

21. A Paramagnetic Organic Compound.

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A FEW years ago one of us, in collaboration with Dr. F. H. Banfield (J., 1926, 1612), showed that the substance $C_{18}H_{22}O_2N_2$ of structure (I) gives on mild oxidation a red compound $C_{18}H_{21}O_2N_2$ to which the structure (II) was assigned. The red substance has an odd number of electrons in its molecule due either to a quadrivalent nitrogen atom (marked *) or to the valency of 1 for the adjacent oxygen atom.



Compounds with an odd number of electrons must contain an unpaired electron and should exhibit paramagnetism (Taylor and Lewis, *Proc. Nat. Acad. Sci.*, 1925, **11**, 456). We have therefore measured the magnetic susceptibilities of the substances (I) and (II) and find that, whilst (I), in common with nearly all organic compounds, is diamagnetic, (II) is strongly paramagnetic and its molecule has a magnetic moment very close to the value predicted for one unbalanced electron, *viz.*, $\mu = 1.73$ Bohr magnetons.

The susceptibilities were measured by the Guoy method in the apparatus described by one of us (preceding paper). The following results were obtained for the solid substances :

Substance.	<i>t.</i>	χ .	χ_M .	δ .	χ_A .	μ .
I	22°	-0.44*	- 131	(193)	—	—
II	17	+3.95	+1165	-128	+1293	1.73

* All susceptibilities are quoted in units of 10^{-6} e.m.u.

The molecular susceptibility of (I) is lower than the value predicted from Pascal's constants (193); it seems preferable to use the experi-

mental value in computing the diamagnetic correction, δ , for (II). The moment is obtained by the equation $\mu = 2.83\sqrt{\chi_A T}$, which assumes Curie's law.

Since solutions usually give very close approximations to Curie's law, measurements were also made on (II) dissolved in benzene. For this experiment a tube of larger cross-section was used to increase the accuracy, and was calibrated with water ($\chi = -0.719$) and with a solution of copper sulphate; for the latter it was assumed that the cupric ion had a moment of 1.93 (Weiss, *J. Physique*, 1924, 5, 129). A solution containing 20.33% of (II) in benzene gave $\chi = +0.471$. The benzene used had $\chi = -0.723$ ("International Critical Tables," vol. VI, p. 362, give -0.712). A mixture law being assumed, these results give for substance (II) in solution $\chi = +3.64$, whence $\mu = 1.68$.

The solution method is inevitably subject to a rather larger error than the solid method: the limit of accuracy in determining the pull exerted by the magnet being assumed to be ± 0.1 milligram, then for the solid $\mu = 1.73 \pm 0.02$ and in solution $\mu = 1.68 \pm 0.05$. If, as in the first transition series elements, the spin of the unbalanced electron determines the magnetic moment, then $\mu = \sqrt{4s(s+1)}$, which, for $s = \frac{1}{2}$, gives $\mu = 1.73$.

Substances which contain transition elements being excluded, the magnetic moments found for other "odd molecules" are (a) nitric oxide, 1.85 (Bauer and Piccard, *J. Physique*, 1920, 1, 97); chlorine dioxide, 1.75 (Taylor and Lewis, *loc. cit.*); and (c) nitrogen peroxide, which Soné (*Sci. Rep. Tôhoku*, 1922, 11, 139) finds is paramagnetic with χ_M at $135^\circ = 153$. This is much smaller than the value expected for $\mu = 1.73$, viz., 918. In addition, Taylor and Lewis (*loc. cit.*) state that α -naphthyldiphenylmethyl is paramagnetic in benzene solution (compare Taylor, *J. Amer. Chem. Soc.*, 1926, 48, 858) and find χ_M at $20^\circ = 570 \times 10^{-6}$ on the assumption that one-third of the substance is dissociated in solution to give the free radical.

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