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Further investigations on the electronic structure of free radicals *

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The Electron Spin Resonance (E.S.R.) spectra of a group of hydrazyl free radicals have been studied in X-band and in very diluted solutions of CCl_4 . Accounts of the results have been published [1] or are being published [2]. These radicals, which are obtained from the 1-1-diphenyl-2-benzoyl-hydrazyl (fig. 1) by substitution of one or more hydrogen atoms of the benzoylic ring with nitric groups, are stable at -20°C for considerable lengths of time, and they have been investigated at that temperature.

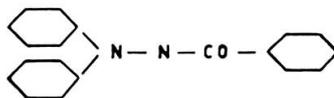


Fig. 1

The E.S.R. spectrum of the radical of figure 1 consists of 5 equally spaced lines, their separation being about 8 gauss (fig. 2a). The five lines are due to the I.S interaction with the two nuclei of hydrazyl nitrogen which are in magnetically equivalent positions. Accordingly, the spectrum may be described by the following spin Hamiltonian

$$\mathcal{H} = g \beta H \cdot S + a_1 I_{N_1} \cdot S + a_2 I_{N_2} \cdot S$$

with $a_1 = a_2$.

The hyperfine structure, due to the interaction of the paramagnetic electron with the hydrogen nuclei is not evidenced.

The spectrum of the radical obtained by that of figure 1 by substituting an hydrogen atom at ortho position to the carbonyl group, with a nitric group, is significantly different from the former and it is shown in figure 2b. It may be described taking into account one extra term in the spin Hamil-

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tonian, corresponding to a not so strong interaction with the nitrogen nucleus of the nitric group. The spin Hamiltonian thus becomes

$$\mathcal{H} = g \beta H \cdot S + a_1 I_{N_1} \cdot S + a_2 I_{N_2} \cdot S + a_3 I_{N_3} \cdot S$$

where I_{N_1} and I_{N_2} refer to the nuclear spins of the hydrazyl nitrogens and I_{N_3} to that of the nitric nitrogen, and $a_1 = a_2 \gg a_3$.

A spectrum similar to that of figure 2b is again found in the radical containing two nitric groups, respectively at ortho and para positions to the carbonyl group, while the radical containing only one nitric group in para position exhibits a spectrum similar to that of figure 2a.

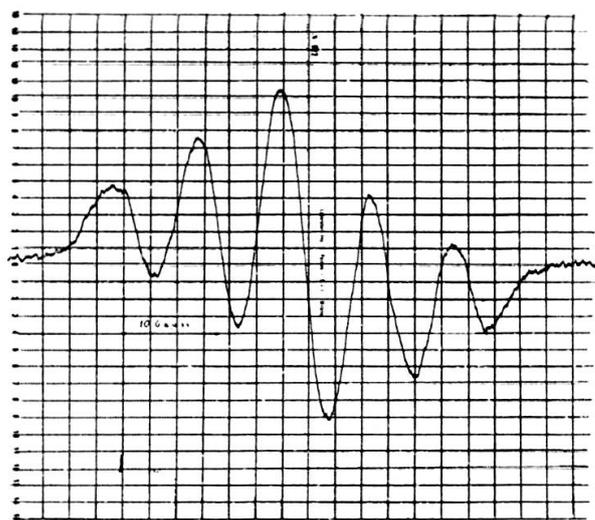


Fig. 2 a)

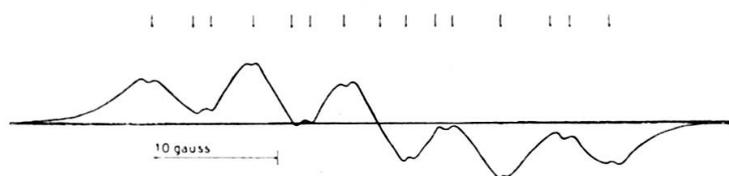


Fig. 2 b)

The following unexpected points in our results are relevant:

- a) The I.S interaction with the nitrogen nucleus at ortho position to the carbonyl group has been evidenced and it has been shown to be dominant, after that with the hydrazyl nitrogen nuclei.
- b) If two nitric groups are present in the benzoic ring (respectively at ortho and para positions) the I.S interaction occurs in practice with

only one of them i.e. with that at ortho position. If only one nitric group is present at para position no I.S interaction is observed with its nitrogen nucleus.

This behaviour is exhibited not only by the hydrazyl radicals. While our work was in progress, Ward [3] has studied the E.S.R. spectra of the potassium salt of m-dinitrobenzene negative ion in diluted solutions of 1-2-dimethoxy-ethane (DME). Consistently with our results he has observed an I.S interaction only with one of the nitrogen nuclei belonging to the two nitric groups which are present in the ion. This interaction is dominant compared with the I.S interaction due to the hydrogen nuclei.

On the basis of these experimental data, we have extended the investigation to the DPPH radical. The latter has a nuclear structure very similar to the radicals which we had investigated and there are two nitric groups at ortho positions. One should then expect a sizable I.S interaction concerned with the two mentioned nitrogen nuclei. This interaction is not evident from the E.S.R. spectrum of a diluted solution of DPPH: it should be possibly evidenced by a comparison of that spectrum with the similar one obtained using a DPPH in which the nitric nitrogen has been substituted by N^{15} . In fact, in that case, the substructure lines due to the nitric nitrogen nuclei should be 15 instead of 25 and they should either become individually detectable, or give an appreciably smaller contribution to the width of the 5 principal lines. We have performed that substitution (90% of N^{15}) but in spite of the above expectation, we have found no detectable difference in the two spectra. It has to be noted that these are only preliminary results taken (in very diluted solutions of CCl_4) at room temperature. Further work is being made along this line.

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