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E.S.R. EVIDENCE FOR A π GROUND-STATE OF AMIDO RADICALS

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Because of the growing interest in organic synthesis via amido radicals (1), the ground state structure of these radicals has been the subject of much speculation. They can exist in either a σ or a π ground state. This is shown below (fig.1) making the reasonable assumption that the amido moiety in the amido radical is planar as it is in amide molecules.

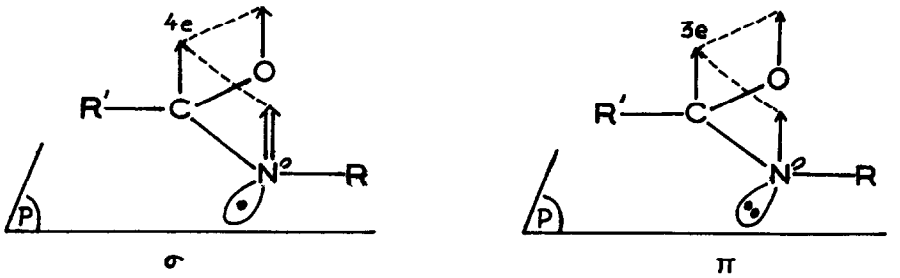


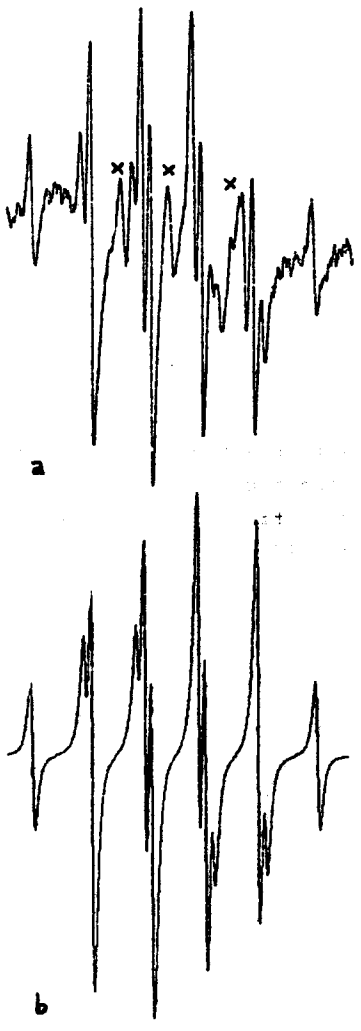
Figure 1

Although many suggestions based on chemical (2,3,4) spectroscopic (5) or theoretical (6) evidence have been published no unambigous proof exists for a σ or a π structure.

In our opinion only a direct E.S.R. study of an amido radical could give a definitive answer to this problem.

To realize this experiment we prepared 1,4-diacyl 1,4-dimethyl tetrazene-2 by the method of Ronco et al (7). A toluene solution of this tetrazene (2 mg in 200 µl of solvent) was then irradiated with a Philips SP 500 W lamp at -90°C in the cavity of an E.S.R. spectrometer (varian type E_3)

The features of the spectrum obtained (fig. 2) (a_N = 7 gauss, $a_H^{N-CH_3}$ = 8 gauss) are characteristic of a π acylamino radical. For a σ radical a higher a_N value would have been expected (8) since the 2s character of the odd electron is important.



For example in the iminoxy radical where the odd electron is in a σ orbital $a_N \cong 30$ gauss (9) although the σ orbital is delocalized on the nitrogen and the oxygen atoms.
A preliminary I.N.D.O. calculation with the geometry of trans acetamide (10) except d_{C-N}^{O} = 1,30 Å) gave us a π description with a_N = 10, 4 gauss. We believe therefore that the π structure of amido radicals is strongly indicated by these results and we are now trying to explain some "anomalies" in their behaviour by chemical and E.S.R. experiments.

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Figure 2: E.S.R. spectra of acylamino radical
a : experimental (toluene -90°C)
b : simulated (a_N = 7 gauss, $a_N^{N-CH_3}$ = 8 gauss)
x : unknown radical

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