Tetrahedron Letters No.35, pp. 3035-3038, 1970. Pergamon Press. Printed in Great Britain.

# ELECTRON SPIN RESONANCE SPECTRA OF SOME IMINOXY RADICALS.[1] II.

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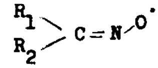
(Received in UK 13 April 1970; accepted for publication 25 June 1970)

The present paper reports new e.s.r. data on iminoxy radicals. They have the general formula  $\begin{matrix}R_1\\R_2\end{matrix}\!>C=N\diagup^{O^{\cdot}}$ with the single electron being in a σ-type orbital. A large (~30 gauss) nitrogen hyperfine splitting (h.f.s.) constant is characteristic of these radicals.

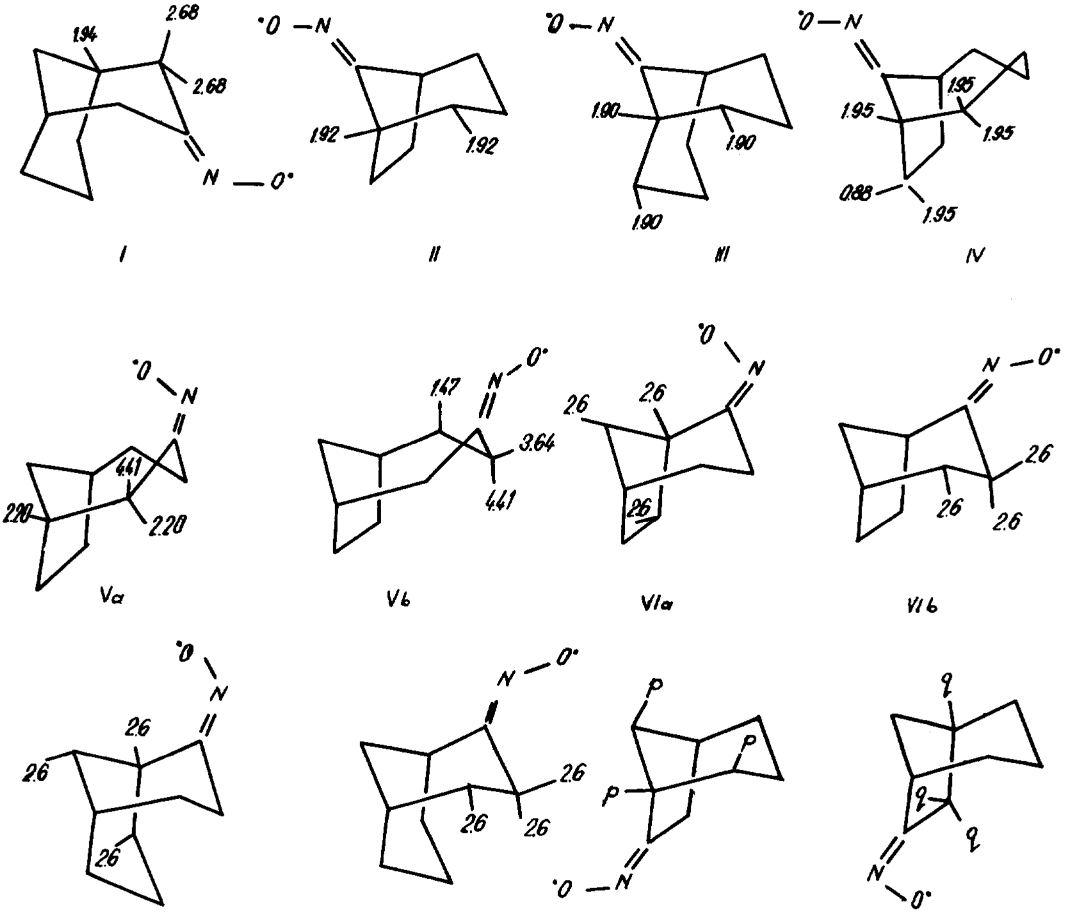
B.C.Gilbert and R.O.C.Norman[2] established some of the empirical rules which control the long-range spin density transmission in these σ-type radicals, studying the dependence of the α and β hydrogen h.f.s. constants on the molecular geometry. Nevertheless a quantitative angle-h.f.s. constant correlation has not been established, data on geometrically well characterised, rigid molecules being still necessary.

We have obtained iminoxy radicals from a series of bicyclic compounds[3] by oxidizing the corresponding oximes (Table 1) with lead tetraacetate. Experimental details were previously[1] reported. All spectra were recorded on a JES-3B spectrometer using X- as well as K-band frequencies, the last to identify overlapping spectra when two isomeric radicals were expected.

The measured h.f.s. constants are recorded in Table 1. A possible assignment of these constants is that indicated on the structural formulae (fig.1). This is based on the general conclusions of Gilbert and Norman[2] that most effective coupling occurs via a planar σ-framework, cis to the iminoxy oxygen. The radical from bicyclo[3.2.1]octan-3-one oxime[2] (fig.2) was chosen as a geometrical model to be compared with the investigated compounds.

The most h.f.s. constants can be accounted for in this framework. Nevertheless, two unexpected facts have to be discussed:

(i) The two α hydrogen atoms in (I) are equivalent, having $a_H$ 2.68 gauss, a result very close to the cyclohexanone oxime radical in which a "chair"-"chair" inversion occurs. Thus we suppose the cyclohexanone ring in compound (I) undergoes "chair"-"boat" isomerisation at a high-enough frequency as to result in an average splitting for the two



I II III IV

Va Vb VIa VIb

VIIa VIIb VIII

(p represents either the 2.4 or the 2.6 gauss h.f.s., and q represents the other one)

**Fig.1** - The numbers indicate the h.f.s. constants of the corresponding hydrogen atoms.

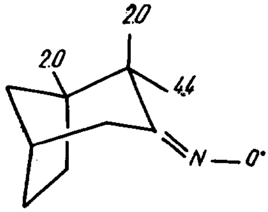


**Fig. 2**

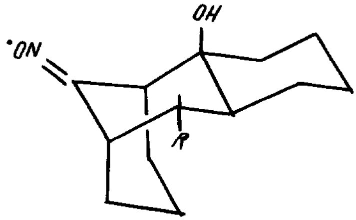


**Fig. 3**

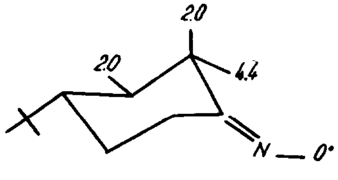


**Fig. 4**

<u>TABLE 1</u>. Hyperfine splitting constants (gauss) measured at room temperature in benzene. The number of equivalent protons is indicated in parentheses.

| Radical | The parent oxime | $a_N$ | $a_H$ | | |
|---|---|---|---|---|---|
| I | bicyclo[3.3.1]nonan-3-one oxime | 30.5 | 2.68(2); | 1.94(1); | 0.60(1) |
| II | bicyclo[3.2.1]octan-8-one oxime | 30.7 | 1.92(2) | | |
| III | bicyclo[3.3.1]nonan-9-one oxime | 30.2 | 1.90(3) | | |
| IV | bicyclo[4.2.1]nonan-9-one oxime | 28.4 | 1.95(4); | 0.88(1) | |
| Va | bicyclo[4.2.1]nonan-3-one oxime | 30.7 | 4.41(1); | 2.20(2); | 0.73(1) |
| b | | 30.7 | 4.41(1); | 3.67(1); | 1.47(1) |
| VI | bicyclo[3.2.1]octan-2-one oxime | 28.6 | 2.6(3) | | |
| VII | bicyclo[3.3.1]nonan-2-one oxime | 30.9 | 2.6(3) | | |
| VIIIa | bicyclo[3.2.1]octan-6-one oxime | 30.1 | 2.4(3) | | |
| b | | 29.8 | 2.6(3) | | |

α hydrogen atoms. X-ray analysis[4] of some 3-substituted derivatives of the bicyclo[3.3.1] nonane system showed some of them to have a tween "chair"-"boat" conformation.

(ii) The splitting of about 4 gauss expected from interaction with the α equatorial hydrogen atom could not be observed in the spectra of (II),(III) and (IV). A splitting of about 2 gauss was found instead. The same is true for a series of compounds of general formula (fig.3) which are the subject of another paper.[5] Geometrical changes cannot be the only cause for the lowering of the $a_H$ value. In the radical(III), for instance, the equatorial α-hydrogen atom lies exactly as in the model compound, i.e. <u>in</u> the plane of the oxime group σ-bonds.

It seems that the 50% lowering of the equatorial α-proton h.f.s. is due to the substitution of a hydrocarbon chain at the α-carbon atom. It is not clear why similar substitution at the β-carbon atom does not affect the value of the equatorial β-proton h.f.s. (the spectra of t-butyl-cyclohexanone oxime (fig.4) and bicyclo[3.2.1]octan-3-one oxime (fig.2) are identical).

An alternative explanation for the disappearance of the 4 gauss splitting in the spectra of (II),(III) and (IV) exists: it is possible to suppose that the assignments of the 4.4 gauss and 2.0 gauss splittings to the equatorial and axial α-protons respectively, in the model compound (fig.2), have to be interchanged. No direct proof for any of these two assignments was found so far. Nevertheless the initial assignments (fig.2) seem more probable, as they are in accordance with the general conclusion regarding the optimal coupling in planar conformations.

For (VI) and (VII) two isomers are expected. In our first report[1] a single radical was observed in each case. These data are now supported by experiments on three analysed (40%, 50% and 78% anti-$C_1$) mixtures of isomeric oximes for (VI) and on the pure anti-$C_1$ isomer for (VII). In all cases a single radical was again observed in measurable concentration in X- as well as in K-band spectra.

If the observed spectra could be assigned to the syn-$C_1$ radicals (fig.1, VIa and VIIa), our previous statement about the lowering of the h.f.s. of the α-proton, when on a tertiary carbon atom, would be confirmed. Alternatively, for the radicals supposed to have the anti-$C_1$ conformation (fig.1, VIb and VIIb) the equivalence of the two α-hydrogen atoms can be explained on the basis of a "boat"-"chair" inversion only.

The spectrum of (V) was interpreted in terms of two radicals with identical $a_N$ and g factors: the low and high field parts are identical and do not change when recorded in the K-band. A tentative assignment is indicated on the structural formulae. We notice the expected 4.4 and 3.7 gauss splittings for hydrogen atoms on secondary α-carbon atoms, when the C-H bond is almost in the plane of the oxime σ-bonds.

The spectra of both the syn- and the anti-isomers of (VIII) have been observed and are in good agreement with the expectations. The analogy in both structure and spectra of the anti-$C_5$ isomer with the corresponding isomer of camphoroxime[2] is noted. The syn-$C_5$ isomer also shows interaction with three equivalent protons. That is what one expects when taking into account the conclusion at (ii), indicating that h.f.s. of protons on tertiary α-carbon atoms are of about 2 gauss and thus comparable with protons on β-carbon atoms.

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