109. *Steric Inhibition of Resonance. Part I. The Dichloronitrobenzenes.*

By George Thomson.

The molecular solution volumes and molecular refractivities of the six isomeric dichloronitrobenzenes are interpreted as supporting the view that in 2 : 6-dichloronitrobenzene resonance between the nitro-group and the benzene nucleus is to a large extent inhibited and that even one chlorine ortho to a nitro-group will have a certain inhibitory effect on the resonance. Variations in the parachors are of the same magnitude and sign as the variations in molecular solution volumes.

Values found for their dipole moments are not inconsistent with this view.

The abnormally low reactivity of the chlorine atoms in 2 : 6-dichloronitrobenzene noted by Holleman and de Mooy (*Rec. Trav. chim.*, 1915, **35**, 19) has been discussed by Hückel (" Theoretische Grundlagen der organischen Chemie," 1931, ii, 256, 272; *Ber.*, 1929, **62**, 2041), who has calculated the energy of activation from Holleman's measurements. More recently, Loudon and Shulman (J., 1941, 725) have suggested that the low reactivity results from inhibition by the chlorine atoms of the resonance between the nitro-group and the benzene nucleus. Such steric inhibition of resonance was first postulated by Hampson and his collaborators (J., 1937, 10; 1939, 981) to account for the unexpectedly low dipole moments of nitro- and dimethylamino-durene derivatives. Hammick and Hellicar (J., 1938, 761), discussing the steric effects of chlorine and methyl substituents, point out that, the radius of the chlorine atom being taken as 0·99 A., and the radius of revolution of C–H in methyl as 1·09 A., a scale diagram shows that the surface of the chlorine atom will be 0·07 A. nearer than the sphere of revolution of the methyl group to an atom or group on the benzene nucleus between them. The chlorine atom would therefore be expected to be just as effective as the methyl group in inhibiting resonance.

If in 2 : 6-dichloronitrobenzene the vicinal chlorine atoms inhibit resonance between the nitro-group and the benzene nucleus, certain physical properties may be expected to differentiate this compound from its isomers.

Since the oxygen atoms of the nitro-group will be forced out of the plane of the benzene ring, the carbon–nitrogen bond will revert from partial double-bond to single-bond character with consequent lengthening: the molecules will be less easily packed and one would expect the molecular volume to be greater than that of an isomer such as 3 : 4- or 3 : 5-dichloronitrobenzene in which resonance is likely to be quite uninhibited. Such a volume change may be reflected in the parachor.

Further, inhibition of the resonance between the nitro-group and the benzene ring would be expected to result in a lowering of the molecular refractivity. It is known that the atomic refractivity of the nitro-group is lower in nitroparaffins than in nitrobenzenes, and the relevant structural difference appears to be the occurrence in the latter of resonance between the nitro-group and the benzene nucleus. Brühl (*Z. physikal. Chem.*, 1898, **25**, 613) gives the atomic refractivity (for the D line) of the nitro-group in nitrobenzenes as 7·30 and in nitroparaffins as 6·72, a difference of 0·58 unit. If Eisenlohr's recalculated values of atomic refractivity are used a rather larger difference is found: his value (*ibid.*, 1912, **79**, 129) for the nitro-group in nitroparaffins containing up to five carbon atoms is 6·638, and in those containing 6—10 carbon atoms 6·582. On the same basis the value for the nitro-group in nitrobenzene is calculated as 7·53, giving a difference between the aliphatic and the aromatic nitro-group of 0·95.

Finally, the dipole moment of 2 : 6-dichloronitrobenzene would be expected, like that of nitrodurene, to be lower than the value calculated by vectorial addition of the constituent moments after allowance for induction effects.

In order to test these points, measurements of molecular solution volume, molecular refractivity, and dipole moment have been made in benzene solution at 25°, and the parachors have been calculated from measurements of density and surface tension made on liquid dichloronitrobenzenes at 100°. All six isomers have been investigated.

Discussion of Results.—In Table I are collected the values of molecular solution volumes (M.S.V.), parachor, and molecular refractivity for sodium yellow ($\lambda = 5893$ A.) and mercury green ($\lambda = 5461$ A.). Measurements were made on solutions in which the concentration of dichloronitrobenzene varied between about 4 and 6 mols. %. The last col. contains the values of energy of activation (for the reaction with sodium methoxide) calculated by Hückel (*loc. cit.*).

TABLE I.

Data for dichloronitrobenzenes.

Isomer.	M.S.V.	$[P]$.	$[R_L]_D$.	$[R_L]_{5461}$.	Q.	Isomer.	M.S.V.	$[P]$.	$[R_L]_D$.	$[R_L]_{5461}$.	Q.
3 : 4-	125·7	333·4	43·00	43·15	22·3	2 : 4-	126·7	335·7	42·62	42·84	22·7
3 : 5-	125·6	334·5	42·94	43·19	—	2 : 5-	126·7	336·2	42·50	42·72	23·2
2 : 3-	126·4	335·8	42·63	42·79	23·0	2 : 6-	130·4	340·1	42·32	42·46	25

It will be seen that the values fall into three well-defined groups, depending on the extent to which the ortho-positions to the nitro-group are substituted by chlorine, the regularities in molecular refractivity being better defined in the values for mercury green. The lowest values of molecular solution volume and parachor and the highest values of molecular refractivity are those of 3 : 5- and 3 : 4-dichloronitrobenzenes: the values for these two isomers are identical within the limits of experimental error. When one chlorine occupies a position ortho to the nitro-group, both the molecular solution volume and the parachor are slightly raised and the molecular refractivity is lowered: the values for 2 : 3-, 2 : 4-, and 2 : 5-dichloronitrobenzenes are indistinguishable from one another but differ from those for 3 : 4- and 3 : 5-dichloronitrobenzenes by more than the experimental error. In the 2 : 6-isomer there is a further considerable increase in molecular solution volume and in parachor and a decrease in molecular refractivity approximately the same as that occasioned by the presence of one chlorine as an ortho-substituent. Much the same grouping of the isomers is possible on the basis of Hückel's values for their energies of activation. The difference in molecular refractivity for sodium yellow between 3 : 5- and 2 : 6-dichloronitrobenzene is 0·62, indicating that in the latter compound the atomic refractivity of the nitro-group is closer to the value for the group in a nitroparaffin than to the value in nitrobenzene. Values collected in Table II, where Δ is the difference due to one nitro-group, show that a reduction in molecular refractivity is observed whenever the 2 : 6 positions in nitrobenzene are substituted by methyl, chlorine, or bromine. The effect is most easily demonstrated by comparing the differences between the nitro- and the corresponding unnitrated compounds.

TABLE II.

Compound.	$[R_L]_D$.	Δ.	$[R_L]_{5461}$.	Δ.
Benzene	26·18 [1]	6·56	26·36 [2]	6·68
Nitrobenzene	32·74 [1]		33·04 [2]	
Mesitylene	40·76	6·22	41·06	6·16
Nitromesitylene	46·98		47·22	
s-Trichlorobenzene	40·9 [3]	6·2	—	—
1 : 3 : 5-Trichloro-2 : 4 : 6-trinitrobenzene	59·5 [3]		—	—
s-Tribromobenzene	49·9 [3]	6·07	—	—
1 : 3 : 5-Tribromo-2 : 4 : 6-trinitrobenzene	68·1 [3]		—	—
m-Dichlorobenzene	36·16	6·78	36·40	6·79
3 : 5-Dichloronitrobenzene	42·94		43·19	
m-Dichlorobenzene	36·16	6·16	36·40	6·06
2 : 6-Dichloronitrobenzene	42·32		42·46	
Chloroform	21·40 [1]	5·92	21·49 [2]	5·94
Chloropicrin	27·32 [1]		27·43 [2]	

[1] Landolt–Börnstein "Tabellen." [2] *Ibid.*, by interpolation. [3] Tiganik, *Z. physikal. Chem.*, 1931, *B*, **13**, 425.

It might be objected that, in the aromatic compounds instanced, possibly not the nitro-group but one or both of the other groups is suffering distortion. This seems unlikely, since trichlorination of mesitylene results in the same increase of molecular refractivity as trichlorination of benzene to give *s*-trichlorobenzene. Admittedly, the differences in molecular refractivity in the dichloronitrobenzene series are small but they appear to be real, and if it is granted that the reduction in the atomic refractivity of the nitro-group occasioned by two bulky ortho-substituents is due to inhibition of resonance, it is difficult to avoid the conclusion that even one such ortho-substituent can have some inhibitory effect on the resonance between the nitro-group and the benzene nucleus. Baddeley (*Nature,* 1939, **144**, 444) has explained some " ortho " phenomena due to a single ortho-substituent on the basis of inhibited resonance, and Loudon and Shulman (*loc. cit.*) also refer to this possibility.

Interpretation of the dipole moments of the dichloronitrobenzenes is complicated by the necessity for a knowledge of the magnitude of the inductive effects between the substituents. Exact calculation of these effects is impossible in view of the uncertainty of the locus of the resultant moment of the nitro-group : small changes in its location produce large changes in the induced moments in groups in its immediate neighbourhood, and it seems probable that in considering inductive interaction between ortho-substituents and a nitro-group it would be necessary to analyse the nitro-group into its component dipoles and consider the induction due to each separately. Smallwood and Herzfeld (*J. Amer. Chem. Soc.*, 1930, **52**, 1919), who first attempted to calculate the induction effects in disubstituted benzene derivatives, invariably found discrepancies when a nitro-group was one of the substituents, and Brown, de Bruyne, and Gross (*ibid.*, 1934, **56**, 1291), who applied Smallwood and Herzfeld's treatment to mesitylene derivatives, failed to get agreement between their experimental and calculated moments for nitromesitylene, though in this case the discrepancy could no doubt be explained in part by inhibition of resonance due to the vicinal methyl groups. In Hampson's approximate calculations of the induced moments in nitrodurene, it was possible on account of the low moment of the H_3C–C link to neglect its inductive effect on the nitro-group. This is not possible with the Cl–C link, and so resort has been made to empirical methods in order to obtain the " calculated " values of moment of the dichloronitrobenzenes set out in Table IV. (All values of dipole moments in this paper are in Debye units.) The A series of values are obtained by compounding the moments of nitrobenzene and the appropriate dichlorobenzene : in this way some correction is made for the interaction of the two chlorine atoms. The B series embody a further correction for the interaction of the chlorine atoms and the nitro-group estimated from the deviations of the observed moments of the chloronitrobenzenes from the values calculated by vector addition. Tiganik's values (*loc. cit.*) for the chloronitrobenzenes have been used in preference to Lutgert's (*Z. physikal. Chem.*, 1931, *B*, **14**, 350), which seem improbably low in comparison with the values found in the vapour phase by Groves and Sugden (J., 1937, 1782) and, moreover, are open to the objection that they were determined by the temperature–solution method.

Table III.

Dipole moments of the chloronitrobenzenes.

	Tiganik.		Groves and Sugden.		Lutgert.
	Obs.	Calc.	Obs.	Calc.	Obs.
o-$C_6H_4Cl{\cdot}NO_2$	4·33	4·92	4·59	5·32	3·96
m-$C_6H_4Cl{\cdot}NO_2$	3·40	3·46	3·69	3·69	3·12
p-$C_6H_4Cl{\cdot}NO_2$	2·57	2·42	2·78	2·51	2·34

Since Tiganik's values for the chloronitrobenzenes are to be used, it has been thought desirable to use also his values (*loc. cit.*) for nitrobenzene and the dichlorobenzenes, *viz.*, $C_6H_5{\cdot}NO_2$, 3·97; o-$C_6H_4Cl_2$, 2·25; m-$C_6H_4Cl_2$, 1·48; p-$C_6H_4Cl_2$, 0. The following assumptions are made regarding interaction of chlorine and nitro-groups. (*a*) Each chlorine ortho to a nitro-group will result in a diminution of moment of 0·59 D. (the difference between the observed and calculated values for *o*-chloronitrobenzene in benzene solution). This correction includes at least two factors, *viz.*, the effect of induction and the effect of inhibition of resonance; in the present state of our knowledge it is impossible to assess them separately. (*b*) A chlorine meta to a nitro-group will have no effect (cf. identity of calculated and experimental gas values for *m*-chloronitrobenzene and the closeness of the corresponding solution values). (*c*) A chlorine para to a nitro-group will result in an increase of moment to 0·15 D. (the difference between observed and calculated values for *p*-chloronitrobenzene).

The experimental and the calculated values of dipole moments of the dichloronitrobenzenes are given in Table IV. In the case of 2 : 5-dichloronitrobenzene, the only isomer whose moment has previously been measured, the value now found is identical with that found by Hassel and Naeshagen (*Z. physikal. Chem.*, 1931, *B*, **12**, 79).

Table IV.

Dipole moments of dichloronitrobenzenes.

Isomer.	2 : 3.	2 : 4.	2 : 5.	2 : 6.	3 : 4.	3 : 5.
Found	3·86	2·66	3·45	4·18	2·17	2·66
Calc. (A)	4·56	3·47	3·97	5·45	2·31	2·49
Calc. (B)	3·97	3·03	3·38	4·27	2·46	2·49

Despite the empirical nature of the treatment, the calculated results show a fair agreement with the experimental (within 2—7%), with the notable exceptions of the values for 2 : 4- and 3 : 4-dichloronitrobenzenes, *i.e.*, the only two isomers which have a chlorine substituted para to the nitro-group. Now a para-substituted nitrobenzene normally has a value of moment higher than that calculated as the vector sum of the moments. It is unlikely that this exaltation of moment is due to induction; more probably it results from interaction of resonance effects as shown so much more markedly in the familiar case of *p*-nitroaniline. In the case of

2 : 4-dichloronitrobenzene the chlorine ortho to the nitro-group will, if it inhibits the resonance between the nitro-group and the benzene nucleus, in a proportionate degree cause a departure from the character of nitrophenyl so that the second chlorine entering para to the nitro-group will not increase the moment by 0·15. This argument, however, cannot apply in the case of 3 : 4-dichloronitrobenzene, in which the resonance of the nitro-group with the benzene nucleus would be expected to be unimpaired as will that of the para-chlorine.*

The case of 3 : 5-dichloronitrobenzene is rather surprising. It should not be complicated by induction effects or inhibition of resonance, and one would expect a rather closer agreement between the observed and the calculated moment than is shown here.

EXPERIMENTAL.

Materials.—Solvent benzene was purified in the usual manner. Mesitylene had b. p. 163·5°, $d_{4^\circ}^{25^\circ}$ 0·85948, $n_{\mathrm{D}}^{25^\circ}$ 1·49698, whence $[R_L]_{\mathrm{D}}$ 40·76, in good agreement with the value 40·79 ± 0·05 given by Mulliken (*J. Chem. Physics*, 1939, **7**, 356) quoting from Egloff's " Physical Constants of Hydrocarbons "; $n_{5461}^{25^\circ}$ 1·5000, whence $[R_L]_{5461}$ 41·06. *m*-Dichlorobenzene had b. p. 171—171·4°/755 mm., $d_{4^\circ}^{25^\circ}$ 1·2824, $n_{\mathrm{D}}^{25^\circ}$ 1·54400, whence $[R_L]_{\mathrm{D}}$ 36·16, $n_{5461}^{25^\circ}$ 1·54834, whence $[R_L]_{5461}$ 36·40. Nitromesitylene (m. p. 44°) was prepared as in *Organic Syntheses*, **14**, 68.

3 : 4- and 2 : 5-Dichloronitrobenzenes were purchased from B.D.H., distilled under reduced pressure, and recrystallised: m. p.'s 43° and 55°, respectively. 2 : 3-Dichloronitrobenzene (m. p. 61°) was prepared as described by Kremer and Bendich (*J. Amer. Chem. Soc.*, 1939, **61**, 2658). 3 : 5-, 2 : 4-, and 2 : 6-Dichloronitrobenzene (m. p.'s 65°, 33°, and 71°, respectively) were prepared by the methods of Holleman and Reiding (*Rev. Trav. chim.*, 1904, **23**, 357).

Measurements.—Refractive indices were measured on a Hilger–Pulfrich refractometer, and dielectric constants by means of the apparatus described in previous papers.

For measurements of surface tension at 100°, Ferguson's method (*Proc. Physical Soc.*, 1932, **44**, 511) was adopted. The horizontal capillary tube (0·0592 cm. bore) was a sliding fit in a brass tube which was steam-jacketed. The manometer liquid was high-boiling (>120°) light petroleum, and the differences in level were measured by means of a cathetometer. To test the apparatus, the surface tension of a purified specimen of *p*-chloronitrobenzene was measured. The values found, 35·33 and 35·27 dynes/cm., are in good agreement with Sugden's value 35·40 (J., 1924, 1167) and, like his, rather higher than that of Jaeger (*Z. anorg. Chem.*, 1917, **101**, 138).

Densities at 100° were measured under comparable conditions. The pyknometer (kindly lent by Dr. James Bell) was made from pyrex tubing of about 1 mm. bore, and fitted into a slot in a plate of brass enclosed in a vessel through which was passed a vigorous stream of steam. Densities of 2 : 4-, 2 : 5-, and 3 : 4-dichloronitrobenzenes have been measured over a range of temperatures by Jaeger (*loc. cit.*), and the values now recorded are in good agreement with those obtained by interpolation from his data.

Densities, surface tensions, and parachors of dichloronitrobenzenes at 100°.

[J. = Value due to Jaeger (*loc. cit.*).]

Compound.	γ^{100° (dynes/cm.)	$d_{4^\circ}^{100^\circ}$.	[*P*].
2 : 3-Isomer	38·26, 38·21, 38·22, 38·20; mean 38·22	1·421, 1·421	335·8
2 : 4-Isomer	37·18, 37·17, 37·32, 37·20; mean 37·22 (J. 34·8)	1·411, 1·413 (J. 1·416)	335·7
2 : 5-Isomer	37·14, 37·13, 37·15, 37·09, 37·06, 37·06; mean 37·10 (J. 34·9)	1·409, 1·408 (J. 1·410)	336·2
2 : 6-Isomer	36·21, 36·17, 36·21; mean 36·20	1·383, 1·385	340·1
3 : 4-Isomer	37·43, 37·48, 37·49, 37·44; mean 37·46 (J. 35·2)	1·422, 1·424 (J. 1·424)	333·4
3 : 5-Isomer	35·55, 35·60, 35·55, 35·50, 35·52, 35·59, 35·66; mean 35·57	1·399, 1·402	334·5

Refractivity measurements in benzene solution at 25°.

Solute.	Mol.-fraction solute.	$d_{4^\circ}^{25^\circ}$.	M.S.V.	$n_{\mathrm{D}}^{25^\circ}$.	$[R_L]_{\mathrm{D}}$.	$n_{5461}^{25^\circ}$.	$[R_L]_{5461}$.
(Benzene)	—	0·87342	—	1·49786	26·174	1·50201	26·361
Nitromesitylene	0·044389	0·88797	—	1·49956	47·04	1·50362	47·21
	0·058526	0·89251	—	1·49998	46·92	0·50418	47·23
2 : 3-Dichloronitrobenzene	0·04783	0·91623	126·4	1·50365	42·59	1·50776	42·71
	0·063181	0·92852	126·3	1·50490	42·66	1·50911	42·88
	0·046188	0·91485	126·2	1·50356	42·65	1·50767	42·78
2 : 4-Dichloronitrobenzene	0·050586	0·91847	126·7	1·50393	42·62	1·50813	42·86
	0·044671	0·91330	126·7	1·50323	42·62	1·50738	42·82
2 : 5-Dichloronitrobenzene	0·057529	0·92456	126·7	1·50454	42·52	1·50869	42·68
	0·054260	0·92163	126·8	1·50416	42·44	1·50841	42·77
	0·044683	0·91335	126·5	1·50318	42·57	1·50724	42·70
2 : 6-Dichloronitrobenzene	0·050841	0·91690	130·3	1·50242	42·29	1·50654	42·48
	0·054156	0·91963	130·4	1·50276	42·36	1·50682	42·51
	0·053725	0·91918	130·4	1·50261	42·31	1·50659	42·38
3 : 4-Dichloronitrobenzene	0·052012	0·92020	125·8	1·50477	42·93	1·50896	43·20
	0·035684	0·90585	125·5	1·50280	43·07	1·50682	43·10
3 : 5-Dichloronitrobenzene	0·044626	0·91370	125·8	1·50379	42·93	1·50799	43·16
	0·054092	0·92214	125·6	1·50509	42·93	1·50925	43·15
	0·058348	0·92587	125·7	1·50574	42·97	1·51001	43·27

In the following tables the symbols have their usual significance. The solvent benzene used had $d_{4^\circ}^{25^\circ}$ 0·87368, $n_{\mathrm{D}}^{25^\circ}$ 1·49818, ε_{25° 2·2725. In calculating P_{O}, P_{E} has been taken as 42·7 (the sum of the atomic refractivities) and P_{A} as 5% of P_{E}.

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* Resonance between a substituent such as chlorine and the benzene ring is unaffected by bulky ortho-substituents; *e.g.*, the moments of chloromesitylene and chlorobenzene are identical, as are the moments of bromomesitylene and bromobenzene, and bromodurene has a moment of 1·55 as compared with 1·52 for bromobenzene.

Dipole-moment measurements.

2 : 3-Dichloronitrobenzene.

f_2.	$d_{4°}^{25°}$.	$\varepsilon_{25°}$.	P_2.
0·0074465	0·88032	2·4307	340·5
0·009436	0·88206	2·4730	337·9
0·010579	0·88304	2·4980	336·7
0·012712	0·88502	2·5433	333·5
0·015363	0·88742	2·6019	332·4
0·019626	0·89118	2·6930	326·9

$P_2 = 352$; $P_O = 308{\cdot}2$; $\mu = 3{\cdot}86$.

2 : 5-Dichloronitrobenzene.

f_2.	$d_{4°}^{25°}$.	$\varepsilon_{25°}$.	P_2.
0·0049737	0·87828	2·3559	280·2
0·006804	0·88003	2·3837	273·2
0·008382	0·88160	2·4070	266·3
0·0096347	0·88252	2·4270	265·9
0·012828	0·88550	2·4728	257·6

$P_2 = 291{\cdot}5$; $P_O = 246{\cdot}7$; $\mu = 3{\cdot}45$.

3 : 4-Dichloronitrobenzene.

f_2.	$d_{4°}^{25°}$.	$\varepsilon_{25°}$.	P_2.
0·004548	0·87791	2·3050	141·1
0·006893	0·88001	2·3218	141·4
0·008248	0·88156	2·3316	140·2
0·010161	0·88304	2·3445	139·9
0·014641	0·88713	2·3759	139·1

$P_2 = 142{\cdot}2$; $P_O = 97{\cdot}4$; $\mu = 2{\cdot}17$.

2 : 4-Dichloronitrobenzene.

f_2.	$d_{4°}^{25°}$.	$\varepsilon_{25°}$.	P_2.
0·0037364	0·87721	2·3115	190·1
0·006558	0·87960	2·3408	189·2
0·0091498	0·88212	2·3679	188·1
0·012787	0·88540	2·4051	188·9
0·016389	0·88849	2·4416	184·7

$P_2 = 192{\cdot}2$; $P_O = 147{\cdot}4$; $\mu = 2{\cdot}66$.

2 : 6-Dichloronitrobenzene.

f_2.	$d_{4°}^{25°}$.	$\varepsilon_{25°}$.	P_2.
0·0041762	0·87744	2·3772	399·0
0·0049204	0·87808	2·3965	399·3
0·0081384	0·88088	2·4760	390·7
0·012275	0·88448	2·5785	382·2
0·015039	0·88688	2·6475	377·6

$P_2 = 407$; $P_O = 362{\cdot}2$; $\mu = 4{\cdot}18$.

3 : 5-Dichloronitrobenzene.

f_2.	$d_{4°}^{25°}$.	$\varepsilon_{25°}$.	P_2.
0·0035416	0·87693	2·3073	182·2
0·004519	0·87804	2·3174	181·7
0·006930	0·88009	2·3347	173·5
0·01023	0·88298	2·3628	165·5
0·011587	0·88430	2·3722	161·7

$P_2 = 191{\cdot}2$; $P_O = 146{\cdot}4$; $\mu = 2{\cdot}66$.

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