106. *Further Examples of the Use of Paramagnetism as a Test for Free Radicals.*

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In continuation of our work on the magnetism of organic substances which contain an odd number of electrons (Kenyon and Sugden, J., 1932, 170; Sugden, *Trans. Faraday Soc.*, 1934, **30**, 18) we have examined the susceptibility of the substances referred to below. The molecular susceptibility should be given by $\chi_M = \chi_\mu + \chi_d + \chi_r$, where χ_d is the diamagnetic contribution, which can be computed with sufficient accuracy by adding Pascal's constants for the atoms and links in the molecule, and χ_r is a small residual term due to "high frequency" elements in the quantum-theory treatment (van Vleck, "Theory of Electric and Magnetic Susceptibilities," 1932, p. 274) which can be neglected in a discussion of strongly paramagnetic substances; χ_μ can therefore be obtained as the algebraic difference between χ_M and χ_d, and the effective magnetic moment is then given by $\mu_{eff.} = 2{\cdot}83\sqrt{\chi_\mu T}$. For a free radical with one electron with an unbalanced spin at 20°, χ_μ should be 1270 × 10^{-6} e.m.u. and $\mu_{eff.}$ should be 1·73 Bohr magnetons.

		t.	χ.*	χ_M.	χ_d.	χ_μ.	$\mu_{eff.}$.
1	$Ph_2N{\cdot}\overset{\mid}{N}{\cdot}C_6H_2(NO_2)_3$	16°	2·30	906	−212	1118	1·61
1a	$Ph_2N{\cdot}NH{\cdot}C_6H_2(NO_2)_3$	16	−0·537	−215	—	—	—
2	$(p\text{-}NO_2{\cdot}C_6H_4)_3C—$	18	1·723	651	−141	792	1·36
2a	$(p\text{-}NO_2{\cdot}C_6H_4)_3CBr$	16	−0·376	−172	—	—	—
3	$Ph_2C—O—K$	17	3·546	784	−124	908	1·45
3a	$Ph_2C{=}O$	17	−0·594	−108	—	—	—

* All susceptibilities are recorded in e.m.u. × 10^{-6}.

The above table contains the data for three substances which we have found to exhibit a large paramagnetism in the solid state. αα-Diphenyl-β-trinitrophenylhydrazyl (No. 1) appears to be a very stable free radical (see below) and, from the observed paramagnetism, contains at least 90% of the free radical form in the solid state. The diamagnetic correction for this substance was calculated from the susceptibility of the parent hydrazine (No. 1a) which, as theory predicts, is diamagnetic. Since this work was completed E. Müller, Müller-Rodloff, and Bunge (*Annalen*, 1935, **520**, 235) have published observations on the magnetic susceptibility of a number of substances including the hydrazyl (1) and conclude that it is entirely in the free-radical form.

Substance No. 2 is of interest since it is of the triphenylmethyl type. Its large paramagnetism shows that in the solid state it consists largely of the free radical. The low values found for the susceptibility and the moment are probably due to oxidation during the handling of this very unstable substance in spite of the precautions taken to avoid exposure to air. The diamagnetic correction for this compound was obtained from the susceptibility of the parent bromide (No. 2a) by taking Br as − 30·6.

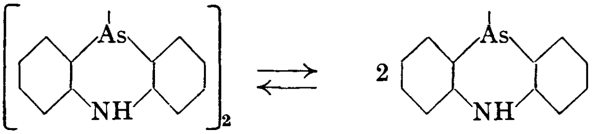
The ketyl (No. 3) has already been shown to be paramagnetic in dioxan solution (Sugden, *loc. cit.*), and is now found to be so in the solid state also. The susceptibility found for the solid is a little lower than that found in solution; it may be interpreted as indicating at least 70% of free radical. This is a minimum estimate, since any oxidation would give too low a value.

The relative stabilities of the hydrazyl (1) and the triphenylmethyl derivative (2) were studied by measuring specimens stored in corked tubes from time to time. The following results were obtained.

	αα-Diphenyl-β-trinitrophenylhydrazyl.				*Tri-*p*-nitrophenylmethyl.*		
Time (days)	0	2	7	42	0	2	9
χ_M	1118	1123	1117	1082	792	270	16

We have also examined two other substances which might be free radicals, but with negative results. 10 : 10′-Bis-5 : 10-dihydrophenarsazine (I) from its orange-yellow colour and its ready oxidation might be supposed to exist to some extent in the solid state as the free radical (II). We are indebted to Prof. C. S. Gibson, F.R.S., for a specimen of the parent chloride from which the phenarsazine was prepared. The phenarsazine was found to be diamagnetic ($\chi = -0{\cdot}764$), hence the solid must consist of the dimeric form (I) with no detectable amount of the free radical (II).

(I.)



(II.)

On both chemical and physical grounds it has been suggested that thiobenzophenone is a biradical $\mathrm{Ph_2\underset{\vdots}{C}{—}\underset{|}{S}}$ (Bergmann, Magat, and Wagenburg, *Ber.*, 1930, **63**, 2576; Hunter and Partington, J., 1933, 87). We have found, however, that it is diamagnetic with a mass susceptibility of $-0{\cdot}677$. E. Müller and Müller-Rudloff (*Ber.*, 1935, **68**, 1276) also find from the susceptibility of *pp*′-tetramethyldiaminothiobenzophenone that it exists to the extent of less than 1% as free radical in chloroform solution. It should, however, be noted that in these substances two free electrons are present in the biradical, and if their spins are opposed then no paramagnetism would result. The magnetic test is therefore not decisive for biradicals.

EXPERIMENTAL.

Magnetical susceptibilities were measured by the Gouy method as described earlier (J., 1932, 163).

αα-Diphenyl-β-trinitrophenylhydrazyl. The parent hydrazine, m. p. 173° (decomp.), was prepared by condensation of αα-diphenylhydrazine with picryl chloride. Oxidation of this with lead peroxide (Goldschmidt and Renn, *Ber.*, 1922, **55**, 636) afforded the hydrazyl as violet-black prisms, which were crystallised from chloroform–ether; m. p. 138—140°.

*Tri-*p*-nitrophenylmethyl.* Tri-*p*-nitrophenylmethane, prepared by the method of Hantzsch and Hein (*Ber.*, 1919, **52**, 495), was converted into the dark green free radical in an atmosphere of nitrogen as described by Ziegler and Boye (*Annalen*, 1927, **458**, 252).

Benzophenone-potassium. 12 G. of benzophenone in 120 c.c. of dry ether were shaken with 2·5 g. of potassium dust for 2 hours in an atmosphere of nitrogen. The deep blue precipitate was dried in a current of nitrogen, the measurement tube quickly fitted to the vessel containing the ketyl, and the substance packed evenly into the tube by means of a glass rod passing through a rubber sleeve in the preparation vessel. A current of nitrogen was passed continuously through the apparatus to minimise decomposition.

10 : 10′-Bis-5 : 10-dihydrophenarsazine was prepared from the chloride by reduction with hypophosphorous acid (Burton and Gibson, J., 1926, 2246) and obtained as orange needles, m. p. 306—307°. Its solutions in acetone, alcohol, or benzene did not darken on heating.

Thiobenzophenone was prepared as described in "Organic Syntheses," XI, 94. The deep blue product was recrystallised three times from ligroin and melted at 53°.

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