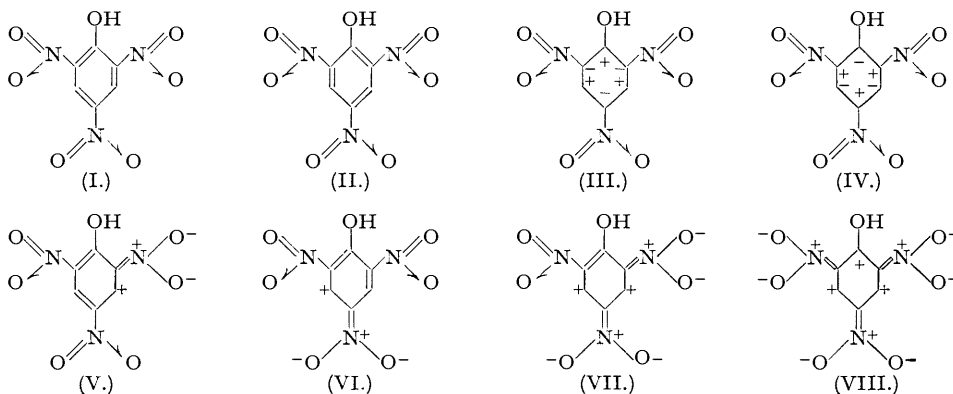


618. *The Magnetic Susceptibility of Certain Organic Compounds. Part II. The Constitution of Picric Acid, Naphthalene, and Naphthalene Picrate.*

By F. G. BADDAR and H. MIKHAIL.

Magnetic susceptibilities of naphthalene picrate and its constituents showed that the latter are linked together by weak electrostatic forces. The abnormally high value obtained for picric acid ($\chi_M \times 10^6 = -84.38$) suggests the contribution of several coplanar structures to the normal state of the molecule.

IN Part I (*J.*, 1944, 590) it was shown that the additivity law holds for quinhydrone and that the bond linking the quinone to the quinol molecule cannot be represented more precisely than by a dotted line, or that the individual molecules are held together by weak electrostatic forces (cf. Lal and Khan, *Current Sci.*, 1944, **13**, 312). In the present investigation the study was extended to naphthalene picrate in a similar attempt to investigate the type of linkage between its components. The magnetic susceptibility for naphthalene is found to be (-92.8×10^{-6}) which agrees, within the experimental errors, with the theoretical values based on either the Pascal (*Bull. Soc. chim.*, 1911, **9**, 79, 336, 868) or the Gray-Cruickshank method (*Trans. Faraday Soc.*, 1935, **31**, 1491).



The experimental value for picric acid (-84.38×10^{-6}) is exceptionally high, compared with the mean calculated value (-73.145×10^{-6}) for the structures (I)—(IV) (55.125, 55.125,

90·965, and 91·366, respectively). This showed that the coplanar structures (V), (VI), and (VII) and their corresponding internal ionic structures, as well as structure (VIII), may contribute to the normal state of the molecule.

The agreement between the experimental and calculated values for structure (VIII) cannot be taken as an evidence that this is the sole structure contributing to the normal state of the molecule. Such a structure is less stable than are structures (I) and (II) as it involves the unstable separation of charge. Table I shows the method of calculation based on the Gray-Cruickshank method (*loc. cit.*) for structure (VIII).

Singh *et al.* (*J. Indian Chem. Soc.*, 1946, **23**, 335) considered the high magnetic susceptibility ($-74\cdot55 \times 10^{-6}$) of *s*-trinitrobenzene to be an indication of the existence of three resonance structures which contribute equally to the actual state of the molecule. These, however, are not equally stable, for the same reason as stated above. Such less stable structures should, therefore, contribute less to the actual state of the molecule than do the more stable structures.

The value for naphthalene (see Table II) is in good agreement with that obtained by Lonsdale (*Proc. Roy. Soc.*, 1937, **159**, 153) and is not too far from the calculated value.

The experimental value for naphthalene picrate ($-185\cdot9 \times 10^{-6}$) does not deviate widely from the additive value for naphthalene and picric acid ($-177\cdot62 \times 10^{-6}$). This small deviation from additivity supports the assumption that the components are linked together by weak electrostatic forces.

TABLE I.

No. of atoms.	Charge on each.	Diamagnetism of each.	Total diamagnetism.	Bond depression.
2 C	+0·96	C ⁺¹ = 0·96 × 6·64 = 6·3744 C ⁰ = 0·04 × 9·96 = 0·3984	13·5456	6C—C = 11·88
1 C	+1·13	C ⁺² = 0·13 × 4·23 = 0·5499 C ⁺¹ = 0·87 × 6·64 = 5·7768	6·3267	3C=N = 35·31
3 C	+0·25	C ⁺¹ = 0·25 × 6·64 = 1·6600 C ⁰ = 0·75 × 9·96 = 7·4700	27·3900	1C—O = 1·92
2 H	+0·04	H ⁺¹ = 0·04 × 0·00 = 0·0000 H ⁰ = 0·96 × 2·373 = 2·2781	4·5562	1O—H = 0·67
1 H	+0·31	H ⁺¹ = 0·31 × 0·00 = 0·0000 H ⁰ = 0·69 × 2·373 = 1·6374	1·6374	6N → O = 3·12
1 O	-0·44	O ⁻¹ = 0·44 × 9·4 = 4·1360 O ⁰ = 0·56 × 7·09 = 3·9704	8·1064	2C—H = 1·06
				53·96
6 O	-1·08	O ⁻² = 0·08 × 12·66 = 1·0128 O ⁻¹ = 0·92 × 9·4 = 8·6480	57·9648	
3 N	+0·91	N ⁺¹ = 0·91 × 5·91 = 5·3781 N ⁰ = 0·09 × 8·28 = 0·7452	18·3699	
		Total	137·8970	
		Bond depression	53·96	
		Molecular diamagnetism	83·9370	

EXPERIMENTAL.

The Gouy method was adopted, details of which are described in Part I (*loc. cit.*).

The following formula was used in calculating the experimental magnetic susceptibility, *viz.*,

$$\chi_s = \frac{W}{[1 + v/V]S} \times \frac{\partial S}{\partial W} + \left[1/\sigma - \frac{W}{S} \times \frac{\partial S}{\partial W} \times \frac{1}{d} \right]$$

where the symbols have their usual meanings (cf. Hoare, *Proc. Roy. Soc.*, 1934, **147**, 88). The term v/V is the meniscus correction where v is the volume of the meniscus and V is the volume of the tube to an arbitrary mark (cf. Nettleton and Sugden, *Proc. Roy. Soc.*, 1939, *A*, **173**, 313). χ_w for pure water at 20–25° was taken as $-0\cdot72 \times 10^{-6}$.

Two tubes were chosen, for which the meniscus correction contributed an error of about 0·7%, if neglected in case of solids.

Purification of Materials.—The solvents which were used for crystallisation were purified according to Weissberger and Proskauer (*Organic Solvents*, 1935).

Picric Acid.—Three different samples were used which were purified as follows:

(i) A pure Kahlbaum sample of picric acid and an AnalaR sample were purified by repeated crystallisation from water. The dry product was then crystallised from alcohol or benzene to give pale yellow needles, *m. p.* 122·5°.

(ii) Kahlbaum picric acid was nitrated with a mixture of concentrated sulphuric acid and nitric

acids to convert any incompletely nitrated phenol into the fully nitrated product (cf. Arundel, Davies, and Imp. Chem. Ind., B.P. 370,436), and then purified as above.

(iii) Picric acid was precipitated as its sodium salt which was crystallised from water, and the free acid was then liberated by pure hydrochloric acid and purified as in (i).

Naphthalene.—B.D.H. "Naphthalene for molecular weight determination" was crystallised from alcohol to give colourless leaflets, m. p. 81·6°.

Naphthalene Picrate.—Equimolecular amounts of pure naphthalene and picric acid were dissolved in benzene and the solutions mixed in the cold. The picrate crystallised from ethyl acetate in yellow needles, m. p. 152—152·5°.

The usual method of producing uniformity in packing was followed (see Part I, *loc. cit.*).

Typical results for $-\chi_M \times 10^6$ are given in Table II.

TABLE II.

Substance.	Experimental values.				Calculated values.	
	(i).	(ii).	(iii).	(iv).	Pascal.	Gray <i>et al.</i>
Naphthalene	92·88	91·80	—	93·0	91·49	91·87
Picric acid	84·38	—	—	—	80·06	—
Naphthalene picrate	185·94	—	187·1	—	171·55	—

(i) Author's values. (ii) Pascal, *loc. cit.* (iii) Bhatnagar and Nevgi, *Indian J. Physics*, 1935, **2**, 311.
(iv) Lonsdale, *Proc. Roy. Soc.*, 1937, **159**, 153.

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