# The Stereochemistry of Acorone

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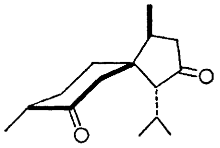
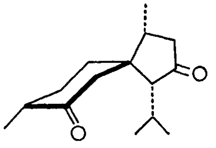
THE sesquiterpene acorone has been the subject of considerable chemical study.[1,2] In their latest publication on the matter Šorm and his colleagues deduced the stereochemistry shown in (I) and then in an appendix to the paper revised their decision to formula (II).[2]

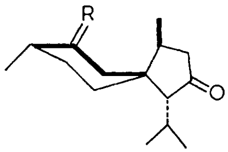
In order to define the stereochemistry unambiguously we have determined the crystal structure of acorone *p*-bromophenylsulphonylhydrazone and our conclusions concerning the constitution and stereochemistry are summarized in formula (III; $R = N{\cdot}NH{\cdot}SO_2{\cdot}C_6H_4{\cdot}Br$). The stereochemistry shown in (III) differs from that shown in (I) only in the conformation adopted by the six-membered ring; in (I) the methyl group at C(8) is equatorial whereas in (III) the methyl group is axial. Šorm *et al.* report that optical rotatory dispersion measurements are in accord with the cyclohexanone ring of acorone adopting in solution predominantly the chair conformation with the methyl group at C(8) equatorial;[2] this is the expected result, for the chair conformer of 2-methylcyclohexanone with the methyl group equatorial is more stable, by about 1·6kcal./mole, than the alternative chair conformer with the methyl group axial.[3] The adoption by the *p*-bromophenylsulphonylhydrazone in the solid state of the conformation in which the methyl group at C(8) is axial suggests that where conformers differing only slightly in energy are involved the packing forces (van der Waals, etc.) can favour in the crystal a conformation which is present only to a small extent in solution. We conclude that it is advisable to be cautious in the extrapolation of solid-state conformational results to solution chemistry.



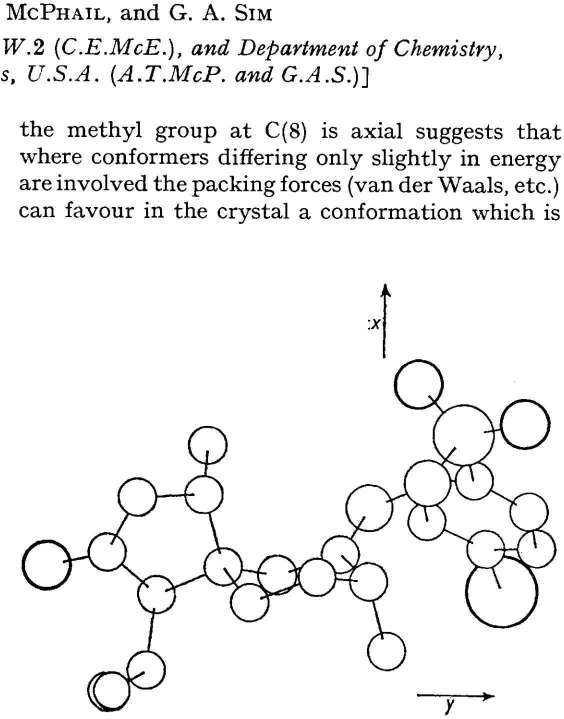
(I)



(II)



(III)



*The molecular structure as viewed along the* c *axis.*

Acorone *p*-bromophenylsulphonylhydrazone crystallizes in the monoclinic system, space group $P2_1$, with two molecules of $C_{21}H_{29}N_2BrSO_3$ in a unit cell with dimensions $a = 11{\cdot}45$, $b = 9{\cdot}95$, $c = 11{\cdot}03$ Å, $\beta = 109° 15'$. Three-dimensional intensity data were recorded by the equi-inclination Weissenberg technique and were estimated visually; in all **1453** independent $|F_0|$ values were derived. The structure was elucidated by the heavy-atom method and refined by Fourier and least-squares methods. The value of $R$ is 14·5%.

The arrangement of atoms within the molecule as seen when viewed along the *c* axis is shown in the Figure. The cyclopentanone ring adopts the half-chair conformation, not the envelope conformation

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[1] V. Sýkora, V. Herout, J. Plíva, and F. Šorm, *Chem. and Ind.*, 1956, 1231; V. Sýkora, V. Herout, J. Plíva, and F. Šorm, *Coll. Czech. Chem. Comm.*, 1958, **23**, 1072; V. Sýkora, V. Herout, A. Reiser, and F. Šorm, *Coll. Czech. Chem. Comm.*, 1959, **24**, 1306; J. Vrkoč, V. Herout, and F. Šorm, *Coll. Czech. Chem. Comm.*, 1963, **28**, 1084.

[2] J. Vrkoč, J. Jonáš, V. Herout, and F. Šorm, *Coll. Czech. Chem. Comm.*, 1964, **29**, 539.

[3] N. L. Allinger and H. M. Blatter, *J. Amer. Chem. Soc.*, 1961, **83**, 994.

which is usually encountered in crystal-structure studies of five-membered rings.[4]

The calculations were performed on the DEUCE computer at the University of Glasgow and the IBM 7094 computer at the University of Illinois. Dr. V. Herout supplied the crystals.

(*Received, May 3rd,* 1965.)

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[4] A. T. McPhail and G. A. Sim, *J. Chem. Soc.*, 1965, 1663; J. D. M. Asher and G. A. Sim, *J. Chem. Soc.*, 1965, 1584; and references cited therein.