The Geometry of the 1,4-Dihydronaphthalene Ring

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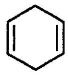
1,4,5,8,9,12-Hexahydrotriphenylene **4** has been studied as a crystalline model for 1,4-dihydronaphthalene; X-ray analysis shows this compound to be planar to within 0.06 Å, in agreement with molecular mechanics calculations.

The preferred conformations of cyclohexa-1,4-diene **1**, 1,4-dihydronaphthalene **2**, 9,10-dihydroanthracene **3**, and their derivatives have been the source of considerable controversy.[1,2] Mostly at issue has been the geometry of the partially saturated six-membered ring–planar or boat shaped. In the solid state, **3** is considerably puckered, with X-ray analysis[3] indicating an angle of 145° between the planes containing each of the aromatic rings (*i.e.* α). A number of X-ray studies[1] on derivatives of **3** show a range of ring folding from $\alpha = 129°$ to $\alpha = 180°$. The latter value, of course, represents a planar structure. In general, monosubstitution or *cis*-disubstitution favour folded structures while 9,9- or *trans*-9,10-disubstitution results in planarity (especially where the substituents are identical). The structure of **3** is probably much flatter in solution, or in the gas phase, and may be planar. At any rate, an inversion barrier has never been observed, and recent *ab initio* calculations suggest a value of 8 kJ mol^{-1} or less.[4]

On the other hand, there now seems to be general agreement that **1** is planar,[2] albeit with a wide amplitude vibration about the axis defined above as α. Some X-ray results have been reported for *trans*-3,6-disubstituted derivatives of **1** that confirm the planar structure. The situation is not quite as clear for **2**. Calculations suggest that nonplanar structures should be increasingly favoured in the series **1** < **2** < **3**. An X-ray study of 1,4-dihydro-1-naphthoic acid[5] has appeared indicating the substituted ring to be folded with $\alpha = 169.2°$. Similarly, an NMR study[6] of 1-phenyl-1,4-dihydronaphthalene indicates it to be very flat and molecular mechanics calculations[7] predicts a folding angle of 170°. Molecular mechanics calculations indicate **2** itself to be



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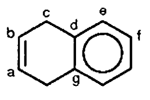

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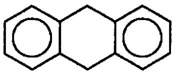

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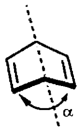

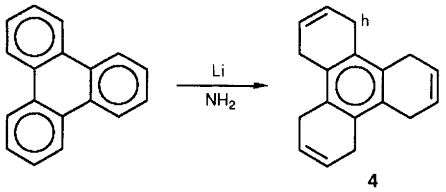

Scheme 1

Table 1 Selected molecular mechanics calculated bond angles and lengths for **2** and **4**

	$C_dC_cC_bC_a$ (°)	$C_hC_eC_dC_c$ (°)	$C_dC_cC_b$ (°)	C_eC_d/Å	C_dC_g/Å
2	0.40	—	115.22	1.40	1.41
4	0.04	0.00	116.81	1.41	1.40
	[0.1–4.6 (4)	0.3–1.6 (3)	114.8–115.2 (2)	1.408–1.414 (3)	1.387–1.391 (3)]^a

^{a} Quantities derived from the X-ray experiment for **4** giving the range of magnitude observed with esds in parentheses.

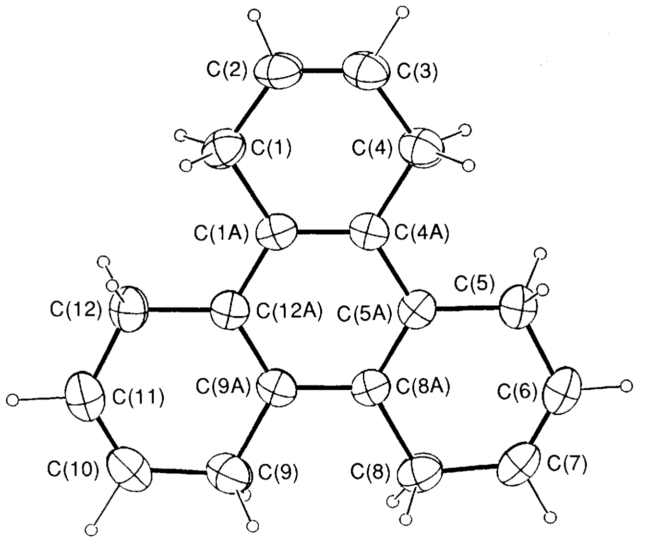

Fig. 1 ORTEP view of the structure of 1,4,5,8,9,12-hexahydrotriphenylene **4**. Thermal parameters drawn at the 40% probability level. Bond lengths of the type C(1a)–C(4a) average 1.389; C(1a)–C(12a) 1.411; C(1a)–C(1) 1.510; C(1)–C(2) 1.486; C(2)–C(3) 1.308 Å.

planar.[8] Herein, we report the first X-ray study† of a derivative of **2** without substitution in the cyclohexadiene ring.

The compound, 1,4,5,8,9,12-hexahydrotriphenylene **4**, was formed in 3% yield as one of a number of products from the reduction of triphenylene with lithium metal in anhydrous, liquid ammonia (see Scheme 1).[9] Molecular mechanics calculations predict both **2** and **4** to be planar, and a comparison of the data for both compounds (see Table 1) suggests that the 1,4-dihydronaphthalene substructure in **4** compares very closely with the calculated structure of **2**. Hence **4** represents a good model for the structure of **2**, and since **4** is crystalline, this represents an opportunity to deduce information about the structure of 1,4-dihydronaphthalenes in general.

The crystal structure of **4** is illustrated in Fig. 1. The 18 carbon atoms of the molecule are nearly coplanar, exhibiting average deviation 0.029 Å with maximum deviation 0.055(3) Å for C(6). The central phenyl ring is planar with maximum deviation 0.007(2) Å. The peripheral sp^2 carbon atoms lie 0.066(3)–0.120(3) Å out of this plane. The non-phenyl C atoms do not exhibit large displacement parameters at 299 K, having B_{eq} values of 3.79(6)–4.66(7) Å^2.

In summary, the planar structure for **4** in the solid state argues strongly for the preference of planar geometries in the solid state of 1,4-dihydronaphthalenes, and suggests that solid 1,4-dihydronaphthalene itself is most probably planar, in agreement with calculations.

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† The crystal structure was determined using intensity data collected on an Enraf-Nonius CAD4 diffractometer with graphite monochromated Cu-Kα radiation. *Crystal data*: $C_{18}H_{18}$, orthorhombic space group $P2_12_12_1$, $a = 5.3441(5)$, $b = 13.0943(11)$, $c = 17.5834(13)$ Å, $V = 1230.4(3)$ Å^3, $Z = 4$, $D_c = 1.265$ g cm^{-3}, μ(Cu-Kα) = 5.0 cm^{-1}, $R = 0.045$, $R_w = 0.048$ for 1192 observed data having $I > 1\sigma(I)$. H atoms were located and refined. Atomic coordinates, bond distances and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1 1991.

References

1 P. W. Rabideau, *Acc. Chem. Res.*, 1978, **11**, 141.
2 P. W. Rabideau, in *The Conformational Analysis of Cyclohexenes, Cyclohexadienes and Related Hydroaromatic Compounds*, ed. P. W. Rabideau, VCH, New York, 1989, ch. 4.
3 W. G. Ferrier and J. Iball, *J. Chem. Ind. (London)*, 1954, 1296; F. H. Herbstein, M. Kapon and G. M. Reisner, *Acta Crystallogr., Sect. B*, 1986, **42**, 181.
4 T. Schaefer and R. Sebastian, *J. Mol. Struct., Theochem.*, 1987, **153**, 55.
5 A. K. Cheetham, M. C. Grossel and D. James, *J. Org. Chem.*, 1982, **47**, 566.
6 J. J. M. Lamberts, C. A. G. Haasnoot and W. H. Laarhoven, *J. Org. Chem.*, 1984, **49**, 2490.
7 P. W. Rabideau, J. L. Mooney and J. N. Hardin, *J. Org. Chem.*, 1985, **50**, 5737.
8 K. B. Lipkowitz, P. W. Rabideau, D. J. Raber, L. E. Hardee, P. v. R. Schleyer, A. J. Kos and R. A. Kahn, *J. Org. Chem.*, 1982, **47**, 1002.
9 Z. Marcinow, A. Sygula and P. W. Rabideau, *J. Org. Chem.*, 1988, **53**, 3603.

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