Paracyclophanes. Resolution of a Dissymmetric Tetramethyl[2,2]paracyclophane

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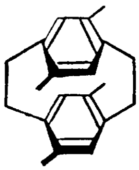
RESTRICTED rotation of the aromatic rings in [*mn*]paracyclophanes and [*m*]paracyclophanes may allow resolution of suitably substituted derivatives.[1] Here we report the first resolution of an [*mn*]paracyclophane devoid of functional groups.

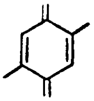
The generation of 2,5-dimethyl-*p*-xylylene (I) affords, among other products, a tetramethyl[2,2]-paracyclophane dimer.[2] We previously assigned to the dimer structure (III) with methyl groups on opposed rings in non-eclipsed positions. The alternative isomer, (II) with all methyl groups eclipsed, appeared less likely on the basis of obvious steric arguments and our failure to observe spectral abnormalities that would be anticipated from such serious eclipsing.[2] The same dimer is obtained from the intramolecular Wurtz coupling of 4,4′-bisbromomethyl-2,2′,5,5′-tetramethylbibenzyl.[3] (In this connection, it is pertinent to note that the Woodward–Hoffmann selection rules[4] predict a multistep process for the dimerization of a *p*-xylylene.) That the dimer possesses the dissymmetric structure (III) rather than the symmetric one (II) has now been confirmed. Partial resolution of racemic (III) has been accomplished through the use of the complexing agent α-(2,4,5,7-tetranitro-9-fluorenylideneamino-oxy)propionic acid.[5]

A solution containing 100 mg. of (III) dissolved in the minimum amount of hot glacial acetic acid was added to a like solution containing 185 mg. of (—)-α-(2,4,5,7-tetranitro-9-fluorenylideneamino-oxy)propionic acid. Concentration and cooling afforded a mixture of the diastereomeric complexes as dark red crystals.* The mixture was triturated with three 2 ml. portions of Skellysolve B and the resulting combined filtrates passed through a short column of alumina to remove the resolving agent. This treatment afforded 34 mg. of analytically pure (III), m.p. 103—106° and $[\alpha]_D^{27}$ $-3{\cdot}2°$ (c = 1·52 g./100 ml., chloroform). The residue from the above trituration gave, after dissolution in benzene and removal of the resolving agent, 29 mg. of dextrorotatory (III). This material had m.p. 103—106° and $[\alpha]_D^{27}$ $+ 4{\cdot}2°$ (c = 1·14 g./100 ml., chloroform). The dextrorotatory sample was examined at shorter wavelengths.† In the range 279 to 500 mμ it exhibited a plain positive curve with $[\alpha]_{279}^{25}$ $+ 72°$ (c = 0·246 g./100 ml., ethanol).

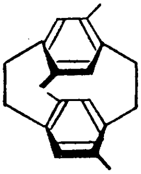
We are currently attempting to define the optical purity of our resolved material.



(II)



(I)



(III)

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* Attempts to separate and characterize the diastereomeric complexes were not rewarding. The complexes characteristically exhibit irregular decomposition points and crystallize as solvates (see ref. 5).

† The rotatory dispersion curve was obtained using a JASCO Model ORD/UV5 instrument. We are indebted to Dr. Robert Zand, Institute of Science and Technology, The University of Michigan, for providing this curve. The sodium D-line measurements were obtained with a Bendix Ericsson ETL-NPL Automatic Polarimeter, Type 143A.

[1] *Cf.* B. H. Smith, "Bridged Aromatic Compounds," Academic Press, New York, 1964, pp. 333–358.

[2] D. T. Longone and C. L. Warren, *J. Amer. Chem. Soc.*, 1962, **84**, 1507. D. T. Longone and F. P. Boettcher, *ibid.*, 1963, **85**, 3436.

[3] D. T. Longone and L. Simanyi, unpublished results.

[4] R. Hoffmann and R. B. Woodward, *J. Amer. Chem. Soc.*, 1965, **87**, 2046.

[5] M. S. Newman and W. B. Lutz, *J. Amer. Chem. Soc.*, 1956, **78**, 2469; M. S. Newman and D. Lednicer, *ibid.*, p. 4765.