Electron Spin Resonance Studies. Part XV.¹ Iminoxy-radicals from Acetophenone Oxime and Related Oximes²

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The electron spin resonance spectra of the iminoxy-radicals derived by the oxidation of acetophenone oxime, some of its derivatives, and related oximes have been measured in solution. The spectra of some of these radicals have also been examined in the solid state, in which they have been generated by y-irradiation of powdered oximes. In some cases, both syn- and anti-radicals are observed, and in other cases only one isomer; each spectrum has been assigned to a radical of a particular configuration. The results for the 2-halogenoacetophenone iminoxy-radicals in which the methyl group is trans to the iminoxy-oxygen atom show that of the two possible conformations in which the aromatic ring and the iminoxy-function are coplanar, the one in which the halogen atom is close to the iminoxy-oxygen atom is the more heavily populated. This is in marked contrast to the situation in the radicals of the same configuration from 2-halogenobenzaldoximes, and the reason for the difference is discussed. The halogen-splittings in the 2-halogenoacetophenone iminoxy-radicals are strongly dependent on both the nature of the solvent and the temperature, unlike those in 1-halogenofluorenone iminoxy-radicals, and it is argued that, in the former series of radicals, non-planar conformations are significantly populated, though to a decreasing extent as the polarity of the solvent is increased or the temperature is lowered.

WE previously described the electron spin resonance (e.s.r.) spectra of the isomeric syn- and anti-iminoxyradicals derived from benzaldoxime and related oximes, and showed how the spectral characteristics provide information about the conformational preferences of these radicals.³ We now report on the e.s.r. spectra of the iminoxy-radicals from acetophenone oxime and related oximes, including studies of the solvent- and temperature-dependence of halogen-splittings in the radicals from 2-halogenoacetophenone oximes. A preliminary account of some of our results has been published.4

The iminoxy-radicals from the ketoximes were stable enough to be studied in a static system, in which they were generated by oxidation with lead tetra-acetate.⁵ The radicals from the aldoximes which we studied were less stable and, at least for solution in methylene dichloride, they decayed too rapidly to be observed in a static system, so they were generated by a flow technique⁶ with ceric sulphate as oxidant and aqueous acetone as solvent.³ Some of these radicals (those from 9-anthraldehyde and trimethylacetaldehyde) were also examined in a static system with dimethyl sulphoxide as solvent; the spectral characteristics were the same as those with the flow technique and aqueous acetone. The results for studies in methylene dichloride at 25° and, for the aldoximes, in aqueous acetone at room temperature are in Table 1, and the assignments of the spectra are discussed in the sequel. Studies under other conditions are described and discussed later.

Acetophenone Oxime.—Only one radical was detected. It showed interaction with five protons $(a_{\rm H}, 1.4 \text{ oersted})$ and is accordingly 3,5,7 assigned structure (I), the interacting protons being those in the methyl group and at the ortho-positions of the aromatic ring, and there being rapid rotation about the bond joining the benzene ring and the iminoxy-function. It is interesting that this radical should predominate, since the parent oxime almost certainly exists in the isomeric configuration;⁸ it may be relevant that steric effects should be less significant in the radical than in the oxime, since the CNO bond angle is larger in the former.⁹

Spectra from meta- and para-substituted acetophenone oximes were identical with that from the unsubstituted compound, providing further confirmation of the conclusion ⁵ that interactions with protons in these (σ -type) iminoxy-radicals are insensitive to the introduction of substituents such as p-NO₂ which interact with the π system. Weak lines in some of the spectra may have been due to the geometrically isomeric radicals, but analysis was not possible.



1- and 2-Acetylnaphthalene Oximes and Related Aldox*imes.*—The only radical observed when 2-acetylnaphthalene oxime was oxidised showed interaction with five

- ⁵ B. C. Gilbert and R. O. C. Norman, J. Chem. Soc. (B), 1966, 86. 6
- W. T. Dixon and R. O. C. Norman, J. Chem. Soc., 1963,
- 3119. ⁷ M. Bethoux, H. Lemaire, and A. Rassat, Bull. Soc. chim. France, 1964, 1985.
- ⁸ L. G. Donaruma and W. Z. Heldt, Org. Reactions, 1960, 11, 1; E. Lustig, J. Phys. Chem., 1961, 65, 491.
- ⁹ W. M. Fox and M. C. R. Symons, J. Chem. Soc. (A), 1966, 1503.

¹ Part XIV, C. R. E. Jefcoate and R. O. C. Norman, J. Chem. Soc. (B), 1968, 48.

² This paper is regarded as Part V of the series Iminoxy-radicals [Part IV, B. C. Gilbert and R. O. C. Norman, J. Chem. Soc. (B), 1967, 9817.

B. C. Gilbert and R. O. C. Norman, J. Chem. Soc. (B), 1966,

⁴ R. O. C. Norman and B. C. Gilbert, J. Phys. Chem., 1967, 71, 14.

TABLE 1

Coupling constants $(\pm 0.1 \text{ oersted})$ of iminoxy-radicals ^a in methylene dichloride at 25° (except where otherwise stated)

		Other hyperfine splitting			
Parent carbonyl compound	a _N	а	No. of inter- acting nuclei		
Acetophenone ^e 1-Acetylnaphthalene	$31 \cdot 6 \\ 30 \cdot 8$	1·4 1·4 1·0	5 3 1		
2-Acetylnaphthalene	31.0	1.4	5		
1-Naphthaldehyde ⁴	(i) 32·4	$7.05 \\ 2.8$	1 1		
	(ii) 31 ·0	27.5	1		
2-Naphthaldehyde ^d	$32 \cdot 4$	$6 \cdot 4$ $1 \cdot 4$	$\frac{1}{2}$		
9-Anthraldehyde ^d , e	(i) 32·5(ii) 31·0	$7.0 \\ 27.0$	1 1		
Pivalophenone	(i) 31·5 (ii) 30·7	$1.4 \\ 1.05$	2 9		
Trimethylacetaldehyde ^{d, e}	(i) 32·2	$7 \cdot 4$ $0 \cdot 95$	1 9		
	(ii) 30·5	27.0	1		
ω -Trifluoroacetophenone	(i) 32·2	$1.45 \\ 0.5$	2 3 (F)		
	(ii) 31 ·6	8.65	3 (F)		
ω-Trifluoro-2-methylaceto- phenone	(i) 30·4	$0.75 \\ 0.5$	3 3 (F)		
	(ii) 31·4	8.1	3 (F)		
2,4-Dimethylacetophenone	$32 \cdot 8$	1.4	6		
2-Fluoroacetophenone	(i) 32·3	$1 \cdot 4$ $7 \cdot 5$	3 1 (F)		
	(ii) 32·0	1.4	3		
2-Chloroacetophenone	33.5	$rac{1\cdot 4}{1\cdot 5^{f}}$	3 1 (Cl)		
2-Bromoacetophenone	33.2	$1{\cdot}4 \\ 8{\cdot}35/7{\cdot}85$	3 1 (⁸¹ Br/ ⁷⁹ Br)		
2-Iodoacetophenone ^g	30	10	1 (¹²⁷ I)		
2-Nitroacetophenone	32.0	1.45	3		
2-Methoxyacetophenone	$33 \cdot 2$	1.5	3		
2-Chloro-5-nitroaceto- phenone	33.5	1·4 1·7 ⁵	3 1 (Cl)		
2,5-Dichloroacetophenone	$33 \cdot 5$	$1.4 \\ 1.55$	3 1 (Cl)		
2-Bromo-5-nitroaceto- phenone	33.3	1·4 8·85 ^b	3 1 (Br)		

^a Where two radicals were observed, that present in the larger concentration is designated (i). ^b Interaction with protons unless stated otherwise. ^c A similar spectrum was observed when each of the following substituents was present in acetophenone oxime: p-OMe, p-NO₂, p-Cl, m-NO₂, m-Cl, m-F. ^d In acetone-water (2:3, v/v) at room temperature. ^e The same splittings were obtained for solutions in dimethyl sulphoxide. ^f Mean for ³⁵Cl and ³⁷Cl. ^e ± 1 oersted. ^b Mean for ⁷⁹Br and ⁸¹Br.

protons $(a_{\rm H}, 1.4 \text{ oersted})$ and is therefore assigned structure (II; R = Me), with the 1-, 3-, and Me protons interacting. The radical from 1-acetylnaphthalene oxime showed interaction with four protons; of these, the three with a coupling constant of 1.4 oersted are attributed to the methyl group, but the fourth $(a_{\rm H}, 1.0$ oersted) cannot immediately be assigned. The significant splitting from a fourth proton indicates³ that the radical is the geometrical isomer (III; R = Me), but the splitting constant is atypical ^{3,5} of structures of this type. However, the result is satisfactorily interpreted in the light of observations on the radicals from the two naphthaldoximes and 9-anthraldoxime.

2-Naphthaldoxime gave only one detectable radical. By analogy with the data for benzaldoximes,³ the doublet splitting of 6.4 oersted is due to the aldehydic proton, the triplet splitting of 1.4 oersted is due to the 1- and 3-protons, and the radical has the configuration (II; R = H). The centre lines of the three triplets were broader than the wing lines, for a reason which is discussed below.

Of the two radicals derived from 1-naphthaldoxime, that which showed significant interaction with two protons ($a_{\rm H}$, 7.05, 2.8 oersted) has structure ³ (III; R = H) and the other $(a_{\rm H}, 27.5 \text{ oersted})$ is the geometrical isomer; the splittings of 7.05 and 27.5 oersted are attributed to the aldehydic protons. Now, the smaller proton-splitting in the former radical (2.8 oersted) is twice as great as the average value for the 1- and 3protons in the isomeric radical (II; R = H) and for ortho-protons in related radicals in which two planar conformations are equally populated. It follows that, for the radical (III; R = H), essentially all the species adopt the conformation shown (the smaller protonsplitting being due to the 2-proton) rather than the alternative planar conformation (IV; R = H) evidently because, in the latter, there is strong steric repulsion between the iminoxy-oxygen atom and the 8-hydrogen atom (peri).

9-Anthraldoxime gave two radicals; that with the smaller doublet splitting is assigned ³ configuration (V), and that with the larger doublet splitting is its geometrical isomer. In the former radical, there was no detectable interaction with either of the two *peri*-protons.

In view of this last observation, it is reasonable to conclude that the splitting of 1.0 oersted in the radical (III; R = Me) is due to the 2- and not the 8-proton. Now, since the conformation (IV) is sterically compressed for R = H, it would also be compressed for R = Me. However, in the latter case, conformation (III) would also be expected to be sterically compressed as a result of interaction of the methyl group and the peri-hydrogen atom. We therefore attribute the relatively low coupling constant for the 2-proton in (III; R = Me) to the fact that non-planar conformations, in which $a_{\rm H}$ should be less than the expected value of 2.8 oersted for the planar conformation (III; R = H), are more significantly populated than in those iminoxyradicals in which there is less strain in the coplanar conformations.

Pivalophenone and Trimethylacetaldehyde Oximes.— Each oxime gave two radicals on oxidation. That from pivalophenone oxime which showed interaction with two protons $(a_{\rm H}, 1.4 \text{ oersted})$ is assigned structure (VI), and that from trimethylacetaldehyde oxime which had a proton-splitting of 27 oersted is assigned structure (VIII). In the isomeric radicals, (VII) and (IX), respectively, there was significant interaction with the nine protons of the t-butyl group which are removed from the iminoxy-oxygen atom by five bonds. This is a further example of the long-range interactions which are characteristic of certain iminoxy-radicals.⁴



 ω -Trifluoroacetophenone Oxime.—Of the two iminoxyradicals which were detected, one showed interaction with two nuclei of spin $\frac{1}{2}$ whose magnitude, 1.45 oersted, indicates that they are the ortho-protons of the phenyl group in the radical (X). The other three nuclei of spin $\frac{1}{2}$, with which a small interaction ($a_{\rm H}$, 0.5 oersted) was observed (and which, in our preliminary examination,⁴ was not detected), are therefore those of the fluorine substituents. In the isomeric radical (XI) the only observed interaction was with three nuclei of spin $\frac{1}{2}$ (a, 8.65 oersted) which are therefore those of the fluorine atoms.

The interaction with fluorine is far stronger in radical (XI) than in its isomer (X), and this observation is applicable to the assignment of structures to the two radicals observed from ω -trifluoro-2-methylacetophenone oxime. Thus, the radical in which there is interaction with three nuclei of spin $\frac{1}{2}$, $a = 8\cdot 1$ oersted, is assigned structure (XII), the interaction being with the fluorine nuclei, and that in which there are very much smaller interactions with each of two sets of three nuclei of spin $\frac{1}{2}$ is attributed to its isomer (XIII). Of these two sets, that for which the coupling constant is 0.5 oersted is ascribed to the three fluorine nuclei, by comparison with a_F for the radical (X), and the larger coupling constant (0.75 oersted) is evidently due to the methyl protons.

That there should be a detectable interaction with the methyl protons in (XIII) but not in (XII) is in accord with our observations on related systems, that nuclei on an aromatic ring interact more strongly with the unpaired spin in an *ortho*-substituted iminoxy-function when its oxygen atom is directed towards the aromatic ring.²⁻⁵ In this case, there was no detectable interaction from the *ortho*-proton, implying that the planar conformation (XIII) is of lower energy than the alternative planar conformation in which the positions of *o*-Me and *o*-H are reversed with respect to the iminoxy-function; this is presumably a result of steric repulsion, in the latter

conformation, between the 2-methyl and the trifluoromethyl groups.

ortho-Substituted Acetophenone Oximes.-The main problem in the assignment of structures to the radicals detected from the oxidation of ortho-substituted acetophenone oximes is that the methyl splitting provides no information as to whether the iminoxy-function points towards or away from the benzene ring; the coupling constant is 1.4 oersted in each case.* This is in contrast to the results for the benzaldoximes and the ω-trifluoroacetophenone oximes, where the splittings due to the aldehydic proton and the fluorine nuclei, respectively, are markedly different in the syn- and the anti-isomers. However, the oxidation of all the benzaldoximes, naphthaldoximes, acetylnaphthalene oximes, and ω trifluoroacetophenone oximes we have studied, and that of acetophenone oxime itself, invariably gives a preponderance of the isomer in which the iminoxyoxygen is directed towards the aromatic ring; this is true even when the reasonably bulky methyl group is introduced into the 2-position of ω -trifluoroacetophenone oxime (Table 1). We therefore conclude that the major radicals (or, in some cases, the only detectable radical) which are observed during the oxidation of orthosubstituted acetophenone oximes likewise have the configuration in which the aromatic ring is cis to the iminoxy-oxygen. Moreover, of the two radicals from ω-trifluoro-2-methylacetophenone oxime, only that with this cis-configuration shows methyl splitting, so the splitting from the o-methyl group in the only radical detected from 2,4-dimethylacetophenone oxime reinforces our conclusion that the latter radical has the cisconfiguration.

The absence of detectable interaction with the orthoproton in this radical indicates that it prefers the planar conformation (XIV) to the alternative one obtained by rotation about the C(NO)-Ar bond. Interaction with the o-methyl protons is significantly greater in (XIV) than in the fluorine analogue (XIII), suggesting, at least in the latter case, that non-planar conformations in which the o-methyl protons and the iminoxy-oxygen are further removed than in the planar conformation (XIII), are significantly populated. It is perhaps relevant that, in the radical-anion from acetophenone, the aromatic ring and the carbonyl group are not coplanar; this is attributed to the steric effect of the methyl group.¹⁰

The spectrum obtained by oxidising 2-fluoroacetophenone oxime showed the presence of the isomeric iminoxy-radicals and a nitroxide radical; Figure 1 shows the spectrum obtained in dimethyl sulphoxide. Each iminoxy-radical showed interaction with three equivalent nuclei of spin $\frac{1}{2}$ (a, 1.4 oersted), which are evidently the protons of the methyl group, and the major radical showed an additional interaction with a nucleus of spin $\frac{1}{2}$ (a, 7.5 oersted). Application of our arguments above indicates that the radical in lower

^{*} We previously suggested a reason for the (numerically) equal splittings from the two sets of methyl protons in the radical from acetone.⁴

¹⁰ N. Steinberger and G. K. Fraenkel, *J. Chem. Phys.*, 1964 **40**, 723.

concentration, which shows interaction only with the methyl group, has structure (XV) and that the other is the geometrical isomer (XVI; R = F, R' = H). In the latter, the coupling constant of 7.5 oersted is far greater than that associated with an *ortho*-proton in radicals of related type, for which the maximum value [corresponding to conformation (XVII)] is *ca.* 2.8 oersted, and we conclude that the interaction is due to the *o*-fluorine nucleus; splittings from fluorine of this magnitude have been observed in radicals of related structure.³ Further, the fact that interaction with the *ortho*-proton was not detectable in the radical (XVI; R = F, R' = H) implies that, of the two possible planar conformations, (XVI) is preferred to (XVII).



Each of the other ortho-substituted acetophenone oximes which we studied gave only one detectable radical.



FIGURE 1 E.s.r. spectrum from the oxidation of 2-fluoroacetophenone oxime in dimethyl sulphoxide

The chloro-, bromo-, and iodo-substituted radicals each showed interaction with the halogen nucleus, so that, by analogy with the data for the fluoro-substituted radicals, they may be assigned structures (XVI; $\mathbf{R} = \mathbf{Cl}$, Br, or I, $\mathbf{R'} = \mathbf{H}$). Moreover, the magnitude of the halogen splittings,² and the fact that no splitting from the ortho-proton could be detected in the spectra from the chloro- or bromo-substituted radicals (where splittings as low as 0.5 oersted would have been observed), indicate that the radicals adopt the planar conformation (XVI) in preference to the alternative planar conformations are adopted is discussed later. [The lines in the spectrum of the iodine-substituted radical were so broad (see below) that not even the expected splitting from the methyl protons could be detected.] Likewise, the iminoxy-radicals from the three 2,5-disubstituted acetophenones are assigned the structures (XVI; $R = Cl, R' = NO_2$; $R = R' = Cl; R = Br, R' = NO_2$),



FIGURE 2 (a) Hyperfine splitting in the $(m_{\rm N}=+1)$ peak of the e.s.r. spectrum (second derivative) of the iminoxy-radical from 2-bromoacetophenone oxime in acetonitrile at 25° (resonances due to a second radical are marked \times). (b) Reconstruction for ⁸¹Br (a, 8.9 oersted). (c) Reconstruction for ⁷⁹Br (a, 8.25 oersted)

with the preferred planar conformation as shown. Finally, the iminoxy-radicals from 2-nitro- and 2-methoxy-acetophenone showed interaction only with the methyl protons, and we presume that these radicals also have the configuration and preferred conformations (XVI; $R = NO_2$ or OMe, R' = H).

The e.s.r. data for these radicals are in marked contrast with those for the radicals of anti-configuration from ortho-substituted benzaldoximes.³ In these, there is an interaction with the ortho-proton of 2.4-2.7 oersted but no detectable interaction with a paramagnetic orthosubstituent, from which it has been inferred that the radicals preferentially adopt the planar conformation (XVIII), in which the iminoxy-oxygen atom and the ortho-proton are minimally separated. That the corresponding radicals from ortho-substituted acetophenone oximes should prefer the planar conformation in which the ortho-substituent is near the iminoxy-oxygen atom is evidently the result of the fact that, in the alternative planar conformation, there is a powerful repulsive interaction between the ortho-substituent and the methyl group.

The spectrum of the radical from 2-bromoacetophenone oxime showed separate resonances due to the ⁷⁹Br and ⁸¹Br nuclei; the ratio of the splitting constants for the two nuclei (0.94:1) is in good agreement with that calculated from the respective nuclear g-factors ¹¹ (0.93:1). Figure 2 shows the group of lines correspond-

¹¹ ' Table of Nuclear Magnetic Properties,' Varian Associates.

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ing to the high-field nitrogen resonance in the spectrum obtained in acetonitrile, together with a reconstruction; the two resonances in the centre of the group are probably part of a 1:3:3:1 quartet, whose wing lines are obscured (a, 1.3 oersted), due to the geometrical isomer.

The spectrum of the iodo-substituted radical had very broad lines whose widths varied across the spectrum; in particular, the lines corresponding to the $m_{\rm I} = \pm 5/2$ resonances were sharper than the remainder (peak-to-peak line-width, *ca.* 5 oersted). These characteristics are similar to those shown by the iminoxy-radical from 1-iodofluorenone, and we attribute them, as for the fluorenone radical,² to the occurrence of nuclear quadrupole relaxation.

Dependence of Halogen Splittings on Solvent and Temperature.—The halogen splittings in the 2-halogenoacetophenone iminoxy-radicals, unlike those in the 1halogenofluorenone iminoxy-radicals, are strongly dependent both on the nature of the solvent (Tables 2 and 3) and on the temperature (Table 4); however, the nitrogen and proton splittings are not significantly affected.

(a) Solvent dependence. For each radical, the halogen splitting increases with the dielectric constant of the solvent (Table 2). The biggest variation is given by the 2-fluoro-substituted radical; to a first approximation, the fluorine splitting increases linearly with the dielectric constant.

These trends, together with the independence of solvent of the halogen splittings in 1-halogenofluorenone iminoxy-radicals, are most reasonably interpreted as follows. The halogen splitting should be maximal for the planar conformation (XVI; R = Hal) in which the halogen atom is closest to the iminoxy-function.²⁻⁵

TABLE 2

Coupling constants (± 0.05 oersted) for the halogen substituent in the iminoxy-radicals (XVI) at 25°

	R = Dielectric $R' =$	$_{ m H}^{ m F}$	Cl H	Br H	Cl Cl	Cl NO.	Br NO.
Solvent	constant	$a_{\rm F}$	$a_{\rm Cl}$ a	$a_{\rm Br} b$	a_{Cl} a	a_{Cl}	$a_{\mathbf{Br}} {}^{\tilde{b}}$
PhH	. 2·29 ·	6.6	1.5	7.6	1.5	1.6	
CH2Cl2	. 9·08 °	$7 \cdot 5$	1.55	8.35 °	1.55	1.7	8.85
				7.85 d			
MeCN	. 37.5 °	9.25	1.6	8.90		1.8	9.0
				8·25 d			
HCO•NMe,	36.7^{f}	10.0	1.65		1.85	1.95	
Me,SO	$. 45.5^{g}$	10.5	1.75	9.6 °	$2 \cdot 0$	$2 \cdot 05$	9.85
-				8.9 d			

^a Mean for ³⁵Cl and ³⁷Cl. ^b Mean for ⁷⁹Br and ⁸¹Br except where two values are quoted. ^c For ⁸¹Br. ^d For ⁷⁹Br. ^e Values for 20° from 'Technique in Organic Chemistry,' ed. A. Weissberger, 2nd edn., vol. 7, Interscience, New York, 1955. ^f Value for 25° from G. R. Leader and J. F. Gormley, J. Amer. Chem. Soc., 1951, **73**, 5731. ^g Value for 25° from J. J. Lindberg and R. Hakalax, Finska Kemistsamfundets Medd., 1962, **71**, 97.

This conformation will become increasingly stable, relative to those in which the aromatic ring and the iminoxy-function are not coplanar, as the contribution of the canonical structure (XIX; R = Hal) is increased.

¹² R. E. Klinck, D. H. Marr, and J. B. Stothers, *Chem. Comm.*, 1967, 409.

TABLE 3

Coupling constants (± 0.05 oersted) for ¹⁹F in the iminoxyradical from 2-fluoroacetophenone in benzene-dimethyl sulphoxide mixtures at 25°

Mole $\%$ benzene $a_{\rm F}$	$\begin{array}{c} 0 \\ 10 \cdot 5 \end{array}$	$21.0 \\ 9.9$	$28.5 \\ 9.75$	$44.5 \\ 9.35$	61·6 8·9
Mole $\frac{0}{0}$ benzene $a_{\mathbf{F}}$	$70.6 \\ 8.45$	$76.2 \\ 8.2$	80·0 8·0	$83.0 \\ 7.8$	$100 \\ 6 \cdot 6$

TABLE 4

Coupling constants (± 0.05 oersted) for the halogen substituent ^a in the iminoxy-radicals (XVI) as a function of temperature

Т

-	R = R' =	F H				C N	l O ₂	Br H
			$a_{ m F}$			a	cı	$a_{\rm Br}$
emp.»		\mathbf{PhH}	CH ₂ Cl	DMF	Me_2SO	DMF	Me2SO	CH2Cl2
– 60°						2.45		
-50			9.35					
-40						2.35		$9 \cdot 8$
- 30			8.75					
20				11.35		$2 \cdot 2$		$8 \cdot 9$
-10			8 ∙3					
0			7.95	10.7		2.05		8.35
10			7.8				~ ~ ~	
20		6.75	7.65	10.1	10.6	1.95	2.02	8.12
25		6.6	7.5	10.0	10.5	1.95	2.05	$8 \cdot 1$
30		6.55						
40		6.45		9.7	10.1	1.85	1.95	
50		$6 \cdot 3$						
60		$6 \cdot 2$					1.9	
70		6.05						

^{*a*} Separate splittings for ³⁵Cl and ³⁷Cl, and for ⁷⁹Br and ⁸¹Br were not always resolved; mean values are quoted. ^{*b*} $\pm 0.2^{\circ}$. ^{*c*} Dimethylformamide.

Since this structure is dipolar, its stability, and hence its contribution to the hybrid, should increase with the polarity of the solvent, and hence the halogen splitting should increase with the dielectric solvent. The I-halogenofluorenone iminoxy-radicals, on the other hand, are held planar by the fixed geometry of the system, so corresponding changes in the halogen splitting are not to be expected. A similar explanation has been advanced to account for the solvent dependence of the n.m.r. spectra of some *para*-substituted acetophenones and benzaldehydes.¹²



For a solution of a radical in a mixture of solvents S_A and S_B , Gendell *et al.* have suggested ¹³ a model of localised radical-solvent complexes which undergo rapid exchange ($\mathbf{R}\cdot\mathbf{S}_A + \mathbf{S}_B \Longrightarrow \mathbf{S}_A + \mathbf{R}\cdot\mathbf{S}_B$); the treatment has been successfully applied to various radical-anions.^{13,14} We have applied this model to solutions

¹³ J. Gendell, J. H. Freed, and G. K. Fraenkel, *J. Chem. Phys.*, 1962, **37**, 2832.

¹⁴ P. H. Rieger and G. K. Fraenkel, *J. Chem. Phys.*, 1963, **39**, 609.

of the radical (XVI; R = F, R' = H) in mixtures of benzene and dimethyl sulphoxide, using the data in Table 3, and found satisfactory agreement between the observed values for a_F and those derived from the model by introducing an equilibrium constant of 2.3 in favour of the complex between the radical and dimethyl sulphoxide.

One other aspect of the data in Table 2 is notable. The splitting due to chlorine (or bromine) in the radicals (XVI; R = Cl or Br, $R' = NO_2$) is greater, for a given solvent, than in the radicals (XVI; R = Cl or Br, R' = H). This may be the result of the fact that, in the former radicals, conjugation between the halogen substituent and the nitro-group, represented by the contribution of structure (XX; R = Cl or Br) to the hybrid, should result in one of the pairs of electrons on the halogen (namely, that which takes part in the conjugated system) having greater p-character than in the radicals (XVI; R = Cl or Br, R' = H). Consequently, the remaining pairs should have relatively greater s-character, so interaction between the orbital containing the unpaired spin on the iminoxy-function and the halogen orbital which is directed towards this function should lead to a relatively greater spin density at the halogen nucleus in the radicals (XVI; $R' = NO_2$) than in (XVI; R' = H).

(b) Temperature dependence. The data for the effect of temperature on halogen splittings (Table 4) are limited not only by the melting points and volatilities of the solvents used, but also by two properties of iminoxyradicals: the radicals decay more rapidly at higher temperatures, and the signal intensity also decreases reversibly at rather low temperatures, probably as a result of dimerisation.9 Nevertheless, the available data show clearly that the halogen splitting increases as the temperature is lowered, and this is consistent with the view that planar conformations of the type (XVI), in which the halogen splitting is maximal, are relatively more stable than the alternative planar conformations and those in which the iminoxy-function and the aromatic ring are not coplanar, so that, as the temperature is lowered, the planar conformations (XVI) become more heavily populated and the average splitting increases.

According to our interpretation, the splitting constant for fluorine in the radical (XVI; R = F, R' = H) at very low temperatures, when essentially all the radicals are in the planar conformation (XVI), should be twice that at high temperatures when all conformations are equally populated. It is therefore interesting that the highest value for a_F (11.35 oersted at -20° in dimethylformamide) is approaching twice the lowest value (6.05 oersted at 70° in benzene).* The former value is close to that (13.5 oersted) in the radical from 1-fluorofluorenone oxime where the geometry is fixed.³

Restricted Rotation in the Radical (II; R = H).—The centre line of each of the triplet splittings due to the two ortho-protons (C-1 and C-3) in the radical (II; R = H) was significantly broadened with respect to the wing lines. It follows that the rate of interconversion of the two planar conformations of this radical, under the conditions employed, is of the order of the difference in hyperfine interactions between the 1- and 3-protons for a particular planar conformation. From our previous studies,^{3,5} we would expect these interactions to be *ca*. 0 and 2.8 oersted, *i.e.*, 0 and 7.8 Mc./sec., for the 1- and 3-protons, respectively, so interconversion is occurring at *ca*. 8 Mc./sec.

Alternating line-widths have not been observed for related radicals; for example, the triplet splittings due to the ortho-protons in the iminoxy-radicals from benzophenone⁵ and benzaldehyde (anti-configuration)³ have a 1:2:1 pattern with equal line-widths, indicating that the rates of interconversion between the planar conformations are greater than 8 Mc./sec. One possible explanation for the slower rate of interconversion in the radical (II; R = H) than in related radicals is that there is a greater degree of double-bond character in this radical than in, for example, the radical (XXI; R = H). This would follow if there were a greater contribution to the hybrid from dipolar structures such as (XXII) than from those such as (XXIII). If this explanation were correct, then, since the σ -value of p-OMe is very much greater (more negative) than that of the 3,4benzo-substituent,¹⁵ we should expect a relatively greater contribution from structure (XXIV) to the hybrid which describes the radical (XXI; R = OMe), and therefore a slower rate of interconversion of the two planar conformations of this radical. However, the radical (XXI; R = OMe), generated from p-methoxybenzaldoxime, showed a simple 1:2:1 triplet from interaction with the ortho-protons $(a_{\rm H}, 1.4 \text{ oersted})$, in addition to a nitrogen splitting of 32.4 and an aldehydic proton splitting of 6.4 oersted.[†]

We therefore suggest an alternative explanation, namely, that the slower rate for the radical (II; R = H) than for the related radicals we have studied results from the greater moment of inertia of the aromatic ring in the former case. If this is so, we should expect an alternating line-width effect in the radical (II; R = Me). However, it is not possible to distinguish clearly in this case between a set of lines of binomial

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^{*} The justification for comparing data in different solvents is that $a_{\rm F}$ in the 1-fluorofluorenone iminoxy-radical is independent of the solvent as well as the temperature. Thus, because the planar conformation is less stabilised, by the conjugative effect we have discussed above, in benzene than in dimethylformamide, the minimum value for $a_{\rm F}$ will be more rapidly approached as the temperature is raised in the benzene than in the dimethylformamide solution, and the maximum value will be more rapidly approached as the temperature is lowered in the dimethylformamide than in the benzene solution.

[†] We also studied the oxidation of p-dimethylaminobenzaldoxime, since the p-NMe₂ group has a particularly large (negative) σ -value. However, on oxidation with ceric sulphate in aqueous acetone, it gave an intense complex spectrum typical of those obtained by the oxidation of other *para*-substituted dimethylanilines ¹⁶ and attributable ¹⁶ to the radical-cation formed by the (formal) loss of one electron from the aminonitrogen atom.

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intensity distribution (and equal widths) and one showing the alternating effect, partly because the resolution of individual resonances was not complete and partly because the methyl protons have the same coupling constant as the aromatic 1- and 3-protons.



g-Factors.—The average g-factors for iminoxy-radicals derived from acetophenone and some of its derivatives, measured to within ± 0.0001 (except where stated) for solutions in methylene dichloride at room temperature, were as follows: unsubstituted compound, 2.0057; 4-NO₂, 2.0057; 4-Cl, 2.0057; 2-F, 2.0062; 2-Cl, 2.0058; 2-Br, 2.0064; 2-I, 2.0090 ± 0.0003 ; 2,5-di-Cl, 2.0056; 2-Cl-5-NO₂, 2.0056; 2-Br-5-NO₂, 2.0062. These values were the same, within the limits of experimental error, when other solvents and temperatures were employed. As is the case for the nitrogen and the *ortho*-proton splittings, the g-factor is unaffected by para-substituents. However, it is affected by the introduction of an orthohalogeno-substituent, although only in the case of the o-iodo-containing radical is the effect marked. The values for the series 2-F, 2-Cl, 2-Br, and 2-I are closely similar to those for the 1-halogenofluorenone iminoxyradicals, and the relatively small g-shifts may be reconciled with the relatively large halogen splittings in the way we have suggested for the fluorenone series.²

The Spectra of Some Iminoxy-radicals in Solids.—The γ -irradiation of a single crystal of dimethylglyoxime gives a radical 17 which has been shown to be of the iminoxy-type.^{17,18} Similar single-crystal studies of trapped iminoxy-radicals have since been made,¹⁹ and the e.s.r. spectra of randomly oriented trapped iminoxyradicals have also been examined, the radicals being generated both by the freezing of liquid samples and by y-irradiation of powdered solids.⁹ We have applied the last two techniques to some ortho-halogeno-oximes in order to search for anisotropic halogen interactions.

When solutions containing iminoxy-radicals from each of the 2-halogenoacetophenones, benzophenone, and 1-fluoro-, 1-chloro-, and 1-bromo-fluorenone were cooled to -150° (methylene dichloride) or -50° (dimethyl sulphoxide), the resulting glasses did not show e.s.r. absorption, probably ⁹ because of dimerisation of the radicals. However, a spectrum was obtained from 1-iodofluorenone oxime, and this is discussed below.

The γ -irradiation of powder samples of each of the four ortho-halogenoacetophenone oximes gave spectra characteristic of iminoxy-radicals,⁹ but in no case could halogen splittings be detected, possibly because under these conditions the radical maintains the configuration of the parent oxime so that the iminoxy-oxygen atom is directed away from the aromatic ring. The same technique when applied to benzophenone oxime and ω -trifluoroacetophenone oxime yielded iminoxy-radicals in which a proton interaction (a, ca. 4 oersted) was detected in the high-field (parallel) nitrogen features. It is probable that in each case the interaction is with an ortho-proton; the fact that it is weaker than that in the radical from fluorenone oxime 9 (ca. 7 oersted) suggests that the ring is rotated out of the plane of the iminoxygroup (the benzene ring is twisted about 19° out of the plane of the oxime function in a related oxime 20).

Each of the four 1-halogenofluorenone oximes (the radicals from which show particularly large halogen splittings in solution²) likewise gave spectra typical of iminoxy-radicals. That from the 1-chloro-derivative showed nitrogen features but no hyperfine splitting. That from the 1-fluoro-derivative showed anisotropic hyperfine splittings on the high-field (parallel) feature, but no analysis was possible. However, those from the 1-bromo- and 1-iodo-derivatives showed halogen splittings in the wings. In the former, the spacing of the peaks in the extreme nitrogen features was approximately 10 oersted (i.e., similar to the value obtained in solution), suggesting that the radical has the same configuration as that observed in solution, and that the anisotropy is small. The spectrum for the iodosubstituted radical was closely similar to that obtained by freezing a solution of the radical; the iodine splitting, detectable in the high-field (parallel) nitrogen features, was approximately the same as that of the radical in solution, so here also the anisotropy is small. These results are reasonable in that the interaction of the unpaired spin with the halogen probably involves the transmission of only a very small proportion of the spin into a halogen orbital but, since this orbital has significant s-character, there is a substantial isotropic splitting.

EXPERIMENTAL

A Varian V4502 electron spin resonance spectrometer was used. Hyperfine splitting constants were measured with the Varian 'Fieldial' attachment and by comparison with Frémy's salt ($a_N = 13.0$ oersted). g-Factors were determined with a dual cavity by comparison with Frémy's salt (g = 2.0055). The flow system,⁶ the use of ceric ion as oxidant,²¹ and the procedure for oxidations with lead tetraacetate 5 have been described. The temperature, for experiments in the static system, was maintained to within $\pm 2^{\circ}$ using the Varian variable-temperature accessory.

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y-Irradiations were carried out by Dr. W. M. Fox using a Gammacell source.

Materials .- Oximes were prepared from the parent aldehydes or ketones by a standard method,²² and their m. p.s agreed with those reported ²³ except where indicated. In cases where two isomeric oximes have been described, only one was isolated; *p*-anisaldehyde gave the α -oxime,²³ p-dimethylaminobenzaldehyde gave the anti-oxime,23 and 9-anthraldehyde gave the anti-oxime.24 2-Naphthaldoxime had m. p. 154-155.5° (from ethanol) (lit.,²⁵ 156°). 2-Chloro-5-nitroacetophenone, by the nitration of 2-chloroacetophenone,26 gave an oxime, m. p. 166-167° (from aqueous ethanol) (Found: C, 44.6; H, 3.4; Cl, 16.3; N, 12.9. C₈H₇ClN₂O₃ requires C, 44.7; H, 3.3; Cl, 16.5; N, 13.0%). 2-Bromoacetophenone oxime had m. p. $124-125^{\circ}$ (from ethanol) (lit.,²⁷ 127.5-129°). 2-Bromo-5-nitroacetophenone, by the nitration of 2-bromoacetophenone,28 gave an oxime, m. p. 173-174° (from ethanol) (lit.,28 for the syn-isomer, 171°). 2-Iodoacetophenone oxime had m. p. 130·5-131° (from ethanol) (lit.,²⁹ 130-132°). ω-Tri-

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fluoroacetophenone was converted into an oxime, m. p. 86—86.5° [from light petroleum (b. p. $40-60^{\circ}$)] (Found: C, 50.9; H, 3.3; F, 29.6; N, 7.4. C₈H₆F₃NO requires C, 50.8; H, 3.2; F, 30.2; N, 7.4%). ω -Trifluoro-2-methylacetophenone, prepared from o-bromotoluene and trifluoroacetic acid following Bergmann et al.,30 had b. p. 63-65°/17 mm. (lit.,³⁰ 75-76°/19 mm.). No oxime could be prepared from this ketone by the usual method, but an oxime was isolated in small yield as a viscous yellow liquid after treatment with hydroxylamine hydrochloride in pyridine for 1 month (the method of Greer and Pearson ³¹); it could not be fully characterised, but the e.s.r. spectrum obtained on oxidation indicated that the oxime had been formed.

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