The Bicyclo[2,2,2]octane Conformation: *X*-ray Analysis of 1-*p*-Bromobenzenesulphonyloxymethylbicyclo[2,2,2]octane

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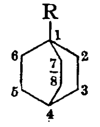
THE conformation of the bicyclo[2,2,2]octane system (I) has been the subject of conflicting reports in the literature. A staggered conformation (II) with C_3 symmetry has been inferred from heats of hydrogenation studies,[1] but this has been opposed by Gleicher and Schleyer[2] who favoured the eclipsed structure (III) with D_3h symmetry on the basis of calculations with admittedly empirical potential functions.

It has been suggested[1] that as much as 10° of twist about the C(1) · · · C(4) axis could be accommodated without undue distortion of bond angles and also that a relatively large total energy change may be brought about by small reductions in each of the six 1 : 2 and 1 : 3 opposed H · · · H interactions. The importance of avoiding zero dihedral angles and the energy-lowering effect of even a small torsional angle increase has recently been emphasised by Wiberg.[3] Attempts to determine the conformation of the bicyclo[2,2,2]octane system by infrared[4,5] and polarised Raman spectroscopy,[5] and by microwave spectroscopy[6] using either the parent hydrocarbon or a suitable derivative, have been inconclusive. To establish the conformation in the solid phase we have synthesised and completed a single-crystal *X*-ray analysis of a new compound, 1-*p*-bromobenzenesulphonyloxymethylbicyclo[2,2,2]octane (IV).†

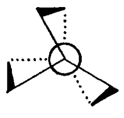
The crystals are monoclinic, space group $P2_1/c$ with four molecules of $C_{15}H_{19}O_3SBr$ in a unit cell of dimensions $a = 18{\cdot}99$, $b = 6{\cdot}65$, $c = 12{\cdot}56$Å, $\beta = 96{\cdot}0°$. The structure was solved by way of the heavy atom and refined by three-dimensional least-squares methods using 1715 three-dimensional data which were estimated from Weissenberg films using a Joyce Loebl integrating photomicrodensitometer. R is now 10·4%.

Our molecular geometry calculations determine unambiguously that the bicyclo[2,2,2]octane skeleton in (IV) closely conforms to symmetry C_3 (II) with the group of atoms C(2), C(6), C(7) rotated 3° about the C(1) · · · C(4) axis with respect to the C(3), C(5), C(8) group. This has the effect of increasing the torsional angles at C(2)–C(3), C(5)–C(6), and C(7)–C(8) to 5° whereas with an eclipsed D_3h model a zero value would hold.

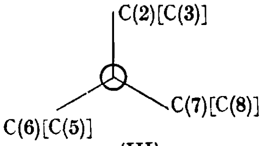
The *p*-bromobenzenesulphonyloxymethyl group appears to have had little or no effect on the conformation of the carbocycle; there are no close intramolecular contacts between them, and all intermolecular distances correspond to or are greater than normal van der Waal's distances.



(I) R=H
(IV) R=p-Br·C_6H_4·SO_2OCH_2



(II)



(III)

Bond-length and undue bond-angle strain appear to be absent in our molecule and we infer that the staggered conformation is adopted solely to release strain arising from torsional and nonbonded intramolecular interaction. Although we have proved the existence of a staggered conformation in the solid, in view of the danger in extrapolating conformational results from solid to solution phase it is open to question whether or not a staggered conformation is exclusively adopted in solution.

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† Satisfactory elemental analyses and spectroscopic data have been obtained for this compound.

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