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Additivity Methods in Molecular Polarizability

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Abstract: Empirical methods to calculate average molecular polarizabilities based on atomic hybrid parameters are reexamined. New sets of optimized atomic hybrid components, τ_A(ahc), and atomic hybrid polarizabilities, α_A(ahp), are presented. They yield average molecular polarizabilities with complementary empirical formulas, $\alpha(\text{ahc}) = (4/N)[\sum_A \tau_A(\text{ahc})]^2$ (N = number of electrons in the molecule) and $\alpha(\text{ahp}) = \sum_A \alpha_A(\text{ahp})$, which reproduce the experimental polarizabilities to an average error of 2.2% and 2.8% respectively for approximately 400 compounds containing H, C, N, O, S, F, Cl, B, I, and P. Only one parameter, τ_A or α_A, in each formula is required for each atom, A, in a particular atomic hybridization state. Conjugate parameters, $\alpha_A^*(\text{ahp}) = (4/N_A)\tau_A(\text{ahc})^2$ and $\tau_A^*(\text{ahp}) = [N_A \alpha_A(\text{ahp})/4]^{1/2}$ (N_A = number of electrons in atom A) used as alternate sets in these two empirical formulas, yield average molecular polarizabilities to a root-mean-square standard deviation of 5.6% and 6.4%, respectively. These two partitioning schemes are discussed. The atomic hybrid polarizabilities can be combined to generate bond polarizabilities, bp and two possible sets are discussed. In addition, the atomic polarizabilities are related to group polarizabilities, gp. The atomic hybrid methods require fewer parameters than the bond or group polarizability methods, but the ahc, ahp, bp, and gp methods yield comparable results.

Introduction

The most successful empirical approaches to the calculation of average molecular polarizabilities include the environment through atomic hybridization about the central atom or with the atoms defining a bond or groups. Miller and Savchik[1] were the first to propose a method that features atom hybridization (ah) in which each atom is characterized by its state of atomic hybridization. They used a functional form

$$\alpha(\text{ahc}) = (4/N)[\sum_A \tau_A(\text{ahc})]^2 \qquad (1)$$

where τ_A is an atomic hybrid component (ahc) for each atom A in a given state of hybridization, and N is the total number of electrons. This formula was based on a theoretical interpretation of variational perturbation results[1-4] and interpreted with molecular orbital theory.[1] Their optimized atomic hybrid components, τ_A(ahc), reproduce α(ahc) to 1-3% and within experimental error for most of the approximately 240 molecules studied. They wrote the average atomic polarizability as

$$\alpha_A^*(\text{ahc}) = (4/N_A)\tau_A^2 \qquad (2)$$

using the set of τ_A from the ahc optimization, where N_A is the number of electrons in atom A. α_A^*(ahc) will be referred to as the conjugate (*) ahc polarizability. In this paper it will be useful to compute the conjugate ahc molecular polarizability

$$\alpha^*(\text{ahc}) = \sum_A \alpha_A^*(\text{ahc}) \qquad (3)$$

to compare the two schemes of partitioning, eqs 1 and 3, and the conjugate relationship through eq 2.

Subsequently, Yoffe and Maggiora[5] used eqs 2 and 3 in a study of London dispersion interaction energies and Kang and Jhon[6] tabulated values of α^*(ahc) for approximately 100 molecules. α^*(ahc) are consistently larger than α(ahc) by only 1-5% in most cases studied. Kang and Jhon[6] refined the atomic polarizabilities to obtain an optimum set of atomic hybrid polarizabilities, α_A(ahp), which reproduce the molecular polarizabilities

$$\alpha(\text{ahp}) = \sum_A \alpha_A(\text{ahp}) \qquad (4)$$

to approximately 1-3%. In this paper it will be convenient to define a conjugate (*) ahc parameter

$$\tau_A^*(\text{ahp}) = [N_A \alpha_A(\text{ahp})/4]^{1/2} \qquad (5)$$

calculated with the optimum parameters α_A(ahp) from which the conjugate (*) ahp molecular polarizability becomes

$$\alpha^*(\text{ahp}) = (4/N)[\sum_A \tau_A^*(\text{ahp})]^2 \qquad (6)$$

to relate eqs 4 and 6 through eq 5.

Comparisons between the ahc and ahp methods of eqs 1 and 4 calculated with newly optimized τ_A(ahc) and α_A(ahp) and the conjugate methods of eqs 3 and 6 will be made to examine the interchangability of parameters, the equivalence of the two methods of partitioning the molecular polarizability, and the atomic size.

The simplicity of the ahc and ahp atomic hybrid methods is understood by noting that the molecular polarizability cannot be written as a sum of atomic polarizabilities[7,8] when atoms are defined *only* by the atomic number. Eisenlohr[8,9] and more recently Vogel[10] set up an extensive system of atomic refractions[11] that have been supplemented by Batsanov[12] in which each atom must be assigned a polarizability depending on the atoms to which it is bonded. Silberstein[7] pointed out that atomic polarizabilities are not additive unless the atomic environment is considered in great detail. The methods that consider atoms in atomic hybrid states eliminate the need to develop an extensive set of rules that consider the specific atoms involved in bonding.

A third method of calculating molecular polarizabilities originated with the early work by von Steiger,[13] Smyth,[14] and Denbigh,[15] who demonstrated additivity of bond polarizabilities (bp)

$$\alpha(\text{bp}) = \sum_B \alpha_B(\text{bp}) \qquad (7)$$

where the sum is over all bonds B in the molecule. Denbigh[15] and Vickery and Denbigh[16] obtained a set of α_B(bp) that reproduce α(bp) to 1-2% for 52 molecules, and Vogel et al.[17] have obtained

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(2) Hylleraas, E. *Z. Phys.* **1930**, *65*, 209.

(3) Hasse, H. R. *Proc. Cambridge Philos. Soc.* **1930**, *26*, 542.

(4) Hirshfelder, J. O.; Curtiss, C. F.; Bird, R. B. *Molecular Theory of Gases and Liquids*; Wiley: New York, 1954; pp 942-948.

(5) Yoffe, J. A.; Maggiora, G. M. *Theor. Chim. Acta* **1980**, *56*, 191.

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(10) Vogel, A. *J. Chem. Soc.* **1948**, 1833.

(11) Molar refraction R (cm^3) is related to polarizability through Avogadro's number, L, by $\alpha(\text{Å}^3) = 3R/(4\pi L) = 0.3964R$.

(12) Batsanov, S. S. *Refractometry and Chemical Structure*; Consultants Bureau: New York, 1961.

(13) von Steiger, A. L. *Berichte* **1921**, *54*, 1381.

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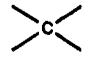
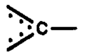
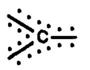
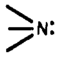
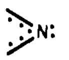
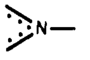
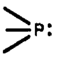
Table I. Parameters for Atoms in Hybrid Configurations

symbol[a]	hybrid[b]	group[c]	τ_A(ahc),[d] Å$^{3/2}$	α_A(ahp),[d] Å^3	$\alpha_A{}^*$(ahc),[e] Å^3	$\tau_A{}^*$(ahp),[e] Å$^{3/2}$	ρ_A(ahc),[f] Å	ρ_A(ahp),[f] Å	ρ_A(exp),[f] Å	α_A(exp),[g] Å^3
H	σ	-H	0.313	0.387	0.392	0.311	1.227	1.223	1.200	0.358
F	σ	-F	1.089	0.296	0.527	0.816	1.322	1.144	1.470	0.807
Cl	σ	-Cl	3.165	2.315	2.357	3.137	1.922	1.913	1.750	1.620
Br	σ	-Br	5.566	3.013	3.541	5.135	2.128	2.044	1.850	2.023
I	σ	-I	8.593	5.415	5.573	8.470	2.383	2.366	1.980	2.655
CTE	tetetete		1.294	1.061	1.116	1.262	1.594	1.574	1.700	1.443
CTR	trtrtrπ		1.433	1.352	1.369	1.424	1.678	1.673	1.700	1.443
CBR	trtrtrπ		1.707	1.896	1.943	1.686	1.831	1.820	1.700	1.443
CDI	didi$\pi\pi$	—C≡	1.393	1.283	1.294	1.387	1.654	1.651	1.700	1.443
NTE	te^{2}tetete		1.373	0.964	1.077	1.299	1.580	1.537	1.550	0.997
NTR2	tr^{2}trtrπ		1.262	1.030	0.910	1.343	1.515	1.563	1.550	0.997
NPI2	trtrtrπ^2		1.220	1.090	0.851	1.381	1.490	1.585	1.550	0.997
NDI	di^{2}di$\pi\pi$	≡N:	1.304	0.956	0.972	1.293	1.540	1.534	1.550	0.997
OTE	te^{2}te^{2}tete		1.249	0.637	0.780	1.129	1.458	1.386	1.520	0.922
OTR4	tr^{2}tr^{2}trπ	=O:	1.216	0.569	0.739	1.067	1.438	1.347	1.520	0.922
OPI2	tr^{2}trtrπ^2		1.083	0.274	0.586	0.740	1.357	1.122	1.520	0.922
STE	te^{2}te^{2}tete		3.496	3.000	3.056	3.464	2.051	2.041	1.800	1.813
STR4	tr^{2}tr^{2}trπ	=S:	3.827	3.729	3.661	3.862	2.146	2.156	1.800	1.813
SPI2	tr^{2}trtrπ^2		2.982	2.700	2.223	3.286	1.894	1.988	1.800	1.813
PTE	tetetete		2.485	1.538	1.647	2.402	1.757	1.727	1.800	1.813

[a] Atom A is represented as an atomic hybrid. The first (and sometimes second) letters denote the atom, and the remaining letters denote the atomic hybridization state. [b] Atomic orbitals are hybridized to form molecular orbitals in the states of hybridization: σ, te (tetrahedral), tr (trigonal), di (digonal), and π. [c] Examples from portions of molecules or molecular groups. [d] Optimized parameters: atomic hybrid component, τ_A(ahc), or atomic hybrid polarizability, α_A(ahp). [e] The conjugate (*) set of parameters $\tau_A{}^*$(ahc) or $\alpha_A{}^*$(ahp) used with eq 3 or 6 indicate the extent of transferability of parameters between the two methods. [f] Theoretical van der Waals radii ρ_A(ahc) and ρ_A(ahp) obtained from the two methods relate α(ahc) and α(ahp) to atomic size with eq 12′ and are compared to the experimental van der Waals radii, ρ_A(exp), ref 18. [g] $\alpha(\exp) = [\rho_A(\exp)/(1.05\sqrt{3})]^3/a_0$ provides an estimate of the experimental polarizability.

the most refined set of bond polarizabilities. This method has been used very successfully. It introduces the environment into the parametrization through bonds linking pairs of atoms. Single, double, triplet, aromatic, etc. bonds indirectly incorporate atomic hybridization.

A fourth method of calculating molecular polarizability was developed extensively by Vogel and co-workers and culminated in a set of group polarizabilities, gp.[10] They very cleverly represented different types of bonding with a set of characteristic groups that can be interpreted with atomic hybrids and represented by the present ahp method.

In this paper optimum sets of ahc and ahp parameters will be presented and the bp and gp methods will be related to the ahp method. Unlike the atomic hybrid methods in which one parameter is required for each of M atoms or types, the bond method requires $M(M-1)/2$ bond parameters, and a distinction for carbon atoms in aromatic, naphthalenic, etc. bonds is generally made. The group method requires parameters for each unique group. However, a relationship between the bp, gp, and ahp methods will be shown.

Optimized ahc and ahp Parameters

Atomic parameters are characterized according to atomic hybridization and listed in Table I. Molecular polarizabilities

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(18) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

(19) Landolt-Bornstein, *Atom und Molekularphysik*; Springer-Verlag: West Berlin, 1951; Vol. 1, Part 3, pp 511–513.

(20) Applequist, J.; Carl, J. R.; Fung, K.-K. *J. Am. Chem. Soc.* **1972**, *94*, 2953.

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(28) LeFevre, R. J. W.; Sundaram, K. M. S. *J. Chem. Soc.* **1963**, 4442.

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(32) Aroney, M. J.; Fisher, L. R.; LeFevre, R. J. W. *J. Chem. Soc.* **1963**, 4450.

(33) Bottcher, C. F. J. *Theory of Electric Polarization*; Elsevier Publishing Co.: Amsterdam, 1952, p 289.

(34) Aroney, M. J.; LeFevre, R. J. W.; Saxby, J. *J. Chem. Soc.* **1963**, 4938.

are presented for approximately 400 compounds in Table II for the ahc and ahp methods. The compounds are arranged to introduce new atomic hybrids. In order they are as follows: (1) alkanes and halogenated alkanes, (2) alkenes and halogenated alkenes, (3) alkynes, (4) benzene and its derivatives, (5) condensed ring systems and their derivatives, (6) amines, aniline, pyrrole, and nitriles, (7) heterocycles containing nitrogen, (8) alcohols and ethers, (9) ketones, (10) acids and esters, (11) amides, etc., (12) molecules containing sulfur, (13) isomers of $C_{10}H_{18}O$, (14) molecules of biological interest, and (15) molecules containing phosphate. Atomic hybridization is introduced in the approximate order H, F, Cl, Br, I, CTE, CTR, CBR, CDI, NTE, NTR2, NDI2, NDI, OTE, OTR4, OPI2, STE, STR4, SPI2, and PTE. This notation denotes the atomic hybridization listed in Table I.

The optimization of parameters τ_A(ahc) and α_A(ahp) separately for the ahc and ahp methods, eqs 1 and 4, was performed by increasing the number of molecules with various types of hybridization. In Table II α(exp), α(ahc), and α(ahp) are presented along with the percent error $\delta\alpha$(ahc), $\delta\alpha$(ahp), $\delta\alpha^*$(ahc), and $\delta\alpha^*$(ahp) for each molecule calculated with the optimized ahc and ahp and their conjugate (*) methods as

$$\delta\alpha_M(\text{calc}) = 100[\alpha_M(\text{calc}) - \alpha_M(\text{exp})]/\alpha_M(\text{exp})\ \% \qquad (8)$$

where calc refers to the ahc and ahp methods, and the subscript is introduced to denote molecule M. The parameters τ_A(ahc) and α_A(ahp) are obtained by minimizing the root-mean-square deviation

$$\sigma(\text{calc}) = \{[\sum_M \delta\alpha_M(\text{calc})^2]/(T-1)\}^{1/2} \qquad (9)$$

for a sum over all molecules $M = 1, 2, 3, ..., T$. σ(ahc) = 5.6% and σ(ahp) = 6.4%, and calculation of the average magnitude error yields σ(ahc) = 2.2% and σ(ahp) = 2.8% where

$$a(\text{calc}) = \{\sum_M |\delta\alpha_M(\text{calc})|\}/(T-1) \qquad (10)$$

for approximately 400 molecules studied. Optimization of the parameters τ_A(ahc) and α_A(ahp) yielded a smaller standard deviation for the ahc method. As one scans through classes of compounds in Table II, several trends appear. For the alkanes both methods yield uniform errors of approximately 1%. In the fluorinated hydrocarbons, the ahp method is about 1% better except for $C_1H_xF_y$ ($x + y = 4$) in the series for which the ahp gives poor results. The brominated alkanes yield a uniform error of approximately 1% for the ahc method but a uniform increase from −5.3% for CH_3Br to 1.4% for $C_{18}H_{37}Br$ in the ahp method. Once again results for $C_1H_xBr_y$ ($x + y = 4$) yield larger errors with the ahp than the ahc method. Several cases contrast the two methods: For HCl, O_2, CO_2, and guanine, the ahc results are significantly better than the ahp method. Results for 2,3:4,5-dibenzophenazine, ethyl nitrite, $(CN)_2$, $CH_2(CN)_2$, N_2, and formaldehyde are equally poor for both methods.

The experimental polarizabilities were included in the data set without evaluation. They were obtained in the gas phase and the liquid phase or by considering the molecule as a solute in an inert solvent such as CCl_4, CH_3Cl, or C_6H_6 by determining the refraction at infinite dilution with the sodium D line. Three or more experimental measurements on benzene, toluene, *o*- and *p*-xylene, naphthalene, anthracene, aniline, pyridine, quinoline, isoquinoline, methanol, acetone, and formamide and two measurements on many additional compounds yield differences in the experimental results ranging between 0 and 4% in most cases and as high as 8%. This simple interpretation of the errors in the reported experimental results suggests that the average errors associated with the empirical formulas, a(ahc) = 2.2% and a(ahp) = 2.8%, and the standard deviations, σ(ahc) = 5.6% and σ(ahp) = 6.4%, are competitive with those expected from experimental results.

It is interesting to note that errors in the conjugate calculations $\delta\alpha^*$(ahc) and $\delta\alpha^*$(ahp) are usually approximately of the same magnitude but opposite in sign. The parameters τ_A(ahc) and α_A(ahp) and the conjugate parameters τ_A^*(ahp) and α_A^*(ahc) are in reasonable agreement as seen from results listed in Table I. Those for fluorine and oxygen in the OPI2 ($tr^2trtr\pi^2$) exhibit the greatest deviation because they are small and affect α(ahc) and α(ahp) the least. These values can be influenced the most by eliminating the fluorinated benzenes and fused ring systems from the optimization process. Although τ_H and α_H are small, adjustment of these parameters was biased because the aliphatic systems were optimized first and in addition because data on the aliphatic hydrocarbons from several experimental sets is consistently within 1.0%. Although a complete optimization was performed, the standard deviation is somewhat insensitive to small adjustments. A change in τ_H or α_H can be offset by a comparable change in τ_{CTE} and τ_{CTR} or α_{CTE} and α_{CTR}, which does not affect σ because of the appearance of CH_2 and CH units somewhat consistently throughout the data set.

Theoretical van der Waals Radii

Classically, the polarizability may be interpreted as the volume of the system. The Slater–Kirkwood approximation[35] relates the polarizability to the atomic size with

$$\alpha_A = (4/a_0)[r_A^2/3]^2 \qquad (11)$$

which can be combined with α_A^*(ahc) from eq 2 or the optimum values α_A(ahp) to yield an approximation to the van der Waals radius of atom A with

$$\rho_A = 1.05\sqrt{2}[r_A^2]^{1/2} \qquad (12)$$

$$\rho_A = 1.05\sqrt{3}[a_0\alpha_A]^{1/4} \qquad (12')$$

where a_0 = 0.529177 Å is the Bohr radius and $1.05\sqrt{2}$ is a correction to adjust the theoretical radii of each atom A, $[r_A^2]^{1/2}$, to approximate the experimental van der Waals radii[18] listed in Table I. The experimental van der Waals radii agree well with the empirical values except for ρ_F because α_F(ahp) and τ_F(ahc) are small and more insensitive than other atomic parameters to the fit of the empirical molecular polarizability to the experimental values.

An Update of an ahp Method

The following corrections to the molecular polarizabilities calculated by Kang and Jhon with the atomic polarizabilities taken from Table I of ref 6 should be noted: aniline (11.17 Å^3), *N*-methylaniline (13.01 Å^3), *N*,*N*-dimethylaniline (14.84 Å^3), *N*-ethylaniline (14.84 Å^3), *N*,*N*-diethylaniline (18.52 Å^3), quinoline (15.40 Å^3), HCN (2.52 Å^3), *p*-cyanotoluene (13.28 Å^3), *p*-nitrotoluene (13.56 Å^3), nitrobenzene (11.73 Å^3), furan (7.53 Å^3), benzamide (12.86 Å^3), and anthraquinone (25.41 Å^3). Corrections to all but quinoline lead to a larger deviation from experimental results. For this reason too, the α_A(ahp) parameters are reoptimized and the results presented in an extended list of molecules in Table II.

Kang and Jhon[6] used three types of trigonal carbon atoms with $trtrtr\pi$ hybridization. Treated differently were the double bond in the alkenes and the aromatic bond in benzene (as in the case of the bond polarizability method, ref 14–17) and a branched carbon atom (as at the 9 and 10 positions of naphthalene in the ahc method, ref 1). In the present investigation, the idea that one CTR parameter fits all trigonal carbon atoms attached to at least one hydrogen atom was tested. The alkenes and aromatic systems yielded optimized values of α_{CTR} = 1.343 Å^3 and α_{CTR} = 1.352 Å^3, respectively, and of τ_{CTR} = 1.444 Å$^{3/2}$ and 1.433 Å$^{3/2}$, respectively. The small difference is within experimental error, and consequently, separate parameters for ethylene and benzene type CTR atoms are not needed as found previously.[1] Therefore, only two types of $trtrtr\pi$ hybridization are used: one for branched trigonal carbon atoms (CBR) in trigonal carbon atoms not bonded to hydrogen atoms, and the other for alkenes and aromatic systems (CTR) in trigonal carbon atoms bonded to at least one hydrogen atom. As discussed by Miller and Savchik,[1] this is the only exception to the rule that atomic hybridization alone characterizes

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(35) Slater, J. C.; Kirkwood, J. G. *Phys. Rev.* **1931**, *37*, 682.

Table II. Empirical (ahc) and (ahp) and Experimental Polarizabilities (exp) with Empirical Atomic Hybrid Formulas[a]

molecule	N	α, Å^3			$\delta\alpha$, %		$\delta\alpha^*$, %		ref	empirical formula (atomic hybrids)		
		exp	ahc	ahp	ahc	ahp	ahc	ahp				
Alkanes and Halogenated Alkanes: CTE (tetetete), H(σ), F(σ), Cl(σ), Br(σ), I(σ) Hybridization												
H_2	2	0.79	0.78	0.77	−0.8	−2.0	−0.8	−2.0	19	2H		
methane	10	2.60	2.59	2.61	−0.3	0.3	3.2	−3.4	19	1CTE	4H	
ethane	18	4.47	4.43	4.44	−0.8	−0.6	2.5	−4.2	19	2CTE	6H	
n-propane	26	6.29	6.27	6.28	−0.3	−0.2	3.1	−3.8	19	3CTE	8H	
n-butane	34	8.12	8.12	8.11	0.0	−0.1	3.3	−3.6	19	4CTE	10H	
n-pentane	42	9.95	9.96	9.95	0.1	0.0	3.4	−3.5	19	5CTE	12H	
n-pentane	42	10.02	9.96	9.95	−0.6	−0.7	2.6	−4.2	5	5CTE	12H	
n-hexane	50	11.78	11.80	11.78	0.2	0.0	3.4	−3.4	19	6CTE	14H	
n-hexane	50	11.84	11.80	11.78	−0.3	−0.5	2.9	−3.9	15	6CTE	14H	
n-heptane	58	13.61	13.64	13.62	0.3	0.1	3.5	−3.4	19	7CTE	16H	
n-heptane	58	13.68	13.64	13.62	−0.3	−0.5	2.9	−3.9	15	7CTE	16H	
n-octane	66	15.44	15.49	15.45	0.3	0.1	3.5	−3.4	19	8CTE	18H	
n-octane	66	15.51	15.49	15.45	−0.2	−0.4	3.0	−3.8	15	8CTE	18H	
n-nonane	74	17.36	17.33	17.29	−0.1	−0.4	3.0	−3.8	15	9CTE	20H	
n-nonane	74	17.36	17.33	17.29	−0.1	−0.4	3.0	−3.8	15	9CTE	20H	
n-decane	82	19.10	19.17	19.12	0.4	0.1	3.6	−3.3	19	10CTE	22H	
n-decane	82	19.19	19.17	19.12	−0.1	−0.4	3.1	−3.8	15	10CTE	22H	
n-undecane	90	21.03	21.02	20.96	−0.1	−0.4	3.1	−3.8	15	11CTE	24H	
n-undecane	90	21.03	21.02	20.96	−0.1	−0.4	3.1	−3.8	15	11CTE	24H	
n-dodecane	98	22.75	22.86	22.79	0.5	0.2	3.7	−3.2	19	12CTE	26H	
n-dodecane	98	22.86	22.86	22.79	0.0	−0.3	3.2	−3.7	15	12CTE	26H	
isobutane	34	8.14	8.12	8.11	−0.3	−0.3	3.0	−3.8	19	4CTE	10H	
neopentane	42	10.20	9.96	9.95	−2.4	−2.5	0.8	−5.9	20	5CTE	12H	
cyclopentane	40	9.09	9.22	9.18	1.4	0.9	4.5	−2.4	15	5CTE	10H	
cyclopentane	40	9.15	9.22	9.18	0.7	0.3	3.8	−3.1	21	5CTE	10H	
cyclohexane	48	10.99	11.06	11.01	0.6	0.2	3.7	−3.2	15	6CTE	12H	
cyclohexane	48	10.87	11.06	11.01	1.7	1.3	4.9	−2.1	19	6CTE	12H	
3-methylheptane	66	15.44	15.49	15.45	0.3	0.1	3.5	−3.4	19	8CTE	18H	
2,2,4-trimethylpentane	66	15.44	15.49	15.45	0.3	0.1	3.5	−3.4	19	8CTE	18H	
n-CH_3F	18	2.62	2.45	2.52	−6.4	−3.9	7.6	−23.1	20	1CTE	3H	1F
n-$C_5H_{11}F$	50	9.95	9.68	9.86	−2.7	−1.0	4.7	−10.6	22	5CTE	11H	1F
n-$C_6H_{13}F$	58	11.80	11.52	11.69	−2.4	−0.9	4.4	−9.7	22	6CTE	13H	1F
n-$C_7H_{15}F$	66	13.66	13.35	13.53	−2.2	−0.9	4.1	−9.1	22	7CTE	15H	1F
n-$C_8H_{17}F$	74	15.46	15.19	15.36	−1.8	−0.6	4.3	−8.3	22	8CTE	17H	1F
n-$C_9H_{19}F$	82	17.34	17.03	17.20	−1.8	−0.8	3.9	−8.1	22	9CTE	19H	1F
n-$C_{10}H_{21}F$	90	19.18	18.86	19.03	−1.7	−0.8	3.8	−7.7	22	10CTE	21H	1F
n-$C_{11}H_{23}F$	98	21.00	20.70	20.87	−1.4	−0.6	3.9	−7.2	22	11CTE	23H	1F
n-$C_{12}H_{25}F$	106	22.83	22.54	22.70	−1.3	−0.6	3.9	−6.9	22	12CTE	25H	1F
n-$C_{14}H_{33}F$	122	26.57	26.23	26.37	−1.3	−0.7	3.6	−6.7	22	14CTE	26H	1F
n-C_1H_3Br	44	5.53	5.53	5.23	0.0	−5.3	5.5	−11.7	23	1CTE	3H	1Br
n-C_2H_5Br	52	7.28	7.27	7.07	−0.2	−2.9	6.2	−10.3	23	2CTE	5H	1Br
n-C_3H_7Br	60	9.07	9.03	8.90	−0.4	−1.8	6.2	−9.5	23	3CTE	7H	1Br
n-C_4H_9Br	68	10.86	10.81	10.74	−0.4	−1.1	6.2	−8.7	23	4CTE	9H	1Br
n-$C_5H_{11}Br$	76	12.65	12.61	12.57	−0.3	−0.6	6.2	−8.1	23	5CTE	11H	1Br
n-$C_6H_{13}Br$	84	14.44	14.42	14.41	−0.2	−0.2	6.2	−7.5	23	6CTE	13H	1Br
n-$C_7H_{15}Br$	92	16.23	16.23	16.24	0.0	0.1	6.2	−7.0	23	7CTE	15H	1Br
n-$C_8H_{17}Br$	100	18.02	18.04	18.08	0.1	0.3	6.2	−6.6	23	8CTE	17H	1Br
n-$C_9H_{19}Br$	108	19.81	19.86	19.91	0.3	0.5	6.2	−6.2	23	9CTE	19H	1Br
n-$C_{10}H_{21}Br$	116	21.60	21.69	21.75	0.4	0.7	6.2	−5.9	23	10CTE	21H	1Br
n-$C_{12}H_{25}Br$	132	25.18	25.34	25.42	0.6	1.0	6.2	−5.3	23	12CTE	25H	1Br
n-$C_{16}H_{33}Br$	164	32.34	32.67	32.76	1.0	1.3	6.2	−4.5	23	16CTE	33H	1Br
n-$C_{18}H_{37}Br$	180	35.92	36.34	36.43	1.2	1.4	6.2	−4.2	23	18CTE	37H	1Br
CHF_3	34	2.81	2.79	2.34	−0.5	−16.9	9.9	−32.3	20	1CTE	1H	3F
CF_4	42	2.92	3.04	2.25	4.1	−23.1	10.4	−33.2	20	1CTE	4F	
CH_3Br	44	5.61	5.53	5.23	−1.4	−6.7	4.0	−13.0	20	1CTE	3H	1Br
CH_2Br_2	78	8.68	8.74	7.86	0.6	−9.4	3.5	−12.7	20	1CTE	2H	2Br
$CHBr_3$	112	11.84	11.97	10.49	1.1	−11.4	2.4	−13.1	20	1CTE	1H	3Br
CH_3I	62	7.59	7.56	7.64	−0.4	0.6	3.6	−3.3	20	1CTE	3H	1I
CH_2I_2	114	12.90	12.81	12.66	−0.7	−1.8	1.1	−3.6	20	1CTE	2H	2I
CHI_3	166	18.04	18.07	17.69	0.2	−1.9	1.0	−2.7	20	1CTE	1H	3I
CH_3Cl	26	4.56	4.48	4.54	−1.7	−0.5	1.9	−4.1	19	1CTE	3H	1Cl
CH_3Cl	26	4.55	4.48	4.54	−1.5	−0.3	2.2	−3.9	20	1CTE	3H	1Cl
CH_2Cl_2	42	6.48	6.48	6.46	0.0	−0.2	2.1	−2.2	19	1CTE	2H	2Cl
CH_2Cl_2	42	6.82	6.48	6.46	−5.0	−5.2	−3.0	−7.1	20	1CTE	2H	2Cl
CH_2Cl_2	42	6.56	6.48	6.46	−1.2	−1.5	0.8	−3.4	15	1CTE	2H	2Cl
$CHCl_3$	58	8.23	8.50	8.39	3.3	2.0	4.2	1.1	19	1CTE	1H	3Cl
$CHCl_3$	58	8.53	8.50	8.39	−0.3	−1.6	0.6	−2.5	20	1CTE	1H	3Cl
CCl_4	74	10.50	10.53	10.32	0.2	−1.7	0.4	−1.8	19	1CTE	4Cl	
CCl_4	74	10.51	10.53	10.32	0.1	−1.8	0.3	−1.9	20	1CTE	4Cl	
CCl_4	74	10.47	10.53	10.32	0.5	−1.5	0.7	−1.6	15	1CTE	4Cl	
ethyl chloride	34	6.40	6.30	6.37	−1.6	−0.4	2.3	−4.3	19	2CTE	5H	1Cl
Cl_2	34	4.61	4.71	4.63	2.3	0.4	2.3	0.4	19	2Cl		
HF	10	0.80	0.79	0.68	−1.7	−14.6	14.9	−36.5	19	1H	1F	
HCl	18	2.63	2.69	2.70	2.2	2.7	4.5	0.4	19	1H	1Cl	
HBr	36	3.61	3.84	3.40	6.4	−5.8	8.9	−8.7	19	1H	1Br	
HI	54	5.45	5.88	5.80	7.8	6.5	9.4	4.8	19	1H	1I	

Table II (Continued)

molecule	*N*	α, Å^3			$\delta\alpha$, %		$\delta\alpha^*$, %		ref	empirical formula (atomic hybrids)			
		exp	ahc	ahp	ahc	ahp	ahc	ahp					
Alkenes and Halogenated Alkenes: CTR (trtrtrπ) Hybridization													
ethylene	16	4.26	4.24	4.25	−0.5	−0.2	1.1	−1.7	19	2CTR	4H		
1-pentene	40	9.65	9.76	9.76	1.1	1.1	3.7	−1.6	15	2CTR	3CTE	10H	
2-pentene	40	9.84	9.76	9.76	−0.9	−0.9	1.6	−3.6	15	2CTR	3CTE	10H	
1,4-pentadiene	46	11.49	11.40	11.40	−0.8	−0.8	1.2	−2.9	15	4CTR	2CTE	10H	
1-hexene	48	11.65	11.60	11.59	−0.4	−0.5	2.2	−3.3	15	2CTR	4CTE	12H	
1-heptene	56	13.51	13.44	13.43	−0.5	−0.6	2.2	−3.5	15	2CTR	5CTE	14H	
$CH_2{=}CCl_2$	48	7.83	8.04	8.11	2.7	3.6	5.2	1.0	24	2CTR	2Cl	2H	
trans-dichloroethylene	48	8.15	8.04	8.11	−1.4	−0.5	1.0	−2.9	12	2CTR	2Cl	2H	
cis-dichloroethylene	48	8.03	8.04	8.11	0.1	1.0	2.6	−1.4	12	2CTR	2Cl	2H	
cis-dichloroethylene	48	7.78	8.04	8.11	3.3	4.2	5.9	1.7	24	2CTR	2Cl	2H	
$CHCl{=}CCl_2$	64	10.03	10.04	10.04	0.1	0.1	1.7	−1.6	24	2CTR	3Cl	1H	
trans-Chlorobromoethylene	66	9.28	9.05	8.81	−2.4	−5.1	1.5	−9.9	12	2CTR	2H	1Cl	1Br
cis-chlorobromoethylene	66	9.19	9.05	8.81	−1.5	−4.2	2.5	−9.1	12	2CTR	2H	1Cl	1Br
Alkynes: CDI (didi$\pi\pi$) Hybridization													
acetylene	14	3.33	3.33	3.34	−0.1	0.3	1.2	−1.0	19	2CDI	2H		
1-heptyne	54	12.87	12.54	12.52	−2.5	−2.7	0.0	−5.5	15	2CDI	5CTE	12H	
1,5-hexadiyne	42	10.21	9.60	9.58	−6.0	−6.2	−4.4	−7.8	15	4CDI	2CTE	6H	
Benzene and Its Derivatives: CTR (trtrtrπ) Hybridization													
benzene	42	10.39	10.45	10.43	0.6	0.5	1.7	−0.6	25	6CTR	6H		
benzene	42	10.32	10.45	10.43	1.3	1.1	2.4	0.0	19	6CTR	6H		
benzene	42	10.42	10.45	10.43	0.3	0.2	1.4	−0.9	15	6CTR	6H		
toluene	50	11.83	12.29	12.27	3.9	3.7	5.4	2.2	23	6CTR	1CTE	8H	
toluene	50	12.26	12.29	12.27	0.3	0.1	1.7	−1.4	19	6CTR	1CTE	8H	
toluene	50	12.31	12.29	12.27	−0.2	−0.4	1.2	−1.8	15	6CTR	1CTE	8H	
toluene	50	12.26	12.29	12.27	0.3	0.1	1.7	−1.4	19	6CTR	1CTE	8H	
toluene	50	11.83	12.29	12.27	3.9	3.7	5.4	2.2	26	6CTR	1CTE	8H	
1,3,5-trimethylbenzene	66	16.14	15.98	15.94	−1.0	−1.3	0.8	−3.1	15	6CTR	3CTE	12H	
1,3,5-trimethylbenzene	66	15.38	15.98	15.94	3.9	3.6	5.8	1.7	23	6CTR	3CTE	12H	
1,2,4,5-pentamethylbenzene	74	17.40	17.82	17.77	2.4	2.1	4.4	0.0	23	6CTR	4CTE	14H	
hexamethylbenzene	90	20.81	21.50	21.44	3.3	3.0	5.6	0.7	23	6CTR	6CTE	18H	
fluorobenzene	50	9.86	10.13	10.34	2.7	4.9	8.5	−3.3	27	6CTR	5H	1F	
chlorobenzene	58	12.25	12.25	12.36	0.0	0.9	2.3	−1.4	19	6CTR	5H	1Cl	
bromobenzene	76	13.62	13.02	13.06	−4.4	−4.1	0.7	−10.3	19	6CTR	5H	1Br	
1,2-difluorobenzene	58	9.80	9.98	10.25	1.8	4.6	10.6	−8.2	27	6CTR	4H	2F	
o-dichlorobenzene	74	14.17	14.15	14.29	−0.1	0.8	2.3	−1.6	19	6CTR	4H	2Cl	
o-dichlorobenzene	74	14.27	14.15	14.29	−0.8	0.2	1.6	−2.3	15	6CTR	4H	2Cl	
m-dichlorobenzene	74	14.23	14.15	14.29	−0.6	0.4	1.9	−2.0	19	6CTR	4H	2Cl	
m-dichlorobenzene	74	14.32	14.15	14.29	−1.1	−0.2	1.3	−2.6	15	6CTR	4H	2Cl	
p-dichlorobenzene	74	14.20	14.15	14.29	−0.3	0.6	2.1	−1.8	19	6CTR	4H	2Cl	
1,4-difluorobenzene	58	9.80	9.98	10.25	1.8	4.6	10.6	−8.2	27	6CTR	4H	2F	
1,3,5-trifluorobenzene	66	9.74	9.94	10.16	2.0	4.3	12.6	−11.5	27	6CTR	3H	3F	
1,2,3,4-tetrafluorobenzene	74	9.69	9.97	10.07	2.9	3.9	14.6	−13.8	27	6CTR	2H	4F	
1,2,4,5-tetrafluorobenzene	74	9.69	9.97	10.07	2.9	3.9	14.6	−13.8	27	6CTR	2H	4F	
pentafluorobenzene	82	9.63	10.05	9.98	4.4	3.6	16.7	−15.2	27	6CTR	1H	5F	
hexafluorobenzene	90	9.58	10.18	9.89	6.2	3.2	18.8	−16.2	27	6CTR	6F		
p-fluorotoluene	58	11.70	11.97	12.18	2.3	4.1	7.7	−3.4	23	6CTR	1CTE	7H	1F
p-chlorotoluene	66	13.70	14.09	14.20	2.9	3.6	5.3	1.1	23	6CTR	1CTE	7H	1Cl
p-bromotoluene	84	14.80	14.83	14.89	0.2	0.6	5.5	−5.7	23	6CTR	1CTE	7H	1Br
p-iodotoluene	102	17.10	16.76	17.30	−2.0	1.2	3.2	−4.1	23	6CTR	1CTE	7H	1I
o-xylene	58	14.10	14.13	14.10	0.2	0.0	1.9	−1.7	19	6CTR	2CTE	10H	
o-xylene	58	14.17	14.13	14.10	−0.3	−0.5	1.4	−2.2	15	6CTR	2CTE	10H	
o-xylene	58	14.18	14.13	14.10	−0.3	−0.5	1.3	−2.2	12	6CTR	2CTE	10H	
m-xylene	58	14.18	14.13	14.10	−0.3	−0.5	1.3	−2.2	19	6CTR	2CTE	10H	
m-xylene	58	14.23	14.13	14.10	−0.7	−0.9	0.9	−2.6	15	6CTR	2CTE	10H	
p-xylene	58	13.70	14.13	14.10	3.2	2.9	4.9	1.2	23	6CTR	2CTE	10H	
p-xylene	58	14.28	14.13	14.10	−1.0	−1.2	0.6	−2.9	12	6CTR	2CTE	10H	
p-xylene	58	14.20	14.13	14.10	−0.5	−0.7	1.2	−2.4	19	6CTR	2CTE	10H	
p-xylene	58	14.26	14.13	14.10	−0.9	−1.1	0.8	−2.8	15	6CTR	2CTE	10H	
Condensed Ring Systems and Their Derivatives: CBR (trtrtrπ) Branched Carbon Hybridization													
naphthalene	68	16.46	17.77	17.70	8.0	7.6	9.2	6.4	23	8CTR	2CBR	8H	
naphthalene	68	17.48	17.77	17.70	1.7	1.3	2.8	0.2	25	8CTR	2CBR	8H	
naphthalene	68	17.59	17.77	17.70	1.0	0.7	2.2	−0.4	15	8CTR	2CBR	8H	
naphthalene	68	16.57	17.77	17.70	7.3	6.8	8.5	5.7	26	8CTR	2CBR	8H	
anthracene	94	25.36	25.10	24.97	−1.0	−1.5	0.1	−2.6	23	10CTR	4CBR	10H	
anthracene	94	25.93	25.10	24.97	−3.2	−3.7	−2.1	−4.7	25	10CTR	4CBR	10H	
anthracene	94	25.37	25.10	24.97	−1.1	−1.6	0.0	−2.6	26	10CTR	4CBR	10H	
phenanthrene	94	24.70	25.10	24.97	1.6	1.1	2.8	0.0	25	10CTR	4CBR	10H	
naphthacene	120	32.27	32.44	32.24	0.5	−0.1	1.6	−1.1	25	12CTR	6CBR	12H	
1,2-benzanthracene	120	32.86	32.44	32.24	−1.3	−1.9	−0.2	−2.9	25	12CTR	6CBR	12H	
chrysene	120	33.06	32.44	32.24	−1.9	−2.5	−0.8	−3.5	25	12CTR	6CBR	12H	
chrysene	120	32.15	32.44	32.24	0.9	0.3	2.0	−0.7	26	12CTR	6CBR	12H	
1,2:5,6-dibenzanthracene	146	41.31	39.77	39.51	−3.7	−4.3	−2.7	−5.3	25	14CTR	8CBR	14H	
acenaphthene	82	20.61	20.69	20.60	0.4	−0.1	1.8	−1.5	25	8CTR	2CBR	2CTE	10H
fluoranthene	106	28.34	27.82	27.68	−1.8	−2.4	−0.8	−3.3	25	12CTR	4CBR	10H	
pyrene	106	29.34	28.96	28.77	−1.3	−1.9	−0.2	−2.9	25	10CTR	6CBR	10H	
pyrene	106	28.22	28.96	28.77	2.6	1.9	3.7	0.9	26	10CTR	6CBR	10H	
dodecahydrotriphenyl	132	29.89	30.33	30.13	1.5	0.8	3.8	−1.6	25	6CTR	12CTE	24H	

Table II (Continued)

		α, Å^3			$\delta\alpha$, %		$\delta\alpha^*$, %			empirical formula (atomic hybrids)				
molecule	*N*	exp	ahc	ahp	ahc	ahp	ahc	ahp	ref					
fluorene	88	21.68	21.25	21.15	-2.0	-2.4	-1.0	-3.5	25	12CTR	1CTE	10H		
2,3-benzfluorene	114	30.21	28.55	28.42	-5.5	-5.9	-4.4	-6.9	25	14CTR	2CBR	1CTE	12H	
difluorenyl	174	42.81	43.92	43.71	2.6	2.1	3.8	0.9	25	20CTR	4CBR	2CTE	18H	
brazan	106	29.89	28.96	28.77	-3.1	-3.8	-2.1	-4.7	25	10CTR	6CBR	10H		
triphenylene	120	31.07	32.44	32.24	4.4	3.8	5.5	2.7	28	12CTR	6CBR	12H		
coronene	156	42.50	44.02	43.62	3.6	2.6	4.6	1.7	25	12CTR	12CBR	12H		
coronene	156	44.77	44.02	43.62	-1.7	-2.6	-0.7	-3.4	28	12CTR	12CBR	12H		
β-truxene	180	45.55	46.11	45.86	1.2	0.7	2.5	-0.6	25	18CTR	6CBR	3CTE	18H	
α-methylnaphthalene	76	19.35	19.61	19.54	1.3	1.0	2.7	-0.4	12	8CTR	1CTE	2CBR	10H	
β-methylnaphthalene	76	19.52	19.61	19.54	0.5	0.1	1.8	-1.3	12	8CTR	1CTE	2CBR	10H	
α-ethylnaphthalene	84	21.19	21.45	21.37	1.2	0.9	2.7	-0.7	12	8CTR	2CTE	2CBR	12H	
β-ethylnaphthalene	84	21.36	21.45	21.37	0.4	0.1	1.9	-1.5	12	8CTR	2CTE	2CBR	12H	
α-chloronaphthalene	84	19.30	19.50	19.63	1.0	1.7	3.3	-0.5	12	8CTR	2CBR	7H	1Cl	
β-chloronaphthalene	84	19.58	19.50	19.63	-0.4	0.3	1.8	-1.9	12	8CTR	2CBR	7H	1Cl	
α-bromonaphthalene	102	20.34	19.13	19.24	-6.0	-5.4	-1.8	-10.5	15	10CTR	7H	1Br		
α-iodonaphthalene	120	22.41	21.95	22.73	-2.1	1.4	3.3	-4.0	12	8CTR	8CBR	7H	1I	
β-iodonaphthalene	120	22.95	21.95	22.73	-4.3	-0.9	0.9	-6.2	12	8CTR	2CBR	7H	1I	
octafluoronaphthalene	132	17.64	16.86	16.98	-4.4	-3.8	8.0	-22.1	27	8CTR	8F	2CBR		
α-naphthalenecarboxaldehyde	82	19.75	20.11	20.17	1.8	2.1	4.6	-1.1	12	8CTR	1OTR4	3CBR	8H	
β-naphthalenecarboxaldehyde	82	20.06	20.11	20.17	0.3	0.6	3.0	-2.6	12	8CTR	1OTR4	3CBR	8H	
α-naphthylamine	76	19.50	18.83	19.18	-3.4	-1.6	-1.4	-3.1	12	8CTR	1NPI2	2CBR	9H	
β-naphthylamine	76	19.73	18.83	19.18	-4.6	-2.8	-2.6	-4.3	12	8CTR	1NPI2	2CBR	9H	
α-bromonaphthalene	102	20.34	20.09	20.33	-1.2	-0.1	3.8	-6.0	15	8CTR	2CBR	7H	1Br	
styrene	56	14.41	14.49	14.46	0.6	0.3	1.8	-0.8	7	7CTR	1CBR	8H		
styrene	56	14.41	13.94	13.91	-3.3	-3.4	-2.2	-4.5	7	8CTR	8H			
α-methylstyrene	64	16.05	16.33	16.29	1.7	1.5	3.2	0.0	7	7CTR	1CBR	1CTE	10H	
α,β,β-trimethylstyrene	80	19.64	20.00	19.96	1.8	1.6	3.7	-0.3	7	7CTR	3CTE	1CBR	14H	
9-chloroanthracene	110	27.35	26.78	26.90	-2.1	-1.6	0.0	-3.6	23	10CTR	4CBR	9H	1Cl	
9-bromoanthracene	128	28.32	27.27	27.60	-3.7	-2.5	0.7	-7.7	23	10CTR	4CBR	9H	1Br	
Amines: NTE (te^{2}tetete) Hybridization														
NH_3	10	2.26	2.14	2.13	-5.4	-6.0	-0.3	-11.8	19	1NTE	3H			
dimethylamine	34	7.21	7.23	7.15	0.3	-0.8	4.4	-5.5	12	2NTE	2CTE	8H		
n-propylamine	34	7.70	7.67	7.63	-0.5	-0.9	3.2	-5.1	15	1NTE	3CTE	9H		
isopropylamine	34	7.77	7.67	7.63	-1.3	-1.8	2.4	-5.9	15	1NTE	3CTE	9H		
diethylamine	42	9.61	9.51	9.46	-1.0	-1.5	2.6	-5.4	15	1NTE	4CTE	11H		
di-*n*-propylamine	58	13.29	13.19	13.13	-0.7	-1.2	2.7	-5.0	15	1NTE	6CTE	15H		
triethylamine	58	13.38	13.19	13.13	-1.4	-1.8	2.1	-5.6	15	1NTE	6CTE	15H		
tri-*n*-propylamine	82	18.87	18.72	18.64	-0.8	-1.2	2.5	-4.9	15	1NTE	9CTE	21H		
Anilines: NPI2 (trtrtrπ^2) Hybridization														
aniline	50	11.58	11.54	11.91	-0.4	2.8	1.9	1.2	12	6CTR	1NPI2	7H		
aniline	50	11.53	11.54	11.91	0.1	3.3	2.4	1.6	23	6CTR	1NPI2	7H		
aniline	50	12.12	11.54	11.91	-4.8	-1.7	-2.6	-3.3	15	6CTR	1NPI2	7H		
N-methylaniline	58	13.49	13.38	13.75	-0.8	1.9	1.6	0.0	12	6CTR	1NPI2	1CTE	9H	
N-methylaniline	58	14.14	13.38	13.75	-5.4	-2.8	-3.1	-4.6	15	6CTR	1NPI2	1CTE	9H	
N-ethylaniline	66	15.32	15.22	15.58	-0.6	1.7	1.9	-0.4	12	6CTR	1NPI2	2CTE	11H	
N,*N*-dimethylaniline	66	15.40	15.22	15.58	-1.1	1.2	1.4	-0.9	12	6CTR	1NPI2	2CTE	11H	
N,*N*-dimethylaniline	66	15.23	15.22	15.58	0.0	2.3	2.5	0.2	23	6CTR	1NPI2	2CTE	11H	
N,*N*-diethylaniline	82	19.01	18.91	19.25	-0.5	1.3	2.1	-1.1	12	6CTR	1NPI2	4CTE	15H	
p-fluoroaniline	58	11.51	11.27	11.82	-2.1	2.7	3.8	-4.8	23	6CTR	1NPI2	6H	1F	
p-chloroaniline	66	13.50	13.38	13.84	-0.9	2.5	2.0	0.1	23	6CTR	1NPI2	6H	1Cl	
p-bromoaniline	84	14.55	14.19	14.54	-2.5	-0.1	2.8	-6.2	23	6CTR	1NPI2	6H	1Br	
dichloroaniline	82	15.18	15.30	15.77	0.8	3.9	3.7	1.3	23	6CTR	1NPI2	5H	2Cl	
2,6-dimethylaniline	66	16.21	15.22	15.58	-6.1	-3.9	-3.7	-5.9	29	6CTR	1NPI2	2CTE	11H	
2,6-dimethylaniline	66	16.02	15.22	15.58	-4.9	-2.7	-2.5	-4.7	29	6CTR	1NPI2	2CTE	11H	
3,5-dimethylaniline	66	16.37	15.22	15.58	-7.0	-4.8	-4.7	-6.8	29	6CTR	1NPI2	2CTE	11H	
3,5-dimethylaniline	66	16.25	15.22	15.58	-6.3	-4.1	-4.0	-6.1	29	6CTR	1NPI2	2CTE	11H	
2,6-dichloroaniline	82	16.41	15.30	15.77	-6.7	-3.9	-4.1	-6.3	29	6CTR	1NPI2	5H	2Cl	
2,6-dichloroaniline	82	15.98	15.30	15.77	-4.2	-1.3	-1.5	-3.8	29	6CTR	1NPI2	5H	2Cl	
3,5-dichloroaniline	82	16.69	15.30	15.77	-8.3	-5.5	-5.7	-7.9	29	6CTR	1NPI2	5H	2Cl	
3,5-dichloroaniline	82	16.45	15.30	15.77	-7.0	-4.2	-4.3	-6.5	29	6CTR	1NPI2	5H	2Cl	
pyrrole	36	7.94	8.06	8.43	1.5	6.2	4.4	4.3	21	4CTR	1NPI2	5H		
p-toluidine	58	13.47	13.38	13.75	-0.7	2.0	1.8	0.2	23	6CTR	1NPI2	1CTE	9H	
Heterocycles: NTR2 (tr^{2}trtrπ) Hybridization														
pyridine	42	9.18	9.51	9.72	3.6	5.9	5.8	4.1	23	5CTR	1NTR2	5H		
pyridine	42	9.14	9.51	9.72	4.0	6.4	6.3	4.6	30	5CTR	1NTR2	5H		
pyridine	42	9.47	9.51	9.72	0.4	2.7	2.6	0.9	19	5CTR	1NTR2	5H		
pyridine	42	9.20	9.51	9.72	3.4	5.7	5.6	3.9	21	5CTR	1NTR2	5H		
quinoline	68	15.70	16.80	16.99	7.0	8.2	9.1	6.5	21	7CTR	1NTR2	2CBR	7H	
quinoline	68	16.57	16.80	16.99	1.4	2.6	3.3	0.9	25	7CTR	1NTR2	2CBR	7H	
quinoline	68	16.60	16.80	16.99	1.2	2.4	3.1	0.8	12	7CTR	1NTR2	2CBR	7H	
isoquinoline	68	16.43	16.80	16.99	2.2	3.4	4.2	1.8	12	7CTR	1NTR2	2CBR	7H	
isoquinoline	68	16.49	17.35	17.54	5.2	6.4	7.3	4.6	25	6CTR	1NTR2	3CBR	7H	
isoquinoline	68	15.62	16.80	16.99	7.5	8.8	9.6	7.1	21	7CTR	1NTR2	2CBR	7H	
1-methylquinoline	74	18.65	17.89	18.06	-4.1	-3.2	-2.2	-4.8	12	7CTR	2CBR	1CTE	1NTR2	7H
1-methylisoquinoline	74	18.28	17.89	18.06	-2.1	-1.2	-0.2	-2.9	12	7CTR	2CBR	1CTE	1NTR2	7H

Table II (Continued)

molecule	*N*	α, Å^3			$\delta\alpha$, %		$\delta\alpha^*$, %		ref	empirical formula (atomic hybrids)				
		exp	ahc	ahp	ahc	ahp	ahc	ahp						
quinoxaline	68	15.13	15.85	16.29	4.7	7.6	7.5	5.4	31	6CTR	2CBR	2NTR2	6H	
2,3-dimethylquinoxaline	84	18.70	19.53	19.96	4.5	6.7	7.3	4.3	31	6CTR	2CBR	2NTR2	2CTE	10H
phenazine	94	23.43	23.14	23.56	−1.2	0.5	1.1	−1.3	23	8CTR	2NTR2	4CBR	8H	
phenazine	94	23.42	23.14	23.56	−1.2	0.6	1.1	−1.3	31	8CTR	2NTR2	4CBR	8H	
2,3:4,5-dibenzophenazine	146	33.42	37.77	38.10	13.0	14.0	15.2	12.2	31	12CTR	8CBR	2NTR2	12H	
ethyl nitrite	40	7.00	6.21	6.29	−11.3	−10.1	−5.4	−17.1	19	2CTE	1OTE	1NTR2	1OTR4	5H
Nitriles: NDI (di^{2}di$\pi\pi$) Hybridization														
HCN	14	2.59	2.59	2.63	−0.1	1.4	2.6	−1.3	19	1H	1CDI	1NDI		
$(CN)_2$	26	5.01	4.48	4.48	−10.7	−10.6	−9.6	−11.7	19	2CDI	2NDI			
acetonitrile	22	4.48	4.42	4.46	−1.4	−0.4	1.7	−3.5	20	1CTE	3H	1CDI	1NDI	
CH_3CH_2CN	30	6.24	6.26	6.30	0.3	0.9	3.5	−2.4	20	2CTE	5H	1CDI	1NDI	
$(CH_3)_2CHCN$	38	8.05	8.10	8.13	0.6	1.0	3.8	−2.3	20	3CTE	7H	1CDI	1NDI	
$(CH_3)_3CCN$	46	9.59	9.94	9.97	3.6	3.9	7.0	0.5	20	4CTE	9H	1CDI	1NDI	
$CH_2(CN)_2$	34	5.79	6.29	6.31	8.7	9.0	11.1	6.7	20	1CTE	2H	2CDI	2NDI	
CH_2ClCN	38	6.10	6.37	6.39	4.5	4.7	6.9	2.3	20	1CTE	2H	1Cl	1CDI	1NDI
CCl_3CN	70	10.42	10.39	10.24	−0.3	−1.7	0.3	−2.2	20	1CTE	3Cl	1CDI	1NDI	
9-cyanoanthracene	106	28.32	26.85	26.83	−5.2	−5.3	−3.8	−6.7	23	10CTR	4CBR	1CDI	1NDI	9H
N_2	14	1.76	1.94	1.91	10.4	8.6	10.4	8.6	19	2NDI				
Mixed Hybridization: NTE (te^{2}tetete), NPI2 (trtrtrπ^2), NTR2 (tr^{2}trtrπ) Hybridization														
hydrazine	18	3.46	3.55	3.48	2.8	0.6	7.7	−5.1	12	2NTE	4H			
phenylhydrazine	58	12.91	12.93	13.26	0.2	2.7	2.9	0.5	12	1NTE	6CTR	1NPI2	8H	
1,1-methylphenylhydrazine	66	14.81	14.78	15.10	−0.2	2.0	2.5	−0.4	12	1NTE	6CTR	1NPI2	10H	1CTE
1,1-ethylphenylhydrazine	74	16.62	16.62	16.93	0.0	1.9	2.7	−0.6	12	1NTE	6CTR	1NPI2	12H	2CTE
3-aminobutyronitrile	46	9.17	9.51	9.48	3.6	3.4	7.1	−0.4	12	3CTE	1CDI	1NDI	1NTE	8H
p-cyanotoluene	62	13.90	14.09	14.12	1.4	1.6	3.2	−0.2	23	6CTR	1CTE	1CDI	1NDI	7H
3-(dimethylamino)butyronitrile	62	12.87	13.19	13.15	2.5	2.2	5.9	−1.5	12	5CTE	1CDI	1NDI	1NTE	12H
pyrazole	36	7.23	7.17	7.72	−0.8	6.8	2.8	4.3	12	3CTR	1NTR2	1NPI2	4H	
N-methylpyrazole	44	8.99	9.01	9.56	0.2	6.4	3.9	3.7	12	3CTR	1NTR2	1NPI2	1CTE	6H
1,5-dimethylpyrazole	52	10.72	10.84	11.39	1.2	6.3	4.8	3.5	12	3CTR	1NTR2	1NPI2	2CTE	8H
1-ethyl-5-methylpyrazole	60	12.50	12.68	13.23	1.5	5.9	5.1	2.9	12	3CTR	1NTR2	1NPI2	3CTE	10H
imidazole	36	7.19	7.17	7.72	−0.2	7.5	3.4	5.0	12	3CTR	1NTR2	1NPI2	4H	
N-methylimidazole	44	8.86	9.01	9.56	1.6	7.9	5.4	5.2	12	3CTR	1NTR2	1NPI2	1CTE	6H
N-*n*-propylimidazole	60	12.40	12.68	13.23	2.2	6.6	5.9	3.7	12	3CTR	1NTR2	1NPI2	3CTE	10H
Alcohols and Ethers: OTE (te^{2}te^{2}tete) Hybridization														
water	10	1.45	1.41	1.41	−3.1	−2.8	7.8	−15.5	12	1OTE	2H			
methanol	18	3.26	3.20	3.25	−1.9	−0.5	6.2	−10.0	15	1CTE	1OTE	4H		
methanol	18	3.20	3.20	3.25	0.2	1.6	8.4	−8.1	12	1CTE	1OTE	4H		
methanol	18	3.23	3.20	3.25	−0.9	0.5	7.2	−9.1	19	1CTE	1OTE	4H		
ethanol	26	5.07	5.02	5.08	−0.8	0.3	5.9	−7.5	15	2CTE	1OTE	6H		
ethanol	26	4.94	5.02	5.08	1.7	2.9	8.6	−5.2	12	2CTE	1OTE	6H		
1-propanol	34	6.77	6.86	6.92	1.3	2.2	7.3	−4.8	12	3CTE	1OTE	8H		
2-propanol	34	6.97	6.86	6.92	−1.6	−0.8	4.2	−7.5	20	3CTE	1OTE	8H		
cyclohexanol	56	11.56	11.65	11.65	0.7	0.8	5.4	−4.5	20	6CTE	1OTE	12H		
glycol	34	5.71	5.71	5.72	−0.1	0.2	7.6	−9.0	15	2CTE	2OTE	6H		
dimethyl ether	26	5.16	5.02	5.08	−2.6	−1.5	4.0	−9.2	19	2CTE	1OTE	6H		
diethyl ether	42	8.73	8.70	8.75	−0.4	0.2	5.0	−5.9	19	4CTE	1OTE	10H		
methyl propyl ether	42	8.86	8.70	8.75	−1.9	−1.2	3.4	−7.3	15	4CTE	1OTE	10H		
methyl propyl ether	42	8.64	8.70	8.75	0.6	1.3	6.0	−5.0	12	4CTE	1OTE	10H		
ethyl propyl ether	50	10.49	10.53	10.59	0.5	1.0	5.5	−4.8	12	5CTE	1OTE	12H		
ethyl propyl ether	50	10.68	10.53	10.59	−1.4	−0.9	3.6	−6.6	15	5CTE	1OTE	12H		
dipropyl ether	58	12.55	12.37	12.42	−1.4	−1.0	3.3	−6.4	15	6CTE	1OTE	14H		
di-*n*-propyl ether	58	12.53	12.37	12.42	−1.2	−0.9	3.5	−6.2	19	6CTE	1OTE	14H		
ethylene oxide	24	4.43	4.32	4.31	−2.6	−2.8	3.4	−9.8	20	2CTE	2OTE	4H		
dioxane	48	9.44	8.63	8.61	−8.6	−8.7	−3.0	−15.4	19	4CTE	2OTE	8H		
dioxane	48	8.60	8.63	8.61	0.4	0.2	6.5	−7.1	20	4CTE	2OTE	8H		
Ketones: OTR4 (tr^{2}tr^{2}trπ) Hybridization														
O_2	16	1.60	1.48	1.14	−7.6	−28.9	−7.6	−28.9	19	2OTR4				
CO	14	1.95	1.94	1.85	−0.3	−5.0	4.3	−11.8	19	1CDI	1OTR4			
CO_2	22	2.65	2.66	2.42	0.4	−8.6	4.6	−14.9	19	1CDI	2OTR4			
acetone	32	6.40	6.33	6.36	−1.2	−0.6	4.5	−7.6	15	2CTE	1CTR	1OTR4	6H	
acetone	32	6.33	6.33	6.36	0.0	0.6	5.7	−6.5	19	2CTE	1CTR	1OTR4	6H	
acetone	32	6.39	6.33	6.36	−1.0	−0.4	4.7	−7.4	20	2CTE	1CTR	1OTR4	6H	
methyl ethyl ketone	40	8.13	8.16	8.20	0.4	0.9	5.7	−5.5	19	3CTE	1CTR	1OTR4	8H	
methyl ethyl ketone	40	8.19	8.16	8.20	−0.4	0.1	4.9	−6.3	15	3CTE	1CTR	1OTR4	8H	
diethyl ketone	48	9.93	10.00	10.04	0.7	1.1	5.7	−4.9	19	4CTE	1CTR	1OTR4	10H	
n-methyl propyl ketone	48	9.93	10.00	10.04	0.7	1.1	5.7	−4.9	19	4CTE	1CTR	1OTR4	10H	
diisopropyl ketone	64	13.53	13.68	13.70	1.1	1.3	5.6	−4.0	19	6CTE	1CTR	1OTR4	14H	
formaldehyde	16	2.45	2.68	2.69	9.4	10.0	18.0	−1.1	20	1CTR	2H	1OTR4		
acetaldehyde	24	4.59	4.74	4.82	3.3	5.0	9.9	−3.4	20	2CTR	4H	1OTR4		
propionaldehyde	32	6.35	6.33	6.36	−0.4	0.2	5.4	−6.8	15	2CTE	1CTR	1OTR4	6H	
n-butyraldehyde	40	8.18	8.16	8.20	−0.2	0.2	5.0	−6.1	15	3CTE	1CTR	1OTR4	8H	
anthraquinone	108	24.46	25.22	25.34	3.1	3.6	6.6	−0.7	25	10CTR	4CBR	2OTR4	8H	
OPI2 (tr^{2}trtrπ^2) Hybridization														
furan	36	7.23	7.23	7.23	0.0	0.0	5.5	−9.3	21	4CTR	1OPI2	4H		
dixanthylene	188	45.27	47.34	47.33	4.6	4.5	7.7	−0.1	25	16CTR	10CBR	2OPI2	16H	

Table II (Continued)

molecule	N	α, Å^3			$\delta\alpha$, %		$\delta\alpha^*$, %			empirical formula (atomic hybrids)					
		exp	ahc	ahp	ahc	ahp	ahc	ahp	ref						
Acids and Esters: OTE and OTR4 Mixed Hybridization															
formic acid	24	3.32	3.41	3.33	2.8	0.4	10.7	−9.6	12	1CTR	1OTR4	1OTE	2H		
acetic acid	32	5.15	5.19	5.17	0.8	0.3	8.2	−8.9	15	1CTR	1OTR4	1OTE	1CTE	4H	
acetic acid	32	5.05	5.19	5.17	2.7	2.2	10.2	−7.2	12	1CTR	1OTR4	1OTE	1CTE	4H	
propionic acid	40	6.96	7.00	7.00	0.5	0.6	7.3	−7.9	15	1CTR	1OTR4	1OTE	2CTE	6H	
propionic acid	40	6.80	7.00	7.00	2.8	2.9	9.8	−5.7	12	1CTR	1OTR4	1OTE	2CTE	6H	
butyric acid	48	8.58	8.81	8.84	2.7	3.0	9.2	−5.0	12	1CTR	1OTR4	1OTE	3CTE	8H	
methyl formate	32	5.05	5.19	5.17	2.7	2.2	10.2	−7.2	12	1CTR	1OTR4	1OTE	1CTE	4H	
ethyl formate	40	6.88	7.00	7.00	1.7	1.8	8.6	−6.7	12	1CTR	1OTR4	1OTE	2CTE	6H	
methyl acetate	40	6.81	7.00	7.00	2.8	2.9	9.8	−5.8	12	1CTR	1OTR4	1OTE	2CTE	6H	
ethyl acetate	48	8.62	8.81	8.84	2.3	2.5	8.7	−5.4	12	1CTR	1OTR4	1OTE	3CTE	8H	
methyl propionate	48	8.79	8.81	8.84	0.3	0.5	6.6	−7.2	15	1CTR	1OTR4	1OTE	3CTE	8H	
methyl propionate	48	8.53	8.81	8.84	2.6	2.9	9.1	−5.0	12	1CTR	1OTR4	1OTE	3CTE	8H	
ethyl propionate	56	10.41	10.64	10.67	2.2	2.6	8.3	−4.8	12	1CTR	1OTR4	1OTE	4CTE	10H	
methyl butyrate	56	10.41	10.64	10.67	2.2	2.5	8.3	−4.8	12	1CTR	1OTR4	1OTE	4CTE	10H	
ethyl butyrate	64	12.23	12.47	12.51	1.9	2.3	7.7	−4.6	12	1CTR	1OTR4	1OTE	5CTE	12H	
CH_2OHCH_2OH	34	5.61	5.71	5.72	1.6	1.9	9.4	−7.4	12	2CTE	2OTE	6H			
$CH_2OHCH_2OCH_3$	42	7.44	7.52	7.55	1.0	1.5	8.1	−6.9	12	3CTE	2OTE	8H			
$CH_2OHCH_2OC_2H_5$	50	9.28	9.34	9.39	0.7	1.2	7.2	−6.5	12	4CTE	2OTE	10H			
CH_2ClCH_2OH	42	6.88	6.99	7.01	1.6	1.8	6.5	−3.7	12	2CTE	1OTE	5H	1Cl		
$CH_2ClCH_2OCH_3$	50	8.71	8.80	8.84	1.1	1.6	6.0	−3.9	12	3CTE	1OTE	7H	1Cl		
$CH_2ClCH_2OC_2H_5$	58	10.56	10.62	10.68	0.5	1.1	5.4	−4.2	12	4CTE	1OTE	9H	1Cl		
$CH_2ClCH_2CH_2COOH$	64	10.45	10.78	10.76	3.2	3.1	8.5	−3.2	12	1CTR	1OTR4	1OTE	3CTE	7H	1Cl
$CH_2ClCH_2CH_2COOCH_3$	72	12.27	12.59	12.60	2.6	2.7	7.9	−3.5	12	1CTR	1OTR4	1OTE	4CTE	9H	1Cl
$CH_2ClCH_2CH_2COOC_2H_5$	80	14.11	14.41	14.43	2.1	2.3	7.3	−3.7	12	1CTR	1OTR4	1OTE	5CTE	11H	1Cl
$CH_3CHClCH_2COOH$	64	10.54	10.78	10.76	2.3	2.1	7.6	−4.1	12	1CTR	1OTR4	1OTE	3CTE	7H	1Cl
$CH_3CHClCH_2COOCH_3$	72	12.31	12.59	12.60	2.3	2.3	7.5	−3.8	12	1CTR	1OTR4	1OTE	4CTE	9H	1Cl
$CH_3CHClCH_2COOC_2H_5$	80	14.13	14.41	14.43	2.0	2.1	7.1	−3.9	12	1CTR	1OTR4	1OTE	5CTE	11H	1Cl
$CH_3CH_2CHClCOOH$	64	10.61	10.78	10.76	1.7	1.5	6.9	−4.7	12	1CTR	1OTR4	1OTE	3CTE	7H	1Cl
$CH_3CH_2CHClCOOCH_3$	72	12.33	12.59	12.60	2.2	2.2	7.4	−3.9	12	1CTR	1OTR4	1OTE	4CTE	9H	1Cl
$CH_3CH_2CHClCOOC_2H_5$	80	14.16	14.41	14.43	1.8	1.9	6.9	−4.0	12	1CTR	1OTR4	1OTE	5CTE	11H	1Cl
$C_2H_5CHClCH_2OH$	58	10.70	10.62	10.68	−0.8	−0.2	4.0	−5.5	12	4CTE	1OTE	9H	1Cl		
$CH_3CHClCH_2CH_2OH$	58	10.38	10.62	10.68	2.3	2.9	7.2	−2.5	12	4CTE	1OTE	9H	1Cl		
$CH_3CHClCH_2OH$	50	8.89	8.80	8.84	−1.0	−0.5	3.8	−5.9	12	3CTE	1OTE	7H	1Cl		
$CH_2ClCH_2CH_2OH$	50	8.84	8.80	8.84	−0.5	0.0	4.3	−5.4	12	3CTE	1OTE	7H	1Cl		
$CH_3CH_2CHClCOOH$	64	10.87	10.78	10.76	−0.8	−1.0	4.3	−7.0	12	3CTE	1CTR	1OTR4	1OTE	7H	1Cl
$CH_3CHClCH_2COOH$	64	10.80	10.78	10.76	−0.2	−0.3	4.9	−6.4	12	3CTE	1CTR	1OTR4	1OTE	7H	1Cl
$CH_2ClCH_2CH_2COOH$	64	10.69	10.78	10.76	0.9	0.7	6.0	−5.4	12	3CTE	1CTR	1OTR4	1OTE	7H	1Cl
$CH_3CH_2CH_2CHClCOOH$	72	12.69	12.59	12.60	−0.7	−0.7	4.3	−6.6	12	4CTE	1CTR	1OTR4	1OTE	9H	1Cl
$CH_3CH_2CHClCH_2COOH$	72	12.57	12.59	12.60	0.1	0.2	5.3	−5.8	12	4CTE	1CTR	1OTR4	1OTE	9H	1Cl
$CH_3CHClCH_2CH_2COOH$	72	12.53	12.59	12.60	0.5	0.5	5.6	−5.5	12	4CTE	1CTR	1OTR4	1OTE	9H	1Cl
ethyl ester, α-naphthoic acid	106	23.97	24.33	24.48	1.5	2.1	5.3	−2.4	12	8CTR	3CBR	2CTE	1OTR4	1OTE	12H
ethyl ester, β-naphthoic acid	106	24.19	24.33	24.48	0.6	1.2	4.3	−3.3	12	8CTR	3CBR	2CTE	1OTR4	1OTE	12H
ethyl ester, α-naphthol	98	22.03	21.97	22.10	−0.3	0.3	3.3	−4.1	12	9CTR	2CBR	1CTE	1OTR4	1OTE	10H
ethyl ester, β-naphthol	98	22.21	21.97	22.10	−1.1	−0.5	2.5	−4.8	12	9CTR	2CBR	1CTE	1OTR4	1OTE	10H
Amides, etc.: NPI2 and OTR4 Mixed Hybridization															
formamide	24	4.08	3.85	4.17	−5.6	2.3	1.4	−5.7	12	1CTR	1OTR4	1NPI2	3H		
formamide	24	3.88	3.85	4.17	−0.7	7.5	6.6	−0.8	23	1CTR	1OTR4	1NPI2	3H		
formamide	24	4.08	3.85	4.17	−5.6	2.3	1.3	−5.7	20	1CTR	1OTR4	1NPI2	3H		
acetamide	32	5.39	5.66	6.01	5.0	11.4	12.0	3.8	23	1CTR	1OTR4	1NPI2	1CTE	5H	
acetamide	32	5.67	5.66	6.01	−0.2	5.9	6.4	−1.4	20	1CTR	1OTR4	1NPI2	1CTE	5H	
N-methylformamide	32	5.89	5.66	6.01	−3.9	2.0	2.5	−5.0	12	1CTR	1OTR4	1NPI2	1CTE	5H	
N-methylformamide	32	5.91	5.66	6.01	−4.3	1.6	2.1	−5.4	20	1CTR	1OTR4	1NPI2	1CTE	5H	
N,*N*-dimethylformamide	40	7.69	7.48	7.84	−2.8	2.0	3.2	−4.4	12	1CTR	1OTR4	1NPI2	2CTE	7H	
N,*N*-dimethylformamide	40	7.81	7.48	7.84	−4.2	0.4	1.6	−5.9	20	1CTR	1OTR4	1NPI2	2CTE	7H	
N-ethylacetamide	48	9.45	9.31	9.68	−1.5	2.4	4.1	−3.6	12	1CTR	1OTR4	1NPI2	3CTE	9H	
N-methylacetamide	40	7.82	7.48	7.84	−4.4	0.3	1.5	−6.0	20	1CTR	1OTR4	1NPI2	2CTE	7H	
N,*N*-diethylacetamide	64	12.96	12.97	13.35	0.1	3.0	5.2	−2.5	12	1CTR	1OTR4	1NPI2	5CTE	13H	
benzamide	64	12.75	13.43	13.83	5.3	8.5	9.1	4.4	23	7CTR	1OTR4	1NPI2	7H		
p-nitroaniline	72	13.90	13.20	13.89	−5.0	−0.1	−0.5	−4.8	23	6CTR	2NPI2	2OTE	6H		
NO	15	1.70	1.64	1.60	−3.7	−5.9	−3.0	−8.9		1NTR2	1OTR4				
N_2O	22	3.00	2.54	2.61	−15.2	−12.8	−14.6	−15.2	19	1NPI2	1NDI	1OTR4			
p-nitrotoluene	72	14.10	13.87	14.25	−1.6	1.0	2.7	−3.8	23	6CTR	1CTE	1NPI2	2OTE	7H	
nitrobenzene	64	12.92	12.04	12.41	−6.8	−3.9	−2.6	−8.7	19	6CTR	1NPI2	2OTE	5H		
Sulfur: STE (te^{2}te^{2}tete), STR4 (tr^{2}tr^{2}trπ) and SPI2 (tr^{2}trtrπ^2) Hybridization															
H_2S	18	3.83	3.78	3.77	−1.4	−1.5	0.2	−3.1	19	2H	1STE				
C_2H_5SH	34	7.38	7.46	7.44	1.1	0.9	3.5	−1.6	12	2CTE	6H	1STE			
$(C_2H_5)_2S$	50	11.00	11.14	11.11	1.3	1.0	4.0	−1.8	12	4CTE	10H	1STE			
$(CH_3)_2S$	34	7.53	7.46	7.44	−1.0	−1.2	1.4	−3.7	32	2CTE	6H	1STE			
$(CH_3)_2SO$	42	7.97	8.08	8.08	1.4	1.4	5.7	−3.6	32	2CTE	6H	1STE	1OTE		
$(CH_3)_2SO_2$	50	8.40	8.75	8.72	4.1	3.7	9.5	−2.7	32	2CTE	6H	1STE	2OTE		
$(C_6H_5)_2S$	98	23.79	23.16	23.09	−2.6	−2.9	−1.6	−3.9	32	12CTR	10H	1STE			
$(C_6H_5)_2SO$	106	24.34	23.72	23.73	−2.6	−2.5	−0.7	−4.7	32	12CTR	10	1STE	1OTE		
$(C_6H_5)_2SO_2$	114	24.66	24.31	24.37	−1.4	−1.2	1.2	−4.4	32	12CTR	10H	1STE	2OTE		
thiophene	44	9.00	9.03	9.66	0.3	7.3	3.0	5.6	21	4CTR	4H	1SPI2			
SO_2	32	3.90	3.71	3.91	−4.9	0.2	−4.0	−3.7	19	1SPI2	1OTR4	1OTE			
CS_2	38	8.74	8.62	8.74	−1.4	0.0	−1.4	0.0	19	1CDI	2STR4				
diperinaphthylenethiophene	172	43.25	45.88	46.32	6.1	7.1	7.9	5.7	25	12CTR	12CBR	1SPI2	12H		

Table II (Continued)

molecule	N	α, Å^3			$\delta\alpha$, %		$\delta\alpha^*$, %		ref	empirical formula (atomic hybrids)					
		exp	ahc	ahp	ahc	ahp	ahc	ahp							
Isomers of $C_{10}H_{18}O$ with OTE and OTR4 Hybridization															
$C_{10}H_{18}O$; acetylenic alcohols	86	18.99	18.64	18.66	−1.8	−1.7	1.9	−6.0	12	8CTE	2CDI	1OTE	18H		
$C_{10}H_{18}O$; acetylenic ethers	86	19.04	18.64	18.66	−2.1	−2.0	1.7	−6.2	12	8CTE	2CDI	1OTE	18H		
$C_{10}H_{18}O$; diethylenic alcohols	86	19.41	19.32	19.38	−0.5	−0.2	3.1	−4.2	12	6CTE	4CTR	1OTE	18H		
$C_{10}H_{18}O$; diethylenic ethers	86	19.46	19.32	19.38	−0.7	−0.4	2.8	−4.5	12	6CTE	4CTR	1OTE	18H		
$C_{10}H_{18}O$; cyclic alcohol, with double bond	86	18.72	18.79	18.80	0.4	0.4	4.2	−3.9	12	8CTE	2CTR	1OTE	18H		
$C_{10}H_{18}O$; cyclic ethers, with double bond	86	18.77	18.79	18.80	0.1	0.1	3.9	−4.1	12	8CTE	2CTR	1OTE	18H		
$C_{10}H_{18}O$; ethylenic C=O or CHO	86	19.00	18.99	19.02	0.0	0.1	3.8	−4.3	12	7CTE	3CTR	1OTR4	18H		
$C_{10}H_{18}O$; cyclic C=O or CHO	86	18.31	18.47	18.44	0.9	0.7	4.9	−4.0	12	9CTE	1CTR	1OTR4	18H		
$C_{10}H_{18}O$; bicyclic alcohols	86	18.04	18.28	18.21	1.3	1.0	5.3	−3.5	12	10CTE	1OTE	18H			
$C_{10}H_{18}O$; bicyclic ethers	86	18.09	18.28	18.21	1.1	0.7	5.0	−3.8	12	10CTE	1OTE	18H			
Biological Molecules															
guanine	78	13.60	14.26	15.68	4.9	15.3	10.8	10.2	33	3CTR	2CBR	3NPI2	2NTR2	1OTR4	5H
adenine	70	13.10	13.74	15.05	4.9	14.9	9.8	11.5	33	3CTR	2CBR	2NPI2	3NTR2	5H	
cytosine	58	10.30	10.29	11.12	−0.1	8.0	4.7	3.3	33	4CTR	2NPI2	1NTR2	1OTR4	5H	
thymine	66	11.23	11.50	12.11	2.4	7.8	8.0	1.6	33	4CTR	1CTE	2NPI2	2OTR4	6H	
acridine	94	25.49	24.11	24.26	−5.4	−4.8	−3.8	−6.2	25	9CTR	4CBR	1NTR2	9H		
Phosphate: PTE (te^{2}tetete)															
trimethyl phosphate	74	10.86	10.87	10.75	0.1	−1.0	7.2	−9.3	34	3CTE	1PTE	4OTE	9H		
$(CH_3)_3C(CH_2O)_3P$	78	13.32	12.35	12.24	−7.3	−8.1	−1.7	−14.6	34	5CTE	3OTE	1PTE	9H		
$(CH_3)_3C(CH_2O)_3PO$	86	12.84	13.08	12.87	1.8	0.3	8.1	−7.0	34	5CTE	4OTE	1PTE	9H		
$(CH_3)_3C(CH_2O)_3PS$	94	15.74	15.39	15.24	−2.2	−3.2	2.6	−8.9	34	5CTE	3OTE	1PTE	1STE	9H	

[a] α(ahc) is calculated with eq 1, and α(ahp) is calculated with eq 4 using optimum τ_A(ahc) and α_A(ahp) parameters. An asterisk (*) refers to the conjugate formulas, eqs 3 and 6. The errors, $\delta\alpha$(ahc), $\delta\alpha$(ahp), $\delta\alpha^*$(ahc), and $\delta\alpha^*$(ahp), are calculated with eq 8 with the appropriate α(ahc), α(ahp), α^*(ahc), and α^*(ahp) from eqs 1, 4, 3, and 6. The empirical formula is presented with the number of each atomic hybrid. N is the total number of electrons in the molecule.

Table III. Classical Bond Polarizabilities (Å^3) Obtained from α(ahp)

bond X-Y	Denbigh[a] (ref 15)	Vogel[a] (ref 17)	$\alpha_{X\text{-}Y}{}^+(bp)$[b] (eq 13)	formula[b]
Single Bond Polarizabilities				
C—H	0.670	0.664	0.652	$(1/4)\alpha_{CTE} + \alpha_H$
C—F	0.682	0.575	0.555	$(1/4)\alpha_{CTE} + \alpha_F$
C—Cl	2.588	2.580	2.580	$(1/4)\alpha_{CTE} + \alpha_{Cl}$
C—Br	3.714	3.722	3.278	$(1/4)\alpha_{CTE} + \alpha_{Br}$
C—I	5.768	5.791	5.680	$(1/4)\alpha_{CTE} + \alpha_I$
C—C	0.496	0.514	0.531	$2(1/4)\alpha_{CTE}$
N—H	0.718	0.698	0.708	$(1/3)\alpha_{NTE} + \alpha_H$
O—H	0.686	0.658 (alcohols) 0.713 (acids)	0.706	$(1/2)\alpha_{OTE} + \alpha_H$
C—O	0.599	0.610 (ether) 0.578 (acetals)	0.584	$(1/4)\alpha_{CTE} + (1/2)\alpha_{OTE}$
C—O	0.599		0.769	$(1/3)\alpha_{CTR} + (1/2)\alpha_{OTE}$
C—N	0.611	0.246	0.587	$(1/4)\alpha_{CTE} + (1/3)\alpha_{NTE}$
Multiple Bond Polarizabilities				
C=C	1.649	1.653	1.643	$2[\alpha_{CTR} - 2(1/4)\alpha_{CTE}]$
C_{ar}—C_{ar}	1.082	1.066	1.087	$\alpha_{CTR} - (1/4)\alpha_{CTE}$
C_{na}—C_{na}	1.102		1.249	$[\alpha(\text{naph}) - 8\alpha_{C\text{-}H}]/10$
C_{ant}—C_{ant}			1.318	$[\alpha(\text{anth}) - 10\alpha_{C\text{-}H}]/14$
C≡C	2.537	2.327	2.036	$2[\alpha_{CDI} - (1/4)\alpha_{CTE}]$
C=O	1.340	1.383	1.020	$(1/3)\alpha_{CTR} + \alpha_{OTR4}$

[a] Bond polarizabilities, bp, from refs 13 and 15 are calibrated against refractions obtained with the sodium D line. [b] The nonclassical bond polarizability defined by eq 13 is one partitioning method to relate atomic hybrid polarizabilites to $\alpha_{X\text{-}Y}{}^+(bp)$. $\alpha_{X\text{-}Y}{}^+(bp)$ is calculated with eq 13 for single bonds and the indicated formula for multiply bonded atoms.

the parameters and the environment and not the atoms attached to a given atom A. The requirement that bridged nitrogen atoms of the type NPI2 be considered differently could not be tested because the necessary molecular polarizability data were not available.

Bond Polarizability Methods and the ahp Method

In the classical set of bond polarizabilities proposed by von Steiger,[7] Smyth,[8] and Denbigh,[9] each type of bond is assigned a unique value in a heirarchecal procedure. For example,

$$\alpha_{CTE\text{-}H} = (1/4)\alpha(CH_4) \qquad (13)$$

and

$$\alpha(C_nH_{2n+2}) = (n-1)\alpha_{CTE\text{-}CTE} + (2n+2)\alpha_{CTE\text{-}H} \qquad (14)$$

are used to obtain $\alpha_{C\text{-}H}$ and $\alpha_{C\text{-}C}$ in the alkanes. In addition, all single bond polarizabilities, X-Y, can be fit by formulas given in (13) and (14) by including the appropriate number of terms $\alpha_{X\text{-}Y}$. These single bond polarizabilities can be defined uniquely if the atoms have tetrahedral or σ hybridization because all bonds are equivalent. They are listed in Table III for atoms involved in this study and compared to results of Denbigh[15] and Vogel.[17]

A problem arises for atoms participating in multiple bonding because the bonds are in general not equivalent. For example, the C_{ar}—C_{ar} and C=C bond polarizabilities depend on the assumption that a C—H bond is independent of the type of hybridization and environment. Its effect is removed from alkenes, benzene, naphthalene, etc., with equations of the type

$$\alpha_{C=C} = \alpha(C_2H_4) - 4\alpha_{CTE\text{-}H} \qquad (15)$$

$$\alpha_{C_{ar}\text{-}C_{ar}} = [\alpha(C_6H_6) - 6\alpha_{CTE\text{-}H}]/6 \qquad (15')$$

$$\alpha_{C_{na}\text{-}C_{na}} = [\alpha(C_{10}H_8) - 8\alpha_{CTE\text{-}H}]/10 \qquad (15'')$$

to obtain parameters for the double, aromatic, and naphthalenic bonds. The fact that $\alpha_{C_{ar}-C_{ar}}$ and $\alpha_{C_{na}-C_{na}}$ differ[15] suggests that bond polarizabilities will be required for anthracenes and all other fused rings. Some formulas are presented in Table III to relate α(ahp) to the classical results of Denbigh[15] and Vogel.[17] Adjustment of the bond polarizabilities to accurately predict molecular polarizabilities results in a trade-off among the parameters with a small improvement. Optimum bond polarizabilities and special consideration of multiply bonded and fused ring systems has been carefully documented elsewhere (refs 15–17); however, comparisons between the literature values (refs 15 and 17) and a partitioning with formulas of the type in eqs 15–15″ demonstrates similarity of results. The purpose of this discussion is to demonstrate a relationship between the α_A(ahp) and $\alpha_{X-Y}{}^{+}$(bp) and to demonstrate that it depends on the method of partitioning the atomic hybrid among the bonds. The atomic hybrid method avoids these difficulties by assigning each atom a unique state of hybridization without regard to the atom to which it is attached.

The Group Polarizability Method and the ahp Method

Vogel[10] has presented a set of atomic and groups refractivities that include atoms H, F, Cl, Br, I, O, N, and S, bonds C═O, OH, NH, SH, C═C, C≡C, C≡N, etc., and groups CH_2, CH_3, COO (esters), CO_2H, NH_2, etc. These are listed in Table IV. To use these data the molecule must be represented as a sum of groups. For example

$$\alpha(C_nH_{2n+2}) = n\alpha(CH_2) + 2\alpha(H) \text{ (all } n)$$
$$= (n-2)\alpha(CH_2) + 2\alpha(CH_3) \ (n > 1)$$

$$\alpha(\text{acetone}) = 2\alpha(CH_2) + 2\alpha(H) + \alpha(C{=}O)$$
$$= 2\alpha(CH_3) + \alpha(C{=}O)$$

$$\alpha(\text{ethylene}) = \alpha(C{=}C) + 2\alpha(CH_2)$$

$$\alpha(HC{\equiv}N) = \alpha(C{\equiv}N) + \alpha(H)$$

Interestingly enough, the methods developed by Vogel[10] implicitly contain hybridization. A formula relating each group to an appropriate sum over ahp's is presented and data from both methods are compared. For example, the H, C, CH_2, and CH_3 aliphatic units are directly related by differential increments of α(H) added to α(CTE). The carbon atom in ketones, esters, and acids is CTR; the oxygen atom in ethers and alcohols and one oxygen atom in esters and acids is OTE, and the other in acids and esters is OTR4; aliphatic nitrogen atoms are NTE in primary, secondary, and tertiary amines; aromatic nitrogen atoms are NPI2 in primary, secondary, and tertiary amines; sulfides and thiols have STE and SPI2 sulfur atoms, respectively; CDI and NDI are used for triple bond contributions in C≡N. The atom, bond, and group polarizabilities are listed in Table XXII of ref 10. Most can be represented as a sum of ahp's. Several are expressed as a differential contribution to one of the other groups. For example, the double bond, C═C, and terminal triple bond, C≡C, are differential contributions added to CH and CH_2 groups. Also, 3-, 4-, 5- and 6-carbon-ring contributions are differential corrections to an appropriate sum over aliphatic CH_2 groups.

The gp's may be obtained from sums over appropriate ahp's, and conversely, the gp's may be factored into a set of ahp's because the units represented by Vogel[10] coincidently coincide with atoms in classical states of hybridization. The present empirical ahc and ahp methods may be interpreted as a continuation of the factorization to the atomic hybrid level for all groups.

Table IV. Group Polarizabilities (Å^3) as a Sum of Atomic Hybrid Polarizabilities[a]

	Vogel (ref 10)	α(gp)	formula
H	0.408	0.387	α(H)
C (in CH_2)	1.027	1.061	α(CTE)
CH_2	1.842	1.835	α(CTE) + α(H)
CH_3	2.241	2.222	α(CTE) + 3α(H)
O (ethers)	0.699	0.637	α(OTE)
C═O (ketones)	1.824	1.921	α(CTR) + α(OTR4)
COO (esters)	2.458	2.558	α(CTR) + α(OTR4) + α(OTE)
OH (alcohols)	1.009	1.024	α(OTE) + α(H)
CO_2H	2.864	2.945	α(COO) + α(H)
F	0.321	0.296	α(F)
Cl	2.317	2.315	α(Cl)
Br	3.465	3.013	α(Br)
I	5.531	5.415	α(I)
NH_2 (primary aliphatic)	1.759	1.738	α(NTE) + 2α(H)
NH (secondary aliphatic)	1.431	1.351	α(NTE) + α(H)
NH (secondary aromatic)	1.854	1.477	α(NPI2) + α(H)
N (tertiary aliphatic)	1.088	0.964	α(NTE)
N (tertiary aromatic)	1.678	1.090	α(NPI2)
S (sulfides)	3.140	3.000	α(STE)
SH (thiols)	3.471	3.087	α(SPI2) + α(H)
C═C (double bond)	0.624	0.582	2[α(CTR) − α(CTE)]
C≡C (triple bond)	0.784	0.444	2[α(CDI) − α(CTE)]
C≡N (nitrile)	2.164	2.239	α(CDI) + α(NDI)

[a] Group polarizabilities, α(gp), are calculated with the indicated formula and ahp's in Table I.

Discussion and Conclusion

This study of the empirical approaches to the calculation of molecular polarizability was undertaken for several purposes: (1) to obtain an updated set of parameters τ_A(ahc) and α_A(ahp) for the calculation of molecular polarizability with the ahc or ahp methods, with eqs 1 and 4; (2) to obtain a set of atomic polarizabilities that can be used in the semiempirical approach in which a 6 − n potential

$$U_{ij} = [A_{ij}/\rho_{ij}{}^6][-s_{ij}{}^{-6} + (6/n)s_{ij}{}^{-n}] \qquad (16)$$

is used, where $s_{ij} = r_{ij}/(\rho_i + \rho_j)$ is the reduced distance between atoms i and j and ρ_i and ρ_j are the van der Waals radii of atoms i and j and n = 9 to 14 depends on the repulsive potential, and the London dispersion coefficient[36]

$$A_{ij} = 1.5\alpha_i\alpha_j I_i I_j/(I_i + I_j) \qquad (17)$$

contains the polarizabilities and ionization potentials of atoms, bonds or groups i and j; (3) to assess the accuracy of the ahc and ahp empirical formulas, eqs 1 and 4, in calculating molecular polarizabilities; (4) to assess the "invariance" of the results to partitioning by comparing the ahc and ahp methods to their conjugate calculations; and (5) to obtain average atomic and molecular polarizabilities as a first step in the calculation of the molecular polarizability tensor and principal axes of polarizability reported in the next paper (ref 37).

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