

Extended Hückel Calculations on Some 2-Iminoxy- 1,3-dicarbonyl Radicals

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Extended Hückel calculations have been carried out on the iminoxy radicals formed by oxidation of 5-isonitrosobarbituric acid (violuric acid) (I), indane-1,3-dione-2-oxime (II), pentane-2,4-dione-3-oxime (III), and methyl 3-oxo-butanoate-2-oxime (IV). The results show a qualitative agreement with the ESR spectra of the radicals, and were found to give valuable information for distinguishing between several possible conformations. The calculations predict an unsymmetrical spin density in agreement with experiments, the atoms situated *cis* (*syn*) to the iminoxy group having the larger spin densities.

Preliminary extended Hückel (EH)¹ calculations on the violuric acid radical, *i.e.* the iminoxy radical derived from 5-isonitrosobarbituric acid² (violuric acid) showed that the EH method was able to account qualitatively for the ESR spectrum of this radical.³ In this paper we wish to report the results of further EH calculations carried out on radicals of the same type,² *i.e.* the radicals derived by oxidation of violuric acid (I), indane-1,3-dione-2-oxime (II), pentane-2,4-dione-2-oxime (III), and methyl 3-oxo-butanoate-2-oxime (IV).

METHOD OF CALCULATIONS

The EH method¹ has been much used for theoretical studies of organic molecules. Allen and Russell⁴ have made an extensive comparison of the results of EH calculations with those of *ab initio* MO—SCF calculations and conclude that while the EH method is very good for the prediction of properties such as the order of energy levels and molecular shape, it gives less

reliable results in the case of MO coefficients and properties derived from these. This unhappy fact makes the EH method less suited for the prediction of spin densities, since these are calculated directly from the MO coefficients. However, the EH method has the advantage of being simple and straight forward, and of giving easily interpreted results. As will be seen, the EH method gives fair agreement with experiments concerning some important features of the radicals here investigated. Previous investigators⁵⁻⁸ of radicals have used the EH method with some success, which suggests that the use of the EH method is justified for this type of problem.

In the EH calculations we have used the Wolfsberg-Helmholtz⁹ approximation for the Hamiltonian off-diagonal elements with $K=1.75$.¹ The diagonal elements were given the conventional values (Table 1),^{1,10} and the ordinary Slater orbitals were used for atomic orbitals.¹ The spin densities were calculated using a Mulliken population analysis¹¹ of the highest occupied orbital. Some investigators have used the MO coefficients directly,⁵ but the difference in result is very small.

Table 1. Valence state ionization potentials (eV).

	$H_{ii}(1s)$	$H_{ii}(2s)$	$H_{ii}(2p)$
H	-13.6		
C		-21.4	-11.4
N		-26.0	-13.4
O		-35.0	-17.5

The relationship between calculated $2s$ and $2p$ spin densities on the nitrogen atom of the iminoxy group and the ^{14}N splitting constant has been investigated for some iminoxy radicals by Cramer and Drago,⁸ and by Berthier *et al.*¹² When applied to the radicals of the present series, the equations derived by these authors^{8,12} gave results which in general were not in agreement with the experimental splittings. Thus, the regression coefficients evaluated by Cramer and Drago⁸ led to ^{14}N splittings which were between 10 and 30 % too low, while the theoretically derived coefficients of Berthier *et al.*¹² gave rise to splittings 10 to 30 % above the experimental values. However, the most serious objection was the large spread in calculated values in either case, as contrasted with the experimental ^{14}N splittings which were very close to 30 gauss (28-31) for all radicals concerned. The correlation between calculated spin densities and experimental splitting constants was also rather low in the case of the hydrogen atoms. In view of this fact we shall refrain from tabulating evaluated splitting constants, and have preferred to consider spin densities only. Since the population analysis gives separate spin densities for each AO (hydrogen $1s$, carbon, nitrogen and oxygen $2s$, $2p_x$, $2p_y$, and $2p_z$) some kind of weighting between $2s$ and $2p$ densities must be made regarding

their influence on the ^{14}N splittings, even in the absence of evaluated theoretical splitting constants. In Table 2 separate spin densities for $2s$ and $2p$ are tabulated, while Table 3 shows the values of a weighted sum of $2s$ and $2p$ with the value 10 used for the weighting factor for the $2s$ density ($S=10 Q_{2s}+Q_{2p}$). The factor 10 was chosen on the basis of the theoretical considerations made by Berthier *et al.*¹² for ^{14}N splittings, and was used rather arbitrarily in the case of ^{13}C splittings as well.

$Q_{2p}=Q_{2p_x}+Q_{2p_y}$, since Q_{2p_z} becomes zero in all calculations, which is consistent with the assumption that the investigated radicals are sigma-radicals.²

The spin densities of the methyl hydrogens in radicals III and IV were calculated in the following way: The computed spin density of the hydrogen atom lying in the molecular plane was divided by three, and each hydrogen atom of the methyl group was then assumed to have this effective spin density.

GEOMETRIES OF THE RADICALS

In all calculations the same geometry was assumed for the CNO group (Fig. 1). The angle α was given the value 135° since preliminary calculations gave energy minima for $\alpha=135^\circ$ in both radical I and radical II. The following bond lengths were taken for the CNO group: $a=1.29 \text{ \AA}$ and $b=1.36 \text{ \AA}$, which are mean values of those found for conjugated oximes.¹³⁻¹⁵

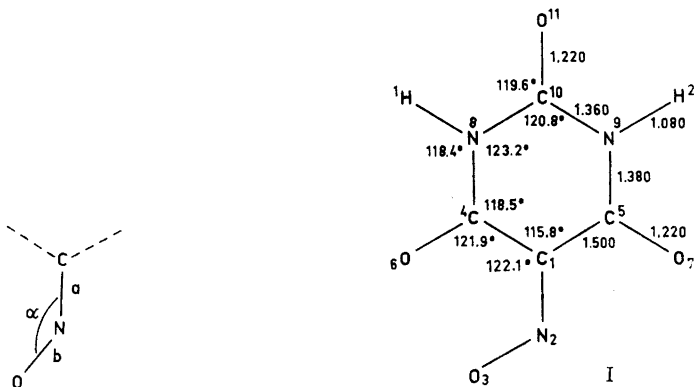
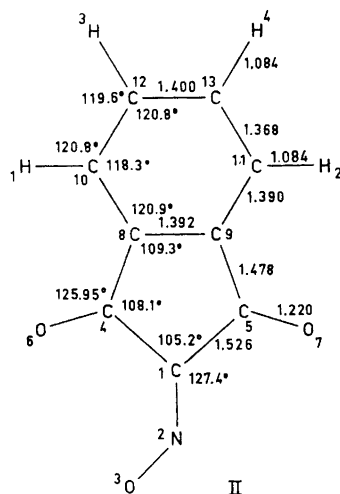


Fig. 1. Geometry of the iminoxy group. Fig. 2. Geometry and numbering of radical I.

For the geometry of violuric acid (Fig. 2) the model was barbituric acid,^{16,17} and triketoindane¹⁸ provided pertinent values for the geometry of radical II (Fig. 3). The geometries of radicals III and IV (Figs. 4 and 5) have been generated using standard values¹⁹ for bond lengths and angles together with values from pentane-2,4-dioldiacetate,²⁰ methyl bromocinnamate,²¹ and ethyl stearate.²² Planar conformations have been assumed with only the hydrogen

Fig. 3. Geometry and numbering of radical II.



atoms of the methyl groups lying outside the molecular planes. Conformations with exchanged positions of the carbonyl and methyl groups were not included in the case of radical IV since the analogous conformations of radical III, *i.e.* III b, c, and d, were found to be energetically unfavourable.

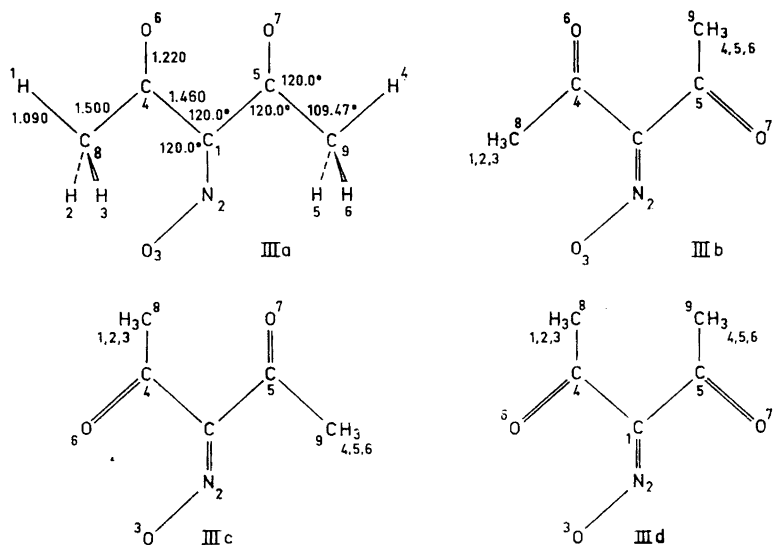


Fig. 4. Geometry and numbering of radical III.

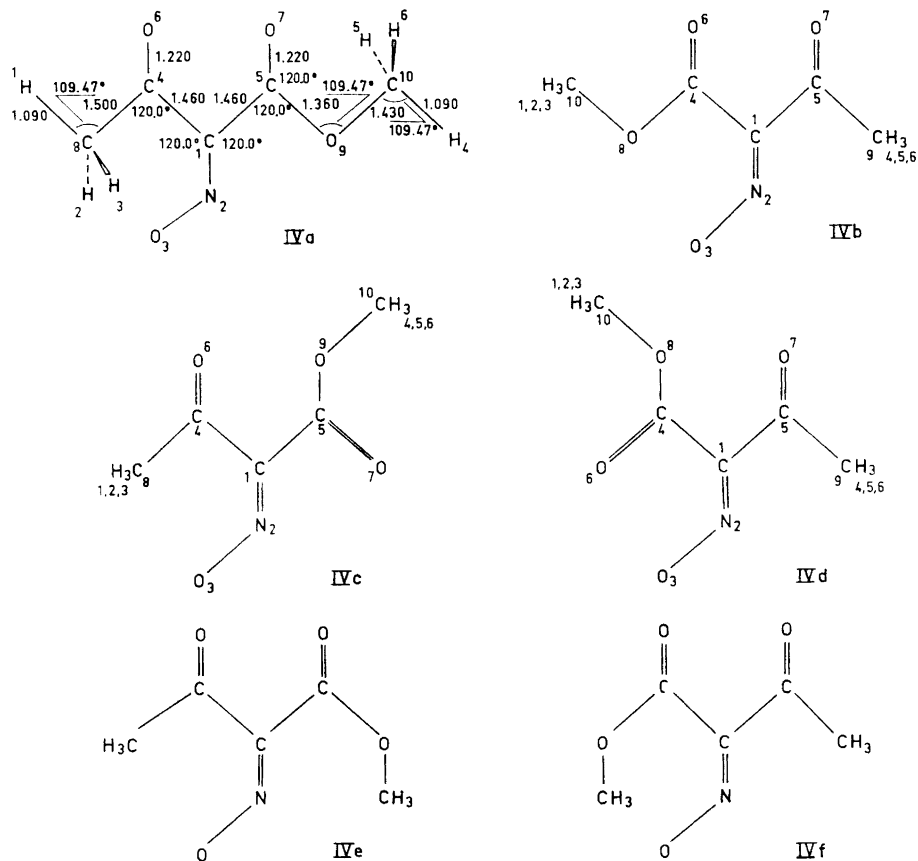


Fig. 5. Geometry and numbering of radical IV.

RESULTS

The calculated spin densities of radical conformations I, II, III a–c, and IV a–d are collected in Table 2, together with the electronic energies. The numbering of the atoms of the radicals is shown in Figs. 2–5. The conformations III d, IV d, e, and f had a much higher electronic energy than the other forms (more than 2 eV), and were therefore excluded. The experimental values quoted below are taken from Ref. 2.

Radical I. The ESR spectrum shows a ¹⁴N triplet splitting of 31.0 gauss together with a secondary ¹⁴N triplet splitting of 2.48 gauss and a secondary hydrogen doublet splitting of 1.79 gauss. As can be seen from Table 2 the large splitting arises from the nitrogen atom of the iminoxy group, and the smaller one from one of the nitrogen atoms of the ring, evidently the one (atom 8) situated *cis* (*syn*) to the oxygen atom of the iminoxy group. This nitrogen atom (8) has more than seven times as large a spin density as the one (atom 9)

Table 2. Computed spin densities and electronic energies for radicals I-IV.

Atom Radical	1		2		3		4		5		6		7		8		9	
	2s	2p	2s	2p	2s	2p	2s	2p	2s	2p	2s	2p	2s	2p	2s	2p	2s	2p
I	.0009	.1176	.0125	.5712	.0006	.0609	.0120	.1114	.0043	.0281	.0003	.0223	.0002	.0074	.0023	.0335	.0004	.0037
II	.0001	.1352	.0076	.2915	.0006	.0299	.0011	.1727	.0001	.0656	.0001	.0305	.0000	.0119	.0008	.0798	.0001	.0286
III a	.0006	.1589	.0098	.3562	.0006	.0409	.0054	.1619	.0013	.0827	.0002	.0294	.0000	.0122	.0029	.0657	.0010	.0548
b	.0004	.1536	.0122	.4171	.0006	.0491	.0051	.1568	.0040	.0395	.0002	.0317	.0002	.0127	.0028	.0642	.0007	.0138
c	.0002	.1433	.0083	.4296	.0006	.0431	.0049	.1584	.0008	.0524	.0002	.0277	.0000	.0092	.0027	.0648	.0006	.0392
IV a	.0000	.1384	.0109	.4812	.0005	.0538	.0052	.1578	.0076	.0261	.0002	.0319	.0000	.0036	.0028	.0613	.0005	.0064
b	.0035	.1137	.0132	.5410	.0007	.0589	.0206	.0790	.0006	.0677	.0006	.0214	.0000	.0111	.0010	.0111	.0007	.0503
c	.0000	.1426	.0105	.4676	.0005	.0520	.0054	.1631	.0075	.0286	.0002	.0321	.0003	.0090	.0029	.0635	.0002	.0017
d	.0039	.1182	.0138	.5154	.0007	.0578	.0210	.0803	.0008	.0786	.0005	.0201	.0000	.0126	.0011	.0122	.0008	.0568
Atom Radical	H ₁		H ₂		H ₃		H ₃		H ₄		H ₅		H ₅		H ₆		E _{el} (eV)	
I	0.0086		0.0016		0.0104		0.0071		0.0013		0.0013		0.0013		0.0013		-991.849	
II	0.0020		0.0000		0.0039		0.0013		0.0008		0.0008		0.0008		0.0008		-991.667	
III a	0.0039		0.0039		0.0040		0.0012		0.0012		0.0012		0.0012		0.0012		-991.419	
b	0.0040		0.0040		0.0039		0.0001		0.0001		0.0001		0.0001		0.0001		-1137.410	
c	0.0039		0.0039		0.0040		0.0011		0.0011		0.0011		0.0011		0.0011		-1137.441	
IV a	0.0039		0.0039		0.0040		0.0000		0.0000		0.0000		0.0000		0.0000		-1137.413	
b	0.0001		0.0001		0.0001		0.0013		0.0013		0.0013		0.0013		0.0013		-1137.423	
c	0.0040		0.0040		0.0001		0.0013		0.0013		0.0013		0.0013		0.0013		-1137.423	
d	0.0001		0.0001		0.0001		0.0013		0.0013		0.0013		0.0013		0.0013		-1137.423	

Table 3. Computed values of $S=10 \rho_{2s} + \rho_{2p}$.

Radical ^{Atom}	1	2	4	5	8	9
I	.1266	.6962	.2314	.0711	.0565	.0077
II	.1362	.3675	.1837	.0666	.0878	.0296
III a	.1649	.4542	.2159	.0957	.0947	.0648
IV b	.1487	.6730	.2850	.0737		.0573
IV d	.1572	.6534	.2903	.0866		.0648

situated *trans* (*anti*) to the iminoxy group. Assuming that the coupling is proportional to the weighted sum, S , of the spin densities, tabulated in Table 3, we find the theoretical quotient between the nitrogen splittings originating from atoms 2 and 8, to be 12.3, in good agreement with the experimental value of 12.5 (31.0/2.48). The hydrogen splitting arises obviously from hydrogen atom No. 1, *i.e.* the one situated *cis* (*syn*) to the iminoxy group.

Radical II. The ESR spectrum shows only a large ^{14}N triplet splitting of 30.0 gauss and a secondary hydrogen doublet splitting of 0.40 gauss. Obviously, the nitrogen splitting comes from the nitrogen atom (2) of the iminoxy group, while the hydrogen splitting is effected probably by hydrogen atom No. 3, situated *cis* (*syn*) to the iminoxy group. However, the spin density on hydrogen atom No. 3 is very large, *viz.* 0.0104, predicting a larger splitting than that present in radical I, in which the corresponding density was only 0.0086, obviously in disagreement with the experimental results. In fact the hydrogen splitting of radical I is 4.5 times larger than that of radical II. Also the spin density on the nitrogen atom of the iminoxy group is unrealistic. The large experimental splitting of 30.0 gauss indicates that the spin density would be of the same magnitude as that on the corresponding atom of radical I, *i.e.* about twice the calculated value.

Radical III. The conformation III a (Fig. 4) has by far the lowest electronic energy, and is the only one to be considered. Besides the ^{14}N triplet splitting of the iminoxy group of 28.0 gauss, the spectrum shows two quartets (1:3:3:1) with splitting constants of 0.39 and 0.12 gauss, respectively. Spectra recorded under high amplification reveal the presence of at least three sets of ^{13}C doublet splittings: 10.0, 8.12, and 4.90 gauss, respectively. The two quartets originate from the hydrogen atoms of two non-equivalent methyl groups, the one situated *cis* (*syn*) (hydrogen atoms Nos. 1, 2, 3) to the iminoxy group giving rise to the quartet with the larger splitting constant. The quotient between the calculated spin densities of the hydrogen atoms concerned is equal to 3.0, in good agreement with the quotient between the experimental splittings, which is equal to 3.3 (0.39/0.12).

The origin of the ^{13}C splittings is more difficult to assign since the $2s$ density decreases in the order (Fig. 4) 8, 5, and 7, while ordering according to $2p$

spin densities gives the sequence 4, 1, 5, 8, and 9. Finally, ordering according to S -values evaluated with the weighting factor equal to 10 (Table 3), also for the carbon splittings, gives the sequence 4, 1, and 8 (or 5) with the relative values of spin density 1.0:0.74:0.44 (experimental:1.0:0.81:0.49).

Radical IV. The ESR spectrum shows the presence of two different radical forms, of which one is quantitatively predominant over the other. The dominant form exhibits a ^{14}N triplet splitting of 29.8 gauss together with narrow incompletely resolved secondary splittings. These findings agree well with the conformations IV b and d (Fig. 5), which have lower electronic energy than the conformations IV a and c, and everywhere a low spin density on the hydrogen atoms. The dominant radical form exhibits ^{13}C doublet splittings of 9.60, 7.74, and 4.53 gauss, again difficult to assign. The S order is 4, 1, and 5, however. When the S -values of these atoms are compared with those of radical III, we obtain the quotients 1.32:0.69:0.34, while the experimental splittings give the quotients 0.96:0.77:0.46.

The less predominant radical form shows a ^{14}N triplet splitting from the iminoxy group of 31.0 gauss together with a secondary quartet (1:3:3:1) with a splitting constant of 0.50 gauss. This spectrum agrees well with the calculated spin densities of conformers IV a and c, the secondary quartet originating from the hydrogen atoms of the methyl group situated in the position *cis* (*syn*) to the iminoxy group. These results are consistent with our experimental findings that the quartet splittings arise from an interaction with the methyl protons of the carboxylic acid part of the radical molecule.²

CONCLUSIONS

The EH method has proved to be a valuable tool for qualitative analysis of the ESR spectra of the iminoxy radicals of this series, especially for distinguishing between several possible conformers. The EH method predicts an unsymmetrical spin distribution in agreement with experiment,² the atoms situated *cis* (*syn*) to the iminoxy group having the larger spin densities. The question whether this state of affairs is due to a direct polarization by the oxygen atom of the iminoxy group, or is an effect transmitted through the sigma-bonds, is in our opinion rather futile. It can be seen (Table 2), however, that the hydrogen atoms of the different conformers III a, b, and c have the same spin densities, which shows that the distance to the oxygen atom of the iminoxy group is of minor importance.

On the other hand, the EH calculations led to spin densities which could not be satisfactorily related to the experimental splittings. This failure is to be expected partly on basis of the comparative studies made by Allen and Russel⁴ but is nevertheless in contrast to the results of Cramer and Drago⁸ who obtained a rather good correlation for several iminoxy radicals derived from aldoximes. The reason for this discrepancy is not obvious, but may be connected with a different choice of molecular parameters.

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