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FACTORS AFFECTING STABILITY AND EQUILIBRIA OF FREE RADICALS—VIII[1]

1-CYANO-2,2-DIPHENYLHYDRAZYL

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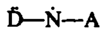
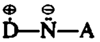
Abstract—The oxidation of 3,3-diphenylcarbazonitrile (1-cyano-2,2-diphenylhydrazine) with lead dioxide or tetraacetate affords the stable violet free radical 1-cyano-2,2-diphenylhydrazyl whose ESR spectra in solution and solid state are reported and discussed.

All hydrazyl free radicals which are stable[1-5] have an acceptor group bonded to the dicoordinated nitrogen, and thus constitute a particular case of aminyls[6] (**1**) with "push-pull" electronic effect in which a N atom has both a donor D and an acceptor substituent A.[1,2,7] We report the first example of a hydrazyl in which the acceptor is a cyano group.



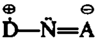
$\ddot{D}-\dot{N}-A$

1a



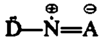
$\overset{\oplus}{\dot{D}}-\overset{\ominus}{\ddot{N}}-A$

1b



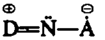
$\overset{\oplus}{\dot{D}}-\ddot{N}=\overset{\ominus}{A}$

1c



$\ddot{D}-\overset{\oplus}{\dot{N}}=\overset{\ominus}{A}$

1d



$\overset{\oplus}{D}=\ddot{N}-\overset{\ominus}{\dot{A}}$

1e

3,3-Diphenylcarbazonitrile or 1-cyano-2,2-diphenylhydrazine (**2**) was prepared from 1,1-diphenylhydrazine[8] and cyanogen bromide[9] in anhydrous ethanol or benzene. It had m.p. 97° in agreement with literature data.[10] Its IR spectrum presents in KBr disk a strong νCN band at 2230 cm^{-1}, strong aromatic bands at 1497 and 1595 cm^{-1} (νCC), 692 and 758 cm^{-1} (δCH) and a medium νNH band at 3390 cm^{-1}.

Tivoli[10] had noted that **2** cannot be kept indefinitely, becoming oxidized to a violet product. We investigated by electronic paramagnetic resonance (ESR) spectroscopy the nature of the violet product, and found that it is a stable free radical **3**.

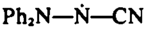
The violet colour can best be studied by oxidizing **2** with lead dioxide in benzene. The solution presents an absorption max at 501 nm (2,2-diphenyl-1-picrylhydrazyl has the absorption max in chloroform[8,11] at 530 nm), whereas 1-arenesulphonyl-2,2-diphenylhydrazyls **4** have absorption maxima[1] around 495 nm).

The oxidation of **2** with lead tetraacetate in benzene affords a violet solution presenting a well—resolved ESR spectrum (Fig) with a pattern evidencing a 1:2:3:2:1 multiplet. The g-factor (2·0037 ± 0·0003) excludes other structures than **3**.

The large number of lines (69 lines) in the ESR spectrum makes a straightforward interpretation difficult. However, by using a method based on partitions,[12,13] the following approximate hyperfine coupling constants were determined: 9·0 G for the two hydrazinic nitrogens 3·0 G for the cyano nitrogen; for one phenyl group, $a_{o-H} = 1{\cdot}5$ G, $a_{p-H} = 2{\cdot}25$ G, $a_{m-H} = 0{\cdot}75$ G; for the second phenyl group, $a_{o-H} = a_{p-H} = 0{\cdot}75$ G. These coupling constants agree with those determined for 1-arenesulphonyl-2,2-diphenylhydrazyls (**4**).[1]

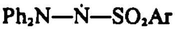
$Ph_2N—N—CN$

2



$Ph_2N-\dot{N}-CN$

3



$Ph_2N-\dot{N}-SO_2Ar$

4

After two weeks at room temperature in a degassed closed vial, the ESR signal of **3** in benzene shows no decrease in intensity. The radical **3** can also be obtained in crystalline state and thus seems to be at least as stable as the parent hydrazine **2**: by oxidizing **2** with lead dioxide and evaporating the solvent, a crystalline violet-black product was obtained whose IR spectrum no longer presents an N—H stretching band. By recording the ESR spectrum of the solid product and by comparing the integrated area with that of a standard diphenylpicrylhydrazyl sample, the number of unpaired spins in the solid **3** is about 1% of the theoretical amount.

EXPERIMENTAL

1-*Cyano*-2,2-*diphenylhydrazine* (**2**). To a soln of 1,1-diphenylhydrazine[8] (7 g) in 25 ml abs EtOH or benzene, cyanogen bromide[9] (2 g) was added and the soln stirred

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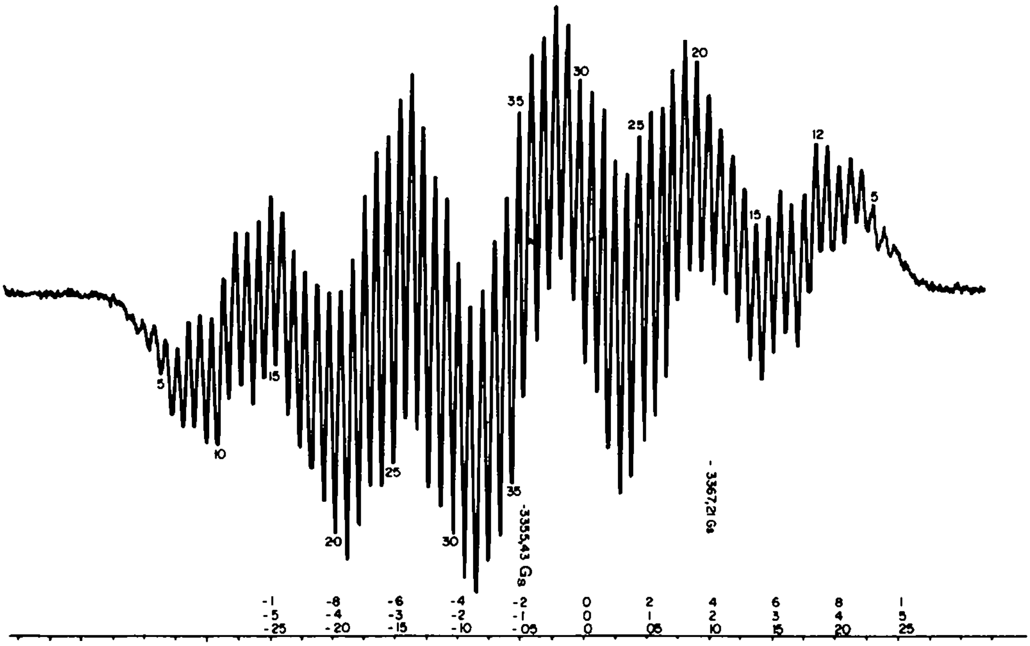

Fig 1. First-derivative ESR spectrum of 1-cyano-2,2-diphenylhydrazyl (2) in benzene.

for 1 h at room temp. The precipitated diphenylhydrazonium bromide was filtered off, and the filtrate was concentrated in vacuum yielding 2, m.p. 97° (from benzene-light petroleum).[10] (Found, N, 20·22. Calc. for $C_{13}H_{11}N_3$: N 20·03%).

Spectra. IR absorption spectra were recorded with a Zeiss (Jena) UR-10 instrument, visible spectra were recorded with an Optica CF4 (Milan) instrument, and ESR spectra were determined with a Jeol-ME3X and a Varian-E12 instrument.

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