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The equivalence of bond-energy schemes and the determination of resonance energies

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Abstract. It is argued that the preservation of algebraic equivalence between the Allen and Laidler bond-energy schemes for nonconjugated alkenes logically determines that the Allen scheme should apply to a classical structure of a conjugated hydrocarbon exactly as it stands, i.e. no additional parameters are needed. Extending the requirement of equivalence to conjugated alkenes implies that, in the Laidler scheme, the bond energy of the pure single CC bond in a conjugated system is a combination of the bond-energies of the semiconjugated and normal CC single bonds: $E(\mathrm{C_d{-}C_d}) = 2E(\mathrm{C_d{-}C}) - E(\mathrm{C{-}C})$. This result is a deduction and is not an independent hypothesis. The equivalence of the two schemes for conjugated hydrocarbons is demonstrated numerically, by calculating the resonance energies of some selected molecules by both methods.

Key words: Equivalence – Bond energies – Resonance energies

1 Introduction

The traditional measure [1] of the resonance energy (RE) of a conjugated molecule is the difference between the observed atomisation enthalpy, ΔH_a, and the value of ΔH_a obtained by applying a bond-energy scheme to a classical structure. Since the classical structure of a resonating molecule does not exist by definition, REs can be criticised for not being empirical quantities. They are nonetheless interesting from a theoretical point of view and the concept of RE in the traditional sense is often invoked for the interpretation of other, strictly empirical definitions of RE.

There is, however, a related criticism which could be made of the traditional RE and which is the concern of this article. REs are not well defined by the above prescription, because there is no agreed way of extending the application of bond-energy schemes from nonconjugated molecules to the hypothetical structures of conjugated molecules. For example, the Laidler scheme [2] requires an additional parameter, $E(\mathrm{C_d{-}C_d})$, for the energy contribution of the single bond which connects two nonresonating double bonds. In the absence of molecules known to contain such single bonds, the value of $E(\mathrm{C_d{-}C_d})$ cannot be determined by the usual thermochemical method of fitting calculated values of ΔH_a to observed values.

Estimates of $E(\mathrm{C_d{-}C_d})$, in relation to other bond energies, were made long ago [3, 4] by combining thermochemical data with assumptions about the detailed electronic structure of bonds (e.g. π bond orders, hybridisation). More recently [5] assumptions of a similar kind were used to estimate the RE of butadiene directly, from a (spectroscopically determined) barrier to rotation. The result of this study differs from the RE of butadiene as inferred from the earlier work [3, 4] by more than 5 kcal mol^{-1}.

In a quite different approach, REs can be defined empirically – and they should then be called stabilisation energies – by identifying them with the enthalpy changes in certain chemical reactions. Classical structures and bond energies then have no part in the calculation of the stabilisation energy, but they can be involved in its interpretation. For example, a stabilisation energy could be defined as the enthalpy change in a reaction where a conjugated hydrocarbon combines with n ethane molecules to give a saturated molecule plus n ethenes. In this case, however, questions arise as to how much of the enthalpy change is due to loss of conjugation and how much is due to changes in the nature of the single bonds [3]. These questions lead back to the concepts, and to the problems, of the traditional approach.

An important empirical approach [6, 7] which focuses specifically on the conjugation energy uses the enthalpy changes in homodesmotic reactions. These are rearrangement reactions in which the number of bonds of each formal type does not change. The homodesmotic stabilisation energy (HSE) of a molecule with n $\mathrm{C_d{-}C_d}$ bonds may then be defined as (minus) the enthalpy change in the homodesmotic reaction where the molecule of interest is produced from reagents which include, apart from nonresonating molecules, n butadiene molecules.

For an important class of molecules, i.e. homoaromatic species, there is an approximate relationship between HSEs and the REs determined by the Laidler method:

$$\mathrm{HSE\,(molecules)} \approx \mathrm{RE\,(molecule)} - n\,\mathrm{RE\,(butadiene)}\ . \qquad (1)$$

This relation shows that the HSE is not a convenient explanation of the stability of a molecule and indeed is not a molecular property, unless the RE of butadiene really is zero. The question as to whether butadiene itself derives any stabilisation from conjugation is very old [3] and comes back to the problem of determining $E(\mathrm{C_d{-}C_d})$.

REs are conceptually more convenient and theoretically more interesting than empirical stabilisation energies; however, these advantages cannot be realised until REs are better defined in thermochemical terms. The present article aims to show that conjectural elements in the application of bond-energy schemes to the classical structures of conjugated molecules can be eliminated by purely logical considerations. The requirement of algebraic equivalence [8] between the Allen [9] and the Laidler [2] bond-energy schemes determines how both schemes should apply to classical structures. There are no new parameters. Firstly, however, elements of the Laidler scheme will be recapitulated.

2 The Laidler scheme

This scheme distinguishes different types of single CC and CH bonds according to whether the carbon atoms involved in the bond are singly or doubly bonded to other atoms. It has become usual to think of this classification in terms of hybridisation. Thus, the bond energies $E(\mathrm{C_d{-}C})$ and $E(\mathrm{C{-}C})$ refer to sp^2—sp^3 and sp^3—sp^3 bonds, respectively. The elusive $E(\mathrm{C_d{-}C_d})$ parameter refers to an sp^2—sp^2 bond. The CH bonds are differentiated both by the hybridisation of the C atom and by the number of H atoms joined to it. Thus, $E(\mathrm{C{-}H})_\mathrm{p}$, $E(\mathrm{C{-}H})_\mathrm{s}$ and $E(\mathrm{C{-}H})_\mathrm{t}$ are the energies of primary, secondary and tertiary CH bonds at an sp^3 carbon, while $E(\mathrm{C_d{-}H})_2$ and $E(\mathrm{C_d{-}H})_1$ refer to the two kinds of CH bond at an sp^2 carbon. Hybridisation is used here simply as a way of referring to bonds which make different contributions to the estimated ΔH_a. It is not meant to suggest a precise description of the electronic structure of a bond. Hybridisation in this sense was used – with reservations – by Dewar and Schmeising [3].

The values of these parameters as determined by Cox and Pilcher [8] from the "best" group method [10] parameters using the equivalence relationships are shown in Table 1. Because the parameters in Table 1 have been widely used and because the purpose of the present work is methodological, the bond energies have not been revised to take account of the latest values of certain formation enthalpies, including that of gaseous carbon.

The Laidler classification of bonds is identical to that used in the HSE method. It is therefore easy to deduce Eq. (1) by first expressing the enthalpy change for the appropriate homodesmotic reaction in terms of the atomisation enthalpies of the participating molecules and then expressing the latter quantities in terms of Laidler bond energies and (where appropriate) REs. The bond-energy terms cancel out, so Eq. (1) is independent of the particular values chosen for the bond energies and, in particular, is independent of $E(\mathrm{C_d{-}C_d})$. This cancellation was, of course, the main reason for adopting the HSE approach. Equation (1) is not exact, because the Laidler method does not reproduce exactly the atomisation enthalpies of the nonresonating molecules involved in the homodesmotic reactions. In particular, ΔH_a for propene is overestimated by 0.13 kcal mol^{-1}, using the parameters in Table 1.

Table 1. Laidler parameters (298 K) from Ref. [8]. For an explanation of the symbols see the text

Symbol	Energy/kcal mol^{-1}
$E(\mathrm{C{-}C})$	85.48
$E(\mathrm{C{-}H})_\mathrm{p}$	98.19
$E(\mathrm{C{-}H})_\mathrm{s}$	97.27
$E(\mathrm{C{-}H})_\mathrm{t}$	96.53
$E(\mathrm{C{=}C})$	133.00
$E(\mathrm{C_d{-}H})_2$	101.19
$E(\mathrm{C_d{-}H})_1$	100.53
$E(\mathrm{C_d{-}C})$	90.07
$E(\mathrm{C_d{-}C_d})$	?

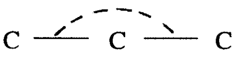
The various attempts to estimate $E(\mathrm{C_d{-}C_d})$ have been discussed elsewhere [8, 11] and only one approach need be mentioned here. If the vinyl groups in 1,3-butadiene are rotated relative to each other about the central bond then the overlap between the p orbitals on carbon atoms 2 and 3 vanishes when the angle of twist is 90°. The barrier to rotation (measured from the trans structure) is known to be 7.2 kcal mol^{-1} from Raman spectroscopy [12]. George et al. [5] identify this barrier with the conjugation energy (i.e. RE) of butadiene, and this implies a value of 91.1 kcal mol^{-1} for $E(\mathrm{C_d{-}C_d})$ assuming that the other bond energies are those given in Table 1. It seems wrong, however, to use a nonplanar structure as a model for classical butadiene. Put another way, it seems unlikely that the whole of the barrier is due to the effects of conjugation; therefore, the value of 91.1 kcal mol^{-1} is here regarded as a lower limit.

The idea that the classical structure for a conjugated molecule contains a new type of single CC bond, for which no thermochemical model is suggested by nonconjugated molecules, arises from a literal interpretation of the Laidler scheme in terms of hybridisation. This idea is brought into question by the Allen scheme, which recognises the state of coordination of the carbon centres but not their hybridisation.

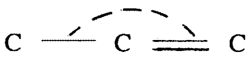
3 The Allen scheme

This scheme has been shown by Cox and Pilcher [8] to be algebraically equivalent to the Laidler scheme for nonconjugated molecules. This result is more interesting because the Allen scheme does not recognise different types of single CC and CH bonds; in considering the interactions between bonds and between nonbonded centres, the possibility of recognising carbon centres in different states of hybridisation is actually suppressed.

According to the Allen Scheme, there are only three types of bond in alkenes, self-evidently designated by their energy parameters $B(C—C)$, $B(C—H)$ and $B(C{=}C)$. Interactions between bonds emanating from the same centre are then introduced: $\Gamma(CCC)$ is the interaction between two single bonds; $\Gamma(CC_dC_d)$ is the interaction between a single and a double bond.



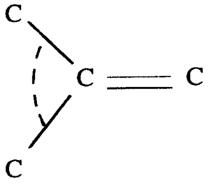
$\Gamma(CCC)$



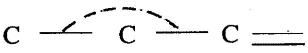
$\Gamma(CC_dC_d)$

In alkanes there are three interactions $\Gamma(CCC)$ at a tertiary centre and six at a quaternary. There would be two interactions $\Gamma(CC_dC_d)$ in isobutene.

In the monoalkenes there appear to be, in addition to $\Gamma(CCC)$, two other types of interaction between single bonds: one where the central atom is *sp*^{2} hybridised and the other where one of the extreme atoms is *sp*^{2} hybridised.



$\Gamma(CC'_dC)$



$\Gamma(CCC'_d)$

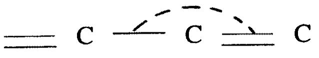
In the above notation C'_d indicates a double- bonded centre, where the double bond is not involved in the pair interaction. In fact, both the above interactions are implicitly assumed by Cox and Pilcher to be the same as $\Gamma(CCC)$. Any other assumption would destroy equivalence with the Laidler scheme.

Alkadienes appear to introduce a new interaction between single bonds, $\Gamma(C'_dCC'_d)$, where both the extreme atoms are *sp*^{2} hybridised:

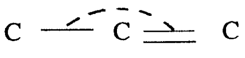
$\Gamma(C'_dCC'_d)$

Now the algebraic equivalence of the Allen and Laidler schemes has not been shown for the alkadienes, but it is possible to demonstrate the equivalence numerically by calculating ΔH_a for 1,4-pentadiene by both methods. A value of 1246.46 kcal mol^{-1} is obtained by the Allen method, assuming that $\Gamma(C'_dCC'_d) = \Gamma(CCC)$. The value obtained by the Laidler method is 1246.50 kcal mol^{-1}. Equivalence would be lost if $\Gamma(C'_dCC'_d)$ were given a different value from $\Gamma(CCC)$.

Now, when one comes to consider conjugated structures, it would be logically inconsistent with what has been said so far if a "new" type of interaction, $\Gamma(C'_dC_dC_d)$, were to be recognised by giving it a value different from $\Gamma(CC_dC_d)$.



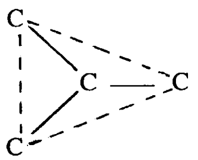
$\Gamma(C'_dC_dC_d)$



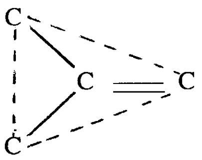
$\Gamma(CC_dC_d)$

Cox and Pilcher appear to entertain the idea that these interactions could be different, although they did not consider the possibility of C'_d centres in monoalkenes. The requirement $\Gamma(C'_dC_dC_d) = \Gamma(CC_dC_d)$ implies that the Allen scheme be applied to 1,3-butadiene exactly as it stands.

The same line of argument can be extended to the triangular interactions between non-bonded centres. The interaction between the trio of atoms around a single-bonded centre is designated $\Delta(CCC)$, while the interaction between the trio around a double-bonded centre is $\Delta(CCC_d)$.



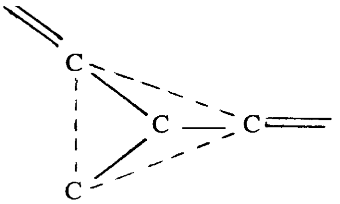
$\Delta(CCC)$



$\Delta(CCC_d)$

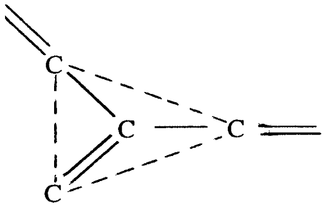
There are four interactions $\Delta(CCC)$ around a quaternary carbon. Now the alkadienes appear to introduce the possibility of a "new" interaction $\Delta(CC'_dC'_d)$ between the trio of atoms around a saturated centre, where two of the peripheral atoms are *sp*^{2} hybridised.

$\Delta(CC'_dC'_d)$

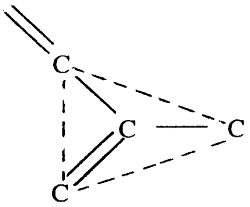


The notation $\Delta(CC'_dC'_d)$ indicates that the double bonds on the primed centres are outside the triangle. Once again, the numerical equivalence of the Allen and Laidler schemes is maintained (e.g. in the case of 3-methyl-1,4-pentadiene), only by the assumption $\Delta(CC'_dC'_d) = \Delta(CCC)$.

Finally, considering triangular interactions in conjugated systems, it would be inconsistent with previous arguments to recognise new interactions $\Delta(C_dC'_dC'_d)$ and $\Delta(C_dC'_dC)$ as being different from $\Delta(C_dCC)$.



$\Delta(C_dC'_dC'_d)$



$\Delta(C_dC'_dC)$

To sum up: the Allen scheme for nonconjugated alkenes would not be equivalent to the Laidler scheme if C'_d centres were differentiated from plain C. The

Table 2. Allen parameters (298 K) from Ref. [8]. For an explanation of the symbols see the text

Symbol	Energy/kcal mol^{-1}
$B(\mathrm{C{-}H})$	99.30
$B(\mathrm{C{-}C})$	78.84
$B(\mathrm{C{=}C})$	140.55
$\Gamma(\mathrm{CCC})$	2.58
$\Gamma(\mathrm{CC_dC_d})$	5.35
$\Delta(\mathrm{CCC})$	−0.55
$\Delta(\mathrm{CCC_d})$	−1.25

absence of recognisable $\mathrm{C'_d}$ centres means that the Allen scheme applies to classical, conjugated structures without introducing any parameters beyond those in Table 2.

4 Equivalence of the schemes for classical structures

Cox and Pilcher [8] demonstrated the equivalence of the Allen [9] and Laidler [2] schemes for alkanes and alkenes by showing that both schemes were equivalent to the group method of Benson and Buss [10]. Since the Allen scheme applies to classical structures as it stands, there must be a relationship between existing Laidler parameters which will ensure that the Laidler scheme gives the same results as the Allen scheme for classical structures. This relationship is discovered by equating a Laidler expression for ΔH_a with an Allen expression for each of the following molecules: ethane, ethene, tetramethylethene and 2,3-dimethyl-1,3-butadiene. These molecules were chosen simply to make the algebra easy, and the results of the derivation which follows do not depend on a particular choice. The molecule 2,3-dimethyl-1,3-butadiene was chosen as the exemplar of conjugation because choosing butadiene itself would have required an additional equation (for 2-butene).

Ethane: $$1/2E(\mathrm{C{-}C}) + 3E(\mathrm{C{-}H})_\mathrm{p} = 1/2B(\mathrm{C{-}C}) + 3B(\mathrm{C{-}H}) \tag{2}$$

Ethene: $$1/2E(\mathrm{C{=}C}) + 2E(\mathrm{C_d{-}H})_2 = 1/2B(\mathrm{C{=}C}) + 2B(\mathrm{C{-}H}) \tag{3}$$

Tetramethylethene:

$$\begin{aligned}1/2E(\mathrm{C{=}C}) + 6E(\mathrm{C{-}H})_\mathrm{p} + 2E(\mathrm{C_d{-}C}) &= 1/2B(\mathrm{C{=}C}) + 6B(\mathrm{C{-}H}) + 2B(\mathrm{C{-}C})\\ &\quad + 2\Gamma(\mathrm{CC_dC_d}) + \Gamma(\mathrm{CCC}) + \Delta(\mathrm{C_dCC})\end{aligned} \tag{4}$$

2,3-Dimethyl-1,3 butadiene:

$$\begin{aligned}&E(\mathrm{C{=}C}) + 2E(\mathrm{C_d{-}H})_2 + E(\mathrm{C_d{-}C}) + 1/2E(\mathrm{C_d{-}C_d})\\ &\quad + 3E(\mathrm{C{-}H})_\mathrm{p} = B(\mathrm{C{=}C}) + 2B(\mathrm{C{-}H}) + B(\mathrm{C{-}C})\\ &\qquad + 1/2B(\mathrm{C{-}C}) + 3B(\mathrm{C{-}H})\\ &\qquad + 2\Gamma(\mathrm{CC_dC_d}) + \Gamma(\mathrm{CCC}) + \Delta(\mathrm{C_dCC})\end{aligned} \tag{5}$$

Now, Eq. (5) minus Eq. (4) gives

$$\begin{aligned}&1/2E(\mathrm{C{=}C}) + 2E(\mathrm{C_d{-}H})_2 - E(\mathrm{C_d{-}C})\\ &\quad + 1/2E(\mathrm{C_d{-}C_d}) - 3E(\mathrm{C{-}H})_\mathrm{p}\\ &\quad = 1/2B(\mathrm{C{=}C}) - B(\mathrm{C{-}H}) - 1/2B(\mathrm{C{-}C})\end{aligned} \tag{6}$$

and Eq. (6) minus Eq. (3) yields

$$\begin{aligned}&-E(\mathrm{C_d{-}C}) + 1/2E(\mathrm{C_d{-}C_d}) - 3E(\mathrm{C{-}H})_\mathrm{p}\\ &\quad = -1/2B(\mathrm{C{-}C}) - 3B(\mathrm{C{-}H}).\end{aligned} \tag{7}$$

Finally, Eq. (7) plus Eq. (2) gives

$$-E(\mathrm{C_d{-}C}) + 1/2E(\mathrm{C_d{-}C_d}) + 1/2E(\mathrm{C{-}C}) = 0$$

or

$$2E(\mathrm{C_d{-}C}) - E(\mathrm{C{-}C}) - E(\mathrm{C_d{-}C_d}) = 0 \tag{8}$$

The result is very familiar in as much as it has often been assumed in calculations as a convenient physical hypothesis. Here it is a logical consequence of equivalence. Any other assumption about $E(\mathrm{C_d{-}C_d})$ would lose equivalence with the Allen scheme. Of course, it might be argued that this loss of equivalence would not matter if it led to the Laidler scheme having more empirical content; however, this empirical content is lacking. So far as the author is aware, there is no thermochemical fact which falsifies Eq. (8).

The value of $E(\mathrm{C_d{-}C_d})$ as determined from the parameters in Table 1 and Eq. (8) is 94.66 kcal mol^{-1}. Possibly because of rounding in the published Laidler and Allen parameters, this value does not quite give the same estimated values of ΔH_a for the conjugated molecules in Table 3. Excellent agreement is obtained, however, using 94.63 kcal mol^{-1}.

The RE of butadiene as indicated in Table 3 is 3.6 kcalmol^{-1}. This value happens to be in close agreement with the empirical resonance energy of butadiene, as determined by the difference between the heat of hydrogenation of butadiene and that of two molecules of 1-butene. The agreement would be exact if the bond-energy scheme(s) exactly reproduced the formation enthalpies of 1-butene and butane. This result follows from Eq. (8), as does the fact that for the rearrangement

Table 3. Observed [8] and estimated atomisation enthalpies (kcal mol^{-1} at 298 K)

Molecule	ΔH_a (obs)	ΔH_a (est) Laidler[a]	ΔH_a (est) Allen	ΔH_a (obs) $-\Delta H_\mathrm{a}$ (est)
1,3-Butadiene	970.09	966.45	966.44	3.6
Benzene	1318.19	1286.07	1286.07	32.1
Toluene	1601.11	1570.18	1570.19	30.9
Diphenylmethane	2807.51[b]	2745.76	2745.76	61.7
1,2-Diphenylethane	3089.60	3025.78	3025.78	63.8
Triphenylmethane	4015.9	3923.36	3923.36	92.5
Biphenyl	2528.27	2465.71	2465.74	62.6
1,3,5-Triphenyl benzene	4951.40	4824.99	4825.08	126.4
Naphthalene	2089.75	2037.02	2037.05	52.7
Anthracene	2858.40	2787.97	2788.03	70.4
Phenantrene	2864.10	2787.97	2788.03	76.1
trans-Stilbene	2985.08	2894.40	2894.43	90.6

[a] Calculated using $E(\mathrm{C_d{-}C_d}) = 94.63$ kcal mol^{-1}

[b] Calculated using the formation enthalpy given in Ref. [16]

$$CH_2{=}CH{-}CH{=}CH_2 + CH_3{-}CH_3$$
$$\rightarrow 2CH_3{-}CH{=}CH_2$$

ΔH is the same as the RE of butadiene to within 0.3 kcal mol^{-1}.

5 Discussion

The entries in the last column of Table 3 should, strictly speaking, be called conventional stabilisation energies (CSEs), after Cox and Pilcher [8]. These quantities are the same as REs provided that the conjugated molecule is not destabilised to any extent by strain or steric interactions. The molecules in Table 3 were chosen primarily to demonstrate the numerical equivalence of the two schemes for a sufficient number of different conjugated structures.

REs are now quite narrowly defined in terms of thermochemical data, the only latitude being in the choice of the "best" parameters of the group method [10] from which both the Laidler and Allen parameters have been derived [8]. This latitude is small compared with the margin of uncertainty which hitherto came from regarding $E(C_d{-}C_d)$ as an extraneous parameter.

No assumptions have been made about the detailed nature (e.g. molecular geometry, electronic structure) of a classical structure. Only the structural formula has been assumed, as in Pauling's original approach [1]. The bond-energy schemes employed here, however, are much more sophisticated than Pauling's. The belief that using sophisticated schemes requires additional parameters beyond those determined from the thermochemistry of nonresonating molecules has been shown to be incorrect.

Although considerations of molecular geometry and electronic structure have not been involved in the calculation of REs, such considerations are the only means of investigating whether the results are reasonable. For example, the external validity of Eq. (8) is currently under investigation by the author using bond-energy/bond-length relationships. These calculations are essentially a reinvestigation of methods pioneered by Dewar and Schmeising [3] and by Bernstein [13].

Another possible check on the results is suggested by theoretical studies on biphenyl. This molecule could provide a more convenient model of the pure $sp^2{-}sp^2$ bond than twisted (90°) butadiene. The suggestion that there is no resonance between the ring systems of biphenyl in the electronic ground state is not new [14]. It can be understood by first imagining biphenyl to be planar (D_{2h}) and then considering that the (12) π molecular orbitals (MOs) of biphenyl are linear combinations of the bonding π MOs of two benzene molecules. The π bond order in the central bond is exactly zero when the lowest six π MOs are fully occupied. Recently it has been shown that model (D_{2h}) wavefunctions of the latter kind can give a qualitative interpretation of the electronic spectrum of biphenyl, as calculated ab initio at the CASPT2 level [15]. Less sophisticated (STO-3G) calculations in this laboratory have shown that the Mulliken bond orders in the rings of biphenyl are almost identical to those of benzene.[1] The central bond order is 1.03 for the planar molecule and it drops to 1.01 at the (experimental) dihedral angle of 44°. The π contribution to the central bond order was only 0.04 in the planar molecule (with the central bond length at 1.489 Å). There is thus a reasonable presumption that the RE of biphenyl should be twice the RE of benzene.

The results in Table 3 show that the CSE of biphenyl is 1.6 kcal mol^{-1} less than the CSE of two benzene molecules. A possible interpretation is that the RE of biphenyl is indeed twice the RE of benzene, but that steric repulsion between the hydrogens in the 2 and 2′ positions destabilises biphenyl to the extent of 1.6 kcal mol^{-1}. This estimate of the steric effect agrees well with the value (1.4 kcal mol^{-1}) given by George et al. [6]. However, other evidence is needed that a substituted benzene ring carries the same RE as benzene itself.

Table 3 indicates that the RE of toluene is 1.2 kcal mol^{-1} less than that of benzene, i.e. the opposite of what might be expected from the idea of hyperconjugation. This difference between the REs of toluene and benzene is not large, but it is significant when compared with typical failures of the bond-energy schemes to reproduce the ΔH_a values of nonresonating molecules. A possible explanation of the differences between the REs of benzene and toluene is that the CH bond in benzene has a greater bond energy than the "classical" value $E(C_d{-}H)_1$ and/or that the $C{-}CH_3$ bond in toluene has a smaller bond energy than $E(C_d{-}C)$. The same explanation would lead one to predict that diphenyl methane has the same RE as two toluenes and that triphenylmethane has the same RE as three toluenes.

These predictions are confirmed to a remarkable degree by Table 3, provided that the latest value [16] of the formation enthalpy of diphenylmethane is used to determine the observed value of ΔH_a. Since the systems being compared have the same number of $C_d{-}C_d$ bonds, the agreement has nothing to do with the value of $E(C_d{-}C_d)$. Very similar conclusions, therefore, can be reached by the HSE method. The HSE of diphenylmethane can be shown to be equal to the sum of the HSEs of toluene and ethylbenzene. The HSE of benzene is 1.3 kcal mol^{-1} more than the HSE of toluene.

Two other results in Table 3, however, cannot be explained so neatly either by the conjecture that the ring systems are like toluene or that they are like benzene. The CSE of 1,2-diphenylethane is closer to the CSE of two benzenes than it is to two toluenes and the CSE of 1,3,5-triphenylbenzene is only 2 kcal mol^{-1} less than the CSE of four benzenes. The latter result suggests either that 1,3,5-triphenylbenzene has slightly more resonance stabilisation in each ring system than biphenyl or that the molecule is subject to less steric destabilisation (for each link between the rings) than biphenyl, both of which are hard to explain.

In order to use the formation enthalpy of biphenyl as an empirical check on the value of $E(C_d{-}C_d)$, it would be necessary to know whether the ring systems carry the

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[1] Calculations using the SPARTAN suite of programs by the author and M J Bearpark.

same RE as benzene or whether they are more like toluene. To this end, it would probably be worthwhile to look at the whole problem again using thermochemical data at 0 K. In this way bond energies would not carry contributions from rotation and thermally excited vibrations, and in the case of biphenyl the contribution of the torsional motion to ΔH_a would be reduced.

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