Electron Spin Resonance Studies. Part XII.[1] Characteristics of the Iminoxy-radicals from the 1-Halogenofluorenone Oximes[2]

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The hyperfine splittings of the halogen nuclei in the 1-halogenofluorenone iminoxy-radicals are remarkably large; they are discussed in terms of an interaction between the orbital of the unpaired electron on the iminoxy-function and one on the halogen which, though four bonds removed, is suitably sited by virtue of the fixed geometry of the system. The lines in the spectrum of the iodine-containing radical are markedly broadened, and their widths vary with the temperature and viscosity of the medium in a manner which indicates the operation of nuclear-quadrupole relaxation.

We have recently drawn attention to the unusually large coupling constants associated with halogen nuclei which are appropriately situated in iminoxy (RR′C=NO·) radicals.[2,3] We have now examined in detail the electron spin resonance spectra of the iminoxy-radicals obtained by oxidising 1-bromo- and 1-iodo-fluorenone oxime with lead tetra-acetate and have compared the results with those for the corresponding fluoro- and chloro-containing radicals.

Spectral Characteristics and Assignments.—Unlike 1-fluoro- and 1-chloro-fluorenone oxime, 1-bromo- and 1-iodo-fluorenone oxime each gave only one detectable radical on oxidation. That from the bromo-compound showed interaction with nitrogen (*a*, 33·6 oersted), one proton (*a*, 2·9 oersted), and the halogen (four lines; *a*, 10·4 oersted). Separate resonances due to ^{79}Br and ^{81}Br, the ratio of whose nuclear *g*-factors is close to unity,[4] were not completely resolved; the relatively large line-widths, *ca.* 1·5 oersted, compared with values of *ca.* 0·5 oersted for other iminoxy-radicals which have been generated in the same conditions, result, at least in part, from the overlap of lines due to ^{79}Br and ^{81}Br.

Table 1

Splitting constants (oersted)[a] and *g*-factors[b] for 1-halogenofluorenone iminoxy-radicals

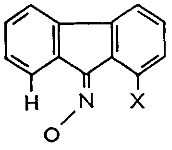
		Radical (I)				
X	=	H	F	Cl	Br[c]	I[d]
a_N	=	30·85	32·6	31·5	33·6	35·0
a_H	=	2·7	2·85	2·7	2·9	—
a_X	=	1·0	4·4	0·85[e]	10·4[f]	13·5
g	=	2·0064	2·0061	2·0061	2·0068	2·0090[g]

		Radical (II)		
X	=	H	F	Cl
a_N	=	30·85	31·1	31·5
a_H	=	1·0	0·8	—
a_X	=	2·7	13·5	2·7[e]
g	=	2·0064	2·0059	2·0061

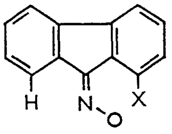
[a] To within ±0·05 except where stated. [b] To within ±0·0001 except where stated. [c] ±0·1. [d] ±0·2. [e] Mean for the radicals containing ^{35}Cl and ^{37}Cl. [f] Mean for the radicals containing ^{79}Br and ^{81}Br. [g] ±0·0003.

The magnitude of the proton-splitting enables us, by the arguments discussed previously,[3] to assign the spectrum to the radical (I; X = Br) in which the halogen and oxygen atoms bear a *trans* relationship with respect to the C=N bond. We infer that the failure to detect the isomeric radical (II; X = Br) arises from steric repulsion between the oxygen and bromine atoms in this radical such that the expected[5] equilibrium between the isomers lies relatively further towards the radical (I; X = Br) as compared with the position of equilibrium between the corresponding chloro-substituted radicals. The effect of steric hindrance on the relative stabilities of different conformations of halogen-substituted iminoxy-radicals has already been established.[2,3]

The iodo-substituted radical showed interaction with nitrogen (*a*, 35·0 oersted) and iodine (six lines; *a*, 13·5 oersted). The lines were so broad (see below) that no further splitting could be detected. Analogy with the behaviour of the bromo-compound leads us to assume that the iodo-radical has the structure (I; X = I), the the expected proton-splitting of[3] *ca.* 2·8 oersted being obscured.



(I)



(II)

The splitting constants and *g*-factors are in Table 1 together with those for other members of the series. These values were constant, within the limits of experimental error, for solutions in methylene dichloride, acetonitrile, benzene, and dimethyl sulphoxide at 20°.

Magnitude of Halogen-splittings.—Splitting due to interaction between an unpaired electron and an iodine nucleus has not, to our knowledge, been observed previously. Interaction with a bromine nucleus in an organic radical in solution has been detected only in the case of the radical (III; X = Br) for which $a_{Br} = 3·7$ oersted.[6]

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[1] Part XI, R. O. C. Norman and R. J. Pritchett, *J. Chem. Soc.* (*B*), 1967, 926.

[2] This Paper is regarded as Part IV of the Series, Iminoxy-radicals (Part III, R. O. C. Norman and B. C. Gilbert, *J. Phys. Chem.*, 1967, **71**, 14).

[3] B. C. Gilbert and R. O. C. Norman, *J. Chem. Soc.* (*B*), 1966, 722.

[4] 'Table of Nuclear Magnetic Properties,' Varian Associates.

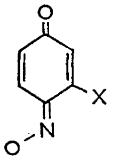
[5] B. C. Gilbert and R. O. C. Norman, *J. Chem. Soc.* (*B*), 1966, 86.

[6] W. M. Fox and W. A. Waters, *J. Chem. Soc.*, 1965, 4628.

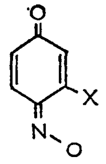
Previous studies of halogen-containing radicals have been concerned almost entirely with those of π-type. In these cases, the splitting constants for equivalently placed nuclei usually decrease in the order, F > H > Cl, with no splitting detectable from equivalently placed bromine or iodine nuclei, as in substituted *p*-benzosemiquinones [7] and nitrobenzene radical-anions.[8] This order is doubtless associated not only with the magnitudes of the nuclear *g*-factors (*e.g.*, Cl ≪ F) but also with the mechanisms by which spin-density is transmitted to a halogen nucleus. Thus, for the isotropic interaction in the radical $\cdot CHF\cdot CONH_2$, Whiffen and his colleagues have concluded [9] that spin-polarisation of the C–F bonding-electrons induces negative spin-density at fluorine, while conjugation, represented by the contribution of the structure $\overset{+}{F}$–$\overset{-}{C}H\cdot CONH_2$, provides considerable fluorine 2*p*-character for the unpaired electron which in turn polarises the spin in the fluorine 2*s* shell and leads to positive spin-density at the nucleus; the overall effect is that there is a small (positive) spin-density at the nucleus which is determined by the difference between two large quantities. Since two mechanisms are in operation, it is not surprising that the ratio $a_F : a_H$ varies with the structures of the radicals.

In contrast, iminoxy-radicals are of σ-type,[5,10] and the transmission of spin through the π-system is, at most, relatively ineffective.[5] It is consequently not surprising that the magnitudes of halogen-splittings lie in different orders. For the series (I) and (II), the orders are, respectively, H ~ Cl < F < Br < I, and H ~ Cl < F. The results may be compared with those for the series of related radicals (III) and (IV) for which the following tentative assignments have been made:[6] for (III), X = H, 1·4; F, 3—4; Cl, not detectable; Br, 3·7; and for (IV), X = H, 3·9; F, 8—10; Cl, 2 oersted. As in the fluorenone iminoxy-radicals, the splitting for X = H, F, or Cl is larger when X is *cis* with respect to the iminoxy-oxygen, but it is notable that, although the proton-splittings in (III) and (IV) are larger than those in (I) and (II), respectively, the opposite is true of the halogen-splittings. Now, although the halogen nucleus in (I) or (II) is further removed from the iminoxy-function, in terms of the number of intervening bonds, as compared with (III) or (IV), it is held nearer to this function, in terms of the non-bonding separation, by the fixed geometry of the radical. Thus, the data are in accord with our view [3] that splitting arises in radicals of this type as a result of an interaction through space, and they indicate that such interactions may be of particular significance for the halogen nuclei.

In order to probe further the nature of this interaction and to rationalise the order of splitting constants for the halogens, it is helpful to derive the spin-population in the outermost populated *s*-orbital of the halogen (or an equivalently placed hydrogen). This is given by the fraction $a(X)/A_0(X)$, where $a(X)$ is the observed splitting due to the nucleus X and $A_0(X)$ is the splitting which would be observed if there were an unpaired electron in the outermost populated *s*-orbital. [A_0 is given by $g_e\beta_e g_n\beta_n \boldsymbol{h}^{-1} (8\pi/3)\, \psi^2(O)$ where $\psi^2(O)$ is the square of the value of the valence-shell *s* wave function at the nucleus. In this treatment, contributions to the splitting from inner *s*-orbital polarisation are neglected.] The following values for A_0 are available:[11] H, 508; ^{19}F, 17,400; ^{35}Cl, 1665; ^{37}Cl, 1385; ^{79}Br, 7850; ^{81}Br, 8160 oersted; and we have calculated a value of A_0 for ^{127}I of 7300 oersted, using [12] $\psi^2(O) = 22{\cdot}84$ a.u. Since separate resonances for ^{35}Cl and ^{37}Cl and for ^{79}Br and ^{81}Br were not resolved, it is appropriate to employ the weighted means of the A_0-values in these cases. The derived spin-populations are then as in Table 2.



(III)



(IV)

TABLE 2

Radical (I), X =	H	F	Cl	Br	I
Spin-population, ×10²(%)	19·7	2·5	5·3	13·2	18·5
Radical (II), X =	H	F	Cl		
Spin-population, ×10²(%)	53·1	7·8	16·9		

Amongst the halogens, the spin-population increases with the size of the atom and its covalent radius; simple models show that the distance between the halogen and the iminoxy-nitrogen [in (I)] or oxygen [in (II)] decreases in the order F > Cl > Br > I. Thus, the order of spin-populations could be the result of an interaction between the in-plane orbital of the iminoxy-function which contains the unpaired electron [5] and an appropriate orbital of the halogen which lies in the same plane. This type of interaction may be contrasted with that which has been invoked to account for the β-fluorine splittings in the radicals [13,14] $(CF_3)_2NO\cdot$ and $CF_3\cdot\dot{C}F\cdot CONH_2$; here, it is suggested that there is a direct 1,3-conjugation, of *p*π–*p*π type, between a *p*-orbital on fluorine and the p_z orbital containing the unpaired electron, on nitrogen and on carbon, respectively.

It is to be noted that, whereas the fluorenone iminoxy-

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[7] D. H. Anderson, P. J. Frank, and H. S. Gutowsky, *J. Chem. Phys.*, 1960, **32**, 196; T. C. Hollocher, M. Tooney, and R. Adman, *Nature*, 1963, **197**, 74.

[8] P. L. Kolker and W. A. Waters, *J. Chem. Soc.*, 1964, 1136.

[9] R. J. Cook, J. R. Rowlands, and D. H. Whiffen, *Proc. Chem. Soc.*, 1962, 252; *Mol. Phys.*, 1963, **7**, 31.

[10] M. C. R. Symons, *J. Chem. Soc.*, 1965, 2276.

[11] J. R. Morton, J. R. Rowlands, and D. H. Whiffen, 'Atomic Properties for Determining Electron Spin Resonance Data,' No. BPR 13, Basic Physics Division, National Physical Laboratory.

[12] D. F. Mayers, personal communication.

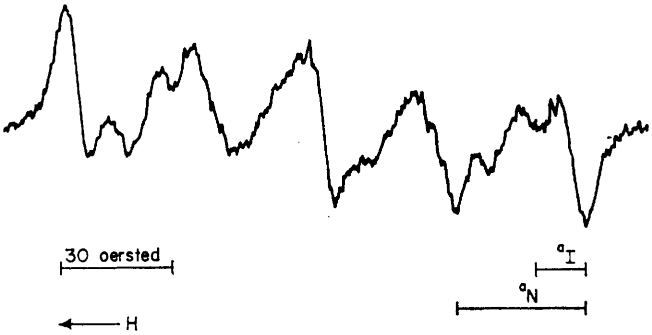
[13] P. J. Scheidler and J. R. Bolton, *J. Amer. Chem. Soc.*, 1966, **88**, 371.

[14] R. J. Lontz, *J. Chem. Phys.*, 1966, **45**, 1339.

radicals are characterised by large splittings from the 1-halogeno-substituents, the effect on $g_{av.}$ of replacing hydrogen by halogen is small, although g increases, as expected, with the size of the halogen. This is in marked contrast with the data for substituted *p*-benzosemiquinone radicals: in these, splittings from chlorine, bromine, or iodine substituents have not been observed, and are evidently much smaller than a_H, whereas the g-factors are considerably greater than for the unsubstituted semiquinone.[15] A possible explanation is as follows. Conjugation between the halogen and aromatic carbon in the semiquinones should give a significant spin-population in a *p*-orbital on the halogen and hence [15] a significant g-shift. This unpaired spin should produce spin-density in the valence-shell *s*-orbital of the halogen by spin-polarisation, but this effect should be opposed by the induction of spin-density in this orbital *via* spin-polarisation of the electrons in the carbon–halogen bond by the spin-population on carbon, resulting in an overall small splitting. For the iminoxy-radicals, on the other hand, evidently only a comparatively small spin-population is transferred to a halogen orbital (giving only a small g-shift), but, since this orbital has significant *s*-character, an appreciable splitting results.

The Spectrum of the Radical (I; X = I).—The spectrum (Figure) of the radical obtained by the oxidation of 1-iodofluorenone oxime in methylene dichloride at 20° cannot, on first inspection, be unambiguously assigned to an iminoxy-radical. That it is the spectrum of an iminoxy-radical is, however, consistent with three observations. First, the spectrum can be analysed in terms of a splitting from nitrogen of 35·0 oersted (see Figure) which is in the range of the relatively large values which characterise iminoxy-radicals.[3,5] Secondly, when a solution of the radical is cooled to −140°, a three-line spectrum whose shape is characteristic of trapped iminoxy-radicals [16] is observed. Thirdly, at higher temperatures the individual lines become sharper and the resonances due to one nitrogen and one iodine nucleus can be more clearly distinguished; however, in these conditions the radical decays rapidly. The appearance of the spectrum at 20° is the result of the lines being in general very broad and yet not being of uniform width across the spectrum; in particular, the lines corresponding to m_I(Iodine) = $\pm\frac{5}{2}$ are sharper than the remainder.

The breadths of the lines are far too large to be due to anisotropy in the hyperfine splittings or the g-factor. There are, however, two possible causes of line-broadening of this magnitude, namely, spin–orbit interaction and nuclear-quadrupole relaxation. In order to distinguish between these possibilities, we measured the line-broadening as a function of the viscosity, η, and temperature of the solvent. For relatively low values of η/T, the line-shape of the extreme high-field line was found to be approximately Lorentzian; the peak-to-peak line-width was then estimated from the shape of the peak (Table 3). For relatively high values of η/T, the line-width was of the same magnitude as the iodine hyperfine splitting and only a crude estimate could be made.



Electron spin resonance spectrum of the iminoxy-radical from 1-iodofluorenone oxime in methylene dichloride at 20°

TABLE 3

Estimated peak-to-peak line-widths of the extreme high-field line in the radical (I; X = I)

Solvent	T [a]	Viscosity (η) (centi-poise)	$10^3\eta/T$(°K)	Line-width [g]
MeCN	15°	0·375 [b]	1·30	8
	30	0·325 [b]	1·05	5·5
	60	0·246 [c]	0·74	4
CH_2Cl_2	−80	1·652 [d]	8·55	*ca.* 20
	−60	1·235 [d]	5·80	*ca.* 14
	−40	0·908 [d]	3·90	*ca.* 12
	−20	0·690 [d]	2·77	10·5
	0	0·533 [d]	1·97	9
	20	0·440 [d]	1·50	7
PhH	20	0·652 [e]	2·22	10
	50	0·442 [e]	1·36	7
	70	0·358 [e]	1·04	5
Me_2SO	25	2·00 [f]	6·72	*ca.* 17
MeOH	25	0·544 [b]	1·82	8

[a] ±2°. [b] 'Technique in Organic Chemistry,' ed. A. Weissberger, vol. 7, 2nd edn., Interscience, New York, 1955. [c] Calculated assuming [b] an exponential dependnce of η on T. [d] Calculated [c] from data [b] for other temperatures. [e] 'Handbook of Chemistry and Physics,' 46th edn., The Chemical Rubber Co., 1965. [f] J. J. Lindberg and R. Lauren, *Finska Kemistsamfundets Medd.*, 1962, **71**, 37. [g] ±0·5 oersted, except where indicated as approximate; see text.

The large line-widths of some peroxy-radicals and other radicals with high g-factors have been attributed to spin–orbit interaction.[17] A study of the t-butylperoxy-radical has shown [17] that the line-width increases with increase in T and decrease in η; the phenomenon is probably an example of the spin–rotation effects discussed by Kivelson and his colleagues.[18] In the present case, however, the opposite behaviour is observed: the line-width decreases with increase in temperature and with decrease in viscosity. This is as expected for nuclear-quadrupole relaxation: this process should become less rapid, and the lines correspondingly narrower,

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[15] M. S. Blois, H. W. Brown, and J. E. Maling, in 'Free Radicals in Biological Systems,' ed. M. S. Blois *et al.*, Academic Press, New York and London, 1961, p. 117.

[16] W. M. Fox and M. C. R. Symons, *J. Chem. Soc.* (*A*), 1966, 1503.

[17] J. R. Thomas, *J. Amer. Chem. Soc.*, 1966, **88**, 2064.

[18] R. Wilson and D. Kivelson, *J. Chem. Phys.*, 1966, **44**, 154, 4440, 4445; P. W. Atkins and D. Kivelson, *ibid.*, p. 169.

when the fluctuating field is more nearly averaged, that is, at high temperatures and low viscosities.

Moreover, the data in Table **3** show that, for the smaller values of η/T, the line-width is approximately proportional to η/T, in accord with Freed and Fraenkel's treatment [19] for the contribution to the line-width of nuclear-quadrupole relaxation in cases where the line-width is less than the hyperfine splitting. (Since the line-width obtained by extrapolation to $\eta/T = 0$ is close to zero, this form of relaxation is apparently dominant in governing the line-width.)

According to the treatment, the relaxation time, T_2^Q, due to nuclear quadrupole interaction is given by

$$\frac{1}{T_2^Q} = \frac{\tau_c}{20}\left(\frac{e^2Qq}{\hbar}\right)^2 \left\{\frac{I(I+1)[I(I+1)-1+2m^2]-3m^4}{[I(2I-1)]^2}\right\}$$

where τ_c is the molecular tumbling correlation time, Q is the nuclear quadrupole moment, q is the electric-field gradient at the nucleus, I is the nuclear spin, and m is the z-component of the nuclear spin; τ_c can be expressed as [20] $4\pi\eta a^3/3kT$, for a spherical molecule of radius a in a solvent of viscosity η. The peak-to-peak line-width, ΔH (oersted), is given by

$$\Delta H = (2{\cdot}8\pi\sqrt{3})^{-1}/10^6 T_2^Q$$

The application of this theory to halogen-containing radicals leads to the prediction that for nuclei with $I = \frac{3}{2}$ (the chlorine and bromine isotopes) the line-width is independent of m ($\pm\frac{1}{2}$, $\pm\frac{3}{2}$). For iodine, however, for which $I = \frac{5}{2}$, the line-widths should vary with m, having the following relative values:

m	$\pm\frac{1}{2}$	$\pm\frac{3}{2}$	$\pm\frac{5}{2}$
ΔH	1·2	1·53	1

Qualitatively, this is in agreement with the observation that the $m = \pm\frac{5}{2}$ resonances in the 1-iodofluorenone iminoxy-radical are the least broadened.

It is more difficult to calculate the absolute line-widths, or the relative line-widths to be expected for the iodo- as compared with, *e.g.*, the bromo-substituted iminoxy-radical. It has been suggested [21] that the most suitable approach is to employ typical values [22] for the nuclear quadrupole coupling constants ($e^2Qq/\hbar$) of covalently bonded halogen compounds (Table 4).

TABLE 4

Halogen	^{35}Cl	^{79}Br	^{127}I	
$e^2Qq/\hbar$	80	500	2,000	Mc./sec.

These values give predicted line-widths for the $m = \pm\frac{3}{2}$ resonances in the ratio, ^{35}Cl : ^{79}Br : ^{127}I = ~1 : 40 : 450, in agreement with the observation that only the iodine-containing radical shows marked line-broadening. Moreover, if we assume the reasonable [23] value of 10^{-11} sec. for the correlation time τ_c for these radicals, we obtain the following absolute values for the line-widths: ^{35}Cl, 0·01; ^{79}Br, 0·45; ^{127}I, 3·1 ($m = \pm\frac{5}{2}$), 4·7 ($m = \pm\frac{3}{2}$), 3·8 oersted ($m = \pm\frac{1}{2}$). (For ^{37}Cl and ^{81}Br, slightly smaller values would be expected because Q is smaller than the values for ^{35}Cl and ^{79}Br, respectively.) For iodine, the prediction is in agreement with the observed value for acetonitrile solution at *ca.* 60°. For chlorine, there should be no observable contribution to the line-width. For bromine, it seems likely that the observed broad lines (*ca.* 1·5 oersted) are due at least in part to nuclear quadrupole relaxation, but confirmation of this is difficult because of the overlapping of individual resonances due to ^{79}Br and ^{81}Br.

EXPERIMENTAL

The spectrometer and the general procedure have been described.[3,5] Radicals were generated by oxidation of the oxime with lead tetra-acetate and were examined in a static system except for the reaction in methanol which was carried out with ceric ion as oxidant [24] and a flow technique. Hyperfine splitting constants and g-factors were measured by comparison with Fremy's salt by use of a dual cavity.

Oximes.—The oximation of 1-bromofluorenone [25] gave the *oxime*, m. p. 214—215° (from aqueous ethanol) (Found: C, 56·8; H, 2·9; Br, 29·0; N, 5·35. $C_{13}H_8BrNO$ requires C, 57·0; H, 2·9; Br, 29·2; N, 5·1%) and likewise 1-iodofluorenone [26] gave the *oxime*, m. p. 217·5—219° (from aqueous ethanol followed by sublimation *in vacuo*) (Found: C, 50·3; H, 2·7; I, 37·9; N, 4·2. $C_{13}H_8INO$ requires C, 48·6; H, 2·5; I, 39·5; N, 4·4%).

We thank Professor J. H. Freed and Dr. H. Sillescu for discussions and for drawing our attention to the applicability of the line-width treatment we used, and Dr. D. F. Mayers for computing the appropriate $\psi^2(0)$ value for iodine.

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[19] J. H. Freed and G. K. Fraenkel, *J. Chem. Phys.*, 1963, **39**, 326.

[20] N. Bloembergen, E. M. Purcell, and R. V. Pound, *Phys. Rev.*, 1948, **73**, 679.

[21] H. Sillescu, personal communication.

[22] C. P. Slichter, ' Principles of Magnetic Resonance,' Harper and Row, New York, 1963, p. 175.

[23] See, *e.g.*, B. L. Silver, Z. Luz, and C. Eden, *J. Chem. Phys.*, 1966, **44**, 4258; J. W. H. Schreurs and G. K. Fraenkel, *ibid.*, 1961, **34**, 756; T. A. Miller, R. N. Adams, and P. M. Richards, *ibid.*, 1966, **44**, 4022.

[24] J. R. Thomas, *J. Amer. Chem. Soc.*, 1964, **86**, 1446.

[25] E. H. Huntress, K. Pfister, and K. H. T. Pfister, *J. Amer. Chem. Soc.*, 1942, **64**, 2845.

[26] N. Kharasch and T. C. Bruice, *J. Amer. Chem. Soc.*, 1951, **73**, 3240.