

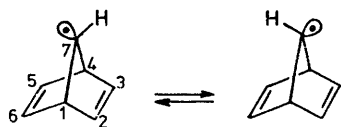
Pyramidal Geometry of the Tervalent Carbon Atom of the Norbornadien-7-yl Radical; Electron Spin Resonance Study

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Summary The e.s.r. spectrum of the norbornadien-7-yl radical shows that its trigonal carbon atom (C_α) is more pyramidal than that of the cyclopropyl radical; it is suggested that the pyramidal deformation of the former is due to electron transfer interaction from the etheno bridges to C_α as well as to the small bond angle around C_α .

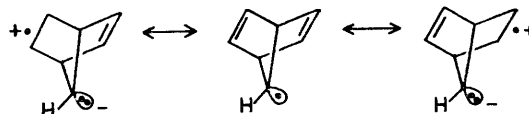
THE bending of the radical centre of substituted alkyl radicals is of current interest.¹ We report here the e.s.r. spectrum of the norbornadien-7-yl radical and that its trivalent carbon atom is more pyramidal than that of the cyclopropyl radical.



Irradiation of a cyclopropane solution of a mixture of 7-bromonorbornadiene,² triethylsilane, and di-*t*-butyl peroxide at -108°C led to an e.s.r. spectrum³ which was analysed as a doublet (0.449 mT) of triplets (0.187 mT) further split into quintets (0.008 mT) with a *g* factor of 2.00228.† We attribute the spectrum to the norbornadien-7-yl radical.⁴ The doublet, triplet, and quintet splittings can be reasonably assigned to α (7-H), bridgehead (1- and 4-H), and etheno bridge (2-, 3-, 5-, and 6-H) protons, respectively. These hyperfine splitting constants (h.f.s.c.) fit well the correlation⁵ between α and β proton h.f.s.c.s observed for norbornen-7-yl⁶ and related radicals. The α -proton h.f.s.c. of $(-)$ 0.449 mT of the norbornadien-7-yl

radical is more positive than that of the cyclopropyl radical (-0.65 mT),⁷ showing that the radical centre of the former is more bent than that of the latter, although the C(1)–C(7)–C(4) bond angles in the former would be expected to be around 92° ⁸ and far larger than the corresponding bond angle in the latter.

We suggested previously that the extent of radical-centre bending of the norbornen-7-yl and related radicals should correlate with the angle between the C(1)–C(7) and C(7)–C(4) bonds. The present results suggest that this bond angle may not be the only major factor inducing pyramidal deformation of the norbornadien-7-yl and related radicals. The symmetry of the π orbitals on the etheno bridges and the odd electron orbital on C-7 only allows electron transfer away from the etheno bridges to C-7 (Scheme).⁹ The



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resulting carbanion-like character of the trivalent carbon atom as well as the small angle between the C(7)–C(1) and C(7)–C(4) bonds seems to have led to a pyramidal deformation of the trivalent carbon atom. The relative importance of π electron delocalization and σ inductive effects in radical-centre bending of substituted alkyl radicals such as $\cdot\text{CF}_3$ is a subject of continuing discussion.¹ However, σ inductive effects are not involved in the pyramidal deformation of the radical centre of the present species.

(Received, 19th May 1978; Com. 541.)

† This analysis was confirmed by comparing observed and simulated spectra; these spectra were made available to the referees.

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