Large Long-range Coupling in the Electron Spin Resonance Spectra of the Bicyclo[2.1.1]hexan-1-yl Radical

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Summary The bridgehead proton hyperfine splitting constant of the bicyclo[2.1.1]hexan-1-yl radical is unexpectedly large (22·49 G); INDO calculations show that this is due to 'through-space' as well as 'through-bond' spin transfer from C–1 to 4–H.

The e.s.r. spectrum of the bicyclo[2.1.1]hexan-1-yl radical was observed during irradiation of a cyclopropane solution of bis(bicyclo[2.1.1]hexane-1-carbonyl) peroxide at −116 °C. The g factor was 2·00257 ± 0·00003. The spectrum was analysed as a doublet (22·49 ± 0·04 G) split further into three sets of 1:2:1 triplets (5·01 ± 0·01, 2·01 ± 0·1, and 0·84 ± 0·01 G). The assignment of the 22·49 G doublet to 4-H was straightforward from the molecular symmetry of the radical. The proton hyperfine splitting constants (h.f.s.c.) of the radical were calculated by the INDO method[1] (Table). INDO calculations were performed for the structure with 1-H removed from the parent hydrocarbon[2] and also with structures in which C-1 was displaced Z Å inward along the C-1—1-H axis in the parent molecule. From a comparison between the calculated and observed h.f.s.c.s, the triplet splitting of 5·01 G is assigned to *exo*-5-H. Further experimental studies are needed for assignment of the remaining triplets.

The bridgehead proton h.f.s.c. of the present radical is large in comparison with those of the 1-norbornyl (2·45 G)[3] and bicyclo[2.2.2]octan-1-yl (2·69 G)[4] radicals. The calculated results in the Table show the importance of both 'through-space' and 'through-bond' mechanisms for the large bridgehead proton h.f.s.c. of the present radical. In agreement with the significant bridgehead proton h.f.s.c., a non-empirical SCF LCAO MO study of the parent hydrocarbon revealed a strong interaction between the two bridgehead sites,[5] and a large long-range coupling between the bridgehead protons (7·0 Hz) was observed in the n.m.r. spectrum of 2-methylenebicyclo[2.1.1]hexane.[6]

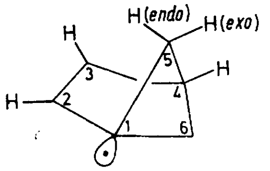

Table. INDO hyperfine splitting constants (in G) for the bicyclo[2.1.1]hexan-1-yl radical

Z/Å	4-H[a]	*exo*-5-H	*endo*-5-H	3-H	2-H	E/(kcal mol^{-1})[b]
0·0	15·7 (8·0)	3·06	1·33	0·81	0·56	−0·8
0·1	21·4 (10·4)	4·52	1·78	1·00	0·64	3·3
0·2	29·9 (13·9)	6·05	2·24	1·31	0·62	9·3
Obsd.	22·49	5·01	(2·01)	0·84,	0·0)	—

[a] Numbers in parentheses are h.f.s.c.s obtained in calculations in which the C–1—C–4 'through-space' interactions are artificially removed. [b] Calculated destabilization accompanying the artificial removal of the C–1—C–4 'through-space' interactions.

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