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Extension of the platform of applicability of the SM5.42R universal solvation model

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Abstract. We present eight new parameterizations of the SM5.42R solvation model: in particular we present parameterizations for HF/MIDI!, HF/6-31G*, HF/6-31+G*, HF/cc-pVDZ, AM1, PM3, BPW91/MIDI!, and B3LYP/MIDI!. Two of the new cases are parameterized using the reaction-field operator presented previously, and six of the new cases are parameterized with a simplified reaction-field operator; results obtained by the two methods are compared for selected examples. For a training set of 2135 data for 275 neutral solutes containing H, C, N, O, F, S, P, Cl, Br, and I in 91 solvents (water and 90 nonaqueous solvents), seven of the eight new parameterizations give mean unsigned errors in the range 0.43–0.46 kcal/mol, and the eighth – for a basis set containing diffuse functions – gives a mean unsigned error of 0.53 kcal/mol. The mean unsigned error for 49 ionic solutes (containing the same elements) in water is 3.5–3.9 kcal/mol for the Hartree–Fock, Becke–Perdew–Wang-1991 and Becke three-parameter Lee–Yang–Parr cases and 4.1 and 4.0 kcal/mol for parameterized model 3 and Austin model 1, respectively. The methods are tested for sensitivity of solvation free energies to geometry and for predicting partition coefficients of carbonates, which were not included in the training set.

1 Introduction

In two recent papers, we have presented parameterizations of the SM5.42R universal solvation model for use with density functional theory (DFT) employing the Becke–Perdew–Wang-1991 (BPW91) functional and the MIDI!6D, DZVP, and 6-31G* basis sets [1] and for use with ab initio Hartree–Fock calculations employing the MIDI!6D basis set [2]. In the present paper we present eight additional parameterizations of the SM5.42R universal solvation model, namely:

- Ab initio Hartree–Fock theory with the MIDI!, 6-31G*, 6-31+G*, and cc-pVDZ basis sets.
- semiempirical Hartree–Fock theory with the neglect-of-diatomic-differential overlap (NDDO) approximation and the Austin model 1 (AM1) and parameterized model 3 (PM3) parameterizations of the Fock operator.
- DFT with the BPW91 density functional and the MIDI! basis set.
- Becke's semiempirical three-parameter hybrid Hartree–Fock-DFT with the Becke nonlocal exchange functional and Lee–Yang–Parr (LYP) nonlocal correlation functional (B3LYP) and the MIDI! basis set.

Section 2 reviews the background and gives background references. The new parameterizations and their mean errors are presented in Sect. 3, while Sect. 4 provides discussion.

2 Background

2.1 Basis Sets

The basis sets have all been presented elsewhere: MIDI! [3, 4], MIDI!6D [3, 4], DZVP [5], 6-31G* [6–8], 6-31+G* [6–10], and cc-pVDZ [11, 12].[1] We note that the MIDI! basis uses five spherical harmonic basis functions for a *d* shell, and it may be called MIDI!5D.

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[1] The 6-31G* and 6-31+G* bases for Br were obtained from Ref. [52]. The cc-pVDZ basis is unavailable for Br and I, and in both cases it was substituted by the MIDI! basis. The 6-31G* basis is unavailable for I, and it was substituted by the MIDI!6D basis. A 6-31+G* basis for I was obtained by augmenting the MIDI!6D basis with diffuse s and p functions with exponential parameter 0.03.

Table 1. Electrostatic radii (Å). SM5*x* models with various parameterizations, including Hartree–Fock. (HF), density functional theory (*DFT*), hybrid HF-DFT, Austin model 1 (AM1) and parameterized model 3 (PM3) parameterizations

Atom	SM5.4/all	SM5.2R/all	SM5.42R/HF, DFT, HF-DFT	SM5.42R/ AM1, PM3
H	≤1.2	0.91	0.91	0.91
C	1.78	1.78	1.78	1.78
N	1.92	1.92	1.92	1.92
O	1.60	1.60	1.60	1.60
F	1.50	1.50	1.50	1.50
P	–	2.40	2.27	2.40
S	1.92	2.05	1.98	2.15
Cl	2.13	2.13	2.13	2.13
Br	2.31	2.31	2.31	2.31
I	2.66	2.66	2.66	2.66

Table 2. Surface-tension coefficients (cal mol^{-1} Å^{-2}) for SM5.42R/HF/MIDI![a]

Atom (or atom pair)	$\sigma^{(n)}$	$\sigma^{(\alpha)}$	$\sigma^{(\beta)}$	$\sigma^{(\text{water})}$
H	40.46			99.13
C	60.17	24.39	−7.88	89.61
N	6.05	−87.36	91.03	−69.48
O	−39.40	−23.79		−185.04
F	3.45			45.27
P	−427.64			−69.57
S	−77.96	−68.66	60.41	−84.39
Cl	−34.02			−2.01
Br	−45.21			−16.55
I	−48.68			−19.83
H, C	−103.35			−132.85
H, N	−81.20		−150.19	−223.07
H, N (2)	−190.58			−222.01
H, O	−11.29	−291.72	−333.36	−246.83
H, O (2)	195.45			435.15
H, S	58.73			41.34
C, C	−73.66			−74.99
C, C (2)	−0.79			−5.91
O, C	70.26		44.90	243.64
O, O	−39.55	112.06	−22.76	35.30
C, N	−71.04	96.15		30.88
N, C	−13.71	−58.87	0.76	−66.85
N, C (2)				−259.78
N, C (3)	59.44			75.70
O, N	73.23	−7.28	46.75	291.22
O, P	135.42			166.73
S, P	179.23			286.47
S, S	7.60			40.35
	$\sigma^{(\gamma)}$	$\sigma^{(\beta^2)}$	$\sigma^{(\phi^2)}$	$\sigma^{(\psi^2)}$
	0.3293	5.47	−3.91	−8.76

[a] The notation for the parameters in Tables 1–8 is the same as in Ref. [1]

MIDI!6D is the same as MIDI! except that six Cartesian basis functions are employed to span the *d* space (as is well known, this is equivalent to having an extra *s* function). By definition the DZVP, 6-31G*, and 6-31+G* basis sets use the 6D option, and the cc-pVDZ basis uses the 5D option.

Table 3. Surface-tension coefficients (cal mol^{-1} Å^{-2}) for SM5.42R/HF/6-31G*

Atom (or atom pair)	$\sigma^{(n)}$	$\sigma^{(\alpha)}$	$\sigma^{(\beta)}$	$\sigma^{(\text{water})}$
H	40.00			98.93
C	68.57	27.96	−0.98	106.51
N	−0.54	−106.57	86.69	−96.68
O	−37.78	−37.13		−179.41
F	−0.09			38.16
P	−411.55			−68.09
S	−76.49	−63.04	59.97	−73.37
Cl	−34.83			−2.37
Br	−47.25			−20.70
I	−51.14			−23.29
H, C	−107.64			−142.59
H, N	−80.44		−142.60	−217.42
H, N (2)	−184.77			−201.18
H, O	−8.50	−274.28	−315.14	−247.26
H, O (2)	200.40			467.56
H, S	52.70			12.18
C, C	−74.24			−73.82
C, C (2)	−5.64			−13.36
O, C	51.94		23.46	191.89
O, O	−33.13	116.62	−9.41	54.65
C, N	−65.26	123.41		51.63
N, C	−14.39	−60.96	−0.09	−67.19
N, C (2)				−258.26
N, C (3)	46.47			56.23
O, N	65.35	16.88	51.15	269.09
O, P	103.00			92.50
S, P	152.96			250.93
S, S	10.63			39.74
	$\sigma^{(\gamma)}$	$\sigma^{(\beta^2)}$	$\sigma^{(\phi^2)}$	$\sigma^{(\psi^2)}$
	0.3340	3.62	−3.94	−8.29

2.2 CM2 class IV charges

Solute electrostatic interactions with the bulk solvent are computed from the partial charges of the solute atoms. In the SM5.42R solvation model, these are calculated using the CM2 class IV charge model [13a, 13b]. In this model the charge q_k on atom k is given by

$$q_k = q_k^{\mathrm{L}} + q_k^{\mathrm{M}} \ , \tag{1}$$

where q_k^{L} is the Löwdin charge, and q_k^{M} is the CM2 modification. The former is given by [14]

$$q_k^{\mathrm{L}} = Z_k - \sum_{\mu \in k} \left(\mathbf{S}^{1/2}\mathbf{P}\mathbf{S}^{1/2}\right)_{\mu\mu} \ , \tag{2}$$

where Z is the nuclear charge (or core charge in NDDO theory), μ is a basis function label, $\mathbf{S}$ is the overlap matrix, and $\mathbf{P}$ is the density matrix; q_k^{M} is given by [13]

$$q_k^{\mathrm{M}} = \sum_{k' \neq k} B_{kk'}(D_{kk'} + C_{kk'}B_{kk'}) \ , \tag{3}$$

where $B_{kk'}$ is Mayer's bond order [15] (which is a function of $\mathbf{P}$), and $\mathbf{D}$ and $\mathbf{C}$ are matrices of semiempirical parameters.

Table 4. Surface-tension coefficients (cal mol^{-1} Å^{-2}) for SM5.42R/HF/6-31+G*

Atom (or atom pair)	$\sigma^{(n)}$	$\sigma^{(\alpha)}$	$\sigma^{(\beta)}$	$\sigma^{(\text{water})}$
H	35.62			97.24
C	84.61	30.16	−8.25	111.00
N	−9.02	−96.08	83.74	−68.23
O	−39.56	−61.08		−156.72
F	1.78			36.43
P	−77.91			−34.43
S	−89.79	−50.12	55.30	−81.02
Cl	−36.62			−2.32
Br	−48.39			−20.96
I	−46.64			−23.69
H, C	−100.64			−132.21
H, N	−73.66		−149.43	−241.31
H, N (2)	−176.87			−203.37
H, O	0.21	−230.78	−280.79	−259.87
H, O (2)	258.50			581.84
H, S	99.24			42.76
C, C	−88.98			−85.65
C, C (2)	−23.39			−33.10
O, C	59.71		34.32	156.71
O, O	−19.73	175.95	−53.61	101.24
C, N	−61.68	152.14		59.58
N, C	−17.41	−61.28	4.94	−71.44
N, C (2)				−389.89
N, C (3)	37.35			−59.58
O, N	57.51	2.35	91.95	195.84
O, P	31.67			12.38
S, P	192.62			366.11
S, S	11.94			29.98
	$\sigma^{(\gamma)}$	$\sigma^{(\beta^2)}$	$\sigma^{(\phi^2)}$	$\sigma^{(\psi^2)}$
	0.3538	4.80	−3.62	−8.09

Table 5. Surface-tension coefficients (cal mol^{-1} Å^{-2}) for SM5.42R/HF/cc-pVDZ

Atom (or atom pair)	$\sigma^{(n)}$	$\sigma^{(\alpha)}$	$\sigma^{(\beta)}$	$\sigma^{(\text{water})}$
H	39.92			98.79
C	74.12	28.73	1.20	114.50
N	2.85	−108.24	72.15	−94.76
O	−36.11	−46.38		−184.25
F	0.40			38.78
P	−261.61			−73.57
S	−84.06	−71.90	66.97	−88.34
Cl	−35.78			−4.39
Br	−48.15			−21.16
I	−52.24			−26.31
H, C	−109.09			−144.23
H, N	−86.25		−138.62	−231.94
H, N (2)	−178.10			−182.29
H, O	−17.51	−266.18	−316.75	−256.18
H, O (2)	210.16			475.62
H, S	132.00			173.69
C, C	−77.23			−76.81
C, C (2)	−31.11			−65.94
O, C	51.98		23.16	194.09
O, O	−39.98	124.79	−22.4	48.84
C, N	−73.91	122.75		35.87
N, C	−13.39	−59.96	1.49	−63.95
N, C (2)				−236.18
N, C (3)	42.26			103.24
O, N	43.64	−49.16	35.95	198.09
O, P	71.84			77.91
S, P	170.91			300.52
S, S	13.93			44.91
	$\sigma^{(\gamma)}$	$\sigma^{(\beta^2)}$	$\sigma^{(\phi^2)}$	$\sigma^{(\psi^2)}$
	0.3340	3.26	−3.91	−8.16

2.3 Fock, Kohn–Sham, and hybrid Fock–Kohn–Sham operators

In all the theories considered here the gas-phase molecular orbitals $\phi_\mu^{(0)}$ satisfy a pseudo-eigenvalue equation of the form

$$\hat{F}^{(0)}\phi_\mu^{(0)} = \varepsilon_\mu^{(0)}\phi_\mu^{(0)} \ , \tag{4}$$

where $\varepsilon_\mu^{(0)}$ is the gas-phase orbital eigenvalue, and $\hat{F}^{(0)}$ is the gas-phase Fock operator (in ab initio [16], AM1 [17], and PM3 [18] Hartree–Fock theories), the Kohn–Sham operator (in DFT [19]), or the hybrid Fock–Kohn–Sham operator (in hybrid Hartree–Fock–DFT theory [20]). In liquid-phase solution, $\hat{F}^{(0)}$ is replaced by

$$\hat{F} = \hat{F}^{(0)} + \hat{V} \ , \tag{5}$$

where $\hat{V}$ is an operator representing the effect on the Fock operator of the solvent reaction field, as evaluated by the generalized Born approximation [21–31]. In addition, $\varepsilon_\mu^{(0)}$ is replaced by ε_μ, the condensed-phase orbital eigenvalue. $\hat{F}^{(0)}$ and $\hat{F}$ are in each case determined by iterating to a self-consistent field [25, 26, 29–31]. Since $\hat{V}$ includes the reaction field, this is called the self-consistent reaction field (SCRF) method [32–36].

The expectation values of the gas-phase Hamiltonian (electronic plus nuclear repulsion) are calculated from wave functions determined variationally using Eqs. (4) and (5) for the solute electronic system and are denoted E_0 and E, respectively.

2.4 The reaction-field operator

The reaction-field contribution $\hat{V}$ to the Fock operator appearing in Eq. (5) may be obtained by the variational principle [31, 37, 38]. In our first paper [1] on SCRF calculations employing CM2 charges, we used the variational principle to derive the following expression:

$$\langle\mu|\hat{V}|\upsilon\rangle = \sum_\sigma V_{k_\sigma} g_{\sigma\mu\upsilon} \ , \tag{6}$$

where

$$V_k = -\sum_{k'}\left(1-\frac{1}{\varepsilon}\right) q_{k'}\gamma_{kk'} \ . \tag{7}$$

σ, μ, and υ label basis functions, k and k' label atoms, k_σ denotes the atom on which basis function σ is centered, ε is the dielectric constant (relative permittivity), $q_{k'}$ is the charge on atom k', $\gamma_{kk'}$ is the generalized Born Coulomb integral between atoms k and k',

Table 6. Surface-tension coefficients (cal mol^{-1} Å^{-2}) optimized for SM5.42R/AM1

Atom (or atom pair)	$\hat{\sigma}_k^{(n)}$	$\hat{\sigma}_k^{(\alpha)}$	$\hat{\sigma}_k^{(\beta)}$	$\hat{\sigma}_k^{(\text{water})}$
H	39.40			99.48
C	70.44	28.13	11.40	113.37
N	42.07	−70.23	115.66	37.02
O	−24.56	−4.37		−148.98
F	1.57			44.97
P	−29.90			−40.88
S	−74.94	−55.10	64.39	−56.49
Cl	−36.15			−2.72
Br	−47.41			−20.37
I	−50.90			−18.82
H, C	−112.19			−151.17
H, N	−95.42		−142.81	−270.26
H, N (2)	−207.45			−253.16
H, O	−10.73	−325.77	−263.31	−243.75
H, O (2)	226.66			534.56
H, S	37.67			−34.36
C, C	−72.83			−67.68
C, C (2)	5.41			16.10
O, C	45.06		74.93	231.29
O, O	−30.49	100.15	−48.56	41.82
C, N	−69.86	149.73		35.02
N, C	−15.34	−66.82	−0.59	−69.62
N, C (2)				−238.94
N, C (3)	−14.41			−3.55
O, N	36.18	−12.23	101.68	240.69
O, P	54.90			149.34
S, P	282.36			503.51
S, S	16.77			49.21
	$\sigma^{(\gamma)}$	$\sigma^{(\beta^2)}$	$\sigma^{(\phi^2)}$	$\sigma^{(\psi^2)}$
	0.3871	−0.37	−4.61	−6.98

Table 7. Surface-tension coefficients (cal mol^{-1} Å^{-2}) optimized for SM5.42R/PM3

Atom (or atom pair)	$\hat{\sigma}_k^{(n)}$	$\hat{\sigma}_k^{(\alpha)}$	$\hat{\sigma}_k^{(\beta)}$	$\hat{\sigma}_k^{(\text{water})}$
H	39.47			99.31
C	64.86	27.68	7.59	103.78
N	42.88	−75.43	115.23	35.42
O	−41.08	−12.18		−184.68
F	−1.37			39.23
P	−137.51			−63.31
S	−74.75	−51.10	58.10	−48.17
Cl	−35.41			−0.74
Br	−47.89			−20.03
I	−50.79			−18.03
H, C	−108.95			−145.69
H, N	−105.76		−147.61	−285.67
H, N (2)	−197.85			−241.71
H, O	17.26	−308.95	−267.50	−176.86
H, O (2)	209.43			489.79
H, S	36.92			−78.18
C, C	−71.03			−66.43
C, C (2)	9.79			21.86
O, C	76.79		100.40	306.30
O, O	−34.44	110.31	−67.36	23.90
C, N	−77.47	154.20		27.40
N,C	−14.58	−69.00	−1.44	−71.16
N, C (2)				−336.91
N, C (3)	−2.28			21.21
O, N	89.27	25.23	133.40	370.94
O, P	47.66			101.92
S, P	172.91			284.09
S, S	11.95			23.54
	$\sigma^{(\gamma)}$	$\sigma^{(\beta^2)}$	$\sigma^{(\phi^2)}$	$\sigma^{(\psi^2)}$
	0.3755	0.52	−4.54	−7.21

$$g_{\sigma\mu\upsilon} = g^{\mathrm{L}}_{\sigma\mu\upsilon} + g^{\mathrm{M}}_{\sigma\mu\upsilon} \tag{8}$$

$$g^{\mathrm{L}}_{\sigma\mu\upsilon} = -(\mathbf{S}^{1/2})_{\mu\sigma}(\mathbf{S}^{1/2})_{\sigma\upsilon} \tag{9}$$

and

$$g^{\mathrm{M}}_{\sigma\mu\upsilon} = \frac{1}{2}\sum_{k'\neq k_\sigma} T'_{k_\sigma k'} h_{k_\sigma k'\mu\upsilon} \quad , \tag{10}$$

where

$$T'_{kk'} = D_{kk'} + 2C_{kk'}B_{kk'} \tag{11}$$

and

$$h_{kk'\mu\upsilon} = \sum_{\lambda\in k}\sum_{\omega\in k'}\left[\left(\delta_{\mu\lambda}S_{\upsilon\omega} + \delta_{\nu\lambda}S_{\mu\omega}\right)(\mathbf{PS})_{\omega\lambda} + \left(\delta_{\mu\omega}S_{\upsilon\lambda} + \delta_{\upsilon\omega}S_{\mu\lambda}\right)(\mathbf{PS})_{\lambda\omega}\right] \quad , \tag{12}$$

where **P** is the condensed-phase density matrix.

In our second paper [2] we showed that Eq. (6) can be simplified to

$$\langle\mu|\hat{V}|\upsilon\rangle = \sum_\sigma\left[V_{k_\sigma}g^{\mathrm{L}}_{\sigma\mu\upsilon} + \frac{1}{2}T'_{k_\mu k_\sigma}S_{\upsilon\sigma}(\mathbf{PS})_{\sigma\mu}\left(V_{k_\mu} - V_{k_\sigma}\right) + \frac{1}{2}T'_{k_\upsilon k_\sigma}S_{\mu\sigma}(\mathbf{PS})_{\sigma\upsilon}\left(V_{k_\upsilon} - V_{k_\sigma}\right)\right] \tag{13}$$

which is computationally more efficient.

Use of Eqs. (6)–(12) or the equivalent Eq. (13) is called scheme 1. In our programs, it is denoted by ISCRF = 1.

One can, however, propose a slightly different model. In this model, the solution-phase charges are calculated using the gas-phase bond orders in Eq. (3). In this case, q_k^{M} does not depend on the condensed-phase **P** and the variational procedure leads to

$$\langle\mu|\hat{V}|\nu\rangle = \sum_\sigma V_{k_\sigma}g^{\mathrm{L}}_{\sigma\mu\upsilon} \tag{14}$$

Use of Eq. (14) in the Fock operator is called scheme 2. In our programs, it is denoted by ISCRF = 2.

One could think of scheme 2 as an approximation to scheme 1 that is not fully variational. Alternatively, one can think of scheme 2 as the fully variational implementation of a different model. In this model one recognizes that CM2 charges are obtained by modifying Löwdin charges using Eqs. (1) and (3). The modification involves semiempirical parameters, $C_{kk'}$ and $D_{kk'}$, fit to gas-phase dipole moments, and in scheme 2 one assumes that the same modification applies to a solvated molecule, while the change in atomic partial charges due to solvation effects is reflected solely in the change in Löwdin charges. Thus the q_k^{M} are constants for a given molecule.

Table 8. Surface-tension coefficients (cal mol^{-1} Å^{-2}) for SM5.42R/BPW91/MIDI!

Atom (or atom pair)	$\sigma^{(n)}$	$\sigma^{(\alpha)}$	$\sigma^{(\beta)}$	$\sigma^{(\text{water})}$
H	40.46			99.36
C	74.09	26.55	2.74	115.02
N	13.64	−94.79	84.31	−54.47
O	−33.77	−29.38		−175.89
F	3.44			47.15
P	−381.96			−75.30
S	−80.04	−62.39	55.64	−92.89
Cl	−35.76			−4.39
Br	−47.18			−21.37
I	−51.97			−26.47
H, C	−110.37			−143.85
H, N	−87.35		−139.08	234.69
H, N (2)	−191.13			−222.50
H, O	−21.38	−274.58	−326.64	−261.67
H, O (2)	194.39			433.73
H, S	62.05			68.59
C, C	−77.35			−79.64
C, C (2)	−12.87			−25.21
O, C	53.61		44.68	211.26
O, O	−47.92	101.35	−26.22	18.80
C, N	−83.26	125.10		16.24
N, C	−13.00	−61.95	−0.54	−65.44
N, C (2)				−389.89
N, C (3)	34.42			85.79
O, N	62.64	31.79	31.00	273.78
O, P	128.56			166.00
S, P	145.40			241.83
S, S	11.11			55.03
	$\sigma^{(\gamma)}$	$\sigma^{(\beta^2)}$	$\sigma^{(\phi^2)}$	$\sigma^{(\psi^2)}$
	0.3428	3.03	−4.11	−8.51

Table 9. Surface-tension coefficients (cal mol^{-1} Å^{-2}) for SM5.42R/B3LYP/MIDI!

Atom (or atom pair)	$\sigma^{(n)}$	$\sigma^{(\alpha)}$	$\sigma^{(\beta)}$	$\sigma^{(\text{water})}$
H	40.41			99.26
C	71.79	26.62	−0.59	110.03
N	13.45	−98.11	85.42	−61.63
O	−40.57	−32.70		−189.48
F	2.90			45.91
P	−298.23			−75.77
S	−80.31	−64.45	56.14	−92.46
Cl	−35.38			−4.16
Br	−46.58			−20.35
I	−51.35			−25.45
H, C	−108.74			−141.36
H, N	−92.72		−146.15	−243.13
H, N (2)	−187.63			−213.67
H, O	−6.12	−267.40	−325.42	−232.30
H, O (2)	191.75			431.46
H, S	63.87			61.49
C, C	−77.26			−79.53
C, C (2)	−10.82			−21.69
O, C	62.67		41.28	229.38
O, O	−45.36	106.03	−26.99	23.25
C, N	−85.19	129.22		19.70
N, C	−12.69	−62.81	−5.32	−65.65
N, C (2)				−393.69
N, C (3)	41.09			101.26
O, N	73.58	29.61	37.64	297.28
O, P	120.78			181.46
S, P	151.74			264.71
S, S	10.50			51.83
	$\sigma^{(\gamma)}$	$\sigma^{(\beta^2)}$	$\sigma^{(\phi^2)}$	$\sigma^{(\psi^2)}$
	0.3379	3.70	−4.03	−8.64

The four SM5.42R parameterizations presented previously [1, 2] were carried out with scheme 1. For the present analysis, the AM1 and PM3 parameterizations were carried out with scheme 1, and the other six new parameterizations were carried out with scheme 2.

One advantage of scheme 2 is that it is simpler. In addition, it sometimes converges when scheme 1 does not.

After the self-consistent wave function is obtained, the polarization contribution to the free energy of solvation is given by

$$G_{\text{P}} = \frac{1}{2}\sum_k V_k q_k \quad . \tag{15}$$

2.5 SM5.42R model

In all SMx models, including SM5.42R (in which $x = .42\text{R}$), the standard-state free energy of solvation is

$$\Delta G^0_{\text{S}} = E - E_0 + G_{\text{P}} + G_{\text{CDS}} \quad , \tag{16}$$

where, in cases where gas-phase geometries are not reoptimized in solution, $(E + G_{\text{P}} - E_0)$ is also called ΔG_{EP} (the change in solute-electronic and solvent-polarization free energy), and G_{CDS} is the "cavity-dispersion-solvent-structure" free energy, also called the first-solvation-shell term. The contribution $E - E_0$ from the gas-phase Hamiltonian is called the distortion energy. The standard-state free energy of solvation is the free energy of transfer of the solute from the gas phase (air at 1 atm and 298 K) to a liquid solution in a specified solvent at 298 K and under 1 atm of external pressure. The standard state for all our work is 1 mol of solute per liter, both in the gas phase and in liquid-phase solutions. If we had used a standard of 1 atm of solute in the gas phase, there would have been another term in Eq. (16) [39] to account for the change in number entropy. In general we write G_{CDS} as a sum of atomic surface tensions σ_k times solvent-accessible surface areas A_k for all the atoms k in the solute:

$$G_{\text{CDS}} = \sum_k \sigma_k A_k \quad . \tag{17}$$

Each σ_k is a multilinear function of semiempirical surface tension coefficients $\tilde{\sigma}_{km}$:

$$\sigma_k = \sum_m \tilde{\sigma}_{km} T_m \quad , \tag{18}$$

where the T_m are nonlinear functions of interatomic distances, atomic numbers, and a small number of solvent properties (called solvent descriptors). In early SMx models the T_m functions depend on bond orders [39–41], but those dependencies are replaced by depen-

Table 10. Performance of the SM5.42R model by solute functional class as measured by the mean signed error (MSE) and the mean unsigned error (MUE) (kcal mol^{-1})

Solute class	Number of			HF/MIDI!		HF/6-31G*	
	Solutes	Solvent classes	Data	MSE	MUE	MSE	MUE
Unbranched alkanes	9	19	84	0.07	0.37	0.09	0.39
Branched alkanes	5	3	12	0.14	0.44	0.12	0.43
Cycloalkanes	5	6	18	−0.34	0.43	−0.38	0.44
Alkenes	9	4	27	−0.06	0.25	0.01	0.26
Alkynes	5	3	14	0.02	0.16	0.01	0.16
Arenes	9	19	134	−0.45	0.51	−0.42	0.50
Alcohols	17	19	385	0.02	0.35	0.01	0.36
Ethers	12	19	93	0.10	0.45	0.11	0.44
Aldehydes	7	8	38	−0.17	0.39	−0.09	0.39
Ketones	12	18	203	−0.20	0.42	−0.20	0.41
Carboxylic acids	5	14	124	−0.11	0.45	−0.07	0.43
Esters	14	8	249	0.10	0.34	0.08	0.31
Non-halo bifunctional compounds	5	8	28	0.76	1.05	0.77	1.03
Inorganic compounds	2	9	22	0.03	0.62	0.03	0.63
Aliphatic amines	15	10	168	0.07	0.32	0.07	0.32
Aromatic amines	11	12	81	0.06	0.35	0.04	0.34
Nitriles	4	6	22	−0.12	0.37	−0.13	0.34
Nitrohydrocarbons	6	8	38	0.01	0.31	0.00	0.26
Amides and ureas	4	6	11	0.74	1.24	0.78	1.14
Bifunctional HCN and HCNO	6	3	11	−0.45	0.68	−0.46	0.64
Inorganic HCN	2	8	15	−0.38	0.67	−0.39	0.68
Thiols	4	5	14	0.34	0.37	0.32	0.33
Sulfides	6	6	23	−0.11	0.67	−0.10	0.59
Disulfides	2	3	5	0.00	0.22	0.00	0.24
Fluorinated hydrocarbons	9	5	19	−0.47	0.56	−0.46	0.49
Chloroalkanes	13	5	35	0.05	0.28	−0.15	0.29
Chloroalkenes	5	4	16	0.62	0.62	0.67	0.67
Chloroarenes	8	6	37	−0.58	0.59	−0.39	0.42
Brominated hydrocarbons	14	6	50	−0.25	0.34	−0.22	0.33
Iodinated hydrocarbons	9	6	28	−0.06	0.32	−0.04	0.29
Other halo compounds	26	9	80	0.18	0.66	0.18	0.66
P, H, C and O compounds	5	6	28	−0.09	1.01	−0.07	0.98
Other P compounds	10	4	23	0.01	1.23	0.00	1.28
Total	275	19	2135	−0.04	0.43	−0.04	0.42

dencies on interatomic distances for $x = 5$–5.42 [42]. The T_m are sometimes called the first-solvation-shell functional forms.

Universal solvation models [1, 2, 42–45] are in principle valid for all solvents (that is why they are called universal) because the properties of the solvent enter only through the dielectric constant in $\hat{V}$ and through a small number of solvent descriptors in the first-solvation-shell functional forms. Thus, universal solvation models can be applied to any solvent for which the dielectric constant and these few solvent descriptors are known or can be estimated.

SM5 universal solvation models are based on the SM5 approach [42–49] to the first-solvation-shell functional forms. The essential element of this approach is that T_m depends on interatomic distances primarily of atoms within bonding distance and sometimes within the range of distances characteristic of geminal interactions. The T_m do not depend on bond orders, and external "typing" is not required (e.g., one does not have to label oxygens as being of alcohol type, carbonyl type, etc.)

SM5.4 and SM5.42 models are SM5 models employing class IV [13, 50] point charges (denoted by .4). SM5.4 models employ the CM1 class IV charge model [50], and SM5.42 models employ the CM2 class IV charge model [13a]. The 2 in 5.42 denotes that it is our second model of the 5.4 type.

In the SM5.42R model, the gas-phase geometry of the solute is taken as rigid (denoted R) during the determination of the semiempirical $\tilde{\sigma}_{km}$ values, i.e., the parameterization is based on calculations in which the geometry is not relaxed upon dissolution.

Although the G_{CDS} term nominally models first-solvation-shell effects, it is also designed to make up for systematic deficiencies and/or intrinsic uncertainties in $E + G_P - E_0$. The latter arise from the intrinsic uncertainty in the dielectric constant of the solvent in the microscopic region near the solute (the "cosphere"), and the former can arise from the approximations in obtaining Eqs. (1) and (2), such as lack of correlation in Hartree–Fock theory, inexact density functionals in DFT, NDDO approximations in AM1

Table 11. Performance of the SM5.42R model by solute functional class

Solute class	Number of			HF/6-31+G*		HF/cc-pVDZ	
	Solutes	Solvent classes	Data	MSE	MUE	MSE	MUE
Unbranched alkanes	9	19	84	0.34	0.48	0.12	0.42
Branched alkanes	5	3	12	0.45	0.57	0.09	0.43
Cycloalkanes	5	6	18	−0.14	0.27	−0.46	0.50
Alkenes	9	4	27	0.35	0.45	−0.03	0.28
Alkynes	5	3	14	−0.06	0.25	0.01	0.24
Arenes	9	19	134	−0.42	0.46	−0.46	0.54
Alcohols	17	19	385	−0.08	0.38	0.00	0.38
Ethers	12	19	93	0.25	0.51	0.12	0.45
Aldehydes	7	8	38	0.89	0.94	0.06	0.42
Ketones	12	18	203	−0.30	0.49	−0.25	0.43
Carboxylic acids	5	14	124	0.18	0.49	−0.08	0.42
Esters	14	8	249	−0.09	0.56	0.08	0.32
Non-halo bifunctional compounds	5	8	28	0.75	1.13	0.87	1.07
Inorganic compounds	2	9	22	0.00	0.69	0.02	0.63
Aliphatic amines	15	10	168	0.06	0.31	0.06	0.33
Aromatic amines	11	12	81	0.12	0.34	0.07	0.33
Nitriles	4	6	22	−0.30	0.40	0.00	0.27
Nitrohydrocarbons	6	8	38	0.00	0.48	−0.01	0.26
Amides and ureas	4	6	11	0.39	0.78	0.86	1.16
Bifunctional HCN and HCNO	6	3	11	−0.42	0.53	−0.49	0.70
Inorganic HCN	2	8	15	−0.37	0.67	−0.45	0.74
Thiols	4	5	14	0.34	0.48	0.37	0.37
Sulfides	6	6	23	−0.08	0.82	−0.13	0.59
Disulfides	2	3	5	0.00	0.24	0.00	0.22
Fluorinated hydrocarbons	9	5	19	−0.48	0.59	−0.37	0.42
Chloroalkanes	13	5	35	0.15	0.32	−0.23	0.32
Chloroalkenes	5	4	16	0.84	0.84	0.67	0.67
Chloroarenes	8	6	37	−0.42	0.45	−0.23	0.32
Brominated hydrocarbons	14	6	50	−0.13	0.31	−0.32	0.41
Iodinated hydrocarbons	9	6	28	−0.06	1.08	−0.05	0.26
Other halo compounds	26	9	80	0.09	0.79	0.25	0.71
P, H, C and O compounds	5	6	28	−0.17	1.44	0.07	1.17
Other P compounds	10	4	23	0.26	2.52	0.33	1.32
Total	275	19	2135	−0.02	0.52	−0.03	0.44

and PM3, choice of basis set, generalized Born approximation, etc. For this reason, whenever $\hat{F}^{(0)}$ is changed, including a change in the Fock, Kohn–Sham, or hybrid operator or the basis set used to represent this operator, a new set of $\tilde{\sigma}_{km}$ should be determined for optimal performance. The present paper presents eight such new sets of $\tilde{\sigma}_{km}$.

2.6 Computer codes

The ab initio Hartree–Fock calculations and the DFT and hybrid Hartree–Fock-DFT calculations were carried out with the Minnesota Gaussian Solvation Module (MN-GSM [51]), which is a package for updating GAUSSIAN94 [52] to carry out SM5.42R calculations with ab initio Hartree–Fock, DFT, or hybrid DFT methods. The semiempirical AM1 and PM3 calculations were carried out with AMSOL [53].

The previous parameterizations [1, 2] of SM5.42R were carried out with DGSOL [54], which is a module for inserting the SM5.42R capability into DGAUSS [55], and with GAMESOL [56], a module for inserting the SM5.42R capability into GAMESS [57].

The numerical methods used for the calculations are described elsewhere [58]. In particular the exposed surface areas, which are needed in both the ENP and CDS calculations, are computed using the ASA algorithm [58], and the radial quadratures in the dielectric screening algorithm are carried out using the force trapezoid algorithm [58].

We note that DG-SOL contains ISCRF = 1 based on Eqs. (6)–(13). GAMESOL and MN-GSM contain ISCRF = 1 based on Eq. (14), and they also contain ISCRF = 2. AMSOL contains ISCRF = 1 based on Eq. (14), but in the case of the semiempirical methods in AMSOL, $\mathbf{S} = \mathbf{1}$, which leads to great simplification.

3 Parameterizations

All parameterizations of the SM5.42R model use the same functional forms for ENP and CDS terms, and, with two exceptions, they use the same nonlinear parameters in ENP and CDS terms. These functional forms and nonlinear parameters have been specified elsewhere [1, 2]. The only two exceptions are the Coulomb radii for P and S. For all the Hartree–Fock,

Table 12. Performance of the SM5.42R model by solute functional group class

Solute class	Number of			SM5.42R/AM1		SM5.42R/PM3	
	Solutes	Solvent classes	Data	MSE	MUE	MSE	MUE
Unbranched alkanes	9	19	84	0.10	0.40	0.14	0.41
Branched alkanes	5	3	12	0.08	0.41	0.13	0.41
Cycloalkanes	5	6	18	−0.27	0.33	−0.19	0.31
Alkenes	9	4	27	0.20	0.31	0.17	0.28
Alkynes	5	3	14	−0.01	0.15	−0.01	0.14
Arenes	9	19	134	−0.44	0.50	−0.49	0.53
Alcohols	17	19	385	−0.04	0.37	−0.03	0.38
Ethers	12	19	93	0.18	0.53	0.20	0.51
Aldehydes	7	8	38	−0.39	0.47	−0.49	0.54
Ketones	12	18	203	−0.13	0.42	−0.14	0.44
Carboxylic acids	5	14	124	−0.03	0.46	−0.04	0.47
Esters	14	8	249	0.02	0.40	0.03	0.39
Bifunctional compounds containing H, C, O	5	8	28	0.83	1.00	0.81	1.00
Inorganic compounds containing H and O	2	9	22	0.00	0.68	0.00	0.66
Aliphatic amines	15	10	168	0.06	0.34	0.05	0.31
Aromatic amines	11	12	81	0.04	0.35	0.00	0.33
Nitriles	4	6	22	0.00	0.54	0.00	0.54
Nitrohydrocarbons	6	8	38	0.00	0.24	0.00	0.29
Amides and ureas	4	6	11	0.64	1.08	0.63	1.01
Bifunctional compounds containing N	6	3	11	−0.36	0.66	−0.27	0.64
Inorganic compounds containing N	2	8	15	−0.40	0.69	−0.24	0.57
Compounds containing P, C, H, and/or O	5	6	28	−0.12	1.08	−0.07	1.16
Other phosphorus compounds	10	4	23	0.13	1.24	0.07	1.22
Thiols	4	5	14	0.28	0.32	0.33	0.34
Sulfides	6	6	23	−0.08	0.53	−0.01	0.67
Disulfides	2	3	5	0.00	0.26	0.00	0.22
Fluorinated hydrocarbons	9	5	19	−0.26	0.46	−0.29	0.50
Chloroalkanes	13	5	35	−0.34	0.40	−0.39	0.48
Chloroalkenes	5	4	16	0.64	0.64	0.58	0.58
Chloroarenes	8	6	37	−0.40	0.45	−0.33	0.39
Brominated hydrocarbons	14	6	50	−0.31	0.37	−0.39	0.44
Iodinated hydrocarbons	9	6	28	−0.05	0.26	−0.09	0.37
Multifunctional halogenated solutes	26	9	80	0.28	0.71	0.31	0.72
Total	275	19	2135	−0.03	0.45	−0.03	0.46

DFT, and hybrid Hartree–Fock-DFT calculations they were set to 2.27 Å for P and 1.98 Å for S, as in Refs. [1, 2]; however for AM1 and PM3 they were separately optimized to 2.40 Å for P and 2.15 Å for S. The radii used in various SM5 solvation models are compared in Table 1. With the exception of the P and S Coulomb radii, the only differences among the 12 parameterizations of the SM5.42R model are the linear parameters, namely the $\tilde{\sigma}_{km}$ surface-tension coefficients.

All SM5.42R solvation models were parameterized against the same training set of experimental data and were parameterized using the same set of HF/MIDI! geometries. The data set has been explained previously [1, 45–47]. It consists of 2135 solvation free energies for 275 neutral solutes composed of H, C, N, O, F, P, S, Cl, Br, and I in 91 solvents. The parameterization process has been explained previously [1] and was used here without change.

The final values of the surface-tension coefficients for the eight new parameterizations presented in this paper are given in Tables 2–9.

4 Results

The mean unsigned errors (MUEs) and mean signed errors (MSEs) for the neutral molecules are given in Tables 10–13 organized by type of solute. Tables 14–17 present MUEs and MSEs for neutral molecules organized by type of solvent. Notice that Tables 10–13 include solutes containing P, but Tables 14–17 do not; however, the trends in Tables 14–17 would be the same if P compounds were included. Tables 18 and 19 provide samples of the detailed results for neutral molecules.

The model was also tested for aqueous solvation free energies of ions, again using HF/MIDI! geometries. We used the same 49 ions that were used in Ref. [47] (43 non-phosphorus ions given in the text of that paper and six monocharged phosphorus ions specified in the appendix). (The experimental value for protonated acetamide was taken from the paper of Florian and Warshel [59]; the value given in their table is assumed to be more accurate than the older value we used previously.) The 49 data used to test the model for charged species are

Table 13. Performance of the SM5.42R model by solute functional class

Solute class	Number of			BPW91/MIDI!		B3LYP/MIDI!	
	Solutes	Solvent classes	Data	MSE	MUE	MSE	MUE
Unbranched alkanes	9	19	82	0.08	0.40	0.10	0.39
Branched alkanes	5	3	12	0.12	0.42	0.17	0.40
Cycloalkanes	5	6	18	0.48	0.53	−0.37	0.42
Alkenes	9	4	27	−0.02	0.29	0.14	0.29
Alkynes	5	3	14	−0.01	0.20	0.13	0.23
Arenes	9	19	134	−0.49	0.56	−0.25	0.48
Alcohols	17	19	385	0.03	0.38	0.15	0.42
Ethers	12	19	93	0.04	0.47	0.08	0.48
Aldehydes	7	8	38	−0.15	0.40	0.08	0.48
Ketones	12	18	203	−0.23	0.42	−0.05	0.42
Carboxylic acids	5	14	124	−0.14	0.44	−0.08	0.43
Esters	14	8	249	0.13	0.33	0.07	0.33
Non-halo bifunctional compounds	5	8	28	0.85	1.09	1.08	1.27
Inorganic compounds	2	9	22	0.03	0.61	0.12	0.60
Aliphatic amines	15	10	168	0.09	0.36	−0.01	0.32
Aromatic amines	11	12	81	0.01	0.33	0.20	0.41
Nitriles	4	6	22	0.00	0.40	0.11	0.39
Nitrohydrocarbons	6	8	38	0.02	0.47	0.01	0.47
Amides and ureas	4	6	11	0.84	1.37	1.04	1.46
Bifunctional HCN and HCNO	6	3	11	−0.40	0.65	−0.45	0.73
Inorganic HCN	2	8	15	−0.42	0.71	−0.45	0.72
Thiols	4	5	14	0.29	0.32	0.19	0.22
Sulfides	6	6	23	−0.15	0.62	−0.10	0.74
Disulfides	2	3	5	0.00	0.24	0.15	0.24
Fluorinated hydrocarbons	9	5	19	−0.37	0.47	−0.26	0.45
Chloroalkanes	13	5	35	−0.09	0.33	0.04	0.34
Chloroalkenes	5	4	16	0.69	0.69	0.70	0.70
Chloroarenes	8	6	37	−0.40	0.43	−0.24	0.39
Brominated hydrocarbons	14	6	50	−0.22	0.33	−0.10	0.31
Iodinated hydrocarbons	9	6	28	−0.03	0.28	0.08	0.34
Other halo compounds	26	9	80	0.20	0.66	0.36	0.77
P, H, C and O compounds	5	6	28	0.22	0.98	0.13	1.00
Other P compounds	10	4	23	0.41	1.38	0.57	1.28
Total	275	19	2135	−0.04	0.46	0.06	0.46

solvation free energies of ions composed of H, C, N, O, F, P, S, Cl, Br, and I in water. The geometries were examined at the HF/MIDI!, BPW91/MIDI!//HF/MIDI!, and B3LYP/MIDI!//HF/MIDI! levels for two ions where there are conformational issues. For both formamide and acetamide, O protonation is strongly favored over N protonation in both the gas phase and in solution. In both O-protonated species, the proton anti to the amino group is favored (by about 2.5–3 kcal/mol), and in $CH_3C(OH)NH_2^+$, the methyl group prefers to have a C—H bond anti to the C═O bond. The results for all ions are presented in Tables 20–23.

Table 24 presents the overall MUEs, which are the mean absolute values of the deviation from experiment, for the eight new parameterizations plus the four parameterizations presented previously [1, 2]. All results in Tables 10–24 are based on HF/MIDI! geometries.

5 Discussion

Table 24 shows rather uniform overall performance across the eight new parameterizations. The errors for neutral molecules are only 2–2.5 times larger than our estimated typical uncertainty in the experimental data for neutral molecules, which is about 0.2 kcal/mol. The errors for ions are actually smaller than our estimated uncertainty in the typical experimental free energy of solvation for ions, which is 5 kcal/mol.

Tables 10–13 show that trends in the errors by solute class are similar for the eight parameterizations. MSEs tend to be largest for functional groups containing nitrogen or chlorine atoms. Tables 18 and 19 show that individual solvation free energies of neutral molecules also tend to be predicted similarly by the various parameterizations. There is a small, but consistent, tendency for the HF/6-31G* and HF/6-31 + G* parameterizations to predict less negative solvation free energies than the other parameterizations for aromatics; this derives from smaller polarization of the aromatic C—H bonds in the former two cases.

Tables 14–17 show that the largest systematic errors for solvents are for aromatic ethers, nitriles, nitro compounds, and haloaromatics. MUEs for solvent classes tend to be reasonably uniform, with only 9% of the values exceeding 0.60 kcal/mol.

Tables 20–23 show that, as expected, solvation free energies of ions are dominated by the electrostatic terms.

Table 14. Performance of the SM5.42R model by solvent functional class

Solvent class	Number of			HF/MIDI!		HF/6-31G*	
	Solvents	Solute classes[a]	Data	MSE	MUE	MSE	MUE
Aqueous	1	31	248	−0.03	0.43	−0.03	0.46
Alkanes	11	30	475	−0.04	0.31	−0.04	0.30
Cycloalkanes	2	24	106	0.06	0.38	0.07	0.37
Arenes	12	16	256	0.25	0.40	0.23	0.38
Aaliphatic alcohols	12	31	299	−0.06	0.50	−0.05	0.50
Aromatic alcohols	2	7	12	0.09	0.55	0.13	0.55
Ketones	4	10	35	−0.18	0.46	−0.16	0.44
Esters	2	8	36	0.35	0.53	0.37	0.53
Aliphatic ethers	4	19	99	−0.03	0.49	−0.01	0.49
Aromatic ethers	3	5	15	−0.54	0.55	−0.50	0.53
Amines	2	6	12	0.02	0.37	0.07	0.34
Pyridines	3	5	15	−0.26	0.42	−0.23	0.40
Nitriles	2	5	10	−0.63	0.63	−0.63	0.63
Nitro compounds	4	8	27	−0.27	0.62	−0.27	0.57
Tertiary amides	2	5	10	−0.06	0.28	−0.05	0.28
Haloaliphatics	12	27	269	−0.12	0.46	−0.12	0.44
Haloaromatics	6	11	106	−0.28	0.39	−0.29	0.40
Miscellaneous acidic solvents	3	5	15	0.07	0.38	0.09	0.42
Miscellaneous nonacidic solvents	4	12	39	−0.05	0.41	−0.07	0.39
Total	91	31	2084	−0.03	0.42	−0.03	0.40

[a] Excluding phosphorus compounds

Table 15. Performance of the SM5.42R model by solvent functional class

Solvent class	Number of			HF/6-31 + G*		HF-cc-pVDZ	
	Solvents	Solute classes[a]	Data	MSE	MUE	MSE	MUE
Aqueous	1	31	248	−0.01	0.54	−0.02	0.40
Alkanes	11	30	475	0.02	0.38	−0.05	0.32
Cycloalkanes	2	24	106	0.07	0.46	0.07	0.36
Arenes	12	16	256	0.17	0.39	0.23	0.39
Aliphatic alcohols	12	31	299	−0.04	0.65	−0.04	0.56
Aromatic alcohols	2	7	12	0.36	0.75	0.09	0.58
Ketones	4	10	35	−0.07	0.45	−0.16	0.47
Esters	2	8	36	0.30	0.49	0.41	0.60
Aliphatic ethers	4	19	99	−0.01	0.55	0.00	0.49
Aromatic ethers	3	5	15	−0.37	0.56	−0.53	0.57
Amines	2	6	12	0.19	0.40	0.05	0.33
Pyridines	3	5	15	−0.16	0.45	−0.28	0.43
Nitriles	2	5	10	−0.59	0.65	−0.72	0.72
Nitro compounds	4	8	27	−0.20	0.59	−0.25	0.63
Tertiary amides	2	5	10	−0.05	0.37	−0.12	0.33
Haloaliphatics	12	27	269	−0.17	0.54	−0.11	0.46
Haloaromatics	6	11	106	−0.38	0.52	−0.28	0.40
Miscellaneous acidic solvents	3	5	15	0.09	0.54	0.02	0.49
Miscellaneous nonacidic solvents	4	12	39	−0.06	0.44	−0.07	0.41
Total	91	31	2084	−0.02	0.49	−0.03	0.42

[a] Excluding phosphorus compounds

The solvation free energy of the hydronium ion and of protonated alcohols is systematically underestimated, whereas ammonium and protonated methylamine are systematically oversolvated. The model does quite well for the hydroxide ion.

Although six of the 12 SM5.42R parameterizations were carried out with ISCRF = 1, and six were carried out with ISCRF = 2, any of the resulting parameterizations can usually be used with either choice of reaction-field operator because in most cases the results are

Table 16. Performance of the SM5.42R model by solvent functional group class

Solvent class	Number of			SM5.42R/AM1		SM5.42R/PM3	
	Solvents	Solute classes[a]	Data	MSE	MUE	MSE	MUE
Aqueous	1	31	248	−0.04	0.42	−0.09	0.66
Alkanes	11	30	475	−0.03	0.31	−0.10	0.34
Cycloalkanes	2	24	106	0.13	0.39	−0.08	0.37
Arenes	12	16	256	0.27	0.40	−0.07	0.33
Aliphatic alcohols	12	31	299	−0.06	0.53	−0.22	0.59
Aromatic alcohols	2	7	12	0.17	0.54	0.08	0.59
Ketones	4	10	35	−0.27	0.53	−0.27	0.64
Esters	2	8	36	0.36	0.52	0.36	0.51
Aliphatic ethers	4	19	99	−0.02	0.52	−0.09	0.48
Aromatic ethers	3	5	15	−0.48	0.52	−0.34	0.43
Amines	2	6	12	0.22	0.39	−0.14	0.58
Pyridines	3	5	15	−0.24	0.42	−0.04	0.39
Nitriles	2	5	10	−0.76	0.76	−0.24	0.48
Nitro compounds	4	8	27	−0.41	0.58	−0.28	0.87
Tertiary amides	2	5	10	−0.10	0.34	0.18	0.38
Haloaliphatics	12	27	269	−0.16	0.48	−0.21	0.59
Haloaromatics	6	11	106	−0.43	0.54	−0.12	0.34
Miscellaneous acidic solvents	3	5	15	0.19	0.48	0.21	0.45
Miscellaneous nonacidic solvents	4	12	39	−0.05	0.39	−0.26	0.56
Total	91	19	2084	−0.03	0.43	−0.12	0.48

[a] Excluding phosphorus compounds

Table 17. Performance of the SM5.42R model by solvent functional class

Solvent class	Number of			BPW91/MIDI!		B3LYP/MIDI!	
	Solvents	Solute classes[a]	Data	MSE	MUE	MSE	MUE
Aqueous	1	31	248	−0.02	0.45	0.21	0.52
Alkanes	11	30	475	−0.05	0.32	0.00	0.32
Cycloalkanes	2	24	106	0.08	0.38	0.08	0.37
Arenes	12	16	256	0.24	0.40	0.29	0.43
Aliphatic alcohols	12	31	299	−0.05	0.53	0.14	0.54
Aromatic alcohols	2	7	12	0.06	0.54	0.19	0.59
Ketones	4	10	35	−0.21	0.48	−0.20	0.46
Esters	2	8	36	0.39	0.58	0.38	0.56
Aliphatic ethers	4	19	99	0.00	0.52	−0.01	0.52
Aromatic ethers	3	5	15	−0.54	0.58	−0.49	0.50
Amines	2	6	12	0.05	0.34	0.10	0.36
Pyridines	3	5	15	−0.30	0.46	−0.18	0.38
Nitriles	2	5	10	−0.74	0.74	−0.69	0.69
Nitro compounds	4	8	27	−0.35	0.58	0.12	0.71
Tertiary amides	2	5	10	−0.12	0.34	−0.09	0.31
Haloaliphatics	12	27	269	−0.11	0.46	−0.10	0.46
Haloaromatics	6	11	106	−0.30	0.41	−0.24	0.39
Miscellaneous acidic solvents	3	5	15	0.03	0.45	0.25	0.41
Miscellaneous nonacidic solvents	4	12	39	−0.07	0.40	−0.01	0.44
Total	91	31	2084	−0.03	0.43	0.06	0.44

[a] Excluding phosphorus compounds

nearly the same. This is illustrated in Table 25. This is partially explained by comparing the relative sizes of the contributions of the various terms, which is done in Table 26. Table 26 shows the values of trace $\hat{\mathbf{V}}\mathbf{P}$, where $\mathbf{P}$ is the liquid-phase density matrix calculated with ISCRF = 1. In the first numerical column of Table 26, we use both terms in Eq. (8), but in the final columns we separately tabulate the contributions of the individual terms. (Notice that trace $\hat{\mathbf{V}}\mathbf{P}$ does not include the contributions from the interaction of the reaction field with the solute nuclei.) All results in Table 26 were calculated with wave functions converged with ISCRF = 1. Clearly, the first term is much bigger than the second one in Eq. (8).

Although the parameterizations were carried out using HF/MIDI! gas-phase geometries, the results are not overly sensitive to the geometry, as long as reasonable geometries are used. To illustrate this, Table 27

Table 18. Calculated and experimental free energies of solvation, ΔG_S^0 (kcal/mol), electronic-nuclear-polarization free energy changes, ΔG_{ENP}, and cavity-dispersion-solvent-structure free energies, G_{CDS}, for all neutral solutes used in the parameterizations of the SM5.42R model

Solute	SM5.42R/AM1			SM5.42R/PM3			Expt.
	ΔG_{ENP}	G_{CDS}	ΔG_S^0	ΔG_{ENP}	G_{CDS}	ΔG_S^0	ΔG_S^0
Solvent: *n*-pentane							
Methanol	−1.83	0.35	−1.48	−1.75	0.24	−1.50	−1.29
Ethanol	−1.75	−0.76	−2.50	−1.67	−0.83	−2.50	−2.15
1-Propanol	−1.66	−1.53	−3.19	−1.60	−1.59	−3.19	−2.76
1-Butanol	−1.53	−2.29	−3.82	−1.49	−2.34	−3.83	−3.77
1-Pentanol	−1.50	−3.04	−4.54	−1.47	−3.06	−4.54	−3.92
Phenol	−2.35	−3.02	−5.37	−2.17	−3.13	−5.31	−5.67
1-Hexanol	−1.51	−3.80	−5.31	−1.48	−3.83	−5.32	−4.97
1-Heptanol	−1.49	−4.55	−6.04	−1.47	−4.56	−6.03	−5.62
2-Pentanone	−1.87	−2.47	−4.34	−1.95	−2.37	−4.32	−4.16
2-Hexanone	−1.80	−3.23	−5.03	−1.88	−3.10	−4.98	−4.79
3,3-Dimethylbutanone	−1.76	−2.39	−4.15	−1.82	−2.29	−4.10	−4.43
2-Heptanone	−1.84	−3.96	−5.80	−1.93	−3.83	−5.75	−5.40
Methyl ethanoate	−2.37	−0.56	−2.93	−2.22	−0.71	−2.93	−3.13
Methyl propanoate	−2.15	−1.33	−3.49	−2.01	−1.46	−3.48	−3.69
Ethyl ethanoate	−2.26	−1.57	−3.83	−2.14	−1.69	−3.83	−3.69
Propyl ethanoate	−2.19	−2.33	−4.52	−2.10	−2.42	−4.53	−4.21
Methyl pentanoate	−2.04	−2.80	−4.84	−1.92	−2.90	−4.82	−4.96
Butyl ethanoate	−2.16	−3.07	−5.23	−2.08	−3.15	−5.23	−4.88
Methyl hexanoate	−2.02	−3.55	−5.56	−1.91	−3.62	−5.53	−5.67
Pentyl ethanoate	−2.14	−3.82	−5.95	−2.07	−3.88	−5.94	−5.62
Ethylamine	−0.83	−1.66	−2.49	−0.71	−1.82	−2.53	−2.18
Propylamine	−0.80	−2.44	−3.23	−0.68	−2.58	−3.26	−3.13
Butylamine	−0.77	−3.18	−3.95	−0.65	−3.31	−3.96	−3.62
Aniline	−1.90	−3.68	−5.58	−1.64	−4.01	−5.65	−5.15
Trichloromethane	−0.54	−3.35	−3.89	−0.51	−3.30	−3.81	−3.26
Tribromomethane	−0.28	−5.48	−5.75	−0.20	−5.58	−5.78	−4.83
Solvent: *n*-hexane							
n-Octane	0.02	−5.40	−5.38	0.02	−5.29	−5.27	−5.46
Benzene	−1.05	−3.63	−4.69	−0.94	−3.78	−4.72	−3.96
Toluene	−1.08	−4.07	−5.15	−0.98	−4.20	−5.18	−4.84
Ethylbenzene	−0.99	−4.73	−5.72	−0.90	−4.85	−5.75	−4.99
o-Xylene	−1.13	−4.51	−5.64	−1.03	−4.63	−5.66	−5.22
m-Xylene	−1.11	−4.50	−5.61	−1.01	−4.62	−5.63	−4.99
p-Xylene	−1.10	−4.50	−5.60	−1.00	−4.62	−5.62	−5.01
Methanol	−1.88	0.43	−1.45	−1.79	0.32	−1.48	−1.49
Ethanol	−1.79	−0.67	−2.46	−1.71	−0.74	−2.46	−2.61
1-Propanol	−1.71	−1.43	−3.13	−1.64	−1.48	−3.13	−2.81
1-Butanol	−1.57	−2.17	−3.74	−1.53	−2.22	−3.75	−3.77
1-Pentanol	−1.54	−2.90	−4.44	−1.51	−2.93	−4.44	−4.38
Phenol	−2.41	−2.91	−5.32	−2.23	−3.03	−5.26	−5.49
1-Hexanol	−1.55	−3.65	−5.20	−1.52	−3.68	−5.20	−5.14
o-Cresol	−2.38	−3.38	−5.76	−2.22	−3.49	−5.71	−6.25
p-Cresol	−2.42	−3.36	−5.77	−2.25	−3.48	−5.72	−5.86
1-Heptanol	−1.53	−4.38	−5.91	−1.51	−4.39	−5.90	−5.75
1,4-Dioxane	−1.89	−2.11	−4.00	−1.52	−2.64	−4.17	−4.08
Benzaldehyde	−2.56	−3.08	−5.64	−2.56	−3.17	−5.73	−5.53
Propanone	−2.14	−0.86	−3.00	−2.23	−0.80	−3.02	−2.60
Butanone	−1.99	−1.64	−3.64	−2.07	−1.56	−3.64	−3.48
2-Hexanone	−1.85	−3.07	−4.92	−1.94	−2.95	−4.89	−4.68
3,3-Dimethylbutanone	−1.81	−2.23	−4.04	−1.87	−2.13	−4.00	−4.34
2-Heptanone	−1.89	−3.79	−5.68	−1.98	−3.66	−5.64	−5.36
Methyl phenyl ketone	−2.52	−3.89	−6.41	−2.48	−3.97	−6.45	−6.05
Ethanoic acid	−2.97	−0.21	−3.18	−2.98	−0.17	−3.16	−2.83
Propanoic acid	−2.73	−0.98	−3.70	−2.74	−0.92	−3.66	−2.98
Methyl ethanoate	−2.44	−0.44	−2.87	−2.29	−0.59	−2.88	−3.12
Methyl propanoate	−2.21	−1.20	−3.41	−2.07	−1.33	−3.40	−3.65
Ethyl ethanoate	−2.32	−1.43	−3.76	−2.20	−1.56	−3.76	−3.62
Propyl ethanoate	−2.25	−2.18	−4.43	−2.16	−2.28	−4.44	−4.10
Methyl pentanoate	−2.10	−2.63	−4.72	−1.98	−2.73	−4.71	−4.94
Butyl ethanoate	−2.22	−2.90	−5.12	−2.14	−2.99	−5.12	−4.86
Methyl hexanoate	−2.07	−3.36	−5.43	−1.96	−3.44	−5.40	−5.64
Pentyl ethanoate	−2.20	−3.63	−5.83	−2.12	−3.70	−5.82	−5.52

Table 18. (Cont.)

Solute	SM5.42R/AM1			SM5.42R/PM3			Expt.
	ΔG_{ENP}	G_{CDS}	ΔG_S^0	ΔG_{ENP}	G_{CDS}	ΔG_S^0	ΔG_S^0
p-Hydroxybenzaldehyde	−3.95	−2.32	−6.27	−3.91	−2.37	−6.28	−9.18
Ethylamine	−0.86	−1.57	−2.43	−0.72	−1.75	−2.47	−2.09
Propylamine	−0.82	−2.33	−3.15	−0.69	−2.49	−3.18	−3.13
Butylamine	−0.79	−3.06	−3.85	−0.67	−3.20	−3.86	−3.55
Pyridine	−1.98	−2.65	−4.62	−1.85	−2.88	−4.73	−3.81
Aniline	−1.96	−3.57	−5.53	−1.68	−3.91	−5.59	−5.43
Nitroethane	−1.95	−1.75	−3.71	−2.67	−1.06	−3.73	−3.19
1-Nitrobutane	−1.72	−3.20	−4.92	−2.51	−2.48	−4.99	−4.64
Nitrobenzene	−2.32	−3.85	−6.16	−2.73	−3.35	−6.08	−6.09
$OP(OCH_3)_3$	−4.82	0.29	−4.53	−2.69	−2.33	−5.02	−5.82
$OP(OC_2H_5)_3$	−4.48	−2.88	−7.37	−2.48	−5.39	−7.87	−6.78
$OP(OC_3H_7)_3$	−4.12	−5.14	−9.26	−2.25	−7.59	−9.84	−7.24
Fluorobenzene	−1.19	−3.03	−4.22	−1.09	−3.26	−4.34	−4.15
Trichloromethane	−0.56	−3.27	−3.83	−0.53	−3.22	−3.75	−3.17
Chlorobenzene	−1.05	−4.36	−5.41	−0.90	−4.48	−5.39	−5.14
p-Dichlorobenzene	−0.90	−5.07	−5.98	−0.78	−5.18	−5.96	−5.69
Tribromomethane	−0.28	−5.41	−5.69	−0.21	−5.52	−5.72	−4.38
Bromobenzene	−1.04	−5.06	−6.09	−0.88	−5.24	−6.11	−5.66
p-Bromophenol	−2.44	−4.29	−6.74	−2.22	−4.46	−6.68	−6.96
3,5-Dibromo-4-hydroxybenzonitrile	−2.71	−4.69	−7.40	−2.61	−4.82	−7.43	−9.67
Solvent: *n*-heptane							
Benzene	−1.07	−3.57	−4.64	−0.96	−3.72	−4.68	−4.00
Toluene	−1.10	−3.99	−5.09	−1.00	−4.13	−5.12	−4.78
o-Xylene	−1.16	−4.42	−5.58	−1.05	−4.54	−5.60	−5.52
m-Xylene	−1.13	−4.41	−5.54	−1.03	−4.53	−5.56	−5.67
p-Xylene	−1.12	−4.41	−5.53	−1.02	−4.53	−5.55	−5.52
Naphthalene	−1.74	−5.76	−7.51	−1.56	−5.99	−7.55	−7.02
Anthracene	−2.33	−7.95	−10.28	−2.10	−8.26	−10.35	−10.00
Methanol	−1.92	0.49	−1.43	−1.83	0.37	−1.46	−1.29
Ethanol	−1.83	−0.60	−2.43	−1.74	−0.68	−2.42	−2.15
1-Propanol	−1.74	−1.35	−3.09	−1.67	−1.41	−3.08	−3.01
1-Butanol	−1.60	−2.08	−3.68	−1.56	−2.13	−3.69	−3.66
1-Pentanol	−1.57	−2.80	−4.37	−1.54	−2.83	−4.37	−4.09
Phenol	−2.46	−2.83	−5.29	−2.28	−2.96	−5.23	−5.32
1-Hexanol	−1.58	−3.53	−5.11	−1.55	−3.57	−5.12	−4.89
o-Cresol	−2.42	−3.29	−5.71	−2.26	−3.41	−5.67	−6.01
m-Cresol	−2.48	−3.25	−5.73	−2.30	−3.37	−5.67	−5.01
p-Cresol	−2.46	−3.26	−5.72	−2.29	−3.39	−5.68	−5.77
1-Heptanol	−1.56	−4.25	−5.81	−1.54	−4.27	−5.81	−5.60
Anisole	−1.74	−3.07	−4.81	−1.43	−3.38	−4.81	−5.35
Benzaldehyde	−2.61	−2.99	−5.60	−2.61	−3.09	−5.70	−5.50
Propanone	−2.19	−0.78	−2.97	−2.27	−0.72	−3.00	−2.61
Butanone	−2.04	−1.56	−3.59	−2.11	−1.48	−3.60	−3.36
2-Pentanone	−1.96	−2.23	−4.20	−2.05	−2.14	−4.19	−4.07
2-Hexanone	−1.89	−2.96	−4.85	−1.98	−2.84	−4.82	−4.55
3,3-Dimethylbutanone	−1.85	−2.12	−3.97	−1.91	−2.02	−3.93	−4.30
2-Heptanone	−1.93	−3.67	−5.60	−2.02	−3.54	−5.56	−5.22
Methyl phenyl ketone	−2.57	−3.80	−6.37	−2.53	−3.88	−6.41	−6.14
2-Octanone	−1.92	−4.38	−6.29	−2.01	−4.23	−6.25	−5.68
Propanoic acid	−2.78	−0.89	−3.67	−2.80	−0.84	−3.64	−4.06
Butanoic acid	−2.68	−1.59	−4.26	−2.72	−1.52	−4.23	−5.05
Pentanoic acid	−2.66	−2.30	−4.96	−2.70	−2.21	−4.92	−5.23
Hexanoic acid	−2.64	−3.02	−5.65	−2.69	−2.91	−5.60	−6.54
Methyl ethanoate	−2.48	−0.35	−2.83	−2.33	−0.51	−2.84	−2.97
Methyl propanoate	−2.26	−1.10	−3.36	−2.11	−1.24	−3.35	−3.63
Ethyl ethanoate	−2.37	−1.33	−3.71	−2.25	−1.46	−3.71	−3.50
Propyl ethanoate	−2.29	−2.06	−4.36	−2.20	−2.17	−4.38	−4.09
Methyl pentanoate	−2.14	−2.50	−4.64	−2.02	−2.61	−4.63	−4.92
Butyl ethanoate	−2.26	−2.78	−5.04	−2.18	−2.87	−5.05	−4.83
Methyl hexanoate	−2.11	−3.22	−5.33	−2.00	−3.31	−5.31	−5.63
Pentyl ethanoate	−2.24	−3.50	−5.74	−2.17	−3.57	−5.73	−5.42
Ethylamine	−0.87	−1.51	−2.38	−0.74	−1.69	−2.43	−2.09
Propylamine	−0.83	−2.26	−3.09	−0.71	−2.42	−3.12	−3.03
Butylamine	−0.80	−2.98	−3.78	−0.68	−3.12	−3.79	−3.44

Table 18. (Cont.)

Solute	SM5.42R/AM1			SM5.42R/PM3			Expt.
	ΔG_{ENP}	G_{CDS}	ΔG_S^0	ΔG_{ENP}	G_{CDS}	ΔG_S^0	ΔG_S^0
Pyridine	−2.01	−2.58	−4.59	−1.89	−2.81	−4.71	−4.28
Aniline	−1.99	−3.50	−5.49	−1.72	−3.84	−5.56	−5.38
Ethanonitrile	−2.86	0.29	−2.57	−2.83	0.32	−2.51	−2.06
Benzonitrile	−2.34	−2.70	−5.04	−2.24	−2.80	−5.04	−5.33
Nitrobenzene	−2.37	−3.76	−6.13	−2.79	−3.27	−6.05	−6.14
$OP(OCH_3)_3$	−4.92	0.44	−4.48	−2.75	−2.21	−4.96	−5.59
$OP(OC_2H_5)_3$	−4.57	−2.71	−7.28	−2.53	−5.25	−7.78	−6.67
$OP(OC_3H_7)_3$	−4.20	−4.93	−9.13	−2.29	−7.42	−9.70	−7.50
Thiophene	−0.90	−3.14	−4.04	−0.86	−3.29	−4.15	−4.09
Fluorobenzene	−1.21	−2.96	−4.17	−1.11	−3.19	−4.30	−4.13
Chlorobenzene	−1.07	−4.29	−5.36	−0.92	−4.42	−5.34	−5.15
o-Dichlorobenzene	−1.17	−4.92	−6.09	−0.98	−5.04	−6.02	−6.01
p-Dichlorobenzene	−0.92	−5.00	−5.92	−0.79	−5.11	−5.90	−5.81
2,2′-Dichlorobiphenyl	−1.84	−8.12	−9.96	−1.58	−8.36	−9.94	−9.22
Bromobenzene	−1.06	−4.99	−6.04	−0.89	−5.17	−6.07	−5.72
p-Dibromobenzene	−0.88	−6.40	−7.28	−0.73	−6.62	−7.36	−7.55
Iodobenzene	−0.95	−5.55	−6.50	−0.84	−5.71	−6.55	−6.27
Solvent: *n*-octane							
Toluene	−1.12	−3.92	−5.04	−1.02	−4.06	−5.08	−4.82
Methanol	−1.95	0.54	−1.42	−1.86	0.41	−1.45	−1.29
Ethanol	−1.86	−0.54	−2.40	−1.77	−0.63	−2.40	−2.15
1-Propanol	−1.77	−1.28	−3.05	−1.71	−1.34	−3.05	−2.76
1-Butanol	−1.63	−2.00	−3.63	−1.59	−2.05	−3.64	−3.69
1-Pentanol	−1.60	−2.70	−4.31	−1.57	−2.74	−4.31	−4.10
Phenol	−2.50	−2.76	−5.27	−2.32	−2.89	−5.21	−5.47
1-Hexanol	−1.61	−3.43	−5.04	−1.58	−3.47	−5.05	−4.86
o-Cresol	−2.47	−3.21	−5.68	−2.30	−3.33	−5.63	−6.16
m-Cresol	−2.52	−3.17	−5.69	−2.35	−3.29	−5.64	−5.19
p-Cresol	−2.51	−3.18	−5.69	−2.33	−3.31	−5.64	−6.19
1-Heptanol	−1.59	−4.13	−5.72	−1.57	−4.16	−5.73	−5.56
Propanone	−2.23	−0.72	−2.95	−2.32	−0.66	−2.98	−2.46
Butanone	−2.08	−1.48	−3.56	−2.16	−1.41	−3.56	−3.24
2-Pentanone	−2.00	−2.15	−4.15	−2.09	−2.06	−4.15	−3.97
2-Hexanone	−1.93	−2.86	−4.79	−2.02	−2.75	−4.76	−4.60
3,3-Dimethylbutanone	−1.89	−2.01	−3.90	−1.95	−1.92	−3.87	−4.21
2-Heptanone	−1.97	−3.55	−5.52	−2.07	−3.43	−5.50	−5.25
Methyl ethanoate	−2.53	−0.27	−2.80	−2.38	−0.43	−2.81	−3.06
Methyl propanoate	−2.30	−1.01	−3.31	−2.15	−1.15	−3.31	−3.57
Ethyl ethanoate	−2.42	−1.25	−3.66	−2.29	−1.38	−3.67	−3.48
Propyl ethanoate	−2.34	−1.97	−4.31	−2.25	−2.08	−4.33	−4.09
Methyl pentanoate	−2.18	−2.39	−4.57	−2.06	−2.50	−4.56	−4.86
Butyl ethanoate	−2.31	−2.67	−4.97	−2.22	−2.76	−4.99	−4.80
Methyl hexanoate	−2.15	−3.10	−5.25	−2.04	−3.19	−5.23	−5.53
Pentyl ethanoate	−2.28	−3.38	−5.66	−2.21	−3.45	−5.66	−5.36
Ethylamine	−0.89	−1.46	−2.34	−0.75	−1.64	−2.39	−2.04
Propylamine	−0.85	−2.19	−3.04	−0.72	−2.35	−3.07	−3.00
Butylamine	−0.81	−2.90	−3.71	−0.69	−3.04	−3.73	−3.55
Diethylamine	−0.47	−2.92	−3.39	−0.41	−2.99	−3.40	−3.42
2-Methylpyrazine	−2.69	−2.03	−4.72	−2.27	−2.31	−4.59	−4.70
Aniline	−2.03	−3.43	−5.46	−1.75	−3.78	−5.53	−4.84
2-Ethylpyrazine	−2.48	−2.69	−5.18	−2.10	−2.96	−5.07	−5.51
1-Nitropropane	−1.84	−2.31	−4.16	−2.65	−1.60	−4.25	−3.95
Solvent: *n*-nonane							
Methanol	−1.97	0.58	−1.40	−1.88	0.45	−1.43	−1.29
Ethanol	−1.88	−0.50	−2.38	−1.80	−0.58	−2.38	−2.15
1-Propanol	−1.79	−1.22	−3.01	−1.73	−1.29	−3.01	−2.76
1-Butanol	−1.65	−1.93	−3.58	−1.61	−1.99	−3.60	−3.77
1-Pentanol	−1.62	−2.63	−4.25	−1.59	−2.67	−4.25	−3.92
Phenol	−2.53	−2.70	−5.24	−2.35	−2.83	−5.18	−5.60
1-Hexanol	−1.63	−3.34	−4.97	−1.60	−3.39	−4.99	−4.97
o-Cresol	−2.50	−3.14	−5.63	−2.33	−3.26	−5.59	−6.20
1-Heptanol	−1.61	−4.04	−5.65	−1.59	−4.07	−5.65	−5.62
Butanone	−2.10	−1.42	−3.52	−2.18	−1.34	−3.53	−3.20

Table 18. (Cont.)

Solute	SM5.42R/AM1			SM5.42R/PM3			Expt.
	ΔG_{ENP}	G_{CDS}	ΔG_S^0	ΔG_{ENP}	G_{CDS}	ΔG_S^0	ΔG_S^0
2-Pentanone	−2.03	−2.07	−4.10	−2.12	−1.98	−4.10	−3.97
2-Hexanone	−1.96	−2.78	−4.73	−2.04	−2.67	−4.71	−4.59
3,3-Dimethylbutanone	−1.91	−1.93	−3.84	−1.97	−1.83	−3.81	−4.19
2-Heptanone	−2.00	−3.46	−5.46	−2.09	−3.34	−5.43	−5.24
Methyl ethanoate	−2.56	−0.21	−2.77	−2.40	−0.37	−2.78	−3.02
Methyl propanoate	−2.33	−0.94	−3.27	−2.18	−1.08	−3.26	−3.50
Ethyl ethanoate	−2.44	−1.18	−3.62	−2.32	−1.31	−3.63	−3.45
Propyl ethanoate	−2.37	−1.89	−4.25	−2.27	−2.00	−4.27	−4.07
Methyl pentanoate	−2.20	−2.30	−4.50	−2.08	−2.42	−4.50	−4.85
Butyl ethanoate	−2.33	−2.58	−4.91	−2.25	−2.68	−4.93	−4.69
Methyl hexanoate	−2.18	−3.00	−5.17	−2.06	−3.09	−5.15	−5.51
Pentyl ethanoate	−2.31	−3.27	−5.58	−2.24	−3.35	−5.59	−5.33
Ethylamine	−0.90	−1.41	−2.31	−0.76	−1.59	−2.35	−1.98
Propylamine	−0.86	−2.14	−3.00	−0.73	−2.30	−3.03	−2.96
Butylamine	−0.82	−2.83	−3.66	−0.70	−2.98	−3.68	−3.55
Solvent: *n*-decane							
n-Octane	0.02	−4.98	−4.96	0.02	−4.88	−4.86	−5.18
Benzene	−1.12	−3.42	−4.55	−1.01	−3.58	−4.59	−3.80
Toluene	−1.16	−3.81	−4.96	−1.05	−3.95	−5.00	−4.65
Ethylbenzene	−1.06	−4.43	−5.49	−0.96	−4.56	−5.53	−5.25
Methanol	−2.00	0.61	−1.40	−1.91	0.48	−1.43	−1.29
Ethanol	−1.91	−0.46	−2.37	−1.83	−0.54	−2.37	−2.44
1-Propanol	−1.82	−1.17	−2.99	−1.75	−1.24	−3.00	−2.76
1-Butanol	−1.67	−1.88	−3.55	−1.63	−1.94	−3.57	−3.77
1-Pentanol	−1.65	−2.56	−4.21	−1.61	−2.61	−4.22	−3.92
Phenol	−2.58	−2.65	−5.23	−2.39	−2.79	−5.17	−5.50
1-Hexanol	−1.65	−3.27	−4.92	−1.63	−3.32	−4.95	−4.97
p-Cresol	−2.58	−3.05	−5.63	−2.40	−3.18	−5.58	−6.00
1-Heptanol	−1.64	−3.96	−5.59	−1.61	−3.99	−5.60	−5.62
1,4-Dioxane	−2.02	−1.85	−3.86	−1.63	−2.40	−4.03	−3.97
Propanone	−2.30	−0.62	−2.92	−2.39	−0.56	−2.95	−2.47
Butanone	−2.14	−1.36	−3.50	−2.23	−1.29	−3.52	−3.30
2-Pentanone	−2.07	−2.01	−4.08	−2.16	−1.92	−4.08	−3.93
2-Hexanone	−1.99	−2.71	−4.70	−2.08	−2.60	−4.68	−4.61
3,3-Dimethylbutanone	−1.95	−1.86	−3.80	−2.01	−1.76	−3.77	−4.15
2-Heptanone	−2.03	−3.38	−5.41	−2.13	−3.26	−5.39	−5.18
Methyl ethanoate	−2.61	−0.15	−2.76	−2.45	−0.32	−2.77	−2.98
Methyl propanoate	−2.37	−0.88	−3.25	−2.22	−1.03	−3.24	−3.49
Ethyl ethanoate	−2.49	−1.12	−3.60	−2.36	−1.25	−3.61	−3.43
Propyl ethanoate	−2.41	−1.82	−4.23	−2.31	−1.94	−4.25	−4.02
Methyl pentanoate	−2.24	−2.22	−4.47	−2.12	−2.34	−4.46	−4.77
Butyl ethanoate	−2.37	−2.50	−4.88	−2.29	−2.60	−4.89	−4.66
Methyl hexanoate	−2.22	−2.91	−5.13	−2.10	−3.01	−5.11	−5.48
Pentyl ethanoate	−2.35	−3.19	−5.54	−2.27	−3.27	−5.55	−5.31
Ethylamine	−0.91	−1.37	−2.28	−0.77	−1.55	−2.33	−1.92
Propylamine	−0.87	−2.09	−2.96	−0.74	−2.26	−3.00	−2.96
Butylamine	−0.84	−2.78	−3.62	−0.71	−2.93	−3.63	−3.55
Ethanamide	−3.79	0.01	−3.78	−3.56	−0.14	−3.70	−2.85
Fluorobenzene	−1.27	−2.79	−4.06	−1.16	−3.03	−4.19	−3.48
Trichloroethene	−0.41	−2.87	−3.27	−0.36	−2.89	−3.25	−3.84
Chlorobenzene	−1.12	−4.12	−5.24	−0.97	−4.26	−5.22	−4.93
Bromobenzene	−1.11	−4.82	−5.93	−0.94	−5.02	−5.96	−5.43
Solvent: *n*-undecane							
Benzene	−1.12	−3.48	−4.60	−1.01	−3.64	−4.65	−4.05
Toluene	−1.16	−3.86	−5.02	−1.05	−4.01	−5.06	−4.81
Ethylbenzene	−1.06	−4.49	−5.55	−0.96	−4.63	−5.59	−5.44
Trichloromethane	−0.59	−3.12	−3.72	−0.56	−3.08	−3.65	−3.42
1,1,1-Trichloroethane	−0.74	−3.66	−4.40	−0.63	−3.61	−4.24	−3.82
E-1,2-Dichloroethene	−0.47	−1.99	−2.46	−0.52	−2.03	−2.54	−3.60
Trichloroethene	−0.41	−2.90	−3.31	−0.36	−2.93	−3.29	−3.87
Chlorobenzene	−1.12	−4.18	−5.30	−0.97	−4.32	−5.29	−5.12
o-Dichlorobenzene	−1.23	−4.81	−6.04	−1.03	−4.94	−5.97	−6.11
Tribromomethane	−0.30	−5.32	−5.62	−0.22	−5.44	−5.67	−4.84
Tetrachloroethene	0.00	−3.76	−3.76	0.00	−3.77	−3.77	−4.63

Table 18. (Cont.)

Solute	SM5.42R/AM1			SM5.42R/PM3			Expt.
	ΔG_{ENP}	G_{CDS}	ΔG_S^0	ΔG_{ENP}	G_{CDS}	ΔG_S^0	ΔG_S^0
Solvent: *n*-dodecane							
Ethanol	−1.93	−0.40	−2.33	−1.85	−0.49	−2.33	−2.06
1-Propanol	−1.84	−1.11	−2.95	−1.77	−1.18	−2.95	−2.74
1-Butanol	−1.69	−1.80	−3.49	−1.65	−1.86	−3.51	−3.47
1-Pentanol	−1.67	−2.47	−4.14	−1.63	−2.52	−4.15	−4.09
1-Hexanol	−1.67	−3.17	−4.84	−1.64	−3.22	−4.87	−4.28
1-Heptanol	−1.65	−3.85	−5.50	−1.63	−3.88	−5.51	−5.41
Methyl phenyl ketone	−2.73	−3.48	−6.22	−2.69	−3.58	−6.27	−6.11
Solvent: *n*-pentadecane							
Methyl ethanoate	−2.67	0.01	−2.65	−2.50	−0.16	−2.66	−2.82
Methyl propanoate	−2.42	−0.69	−3.11	−2.27	−0.84	−3.11	−3.35
Ethyl ethanoate	−2.54	−0.93	−3.47	−2.41	−1.07	−3.49	−3.37
Propyl ethanoate	−2.46	−1.60	−4.07	−2.37	−1.73	−4.10	−3.91
Methyl pentanoate	−2.29	−1.98	−4.28	−2.16	−2.11	−4.27	−4.59
Butyl ethanoate	−2.43	−2.26	−4.69	−2.34	−2.37	−4.72	−4.49
Methyl hexanoate	−2.27	−2.64	−4.91	−2.14	−2.75	−4.90	−5.35
Pentyl ethanoate	−2.40	−2.93	−5.33	−2.33	−3.02	−5.35	−5.18
Solvent: *n*-hexadecane							
Methane	−0.03	0.59	0.56	−0.01	0.55	0.54	0.45
Ethane	−0.06	−0.67	−0.73	−0.03	−0.69	−0.72	−0.67
Propane	−0.07	−1.40	−1.47	−0.04	−1.40	−1.44	−1.43
n-Butane	−0.05	−2.06	−2.12	−0.04	−2.04	−2.07	−2.20
n-Pentane	−0.04	−2.72	−2.76	−0.02	−2.68	−2.71	−2.95
n-Hexane	−0.02	−3.38	−3.40	−0.01	−3.33	−3.33	−3.64
n-Heptane	0.00	−4.04	−4.04	0.01	−3.97	−3.96	−4.33
n-Octane	0.02	−4.70	−4.68	0.02	−4.61	−4.59	−5.02
n-Hexadecane	0.18	−9.97	−9.79	0.15	−9.76	−9.61	−10.52
2-Methylpropane	−0.06	−1.76	−1.82	−0.04	−1.74	−1.78	−1.92
2,2-Dimethylpropane	−0.07	−1.94	−2.01	−0.05	−1.91	−1.96	−2.48
2-Methylpentane	−0.02	−2.93	−2.95	−0.01	−2.89	−2.90	−3.48
2,4-Dimethylpentane	0.02	−3.23	−3.21	0.02	−3.17	−3.15	−3.87
2,2,4-Trimethylpentane	0.02	−3.43	−3.40	0.02	−3.36	−3.34	−4.24
Cyclopropane	−0.25	−2.23	−2.48	−0.20	−2.26	−2.47	−1.78
Cyclopentane	−0.14	−3.32	−3.46	−0.10	−3.28	−3.38	−3.38
Cyclohexane	−0.09	−3.98	−4.06	−0.06	−3.90	−3.96	−4.04
Methylcyclohexane	−0.04	−4.21	−4.25	−0.03	−4.13	−4.15	−4.43
Ethene	−0.26	0.09	−0.17	−0.21	−0.01	−0.21	−0.39
Propene	−0.32	−0.85	−1.17	−0.27	−0.92	−1.19	−1.29
s-trans-1,3-Butadiene	−0.51	−0.98	−1.49	−0.43	−1.13	−1.56	−2.10
1-Butene	−0.27	−1.50	−1.77	−0.23	−1.56	−1.79	−2.03
1-Pentene	−0.24	−2.16	−2.40	−0.21	−2.20	−2.41	−2.79
1-Hexene	−0.22	−2.82	−3.04	−0.20	−2.85	−3.04	−3.51
Ethyne	−1.18	1.12	−0.06	−1.13	1.07	−0.07	−0.20
Propyne	−1.43	−0.15	−1.58	−1.36	−0.19	−1.55	−1.40
1-Butyne	−1.30	−0.79	−2.09	−1.24	−0.82	−2.05	−2.07
1-Pentyne	−1.21	−1.45	−2.66	−1.16	−1.47	−2.63	−2.74
1-Hexyne	−1.19	−2.11	−3.30	−1.15	−2.11	−3.26	−3.42
Benzene	−1.17	−3.29	−4.45	−1.05	−3.45	−4.50	−3.80
Toluene	−1.20	−3.64	−4.84	−1.09	−3.79	−4.88	−4.54
Ethylbenzene	−1.10	−4.23	−5.33	−1.00	−4.37	−5.37	−5.15
o-Xylene	−1.26	−4.01	−5.27	−1.15	−4.15	−5.30	−5.37
m-Xylene	−1.23	−3.98	−5.22	−1.12	−4.13	−5.25	−5.24
p-Xylene	−1.23	−3.98	−5.21	−1.12	−4.13	−5.25	−5.24
Naphthalene	−1.90	−5.38	−7.28	−1.71	−5.63	−7.34	−7.29
Anthracene	−2.54	−7.46	−10.00	−2.29	−7.80	−10.09	−10.32
Chrysene	−3.19	−9.29	−12.48	−2.89	−9.74	−12.64	−14.10
Methanol	−2.08	0.73	−1.35	−1.99	0.60	−1.39	−1.32
Ethanol	−1.98	−0.32	−2.30	−1.89	−0.41	−2.30	−2.03
1,2-Ethanediol	−2.87	−0.46	−3.32	−2.81	−0.71	−3.52	−2.81
1-Propanol	−1.89	−1.01	−2.89	−1.82	−1.08	−2.90	−2.77
2-Propanol	−1.58	−0.88	−2.46	−1.56	−0.96	−2.52	−2.47
1-Butanol	−1.73	−1.68	−3.41	−1.69	−1.75	−3.44	−3.55
2-Methyl-2-Propanol	−1.55	−1.14	−2.69	−1.51	−1.20	−2.71	−2.74
Cyclopentanol	−1.49	−2.74	−4.23	−1.46	−2.80	−4.26	−4.42

Table 18. (Cont.)

Solute	SM5.42R/AM1			SM5.42R/PM3			Expt.
	ΔG_{ENP}	G_{CDS}	ΔG_S^0	ΔG_{ENP}	G_{CDS}	ΔG_S^0	ΔG_S^0
1-Pentanol	−1.71	−2.34	−4.05	−1.67	−2.39	−4.06	−4.24
Phenol	−2.67	−2.48	−5.16	−2.48	−2.62	−5.10	−5.14
1-Hexanol	−1.71	−3.02	−4.73	−1.69	−3.08	−4.76	−4.92
o-Cresol	−2.64	−2.88	−5.51	−2.46	−3.01	−5.47	−5.78
m-Cresol	−2.69	−2.84	−5.53	−2.50	−2.97	−5.48	−5.91
p-Cresol	−2.68	−2.85	−5.52	−2.49	−2.99	−5.48	−5.88
1-Heptanol	−1.70	−3.68	−5.38	−1.67	−3.72	−5.39	−5.62
1-Octanol	−1.65	−4.31	−5.96	−1.63	−4.32	−5.94	−6.30
1-Decanol	−1.74	−5.62	−7.36	−1.71	−5.58	−7.29	−7.68
Dimethyl ether	−1.21	0.47	−0.73	−0.96	0.16	−0.80	−1.49
Tetrahydrofuran	−1.37	−1.96	−3.33	−1.13	−2.23	−3.37	−3.60
1,4-Dioxane	−2.09	−1.67	−3.76	−1.69	−2.24	−3.93	−3.82
Diethyl ether	−1.03	−1.46	−2.49	−0.83	−1.71	−2.54	−2.81
1,2-Dimethoxyethane	−1.70	−0.29	−1.99	−1.34	−0.84	−2.18	−3.63
Anisole	−1.90	−2.65	−4.55	−1.56	−2.98	−4.54	−5.35
Tetrahydropyran	−1.08	−2.72	−3.80	−0.89	−2.95	−3.84	−4.08
Isopropyl ether	−0.81	−2.39	−3.20	−0.68	−2.61	−3.29	−4.02
Ethyl phenyl ether	−1.75	−3.57	−5.32	−1.45	−3.88	−5.33	−5.64
Formaldehyde	−2.68	1.73	−0.94	−2.77	1.74	−1.03	−0.99
Ethanal	−2.48	0.34	−2.15	−2.62	0.37	−2.24	−1.68
Propanal	−2.33	−0.40	−2.73	−2.44	−0.35	−2.79	−2.48
Butanal	−2.25	−1.03	−3.28	−2.38	−0.96	−3.34	−3.10
Pentanal	−2.22	−1.68	−3.89	−2.40	−1.59	−3.99	−3.89
Benzaldehyde	−2.85	−2.59	−5.45	−2.85	−2.71	−5.56	−5.44
Octanal	−2.18	−3.66	−5.84	−2.32	−3.53	−5.85	−5.98
Propanone	−2.39	−0.45	−2.85	−2.49	−0.40	−2.89	−2.31
Butanone	−2.23	−1.18	−3.40	−2.32	−1.11	−3.43	−3.12
Cyclopentanone	−2.13	−2.37	−4.50	−2.25	−2.28	−4.53	−4.39
2-Pentanone	−2.15	−1.79	−3.94	−2.25	−1.71	−3.96	−3.76
3-Pentanone	−2.06	−1.89	−3.96	−2.15	−1.82	−3.96	−3.83
2-Hexanone	−2.07	−2.46	−4.54	−2.17	−2.36	−4.53	−4.45
3,3-Dimethylbutanone	−2.03	−1.61	−3.63	−2.09	−1.52	−3.61	−3.94
2-Heptanone	−2.12	−3.11	−5.23	−2.22	−3.00	−5.22	−5.13
4-Heptanone	−1.90	−3.13	−5.03	−2.00	−3.02	−5.03	−5.20
Methyl phenyl ketone	−2.81	−3.35	−6.17	−2.77	−3.46	−6.22	−6.14
5-Nonanone	−1.87	−4.45	−6.32	−1.99	−4.31	−6.29	−6.46
2-Octanone	−2.10	−3.77	−5.87	−2.21	−3.64	−5.84	−5.81
Ethanoic acid	−3.29	0.17	−3.12	−3.31	0.19	−3.11	−2.39
Propanoic acid	−3.02	−0.53	−3.55	−3.04	−0.49	−3.53	−3.12
Butanoic acid	−2.91	−1.17	−4.08	−2.95	−1.11	−4.06	−3.86
Pentanoic acid	−2.89	−1.82	−4.71	−2.94	−1.75	−4.69	−4.61
Hexanoic acid	−2.87	−2.48	−5.35	−2.92	−2.39	−5.31	−5.35
Methyl methanoate	−2.91	1.17	−1.74	−2.81	0.98	−1.82	−1.99
Ethyl methanoate	−2.78	0.22	−2.56	−2.71	0.06	−2.65	−2.59
Methyl ethanoate	−2.71	0.03	−2.67	−2.54	−0.14	−2.68	−2.67
Methyl propanoate	−2.46	−0.66	−3.12	−2.30	−0.82	−3.12	−2.68
Ethyl ethanoate	−2.58	−0.91	−3.49	−2.45	−1.05	−3.50	−3.25
Methyl butanoate	−2.35	−1.30	−3.65	−2.21	−1.44	−3.65	−4.01
Propyl ethanoate	−2.50	−1.58	−4.08	−2.40	−1.71	−4.11	−3.93
Methyl pentanoate	−2.33	−1.95	−4.28	−2.20	−2.08	−4.28	−4.69
Butyl ethanoate	−2.47	−2.24	−4.70	−2.38	−2.35	−4.72	−4.61
Methyl hexanoate	−2.30	−2.61	−4.91	−2.18	−2.72	−4.90	−5.43
Pentyl ethanoate	−2.44	−2.89	−5.34	−2.36	−2.99	−5.35	−5.20
Ethyloctadecanoate	−1.95	−11.46	−13.42	−1.91	−11.36	−13.27	−13.69
Methyl benzoate	−2.80	−2.78	−5.58	−2.55	−3.09	−5.64	−6.31
2-Propen-1-ol	−1.78	−0.45	−2.23	−1.70	−0.62	−2.33	−2.73
Water	−3.63	3.83	0.20	−3.51	3.69	0.18	−0.35
Hydrogen	0.00	1.70	1.70	0.00	1.69	1.69	1.64
Ethylamine	−0.94	−1.24	−2.18	−0.80	−1.43	−2.23	−2.29
Dimethylamine	−0.92	−1.26	−2.18	−0.76	−1.42	−2.18	−2.18
Propylamine	−0.90	−1.93	−2.83	−0.77	−2.10	−2.87	−2.92
Trimethylamine	−0.87	−1.88	−2.75	−0.67	−1.96	−2.62	−2.21
Butylamine	−0.86	−2.59	−3.46	−0.73	−2.75	−3.48	−3.57
Diethylamine	−0.50	−2.61	−3.11	−0.43	−2.70	−3.13	−3.27

Table 18. (Cont.)

Solute	SM5.42R/AM1			SM5.42R/PM3			Expt.
	ΔG_{ENP}	G_{CDS}	ΔG_S^0	ΔG_{ENP}	G_{CDS}	ΔG_S^0	ΔG_S^0
Pentylamine	−0.84	−3.25	−4.09	−0.71	−3.39	−4.10	−4.28
Dipropylamine	−0.41	−3.98	−4.39	−0.39	−4.03	−4.41	−4.57
Pyridine	−2.20	−2.28	−4.47	−2.07	−2.53	−4.60	−4.10
Aniline	−2.16	−3.15	−5.31	−1.86	−3.52	−5.38	−5.44
2-Methylpyridine	−2.23	−2.72	−4.95	−2.07	−2.94	−5.01	−4.68
3-Methylpyridine	−2.16	−2.63	−4.79	−2.03	−2.87	−4.90	−4.91
4-Methylpyridine	−2.19	−2.63	−4.82	−2.07	−2.87	−4.94	−4.89
N-Methylaniline	−1.88	−3.80	−5.68	−1.61	−4.11	−5.72	−6.19
2,4-Dimethylpyridine	−2.22	−3.08	−5.30	−2.06	−3.29	−5.35	−5.52
2,5-Dimethylpyridine	−2.18	−3.09	−5.27	−2.02	−3.29	−5.31	−5.52
2,6-Dimethylpyridine	−2.24	−3.20	−5.45	−2.07	−3.39	−5.46	−5.27
Ethanonitrile	−3.14	0.56	−2.57	−3.10	0.58	−2.52	−2.37
Propanonitrile	−2.81	−0.09	−2.89	−2.78	−0.04	−2.82	−2.84
Butanonitrile	−2.64	−0.75	−3.39	−2.62	−0.69	−3.31	−3.48
Benzonitrile	−2.56	−2.31	−4.87	−2.44	−2.42	−4.87	−5.51
Nitroethane	−2.18	−1.36	−3.55	−2.96	−0.65	−3.62	−3.29
1-Nitropropane	−1.98	−2.01	−3.99	−2.83	−1.30	−4.13	−3.95
2-Nitropropane	−2.04	−1.74	−3.78	−2.66	−1.02	−3.69	−3.47
1-Nitrobutane	−1.92	−2.67	−4.59	−2.79	−1.94	−4.73	−4.66
Nitrobenzene	−2.59	−3.38	−5.97	−3.04	−2.89	−5.92	−6.22
2-Methyl-1-nitrobenzene	−2.57	−3.77	−6.34	−2.86	−3.29	−6.15	−6.52
Ethanamide	−3.94	0.18	−3.76	−3.70	0.01	−3.69	−3.33
Ammonia	−1.63	0.36	−1.28	−1.25	0.07	−1.18	−0.93
Dimethyl methylphosphonate	−4.61	1.26	−3.35	−2.58	−1.16	−3.74	−5.43
Ethanethiol	−0.66	−1.98	−2.63	−0.50	−2.00	−2.50	−2.96
1-Propanethiol	−0.56	−2.66	−3.22	−0.42	−2.67	−3.09	−3.66
Thiophenol	−1.13	−4.28	−5.41	−1.13	−4.46	−5.59	−5.61
Thiophene	−0.98	−2.87	−3.86	−0.93	−3.04	−3.97	−4.01
Dimethyl sulfide	−0.92	−1.48	−2.40	−0.73	−1.53	−2.26	−3.05
Diethyl sulfide	−0.84	−3.29	−4.13	−0.68	−3.30	−3.98	−4.23
Dipropyl sulfide	−0.66	−4.67	−5.33	−0.52	−4.64	−5.16	−5.61
Hydrogen sulfide	−0.29	−0.75	−1.05	−0.28	−0.78	−1.06	−0.72
Dimethyl disulfide	−1.44	−2.83	−4.27	−1.21	−3.12	−4.33	−4.84
Diethyl disulfide	−1.24	−4.50	−5.73	−1.04	−4.73	−5.77	−5.74
Fluoroethane	−0.95	−0.25	−1.19	−0.76	−0.34	−1.10	−0.76
Fluorobenzene	−1.32	−2.62	−3.95	−1.21	−2.88	−4.09	−4.03
1-Fluorohexane	−0.80	−2.92	−3.73	−0.65	−2.95	−3.60	−4.03
1-Fluorooctane	−0.77	−4.24	−5.00	−0.62	−4.23	−4.85	−5.25
Dichloromethane	−1.00	−1.85	−2.85	−1.07	−1.83	−2.91	−2.76
Trichloromethane	−0.62	−2.95	−3.57	−0.59	−2.92	−3.50	−3.38
Chloroethane	−0.82	−1.67	−2.49	−0.96	−1.66	−2.62	−2.29
1,1,1-Trichloroethane	−0.77	−3.45	−4.22	−0.65	−3.41	−4.06	−3.73
1,1,2-Trichloroethane	−1.09	−3.57	−4.66	−1.18	−3.52	−4.70	−4.49
1-Chloropropane	−0.70	−2.37	−3.07	−0.84	−2.35	−3.18	−2.86
2-Chloropropane	−0.79	−2.22	−3.01	−0.91	−2.19	−3.10	−2.69
3-Chloropropene	−0.80	−1.78	−2.59	−0.89	−1.84	−2.73	−2.88
Z-1,2-Dichloroethene	−0.97	−1.80	−2.77	−0.94	−1.85	−2.79	−3.33
E-1,2-Dichloroethene	−0.49	−1.82	−2.31	−0.54	−1.87	−2.40	−3.11
Trichloroethene	−0.42	−2.71	−3.14	−0.38	−2.74	−3.12	−4.08
Chlorobenzene	−1.17	−3.96	−5.13	−1.00	−4.11	−5.11	−4.99
o-Dichlorobenzene	−1.28	−4.56	−5.84	−1.07	−4.70	−5.77	−6.16
p-Dichlorobenzene	−1.00	−4.63	−5.63	−0.86	−4.76	−5.62	−6.02
Dibromomethane	−0.68	−3.32	−4.00	−0.60	−3.42	−4.02	−3.94
Tribromomethane	−0.32	−5.12	−5.43	−0.23	−5.25	−5.47	−5.16
Bromoethane	−0.68	−2.40	−3.08	−0.76	−2.45	−3.21	−2.89
1-Bromopropane	−0.57	−3.10	−3.67	−0.63	−3.12	−3.75	−3.57
2-Bromopropane	−0.64	−2.94	−3.58	−0.75	−2.97	−3.72	−3.26
3-Bromopropene	−0.69	−2.47	−3.16	−0.71	−2.59	−3.31	−3.42
1-Bromobutane	−0.55	−3.75	−4.30	−0.60	−3.76	−4.37	−4.24
1-Bromo-2-methylpropane	−0.48	−3.29	−3.77	−0.56	−3.30	−3.86	−4.04
1-Bromopentane	−0.52	−4.41	−4.93	−0.58	−4.41	−4.99	−4.93
Bromobenzene	−1.15	−4.67	−5.82	−0.97	−4.87	−5.85	−5.51
Bromotoluene	−1.63	−5.17	−6.79	−1.57	−5.36	−6.93	−6.36
p-Bromotoluene	−1.24	−4.98	−6.22	−1.07	−5.17	−6.24	−6.19

Table 18. (Cont.)

Solute	SM5.42R/AM1			SM5.42R/PM3			Expt.
	ΔG_{ENP}	G_{CDS}	ΔG_S^0	ΔG_{ENP}	G_{CDS}	ΔG_S^0	ΔG_S^0
Diiodomethane	−0.49	−4.44	−4.94	−0.26	−4.49	−4.75	−5.26
Iodomethane	−0.65	−1.94	−2.59	−0.57	−1.98	−2.56	−2.88
Iodoethane	−0.60	−2.96	−3.55	−0.69	−2.98	−3.67	−3.51
3-Iodopropene	−0.58	−3.07	−3.65	−0.57	−3.16	−3.73	−4.10
1-Iodopropane	−0.50	−3.65	−4.16	−0.54	−3.66	−4.20	−4.27
1-Iodobutane	−0.48	−4.31	−4.79	−0.51	−4.30	−4.80	−4.95
1-Iodopentane	−0.45	−4.97	−5.42	−0.48	−4.94	−5.42	−5.63
Iodobenzene	−1.04	−5.22	−6.26	−0.91	−5.40	−6.32	−6.25
Bromotrichloromethane	0.00	−4.50	−4.50	−0.05	−4.50	−4.55	−4.46
1-Bromo-1-chloro-2,2,2-trifluoroethane	−0.69	−1.96	−2.65	−0.54	−2.22	−2.76	−2.97
1-Bromo-1,2,2,2-tetrafluoroethane	−1.03	−0.59	−1.62	−0.77	−0.96	−1.73	−1.87
Tetrachloroethene	0.00	−3.54	−3.54	0.00	−3.56	−3.56	−4.88
1,1,2-Trichloro-1,2,2-trifluoroethane	−0.12	−2.12	−2.25	−0.14	−2.31	−2.46	−2.89
2,2,2-Trifluoroethanol	−3.17	1.01	−2.16	−2.90	0.68	−2.22	−1.67
1,1-Dichloro-2,2-difluoroethyl methyl ether	−1.48	−1.25	−2.73	−1.17	−1.50	−2.67	−3.90
2,2,2-Trifluoroethyl vinyl ether	−1.71	0.77	−0.94	−1.36	0.29	−1.07	−1.91
Solvent: isooctane							
n-Pentane	−0.04	−3.44	−3.47	−0.02	−3.38	−3.40	−3.21
n-Hexane	−0.02	−4.21	−4.23	−0.01	−4.13	−4.14	−3.08
n-Octane	0.02	−5.76	−5.75	0.02	−5.65	−5.63	−5.44
Propene	−0.30	−1.28	−1.58	−0.25	−1.34	−1.59	−1.61
1-Butene	−0.25	−2.05	−2.30	−0.22	−2.09	−2.31	−2.26
1-Pentene	−0.23	−2.82	−3.05	−0.20	−2.85	−3.05	−2.36
Benzene	−1.09	−3.87	−4.96	−0.98	−4.02	−5.00	−4.01
Toluene	−1.12	−4.33	−5.46	−1.02	−4.47	−5.49	−4.68
m-Xylene	−1.15	−4.80	−5.95	−1.05	−4.92	−5.97	−5.12
Ethanol	−1.86	−0.73	−2.59	−1.77	−0.81	−2.59	−2.44
1-Propanol	−1.77	−1.54	−3.31	−1.71	−1.60	−3.30	−3.00
1-Butanol	−1.63	−2.33	−3.96	−1.59	−2.38	−3.97	−3.56
1-Pentanol	−1.60	−3.10	−4.71	−1.57	−3.13	−4.70	−4.17
Phenol	−2.50	−3.11	−5.61	−2.32	−3.23	−5.55	−5.30
1-Hexanol	−1.61	−3.90	−5.51	−1.58	−3.94	−5.52	−5.10
o-Cresol	−2.47	−3.61	−6.08	−2.30	−3.73	−6.03	−5.68
p-Cresol	−2.51	−3.59	−6.09	−2.33	−3.71	−6.04	−5.59
1,4-Dioxane	−1.96	−2.27	−4.22	−1.58	−2.82	−4.41	−4.02
Butanal	−2.10	−1.62	−3.72	−2.21	−1.54	−3.75	−3.45
Pentanal	−2.07	−2.39	−4.46	−2.24	−2.29	−4.52	−4.24
Propanone	−2.23	−0.94	−3.16	−2.32	−0.87	−3.19	−2.44
Butanone	−2.08	−1.77	−3.85	−2.16	−1.69	−3.84	−3.40
2-Pentanone	−2.00	−2.50	−4.51	−2.09	−2.40	−4.50	−4.14
2-Hexanone	−1.93	−3.29	−5.22	−2.02	−3.17	−5.18	−4.72
Methyl benzoate	−2.62	−3.62	−6.25	−2.39	−3.92	−6.30	−6.71
Aniline	−2.03	−3.81	−5.84	−1.75	−4.17	−5.91	−5.20
1-Nitropropane	−1.84	−2.64	−4.49	−2.65	−1.90	−4.55	−3.94
Ethanethiol	−0.61	−2.47	−3.08	−0.47	−2.47	−2.94	−3.13
1-Propanethiol	−0.52	−3.27	−3.79	−0.39	−3.26	−3.65	−3.78
Trichloromethane	−0.58	−3.48	−4.06	−0.55	−3.43	−3.98	−3.06
Solvent: cyclohexane							
Propane	−0.07	−1.51	−1.57	−0.04	−1.50	−1.54	−2.09
n-Butane	−0.05	−2.19	−2.25	−0.03	−2.17	−2.20	−2.86
n-Pentane	−0.04	−2.88	−2.91	−0.02	−2.83	−2.86	−3.50
n-Octane	0.02	−4.92	−4.91	0.02	−4.83	−4.81	−5.63
Cyclohexane	−0.08	−4.12	−4.21	−0.06	−4.04	−4.11	−4.43
Benzene	−1.14	−3.40	−4.55	−1.03	−3.56	−4.59	−4.19
Toluene	−1.18	−3.78	−4.95	−1.06	−3.93	−4.99	−4.90
Ethylbenzene	−1.08	−4.40	−5.47	−0.98	−4.53	−5.51	−4.97
o-Xylene	−1.23	−4.17	−5.41	−1.12	−4.31	−5.44	−5.54
m-Xylene	−1.21	−4.15	−5.36	−1.10	−4.29	−5.39	−5.52
Naphthalene	−1.86	−5.54	−7.40	−1.67	−5.79	−7.46	−7.17
Methanol	−2.04	0.65	−1.39	−1.95	0.52	−1.42	−1.29
Ethanol	−1.94	−0.42	−2.36	−1.85	−0.51	−2.36	−2.59
1-Propanol	−1.85	−1.13	−2.98	−1.78	−1.20	−2.98	−2.73
2-Propanol	−1.55	−1.00	−2.56	−1.52	−1.08	−2.60	−2.37

Table 18. (Cont.)

Solute	SM5.42R/AM1			SM5.42R/PM3			Expt.
	ΔG_{ENP}	G_{CDS}	ΔG_S^0	ΔG_{ENP}	G_{CDS}	ΔG_S^0	ΔG_S^0
1-Butanol	−1.70	−1.83	−3.53	−1.66	−1.89	−3.55	−3.52
2-Methyl-2-propanol	−1.52	−1.29	−2.81	−1.48	−1.34	−2.82	−2.93
1-Pentanol	−1.67	−2.51	−4.18	−1.64	−2.56	−4.20	−3.61
Phenol	−2.62	−2.62	−5.24	−2.43	−2.75	−5.18	−5.57
1-Hexanol	−1.68	−3.21	−4.89	−1.65	−3.27	−4.92	−5.31
o-Cresol	−2.58	−3.04	−5.62	−2.41	−3.17	−5.57	−6.02
m-Cresol	−2.64	−3.00	−5.63	−2.45	−3.13	−5.58	−5.20
p-Cresol	−2.62	−3.01	−5.63	−2.44	−3.14	−5.58	−5.89
1-Heptanol	−1.66	−3.90	−5.56	−1.64	−3.93	−5.57	−6.02
1,4-Dioxane	−2.05	−1.80	−3.85	−1.65	−2.37	−4.02	−4.17
Diethyl ether	−1.00	−1.61	−2.62	−0.81	−1.85	−2.67	−3.03
Anisole	−1.86	−2.81	−4.67	−1.53	−3.13	−4.66	−5.38
Tetrahydropyran	−1.06	−2.86	−3.92	−0.87	−3.08	−3.96	−4.41
Ethyl phenyl ether	−1.71	−3.75	−5.47	−1.42	−4.05	−5.48	−6.00
Benzaldehyde	−2.79	−2.75	−5.54	−2.79	−2.86	−5.64	−5.71
Propanone	−2.34	−0.57	−2.91	−2.43	−0.52	−2.95	−2.67
Butanone	−2.18	−1.31	−3.49	−2.27	−1.25	−3.51	−3.48
2-Pentanone	−2.10	−1.96	−4.06	−2.20	−1.87	−4.07	−4.19
3-Pentanone	−2.02	−2.05	−4.07	−2.10	−1.97	−4.07	−4.30
2-Hexanone	−2.03	−2.65	−4.68	−2.12	−2.54	−4.66	−4.77
3,3-Dimethylbutanone	−1.98	−1.79	−3.77	−2.04	−1.70	−3.75	−4.42
2-Heptanone	−2.07	−3.32	−5.39	−2.17	−3.20	−5.37	−5.47
Methyl phenyl ketone	−2.75	−3.53	−6.28	−2.71	−3.62	−6.33	−6.29
Ethanoic acid	−3.22	0.06	−3.16	−3.24	0.09	−3.15	−1.73
Propanoic acid	−2.96	−0.66	−3.62	−2.98	−0.61	−3.59	−3.78
Methyl ethanoate	−2.65	−0.10	−2.75	−2.49	−0.27	−2.76	−3.06
Methyl propanoate	−2.41	−0.82	−3.23	−2.25	−0.97	−3.22	−3.71
Ethyl ethanoate	−2.53	−1.06	−3.59	−2.40	−1.20	−3.60	−3.56
Propyl ethanoate	−2.45	−1.76	−4.21	−2.35	−1.88	−4.23	−4.36
Methyl pentanoate	−2.28	−2.15	−4.43	−2.15	−2.28	−4.43	−5.04
Butyl ethanoate	−2.41	−2.44	−4.85	−2.33	−2.54	−4.87	−4.94
Methyl hexanoate	−2.25	−2.84	−5.09	−2.13	−2.94	−5.07	−5.75
Pentyl ethanoate	−2.39	−3.12	−5.51	−2.31	−3.21	−5.52	−5.71
Methyl benzoate	−2.74	−2.96	−5.71	−2.50	−3.27	−5.77	−7.01
m-Hydroxybenzaldehyde	−4.11	−1.95	−6.06	−4.04	−2.03	−6.07	−6.88
p-Hydroxybenzaldehyde	−4.30	−1.93	−6.23	−4.26	−1.99	−6.25	−7.19
Water	−3.56	3.76	0.20	−3.44	3.62	0.18	−0.39
Ethylamine	−0.93	−1.34	−2.26	−0.79	−1.53	−2.31	−2.04
Trimethylamine	−0.85	−2.00	−2.85	−0.65	−2.08	−2.73	−2.63
Butylamine	−0.85	−2.74	−3.59	−0.72	−2.89	−3.61	−3.72
Diethylamine	−0.49	−2.76	−3.25	−0.42	−2.84	−3.27	−3.61
Pyridine	−2.15	−2.40	−4.55	−2.02	−2.64	−4.67	−4.30
Aniline	−2.12	−3.29	−5.41	−1.83	−3.65	−5.48	−5.52
2-Methylpyridine	−2.18	−2.86	−5.04	−2.02	−3.08	−5.10	−5.05
3-Methylpyridine	−2.11	−2.77	−4.88	−1.98	−3.01	−4.99	−5.14
4-Methylpyridine	−2.15	−2.77	−4.92	−2.02	−3.01	−5.03	−5.23
2,6-Dimethylpyridine	−2.19	−3.37	−5.56	−2.02	−3.55	−5.57	−5.51
Ethanonitrile	−3.07	0.47	−2.59	−3.03	0.50	−2.54	−1.87
Benzonitrile	−2.50	−2.46	−4.96	−2.39	−2.57	−4.96	−5.54
1-Nitropropane	−1.93	−2.15	−4.09	−2.77	−1.44	−4.21	−4.06
Nitrobenzene	−2.53	−3.53	−6.07	−2.97	−3.04	−6.01	−6.62
2-Methyl-1-nitrobenzene	−2.52	−3.94	−6.45	−2.80	−3.46	−6.26	−6.71
$OP(OCH_3)_3$	−5.24	0.85	−4.39	−2.93	−1.89	−4.81	−5.67
$OP(OC_2H_5)_3$	−4.87	−2.23	−7.09	−2.70	−4.85	−7.55	−7.60
$OP(OC_3H_7)_3$	−4.47	−4.35	−8.82	−2.44	−6.92	−9.36	−7.71
1-Propanethiol	−0.55	−2.79	−3.34	−0.41	−2.79	−3.20	−3.12
Thioanisole	−1.53	−4.85	−6.38	−1.45	−5.03	−6.48	−5.66
Fluorobenzene	−1.30	−2.75	−4.05	−1.18	−3.00	−4.19	−3.59
1,1,1-Trichloroethane	−0.75	−3.58	−4.34	−0.64	−3.53	−4.17	−4.08
Trichloroethene	−0.42	−2.84	−3.25	−0.37	−2.86	−3.23	−4.29
Chlorobenzene	−1.14	−4.09	−5.24	−0.98	−4.24	−5.22	−5.10
p-Dichlorobenzene	−0.98	−4.78	−5.76	−0.84	−4.91	−5.75	−5.89
Bromobenzene	−1.13	−4.81	−5.93	−0.95	−5.00	−5.96	−5.29
Iodobenzene	−1.02	−5.37	−6.38	−0.90	−5.54	−6.43	−6.26

Table 18. (Cont.)

Solute	SM5.42R/AM1			SM5.42R/PM3			Expt.
	ΔG_{ENP}	G_{CDS}	ΔG_S^0	ΔG_{ENP}	G_{CDS}	ΔG_S^0	ΔG_S^0
Difluorodichloromethane	−0.11	−1.31	−1.42	−0.10	−1.45	−1.56	−1.81
Fluorotrichloromethane	−0.05	−2.69	−2.74	−0.07	−2.73	−2.80	−2.63
2,2,2-Trifluoroethanol	−3.11	0.88	−2.23	−2.85	0.56	−2.28	−1.53
p-Bromophenol	−2.65	−3.97	−6.63	−2.41	−4.17	−6.58	−7.14
3,5-Dibromo-4-hydroxybenzonitrile	−2.95	−4.26	−7.21	−2.84	−4.41	−7.25	−6.83
Solvent: decalin							
Toluene	−1.28	−3.55	−4.83	−1.16	−3.71	−4.87	−4.37
Phenol	−2.85	−2.38	−5.23	−2.64	−2.53	−5.17	−5.38
m-Cresol	−2.87	−2.71	−5.58	−2.67	−2.85	−5.53	−5.11
p-Cresol	−2.85	−2.72	−5.57	−2.65	−2.87	−5.53	−5.68
Anisole	−2.03	−2.52	−4.55	−1.67	−2.87	−4.53	−5.00
Methyl phenyl ketone	−3.01	−3.23	−6.24	−2.96	−3.34	−6.30	−6.23
Ethanoic acid	−3.50	0.29	−3.21	−3.52	0.32	−3.21	−4.49
Propanoic acid	−3.22	−0.39	−3.61	−3.24	−0.35	−3.59	−4.42
Methyl ethanoate	−2.89	0.19	−2.70	−2.71	0.00	−2.71	−2.90
Methyl propanoate	−2.63	−0.49	−3.12	−2.46	−0.66	−3.12	−3.50
Ethyl ethanoate	−2.76	−0.74	−3.51	−2.62	−0.90	−3.52	−3.47
Propyl ethanoate	−2.67	−1.41	−4.08	−2.57	−1.54	−4.11	−4.05
Methyl pentanoate	−2.49	−1.76	−4.25	−2.35	−1.90	−4.25	−4.83
Butyl ethanoate	−2.63	−2.05	−4.68	−2.54	−2.17	−4.71	−4.71
Methyl hexanoate	−2.46	−2.40	−4.86	−2.33	−2.53	−4.85	−5.51
Pentyl ethanoate	−2.61	−2.69	−5.30	−2.52	−2.80	−5.32	−5.44
Methyl benzoate	−3.00	−2.62	−5.61	−2.73	−2.95	−5.67	−6.76
Aniline	−2.31	−3.05	−5.36	−1.99	−3.44	−5.43	−5.78
Benzonitrile	−2.74	−2.18	−4.92	−2.62	−2.31	−4.93	−5.86
Nitrobenzene	−2.78	−3.28	−6.05	−3.24	−2.77	−6.01	−6.36
Thioanisole	−1.68	−4.60	−6.28	−1.59	−4.80	−6.38	−5.54
Fluorobenzene	−1.42	−2.53	−3.95	−1.30	−2.79	−4.09	−3.44
Chlorobenzene	−1.25	−3.89	−5.13	−1.07	−4.04	−5.12	−4.61
Bromobenzene	−1.23	−4.61	−5.84	−1.04	−4.83	−5.87	−5.25
Iodobenzene	−1.11	−5.17	−6.28	−0.98	−5.36	−6.33	−5.96
Solvent: benzene							
n-Pentane	−0.04	−3.42	−3.46	−0.03	−3.39	−3.41	−2.99
n-Hexane	−0.02	−4.20	−4.22	−0.01	−4.15	−4.16	−3.62
n-Octane	0.02	−5.77	−5.75	0.02	−5.69	−5.67	−5.35
Cyclohexane	−0.09	−4.73	−4.82	−0.07	−4.66	−4.73	−4.05
Benzene	−1.28	−3.85	−5.13	−1.15	−4.04	−5.20	−4.55
Toluene	−1.32	−4.31	−5.62	−1.19	−4.49	−5.69	−5.32
Methanol	−2.27	0.27	−2.00	−2.17	0.13	−2.04	−2.58
Ethanol	−2.17	−0.91	−3.08	−2.07	−1.02	−3.09	−3.42
1-Propanol	−2.06	−1.73	−3.79	−1.99	−1.81	−3.81	−3.87
2-Propanol	−1.73	−1.59	−3.32	−1.70	−1.68	−3.38	−3.48
1-Butanol	−1.90	−2.52	−4.42	−1.85	−2.60	−4.46	−4.45
2-Methyl-2-propanol	−1.70	−1.95	−3.65	−1.65	−2.02	−3.67	−3.70
1-Pentanol	−1.87	−3.31	−5.17	−1.83	−3.37	−5.20	−5.10
Phenol	−2.93	−3.25	−6.19	−2.72	−3.42	−6.13	−7.12
1-Hexanol	−1.87	−4.09	−5.97	−1.84	−4.17	−6.01	−6.13
o-Cresol	−2.89	−3.75	−6.65	−2.70	−3.91	−6.61	−7.44
m-Cresol	−2.95	−3.71	−6.66	−2.75	−3.87	−6.62	−6.66
p-Cresol	−2.93	−3.73	−6.66	−2.73	−3.89	−6.62	−7.35
1-Heptanol	−1.85	−4.88	−6.73	−1.83	−4.93	−6.76	−6.85
1-Octanol	−1.80	−5.65	−7.46	−1.78	−5.67	−7.45	−8.06
1,4-Dioxane	−2.29	−2.27	−4.56	−1.85	−2.89	−4.74	−5.21
Propanone	−2.65	−0.75	−3.40	−2.75	−0.66	−3.41	−3.79
Butanone	−2.47	−1.60	−4.06	−2.56	−1.50	−4.06	−4.46
2-Pentanone	−2.38	−2.34	−4.72	−2.49	−2.22	−4.71	−5.14
2-Hexanone	−2.29	−3.13	−5.42	−2.40	−2.99	−5.39	−5.76
2-Heptanone	−2.34	−3.90	−6.24	−2.45	−3.76	−6.21	−6.36
Ethanoic acid	−3.60	−0.37	−3.97	−3.62	−0.34	−3.96	−4.02
Propanoic acid	−3.31	−1.19	−4.50	−3.33	−1.14	−4.48	−4.75
Butanoic acid	−3.19	−1.95	−5.13	−3.23	−1.89	−5.12	−5.30
Pentanoic acid	−3.17	−2.73	−5.89	−3.22	−2.65	−5.87	−6.01
Hexanoic acid	−3.14	−3.51	−6.65	−3.20	−3.42	−6.62	−6.94

Table 18. (Cont.)

Solute	SM5.42R/AM1			SM5.42R/PM3			Expt.
	ΔG_{ENP}	G_{CDS}	ΔG_S^0	ΔG_{ENP}	G_{CDS}	ΔG_S^0	ΔG_S^0
Methyl ethanoate	−2.98	−0.36	−3.34	−2.79	−0.54	−3.33	−4.04
Methyl propanoate	−2.71	−1.18	−3.89	−2.53	−1.34	−3.88	−4.58
Ethyl ethanoate	−2.84	−1.44	−4.28	−2.69	−1.59	−4.28	−4.53
Propyl ethanoate	−2.75	−2.23	−4.98	−2.64	−2.36	−5.00	−5.21
Methyl pentanoate	−2.56	−2.72	−5.28	−2.42	−2.85	−5.27	−5.83
Butyl ethanoate	−2.71	−3.01	−5.72	−2.62	−3.12	−5.74	−5.78
Methyl hexanoate	−2.53	−3.50	−6.03	−2.39	−3.62	−6.01	−6.47
Pentyl ethanoate	−2.69	−3.79	−6.48	−2.60	−3.89	−6.49	−6.53
Methyl benzoate	−3.08	−3.50	−6.58	−2.81	−3.84	−6.65	−6.27
m-Hydroxybenzaldehyde	−4.61	−2.50	−7.11	−4.53	−2.57	−7.11	−9.29
p-Hydroxybenzaldehyde	−4.83	−2.48	−7.31	−4.79	−2.52	−7.32	−9.73
Water	−3.96	3.35	−0.61	−3.84	3.20	−0.64	−1.71
Methylamine	−1.29	−0.85	−2.15	−1.06	−1.11	−2.17	−2.66
Ethylamine	−1.03	−1.76	−2.79	−0.88	−1.98	−2.85	−2.73
Dimethylamine	−1.01	−1.69	−2.70	−0.83	−1.87	−2.70	−3.01
Propylamine	−0.98	−2.58	−3.56	−0.84	−2.78	−3.61	−3.68
Trimethylamine	−0.94	−2.34	−3.29	−0.73	−2.44	−3.16	−2.80
Butylamine	−0.94	−3.36	−4.31	−0.80	−3.54	−4.35	−4.33
Diethylamine	−0.55	−3.29	−3.84	−0.47	−3.40	−3.88	−4.02
Piperidine	−0.65	−4.70	−5.35	−0.59	−4.76	−5.35	−5.03
Dipropylamine	−0.45	−4.90	−5.35	−0.42	−4.97	−5.39	−5.09
Pyridine	−2.42	−2.61	−5.03	−2.28	−2.90	−5.18	−5.28
Aniline	−2.37	−3.88	−6.25	−2.04	−4.30	−6.34	−6.88
2-Methylpyridine	−2.46	−3.17	−5.62	−2.28	−3.42	−5.70	−5.86
4-Methylpyridine	−2.41	−3.07	−5.48	−2.28	−3.35	−5.63	−6.17
2,6-Dimethylpyridine	−2.47	−3.77	−6.24	−2.29	−3.99	−6.27	−6.39
Nitrobenzene	−2.86	−3.84	−6.70	−3.33	−3.29	−6.63	−7.60
1,1-Dimethyl-3-phenylurea	−4.55	−5.34	−9.90	−4.19	−5.86	−10.05	−12.18
Ammonia	−1.78	0.01	−1.77	−1.36	−0.30	−1.66	−1.12
Hydrazine	−1.53	−4.66	−6.19	−1.39	−4.83	−6.21	−7.05
OP(OCH3)3	−5.86	0.14	−5.71	−3.28	−2.84	−6.12	−8.02
OP(OC2H5)3	−5.45	−3.27	−8.72	−3.03	−6.15	−9.18	−8.58
OP(OC3H7)3	−5.00	−5.70	−10.70	−2.73	−8.52	−11.26	−9.34
2,2-Dichloroethenyl dimethyl phosphate	−4.96	−2.07	−7.02	−2.92	−4.99	−7.91	−9.09
Dimethyl 4-nitrophenyl thiophosphate	−10.09	3.38	−6.71	−6.92	−1.73	−8.66	−9.21
Diethyl 4-nitrophenyl thiophosphate	−9.10	0.99	−8.11	−6.49	−3.94	−10.44	−8.58
p-Bromophenol	−2.97	−4.77	−7.74	−2.70	−4.99	−7.69	−8.81
Solvent: toluene							
n-Octane	0.02	−5.53	−5.51	0.02	−5.46	−5.43	−5.38
Methanol	−2.36	0.33	−2.03	−2.26	0.19	−2.06	−2.18
Ethanol	−2.25	−0.82	−3.08	−2.15	−0.93	−3.08	−3.33
1-Propanol	−2.15	−1.61	−3.76	−2.07	−1.70	−3.77	−3.71
1-Butanol	−1.97	−2.38	−4.35	−1.93	−2.46	−4.39	−4.31
1-Pentanol	−1.94	−3.14	−5.08	−1.90	−3.21	−5.11	−5.17
Phenol	−3.05	−3.12	−6.17	−2.83	−3.28	−6.11	−6.93
1-Hexanol	−1.95	−3.90	−5.85	−1.92	−3.97	−5.89	−6.12
o-Cresol	−3.01	−3.59	−6.60	−2.81	−3.75	−6.56	−7.43
p-Cresol	−3.05	−3.56	−6.61	−2.84	−3.73	−6.57	−7.56
1-Heptanol	−1.93	−4.66	−6.58	−1.90	−4.71	−6.62	−6.75
1,4-Dioxane	−2.38	−2.15	−4.52	−1.92	−2.76	−4.68	−4.91
Propanone	−2.76	−0.65	−3.41	−2.87	−0.56	−3.43	−3.59
Butanone	−2.58	−1.47	−4.04	−2.68	−1.37	−4.05	−4.27
2-Pentanone	−2.49	−2.18	−4.67	−2.60	−2.07	−4.67	−5.02
2-Hexanone	−2.40	−2.95	−5.35	−2.50	−2.81	−5.32	−5.60
3,3-Dimethylbutanone	−2.34	−2.05	−4.39	−2.41	−1.93	−4.35	−5.00
2-Heptanone	−2.45	−3.69	−6.14	−2.56	−3.55	−6.11	−6.30
Ethanoic acid	−3.75	−0.28	−4.02	−3.77	−0.25	−4.02	−4.00
Propanoic acid	−3.44	−1.07	−4.52	−3.47	−1.03	−4.50	−4.57
Butanoic acid	−3.31	−1.80	−5.12	−3.37	−1.75	−5.11	−5.24
Pentanoic acid	−3.29	−2.56	−5.85	−3.35	−2.48	−5.83	−5.89
Hexanoic acid	−3.26	−3.31	−6.58	−3.33	−3.23	−6.55	−6.97
Methyl ethanoate	−3.10	−0.25	−3.35	−2.91	−0.43	−3.34	−3.81
Methyl propanoate	−2.82	−1.04	−3.86	−2.64	−1.21	−3.84	−4.62
Ethyl ethanoate	−2.96	−1.29	−4.26	−2.81	−1.45	−4.25	−4.41

Table 18. (Cont.)

Solute	SM5.42R/AM1			SM5.42R/PM3			Expt.
	ΔG_{ENP}	G_{CDS}	ΔG_S^0	ΔG_{ENP}	G_{CDS}	ΔG_S^0	ΔG_S^0
Propyl ethanoate	−2.87	−2.06	−4.93	−2.75	−2.20	−4.95	−5.00
Methyl pentanoate	−2.67	−2.53	−5.19	−2.52	−2.66	−5.18	−5.65
Butyl ethanoate	−2.82	−2.82	−5.64	−2.72	−2.94	−5.66	−5.57
Methyl hexanoate	−2.63	−3.28	−5.92	−2.49	−3.40	−5.89	−6.38
Pentyl ethanoate	−2.80	−3.57	−6.37	−2.71	−3.67	−6.38	−6.41
Methyl benzoate	−3.21	−3.31	−6.53	−2.92	−3.66	−6.58	−7.96
Water	−4.12	3.38	−0.74	−3.99	3.23	−0.76	−1.69
Methylamine	−1.34	−0.78	−2.12	−1.10	−1.04	−2.14	−2.65
Ethylamine	−1.07	−1.66	−2.73	−0.91	−1.88	−2.79	−2.67
Dimethylamine	−1.04	−1.59	−2.64	−0.86	−1.77	−2.64	−2.68
Propylamine	−1.02	−2.46	−3.48	−0.87	−2.65	−3.52	−3.51
Trimethylamine	−0.98	−2.22	−3.20	−0.76	−2.31	−3.07	−2.71
Butylamine	−0.98	−3.21	−4.19	−0.83	−3.39	−4.23	−4.43
Diethylamine	−0.57	−3.14	−3.71	−0.49	−3.26	−3.75	−3.75
Dipropylamine	−0.47	−4.70	−5.17	−0.44	−4.77	−5.21	−5.24
Pyridine	−2.52	−2.49	−5.01	−2.38	−2.78	−5.16	−5.13
Aniline	−2.46	−3.73	−6.19	−2.13	−4.15	−6.28	−6.69
1-Nitropropane	−2.27	−2.25	−4.52	−3.23	−1.46	−4.69	−5.25
Ammonia	−1.85	0.06	−1.79	−1.41	−0.26	−1.67	−2.38
p-Bromophenol	−3.09	−4.60	−7.69	−2.81	−4.82	−7.63	−8.70
Solvent: ethylbenzene							
Methanol	−2.40	0.39	−2.01	−2.29	0.25	−2.04	−1.43
Ethanol	−2.29	−0.74	−3.03	−2.19	−0.84	−3.03	−2.49
1-Propanol	−2.18	−1.50	−3.67	−2.10	−1.59	−3.69	−3.71
1-Butanol	−2.00	−2.24	−4.24	−1.96	−2.32	−4.28	−3.77
1-Pentanol	−1.97	−2.96	−4.94	−1.93	−3.04	−4.97	−4.72
Phenol	−3.10	−2.97	−6.07	−2.87	−3.14	−6.01	−6.82
1-Hexanol	−1.98	−3.70	−5.67	−1.95	−3.78	−5.72	−5.68
o-Cresol	−3.06	−3.42	−6.48	−2.85	−3.59	−6.44	−7.25
1-Heptanol	−1.96	−4.42	−6.38	−1.93	−4.49	−6.42	−6.70
Propanone	−2.81	−0.51	−3.33	−2.92	−0.43	−3.35	−3.41
Butanone	−2.62	−1.31	−3.93	−2.73	−1.21	−3.94	−4.12
2-Pentanone	−2.53	−2.00	−4.53	−2.64	−1.89	−4.53	−4.85
2-Hexanone	−2.44	−2.73	−5.17	−2.55	−2.60	−5.15	−5.49
3,3-Dimethylbutanone	−2.38	−1.84	−4.22	−2.46	−1.72	−4.18	−4.92
2-Heptanone	−2.49	−3.45	−5.94	−2.61	−3.31	−5.92	−6.10
Methyl ethanoate	−3.15	−0.11	−3.26	−2.96	−0.29	−3.25	−3.74
Methyl propanoate	−2.87	−0.88	−3.74	−2.68	−1.04	−3.73	−4.29
Ethyl ethanoate	−3.01	−1.13	−4.14	−2.86	−1.28	−4.14	−4.31
Propyl ethanoate	−2.92	−1.87	−4.78	−2.80	−2.00	−4.80	−4.95
Methyl pentanoate	−2.71	−2.30	−5.01	−2.56	−2.44	−5.00	−5.56
Butyl ethanoate	−2.87	−2.59	−5.47	−2.77	−2.71	−5.49	−5.48
Pentyl ethanoate	−2.85	−3.32	−6.17	−2.75	−3.43	−6.18	−6.20
Water	−4.18	3.39	−0.80	−4.05	3.23	−0.81	−1.51
Ethylamine	−1.08	−1.56	−2.64	−0.92	−1.78	−2.70	−2.59
Propylamine	−1.04	−2.32	−3.36	−0.88	−2.52	−3.41	−3.44
Trimethylamine	−1.00	−2.07	−3.07	−0.77	−2.17	−2.94	−2.64
Butylamine	−0.99	−3.05	−4.04	−0.85	−3.24	−4.08	−4.06
p-Bromophenol	−3.14	−4.43	−7.57	−2.85	−4.66	−7.51	−8.54
Solvent: isopropylbenzene							
Ethanol	−2.25	−0.75	−3.00	−2.15	−0.86	−3.00	−2.90
Propanone	−2.75	−0.50	−3.25	−2.86	−0.41	−3.27	−3.32
Butanone	−2.57	−1.30	−3.86	−2.67	−1.20	−3.86	−4.02
2-Pentanone	−2.48	−1.98	−4.46	−2.59	−1.87	−4.45	−4.84
2-Hexanone	−2.39	−2.71	−5.10	−2.50	−2.58	−5.08	−5.39
3,3-Dimethylbutanone	−2.33	−1.82	−4.16	−2.40	−1.71	−4.11	−4.81
2-Heptanone	−2.44	−3.43	−5.87	−2.55	−3.29	−5.84	−5.99
Propanoic acid	−3.43	−0.96	−4.39	−3.46	−0.92	−4.38	−4.23
Butanoic acid	−3.30	−1.66	−4.97	−3.35	−1.61	−4.96	−4.93
Methyl propanoate	−2.81	−0.87	−3.68	−2.63	−1.04	−3.66	−4.19
Ethyl ethanoate	−2.95	−1.12	−4.07	−2.80	−1.27	−4.07	−4.22
Propyl ethanoate	−2.86	−1.86	−4.72	−2.74	−2.00	−4.74	−4.78
Methyl pentanoate	−2.66	−2.29	−4.95	−2.51	−2.43	−4.94	−5.45

Table 18. (Cont.)

Solute	SM5.42R/AM1			SM5.42R/PM3			Expt.
	ΔG_{ENP}	G_{CDS}	ΔG_S^0	ΔG_{ENP}	G_{CDS}	ΔG_S^0	ΔG_S^0
Butyl ethanoate	−2.81	−2.58	−5.40	−2.71	−2.70	−5.42	−5.36
Methyl hexanoate	−2.63	−3.02	−5.64	−2.48	−3.14	−5.63	−6.19
Pentyl ethanoate	−2.79	−3.31	−6.10	−2.70	−3.41	−6.11	−6.13
Water	−4.10	3.34	−0.76	−3.97	3.19	−0.79	−1.41
Solvent: *n*-butylbenzene							
Phenol	−3.03	−2.85	−5.87	−2.81	−3.01	−5.82	−6.76
2-Pentanone	−2.47	−1.85	−4.32	−2.58	−1.75	−4.32	−4.74
2-Hexanone	−2.38	−2.56	−4.95	−2.49	−2.44	−4.92	−5.31
3,3-Dimethylbutanone	−2.32	−1.68	−4.00	−2.40	−1.57	−3.96	−4.77
2-Heptanone	−2.43	−3.26	−5.69	−2.54	−3.12	−5.67	−5.93
Methyl propanoate	−2.80	−0.75	−3.55	−2.62	−0.92	−3.54	−4.19
Methyl pentanoate	−2.65	−2.13	−4.77	−2.50	−2.27	−4.77	−5.37
Butyl ethanoate	−2.80	−2.42	−5.22	−2.70	−2.54	−5.25	−5.28
Methyl hexanoate	−2.62	−2.83	−5.45	−2.48	−2.96	−5.43	−6.09
Solvent: *sec*-butylbenzene							
Methyl ethanoate	−3.06	−0.04	−3.10	−2.87	−0.22	−3.09	−3.91
Ethyl ethanoate	−2.92	−1.04	−3.96	−2.77	−1.20	−3.96	−4.11
Propyl ethanoate	−2.83	−1.76	−4.59	−2.71	−1.90	−4.62	−4.62
Butyl ethanoate	−2.78	−2.47	−5.26	−2.69	−2.60	−5.28	−5.22
Pentyl ethanoate	−2.76	−3.18	−5.94	−2.67	−3.29	−5.96	−5.98
Solvent: *tert*-butylbenzene							
Butanone	−2.54	−1.25	−3.79	−2.63	−1.16	−3.79	−3.94
2-Pentanone	−2.45	−1.93	−4.38	−2.56	−1.82	−4.38	−4.72
2-Hexanone	−2.36	−2.66	−5.02	−2.47	−2.52	−4.99	−5.27
3,3-Dimethylbutanone	−2.31	−1.77	−4.07	−2.38	−1.65	−4.03	−4.79
2-Heptanone	−2.41	−3.37	−5.77	−2.52	−3.22	−5.75	−5.88
Methyl ethanoate	−3.06	−0.07	−3.12	−2.87	−0.25	−3.12	−3.57
Methyl propanoate	−2.78	−0.82	−3.60	−2.60	−0.99	−3.59	−4.17
Ethyl ethanoate	−2.92	−1.07	−3.99	−2.77	−1.23	−4.00	−4.22
Propyl ethanoate	−2.83	−1.81	−4.63	−2.71	−1.94	−4.66	−4.72
Methyl pentanoate	−2.63	−2.23	−4.86	−2.48	−2.37	−4.85	−5.39
Butyl ethanoate	−2.78	−2.52	−5.30	−2.69	−2.64	−5.33	−5.25
Methyl hexanoate	−2.60	−2.95	−5.55	−2.46	−3.07	−5.53	−6.13
Pentyl ethanoate	−2.76	−3.24	−6.00	−2.67	−3.35	−6.01	−5.92
Solvent: xylenes (technical mixture)							
n-Octane	0.02	−5.28	−5.26	0.02	−5.21	−5.19	−5.29
Toluene	−1.38	−3.98	−5.36	−1.25	−4.18	−5.43	−5.06
Methanol	−2.37	0.38	−1.99	−2.26	0.23	−2.03	−1.73
Ethanol	−2.26	−0.75	−3.02	−2.16	−0.86	−3.02	−3.32
1-Propanol	−2.15	−1.51	−3.67	−2.08	−1.61	−3.68	−3.57
1-Butanol	−1.98	−2.26	−4.24	−1.93	−2.35	−4.28	−4.17
1-Pentanol	−1.95	−2.99	−4.93	−1.91	−3.06	−4.97	−4.72
Phenol	−3.06	−2.99	−6.05	−2.84	−3.16	−6.00	−6.83
1-Hexanol	−1.95	−3.72	−5.67	−1.92	−3.80	−5.72	−5.85
o-Cresol	−3.02	−3.44	−6.46	−2.81	−3.61	−6.42	−7.25
m-Cresol	−3.08	−3.40	−6.47	−2.87	−3.56	−6.43	−6.32
p-Cresol	−3.06	−3.41	−6.47	−2.85	−3.58	−6.43	−7.18
1-Heptanol	−1.93	−4.45	−6.38	−1.91	−4.52	−6.42	−6.74
1,4-Dioxane	−2.39	−2.01	−4.39	−1.93	−2.63	−4.56	−4.86
Propanone	−2.77	−0.51	−3.28	−2.88	−0.42	−3.30	−3.26
Butanone	−2.59	−1.30	−3.89	−2.69	−1.21	−3.89	−4.23
2-Pentanone	−2.50	−1.99	−4.49	−2.61	−1.88	−4.49	−4.87
2-Hexanone	−2.41	−2.73	−5.14	−2.51	−2.60	−5.11	−5.49
3,3-Dimethylbutanone	−2.35	−1.83	−4.18	−2.42	−1.72	−4.14	−4.91
2-Heptanone	−2.46	−3.45	−5.91	−2.57	−3.31	−5.88	−6.15
Ethanoic acid	−3.76	−0.20	−3.96	−3.78	−0.17	−3.95	−4.08
Propanoic acid	−3.46	−0.97	−4.42	−3.48	−0.93	−4.41	−4.72
Butanoic acid	−3.33	−1.67	−5.00	−3.38	−1.62	−4.99	−5.30
Pentanoic acid	−3.30	−2.40	−5.70	−3.36	−2.33	−5.69	−5.71
Hexanoic acid	−3.27	−3.13	−6.40	−3.34	−3.04	−6.38	−6.67
Methyl ethanoate	−3.11	−0.11	−3.22	−2.92	−0.29	−3.21	−3.70
Methyl propanoate	−2.83	−0.87	−3.70	−2.65	−1.04	−3.69	−4.20

Table 18. (Cont.)

Solute	SM5.42R/AM1			SM5.42R/PM3			Expt.
	ΔG_{ENP}	G_{CDS}	ΔG_S^0	ΔG_{ENP}	G_{CDS}	ΔG_S^0	ΔG_S^0
Ethyl ethanoate	−2.97	−1.13	−4.10	−2.82	−1.28	−4.10	−4.26
Propyl ethanoate	−2.88	−1.87	−4.75	−2.76	−2.01	−4.77	−4.87
Methyl pentanoate	−2.67	−2.31	−4.98	−2.52	−2.45	−4.97	−5.61
Butyl ethanoate	−2.83	−2.60	−5.43	−2.73	−2.72	−5.45	−5.40
Methyl hexanoate	−2.64	−3.03	−5.68	−2.50	−3.16	−5.66	−6.26
Pentyl ethanoate	−2.81	−3.33	−6.13	−2.71	−3.43	−6.15	−6.19
Water	−4.13	3.36	−0.77	−4.00	3.21	−0.79	−1.56
Methylamine	−1.34	−0.71	−2.06	−1.10	−0.97	−2.08	−3.20
Ethylamine	−1.07	−1.57	−2.64	−0.91	−1.79	−2.70	−3.01
Dimethylamine	−1.05	−1.49	−2.53	−0.87	−1.67	−2.54	−3.36
Propylamine	−1.02	−2.33	−3.36	−0.87	−2.54	−3.41	−3.69
Trimethylamine	−0.98	−2.07	−3.06	−0.76	−2.17	−2.93	−2.63
Butylamine	−0.98	−3.06	−4.05	−0.84	−3.25	−4.09	−4.22
Diethylamine	−0.57	−2.98	−3.55	−0.49	−3.10	−3.60	−3.93
Piperidine	−0.68	−4.39	−5.07	−0.61	−4.46	−5.07	−5.15
Pentylamine	−0.95	−3.79	−4.75	−0.81	−3.97	−4.78	−4.70
Dipropylamine	−0.47	−4.49	−4.96	−0.44	−4.56	−5.00	−5.35
Pyridine	−2.53	−2.33	−4.86	−2.38	−2.63	−5.01	−5.12
Aniline	−2.47	−3.59	−6.06	−2.13	−4.01	−6.15	−6.10
p-Bromophenol	−3.10	−4.45	−7.55	−2.82	−4.68	−7.50	−8.69
Solvent: *p*-isopropyltoluene							
Methyl ethanoate	−2.93	−0.10	−3.03	−2.75	−0.28	−3.03	−3.32
Methyl propanoate	−2.66	−0.87	−3.53	−2.49	−1.03	−3.53	−4.14
Methyl pentanoate	−2.52	−2.29	−4.81	−2.38	−2.43	−4.81	−5.33
Methyl hexanoate	−2.49	−3.02	−5.51	−2.35	−3.15	−5.50	−6.06
Pentyl ethanoate	−2.64	−3.31	−5.95	−2.56	−3.42	−5.97	−6.02
Solvent: 1,2,4-trimethylbenzene							
Butanone	−2.57	−1.19	−3.76	−2.67	−1.09	−3.75	−3.97
2-Pentanone	−2.48	−1.86	−4.34	−2.59	−1.75	−4.33	−4.83
2-Hexanone	−2.39	−2.59	−4.97	−2.50	−2.45	−4.94	−5.39
3,3-Dimethylbutanone	−2.33	−1.69	−4.02	−2.40	−1.57	−3.98	−4.80
2-Heptanone	−2.44	−3.29	−5.73	−2.55	−3.15	−5.70	−6.01
Methyl ethanoate	−3.09	−0.01	−3.10	−2.90	−0.20	−3.10	−3.58
Methyl propanoate	−2.81	−0.77	−3.58	−2.63	−0.94	−3.56	−4.14
Methyl pentanoate	−2.66	−2.17	−4.82	−2.51	−2.31	−4.82	−5.41
Methyl hexanoate	−2.63	−2.88	−5.51	−2.48	−3.01	−5.50	−6.16
Pentyl ethanoate	−2.79	−3.17	−5.96	−2.70	−3.29	−5.98	−6.09
Solvent: mesitylene							
Phenol	−2.93	−3.03	−5.96	−2.72	−3.20	−5.92	−6.80
Butanone	−2.47	−1.28	−3.75	−2.56	−1.18	−3.74	−3.95
2-Pentanone	−2.38	−1.97	−4.35	−2.49	−1.85	−4.34	−4.80
2-Hexanone	−2.29	−2.71	−5.01	−2.40	−2.57	−4.97	−5.34
3,3-Dimethylbutanone	−2.24	−1.82	−4.06	−2.31	−1.70	−4.01	−4.77
2-Heptanone	−2.34	−3.43	−5.78	−2.45	−3.29	−5.74	−5.99
Solvent: tetralin							
Ethanol	−2.50	−0.57	−3.07	−2.40	−0.69	−3.08	−1.54
Propanone	−3.11	−0.20	−3.32	−3.24	−0.11	−3.35	−2.54
Butanone	−2.91	−0.96	−3.87	−3.02	−0.86	−3.88	−3.12
2-Pentanone	−2.81	−1.60	−4.41	−2.93	−1.49	−4.42	−3.99
2-Hexanone	−2.71	−2.29	−5.00	−2.83	−2.16	−4.99	−4.64
3,3-Dimethylbutanone	−2.64	−1.39	−4.03	−2.72	−1.27	−4.00	−4.19
2-Heptanone	−2.76	−2.96	−5.73	−2.89	−2.83	−5.72	−5.33
Water	−4.56	3.47	−1.09	−4.42	3.31	−1.11	0.07
Solvent: ethanol							
n-Octane	0.03	−4.02	−3.99	0.04	−4.00	−3.96	−4.23
Toluene	−2.49	−2.69	−5.17	−2.27	−2.93	−5.20	−4.57
1,4-Dioxane	−4.18	−1.36	−5.54	−3.37	−2.01	−5.39	−4.68
Butanone	−5.05	−0.46	−5.52	−5.23	−0.35	−5.59	−4.32
Chlorobenzene	−2.49	−3.13	−5.63	−2.15	−3.35	−5.50	−3.30
Solvent: propanol							
n-Octane	0.03	−4.00	−3.97	0.04	−3.98	−3.94	−4.39

Table 18. (Cont.)

Solute	SM5.42R/AM1			SM5.42R/PM3			Expt.
	ΔG_{ENP}	G_{CDS}	ΔG_S^0	ΔG_{ENP}	G_{CDS}	ΔG_S^0	ΔG_S^0
Toluene	−2.46	−2.68	−5.14	−2.24	−2.93	−5.17	−4.47
Ethanol	−3.91	−1.73	−5.64	−3.76	−1.85	−5.61	−5.01
1,4-Dioxane	−4.14	−1.33	−5.46	−3.34	−2.00	−5.33	−4.61
Butanone	−4.99	−0.42	−5.41	−5.17	−0.31	−5.48	−4.15
Solvent: isopropanol							
n-Octane	0.03	−4.25	−4.22	0.04	−4.22	−4.18	−4.50
Toluene	−2.45	−2.85	−5.29	−2.23	−3.10	−5.33	−4.38
Ethanol	−3.89	−1.89	−5.78	−3.74	−2.00	−5.75	−4.84
1,4-Dioxane	−4.12	−1.51	−5.63	−3.33	−2.17	−5.50	−4.49
Butanone	−4.96	−0.51	−5.47	−5.14	−0.36	−5.50	−4.07
Solvent: butanol							
n-Octane	0.03	−3.90	−3.87	0.04	−3.88	−3.84	−4.45
Benzene	−2.35	−2.34	−4.70	−2.13	−2.60	−4.73	−3.39
Toluene	−2.43	−2.62	−5.05	−2.21	−2.88	−5.09	−4.50
Ethylbenzene	−2.22	−3.13	−5.35	−2.04	−3.38	−5.41	−4.46
Methanol	−4.02	−0.73	−4.75	−3.87	−0.88	−4.75	−4.73
Ethanol	−3.87	−1.68	−5.54	−3.72	−1.80	−5.51	−5.02
1,2-Ethanediol	−5.54	−3.00	−8.54	−5.46	−3.34	−8.80	−8.69
Formaldehyde	−5.73	2.30	−3.43	−5.91	2.37	−3.54	−3.49
Butanone	−4.92	−0.35	−5.27	−5.09	−0.24	−5.34	−4.12
Ethanoic acid	−6.53	−0.38	−6.92	−6.58	−0.34	−6.92	−6.81
Propanoic acid	−6.01	−1.01	−7.02	−6.07	−0.96	−7.03	−7.17
Butanoic acid	−5.77	−1.56	−7.33	−5.87	−1.50	−7.37	−7.66
Pentanoic acid	−5.74	−2.14	−7.88	−5.85	−2.07	−7.92	−8.02
Hexanoic acid	−5.69	−2.71	−8.40	−5.81	−2.63	−8.45	−8.75
Ethylamine	−1.78	−2.21	−3.99	−1.53	−2.50	−4.03	−4.50
Propylamine	−1.71	−2.83	−4.54	−1.47	−3.10	−4.58	−5.04
Butylamine	−1.63	−3.40	−5.04	−1.41	−3.67	−5.08	−5.52
Diethylamine	−0.96	−3.42	−4.38	−0.84	−3.63	−4.47	−5.15
Solvent: *sec*-butanol							
Formaldehyde	−5.69	2.30	−3.39	−5.87	2.40	−3.46	−2.86
Ethanoic acid	−6.49	−0.59	−7.08	−6.54	−0.55	−7.08	−6.81
Propanoic acid	−5.97	−1.24	−7.22	−6.03	−1.19	−7.22	−7.00
Butanoic acid	−5.73	−1.83	−7.56	−5.83	−1.76	−7.59	−7.34
Pentanoic acid	−5.71	−2.43	−8.14	−5.82	−2.36	−8.17	−7.61
Hexanoic acid	−5.65	−3.04	−8.69	−5.77	−2.95	−8.72	−8.11
Water	−6.90	0.25	−6.65	−6.73	0.12	−6.61	−5.71
Solvent: isobutanol							
Butanal	−4.89	−0.35	−5.24	−5.15	−0.23	−5.38	−4.82
Ethanoic acid	−6.52	−0.49	−7.01	−6.56	−0.45	−7.01	−6.80
Propanoic acid	−6.00	−1.14	−7.14	−6.05	−1.09	−7.14	−6.98
Butanoic acid	−5.75	−1.72	−7.47	−5.85	−1.66	−7.51	−7.62
Pentanoic acid	−5.73	−2.32	−8.05	−5.84	−2.25	−8.09	−8.06
Hexanoic acid	−5.67	−2.92	−8.60	−5.80	−2.84	−8.64	−8.77
Ethyl ethanoate	−5.32	0.06	−5.26	−5.03	−0.10	−5.13	−4.27
Methylamine	−2.23	−1.59	−3.82	−1.85	−1.91	−3.76	−4.56
Dimethylamine	−1.75	−2.38	−4.13	−1.46	−2.65	−4.11	−4.43
Trimethylamine	−1.64	−2.74	−4.38	−1.28	−2.92	−4.20	−3.90
Piperazine	−2.69	−6.24	−8.93	−2.22	−6.61	−8.83	−6.58
Butylamine	−1.63	−3.57	−5.20	−1.41	−3.83	−5.23	−5.55
Diethylamine	−0.96	−3.58	−4.54	−0.84	−3.79	−4.62	−4.86
Piperidine	−1.15	−4.96	−6.11	−1.05	−5.13	−6.18	−6.17
Dipropylamine	−0.80	−4.92	−5.72	−0.76	−5.10	−5.86	−5.87
Pyridine	−4.55	−1.61	−6.16	−4.39	−1.98	−6.37	−5.87
Solvent: 1-pentanol							
Benzene	−2.33	−2.35	−4.68	−2.11	−2.61	−4.72	−3.53
Toluene	−2.40	−2.63	−5.04	−2.19	−2.89	−5.08	−4.25
Ethylbenzene	−2.20	−3.14	−5.34	−2.01	−3.39	−5.40	−4.48
Phenol	−5.27	−3.05	−8.32	−4.90	−3.26	−8.16	−8.55
o-Cresol	−5.21	−3.35	−8.57	−4.88	−3.56	−8.44	−8.57
p-Cresol	−5.27	−3.31	−8.58	−4.92	−3.53	−8.45	−9.25
Formaldehyde	−5.66	2.32	−3.34	−5.84	2.39	−3.44	−3.44

Table 18. (Cont.)

Solute	SM5.42R/AM1			SM5.42R/PM3			Expt.
	ΔG_{ENP}	G_{CDS}	ΔG_S^0	ΔG_{ENP}	G_{CDS}	ΔG_S^0	ΔG_S^0
Ethanoic acid	−6.46	−0.37	−6.83	−6.51	−0.33	−6.84	−6.65
Propanoic acid	−5.95	−1.00	−6.95	−6.00	−0.95	−6.96	−7.09
Butanoic acid	−5.71	−1.55	−7.26	−5.81	−1.50	−7.30	−7.74
Pentanoic acid	−5.68	−2.13	−7.81	−5.79	−2.06	−7.86	−8.17
Hexanoic acid	−5.63	−2.71	−8.33	−5.75	−2.63	−8.38	−8.99
Methylamine	−2.21	−1.51	−3.72	−1.84	−1.83	−3.66	−3.95
Ethylamine	−1.76	−2.21	−3.97	−1.52	−2.50	−4.02	−4.27
Propylamine	−1.69	−2.83	−4.52	−1.46	−3.11	−4.57	−4.88
Butylamine	−1.62	−3.41	−5.03	−1.39	−3.67	−5.07	−5.50
Diethylamine	−0.95	−3.42	−4.38	−0.83	−3.64	−4.47	−5.30
Aniline	−4.19	−3.00	−7.19	−3.66	−3.52	−7.17	−6.44
Ammonia	−3.03	−0.61	−3.65	−2.34	−0.96	−3.31	−3.13
p-Bromophenol	−5.34	−4.46	−9.80	−4.86	−4.72	−9.58	−10.62
Solvent: 1-hexanol							
Benzene	−2.29	−2.35	−4.64	−2.07	−2.61	−4.68	−3.68
Toluene	−2.36	−2.63	−4.99	−2.15	−2.89	−5.04	−4.27
Ethylbenzene	−2.16	−3.14	−5.30	−1.98	−3.39	−5.36	−4.54
Phenol	−5.17	−3.04	−8.22	−4.81	−3.25	−8.06	−8.76
o-Cresol	−5.12	−3.34	−8.46	−4.79	−3.56	−8.34	−8.76
m-Cresol	−5.19	−3.29	−8.48	−4.85	−3.50	−8.35	−8.42
p-Cresol	−5.17	−3.30	−8.47	−4.83	−3.52	−8.35	−9.21
Formaldehyde	−5.54	2.34	−3.21	−5.72	2.41	−3.31	−3.42
Ethanoic acid	−6.35	−0.36	−6.71	−6.39	−0.32	−6.71	−6.51
Ethylamine	−1.74	−2.20	−3.94	−1.50	−2.49	−3.98	−4.20
Propylamine	−1.66	−2.82	−4.48	−1.43	−3.10	−4.53	−4.83
Butylamine	−1.59	−3.40	−4.99	−1.37	−3.67	−5.04	−5.40
p-Bromophenol	−5.24	−4.46	−9.70	−4.78	−4.72	−9.49	−10.51
Solvent: 1-heptanol							
Benzene	−2.26	−2.33	−4.59	−2.04	−2.60	−4.64	−3.73
Toluene	−2.33	−2.61	−4.94	−2.12	−2.86	−4.99	−4.33
Ethylbenzene	−2.13	−3.11	−5.25	−1.95	−3.36	−5.32	−4.58
Phenol	−5.12	−3.02	−8.13	−4.76	−3.23	−7.99	−8.69
o-Cresol	−5.07	−3.31	−8.38	−4.74	−3.53	−8.26	−8.78
p-Cresol	−5.12	−3.27	−8.39	−4.78	−3.49	−8.27	−9.16
Ethanoic acid	−6.28	−0.33	−6.61	−6.32	−0.29	−6.62	−6.70
Ethylamine	−1.72	−2.18	−3.90	−1.48	−2.47	−3.95	−4.15
Propylamine	−1.65	−2.80	−4.44	−1.42	−3.08	−4.50	−4.80
Butylamine	−1.58	−3.37	−4.95	−1.36	−3.64	−5.00	−5.33
p-Bromophenol	−5.19	−4.43	−9.62	−4.72	−4.69	−9.42	−10.49
Solvent: 1-octanol							
Methane	−0.04	0.83	0.78	−0.02	0.77	0.75	0.51
Ethane	−0.11	−0.33	−0.44	−0.06	−0.37	−0.43	−0.64
Propane	−0.12	−0.97	−1.09	−0.08	−1.00	−1.08	−1.26
n-Butane	−0.10	−1.54	−1.64	−0.06	−1.56	−1.62	−1.86
n-Pentane	−0.07	−2.11	−2.18	−0.04	−2.12	−2.17	−2.45
n-Hexane	−0.04	−2.68	−2.72	−0.02	−2.68	−2.70	−3.01
n-Heptane	−0.01	−3.25	−3.26	0.01	−3.24	−3.23	−3.74
n-Octane	0.03	−3.82	−3.79	0.03	−3.80	−3.77	−4.18
2-Methylpropane	−0.11	−1.25	−1.36	−0.08	−1.27	−1.35	−1.45
2,2-Dimethylpropane	−0.13	−1.37	−1.50	−0.09	−1.38	−1.48	−1.74
Cyclopropane	−0.45	−1.73	−2.18	−0.37	−1.80	−2.17	−1.60
Cyclopentane	−0.25	−2.76	−3.01	−0.19	−2.76	−2.95	−2.65
Cyclohexane	−0.16	−3.39	−3.54	−0.12	−3.35	−3.47	−3.46
Methylcyclohexane	−0.08	−3.54	−3.62	−0.05	−3.51	−3.56	−3.21
Ethene	−0.47	0.56	0.09	−0.38	0.42	0.04	−0.27
Propene	−0.59	−0.29	−0.88	−0.50	−0.42	−0.91	−1.14
s-trans-1,3-Butadiene	−0.96	−0.21	−1.17	−0.81	−0.43	−1.24	−2.10
2-Methylpropene	−0.73	−0.65	−1.37	−0.63	−0.77	−1.40	−2.03
1-Butene	−0.50	−0.85	−1.35	−0.43	−0.97	−1.40	−1.89
1-Hexene	−0.40	−1.99	−2.39	−0.35	−2.09	−2.44	−2.94
Ethyne	−2.21	1.73	−0.48	−2.13	1.61	−0.52	−0.51
Propyne	−2.73	0.55	−2.19	−2.60	0.43	−2.17	−1.59
1-Pentyne	−2.31	−0.57	−2.88	−2.22	−0.68	−2.90	−2.79

Table 18. (Cont.)

Solute	SM5.42R/AM1			SM5.42R/PM3			Expt.
	ΔG_{ENP}	G_{CDS}	ΔG_S^0	ΔG_{ENP}	G_{CDS}	ΔG_S^0	ΔG_S^0
1-Hexyne	−2.27	−1.14	−3.41	−2.20	−1.23	−3.43	−3.43
Benzene	−2.22	−2.32	−4.54	−2.01	−2.58	−4.59	−3.72
Toluene	−2.29	−2.58	−4.88	−2.09	−2.84	−4.93	−4.55
Ethylbenzene	−2.10	−3.08	−5.18	−1.92	−3.34	−5.26	−5.08
o-Xylene	−2.43	−2.88	−5.31	−2.22	−3.13	−5.36	−5.07
m-Xylene	−2.38	−2.85	−5.22	−2.17	−3.10	−5.27	−5.25
p-Xylene	−2.35	−2.84	−5.20	−2.15	−3.10	−5.25	−5.19
Naphthalene	−3.74	−3.92	−7.66	−3.37	−4.32	−7.69	−6.97
Anthracene	−5.03	−5.50	−10.54	−4.55	−6.05	−10.60	−10.47
Methanol	−3.81	−0.66	−4.48	−3.66	−0.82	−4.48	−3.87
Ethanol	−3.66	−1.61	−5.27	−3.52	−1.74	−5.25	−4.36
1,2-Ethanediol	−5.26	−2.92	−8.18	−5.17	−3.28	−8.45	−7.44
1-Propanol	−3.49	−2.21	−5.70	−3.38	−2.33	−5.70	−5.02
2-Propanol	−2.93	−2.05	−4.97	−2.88	−2.17	−5.06	−4.62
1-Butanol	−3.18	−2.79	−5.97	−3.12	−2.90	−6.03	−5.71
2-Methyl-2-propanol	−2.89	−2.22	−5.11	−2.82	−2.33	−5.14	−4.78
1-Pentanol	−3.13	−3.35	−6.49	−3.09	−3.46	−6.55	−6.40
Phenol	−5.03	−2.99	−8.02	−4.68	−3.20	−7.88	−8.69
1-Hexanol	−3.14	−3.84	−6.97	−3.10	−3.96	−7.06	−7.06
o-Cresol	−4.98	−3.28	−8.26	−4.66	−3.50	−8.15	−8.49
m-Cresol	−5.05	−3.23	−8.28	−4.72	−3.44	−8.16	−8.20
p-Cresol	−5.03	−3.24	−8.27	−4.70	−3.46	−8.16	−8.84
1-Heptanol	−3.11	−4.41	−7.52	−3.08	−4.52	−7.60	−7.75
1-Octanol	−3.04	−5.06	−8.10	−3.01	−5.14	−8.15	−8.13
1-Decanol	−3.23	−6.20	−9.42	−3.18	−6.25	−9.42	−9.88
Dimethyl ether	−2.26	0.80	−1.47	−1.82	0.43	−1.39	−2.06
Tetrahydrofuran	−2.62	−1.50	−4.12	−2.17	−1.85	−4.02	−3.93
1,4-Dioxane	−3.88	−1.19	−5.07	−3.13	−1.88	−5.01	−4.89
Diethyl ether	−1.96	−0.94	−2.90	−1.60	−1.26	−2.86	−2.89
Methyl propyl ether	−1.96	−0.67	−2.63	−1.59	−1.00	−2.60	−3.63
Methyl isopropyl ether	−1.95	−0.54	−2.49	−1.59	−0.86	−2.46	−4.64
1,2-Dimethoxyethane	−3.14	0.21	−2.93	−2.49	−0.43	−2.92	−4.55
t-Butyl methyl ether	−1.86	−0.70	−2.56	−1.52	−1.01	−2.53	−3.49
Anisole	−3.67	−1.53	−5.20	−3.02	−1.97	−4.99	−5.47
Tetrahydropyran	−2.04	−2.22	−4.27	−1.70	−2.52	−4.22	−4.21
Ethyl phenyl ether	−3.40	−2.36	−5.76	−2.83	−2.78	−5.61	−5.65
Formaldehyde	−5.37	2.38	−2.99	−5.54	2.46	−3.09	−3.23
Propanal	−4.74	0.41	−4.32	−4.96	0.52	−4.45	−4.13
Butanal	−4.58	−0.12	−4.71	−4.83	−0.01	−4.84	−4.62
Benzaldehyde	−5.70	−1.15	−6.86	−5.70	−1.29	−6.99	−6.13
Propanone	−4.88	0.38	−4.51	−5.06	0.48	−4.58	−3.15
Butanone	−4.59	−0.27	−4.86	−4.76	−0.17	−4.92	−3.78
Cyclopentanone	−4.24	−1.41	−5.65	−4.46	−1.27	−5.74	−5.01
2-Pentanone	−4.43	−0.80	−5.23	−4.61	−0.69	−5.30	−4.35
3-Pentanone	−4.29	−0.92	−5.21	−4.46	−0.81	−5.27	−4.36
2-Hexanone	−4.30	−1.38	−5.68	−4.47	−1.25	−5.71	−5.02
3,3-Dimethylbutanone	−4.16	−0.58	−4.73	−4.27	−0.46	−4.74	−4.53
2-Heptanone	−4.37	−1.94	−6.31	−4.57	−1.80	−6.37	−5.65
Methyl phenyl ketone	−5.72	−1.84	−7.56	−5.62	−1.97	−7.59	−6.74
2-Octanone	−4.35	−2.50	−6.86	−4.55	−2.36	−6.91	−6.38
Ethanoic acid	−6.17	−0.30	−6.48	−6.22	−0.27	−6.49	−6.35
Propanoic acid	−5.68	−0.93	−6.61	−5.73	−0.88	−6.61	−6.86
Butanoic acid	−5.45	−1.47	−6.92	−5.54	−1.42	−6.96	−7.58
Pentanoic acid	−5.42	−2.04	−7.47	−5.53	−1.98	−7.51	−8.22
Hexanoic acid	−5.37	−2.61	−7.99	−5.49	−2.54	−8.03	−8.82
Methyl methanoate	−5.62	2.23	−3.39	−5.43	2.04	−3.40	−2.82
Methyl ethanoate	−5.24	1.17	−4.07	−4.91	0.97	−3.94	−3.54
Methyl propanoate	−4.77	0.54	−4.23	−4.47	0.36	−4.11	−4.06
Ethyl ethanoate	−5.02	0.32	−4.70	−4.75	0.14	−4.61	−4.06
Methyl butanoate	−4.53	0.00	−4.53	−4.27	−0.18	−4.45	−4.59
Propyl ethanoate	−4.85	−0.26	−5.12	−4.65	−0.42	−5.07	−4.55
Methyl pentanoate	−4.50	−0.57	−5.07	−4.26	−0.74	−5.00	−5.13
Butyl ethanoate	−4.77	−0.83	−5.60	−4.59	−0.98	−5.58	−4.96
Methyl benzoate	−5.47	−0.96	−6.44	−4.96	−1.38	−6.33	−7.26

Table 18. (Cont.)

Solute	SM5.42R/AM1			SM5.42R/PM3			Expt.
	ΔG_{ENP}	G_{CDS}	ΔG_S^0	ΔG_{ENP}	G_{CDS}	ΔG_S^0	ΔG_S^0
2-Propen-1-ol	−3.25	−1.50	−4.76	−3.13	−1.73	−4.86	−5.27
2-Methoxyethanol	−4.69	−1.33	−6.02	−4.36	−1.76	−6.12	−5.83
m-Hydroxybenzaldehyde	−8.05	−1.82	−9.87	−7.94	−1.90	−9.84	−11.39
p-Hydroxybenzaldehyde	−8.63	−1.78	−10.42	−8.60	−1.84	−10.44	−12.36
Water	−6.59	0.52	−6.07	−6.42	0.39	−6.03	−4.43
Hydrogen	0.00	1.69	1.69	0.00	1.69	1.69	1.76
Methylamine	−2.12	−1.46	−3.59	−1.76	−1.79	−3.55	−3.78
Ethylamine	−1.69	−2.16	−3.85	−1.46	−2.45	−3.91	−4.09
Propylamine	−1.62	−2.77	−4.39	−1.40	−3.06	−4.45	−4.77
Trimethylamine	−1.56	−2.55	−4.11	−1.22	−2.75	−3.96	−3.60
Piperazine	−2.56	−6.07	−8.62	−2.11	−6.45	−8.56	−5.80
Butylamine	−1.55	−3.34	−4.89	−1.34	−3.62	−4.95	−5.35
Diethylamine	−0.91	−3.36	−4.27	−0.79	−3.58	−4.37	−4.75
Piperidine	−1.09	−4.78	−5.87	−0.99	−4.95	−5.95	−6.27
Dipropylamine	−0.76	−4.64	−5.40	−0.72	−4.83	−5.55	−6.02
Pyridine	−4.29	−1.44	−5.72	−4.12	−1.82	−5.95	−5.34
2-Methylpyrazine	−5.49	−0.99	−6.48	−4.66	−1.47	−6.13	−5.87
Aniline	−4.01	−2.95	−6.96	−3.50	−3.47	−6.97	−6.71
2-Methylpyridine	−4.39	−1.85	−6.24	−4.16	−2.21	−6.37	−6.14
3-Methylpyridine	−4.21	−1.71	−5.92	−4.04	−2.09	−6.12	−6.40
4-Methylpyridine	−4.25	−1.71	−5.96	−4.09	−2.09	−6.18	−6.60
2-Ethylpyrazine	−5.08	−1.53	−6.61	−4.33	−1.99	−6.32	−6.40
Ethanonitrile	−6.45	1.93	−4.53	−6.48	1.88	−4.60	−3.15
Propanonitrile	−5.73	1.35	−4.38	−5.74	1.31	−4.43	−3.66
Butanonitrile	−5.35	0.77	−4.58	−5.37	0.75	−4.62	−4.25
Benzonitrile	−5.07	−0.27	−5.33	−4.91	−0.53	−5.43	−6.09
Nitroethane	−4.38	0.14	−4.24	−5.69	1.27	−4.43	−3.93
1-Nitropropane	−3.92	−0.47	−4.39	−5.40	0.64	−4.76	−4.44
2-Nitropropane	−4.10	−0.22	−4.33	−5.10	0.89	−4.21	−4.23
1-Nitrobutane	−3.82	−1.04	−4.86	−5.35	0.09	−5.26	−5.11
Nitrobenzene	−5.30	−1.14	−6.44	−5.85	−0.31	−6.16	−6.63
2-Methyl-1-nitrobenzene	−5.30	−1.50	−6.81	−5.56	−0.73	−6.29	−6.80
1,1-Dimethyl-3-phenylurea	−8.34	−3.01	−11.34	−7.72	−3.62	−11.34	−13.12
9-Methyladenine	−9.97	−3.19	−13.15	−8.65	−4.65	−13.30	−13.56
Morpholine	−3.21	−3.56	−6.77	−2.65	−4.07	−6.72	−5.99
3-Ethyl-2-methoxypyrazine	−5.20	−0.77	−5.97	−4.16	−1.35	−5.51	−6.85
Hydrazine	−2.48	−5.11	−7.60	−2.26	−5.35	−7.61	−6.48
$OP(OCH_3)_3$	−10.01	2.03	−7.98	−5.70	−1.10	−6.79	−7.81
$OP(OC_2H_5)_3$	−9.35	−0.70	−10.05	−5.28	−3.73	−9.01	−8.88
$OP(OC_3H_7)_3$	−8.55	−2.49	−11.04	−4.75	−5.49	−10.23	−8.65
2,2-Dichloroethenyl dimethyl phosphate	−8.38	0.23	−8.14	−4.99	−2.82	−7.81	−8.59
Dimethyl 4-bromo-2,5-dichlorophenyl thiophosphate	−13.63	2.94	−10.69	−7.10	−2.88	−9.98	−12.30
Dimethyl 2,4,5-trichlorophenyl thiophosphate	−13.69	3.64	−10.05	−7.16	−2.13	−9.30	−11.69
Dimethyl 4-nitrophenyl thiophosphate	−17.84	6.99	−10.85	−12.12	2.26	−9.87	−11.70
Diethyl 2,4-dichlorophenyl thiophosphate	−13.47	2.46	−11.01	−7.00	−3.25	−10.25	−10.87
Dimethyl 3-methyl-4-thiomethoxyphenyl thiophosphate	−18.53	2.88	−15.65	−11.96	−3.02	−14.97	−12.55
Diethyl 4-nitrophenyl thiophosphonate	−16.00	5.06	−10.93	−11.30	0.50	−10.80	−11.31
O-Ethyl *O*′-4-bromo-2-chlorophenyl *S*-propyl phosphorothioate	−9.70	−0.75	−10.45	−5.06	−5.85	−10.91	−10.49
Ethyl 4-cyanophenyl phenylthiophosphonate	−17.52	4.27	−13.24	−11.31	−1.21	−12.52	−11.06
1-Propanethiol	−1.12	−2.02	−3.14	−0.82	−2.08	−2.90	−3.52
Thiophenol	−2.20	−3.11	−5.31	−2.18	−3.41	−5.59	−5.99
Thiophene	−1.84	−1.93	−3.77	−1.76	−2.20	−3.96	−3.89
Diethyl sulfide	−1.72	−2.52	−4.23	−1.35	−2.60	−3.95	−4.09
Thioanisole	−3.10	−3.40	−6.51	−2.92	−3.72	−6.64	−6.47
Dimethyl disulfide	−2.82	−2.00	−4.82	−2.35	−2.37	−4.72	−4.24
1,1-Difluoroethane	−2.68	0.42	−2.25	−2.02	0.24	−1.78	−1.13
Fluorobenzene	−2.64	−1.70	−4.34	−2.41	−2.05	−4.46	−3.87
Dichloromethane	−1.98	−1.72	−3.70	−2.18	−1.70	−3.88	−3.07
Trichloromethane	−1.21	−2.87	−4.08	−1.16	−2.82	−3.98	−3.81
Chloroethane	−1.62	−1.39	−3.00	−1.96	−1.40	−3.35	−2.58

Table 18. (Cont.)

Solute	SM5.42R/AM1			SM5.42R/PM3			Expt.
	ΔG_{ENP}	G_{CDS}	ΔG_S^0	ΔG_{ENP}	G_{CDS}	ΔG_S^0	ΔG_S^0
1,1,1-Trichloroethane	−1.51	−3.27	−4.78	−1.28	−3.22	−4.50	−3.69
1,1,2-Trichloroethane	−2.10	−3.40	−5.50	−2.32	−3.34	−5.67	−4.53
1-Chloropropane	−1.36	−2.00	−3.36	−1.68	−2.00	−3.67	−3.06
2-Chloropropane	−1.58	−1.85	−3.42	−1.85	−1.85	−3.70	−2.84
Z-1,2-Dichloroethene	−1.99	−1.46	−3.45	−1.99	−1.53	−3.52	−3.71
E-1,2-Dichloroethene	−0.93	−1.48	−2.41	−1.03	−1.55	−2.58	−3.61
Trichloroethene	−0.86	−2.43	−3.29	−0.77	−2.47	−3.24	−3.75
Chlorobenzene	−2.29	−3.05	−5.34	−1.97	−3.29	−5.26	−5.00
o-Dichlorobenzene	−2.64	−3.71	−6.35	−2.23	−3.92	−6.15	−6.01
p-Dichlorobenzene	−1.90	−3.79	−5.68	−1.64	−4.00	−5.64	−5.67
2,2′-Dichlorobiphenyl	−4.04	−5.93	−9.97	−3.48	−6.36	−9.84	−9.41
2,3-Dichlorobiphenyl	−3.66	−5.94	−9.60	−3.15	−6.37	−9.52	−9.23
2,2′,3-Trichlorobiphenyl	−4.13	−6.59	−10.71	−3.51	−6.99	−10.50	−9.12
Bromomethane	−1.44	−1.21	−2.64	−1.51	−1.28	−2.79	−2.43
Dibromomethane	−1.36	−3.19	−4.55	−1.21	−3.28	−4.50	−4.18
Tribromomethane	−0.61	−5.03	−5.64	−0.45	−5.14	−5.59	−5.62
Bromoethane	−1.35	−2.12	−3.47	−1.55	−2.18	−3.73	−2.90
1-Bromopropane	−1.13	−2.72	−3.85	−1.26	−2.77	−4.04	−3.42
2-Bromopropane	−1.28	−2.56	−3.85	−1.55	−2.62	−4.17	−3.40
3-Bromopropene	−1.34	−1.98	−3.32	−1.42	−2.13	−3.55	−3.30
1-Bromobutane	−1.08	−3.29	−4.37	−1.22	−3.33	−4.55	−4.16
1-Bromopentane	−1.04	−3.86	−4.90	−1.19	−3.89	−5.08	−4.68
Bromobenzene	−2.25	−3.76	−6.01	−1.89	−4.05	−5.94	−5.46
p-Dibromobenzene	−1.79	−5.21	−7.00	−1.50	−5.53	−7.02	−7.47
Bromotoluene	−3.12	−4.17	−7.30	−3.05	−4.46	−7.50	−6.36
Diiodomethane	−0.99	−4.30	−5.29	−0.53	−4.34	−4.88	−5.63
Iodomethane	−1.32	−1.75	−3.07	−1.24	−1.80	−3.04	−3.07
Iodoethane	−1.21	−2.67	−3.88	−1.49	−2.70	−4.19	−3.45
2-Iodopropane	−1.13	−3.11	−4.24	−1.63	−3.14	−4.76	−4.40
Iodobenzene	−2.02	−4.32	−6.33	−1.75	−4.58	−6.33	−6.18
Bromotrifluoromethane	−0.34	−0.47	−0.80	−0.25	−0.76	−1.01	−0.75
Chlorodifluoromethane	−2.63	0.03	−2.60	−1.92	−0.14	−2.05	−1.97
Difluorodichloromethane	−0.19	−1.15	−1.35	−0.19	−1.28	−1.47	−1.25
Fluorotrichloromethane	−0.10	−2.53	−2.62	−0.12	−2.56	−2.68	−2.63
Tetrafluoromethane	−0.76	1.70	0.94	−0.46	1.36	0.90	1.50
1-Bromo-1-chloro-2,2,2-trifluoroethane	−1.34	−1.86	−3.20	−1.04	−2.11	−3.16	−3.27
Tetrachloroethene	−0.01	−3.31	−3.31	0.00	−3.33	−3.33	−4.24
1,1,2-Trichloro-1,2,2-trifluoroethane	−0.22	−2.07	−2.29	−0.27	−2.24	−2.51	−2.54
2,2,2-Trifluoroethanol	−6.07	−0.42	−6.49	−5.52	−0.75	−6.27	−4.81
1,1-Dichloro-2,2-difluoroethyl methyl ether	−2.77	−0.91	−3.68	−2.20	−1.15	−3.35	−4.02
1,1,1-Trifluoropropan-2-ol	−4.02	−0.76	−4.78	−3.47	−1.12	−4.58	−5.12
1,1,1,3,3,3-Hexafluoropropan-2-ol	−4.00	0.56	−3.44	−3.30	−0.01	−3.31	−5.76
p-Bromophenol	−5.10	−4.41	−9.50	−4.64	−4.67	−9.31	−10.59
2,6-Dichlorobenzonitrile	−5.32	−1.75	−7.07	−5.16	−1.94	−7.10	−9.18
4-Amino-3,5,6-trichloropyridine-2-carboxylic acid	−7.55	−4.28	−11.83	−7.76	−4.65	−12.41	−12.37
Solvent: 1-nonanol							
Benzene	−2.18	−2.28	−4.46	−1.97	−2.55	−4.51	−3.82
Toluene	−2.25	−2.54	−4.79	−2.04	−2.80	−4.85	−4.34
Ethylbenzene	−2.05	−3.03	−5.09	−1.88	−3.29	−5.17	−4.61
Phenol	−4.93	−2.95	−7.88	−4.58	−3.16	−7.75	−8.61
2-Methoxyethanol	−4.60	−1.28	−5.88	−4.28	−1.71	−5.99	−5.61
Ethylamine	−1.66	−2.13	−3.79	−1.43	−2.42	−3.85	−4.02
Propylamine	−1.59	−2.73	−4.33	−1.37	−3.02	−4.39	−4.66
Butylamine	−1.52	−3.30	−4.82	−1.31	−3.57	−4.88	−5.22
p-Bromophenol	−5.00	−4.36	−9.36	−4.55	−4.62	−9.18	−10.36
Solvent: 1-decanol							
Phenol	−4.82	−2.92	−7.74	−4.48	−3.14	−7.62	−8.58
o-Cresol	−4.77	−3.20	−7.97	−4.46	−3.42	−7.88	−8.58
m-Cresol	−4.84	−3.15	−7.99	−4.52	−3.36	−7.88	−8.01
p-Cresol	−4.82	−3.16	−7.98	−4.50	−3.38	−7.89	−8.91
2-Methoxyethanol	−4.51	−1.25	−5.75	−4.18	−1.68	−5.87	−5.41
Ethylamine	−1.63	−2.10	−3.73	−1.40	−2.40	−3.80	−3.91

Table 18. (Cont.)

Solute	SM5.42R/AM1			SM5.42R/PM3			Expt.
	ΔG_{ENP}	G_{CDS}	ΔG_S^0	ΔG_{ENP}	G_{CDS}	ΔG_S^0	ΔG_S^0
Propylamine	−1.56	−2.71	−4.27	−1.34	−2.99	−4.33	−4.59
Butylamine	−1.49	−3.27	−4.76	−1.28	−3.54	−4.83	−5.15
Chlorobenzene	−2.18	−2.99	−5.17	−1.88	−3.23	−5.11	−4.83
p-Bromophenol	−4.89	−4.33	−9.21	−4.45	−4.59	−9.04	−10.32
Solvent: benzyl alcohol							
n-Octane	0.03	−4.09	−4.06	0.04	−4.08	−4.04	−3.77
Toluene	−2.35	−2.81	−5.16	−2.14	−3.10	−5.24	−4.46
Ethanol	−3.74	−1.65	−5.39	−3.60	−1.78	−5.38	−4.84
1,4-Dioxane	−3.96	−1.31	−5.27	−3.20	−2.05	−5.25	−5.39
Formaldehyde	−5.51	2.61	−2.90	−5.69	2.71	−2.98	−3.48
Butanone	−4.72	−0.24	−4.96	−4.89	−0.11	−5.00	−4.57
Ethanoic acid	−6.32	−0.34	−6.66	−6.36	−0.31	−6.67	−6.96
Solvent: *m*-cresol							
n-Octane	0.03	−3.77	−3.73	0.04	−3.75	−3.72	−4.02
Toluene	−2.37	−2.47	−4.84	−2.15	−2.74	−4.89	−4.58
Ethanol	−3.77	−1.67	−5.44	−3.62	−1.81	−5.42	−5.58
1,4-Dioxane	−3.99	−0.97	−4.95	−3.22	−1.72	−4.94	−6.82
Butanone	−4.76	−0.24	−5.00	−4.93	−0.20	−5.13	−5.98
Solvent: butanone							
n-Octane	0.03	−4.45	−4.42	0.04	−4.42	−4.38	−4.64
Toluene	−2.44	−3.27	−5.71	−2.22	−3.52	−5.74	−5.06
Ethanol	−3.88	−1.15	−5.03	−3.73	−1.26	−4.99	−4.46
1,4-Dioxane	−4.11	−1.73	−5.83	−3.31	−2.35	−5.66	−5.02
Formaldehyde	−5.75	2.15	−3.61	−5.94	2.28	−3.65	−1.77
Ethanoic acid	−6.56	−0.50	−7.06	−6.60	−0.47	−7.08	−6.88
Propanoic acid	−6.04	−1.17	−7.21	−6.09	−1.13	−7.22	−7.05
Butanoic acid	−5.79	−1.78	−7.57	−5.89	−1.73	−7.62	−7.34
Pentanoic acid	−5.76	−2.41	−8.17	−5.88	−2.35	−8.22	−7.54
Hexanoic acid	−5.71	−3.03	−8.74	−5.83	−2.96	−8.80	−8.07
Solvent: 4-methyl-2-pentanone							
Naphthalene	−3.87	−4.99	−8.86	−3.49	−5.37	−8.86	−7.45
Phenol	−5.19	−3.02	−8.21	−4.83	−3.21	−8.03	−9.38
m-Cresol	−5.21	−3.35	−8.56	−4.87	−3.54	−8.41	−8.79
Ethanoic acid	−6.37	−0.55	−6.92	−6.41	−0.52	−6.93	−6.33
Propanoic acid	−5.86	−1.25	−7.11	−5.91	−1.20	−7.12	−6.85
Butanoic acid	−5.62	−1.87	−7.50	−5.72	−1.82	−7.54	−7.44
Methylamine	−2.18	−0.83	−3.01	−1.81	−1.10	−2.92	−4.14
Trimethylamine	−1.61	−1.57	−3.18	−1.25	−1.71	−2.96	−2.86
Diethylamine	−0.94	−2.63	−3.57	−0.82	−2.79	−3.61	−3.63
Pyridine	−4.43	−1.48	−5.92	−4.27	−1.82	−6.09	−5.33
Aniline	−4.13	−3.31	−7.44	−3.60	−3.79	−7.39	−7.54
Ammonia	−2.99	−0.35	−3.34	−2.31	−0.67	−2.98	−2.52
Solvent: cyclohexanone							
n-Octane	0.03	−3.62	−3.59	0.04	−3.62	−3.58	−4.57
Toluene	−2.41	−2.75	−5.16	−2.20	−3.03	−5.22	−5.05
Ethanol	−3.84	−0.82	−4.66	−3.69	−0.95	−4.64	−4.41
1,4-Dioxane	−4.06	−1.22	−5.28	−3.28	−1.90	−5.17	−4.95
Butanone	−4.87	−0.06	−4.93	−5.04	0.11	−4.94	−4.42
Ethanoic acid	−6.48	−0.12	−6.61	−6.53	−0.10	−6.63	−6.43
Propanoic acid	−5.96	−0.72	−6.68	−6.02	−0.69	−6.71	−7.18
Solvent: methyl phenyl ketone							
n-Octane	0.03	−4.04	−4.01	0.04	−4.04	−4.00	−4.24
Toluene	−2.43	−3.09	−5.52	−2.22	−3.37	−5.58	−4.90
Ethanol	−3.87	−0.76	−4.63	−3.72	−0.90	−4.62	−4.12
1,4-Dioxane	−4.09	−1.38	−5.47	−3.31	−2.08	−5.38	−5.03
Butanone	−4.92	−0.28	−5.20	−5.10	−0.13	−5.23	−4.39
Ethanoic acid	−6.54	−0.07	−6.60	−6.58	−0.05	−6.63	−6.20
Solvent: ethyl acetate							
n-Octane	0.03	−4.51	−4.48	0.03	−4.47	−4.44	−4.72
Toluene	−2.09	−3.33	−5.42	−1.90	−3.56	−5.47	−5.05
Methanol	−3.51	−0.08	−3.58	−3.36	−0.22	−3.58	−3.37

Table 18. (Cont.)

Solute	SM5.42R/AM1			SM5.42R/PM3			Expt.
	ΔG_{ENP}	G_{CDS}	ΔG_S^0	ΔG_{ENP}	G_{CDS}	ΔG_S^0	ΔG_S^0
Ethanol	−3.36	−1.08	−4.44	−3.22	−1.19	−4.41	−4.24
1,2-Ethanediol	−4.83	−2.06	−6.89	−4.75	−2.43	−7.17	−6.82
1-Propanol	−3.20	−1.74	−4.94	−3.09	−1.84	−4.94	−4.90
1-Butanol	−2.92	−2.38	−5.31	−2.87	−2.48	−5.35	−5.77
1-Pentanol	−2.88	−3.02	−5.89	−2.83	−3.10	−5.94	−6.13
Phenol	−4.60	−2.88	−7.48	−4.27	−3.07	−7.34	−8.70
1-Hexanol	−2.88	−3.62	−6.50	−2.85	−3.72	−6.56	−6.92
1-Heptanol	−2.86	−4.25	−7.11	−2.83	−4.34	−7.17	−7.56
1-Octanol	−2.79	−4.92	−7.71	−2.76	−4.97	−7.74	−8.41
1,4-Dioxane	−3.56	−1.75	−5.30	−2.87	−2.36	−5.23	−5.03
Ethanoic acid	−5.65	−0.46	−6.11	−5.69	−0.43	−6.12	−6.46
Propanoic acid	−5.19	−1.13	−6.33	−5.24	−1.09	−6.33	−6.95
Butanoic acid	−4.99	−1.74	−6.73	−5.07	−1.70	−6.77	−7.34
Water	−6.07	2.04	−4.03	−5.91	1.89	−4.01	−4.26
Solvent: *n*-butyl acetate							
Naphthalene	−3.22	−4.90	−8.12	−2.90	−5.27	−8.17	−7.59
Methanol	−3.35	−0.03	−3.38	−3.21	−0.18	−3.39	−3.04
Ethanol	−3.21	−1.04	−4.25	−3.08	−1.15	−4.23	−3.97
1,2-Ethanediol	−4.62	−2.02	−6.64	−4.54	−2.39	−6.92	−6.27
1-Propanol	−3.06	−1.70	−4.75	−2.95	−1.80	−4.76	−4.52
1-Butanol	−2.79	−2.34	−5.13	−2.74	−2.44	−5.18	−5.23
1-Pentanol	−2.75	−2.97	−5.72	−2.71	−3.06	−5.77	−5.78
Phenol	−4.38	−2.85	−7.24	−4.07	−3.04	−7.12	−8.96
1-Hexanol	−2.76	−3.57	−6.33	−2.72	−3.67	−6.39	−6.62
o-Cresol	−4.34	−3.23	−7.56	−4.05	−3.42	−7.47	−8.90
m-Cresol	−4.41	−3.17	−7.58	−4.11	−3.37	−7.48	−8.44
p-Cresol	−4.38	−3.19	−7.57	−4.09	−3.39	−7.48	−9.28
1-Heptanol	−2.73	−4.20	−6.93	−2.70	−4.29	−7.00	−7.14
1-Octanol	−2.66	−4.87	−7.53	−2.64	−4.92	−7.56	−8.17
Ethanoic acid	−5.38	−0.41	−5.79	−5.42	−0.38	−5.80	−6.11
Water	−5.81	2.12	−3.69	−5.65	1.97	−3.68	−4.13
Pyridine	−3.70	−1.49	−5.19	−3.53	−1.82	−5.35	−5.31
Aniline	−3.51	−3.19	−6.70	−3.05	−3.65	−6.71	−7.30
p-Bromophenol	−4.44	−4.21	−8.65	−4.04	−4.45	−8.49	−10.57
Solvent: di-*n*-butyl ether							
n-Octane	0.02	−4.76	−4.74	0.03	−4.72	−4.69	−5.24
Toluene	−1.62	−3.51	−5.13	−1.47	−3.74	−5.21	−4.87
Ethanol	−2.65	−1.15	−3.80	−2.53	−1.26	−3.79	−3.51
1,4-Dioxane	−2.80	−1.87	−4.67	−2.26	−2.49	−4.75	−4.37
Butanone	−3.10	−0.86	−3.96	−3.22	−0.70	−3.92	−3.78
Ethanoic acid	−4.42	−0.52	−4.94	−4.45	−0.49	−4.93	−5.21
Propanoic acid	−4.06	−1.23	−5.29	−4.09	−1.18	−5.28	−6.11
Diethylamine	−0.66	−2.71	−3.38	−0.57	−2.86	−3.44	−3.80
Pyridine	−3.00	−1.64	−4.63	−2.84	−1.97	−4.80	−4.65
2-Methylpyrazine	−3.90	−0.60	−4.50	−3.30	−0.99	−4.28	−5.12
2-Methylpyridine	−3.05	−2.10	−5.15	−2.85	−2.39	−5.24	−5.20
2-Ethylpyrazine	−3.60	−1.23	−4.83	−3.05	−1.60	−4.66	−5.87
Solvent: tetrahydrofuran							
n-Octane	0.03	−4.33	−4.30	0.03	−4.30	−4.27	−5.39
Toluene	−2.19	−3.22	−5.41	−1.99	−3.47	−5.46	−5.50
Ethanol	−3.51	−1.02	−4.53	−3.37	−1.14	−4.51	−4.56
1,4-Dioxane	−3.71	−1.63	−5.34	−3.00	−2.27	−5.26	−5.17
Butanone	−4.35	−0.59	−4.94	−4.51	−0.42	−4.93	−4.54
Solvent: diethyl ether							
n-Octane	0.03	−5.18	−5.15	0.03	−5.12	−5.09	−5.62
Benzene	−1.83	−3.36	−5.19	−1.65	−3.58	−5.23	−4.21
Toluene	−1.89	−3.77	−5.66	−1.72	−3.98	−5.70	−5.23
Ethylbenzene	−1.73	−4.41	−6.14	−1.58	−4.61	−6.19	−5.45
o-Xylene	−1.99	−4.20	−6.19	−1.82	−4.40	−6.22	−5.58
m-Xylene	−1.95	−4.18	−6.13	−1.78	−4.39	−6.17	−5.56
Naphthalene	−3.04	−5.42	−8.46	−2.74	−5.76	−8.49	−7.25
Methanol	−3.19	−0.23	−3.42	−3.05	−0.37	−3.42	−3.61

Table 18. (Cont.)

Solute	SM5.42R/AM1			SM5.42R/PM3			Expt.
	ΔG_{ENP}	G_{CDS}	ΔG_S^0	ΔG_{ENP}	G_{CDS}	ΔG_S^0	ΔG_S^0
Ethanol	−3.05	−1.30	−4.35	−2.92	−1.40	−4.33	−4.41
1,2-Ethanediol	−4.39	−2.24	−6.63	−4.31	−2.58	−6.89	−6.20
1-Propanol	−2.90	−2.03	−4.94	−2.81	−2.12	−4.93	−4.90
2-Propanol	−2.44	−1.90	−4.33	−2.40	−1.99	−4.39	−4.44
1-Butanol	−2.66	−2.75	−5.41	−2.60	−2.83	−5.44	−5.69
2-Methyl-2-Propanol	−2.40	−2.22	−4.62	−2.33	−2.29	−4.63	−4.80
Cyclopentanol	−2.27	−3.74	−6.01	−2.24	−3.81	−6.05	−6.50
1-Pentanol	−2.62	−3.45	−6.07	−2.57	−3.52	−6.10	−6.11
Phenol	−4.16	−3.24	−7.40	−3.86	−3.41	−7.27	−8.75
1-Hexanol	−2.62	−4.13	−6.75	−2.59	−4.21	−6.79	−6.82
m-Cresol	−4.18	−3.64	−7.82	−3.90	−3.81	−7.71	−7.95
1-Heptanol	−2.60	−4.83	−7.43	−2.57	−4.90	−7.46	−7.51
1-Octanol	−2.53	−5.57	−8.10	−2.51	−5.60	−8.10	−7.25
1,4-Dioxane	−3.23	−2.13	−5.36	−2.60	−2.72	−5.32	−4.67
Anisole	−3.01	−2.82	−5.83	−2.47	−3.17	−5.64	−5.71
Ethanal	−4.04	0.42	−3.62	−4.25	0.56	−3.69	−2.85
Propanal	−3.80	−0.37	−4.17	−3.99	−0.23	−4.21	−3.85
Benzaldehyde	−4.61	−2.45	−7.06	−4.60	−2.51	−7.11	−6.08
Butanone	−3.67	−1.19	−4.86	−3.80	−1.03	−4.83	−4.09
Methyl phenyl ketone	−4.58	−3.25	−7.83	−4.51	−3.30	−7.81	−6.79
Ethanoic acid	−5.11	−0.71	−5.82	−5.14	−0.67	−5.82	−6.26
Propanoic acid	−4.70	−1.45	−6.15	−4.74	−1.40	−6.14	−6.75
Butanoic acid	−4.51	−2.13	−6.65	−4.59	−2.07	−6.66	−7.32
Pentanoic acid	−4.49	−2.84	−7.33	−4.57	−2.76	−7.33	−7.87
Hexanoic acid	−4.45	−3.54	−7.99	−4.54	−3.46	−8.00	−8.85
2-Propen-1-ol	−2.72	−1.42	−4.14	−2.61	−1.61	−4.22	−4.87
2-Methoxyethanol	−3.92	−1.25	−5.16	−3.63	−1.60	−5.23	−5.12
m-Hydroxybenzaldehyde	−6.61	−2.32	−8.93	−6.51	−2.33	−8.84	−11.36
p-Hydroxybenzaldehyde	−7.01	−2.29	−9.30	−6.97	−2.27	−9.24	−12.07
Water	−5.53	2.00	−3.53	−5.37	1.86	−3.52	−3.85
Methylamine	−1.79	−0.97	−2.75	−1.48	−1.22	−2.70	−2.32
Ethylamine	−1.43	−1.78	−3.21	−1.22	−2.00	−3.23	−2.89
Dimethylamine	−1.40	−1.54	−2.94	−1.16	−1.73	−2.89	−2.63
Propylamine	−1.36	−2.52	−3.88	−1.17	−2.73	−3.90	−3.65
Trimethylamine	−1.31	−1.94	−3.26	−1.02	−2.06	−3.07	−2.78
Butylamine	−1.31	−3.23	−4.53	−1.12	−3.42	−4.54	−4.44
Diethylamine	−0.76	−2.99	−3.75	−0.66	−3.12	−3.78	−3.83
Piperidine	−0.91	−4.25	−5.17	−0.83	−4.34	−5.17	−4.82
Dipropylamine	−0.63	−4.42	−5.05	−0.60	−4.51	−5.11	−4.96
Pyridine	−3.50	−1.92	−5.41	−3.33	−2.22	−5.55	−4.81
Aniline	−3.34	−3.60	−6.94	−2.90	−4.04	−6.93	−6.51
Ethanonitrile	−5.17	1.19	−3.98	−5.16	1.18	−3.98	−3.59
Benzonitrile	−4.11	−1.61	−5.72	−3.96	−1.80	−5.76	−6.36
Nitrobenzene	−4.24	−2.89	−7.13	−4.79	−2.35	−7.14	−6.85
2-Methyl-1-nitrobenzene	−4.23	−3.35	−7.58	−4.54	−2.83	−7.37	−7.21
Ethanamide	−6.30	−0.09	−6.40	−5.94	−0.16	−6.11	−6.16
Ammonia	−2.46	−0.37	−2.83	−1.89	−0.67	−2.56	−1.41
Hydrazine	−2.10	−4.53	−6.63	−1.91	−4.71	−6.62	−6.11
Hydrogen sulfide	−0.47	−0.15	−0.62	−0.44	−0.24	−0.68	−0.60
Chlorobenzene	−1.86	−4.10	−5.96	−1.60	−4.29	−5.89	−5.42
p-Dichlorobenzene	−1.57	−4.83	−6.40	−1.35	−5.00	−6.35	−6.18
Bromobenzene	−1.83	−4.79	−6.62	−1.55	−5.03	−6.58	−5.99
Iodomethane	−1.06	−2.16	−3.22	−0.97	−2.20	−3.17	−3.51
Iodobenzene	−1.65	−5.34	−6.99	−1.44	−5.56	−7.00	−6.64
Solvent: isopropyl ether							
n-Octane	0.03	−5.19	−5.17	0.03	−5.14	−5.11	−5.38
Toluene	−1.81	−3.79	−5.60	−1.64	−4.00	−5.64	−4.91
Naphthalene	−2.91	−5.45	−8.36	−2.62	−5.79	−8.41	−7.24
Ethanol	−2.93	−1.29	−4.22	−2.81	−1.39	−4.20	−3.90
Phenol	−4.00	−3.24	−7.24	−3.71	−3.41	−7.12	−8.35
1,4-Dioxane	−3.10	−2.13	−5.23	−2.50	−2.72	−5.22	−4.42
Formaldehyde	−4.15	1.84	−2.31	−4.28	1.96	−2.32	−1.04
Butanone	−3.50	−1.18	−4.68	−3.63	−1.02	−4.65	−3.96
Ethanoic acid	−4.91	−0.69	−5.60	−4.94	−0.66	−5.59	−5.73

Table 18. (Cont.)

Solute	SM5.42R/AM1			SM5.42R/PM3			Expt.
	ΔG_{ENP}	G_{CDS}	ΔG_S^0	ΔG_{ENP}	G_{CDS}	ΔG_S^0	ΔG_S^0
Propanoic acid	−4.51	−1.44	−5.95	−4.55	−1.39	−5.94	−6.37
Butanoic acid	−4.34	−2.12	−6.46	−4.41	−2.06	−6.47	−6.85
Pentanoic acid	−4.31	−2.83	−7.14	−4.39	−2.76	−7.14	−7.59
Hexanoic acid	−4.27	−3.54	−7.81	−4.36	−3.45	−7.81	−8.23
p-Hydroxybenzaldehyde	−6.71	−2.28	−8.99	−6.67	−2.27	−8.93	−11.63
Water	−5.32	2.05	−3.27	−5.17	1.90	−3.27	−3.58
Trimethylamine	−1.26	−1.94	−3.21	−0.98	−2.06	−3.03	−2.74
Butylamine	−1.26	−3.23	−4.49	−1.08	−3.42	−4.50	−4.24
Diethylamine	−0.73	−2.99	−3.73	−0.64	−3.13	−3.76	−3.78
Pyridine	−3.35	−1.92	−5.27	−3.19	−2.23	−5.42	−4.88
Aniline	−3.21	−3.61	−6.82	−2.78	−4.05	−6.83	−6.67
Solvent: anisole							
n-Octane	0.03	−4.59	−4.56	0.03	−4.56	−4.53	−4.62
Toluene	−1.89	−3.50	−5.38	−1.71	−3.74	−5.45	−4.95
Ethanol	−3.05	−0.68	−3.72	−2.92	−0.80	−3.72	−3.59
1,4-Dioxane	−3.22	−1.64	−4.86	−2.60	−2.31	−4.90	−5.06
Butanone	−3.66	−0.78	−4.44	−3.80	−0.66	−4.46	−4.43
Solvent: ethoxybenzene							
n-Octane	0.03	−4.68	−4.66	0.03	−4.65	−4.62	−4.75
Toluene	−1.88	−3.54	−5.42	−1.71	−3.78	−5.48	−4.99
Ethanol	−3.04	−0.79	−3.83	−2.91	−0.91	−3.82	−3.45
1,4-Dioxane	−3.21	−1.72	−4.93	−2.59	−2.37	−4.96	−4.87
Butanone	−3.65	−0.83	−4.47	−3.78	−0.70	−4.49	−4.28
Solvent: diphenyl ether							
n-Octane	0.03	−6.17	−6.14	0.03	−6.09	−6.06	−4.38
Toluene	−1.79	−4.58	−6.38	−1.63	−4.78	−6.41	−4.86
Ethanol	−2.91	−1.09	−4.00	−2.79	−1.20	−3.99	−3.22
1,4-Dioxane	−3.07	−2.47	−5.54	−2.48	−3.12	−5.60	−4.83
Butanone	−3.46	−1.70	−5.16	−3.59	−1.58	−5.17	−4.08
Solvent: triethylamine							
n-Octane	0.02	−4.84	−4.82	0.02	−4.79	−4.76	−5.62
Toluene	−1.37	−3.44	−4.81	−1.24	−3.70	−4.95	−4.98
Ethanol	−2.25	−1.76	−4.01	−2.15	−1.87	−4.03	−3.87
1,4-Dioxane	−2.38	−2.02	−4.40	−1.92	−2.67	−4.59	−4.41
Butanone	−2.58	−0.62	−3.19	−2.68	−0.36	−3.03	−3.86
Solvent: Aniline							
n-Octane	0.03	−3.87	−3.85	0.03	−3.87	−3.84	−3.48
Toluene	−2.16	−2.80	−4.96	−1.96	−3.08	−5.05	−4.57
Ethanol	−3.46	−1.10	−4.56	−3.32	−1.24	−4.56	−4.45
1,4-Dioxane	−3.66	−1.13	−4.79	−2.96	−1.88	−4.83	−5.65
Butanone	−4.28	−0.20	−4.47	−4.43	−0.10	−4.53	−4.87
Ethanoic acid	−5.82	0.05	−5.77	−5.86	0.07	−5.79	−6.30
Propanoic acid	−5.35	−0.60	−5.95	−5.40	−0.57	−5.97	−6.20
Solvent: pyridine							
n-Octane	0.03	−4.37	−4.34	0.04	−4.36	−4.33	−4.50
Toluene	−2.37	−3.28	−5.65	−2.16	−3.55	−5.71	−5.10
Ethanol	−3.78	−0.99	−4.77	−3.63	−1.12	−4.75	−5.08
1,4-Dioxane	−4.00	−1.60	−5.59	−3.23	−2.29	−5.51	−5.14
Butanone	−4.77	−0.47	−5.24	−4.94	−0.30	−5.24	−4.61
Solvent: 2-methylpyridine							
n-Octane	0.03	−4.49	−4.46	0.03	−4.47	−4.44	−4.73
Toluene	−2.30	−3.33	−5.62	−2.09	−3.60	−5.69	−5.06
Ethanol	−3.67	−1.16	−4.82	−3.52	−1.29	−4.81	−5.01
1,4-Dioxane	−3.88	−1.69	−5.57	−3.13	−2.38	−5.51	−5.01
Butanone	−4.60	−0.50	−5.09	−4.76	−0.31	−5.08	−4.52
Solvent: 2,6-dimethylpyridine							
n-Octane	0.03	−4.59	−4.56	0.03	−4.56	−4.53	−4.88
Toluene	−2.18	−3.37	−5.55	−1.98	−3.65	−5.63	−5.03
Ethanol	−3.49	−1.28	−4.77	−3.35	−1.41	−4.75	−4.87
1,4-Dioxane	−3.69	−1.76	−5.45	−2.98	−2.45	−5.43	−4.90
Butanone	−4.32	−0.51	−4.83	−4.47	−0.31	−4.78	−4.34

Table 18. (Cont.)

Solute	SM5.42R/AM1			SM5.42R/PM3			Expt.
	ΔG_{ENP}	G_{CDS}	ΔG_S^0	ΔG_{ENP}	G_{CDS}	ΔG_S^0	ΔG_S^0
Solvent: acetonitrile							
n-Octane	0.03	−3.73	−3.70	0.04	−3.71	−3.68	−3.57
Toluene	−2.53	−2.80	−5.33	−2.31	−3.03	−5.33	−4.68
Ethanol	−4.01	−0.73	−4.74	−3.86	−0.84	−4.70	−4.43
1,4-Dioxane	−4.25	−1.26	−5.51	−3.43	−1.86	−5.29	−5.33
Butanone	−5.16	−0.45	−5.61	−5.34	−0.34	−5.69	−4.73
Solvent: benzonitrile							
n-Octane	0.03	−5.11	−5.08	0.04	−5.07	−5.03	−4.34
Toluene	−2.49	−3.83	−6.32	−2.27	−4.06	−6.33	−4.95
Ethanol	−3.96	−0.94	−4.90	−3.80	−1.06	−4.87	−4.05
1,4-Dioxane	−4.19	−1.94	−6.13	−3.38	−2.61	−5.99	−5.14
Butanone	−5.06	−1.03	−6.09	−5.24	−0.90	−6.14	−4.58
Solvent: nitromethane							
n-Octane	0.03	−3.08	−3.04	0.04	−3.08	−3.04	−3.15
Toluene	−2.53	−2.40	−4.93	−2.30	−2.65	−4.95	−4.52
Ethanol	−4.01	−0.38	−4.39	−3.86	−0.51	−4.37	−4.16
1,4-Dioxane	−4.25	−0.86	−5.11	−3.43	−1.49	−4.92	−5.46
Butanone	−5.16	−0.04	−5.19	−5.34	0.06	−5.28	−4.72
Solvent: nitroethane							
n-Octane	0.03	−3.67	−3.64	0.04	−3.66	−3.62	−3.89
Toluene	−2.50	−2.82	−5.33	−2.28	−3.06	−5.34	−4.88
Ethanol	−3.97	−0.56	−4.53	−3.82	−0.68	−4.50	−3.98
1,4-Dioxane	−4.21	−1.21	−5.42	−3.39	−1.84	−5.23	−5.28
Butanone	−5.09	−0.35	−5.44	−5.27	−0.24	−5.51	−4.73
Solvent: nitrobenzene							
Methanol	−4.17	0.70	−3.46	−4.00	0.54	−3.47	−2.93
Phenol	−5.53	−2.21	−7.74	−5.14	−2.43	−7.57	−7.86
o-Cresol	−5.47	−2.50	−7.97	−5.12	−2.73	−7.84	−8.16
m-Cresol	−5.54	−2.45	−7.99	−5.18	−2.67	−7.85	−7.29
p-Cresol	−5.52	−2.46	−7.98	−5.16	−2.69	−7.85	−8.13
Ethanoic acid	−6.78	0.35	−6.42	−6.82	0.36	−6.46	−4.78
Propanoic acid	−6.24	−0.27	−6.51	−6.30	−0.25	−6.55	−5.38
Butanoic acid	−5.98	−0.82	−6.80	−6.09	−0.79	−6.88	−5.84
Pentanoic acid	−5.96	−1.39	−7.34	−6.07	−1.35	−7.43	−6.47
Hexanoic acid	−5.90	−1.96	−7.86	−6.03	−1.92	−7.95	−7.26
Aniline	−4.38	−2.71	−7.09	−3.83	−3.21	−7.04	−7.15
p-Bromophenol	−5.60	−3.56	−9.15	−5.10	−3.84	−8.94	−9.76
Solvent: *o*-nitrotoluene							
Phenol	−5.45	−2.28	−7.74	−5.07	−2.49	−7.57	−7.79
Ethanoic acid	−6.69	0.29	−6.39	−6.74	0.30	−6.43	−4.68
Propanoic acid	−6.16	−0.34	−6.50	−6.21	−0.32	−6.53	−5.30
Butanoic acid	−5.91	−0.90	−6.80	−6.01	−0.87	−6.88	−5.76
p-Bromophenol	−5.53	−3.63	−9.16	−5.04	−3.91	−8.94	−9.57
Solvent: dimethylformamide							
n-Octane	0.03	−3.35	−3.31	0.04	−3.34	−3.31	−3.77
Toluene	−2.53	−2.50	−5.03	−2.31	−2.80	−5.10	−4.88
Ethanol	−4.01	−1.04	−5.05	−3.86	−1.17	−5.03	−5.23
1,4-Dioxane	−4.25	−1.14	−5.38	−3.43	−1.82	−5.25	−5.03
Butanone	−5.16	0.23	−4.93	−5.34	0.45	−4.90	−4.56
Solvent: dimethylacetamide							
n-Octane	0.03	−3.60	−3.56	0.04	−3.58	−3.55	−3.94
Toluene	−2.53	−2.65	−5.19	−2.31	−2.95	−5.25	−4.94
Ethanol	−4.02	−1.20	−5.21	−3.86	−1.33	−5.19	−5.40
1,4-Dioxane	−4.25	−1.28	−5.54	−3.43	−1.97	−5.40	−5.01
Butanone	−5.16	0.13	−5.04	−5.35	0.36	−4.98	−4.52
Solvent: 1-fluorooctane							
Methyl ethanoate	−4.14	−0.07	−4.21	−3.89	−0.24	−4.13	−3.59
Methyl propanoate	−3.77	−0.77	−4.54	−3.53	−0.93	−4.46	−4.09
Ethyl ethanoate	−3.96	−1.01	−4.97	−3.76	−1.15	−4.91	−4.16
Propyl ethanoate	−3.84	−1.69	−5.53	−3.68	−1.81	−5.49	−4.65

Table 18. (Cont.)

Solute	SM5.42R/AM1			SM5.42R/PM3			Expt.
	ΔG_{ENP}	G_{CDS}	ΔG_S^0	ΔG_{ENP}	G_{CDS}	ΔG_S^0	ΔG_S^0
Methyl pentanoate	−3.56	−2.08	−5.65	−3.36	−2.21	−5.58	−5.33
Butyl ethanoate	−3.78	−2.36	−6.13	−3.64	−2.47	−6.11	−5.22
Solvent: dichloromethane							
n-Octane	0.03	−5.07	−5.04	0.03	−5.02	−4.99	−5.18
Toluene	−2.26	−3.77	−6.03	−2.05	−3.96	−6.01	−5.53
Ethanol	−3.61	−0.79	−4.39	−3.46	−0.89	−4.36	−3.82
Phenol	−4.95	−2.89	−7.84	−4.60	−3.06	−7.66	−7.50
p-Cresol	−4.95	−3.29	−8.24	−4.62	−3.47	−8.09	−7.71
1,4-Dioxane	−3.82	−1.87	−5.69	−3.08	−2.47	−5.55	−4.82
Water	−6.50	3.08	−3.42	−6.33	2.94	−3.38	−2.63
Thiophenol	−2.16	−4.51	−6.67	−2.14	−4.71	−6.86	−7.11
p-Bromophenol	−5.02	−4.30	−9.32	−4.57	−4.53	−9.10	−9.09
Solvent: chloroform							
n-Octane	0.03	−5.35	−5.32	0.03	−5.29	−5.26	−5.25
Cyclohexane	−0.14	−4.42	−4.55	−0.10	−4.36	−4.46	−4.45
Benzene	−1.90	−3.50	−5.40	−1.71	−3.69	−5.41	−4.64
Toluene	−1.96	−3.93	−5.88	−1.78	−4.11	−5.89	−5.48
Ethylbenzene	−1.79	−4.59	−6.38	−1.64	−4.76	−6.40	−5.84
o-Xylene	−2.06	−4.37	−6.43	−1.89	−4.54	−6.43	−6.23
m-Xylene	−2.02	−4.35	−6.37	−1.85	−4.52	−6.37	−5.86
Naphthalene	−3.16	−5.67	−8.84	−2.85	−5.96	−8.81	−7.89
Methanol	−3.29	0.18	−3.11	−3.16	0.04	−3.12	−3.32
Ethanol	−3.16	−0.94	−4.09	−3.02	−1.04	−4.07	−3.94
1,2-Ethanediol	−4.54	−1.26	−5.80	−4.46	−1.53	−5.99	−5.98
1-Propanol	−3.00	−1.70	−4.70	−2.90	−1.79	−4.70	−4.41
2-Propanol	−2.52	−1.56	−4.08	−2.48	−1.66	−4.14	−4.28
1-Butanol	−2.75	−2.44	−5.19	−2.69	−2.53	−5.23	−5.28
2-Methyl-2-propanol	−2.48	−1.89	−4.37	−2.42	−1.97	−4.38	−4.48
1-Pentanol	−2.71	−3.18	−5.88	−2.66	−3.25	−5.92	−5.90
Phenol	−4.31	−3.09	−7.40	−4.00	−3.25	−7.25	−7.14
1-Hexanol	−2.71	−3.91	−6.62	−2.67	−3.99	−6.67	−6.67
o-Cresol	−4.26	−3.54	−7.80	−3.98	−3.71	−7.69	−7.55
m-Cresol	−4.33	−3.51	−7.83	−4.04	−3.67	−7.71	−6.70
p-Cresol	−4.31	−3.52	−7.83	−4.02	−3.69	−7.71	−7.59
1-Heptanol	−2.69	−4.64	−7.32	−2.65	−4.71	−7.37	−7.53
1,4-Dioxane	−3.34	−1.99	−5.32	−2.69	−2.60	−5.29	−6.21
Diethyl ether	−1.67	−1.86	−3.54	−1.36	−2.15	−3.51	−4.32
Anisole	−3.12	−2.97	−6.09	−2.56	−3.35	−5.91	−6.24
Tetrahydropyran	−1.75	−3.14	−4.89	−1.45	−3.40	−4.85	−5.84
Isopropyl ether	−1.33	−2.92	−4.25	−1.12	−3.18	−4.29	−3.78
Ethyl phenyl ether	−2.88	−3.97	−6.86	−2.40	−4.32	−6.72	−7.16
Formaldehyde	−4.51	1.61	−2.90	−4.66	1.59	−3.07	0.12
Ethanal	−4.20	0.14	−4.07	−4.42	0.14	−4.28	−3.65
Benzaldehyde	−4.79	−2.87	−7.66	−4.78	−3.03	−7.82	−7.09
Propanone	−4.08	−0.73	−4.81	−4.23	−0.71	−4.94	−4.42
Butanone	−3.82	−1.52	−5.34	−3.96	−1.49	−5.45	−5.43
Methyl phenyl ketone	−4.77	−3.70	−8.47	−4.69	−3.85	−8.54	−7.81
Ethanoic acid	−5.29	−0.18	−5.48	−5.33	−0.16	−5.49	−4.74
Propanoic acid	−4.87	−0.96	−5.82	−4.91	−0.92	−5.83	−5.37
Butanoic acid	−4.67	−1.67	−6.34	−4.75	−1.62	−6.37	−5.99
Pentanoic acid	−4.65	−2.40	−7.04	−4.73	−2.34	−7.07	−6.61
Hexanoic acid	−4.61	−3.13	−7.74	−4.70	−3.06	−7.76	−7.51
Methyl ethanoate	−4.45	−0.07	−4.51	−4.17	−0.27	−4.44	−4.90
Methyl propanoate	−4.05	−0.84	−4.88	−3.79	−1.02	−4.81	−5.48
Ethyl ethanoate	−4.26	−1.08	−5.34	−4.03	−1.26	−5.29	−5.58
Propyl ethanoate	−4.12	−1.83	−5.95	−3.95	−1.99	−5.94	−6.35
Methyl pentanoate	−3.82	−2.27	−6.10	−3.61	−2.44	−6.05	−6.68
Butyl ethanoate	−4.05	−2.56	−6.61	−3.90	−2.70	−6.61	−6.71
Methyl hexanoate	−3.77	−3.01	−6.78	−3.58	−3.16	−6.73	−7.24
Pentyl ethanoate	−4.02	−3.29	−7.31	−3.88	−3.42	−7.30	−7.36
Methyl benzoate	−4.63	−2.96	−7.59	−4.20	−3.31	−7.51	−7.81
2-Propen-1-ol	−2.81	−1.06	−3.87	−2.70	−1.25	−3.95	−4.34
p-Hydroxybenzaldehyde	−7.28	−2.43	−9.71	−7.24	−2.54	−9.78	−10.30

Table 18. (Cont.)

Solute	SM5.42R/AM1			SM5.42R/PM3			Expt.
	ΔG_{ENP}	G_{CDS}	ΔG_S^0	ΔG_{ENP}	G_{CDS}	ΔG_S^0	ΔG_S^0
Water	−5.71	2.98	−2.74	−5.55	2.84	−2.71	−2.05
Methylamine	−1.85	−1.06	−2.90	−1.52	−1.32	−2.84	−3.17
Ethylamine	−1.47	−1.91	−3.38	−1.26	−2.13	−3.40	−4.02
Dimethylamine	−1.44	−2.06	−3.50	−1.20	−2.25	−3.46	−3.69
Propylamine	−1.41	−2.68	−4.09	−1.21	−2.89	−4.10	−4.73
Trimethylamine	−1.36	−2.78	−4.13	−1.05	−2.90	−3.95	−3.90
Butylamine	−1.35	−3.42	−4.76	−1.16	−3.61	−4.77	−5.35
Diethylamine	−0.79	−3.54	−4.33	−0.69	−3.67	−4.36	−5.23
Piperidine	−0.94	−4.93	−5.87	−0.85	−5.01	−5.87	−6.37
Pyridine	−3.63	−2.72	−6.35	−3.46	−3.01	−6.47	−6.45
2-Methylpyrazine	−4.69	−2.48	−7.17	−3.97	−2.83	−6.81	−6.99
Aniline	−3.45	−3.62	−7.07	−3.00	−4.03	−7.03	−7.34
2-Methylpyridine	−3.71	−3.25	−6.96	−3.49	−3.51	−7.00	−6.98
3-Methylpyridine	−3.56	−3.14	−6.71	−3.39	−3.42	−6.82	−7.35
4-Methylpyridine	−3.61	−3.14	−6.75	−3.45	−3.42	−6.87	−7.50
2-Ethylpyrazine	−4.33	−3.17	−7.50	−3.68	−3.51	−7.20	−7.72
2,6-Dimethylpyridine	−3.75	−3.81	−7.56	−3.51	−4.04	−7.55	−7.74
Ethanonitrile	−5.38	0.40	−4.98	−5.38	0.40	−4.98	−4.44
Benzonitrile	−4.27	−2.56	−6.84	−4.12	−2.72	−6.84	−7.22
Nitrobenzene	−4.42	−3.49	−7.91	−4.97	−2.90	−7.87	−7.78
2-Methyl-1-nitrobenzene	−4.41	−3.94	−8.35	−4.71	−3.38	−8.09	−8.30
Ethanamide	−6.55	−0.28	−6.82	−6.18	−0.48	−6.66	−7.05
1,1-Dimethyl-3-phenylurea	−6.97	−5.12	−12.09	−6.44	−5.67	−12.11	−13.64
9-Methyladenine	−8.49	−5.91	−14.40	−7.35	−7.19	−14.54	−12.51
1-Methylthymine	−8.27	−2.10	−10.37	−7.39	−2.55	−9.94	−9.71
Morpholine	−2.77	−3.60	−6.37	−2.29	−4.01	−6.30	−6.72
Ammonia	−2.54	0.02	−2.52	−1.95	−0.29	−2.24	−2.41
Hydrazine	−2.17	−4.59	−6.76	−1.97	−4.77	−6.74	−7.46
$OP(OCH_3)_3$	−8.59	1.04	−7.55	−4.86	−1.77	−6.64	−9.74
$OP(OC_2H_5)_3$	−8.01	−2.21	−10.22	−4.50	−4.93	−9.42	−10.90
$OP(OC_3H_7)_3$	−7.34	−4.48	−11.82	−4.05	−7.16	−11.21	−11.11
Dimethyl 4-nitrophenyl thiophosphate	−15.13	3.46	−11.67	−10.31	−1.34	−11.65	−9.51
Thiophenol	−1.86	−4.81	−6.67	−1.85	−5.00	−6.85	−7.61
Thiophene	−1.58	−3.29	−4.87	−1.50	−3.46	−4.97	−5.83
Diethyl sulfide	−1.43	−3.90	−5.33	−1.14	−3.92	−5.06	−6.40
Hydrogen sulfide	−0.49	−1.18	−1.67	−0.45	−1.19	−1.65	−0.51
Thioanisole	−2.62	−5.24	−7.85	−2.47	−5.44	−7.91	−5.98
Fluorobenzene	−2.22	−2.88	−5.10	−2.03	−3.15	−5.18	−4.25
Chlorobenzene	−1.93	−4.27	−6.21	−1.67	−4.45	−6.11	−5.45
p-Dichlorobenzene	−1.62	−5.04	−6.66	−1.40	−5.20	−6.60	−6.32
Bromobenzene	−1.90	−5.01	−6.91	−1.60	−5.24	−6.84	−6.07
Iodobenzene	−1.71	−5.60	−7.30	−1.49	−5.80	−7.29	−6.60
Difluorodichloromethane	−0.17	−1.60	−1.77	−0.16	−1.75	−1.92	−1.55
Fluorotrichloromethane	−0.08	−3.03	−3.11	−0.11	−3.08	−3.19	−2.62
2,2,2-Trifluoroethanol	−5.18	0.29	−4.88	−4.72	−0.05	−4.76	−3.03
p-Bromophenol	−4.37	−4.55	−8.92	−3.97	−4.78	−8.75	−8.59
Solvent: carbon tetrachloride							
n-Octane	0.02	−5.80	−5.78	0.02	−5.74	−5.72	−5.25
2-Methylpropene	−0.42	−1.84	−2.27	−0.37	−1.92	−2.29	−2.63
1-Butene	−0.29	−2.06	−2.35	−0.25	−2.14	−2.39	−2.48
E-2-Pentene	−0.34	−3.11	−3.44	−0.29	−3.16	−3.46	−3.46
Benzene	−1.26	−3.90	−5.16	−1.14	−4.08	−5.21	−4.50
Toluene	−1.30	−4.36	−5.66	−1.18	−4.54	−5.71	−5.12
Ethylbenzene	−1.19	−5.08	−6.26	−1.08	−5.24	−6.32	−5.67
o-Xylene	−1.36	−4.84	−6.20	−1.24	−5.01	−6.25	−6.07
m-Xylene	−1.33	−4.83	−6.16	−1.22	−5.00	−6.21	−5.71
Naphthalene	−2.06	−6.26	−8.32	−1.85	−6.54	−8.39	−7.55
Methanol	−2.24	0.44	−1.80	−2.14	0.30	−1.84	−2.25
Ethanol	−2.14	−0.73	−2.87	−2.04	−0.84	−2.88	−2.96
1-Propanol	−2.03	−1.55	−3.58	−1.96	−1.64	−3.60	−3.64
2-Propanol	−1.71	−1.41	−3.12	−1.68	−1.51	−3.19	−3.15
1-Butanol	−1.87	−2.35	−4.21	−1.82	−2.43	−4.25	−4.20
2-Methyl-2-propanol	−1.67	−1.78	−3.46	−1.63	−1.86	−3.49	−3.40

Table 18. (Cont.)

Solute	SM5.42R/AM1			SM5.42R/PM3			Expt.
	ΔG_{ENP}	G_{CDS}	ΔG_S^0	ΔG_{ENP}	G_{CDS}	ΔG_S^0	ΔG_S^0
1-Pentanol	−1.84	−3.13	−4.96	−1.80	−3.20	−5.00	−4.73
Phenol	−2.88	−3.13	−6.01	−2.67	−3.29	−5.96	−6.14
1-Hexanol	−1.84	−3.93	−5.77	−1.81	−4.01	−5.82	−5.04
o-Cresol	−2.85	−3.64	−6.48	−2.65	−3.79	−6.45	−6.51
p-Cresol	−2.89	−3.61	−6.50	−2.69	−3.77	−6.46	−6.32
1-Heptanol	−1.83	−4.71	−6.53	−1.80	−4.78	−6.58	−6.49
1,4-Dioxane	−2.25	−2.28	−4.53	−1.82	−2.88	−4.69	−4.97
Anisole	−2.06	−3.40	−5.46	−1.69	−3.76	−5.45	−5.49
Benzaldehyde	−3.10	−3.31	−6.41	−3.09	−3.45	−6.54	−6.11
Propanone	−2.60	−0.94	−3.54	−2.70	−0.90	−3.60	−3.35
Butanone	−2.42	−1.78	−4.21	−2.52	−1.73	−4.25	−4.09
Cyclopentanone	−2.31	−3.02	−5.33	−2.44	−2.94	−5.37	−5.26
2-Pentanone	−2.34	−2.52	−4.86	−2.44	−2.46	−4.90	−4.81
2-Hexanone	−2.26	−3.31	−5.57	−2.36	−3.23	−5.59	−5.47
2-Heptanone	−2.30	−4.08	−6.38	−2.41	−3.99	−6.41	−6.12
Methyl phenyl ketone	−3.05	−4.18	−7.24	−3.00	−4.31	−7.31	−7.10
Ethanoic acid	−3.55	−0.25	−3.80	−3.57	−0.24	−3.80	−3.64
Propanoic acid	−3.26	−1.07	−4.33	−3.28	−1.04	−4.32	−4.09
Butanoic acid	−3.14	−1.83	−4.96	−3.19	−1.78	−4.97	−4.81
Hexanoic acid	−3.09	−3.39	−6.48	−3.15	−3.32	−6.47	−6.99
Methyl ethanoate	−2.93	−0.50	−3.43	−2.75	−0.69	−3.44	−3.82
Methyl propanoate	−2.66	−1.31	−3.98	−2.49	−1.49	−3.98	−4.43
Ethyl ethanoate	−2.80	−1.56	−4.36	−2.65	−1.73	−4.38	−4.40
Propyl ethanoate	−2.71	−2.36	−5.07	−2.60	−2.51	−5.11	−5.03
Methyl pentanoate	−2.52	−2.85	−5.37	−2.38	−3.00	−5.38	−5.71
Butyl ethanoate	−2.67	−3.14	−5.80	−2.57	−3.27	−5.84	−5.59
Methyl hexanoate	−2.49	−3.63	−6.12	−2.35	−3.77	−6.12	−6.39
Pentyl ethanoate	−2.64	−3.92	−6.56	−2.56	−4.04	−6.60	−6.35
Methyl benzoate	−3.03	−3.65	−6.68	−2.76	−3.99	−6.75	−7.19
p-Hydroxybenzaldehyde	−4.75	−2.52	−7.27	−4.71	−2.60	−7.32	−8.16
Water	−3.90	3.71	−0.19	−3.78	3.56	−0.21	−0.85
Methylamine	−1.27	−0.80	−2.07	−1.04	−1.04	−2.08	−2.53
Ethylamine	−1.01	−1.70	−2.71	−0.86	−1.91	−2.77	−2.77
Dimethylamine	−0.99	−1.72	−2.71	−0.82	−1.89	−2.71	−2.75
Propylamine	−0.97	−2.52	−3.48	−0.82	−2.71	−3.53	−3.59
Trimethylamine	−0.93	−2.46	−3.39	−0.72	−2.55	−3.26	−3.09
Butylamine	−0.93	−3.30	−4.23	−0.79	−3.47	−4.26	−4.34
Diethylamine	−0.54	−3.31	−3.85	−0.47	−3.42	−3.89	−4.12
Pyridine	−2.38	−2.84	−5.22	−2.24	−3.12	−5.36	−5.01
Aniline	−2.33	−3.83	−6.17	−2.01	−4.23	−6.24	−6.10
Benzonitrile	−2.77	−3.00	−5.78	−2.65	−3.14	−5.79	−6.28
1-Nitropropane	−2.14	−2.66	−4.81	−3.06	−1.95	−5.00	−4.49
Nitrobenzene	−2.81	−4.13	−6.94	−3.28	−3.64	−6.92	−6.92
2-Methyl-1-nitrobenzene	−2.80	−4.61	−7.41	−3.09	−4.15	−7.24	−7.49
Ammonia	−1.75	0.15	−1.60	−1.34	−0.15	−1.49	−1.06
$OP(OCH_3)_3$	−5.76	0.26	−5.51	−3.23	−2.57	−5.80	−7.24
$OP(OC_2H_5)_3$	−5.36	−3.14	−8.50	−2.98	−5.86	−8.84	−7.51
$OP(OC_3H_7)_3$	−4.92	−5.56	−10.48	−2.69	−8.24	−10.93	−8.60
Thioanisole	−1.70	−5.54	−7.24	−1.61	−5.75	−7.35	−5.66
Fluorobenzene	−1.44	−3.25	−4.69	−1.31	−3.53	−4.84	−3.64
Chlorobenzene	−1.27	−4.67	−5.93	−1.09	−4.83	−5.92	−5.21
p-Dichlorobenzene	−1.08	−5.43	−6.52	−0.93	−5.59	−6.52	−6.28
Bromobenzene	−1.25	−5.41	−6.66	−1.05	−5.64	−6.69	−5.85
Iodobenzene	−1.12	−6.01	−7.13	−0.99	−6.21	−7.20	−6.50
p-Bromophenol	−2.92	−4.60	−7.53	−2.66	−4.83	−7.48	−7.86
Solvent: 1,2-dichloroethane							
Methanol	−3.83	0.44	−3.39	−3.68	0.29	−3.39	−2.53
Ethanol	−3.68	−0.57	−4.25	−3.53	−0.69	−4.22	−2.83
1-Propanol	−3.50	−1.23	−4.73	−3.39	−1.33	−4.72	−3.85
1-Butanol	−3.19	−1.86	−5.06	−3.14	−1.96	−5.10	−4.92
1-Pentanol	−3.15	−2.49	−5.63	−3.10	−2.58	−5.68	−5.45
Phenol	−5.05	−2.53	−7.58	−4.70	−2.71	−7.40	−7.48
1-Hexanol	−3.15	−3.11	−6.26	−3.11	−3.21	−6.32	−6.02
o-Cresol	−5.00	−2.88	−7.88	−4.67	−3.06	−7.74	−7.73

Table 18. (Cont.)

Solute	SM5.42R/AM1			SM5.42R/PM3			Expt.
	ΔG_{ENP}	G_{CDS}	ΔG_S^0	ΔG_{ENP}	G_{CDS}	ΔG_S^0	ΔG_S^0
m-Cresol	−5.07	−2.84	−7.91	−4.74	−3.02	−7.75	−6.91
p-Cresol	−5.05	−2.85	−7.90	−4.72	−3.03	−7.75	−7.75
1-Heptanol	−3.12	−3.73	−6.85	−3.09	−3.82	−6.91	−6.79
Benzaldehyde	−5.73	−2.15	−7.88	−5.73	−2.29	−8.02	−7.23
Methyl phenyl ketone	−5.74	−2.88	−8.62	−5.65	−3.02	−8.67	−7.83
Ethanoic acid	−6.20	0.13	−6.07	−6.24	0.15	−6.10	−4.89
Propanoic acid	−5.70	−0.54	−6.24	−5.76	−0.51	−6.26	−5.12
Butanoic acid	−5.47	−1.14	−6.61	−5.57	−1.10	−6.67	−5.83
Pentanoic acid	−5.45	−1.76	−7.21	−5.55	−1.71	−7.26	−6.47
Hexanoic acid	−5.40	−2.38	−7.78	−5.51	−2.32	−7.83	−7.33
Methyl ethanoate	−5.26	0.41	−4.85	−4.94	0.21	−4.72	−4.55
Methyl propanoate	−4.79	−0.25	−5.04	−4.49	−0.44	−4.93	−4.87
Ethyl ethanoate	−5.04	−0.49	−5.54	−4.77	−0.67	−5.44	−4.93
Propyl ethanoate	−4.87	−1.13	−6.00	−4.67	−1.29	−5.96	−5.40
Methyl pentanoate	−4.52	−1.47	−5.99	−4.28	−1.64	−5.92	−5.97
Butyl ethanoate	−4.79	−1.75	−6.54	−4.62	−1.90	−6.52	−5.93
Methyl hexanoate	−4.46	−2.09	−6.56	−4.23	−2.25	−6.48	−6.57
Pentyl ethanoate	−4.75	−2.37	−7.12	−4.59	−2.51	−7.10	−6.64
m-Hydroxybenzaldehyde	−8.08	−1.69	−9.78	−7.97	−1.81	−9.78	−10.11
p-Hydroxybenzaldehyde	−8.67	−1.67	−10.34	−8.64	−1.76	−10.40	−10.70
Ethylamine	−1.70	−1.42	−3.12	−1.46	−1.65	−3.11	−3.19
Propylamine	−1.63	−2.08	−3.70	−1.40	−2.30	−3.70	−4.04
Butylamine	−1.56	−2.70	−4.26	−1.34	−2.91	−4.25	−4.49
Diethylamine	−0.92	−2.73	−3.65	−0.80	−2.88	−3.68	−4.00
Pyridine	−4.31	−2.02	−6.33	−4.14	−2.33	−6.47	−5.53
Aniline	−4.02	−3.02	−7.04	−3.51	−3.45	−6.96	−7.39
$OP(OCH_3)_3$	−10.05	1.49	−8.56	−5.72	−1.40	−7.12	−8.55
$OP(OC_2H_5)_3$	−9.39	−1.42	−10.81	−5.30	−4.22	−9.52	−9.59
p-Bromophenol	−5.12	−3.87	−8.99	−4.66	−4.12	−8.78	−9.10
Solvent: tetrachloroethene							
Phenol	−2.93	−2.71	−5.64	−2.72	−2.88	−5.60	−6.10
Propanone	−2.65	−0.56	−3.21	−2.75	−0.52	−3.27	−3.09
Methyl ethanoate	−2.98	−0.06	−3.04	−2.79	−0.26	−3.05	−3.63
Methyl propanoate	−2.71	−0.81	−3.52	−2.53	−1.00	−3.53	−4.39
Ethyl ethanoate	−2.84	−1.06	−3.91	−2.69	−1.24	−3.94	−4.22
Propyl ethanoate	−2.75	−1.79	−4.54	−2.64	−1.95	−4.59	−4.80
Methyl pentanoate	−2.56	−2.20	−4.76	−2.42	−2.37	−4.78	−5.41
Butyl ethanoate	−2.71	−2.50	−5.21	−2.62	−2.64	−5.26	−5.35
Solvent: chlorohexane							
Propanone	−4.39	−0.40	−4.79	−4.55	−0.33	−4.88	−3.45
Butanone	−4.12	−1.12	−5.24	−4.27	−1.04	−5.31	−4.10
2-Pentanone	−3.97	−1.75	−5.72	−4.14	−1.65	−5.79	−4.84
2-Hexanone	−3.85	−2.42	−6.27	−4.01	−2.30	−6.31	−5.42
3,3-Dimethylbutanone	−3.73	−1.57	−5.30	−3.84	−1.47	−5.31	−4.98
Methyl ethanoate	−4.75	0.02	−4.73	−4.46	−0.15	−4.62	−3.66
Methyl propanoate	−4.33	−0.68	−5.00	−4.05	−0.84	−4.89	−4.20
Ethyl ethanoate	−4.55	−0.92	−5.47	−4.31	−1.06	−5.38	−4.25
Propyl ethanoate	−4.40	−1.59	−6.00	−4.22	−1.72	−5.94	−4.84
Methyl pentanoate	−4.09	−1.97	−6.06	−3.86	−2.11	−5.97	−5.41
Butyl ethanoate	−4.33	−2.25	−6.58	−4.17	−2.37	−6.54	−5.37
Solvent: bromoform							
Methanol	−3.19	0.71	−2.48	−3.06	0.53	−2.52	−2.79
Ethanol	−3.05	−0.34	−3.39	−2.93	−0.48	−3.40	−3.24
1-Propanol	−2.91	−0.99	−3.89	−2.81	−1.12	−3.93	−4.03
1-Butanol	−2.66	−1.62	−4.27	−2.61	−1.75	−4.35	−4.72
1-Pentanol	−2.62	−2.23	−4.85	−2.58	−2.36	−4.93	−5.34
Phenol	−4.16	−2.37	−6.54	−3.87	−2.59	−6.46	−6.88
1-Hexanol	−2.62	−2.85	−5.47	−2.59	−2.99	−5.58	−6.20
o-Cresol	−4.12	−2.69	−6.81	−3.85	−2.91	−6.76	−7.45
1-Heptanol	−2.60	−3.46	−6.06	−2.57	−3.60	−6.17	−7.10
Ethanoic acid	−5.12	0.49	−4.62	−5.15	0.50	−4.65	−4.54
p-Bromophenol	−4.22	−3.79	−8.01	−3.84	−4.08	−7.92	−8.49

Table 18. (Cont.)

Solute	SM5.42R/AM1			SM5.42R/PM3			Expt.
	ΔG_{ENP}	G_{CDS}	ΔG_S^0	ΔG_{ENP}	G_{CDS}	ΔG_S^0	ΔG_S^0
Solvent: 1,2-bromoethane							
n-Octane	0.03	−5.10	−5.07	0.03	−5.04	−5.00	−5.54
Toluene	−2.27	−3.85	−6.12	−2.06	−4.03	−6.09	−5.55
1,4-Dioxane	−3.83	−1.95	−5.78	−3.09	−2.53	−5.62	−5.39
Butanone	−4.52	−1.32	−5.84	−4.68	−1.23	−5.92	−5.13
Propanoic acid	−5.61	−0.92	−6.53	−5.66	−0.88	−6.54	−5.52
Solvent: dibromoethane							
Methanol	−3.34	0.69	−2.65	−3.20	0.53	−2.67	−2.38
Ethanol	−3.20	−0.32	−3.52	−3.07	−0.44	−3.51	−2.69
1-Propanol	−3.04	−0.95	−3.99	−2.94	−1.06	−4.01	−3.82
1-Butanol	−2.78	−1.56	−4.34	−2.73	−1.67	−4.40	−4.65
1-Pentanol	−2.74	−2.15	−4.90	−2.70	−2.26	−4.96	−5.44
Phenol	−4.37	−2.30	−6.67	−4.06	−2.50	−6.56	−7.22
1-Hexanol	−2.75	−2.75	−5.50	−2.71	−2.87	−5.59	−6.08
p-Cresol	−4.37	−2.58	−6.94	−4.08	−2.78	−6.86	−7.52
1-Heptanol	−2.72	−3.35	−6.07	−2.69	−3.46	−6.15	−6.64
p-Bromophenol	−4.43	−3.66	−8.09	−4.03	−3.93	−7.96	−9.01
Solvent: 1-bromooctane							
Methyl ethanoate	−4.54	0.18	−4.36	−4.26	−0.01	−4.26	−3.35
Ethyl ethanoate	−4.34	−0.75	−5.10	−4.12	−0.91	−5.02	−3.97
Propyl ethanoate	−4.20	−1.41	−5.61	−4.03	−1.55	−5.58	−4.48
Butyl ethanoate	−4.13	−2.05	−6.19	−3.98	−2.18	−6.16	−5.11
Pentyl ethanoate	−4.10	−2.70	−6.80	−3.96	−2.81	−6.77	−5.81
Solvent: 1-iodohexadecane							
n-Pentane	−0.06	−2.42	−2.47	−0.03	−2.40	−2.44	−2.59
n-Hexane	−0.03	−3.03	−3.06	−0.01	−3.01	−3.02	−3.26
n-Heptane	0.00	−3.65	−3.65	0.01	−3.62	−3.61	−3.90
Cyclohexane	−0.12	−3.72	−3.84	−0.09	−3.67	−3.76	−3.66
Methylcyclohexane	−0.06	−3.90	−3.96	−0.04	−3.84	−3.88	−4.07
Benzene	−1.70	−3.02	−4.72	−1.53	−3.24	−4.77	−3.71
Toluene	−1.75	−3.33	−5.08	−1.59	−3.53	−5.12	−4.41
Dichloromethane	−1.49	−1.69	−3.18	−1.61	−1.69	−3.30	−2.76
Trichloromethane	−0.91	−2.80	−3.71	−0.87	−2.77	−3.64	−3.36
Solvent: fluorobenzene							
n-Octane	0.03	−5.58	−5.55	0.03	−5.49	−5.46	−4.99
Toluene	−2.04	−4.18	−6.23	−1.86	−4.36	−6.22	−5.27
Ethanol	−3.29	−0.81	−4.09	−3.15	−0.90	−4.06	−3.45
1,4-Dioxane	−3.48	−2.18	−5.66	−2.81	−2.77	−5.58	−5.18
Butanone	−4.02	−1.56	−5.57	−4.17	−1.47	−5.63	−4.60
Solvent: chlorobenzene							
n-Octane	0.03	−5.18	−5.16	0.03	−5.11	−5.08	−5.16
Toluene	−2.07	−3.96	−6.03	−1.88	−4.15	−6.03	−5.18
Methanol	−3.47	0.59	−2.87	−3.32	0.45	−2.87	−2.44
Ethanol	−3.32	−0.54	−3.86	−3.19	−0.64	−3.83	−3.30
1-Propanol	−3.16	−1.29	−4.45	−3.06	−1.38	−4.44	−3.82
1-Butanol	−2.89	−2.02	−4.91	−2.83	−2.11	−4.94	−4.31
1-Pentanol	−2.85	−2.75	−5.59	−2.80	−2.81	−5.62	−5.25
Phenol	−4.54	−2.83	−7.37	−4.22	−2.99	−7.22	−6.96
1-Hexanol	−2.85	−3.48	−6.33	−2.81	−3.56	−6.38	−5.98
o-Cresol	−4.50	−3.27	−7.76	−4.20	−3.43	−7.63	−7.33
p-Cresol	−4.54	−3.23	−7.78	−4.24	−3.40	−7.65	−7.23
1-Heptanol	−2.83	−4.20	−7.03	−2.79	−4.27	−7.06	−6.78
1,4-Dioxane	−3.51	−1.91	−5.42	−2.84	−2.53	−5.37	−5.08
Propanone	−4.34	−0.51	−4.85	−4.50	−0.45	−4.95	−3.86
Butanone	−4.07	−1.30	−5.37	−4.22	−1.22	−5.44	−4.47
2-Pentanone	−3.92	−1.98	−5.90	−4.09	−1.89	−5.98	−5.29
2-Hexanone	−3.80	−2.71	−6.51	−3.96	−2.60	−6.55	−5.84
3,3-Dimethylbutanone	−3.68	−1.80	−5.48	−3.79	−1.70	−5.50	−5.25
2-Heptanone	−3.87	−3.42	−7.29	−4.04	−3.30	−7.34	−6.46
Propanoic acid	−5.13	−0.76	−5.89	−5.18	−0.72	−5.90	−4.38
Methyl ethanoate	−4.70	−0.04	−4.75	−4.42	−0.23	−4.65	−4.00
Methyl propanoate	−4.28	−0.80	−5.08	−4.01	−0.98	−4.99	−4.55

Table 18. (Cont.)

Solute	SM5.42R/AM1			SM5.42R/PM3			Expt.
	ΔG_{ENP}	G_{CDS}	ΔG_S^0	ΔG_{ENP}	G_{CDS}	ΔG_S^0	ΔG_S^0
Ethyl ethanoate	−4.50	−1.06	−5.57	−4.27	−1.22	−5.49	−4.63
Propyl ethanoate	−4.36	−1.80	−6.15	−4.18	−1.94	−6.12	−5.15
Methyl pentanoate	−4.04	−2.22	−6.26	−3.82	−2.36	−6.18	−5.83
Butyl ethanoate	−4.29	−2.52	−6.80	−4.13	−2.64	−6.77	−5.74
Pentyl ethanoate	−4.25	−3.24	−7.49	−4.10	−3.35	−7.45	−6.49
Methylamine	−1.94	−0.60	−2.54	−1.60	−0.86	−2.46	−2.16
Ethylamine	−1.55	−1.45	−2.99	−1.32	−1.67	−2.99	−2.73
Dimethylamine	−1.52	−1.42	−2.94	−1.26	−1.61	−2.87	−2.75
Propylamine	−1.48	−2.21	−3.68	−1.27	−2.40	−3.67	−3.59
Trimethylamine	−1.43	−2.06	−3.49	−1.10	−2.16	−3.26	−2.82
Butylamine	−1.42	−2.93	−4.34	−1.22	−3.11	−4.33	−4.22
Aniline	−3.63	−3.49	−7.13	−3.16	−3.91	−7.07	−6.72
Ammonia	−2.66	0.25	−2.42	−2.05	−0.07	−2.12	−1.22
p-Bromophenol	−4.61	−4.28	−8.89	−4.19	−4.51	−8.70	−8.54
Solvent: bromobenzene							
n-Octane	0.03	−5.11	−5.08	0.03	−5.05	−5.01	−5.02
Toluene	−2.04	−3.92	−5.96	−1.85	−4.12	−5.97	−5.13
Methanol	−3.42	0.64	−2.79	−3.28	0.49	−2.79	−2.31
Ethanol	−3.28	−0.50	−3.78	−3.14	−0.61	−3.76	−3.26
1-Propanol	−3.12	−1.25	−4.37	−3.02	−1.35	−4.37	−3.74
1-Butanol	−2.85	−1.98	−4.83	−2.80	−2.08	−4.87	−4.08
1-Pentanol	−2.81	−2.70	−5.51	−2.76	−2.78	−5.54	−5.06
Phenol	−4.48	−2.80	−7.28	−4.16	−2.98	−7.14	−6.87
1-Hexanol	−2.81	−3.43	−6.25	−2.78	−3.52	−6.30	−5.92
o-Cresol	−4.43	−3.23	−7.66	−4.14	−3.40	−7.54	−7.26
p-Cresol	−4.48	−3.19	−7.68	−4.18	−3.38	−7.56	−7.12
1-Heptanol	−2.79	−4.15	−6.94	−2.76	−4.22	−6.98	−6.68
1,4-Dioxane	−3.47	−1.85	−5.32	−2.80	−2.49	−5.29	−5.02
Butanone	−4.00	−1.20	−5.20	−4.15	−1.12	−5.27	−4.37
Methyl ethanoate	−4.63	0.06	−4.57	−4.35	−0.14	−4.49	−3.87
Ethyl ethanoate	−4.44	−0.96	−5.40	−4.20	−1.13	−5.33	−4.57
Propyl ethanoate	−4.29	−1.69	−5.98	−4.12	−1.84	−5.96	−4.93
Butyl ethanoate	−4.22	−2.40	−6.63	−4.07	−2.54	−6.61	−5.58
Pentyl ethanoate	−4.19	−3.12	−7.31	−4.04	−3.24	−7.29	−6.35
Ethylamine	−1.53	−1.41	−2.94	−1.31	−1.64	−2.95	−2.73
Propylamine	−1.46	−2.17	−3.63	−1.25	−2.38	−3.63	−3.57
Butylamine	−1.40	−2.88	−4.28	−1.20	−3.08	−4.28	−4.19
Aniline	−3.58	−3.46	−7.05	−3.12	−3.90	−7.02	−6.66
p-Bromophenol	−4.54	−4.27	−8.81	−4.13	−4.51	−8.64	−8.49
Solvent: iodobenzene							
n-Octane	0.03	−5.00	−4.98	0.03	−4.95	−4.92	−4.72
Toluene	−1.94	−3.87	−5.80	−1.76	−4.08	−5.84	−4.99
Methanol	−3.26	0.70	−2.56	−3.12	0.55	−2.58	−2.18
Ethanol	−3.12	−0.44	−3.56	−2.99	−0.56	−3.56	−3.18
1-Propanol	−2.97	−1.19	−4.16	−2.87	−1.29	−4.17	−3.52
1-Butanol	−2.72	−1.91	−4.63	−2.67	−2.02	−4.68	−4.05
1-Pentanol	−2.68	−2.63	−5.30	−2.63	−2.71	−5.35	−5.02
Phenol	−4.26	−2.76	−7.02	−3.96	−2.95	−6.90	−6.76
1-Hexanol	−2.68	−3.35	−6.03	−2.65	−3.45	−6.10	−5.71
o-Cresol	−4.21	−3.17	−7.38	−3.94	−3.36	−7.29	−7.14
m-Cresol	−4.28	−3.12	−7.40	−4.00	−3.31	−7.30	−6.04
p-Cresol	−4.26	−3.13	−7.39	−3.98	−3.33	−7.31	−7.01
1-Heptanol	−2.66	−4.06	−6.72	−2.63	−4.15	−6.78	−6.53
1,4-Dioxane	−3.30	−1.75	−5.05	−2.67	−2.43	−5.09	−4.94
Butanone	−3.77	−1.05	−4.82	−3.91	−0.97	−4.88	−4.22
Ethylamine	−1.46	−1.35	−2.81	−1.25	−1.59	−2.84	−2.73
Propylamine	−1.39	−2.10	−3.50	−1.20	−2.33	−3.52	−3.54
Butylamine	−1.34	−2.82	−4.15	−1.15	−3.03	−4.17	−4.13
p-Bromophenol	−4.32	−4.25	−8.57	−3.93	−4.51	−8.44	−8.45
Solvent: *o*-dichlorobenzene							
Methanol	−3.82	0.79	−3.03	−3.67	0.64	−3.03	−1.73
Ethanol	−3.67	−0.32	−3.98	−3.52	−0.43	−3.95	−2.34
1-Propanol	−3.49	−1.03	−4.53	−3.38	−1.13	−4.51	−3.47

Table 18. (Cont.)

Solute	SM5.42R/AM1			SM5.42R/PM3			Expt.
	ΔG_{ENP}	G_{CDS}	ΔG_S^0	ΔG_{ENP}	G_{CDS}	ΔG_S^0	ΔG_S^0
1-Butanol	−3.19	−1.74	−4.92	−3.13	−1.83	−4.96	−3.90
1-Pentanol	−3.14	−2.42	−5.56	−3.09	−2.50	−5.59	−4.93
1-Hexanol	−3.14	−3.13	−6.27	−3.10	−3.22	−6.32	−5.70
1-Heptanol	−3.11	−3.82	−6.93	−3.08	−3.89	−6.97	−6.50
Ethylamine	−1.70	−1.26	−2.96	−1.46	−1.49	−2.94	−2.59
Propylamine	−1.62	−1.99	−3.61	−1.40	−2.19	−3.59	−3.44
Butylamine	−1.55	−2.67	−4.23	−1.34	−2.87	−4.20	−4.13
Solvent: perfluorobenzene							
Propanone	−2.35	−0.92	−3.27	−2.45	−0.87	−3.31	−3.82
2-Pentanone	−2.12	−2.42	−4.54	−2.21	−2.34	−4.55	−5.10
2-Hexanone	−2.04	−3.18	−5.22	−2.13	−3.08	−5.21	−5.55
3,3-Dimethylbutanone	−1.99	−2.33	−4.33	−2.06	−2.25	−4.31	−5.26
2-Heptanone	−2.08	−3.91	−5.99	−2.18	−3.80	−5.98	−6.15
Methyl ethanoate	−2.67	−0.50	−3.17	−2.50	−0.67	−3.17	−4.23
Ethyl ethanoate	−2.54	−1.52	−4.06	−2.41	−1.65	−4.07	−4.56
Propyl ethanoate	−2.46	−2.27	−4.74	−2.37	−2.39	−4.76	−5.06
Methyl pentanoate	−2.29	−2.74	−5.03	−2.16	−2.86	−5.02	−5.59
Butyl ethanoate	−2.43	−3.02	−5.44	−2.34	−3.12	−5.46	−5.52
Methyl hexanoate	−2.27	−3.48	−5.75	−2.14	−3.59	−5.73	−6.21
Pentyl ethanoate	−2.40	−3.76	−6.16	−2.33	−3.85	−6.17	−6.16
Solvent: methylformamide							
n-Octane	0.03	−2.45	−2.42	0.04	−2.47	−2.44	−3.34
Toluene	−2.60	−1.65	−4.25	−2.37	−1.94	−4.31	−4.34
Ethanol	−4.12	−1.24	−5.36	−3.96	−1.38	−5.34	−5.12
1,4-Dioxane	−4.36	−0.42	−4.78	−3.52	−1.15	−4.66	−4.86
Butanone	−5.33	0.58	−4.76	−5.52	0.67	−4.85	−4.34
Solvent: acetic acid							
n-Octane	0.03	−3.16	−3.13	0.03	−3.16	−3.12	−3.93
Toluene	−2.11	−1.94	−4.06	−1.92	−2.20	−4.12	−4.53
Ethanol	−3.39	−1.88	−5.27	−3.25	−2.00	−5.25	−5.25
1,4-Dioxane	−3.59	−0.76	−4.35	−2.90	−1.46	−4.35	−5.80
Butanone	−4.17	0.01	−4.17	−4.33	0.06	−4.26	−4.80
Solvent: 2-methoxyethanol							
n-Octane	0.03	−3.17	−3.14	0.04	−3.16	−3.12	−3.71
Toluene	−2.43	−2.09	−4.52	−2.21	−2.39	−4.60	−4.49
Ethanol	−3.86	−1.84	−5.70	−3.71	−1.97	−5.68	−4.71
1,4-Dioxane	−4.09	−0.98	−5.07	−3.30	−1.69	−4.99	−4.91
Butanone	−4.91	0.38	−4.54	−5.09	0.59	−4.50	−4.28
Solvent: tributylphosphate							
Methanol	−3.72	−1.18	−4.89	−3.57	−1.31	−4.88	−4.16
Ethanol	−3.57	−2.16	−5.72	−3.42	−2.26	−5.68	−4.57
1-Propanol	−3.39	−2.79	−6.18	−3.29	−2.87	−6.15	−5.42
1-Butanol	−3.10	−3.39	−6.49	−3.04	−3.46	−6.50	−6.28
1-Pentanol	−3.05	−3.99	−7.04	−3.01	−4.04	−7.04	−6.69
1-Hexanol	−3.06	−4.47	−7.52	−3.02	−4.52	−7.54	−7.68
1-Heptanol	−3.03	−5.07	−8.10	−3.00	−5.10	−8.09	−7.98
Ethanoic acid	−6.00	−1.25	−7.25	−6.05	−1.16	−7.20	−7.11
Propanoic acid	−5.52	−1.90	−7.42	−5.57	−1.79	−7.36	−7.73
Butanoic acid	−5.30	−2.48	−7.78	−5.39	−2.35	−7.74	−8.29
Pentanoic acid	−5.28	−3.08	−8.35	−5.38	−2.93	−8.31	−8.82
2-Methoxyethanol	−4.57	−1.90	−6.47	−4.24	−2.25	−6.49	−6.14
Water	−6.43	−0.46	−6.88	−6.26	−0.61	−6.87	−4.69
Ethylamine	−1.65	−1.86	−3.52	−1.42	−2.13	−3.55	−3.29
Propylamine	−1.58	−2.50	−4.08	−1.36	−2.74	−4.11	−3.98
Butylamine	−1.51	−3.10	−4.61	−1.30	−3.33	−4.63	−4.25
Aniline	−3.90	−3.29	−7.19	−3.40	−3.85	−7.25	−7.60
Solvent: tetrahydrothiophene-1,1-dioxide							
n-Octane	0.03	−1.47	−1.43	0.04	−1.51	−1.47	−2.44
Toluene	−2.54	−1.26	−3.80	−2.32	−1.60	−3.92	−4.23
Ethanol	−4.03	−0.46	−4.49	−3.88	−0.62	−4.50	−4.30
1,4-Dioxane	−4.27	−0.07	−4.34	−3.44	−0.82	−4.26	−4.90
Butanone	−5.19	1.48	−3.71	−5.38	1.72	−3.66	−4.09

Table 18. (Cont.)

Solute	SM5.42R/AM1			SM5.42R/PM3			Expt.
	ΔG_{ENP}	G_{CDS}	ΔG_S^0	ΔG_{ENP}	G_{CDS}	ΔG_S^0	ΔG_S^0
Solvent: dimethylsulfoxide							
n-Octane	0.03	−2.34	−2.31	0.04	−2.35	−2.32	−2.84
Toluene	−2.55	−1.80	−4.34	−2.32	−2.12	−4.44	−4.42
Ethanol	−4.04	−0.89	−4.93	−3.88	−1.03	−4.91	−5.25
1,4-Dioxane	−4.28	−0.62	−4.89	−3.45	−1.31	−4.77	−4.90
Butanone	−5.21	0.91	−4.29	−5.39	1.16	−4.23	−4.23
Solvent: carbon disulfide							
n-Octane	0.02	−5.21	−5.19	0.03	−5.13	−5.11	−5.68
Toluene	−1.47	−4.03	−5.50	−1.33	−4.22	−5.56	−5.39
Ethanol	−2.41	−0.43	−2.84	−2.31	−0.54	−2.85	−2.95
Phenol	−3.27	−2.82	−6.09	−3.03	−3.00	−6.02	−6.27
1,4-Dioxane	−2.54	−1.85	−4.39	−2.05	−2.51	−4.57	−4.67
Propanone	−2.98	−0.39	−3.37	−3.10	−0.32	−3.42	−3.14
Butanone	−2.78	−1.20	−3.98	−2.89	−1.12	−4.01	−3.85
Ethanoic acid	−4.01	0.15	−3.86	−4.04	0.18	−3.86	−2.98
Methyl ethanoate	−3.33	0.13	−3.20	−3.12	−0.07	−3.20	−3.67
Ethyl ethanoate	−3.18	−0.92	−4.11	−3.02	−1.10	−4.11	−4.08
Propyl ethanoate	−3.08	−1.68	−4.75	−2.96	−1.83	−4.78	−4.63
1-Nitropropane	−2.45	−2.10	−4.54	−3.47	−1.27	−4.74	−4.50
Solvent: water							
Methane	−0.05	1.66	1.61	−0.02	1.63	1.61	2.00
Ethane	−0.12	1.43	1.31	−0.07	1.41	1.34	1.83
Propane	−0.13	1.51	1.38	−0.09	1.51	1.42	1.96
n-Butane	−0.11	1.65	1.54	−0.07	1.66	1.58	2.08
n-Pentane	−0.08	1.78	1.70	−0.05	1.80	1.75	2.33
n-Hexane	−0.04	1.91	1.87	−0.02	1.95	1.93	2.49
n-Heptane	−0.01	2.04	2.04	0.01	2.09	2.10	2.62
n-Octane	0.03	2.18	2.21	0.04	2.24	2.28	2.89
2-Methylpropane	−0.13	1.81	1.69	−0.09	1.82	1.74	2.32
2,2-Dimethylpropane	−0.14	2.19	2.05	−0.10	2.23	2.12	2.50
2-Methylpentane	−0.04	2.11	2.07	−0.02	2.14	2.12	2.52
2,4-Dimethylpentane	0.03	2.44	2.46	0.04	2.49	2.52	2.88
2,2,4-Trimethylpentane	0.04	2.77	2.81	0.04	2.84	2.88	2.85
Cyclopropane	−0.50	0.77	0.28	−0.41	0.69	0.28	0.75
Cyclopentane	−0.28	0.91	0.63	−0.21	0.92	0.71	1.20
Cyclohexane	−0.18	0.91	0.73	−0.13	0.96	0.83	1.23
Methylcyclohexane	−0.09	1.29	1.20	−0.06	1.35	1.29	1.71
cis-1,2-Dimethylcyclohexane	−0.01	1.66	1.64	0.00	1.73	1.74	1.58
Ethene	−0.52	1.89	1.37	−0.42	1.75	1.33	1.27
Propene	−0.65	1.84	1.19	−0.55	1.72	1.17	1.27
s-trans-1,3-Butadiene	−1.08	2.26	1.18	−0.91	2.03	1.12	0.61
2-Methylpropene	−0.81	2.09	1.28	−0.70	1.99	1.28	1.16
1-Butene	−0.55	1.98	1.42	−0.47	1.87	1.40	1.38
Cyclopentene	−1.04	1.06	0.02	−0.91	0.95	0.04	0.56
1-Pentene	−0.49	2.11	1.62	−0.43	2.02	1.59	1.66
E-2-Pentene	−0.65	1.95	1.29	−0.57	1.86	1.29	1.34
1-Hexene	−0.45	2.24	1.80	−0.40	2.16	1.77	1.68
Ethyne	−2.47	2.80	0.33	−2.38	2.66	0.28	−0.01
Propyne	−3.07	2.50	−0.57	−2.92	2.36	−0.56	−0.31
1-Butyne	−2.79	2.64	−0.16	−2.67	2.51	−0.15	−0.16
1-Pentyne	−2.59	2.77	0.18	−2.49	2.65	0.16	0.01
1-Hexyne	−2.55	2.90	0.35	−2.47	2.80	0.33	0.29
Benzene	−2.49	1.20	−1.29	−2.26	0.89	−1.36	−0.87
Toluene	−2.58	1.53	−1.05	−2.35	1.23	−1.12	−0.89
Ethylbenzene	−2.35	1.70	−0.65	−2.16	1.42	−0.74	−0.80
o-Xylene	−2.73	1.77	−0.95	−2.50	1.49	−1.01	−0.90
m-Xylene	−2.67	1.85	−0.82	−2.44	1.57	−0.88	−0.84
p-Xylene	−2.65	1.86	−0.79	−2.42	1.57	−0.85	−0.81
Naphthalene	−4.23	1.35	−2.88	−3.82	0.87	−2.95	−2.39
Anthracene	−5.71	1.51	−4.20	−5.17	0.85	−4.31	−4.23
Methanol	−4.24	−1.50	−5.74	−4.08	−1.62	−5.70	−5.11
Ethanol	−4.08	−1.53	−5.61	−3.92	−1.62	−5.54	−5.01
1,2-Ethanediol	−5.84	−3.72	−9.56	−5.75	−4.11	−9.86	−9.30

Table 18. (Cont.)

Solute	SM5.42R/AM1			SM5.42R/PM3			Expt.
	ΔG_{ENP}	G_{CDS}	ΔG_S^0	ΔG_{ENP}	G_{CDS}	ΔG_S^0	ΔG_S^0
1-Propanol	−3.89	−1.42	−5.31	−3.77	−1.49	−5.26	−4.83
2-Propanol	−3.26	−1.31	−4.57	−3.22	−1.39	−4.61	−4.76
1-Butanol	−3.54	−1.32	−4.86	−3.48	−1.40	−4.88	−4.72
2-Methyl-2-propanol	−3.23	−0.85	−4.08	−3.15	−0.90	−4.05	−4.51
Cyclopentanol	−3.02	−1.90	−4.92	−2.99	−1.98	−4.97	−5.49
1-Pentanol	−3.48	−1.19	−4.68	−3.44	−1.25	−4.69	−4.47
Phenol	−5.64	−0.93	−6.56	−5.25	−1.12	−6.37	−6.62
1-Hexanol	−3.49	−1.04	−4.53	−3.45	−1.12	−4.58	−4.36
o-Cresol	−5.58	−0.60	−6.18	−5.22	−0.80	−6.02	−5.87
m-Cresol	−5.65	−0.59	−6.24	−5.28	−0.78	−6.06	−5.49
p-Cresol	−5.63	−0.62	−6.25	−5.27	−0.82	−6.09	−6.14
1-Heptanol	−3.46	−0.91	−4.37	−3.43	−0.98	−4.41	−4.24
1-Octanol	−3.38	−0.78	−4.16	−3.36	−0.80	−4.16	−4.09
Dimethyl ether	−2.53	0.68	−1.85	−2.04	0.25	−1.78	−1.92
Tetrahydrofuran	−2.94	−0.29	−3.23	−2.45	−0.71	−3.16	−3.47
1,4-Dioxane	−4.32	−1.25	−5.57	−3.49	−2.15	−5.63	−5.05
Diethyl ether	−2.20	0.70	−1.50	−1.81	0.34	−1.47	−1.76
Methyl propyl ether	−2.20	0.80	−1.39	−1.79	0.42	−1.37	−1.66
Methyl isopropyl ether	−2.19	0.90	−1.29	−1.79	0.53	−1.26	−2.01
1,2-Dimethoxyethane	−3.50	−0.01	−3.51	−2.77	−0.79	−3.56	−4.84
t-Butyl methyl ether	−2.09	1.30	−0.79	−1.71	0.95	−0.76	−2.21
Anisole	−4.14	1.17	−2.97	−3.41	0.65	−2.75	−2.45
Tetrahydropyran	−2.29	−0.28	−2.57	−1.91	−0.65	−2.56	−3.12
Isopropyl ether	−1.76	1.22	−0.55	−1.49	0.88	−0.61	−0.53
Ethyl phenyl ether	−3.85	1.19	−2.65	−3.20	0.70	−2.50	−4.28
Ethanal	−5.71	1.55	−4.16	−6.00	1.70	−4.30	−3.50
Propanal	−5.42	1.63	−3.79	−5.67	1.79	−3.89	−3.44
Butanal	−5.25	1.78	−3.47	−5.52	1.95	−3.57	−3.18
Pentanal	−4.94	1.92	−3.02	−5.36	2.12	−3.25	−3.03
Benzaldehyde	−6.51	1.66	−4.85	−6.50	1.52	−4.98	−4.02
Octanal	−5.14	2.32	−2.81	−5.42	2.55	−2.87	−2.29
Propanone	−5.59	1.58	−4.01	−5.79	1.74	−4.05	−3.85
Butanone	−5.27	1.68	−3.60	−5.46	1.84	−3.62	−3.64
Cyclopentanone	−4.82	0.99	−3.83	−5.07	1.17	−3.90	−4.68
2-Pentanone	−5.10	1.83	−3.26	−5.30	2.01	−3.28	−3.53
3-Pentanone	−4.95	1.77	−3.18	−5.14	1.94	−3.19	−3.41
2-Hexanone	−4.95	1.96	−2.99	−5.14	2.16	−2.98	−3.29
3,3-Dimethylbutanone	−4.77	2.38	−2.39	−4.90	2.58	−2.32	−2.89
2-Heptanone	−5.03	2.10	−2.94	−5.25	2.30	−2.94	−3.04
4-Heptanone	−4.57	2.09	−2.48	−4.79	2.28	−2.51	−2.93
Methyl phenyl ketone	−6.56	1.67	−4.89	−6.44	1.53	−4.91	−4.58
5-Nonanone	−4.57	2.35	−2.22	−4.80	2.57	−2.23	−2.67
2-Octanone	−5.01	2.24	−2.77	−5.23	2.46	−2.77	−2.88
Ethanoic acid	−6.91	0.26	−6.65	−6.96	0.31	−6.65	−6.70
Propanoic acid	−6.36	0.35	−6.01	−6.42	0.41	−6.01	−6.47
Butanoic acid	−6.10	0.49	−5.61	−6.21	0.57	−5.64	−6.36
Pentanoic acid	−6.08	0.62	−5.45	−6.20	0.71	−5.48	−6.16
Hexanoic acid	−6.02	0.76	−5.26	−6.15	0.86	−5.29	−6.21
Methyl methanoate	−6.33	2.44	−3.89	−6.12	2.18	−3.94	−2.78
Ethyl methanoate	−6.07	2.42	−3.65	−5.92	2.19	−3.73	−2.65
Methyl ethanoate	−5.90	2.21	−3.69	−5.54	1.94	−3.60	−3.32
Methyl propanoate	−5.39	2.30	−3.08	−5.05	2.05	−3.00	−2.93
Ethyl ethanoate	−5.67	2.20	−3.46	−5.36	1.96	−3.40	−3.10
Methyl butanoate	−5.11	2.45	−2.66	−4.82	2.20	−2.62	−2.83
Propyl ethanoate	−5.47	2.34	−3.13	−5.24	2.12	−3.13	−2.86
Methyl pentanoate	−5.08	2.58	−2.50	−4.81	2.35	−2.46	−2.57
Butyl ethanoate	−5.38	2.48	−2.90	−5.18	2.27	−2.91	−2.55
Methyl hexanoate	−5.02	2.71	−2.30	−4.76	2.49	−2.26	−2.49
Methyl octanoate	−4.97	2.99	−1.98	−4.72	2.80	−1.92	−2.04
Pentyl ethanoate	−5.33	2.61	−2.73	−5.15	2.41	−2.74	−2.45
Methyl benzoate	−6.20	2.42	−3.78	−5.61	1.89	−3.72	−2.22
2-Propen-1-ol	−3.62	−1.11	−4.73	−3.48	−1.32	−4.80	−5.08
2-Methoxyethanol	−5.22	−2.26	−7.48	−4.86	−2.73	−7.59	−6.77
Butenyne	−3.28	2.93	−0.35	−2.95	2.69	−0.27	0.04

Table 18. (Cont.)

Solute	SM5.42R/AM1			SM5.42R/PM3			Expt.
	ΔG_{ENP}	G_{CDS}	ΔG_S^0	ΔG_{ENP}	G_{CDS}	ΔG_S^0	ΔG_S^0
m-Hydroxybenzaldehyde	−9.06	−0.45	−9.52	−8.95	−0.47	−9.42	−9.51
p-Hydroxybenzaldehyde	−9.82	−0.36	−10.17	−9.79	−0.35	−10.13	−10.48
Water	−7.31	1.00	−6.31	−7.13	0.82	−6.31	−6.31
Hydrogen	0.00	2.36	2.36	0.00	2.35	2.35	2.33
Methylamine	−2.35	−2.27	−4.62	−1.95	−2.60	−4.56	−4.56
Ethylamine	−1.87	−2.19	−4.06	−1.62	−2.48	−4.10	−4.50
Dimethylamine	−1.84	−2.33	−4.17	−1.55	−2.63	−4.18	−4.29
Azetidine	−2.13	−3.28	−5.42	−1.91	−3.61	−5.52	−5.56
Propylamine	−1.79	−2.10	−3.89	−1.55	−2.38	−3.93	−4.39
Trimethylamine	−1.73	−1.73	−3.46	−1.35	−1.96	−3.31	−3.23
Pyrrolidine	−1.60	−3.18	−4.78	−1.50	−3.44	−4.94	−5.48
Piperazine	−2.83	−6.64	−9.47	−2.34	−7.11	−9.46	−7.40
Butylamine	−1.72	−1.96	−3.68	−1.48	−2.23	−3.71	−4.29
Diethylamine	−1.01	−1.93	−2.94	−0.89	−2.17	−3.05	−4.07
N-Methylpiperazine	−2.67	−5.90	−8.57	−2.14	−6.30	−8.44	−7.77
Piperidine	−1.21	−2.97	−4.18	−1.11	−3.18	−4.29	−5.11
Pentylamine	−1.67	−1.83	−3.50	−1.45	−2.09	−3.53	−4.10
N,*N*′-Dimethylpiperazine	−2.38	−5.18	−7.56	−1.80	−5.52	−7.31	−7.58
Dipropylamine	−0.84	−1.93	−2.77	−0.81	−2.13	−2.94	−3.66
Pyridine	−4.85	0.31	−4.54	−4.70	−0.13	−4.83	−4.70
2-Methylpyrazine	−6.17	−0.40	−6.57	−5.24	−0.95	−6.19	−5.57
Aniline	−4.46	−0.84	−5.30	−3.91	−1.40	−5.30	−5.49
2-Methylpyridine	−4.99	0.51	−4.48	−4.75	0.10	−4.66	−4.63
3-Methylpyridine	−4.76	0.64	−4.13	−4.59	0.20	−4.39	−4.77
4-Methylpyridine	−4.80	0.62	−4.18	−4.64	0.19	−4.45	−4.94
2-Ethylpyrazine	−5.71	−0.25	−5.96	−4.87	−0.78	−5.65	−5.51
2,4-Dimethylpyridine	−4.93	0.83	−4.10	−4.68	0.43	−4.25	−4.86
2,5-Dimethylpyridine	−4.88	0.83	−4.05	−4.62	0.44	−4.19	−4.72
2,6-Dimethylpyridine	−5.06	0.75	−4.31	−4.80	0.37	−4.42	−4.60
Ethanonitrile	−7.39	2.47	−4.92	−7.45	2.52	−4.92	−3.89
Propanonitrile	−6.55	2.58	−3.97	−6.59	2.65	−3.94	−3.85
Butanonitrile	−6.11	2.71	−3.40	−6.15	2.79	−3.36	−3.64
Benzonitrile	−5.75	2.57	−3.19	−5.59	2.35	−3.24	−4.10
Nitroethane	−4.98	1.34	−3.64	−6.41	2.56	−3.84	−3.71
1-Nitropropane	−4.45	1.38	−3.07	−6.07	2.59	−3.48	−3.34
2-Nitropropane	−4.67	1.56	−3.11	−5.74	2.78	−2.96	−3.14
1-Nitrobutane	−4.33	1.51	−2.82	−6.01	2.74	−3.27	−3.08
Nitrobenzene	−6.09	1.81	−4.29	−6.61	2.67	−3.94	−4.12
2-Methyl-1-nitrobenzene	−6.11	2.01	−4.10	−6.31	2.83	−3.48	−3.59
Ethanamide	−8.77	−1.77	−10.54	−8.31	−2.33	−10.63	−9.71
E-*N*-Methylacetamide	−7.83	−0.75	−8.58	−7.34	−1.12	−8.46	−10.00
Z-*N*-Methylacetamide	−8.76	−0.74	−9.50	−8.61	−1.12	−9.73	−10.00
1,1-Dimethyl-3-phenylurea	−9.54	−0.64	−10.19	−8.86	−1.69	−10.55	−11.87
9-Methyladenine	−11.22	−2.50	−13.72	−9.76	−4.01	−13.77	−13.60
1-Methylthymine	−11.24	−0.46	−11.70	−10.01	−1.35	−11.35	−10.40
2-Methoxyethanamine	−3.71	−2.92	−6.63	−3.18	−3.60	−6.77	−6.55
Morpholine	−3.58	−4.07	−7.65	−2.96	−4.71	−7.67	−7.17
N-Methylmorpholine	−3.32	−3.33	−6.65	−2.63	−3.89	−6.52	−6.34
Ammonia	−3.21	−1.99	−5.20	−2.49	−2.31	−4.80	−4.29
Hydrazine	−2.74	−6.56	−9.30	−2.49	−6.81	−9.30	−9.30
Phosphine	−1.27	1.86	0.60	−0.72	1.29	0.57	0.60
$OP(OCH_3)_3$	−11.19	2.70	−8.49	−6.40	−1.62	−8.02	−8.70
$OP(OC_2H_5)_3$	−10.47	2.49	−7.98	−5.94	−1.67	−7.61	−7.80
$OP(OC_3H_7)_3$	−9.57	2.83	−6.74	−5.34	−1.27	−6.60	−6.10
2,2-Dichloroethenyl dimethyl phosphate	−9.33	2.84	−6.50	−5.58	−1.24	−6.82	−6.61
Dimethyl 4-bromo-2,5-dichlorophenyl thiophosphate	−15.45	11.23	−4.22	−8.06	4.03	−4.03	−5.70
Dimethyl 2,4,5-trichlorophenyl thiophosphate	−15.52	11.84	−3.68	−8.13	4.68	−3.45	−5.06
Dimethyl 4-nitrophenyl thiophosphate	−20.14	12.84	−7.30	−13.66	6.66	−7.00	−7.62
Dimethyl 5-(4-chloro)bicyclo[3.2.0]heptyl phosphate	−10.01	2.83	−7.18	−5.91	−1.39	−7.30	−7.28
Diethyl 2,4-dichlorophenyl thiophosphate	−15.22	11.69	−3.53	−7.90	4.63	−3.27	−3.86

Table 18. (Cont.)

Solute	SM5.42R/AM1			SM5.42R/PM3			Expt.
	ΔG_{ENP}	G_{CDS}	ΔG_S^0	ΔG_{ENP}	G_{CDS}	ΔG_S^0	ΔG_S^0
Dimethyl 3-methyl-4-thiomethoxyphenyl thiophosphate	−20.92	10.21	−10.70	−13.53	2.98	−10.55	−6.92
Diethyl 4-nitrophenyl thiophosphonate	−18.04	12.54	−5.50	−12.71	6.60	−6.11	−6.27
O-Ethyl *O′*-4-bromo-2-chlorophenyl *S*-propyl phosphorothioate	−11.02	8.20	−2.82	−5.76	1.67	−4.09	−4.09
Ethyl 4-cyanophenyl phenylthiophosphonate	−19.76	13.33	−6.43	−12.81	6.74	−6.07	−5.10
Methanethiol	−1.65	0.37	−1.27	−1.19	0.27	−0.92	−1.24
Ethanethiol	−1.53	0.34	−1.19	−1.12	0.24	−0.88	−1.30
1-Propanethiol	−1.28	0.45	−0.83	−0.93	0.37	−0.56	−1.05
Thiophenol	−2.49	0.30	−2.19	−2.46	−0.08	−2.54	−2.55
Thiophene	−2.06	0.55	−1.51	−1.97	0.49	−1.48	−1.42
Dimethyl sulfide	−2.16	0.96	−1.19	−1.64	1.12	−0.52	−1.54
Diethyl sulfide	−1.97	0.95	−1.02	−1.54	1.13	−0.41	−1.43
Dipropyl sulfide	−1.56	1.18	−0.38	−1.18	1.38	0.20	−1.27
Hydrogen sulfide	−0.66	−0.38	−1.03	−0.60	−0.73	−1.33	−0.70
Thioanisole	−3.53	0.85	−2.68	−3.31	0.72	−2.59	−2.73
Dimethyl disulfide	−3.18	1.29	−1.89	−2.64	0.77	−1.87	−1.83
Diethyl disulfide	−2.79	1.23	−1.56	−2.31	0.73	−1.59	−1.63
Fluoromethane	−2.21	2.15	−0.06	−1.63	2.02	0.39	−0.22
1,1-Difluoroethane	−3.02	2.54	−0.48	−2.27	2.33	0.06	−0.11
Tetrafluoromethane	−0.84	3.45	2.61	−0.47	3.03	2.56	3.16
Hexafluoroethane	−0.81	4.70	3.90	−0.52	4.10	3.58	3.94
Octafluoropropane	−0.57	5.86	5.30	−0.39	5.11	4.72	4.28
Fluorobenzene	−3.01	1.92	−1.09	−2.75	1.51	−1.24	−0.78
Chloromethane	−1.93	1.17	−0.76	−2.40	1.20	−1.20	−0.56
Dichloromethane	−2.25	0.68	−1.57	−2.48	0.78	−1.71	−1.36
Trichloromethane	−1.36	0.25	−1.11	−1.31	0.41	−0.90	−1.07
Chloroethane	−1.83	1.07	−0.76	−2.24	1.11	−1.12	−0.63
1,1,1-Trichloroethane	−1.70	0.47	−1.23	−1.45	0.63	−0.82	−0.25
1,1,2-Trichloroethane	−2.37	0.40	−1.97	−2.63	0.57	−2.05	−1.95
1,1,1,2-Tetrachloroethane	−1.88	0.15	−1.73	−1.84	0.37	−1.48	−1.15
Hexachloroethane	−0.01	−0.30	−0.32	−0.04	0.00	−0.04	−1.40
1-Chloropropane	−1.54	1.17	−0.37	−1.91	1.23	−0.68	−0.27
2-Chloropropane	−1.79	1.26	−0.54	−2.12	1.32	−0.80	−0.25
2-Chlorobutane	−1.64	1.42	−0.22	−1.97	1.48	−0.48	0.07
1-Chloropentane	−1.44	1.44	0.00	−1.84	1.53	−0.31	0.07
2-Chloropentane	−1.54	1.55	0.01	−1.88	1.63	−0.25	0.07
Chloroethene	−1.52	1.56	0.05	−1.54	1.50	−0.04	−0.59
3-Chloropropene	−1.76	1.53	−0.24	−2.02	1.47	−0.56	−0.57
Z-1,2-Dichloroethene	−2.28	1.23	−1.06	−2.30	1.23	−1.08	−1.17
E-1,2-Dichloroethene	−1.04	1.22	0.19	−1.16	1.23	0.07	−0.76
Trichloroethene	−0.98	0.91	−0.07	−0.89	0.96	0.08	−0.39
Chlorobenzene	−2.59	1.04	−1.54	−2.23	0.80	−1.43	−1.12
o-Dichlorobenzene	−3.03	0.91	−2.12	−2.57	0.72	−1.85	−1.36
p-Dichlorobenzene	−2.12	0.89	−1.23	−1.84	0.71	−1.13	−1.01
Chlorotoluene	−3.63	1.22	−2.41	−3.68	0.99	−2.69	−1.92
o-Chlorotoluene	−2.71	1.32	−1.38	−2.33	1.09	−1.24	−1.15
2,2′-Dichlorobiphenyl	−4.60	1.50	−3.10	−3.97	1.05	−2.92	−2.73
2,3-Dichlorobiphenyl	−4.18	1.47	−2.71	−3.60	1.02	−2.58	−2.45
2,2′,3-Trichlorobiphenyl	−4.73	1.37	−3.36	−4.03	0.98	−3.05	−1.99
Bromomethane	−1.63	0.53	−1.10	−1.73	0.52	−1.21	−0.82
Dibromomethane	−1.55	−0.57	−2.12	−1.39	−0.56	−1.95	−2.11
Tribromomethane	−0.69	−1.58	−2.27	−0.51	−1.56	−2.07	−1.98
Bromoethane	−1.53	0.44	−1.09	−1.78	0.45	−1.33	−0.70
1-Bromopropane	−1.28	0.55	−0.72	−1.44	0.57	−0.87	−0.56
2-Bromopropane	−1.46	0.64	−0.81	−1.78	0.66	−1.12	−0.48
3-Bromopropene	−1.52	0.91	−0.61	−1.61	0.80	−0.81	−0.86
1-Bromobutane	−1.23	0.69	−0.54	−1.40	0.72	−0.68	−0.41
1-Bromo-isobutane	−1.11	0.92	−0.18	−1.30	0.96	−0.34	−0.03
1-Bromopentane	−1.18	0.82	−0.36	−1.35	0.86	−0.49	−0.08
Bromobenzene	−2.54	0.43	−2.11	−2.13	0.14	−1.99	−1.46
p-Dibromobenzene	−2.00	−0.33	−2.33	−1.67	−0.60	−2.27	−2.30
Bromotoluene	−3.51	0.70	−2.81	−3.44	0.43	−3.01	−2.37
p-Bromotoluene	−2.69	0.80	−1.89	−2.32	0.53	−1.79	−1.39

Table 18. (Cont.)

Solute	SM5.42R/AM1			SM5.42R/PM3			Expt.
	ΔG_{ENP}	G_{CDS}	ΔG_S^0	ΔG_{ENP}	G_{CDS}	ΔG_S^0	ΔG_S^0
Diiodomethane	−1.12	−0.71	−1.84	−0.61	−0.67	−1.28	−2.49
Iodomethane	−1.50	0.47	−1.03	−1.45	0.48	−0.97	−0.89
Iodoethane	−1.38	0.38	−1.00	−1.73	0.40	−1.33	−0.72
1-Iodopropane	−1.14	0.48	−0.65	−1.31	0.52	−0.79	−0.59
2-Iodopropane	−1.29	0.58	−0.71	−1.90	0.61	−1.28	−0.46
1-Iodobutane	−1.09	0.62	−0.47	−1.24	0.67	−0.58	−0.25
1-Iodopentane	−1.04	0.75	−0.29	−1.19	0.81	−0.38	−0.12
Iodobenzene	−2.28	0.36	−1.91	−1.97	0.10	−1.87	−1.73
Bromotrifluoromethane	−0.37	1.95	1.58	−0.28	1.64	1.37	1.79
Chlorofluoromethane	−3.09	1.65	−1.44	−2.75	1.58	−1.17	−0.77
Chlorodifluoromethane	−2.98	2.11	−0.87	−2.17	1.95	−0.23	−0.50
Difluorodichloromethane	−0.21	1.66	1.44	−0.20	1.55	1.35	1.69
Fluorotrichloromethane	−0.11	0.78	0.67	−0.14	0.83	0.69	0.82
Bromotrichloromethane	−0.01	−0.68	−0.68	−0.12	−0.52	−0.64	−0.93
Tetrafluoromethane	−0.83	3.49	2.66	−0.50	3.07	2.56	3.11
1-Bromo-1-chloro-2,2,2-trifluoroethane	−1.51	1.83	0.32	−1.18	1.60	0.42	−0.13
1-Bromo-2-chloroethane	−2.09	0.10	−2.00	−2.31	0.16	−2.15	−1.95
1-Bromo-1,2,2,2-tetrafluoroethane	−2.27	2.72	0.45	−1.67	2.32	0.65	0.52
Chloropentafluoroethane	−0.45	3.89	3.44	−0.35	3.44	3.09	2.86
Tetrachloroethene	−0.01	0.62	0.61	0.00	0.72	0.72	0.05
1-Chloro-2,2,2-trifluoroethane	−3.00	2.76	−0.24	−2.53	2.50	−0.02	0.06
1,1,2-Trichloro-1,2,2-trifluoroethane	−0.25	2.12	1.87	−0.30	1.99	1.69	1.77
2,2,2-Trifluoroethanol	−6.83	0.23	−6.60	−6.19	−0.14	−6.34	−4.31
1-Chloro-2,2,2-trifluoroethyl difluoromethyl ether	−4.33	3.55	−0.77	−3.13	2.89	−0.24	0.11
1,1,1-trifluoropropan-2-ol	−4.47	0.44	−4.04	−3.85	0.04	−3.81	−4.16
1,1,1,3,3,3-hexafluoropropan-2-ol	−4.45	2.19	−2.25	−3.66	1.51	−2.14	−3.77
Bis(2-chloroethyl)sulfide	−2.98	0.24	−2.74	−3.37	0.55	−2.83	−3.92
2,2,2-Trifluoroethyl vinyl ether	−3.66	3.27	−0.39	−2.90	2.65	−0.26	−0.12
p-Bromophenol	−5.71	−1.69	−7.40	−5.21	−1.90	−7.11	−7.13
3,5-Dibromo-4-hydroxybenzonitrile	−6.42	−0.52	−6.94	−6.32	−0.58	−6.90	−9.00
2,6-Dichlorobenzonitrile	−6.17	2.12	−4.05	−6.01	2.03	−3.98	−5.22
2,6-Dichlorothiobenzamide	−10.51	−2.78	−13.29	−11.90	−2.99	−14.89	−10.81
4-Amino-3,5,6-trichloropyridine-2-carboxylic acid	−8.44	−2.50	−10.95	−8.71	−2.82	−11.53	−11.96

shows some examples where the same free energy of solvation is computed with gas-phase geometries calculated at three different levels. These results illustrate that the predicted solvation free energies change by 0.1 to 0.4 kcal/mol when other geometries are used instead of HF/MIDI!, with an average unsigned change of 0.22 kcal/mol over the ten cases. This is about a factor of 2 less than the mean unsigned deviation of the predictions of this model from experiment, so the variation is acceptable.

Since all the models give a similar quality of results (on average), we conclude that the empirical fitting of surface tensions is a very powerful method to complement systematic deviations of the electrostatics from experiment and, furthermore, that the deviations of electrostatics calculated with the generalized Born model and CM2 class IV charges are indeed systematic. This may be reminiscent of a recent study [60] which examined several very different models in which the results were linearly correlated to experiment. With such linear fits, all models gave similar results, perhaps because the linear fit effectively readjusts choices such as cavity sizes. We believe, however, that the ultimate test of all such models is their usefulness in actual applications. That is why we have gone to great lengths to make the fitting as physical as possible. We hope that this will make the methodology more useful in applications to a diverse range of problems.

It has been known for a long time that the free energy of solvation of methyl-substituted amines in water is not a monotonic function of the degree of substitution [61]. The interpretation is unclear, especially because of large enthalpy/entropy compensation. For example, ΔG_S^0 is −4.3 kcal/mol for both ammonia and dimethylamine; however, ammonia has $\Delta H^0 = -8.4$ kcal/mol and $-T\Delta S^0 = 4.1$ kcal/mol, whereas dimethylamine has $\Delta H^0 = -12.7$ kcal/mol and $-T\Delta S^0 = 8.4$ kcal/mol. It appears to be easier to model free-energy changes than separate enthalpy and entropy changes, but even the trend in free-energy changes has proved hard to model. We will compare the present results to seven sets of explicit water calculations, namely: RS89 by Rao and Singh [62], MK95 by Mongantini and Kollman [63], D95N by Ding et al. [64] (nonpolarizable model), D95P by Ding et al. [64] (polarizable model), MCK96 by Meng, Caldwell, and Kollman [65], KGL97 by Kubo, Gallichio, and Levy [66], and SK98 by Spector and Kollman [68].

Table 19. Solvation energies calculated for a few sample cases with a variety of parameterizations

Solute	Solvent	ΔG_S^0 (kcal/mol)						
		HF/MIDI!	HF/6-31G*	HF/6-31+G*	HF/cc-pVDZ	BPW91/MIDI!	B3LYP/MIDI!	Experiment
n-Octane	*n*-Hexadecane	−4.5	−4.6	−4.3	−4.5	−4.6	−4.6	−5.0
Phenol	*n*-Hexadecane	−5.2	−4.7	−4.8	−5.2	−5.2	−5.2	−5.1
Aniline	*n*-Hexadecane	−5.4	−4.9	−5.0	−5.4	−5.5	−5.5	−5.4
Butylamine	Cyclohexane	−3.6	−3.5	−3.4	−3.6	−3.5	−3.6	−3.7
Phenol	Benzene	−6.4	−5.7	−5.9	−6.2	−6.3	−6.3	−7.1
Butylamine	Benzene	−4.3	−4.2	−4.1	−4.3	−4.3	−4.4	−4.3
Butanone	Ethanol	−5.5	−4.6	−4.6	−5.7	−5.6	−5.6	−4.3
Ethyne	1-Octanol	−0.3	0.2	0.3	0.0	−0.2	−0.2	−0.5
1-Butanol	1-Octanol	−4.0	−5.4	−5.9	−5.9	−5.9	−5.9	−5.7
Phenol	1-Octanol	−7.9	−7.1	−7.2	−7.8	−7.9	−7.9	−8.7
Aniline	1-Octanol	−6.9	−6.2	−6.2	−6.8	−7.1	−7.1	−6.7
1,4-Dioxane	Diethyl ether	−5.3	−4.4	−4.6	−5.2	−5.3	−5.3	−4.7
Ethanol	$CHCl_3$	−4.0	−3.4	−3.6	−4.1	−3.9	−4.0	−3.9
Propylamine	$CHCl_3$	−4.1	−3.9	−3.9	−4.1	−4.1	−4.1	−4.7
Ethanol	CCl_4	−2.9	−2.5	−2.5	−3.0	−3.0	−3.0	−3.0
Propylamine	CCl_4	−3.6	−3.4	−3.5	−3.6	−3.6	−3.6	−3.6
Ethanol	Nitromethane	−4.2	−4.8	−3.8	−4.4	−4.3	−4.3	−4.2
n-Octane	Water	2.3	2.2	2.5	2.4	2.4	2.3	2.9
Toluene	Water	−1.1	−0.3	−0.6	−1.1	−1.2	−1.1	−0.9
Methanol	Water	−5.5	−4.8	−5.2	−5.6	−5.4	−5.4	−6.6
Phenol	Water	−6.4	−5.5	−5.5	−6.3	−6.4	−6.4	−5.1
Benzaldehyde	Water	−4.7	−3.5	−2.8	−4.7	−4.4	−4.4	−4.0
Pyridine	Water	−4.5	−3.7	−3.3	−4.4	−4.4	−4.5	−4.7
Aniline	Water	−5.2	−4.4	−4.4	−5.1	−5.4	−5.3	−5.5
1-Iodopropane	Water	−0.7	−0.3	−0.8	−0.7	−0.6	−0.6	−0.6

Only three of these sets of calculations yield absolute free energies of solvation (the others yield substituent effects only), so in addition to Table 28, which compares free energies of solvation, we present the comparison of free-energy differences in Table 29, which gives substituent effects on free energies of solvation. These tables include the two least-expensive methods from the present paper plus the SM5.42R/BPW91/MIDI!6D density functional method from our previous paper [1] on density functional methods. The final row of each table contains the MUE compared to the experimental results. Tables 28 and 29 show typical errors of about 1.5–2.0 kcal/mol for explicit solvent models and about 0.3–0.4 kcal/mol for the SM5.2R implicit solvent models. The typical improvement compared to the previous models is a factor of 5 reduction in error.

Table 30 compares the breakdown in ΔG_{ENP} and G_{CDS} for the SM5.42R results of Table 28. The results are very similar for the three different Hamiltonians because we use CM2 charges in all three cases, and these charges tend to be more similar than the untransformed charges from the various Hamiltonians. For changes in the degree of substitution, Table 30 shows much greater variation in ΔG_{ENP} than in G_{CDS}, but the trend in overall solvation energies is qualitatively similar to that in the G_{CDS} terms, especially for AM1 and PM3. Clearly neither the ENP or CDS terms on their own can account for the experimental results. We note in this respect that G_{CDS} itself results from a cancellation of terms of different signs associated with dispersion, solvent structural perturbation and cavity creation, and specific interactions; variations in all of these may be important.

We close the discussion by turning our attention to selected hydrocarbons. The hydrocarbons in Table 31 allow one to compare normal hexane to cyclohexane and a branched heptane to methylcyclohexane. We do not show the breakdown into ΔG_{ENP} and G_{CDS}, but the former is between 0.0 and −0.3 in every case, so the trends are primarily due to G_{CDS}. The models underestimate the hydrophobic effects by about 0.1 kcal/mol per carbon atom for these molecules, but the trends, summarized in the last three rows, are reasonable. The difference between *n*-hexane and cyclohexane has been particularly difficult for many non-SM5 models to reproduce.

6 Application to carbonates

In order to provide a sample test of the solvation model, we applied it to calculate the free energy of transfer $\Delta G_{o/w}$ from water to 1-octanol for some molecules not in the parameterization suite, namely carbonates. Carbonates differ qualitatively from all molecules in the training suite in that they have oxygen atoms that are geminal to two other oxygen atoms. Thus they provide an interesting test of the model. These results are given in Table 32, along with the standard-state free energies of solvation in water and 1-octanol and the experimental value of the free energy of transfer taken from the MedChem database [67]. For comparison, Table 28 also shows some results calculated by the SM5.4/AM1 [42, 43, 46] method. The results for diethyl carbonate and ethyl 8-quinolinyl carbonate are greatly improved by the new model.

Table 20. Calculated and experimental free energies of solvation (kcal/mol) and components of free-energy calculations for ions in aqueous solution using SM5.42R

	HF/MIDI!			HF/6-31G*			Experiment
	ΔG_{ENP}	G_{CDS}	ΔG_S^0	ΔG_{ENP}	G_{CDS}	ΔG_S^0	ΔG_S^0
HC_2^-	−80.1	1.5	−78.6	−80.4	2.1	−78.4	−73
$CH_3OH_2^+$	−83.5	2.3	−81.2	−83.1	2.7	−80.5	−87
$(CH_3)_2OH^+$	−70.7	0.6	−70.1	−70.5	0.7	−69.8	−70
$CH_3CH_2OH_2^+$	−77.8	2.2	−75.7	−77.4	2.6	−74.8	−81
$CH_3C(OH)CH_3^+$	−67.6	−0.1	−67.7	−67.3	−0.2	−67.5	−64
H_3O^+	−102.4	7.9	−94.5	−102.4	8.9	−94.5	−105
CH_3O^-	−83.7	−0.1	−83.8	−84.6	−0.4	−85.0	−98
$CH_3CO_2^-$	−72.3	0.4	−71.9	−73.2	0.1	−73.1	−77
$CH_3COCH_2^-$	−70.1	0.5	−69.6	−71.2	0.4	−70.8	−81
$C_6H_5O^-$	−63.0	−1.2	−64.2	−65.4	−0.8	−66.2	−75
$C_6H_5CH_2^-$	−57.8	0.2	−57.5	−58.8	1.1	−57.7	−59
OH^-	−102.6	−5.0	−107.6	−102.6	−4.9	−107.5	−110
HO_2^-	−89.5	−6.9	−96.4	−90.2	−6.2	−96.4	−101
O_2^-	−86.8	−6.8	−93.6	−86.8	−6.0	−92.8	−87
$CH_3NH_3^+$	−74.7	−1.5	−76.3	−74.5	−1.4	−75.9	−73
$HC(OH)NH_2^+$	−73.9	−3.8	−77.7	−73.6	−3.9	−77.5	−78
CH_3CNH^+	−67.7	0.7	−67.0	−67.2	0.7	−66.6	−69
$CH_3C(OH)NH_2^+$	−67.0	−4.0	−71.0	−66.7	−4.2	−70.8	−70
$(CH_3)_2NH_2^+$	−67.5	0.2	−67.3	−67.3	0.4	−66.9	−66
$(CH_3)_3NH^+$	−61.8	2.3	−59.5	−61.8	2.6	−59.2	−59
$ImidazoleH^+$	−61.6	−1.2	−62.7	−61.9	−0.2	−62.0	−64
$C_5H_5NH^+$	−58.5	−0.8	−59.3	58.8	0.0	−58.8	−58
$C_6H_5NH_3^+$	−66.2	−2.4	−68.7	−66.7	−1.6	−68.4	−68
NH_4^+	−84.3	−2.7	−87.0	−84.3	−2.7	−87.1	−81
CN^-	−77.8	2.4	−75.4	−77.9	2.4	−75.4	−75
CH_2CN^-	−66.9	0.9	−66.0	−67.4	0.8	−66.6	−75
NH_2^-	−86.1	−2.4	−88.5	−86.3	−2.8	−89.1	−95
NO_2^-	−74.7	−0.6	−75.3	−74.6	−0.8	−75.5	−73
NO_3^-	−69.4	0.5	−69.0	−69.9	0.8	−69.1	−66
N_3^-	−66.2	−3.7	−69.9	−66.4	−5.1	−71.5	−74
$CH_3SH_2^+$	−72.7	1.8	−70.9	−71.9	1.7	−70.3	−74
$(CH_3)_2SH^+$	−64.7	2.1	−62.6	−64.3	2.1	−62.2	−61
HS^-	−82.4	−1.8	−84.2	−82.7	−1.6	−84.3	−76
CH_3S^-	−74.7	−1.4	−76.1	−78.0	−1.1	−79.1	−76
$CH_3CH_2S^-$	−71.3	−1.5	−72.8	−74.6	−1.1	−75.7	−74
$n\text{-}C_3H_7S^-$	−70.0	−1.4	−71.4	−73.8	−1.0	−74.8	−76
$C_6H_5S^-$	−62.4	−2.9	−65.2	−66.2	−1.8	−68.0	−65
F^-	−109.3	1.2	−108.1	−109.3	1.0	−108.3	−107
CHF_2COO^-	−66.4	1.6	−64.8	−66.5	1.0	−65.5	−70
Cl^-	−77.0	−0.1	−77.0	−77.0	−0.1	−77.0	−78
$CHCl_2COO^-$	−59.7	0.1	−59.6	−59.8	−0.3	−60.1	−66
Br^-	−71.0	−0.7	−71.7	−71.0	−0.9	−71.8	−72
I^-	−61.6	−1.0	−62.6	−61.6	−1.1	−62.8	−63
PH_2^-	−72.2	−0.2	−72.4	−72.2	−0.1	−72.3	−67
PH_4^+	−71.9	2.4	−69.5	−71.9	2.4	−69.5	−73
$CH_3PH_3^+$	−67.0	2.9	−64.1	−67.8	3.0	−64.8	−63
$(CH_3)_2PH_2^+$	−63.0	3.5	−59.5	−64.1	3.6	−60.5	−57
$(CH_3)_3PH^+$	−59.7	4.0	−55.6	−60.8	4.1	−56.7	−53
$H_2PO_4^-$	−68.9	−4.7	−73.6	−66.9	−6.7	−73.7	−68

7 Summary

We have extended the applicability of the SM5.42R universal solvation model to hybrid Hartree–Fock-DFT and to additional basis sets for Fock and Kohn–Sham operators. Averaged over the eight new parameterizations, the mean absolute error for 2135 solvation free energies of 275 neutral solutes in 91 solvents (water and 90 organic solvents) is 0.46 kcal/mol, compared to an estimated typical uncertainty of 0.2 kcal/mol in the experimental data, and the mean absolute error in 49 free energies of solvation of ions in water is 3.8 kcal/mol, which is less than the estimated typical uncertainty of 5 kcal/mol in the experimental data. A wide range of solute functional groups and solvent groups are treated with reasonably uniform accuracy across the groups.

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Table 21. Calculated and experimental free energies of solvation (kcal/mol) and components of free-energy calculations for ions in aqueous solution using SM5.42R

	HF/6-31+G*			HF/cc-pVDZ			Experiment
	ΔG_{ENP}	G_{CDS}	ΔG_S^0	ΔG_{ENP}	G_{CDS}	ΔG_S^0	ΔG_S^0
HC_2^-	−80.2	1.5	−78.8	−79.8	1.1	−78.8	−73
$CH_3OH_2^+$	−83.5	3.9	−79.6	−83.2	2.7	−80.6	−87
$(CH_3)_2OH^+$	−70.7	1.1	−69.5	−70.7	0.8	−69.9	−70
$CH_3CH_2OH_2^+$	−77.2	3.8	−73.4	−77.5	2.5	−75.0	−81
$CH_3C(OH)CH_3^+$	−67.3	−0.2	−67.5	−67.2	−0.3	−67.5	−64
H_3O^+	−102.5	7.9	−94.5	−102.1	8.9	−93.3	−105
CH_3O^-	−85.1	−0.1	−85.2	−86.0	−0.4	−86.4	−98
$CH_3CO_2^-$	−77.2	1.2	−76.0	−73.8	−0.1	−73.9	−77
$CH_3COCH_2^-$	−75.2	0.5	−74.7	−71.0	0.5	−70.5	−81
$C_6H_5O^-$	−64.1	−1.2	−65.3	−66.5	−0.7	−67.2	−75
$C_6H_5CH_2^-$	−58.5	0.7	−57.8	−59.0	1.3	−57.7	−59
OH^-	−102.6	−5.3	−107.9	−104.2	−5.1	−109.3	−110
HO_2^-	−92.3	−4.4	−96.7	−89.9	−6.6	−96.5	−101
O_2^-	−86.8	−3.9	−90.7	−86.8	−6.4	−93.2	−87
$CH_3NH_3^+$	−74.6	−1.6	−76.2	−74.7	−1.6	−76.3	−73
$HC(OH)NH_2^+$	−73.1	−3.3	−76.4	−73.1	−4.1	−77.2	−78
CH_3CNH^+	−67.5	0.0	−67.5	−67.5	1.0	−66.5	−69
$CH_3C(OH)NH_2^+$	−66.1	−3.6	−70.6	−66.4	−4.3	−70.7	−70
$(CH_3)_2NH_2^+$	−67.1	0.5	−66.6	−67.4	0.3	−67.1	−66
$(CH_3)_3NH^+$	−61.4	3.0	−58.4	−61.9	2.5	−59.4	−59
ImidazoleH$^+$	−61.1	0.0	−61.1	−61.5	−0.6	−62.1	−64
$C_5H_5NH^+$	−58.0	−0.2	−58.3	−58.6	0.0	−58.6	−58
$C_6H_5NH_3^+$	−65.6	−2.4	−68.0	−66.7	−1.7	−68.4	−68
NH_4^+	−84.4	−3.2	−87.6	−84.3	−3.1	−87.4	−81
CN^-	−78.8	1.8	−77.0	−77.8	1.3	−74.8	−75
CH_2CN^-	−67.5	0.0	−67.5	−67.1	1.4	−65.7	−75
NH_2^-	−87.2	−2.6	−89.8	−86.2	−3.0	−89.2	−95
NO_2^-	−74.6	−0.2	−74.8	−75.5	−2.8	−78.3	−73
NO_3^-	−71.0	1.8	−69.2	−72.0	−2.2	−74.3	−66
N_3^-	−66.7	−3.6	−70.3	−66.2	−5.0	−71.2	−74
$CH_3SH_2^+$	−72.4	2.1	−70.3	−73.9	3.7	−70.3	−74
$(CH_3)_2SH^+$	−64.4	2.5	−61.9	−65.5	3.1	−62.4	−61
HS^-	−83.1	−1.7	−84.8	−83.4	−1.0	−84.4	−76
CH_3S^-	−75.7	−1.1	−76.8	−78.1	−1.5	−79.5	−76
$CH_3CH_2S^-$	−71.7	−1.2	−72.9	−74.6	−1.5	−76.1	−74
n-$C_3H_7S^-$	−71.4	−1.0	−72.4	−73.3	−1.4	−74.7	−76
$C_6H_5S^-$	−67.3	−2.4	−69.7	−65.8	−2.1	−67.9	−65
F^-	−109.3	1.0	−108.3	−109.3	1.1	−108.2	−107
CHF_2COO^-	−66.3	1.9	−64.4	−67.2	0.9	−66.3	−70
Cl^-	−77.0	−0.1	−77.0	−77.0	−0.2	−77.1	−78
$CHCl_2COO^-$	−63.0	0.7	−62.3	−60.6	−0.6	−61.1	−66
Br^-	−71.0	−0.9	−71.9	−71.0	−0.9	−71.9	−72
I^-	−61.6	−1.2	−62.8	−61.6	−1.3	−62.9	−63
PH_2^-	−72.8	0.9	−71.9	−72.2	−0.3	−72.4	−67
PH_4^+	−71.9	3.0	−68.9	−71.9	2.3	−69.6	−73
$CH_3PH_3^+$	−67.9	3.7	−64.3	−68.4	3.0	−65.5	−63
$(CH_3)_2PH_2^+$	−63.5	4.3	−59.2	−65.1	3.6	−61.5	−57
$(CH_3)_3PH^+$	−59.2	5.0	−54.2	−61.7	4.3	−57.5	−53
$H_2PO_4^-$	−67.6	−6.4	−74.0	−66.0	−8.2	−74.2	−68

Table 22. Calculated and experimental free energies of solvation (kcal/mol) and components of free-energy calculations for ions in aqueous solution using SM5.42R

Solute	SM5.42R/AM1			SM5.42R/PM3			Expt.
	ΔG_{ENP}	G_{CDS}	ΔG_S^0	ΔG_{ENP}	G_{CDS}	ΔG_S^0	ΔG_S^0
HC_2^-	−80.8	3.2	−77.6	−82.1	3.0	−79.1	−73
$CH_3OH_2^+$	−84.5	3.6	−80.9	−85.1	3.7	−81.4	−87
$(CH_3)_2OH^+$	−71.0	0.9	−70.2	−71.9	1.0	−70.9	−70
$CH_3CH_2OH_2^+$	−78.7	3.5	−75.2	−79.4	3.6	−75.8	−81
$CH_3C(OH)CH_3^+$	−68.2	0.5	−67.7	−68.6	0.9	−67.6	−64
H_3O^+	−104.0	11.2	−92.8	−103.2	10.9	−92.3	−105
CH_3O^-	−82.8	0.4	−82.4	−84.3	0.4	−83.9	−98
$CH_3CO_2^-$	−73.1	1.8	−71.2	−74.4	1.7	−72.7	−77
$CH_3COCH_2^-$	−71.3	1.5	−69.7	−72.5	1.5	−71.0	−81
$C_6H_5O^-$	−66.0	0.8	−65.2	−67.4	0.6	−66.8	−75
$C_6H_5CH_2^-$	−59.2	1.8	−57.4	−59.9	1.5	−58.4	−59
OH^-	−104.9	−4.2	−109.1	−105.9	−4.6	−110.4	−110
HO_2^-	−91.9	−5.3	−97.2	−92.7	−6.7	−99.4	−101
O_2^-	−86.8	−5.1	−91.9	−86.8	−7.0	−93.8	−87
$CH_3NH_3^+$	−75.2	−1.9	−77.1	−77.0	−2.3	−79.3	−73
$HC(OH)NH_2^+$	−76.2	−2.8	−79.0	−74.5	−3.1	−77.6	−78
CH_3CNH^+	−68.7	1.5	−67.1	−68.0	1.4	−66.6	−69
$CH_3C(OH)NH_2^+$	−68.0	−2.7	−70.7	−67.7	−3.0	−70.7	−70
$(CH_3)_2NH_2^+$	−67.8	−0.2	−68.0	−70.0	−0.6	−70.6	−66
$(CH_3)_3NH^+$	−61.8	2.0	−59.9	−63.8	1.8	−62.1	−59
ImidazoleH$^+$	−63.9	0.3	−63.7	−62.9	−0.5	−63.5	−64
$C_5H_5NH^+$	−59.9	0.6	−59.3	−59.9	0.1	−59.8	−58
$C_6H_5NH_3^+$	−67.8	−1.4	−69.2	−69.3	−2.0	−71.3	−68
NH_4^+	−84.4	−3.0	−87.4	−84.6	−3.4	−88.0	−81
CN^-	−78.8	4.2	−74.7	−78.5	4.1	−74.4	−75
CH_2CN^-	−67.4	2.7	−64.7	−68.7	2.7	−66.0	−75
NH_2^-	−86.4	−0.9	−87.3	−87.9	−1.2	−89.1	−95
NO_2^-	−74.6	1.2	−73.5	−75.6	2.4	−73.2	−73
NO_3^-	−69.4	1.7	−67.7	−69.2	3.3	−65.9	−66
N_3^-	−66.1	1.9	−64.2	−66.3	1.9	−64.4	−74
$CH_3SH_2^+$	−68.4	1.4	−67.1	−69.0	0.9	−68.1	−74
$(CH_3)_2SH^+$	−63.1	2.0	−61.1	−63.3	1.8	−61.5	−61
HS^-	−76.9	−1.3	−78.2	−76.5	−1.3	−77.8	−76
CH_3S^-	−77.3	−0.6	−77.9	−75.0	−0.3	−75.3	−76
$CH_3CH_2S^-$	−75.4	−0.6	−76.0	−73.1	−0.4	−73.5	−74
n-$C_3H_7S^-$	−75.3	−0.5	−75.8	−72.8	−0.2	−73.1	−76
$C_6H_5S^-$	−66.7	−0.6	−67.3	−66.0	−0.7	−66.6	−65
F^-	−109.3	1.2	−108.0	−109.3	1.1	−108.2	−107
CHF_2COO^-	−65.8	3.0	−62.8	−67.3	2.7	−64.6	−70
Cl^-	−76.9	−0.1	−77.0	−76.9	0.0	−77.0	−78
$CHCl_2COO^-$	−57.8	1.5	−56.4	−59.2	1.5	−57.7	−66
Br^-	−70.9	−0.9	−71.8	−70.9	−0.9	−71.8	−72
I^-	−61.6	−0.9	−62.5	−61.6	−0.9	−62.5	−63
PH_2^-	−70.4	0.7	−69.7	−71.6	0.0	−71.5	−67
PH_4^+	−68.0	3.0	−65.0	−68.3	2.5	−65.7	−73
$CH_3PH_3^+$	−66.1	3.4	−62.7	−67.7	3.0	−64.7	−63
$(CH_3)_2PH_2^+$	−65.8	3.8	−62.0	−66.3	3.5	−62.8	−57
$(CH_3)_3PH^+$	−66.9	4.2	−62.7	−63.9	4.0	−59.9	−53
$H_2PO_4^-$	−69.2	−2.5	−71.7	−66.2	−7.3	−73.5	−68

Table 23. Calculated and experimental free energies of solvation (kcal/mol) and components of free-energy calculations for ions in aqueous solution using SM5.42R

	BPW91/MIDI!			B3LYP/MIDI!			Experiment
	ΔG_{ENP}	G_{CDS}	ΔG_S^0	ΔG_{ENP}	G_{CDS}	ΔG_S^0	ΔG_S^0
HC_2^-	−80.3	2.0	−78.4	−80.2	1.8	−78.3	−73
$CH_3OH_2^+$	−83.7	2.3	−81.3	−83.5	2.5	−81.0	−87
$(CH_3)_2OH^+$	−70.7	0.8	−69.9	−70.6	0.9	−69.7	−70
$CH_3CH_2OH_2^+$	−77.8	2.2	−75.7	−77.7	2.4	−75.3	−81
$CH_3C(OH)CH_3^+$	−67.0	−0.1	−67.1	−67.5	0.0	−67.5	−64
H_3O^+	−102.0	7.7	−94.3	−102.3	8.0	−94.3	−105
CH_3O^-	−82.8	−0.1	−82.8	−83.8	−0.2	−84.0	−98
$CH_3CO_2^-$	−71.1	0.0	−71.1	−72.1	−0.1	−72.2	−77
$CH_3COCH_2^-$	−69.5	0.8	−68.7	−69.8	0.6	−69.1	−81
$C_6H_5O^-$	−62.0	−0.5	−62.5	−62.5	−0.8	−63.3	−75
$C_6H_5CH_2^-$	−58.6	1.2	−57.4	−57.8	0.9	−56.9	−59
OH^-	−104.3	−4.9	−109.2	−102.3	−5.1	−107.4	−110
HO_2^-	−90.4	−7.0	−97.4	−89.0	−7.2	−96.5	−101
O_2^-	−86.8	−6.8	−93.6	−86.8	−7.2	−94.1	−87
$CH_3NH_3^+$	−74.6	−1.6	−76.2	−74.6	−1.8	−76.4	−73
$HC(OH)NH_2^+$	−73.4	−4.3	−77.8	−73.5	−4.4	−78.0	−78
CH_3CNH^+	−67.7	1.1	−66.5	−67.7	1.1	−66.6	−69
$CH_3C(OH)NH_2^+$	−66.6	−4.6	−71.2	−66.6	−4.7	−71.3	−70
$(CH_3)_2NH_2^+$	−67.2	0.2	−67.0	−67.3	0.1	−67.3	−66
$(CH_3)_3NH^+$	−61.6	2.3	−59.3	−61.7	2.3	−59.4	−59
$ImidazoleH^+$	−61.4	−0.9	−62.3	−61.6	−1.1	−62.7	−64
$C_5H_5NH^+$	−58.6	−0.1	−58.7	−58.5	−0.4	−58.8	−58
$C_6H_5NH_3^+$	−66.2	−1.8	−68.0	−65.8	−2.2	−68.0	−68
NH_4^+	−84.3	−2.8	−87.1	−84.3	−3.1	−87.4	−81
CN^-	−77.7	3.3	−74.5	−77.8	3.2	−74.5	−75
CH_2CN^-	−67.4	1.7	−65.7	−66.9	1.7	−65.6	−75
NH_2^-	−86.2	−2.2	−88.4	−86.0	−2.5	−88.4	−95
NO_2^-	−74.9	−0.8	−75.7	−74.7	−0.8	−75.5	−73
NO_3^-	−69.2	−0.2	−69.5	−69.4	0.0	−69.5	−66
N_3^-	−66.5	−2.9	−69.3	−66.2	−3.2	−69.5	−74
$CH_3SH_2^+$	−72.7	2.1	−70.6	−74.1	2.0	−72.1	−74
$(CH_3)_2SH^+$	−64.7	2.3	−62.3	−65.3	2.3	−63.0	−61
HS^-	−82.4	−1.9	−84.3	−82.6	−1.9	−84.5	−76
CH_3S^-	−74.3	−1.6	−75.9	−74.5	−1.6	−76.1	−76
$CH_3CH_2S^-$	−71.2	−1.7	−72.8	−71.3	−1.7	−73.0	−74
$n\text{-}C_3H_7S^-$	−69.7	−1.5	−71.3	−69.9	−1.6	−71.4	−76
$C_6H_5S^-$	−61.1	−2.4	−63.4	−62.3	−2.6	−64.9	−65
F^-	−109.3	1.3	−108.0	−109.3	1.2	−108.1	−107
CHF_2COO^-	−65.2	1.2	−63.9	−66.3	1.1	−65.2	−70
Cl^-	−77.0	−0.2	−77.1	−77.0	−0.2	−77.1	−78
$CHCl_2COO^-$	−57.8	−0.5	−58.3	−59.6	−0.5	−60.2	−66
Br^-	−71.0	−0.9	−71.9	−71.0	−0.9	−71.8	−72
I^-	−61.6	−1.3	−62.9	−61.6	−1.3	−62.9	−63
PH_2^-	−72.2	−0.3	−72.6	−72.3	−0.3	−72.6	−67
PH_4^+	−71.9	2.3	−69.6	−71.9	2.3	−69.7	−73
$CH_3PH_3^+$	−65.5	3.0	−62.6	−66.3	2.9	−63.4	−63
$(CH_3)_2PH_2^+$	−60.8	3.7	−57.2	−61.9	3.6	−58.3	−57
$(CH_3)_3PH^+$	−57.3	4.3	−53.0	−58.4	4.3	−54.1	−53
$H_2PO_4^-$	−68.4	−5.2	−73.6	−68.7	−4.8	−73.5	−68

Table 24. MUES (kcal/mol)

Parameterization[a]	Ref.	Neutral molecules		Ions	
		Excl. P[b]	All[c]	Excl. P[d]	All[e]
BPW91/MIDI!6D	[1]	0.43	0.45	3.9	3.7
BPW91/DZVP	[1]	0.43	0.44	3.6	3.6
BPW91/6-31G*	[1]	0.41	0.43	3.9	3.9
HF/MIDI!6D	[2]	0.43	0.45	3.9	3.9
HF/MIDI![f]	present	0.42	0.44	3.8	3.8
HF/6-31G*	present	0.41	0.43	3.7	3.7
HF/6-31 + G*	present	0.50	0.53	3.6	3.5
HF/cc-pVDZ	present	0.43	0.45	3.8	3.9
AM1	present	0.43	0.45	4.0	4.1
PM3	present	0.48	0.46	3.9	4.0
BPW91/MIDI![f]	present	0.43	0.45	3.9	3.8
B3LYP/MIDI!	present	0.43	0.45	3.9	3.7

[a] HF/MIDI! geometries were used in all cases for the calculations in this table and for the calculations in Tables 10–25
[b] 2084 data excluding solutes containing P
[c] All 2135 data
[d] 43 data excluding ions containing P
[e] All 49 data
[f] MIDI! without a 6D qualifier denotes the original 5D-type MIDI! basis

Table 25. Comparison of calculations of distortion energies and standard-state solvation free energies (kcal/mol) and dipole moments (D) in aqueous solution using ISCRF = 1 and ISCRF = 2 options[a]

		ISCRF = 1	ISCRF = 2
HF/MIDI!6D			
H_2O	Distortion energy	0.358	0.355
	Solvation free energy	−6.310	−6.310
	CM2 dipole moment	1.938	1.937
CH_3CH_2OH	Distortion energy	0.268	0.246
	Solvation free energy	−5.514	−5.499
	CM2 dipole moment	1.746	1.720
Thiophene	Distortion energy	0.142	0.119
	Solvation free energy	−2.191	−2.175
	CM2 dipole moment	0.748	0.724
BPW91/MIDI!6D			
H_2O	Distortion energy	0.302	0.302
	Solvation free energy	−6.388	−6.388
	CM2 dipole moment	1.804	1.804
CH_3CH_2OH	Distortion energy	0.254	0.255
	Solvation free energy	−5.487	−5.487
	CM2 dipole moment	1.775	1.776
Thiophene	Distortion energy	0.173	0.167
	Solvation free energy	−2.076	−2.076
	CM2 dipole moment	0.679	0.658
BPW91/6-31G*			
H_2O	Distortion energy	0.405	0.405
	Solvation free energy	−6.310	−6.310
	CM2 dipole moment	2.113	2.113
CH_3CH_2OH	Distortion energy	0.312	0.282
	Solvation free energy	−5.508	−5.487
	CM2 dipole moment	1.822	1.789
Thiophene	Distortion energy	0.198	0.131
	Solvation free energy	−1.850	−1.800
	CM2 dipole moment	0.679	0.658

[a] HF/MIDI! gas-phase geometries

Table 26. Comparison of contributions (kcal/mol) of terms in Eq. (8)

Solute	Solvent	Parameterization	Trace $\hat{\mathbf{V}}\mathbf{P}$		
			Entire $g_{\sigma\mu\upsilon}$	$g^{\mathrm{L}}_{\sigma\mu\upsilon}$	$g^{\mathrm{M}}_{\sigma\mu\upsilon}$
Ethanol	Water	HF/MIDI!	−47.6	−46.7	−0.9
Benzaldehyde	Water	HF/MIDI!	−38.4	−35.0	−3.4
Ethylamine	Water	HF/MIDI!	13.4	15.7	−2.3
Acetonitrile	Water	HF/MIDI!	39.2	45.9	−6.7
Ethanol	Cyclohexane	HF/MIDI!	−23.6	−23.2	−0.4
Ethanol	Water	HF/6-31G*	−55.1	−52.4	−2.7
Acetaldehyde	Water	HF/6-31G*	−77.1	−76.8	−0.3
Ethylamine	Water	HF/6-31G*	10.1	10.2	−0.1
Acetonitrile	Water	HF/6-31G*	32.7	38.6	−5.9
Ethanol	Water	BPW91/MIDI!	−56.9	−54.2	−2.7
Benzaldehyde	Water	BPW91/MIDI!	−75.2	−68.6	−6.6
Ethylamine	Water	BPW91/MIDI!	8.5	11.0	−2.5
Acetonitrile	Water	BPW91/MIDI!	32.4	41.3	−8.9

Table 27. Free energies of solvation calculated with SM5.42R/HF/6-31G* for various choices of geometry

Solute	Solvent	ΔG^0_S(kcal/mol)		
		//HF/MIDI!	//HF/6-31G*	//B3LYP/MIDI!
Methanol	Water	−5.73	−5.30	−5.98
Phenol	Water	−6.64	−6.33	−6.96
1-Butanol	1-Octanol	−6.03	−5.82	−6.19
Phenol	1-Octanol	−8.11	−7.95	−8.32
Propylamine	$CHCl_3$	−4.12	−4.03	−4.21

Table 28. Free energies of solvation (kcal/mol) of ammonia and amines in water

Solute[a]	D95P	KGL97	SK98	SM5.42R/			Expt.
				BPW91[b]	AM1	PM3	
NH_3	−4.0	−4.2	−4.2	−5.1	−5.2	−4.8	−4.3
$MeNH_2$	−3.7	−3.0	−3.6	−4.5	−4.6	−4.6	−4.6
Me_2NH	−1.2	−0.6	−2.0	−4.1	−4.2	−4.2	−4.3
Me_3N	−0.6	2.8	0.4	−3.3	−3.3	−3.3	−3.2
MUE	1.7	2.9	1.8	0.3	0.3	0.2	

[a] Me = methyl
[b] MIDI!6D

Table 29. Changes of free energy of solvation (kcal/mol) of ammonia and amines in water as the number of methyl groups is increased

Substitution[a]	RS89	MK98	D95N	D95P	MCK96	KGL97	SK98	SM5.42R1			Expt.
								BPW91[b]	AM1	PM3	
$Me_0 \rightarrow Me_1$	−0.1	0.6	1.1	0.3	0.4	1.2	0.6	0.6	0.6	0.2	−0.3
$Me_1 \rightarrow Me_2$	1.9	1.6	3.2	2.5	[c]	2.4	1.6	0.4	0.4	0.4	0.3
$Me_2 \rightarrow Me_3$	1.2	2.3	2.3	0.6	[c]	3.4	2.3	0.8	0.7	0.9	1.1
$Me_0 \rightarrow Me_3$	3.0	4.4	6.6	3.4	2.9	7.0	4.5	1.8	1.7	1.5	1.1
MUE	1.0	1.7	2.8	1.4	2.0	3.0	1.7	0.5	0.5	0.3	

[a] Me = methyl
[b] MIDI!6D
[c] Not available

Table 30. Components of free energy of solvation (kcal/mol) of ammonia and amines in water

Solute[b]	BPW91[a]		AM1		PM3	
	ENP	CDS	ENP	CDS	ENP	CDS
NH_3	−2.4	−2.7	−3.2	−2.0	−2.5	−2.3
$MeNH_2$	−1.8	−2.7	−2.3	−2.3	−2.0	−2.6
Me_2NH	−1.5	−2.6	−1.8	−2.3	−1.6	−2.6
Me_3N	−1.5	−1.8	−1.7	−1.7	−1.3	−2.0

[a] MIDI!6D
[b] Me = methyl

Table 31. Free energies of solvation (kcal/mol) of selected hydrocarbons in water

Solute	BPW91[a]	AM1	PM3	Expt.
1. *n*-Hexane	1.9	1.9	1.9	2.5
2. Cyclohexane	0.5	0.7	0.5	1.2
3. 2,4-Dimethylpentane	2.6	2.5	2.6	2.9
4. Methylcyclohexane	1.1	1.2	1.1	1.7
1–2	1.4	1.2	1.4	1.3
3–1	0.7	0.6	0.7	0.4
3–4	1.5	1.3	1.5	1.2

[a] MIDI!6D

Table 32. Free energies of solvation and transfer (kcal/mol) for carbonates

Solute	ΔG_S^0		$\Delta G_{o/w}$	
	Water	1-octanol	Calculated	Expt.
SM5.42R/AM1//HF/MIDI!				
Diethyl carbonate	−2.83	−4.63	−1.80	−1.65
Propylene carbonate	−6.82	−6.89	−0.07	0.56
SM5.42R/AM1//AM1				
Ethyl 8-quinolinyl carbonate	−12.35	−14.50	−2.15	−2.36
SM5.4/AM1				
Diethyl carbonate	−2.82	−6.12	−3.30	−1.65
Propylene carbonate	−6.54	−6.08	0.46	0.56
Ethyl 8-quinolinyl carbonate	−8.37	−13.68	−5.31	−2.36

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