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The Heat of Hydrogenation of (a) Cyclohexatriene

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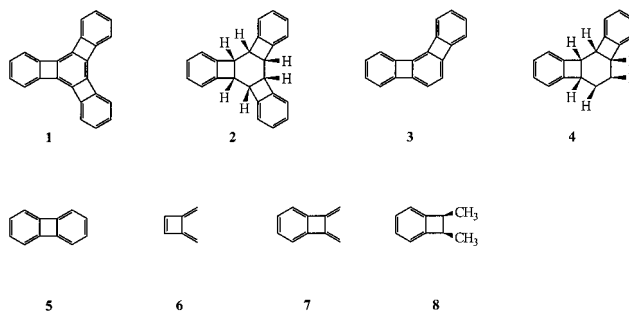
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Benzene is the quintessential protagonist in the fundamental theoretical concept of aromaticity.¹ One of the earliest indications² of the special nature of benzene was its relative thermodynamic stability (and associated lack of reactivity), a feature 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 textbook⁴ 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_{3v}-symmetric [4]phenylene **1**,^{7c} for which various geometric (cf. **6**),^{8,9} dynamic,¹⁰ magnetic,¹¹ spectral,^{7a,c,12} and chemical¹³ 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}



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.

(8) Based on the very similar geometry of the central ring of the hexasilyl derivative 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) Baldrige, K. K.; Siegel, J. S. *J. Am. Chem. Soc.* **1992**, *114*, 9583–9587.

(9) Simply applying $[\sum \text{single bond lengths} - \sum \text{double bond lengths}]/3$ 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.; Otter, 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.; Harcastle, K.; Baldrige, 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**: δ = 148.44 ppm).

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[†] Universität Freiburg.

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[§] Long Island University.

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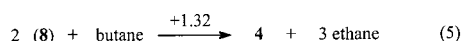
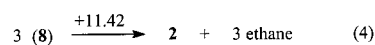
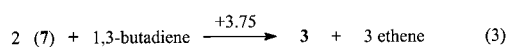
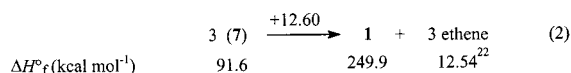
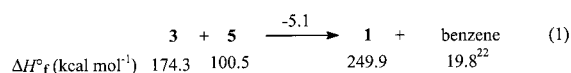
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Table 1. Experimental and Calculated Enthalpies of Formation for **1–4** and Experimental Heats of Hydrogenation for **1** and **3** (All Values in kcal mol⁻¹)

compound	1	2	3	4
$\Delta H_f^\circ(\text{cr})^a$	288.4 ± 1.5		218.1 ± 0.9	
$\Delta H_f^\circ(\text{cr})^a$	218.6 ± 1.5		146.8 ± 0.9	
$\Delta H_{\text{sub}}^\circ$	31.3 ± 1		27.5 ± 0.2	
$\Delta H_f^\circ(\text{g})$	249.9 ± 1.9	178.3 ± 2.4	174.3 ± 0.9	107.5 ± 1.4
$\Delta H_{\text{hyd}}^\circ$	-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 derived²¹ for **5** ($\Delta H_f^\circ = 100.5$):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” homodesmotic²³ reaction eq 1 is slightly exothermic.



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 sp²-Cs (2 × 1.6 kcal mol⁻¹),²⁶ and the bond angle distortion from 135°^{11,27} to

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(21) For the details of the group increment calculations, see Supporting Information.

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

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 $\Delta H_f^\circ = 247.8$ 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 $\Delta H_{\text{hyd}}^\circ$ (**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 $\Delta H_{\text{hyd}}^\circ = -66.8$ 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 $\Delta H_{\text{hyd}}^\circ = -(68.1 \text{ to } 73.6)$ kcal mol⁻¹, > 10 kcal mol⁻¹ less than that corresponding to **1**. Finally, from the experimental²² ΔH_f° (**5**) = 100.5 kcal mol⁻¹ and an increment-calculated^{20b,21} ΔH_f° (cis-**5-H₆**) = 35.7 kcal mol⁻¹, one estimates $\Delta H_{\text{hyd}}^\circ$ (**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.

Acknowledgment. This work is dedicated to Professor R. Neidlein on the occasion of his 70th birthday and was supported by the National Science Foundation (CHE-9610430) and Deutsche Forschungsgemeinschaft. We are grateful for fellowships to R.F. (Kekulé; Fonds der chemischen Industrie), A.J.M. (Syntex; ACS Division of Organic Chemistry, sponsored by Rohm and Haas Co.), and S.W. (DFG), and for intellectual input from Professors R. G. Bergman and A. Streitwieser.

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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(28) Benson’s number for **3** as a cyclohexatriene, but without this correction (which, if proportional, would be 8.4 kcal mol⁻¹) is 174.0 kcal mol⁻¹.

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