687. *Dipole Moments and Molecular Structure. Part III.** *Some Nitro-derivatives of Toluene.*

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The dipole moments of 2 : 4-, 2 : 5-, 2 : 6-, and 3 : 5-dinitrotoluene and 2 : 4 : 6-trinitrotoluene have been measured and the results are used in a discussion of the mechanism of the " activation " of the methyl group in nitrotoluenes. Evidence is presented compatible with the steric suppression of $\overset{+}{\mathrm{Ar}}{=}\overset{+}{\mathrm{N}}\mathrm{O}_2{}^{2-}$ resonance in the 2- and 6-nitro-group in 2 : 6-dinitrotoluene and in 2 : 4 : 6-trinitrotoluene. No evidence has been found for hyperconjugation between the methyl group and the benzene nucleus.

The methyl groups in nitromethane, *p*-nitrotoluene, 2 : 4-dinitrotoluene, and 2 : 4 : 6-trinitrotoluene show many of the properties of active methylene groups: *e.g.*, they condense with benzaldehyde (nitromethane,[1] 2 : 4-dinitro-[2] and trinitro-toluene[3]), and undergo reactions of the Knovenagel–Mannich type with aldehydes and secondary bases (nitromethane,[4] 2 : 4-dinitrotoluene[5]). The effects with trinitrotoluene are in general slightly weaker than those with the other compounds. The methyl groups in 2 : 5-, 2 : 6-, and 3 : 5-dinitrotoluene are not " active."

In this investigation, aimed at the elucidation of the mechanism of the activation of methyl groups in nitrotoluenes, the atom polarisation terms for *p*-dinitrobenzene and *s*.-trinitrobenzene have been evaluated and the dipole moments of 2 : 4-, 2 : 5-, 2 : 6-, and 3 : 5-dinitrotoluene and of 2 : 4 : 6-trinitrotoluene in dilute solution have been determined.

Experimental

Preparation of Materials.—" AnalaR " benzene and dioxan (purified) were frozen four times, refluxed, respectively, over phosphoric oxide and with sodium, and distilled in a stream of dry air immediately before use.

p-Dinitrobenzene (from Hopkin and Williams), recrystallised from ethyl alcohol, had m. p. 173° (Starkey[6] gives m. p. 173°).

2 : 4-Dinitrotoluene (from B.D.H.), recrystallised from acetone, had m. p. 69·0—70° (Garner and Abernethy[7] give m. p. 70·5°).

The 2 : 5-isomer (from Hopkin and Williams), recrystallised from benzene, had m. p. 51—52° (lit.,[7] m. p. 51·2°).

The 2 : 6-isomer (from Kahlbaum), recrystallised from acetone, had m. p. 64·5—65·5° (lit.,[7] m. p. 64·3°).

The 3 : 5-isomer was prepared from *p*-acetamidotoluene by the method of Cohen and McCandlish,[8] and recrystallised from ethyl alcohol; it had m. p. 93° (Cohen and McCandlish[8] give m. p. 92—93°).

2 : 4 : 6-Trinitrotoluene,[9] recrystallised from acetone, had m. p. 81° (Garner and Abernethy[7] give m. p. 81·1°).

s.-Trinitrobenzene, prepared from trinitrotoluene by oxidation and decarboxylation (Clark and Hartman[10]) and recrystallised from acetic acid, had m. p. 122° (lit.,[10] m. p. 121—122°).

Determination of Dipole Moments.—These were made in solution at 25° by the refractivity method, the heterodyne technique being used for measurement of the dielectric constant, as

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* Part II, *J.*, 1957, 188.

[1] Worrall, *Org. Synth.*, Coll. Vol. I, 1948, p. 413.
[2] Thiele and Escale, *Ber.*, 1901, **34**, 2842.
[3] Pfeiffer and Monath, *Ber.*, 1906, **39**, 1306.
[4] Hope and Robinson, *J.*, 1910, **97**, 2114.
[5] McLeod and Robinson, *J.*, 1921, **110**, 1470.
[6] Starkey, *Org. Synth.*, Coll. Vol. II, 1943, p. 225.
[7] Garner and Abernethy, *Proc. Roy. Soc.*, 1921, *A*, **99**, 213.
[8] Cohen and McCandlish, *J.*, 1905, **87**, 1271.
[9] Stettbacher, " Schiess- und Sprengstoffe," Barth, Leipzig, 1933, p. 261.
[10] Clark and Hartman, *Org. Synth.*, Coll. Vol. I, 1948, p. 541.

described in Parts I [11] and II.[12] Parallel determinations in benzene and in dioxan solution were made on all the substances to minimise the risk of not detecting solvent–solute interactions between benzene and the nitro-compounds. The agreement between the dipole results obtained with the two solvents showed that nothing anomalous was happening in the benzene solutions, and the benzene values are used in the theoretical discussions, because the non-polar benzene is, from the point of view of dielectric-constant studies, the more satisfactory solvent.

The results are given in Table 1 (e = dielectric constant).

TABLE 1.

w	*e*	*v*	*n*	*w*	*e*	*v*	*n*
p-*Dinitrobenzene* (*M*, 168·108) : *in benzene*				*in* 1 : 4-*dioxan*			
0·015720	2·2865	1·13481	1·50270	0·012998	2·226	0·96674	1·4236
0·020080	2·2875	1·13225	1·50285	0·016181	2·228	0·96572	1·42385
0·026182	2·2905	1·12979	1·50330	0·024811	2·234	0·96348	1·4252
0·029326	2·2925	1·12803	1·50340	0·037980	2·2425	0·95988	1·4268
s.-*Trinitrobenzene* (*M*, 213·108) : *in benzene*				*in* 1 : 4-*dioxan*			
0·025615	2·287	1·1313	1·5039	0·017010	2·234	0·9675	1·4249
0·039391	2·292	1·1243	1·5046	0·032925	2·243	0·9612	1·4270
0·057245	2·299	1·1139	1·5059	0·036907	2·245	0·9603	1·4270
0·058267	2·300	1·1138	1·5057				
2 : 4-*Dinitrotoluene* (*M*, 182·122) : *in benzene*				*in* 1 : 4-*dioxan*			
0·020229	2·504	1·1364	1·5040	0·010975	2·368	0·9707	1·4241
0·032259	2·641	1·1311	1·5045	0·019742	2·480	0·9682	1·4251
0·048703	2·832	1·1240	1·5053	0·038493	2·746	0·9640	1·4275
0·061784	2·987	1·1183	1·5059	0·058187	3·014	0·9585	1·4299
2 : 5-*Dinitrotoluene* (*M*, 182·134) : *in benzene*				*in* 1 : 4-*dioxan*			
0·0071692	2·280	1·1389	1·50235	0·021480	2·238	0·96479	1·42453
0·014012	2·286	1·1358	1·5027	0·031209	2·2465	0·92642	1·42692
0·021211	2·291	1·1332	1·5030	0·038625	2·253	0·96071	1·42687
0·021940	2·292	1·1318	1·5030	0·057011	2·269	0·95566	1·42934
0·030508	2·299	1·1290	1·5034				
2 : 6-*Dinitrotoluene* (*M*, 182·122) : *in benzene*				*in* 1 : 4-*dioxan*			
0·022776	2·383	1·1356	1·5035	0·021190	2·340	0·9680	1·4255
0·032460	2·432	1·1314	1·5039	0·040131	2·435	0·9590	1·4275
0·047751	2·513	1·1249	1·5045	0·060030	2·579	0·9584	1·4296
0·051291	2·530	1·1232	1·5047				
3 : 5-*Dinitrotoluene* (*M*, 182·134) : *in benzene*				*in* 1 : 4-*dioxan*			
0·007920	2·364	1·13880	1·5022	0·029211	2·558	0·96302	1·4259
0·01084	2·394	1·13766	1·5024	0·035314	2·670	0·96126	1·42636
0·02083	2·511	1·13317	1·5028	0·052210	2·883	0·95693	1·42886
0·02930	2·610	1·12932	1·5032	0·057901	2·964	0·95557	1·4296
				0·061075	3·000	0·95492	1·42997
2 : 4 : 6-*Trinitrotoluene* (*M*, 227·124) : *in benzene*				*in* 1 : 4-*dioxan*			
0·029045	2·306	1·1312	1·5033	0·022650	2·269	0·9674	1·4246
0·045990	2·323	1·1232	1·5041	0·031543	2·277	0·9644	1·4258
0·064720	2·344	1·1138	1·5051	0·035166	2·280	0·9633	1·4261
0·082530	2·362	1·1046	1·5063	0·047543	2·297	0·9591	1·4281

The derived data on the extrapolations of e, v, and n to $w = 0$ and the corresponding slopes α, β, and γ are given in Table 2, together with the molar total and electronic polarisation terms. These are evaluated from the slopes α, β, and γ, by using the expressions: [12]

$$\begin{aligned} {}_{\mathrm{T}}P_2 &= M(0{\cdot}34110 + 0{\cdot}18818\alpha + 0{\cdot}29787\beta) \text{ for benzene solutions} \\ &= M(0{\cdot}28124 + 0{\cdot}16388\alpha + 0{\cdot}28910\beta) \text{ for dioxan solutions} \end{aligned}$$

and

$$\begin{aligned} {}_{\mathrm{E}}P_2 &= M(0{\cdot}33797 + 0{\cdot}29513\beta + 0{\cdot}56986\gamma) \text{ for benzene solutions} \\ &= M(0{\cdot}24782 + 0{\cdot}25475\beta + 0{\cdot}51263\gamma) \text{ for dioxan solutions} \end{aligned}$$

Aromatic polynitro-compounds show rather high atom polarisation (${}_{\mathrm{A}}P_2$) terms.[13] The polarisations at radio frequency and at visible frequency of *p*-dinitrobenzene were measured

[11] Springall, Hampson, May, and Spedding, *J.*, 1949, 1524.

[12] Mortimer, Spedding, and Springall, *J.*, 1957, 188.

[13] Sutton, *Ann. Reports*, 1940, **37**, 63; *Discuss. Faraday Soc.*, 1946, 170.

in both benzene and dioxan; the average difference (12·3 c.c.) for this non-polar substance was taken as that part of the atom polarisation, $_{A}P'_{2}$, neglected in visible-frequency measurements, and this value used for the " neglected " atom polarisation term for dinitrotoluenes. (This procedure is likely to be quite valid for 2 : 5-dinitrotoluene, where the nitro-groups are *para* to one another; but may give a slight overestimate of the $_{A}P'_{2}$ terms for the 2 : 4-, 2 : 6-, and 3 : 5-isomer, where the nitro-groups are *meta* to one another. The derived values of the dipole moments of the last compounds are therefore lower limit values. The possible error so introduced is, however, too small to affect the general conclusions.)

Similar measurements were made on *s.*-trinitrobenzene and the correspondingly derived " neglected " atom polarisation term of 10·9 c.c. was used with trinitrotoluene.

TABLE 2.

No.	Compound	Solvent	e_1'	α	v_1'
1	*p*-Dinitrobenzene	Benzene	2·277	0·572	1·1423
		Dioxan	2·218	0·690	0·9704
2	2 : 4-Dinitrotoluene	Benzene	2·277	11·624	1·1452
		Dioxan	2·214	13·763	0·9734
3	2 : 5-Dinitrotoluene	Benzene	2·276	0·768	1·1426
		Dioxan	2·220	0·870	0·9703
4	2 : 6-Dinitrotoluene	Benzene	2·274	5·178	1·1454
		Dioxan	2·210	6·154	0·9732
5	3 : 5-Dinitrotoluene	Benzene	2·268	11·660	1·1429
		Dioxan	2·202	13·186	0·9705
6	*s.*-Trinitrobenzene	Benzene	2·277	0·392	1·1455
		Dioxan	2·225	0·556	0·9737
7	2 : 4 : 6-Trinitrotoluene	Benzene	2·275	1·055	1·1459
		Dioxan	2·232	1·133	0·9749

No.	β	n_1'	γ	$_{T}P_{2}$	$_{E}P_{2}$	$_{A}P'_{2}$	μ
1	−0·437	1·5018	0·0562	53·55	40·59	12·96	0
	−0·272	1·4217	0·1314	53·08	41·34	11·74	0
2	−0·435	1·5029	0·050	437·8	43·3	12·3	4·33
	−0·254	1·4228	0·122	448·6	44·7	12·3	4·38
3	−0·428	1·5020	0·0470	63·24	43·42	12·3	0·58
	−0·254	1·4217	0·133	64·71	45·77	12·3	0·57
4	−0·432	1·5026	0·040	216·5	42·5	12·3	2·81
	−0·246	1·4230	0·114	221·9	43·4	12·3	2·85
5	−0·435	1·5019	0·0450	438·16	42·84	12·3	4·33
	−0·257	1·4219	0·133	442·17	45·63	12·3	4·33
6	−0·546	1·5025	0·060	54·8	44·9	9·9	0
	−0·370	1·4229	0·120	56·6	44·8	11·9	0
7	−0·498	1·5018	0·0525	88·9	50·2	10·9	1·16 *
	−0·331	1·4217	0·130	84·3	53·0	10·9	1·0 †

* μ for trinitrotoluene in benzene was measured by Le Fèvre and Le Fèvre (*J.*, 1950, 1829) with the results : $_{T}P_{2} = 87{\cdot}2$; $_{E}P_{2} = 48{\cdot}7$; $_{T}P_{2} - {}_{E}P_{2} = 38{\cdot}5$. Our $_{T}P_{2} - {}_{E}P_{2}$ $(= 38{\cdot}7)$ is almost identical with Le Fèvre and Le Fèvre's value, but where we allow the extra 11 c.c. for the $_{A}P'_{2}$ term (yielding a moment = 1·16 D) Le Fèvre and Le Fèvre proceed directly from $_{T}P_{2} - {}_{E}P_{2}$ to the evaluation of the dipole moment and so obtain the value 1·37 D.

† The moment of trinitrotoluene was determined in carbon tetrachloride solution also, and μ = 1·26 D obtained as the result, indicating absence of unexpected solvent effect. Owing, however, to the extremely low solubility in the solvent the result is not of high accuracy and the experimental details are not tabulated.

The dipole moments are evaluated by the Debye expression

$$\mu_{25} = 0{\cdot}2211\sqrt{({}_{T}P_{2} - {}_{E}P_{2} - {}_{A}P'_{2})}\ \text{D}$$

As a further check on the behaviour of trinitrotoluene in benzene solution, the non-existence of a chemical compound between solute and solvent was shown by a freezing-point diagram of the trinitrotoluene–benzene system, which (Fig. 1) shows the typical " single discontinuity–no maximum " form expected for a two-component, single-liquid phase system without compound formation.

DISCUSSION

The dipole moments of the simpler mononitroalkanes $R{\cdot}NO_2$ in solution are as follows: R = Me,[14] 3·1 D; Et,[15] 3·2 D; Bu^t, 3·3 D.[16] The general agreement among these results

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[14] Weissberger and Sängewald, *Ber.*, 1932, **65**, 701.

[15] Hunter and Partington, *J.*, 1933, 309.

[16] Sutton, *Trans. Faraday Soc.*, 1934, **30**, 789.

indicates that there are no mesomeric interaction moments of the hyperconjugation type $\overset{\mathrm{H}+}{\mathrm{C}}\mathrm{H}{=}\overset{+}{\mathrm{N}}\mathrm{O}_2^{2-}$ operating with R = Me or Et. This is also shown by the fact that the C–N bond length in nitromethane has the value $1{\cdot}47 \pm 0{\cdot}02$ Å [17, 18] characteristic of a C–N single bond.[19] The slight variation in the moments is probably due to induction effects and we take the value for $\mathrm{Bu^t{-}NO_2}$ (3·3 D) as being the true $\mathrm{C_{alk}{-}NO_2}$ moment in solution.

In nitrobenzene, however, the extra resonance effect due to contribution from ionic structures of the type $\overset{+}{\mathrm{A}}\mathrm{r} = \overset{+}{\mathrm{N}}\mathrm{O}_2^{2-}$ causes an increase in the moment to 3·94 D,[16, 20] and tends to constrain the $\mathrm{Ar{\cdot}NO_2}$ system to a planar configuration because of C=N double bonding. If, in this system, the nitro-group is forced by bulky *ortho*-substituents to rotate about the C–N bond, the oxygen atoms leaving the plane of the benzene ring, the extra resonance is impaired and the corresponding $\mu(\mathrm{C{-}NO_2})$ is reduced from $\mu(\mathrm{C_{ar}{-}NO_2})$ towards $\mu(\mathrm{C_{alk}{-}NO_2})$. This effect has been investigated (i) in nitrodurene and allied compounds by dipole moments,[21] (ii) in nitromesitylene by dipole moments [22] and Raman spectra,[23] and (iii) in 4-dimethylamino-2-methyl-1-nitrobenzene and in 5-dimethylamino-1 : 3-dimethyl-2-nitrobenzene by ultraviolet absorption spectra.[24]

Fig. 1.

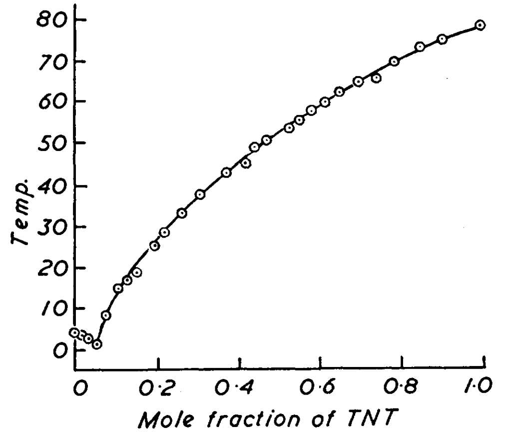
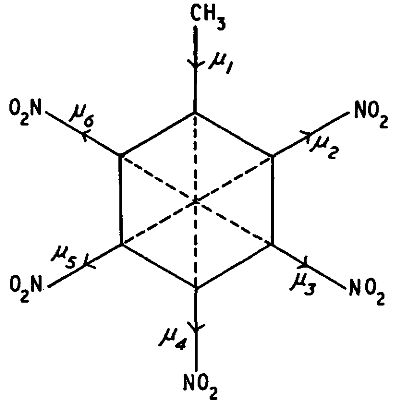
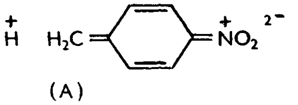


Fig. 2.



The results indicate strong steric suppression of the $\overset{+}{\mathrm{A}}\mathrm{r}{=}\overset{+}{\mathrm{N}}\mathrm{O}_2^{2-}$ resonance when both positions next to the nitro-group have methyl substituents but only weak steric effects with only one *ortho*-substituent.



(A)

In view of the above findings, we may expect with the nitrotoluenes, (*a*) no mesomeric interaction moments of type (A) and (*b*) some steric suppression of the $\overset{+}{\mathrm{A}}\mathrm{r}{=}\overset{+}{\mathrm{N}}\mathrm{O}_2^{2-}$ resonance with nitro-groups adjacent to the methyl group. The suppression is likely to be weak when only one of the *ortho*-positions is substituted by a nitro-group but strong when both are so substituted.

(a) *Mononitrotoluenes*. The dipole moments of *o*-, *m*-, and *p*-mononitrotoluene [25] are susceptible to a simple approximate vector analysis if absence of mesomeric interaction moments is assumed and induction effects are neglected. In Table 3 are listed (i) the

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[17] Brockway, *Rev. Mod. Phys.*, 1936, **8**, 231.

[18] Rogowski, *Ber.*, 1942, **75**, 244.

[19] Pauling, " The Nature of the Chemical Bond," Cornell Univ. Press, Ithaca, 1941, p. 167.

[20] Williams, *Phys. Z.*, 1928, **29**, 174; see also Jenkins, *J.*, 1934, 480.

[21] Birtles and Hampson, *J.*, 1937, 10.

[22] Hammick, New, and Williams, *J.*, 1934, 30.

[23] Saunders, Murray, and Cleveland, *J. Amer. Chem. Soc.*, 1941, **63**, 3121.

[24] Remington, *ibid.*, 1945, **67**, 1841.

[25] Williams, *Phys. Z.*, 1928, **29**, 683.

values of the resultant moments $\bar{\mu}$ calculated on the simple regular hexagon molecular model (Fig. 2) with the assumption that $\mu_1 = 0{\cdot}41$ (the toluene moment[26]) and (*a*) $\overset{+}{\mathrm{Ar}}{=}\overset{+}{\mathrm{N}}\mathrm{O}_2^{2-}$ resonance operating [$\mu(\mathrm{C{-}NO_2}) = 3{\cdot}94$ D] and (*b*) this resonance suppressed [$\mu(\mathrm{C{-}NO_2}) = 3{\cdot}30$ D)], and (ii) the observed resultant moments.

TABLE 3.

	$\bar{\mu}_{calc.}$				$\bar{\mu}_{calc.}$		
	a	*b*	$\bar{\mu}_{obs.}$		*a*	*b*	$\bar{\mu}_{obs.}$
	Mononitrotoluenes				*Dinitrotoluenes*		
o-	3·75	3·14	3·75	2 : 4-	4·16	3·92	4·33
m-	4·16	3·53	4·20	2 : 5-	0·41	0·93	0·58
p-	4·35	3·71	4·50	2 : 6-	3·53	2·89	2·81
2 : 4 : 6-*Trinitrotoluene*				3 : 5-	4·35	4·35	4·33
	0·41	1·05	1·16				

The agreement between $\bar{\mu}_{calc.}$ (*a*) and $\bar{\mu}_{obs.}$ is in accordance with the expectations suggested by the general theory.

The dipole moments of 2 : 4-, 2 : 5-, 2 : 6-, and 3 : 5-dinitrotoluene and of trinitrotoluene were subjected to a similar analysis.

(b) *Dinitrotoluenes.* The results with the mononitrotoluenes encouraged the use of vector models with $\mu_1 = 0{\cdot}41$ D and $\mu_3 = \mu_4 = \mu_5 = 3{\cdot}94$ D. Alternative models were investigated dependent on the setting of μ_2 and μ_6, either (*a*) 3·94 D or (*b*) 3·30 D.

In the results (Table 3) the moderately good agreement between $\bar{\mu}_{calc.}$ (*a*) and $\bar{\mu}_{obs.}$ for 2 : 4- and 2 : 5-dinitrotoluene, and the good agreement between $\bar{\mu}_{calc.}$ (*b*) and $\bar{\mu}_{obs.}$ for the 2 : 6-compound again are in accordance with the expectations. The calculated resultant moment of the 3 : 5-compound is unaffected by (*a*) or (*b*) hypotheses as to μ_2 and μ_6; agreement with observation here too is good.

[Hardung[27] has reported, without experimental details, the measurement of the dipole moments of all six dinitrotoluenes in benzene solution. His results for the 2 : 4-, 2 : 5-, 2 : 6-, and 3 : 5-isomer are respectively 3·75, 0·94, 2·95, and 4·05 D. His aim was to correlate the reactivity of the methyl group with the difference between the calculated and the observed moments. He attributed any such difference to a change in the moment of the $\mathrm{CH_3{-}C}$ grouping, and stated that the correlation was, on the whole, as expected. The most striking discrepancy was with the 2 : 4-isomer (Hardung's experimental result for this compound differs markedly from ours) but the 2 : 5-isomer yields an anomalous result also.]

(c) 2 : 4 : 6-*Trinitrotoluene.* In view of the results with the mono- and dinitrotoluenes, two vector models only were considered : (*a*) using $\mu_1 = 0{\cdot}41$, $\mu_2 = \mu_4 = \mu_6 = 3{\cdot}94$ D; (*b*) using $\mu_1 = 0{\cdot}41$, $\mu_2 = \mu_6 = 3{\cdot}30$, and $\mu_4 = 3{\cdot}94$ D; model (*b*) is the more likely. The results are given in Table 3. The agreement between $\bar{\mu}_{calc.}$ (*b*) and $\bar{\mu}_{obs.}$ again is in accordance with expectations.

The results are compatible with the effects on $\overset{+}{\mathrm{Ar}}{=}\overset{+}{\mathrm{N}}\mathrm{O}_2^{2-}$ resonance summarised in Table 4.

TABLE 4. $\overset{+}{\mathrm{Ar}}{=}\overset{+}{\mathrm{N}}\mathrm{O}_2^{2-}$ *resonance effects* (+ = *operative*; S = *suppressed*).

Posn. of NO_2	MNT	2 : 4-DNT	2 : 5-DNT	2 : 6-DNT	3 : 5-DNT	TNT
2-	+	+	+	S		S
3-	+				+	
4-	+	+				+
5-	+		+		+	
6-	+			S		S

This analysis lends support to the views: (i) that hyperconjugated ionic structures, involving the methyl group, are unlikely to contribute significantly to the resting structures

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[26] Tiganik, *Z. phys. Chem.*, 1931, **13**, *B*, 425.

[27] Hardung, *Helv. Phys. Acta*, 1947, **20**, 1470; 1948, **21**, 445.

of the nitrotoluenes, the difference between the moments of toluene and trinitrotoluene being attributable to the steric lowering of the 2- and 6-NO_2 moments rather than to any mesomeric increase in the CH_3–C moment; (ii) that it is possible to correlate activity of the methyl group in nitrotoluenes with the extent to which excited $\overset{+}{A}r{=}\overset{+}{N}O_2^{2-}$ structures having the nuclear cationic charge located on the methyl-bearing $C_{(1)}$ atom, contribute to the molecule.* The activity is potentially strong in compounds in which the nitro-groups are in the 2-, 4-, or 6-position but is weakened by the steric suppression of $\overset{+}{A}r{=}\overset{+}{N}O_2^{2-}$ structures in the 2 : 6-dinitrotoluene system. Direct steric shielding of the methyl group by 2- and 6-nitro-groups probably assists in the depression of activity.

We are indebted to Drs. G. S. Davy and D. C. C. Smith for assistance with some of the work on the trinitrobenzene–benzene diagram, to Mr. B. C. Jones for polarisation measurements on *p*-dinitrobenzene and on 2 : 5- and 3 : 5-dinitrotoluene, and to Albright and Wilson Limited for a grant.

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[*Received, January 28th*, 1957.]

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* It may be noted that the very reactive methyl group in nitromethane is directly bonded to a cationic " ammonium " nitrogen atom.