Thermochimica Acta, 8 (1974) 225–237

THERMOCHEMICAL PARAMETERS FOR BENZENOID HYDROCARBONS

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(Received 12 July 1973)

ABSTRACT

The heats of atomization of aromatic hydrocarbons are correlated with an incremental 5-term scheme that includes C–H and C–C bond energy terms, resonance energies, and two steric parameters. Regression analysis of the experimental data with respect to the proposed parameters gives reasonable values for each term. A simple method for calculating resonance energies is illustrated that agrees with the results of SCF–LCAO–MO calculations.

INTRODUCTION

Thermochemical data for organic compounds have been summarized by Cox and Pilcher[1]. One finds that empirical parameters to calculate the heats of formation (ΔH_f°(g)) and heats of atomization (ΔH_a°(g)) of aliphatic hydrocarbons are well-established. Both bond-energy and group-increment methods have been refined to the point where agreement to within the estimated limits of experimental uncertainties is easily obtained. For example, a four-parameter group additivity scheme originally proposed by Benson et al.[2], combined with three steric correction terms gives ΔH_f° (g) for 46 saturated hydrocarbons to ± 0.20 kcal mole^{-1} (ref. 3). Quantum theory has had relatively little to do with the development of these enthalpy schemes. A recent graph theoretical analysis makes this point clear, and also graphically demonstrates the essential equivalencies of the several incremental schemes that have been proposed[4].

In contrast, empirical methods for estimating ΔH_f° (g) or ΔH_a° (g) of aromatic hydrocarbons are much less accurate, and theoretical calculations including quantum mechanical calculations have contributed relatively more to the understanding of stabilizing and destabilizing energy terms in these molecules. Destabilizing terms have been best explained on the basis of small out-of-plane and bond angle deformations arising from steric repulsions between non-bonded atoms[5,6]. Calculations based on modified Buckingham potential functions have given reasonable values for the magnitudes of these strain energies, which are of the order of 1–3 kcal per interaction[5].

The main stabilizing force, not found in aliphatic systems, is of course the resonance energy of the delocalized π-electronic system. This is a purely quantum-mechanical concept, and its estimation by non-quantum-mechanical methods would seem to be necessarily inaccurate. Resonance energies are also quite a bit larger than the steric terms referred to above[7], and should be relatively more important in a theoretical scheme to estimate the ΔH_f° (g). As a consequence, the most accurate calculations of ΔH_f° (g) of benzenoid hydrocarbons have been based on semi-empirical LCAO–SCF–MO methods as developed by Dewar and his co-workers[8,9], and Lo and Whitehead[10].

I have recently shown that one can obtain resonance energies for aromatic hydrocarbons that are of SCF quality by a valence-bond method that only requires enumeration of Kekulé structures and their mutual interactions[11]. The method is equivalent to "resonance theory" as applied in the study of elementary organic chemistry[7], and the calculations can be rapidly carried out by hand. Since these resonance energies are so easily obtained, they are used in this paper in conjunction with bond-energy and steric terms to devise methods to estimate ΔH_a° (g) for aromatic compounds.

The results of applying this method are of interest because the latest suggested bond energy scheme for these compounds postulates that the need to allow for resonance stabilization can be circumvented by proper choice of additive bond energy parameters[1]. In the Results and Discussion section, an attempt will be made to assess the intrinsic accuracy of such an approach, and several ways of calculating ΔH_a° (g) will be compared. The magnitudes of steric interactions will also be delineated, and lastly the calculations will provide an experimental thermochemical value for the valence-bond resonance integral to compare with the previously determined theoretical value[11]. This last point is of interest because SCF–MO values of resonance integrals[9] are much smaller than the traditional values used in standard texts of organic chemistry.

EXPERIMENTAL DATA

The most convenient thermodynamic quantity that can be related to the chemical binding energy of a molecule is the heat of atomization ΔH_a° (g), which can be calculated from experimentally known ΔH_f° (g) through eqn (1).

$$\Delta H_a^\circ (g)(C_nH_m) = n\Delta H_f^\circ (g)(C) + m\Delta H_f^\circ (g)(H) - \Delta H_f^\circ (g)(C_nH_m) \qquad (1)$$

The standard heats of formation for gaseous atoms used in this work were the values cited by Cox and Pilcher[1]; ΔH_f° (g)(298.15°)(C) = 170.90 kcal, ΔH_f° (g)(298.15°)(H) = 52.10 kcal. Unfortunately, there are not a large number of accurately determined ΔH_f° (g) for aromatic hydrocarbons. Table 1 is a list of all benzenoid compounds for which experimental values of ΔH_f° (g) are known[1]. The experimental uncertainties associated with the cited values for benzene and naphthalene are of the order of 0.3 kcal or less. However, the remaining compounds have larger uncertainties in ΔH_f° (g) of the order of 1 kcal or more due mostly to imprecisely known heats of vaporization ΔH_v°.

TABLE 1

ΔH_f° AND ΔH_a° (kcal) FOR AROMATIC HYDROCARBONS (297.15°)

Compound	ΔH_f° *(l or c)*	ΔH_v°	ΔH_f° *(g)*	ΔH_a° *(g)*	*Ref.*[a]
1 Benzene	11.72	8.09	19.81	1318.19	
2 Naphthalene	18.58	17.22	35.80	2090.00	1, 12
3 Anthracene	30.88	23.50	54.38	2859.22	1, 13
4 Phenanthrene	27.77	21.72	49.49	2864.11	1, 12
5 Tetracene	37.95	29.8	67.75	3633.65	
6 Benz[a]anthracene	40.83	25.14[b]	65.97	3635.43	
7 Benzo[c]phenanthrene	44.19	25.4	59.59	3631.81	
8 Chrysene	34.72	28.1	62.82	3638.58	
9 Triphenylene	33.72	28.2	61.92	3639.48	
10 Pyrene	27.44	22.5	49.94	3205.46	
11 Perylene	43.69	30.0	73.69	3969.51	
12 Biphenyl	24.03	19.54	43.57	2528.23	1, 12
13 1,3,5-Triphenylbenzene	53.69	34.3	87.99	4951.39	
14 9,10-Diphenylanthracene	73.78	37.5	111.28	5269.92	
15 9,9'-Bianthryl	77.97	30.6	108.57	5614.43	
16 5,6,11,12-Tetraphenyl-tetracene	148.2	38.4	186.6	8450.0	

[a] The first reference number in each row refers to the ΔH_f°, and the second to ΔH_v°. If no reference numbers are listed the values were obtained from the compilation of Cox and Pilcher (ref. 1). [b] This work (see text).

A few values in Table 1 are different from those recommended by Cox and Pilcher. The differences are due to my choices of different experimental values of ΔH_v° to combine with the more precisely known ΔH_f° (C). Calorimetric values of the enthalpies of vaporization reported in 1972 by Morawetz[12] are used for naphthalene, phenanthrene, and biphenyl. The ΔH_v° for anthracene is the most recent determination[13], and is closer to a calculated value of 23.24 kcal[14] than that used by Cox and Pilcher.

The ΔH_v° of benz[a]anthracene was determined calorimetrically at 25°C since no value was listed by Cox and Pilcher. Benz[a]anthracene and naphthalene were purified by preparative gas chromatography. A single vaporization calorimeter was used which was equilibrated after charging with approximately 0.2 g of sample. After evacuation of the calorimeter, the enthalpy of vaporization was balanced by the heat supplied by a constantan wire heater. 8–10 mg of sample were vaporized in each experiment. The heater was electrically connected to a constant current source, a Sargeant IV coulometer, periodically calibrated using a Leeds and Northrop potentiometer. The temperature of the calorimeter was monitored with a 10,000 Ω thermistor (discrimination 5×10^{-5} K) connected to a Wheatstone bridge, amplifier and recorder (W. G. Pye and Co. Ltd. variable resistances, Kiethley Model 150 Microvoltammeter, and Sargeant recorder, Model SR). The ΔH_v° of naphthalene was found to be 17.47 kcal mole^{-1}, literature value 17.37 kcal mole^{-1} (ref. 12). The ΔH°_v of benz[a]anthracene was determined to be 25.14±0.21 kcal mole^{-1} (four experiments).

CALCULATIONS

The contributions of different energy terms to the total ΔH°_a (g) are considered to be additive. The compounds used to establish parameters were the first 12 listed in Table 1. Multiple linear least squares regression analyses with equal weightings of the data for each compound were employed. A weight factor of 3 applied to the benzene and naphthalene values did not change the overall results significantly.

The resonance energies for the 12 standard compounds are all taken from a previous publication[11]. Either SCF–MO values[9] or resonance theory values[11] could be used since their mutual correlation coefficient is 0.998. However, SCF–MO values are not known for compounds 13–16, Table 1, so their resonance stabilization energies were calculated using resonance theory. See Appendix I for a sample calculation. All of the resonance energies are given in Table 2 in units of γ, the permutation integral for three pairs of electrons. The value of γ is 19.32 kcal from SCF–MO theory[9,11].

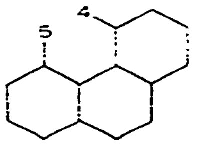
TABLE 2

RESONANCE ENERGIES AND STERIC TERMS

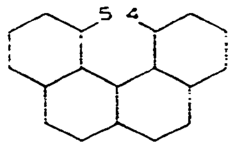
Compound	*Resonance energy* (γ)	*Steric terms*[a]		
		S_1	S_2	S_3
1 Benzene	1.000			
2 Naphthalene	1.580			
3 Anthracene	1.870			
4 Phenanthrene	2.296	1		
5 Tetracene	2.044			
6 Benz[a]anthracene	2.709	1		
7 Benzo[c]phenanthrene	2.963		1	
8 Chrysene	2.963	2		
9 Triphenylene	3.136	3		
10 Pyrene	2.493			
11 Perylene	3.160	2		
12 Biphenyl	2.000			
13 1,3,5-Triphenylbenzene	4.000			3
14 9,10-Diphenylanthracene	3.870			4
15 9,9'-Bianthryl	3.740			2
16 5,6,11,12-Tetraphenyltetracene	6.044			8

[a] The definitions of S_1, S_2, and S_3 are given in the text.

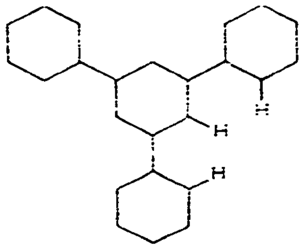
Table 2 also lists steric parameters. Parameter S_1 refers to the 4,5-H,H interaction characteristic of phenanthrene, and S_2 refers to the 4,5-H,H interaction characteristic of benzo[c]phenanthrene. Additional steric parameters, S_3, present in compounds 13 through 16 are simply counted in terms of hydrogen–hydrogen interactions



S_1



S_2



S_3

that differ from S_1 and S_2. The only required comment is to the S_3 terms identified for 1,3,5-triphenylbenzene. These are considered to be different from the interactions of hydrogen atoms in biphenyl because trios of hydrogen atoms interact rather than the pair interactions found in biphenyl. In any event, the enumeration of the S_3 steric terms for this compound is not crucial in any of the later discussions in this paper.

RESULTS AND DISCUSSION

A comparison will be made in this section between a bond-energy scheme that includes terms for C–H and C–C bonds, two steric interaction parameters, and resonance energies, and a Laidler-type[15] method outlined by Cox and Pilcher that employs three different C–C bond energy terms for different types of C–C bonds. A potential criticism of the first method is related to the assumption of a single C–C bond energy parameter. Bernstein has pointed out that aromatic bond lengths are quite variable[16], in contrast to the constant length generally observed in aliphatic hydrocarbons. Recent X-ray work is in agreement as, for example, the C–C bonds in phenanthrene vary in length from 1.35 to 1.46 A[17]. In fact, Bernstein proposed an enthalpy scheme in which the C–C bond energy term for aromatic compounds was adjusted by a relationship involving π-bond orders[18], which gives results comparable to the Laidler-type bond energy method. I have not tried to investigate the Bernstein approach further because it is easy to show that incorporation of resonance energies into a bond energy scheme is tantamount to assumption of a variable C–C bond parameter which is a function of π-bond order (see Appendix II). Inclusion of resonance energies should therefore obviate the necessity for many different C–C bond terms.

Data in Tables 1 and 2, compounds 1–12, were fitted to the function given in eqn (2), where n_{CC} and n_{CH} are numbers of C–C bonds and C–H bonds,

$$\Delta H_a^\circ = b_1 n_{CC} + b_2 n_{CH} + b_3 R.E. + b_4 S_1 + b_5 S_2 \tag{2}$$

respectively, $R.E.$ is the resonance energy, and S_1 and S_2 are the numbers of steric parameters defined and listed in Table 2. The experimental ΔH_a° (g) were also fitted to certain combinations of the terms given in eqn (2) in order to ascertain the relative importance of the steric interaction and resonance parameters. The results are listed in Table 3 as the deviations (calculated—experimental) in the ΔH_a° (g), along with MO results calculated by Dewar and de Llano[9], and with results calculated by the Laidler-type bond energy scheme suggested by Cox and Pilcher.

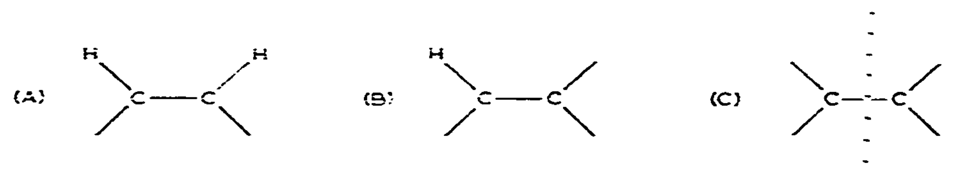
TABLE 3

COMPARISON OF CALCULATED AND EXPERIMENTAL ΔH_f° (g)

Compound	ΔH_f° (g) (calc) $-$ ΔH_f° (g) (exp)					
Number of parameters[a]	2[b]	4[c]	3[d]	4[e]	SCF–MO[f]	5[g]
1 Benzene	−1.36	0.00	−1.27	−1.33	−0.15	−1.57
2 Naphthalene	+0.15	−0.74	+0.13	+0.24	−0.44	+1.01
3 Anthracene	+4.24	+1.06	+2.55	−4.41	−2.34	+2.61
4 Phenanthrene	−0.65	−0.42	−0.01	−0.78	+0.45	+0.52
5 Tetracene	+3.13	−2.35	−0.89	+3.36	−10.65	−2.43
6 Benz[a]anthracene	+1.35	−0.68	+0.97	+1.28	−1.64	+1.53
7 Benzo[c]phenanthrene	+4.97	+6.31	+5.98	0.00	+6.30	0.00
8 Chrysene	−1.80	−0.46	−0.79	−2.17	−4.79	−1.17
9 Triphenylene	−2.70	+2.01	−0.74	−3.36	+2.69	−2.16
10 Pyrene	−7.63	−6.74	−7.39	−7.40	−8.79	−3.48
11 Perylene	+1.64	+7.01	+2.26	+1.34	+0.18	+3.03
12 Biphenyl	+0.64	+0.21	+1.13	+0.74	+2.41	+2.50
Average deviation	±2.52	±2.39	±2.01	±2.20	±3.21	±1.83

[a] Parameters listed in text. [b] *CH* and *CC* terms. [c] *CH*, three *CC* terms, ref. 1. [d] *CH*, *CC*, *R.E.* [e] *CH*, *CC*, S_1, S_2. [f] Ref. 9. [g] *CH*, *CC*, S_1, S_2, *R.E.*.

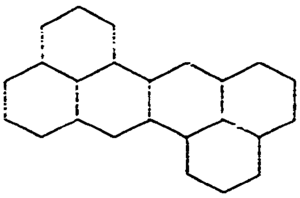
The values of the parameters for each type of calculation are in turn: 2 parameters, $CH = 108.015$, $CC = 111.457$; 3 parameters, $CH = 107.609$, $CC = 110.966$, $\gamma = 5.472$; 4 parameters $CH = 107.999$, $CC = 111.477$, $S_1 = -0.2978$, $S_2 = -5.2018$; 5 parameters, $CH = 106.559$, $CC = 110.826$, $\gamma = 12.317$, $S_1 = -2.448$, $S_2 = -10.728$; SCF–MO calculation (see Dewar and de Llano[9]). Laidler scheme, $CH = 100.53$, CC (A, see figure below) = 119.17, CC (B) = 114.30, CC (C) = 112.80.

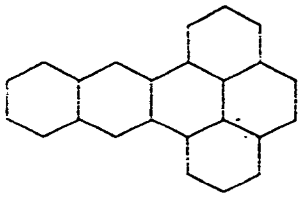


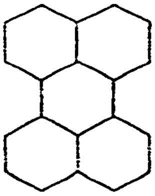
The parameters for the different kinds of C–C bonds in the Laidler-type method are not least-squares values, but are simply those recommended by Cox and Pilcher. A least squares fit of numbers of CH and type A, B, and C bonds to the experimental ΔH_f° (g) gives nonsensical large positive and negative values to the 4 parameters (CH, +5401.9; CC (A), −5182.3; CC (B), −2536.2; CC (C), 112.6). These parameters fit the data slightly better than the Cox and Pilcher parameters, but their unrealistic values are perhaps indicative of an inherent flaw in this particular approach. Increasing the weights assigned to the benzene and the naphthalene data up to a factor of 3 still does not yield realistic results. Also, one should note that the 2 parameter C–H, C–C bond energy scheme fits the data almost as well as the 4 parameter method, further indicating the absence of some critical factor in the theory.

The inclusion of steric factors in the bond energy schemes does improve the average deviation of experimental and calculated heats of atomization, but this is solely due to the fact that benzo[c]phenanthrene is corrected by an S_2 parameter to its exact value. One can see from the Laidler method results in Table 3 that any steric correction for the perylene value ($2S_1$) would cause corresponding increases in negative deviations for the 4 other molecules with S_1-type steric interactions. Furthermore, in the Laidler-type method the data still cannot be fitted by regression analysis to give reasonable values of the parameters, and no obvious steric correction can be invoked to explain the 6.74 kcal of stabilization energy calculated for pyrene.

This brings us to the question of the incorporation of resonance energy into a ΔH_a° (g) scheme for aromatic systems. If either of the methods that only use bond parameters is to yield a good correlation of ΔH_a° (g) data, resonance energies must be capable of incorporation into the bond-energy terms. However, it is now well-established that the resonance energy per C–C bond in aromatic molecules is a variable quantity[9,11], ranging from 0.1678γ (3.2 kcal) in benzene to 0.097γ (1.9 kcal) in tetracene. Even for pairs of compounds with exactly the same number of types A, B, and C C–C bonds, resonance energies differ by several kcal mole^{-1}. Examples are the pair of molecules zethrene and naphtho[2,3-e]pyrene in which the resonance energies differ by 14.6 kcal mole^{-1}, and the pair perylene and benzo[d]pyrene where the resonance energies differ by 4.4 kcal mole^{-1}. These examples show the inherent difficulties in devising additive methods for enthalpies of aromatic compounds that do not include resonance energies explicitly. Calculated values for large molecules not


zethrene


naphtho[2,3-e]pyrene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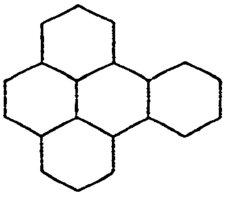

benzo[d]pyrene

included in the set of experimental data used to establish parameters would be *expected* to deviate significantly.

The best fit of the ΔH_a° (g) data is obtained with a 5-term equation incorporating C–C and C–H bond energies, 2 steric terms, and resonance energies. The average deviation is ±1.8 kcal, about twice the claimed limits of error in ΔH_a° (g). The largest negative deviation is for pyrene (−3.48 kcal) and the largest positive deviation is for perylene (+3.03 kcal). Both of these deviations are less than twice the average deviation, giving no basis for rejection of either the experimental data or the theoretical calculation.

The very reasonable values of the steric and resonance parameters that are the results of the regression analysis constitute some support for the essential correctness of this theoretical approach. As mentioned in the Introduction, several different estimates of potential functions give values of −1 to −3 kcal mole^{-1} for S_1 interactions[5], and the present calculated value, −2.45 kcal, is within this range. The present value is also in reasonably good agreement with an estimate of −1.5 kcal derived from hydrogen–deuterium exchange rates and the basicities of aromatic hydrocarbon conjugate bases[19]. The resonance integral parameter, 12.3 kcal, is only 64% of the value calculated from SCF–MO theory by Dewar and de Llano[9]. Considering the known limitations of semi-empirical MO theory this would seem to be sensible agreement. Lastly, the value of the S_2 parameter also seems to be quite reasonable, considering the very close approach of hydrogen atoms required by the geometry of the benzo[c]phenanthrene molecule. No other theoretical values for comparison have been published.

Table 4 gives the results of applying the 5-parameter method to the 4 molecules that were not used to establish the parameters. All of these compounds must be non-planar, and the steric interactions which arise because of the non-planar geometry have not been discussed previously. It is futile to attempt a detailed dissection of the extra steric interactions in these compounds when so little is known about their actual structure. However, it is interesting that a single correction, $S_3 = -4.37$ kcal, based on simple counting of extra S_3 interactions, does bring the calculated ΔH_a° (g) to within the average experimental estimates of error for these compounds (±3 kcal).

TABLE 4

COMPARISON OF CALCULATED AND EXPERIMENTAL ΔH_a° (g) FOR NON-PLANAR AROMATIC HYDROCARBONS

Compound	ΔH_a° *(g) (calc)–* ΔH_a° *(g) (exp)*	S_3	ΔH° *(g) (corr)–* ΔH_a° *(g) (exp)*
1,3,5-Triphenylbenzene	+8.20	3	−4.90
9,10-Diphenylanthracene	+20.57	4	+3.10
Bianthryl	+6.94	2	−1.80
5,6,11,12-Teraphenyltetracene	+38.54	8	+3.60

The small value of the S_3 term is to be expected if the compounds actually are non-planar.

CONCLUSIONS

ΔH°_a (g) for aromatic hydrocarbons can be calculated to within experimental accuracy by additive methods. The scheme advocated here is one that includes a theoretical calculation of the resonance energy and steric correction terms. The approach is intuitively correct and computationally simple. An advantage over methods that only incorporate various kinds of bond-energy terms is that use of the advocated methods allows an examination of resonance energy effects and particular steric effects. Finally, in carrying out this work it was disappointing to note the absence of critical experimental thermochemical data in this area. This situation ought to be rectified, so that the large number of theoreticians working on aromatic systems would have experimental results as standards of evaluations for their calculations.

ACKNOWLEDGEMENT

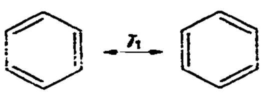
I thank the Robert A. Welch Foundation for generous financial support.

APPENDICES

I. Calculations of resonance energies using resonance theory

The mathematical formulism outlined here for calculating π-resonance energies depends upon the assumption that only equally weighted Kekulé structures contribute to the resonance hybrid. The justification for the assumption is purely empirical, and is based on the fact that resonance energies calculated in this way correlate with resonance energies calculated by semi-empirical SCF–MO methods to a significant degree (corr. coeff. 0.998 for total resonance energies; 0.992 for resonance energies per electron)[11]. The MO calculations referred to were parameterized by reference to experimental heats of formation[9], so I believe they represent the best estimates of resonance energies available.

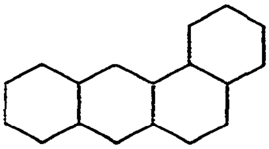
Permutations of pairs of π-electrons that convert one Kekulé structure into another are the resonance interactions considered to give rise to resonance stabilization energies. The exchange integral that permutes three pairs of electrons in a single ring is called γ_1, and the exchange integral permuting five pairs in two annelated rings is called γ_2. The resonance integrals are quantified by referring to electronic transitions of benzene and azulene, which gives the ratio[20] of γ_2 to γ_1 as 0.37. Actual theoretical evaluation of the integrals by a valence-bond method gives $\gamma_2/\gamma_1 = 0.36$[21,22]. Inte-

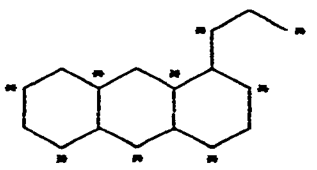


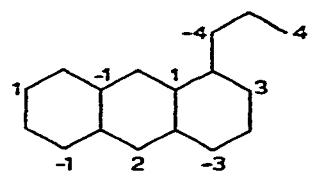
grals for simultaneous permutations of 7 or more pairs of electrons are much smaller than γ_2 and are neglected in this work.

The method is best exemplified by an example, for which we will use the molecule benz[a]anthracene.

The number of Kekulé structures for benz[a]anthracene is determined either by drawing all structures, or by using the graph theoretical concept of the "corrected structure count" (CSC) described in a recent paper[23]. The latter method requires one to delete a vertex from the graph of the molecule, to star the atoms in an alternate manner, and to write the non-arbitrary coefficients (smallest coefficient unity) at starred positions that sum to zero around every vertex as shown below. The sum of the absolute value of the coefficients adjacent to the deleted vertex is the CSC and is equal to the number of Kekulé structures that can be drawn for the molecule. The seven structures for benz[a]anthracene can be quickly drawn, but for larger molecules the CSC method is much faster.







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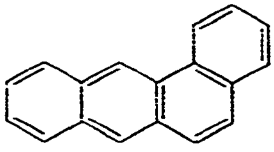

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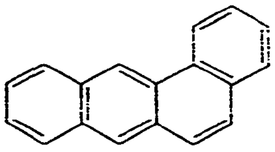

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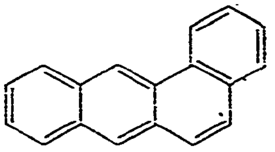

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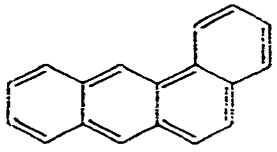
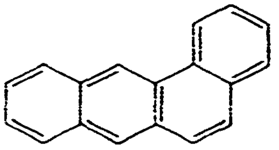


A



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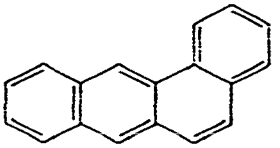

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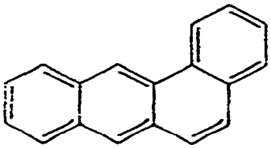
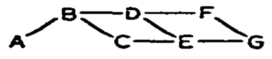


G

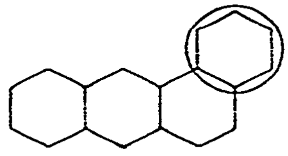
Graphs of the γ_1 interactions and of the γ_2 interactions are drawn below for the benz[a]anthracene system. There are 8 γ_1 interactions and 4 γ_2 interactions. However, it is not necessary to count the interactions as shown below, because it is easy to show that the number of γ_1 interactions for each ring of the molecule is equal to the structure count of the residual molecule with that ring deleted. Similarly, γ_2 integrals are

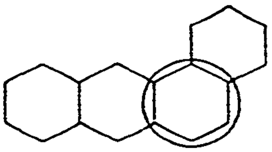


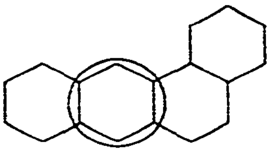
γ_1 interaction diagram

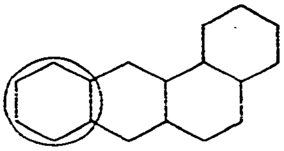
γ_2 interaction diagram

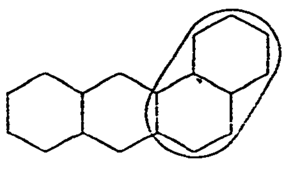
enumerated by deleting adjacent rings two at a time and summing the CSC's for the residual systems as shown. The whole procedure is economically carried out on two single drawings of the molecular graph as shown in the last two figures.

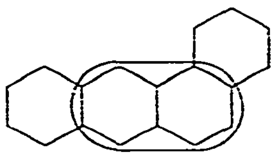

residual CSC = 3

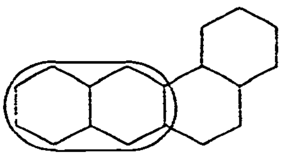

residual CSC = 1

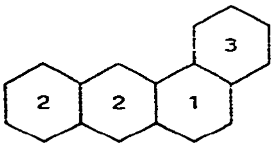

residual CSC = 2


residual CSC = 2

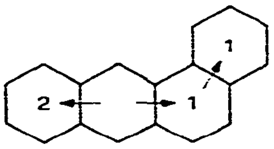

residual CSC = 1


residual CSC = 1


residual CSC = 2



sum $\gamma_1 = 8$



sum $\gamma_2 = 4$

Each structure is assigned equal weight in the resonance hybrid. Then insertion of the linear combination wave function into the integrated form of the Schrödinger wave equation gives a simple additive formula for the π-resonance energy, *R.E.* = (2/CSC) $(n_1\gamma_1+n_2\gamma_2)$, where the terms are defined in context. The calculated resonance energy for benz[a]anthracene is therefore (2/7) $(8\,\gamma_1+4(0.37)\,\gamma_1) = 2.71\,\gamma_1$ or 52.37 kcal. The resonance energy from SCF–MO theory is 52.83 kcal.

II. Equivalence of variable C–C bond energy term method to the resonance energy method

One may assume that a smooth relationship between bond orders and bond energies has been demonstrated. Empirical confirmations for this relationship are the many excellent correlations of bond length and bond order[8,24–26]. In the argument below which to a large extent follows Bartell[27], the energies of bonds are given by power expansions of Pauling bond orders, eqn (3). The resonance energy is found

$$E_{ij} = a_0+a_1\,p_{ij}+a_2\,p_{ij}^2+\ldots \tag{3}$$

by comparing the total energy E_T, summed over all C–C bonds, with the energy calculated for a reference structure, E_R, that has pure alternating single and double bonds, eqns (4), (5), and (6).

$$E_T = \sum_{ij} E_{ij} = a_0 n_{CC}+a_1 \sum_{ij} p_{ij}+a_2 \sum_{ij} (p_{ij})^2+\ldots \tag{4}$$

$$E_R = a_0 n_{CC} + a_1 n_{d.b.}(1) + a_2(n_{d.b.})(1)^2 + \dots \tag{5}$$

$$R.E. = E_T - E_R = a_2 \sum_{ij} [(p_{ij})^2 - n_{d.b.}]. \tag{6}$$

Eqn (6) follows if terms higher than quadratic are small because the sum over all bonds of Pauling bond orders is equal to the number of double bonds, $\sum_{ij} p_{ij} = n_{d.b.}$ The total C–C bond energy, eqn (4), can be rewritten using eqn (6) as given in eqn (7). Now the ΔH_a° (g) is given by eqn (8),

$$E_T = a_0 n_{CC} + a_1 n_{d.b.} + R.E. + a_2 n_{d.b.} \tag{7}$$

$$\Delta H_a^\circ(g) = n_{CH} E_{CH} + E_T \tag{8}$$

which can be simplified with the aid of the mathematical relationship shown in eqn (9)

$$n_{d.b.} = (n_{CH} + 2n_{CC}) \div 6 \tag{9}$$

$$\therefore \Delta H_a^\circ(g) = n_{CH} E_{CH} + a_0 n_{CC} + a_1(n_{CH} + 2n_{CC}) \div 6 + R.E. + a_2(n_{CH} + 2n_{CC}) \div 6$$

or

$$\Delta H_a^\circ(g) = n_{CH}(E_{CH} + a_1/6 + a_2/6) + n_{CC}(a_0 + a_1/3 + a_2/3) + R.E. \tag{10}$$

Eqn (10) is of exactly the form taken to represent the bond energies that was assumed in the text of this paper. Therefore, the sum of a single C–C bond energy parameter and the resonance energy, is equivalent to a method in which every C–C bond is assigned a different energy that depends upon its bond order.

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