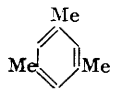
545. *The Ultra-violet Spectra of Certain Substituted Aromatic Nitro-compounds.*

By P. Fielding and R. J. W. Le Fèvre.

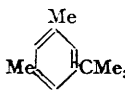
Comparison of the ultra-violet absorption spectra of trinitromesitylene and trinitro-*tert.*-butylxylene with those of mono-, di-, and tri-nitrobenzenes reveals in the first two a diminution of intensity and wave-length of the 260 mμ. (log ε, 3·9) band attributable to the Ar·NO_2 system. An explanation based on the steric inhibition of resonance is in line with previous data in the literature.

In a recent communication (*J.*, 1950, 1829) Le Fèvre and Le Fèvre compared *inter alia* the dipole moments of the hydrocarbons (I)—(III) with those of their symmetrical trinitro-derivatives (IV)—(VI). The apparent orientation polarisation of (VI) was found to exceed that of (III) by 25 c.c., while the corresponding disparities between (IV) and (I), and between (V) and (II) were

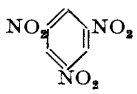
(I.) μ = *ca.* 0D.



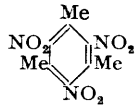
(II.) μ = 0·24D.



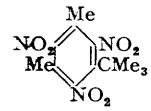
(III.) μ = 0·25D.



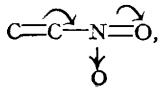
(IV.) μ = 0·68D.



(V.) μ = 0·74D.



(VI.) μ = 1·13D.

both only *ca.* 10 c.c. Trinitration therefore affects polarity most in the case of *tert.*-butylxylene and causes, from (III) to (VI), a change of $\mu_{apparent}$ which is unexpectedly great (cf. Coop and Sutton, *J.*, 1938, 1269). Of the possible reasons for this, those implicit in the phrase "steric inhibition of resonance" seemed applicable, in view of the greater space requirements of CMe_3 than of Me. Scale drawings (such as Figs. 1 and 2 of *J.*, 1935, 957) show overlap between the "*X*-ray" dimensions of *tert.*-butyl and those of two vicinal nitro-groups, while when methyl replaces butyl the interference involves only the "Wirkungsradien." In (VI) therefore, of the three nitro-groups, that *para* to CMe_3 should be least prevented from polarising in the sense  , and—because of this—could outweigh in the molecular resultant the vector sum of the components associated with the other two (less polarised) nitro-substituents.

Such opposition by steric factors to the assumption of planar configurations may be displayed in the ultra-violet absorption spectra of the substances concerned (Remington, *J. Amer. Chem. Soc.*, 1945, **67**, 1838, among others, has set out the qualitative explanation of the variations of wave-length and intensity to be expected between parent structures and their "hindered" derivatives; cf. also Wheland, "The Theory of Resonance," Wiley & Sons, 1944, pp. 160—162). Sherwood and Calvin (*J. Amer. Chem. Soc.*, 1942, **64**, 1350) and Remington (*loc. cit.*) had noted the weakening of the characteristic nitro-absorption band at 2500—2600 by *o*-Me, and Brown and Reagan (*ibid.*, 1947, **69**, 1032) have lately demonstrated that the effect becomes progressively greater as the volume of the *ortho*-hydrocarbon radical is increased.

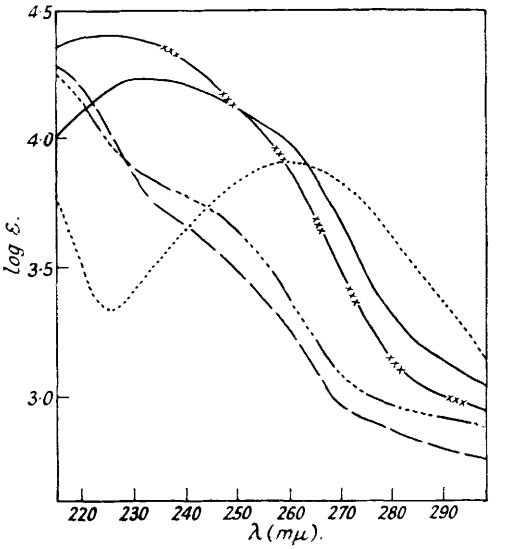
Present Work.—In view of its obvious relevance we have applied the method to structures (IV), (V), and (VI), nitro- and *m*-dinitro-benzene being included for comparison. Absorption determinations were made with the "Beckman photoelectric quartz spectrophotometer, Model DU." Our solvent has been 96% alcohol throughout (Brown and Reagan used *iso*octane).

Results are shown in the figure; details of the clear maxima read from the large-scale originals are tabulated below.

Solute.	$\lambda_{max.}$ (mμ.).	log $\varepsilon_{max.}$
Nitrobenzene	260	3·91
m-Dinitrobenzene	235	4·24
s-Trinitrobenzene	225	4·41
s-Trinitromesitylene	Below 220	Above 4·2
Trinitro-*tert.*-butylxylene	Below 220	Above 4·2

We note that our curve for nitrobenzene in ethyl alcohol agrees with that of Brown and

Reagan (*loc. cit.*; $\lambda_{max.} = 2520$, $\varepsilon_{max.} = 8620$, in *iso*octane). Dinitro- and trinitro-benzenes show slight " shoulders " suggestive of maxima just below 260 mμ., with intensities indicated by log ε values *ca.* 4; with the mesitylene and butylxylene derivatives the corresponding points appear to lie in the region 240—250 mμ. with log ε about 3·2, the butyl compound being the lower. The spectra of the last two substances resemble somewhat those obtained for nitromesitylene and *o*-nitro-*tert.*-butylbenzene by Brown and Reagan. Following these authors we recognise the " shoulders " in the figure as residual 260-mμ. nitro-group absorptions whose positions and intensities indicate reduction or otherwise of resonance conferring a partial double-bond character on the Ar-nitro-link. In this respect therefore mono-, di-, and trinitrobenzenes are approximately equally unaffected, while in compounds (V) and (VI) such resonance is diminished. The broad short-wave maxima of the di- and tri-nitrobenzenes may accordingly be viewed as *E*-bands, displaced towards lower frequencies.



The spectra of the last two substances do not appear to have been much investigated. Rădulescu and Elexa (*Bul. Soc. chim. Romania*, 1935, **17**, 69; *Chem. Abs.*, 1936, **30**, 2111) report certain measurements in absolute alcohol and 0·2N-ethyl-alcoholic sodium ethoxide, but the abstract does not record quantitative data, and the original is not available to us. Kortüm (*Z. physikal. Chem.*, 1939, *B*, **42**, 39) shows graphically, for nitrobenzene and *m*-dinitrobenzene in water and *s*-trinitrobenzene in 10^{-3}N-hydrochloric acid, absorptions at *ca.* 270 mμ. (log ε, 3·9), *ca.* 220 mμ. (log ε, 4·2), and below 230 mμ. (log ε, above 4·4), respectively. His results and ours, therefore, despite the change of solvent, are not very dissimilar.

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