[2](1,4)-Benzeno-[2](1,4)-triptycenophane: Nuclear Magnetic Resonance Evidence of a Skew [2,2]-Paracyclophane Moiety

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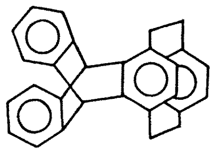
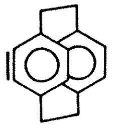
Summary Addition of dehydro-[2,2]-paracyclophane to anthracene gives the title compound containing crossed triptycene and [2,2]-paracyclophane systems, the latter moiety significantly distorted as evidenced by the n.m.r. data.

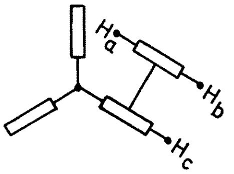
THERE is considerable interest in the synthesis and properties of molecules having two or more π-electron systems held rigidly in close proximity to each other, though not formally conjugated.[1] We report here the synthesis and some properties of [2](1,4)-benzeno-[2](1,4)-triptycenophane[2] (I), a molecule in which one benzenoid ring is held over the face of another and near-orthogonal to a third (see schematic end on structures IA, B).

Compound (I) was obtained *via* Diels–Alder addition of dehydro-[2,2]-paracyclophane (II) to anthracene. The aryne (II) was conveniently generated by dehydrohalogenation of 4-bromo-[2,2]-paracyclophane[3] using the method of Cadogan and his co-workers.[4] A mixture containing t-butylbenzene (15 ml.), 4-bromo-[2,2]-paracyclophane (9·6 mmoles), anthracene (13·0 mmoles) and potassium t-butoxide (10·0 mmoles) was heated with stirring at 150—170° for 27 hr. and then worked-up in the normal manner.[4] An n.m.r. spectrum of the crude product indicated the presence of (I) (*ca.* 15% yield) and considerable amounts of starting bromide and 4-t-butoxy-[2,2]-paracyclophane.[3] Purified (I) (column chromatography and recrystallizations) has m.p. 242—245° and gives a correct analysis for $C_{30}H_{24}$. The structural assignment for (I) is based on the well established precedent for this type of reaction and the spectral data. The mass spectrum has strong peaks at *m/e* 384, 280, and 104, representing the molecular ion and the fragments arising from symmetrical benzylic cleavage, characteristic of the [2,2]-paracyclophane system.[5] The u.v. spectrum exhibits features of both the [2,2]-paracyclophane and triptycene chromophores [λ_{max} in nm. (log ϵ)]: compound (I) (iso-octane), 228 (4·46), 264 (3·70), 271 sh (3·56), 278 (3·57), 293 sh (2·77), and 315 sh (2·40); [2,2]-paracyclophane (cyclohexane),[6] 225 (4·38), 244 sh (3·52), 286 (2·41), and 302 sh (2·19); 1,4-dimethyltriptycene[7] (iso-octane), 261 (3·33), 271 (3·44), 278 (3·53), 293 sh (2·35), and 301 sh (2·24).

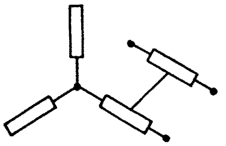
The n.m.r. spectrum of (I) ($CDCl_3$, 100 MHz) reveals a significant geometrical feature. The highest-field aromatic peak at τ 4·83 (2H, m) is readily assigned to the H_a protons (see IA), shielded by both the transannular paracyclophane ring and the neighbouring triptycene face; these are coupled to the H_b protons at τ 3·46 (2H, m); the H_c protons appear as a singlet at τ 3·97 (2H). These chemical shifts strongly suggest that the geometry of (I) is other than that illustrated by (1A). The use of molecular models and the crystallographic data for [2,2]-paracyclophane[8] indicates that in (IA) the H_a protons would lie directly over the face of the neighbouring triptycene ring and at a separation of only 1·8 Å. The Johnson and Bovey ring-current equation[9] gives a calculated up-field shift of *ca.* 3·0 p.p.m. for this interaction; however, the observed shift is only 1·2 p.p.m.† Similarly, the H_b protons in (IA) lie in the same shielding zone of the triptycene face as do the H_a protons but they appear *down-field*† from their position in [2,2]-paracyclophane. A reasonably good agreement between the observed and calculated[9] chemical shifts for H_a, H_b, and H_c results by simply sliding the upper paracyclophane ring over the lower to give the geometry shown in (IB). Less satisfactory agreement is obtained from a combination of a slide and a tilt for the upper ring but such a displacement cannot be excluded with the data at hand. It is clear, however, that the n.m.r. spectrum of (I) is not consistent with that expected for the undistorted structure (IA).


(I)


(II)



(IA)


(IB)

We are examining in detail the properties of (I) as well as the reactivity of (II) as compared to open-chain analogues.

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† Aromatic proton chemical shifts in the appropriate models ($CDCl_3$): [2,2]-paracyclophane, τ 3·63; 1,4-dimethyltriptycene, τ 3·32 (*ortho* to CH_3). The remainder of the observed spectrum for (I) is as expected: τ 2·53—2·87 and 2·81—3·15 (two overlapping A_2B_2 multiplets, 8H, aromatic), 4·56 (s, 2H, bridgehead), and 6·5—7·3 (m, 8H, bridge methylenes).

[1] *Cf.* S. J. Cristol and D. C. Lewis, *J. Amer. Chem. Soc.*, 1967, **89**, 1476.

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[4] J. I. G. Cadogan, J. A. K. Hall, and J. T. Sharp, *J. Chem. Soc. (C)*, 1967, 1860.

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[6] D. J. Cram and H. Steinberg, *J. Amer. Chem. Soc.*, 1951, **73**, 5691.

[7] Prepared in the manner described for compound (I). For another synthesis of this compound, see T. H. Regan and J. B. Miller, *J. Org. Chem.*, 1967, **32**, 2789.

[8] C. J. Brown, *J. Chem. Soc.*, 1953, 3265; K. Lonsdale, H. J. Milledge, and K. V. K. Rao, *Proc. Roy. Soc.*, 1960, *A*, **255**, 82; P. K. Gantzel and K. N. Trueblood, *Acta Cryst.*, 1965, **18**, 958.

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