

ADDITIVITY OF BOND SEPARATION ENERGIES OF HYDROCARBONS AND THEIR THERMOCHEMICAL DATA

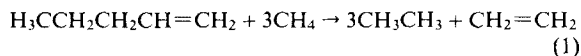
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The additivity of experimental bond separation energies is demonstrated. This thermodynamic function can be reproduced by summation of group equivalents with a correction for the 'stabilization' energy. For this purpose, several group equivalents have been developed for alkanes and alkenes. The correlation between the computed and the experimental bond separation energies is good. These equivalents are then used in evaluating the stabilization (destabilization) energies for aromatic hydrocarbons and polyenes. The results obtained are in good agreement with values reported in the literature.

INTRODUCTION

Energies of reaction can be estimated from *ab initio* calculations. The computed results within the Hartree–Fock approximation generally compare well with experimental data for isodesmic reactions.^{1,2} Bond separation reactions (BSRs) are an important example of this class of reaction.² Specifically, BSRs are processes in which all formal bonds between heavy atoms are separated into the simplest parent (two-heavy-atom) molecules containing the same kinds of linkages. Stoichiometric balance is achieved by the addition of one-heavy-atom hydrides to the left-hand side of the reaction.² For example, the bond separation reaction for 1-pentene is illustrated in the equation.



The enthalpy changes associated with BSRs are called bond separation energies (BSEs), which reflect the stabilization or destabilization in molecules when compared with the corresponding isolated linkages. The BSE from *ab initio* 6-31G* calculations for 1,3-butadiene is 11.2 kcal mol⁻¹ whereas that for cyclopropane is -26.2 kcal mol⁻¹.² The corresponding experimental values are 14.33 and -19.79 kcal mol⁻¹ for 1,3-butadiene and cyclopropane, respectively, as calculated from the heats of formation reported by Cox and Pilcher.³ The positive BSE for 1,3-butadiene indicates stabilization due to conjugation, whereas the negative BSE for cyclopropane reflects destabilization due to the ring strain. BSEs have been used as a measure

of geminal interactions;^{2,4} however, in this paper it is demonstrated that they can also provide direct measures of strain, conjugation and resonance energies.

Many thermodynamic functions are additive, which means that these functions could be obtained by the summation of group, atom or bond contributions with some corrections. Experimental heats of combustion,^{5,6} heats of formation,⁷ heats of atomization⁸ and zero-point energies⁹ are reproduced via different additivity schemes. BSE is calculated from the heats of formation of the reactants and products, which are additive. Therefore, it is expected that experimental BSEs must be reproduced via summation of group equivalents with corrections for stabilization (destabilization) energies (SEs). SE, as defined here, includes the strain energy and any stabilizing interactions in the molecule. Interactions between adjacent C–C bonds in alkanes (branching effect) and the interaction between the π -bonds in conjugated polyenes are examples of such stabilizing interactions. Schleyer *et al.*¹⁰ developed 'strain-free group increments': CH₃, -10.05; CH₂, -5.13; CH, -2.16; C, -0.30 kcal mol⁻¹. These group increments can be used to evaluate the SE in alkanes by taking the difference between the experimental heat of formation and the sum of the group increments. The corresponding increments of Benson *et al.*⁷ are also appropriate for the calculation of the SE of alkanes. Therefore, Schleyer *et al.*¹⁰ used their increments in conjunction with the olefinic increments of Benson *et al.*⁷ (H₂C=, 6.26; HC=, 8.5; C=, 10.34 kcal mol⁻¹) to evaluate the SEs for alkenes. The results obtained by Schleyer *et al.*¹⁰ are in good agreement with those obtained by Mann and co-workers.¹¹ Hence SEs can be calculated with reliability for such compounds.

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DERIVATION OF GROUP EQUIVALENTS

It is found that the experimental BSEs can be reproduced via the empirical equation

$$\text{BSE}_{\text{expt}i} = \sum_{i=1}^k N_i X_i - \text{SE}(\text{kcal mol}^{-1}) \quad (2)$$

where N_i is the number of groups of type i , X_i the equivalent for group i , k the number of different groups in the molecule and SE is the stabilization (destabilization) energy. The group equivalents which have been developed in this work to reproduce the experimental BSE are listed in Table 1 and the compounds that were used in the derivation of the equivalents are listed in Table 2. Compounds whose experimental heats of formation are reliably known were chosen for this purpose because the SE values are dependent on these experimental heats for formation. For each equivalent, averages over as large a set of molecules as possible were taken. Most of the experimental heats of formation of the compounds were taken from the compilations of either Cox and Pilcher³ or Pedley *et al.*¹² SE values for alkane molecules were taken directly from Ref. 10, and those for alkenes were calculated by Schleyer *et al.*'s method.¹⁰

Table 1. The group equivalents

Group	Equivalent
CH ₃	0.07
CH ₂	2.75
CH	7.42
C	13.11
CH ₂ =	0.0
CH=	5.36
C=	11.29

RESULTS AND DISCUSSION

Fifty-seven molecules (Table 2) were used in the derivation of the equivalents. The correlation between the experimental and calculated [via equation (2)] BSEs has an r.m.s. deviation for the 57 molecules of 0.16 kcal mol⁻¹. The reliability of the developed equivalents was then tested by computing the BSEs for an additional 49 molecules (Table 3). This set of molecules includes structural, functional and positional isomers of alkanes and alkenes. The r.m.s. deviation is 0.22 kcal mol⁻¹ for the 49 molecules (Table 3). These

Table 2. Molecules used in the derivation of the group equivalents^a

Molecular formula	Molecule	$\Delta H_f^\circ(\text{g})^b$	SE ^c	BSE		Diff. ^d
				Obsd	Calc.	
CH ₄	Methane	-17.89				
C ₂ H ₄	Ethene	12.45				
C ₂ H ₆	Ethane	-20.24	-0.14			
C ₃ H ₄	Cyclopropene	66.6	54.5	-40.96	-41.03	-0.07
C ₃ H ₆	Propene	4.88	0.08	5.22	5.35	0.13
C ₃ H ₈	Propane	-24.83	0.41	2.24	2.48	0.24
C ₄ H ₆	1-Methylcyclopropene	58.2	54.5	-34.91	-35.03	-0.12
C ₄ H ₆	Cyclobutene	37.5 ^e	30.6	-14.21	-14.38	-0.17
C ₄ H ₈	1-Butene	-0.20	0.13	7.95	8.05	0.10
C ₄ H ₈	<i>trans</i> -2-Butene	-2.99	-0.07	10.74	10.93	0.19
C ₄ H ₈	Isobutene	-4.26	-0.76	12.01	12.19	0.18
C ₄ H ₁₀	Butane	-30.36	0.22	5.42	5.42	0.0
C ₄ H ₁₀	Isobutane	-32.41	0.17	7.47	7.46	-0.01
C ₅ H ₈	1,2-Dimethylcyclopropene	46.4	51.0	-25.46	-25.53	-0.07
C ₅ H ₈	Cyclopentene	8.56	6.8	12.38	12.17	-0.21
C ₅ H ₁₀	1-Pentene	-5.33	0.13	10.73	10.80	0.07
C ₅ H ₁₀	<i>trans</i> -2-Pentene	-7.93	0.12	13.33	13.49	0.16
C ₅ H ₁₀	2-Methyl-1-butene	-8.55	0.08	13.95	14.10	0.15
C ₅ H ₁₀	3-Methyl-1-butene	-6.61	0.80	12.01	12.12	0.11
C ₅ H ₁₀	Cyclopentane	-18.46	7.19	6.71	6.56	-0.15
C ₅ H ₁₂	Pentane	-35.10	0.50	7.81	7.89	0.08
C ₅ H ₁₂	Isopentane	-36.85	0.53	9.56	9.85	0.29
C ₅ H ₁₂	Neopentane	-40.27	0.23	12.98	13.16	0.18
C ₆ H ₁₂	1-Hexene	-9.95	0.64	13.00	13.04	0.04
C ₆ H ₁₂	2-Methyl-1-pentene	-14.19	-0.43	17.24	17.36	0.12
C ₆ H ₁₂	3-Methyl-1-pentene	-11.83	0.71	14.88	14.96	0.08
C ₆ H ₁₂	4-Methyl-1-pentene	-12.25	0.29	15.30	15.38	0.08

(continued)

Table 2. Molecules used in the derivation of the group equivalents^a (continued)

Molecular formula	Molecule	$\Delta H_f^\circ(\text{g})^b$	SE ^c	BSE		Diff. ^d
				Obsd	Calc.	
C ₆ H ₁₂	2-Ethyl-1-butene	-13.39	0.37	16.44	16.56	0.12
C ₆ H ₁₂	3,3-Dimethyl-1-butene	-14.51	1.09	17.56	17.59	0.03
C ₆ H ₁₂	Cyclohexane	-29.50	1.28	15.40	15.22	-0.18
C ₆ H ₁₂	Methylcyclopentane	-25.27	7.46	11.17	11.03	-0.14
C ₆ H ₁₄	Hexane	-39.92	0.68	10.28	10.46	0.18
C ₆ H ₁₄	2-Methylpentane	-41.77	0.93	12.13	12.20	0.07
C ₆ H ₁₄	3-Methylpentane	-41.13	1.56	11.49	11.57	0.08
C ₆ H ₁₄	2,2-Dimethylbutane	-44.48	1.29	14.84	14.85	0.01
C ₇ H ₁₂	Cycloheptene	-2.19	6.28	18.43	18.19	-0.24
C ₇ H ₁₄	2,4-Dimethyl-1-pentene	-20.03	0.81	20.73	20.86	0.13
C ₇ H ₁₄	2-Ethyl-3-methyl-1-butene	-19.01	1.83	19.71	19.84	0.13
C ₇ H ₁₄	2,3,3-Trimethyl-1-butene	-20.43	3.47	21.13	21.21	0.08
C ₇ H ₁₄	Cycloheptane	-28.21	7.70	11.76	11.55	-0.21
C ₇ H ₁₄	Methylcyclohexane	-36.98	0.88	20.53	20.36	-0.17
C ₇ H ₁₄	1,1-Dimethylcyclopentane	-33.04	7.88	16.59	16.37	-0.22
C ₇ H ₁₆	Heptane	-44.85	0.89	12.86	13.00	0.14
C ₇ H ₁₆	2-Methylhexane	-46.52	1.12	14.53	14.76	0.23
C ₇ H ₁₆	3-Ethylpentane	-45.25	2.38	13.26	13.50	0.24
C ₇ H ₁₆	2,2-Dimethylpentane	-49.20	1.48	17.21	17.41	0.20
C ₇ H ₁₆	3,3-Dimethylpentane	-48.08	2.60	16.09	16.29	0.20
C ₇ H ₁₆	2,2,3-Trimethylbutane	-48.87	3.76	16.88	17.12	0.24
C ₈ H ₁₆	2-Methyl-3-ethyl-1-pentene	-23.97	2.00	22.32	22.33	0.01
C ₈ H ₁₆	2,4,4-Trimethyl-1-pentene	-26.37	2.66	24.72	24.77	0.05
C ₈ H ₁₆	Cyclooctane	-29.73	11.31	10.93	10.69	-0.24
C ₈ H ₁₆	Ethylcyclohexane	-41.03	1.96	22.23	22.03	-0.20
C ₈ H ₁₆	1,1-Dimethylcyclohexane	-43.23	2.82	24.43	24.18	-0.25
C ₈ H ₁₈	Octane	-49.86	1.09	15.52	15.55	0.03
C ₈ H ₁₈	2-Methylheptane	-51.47	1.35	17.13	17.28	0.15
C ₈ H ₁₈	2,4-Dimethylhexane	-52.40	2.36	18.06	18.26	0.20
C ₈ H ₁₈	2,2,3-Trimethylpentane	-52.58	5.24	18.24	18.39	0.15
C ₈ H ₁₈	2,2,4-Trimethylpentane	-53.54	4.28	19.20	19.35	0.15
C ₈ H ₁₈	2,3,3-Trimethylpentane	-51.69	6.12	17.35	17.51	0.16
C ₉ H ₁₈	cis-1,3,5-Trimethylcyclohexane	-50.69	1.33	29.54	29.39	-0.15

^a All energies in kcal mol⁻¹.^b $\Delta H_f^\circ(\text{g})$ values were taken from Ref. 3 unless specified otherwise.^c SE values were taken either from Ref. 10 or calculated by Schleyer *et al.*'s method.¹⁰^d Diff. = BSE_{Calc.} - BSE_{Obsd.}^e Ref. 13.

deviations are acceptable as they are similar to the experimental errors. The bicyclic molecules show larger deviations (0.40–0.53 kcal mol⁻¹).

Olefin strain, OS, is defined as the difference between the SE of an olefin and that of its parent hydrocarbon.¹⁴ The heats of formation of many bridgehead olefins and their parent hydrocarbons have been calculated by molecular mechanics (MM1).¹⁴ The SE of a hydrocarbon molecule can be calculated via the equation

$$\text{SE} = \sum_{i=1}^k N_i X_i - \text{BSE}_{\text{exptl}} \quad (3)$$

which is just a rearranged form of equation (2). The developed equivalents were used in the calculation of the SEs of bridgehead molecules and their parent hydrocarbons and then OS was calculated. The results

in Table 4 show excellent agreement between the calculated and the reported OS values.

Resonance energies (RE) are stabilization energies and, therefore, they could be calculated via equation (3). REs of 14 aromatic hydrocarbons were calculated and are listed in the last column of Table 5. Since RE values are usually reported as positive numbers, the RE (Table 5) is taken as the negative of SE. The calculated resonance energies [via equation (3)] are compared with Pople–Pariser–Parr (PPP) and the split p-orbital (SPO) values¹⁶ in Table 6. The comparison shows that there is general agreement between the three sets of figures. However, the difference between the results is relatively large (7–8%) for naphthalene and 3,4-benzophenanthrene.

Resonance energies can also be estimated from heats

Table 3. Molecules used in testing the reliability of the equivalents^a

Molecular formula	Molecule	ΔH_f° (g) ^b	SE ^c	BSE		Diff. ^d
				Obsd	Calc.	
C ₃ H ₆	Cyclopropane	12.74 ^e	28.13	-19.79	-19.88	-0.09
C ₄ H ₆	Methylenecyclopropane	48.0 ^e	41.7	-24.71	-24.91	-0.20
C ₄ H ₆	Bicyclo[1.1.0]butane	51.9 ^e	66.5	-45.76	-46.16	-0.40
C ₄ H ₈	<i>cis</i> -2-Butene	-1.86	1.06	9.61	9.80	0.19
C ₄ H ₈	Cyclobutane	6.38 ^e	26.9	-15.78	-15.90	-0.12
C ₅ H ₈	Bicyclo[2.1.0]pentane	37.6 ^e	57.3	-33.81	-34.21	-0.40
C ₅ H ₁₀	2-Methyl-2-butene	-10.12	1.10	15.52	15.76	0.24
C ₆ H ₁₀	Cyclohexene	-0.84 ^e	2.5	19.43	19.22	-0.21
C ₆ H ₁₀	Bicyclo[3.1.0]hexane	9.07 ^e	33.91	-7.63	-8.07	-0.44
C ₆ H ₁₂	<i>cis</i> -2-Hexene	-12.51	0.67	15.56	15.71	0.15
C ₆ H ₁₂	<i>trans</i> -2-Hexene	-12.88	0.30	15.93	16.06	0.13
C ₆ H ₁₂	<i>cis</i> -3-Hexene	-11.38	1.80	14.43	14.56	0.13
C ₆ H ₁₂	<i>trans</i> -3-Hexene	-13.01	0.17	16.06	16.19	0.13
C ₆ H ₁₂	2-Methyl-2-pentene	-15.98	0.37	19.03	19.24	0.21
C ₆ H ₁₂	2,3-Dimethyl-2-butene	-16.42	3.10	19.47	19.76	0.29
C ₆ H ₁₂	1-Methylcyclohexene	-10.34	1.30	26.58	26.42	-0.16
C ₇ H ₁₂	Bicyclo[4.1.0]heptane	0.32 ^e	30.29	-1.23	-1.70	-0.47
C ₇ H ₁₄	4,4-Dimethyl- <i>cis</i> -2-pentene	-17.36	5.96	18.06	18.15	0.09
C ₇ H ₁₄	4,4-Dimethyl- <i>trans</i> -2-pentene	-21.22	2.10	21.92	22.01	0.09
C ₇ H ₁₄	Ethylcyclopentane	-30.34	7.52	13.89	13.72	-0.17
C ₇ H ₁₄	<i>cis</i> -1,2-Dimethylcyclopentane	-30.95	8.86	14.50	14.37	-0.13
C ₇ H ₁₄	<i>trans</i> -1,2-Dimethylcyclopentane	-32.66	7.15	16.21	16.08	-0.13
C ₇ H ₁₄	<i>cis</i> -1,3-Dimethylcyclopentane	-32.48	7.33	16.03	15.90	-0.13
C ₇ H ₁₄	<i>trans</i> -1,3-Dimethylcyclopentane	-31.92	7.89	15.47	15.34	-0.13
C ₇ H ₁₆	3-Methylhexane	-45.73	1.97	13.74	13.91	0.17
C ₈ H ₁₄	<i>cis</i> -Cyclooctene	-6.2 ^e	7.40	20.09	19.82	-0.27
C ₈ H ₁₄	<i>trans</i> -Cyclooctene	3.1 ^e	16.70	10.79	10.52	-0.27
C ₈ H ₁₄	Bicyclo[5.1.0]octane	-3.87 ^e	31.23	0.61	0.11	-0.50
C ₈ H ₁₆	1-Octene	-19.41	1.44	17.76	17.74	-0.02
C ₈ H ₁₆	2,2,-Dimethyl- <i>cis</i> -3-hexene	-21.34	7.11	19.69	19.75	0.06
C ₈ H ₁₆	2,2-Dimethyl- <i>trans</i> -3-hexene	-25.73	2.72	24.08	24.14	0.06
C ₈ H ₁₆	<i>n</i> -Propylcyclopentane	-35.37	7.62	16.57	16.37	-0.20
C ₈ H ₁₆	<i>cis</i> -1,2-Dimethylcyclohexane	-41.13	3.81	22.33	22.17	-0.16
C ₈ H ₁₆	<i>trans</i> -1,2-Dimethylcyclohexane	-42.99	1.95	24.19	24.03	-0.16
C ₈ H ₁₆	<i>cis</i> -1,3-Dimethylcyclohexane	-44.13	0.81	25.33	25.17	-0.16
C ₈ H ₁₆	<i>trans</i> -1,3-Dimethylcyclohexane	-42.18	2.76	23.38	23.22	-0.16
C ₈ H ₁₆	<i>cis</i> -1,4-Dimethylcyclohexane	-42.20	2.74	23.40	23.24	-0.16
C ₈ H ₁₆	<i>trans</i> -1,4-Dimethylcyclohexane	-44.10	0.84	25.3	25.14	-0.16
C ₈ H ₁₈	2,2-Dimethylhexane	-53.68	2.21	19.34	19.43	0.09
C ₈ H ₁₈	2,3-Dimethylhexane	-51.10	3.68	16.76	16.94	0.18
C ₉ H ₁₆	Bicyclo[6.1.0]nonane	-7.42 ^e	32.81	1.81	1.28	-0.53
C ₉ H ₁₈	Cyclononane	-31.73	14.44	10.58	10.31	-0.27
C ₉ H ₂₀	Nonane	-54.66	1.35	17.97	18.04	0.07
C ₉ H ₂₀	2,2,3,3-Tetramethylpentane	-56.67	9.36	19.98	20.03	0.05
C ₉ H ₂₀	2,2,4,4-Tetramethylpentane	-57.80	8.23	21.11	21.16	0.05
C ₉ H ₂₀	2,3,3,4-Tetramethylpentane	-56.43	8.49	19.74	19.88	0.14
C ₁₀ H ₁₆	Adamantane	-32.17 ^f	6.48	39.75	39.70	-0.05
C ₁₀ H ₂₀	Cyclodecane	-36.88	14.42	13.38	13.08	-0.30
C ₁₀ H ₂₂	Decane	-59.64	1.50	20.60	20.64	0.04

^{a-d} As in Table 2.^e Ref. 10.^f Ref. 12.

Table 4. Calculations of olefin strain energies for bridgehead olefins

Molecular formula	Molecule	$\Delta H_f^0(g)^b$	BSE _{obsd} ^c	$\sum_{i=1}^k N_i X_i$	OS	
					SE ^d	Reported ^e
C ₃ H ₈	Bicyclo [1.1.1] pentane	68.45	-64.66	23.09	87.75	
C ₃ H ₆	Bicyclo [1.1.1] pentane	115.58	-79.10	29.57	108.67	21.0
C ₆ H ₁₀	Bicyclo [2.1.1] hexane	18.33	-16.89	25.84	42.73	
C ₆ H ₈	Bicyclo [2.1.1] hex-1-ene	69.43	-35.30	32.32	67.62	25.0
C ₆ H ₈	Bicyclo [2.1.1] hex-1(5)-ene	77.64	-43.51	32.32	75.83	33.2
C ₇ H ₁₂	Bicyclo [2.2.1] heptane	-13.27	12.36	28.59	16.23	
C ₇ H ₁₀	Bicyclo [2.2.1] hept-1-ene	47.67	-15.89	35.07	50.96	34.9
C ₇ H ₁₀	Bicyclo [2.2.1] hept-1(7)-ene	51.27	-19.49	35.07	54.56	38.5
C ₇ H ₁₂	Bicyclo [3.1.1] heptane	5.98	-6.89	28.59	35.48	
C ₇ H ₁₀	Bicyclo [3.1.1] hept-1-ene	60.92	-29.14	35.07	64.21	28.9
C ₇ H ₁₀	Bicyclo [3.1.1] hept-1(6)-ene	71.21	-39.43	35.07	74.50	39.1
C ₈ H ₁₄	Bicyclo [2.2.2] octane	-23.76	20.50	31.34	10.84	
C ₈ H ₁₂	Bicyclo [2.2.2] oct-1-ene	42.72	-13.29	37.82	51.11	40.4
C ₉ H ₁₆	Bicyclo [3.2.2] nonane	-24.63	19.02	34.09	15.07	
C ₉ H ₁₄	Bicyclo [3.2.2] non-1-ene	21.06	6.02	40.57	34.55	19.5

^a All energies in kcal mol⁻¹.^b $\Delta H_f^0(g)$ are MM1 values reported in Ref. 14.^c From MM1 $\Delta H_f^0(g)$, not from experimental $\Delta H_f^0(g)$.^d The difference between $\sum_{i=1}^k N_i X_i$ and the observed BSE.^e Ref. 14.

Table 5. Calculations of resonance energies for aromatic hydrocarbons^a

Molecular formula	Molecule	ΔH_f° (g) ^b	BSE _{obsd}	$\sum_{i=1}^k N_i X_i$	RE ^c
C ₆ H ₆	Benzene	19·81 ^d	64·16	32·16	32·00
C ₁₀ H ₈	Naphthalene	35·92	119·57	65·46	54·11
C ₁₂ H ₁₀	Biphenyl	43·57 ^e	139·91	76·18	63·73
C ₁₄ H ₁₀	Anthracene	55·19	171·82	98·76	73·06
C ₁₄ H ₁₀	Phenanthrene	49·59	177·42	98·76	78·66
C ₁₆ H ₁₀	Pyrene	53·94	216·60	121·34	95·26
C ₁₈ H ₁₂	Naphthacene	69·65	228·88	132·06	96·82
C ₁₈ H ₁₂	3,4-Benzphenanthrene	70·03	228·50	132·06	96·44
C ₁₈ H ₁₂	1,2-Benzanthracene	69·60	228·93	132·06	96·87
C ₁₈ H ₁₂	Chrysene	62·80 ^d	235·73	132·06	103·67
C ₁₈ H ₁₂	Triphenylene	61·90 ^d	236·63	132·06	104·57
C ₂₀ H ₁₂	Perylene	73·7 ^d	268·36	154·64	113·72
C ₂₄ H ₁₈	1,3,5-Triphenylbenzene	87·83	294·67	164·22	130·45
C ₂₈ H ₁₈	9,9'-Bianthracene	108·58	360·98	209·38	151·60

^a All energies in kcal mol⁻¹.

^b ΔH_f° (g) values from Ref. 12 unless specified otherwise.

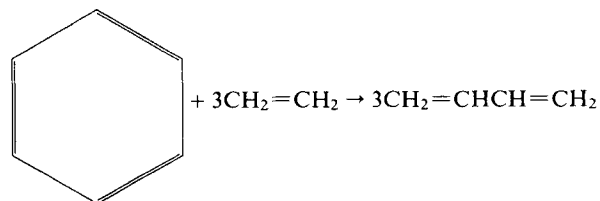
^c Resonance energy (RE) = -SE = $\sum_{i=1}^k N_i X_i$ - BSE_{obsd}.

^d Ref. 3.

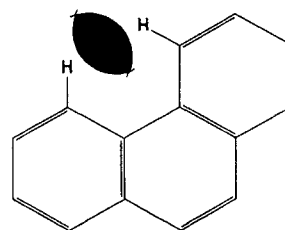
^e Ref. 15.

of hydrogenation or heats of combustion¹⁷ (RE_H). For example, the RE of benzene is the difference between the observed heat of hydrogenation of benzene and three times the heat of hydrogenation of a reference compound, cyclohexene. In both benzene and cyclohexene the configuration around the double bonds is *cis*. In bond separation reactions, the double and single bonds in benzene are isolated into ethylene and ethane molecules. Therefore, to compare the RE obtained via BSE with RE_H, a *cis* correction must be made to the RE calculated via BSE. Since the destabilization of *cis*-2-butene relative to *trans*-2-butene is 1 kcal mol⁻¹, 3 kcal mol⁻¹ per benzene ring should be added to the RE obtained from the BSE to be compared with RE_H. Such calculations were done and the results are listed in Table 6; a good correspondence is found between the two sets of results.

Dewar resonance energy (DRE) is usually calculated from heats of atomization.⁸ Dewar developed parameters to reproduce experimental heats of atomization and also reported parameters for calculating the heats of atomization of molecules which do not have alternative resonance forms.⁸ The difference between the calculated atomization energies for an aromatic molecule by the two sets of parameters then gives the DRE. The DRE differs from the PPP and SPO resonance energies in one respect: in the former the single C—C bonds in Kekulé structures is considered to be purely single, whereas in the others it is not. Therefore, DRE could be considered as the ΔH of a balanced reaction of the aromatic molecule with ethylene to produce 1,3-butadiene. For example, the DRE of benzene is the ΔH of the reaction



The observed and reported DRE for several aromatic hydrocarbons are listed in the last two columns of Table 6; both sets are similar, especially in the absence of steric interactions of the type indicated in the formula shown. With the exception of benzene and naphthalene,



there are differences between the experimental and the reproduced heats of atomization. Therefore, the reported DRE values were recalculated using the experimental rather than the reproduced heats of atomization. The DRE can also be obtained from the present equivalents by subtraction of the conjugation energy from the resonance energy. The conjugation energy is obtained by multiplying the number of C—C single bonds by 3·61, which is the stabilization energy of butadiene. The DREs obtained in this way are listed

Table 6. Comparison of the reported resonance energies of aromatic hydrocarbons with those calculated via equation (3)^{a,b}

Molecule	Equation (3)	RE _H			DRE			
		PPP ^c	SPO ^c	This work ^d	Reported ^e	This work ^f	Obsd ^g	Reported ^h
Benzene	32.0	30.39	30.39	35.0	36.0	21.17	21.17	20.04
Naphthalene	54.11	52.62	52.58	60.11	61.0	32.45	32.38	30.51
Biphenyl	63.73			69.73	71.0			
Anthracene	73.06	71.17	70.98	82.06	83.5	40.57	40.43	37.82
Phenanthrene	78.66	79.68	79.19	87.66	91.3	46.17	46.03	44.12
Pyrene	95.26	92.43	91.62	107.26		55.55	55.34	48.01
Naphthacene	96.82	88.42	87.93	108.82	110.0	53.5	53.29	52.39
3,4-Benzphenanthrene	96.44	104.93	104.23	108.44	109.6	53.12	52.91	50.46
1,2-Benzanthracene	96.87	99.83	99.32	108.87	111.6	53.55	53.34	54.91
Chrysene	103.67	105.0	104.05	115.67	116.5	60.35	60.14	56.34
Triphenylene	104.57	110.51	109.08	116.57	117.7	61.25	61.04	57.05
Perylene	113.72	118.07	116.76	128.72		63.18	62.90	57.86
1,3,5-Triphenylbenzene	130.45			142.45	148.9			
9,9'-Bianthracene	151.60			169.60	170.3			

^aAll energies in kcal mol⁻¹.^bRE, resonance energy; DRE, Dewar RE; RE_H, RE obtained either via hydrogenation or heat of combustion; PPP, Pople-Pariser-Parr; SPO: split p-orbitals.^cReported in Ref. 16.^dObtained from equation (3) with alkene *cis* corrections (see text).^eReported in Ref. 17.^fObtained from equation (3) with corrections for conjugation (see text).^gThe enthalpy change of a balance reaction between the aromatic compound with ethylene to produce 1,3-butadiene.^hReported in Ref. 8. However, with the exception of benzene and naphthalene, the reported values were recalculated using the experimental rather than the reproduced heats of atomization.

Table 7. Calculations of stabilization (destabilization) energies of polyenes^a

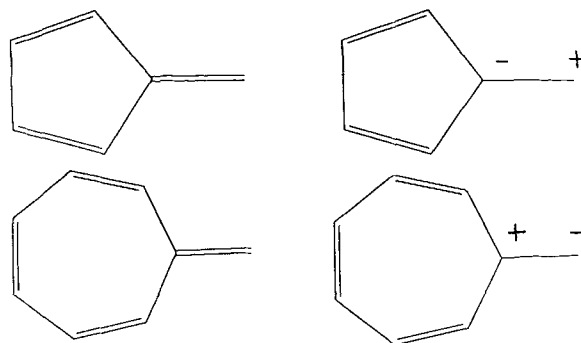
Molecular formula	Molecule	$\Delta H_f^\circ(\text{g})^b$	BSE		SE
			Obsd	Calc.	
C ₄ H ₄	Cyclobutadiene	102.2 ^c	-46.22	21.44	67.66
C ₄ H ₆	1,3-Butadiene	26.11	14.33	10.72	-3.61
C ₅ H ₆	1,3-Cyclopentadiene	31.94	21.69	24.19	2.5
C ₅ H ₈	1, <i>cis</i> -3-Pentadiene	19.13	18.96	16.15	-2.81
C ₅ H ₈	1, <i>trans</i> -3-Pentadiene	18.12	19.97	16.15	-3.81
C ₅ H ₈	1,4-Pentadiene	25.25	12.84	13.47	0.63
C ₅ H ₈	2-Methyl-1,3-butadiene	18.06	20.03	16.72	-3.31
C ₆ H ₆	Fulvene	47.5 ^d	36.47	32.73	-3.74
C ₆ H ₈	1,3-Cyclohexadiene	25.38	25.90	26.94	1.04
C ₆ H ₈	1,4-Cyclohexadiene	26.3	24.89	26.94	2.05
C ₆ H ₁₀	1,5-Hexadiene	20.11	15.63	16.22	0.59
C ₆ H ₁₀	2,3-Dimethyl-1,3-butadiene	10.78	24.96	22.72	-2.24
C ₇ H ₈	1,3,5-Cycloheptatriene	43.90	37.72	34.91	-2.81
C ₇ H ₁₀	1,3-Cycloheptadiene	22.56	26.37	29.69	3.32
C ₈ H ₈	Cyclooctatetraene	71.13	40.83	42.88	2.05
C ₈ H ₈	Heptafulvene	57 ^d	55	43	-12
C ₈ H ₁₀	1,3,5-Cyclooctatriene	43.7 ^e	35.57	37.66	2.09
C ₈ H ₁₀	Dimethylfulvene	32.1	47.17	44.16	-3.01
C ₁₀ H ₈	Azulene	69.1 ^f	86.39	65.46	-20.93
C ₁₈ H ₁₈	[18]Annulene	124.0 ^g	127.91	96.48	-31.43

^aAll energies in kcal mol⁻¹.^b $\Delta H_f^\circ(\text{g})$ values were taken from Ref. 3 unless specified otherwise.^cFrom Ref. 18.^dReported in Ref. 19.^eReported in Ref. 10.^fRef. 12.^gReported in Ref. 15.

in Table 6 and are in agreement with the other DRE values.

The stabilization (destabilization) energies of 20 polyenes were also calculated and are presented in Table 7. The results show that cyclobutadiene has a destabilization energy of 67.66 kcal mol⁻¹, as resulted from its 6.31G* (RMP2) heat of formation (102.2 kcal mol⁻¹) as reported in Ref. 18. The stabilization of 1,3-butadiene via the heat of hydrogenation is reported¹⁷ to be 3.5 kcal mol⁻¹, which agrees with the calculated value of 3.61 kcal mol⁻¹ (Table 7). The calculations via the equivalents show that fulvene, dimethylfulvene and heptafulvene are stabilized, which reflects the resonance shown in the formulae. However, the stabilization energies of these systems are not as important as those for non-benzoid aromatic hydrocarbons, such as azulene and [18]annulene. The difference between the stabilization energies of 1,*cis*-3-pentadiene and the *trans* isomer is 1 kcal mol⁻¹, which agrees with the *cis* correction in alkenes proposed by Benson *et al.*^{7,20}

To conclude, the developed equivalents are able to reproduce the stabilization, destabilization, olefin strain and resonance energies from experimental BSEs for a large number of hydrocarbons.



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