Homodesmotic Reactions for the Assessment of Stabilization Energies in Benzenoid and Other Conjugated Cyclic Hydrocarbons

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New homodesmotic reactions are designed that provide an alternative basis for evaluating stabilization energies of benzenoid and other conjugated cyclic hydrocarbons. As in previous cases, carbon–carbon bonds are matched in the sense of having equal numbers of C_{sp^2}–C_{sp^2}. C_{sp^2}=C_{sp^2}. C_{sp^2}–C_{sp^3}. *etc.* bonds in reactants and products. while simultaneously the various carbon–hydrogen bonds are matched as closely as possible. By minimizing extraneous energy contributions to the reaction heat arising from changes in hybridization and C–H bonding. such reactions single out those structural features resulting in stabilization. These new reactions have the advantage that experimental $\Delta H_f°$ data is currently available for the necessary reactant molecules. thus allowing an explicit evaluation of the homodesmotic stabilization energy to be made. which is compared to quantum theoretical calculations wherever possible.

In previous papers we showed how the enthalpy changes for a particular kind of reaction, which we termed homodesmotic, can be utilized as a measure of the stabilization that characterizes benzenoid hydrocarbons, and the destabilization that characterizes cycloparaffins, cyclic mono-olefins, *etc.*[1,2] The term homodesmotic denotes reactions in which (1) there are equal numbers of each type of carbon–carbon bond (C_{sp^3}–C_{sp^3}, C_{sp^2}–C_{sp^3}, C_{sp^2}–C_{sp^2}, C_{sp^2}=C_{sp^2}, *etc.*) in reactants and products, and (2) there are equal numbers of each type of carbon atom (C_{sp^3}, C_{sp^2}, *etc.*) with zero, one, two, and three hydrogen atoms attached in reactants and products. In these reactions, extraneous energy contributions arising from changes in hybridization and C–H bonding are minimized and structural features resulting in stabilization or destabilization are thus singled out. With similar criteria specified for the hybridization of heteroatoms and the type of heteroatom–carbon bonding, homodesmotic reactions have been designed for the formation of acyl compounds and related structures from simpler molecules, and the enthalpy changes have been calculated as a measure of their stabilization energies.[3]

This paper deals with the design of new homodesmotic reactions for treating polycyclic benzenoid hydrocarbons and other conjugated cyclic hydrocarbons that also contain quaternary C_{sp^2} carbon atoms. Numerical values of the homodesmotic stabilization energies (HSE) are calculated from experimental $\Delta H_f°$ data for 26 compounds. Where the data are available, *viz.* for benzene and to a lesser extent for naphthalene, the HSE values are compared with theoretical evaluations of the reaction heats (HMOSE) based on quantum theoretical computations of $\Delta H_f°$ for the reactants and products, and on *ab initio* calculations of their total molecular energies.

The definition of a *homodesmotic* reaction has been given above. Reactions in which the matching of structural elements is restricted to the number of bonds of a given formal type (without regard to the hybridization of the carbon atoms or the number of hydrogen atoms attached to them) are termed *isodesmic*. For example, the reduction of benzene by methane, the ' bond separation ' reaction of Hehre *et al.*,[4] is isodesmic as is

$$C_6H_6 + 6CH_4 \longrightarrow 3CH_2{=}CH_2 + 3CH_3{-}CH_3 \qquad (1)$$

the formation of naphthalene from butadiene in our previous paper [1] although there is a far greater mismatch

$$6CH_2{=}CH{-}CH{=}CH_2 \longrightarrow C_{10}H_8 + 7CH_2{=}CH_2 \qquad (2)$$

in the C–H bonding in the bond separation reaction (1) than there is in the formation reaction (2).

Benzene, on the other hand, with no quaternary carbon atoms, is formed from butadiene in a truly homodesmotic reaction (3). Homodesmotic reactions are, in

$$3CH_2{=}CH{-}CH{=}CH_2 \longrightarrow C_6H_6 + 3CH_2{=}CH_2 \qquad (3)$$

fact, a special subdivision of isodesmic reactions. All homodesmotic reactions are isodesmic, but few isodesmic reactions are homodesmotic. The extent of matching of structural elements in these reactions of benzene and naphthalene, and also in other reactions that have been utilized to determine stabilization energies, is discussed later.

Design of Homodesmotic Reactions for the Formation of Benzenoid and Other Cyclic Conjugated Hydrocarbons containing Quaternary C_{sp^2} *Carbon Atoms.*—In ref. 1 homodesmotic formation reactions were set up using reactants that contained only C_{sp^2} carbon atoms, so that the entire reaction involved only carbon atoms in this state of hybridization. In the case of the polycyclic benzenoid hydrocarbons, and also fulvene and azulene, which contain quaternary C_{sp^2} carbon atoms, it was therefore necessary to employ one of the vinyl substituted ethylenes to provide this type. For example, naphthalene or its isomer azulene are formed from buta-1,3-diene and divinylethylene (2-vinylbuta-1,3-diene) in reaction (4).

$$2CH_2{=}CH{-}CH{=}CH_2 + 2(CH_2{=}CH)_2C{=}CH_2 \longrightarrow C_{10}H_8 + 5CH_2{=}CH_2 \qquad (4)$$

But $\Delta H_f°$ has not yet been determined for any of the

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[1] P. George, M. Trachtman, C. W. Bock, and A. M. Brett, *Theor. Chim. Acta*, 1975, **38**, 121.

[2] P. George, M. Trachtman, C. W. Bock, and A. M. Brett, *Tetrahedron*, 1976, **32**, 317.

[3] P. George, M. Trachtman, C. W. Bock, and A. M. Brett, in preparation.

[4] W. J. Hehre, R. Ditchfield, L. Radom, and J. A. Pople, *J. Amer. Chem. Soc.*, 1970, **92**, 4796.

vinyl-substituted ethylenes, so it becomes important to set up an alternative homodesmotic reaction for which the necessary data are available. This can be done by utilizing isobutene to furnish the quaternary C_{sp^2} carbon atom as in reaction (5).

$$6CH_2{=}CH{-}CH{=}CH_2 + 2CH_2{=}C(CH_3)_2 \longrightarrow C_{10}H_8 + 5CH_2{=}CH_2 + 4CH_2{=}CHCH_3 \quad (5)$$

Although this reaction now involves both C_{sp^2} and C_{sp^3} carbon atoms, it fulfills the conditions for a homodesmotic reaction. The advantages of defining stabilization energies *via* homodesmotic reactions have been reported previously[1,3] and are discussed later.

Any number of other reactions could be set up with a similarly substituted olefin. Reaction (5), however, has the advantage that it employs the simplest olefin having the required quaternary carbon atom, and for which theoretical computations of $\Delta H_f°$ have already been made[5-8] so a comparison of theoretical with experimental stabilization energies can be carried out. Moreover, isobutene is a 32-electron structure, hence *ab initio* calculations of its total molecular energy in the same basis set(s) as the other reactants and products is entirely feasible, which would enable further very informative comparisons of theoretical and experimental values to be made.

ISE and HSE Values for Polycyclic Benzenoid Hydrocarbons and Other Conjugated Cyclic Hydrocarbons.—Tables 1 and 2 list isodesmic stabilization energy (ISE) and HSE values calculated using $\Delta H_f°$ data largely from Cox and Pilcher.[9]

The isodesmic reactions that utilize only butadiene are given by the general equation (6)[1] while the homodesmotic reactions, in which isobutene is used to furnish the quaternary carbon atoms, are given by (7).

$$\left(\frac{2a-b}{2}\right) C_4H_6 \longrightarrow C_aH_b + \left(\frac{3a-2b}{2}\right) C_2H_4 \quad (6)$$
$$\Delta H° = -\mathrm{ISE}$$

$$\left(\frac{2a-b}{2}\right) C_4H_6 + (a-b)C_4H_8 \longrightarrow C_aH_b + \frac{a}{2} C_2H_4 + 2(a-b)C_3H_6 \quad (7)$$
$$\Delta H° = -\mathrm{HSE}$$

As would be expected, increasing the complexity of the polycyclic structure with a concomitant increase in the number of quaternary carbon atoms causes the ISE values to diverge more and more from the HSE values. Thus for the series naphthalene, anthracene, tetracene, and perylene, in which the number of quaternary carbon atoms increases from 2 to 4, to 6, to 8, the ISE values exceed the HSE values by 3.2, 6.2, 9.4, and 12.5 kcal mol^{-1}, respectively. These diverging values originate in the following way. Taking the difference between the ISE and HSE values is equivalent to evaluating the enthalpy change for the combined reaction obtained by subtracting reaction (6) from (7) *i.e.* $(a-b)[CH_2{=}CH_2 + CH_2{=}C(CH_3)_2 \longrightarrow 2CH_2{=}CHCH_3]$. A direct calculation of $\Delta H°$ for the unit reaction per quaternary carbon atom, within the square bracket, from the $\Delta H_f°$ values for ethylene, isobutene, and propene gives 1.57 ± 0.57 kcal mol^{-1}. Hence the increments in the above series naphthalene, anthracene, tetracene, and perylene are 2, 4, 6, and 8 times $\Delta H°$ for this reaction. A quantitative measure of the alteration in binding energy associated with the mismatch in the bonding in the isodesmic reaction for the formation of conjugated cyclic hydrocarbons is thus afforded by $\Delta H°$ for the disproportionation of methyl groups and hydrogen atoms attached to the C_{sp^2} carbons of an olefinic double bond.

TABLE 1

Stabilization energies for various polycyclic benzenoid hydrocarbons evaluated as $\Delta H°$ for the isodesmic bond separation reaction (8) as $-\Delta H°$ for the isodesmic formation reaction from buta-1,3-diene (6) and as $-\Delta H°$ for the homodesmotic formation reaction from buta-1,3-diene and isobutene (7)[a]

	Isodesmic reactions		Homodesmotic reaction
Compounds	(8) IBSE = ΔH_0	(6) ISE = $-\Delta H°$	(7) HSE = $-\Delta H°$
Benzene	64.2 ± 1.2	21.2 ± 0.9	21.2 ± 0.9
Naphthalene	119.4 ± 2.3	33.5 ± 1.9	30.3 ± 2.6
Biphenyl[b]	141.4 ± 3.0	41.0 ± 2.5	37.9 ± 3.2
Anthracene	171.8 ± 4.1	42.8 ± 3.6	36.6 ± 5.0
Phenanthrene[b]	178.2 ± 4.1	49.2 ± 3.6	43.0 ± 5.0
Pyrene	220.6 ± 4.3	63.0 ± 3.7	53.6 ± 5.9
Tetracene	228.7 ± 5.1	56.8 ± 4.4	47.4 ± 6.6
Benzo[*c*]phenanthrene[b]	233.3 ± 5.2	61.4 ± 4.5	52.0 ± 6.7
Benz[*a*]anthracene[b]	232.5 ± 5.2	60.6 ± 4.5	51.2 ± 6.7
Chrysene[b]	237.1 ± 5.2	65.2 ± 4.5	55.8 ± 6.7
Triphenylene[b]	238.7 ± 5.1	66.8 ± 4.4	57.4 ± 6.6
Perylene[b]	269.7 ± 6.8	69.1 ± 5.0	56.6 ± 8.0
1,3,5-Triphenylbenzene[b]	298.7 ± 6.8	83.8 ± 5.8	74.3 ± 8.0
Graphite (C_2)	40.3 ± 0.9	11.7 ± 0.8	8.5 ± 1.6

[a] Heat of formation values taken from Cox and Pilcher[9] except for benz[*a*]anthracene, which is from A. Magnus, H. Hartman, and F. Becker, *Z. phys. Chem.*, 1951, **197**, 75, and for graphite, where the value per carbon atom in a single infinite sheet is based on an interaction energy of 1.61 ± 0.12 kcal per carbon atom.[11] [b] $\Delta H_f°$ corrected for steric hindrance: biphenyl 1.4; phenanthrene 0.7; 3-benzo[*c*]phenanthrene 4.4; triphenylene 2.1; perylene 1.4; and 1,3,5-triphenylbenzene 4.2 kcal mol^{-1} respectively.[11]

The general isodesmic bond separation reaction[4] is (8). Using current $\Delta H_f°$ data[9] the isodesmic bond separation energy (IBSE) for benzene is 64.16 ± 1.21 kcal mol^{-1}, far larger than the HSE of 21.17 ± 0.88 kcal

$$C_aH_b + (2a-b)CH_4 \longrightarrow \frac{a}{2} C_2H_4 + \left(\frac{2a-b}{2}\right)C_2H_6 \quad (8)$$
$$\Delta H° = \mathrm{IBSE}$$

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[5] M. J. S. Dewar, 'The Molecular Orbital Theory of Organic Chemistry,' McGraw-Hill, New York, 1969, ch. 10.

[6] N. C. Baird and M. J. S. Dewar, *J. Chem. Phys.*, 1969, **50**, 1262.

[7] M. J. S. Dewar and E. Hasselbach, *J. Amer. Chem. Soc.*, 1970, **92**, 590.

[8] R. C. Bingham, M. J. S. Dewar, and D. H. Lo, *J. Amer. Chem. Soc.*, 1975, **97**, 1294.

[9] J. D. Cox and G. Pilcher, 'Thermochemistry of Organic and Organometallic Compounds,' Academic Press, New York, 1970.

mol^{-1}. This feature is even more pronounced for bigger molecules, see Tables 1 and 2. In the most extreme case reported here, 1,3,5-triphenylbenzene, IBSE is 298.7 ± 6.8 compared to the HSE value of 74.3 ± 8.0 kcal mol^{-1}. These very striking differences can again be correlated with the change in hybridization of the carbon atoms and the alteration in the character of the C–H bonding from the point of view of the hybridization of the carbon and the number of hydrogens attached to individual carbon atoms, in the bond separation reaction. For benzene the difference between the IBSE and HSE values amounts to $\Delta H°$ for reaction (9). $\Delta H°$ is +42.99 kcal mol^{-1}, in which the change in hybridization of the

$$3CH_2{=}CH{-}CH{=}CH_2 + 6CH_4 \longrightarrow 6CH_2{=}CH_2 + 3CH_3{-}CH_3 \quad (9)$$

carbon–carbon single bonds ($C_{sp^2}{-}C_{sp^2} \longrightarrow C_{sp^3}{-}C_{sp^3}$) and the alteration in the character of the C–H bonding ($C_{sp^3}{-}H \longrightarrow C_{sp^2}{-}H$) can be clearly seen.

TABLE 2

Stabilization energies for various conjugated cyclic hydrocarbons evaluated as $\Delta H°$ for the isodesmic bond separation reaction (8), as $-\Delta H°$ for the isodesmic formation reaction from buta-1,3-diene (6), and as $-\Delta H°$ for the homodesmotic formation reaction from buta-1,3-diene and isobutene (7) [a]

	Isodesmic reactions		Homodesmotic reaction
Compound	(8) IBSE = $\Delta H°$	(6) ISE = $-\Delta H°$	(7) HSE = $-\Delta H°$
Benzene	64.2 ± 1.2	21.2 ± 0.9	21.2 ± 0.9
Cyclo-octatetraene [d]	40.8 ± 1.8 [e]	−16.5 ± 1.3	−16.5 ± 1.3
[18]annulene	190.9 ± 7.2	61.9 ± 6.3	61.9 ± 6.3
Styrene	76.7 ± 1.7	19.3 ± 1.3	17.8 ± 1.6
trans-Stilbene [b]	159.8 ± 3.0	45.1 ± 2.3	42.0 ± 3.1
trans,trans-1,4-Diphenylbuta-1,3-diene [c]	175.7 ± 3.4	46.8 ± 2.7	43.6 ± 3.4
Acenaphthylene [d]	137.4 ± 3.9 [e]	28.7 ± 3.6	22.4 ± 4.9
Fluoranthene [d]	200.8 ± 4.2 [e]	49.0 ± 3.6	39.6 ± 5.8
Biphenylene [d]	83.8 ± 4.2 [e]	−30.8 ± 3.7	−37.1 ± 5.2
Azulene [d]	82.0 ± 3.0 [e]	8.3 ± 2.5	5.2 ± 3.2
Fulvene [d]	39.7 ± 2.8 [e]	2.6 ± 2.5	1.1 ± 2.8
Heptafulvene [d]	54.4 ± 2.9 [e]	3.5 ± 2.5	1.9 ± 2.9
Heptafulvalene [d]	107.7 ± 4.3 [e]	5.8 ± 3.6	2.7 ± 4.3

[a] $\Delta H_f°$ Data taken from Cox and Pilcher,[9] with the following exceptions. $\Delta H_f°$ (fulvene) calculated from the value for dimethylfulvene, +32.1 ± 1.3 kcal mol^{-1}, using the increment $\Delta H_f°$ [$(CH_3)_2C{=}C(CH_3)_2$] − $\Delta H_f°$ [$(CH_3)_2C{=}CH_2$] = (−16.42 ± 0.25) − (−4.26 ± 0.15) = −12.16 ± 0.40, giving +32.1 ± 1.3 + 12.16 ± 0.4 = +44.26 ± 1.7 kcal mol^{-1}. $\Delta H_f°$ Values for heptafulvene and heptafulvalene were calculated from heat of hydrogenation data in diethylcarbitol solution [18] assuming (i) that the values would be the same in the gas phase, and (ii) $\Delta H_f°$ values for the reduced compounds based on Cox and Pilcher's $\Delta H_f°$ structural parameters and 6.2 kcal mol^{-1} for the strain energy in the seven-membered ring(s), *i.e.* $\Delta H_f°$ (C_8H_{18}) = −35.13 and $\Delta H_f°$ ($C_{14}H_{26}$) = −27.04 kcal mol^{-1}. [b] $\Delta H°_{subl}$ for *trans*-stilbene taken to be 19.0 kcal mol^{-1}, nearer that for 1,2-diphenylethane, 20.1 kcal mol^{-1}, instead of the 16.5 kcal mol^{-1} for the *cis*-isomer,[9] in view of the greater structural similarity to the former. [c] $\Delta H°_{subl}$ for *trans,trans*-1,4-diphenylbuta-1,3-diene taken to be 21 kcal mol^{-1}. [d] Conventional ring strain energy corrections made: 5.91, 6.37, 5.91 + 6.37 = 12.28, and 2(6.37) = 12.74 for the 5, 7, (5 + 7), and (7 + 7) membered ring systems respectively, based on the values for cyclopentadiene and cyclohepta-1,3-diene. These values, 5.91 and 6.37, were calculated from the heats of atomization, taking $E(C_d{-}C_d)$ = 98.27 obtained from $\Delta H_a°$ (buta-1,3-diene) and Cox and Pilcher's values [9] for the bond energy terms $E(C{=}C)$, $E(C_d{-}H)_1$, and $E(C_d{-}H)_2$. This value for $E(C_d{-}C_d)$ thus includes any stabilisation energy there may be in the acyclic structure. [e] No corrections have been made for ring strain energies.

HSE Values for Particular Compounds.—It should be emphasized that while energy contributions arising from changes in the hybridization of the carbon, and from changes in the nature and number of the C–H bonds, have been minimized in setting up the homodesmotic reactions, the HSE values are nevertheless a measure of stabilization relative to that of the number of *trans*-buta-1,3-diene molecules involved in the reactions. Stabilization due to π-electron delocalization and concomitant changes in σ-bonding is generally believed to be far smaller for butadiene and acyclic polyenes than for benzene.[10] Studies are in progress to throw further light on this crucial issue. This proviso, however, must be borne in mind throughout the following discussion.

First, with regard to the polycyclic benzenoid hydrocarbons, we see that the new HSEs show similar correlations with simple structural characteristics as do the classical empirical resonance energies (RE_{II} of ref. 11) calculated on the basis of heats of hydrogenation. For example, there is the approximately linear relationship with the number of formal double bonds in the Kekulé structures: for the 13 compounds listed in Table 1 the mean RE_{II} per double bond is 10.8,[11] compared with a mean HSE of 6.1 with standard errors of 0.13 and 0.15 kcal mol^{-1} respectively. Moreover the same compounds show the greatest individual deviations.

Likewise there is a rough correlation between RE_{II} values, or the new HSE values, and the type of structure when it is considered not as being constituted of alternate double and single bonds, but as aromatic sextets,[12] together with one or more bridging groups, –CH=CH–, that are more aliphatic in character.[13] For example benzene, naphthalene, anthracene, and tetracene constitute a family with one sextet, phenanthrene, benz[*a*]anthracene, benzo[*c*]phenanthrene, and chrysene a family with two, and so on. Other things being equal, the greater the number of sextets the greater the HSE or RE_{II} value, *e.g.* see the values for the isomeric structures.

But, at best, any correlations such as the above are semi-quantitative because there is no exact correspondence in bond length from one structure to another. On the one hand, there is a range of values for the formal $C_{sp^2}{=}C_{sp^2}$ and $C_{sp^2}{-}C_{sp^2}$ bonds of the Kekulé structures, while on the other, the aromatic sextets in the polycyclic structures not only lack the hexagonal symmetry of benzene, but differ in their geometry from one compound to another.

Turning now to the more diverse structures whose

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[10] M. J. S. Dewar and N. N. Schmeising, *Tetrahedron*, 1959, **5**, 166.

[11] P. George, *Chem. Rev.*, 1975, **75**, 85.

[12] R. Robinson, in ' Aromaticity, Chem. Soc. Special Publication, No. 21,' 1967, p. 47.

[13] E. Clar, ' Polycyclic Hydrocarbons,' Academic Press, New York, 1964.

HSE values are listed in Table 2, and recalling that the numerical magnitudes are relative to *trans*-buta-1,3-diene as reference compound, the following features may be noted.

(i) The HSE values for *trans*-stilbene and for *trans,-trans*-1,4-diphenylbuta-1,3-diene are, within experimental uncertainty, twice that for benzene. So there would appear to be no enhancement of stabilization when two benzene rings are joined by a conjugated chain.

(ii) The HSE values for biphenyl and especially 1,3,5-triphenylbenzene are less than the sums for two and four benzene rings respectively, which can be attributed to the non-planarity of these structures in which the rings are tilted *ca.* 45° with respect to each other.

(iii) The HSE value for acenaphthylene, 22.4 kcal mol^{-1}, is substantially less than that for naphthalene, 30.3; and the value for fluoranthene, 39.6 kcal mol^{-1}, despite its being an (almost) planar structure[14,15] is substantially less than that for its constituent ring systems benzene and naphthalene, *i.e.* $21.2 + 30.3 = 51.5$. It may be noted that the five-membered ring, present in both these compounds, results in a further diminution in symmetry.*

(iv) The HSE value for cyclo-octatetraene, uncorrected for ring strain, of -16.5 kcal mol^{-1}, is indicative of net destabilization to this extent. Since the ring strain energy of 1,3,5-cyclo-octatriene is *ca.* 8—11 kcal mol^{-1},† that for cyclo-octatetraene is unlikely to be more than 6—9 kcal mol^{-1} greater, hence the HSE value of -16.5 is in line with the general belief, based upon the alternating C–C bond distance of 1.46 and 1.33 Å[16] that there is no significant bond delocalization in cyclo-octatetraene.

(v) With no correction for strain energy the HSE value for biphenylene is -37.1 kcal mol^{-1}, *i.e.* a net destabilization. Now if the two six-membered rings had the stabilization properties of benzene their contribution would be $2(21.2) = 42.4$ kcal mol^{-1}. Hence, with benzene as baseline, the effective destabilization in biphenylene amounts to $42.4 + 37.1 = 79.5$ kcal mol^{-1}. The strain in the central four-membered ring cannot be established with any certainty, but for the cyclic mono-olefin, cyclobutene, the strain energy is 30.0 kcal mol^{-1}.[9] Even for cyclopropene with greater bond angle distortion the value only rises to 53.8 kcal mol^{-1}. Hence it would appear that in biphenylene the six-membered rings stabilize the structure by an amount considerably less than that characteristic of two benzene rings. This is not altogether surprising since *X*-ray structure determinations have shown these rings to be quite deformed compared with benzene, with bond lengths $C(1)\text{–}C(2) = C(5)\text{–}C(6) = C(6)\text{–}C(1) = 1.38$, $C(2)\text{–}C(3) = C(4)\text{–}C(5) = 1.42$, and $C(3)\text{–}C(4) = 1.35$ Å, and bond angles $C(1)\widehat{C}(2)C(3) = C(4)\widehat{C}(5)C(6) = 114°$ and $C(2)\widehat{C}(3)C(4) = C(3)\widehat{C}(4)C(5) = C(5)\widehat{C}(6)C(1) = C(6)\widehat{C}(1)C(2) = 123°$.[17]

(vi) Turner *et al.*[18] who evaluated the resonance energy as the difference between the observed heat of hydrogenation and a value calculated for a non-resonating reference ring structure, determined resonance energies for azulene, heptafulvene, and heptafulvalene of 28, 13, and 28 kcal mol^{-1}, respectively. On the basis of the homodesmotic reaction, however, the values for fulvene, heptafulvene, and heptafulvalene are zero to within experimental error. The values for the last two compounds are less reliable, being derived from heats of hydrogenation in solution, but the correction for this is such as to diminish HSE still more, giving slightly negative values. Only for azulene is the HSE value indicative of some stabilization, but even this is quite small, about a sixth of that for its benzenoid isomer, naphthalene.

Comparison of Experimental and Theoretical Stabilization Energies.—The stabilization energies considered in this paper are those which, either directly or indirectly, can be identified as the heat for a particular reaction. Hence, in comparing theory with experiment, it is a question of evaluating reaction heats from theoretical calculations of ΔH_f° or the total molecular energies of reactants and products. No idealized structure of any kind enters into the calculations.

Semiempirical calculations. Dewar and his collaborators have reported the results of several semiempirical SCF-MO treatments of organic molecules which (1) include all valence electrons, (2) invoke either a partial neglect of differential overlap (PNDO) or an intermediate neglect of differential overlap (MINDO), and (3) are parametrized to allow the heats of formation of many moderately sized organic structures to be calculated.[5–8,19,20] Using these results we have evaluated reaction heats for several of the stabilization reactions (see Tables 1 and 2). For consistency we have evaluated the reaction heats only within a fixed set of ΔH_f° values.

A comparison of the theoretical and experimental results in Table 3 shows the following. (i) The theoretical results from PNDO are in extremely good agreement with experiment for both the isodesmic and homodesmotic reactions. (ii) The PNDO results are in better agreement with experiment than any of the versions of MINDO. (iii) The latter versions of MINDO (especially MINDO/3) are in many cases in worse agreement with

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* A correction of 5.91 kcal mol^{-1} for strain in the five-membered ring has been incorporated in the calculations: the uncertainty in this estimate is unlikely to be responsible for these appreciably lower HSE values.

† A value of 7.9 kcal mol^{-1} is obtained from ΔH_f° and 98.27 kcal mol^{-1} for the C_{sp^2}—C_{sp^3} bond calculated from ΔH_f° for buta-1,3-diene. This value may be *ca.* 2.7 kcal mol^{-1} too low on account of the ΔH_f° value being too favourable.

[14] G. Ferguson and J. M. Robertson, *Adv. Phys. Org. Chem.*, 1963, **1**, 203.

[15] C. Reid, *J. Mol. Spectroscopy*, 1957, **1**, 18.

[16] O. Bastiansen, L. Hedberg, and K. Hedberg, *J. Chem. Phys.*, 1957, **27**, 1311.

[17] T. C. W. Mak and J. Trotter, *J. Chem. Soc.*, 1962, 1.

[18] R. B. Turner, W. R. Meador, W. Von Doering, L. H. Knox, J. R. Mager, and D. W. Wiley, *J. Amer. Chem. Soc.*, 1957, **79**, 4127.

[19] R. C. Bingham and M. J. S. Dewar, *J. Amer. Chem. Soc.*, 1972, **94**, 9107.

[20] N. Bodor, M. J. S. Dewar, and D. H. Lo, *J. Amer. Chem. Soc.*, 1972, **94**, 5303.

experiment than the earlier versions. (iv) Theory is in better agreement with experiment for the homodesmotic reactions than the isodesmic reactions (note particularly PNDO and MINDO/3). This is certainly due in part to the enhanced cancellation of structural features inherent in the design of homodesmotic reactions.

TABLE 3

Comparison of experimental and theoretical stabilization energies (kcal mol^{-1}), evaluated using semi-empirical SCF-MO methods.[5-8, 19, 20] All values refer to 298 K

Stabilization reaction	Experimental value	Theoretical value				Improved MINDO/2			
		PNDO	MINDO/1	MINDO/C1	MINDO/2	I	II	III	MINDO/3
A Isodesmic bond separation									
Benzene	64.2 ± 1.2	58.7	68.0	78.0	36.2	49.5	76.9	50.8	7.2
Naphthalene	119.4 ± 2.3	106.8	128.6						−4.5
Azulene [a]	82.0 ± 3.0	72.6							
Cyclo-octatetraene [a]	40.8 ± 1.8								−10.1
B Isodesmic									
Naphthalene	33.5 ± 1.9	31.2	30.1						−0.3
Azulene [a]	−4.0 ± 2.5	−3.0			7.7 [b]				
C Homodesmotic									
Benzene	21.2 ± 0.9	20.9	15.5	42.8	18.5 [c]				9.3
Naphthalene	30.3 ± 2.6	30.6	25.1						17.1
Azulene [a]	−7.1 ± 3.2	−3.6							
Cyclo-octatetraene	−16.5 ± 1.3								−7.3

[a] No corrections have been made for ring strain energies. [b,c] Theoretical $\Delta H_f°$ values taken from Tables II and I of ref. 7, respectively.

Several other versions of semiempirical SCF calculations have also appeared in the literature. Wiberg,[21] using a modified version of the complete neglect of differential overlap (CNDO) treatment developed by Pople *et al.*,[22] calculated the ground state energies of several hydrocarbons, from which the heat of the isodesmic bond separation reaction for benzene can be calculated (see Table 4). We have also included in Table 4, a few results using the original INDO parametrization of Pople *et al.*[23] Not enough results are available, however, to make a telling comparison with the PNDO or MINDO results of Dewar *et al.*

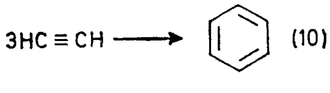
TABLE 4

Comparison of experimental and theoretical stabilization energies (kcal mol^{-1}) for benzene, evaluated using semi-empirical SCF-MO methods (CNDO, INDO).[21-23] All values refer to 0 K

Stabilization reaction	Experimental value [a]	Theoretical value	
		CNDO [b]	INDO [c]
A Isodesmic bond separation			
Benzene	61.1	72.7	89.1
B Homodesmotic			
Benzene	22.4		54.7

[a] Values at 298 K corrected to 0 K using ($H°_{298} - H°_0$) increments, with additional corrections for zero-point vibrational energies to give the reaction heats at 0 K for fixed nuclei. [b] Calculated using results of Wiberg [21] which involved a parameterization different from that of Pople *et al.*[22] [c] Calculated using a program available through the QCPE. Experimental geometries were used throughout.

Ab initio Calculations.—Using the ground state energies currently available from *ab initio* calculations, the homodesmotic stabilization energy and isodesmic bond separation energy of benzene have been evaluated. Only in the STO-3G, LEMAO-6G, and 4-31G basis sets of Hehre *et al.*[4,24] and the Gaussian lobe basis, FGGL, of Buenker and Peyerimhoff [25] have a sufficient number of energies been reported to calculate the reaction heats. The results (Table 5) are in reasonably good agreement with experiment. The agreement using the 4-31G basis set is, in fact, significantly better than the highly parametrized MINDO/3 treatment. However, it must be pointed out that such good agreement is certainly due, in part, to the cancellation of structural features in these reactions. Dewar has noted, for example that in reaction (10) which is neither homodesmotic nor isodesmic,



MINDO/3 is in much better agreement with experiment than 4-31G (and STO-3G) (see Table IV of ref. 8).

TABLE 5

Comparison of experimental and theoretical stabilization energies (kcal mol^{-1}) for benzene, evaluated using total molecular energies calculated in various *ab initio* basis sets.[4,24,25] A Homodesmotic reaction (3), $-\Delta H° =$ HSE; B isodesmic bond separation reaction (1), $\Delta H° =$ IBSE

Stabilization energy	Experimental value [a]	Theoretical value			
		STO-3G	LEMAO-6G	4-31G [b]	FGGL
A	22.4	36.2		26.8	39.7
B	61.1	72.0	78.5	65.2	

[a] Values at 298 K corrected to 0 K using ($H°_{298} - H°_0$) increments, with additional corrections for zero-point vibrational energies to give the reaction heats at 0 K for fixed nuclei. [b] We thank Dr. A. Komornicki for supplying us with the geometry optimized 4-31G benzene result.

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TABLE 6

Matching of structural elements in reactants and products in reactions used to evaluate stabilization energies for benzene and naphthalene (see text). A Isodesmic bond separation reaction;[4] B Dewar and Schmeising's ethane reduction reaction;[10] C empirical resonance energy reaction of Pauling[a] and Wheland[b] (see also Kistiakowsky *et al.*[c]); D isodesmic formation of naphthalene from buta-1,3-diene;[1] E homodesmotic formation of benzene from buta-1,3-diene;[1] F homodesmotic formation of naphthalene from buta-1,3-diene and divinylethylene;[1] G homodesmotic formation of naphthalene from buta-1,3-diene and isobutene

	Reaction	Equal numbers of C_{sp^2} and C_{sp^3} atoms	Equal numbers of $C_{sp^3}-C_{sp^3}$, $C_{sp^2}-C_{sp^3}$, $C_{sp^2}-C_{sp^2}$, and $C_{sp^2}=C_{sp^2}$ bonds	Equal numbers of carbon atoms with 0, 1, 2, 3, and 4 bonded H atoms	Equal numbers of H atoms bonded in CH_3-, $-CH_2-$, $>CH-$, $=CH_2$, and $=CH-$ groups
A	$C_6H_6 + 6CH_4 \longrightarrow 3CH_2=CH_2 + 3CH_3-CH_3$	Yes	No	No	No
B	$C_6H_6 + 3CH_3-CH_3 \longrightarrow C_6H_{12} + 3CH_2=CH_2$	Yes	No	No	No
C	$C_6H_6 + 2C_6H_{12} \longrightarrow 3C_6H_{10}$	Yes	No	Yes	Yes
D	$6CH_2=CH-CH=CH_2 \longrightarrow C_{10}H_8 + 7CH_2=CH_2$	Yes	Yes	No	No
E	$3CH_2=CH-CH=CH_2 \longrightarrow C_6H_6 + 3CH_2=CH_2$	Yes	Yes	Yes	Yes
F	$2CH_2=CH-CH=CH_2 + 2(CH_2=CH)_2C=CH_2 \longrightarrow C_{10}H_8 + 5CH_2=CH_2$	Yes	Yes	Yes	Yes
G	$6CH_2=CH-CH=CH_2 + 2CH_2=C(CH_3)_2 \longrightarrow C_{10}H_8 + 5CH_2=CH_2 + 4CH_2=CHCH_3$	Yes	Yes	Yes	Yes

[a] L. Pauling, ' The Nature of the Chemical Bond,' Cornell University Press, Ithaca, 1940, 2nd edn. [b] G. W. Wheland, ' Resonance in Organic Chemistry,' Wiley, New York, 1955, ch. 3. [c] G. B. Kistiakowsky, J. R. Ruhoff, H. A. Smith, and W. E. Vaughan, *J. Amer. Chem. Soc.*, 1935, **57**, 876; 1936, **58**, 137, 146.

General Aspects of the Matching of Structural Elements in Reactants and Products.—The reactions upon which other stabilization energies are based such as the empirical resonance energy, *etc.* have mismatched structural elements in comparison to homodesmotic reactions, which is one source of extraneous binding energy contributions. All these reactions are isodesmic, in that there are equal numbers of bonds of a given formal type in reactants and products, in this case carbon–carbon single and double bonds and carbon–hydrogen bonds, including, of course, the homodesmotic reaction. But closer examination shows that these other reactions are not all alike in the kind of mismatch.

In Table 6 various stabilization reactions are classified according to the four structural criteria set out at the top of columns 2—5. The first and second relate to the hybridization of the carbon atoms and the C–C bonding, and the third and fourth to the C–H bonding, according to the number of attached hydrogen atoms and the hybridization of the carbon. Reactions A and B, which lead to the IBSE and RE_I values,[11] respectively, are the most mismatched according to these criteria; reactions C and D which lead to RE_{II} [11] and ISE values, respectively, are less mismatched; while reactions E—G which furnish the HSE values, are completely matched according to all four criteria. Hence, leaving aside homodesmotic reactions, there are at least two other categories of isodesmic reaction.

However, even though both reactions we have employed to introduce quaternary C-atoms into the polycyclic structures, one (11) with isobutene and the other

$$\left(\frac{(2a-b)}{2}\right) C_4H_6 + (a-b)C_4H_8 \longrightarrow C_aH_b + \frac{a}{2}C_2H_4 + (a-b)C_3H_6 \quad (11)$$

(12) with divinylethylene meet the criteria for homodesmotic reactions according to our definition, there are nevertheless subtle structural differences between them.

$$(a-b)C_6H_8 + \left(\frac{3b-2a}{2}\right)C_4H_8 \longrightarrow C_aH_b + \frac{a}{2}C_2H_4 \quad (12)$$

While the C/C bonds are matched in terms of the hybridization states of the carbon atoms, there is a residual mismatch in the nearest neighbour carbon atoms around the quaternary carbon atoms. In the isobutene reaction there are two C_{sp^2} and one C_{sp^3} carbon atom around each quaternary carbon atom on the reactant side, compared to three C_{sp^2} carbon atoms on the product side whereas the divinylethylene reaction is perfectly matched in this respect. There are thus different categories of homodesmotic reactions too, and further subdivisions are to be expected if next nearest neighbour atoms are taken into account.

A systematic analysis of these principles which underlie the classification of organic reactions according to structural features is presently underway to establish the various classes.

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