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NON-EQUIVALENCE OF ARYL GROUPS IN 1,1-DIARYL-2-BENZENESULPHONYL-HYDRAZYLS

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Stable hydrazyls ($R_2N-\dot{N}$-Acceptor) constitute a particular case of "push-pull" aminyls (Donor-$\dot{N}$-Acceptor),[1,2] possessing the strongest donor group, R_2N. On the other hand, stable hydrazyls with R being aromatic [3] or aliphatic groups [4] are related to aminyloxides (nitroxides) $R_2N-\dot{O}$ by the analogy between —$\dot{O}$ and —$\dot{N}$-Acceptor groups.

High-resolution ESR spectra of 1,1-diphenyl-2-picrylhydrazyl and related triarylhydrazyls [5] are so complicated that a detailed assignment of hyperfine proton coupling constants is extremely difficult.[6] However, other acceptor groups afford hydrazyls with simpler ESR spectra : CN with one nitrogen coupling constant,[7] SO_2Ar with no coupling ;[8,9] analysis of these ESR spectra indicated that the two aryl groups seem to be magnetically non-equivalent.

We now report the preparation and ESR spectrum of 1,1-bis(3',5'-di-t-butylphenyl)-2-benzenesulphonyl-hydrazyl (I), providing compelling evidence for this non-equivalence.

3,5-Di-t-butylaniline [10] was converted into 3,3',5,5'-tetra-t-butyl-diphenylamine, m. p. 117°, by heating in a Carius tube at 250° equimolar amounts of amine and hydrochloride. Nitrosation with aqueous sodium nitrite in ethanolic hydrochloric acid yielded the nitrosamine, m. p. 108°, which was then reduced with zinc and ethanolic acetic acid to the corresponding hydrazine (two crystalline forms, m. p. 126° and 145°). Refluxation with benzenesulphonyl chloride in benzene yielded 1,1-bis(3',5'-di-t-butylphenyl)-2-benzenesulphonyl-hydrazine, m. p. 204°,* crystallizing from the solution. On oxidation with lead tetraacetate in

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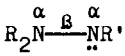
*New compounds with given m. p. were checked by elemental analysis and mass spec.

benzene, hydrazyl I was obtained (visible absorption maximum at 502 nm).

Its ESR spectrum in benzene presents 42 lines (figure). A pattern with intensities in the ratio 1:2:3:2:1, due to splitting by two nitrogen atoms with approximately equal hyperfine coupling constants, is clearly apparent. Each of these components is a multiplet due to proton splittings, consisting in ten lines (partly overlapped in the middle of the spectrum). Taking their intensities into consideration, according to the computer printout presenting all possible ESR spectra with equidistant lines (the complete list for 2 - 15 lines was published [11]), this 10-line multiplet can only be derived from six protons, three of which have a hyperfine coupling constant approximately twice as large as that of the other three. On this basis it was possible to simulate the ESR spectrum, obtaining good agreement between the experimental and simulated spectra with three hyperfine coupling constants : 2N, 9.25 Gauss ; 3H, 2.23 Gauss ; 3H, 1.40 Gauss (figure).

This result leaves no alternative but to assign these hyperfine coupling constants as indicated on the formula accompanying the figure, namely with one aryl group having a larger spin density than the other one.[12]

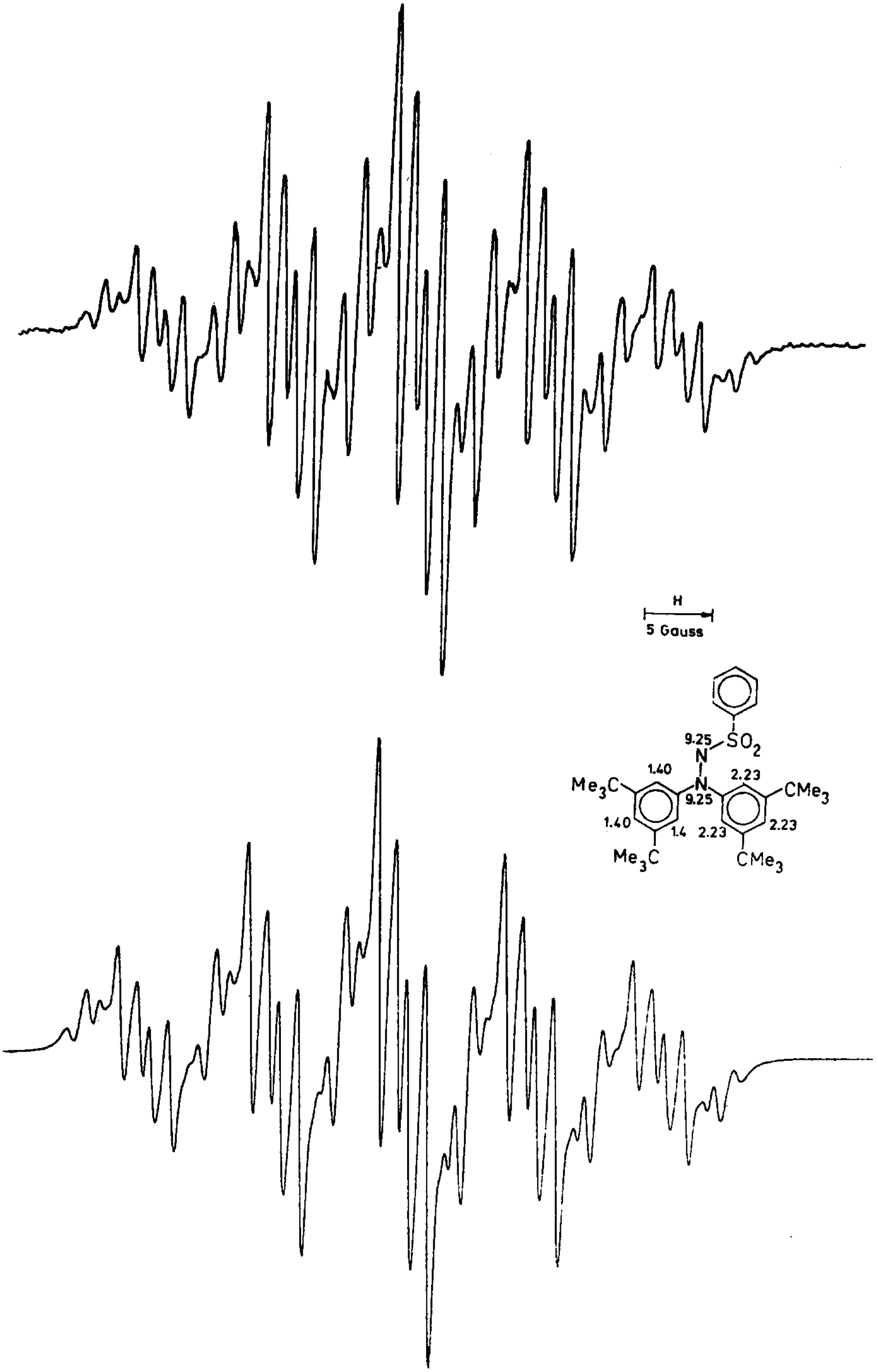
The simplest interpretation of this experimental fact is that the N-N bond in hydrazyls has partial double bond character leading to restricted rotation in agreement with Linnett's theory,[13] and with calculations of the rotation barrier around the N-N bond in hydrazyls.[14] According to Linnett, all atoms in hydrazyls have complete octets of electrons with paired spins α and β if and only if the N-N bond is intermediate between a single and a double bond, according to the formula :



$R_2\overset{\alpha}{N}\overset{\beta}{\text{—}}\underset{\cdot\cdot}{\overset{\alpha}{N}}R'$

The experimental ESR spectrum of the free radical I does not change appreciably in the temperature range -40° to $+80^{\circ}$ in various solvents. At room temperature, benzene solutions of I are stable for several days.

If, as it seems probable, the two aryl groups are non-equivalent not only in I, but in all 1,1-diarylhydrazyls related to diphenylpicrylhydrazyl, this non-equivalence should be taken into consideration both in the assignment of proton hyperfine coupling constants determined by ENDOR experiments,[6] and in theoretical calculations of spin density.[15]



Experimental ESR spectrum of I in benzene (above), and simulated (below).

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12. It is not yet possible to determine which aryl group has the larger and which one the smaller coupling constants. On the formula, the aryl *syn* relative to the arenesulphonyl group was arbitrarily assigned the larger coupling constants. The minor differences between the experimental and simulated ESR spectra may be due to slightly different nitrogen coupling constants ; we hope to determine these by a direct method.
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