Through-space Coupling in a 2-Fluorophenyliminyl Radical

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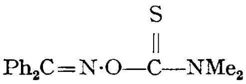
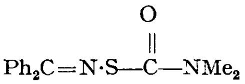
Summary E.s.r. solution spectra of some fluorophenyliminyl free-radicals are reported; the fluorine coupling in a 2-fluorophenyl iminyl suggests a through-space interaction in the nodal plane of the π-system for this radical.

THE iminyl radical (Ia) (Table) has recently been detected[1] by e.s.r. measurements in the thermal rearrangement of the oxime thionocarbamate (II) to the thioxime carbamate (III) in carbon tetrachloride solution at 65 °C.



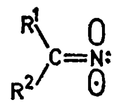
$Ph_2C{=}N{\cdot}O{-}\overset{\overset{\Large S}{\|}}{C}{-}NMe_2$

(II)



$Ph_2C{=}N{\cdot}S{-}\overset{\overset{\Large O}{\|}}{C}{-}NMe_2$

(III)



(I)

	R^1	R^2
a;	Ph	Ph
b;	Ph	2-FC_6H_4
c;	Ph	4-FC_6H_4
d;	4-FC_6H_4	4-FC_6H_4
e;	3-FC_6H_4	3-FC_6H_4

This is therefore a convenient method of generation of aromatic ketimine radicals for e.s.r. study, and we now report the spectra of further iminyls (Ib → e), observed in the thermal rearrangement of the appropriate oxime thionocarbamates. Iminyls are reported to have values of a_N *ca.* 0·95 mT and *g ca.* 2·0030,[2,3] which are in close accord with the values obtained in the present study (Table) Further hyperfine interactions, however, are also recorded in the Table, and these show evidence, in our consideration, of an interesting through-space coupling.

(Ib) has a doublet splitting, attributed to $|a_F|$ *ca.* 0·23 mT. This coupling is greatly reduced in the remaining fluoro-radicals (Ic—e).

TABLE

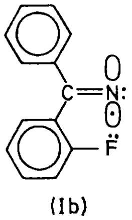
Spectral parameters of iminyls (Ia—e) *in* CCl_4 *at* 65 °C

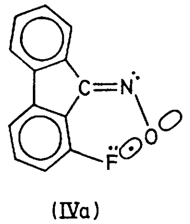
	a_N/mT	a_F/mT	a_H/mT[a]	*g*
a;	1·0		0·04	2·0033
b;	0·98	0·23	0·04	2·0031
c;	0·98		0·04	2·0033
d;	1·02			
e;	1·0		0·04	

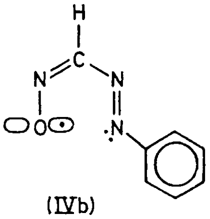
[a] Assignments to individual ring protons have not been made, since imperfect resolution of the multiplet spectra limits analysis of the splitting pattern.

In the study of the e.s.r. spectra of fluoronitrobenzene anions,[4] it was observed that fluorine couplings were generally approximately twice as large as those of the ring hydrogen at the same position in isomeric anion radicals. Since the substitution of weakly electron-withdrawing groups in a radical already containing a strong electron-withdrawing group does not affect the spin-density distribution significantly,[5] $|a_F|$ might therefore be expected to be approximately twice a_H in the iminyls (Ib—e). This value, a_F *ca.* 0·08 mT, is not inconsistent with the imperfectly resolved spectra of (Ic—e), but cannot account for the significantly larger value observed in the 2-fluoro radical (Ib).

The larger coupling of 0·23 mT is uniquely attributable in the series to a 2-fluoro-substituent, since neither 2-hydrogen, 3-fluoro, nor 4-fluoro show this larger splitting. Similar specific interactions in the iminoxyl radicals (IVa and b) have been explained[6,7] by long-range orbital interaction not involving the prevailing π system. Since the unpaired electron in iminyls is believed[2] to occupy a nitrogen orbital of predominantly 2*p* character, orthogonal to the π-orbitals of the molecular framework, a similar explanation is likely for the relatively large fluorine coupling described for the radical (Ib). This explanation is supported by extended Hückel calculations to be reported elsewhere.


(Ib)


(IVa)


(IVb)

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[1] R. F. Hudson, A. J. Lawson, and E. A. C. Lucken, *Chem. Comm.*, 1971, 807.
[2] J. A. Brivati, K. D. J. Root, M. C. R. Symons, and D. J. A. Tinling, *J. Chem. Soc.* (*A*), 1962, 1942.
[3] D. E. Wood, R. V. Lloyd, and D. W. Pratt, *J. Amer. Chem. Soc.*, 1970, **92**, 4115.
[4] A. Carrington, A. Hudson, and H. C. Longuet-Higgins, *Mol. Phys.*, 1968, **9**, 377.
[5] M. Kaplan, J. R. Bolton, and G. K. Fraenkel, *J. Chem. Phys.*, 1965, **42**, 955.
[6] B. C. Gilbert and R. O. C. Norman, *J. Chem. Soc.* (*B*), 1967, 981.
[7] A. F. Neugebauer, *Tetrahedron Letters*, 1970, 2345.