218. *The Dipole Moments of* 1 : 4-*Dinitro-*, 1 : 3 : 5-*Trinitro-*, *and Certain* 2 : 4 : 6-*Trisubstituted*-1 : 3 : 5-*trinitro-benzenes.*

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In connexion with the equivalence of the two oxygen atoms of a nitro-group, several writers have recently referred to the dipole moments of the substances included in the title as being indistinguishable from zero. Such statements are, however, scarcely justified by the literature, for no less than 12 out of the 14 recorded determinations lie between 0·55 and 1·1 units * (see Table I), the solvent being benzene for all cases except ref. 8, where naphthalene was used.

Now whilst the *variations* of the above results can only be ascribed to experimental errors, their *magnitudes* can be explained in at least four ways : (1) that the technique adopted made inadequate allowance for the atomic polarisations during the evaluation of the final moments, (2) that the use of benzene as solvent may have caused the solutes to exhibit abnormally large atomic polarisations, (3) that unsuspected molecular-compound formation between the solutes and the solvent occurred (cf. Bennett, *Ann. Reports*, 1929, **26**, 130)—any of which would operate to give misleadingly large apparent total polarisations—or (4) that the substances do, in fact, possess appreciable permanent moments.

(1) It is impossible to say accurately *a priori* what the atomic polarisations of such molecules would be; the measurements of Sugden and Groves (J., 1934, 1091; cf. also

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* Debye units are referred to throughout.

TABLE I.

	1 : 4-Dinitrobenzene.			*1 : 3 : 5-Trinitrobenzene.*						
Temp.	20°	25°	—	20°	20°	20°	—	20°	85°	25°
Total poln.	45·6	37·0	—	64·5	54	54	—	53·7	50·5	51·5
Moment	0·58	0·32	0·8	1·08	0·8	0·8	0·72	0·70	0·78	0·68
Ref.	4	1, 3	6	3	5	2	6	4	7	8

	Trinitromesitylene.		*Trihalogenotrinitrobenzenes.*	
Temp.	20°	20°	20°	20°
Total poln.	70·5	74·5 ± 1	68·5	77·6
Moment	0·79	0	0·64	0·66
Ref.	4	9	4	4

References.—(1) Williams, *Physikal. Z.*, 1928, **29**, 204. (2) *Idem, J. Amer. Chem. Soc.*, 1928, **50**, 2350. (3) Williams and Schwingel, *ibid.*, p. 362. (4) Tiganik, *Z. physikal. Chem.*, 1931, *B*, **13**, 425. (5) Parts, *ibid.*, 1929, *B*, **4**, 227. (6) Höjendahl, "Studies in Dipole Moment," Copenhagen, 1928; *Physikal. Z.*, 1929, **30**, 391; *Nature*, 1926, **117**, 892. (7) Briegleb, *Naturwiss.*, 1934, **22**, 105. (8) Briegleb and Kambeitz, *Z. physikal. Chem.*, 1934, *B*, **27**, 11. (9) Lütgert, *ibid.*, 1932, *B*, **14**, 27.

McAlpine and Smyth, *J. Chem. Physics*, 1935, **3**, 55) show that nitrobenzene in the vapour state has an atomic polarisation of about 4 c.c.; benzene has only a small value, *ca.* 2 c.c. (Sugden, *Trans. Faraday Soc.*, 1934, **30**, 738). It is therefore evident that to the nitro-group itself an atomic polarisation of *ca.* 2 c.c. must be ascribed; but even though such polarisations are roughly additive (Sugden, *loc. cit.*), the general magnitude of the above polarisation values could only be thus partly accounted for. (2) Briegleb (*Z. physikal. Chem.*, 1932, *B*, **16**, 276) emphasised that for certain solutes the infra-red polarisation is much higher in benzene than in carbon tetrachloride or heptane, and suggested the possibility that this is a general effect, and that all moment values calculated from benzene solution are too high on account of the assumption of a uniformly constant electron plus atomic polarisation in all solvents. (3) It is noteworthy that Kremann (*Monatsh.*, 1908, **29**, 863) has shown cryoscopically that a compound $C_6H_3(NO_2)_3,C_6H_6$ has a definite existence in the solid state. (4) Permanent moments in this group of compounds would arise if the configuration of the nitro-radical were non-planar. This is referred to later.

Present Work.—With these points in mind, therefore, we have (*a*) repeated the measurements for trinitromesitylene and the two polynitrobenzenes in benzene solution, (*b*) sought to avoid as far as possible the difficulties outlined under (1) above, and to minimise experimental errors, by making our observations *on each solution* at the two temperatures 25° and 45°, and (*c*) investigated the possible operation of factors (2) and (3) by using solvents other than benzene.

In connexion with the results under (*b*), it becomes of interest to examine arithmetically how far such data can be trusted to amend the relevant parts of Table I. The relation between polarisation and temperature is accepted as $P_T = A + B/T$, in which A is the distortion polarisation (*i.e.*, the sum of the electronic and the atomic polarisation) and B is $4\pi N\mu^2/9k$; both are assumed to be constant and invariant with temperature (cf. Debye, "Handbuch der Radiologie," Vol. VI) within the limits indicated by Meyer (*Z. physikal. Chem.*, 1930, **8**, *B*, 27) and Goss (J., 1933, 9341). In our present enquiry therefore, we have $P_{25^\circ} - P_{45^\circ} = B/298 - B/318$, and $\mu = 0{\cdot}01273B^{\frac{1}{2}}$. In the following table are set out the differences of polarisation at 25° and 45° which must be measured when compounds having moments ranging from 0 to 1 unit are under investigation:

Moment	0	0·1	0·25	0·5	0·75	1·0
B	0	61·7	385·7	1542·7	3471·1	6170·8
$P_{25^\circ} - P_{45^\circ}$ (c.c.)	0	0·01	0·08	0·33	0·73	1·30

From repeated measurements of the resonance points and densities for a specimen of benzene in the apparatus used in all our observations, we conclude that our polarisation figures are accurate to within ±0·15 c.c., so that, *when the same solution is being compared at two temperatures* 20° *apart*, polarisation differences resulting from the solute molecules having moments of the order 0·5 unit should be detectable with certainty.*

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* The discordance between the P_1 values obtained from a series of solutions at one temperature is probably largely attributable to incorrect relative f_1 data (errors arising from the evaporation of the volatile solvent, weighings, etc.).

EXPERIMENTAL.

Materials.—1 : 4-*Dinitrobenzene.* From *p*-nitroaniline, *via* the nitroso-derivative (Bamberger and Hübner, *Ber.*, 1903, **36**, 3809); recrystallised from benzene; m. p. 171—172°.

1 : 3 : 5-*Trinitrobenzene.* From 2 : 4 : 6-trinitrotoluene by oxidation and decarboxylation (*Centr.*, 1902, i, 149; Friedländer, Vol. 4, 34); recrystallised from benzene; m. p. 121·5—122·5°.

Trinitromesitylene. By direct nitration of the hydrocarbon and recrystallisation from alcohol; m. p. 232—233°.

The benzene and carbon tetrachloride used were purified as detailed by Le Fèvre and Smith (J., 1932, 2239). Dioxan was refluxed over sodium wire for a day, distilled (b. p. 101—102°/760 mm.), fractionally frozen (m. p. 10—11°), and preserved over sodium. Chloroform was dried over phosphoric oxide, and distilled through a long column immediately prior to weighing.

Measurements.—The dielectric constants and densities of dilute solutions in benzene at 25° and 45°, and in the other solvents at 25°, were determined by methods set out before (this vol., p. 480). The polarisations of the solutes were calculated in the usual manner. The significant data are collected in the following tables, in which the symbols *M*, *P*, and *R*, refer respectively to the molecular weights, polarisations, and refractivities of the components, and *f* to their mol.-fraction in the solutions, the subscripts 1 and 2 applying to solute and solvent respectively; ε, *d*, and *n*, in order, denote the dielectric constant, density, and refractive index of the solutions.

1 : 4-*Dinitrobenzene.*

(*a*) In benzene solution, at 25°.

$f_1 . 10^6$	0	2213·4	4520·9	6400·2	9610·4
$M_1f_1 + M_2f_2$	78	78·1992	78·4069	78·5760	78·8649
ϵ	2·2725	2·2743	2·2761	2·2776	2·2802
d	0·87370	0·87542	0·87719	0·87863	0·88112
$P_1f_1 + P_2f_2$	26·5894	26·6313	26·6746	26·7103	26·7709
P_2f_2	26·5894	26·5305	26·4692	26·4192	26·3339
P_1f_1	—	0·1008	0·2054	0·2911	0·4370
P_1	—	45·45	45·44	45·48	45·47

(*b*) In benzene solution, at 45°.

$f_1 . 10^6$	0	2213·4	4520·9	6400·2	9610·4
$M_1f_1 + M_2f_2$	78	78·1992	78·4069	78·5760	78·8649
ϵ	2·2330	2·2349	2·2367	2·2381	2·2407
d	0·85208	0·85380	0·85556	0·85698	0·85951
$P_1f_1 + P_2f_2$	26·6643	26·7076	26·7510	26·7857	26·8449
P_2f_2	26·6643	26·6053	26·5438	26·4936	26·4080
P_1f_1	—	0·1023	0·2072	0·2921	0·4369
P_1	—	45·77	45·80	45·64	45·46

(*c*) In dioxan solution, at 25°.*

$f_1 . 10^6$	0	4003·2	4079·4	7922·3	8745·7
$M_1f_1 + M_2f_2$	88	88·3202	88·3264	88·6338	88·6996
ϵ	2·3060	2·3093	2·3094	2·3127	2·3134
d	1·02798	1·03034	1·03037	1·03260	1·03308
$P_1f_1 + P_2f_2$	25·9637	26·0443	26·0467	26·1267	26·1436
P_2f_2	25·9637	25·8598	25·8578	25·7580	25·7366
P_1f_1	—	0·1845	0·1889	0·3687	0·4070
P_1	—	46·09	46·31	46·54	46·54

(*d*) In chloroform solution, at 25°.†

$f_1 . 10^6$	0	5920·0	7872·0	9096·6	11422·9
$M_1f_1 + M_2f_2$	119·5	119·7871	119·8819	119·9412	119·9551
ϵ	4·7240	4·6916	4·6777	4·6712	4·6576
d	1·46814	1·46811	1·46806	1·46805	1·46803
$P_1f_1 + P_2f_2$	45·0799	45·0128	44·9737	44·9605	44·8912
P_2f_2	45·0799	44·8130	44·7251	44·6698	44·5650
P_1f_1	—	0·1998	0·2486	0·2907	0·3262
P_1	—	33·75	31·58	31·96	28·56

* Values of ε from Smyth and Walls (*J. Amer. Chem. Soc.*, 1931, **53**, 2115).

† Values of ε from Ball (J., 1930, 595).

1 : 3 : 5-*Trinitrobenzene*.

(*a*) In benzene solution, at 25°.

$f_1 . 10^6$	0	6100·5	7520·0	12154·0	16642·0
$M_1f_1 + M_2f_2$	78	78·8235	79·0152	79·6408	80·2466
ϵ	2·2725	2·2790	2·2805	2·2852	2·2897
d	0·87370	0·88049	0·88201	0·88711	0·89203
$P_1f_1 + P_2f_2$	26·5894	26·7583	26·7993	26·9251	27·0464
P_2f_2	26·5894	26·4272	26·3894	26·2662	26·1469
P_1f_1	—	0·3311	0·4099	0·6589	0·8995
P_1	—	54·27	54·51	54·21	54·05

(*b*) In benzene solution, at 45°.

$f_1 . 10^6$	0	6100·5	7520·0	12154·0	16642·0
$M_1f_1 + M_2f_2$	78	78·8235	79·0152	79·6408	80·2466
ϵ	2·2330	2·2396	2·2411	2·2459	2·2494
d	0·85208	0·85869	0·86009	0·86497	0·86917
$P_1f_1 + P_2f_2$	26·6643	26·8396	26·8841	27·0176	27·1447
P_2f_2	26·6643	26·5016	26·4638	26·3402	26·2206
P_1f_1	—	0·3380	0·4203	0·6774	0·9241
P_1	—	55·41	55·89	55·73	55·53

(*c*) In dioxan solution, at 25°.

$f_1 . 10^6$	0	6762·7	7307·4	11446·5	13326·0
$M_1f_1 + M_2f_2$	88	88·8453	88·9135	89·4308	89·6657
ϵ	2·3060	2·3157	2·3158	2·3203	2·3207
d	1·02798	1·03445	1·03498	1·03886	1·04064
$P_1f_1 + P_2f_2$	25·9637	26·1836	26·1917	26·3080	26·3376
P_2f_2	25·9637	25·7881	25·7740	25·6665	25·6177
P_1f_1	—	0·3955	0·4177	0·6415	0·7199
P_1	—	58·48	57·16	56·04	54·02

(*d*) In chloroform solution, at 25°.

$f_1 . 10^6$	0	2665·0	4463·0	5525·4	10279·0
$M_1f_1 + M_2f_2$	119·5	119·7492	119·9173	120·0167	120·4610
ϵ	4·7240	4·7116	4·7018	4·6955	4·6713
d	1·46814	1·46910	1·46976	1·47013	1·47190
$P_1f_1 + P_2f_2$	45·0799	45·0771	45·0668	45·0584	45·0378
P_2f_2	45·0799	44·9598	44·8787	44·8308	44·6165
P_1f_1	—	0·1173	0·1881	0·2276	0·4213
P_1	—	44·02	42·15	41·19	40·99

Trinitromesitylene.

(*a*) In benzene solution, at 25°.

$f_1 . 10^6$	0	1450·0	2891·0	5815·0	9111·0
$M_1f_1 + M_2f_2$	78	78·2566	78·5117	79·0292	79·6126
ϵ	2·2725	2·2744	2·2756	2·2789	2·2826
d	0·87370	0·87529	0·87678	0·87999	0·88359
$P_1f_1 + P_2f_2$	26·5894	26·6563	26·7154	26·8419	26·9845
P_2f_2	26·5894	26·5508	26·5125	26·4348	26·3471
P_1f_1	—	0·1035	0·2029	0·4071	0·6374
P_1	—	71·38	70·18	70·00	69·96

(*b*) In benzene solution, at 45°.

$f_1 . 10^6$	0	1450·0	2891·0	5815·0	9111·0
$M_1f_1 + M_2f_2$	78	78·2566	78·5117	79·0292	79·6126
ϵ	2·2330	2·2345	2·2361	2·2391	2·2432
d	0·85208	0·85353	0·85514	0·85819	0·86201
$P_1f_1 + P_2f_2$	26·6643	26·7295	26·7907	26·9176	27·0593
P_2f_2	26·6643	26·6256	26·5872	26·5092	26·4214
P_1f_1	—	0·1039	0·2035	0·4084	0·6379
P_1	—	71·65	70·39	70·23	70·01

(*c*) In dioxan solution, at 25°.

$f_1 . 10^6$	0	2639·9	3318·3	4095·6	5442·7
$M_1f_1 + M_2f_2$	88	88·4409	88·5542	88·6839	88·9090
ϵ	2·3060	2·3126	2·3133	2·3148	2·3180
d	1·02798	1·03030	1·03033	1·03088	1·03184
$P_1f_1 + P_2f_2$	25·9637	26·1266	26·1690	26·2142	26·3006
P_2f_2	25·9637	25·8952	25·8776	25·8573	25·8224
P_1f_1	—	0·2314	0·2914	0·3569	0·4782
P_1	—	87·65	87·82	87·14	87·86

(*d*) In chloroform solution, at 25°.

$f_1 . 10^6$	0	2991·9	3580·7	6000·0	8571·3
$M_1f_1 + M_2f_2$	119·5	119·9054	119·9852	120·3130	120·6614
ϵ	4·7240	4·7035	4·6993	4·6827	4·6650
d	1·46814	1·46763	1·46753	1·46710	1·46666
$P_1f_1 + P_2f_2$	45·0799	45·1370	45·1472	45·1925	45·2387
P_2f_2	45·0799	44·9450	44·9185	44·8094	44·6935
P_1f_1	—	0·1920	0·2287	0·3831	0·5452
P_1	—	64·17	63·87	63·85	63·61

Estimated P_1 *values for* $f_1 = 0$ *for the above solutions.*

	Dinitrobenzene.	Trinitrobenzene.	Trinitromesitylene.
(*a*)	*ca.* 46	*ca.* 55	*ca.* 70·5
(*b*)	*ca.* 46	*ca.* 55·5	*ca.* 70·5
(*c*)	*ca.* 47	*ca.* 61·5	*ca.* 88
(*d*)	38·9	46·6	64·2

DISCUSSION.

The results (*a*) for benzene solutions at 25° require no special comment and compare satisfactorily with the earlier measurements cited in Table I. For all three compounds in benzene solution the polarisation appears to be higher at 45°; of course, this also happens for the (non-polar) benzene, but comparisons of the P_1 increase per degree for the solutes and for the solvent show clearly that the polarisation increase observed with the solutions cannot arise from this cause alone; *i.e.*, the increase of polarisation per degree for the benzene used is seen to be 0·003745 c.c., as against average increases for the three solutes of 0·0093, 0·0689, and 0·0095 c.c. respectively. We conclude, therefore, that these substances (in benzene solution) cannot have moments much greater than 0·5 unit.

An independent indication that the moment of 1 : 4-dinitrobenzene is actually of a very low order is provided by the measurements of Lippmann (*Z. Elektrochem.*, **1911**, **17**, 15), which relate to the Kerr constants of the three isomeric dinitrobenzenes in dilute benzene solutions. As pointed out by Briegleb and Wolf (*Fortschr. Chem.*, **1931**, **21**, 44), this constant, running in magnitude in the direction of the moment of the molecule concerned, can therefore be used as a guide to this property. It is noteworthy, this being the case, that only for the para-compound is a value for $B\{3/(\varepsilon + 2)\}^2$ obtained of the same order as that for benzene itself; the *m*- and *o*-dinitrobenzenes both give numerically much larger results.

The effects of changing the solvent to dioxan appear to show that these substances are not absolutely non-polar; this follows from the fact that, not even in the case of chloroform, where no combination can reasonably be envisaged, do the total polarisations fall to the $_{\mathrm{E}}P$ and $_{\mathrm{A}}P$ sum * (taken as the $[R_L]_{\mathrm{D}}$ values, *viz.*, 38·5 c.c. for the 1 : 4-dinitro- and 44·7 c.c. for the 1 : 3 : 5-trinitro-benzene, and 59·2 c.c. for trinitromesitylene).† If the differences (0·4, 1·9, and 5·0 c.c., respectively) are regarded as $_{\mathrm{O}}P$ values in chloroform ($\varepsilon_{25^\circ} = 4{\cdot}724$) and are translated into gas values (cf. Le Fèvre, this vol., p. 773) by the equation $_{\mathrm{O}}P_1/_{\mathrm{O}}P_2 . (\varepsilon_1 + 2)/(\varepsilon_2 + 2) = K$ (where K is taken as *ca.* 1·3, and ε_2 as unity), the results (0·69, 3·27, and 8·6 c.c., respectively) would correspond to moments of the orders 0·2, 0·4, and 0·6, respectively. The present work further strongly suggests that these substances associate with benzene and dioxan.

The virtual absence of changes of polarisation with temperature observed experimentally do not militate against such views, because (attachment presumably occurring at the

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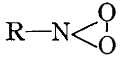
* These results therefore disagree with those of Jenkins (*Nature*, 1934, **134**, 217) in that, according to him, no differences exist between the total and the electronic polarisations of 1 : 4-dinitro- and 1 : 3 : 5-trinitro-benzene in the polar solvent chloroform. The total polarisations are not quoted in the reference cited, but are given as 34 and 41 c.c. respectively in the Faraday Society's tables of dipole moments (*Trans.*, 1934, Appendix, p. 1193). Comparison with the $[R_L]_{\mathrm{D}}$ values for these substances suggests that these figures are too low.

† From the following values of atomic, molecular, and group refractions: NO_2, 7·30; H, 1·100; C_6H_6, 26·14; mesitylene, 40·61. Direct measurements, owing to limited solubilities, do not give trustworthy results.

nitro-groups) from symmetry considerations no *increase* of moment need necessarily parallel the molecular polarisation increase caused by addition.

Configuration of the Nitro-group.—In seeking for an explanation of the finite moments estimated above, it should be emphasised that the possibility of the nitro-group being non-planar does not appear to be excluded by physical evidence. This consists principally of the demonstration of the crystallographic equivalence of the two oxygen atoms and their equidistance from the nitrogen atom (Hertel, *Z. physikal. Chem.*, 1930, *B*, **7**, 188; Hendricks and Hilbert, *J. Amer. Chem. Soc.*, 1931, **53**, 4280; cf. also Schaefer, *Trans. Faraday Soc.*, 1929, **24**, 841, and Banerjee, *Phil. Mag.*, 1934, **18**, 1004)—observations which only rule out (by the fact that elements have larger radii as anions than as covalently attached atoms) the older semipolar bond structure in which one oxygen was represented as carrying a unit anionic charge. The early triangular formula  $R{-}N\langle\begin{smallmatrix}O\\|\\O\end{smallmatrix}$ would satisfy present requirements save for the fact that the O–N–O angle in this group is definitely of the order 120° (above references) and, in consequence, the O–O distance is too great for a single bond.

Raman spectra data seem suggestive. The force constant ($9{\cdot}48 \times 10^{-5}$ dyne) characterising the links in the (aryl) nitro-group (Dadieu, Jele, and Kohlrausch, *Monatsh.*, 1931, **58**, 428) is greater than that required for a single bond ($6{\cdot}7 \times 10^{-5}$ dyne) and less than that for a double bond (14×10^{-5} dyne) (cf. Bailey and Cassie, *Proc. Roy. Soc.*, *A*, 1931, **132**, 236). We therefore envisage a structure in which three electrons from the nitrogen atom participate, with one electron from the carbon and one from each of the oxygen atoms, in three localised bonds (one N–C, and two N–O), and in which one further electron from each of the oxygen atoms forms a non-localised bond over the NO_2 angle. There is thus left an electron pair on the nitrogen atom, and the complex becomes analogous to the ions SO_3^{-2}, ClO_3^{-1}, AsO_3^{-3}, etc., in that it should be pyramidal * (cf. Zachariasen, *J. Amer. Chem. Soc.*, 1931, **53**, 2123). Therefore in, *e.g.*, nitrobenzene a large component moment should exist at an angle to the Ph–N axis, and *p*-dinitro- and *s*.-trinitro-benzenes should become formally analogous to the quinol ethers and other compounds with dipolar groups capable of free rotation, *i.e.*, they should have finite permanent moments which are the root mean squares of the instantaneous resultant moments (varying during the rotation of the nitroxyls about the C–N links). Zahn's observation (*Physikal. Z.*, 1933, **34**, 461), that N_2O_4 has a finite moment ($0{\cdot}6 \pm 0{\cdot}1$; cf., however, *J. Amer. Chem. Soc.*, 1934, **56**, 1427), also becomes on such an hypothesis not incompatible with the conclusions of Hertel and Hendricks, etc., or with those of Harris and King (*J. Chem. Physics*, 1934, **2**, 51), who infer, from the infra-red absorption spectra, that in N_2O_4 the two nitro-groups are non-coplanar (cf. also Sutherland, *Proc. Roy. Soc.*, 1933, *A*, **141**, 342, 535).

An estimate of the degree of departure from plane triangularity is obtained by assuming that the greater part (say 3·2 out of the 3·8 units) of the moment associated with the nitro-group arises within the group itself, *i.e.*, in the N–O and not in the C–N links, and solving the equation (Williams, *J. Amer. Chem. Soc.*, 1928, **50**, 2350) $\mu\,\text{resultant} = \sqrt{2}.\mu.\sin\theta$ for the case of 1 : 4-dinitrobenzene. We have $\sin\theta = 0{\cdot}2/3{\cdot}2\sqrt{2} = 0{\cdot}0442$, whence θ is *ca.* 2·5°; such a small departure from planarity would escape detection by *X*-ray methods.

Effect of Steric Hindrance.—It follows that, if several such pyramidal nitro-groups in a given aromatic molecule are hindered in their rotation by blocking groups which themselves cannot be divided by the plane of the ring as by a plane of symmetry, there is a high chance that the resultant molecular moment would be much greater than for otherwise analogous circumstances in which free rotation is fully possible. Along these lines † the definitely greater moment of trinitromesitylene can be understood. In Fig. 1 are shown the sections which the constituent atoms of this compound would have to make in the plane of the paper during their free rotation; they are drawn from the data of Pauling

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* Compare Pauling, *J. Amer. Chem. Soc.*, 1931, **53**, 1382, who considers that the closely related nitrate ion may be slightly pyramidal.

† Compare, however, the opinions of Placzek ("Molekülstruktur," Leipziger Vorträge, 1931) and Weiler (Z. *Physik*, 1924, **89**, 58) upon which alternative but more speculative explanations could be directly based.

and Huggins (*Proc. Nat. Acad. Sci.*, 1932, **18**, 293) and can be regarded (in the matter of dimension) as minimum estimates. It can be seen that no interference is predicted. Recent resolutions of diphenyl compounds, and other work summarised by Sidgwick (*Ann. Reports*, 1932 and 1933), indicate, however, that the use of considerably greater atomic radii in such questions is justifiable. Accordingly, we have superimposed on the above section the dotted outline obtained when the " Wirkungs-radius " (Stuart, *Z. physikal. Chem.*, 1935, *B*, **27**, 353) of each atom concerned is employed. In such a structure, completely symmetrical arrangements of the three nitro-groups are unlikely, and, if these radicals have the slightly pyramidal configuration referred to above, the molecule should exhibit a finite moment different from that to be expected were free rotation unhindered.

FIG. 1.

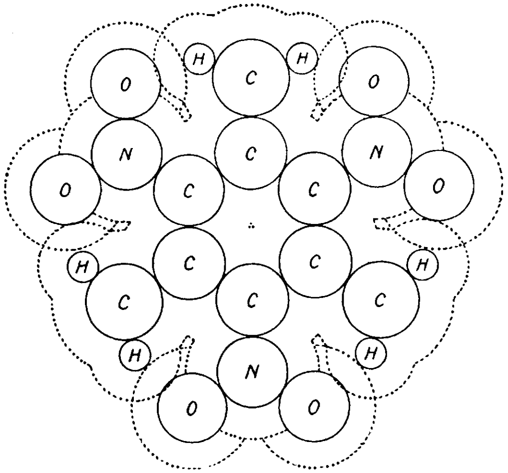
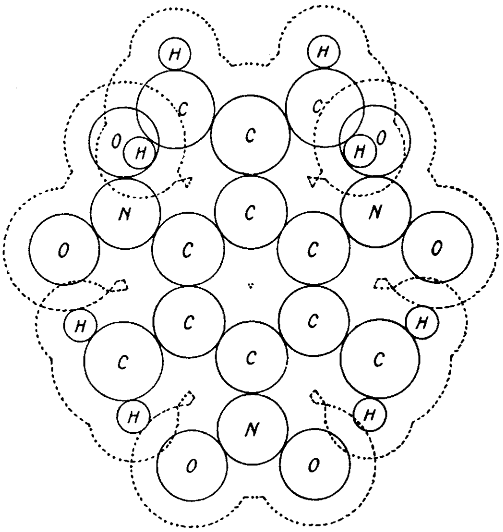


FIG. 2.



In connexion with the above explanation, we have determined the total polarisation and thence the moment of trinitro-5-*tert.*-butyl-*m*-xylene (I ; see p. 964), in which (as the plan, Fig. 2, shows) the situation considered for trinitromesitylene is exaggerated by replacement of methyl by *tert.*-butyl. The measurements have been carried out in carbon tetrachloride as well as benzene, in order to detect solvent effects, if any.

Trinitro-tert.*-butylxylene in benzene.*

$f_1 . 10^6$	0	5214·6	6044·89	8497·29	17404·6
$M_1f_1 + M_2f_2$	78	79·1419	79·3239	79·8609	81·8116
Temperature 25°.					
ϵ	2·2725	2·2829	2·2845	2·2895	2·3074
d	0·87380	0·87930	0·88014	0·88279	0·89224
$P_1f_1 + P_2f_2$	26·5850	26·9608	27·0202	27·1948	27·8308
P_2f_2	26·5850	26·4464	26·4243	26·3591	26·1223
P_1f_1	—	0·5144	0·5959	0·8357	1·7085
P_1	—	98·66	98·66	98·35	98·16
n_2	1·49733	—	1·49790	1·49833	1·49914
n	2·24200	—	2·24370	2·24499	2·24741
$R_1f_1 + R_2f_2$	26·13565	—	26·41346	26·53169	26·92878
R_2f_2	26·13565	—	25·97770	25·91357	25·68076
R_1f_1	—	—	0·43576	0·61812	1·24802
R_1	—	—	72·1	72·7	71·7
Temperature 45°.					
ϵ	2·2330	2·2435	2·2450	2·2500	2·2677
d	0·8521	0·85766	0·85855	0·86115	0·87081
$P_1f_1 + P_2f_2$	26·6640	27·0406	27·0974	27·2757	27·9072
P_2f_2	26·6640	26·5249	26·5028	26·4374	26·1999
P_1f_1	—	0·5156	0·5946	0·8383	1·7073
P_1	—	98·60	98·35	98·30	98·09

*Trinitro-*tert.*-butylxylene in carbon tetrachloride.*

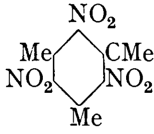
Temperature 25°.

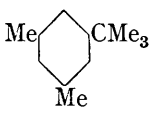
$f_1 . 10^6$	0	8320·4	10078·5	12749·7	19624·4
$M_1f_1 + M_2f_2$	154	155·1898	155·4412	155·8230	156·8064
ϵ	2·2270	2·2442	2·2475	2·2532	2·2668
d	1·5844	1·57910	1·57790	1·57616	1·57162
$P_1f_1 + P_2f_2$	28·2142	28·8102	28·9330	29·1298	29·6225
P_2f_2	28·2142	27·9794	27·9298	27·8544	27·6605
P_1f_1	—	0·8308	1·0032	1·2754	1·9620
P_1	—	99·85	99·54	100·03	99·98

Whence $\mu = 0·22(100 - 73)^{\frac{1}{2}} = 1·14$.

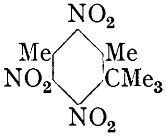
The results are seen to be not inconsistent with expectations based on the foregoing theory, although some of the exaltation of the moment (over that of 5-*tert.*-butyl-*m*-xylene, for which $\mu = 0·25$) is certainly due to induction (cf. Le Fèvre, Le Fèvre, and Robertson, this vol., p. 480). We hope to decide this allotment by an examination of trinitrotri-*tert.*-butylbenzene.

Constitution of the tert.*-Butyl-*m*-xylene.*—Since this substance, believed to be (I), was prepared by trinitration of (II), which might have contained some of its unsymmetrical isomeride (III), it was possible that the product was contaminated with (IV), which would

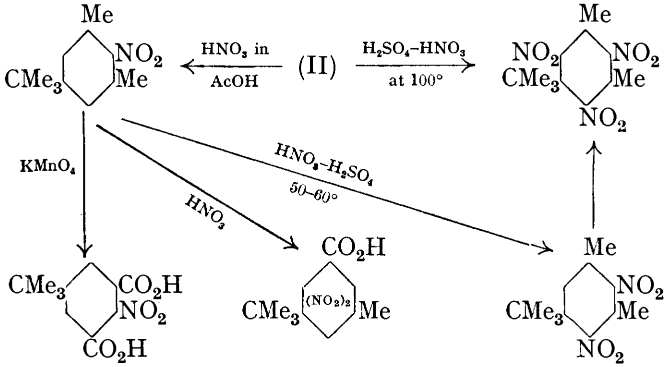

(I.)


(II.)


(III.)


(IV.)

possess a considerable moment in virtue of its *o*-dinitro-groups. The recorded preparations of (II) are from *m*-xylene by either (i) *tert.*-butyl and aluminium chlorides (Baur, *Ber.*, 1891, **24**, 2840) or (ii) *iso*butyl alcohol and concentrated sulphuric acid (Noelting, *Ber.*, 1892, **25**, 791), both of which may give a product of uncertain orientation (cf. Jacobsen, *Ber.*, 1881, **14**, 2624; Bialobrzewski, *Ber.*, 1897, **30**, 1773; Verley, *Bull. Soc. chim.*, 1898, **19**, 67). In these circumstances the isolation of (unstated but evidently small yields of) 3 : 5-dimethylbenzoic, 3-methyl-5-butylbenzoic, and trimesic acids (Baur, *loc. cit.*; *Ber.*, 1898, **31**, 1345) does not suffice to establish the homogeneity of the butylxylene. Baur (*loc. cit.*; *Ber.*, 1900, **33**, 2564) nitrated this hydrocarbon, but only for the mononitro-derivative did he attempt orientation experiments; here again oxidation was employed, the products being given, without discussion, the formulæ shown :



We therefore attempted to assess the purity of (II). This was prepared by Baur's method [(i), above], and fractionated, etc., as closely as possible. Both the step-wise nitrations and the one-stage trinitration of Baur were repeated on a quantitative basis with the material so prepared, the following yields being obtained : Trinitration : 96% crude, 90% recryst. Mononitration : *ca.* 10% recryst. Mononitro- to dinitro-derivative : 90% crude, 85% recryst. Dinitro- to trinitro-derivative : 98% crude, 95% recryst.

We infer that the constitution ascribed by Baur to the trinitro-derivative, m. p. 110°, is correct, because a pure specimen can be heated for several hours in piperidine solution and then recovered quantitatively by dilution with water. Had it possessed the constitution (IV), one of the nitro-groups would undoubtedly have been displaced by piperidine (cf. J., **1927**, 1113); and, because the *crude* trinitro-derivative, subjected to the same process, *also* underwent no change (m. p. and mixed m. p.), we regard the direct trinitration figure as evidence that the hydrocarbon contains at most 4% of the isomeride (III). Such a specimen, after piperidine treatment, was crystallised twice from hot alcohol (forming long, well-developed needles, m. p. 110—111°) and used in the dipole-moment determinations above.

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