Tetrahedron Letters No. 4, pp 325 - 326, 1972. Pergamon Press. Printed in Great Britain.

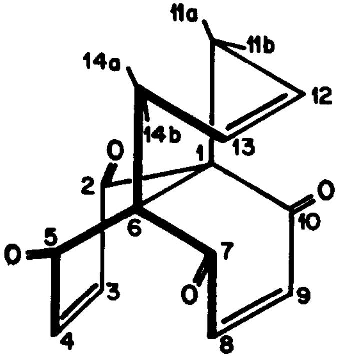
PROPELLANES. XVIII. A PROPELLANE FREE RADICAL[1]

R. Bar-Adon, S. Schlick, B.L. Silver and D. Ginsburg

Department of Chemistry, Technion - Israel Institute of Technology, Haifa

(Received in UK 15 December 1971; accepted for publication 28 December 1971)

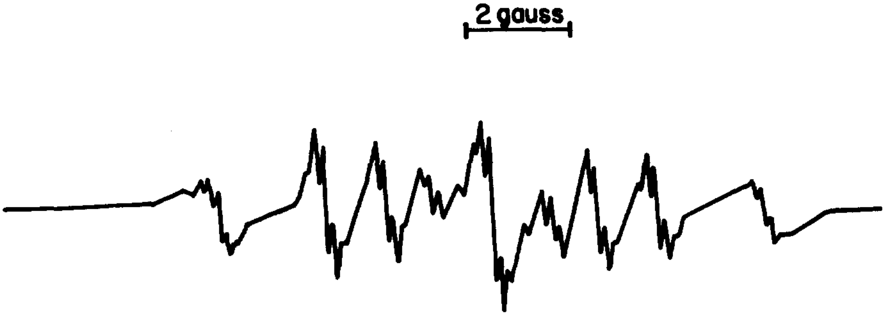
When suitably chosen functional groups are disposed about a propellane framework, interaction may be observed between these groups.[2-4] It could therefore be anticipated that in judiciously chosen propellane derivatives an unpaired free radical would be delocalized over the whole molecule rather than be confined, by the insulating bridgehead carbons, to the ring in which it was generated. Molecules containing carbonyl groups are in general readily reduced to free radicals.[5] 2,5,7,10-Tetraoxo[4.4.4]propella-3,8,12-triene[6] 1 was chosen for preliminary experiments.



1

Electrolytic reduction of ca. 0.1M solutions in DMF with tert-butylammonium perchlorate as supporting electrolyte afforded a room temperature esr spectrum (see figure; Varian model V-4502 spectrophotometer). This consists of a triplet splitting of 2.1 gauss, a second triplet splitting of 3.3 gauss, and a quintet splitting of 0.12 gauss. The spectrum indicates that the radical contains two sets of equivalent pairs of protons and one set of four equivalent protons. The parent molecule has 10 protons and the radical exhibits hyperfine interaction with only 8 of these. The unpaired electron is therefore delocalized over almost the whole molecular framework.

We tentatively propose the conformation shown in 1 for the radical as well; in it protons 3,4,8,9 are equivalent and are associated with the splitting of 0.12 gauss. The p orbitals on their adjacent carbon atoms are at considerable angles with respect to those on the carbonyl



carbons. It is probable that the unpaired electron is localized largely on the four carbonyl groups.

The splittings of the two pairs of equivalent protons 11a, 14a, and 11b, 14b may be rationalized on the basis of their participation in fairly effective "W-arrangements" of the type described by Russell and other workers.[7] Protons 12 and 13 are presumably those that fail to give observable splittings since they are so far from the carbonyl groups.

It should be noted that the triplet excitation in triptycene "hops" between the three aromatic rings though they too are insulated from each other by sp^3 hybridized carbon atoms.[8]

Further work is in progress with respect to the above and other propellane radicals.

References

1. Part XVII. D. Tatarsky, M. Kaufman and D. Ginsburg, Israel J. Chem., in press (1972).
2. J. Altman, E. Babad, J. Itzchaki and D. Ginsburg, Tetrahedron, Suppl. 8, Part 1, 279 (1966).
3. J.J. Bloomfield and R.E. Moser, J. Am. Chem. Soc., 90, 5625 (1968).
4. L.A. Paquette, R.E. Wingard, Jr., J.C. Philips, G.L. Thompson, L.K. Read, and J. Clardy, Ibid., 93, 4508 (1971).
5. B. Venkataraman, B.G. Segal and G.K. Fraenkel, J. Chem. Phys., 30, 1006 (1959).
6. J. Altman, E. Cohen, T. Maymon, J.B. Petersen, N. Reshef and D. Ginsburg, Tetrahedron, 25, 5115 (1969).
7. J.M. Fritsch and J.J. Bloomfield, Spectroscopy Letters, 1, 277 (1968) and references given therein.
8. J. van der Waals and M.S. de Groot, Mol. Phys., 6, 545 (1963).