X-Ray Crystal Structure of (*E*,*E*)-[2_4]Paracyclophane-1,17-diene

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The molecular structure of (*E*,*E*)-[2_4]paracyclophane-1,17-diene, a unique paracyclophane analogue, was established by an *X*-ray crystal structure analysis, and found to be of 2/*m* molecular symmetry with all benzene rings and vinylene groups perpendicular to the molecular ring.

In the preceding paper,[1] we described the preparative method for [2.2]paracyclophane, in which *p*-(trimethylsilylmethyl)benzyltrimethylammonium iodide undergoes the fluoride-induced 1,6-elimination to generate a *p*-xylylene intermediate. Recently, it has been found that an application of the fluoride-induced elimination technique to 4-[4-(trimethylsilylmethyl)styryl]benzyltrimethylammonium iodide (**1**)† (Scheme 1) gave rise to two unique compounds in a total yield of 20% (7:3), which were tentatively assigned as (*E*,*E*)-[2_4]paracyclophane-1,17-diene (**2**) and the (*E*,*E*,*E*)-cyclic trimer (**3**) on the basis of i.r., n.m.r., u.v.,[2] and mass spectra.‡ In this paper the *X*-ray crystal structure of (**2**) is reported. The crystal used in this study was a colourless prism obtained from chloroform solution.

Crystal data: $C_{32}H_{28}$, monoclinic, space group $P2_1/c$, a = 11.721(5), b = 8.298(4), c = 12.483(4) Å, β = 102.36(3)°, Z = 2, D_c = 1.16 g cm^{-3}. Intensity data were collected on a Rigaku AFC-5 diffractometer using monochromated Mo-K_α

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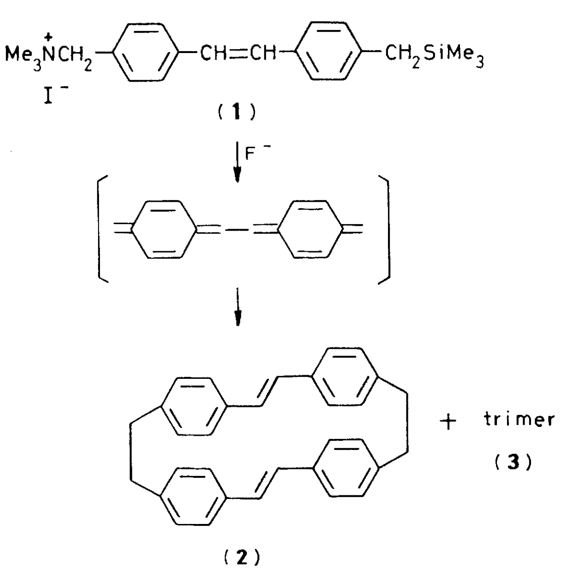
† A *cis–trans*-mixture of (**1**) was prepared by the Wittig reaction of *p*-formylbenzyldimethylamine with [*p*-(trimethylsilylmethyl)benzylidene]triphenylphosphorane, followed by quaternization with methyl iodide.

‡ (**2**): T.l.c. (1:1 C_6H_{14}–$CHCl_3$) R_f 0.59; u.v. ($CHCl_3$) λ_{max} 297 nm (ϵ 3.4 × 10^4); i.r. (KBr) 969 and 812 cm^{-1}; ^{1}H n.m.r. ($CDCl_3$, 60 MHz) δ 3.02 (s, 8H), 6.60, 6.76, 6.88, 7.02 (4s, 20H); mass *m/e* 412. (**3**): T.l.c. (1:1 C_6H_{14}–$CHCl_3$) R_f 0.53; u.v. ($CHCl_3$) λ_{max} 303 nm (ϵ 2.8 × 10^4); i.r. (KBr) 967 and 762 cm^{-1}; ^{1}H n.m.r. ($CDCl_3$, 100 MHz) δ 2.92 (s, 12H), 6.81 (s, 6H, olefinic), 6.70, 6.79, 7.08, 7.17 (AA′BB′, 4s, 24H); ^{13}C n.m.r. ($CDCl_3$) δ 36.65, 126.19, 128.26, 129.56, 135.32, 139.81 p.p.m; mass *m/e* 618.



Scheme 1

radiation ($\lambda = 0.7107$ Å) up to $2\theta = 50°$. Of the 2247 independent reflections thus measured 1030 satisfied the condition $F \geqslant 3\sigma(F)$, and were used for calculations. The structure was solved by direct methods (MULTAN),[3] and refined by the block-diagonal least-squares method (XRAY)[4] using unit weights. The final R-value, applying anisotropic temperature factors to the carbon atoms, was 0.13. The hydrogen atom positions could not be determined owing to the large thermal vibration of the molecule, and this probably also caused the high R-value.§

The asymmetric unit consists of half a molecule. The centre of the molecule coincides with the crystallographic inversion centre, so the molecule is strictly centrosymmetric. The molecular ring is ellipsoid with the ethylene groups at the extremes of the major axis (12.1 Å apart) and the vinylene groups at the ends of the minor axis (4.4 Å apart). As can be clearly seen in Figure 1, the benzene rings and the vinylene groups are all perpendicular to the molecular ring. The angles between the least-squares planes for these groups and that of the ring are in the range 87—90°. The ethylene groups take the eclipsed conformation with a torsion angle of 3°. This arrangement leads to a mirror plane involving the major axis and perpendicular to the molecular ring. Thus, the molecule has $2/m$ symmetry with the two-fold rotation axis passing through the centres of the vinylene groups.

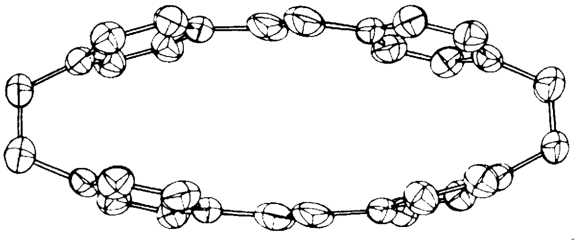


Figure 1. Drawing of the molecule (**2**) as seen normal to the molecular ring.

There are no obvious intermolecular interactions. The molecules seem to be loosely packed in the crystal lattice by weak van der Waals' forces.

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§ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.