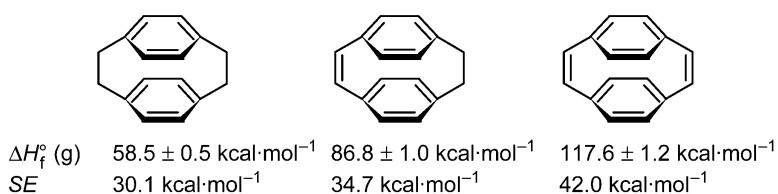Article

Heats of Formation of [2.2]Paracyclophane-1-ene and [2.2]Paracyclophane-1,9-diene – An Experimental Study

Armin de Meijere, Sergei I. Kozhushkov, Karsten Rauch, Heiko Schill, Sergey P. Verevkin, Martin Kmmerlin, Hans-Dieter Beckhaus, Christoph Rchardt, and Dmitrii S. Yufit

ΔH_f° (g)	58.5 ± 0.5 kcal·mol^{-1}	86.8 ± 1.0 kcal·mol^{-1}	117.6 ± 1.2 kcal·mol^{-1}
SE	30.1 kcal·mol^{-1}	34.7 kcal·mol^{-1}	42.0 kcal·mol^{-1}

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Heats of Formation of [2.2]Paracyclophane-1-ene and [2.2]Paracyclophane-1,9-diene – An Experimental Study

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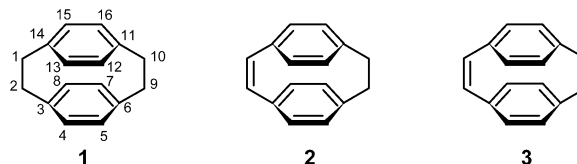University of Durham, Durham, South Road, DH1 3LE, England*

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Abstract: The enthalpies of formation [$\Delta H_f^{\circ}(g)$] of tricyclo[8.2.2.2^{4,7}]hexadeca-1(13),2,4(16),5,7(15),10-(14),11-heptaene (**2**, 1,2-dehydro[2.2]paracyclophane or [2.2]paracyclophane-1-ene) and tricyclo[8.2.2.2^{4,7}]-hexadeca-1(13),2,4(16),5,7(15),8,10(14),11-octaene (**3**, 1,2,9,10-dehydro[2.2]paracyclophane or [2.2]-paracyclophane-1,9-diene) have been determined by measuring their heats of combustion in a microcalorimeter and their heats of sublimation by the transpiration method. Values of the strain energies (SE) [SE(**2**) = 34.7 kcal mol^{-1}, SE(**3**) = 42.0 kcal mol^{-1}] have been derived from the gas-phase heats of formation and are compared with those from MM3 and PM3 calculations and with the corresponding value SE(**1**) = 30.1 kcal mol^{-1} for the parent tricyclo[8.2.2.2^{4,7}]hexadeca-1(13),4(16),5,7(15),10(14),11-hexaene (**1**, [2.2]-paracyclophane). The higher strain energies of **2** and **3** (by 4.6 and 11.9 kcal mol^{-1}) are in accord with the well-known increased reactivities of their aromatic rings as a consequence of their increased bending. As revealed by an X-ray crystal structure analysis, the bending in the monoene **2** corresponds to that of **1** and **3** at one of two bridging corners.

Introduction

[2.2]Paracyclophane (**1**), first prepared by Farthing in 1949[1] and in the following 20 years thoroughly investigated by Cram et al.,[2] has become the archetype of strained compounds with bent aromatic rings.[3] The [2.2]paracyclophane-1-ene (**2**) and the [2.2]paracyclophane-1,9-diene (**3**) have to be strained to the same or an even higher extent, as the bending angle of the benzene moieties increases upon introduction of one or two double bonds into the bridges.[4,5] Consequently, the reactivity

of the benzene rings in **2** and **3** toward cycloadditions of electrophilic reagents increases in the order **1** < **2** < **3**.[6] To quantify the additional strain in **2** and **3**, we have determined heats of formation, $\Delta H_f^{\circ}(g)$, of both compounds by high precision combustion calorimetry and the transpiration method, using carefully purified samples (>99.98% pure form).

Results and Discussion

The hydrocarbons [2.2]paracyclophane-1-ene (**2**)[7–9] and [2.2]-paracyclophane-1,9-diene (**3**)[7,9] were prepared according to established procedures and purified thoroughly (see Experimental Section) for the thermochemical measurements. The heat of combustion measurements, performed as described previ-

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(1) Brown, C. J.; Farthing, A. C. *Nature* **1949**, *164*, 915–916.
(2) (a) Cram, D. J.; Steinberg, H. *J. Am. Chem. Soc.* **1951**, *73*, 5691–5704. (b) Reich, H. J.; Cram, D. J. *J. Am. Chem. Soc.* **1967**, *89*, 3078–3800. (c) Cram, D. J.; Bauer, R. H. *J. Am. Chem. Soc.* **1959**, *81*, 5971–5977. (d) Cram, D. J.; Bauer, R. H.; Allinger, N. L.; Reeves, R. A.; Wechter, W. J.; Heilbronner, E. *J. Am. Chem. Soc.* **1959**, *81*, 5977–5983. (e) Cram, D. J.; Knox, G. R. *J. Am. Chem. Soc.* **1961**, *83*, 2204–2205. (f) Cram, D. J.; Cram, J. M. *Acc. Chem. Res.* **1971**, *4*, 204–213.
(3) For reviews, see: (a) Keehn, P. M.; Rosenfeld, S. M. *Cyclophanes, I, II*; Academic Press: New York, 1983. (b) Vögtle, F. *Cyclophane Chemistry*; Wiley: New York, 1993. (c) Bodwell, G. J. *Angew. Chem.* **1996**, *108*, 2221–2224; *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2085–2088. (d) de Meijere, A.; König, B. *Synlett* **1997**, 1221–1232.
(4) Geometry of **1**: (a) Brown, C. J. *J. Chem. Soc.* **1953**, 3265–3270. (b) Hope, H.; Bernstein, J.; Trueblood, K. N. *Acta Crystallogr., Sect. B* **1972**, *28*, 1733–1743. (c) Lonsdale, K.; Milledge, H. J.; Rao, K. V. K. *Proc. R. Soc. London A* **1960**, *255*, 82–100. Geometry of **3**: (d) Coulter, C. L.; Trueblood, K. N. *Acta Crystallogr.* **1963**, *16*, 667–676.

(5) For the geometries of metal-complexed hydrocarbons **2** and **3**, see also: (a) Albrecht, K.; Hockless, D. C. R.; König, B.; Neumann, H.; Bennett, M. A.; de Meijere, A. *J. Chem. Soc., Chem. Commun.* **1996**, 543–544. (b) de Meijere, A.; Reiser, O.; Stöbbe, M.; Kopf, J.; Adiwidjaja, G.; Sinnwell, V.; Khan, S. I. *Acta Chem. Scand. A* **1988**, *42*, 611–625. For the computational results concerning the geometry of [2.2]paracyclophane (**1**) at different levels of theory, see: (c) Henseler, D.; Hohlneicher, G. *J. Phys. Chem. A* **1998**, *102*, 10828–10833.
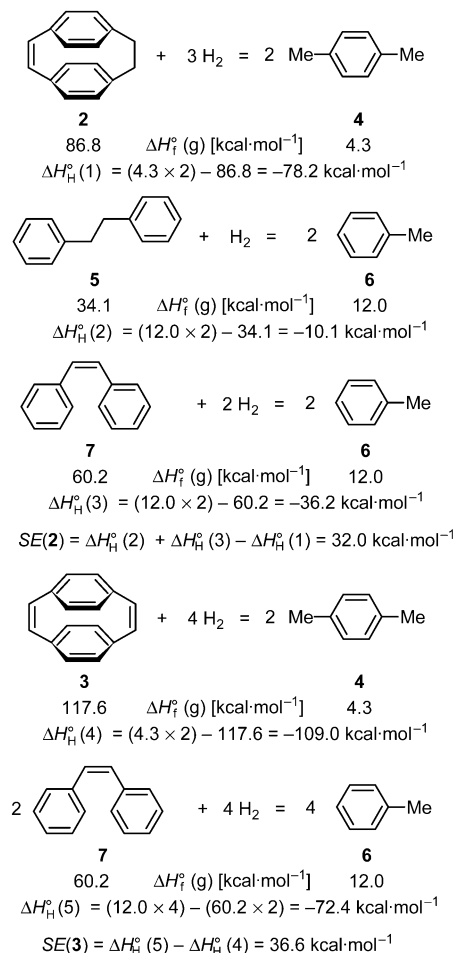
ously,[10] gave $\Delta H_f^\circ(g) = 86.8 \pm 1.0$ kcal mol^{-1} for [2.2]-paracyclophane-1-ene (**2**) and 117.6 ± 1.2 kcal mol^{-1} for [2.2]paracyclophane-1,9-diene (**3**). The corresponding values for paracyclophanes **1**, **2**, and **3** calculated using the MM3 force field were 58.3, 89.9, and 117.8 kcal mol^{-1}, respectively. When the PM3 semiempirical method was applied, $\Delta H_f^\circ(g)$ values of 60.6, 90.9, and 120.8 kcal mol^{-1} were obtained. However, DFT calculations (B3LYP with different basis sets) overestimate these energies by $18-28$ kcal mol^{-1}.

These experimentally determined values exceed the corresponding value of the parent [2.2]paracyclophane (**1**)[11] (58.8 ± 0.8 kcal mol^{-1}) by 28.0 and 58.8 kcal mol^{-1}, respectively. For comparison, the enthalpy of dehydrogenation of 1,2-diphenylethane (**5**) into *cis*-stilbene (**7**) is $60.2 - 34.1 = 26.1$ kcal mol^{-1}.[12] Accordingly, the dehydrogenation of every ethano bridge in **1** is ca. $2-3$ kcal mol^{-1} more endothermic than the transformation of **5** to **7**.
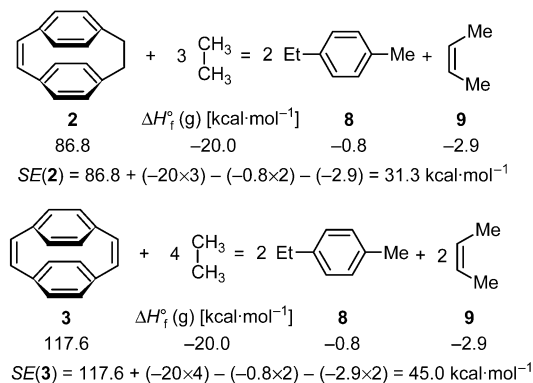
The concept of strain and strain energy (*SE*) provides a basis that helps to correlate structures, stabilities, and reactivities of molecules.[13] Strain enthalpy reflects a nonadditive component of the enthalpy of a molecule and appears to be unique for each molecule. For the parent [2.2]paracyclophane (**1**), *SE* was determined as the difference between the experimentally obtained $\Delta H_f^\circ(g)$ and the calculated sum of the Benson type[14] or of the Cox type[15] increments to be 29.0[11a] and 29.6[11b] kcal mol^{-1}, respectively. When Boyd's approach[16] for qualitative estimation of *SE*'s in cyclophanes was applied by comparing the enthalpy of hydrogenation for **1** and unstrained molecules, values of 31.4[11a] and 31.5[16] kcal mol^{-1} have been obtained. However, with the latter approach, the *SE*'s of di- and tetradehydro[2.2]paracyclophanes **2** and **3** are significantly underestimated (Scheme 1).

Qualitative estimation of *SE*'s using the homodesmotic equations[13] (Scheme 2) gave essentially the same value (31.3 kcal mol^{-1}) for the *SE* in didehydroparacyclophane **2**. The result

(6) The diene **3** reacts more rapidly with diazomethane/copper(I) chloride than **1**. (a) Näder, R.; de Meijere, A. *Angew. Chem.* **1976**, *88*, 153−154; *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 166−167. Under the conditions, under which **3** undergoes cycloaddition of singlet oxygen, **1** is completely inert: (b) Erden, I.; Gölitz, P.; Näder, R.; de Meijere, A. *Angew. Chem.* **1981**, *93*, 605−606; *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 583−585. The [4+2] cycloaddition of *N*-phenyltriazolinedione (PTAD) to **3** proceeds at ambient temperature within 8 h, see: (c) Höfer, J. Dissertation, Universität Hamburg, 1989. The [4+2] cycloaddition of PTAD to **1** requires 138 h at ambient temperature, see: (d) Kleinschroth, J.; Hopf, H. *Angew. Chem.* **1982**, *94*, 485−496; *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 469−480.
(7) Dewhirst, K. C.; Cram, D. J. *J. Am. Chem. Soc.* **1958**, *80*, 3115−3125.
(8) Hopf, H.; Psiorz, M. *Chem. Ber.* **1986**, *119*, 1836−1844.
(9) Stöbbe, M.; Reiser, O.; Näder, R.; de Meijere, A. *Chem. Ber.* **1987**, *120*, 1667−1674.
(10) Beckhaus, H.-D.; Rüchardt, C.; Kozhushkov, S. I.; Belov, V. N.; Verevkin, S. P.; de Meijere, A. *J. Am. Chem. Soc.* **1995**, *117*, 11854−11860.
(11) Three values of $\Delta H_f^\circ(g)$ for the parent [2.2]paracyclophane (**1**) which are all very close to one another have been reported in the literature: (a) Rodgers, D. L.; Westrum, E. F., Jr.; Andrews, J. T. S. *J. Chem. Thermodyn.* **1973**, *5*, 733−739 (57.6 ± 1.0 kcal mol^{-1}). (b) Nishiyama, K.; Sakiyama, M.; Seki, S. *Tetrahedron Lett.* **1977**, 3739−3740 (58.3 ± 0.9 kcal mol^{-1}). (c) Nishiyama, K.; Sakiyama, N.; Seki, S.; Horita, H.; Otsubo, T.; Misumi, S. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 869−877 (58.8 ± 0.8 kcal mol^{-1}). In the present work, we rely upon this last value.
(12) The reference thermochemical data in the present paper were taken from: Domalski, E. S.; Hearing, E. D. *J. Phys. Chem. Ref. Data* **1988**, *17*, 1637−1678.
(13) Greenberg, A.; Liebman, J. F. *Strained Organic Molecules*, Organic Chemistry Series; Academic Press: New York, 1978; Vol. 38.
(14) Benson, S. W. *Thermochemical Kinetics*; Wiley: New York, 1976; p 272 ff.
(15) Cox, J. D.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*; Academic Press: New York, 1970; p 590 ff.
(16) Shieh, C.-F.; McNally, D.; Boyd, R. H. *Tetrahedron* **1969**, *25*, 3653−3665.

Scheme 1. Estimation of Strain Energies (*SE*) for Di- and Tetradehydro[2.2]paracyclophanes **2** and **3** Applying Boyd's Approach[12,16]

2 + 3 H$_2$ = 2 Me—⬡—Me **4**
86.8 $\Delta H_f^\circ(g)$ [kcal·mol^{-1}]   4.3
$\Delta H_H^\circ(1) = (4.3 \times 2) - 86.8 = -78.2$ kcal·mol^{-1}

5 + H$_2$ = 2 ⬡—Me **6**
34.1 $\Delta H_f^\circ(g)$ [kcal·mol^{-1}]   12.0
$\Delta H_H^\circ(2) = (12.0 \times 2) - 34.1 = -10.1$ kcal·mol^{-1}

7 + 2 H$_2$ = 2 ⬡—Me **6**
60.2 $\Delta H_f^\circ(g)$ [kcal·mol^{-1}]   12.0
$\Delta H_H^\circ(3) = (12.0 \times 2) - 60.2 = -36.2$ kcal·mol^{-1}

$SE(\mathbf{2}) = \Delta H_H^\circ(2) + \Delta H_H^\circ(3) - \Delta H_H^\circ(1) = 32.0$ kcal·mol^{-1}

3 + 4 H$_2$ = 2 Me—⬡—Me **4**
117.6 $\Delta H_f^\circ(g)$ [kcal·mol^{-1}]   4.3
$\Delta H_H^\circ(4) = (4.3 \times 2) - 117.6 = -109.0$ kcal·mol^{-1}

2 **7** + 4 H$_2$ = 4 ⬡—Me **6**
60.2 $\Delta H_f^\circ(g)$ [kcal·mol^{-1}]   12.0
$\Delta H_H^\circ(5) = (12.0 \times 4) - (60.2 \times 2) = -72.4$ kcal·mol^{-1}

$SE(\mathbf{3}) = \Delta H_H^\circ(5) - \Delta H_H^\circ(4) = 36.6$ kcal·mol^{-1}

Scheme 2. Estimation of Strain Energies (*SE*) for Di- and Tetradehydro[2.2]paracyclophanes **2** and **3** Applying Homodesmotic Reactions

2 + 3 $\begin{matrix}CH_3\\CH_3\end{matrix}$ = 2 Et—⬡—Me + Me⧸⧹Me **9**
  2   **8**   **9**
86.8 $\Delta H_f^\circ(g)$ [kcal·mol^{-1}]   −20.0   −0.8   −2.9
$SE(\mathbf{2}) = 86.8 + (-20.0 \times 3) - (-0.8 \times 2) - (-2.9) = 31.3$ kcal·mol^{-1}

3 + 4 $\begin{matrix}CH_3\\CH_3\end{matrix}$ = 2 Et—⬡—Me + 2 Me⧸⧹Me
  3   **8**   **9**
117.6 $\Delta H_f^\circ(g)$ [kcal·mol^{-1}]   −20.0   −0.8   −2.9
$SE(\mathbf{3}) = 117.6 + (-20.0 \times 4) - (-0.8 \times 2) - (-2.9 \times 2) = 45.0$ kcal·mol^{-1}

for tetradehydro[2.2]paracyclophane **3** looks better, but is presumably overestimated.

The calculation of *SE*'s for **2** and **3** as the difference between their experimentally obtained $\Delta H_f^\circ(g)$ and the sum of Benson type increments[14] gave the values of 34.7 and 42.0 kcal mol^{-1}, respectively. These results were also checked using a combination of strain-free group additivity increments for hydrocarbons[17] and for arenes.[18] Their advantage with respect to the classic

(17) v. Ragué Schleyer, P.; Williams, J. E.; Blanchard, K. R. *J. Am. Chem. Soc.* **1970**, *92*, 2377−2386.

Benson increments is that they can be used to determine strain enthalpies. However, essentially the same values (34.7 and 41.6 kcal mol^{-1}, respectively) were obtained when the latter systems of strain-free increments were applied. For [2.2]paracyclophane (**1**), the application of Benson[14] and Schleyer–Beckhaus[17,18] additivity increments [using the published value of $\Delta H_f^\circ(g) =$ 58.3 kcal mol^{-1} for **1**][11c] gave *SE* = 30.1 and 30.3 kcal mol^{-1}, respectively.

These data demonstrate moderate but significant increases of the *SE* upon consecutive dehydrogenation of the ethano bridges in **1** on going via **2** to **3**. The strain in the parent hydrocarbon **1**[4b,11c,16,19] has been attributed to six main terms: (a) out-of-plane deformation of the aromatic rings (ca. 9.3 kcal mol^{-1}), (b) bending of the substituent bonds in the para positions (ca. 7.4 kcal mol^{-1}), (c) aliphatic bridge eclipsing (ca. 6.9 kcal mol^{-1}), (d) angle deformation in the aliphatic bridge (ca. 0.7 kcal mol^{-1}), (e) aliphatic bridge bond stretching (ca. 0.7 kcal mol^{-1}), and (f) inter-ring repulsion (ca. 7.1 kcal mol^{-1}). On going from **1** via **2** to **3**, contributions (c) and (d) decrease stepwise, and this would lead to an overall decrease of strain energy. However, the other three terms of strain except (f) should increase, as becomes evident upon comparing the X-ray crystal structure analyses of hydrocarbons **1**,[4a–c] **2**,[20] and **3**[4d,21] (Figure 1).

The bending of the benzene ring, characterized by the angle α and α′, and the out-of-plane bending of the bonds in the para position, characterized by β and β′, both increase on going from [2.2]paracyclophane (**1**) with α = 11.8° and β = 12.8° (at ambient temperature[4b]) via [2.2]paracyclophane-1-ene (**2**) (α = 12.9°, β = 15.0°, α′ = 13.1°, and β′ = 11.5° at ambient temperature; α = 13.1°, β = 14.5°, α′ = 13.1°, and β′ = 11.2° at 100 K[20]) to tetradehydro[2.2]paracyclophane (**3**) with α′ = 13.7° and β′ = 15.2° (at ambient temperature[4d]) or α′ = 13.2° and β′ = 15.5° (at 133 K[21]), respectively, which leads to an
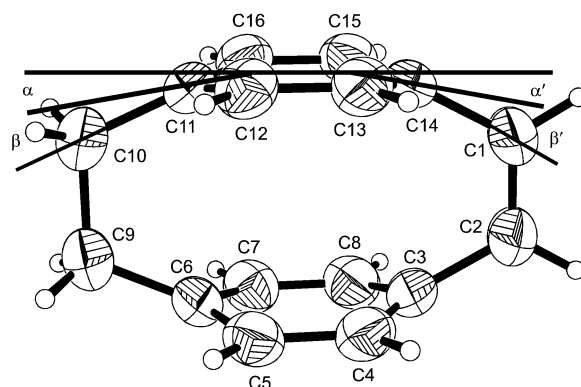

Figure 1. Structure of 1,2-dehydro[2.2]paracyclophane (**2**) in the crystal:[20] bending of benzene rings and adjacent bonds in the [2.2]para-cyclophane skeleton.

increase of the strain energy terms (a) and (b).[22] The aromatic stabilization in the benzene rings of **3** should also be slightly decreased with respect to those in **1**.[23] Concerning the term (f), the distance between two benzene rings in **3** is slightly larger than that in **1** (3.14 vs 3.09 Å), although the C,C-double bond in **3** (1.336 Å) is shorter than the single bond in **1** (1.569 Å). Thus, the inter-ring repulsion, that is, the term (f), must be slightly smaller in **3** than in **1**.

In conclusion, the increased strain energies (by 4.6 and 11.9 kcal mol^{-1}) of **2** and **3** over **1** correlate with the structural changes (Figure 1) and also with the observed increased reactivities in cycloaddition reactions.[6] It is noteworthy that the activation enthalpy $\Delta H^\ddagger$ for the homolytic cleavage of the C,C-single bond in **1** (37.7 kcal mol^{-1})[24] is only 7.6 kcal mol^{-1} higher than its strain energy (30.1 kcal mol^{-1}), and for **2** ($\Delta H^\ddagger$ = 34.4 kcal mol^{-1})[24] it is virtually the same as the *SE* (34.7 kcal mol^{-1}). However, the lower activation enthalpy for the bridge opening in **2** is mainly due to the increased stabilization of the formed diradical and not to its increased strain energy.[24]

Experimental Section

Preparation and Purification of Compounds. The hydrocarbons **2**[8] and **3**[9] were prepared according to previously published procedures. For the thermochemical measurements, both compounds were purified by a sequence of column chromatography on silica gel (eluting with pentane) followed by recrystallization from heptane and repeated (two times) sublimation under reduced pressure (0.01 Torr) at 100 °C. Analysis by gas chromatography established their purities to be ≥99.98%, and this was confirmed by differential scanning calorimetry (DSC) measurements of the melting process.[25]

Combustion Calorimetry. For the measurements of the enthalpies of combustion of the paracyclophanes **2** and **3**, an isoperibolic aneroid microcalorimeter with a stirred water bath was used. The substances were burned in an oxygen atmosphere at a pressure of 3.04 MPa, as has been described in detail previously.[26] The energy equivalent of the

(18) Beckhaus, H.-D. *Chem. Ber.* **1983**, *116*, 86–96.
(19) Boyd, R. H. *J. Chem. Phys.* **1968**, *49*, 2574–2583.
(20) Crystals of compound **2** were grown by slow evaporation of its solution in diethyl ether at 0 °C. The X-ray single-crystal data were collected at 100(2) and 293(2) K on a Bruker SMART CCD 6000 diffractometer ($\lambda_{Mo\ K\alpha}$, graphite monochromator, ω-scan, 0.3°/frame) equipped with an Oxford Cryostream LT-device. The structure was solved by direct methods and refined by full-matrix least squares on F^2 for all data with the Bruker SHELXTL program suite. Non-hydrogen atoms were refined with anisotropic displacement parameters; H-atoms were refined isotropically. The structure contains two independent molecules, located at the special crystallographic positions with symmetry *mmm* and *mm*2. One of these independent molecules is disordered with overlapping of single and double bridging C–C bonds. The geometrical parameters of nondisordered independent molecule **2** are reported in the paper. Crystal data for **2** (parameters at room temperature are given in square parentheses): C$_{16}$H$_{14}$ (206.27), crystal size 0.20 × 0.14 × 0.09 mm^3, orthorhombic, $Z = 12$, space group *Fmmm*, $F(000) = 1320$, $a = 10.6131(3)$ [10.7675(8)] Å, $b = 11.0639(3)$ [11.1550(8)] Å, $c = 27.4860(7)$ [27.708(2)] Å, $V = 3227.47(15)$ [3328.0(4)] Å^3, $\rho = 1.274$ [1.235] g cm^{-3}, $\mu = 0.072$ [0.069] mm^{-1}, intensities measured: 8794 [7172] [2θ_{max} = 58.0°), independent: 1216 [1246] (R_{int} = 0.0637 [0.0547]), 90 parameters refined, R_1 = 0.0419 [0.0443] for 988 [742] reflections with $I > 2\sigma(I_o)$, wR_2 (all data) = 0.1237 [0.1401], GOF = 1.070 [1.010], maximum and minimum residual electron density 0.345 [0.179] and −0.223 [−0.229] e Å^{-3}. Crystallographic data (excluding structure factors) for the hydrocarbon **2** have been deposited as supplementary publication no. CCDC-215005 (measurement at 100 K) and CCDC-215006 (measurement at 293 K) with the Cambridge Crystal-lographic Data Centre. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: (+44)1223-336-033; E-mail: deposit@ccdc.cam.ac.uk).
(21) The X-ray crystal structure of [2.2]paracyclophane-1,9-diene (**3**) was recently reinvestigated with higher precision at low temperature (133 K): Negru, M.; Jones, P. G.; Hopf, H., unpublished results. Cf.: Negru, M. Diplomarbeit, Technische Universität Braunschweig, 2003. The authors are grateful to Professor Dr. Henning Hopf, TU Braunschweig, Germany, for disclosing to us the atomic coordinates of **3**, enabling us to calculate the values of angles α and β in **3**.

(22) For compounds **2** and **3**, the values of angles α, α′, β, and β′ were calculated from atomic coordinates available elsewhere[4d,21] or obtained in this work. The values of angles α and β for paracyclophane (**1**) were taken from its reinvestigated X-ray crystal structure analysis.[4b] However, these values differ significantly from those calculated by us for **1** using a set of atomic coordinates taken from an earlier crystallographic investigation[4c] (α = 14.1°, β = 7.2° at ambient temperature or α = 14.0°, β = 8.9° (at 93 K)).
(23) Cyranski, M. K.; Krygowski, T. M.; Bird, C. W. *Tetrahedron* **1998**, *54*, 9711–9720.
(24) Roth, W. R.; Hopf, H.; de Meijere, A.; Hunold, F.; Börner, S.; Neumann, M.; Wasser, T.; Szurowski, J.; Mlynek, C. *Liebigs Ann.* **1996**, 2141–2154.
(25) Hemminger, W. F.; Cammenga, H. K. *Methoden der Thermischen Analyse*; Springer: Berlin, 1989; p 269 ff.
(26) Beckhaus, H.-D.; Rüchardt, C.; Smisek, M. *Thermochim. Acta* **1984**, *79*, 149–159.

calorimeter ϵ_{calor} (see Table 1 of the Supporting Information) was determined with a standard reference sample of benzoic acid (sample SRM 39i, N.I.S.T.). The summary of auxiliary quantities for the combustion experiments and information necessary for reducing apparent mass (measured in air) to mass, converting the energy of the actual bomb process to that of the isothermal process, and reducing to standard states[27] is given in an earlier publication.[28] The densities of $\rho_{(293)} = 1.24$ g cm^{-3} for [2.2]paracyclophane-1-ene (**2**) and $\rho_{(293)} = 1.25$ g cm^{-3} for [2.2]paracyclophane-1,9-diene (**3**) were determined by flotation of crystals in aqueous KCl solutions. The specific heat capacities (at 298.15 K) $c_p = 0.275$ cal K^{-1} for **1** and $c_p = 0.251$ cal K^{-1} for **2** were measured by DSC. The expansion coefficients were estimated to be $(\delta\nu/\delta T)_p = 0.1 \times 10^{-6}$ dm^3 K^{-1} for both compounds. The energies of combustion of cotton thread, $\Delta_c u°(\text{CH}_{1.774}\text{O}_{0.887}) = -(4050.1 \pm 1.0)$ cal g^{-1}, and of oil, $\Delta_c u°(\text{CH}_{1.940}) = -(10995.1 \pm 1.0)$ cal g^{-1}, were used. Typical combustion experiments for paracyclophanes **2** and **3** are given in Table 1 of the Supporting Information). The individual values of the energies of combustion $\Delta_c u°$ together with the means and its standard deviations are compiled in Table 2 of the Supporting Information. The given standard deviations of the means include the uncertainties from calibration and the combustion energies of the auxiliary materials.

Prior to the combustion experiments, tests were performed to establish the stabilities of paracyclophanes toward oxidation. The pellets of compounds studied were kept in the calorimetric bomb under an oxygen atmosphere of 3.04 MPa for 24 h. No changes in purity of the specimens were detected by means of GC analysis.

Transpiration Method. The enthalpies of sublimation of paracyclophanes were determined by the transpiration method.[15,29] About 0.2 g of the sample was mixed with glass beads and placed in a thermostated U-tube of 20 cm length and 0.5 cm diameter. At constant temperature (± 0.1 K), a nitrogen stream was passed through the U-tube, and the transported amount of material was collected in a cooled trap. A flow of 0.28–0.56 cm^3 s^{-1} of nitrogen was optimal to reach the equilibrium of saturation of transporting gas at each temperature investigated. The amount of condensed substance was determined by GC analysis with an external standard. The vapor pressure p at each saturation temperature was calculated from the amount of product collected within a defined time period with the help of the ideal gas equation, $p = mRT_a/V(\text{N}_2)M$, where $R = 1.987$ cal K^{-1} mol^{-1}, m is the mass of transported compound, $V(\text{N}_2)$ is the volume of transporting gas, M is the molar mass of the compound, and T_a is the ambient temperature (± 0.1 K) of the soap bubble meter (used for the flow rate measurements). The volume of the gas $V(\text{N}_2)$ transferred through the tube was determined from the flow rate and time measurements. The flow rate was maintained constant using a high precision needle valve (Hoke). The vapor pressure p was corrected for the residual vapor pressure at the condensation temperature. The latter was calculated from a linear correlation between $\ln p$ and T^{-1} obtained by iteration. The molar enthalpy of sublimation was calculated from the slope of the linear Clausius–Clapeyron correlation: $\Delta H°_{sub} = -R(\text{d} \ln p/\text{d}T^{-1})$. The observed enthalpies of sublimation $\Delta H°_{sub}(T_{av})$ at the average temperature T_{av} obtained by this procedure are compiled in Table 3 of the Supporting Information. Because of the deviations, the average temperature of measurement for the transpiration method ($T_{av} = 330.8$ K) from $T = 298.15$ K, the observed values of the enthalpies of sublimation of paracyclophanes (Table 3 of the Supporting Information) were adjusted to this reference temperature (see Tables 3 and 4 of the Supporting Information) using the correction:[30]

$$\{\Delta H°_{sub}(T) - \Delta H°_{sub}(298.15\text{ K})\}/(\text{kcal mol}^{-1}) = -0.0076(T/\text{K} - 298.15)$$

DSC Measurements. Enthalpies of fusion and specific heats were measured with a Perkin-Elmer DSC-2C instrument. The temperature scale of the DSC was calibrated by measuring the melting temperatures of the recommended high-purity standards: benzoic acid, tin, and indium. The power scale was calibrated using sapphire as standard material. The samples were studied from 298 to 380 K at a rate of 5 K min^{-1}.

Calculations of $\Delta H°_f(\text{g})$ for paracyclophanes **1**–**3** were performed using the MM3 force field,[31,32] SPARTAN (PM3),[33] and Gaussian 98.A7 (B3LYP)[34] program packages. The results of the calculations using the DFT method (B3LYP with different basis sets) are summarized in Table 5 of the Supporting Information.

Calculation of Strain Energies. The strain of a molecule in general is defined as the difference between the experimental standard enthalpy of formation $\Delta H°_f(\text{g})$ and the calculated sum of the Benson type strain-free increments[14] for a strain-free model.[17] The system of strain-free increments is based on the standard enthalpies of formation $\Delta H°_f(\text{g})$ of simple homologous ("strainless") molecules. Strain-free group additivity increments for hydrocarbons[17] and arenes[18] are well defined. All other increments used in this work are listed in Table 6 of the Supporting Information. Using the group-additivity parameters given in Table 6 of the Supporting Information and the values of $\Delta H°_f(\text{g})$ of the cyclophanes **2** and **3** (Table 4 of the Supporting Information) measured in this study, as well as some experimental results from the literature, we have estimated values for the strain enthalpies ($SE = \Delta H°_f(\text{g}) - \sum$ increments) of compounds **1**–**3** (Table 6 of the Supporting Information).

Supporting Information Available: Detailed data on combustion experiments; determination of vapor pressure; results of DFT calculations; estimation of strain energy (PDF); crystallographic details (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA0374628

(27) Hubbard, W. N.; Scott, D. W.; Waddington, G. In *Experimental Thermochemistry*; Rossini, F. D., Ed.; Interscience: New York, 1956; pp 75–128.

(28) Verevkin, S. P.; Beckhaus, H.-D.; Rüchardt, C.; Haag, R.; Kozhushkov, S. I.; Zywietz, K. T.; de Meijere, A.; Jiao, H.; v. Ragué Schleyer, P. *J. Am. Chem. Soc.* **1998**, *120*, 11130–11135.

(29) Beckhaus, H.-D.; Kratt, G.; Lay, K.; Geiselmann, J.; Rüchardt, C.; Kitschke, B.; Lindner, H. J. *Chem. Ber.* **1980**, *113*, 3441–3455.

(30) Chickos, J. S.; Hosseini, S.; Hesse, D. G.; Liebman, J. F. *Struct. Chem.* **1993**, *4*, 271–278.

(31) Cf.: Kao, J.; Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 975–986; calculated $\Delta H°_f(\text{g}) = 47.61$ kcal mol^{-1}.

(32) Allinger, N. L.; Yuh, Y. H.; Lii, J.-H. *J. Am. Chem. Soc.* **1989**, *111*, 1, 8551–8575.

(33) *PC SPARTAN PRO 1.0.5*; Wave function Inc., 18401 Von Karman Ave., Suite 370, Irvine, CA 92612.

(34) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.