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THE USE OF 90°-1,3-BUTADIENE AS A REFERENCE STRUCTURE FOR THE EVALUATION OF STABILIZATION ENERGIES FOR BENZENE AND OTHER CONJUGATED CYCLIC HYDROCARBONS

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Abstract—Reactions are described that employ 90°-1,3-butadiene as a reference structure for the evaluation of the stabilization energy of the benzenoid and other cyclic conjugated hydrocarbons. The unique benefits of this rotamer of butadiene as a reference molecule within the homodesmotic conceptual framework are discussed. Experimental stabilization energies are presented for a number of cyclic hydrocarbons.

The evaluation of a stabilization energy for benzene from thermochemical data

In several recent papers[1,2] we have shown how the enthalpy changes for especially designed reactions, which we have termed "homodesmotic", provide excellent experimental parameters for characterizing the stabilization present in benzene and other conjugated cyclic hydrocarbons, as well as the destabilization (ring strain) which is typical of many saturated and non-conjugated ring systems.[3] The enthalpy changes, evaluated from ΔH_f^0 data are directly comparable with quantum theoretical values obtained from *ab initio* or semiempirical evaluations of total molecular energies or heats of formation, thus establishing a consistent conceptual framework in which the experimental and the theoretical definitions of stabilization energies involve the same *real* molecules as reference structures.

The special advantage of homodesmotic reactions for this purpose is that energy contributions extraneous to stabilization (or destabilization) are minimized by ensuring that (1) there are equal numbers of each *type* of carbon–carbon bond (C_{sp^3}–C_{sp^3}, C_{sp^3}–C_{sp^2}, C_{sp^2}–C_{sp^2}, C_{sp^2}=C_{sp^2}, etc.) in reactants and products, and (2) there are equal numbers of carbon atoms (C_{sp^3}, C_{sp^2}, etc.) with zero, one, two and three hydrogen atoms attached in reactants and products. The minimization of extraneous energy contributions arising from changes in the types of carbon–carbon and carbon–hydrogen bonds singles out the energetic consequences of those structural features responsible for the stabilization or the destabilization.

A scrutiny of the reactions traditionally and currently used to evaluate the stabilization energy of benzene reveals that none of them are homodesmotic, however all of them are isodesmic,† (Table 1). In such reactions the bonding is matched only in terms of formal type—single, double and triple—irrespective of its chemical nature, e.g. hybridization, C/H bonding, etc. One consequence of this is a considerable variation in the magnitude of the stabilization energy, 64, 49 or 32 kcal/mole according to reaction A, B or C respectively.‡ Furthermore, within the context of bond energy assignments, the very procedure of identifying the stabilization energy as ΔH° for an isodesmic reaction (but one which is *not* also homodesmotic) carries with it the *implicit* assumption that the residue of mismatched bond energy terms can be equated to zero. For example the simplest case, which involves only three mismatched bond energy terms, namely reactions C(i), (ii) and (iii), requires

$$2E(C_{sp^2}\text{–}C_{sp^3}) - E(C_{sp^2}\text{–}C_{sp^2}) - E(C_{sp^3}\text{–}C_{sp^3}) = 0.$$

This expression has been discussed over the years by various authors[4,9,13,14] in connection with reaction C(i)—the classical reaction for the determination of the empirical resonance energy—and the consensus of opinion is that it is unjustified and that an inequality relationship is more likely, namely

$$2E(C_{sp^2}\text{–}C_{sp^3}) > E(C_{sp^2}\text{–}C_{sp^2}) + E(C_{sp^3}\text{–}C_{sp^3}).$$

For reactions A and B the corresponding expressions are more complicated, involving six different bond energy terms in each case (see Ref. 14 for the expression relating to reaction B). Furthermore, since

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†The classification *isodesmic*, which covers many organic reactions, was introduced by Hehre, Ditchfield, Radom and Pople[5] in a study of bond separation processes. *Homodesmotic* reactions constitute a special (and much more restrictive) subclass of isodesmic reactions. None of the reactions discussed by these authors is homodesmotic, see their Table 2.

‡As we shall show later, it is also possible to have a considerable variation in the magnitude of a stabilization energy determined from different homodesmotic reactions. This feature, however, is not due to an alteration in the mismatch in bond types as is the case for reactions which are only isodesmic. Rather, it is due to inherent stabilization or destabilization in the different reactant and product species used as reference structures.

Table 1. The mismatch in the carbon–carbon single bonds in isodesmic reactions used to evaluate[a] a stabilization or resonance energy for benzene, compared to the matching in typical homodesmotic reactions

	Reactions	Reactants C_{sp^3}–C_{sp^3}	Reactants C_{sp^2}–C_{sp^3}	Reactants C_{sp^2}–C_{sp^2}	Products C_{sp^3}–C_{sp^3}	Products C_{sp^2}–C_{sp^3}	Products C_{sp^2}–C_{sp^2}	ΔH^c = SE(RE) kcal/mole
Isodesmic								
A[b]	$C_6H_6 + 6CH_4 \rightarrow 3CH_2{=}CH_2 + 3CH_3{-}CH_3$	0	0	3	3	0	0	64.2 ± 1.2
B[c]	$C_6H_6 + 3CH_3{-}CH_3 \rightarrow 3CH_2{=}CH_2 + C_6H_{12}$	3	0	3	6	0	0	48.8 ± 0.9
C(i)[d]	$C_6H_6 + 2C_6H_{12} \rightarrow 3C_6H_{10}$	12	0	3	9	6	0	32.0 ± 1.0
C(ii)[e]	$C_6H_6 + 3CH_3CH_2CH_2CH_3 \rightarrow C_6H_{12} + 3$ *trans* $CH_3{-}CH{=}CH{-}CH_3$	9	0	3	6	6	0	32.8 ± 1.3
C(iii)[e]	$C_6H_6 + 3CH_3{-}CH_3 + 3CH_2{=}CH_2 \rightarrow 6CH_3{-}CH{=}CH_2$	3	0	3	0	6	0	32.8 ± 1.8
Homodesmotic								
D(i)[f]	$C_6H_6 + 3CH_2{=}CH_2 \rightarrow 3CH_2{=}CH{-}CH{=}CH_2$	0	0	3	0	0	3	21.8 ± 0.9
D(ii)[g]	$C_6H_6 + CH_2{=}CH_2 \rightarrow CH_2{=}(CH{-}CH{=})_3CH_2$	0	0	3	0	0	3	

[a] All values of ΔH° with estimates of the experimental uncertainty have been calculated from ΔH_f° data compiled by Cox and Pilcher.[4]

[b] Reaction A is the "bond separation" reaction employed by Hehre, Radom, Ditchfield and Pople.[5] ΔH^c for this reaction can be shown to be identical to the original empirical resonance energy calculated by Pauling and Sherman,[6] and later by Pauling[7] (about 39 kcal/mole) using thermochemical bond energy terms based on ΔH_f° data for methane, paraffins (ethane) and olefins (ethylene). The numerical discrepancy noted by Glockler,[8] apparently arises through some inconsistency between the ΔH_f° data and the values adopted for the bond energy terms.

[c] Reaction B was proposed by Dewar and Schmeising[9] to avoid the introduction of energy contributions extraneous to the benzene stabilization energy from the strain energy of the cyclohexene utilized in reaction C(i), whereby the stabilization (resonance) energy is evaluated as the difference between the hydrogenation heat of benzene and three times the hydrogenation heat of cyclohexene.[10,11] ΔH° for reaction C(i) is equivalent to this difference in hydrogenation heats.

[d] The value of ΔH° obtained directly from the ΔH_f° data, 35.95 (which rounded off to 36 kcal/mole is the familiar resonance energy value often quoted in the literature) has been corrected here for the strain energy of the cyclohexene ring, 1.32 kcal/mole,[4] i.e. 35.95-3(1.32) = 31.99 kcal/mole.

[e] Reactions C(ii) and C(iii) are identical to reaction C(i) from the point of view of the net difference between the bonds broken and bonds formed. However, despite the differences in chemical structure of reactants and products, especially in the case of C(iii), values of ΔH° identical to within experimental error result, and reaction C(i) can, in no way, be regarded as unique.

[f] Reaction D(i) is the reaction we have employed in previous papers to evaluate the stabilization energy for benzene.[1,2]

[g] Reaction D(ii) is one of many other homodesmotic reactions that can be designed for the same purpose: however, ΔH_f° values have not been measured for any of the acyclic conjugated polyenes beyond 1,3,5-hexatriene,[12] and so ΔH° (SE) values can not yet be quoted.

both carbon–carbon and carbon–hydrogen bonds appear in these expressions, it is less likely there could be any theoretical justification for exact cancellation.

With homodesmotic reactions (e.g. see reaction D(i), Table 1) however, this problem does not arise, since within the context of thermochemical bond energy assignments, the matching of bonds according to chemical *type* leads unequivocally to the simple relationship

$$\Delta H^\circ = \text{Stabilization energy.} \qquad (1)$$

It is to be noted that in writing the homodesmotic reaction in the direction of D(i) it is a fission of the cyclic structure, which is inherently an endothermic process if the structure is stabilized with respect to that of the product(s). ΔH° is then positive without any alteration—in keeping with the usual convention of expressing stabilization energies as positive quantities. In previous papers[1,2] we dealt with the formation of the cyclic structure, namely with the reaction in the reverse direction, which is inherently an exothermic process if the structure is stabilized with respect to that of the reactant(s). It was thus necessary to change the sign of ΔH° in this case to obtain the homodesmotic stabilization energy.

In the second paper[2] we drew attention to the circumstance that the magnitude of the stabilization energy derived from reaction D(i) is substantially less than that for any of the isodesmic reactions. It is a reasonable supposition that the matching of the bonding in the homodesmotic reaction is, in part, responsible for this feature.†

However, as we have stressed in our previous papers, the determination of stabilization (or destabilization) energies from thermochemical data relates the enhanced stability (or relative instability) to the other reactant and product species that complete the reaction—namely the bonding in these species is implicitly adopted as a reference state. Now, in the case under consideration, the stabilization energy in benzene is evaluated relative to the bonding energies in ethylene and *trans*-1,3-butadiene. This latter molecule, however, is certainly stabilized to some extent by π-electron delocalization.‡ Hence, a further reason for the "low" stabilization energy for benzene, evaluated as ΔH° for the homodesmotic reaction D(i), is the fact that the value of 21.8 kcal/mole is relative to whatever the stabilization energy is in three molecules of *trans*-1,3-butadiene.

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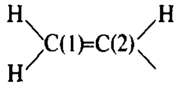
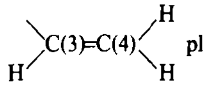
†This conclusion is substantiated by the data for isodesmic compared to homodesmotic isomerization reactions of acyclic (non-conjugated) structures. For example, for twelve isodesmic (but not homodesmotic) isomerizations of hexene ΔH° ranges from 1.9 ± 0.7 to 6.3 ± 0.6, with a mean of 4.2 ± 0.7 kcal/mole; whereas for four homodesmotic isomerizations ΔH° = 0.6 ± 0.7 kcal/mole, i.e. thermoneutral to within experimental error.[4]

‡Dewar and Gleicher[13] have found that it is possible to compensate for this π-interaction within the context of a semiempirical SCF-MO model by absorbing a correction into the empirical bond properties of classical polyenes. The homodesmotic approach to stabilization energies, however, does not employ empirical bond energies in the construction of a hypothetical reference structure. Rather real molecules, with their own unique physical properties are used throughout.

90°-1,3-*Butadiene*

There is no unequivocal method for evaluating the stabilization energy in *trans*-1,3-butadiene from thermochemical data alone, because, in turn, some other chemical structure would be required as reference. Values can be be arrived at by employing isodesmic reactions like those in Table 1, B and C(i) for benzene, giving about 8.9 and 3.7 kcal/mole respectively.[14] But such values have no fundamental significance at all for the same reasons as those given above in the case of benzene. A further homodesmotic reaction would be necessary relating the butadiene to this other chemical structure, which would have to contain a formal C_{sp^2}–C_{sp^2} single bond to match that in butadiene—which is clearly impossible since the 1,3-dienes are themselves the simplest hydrocarbons possessing this structural element. The only type of reference structure that has the appropriate number of carbon atoms in the required hybridization states, the appropriate number of each type of C–C bond, and the required number and type of each carbon–hydrogen bond, is a homodesmotic isomeric form of butadiene. The rotational conformers (rotamers) possess exactly these properties.

One rotamer in particular is of especial interest in the present context, namely the unique conformation of the molecule in which the  plane is twisted 90° relative to the  plane. This 90°-1,3-butadiene, whose properties can be deduced from spectroscopic and other physical data,[16,17] is a real molecule, albeit an unstable one, in which the other bond angles and bond lengths adjust in accord with the minimum energy for the 90°-twist position. In this conformation the planes of the π-bonds between C(1) and C(2), and between C(3) and C(4), are at right angles to each other and the π-overlap otherwise present between C(2) and C(3) is reduced to zero (i.e. the p orbitals on C(2) and C(3) are at right angles and do not overlap).[18] Hence the π-electron delocalization energy and associated effects on σ-bonding should also be reduced to zero. These conclusions are borne out by results obtained by Carriera† using the molecular mechanics program of Allinger, which has been extremely successful in predicting many molecular structures. This program gives a C(2)–C(3) bond length of 1.336 Å, essentially the experimental value for the double bond length in ethylene.‡

Clearly the energy difference between *trans*-1,3-butadiene and 90°-1,3-butadiene provides a measure of the energy contribution that stabilizes the *trans*-conformation in its normal, completely planar structure.

The latest study of the torsional potential function of 1,3-butadiene, utilizing Raman spectrophotometry and a high intensity argon ion laser source, gives the energy difference

$$trans\text{-1,3-butadiene} \rightarrow 90°\text{-1,3-butadiene} \qquad (2)$$

as 7.16 kcal/mole, see Table 3 of Carreira's paper.[17] Following Lowe,[23] who estimates that the experimental uncertainty in the determination of barrier heights by Raman spectroscopy is generally between 10 and 20%, we shall assign an uncertainty of ±0.7 kcal/mole to this value for butadiene. Neglecting the issue of any variation in zero-point vibrational energy contributions,§ this spectroscopically determined energy quantity, combined with the thermochemically determined ΔH_f° for *trans*-1,3-butadiene,[4] namely 26.11 ± 0.15 kcal/mole give for 90°-1,3-butadiene: $\Delta H_f^\circ = 33.27 \pm 0.85$ kcal/mole.

The calculation of stabilization energies for benzene and other conjugated cyclic hydrocarbons using 90°-1,3-*butadiene*

The use of the 90°-conformer has a profound effect on the magnitude of the stabilization energies compared to those reported previously[1,2] using the stable *trans* isomer since the values are increased by 7.16 kcal/mole for each formal C_{sp^2}–C_{sp^2} single bond in the conjugated structure. Thus for benzene,

$$C_6H_6 + 3CH_2{=}CH_2 \rightarrow 3(90°)CH_2{=}CH{-}CH{=}CH_2 \qquad (3)$$

the homodesmotic stabilization energy, ΔH°, becomes 42.65 ± 2.97 kcal/mole compared to the previous value of 21.17 ± 0.87 kcal/mole.

For naphthalene and other polycyclic hydrocarbons that contain sp^2 carbon atoms with no attached hydrogen, we again use isobutene as the source of this structural element which is absent in butadiene, and propylene to make up for the deficiency of C_{sp^2}–H groups and thus satisfy the criteria for homodesmotic reactions,[2] e.g.

$$C_{10}H_8 + 5CH_2{=}CH_2 + 4CH_2{=}CHCH_3 \rightarrow$$
$$6(90°)CH_2{=}CH{-}CH{=}CH_2 + 2CH_2{=}C(CH_3)_2.$$

The two sets of stabilization energies for the polycyclic benzenoid hydrocarbons are presented in Table 2.

Making allowance for the stabilization that is present in *trans*-1,3-butadiene by setting up the reactions with the 90°-conformer thus leads to values that are considerably greater than those based on the traditional procedure involving the difference between hydrogenation heats, e.g. reaction C(i), and that are quite close to those based upon the reduction by ethane suggested by Dewar and Schmeising,[9] e.g. reaction B.

Turning to the stabilization energies for the miscellaneous group of conjugated cyclic hydrocarbons listed in Table 3, the values naturally show the same trend as those for the benzenoid hydrocarbons. The increase in numerical magnitude (greater stabilization) with the 90°-conformer as reference has the effect of shifting the base-line from which one judges the interplay of ring strain (destabilization) and stabilization in some cases, and of changing one's estimate of net stabilization quite significantly in others. Denoting the *trans*—and 90°—butadiene values as "old" and "new" respectively, which are listed as ΔH°(A) and ΔH°(B) in Table 3, the following examples may be noted.

(1) *Cyclooctatetraene.* The old negative value, as large as −16.5, could only be taken to mean that ring strain was such a dominant feature that the bonding could well be

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†We thank Dr. L. A. Carreira for making these data available to us.

‡Allinger's molecular mechanics program predicts C(2)–C(3) and C(3)–C(4) bond lengths in *trans*-1,3-butadiene of 1.468 Å and 1.346 Å respectively, which agree quite well with the most recent experimental data (Table 3, Ref. 19).

§In rigorous calculations combining thermochemical energy data with spectroscopic energy data, due allowance would have to be made for zero-point vibrational energies. But for present purposes it will be assumed that these zero-point energy contributions are similar for the *trans*- and 90°-conformers, and no correction will be attempted.

Table 2. Stabilization energies for various polycyclic benzenoid hydrocarbons evaluated[a] as ΔH° for the homodesmotic reaction.

$$C_aH_b + \frac{a}{2}C_2H_4 + 2(a\text{-}b)C_3H_6 \rightarrow \left(\frac{2a\text{-}b}{2}\right)C_4H_6 + (a\text{-}b)C_4H_8$$

with (A) *trans*-1,3-butadiene, and (B) 90°-1,3-butadiene

Compound	C_2H_4	C_3H_6	C_4H_6	C_4H_8	ΔH° (A)	ΔH° (B)
Benzene	3	—	3	—	21.2 ± 0.9	42.7 ± 3.0
Naphthalene	5	4	6	2	30.3 ± 2.6	73.3 ± 6.8
Biphenyl[b]	6	4	7	2	37.9 ± 3.2	88.0 ± 8.1
Anthracene	7	8	9	4	36.6 ± 5.0	101.0 ± 11.3
Phenanthrene[b]	7	8	9	4	43.0 ± 5.0	107.4 ± 11.3
Pyrene	8	12	11	6	53.6 ± 5.9	132.3 ± 13.6
Tetracene	9	12	12	6	47.4 ± 6.6	133.3 ± 15.0
3,4-Benz-phenanthrene[b]	9	12	12	6	52.0 ± 6.7	137.9 ± 15.1
1,2-Benz-anthracene[b]	9	12	12	6	51.2 ± 6.7	137.1 ± 15.1
Chrysene[b]	9	12	12	6	55.8 ± 6.7	141.7 ± 15.1
Triphenylene[b]	9	12	12	6	57.4 ± 6.6	143.3 ± 15.0
Perylene[b]	10	16	14	8	56.6 ± 8.0	156.8 ± 17.8
1,3,5-Triphenyl-benzene[b]	12	12	15	6	74.3 ± 8.0	181.7 ± 18.5
Graphite (C_2)	1	4	2	2	8.5 ± 1.6	22.8 ± 3.0

[a] Heat of formation values taken from Cox and Pilcher[4] except for 1,2-benzanthracene, which is from Magnus, Hartman and Becker[24] 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/C-atom.[14]

[b] ΔH°_f corrected for steric hindrance:—biphenyl 1.4; phenanthrene 0.7; 1,2-benzanthracene 0.7; 3,4-benzphenanthrene 4.4; triphenylene 2.1; perylene 1.4; and 1,3,5-triphenylbenzene 4.2, kcal/mole respectively.[14]

Table 3. Stabilization energies for various conjugated cyclic hydrocarbons evaluated[a] as ΔH° for the homodesmotic reaction.

$$C_aH_b + \frac{a}{2}C_2H_4 + 2(a\text{-}b)C_3H_6 \rightarrow \frac{2a\text{-}b}{2}C_4H_6 + (a\text{-}b)C_4H_8$$

with (A) *trans*-1,3-butadiene, and (B) 90°-1,3-butadiene[a]

Compound	C_2H_4	C_3H_6	C_4H_6	C_4H_8	ΔH° (A)	ΔH° (B)
Benzene	3	—	3	—	21.2 ± 0.9	42.7 ± 3.0
Cyclooctatetraene[d]	4	—	4	—	−16.5 ± 1.3	12.2 ± 4.1
Styrene	3	2	4	1	17.8 ± 1.6	46.4 ± 4.4
Trans-stilbene[b]	7	4	8	2	42.0 ± 3.1	99.3 ± 8.7
Trans-trans-1,4-diphenyl-1,3-butadiene[c]	8	4	9	2	43.6 ± 3.4	108.1 ± 9.7
Acenaphthylene[d]	6	8	8	4	22.4 ± 4.9	79.7 ± 10.5
Fluoranthene[d]	8	12	11	6	39.6 ± 5.8	118.4 ± 13.5
Biphenylene[d]	6	8	8	4	−37.1 ± 5.2	20.2 ± 10.8
Azulene[d]	5	4	6	2	5.2 ± 3.2	48.1 ± 7.4
Fulvene[d]	2	2	3	1	1.1 ± 2.8	22.5 ± 4.9
Heptafulvene[d]	3	2	4	1	1.9 ± 2.9	30.6 ± 5.7
Heptafulvalene[d]	7	4	8	2	2.7 ± 4.3	60.0 ± 9.9

[a] ΔH°_f data taken from Cox and Pilcher[4] with the following exceptions: ΔH°_f (fulvene) calculated from the value for dimethyl fulvene, +32.1 ± 1.3 kcal/mole, using the increment $[\Delta H^\circ_f((CH_3)_2C{=}C(CH_3)_2) - \Delta H^\circ_f((CH_3)_2C{=}CH_2)] = (-16.42 \pm 0.25) - (-4.26 \pm 0.15) = -12.16 \pm 0.40$, giving $+32.1 \pm 1.3 + 12.16 \pm 0.4 = +44.26 \pm 1.7$ kcal/mole. ΔH°_f values for heptafulvene and heptafulvalene 57.50 ± 1.5 and 103.73 ± 1.5 kcal/mole respectively calculated from heat of hydrogenation data[25] in diethylcarbitol solution assuming (i) that the values would be the same in the gas phase, and (ii) ΔH°_f values for the reduced compounds based on Cox and Pilcher's ΔH°_f structural parameters[4] and 6.2 kcal/mole for the strain energy in the 7-membered ring(s), i.e. ΔH°_f (C_8H_{18}) = −35.13 and ΔH°_f ($C_{14}H_{26}$) = −27.04 kcal/mole.

[b] ΔH°_{subl} for *trans*-stilbene taken to be 19.0 kcal/mole, nearer that for 1,2-diphenyl ethane, 20.1 kcal/mole, instead of the 16.5 kcal/mole for the *cis* isomer[4] in view of the greater structural similarity to the former.

[c] ΔH°_{subl} for *trans–trans*-1,4-diphenyl-1,3-butadiene taken to be 21 kcal/mole.

[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 1,3-cycloheptadiene. These values, 5.91 and 6.37, were calculated from the heats of atomization, taking $E(C_d{-}C_d) = 98.27$ obtained from ΔH°_a (1,3-butadiene) and Cox and Pilcher's values for the bond energy terms E(C=C), $E(C_d{-}H)$, and $E(C_d{-}H)_2$.[4] This value for $E(C_d{-}C_d)$ thus includes any stabilization energy there may be in the acyclic structure.

regarded as localized double and single bonds. The new value of +12.2, although positive and therefore indicative of stabilization, does not contravene the accepted view that the molecule is non-aromatic, but rather that stabilization to the extent possible in the planar acyclic polyene, *trans*-butadiene, is very substantially reduced in this non-planar cyclic structure.

(2) *Biphenylene.* Since the strain energy in cyclobutene is 30.0, and in cyclopropene which clearly has much greater bond angle distortion, 53.8,[4] it would seem improbable that the strain energy associated with the central four-membered ring in biphenylene would much exceed, say, 50, and could be appreciably less. Against this background the net destabilization, represented by the old value of −37.1 suggested that the two benzene-like rings in biphenylene stabilize the structure to an extent far less than that expected for two benzene rings as such. This conclusion in its qualitative sense still holds, but, with the shifted base-line, a net stabilization is now apparent.

(3) *Styrene,* trans-*stilbene,* trans-trans-1,4-*diphenyl*-1,3-*butadiene.* With the old values there was no indication that the increased conjugation resulted in any greater stabilization than that of the constituent benzene ring(s):—styrene and benzene, 17.8 compared to 21.2 (actually less); stilbene and two benzenes, 42.0 compared to 42.4 (same); diphenylbutadiene and two benzenes 43.6 compared to 42.4 (still the same within experimental uncertainty). On the other hand the new values give evidence of a progressive increase in stabilization energy as the conjugation is increased:— styrene and benzene, 46.4 compared to 42.7; stilbene and two benzenes, 99.3 compared to 85.4; diphenyl-butadiene and two benzenes, 108.1 compared to 85.4. A progressive increase is certainly more in keeping with simple expectation, and the enhancement above the contribution computed according to the number of benzene rings would appear to follow closely that based on the butadiene-type structure, i.e. about 7.2 per C_{sp^2}–C_{sp^2} formal bond.

(4) *Acenaphthylene* and *fluoranthene.* The same kind of cumulative, or quasi-additive, relationship shows up in the new values for these compounds. With the old values, 22.4 for acenaphthylene, in which CH=CH bridges the 1,8 carbon atoms of naphthalene, is substantially less than that for the parent naphthalene, 30.3. For fluoranthene, in which two adjacent carbon atoms of a benzene ring bridge the 1,8 carbon atoms of naphthalene, the old value of 39.6 is far lower than that for the component ring systems, 21.2 + 30.3 = 51.5. On the other hand with the new values we have acenaphthylene a little greater than naphthalene, 79.7 compared to 73.3, and fluoranthene, 118.4 very close to the sum of the values for the component rings 42.7 + 73.3 = 116.0.

(5) *Azulene, fulvene, heptafulvene and heptafulvalene.* Turning finally to this group of molecules, which have 5- and/or 7-membered ring structures, the very striking feature about the old values is that they are all very low—zero, in fact to within experimental uncertainty. With reference to *trans*-butadiene, in other words, the thermochemical data for these compounds give no evidence of stabilization at all. But to a varying extent, other physical properties of these molecules suggest some degree of aromatic character.[26] While a difference of this kind is not inconceivable in principle, the sharp contrast is nevertheless surprising. With the new values, on the other hand, all these molecules have sizeable stabilization energies, ranging from 22.5 to 60.0 kcal/mole. Moreover, these values bear favorable comparison to those for their isomeric counterparts. For fulvene, an isomer of benzene, the value is a little more than half that of benzene: and for azulene, an isomer of naphthalene, the value of 48.1 is about two-thirds of the value for naphthalene. The use of 90°-butadiene as the reference structure thus leads to stabilization energies more in keeping with expectation.

DISCUSSION

The stabilization energies in Tables 2 and 3 show that quite different values are arrived at even though each set of reactions is homodesmotic according to the criteria specified at the outset. However, unlike the different values that arise from the various reactions that are only isodesmic, e.g. reactions A, B, C(i), (ii) and (iii) in Table 1, which involve changes in the mismatch in bond types, the different values for the homodesmotic reactions are a consequence of the inherent stabilization of *trans*-1,3-butadiene relative to 90°-1,3-butadiene.

It was clearly recognized in our previous papers[1,2] that in using *trans*-1,3-butadiene as one of the reference compounds, the values for the cyclic conjugated hydrocarbons are necessarily relative to whatever the stabilization energy is in this structure, making due allowance for the stoichiometric factors. This initial approach was entirely practical in conception, utilizing experimental thermochemical data for reactants and products to evaluate the reaction heats, which implicitly employs the appropriate ground state species at 25°. But obviously any stereo-isomer,[†] conformer, or excited state of the molecule(s) that serve as reference would equally well meet the homodesmotic criteria. The use of 90°-butadiene, the unique structure with "localized" double and single bonds, makes allowance for the stabilization in the *trans*-1,3-butadiene structure.

It has been customary to downplay the likely magnitude of the stabilization energy in butadiene (e.g. see Ref. 9) and in acyclic polyenes in general.[15] The classical empirical resonance energy calculations gave for butadiene 3.5 kcal/mole compared to 36.0 for benzene, see Table 3.2 of Ref. 11, or 9.7% that of benzene on a mole basis. This rather small fraction strengthened the view, implied by the nomenclature, that "acyclic aliphatic polyenes" could properly be regarded as in a class apart from the "cyclic aromatic benzenoid hydrocarbons"—and that the difference between the two was truly one of kind and not merely degree.

However, with the stabilization energy of *trans*-1,3-butadiene put at 7.16 kcal/mole relative to the 90°-conformer, and that of benzene at 42.65 for the homodesmotic reaction involving benzene and the 90°-conformer, *trans*-1,3-butadiene now has a stabilization energy 17% that of benzene.

These new values lessen the contrast between the two compounds, and, taking into account the smaller size of the butadiene: C_4 compared to C_6, with fewer bonds, the case for making such a sharp distinction becomes less convincing. A more equitable basis for comparing the stabilization energies of acyclic and cyclic polyenes is obviously needed.

[†] The energy difference between the *cis*- and *trans*-isomers of 1,3-butadiene is 2.50 kcal/mole according to Carriera's recent spectroscopic studies.[17] With the *cis*-isomer as the reference compound instead of the *trans*, i.e. a less stable structure, the stabilization energy of benzene is correspondingly increased from 21.2 to the larger value of 28.7 kcal/mole.

The general structure for the acyclic compounds is

$$CH_2{=}CH{-}(CH{=}CH{-})_nCH{=}CH_2.$$

Butadiene, for which n = 0, is not strictly the first member of the series since it contains formal $C_{sp^2}{=}C_{sp^2}$ double bonds only in terminal positions. Hence, there is a possibility that the magnitude of its stabilization energy is unduly influenced by "end effects" in relation to longer chain compounds. 1,3,5-Hexatriene, with n = 1, is the first member, and at present it appears to be the only one of the longer chain structures for which the necessary combustion heat has been determined, so ΔH_f° can be calculated. Using the value -871.91 ± 3 kcal/mole reported by Kreysig *et al.*,[12] together with $\Delta H_f^\circ\ (CO_2)_g$ and $\Delta H_f^\circ\ (H_2O)_l$ from Cox and Pilcher,[4] we find ΔH_f° (1,3,5-hexatriene) = 34.34 ± 3 kcal/mole. Two points should be noted: first, that the experimental error is larger than usual; secondly, that the value is apparently for the *cis–trans–cis* isomer. In this isomer there would be two pairs of unfavorable C–H interactions like the one pair present in *cis*-1,3-butadiene. With butadiene, the *cis*-isomer is about 2.50 kcal/mole less stable than the *trans*-isomer.[17] Thus for all-*trans*-1,3,5-hexatriene one would expect ΔH_f° to be about 5.0 kcal/mole more favorable, i.e. less positive, about 29.34 kcal/mole.

For the purpose of the following argument, however, it is desirable to underestimate the magnitude of the stabilization energy in the hexatriene to guard against overemphasizing any conclusion that depends on the largeness of the value. We shall therefore take ΔH_f° for the *cis–trans–cis* isomer to be that for the all-*trans* compound.† In view of this compromise, we shall quote the results of calculations to only the nearest kcal. Setting up the homodesmotic reaction with 90°-butadiene as reference, like reaction D(i) for benzene

$$CH_2{=}CH{-}CH{=}CH{-}CH{=}CH_2 + CH_2{=}CH_2 \rightarrow 2(90^\circ)CH_2{=}CH{-}CH{=}CH_2$$

we get ΔH^c, the stabilization energy of the triene, 20 kcal/mole. Thus for the acylic structure which has the *same* number of carbon atoms as benzene, the stabilization energy is nearly 50% of the benzene value. If, as the acyclic polyene chainlength is increased further, the increment in stabilization energy is identical to that between *trans*-1,3-butadiene and *cis–trans–cis*-1,3,5-hexatriene, then the stabilization energy of benzene, 42.7, would be about matched by that of all-*trans*-1,3,5,7,9-decapentaene, i.e. 45 kcal/mole.

Finally, returning to benzene again, the homodesmotic stabilization energy with respect to ethylene and 90°-butadiene as reference compounds is an energy difference relative to structures with localized double and single bonds of lengths about 1.336 and 1.518 Å respectively. Its evaluation at no stage involves any suppositions or assumptions about thermochemical bond energy terms. In this respect it is still a purely experimental quantity.

However, from the known geometry of ethylene, and the geometry of 90°-butadiene obtained from the molecular mechanics program,[19] it is in principle possible to calculate the stabilization of benzene with respect to localized double and single bonds whose lengths would correspond to those in other structures, such as the Kekulé structure, with bond lengths about 1.397 Å, that have played such an important role in the historical development of the theory of aromatic compounds. The results of such compressional energy calculations, as suggested by Lennard-Jones[27] and developed by Hornig[28] and by Coulson and Altman,[29] will be presented in a forthcoming publication.

Note added in proof: The papers by M. H. Palmer and R. H. Findlay (*J. Chem. Soc.* Perkin II, 1885, 1974) and M. H. Palmer and S. M. F. Kennedy (*J. Chem. Soc.* Perkin II, 1893, 1974) have recently come to our attention in which they utilize the 90°-1,3-butadiene structure in theoretical calculations of classical resonance energies.

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†It is more likely that the hexatriene used by Kreysig *et al.* was the all-*trans* compound, i.e. with the s-t T s-t structure, since the rotational barriers about the formal $C_{sp^2}{-}C_{sp^2}$ single bonds are unlikely to be great enough to permit the s-*cis* conformers to be isolated.