Conformation and Stability of 1,1-Diphenylmethyleneiminyl

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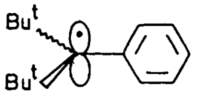
Summary The magnitudes of ring-proton coupling in the title radical are consistent with those calculated for the conformation (III) which is also estimated to be the most stable rotamer.

Aromatic iminyl radicals, such as (I), are surprisingly[1] stable, in view of the apparent lack of π delocalization of the unpaired spin. CIDNP results,[2] however, suggest that p–σ interaction in (Ia) may contribute to this stability. There has been much recent interest in π–σ delocalization in organic radicals,[3] and, in particular, the e.s.r. spectra of 'perpendicular' radicals such as (II) have been studied[4] to check the values of coupling constants predicted[5] by INDO calculations.[6] The radical (II) is forced into a perpendicular conformation by the butyl substituents, and such steric crowding is normally considered to be necessary to produce a significant degree of twisting in aromatic radicals with an exocyclic π centre.

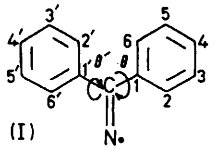
TABLE 1
Proton hyperfine coupling[a] for (I) in CCl_4 solution at 42°

Iminyl	No of lines	Simulation fit X	 a_X/mT	 n equiv.
(Ia)	9	H	0·037	8
(Ib)	8	^{2}H	0·006	1
		H	0·037	7
(Ic)	5	^{2}H	0·006	4
		H	0·037	4
(Id)	5	^{2}H	0·006	4
		H	0·037	4
(Ie)	3	^{2}H	0·006	6
		H	0·037	2
(If)	1	^{2}H	0·006	8

[a] Simulations based on the values given in the table were fitted to the experimental spectra.

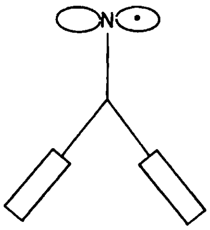


(II)



(I)

a; nondeuteriated
b; [3-^{2}H]
c; [2,3,4,5,6-$^2H_5$]
d; [2,3,4,5,6,4′-$^2H_6$]
e; [2,3,4,5,6,2′,4′,6′-$^2H_8$]
f; [2,3,4,5,6,2′,3′,5′,6′-$^2H_9$]



(III)

TABLE 2. Variation in calculated total energy and *para*-H coupling constant with dihedral angles θ and θ'.

		System A		System B	
θ	θ'	p-coupling	Energy/a.u.	p-coupling constant	Energy/a.u.
0	0	—	—	0·91	−107·311485
30	30	1·65	−107·521076	0·66	−107·546923
60	60	0·58	−107·521933	0·33	−107·549438
90	90	0·25	−107·523611	0·24	−107·551327

System A: $r_{C-N} = 1{\cdot}37$ Å; $r_{C-C(Ar)} = 1{\cdot}40$ Å; $r_{C(Ar)-C(Ar)} = 1{\cdot}40$ Å.
System B: $r_{C-N} = 1{\cdot}30$ Å; $r_{C-C(Ar)} = 1{\cdot}46$ Å; $r_{C(Ar)-C(Ar)} = 1{\cdot}40$ Å.

We now report the results of solution e.s.r. studies and INDO calculations on the iminyl (I), prepared by the thermolysis of *O*-diphenylmethyleneamino dimethylthiocarbamate,[2] which together indicate that the diperpendicular conformation (III) is the most stable for this unusual π radical. The e.s.r. spectrum of (I)[7] is characterized by a nitrogen splitting (*ca.* 1·0 mT) and a further coupling to eight equivalent hydrogen nuclei, $|a_H| = 0{\cdot}037$ mT. Selective deuteriation (Table 1) indicates that these are the two sets of *ortho* and *meta* protons, while the *para* couplings are smaller ($<0{\cdot}02$ mT). INDO calculations (C–C 1·40, C–N 1·37, C–H 1·08 Å) reproduce the nitrogen coupling for all values of θ and θ' (a_N calc. $= 0{\cdot}98 \pm 0{\cdot}05$ mT), but convergence on the experimental proton splittings occurs only when the dihedral angles θ and θ' both approach 90°, and the *para* coupling in particular then reaches a minimum value, close to zero ($|a_H|$ *ortho, meta, para* = 0·13, 0·05, 0·02 mT). The absolute values of these coupling constants change considerably with variation in the geometry of the system and bond distances, but using reasonable values (Table 2) the energy decreases with increasing dihedral angle, and the *para* coupling constant decreases to a minimum value for the most stable configuration (III), with $\theta = \theta' = 90°$.

These conclusions are in complete agreement with very recent INDO calculations[8] on the iso-electronic phenyldiazenyl radical, which however has not been detected by e.s.r. spectroscopy.

These results imply that p–σ hyperconjugation provides greater delocalization energy than the π–π conjugation, usually considered to be the more important.

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