The Conformation of *trans–syn–trans*-1,2,5,6-Tetrabromocylco-octane

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STRAIN-ENERGY calculations on the eight-membered carbocycle have produced four predicted conformations of comparable minimal energy for cyclo-octane.[1] It is therefore not surprising that physicochemical investigations of cyclo-octane and its derivatives have not pointed to one unequivocal preferred conformation.[2] However, two X-ray contributions to the problem have recently established the boat–chair conformation for the eight-membered ring in two derivatives, *trans*-cyclo-octane-1,2-dicarboxylic acid[3] and the dimeric cyclo-octane peroxide;[4] this corresponds to one of the calculated stable conformations.

We now find from an X-ray analysis of crystals of the 1,2,5,6-tetrabromocyclo-octane diastereoisomer of m.p. 137—138° that the eight-membered ring in this derivative possesses another of the predicted favoured conformations, a twisted crown. The crystals are monoclinic, space group $P2_1/c$ with four molecules of $C_8H_{12}Br_4$ in a unit cell of dimensions $a = 9{\cdot}33$, $b = 7{\cdot}38$, $c = 17{\cdot}08$ Å, $\beta = 101.0°$. The structure was solved by the heavy-atom method using 1328 intensity data estimated visually from Weissenberg films. Refinement involved full-matrix least-squares methods using anisotropic thermal parameters; R is now 0·108. The results show that the compound is unequivocally the *trans–syn–trans*-diastereoisomer and a view of the molecule is shown in Figure 1. The parameters of the twisted crown conformation thus established are shown in Figure 2 in terms of the displacements of the carbon atoms from the best plane through them and the torsional angles around each C–C bond; they bear a gratifyingly close similarity to the comparable calculated parameters (shown in brackets) for this cyclo-octane conformation.[1a] The C–C–C bond angles are all significantly greater than tetrahedral and range from 113° to 121° with a mean of 118° (the corresponding mean value in *trans*-cyclo-octane-1,2-dicarboxylic acid was found[3] to be 116°).

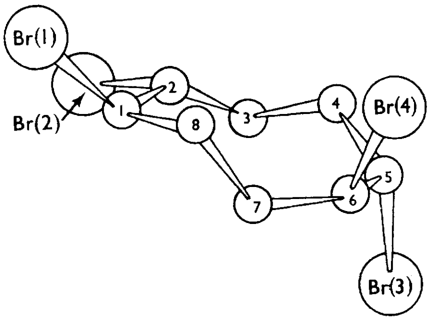

FIGURE 1. *A view of the* trans–syn–trans-1,2,5,6-*tetrabromocyclo-octane system showing the conformation and our numbering scheme.*

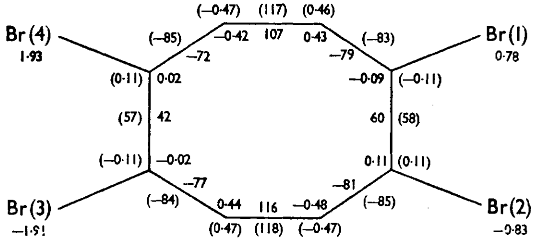

FIGURE 2. *The torsional angles and displacements of the atoms from the best plane through the carbon atoms in* trans–syn–trans-1,2,5,6-*tetrabromocyclo-octane compared with the predicted values (parentheses) for "twisted crown" cyclo-octane.*

It was of obvious interest to examine whether this particular conformation was also favoured in solution. Our refined atomic co-ordinates lead to a calculated dipole moment of 2·54D (assuming a value of 1·9D for the C–Br bond moment). The kind collaboration of Dr. R. A. Y. Jones of the University of East Anglia produced an experimental dipole moment[5] in benzene of 2·44 ± 0·01D (neglecting atomic polarisation). While this finding is very compatible with the X-ray results, it does not rigidly exclude other conformations from being present in solution. A comparison[6] of intensities and frequencies of infrared bands in the 500—750 cm.$^{-1}$ region in both the crystalline phase and in solution in a number of solvents showed close, but not identical, correspondence (full details will be given in a later publication). This would indicate that the twisted crown is a predominating, though not the only, conformer in solution.

The 100 MHz. proton spectrum of a CD_2Cl_2 solution of the tetrabromocyclo-octane at 34° comprises two narrow bands centred at τ 5·40 and 7·50 with relative intensities 1 : 2, which correspond to the methine and methylene protons respectively. Lowering the temperature causes both resonances to broaden markedly and at −75° each is split into a broad doublet, attributable to the slowing up of ring inversion. For ring inversion slow on the n.m.r. time scale two of the adjacent methine protons belong to one magnetic set (*e.g.*, the axial protons H-1 and H-2 in Figure 1) while the other two adjacent methine protons are associated with another distinct magnetic set (the equatorial protons H-5 and H-6 in Figure 1). Such conformational processes as pseudorotation, stretching, and wagging[1c] do not destroy the integrity of these two distinct magnetic sets, but may be expected to average the magnetic environments inside each set;† however, for averaging *between* sets ring inversion is necessitated. At the coalescence temperature of the methine doublet (− 66·5 ± 2°) an approximate value of about 90 sec.^{-1} can be estimated‡ for the rate constant $1/2\,\tau$ for ring inversion. It is interesting that this rate is about two orders of magnitude less than for cyclo-octane itself at the same temperature.[7] The n.m.r. results are in accord with the existence in solution of predominantly one conformer and are compatible with this conformer being the twisted crown indicated by *X*-ray work.

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† At −94° the methine resonance comprises a doublet of separation 40·6 Hz. The lower field component shows some asymmetry which may indicate the presence of another conformer which, on the n.m.r. time scale, is not interconverting rapidly with the conformer(s) giving rise to the doublet. Integration shows this conformer to account for about 10% of the total integrated intensity of the methine resonance.

‡ The estimate was made by the coalescence condition $\frac{1}{2}\tau = \pi\,(\nu_A - \nu_B)/\sqrt{2}$ using the doublet separation $(\nu_A - \nu_B)$ of 40·6 Hz. at −94°. This expression is strictly only valid for the coalescence of two lines of equal intensity which have effectively zero line-width in absence of exchange. In the present case the methine and methylene protons are coupled, but, for the rate comparisons being made, use of the equation for the tetrabromide is justified.

[1] (a) M. Bixon and S. Lifson, *Tetrahedron*, 1967, **23**, 769; (b) K. B. Wiberg, *J. Amer. Chem. Soc.*, 1965, **87**, 1070; (c) J. B. Hendrickson, *ibid.*, 1964, **86**, 4854; (d) N. L. Allinger, *ibid.*, 1959, **81**, 5727.

[2] (a) A. Almenningen, O. Bastiensen, A. Haaland, and H. M. Seip, *Angew Chem. Internat. Edn.*, 1965, **4**, 819 (electron diffraction); (b) H. E. Bellis and E. J. Slowinski, *Spectrochim. Acta*, 1959, **15**, 1102, (infrared and Raman); (c) F. A. L. Anet and M. St. Jacques, *J. Amer. Chem. Soc.*, 1966, **88**, 2585, 2586 (n.m.r.); (d) A. Peak, J. A. Dyer, and L. F. Thomas, *Chem. Comm.*, 1966, 95 (n.m.r.); (e) N. L. Allinger and L. A. Tushaus, *Tetrahedron*, 1967, **23**, 2051, (dipole moments); (f) J. Dale, *Angew Chem. Internat. Edn.*, 1966, **5**, 1005; (g) E. L. Eliel, N. L. Allinger, S. G. Angyal, and G. A. Morrison, "Conformational Analysis", Interscience, New York, 1965, p. 2101.

[3] M. Dobler, J. D. Dunitz, and A. Mugnoli, *Helv. Chim. Acta*, 1966, **49**, 2492.

[4] P. Groth, *Acta Chem. Scand.*, 1965, **19**, 1497.

[5] J. L. Imbach, R. A. Y. Jones, A. R. Katritzky, and R. J. Wyatt, *J. Chem. Soc.* (*B*), 1967, 499.

[6] *e.g.*, W. G. Rothschild, *J. Chem. Phys.*, 1966, **45**, 1214.

[7] F. A. L. Anet and J. S. Hartman, *J. Amer. Chem. Soc.*, 1963, **85**, 1204.