Tetrahedron Letters No. 34, pp. 3183 - 3186, 1971. Pergamon Press. Printed in Great Britain.

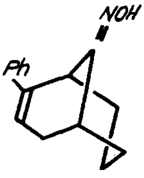
ELECTRON SPIN RESONANCE SPECTRA OF SOME IMINOXY RADICALS. THE STEREOCHEMISTRY OF BICYCLIC SYSTEMS.

H. Căldăraru*, M. Moraru**

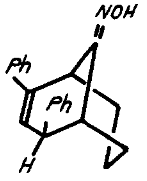
* Institute of Physical Chemistry, Galaţi street 31, Bucharest 13, Romania.
** Department of Organic Chemistry, University, Bucharest, Romania.

(Received UK 13 July 1971; accepted for publication 20 July 1971)

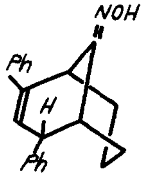
The esr spectra of the iminoxy radicals obtained from molecules with more or less rigid geometry, such as bicyclic compounds, can provide useful information[1,4] about (i) the stereochemistry of the radicals and (ii) the transmission of unpaired spin density. The latter information may be obtained from the correlation between the ring geometry and the hyperfine splitting (hfs) constants. At present the mechanism of this transmission is poorly understood. The present paper reports some new esr data on such radicals obtained from some derivatives of bicyclo [3.3.1] non-2-en-9-one oxime (I, II, III) as a continuation of an earlier study[4].



I



II



III

The radicals were generated in the esr sample tube by adding 1-2 ml of benzene to the solid oxime-lead tetraacetate mixture. The esr spectra were recorded on a JES-3B JEOL spectrometer with 100 KHz field modulation, using X- as well as K-band frequencies. Hfs constants and g-factors were measured in comparison with Frémy's salt (a_N 13.0 G; g 2.0055). The oximes were prepared from parent ketones[5,6], whose absolute stereochemistry at C-4 position is firmly established from nmr data ($J_{3,4}$ = 3.8 Hz, $J_{4,5}$ = 0 Hz and $J_{3,4}$ = 2.8 Hz, $J_{4,5}$ = 6.3 Hz for the ketones of (II) and (III) respectively). The nmr spectra were obtained on a Varian A-60 A spectrometer using 10% solutions in $CDCl_3$.

The X-band spectra obtained from (II) (Fig. 1) and (I) are very similar and come from the overlapping of the spectra of two radicals with almost equal g-factors and different a_N values*. In order to confirm these, K-band spectra were recorded.

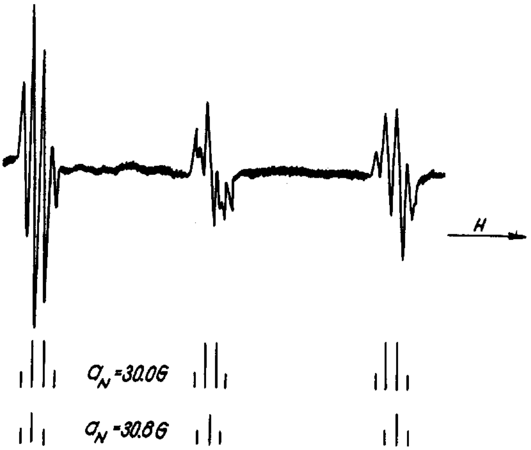


Fig. 1. The esr spectrum and the stick diagram of the two iminoxy radicals obtained from (II).

The measured hfs constants and g-factors of the studied iminoxy radicals together with those of the nitroxides which also appear (the structure of such nitroxides is widely discussed in an other paper[7]) are listed in Table 1.

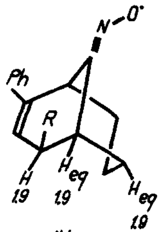
Table 1. Hfs constants (gauss) and g-factors at room temperature in benzene The number of equivalent protons is indicated in parentheses.

Parent oximes	Iminoxy radicals				Nitroxide radicals			
		a_N	a_H	g		a_N	a_{NH}	g
I	(i)	30.1	1.9(3)	2.0064	(a)	13.6		2.0061
	(ii)	30.7	1.9(2)	2.0063	(b)	7.1		2.0068
II	(i)	30.0	1,9(3)	2.0064	(a)	12.6		2.0061
	(ii)	30.8	1.9(2)	2.0063	(b)	7.5		2.0068
					(c)	13.5	8.5	2.0061
III	(i)	30.4	1.9(2)	2.0064	(a)	11,4		2.0061
					(b)	7.5		2.0068

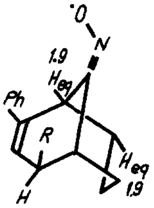
---

* The same spectrum was obtained by an interesting experimental "simulation"; the spectrum of the mixture of iminoxy radicals obtained from bicyclo [3.3.1] nonan-9-one oxime (a_N 30.2 G; $a_H(3)$ 1.9 G)[4] and 2-hydroxy-8-methyl-tricyclo $[7.3.1.0^{2.7}]$ tridecan-13-one oxime (a_N 30.6 G; $a_H(2)$ 1.9 G)[4] was recorded. The particular nitrogen and proton hfs constants as well as the number of interacting protons lead in this case to an overall spectrum which is identical with our spectrum from compounds (I) or (II).

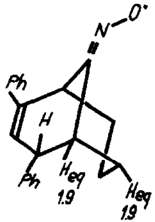
Because of the molecular asymmetry of the parent oximes both iminoxy radical isomers are expected. They were actually observed in the case of (I) and (II). So, of the two radicals obtained from (I), that with the lower nitrogen hfs constant (a_N 30.1 G) and interaction with three protons (a_H 1.9 G) is assigned configuration (IV, R = H) and the other with the greater nitrogen hfs constant (a_N 30.7 G) but interaction with two protons (a_H 1.9 G) is its geometrical isomer (V, R = H). Identical configuration assignments (IV, R = Ph) and (V, R = Ph) respectively can be made for the two iminoxy radical isomers obtained from (II). The iminoxy radical from (III) (a_N 30.4 G) which shows interaction with two protons (a_H 1.9 G) can be represented by one of the isomeric configurations (VI) and (VII).



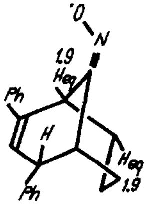
IV



V



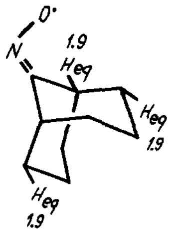
VI



VII

The following observations are worth mentioning :

(i) Although, due to the presence of the double bond, one of the six-membered rings in the iminoxy radicals is distorted as compared to the corresponding saturated compounds, the proton hf splittings are the same as in the radical (VIII). This is explained by the fact that the geometry of the O-N-C-C-C-H fragment is very slightly modified by the double bond. Thus, the conclusions about the optimal planar geometry[1] for long-range coupling are proved once more.



VIII

(ii) The π electron system introduced in the iminoxy radicals studied does not alter the unpaired spin density distribution as compared with a pure σ system such as (VIII). The phenyl group does not even influence the hf splitting of the proton bonded to the same C-atom as ilustrated by the identity of the hfs constants in (IV, R = H) and

(IV, R = Ph). Our results strengthen the more general observation that the π electrons do not play an important part in the σ-spin density transmission.

(iii) The earlier observation[3,4] that the hfs constant for the α-(bridgehead) proton (on a tertiary C-atom) which is coplanar with $\gt C{=}N{-}O$ fragment is only about half (1.9 G) of that for a similar α-proton on a secondary C-atom (4.6 G) holds for the above bicyclic iminoxy radicals too.

Our results suggest the possibility of using esr spectroscopy for the determination of α- and β-substituent stereochemistry in rigid oximes and ketones (it is supposed that the geometry of the iminoxy radical is the same as that of the parent oxime).

REFERENCES

1. B.C. Gilbert and R.O.C. Norman, J.Chem.Soc. (B), 86 (1966).
2. A. Caragheorgheopol, M. Hartmann, R. Kühmstedt and V.E. Sahini, Tetrahedron Letters, 42, 4161 (1967).
3. A. Caragheorgheopol, V. Gräfe, M. Hartmann, V.E. Sahini and K.Wermann, Tetrahedron Letters, 35, 3035 (1970).
4. H. Căldăraru, N. Bărbulescu, L. Ivan and V.E. Sahini, Tetrahedron Letters, 35, 3039 (1970).
5. A.C. Cope and E.C. Herman, J.Am.Chem.Soc., 72, 3405 (1950).
6. H.M. Hellman and R.A. Jerussi, J.Org.Chem., 32, 2148 (1967).
7. A. Caragheorgheopol, H. Căldăraru, T. Constantinescu and V.E. Sahini, J.Am.Chem.Soc., in press.