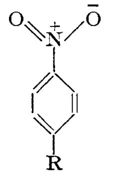
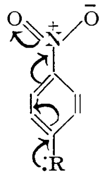
67. *The Magnetic Susceptibility of Certain Organic Compounds. Part III. The Contribution of the Nitro-group to the Magnetic Susceptibility of Aliphatic and Aromatic Nitro-compounds.*

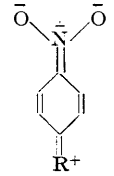
By F. G. Baddar and S. Sugden.

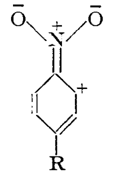
The magnetic susceptibility of certain aromatic and aliphatic nitro-compounds, as well as that of the corresponding parent substances, has been measured in an attempt to determine the contribution of the nitro-group to the magnetic susceptibility of these compounds. Col. 3 in Table III shows that the difference between the magnetic susceptibility of the $\gtrdot C{-}NO_2$ and the $\gtrdot C{-}H$ group is highest in the case of *m*-substituted nitro-compounds. This may be due to the fact that resonance leading to structures such as (III) is impossible in these *m*-compounds.

Several investigators have determined the magnetic susceptibility of the CH_2 group by measuring the susceptibility of a large number of the individuals of a homologous series, *e.g.*, aliphatic acids and their esters (French, *Trans. Faraday Soc.*, 1947, **43**, 356); alcohols, aliphatic acids, and their esters, and aromatic hydrocarbons (Angus and Hill, *ibid.*, 1943, **39**, 190); organic nitrites, nitrates, and nitro-compounds (Gray and Cruickshank, *ibid.*, 1935, **31**, 1491); normal alcohols (Cabrera and Fahlenbrach, *Z. Physik*, 1933, **85**, 568); and acetic acid and its esters (Woodbridge, *Physical Rev.*, 1935, **48**, 672). French (*Trans. Faraday Soc.*, 1945, **41**, 676) measured the susceptibility of certain disubstituted aromatic compounds. She noticed that, where the substituents are *op*-directing, the *o*-compounds have a markedly higher diamagnetic susceptibility value than either the *m*- or the *p*-isomerides. When the substituents are *m*-directing, the *m*-compounds have the highest susceptibility. She attributed this to the fact that in compounds containing two electron-repelling groups *ortho* to each other, there is the highest electron density, whereas in compounds containing two electron-attracting groups, the highest electron density is obtained when the two groups are *meta* to each other. However, she noticed that no such regularity could be traced in substituted aromatic nitro-compounds. It is possible that this irregularity may be due to the fact that in these compounds the contribution of the quinonoid structures (cf. III and IV) to the normal state of the molecule (*i.e.*, resonance) is affected by steric hindrance (cf. Birtles and Hampson, *J.*, 1937, 10; Ingham and Hampson, *J.*, 1939, 981) as well as by the position and polar nature of the substituents. Thus, in a molecule like *p*-R·C_6H_4·NO_2, the contribution of the quinonoid structures (III) or (IV) to the actual state of the molecule (or resonance hybrid) is higher if R is an electron-repelling group than if it is an electron-attracting group.


(I.)


(II.)


(III.)


(IV.)

(R = H, CH_3, or NH_2.)

In the present investigation the magnetic susceptibility of certain aromatic and aliphatic nitro-compounds as well as of the corresponding parent substances was measured in an attempt to determine the contribution of the nitro-group to the magnetic susceptibility both in aliphatic and in aromatic compounds. To avoid inaccuracy due to unequal packing of solid substances, the measurements for such compounds were carried out in solution, using suitable solvents such as benzene, acetone, and ethyl acetate. The fact that the values of the magnetic susceptibility of the solid, deduced from that of its solutions in any two of these solvents at different concentrations, were found to be identical within the experimental errors, was considered to be a sufficient proof for the validity of the additivity law of solutions (see Table I).

In Table III, col. 3 represents the difference between the magnetic suceptibility of the $\succ$C–NO_2 group and the $\succ$C–H group. The unexpectedly low value ($-4·45 \times 10^{-6}$) in the case of *p*-nitroaniline may be due to a solvent effect, whereas that in the case of nitromethane is more difficult to explain. It may be due to the uncertainty in the value of the magnetic susceptibility of methane, which is theoretically deduced (cf. Coulson, *Proc. Physical Soc.*, 1942, **54**, 51; French and Trew, *Trans. Faraday Soc.*, 1945, **41**, 439). It is noticed, however, that in the examples of aromatic nitro-compounds studied (*e.g.*, nitrotoluenes and nitroanilines) the differences in col. 3 of Table III are always highest in case of the *m*-, and lowest in the case of the *p*-derivatives. This may be due to the fact that structures such as (III) are impossible in the case of *m*-substituted nitro-compounds, and although it is possible in the case of the *o*-substituted compounds, yet it may be of less importance owing to steric hindrance (cf. Birtles and Hampson, *loc. cit.*). However, the contribution of the quinonoid structures such as (IV) increases in the case of nitro-compounds substituted by electron-repelling groups in the following order: Unsubstituted nitro-compounds < *m*-nitro- < *o*-nitro- < *p*-nitro-compounds, *i.e.*, nitrobenzene < *m*-nitrotoluene < *o*-nitrotoluene < *p*-nitrotoluene.

EXPERIMENTAL.

The measurements were carried out by the Gouy method using a silica tube which was calibrated by two nickel chloride solutions. Its volume was 25·18 c.c. and its constant (β) was 0·2824 (cf. Baddar, Hilal, and Sugden, *J.*, 1949, 132).

The solid materials used in these measurements were thoroughly purified by repeated crystallisation from pure solvents until a constant value for χ_s was obtained. Similarly, liquid substances were purified by repeated distillation from an all-glass apparatus, the middle fraction always being collected.

Purification of Materials.—Acetone and benzene were purified as stated by Baddar, Hilal, and Sugden (*loc. cit.*).

Ethyl acetate. "AnalaR" Reagent was washed with sodium hydrogen carbonate solution, then with water, and dried over calcium chloride for two weeks. It was fractionally distilled several times, and the fraction, b. p. 76·5—76·6°/756 mm., was collected; $d^{24·95}$ 0·8941.

Toluene. Sulphur-free toluene was shaken with concentrated sulphuric acid, and washed with water, then with sodium carbonate solution to remove any sulphonated product. It was dried ($CaCl_2$), distilled, shaken several times with mercury, and repeatedly fractionated over sodium; b. p. 110·3—110·4°/768 mm.; $d^{24\cdot95}$ 0·8594.

Nitromethane. This was prepared according to *Org. Synth.*, Coll. Vol. I, p. 393; dried ($CaCl_2$), distilled, dried over phosphoric oxide for few hours, and fractionally distilled to give a colourless liquid, b. p. 100—100·4°/752 mm.; $d^{24\cdot95}$ 1·131.

2-*Nitropropane.* A sample kindly provided by I.C.I. Ltd. was washed with sodium carbonate solution, dried ($CaCl_2$), and distilled. The drying and distillation were repeated three times. It was finally kept over phosphoric oxide for two hours, decanted, and distilled in a vacuum to give a colourless liquid, b. p. 42°/40 mm., then redistilled at ordinary pressure, b. p. 119·8—120°/763 mm.; $d^{24\cdot95}$ 0·9828.

Tetranitromethane. Prepared according to Chattaway (*J.*, 1910, **97**, 2099) and purified by washing with sodium hydrogen carbonate solution (cf. Hammick *et al.*, *J.*, 1936, 1464), this was dried ($CaCl_2$) and distilled in vacuum, b. p. 58—59°/100 mm., then dried over phosphoric oxide for 2 hours, decanted, and distilled; b. p. 47·5—48·5°/40 mm. The product was frozen, and the liquid portion rejected, and the residue then twice distilled; b. p. 46°/36 mm.; $d^{24\cdot95}$ 1·6312.

Nitrobenzene and o- *and* m-*nitrotoluene.* A pure sample of each was washed with sodium carbonate solution, then with water, dried ($CaCl_2$), and distilled. It was twice frozen, the liquid portion being rejected, and dried (P_2O_5). By repeated fractional distillation the nitro-compounds were obtained as pale yellow liquids, b. p.s 207°/735 mm., 217—217·1°/738 mm., 228·5—229°/759 mm.; $d^{249\cdot5}$ 1·1974, 1·1580, and 1·1524, respectively.

Aniline. Aniline hydrochloride was crystallised from alcohol, and the pure salt treated with sodium hydroxide solution. The liberated aniline was extracted with ether, dried (KOH) for 3 days, and distilled in a carbon dioxide atmosphere to give a colourless liquid, b. p. 183—183·2°/759 mm. The drying and distillation were repeated several times, and the fraction of b. p. 183·4°/759 mm. was collected.

p-*Nitrotoluene.* This was melted under sodium carbonate solution, washed with water, dried, and crystallised from alcohol several times, to give colourless crystals, m. p. 54·5°.

o-, m-, *and* p-*Nitroaniline.* These were crystallised several times from dilute alcohol, m. p.s 71·6—71·8°, 114°, and 148·2°, respectively.

In all cases the measurement was repeated after redistilling or recrystallising the substance. A series of measurements (usually about 6) were then made with the exciting current alternately off and on and the mean reading was taken as the thrust on the specimen. From this was subtracted the thrust on the empty tube (—27·34 mg.), and then $\chi_s \times 10^6$ of the pure liquids was calculated from the formula of Nettleton and Sugden (*Proc. Roy. Soc.*, 1939, *A*, **173**, 313), *viz.*

$$10^6\chi_s = 0{\cdot}29v/w + \beta f/w$$

The meniscus correction, being negligibly small, was neglected.

For solids the magnetic susceptibility was obtained by preparing solutions of different concentrations of the solid substance in suitable solvents of known magnetic susceptibility. By measuring the susceptibility of the solution, and assuming that the additivity law holds for the constituents of the solution, the susceptibility of the solute can be calculated from the equation

$$10^6\chi_{\text{solution}} = 10^6\chi_{\text{solute}} \times x + 10^6\chi_{\text{solvent}}\ (1 - x), \text{ where } x = \text{concn. of solute in g./g. of solution.}$$

By extrapolation to $x = 1$, the magnetic susceptibility of the solute was obtained.

The measurements were usually carried out in two different solvents, the mean value being taken in each case (see Table I).

To avoid the evaporation of the solvent during the transference of the solution to the specimen tube, the solution was prepared in a small wash-bottle with narrow delivery and pressure tubes closed by stoppers. After the solute and solvent had been weighed into the bottle it was kept in the balance case for ½ hour, The solution was then transferred to the specimen tube by applying a gentle stream of dry air saturated with the vapour of the solvent used.

In Table II sample (*b*) was obtained by redistillation of sample (*a*).

TABLE I.

Substance.	Solvent.	Concn. (x).	No. of detmns.	$-10\chi^6_{\text{sol.}}$	$-10^6\chi_s$.	$-10^6\chi_s$ (extrap.).	Mean.
o-Nitroaniline	Acetone	0·3362	5	0·5516	0·4943	0·4940	0·4954
,, ...	,,	0·3800	6	0·5477	0·4940		
,, ...	$CH_3{\cdot}CO_2Et$	0·3089	6	0·5795	0·4985	0·4967	
,,	,,	0·2424	6	0·5858	0·4939		
m-Nitroaniline ...	Acetone	0·2156	5	0·5632	0·5000	0·4960	0·4985
,, ...	,,	0·2960	5	0·5547	0·4933		
,, ...	$CH_3{\cdot}CO_2Et$	0·1666	6	0·5966	0·5009	0·5009	
p-Nitroaniline ...	Acetone	0·2046	5	0·5596	0·4769	0·4800	0·4842
,, ...	,,	0·2374	5	0·5581	0·4848		
,, ...	,,	0·2456	4	0·5552	0·4772		
,, ...	,,	0·2594	6	0·5544	0·4798		
,, ...	$CH_3{\cdot}CO_2Et$	0·1109	7	0·6016	0·4882	0·4882	
p-Nitrotoluene ...	Acetone	0·3047	5	0·5632	0·5240	0·5253	0·5257
,, ...	,,	0·3556	6	0·5615	0·5270		
,, ...	Benzene	0·3096	6	0·6477	0·5261	0·5261	
,, ...	,,	0·4112	7	0·6299	0·5263		

TABLE II.

Substance.	$-10^6\chi_s$. (*a*), mean of 6 readings.	(*b*), mean of 6 readings.	$-10^6\chi_s$, mean.	$-10^6\chi_M$.
Nitromethane	0·3452 ± 0·0004	0·3462 ± 0·0017	0·3457	21·10
2-Nitropropane	0·5131 ± 0·0004	0·5139 ± 0·0005	0·5135	45·73
Tetranitromethane	0·2195 ± 0·0003	—	0·2195	43·02
Nitrobenzene	0·5024 ± 0·0002	0·5026 ± 0·0003	0·5025	61·81
o-Nitrotoluene	0·5272 ± 0·0004	0·5271 ± 0·0009	0·5272	72·28
m-Nitrotoluene	0·5303 ± 0·0003	0·5305 ± 0·0004	0·5304	72·71
Toluene	0·7142 ± 0·0002	0·7157 ± 0·0010	0·7150	65·83
Aniline	0·6701 ± 0·0004	0·6704 ± 0·0006	0·6703	62·37
Ethyl acetate	0·6156 ± 0·0003	0·6155 ± 0·0003	0·6156	54·21

TABLE III.

Substance.	$-10^6\chi_M$.	$-\Delta 10^6\chi_M$, $\geqslant C{\cdot}NO_2 - \geqslant C{\cdot}H$.	Substance.	$-10^6\chi_M$.	$-\Delta 10^6\chi_M$, $\geqslant C{\cdot}NO_2 - \geqslant C{\cdot}H$.
Nitrobenzene	61·81 (1)	6·99	Nitromethane	21·10	5·1
Benzene	54·82		Methane	16·00	
o-Nitrotoluene	72·28 (2)	6·45	2-Nitropropane	45·37	6·37
Toluene	65·83		Propane	39·36	
m-Nitrotoluene	72·71 (3)	6·88	Tetranitromethane	43·02	6·75 $\frac{(27{\cdot}02)}{4}$
Toluene	65·83 (4)		Methane	16·00	
p-Nitrotoluene	72·06 (5)	6·23			
Toluene	65·83				
o-Nitroaniline	68·42 (6)	6·05			
Aniline	62·37				
m-Nitroaniline	68·96 (7)	6·59			
Aniline	62·37				
p-Nitroaniline	66·82 (8)	4·45			
Aniline	62·37 (9)				

(1) Cf. Cabrera and Fahlenbrach, *Z. Physik*, 1934, **89**, 697; Bhatnagar and Mitra, *J. Indian Chem. Soc.*, 1936, **13**, 329; Bhatnagar *et al.*, *ibid.*, p. 273; *Z. Physik*, 1934, **89**, 506. (2) Cf. Bhatnagar, Mathur, and Mal, *Phil. Mag.*, 1930, **10**, 101; Cabrera and Fahlenbrach, *loc. cit.*; Bhatnagar and Mitra, *loc. cit.* (3) Cf. the first two references in (2). (4) Cf. Kido, *Sci. Rep. Tohoku Univ.*, 1936, **24**, 701; Boeker, *Physical Rev.*, 1933, **43**, 756; Angus and Hill, *loc. cit.* (5) Cf. Cabrera and Fahlenbrach, *loc. cit.*; Subramanian, *Proc. Indian Acad. Sci.*, 1936, **3**, *A*, 420; Bose, *Phil. Mag.*, 1936, **21**, 1119. (6) Cf. Bose, *loc. cit.* (7) Cf. Bose, *loc. cit.*; Krishnan and Banerjee, *Phil. Trans.*, 1935, **234**, *A*, 265. (8) Garssen, *Compt. rend.*, 1933, **196**, 541. (9) Cf. Oxley, *Phil. Trans.*, 1914, **214**, *A*, 109; Rao, *Indian J. Physics*, 1934, **8**, 483.

N.B.—(i) $-10^6\chi_M$ for *p*-nitrotoluene, *o*-, *m*-, and *p*-nitroaniline was determined by multiplying the values in the last column of Table I by the corresponding molecular weight.

(ii) The value for propane was derived from that of methane, the magnetic susceptibility increment for the two CH_2 groups being taken as 2 × 11·68 (cf. Angus and Hill, *loc. cit.*).

THE SIR WILLIAM RAMSAY AND RALPH FORSTER LABORATORIES,
UNIVERSITY COLLEGE, LONDON.

[*Received, October* 10*th*, 1949.]