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The Heat of Hydrogenation of (a) Cyclohexatriene

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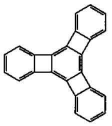
Benzene is the quintessential protagonist in the fundamental theoretical concept of aromaticity.[1] One of the earliest indications[2] of the special nature of benzene was its relative thermodynamic stability (and associated lack of reactivity), a feature quantified in numerous ways as "resonance" or stabilization (SE) energy. The latter is most conveniently based on a comparison of the energy of benzene with that of a "hypothetical" cyclohexatriene, either D_{3h}-1,3,5-cyclohexatriene or D_{6h}-Kekulé benzene. Both species have been the subject of numerous theoretical treatments,[1−3] but only the former may, in principle, be scrutinized experimentally in a system which is designed to distort the regular benzene frame to furnish a bond-alternating array. If, in such, the interaction between double bonds were minimized, it might provide the long-sought textbook[4] model on which to test one of the most frequently quoted first approximations of the empirical resonance energy, namely the difference between the heat of hydrogenation of benzene (-49.1 kcal mol^{-1})[5] and that of three cyclohexenes (-84.8 kcal mol^{-1}),[6] SE $= 35.7$ kcal mol^{-1}. We reported some time ago the synthesis,[7a] and, very recently, structure,[7b] of such a nucleus embedded in the C_3- symmetric [4]phenylene **1**,[7c] for which various geometric (cf. **6**),[8,9] dynamic,[10] magnetic,[11] spectral,[7a,c,12] and chemical[13] criteria point to the presence of three minimally interacting central double bonds.[14] This feature of **1** was originally[7a,8c] interpreted as being the result of avoided antiaromaticity ("π-strain"), but subsequent theoretical treatments have invoked a considerable contribution of a σ-frame distortion effect ["strain-induced bond localization" (SIBL) or "Mills−Nixon effect"][15] to the structure of **1**, sparking a lively discussion that is relevant within the context of the debate on the structure of benzene itself, in which the π-frame is proposed to be distortive, but the σ-frame symmetrizing.[16] Regardless of the factors that might contribute to the bond alternation in **1**, the question arises whether its three reactive alkene units will behave as such quantitatively, for example, and most diagnostically, in a heat of hydrogenation measurement **1** → **2**. We report such data for **1** and, for comparison, also the less "bond-fixed"[17] angular [3]phenylene **3** (to give **4**)[18] and, to place the results on a more absolute thermochemical footing, also the heats of combustion of **1** and **3**. The latter provide the first experimental enthalpies of formation for members of the phenylene class of hydrocarbons[7c] beyond biphenylene **5**, important data for gauging the accuracy of current high level calculational estimates.[11,19]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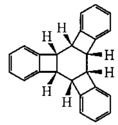
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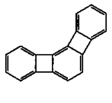
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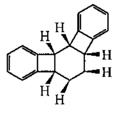
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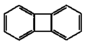
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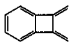
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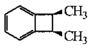
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Details of the experimental techniques and measurements are provided in the Supporting Information. The results are listed in Table 1 together with ΔH°_f estimates of **1−4** by various methods.

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(8) Based on the very similar geometry of the central ring of the hexasilylderivative of **1**:[7a] (a) Bird, C. W. *Tetrahedron* **1998**, *54*, 4641−4646. (b) Kovaček, D.; Margetić, D.; Maksić, Z. B. *J. Mol. Struct. (THEOCHEM)* **1993**, *285*, 195−210. (c) Baldridge, K. K.; Siegel, J. S. *J. Am. Chem. Soc.* **1992**, *114*, 9583−9587.

(9) Simply applying [Σ single bond lengths $-$ Σ double bond lengths]/3 as a measure of bond alternation and using the experimental structural data for the exocyclic diene portion of 3,4-dimethylenecyclobutene **6** (1.497, 1.338 Å; Brown, R. D.; Godfrey, P. D.; Hart, B. T.; Ottrey, A. L.; Onda, M.; Woodruff, M. *Aust. J. Chem.* **1983**, *36*, 639−648) as 100% standard, the central ring in **1** (averaged bond lengths 1.497, 1.343 Å) is 97.3% "bond fixed".

(10) Hindered rotation of attached Cr(CO)$_3$: Nambu, M.; Mohler, D. L.; Hardcastle, K.; Baldridge, K. K.; Siegel, J. S. *J. Am. Chem. Soc.* **1993**, *115*, 6138−6142.

(11) Nucleus independent chemical shift (NICS) values for the central ring of **1**: -1.1 ppm, the "cyclobutadiene" rings: -0.4 ppm, the terminal benzene nuclei: -10.7 ppm. Schulman, J. M.; Disch, R. L.; Jiao, H.; Schleyer, P. v. R. *J. Phys. Chem. A* **1998**, *102*, 8051−8055.

(12) Most striking is the unusually high energy "stilbenoid" chromophore of **1** and the relatively highly shielded central carbons (δ 130.13 ppm; cf. biphenylene: δ 151.7 ppm, or the remaining four-membered ring carbons in **1**: $\delta = 148.44$ ppm).

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(16) See, inter alia: Shaik, S.; Shurki, A.; Danovich, D.; Hiberty, P. C. *J. Mol. Struct. (THEOCHEM)* **1997**, *398−399*, 155−167.

(17) (a) Nambu, M.; Hardcastle, K.; Baldridge, K. K.; Siegel, J. S. *J. Am. Chem. Soc.* **1992**, *114*, 369−371. (b) Nambu, M.; Siegel, J. S. *J. Am. Chem. Soc.* **1988**, *110*, 3675−3676. (c) See also the data for **2** in refs 8 and 11. By the criterion described in ref 9, the central ring is 62% bond-localized.

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Table 1. Experimental and Calculated Enthalpies of Formation for **1**−**4** and Experimental Heats of Hydrogenation for **1** and **3** (All Values in kcal mol^{-1})

compound	1	2	3	4
ΔH°_c (cr)[a]	2884.4 ± 1.5		2181.3 ± 0.9	
ΔH°_f (cr)[a]	218.6 ± 1.5		146.8 ± 0.9	
ΔH°_{sub}[b]	31.3 ± 1		27.5 ± 0.2	
ΔH°_f (g)	249.9 ± 1.9	178.3 ± 2.4	174.3 ± 0.9	107.5 ± 1.4
ΔH°_{hyd}	−71.6 ± 1.5		−66.8 ± 1.0	
HF/6-31G*[c]	250.2		176.7	
BLYP/6-31G*[c]	250.2		176.7	
MMX	263.2	202.1	181.2	114.2
AM1	305.7	201.7	214.5	117.5
PM3	274.3	175.9	193.0	102.5

[a] cr = crystalline. [b] sub = sublimation. [c] Reference 19b.

The agreement between the measured and ab initio calculated[19b] ΔH°_f values for **1** and **3** is extraordinary, whereas more approximate methods fare poorly. Our data provide ($\sigma + \pi$)-strain corrections to ΔH°_f estimates based on ("unstrained") group increment techniques ("Benson numbers")[20] for **1**: 147.9 kcal mol^{-1} and **3**: 99.7 kcal mol^{-1}.[21] Comparison to that derived[21] for **5** (ΔH°_f = 100.5):[22] 53.3 kcal mol^{-1} shows (slight) attenuation of ring strain with increasing benzocyclobutadienofusion of benzene → **5** → **3** → **1**, corroborating calculational results.[19a,b] Consequently, the "experimental" homodesmotic[23] reaction eq 1 is slightly exothermic.

$$\begin{array}{lcccccccc} & \mathbf{3} & + & \mathbf{5} & \xrightarrow{-5.1} & \mathbf{1} & + & \text{benzene} & (1) \\ \Delta H^\circ_f\,(\text{kcal mol}^{-1}) & 174.3 & & 100.5 & & 249.9 & & 19.8^{22} & \end{array}$$

$$\begin{array}{lcccccc} & 3\ (\mathbf{7}) & \xrightarrow{+12.60} & \mathbf{1} & + & 3\ \text{ethene} & (2) \\ \Delta H^\circ_f\,(\text{kcal mol}^{-1}) & 91.6 & & 249.9 & & 12.54^{22} & \end{array}$$

$$2\ (\mathbf{7}) + \text{1,3-butadiene} \xrightarrow{+3.75} \mathbf{3} + 3\ \text{ethene} \qquad (3)$$

$$3\ (\mathbf{8}) \xrightarrow{+11.42} \mathbf{2} + 3\ \text{ethane} \qquad (4)$$

$$2\ (\mathbf{8}) + \text{butane} \xrightarrow{+1.32} \mathbf{4} + 3\ \text{ethane} \qquad (5)$$

With expressed recognition of the caveats associated with such procedures (experimental errors, choice of models, suitability of bond and strain increments, and the symmetry of **1** which may multiply aberrations of the latter),[24] one may attempt to dissect the various strain components in **1**. For this purpose, the central ring is treated as a cyclohexatriene, the σ-strain in the dimethylenebenzocyclobutene (**7**) substructure is equal to that of benzocyclobutene (32.8 kcal mol^{-1})[20b,21,25] plus two sp^2-Cs (2 × 1.6 kcal mol^{-1}),[26] and the bond angle distortion from 135°[11,27] to 120° of the diene unit in **7** (and the associated rehybridization strain) estimated by the homodesmotic reaction ΔH°-calculation (MP2/6-31G**) eq 2: 12.6 kcal mol^{-1}. As a "check", this number can be used in conjunction with the ΔH°_f (exp) of **1** and ethene to suggest a ΔH°_f (**7**) = 91.6 kcal mol^{-1} (eq 2), very close to the Benson value of 91.0 kcal mol^{-1}.[21] Applying the above corrections, the Benson[20b] number for **1** is an encouraging ΔH°_f = 247.8 kcal mol^{-1}.[21] For **3**, similar treatment points to relative stabilization (aromaticity). For example, eq 3 (MP2/6-31G**) (which, subtracting the SE of 1,3-butadiene would be nearly thermoneutral), shows that aromaticity essentially cancels the (here slightly diminished) effect of σ-distortion quantified for **1** in eq 2.[28]

Turning to the heat of hydrogenation experiments, **1** furnishes **2** with a release of 71.6 kcal mol^{-1} (Table 1), thus revealing an experimental ΔH°_f (**2**) = 178.3 kcal mol^{-1}. To relate the former value to that measured for benzene, one has to recognize that the resulting cyclohexane in **2** is planar,[3a,8b,18a] as opposed to cyclohexane itself, and also subject to some additional substituent strain corrections not present in the component benzocyclobutene units. A variant of eq 2, namely eq 4, provides an estimate (MP2/6-31G**) for these deformations: 11.4 kcal mol^{-1}. As another "check", this calculation suggests a ΔH°_f (**8**) = 35.6 kcal mol^{-1}, almost the same as the Benson[20b] value of 35.8 kcal mol^{-1}.[21] Further encouragement for the use of the above strain correction for the cyclohexane moiety in **2** derives from a Benson[20b] calculation of ΔH°_f (**2**) using only its component incremental numbers (including the "normal" cyclohexane correction) and the benzocyclobutene strain: 165.7 kcal mol^{-1},[21] deviating from the measured value by 12.6 kcal mol^{-1}. This would indicate that ΔH°_{hyd} (**1**) should be −(83.0−84.2) kcal mol^{-1}, were it not for the extra strain in **2**, *remarkably close to that expected (−84.8 kcal* mol^{-1}*) based on the cyclohexene model of cyclohexatriene*. On the other hand, a similar treatment of **4** clearly reflects partial aromaticity in **3**. The latter hydrogenates with a lower ΔH°_{hyd} = −66.8 kcal mol^{-1} to a less strained product compared to **2**. While there are no experimental structural data, molecular mechanics simulations show a puckered, half-chair conformation for the cyclohexane portion of **4**, much like that in 1,3-cyclohexadiene.[29] The "extra" energy of this arrangement is indicated by homodesmotic eq 5 (MP2/6-31G**): 1.3 kcal mol^{-1}. Perhaps more pertinently, the Benson ΔH°_f value for **4** uncorrected for this strain is 100.7 kcal mol^{-1},[21] deviating from the measured value by 6.8 kcal mol^{-1}, suggesting a corrected ΔH°_{hyd} = −(68.1 to 73.6) kcal mol^{-1}, >10 kcal mol^{-1} less than that corresponding to **1**. Finally, from the experimental[22] ΔH°_f (**5**) = 100.5 kcal mol^{-1} and an increment-calculated[20b,21] ΔH°_f (cis-**5**-$\mathbf{H_6}$) = 35.7 kcal mol^{-1}, one estimates ΔH°_{hyd} (**5**) = −64.8 kcal mol^{-1}, pointing to further stabilization of **5** relative to **3**, although still reflecting activated character.[30]

In summary, we contend that the σ- and π-strain in **1** act in conjunction to render its core to behave as a true cyclohexatriene not only structurally, spectroscopically, and chemically but also in a quantitative manner in its heat of hydrogenation.

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Supporting Information Available: Experimental details of the determination of the heats of combustion and hydrogenation of **1** and **3**, and information on calculational procedures (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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[21] For the details of the group increment calculations, see Supporting Information.

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[26] Deniz, A. A.; Peters, K. S.; Snyder, G. J. *Science* **1999**, *286*, 1119−1122, especially footnote 32.

[27] We thank Professor Schulman for providing us with the geometric coordinates of calculated **7**.

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