Tetrahedron Letters No.39, pp. 2845-2849, 1964. Pergamon Press Ltd
Printed in Great Britain

ANISOTROPIC EFFECTS OF THREE-MEMBERED RINGS IN PROTON MAGNETIC RESONANCE

Sture Forsén and Torbjörn Norin

Research Group for Nuclear Magnetic Resonance, Division of Physical Chemistry and
Division of Organic Chemistry, The Royal Institute of Technology, Stockholm 70,
Sweden

(Received 30 July 1964)

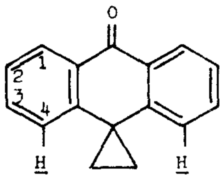
Proton magnetic resonance studies of the structure of thujopsene have indicated a characteristic long-range anisotropic effect of the cyclopropane ring. There seemed to be a rough correlation between the interaction of the cyclopropane ring and the shifts of neighbouring protons[1]. Cyclopropane has an unusually large diamagnetic susceptibility[2], an observation which could be accounted for by assuming three electrons precessing in a ring of radius 1.46 Å. Wiberg and Nist[3] interpreted the high field shift of cyclopropane protons in terms of this ring current effect. From PMR-studies on a large number of cyclopropane derivatives Patel, Howden and Roberts[4] concluded that the chemical shifts observed seemed consistent with a ring current effect. In single cases other authors[5,6] have observed characteristic anisotropic effects of cyclopropane rings. This effect could be of considerable interest for configurational and conformational studies and the determination of its magnitude is therefore desirable. In order to investigate this problem we have studied some model compounds.

The signals due to the C(4)-protons of the anthrone derivative (1)[7] are shifted to a considerably higher field (δ 6.91)*) than those of the C(4)-protons

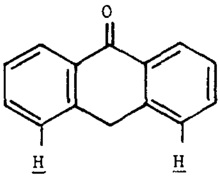
---

*) The proton magnetic resonance spectra were recorded on a Varian A-60 instrument. The spectra of compounds (1)-(3) were recorded in deuterochloroform and those of compounds (4)-(9) in carbontetrachloride. The shifts are given in ppm from tetramethylsilane as internal standard.

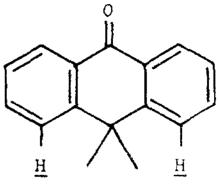
of anthrone (2) (δ 7.41) and dimethylanthrone (3)[8] (δ 7.42). This upfield shift must be due largely to the anisotropy of the cyclopropane ring. It is possible



1



2

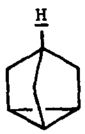


3

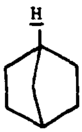
that the π-electron distribution in the aromatic ring in compound (1) may be slightly different from that of compounds (2) and (3) because of conjugative interactions of the cyclopropane ring. The relative constancy of the shifts of the C(1)-, C(2)- and C(3)-protons indicates that the conjugative effects are small. Therefore, taking Δδ = 0.5 ppm for the anisotropy effect of the cyclopropane ring on the C(4)-proton, a rough estimate of the diamagnetic anistrotropy ΔX may be calculated using the point dipole approximation of Mc Connell[9]. The point dipole is simply put in the centre of the cyclopropane ring. The distance from this centre to the centre of a C(4)-proton is taken to be 2.5 Å (as estimated from a Dreiding model) and the angle (θ) to be 90°. The ΔX value thus obtained is 15×10^{-6} cm^3/mole. This value is of the same order of magnitude as the anisotropy value of cyclopropane (27×10^{-6} cm^3/mole) estimated by Lacher, Pollock and Park[2] on the basis of susceptibility measurements.

The C(4)-proton of nortricyclene (tricyclo[2.2.1.0 heptane) (4) appears at a resonance field 0.30 ppm higher than that of the C(4)-proton of norbornane (5

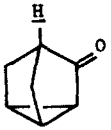
This upfield shift together with a correction added for the anisotropy of the C(1)-C(2)- and C(1)-C(6)-bonds (0.11 ppm, calculated using the point dipole approximation[9] and a $\Delta\chi$-value of 5.5×10^{-30} cm^3/molecule for the carbon-carbon single bond) may approximately be taken as the anisotropic effect of the cyclopropane ring on the C(4)-proton of nortricyclene (4). Using the point dipole approximation discussed above the $\Delta\chi$-value for the cyclopropane ring is computed to 20×10^{-6} cm^3/mole.



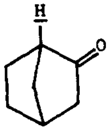
4



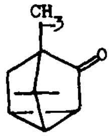
5



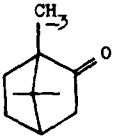
6



7



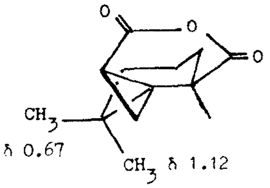
8



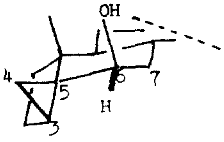
9

The characteristic anisotropic effect of the cyclopropane ring also operates on the C(4)-proton of nortricyclanone (6). The C(4)-proton signal appears at δ 1.8 whereas the corresponding proton of norcamphor (7) has its resonance position at δ 2.49[3]. Similarly the bridgehead methyl group of cyclocamphenone (8) has its resonance position (δ 0.70) at a higher field than that of the corresponding methyl group of camphor (9) (δ 0.82). The compounds (6) and (8) are, however, less suitable for computations of the $\Delta\chi$-value of the cyclopropane ring since these molecules possess a more complex system with a carbonyl group conjugated with the cyclopropane ring.

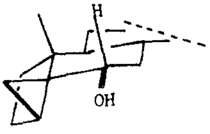
One of the geminal methyl groups of the thujopsene derivative (10) is held in a position above the plane of the cyclopropane ring[10]. This equatorial methyl group has its resonance position at a notably high field[10] and this must be due mainly to the anisotropy of the cyclopropane ring. The large differences in chemical shifts between the two geminal methyl groups of other thujopsene derivatives can similarly be explained by the effect of the cyclopropane ring[1].



10



11



12

Tadanier and Cole[5] have pointed out that the 3α,5α-cyclo-6-hydroxy-steroids, (11) and (12), provide an example where an axial ring proton in a cyclohexane ring absorbs at a lower field than the epimeric equatorial proton. The 6β-hydroxy epimer (11) has its 6-hydrogen above the plane of the cyclopropane ring and this hydrogen is therefore strongly shielded.

From the above examples it is clear that the magnitude of the anisotropy of the cyclopropane ring is greater than the calculated contribution from three carbon-carbon single bonds. An anisotropy value of cyclopropane of about 20×10^{-6} cm^3/mole may serve as a rough estimate for a ΔX-value for computations of long-range anisotropic effects of cyclopropane rings.

Acknowledgements

The cost of the Varian A-60 spectrometer has been defrayed by grants from Knut och Alice Wallenbergs Stiftelse. This work has been supported by the Swedish Technical Research Council.

References

1. S. Forsén and T. Norin, Acta Chem. Scand. 15, 592 (1961).
2. J.R. Lacher, J.W. Pollack and J.D. Park, J.Chem.Phys. 20, 1047 (1952).
3. K.B. Wiberg and B.J. Nist, J.Am.Chem.Soc. 83, 1226 (1961).
4. D.J. Patel, M.E.H. Howden and J.D. Roberts, J.Am.Chem.Soc. 85, 3218 (1963).
5. J. Tadanier and W. Cole, J.Org.Chem. 27, 4610 (1962).
6. R.R. Saners and P.E. Sonnet, Chem. and Ind. 1963, 786.
7. A. Mustafa and M.K. Hilmy, J.Chem.Soc. 1952, 1434.
8. F. Hallgarten, Ber. 21, 2508 (1888).
9. H.M. McConnell, J.Chem.Phys. 27, 226 (1957).
10. T. Norin, Acta Chem. Scand. 17, 738 (1963).