

N-ARENESULPHONYL-N-(2,2,6,6-TETRAMETHYLPYPERIDYL-1)-AMINYLS, HYDRAZYLS WITH
NO NITROGEN-BONDED AROMATIC GROUPS

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All hydrazyls so far known^{1,2} possess at least one aryl group directly attached to nitrogen. We now report the synthesis and the ESR spectra of the first hydrazyls lacking this structural feature.

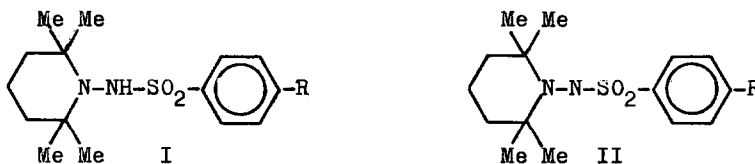
In a review discussing known aminyl free radicals,³ three conditions for stability were pointed out : (i) steric screening of the atom(s) with highest spin density, (ii) substitution of hydrogens by other atoms or groups in positions where disproportionation or dimerization could take place, and (iii) electronic delocalization of spin. The last condition can best be fulfilled in nitrogen free radicals by a donor and an acceptor group attached to the nitrogen atom. Such push-pull nitrogen free radicals were systematically explored³ by combination of donor groups (diarylamino, alkoxy, donor-substituted aryl) with acceptor groups (poly-nitro-,³ -carbomethoxy-,⁴ or -cyano-phenyl,³ arenesulphonyl,^{5,6} acyl,^{5,6} cyano⁷), e.g. by preparing 1-arenesulphonyl-2,2-diphenylhydrazyls,⁵ 1-cyano-2,2-diphenylhydrazyl,⁷ or N-arenesulphonyl-N-(p-dialkylaminophenyl)-aminyls.⁶

Attempts to obtain a stable hydrazyl by oxidation of 1,1-dimethyl-2-picrylhydrazine failed,⁸ because condition (ii) was not fulfilled, and disproportionation could occur : $2 \text{ Pic-N-NMe}_2 \longrightarrow \text{Pic-N}^{\bar{}}\text{-NMe}^{\bar{}}=\text{CH}_2 + \text{Pic-NH-NMe}_2$.

If, however, the dialkylamino group would not be able to disproportionate, all three conditions would be met. Our attempts to oxidize N-picrylamino-2,2,6,6-tetramethylpiperidine will be reported separately because several products are formed. By contrast, N-arenesulphonamido-2,2,6,6-tetramethylpiperidines (I) afford on oxidation hydrazyls (II), which can be considered as push-pull aminyls with a donor dialkylamino group devoid of α -hydrogens (therefore unable to dispropor-

tionate) and an acceptor arenesulphonyl group whose steric effect assists in suppressing dimerization. 1-Amino-2,2,6,6-tetramethylpiperidine⁹⁻¹¹ with an equivalent amount of arenesulphonyl chloride in anhydrous pyridine yielded I in five days at room temperature: Ia, R = H, m.p. 156° dec., Ib, R = NO₂, m.p. 149-151° dec. Infrared spectra in KBr disks: ν_{NH} 3265-75, ν_{SO_2} 1160-70 and 1340-50 cm⁻¹.

Oxidation of I in degassed benzene with lead tetraacetate at room temperature in static systems afforded ESR spectra consisting in a triplet of triplets: IIa, R = H, $g = 2.0034$, $a_{\text{N}} = 11.3$ G, $a_{\text{N}}' = 13.6$ G; IIb, R = NO₂, $g = 2.0036$, $a_{\text{N}} = 11.4$, $a_{\text{N}}' = 13.9$ Gauss. Since detectable hyperfine coupling occurs only with the two ¹⁴N nuclei (in these conditions, no coupling with methyl protons¹² appears), these ESR spectra are the simplest, and the hyperfine coupling constants are the highest, yet recorded for hydrazyls.^{1,2} Since the $a_{\text{N}}/a_{\text{N}}'$ ratio is smaller for IIb than for IIa, one can suppose the sulphonamido nitrogen to possess the larger a_{N}' constant which is more sensitive to para-substitution; for an unequivocal assignment of hyperfine coupling constants, ¹⁵N-labelling is in progress.



The fair stability ($T_{1/2} = \text{ca. } 0.5 \text{ hr at } 30^\circ$) of free radicals II proves that "push-pull" delocalization is essential for the existence of hydrazyls.

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