665. *Ultraviolet and Infrared Spectra of Some Aromatic Nitro-compounds.*

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The ultraviolet and infrared spectra of a series of mono-, di-, and tri-nitro-benzenes and -toluenes have been examined and are interpreted in terms of polar and steric effects. The results yield useful structural correlations for the number and position of substituents in polynitro-aromatic compounds.

SPECTRAL characteristics of the nitro-group in aromatic compounds have often been reported. Doub and Vandenbelt [1] examined a number of nitro-compounds but found no correlations with the ultraviolet spectra of other substituted benzenes. Forbes [2] discussed the part played by polar effects in the electronic spectra of mononitrobenzenes, and there is evidence of steric hindrance in alkylnitrobenzenes.[3,4] In the infrared region the asymmetric stretching vibration has been shown to be sensitive to the electronic properties of other substituents,[5,6] and in sterically hindered compounds polarised infrared studies have demonstrated the rotation of the nitro-group out of the plane of the benzene ring.[7] *X*-Ray work confirms this also for some nitroanthracenes.[8]

Little work has been carried out on polynitrobenzenes.[9] In the present investigation the ultraviolet and infrared spectra of the complete isomeric series of di- and tri-nitro-benzenes and -toluenes have been examined to obtain structural correlations in this class of compound. In particular, steric effects were expected to influence the spectra following the recent observations of Wepster and his co-workers.[10]

EXPERIMENTAL

Ultraviolet Spectra.—The compounds were purified by distillation or crystallisation as appropriate. Weighed amounts (15—30 mg.) were dissolved in 50 ml. of absolute ethanol, and 5 ml. of this solution were diluted to 100 ml. with water. The spectra were measured on a Unicam S.P. 500 spectrophotometer in 10 mm. quartz cells against 5% ethanol–water mixture. Cell corrections were applied to all measurements.

Infrared Spectra.—The measurements were made in chloroform (10—30 mg. in 5 ml. of solvent) on a Grubb-Parsons S3A double-beam prism spectrometer. Rock-salt cells of 0·0251 cm. path length were employed. Each spectrum was scanned from 6 to 8 μ at a constant slit width of 0·2 mm. The frequency values obtained are considered to be accurate to ± 2 cm.$^{-1}$.

The integrated intensities were calculated by use of Ramsay's formula $I = (K\Delta\nu/cl) \ln I_0/I_{\text{max.}}$, where c = molar concentration, l = path length in cm., $\Delta\nu$ = half-intensity band width in cm.$^{-1}$, $\ln I_0/I_{\text{max.}}$ = peak optical density, and K = constant. Ramsay [11] gives values of K for various instrumental conditions but in this work it was taken as 1·56 throughout, the value of $\ln I_0/I_{\text{max.}}$ being kept near to 1·2.

In cases where the nitro-group bands were overlapped by others or by splitting of the nitro-frequencies themselves, graphical resolution was employed, and the frequencies, intensities, and band-widths were calculated for the resolved components. The last two quantities are probably correct to $\pm 5\%$.

[1] Doub and Vandenbelt, *J. Amer. Chem. Soc.*, (*a*) 1947, **69**, 2714; (*b*) 1949, **71**, 2412; (*c*) 1955, **77**, 4535.

[2] Forbes, *Canad. J. Chem.*, 1958, **36**, 1350.

[3] Fielding and Le Fèvre, *J.*, 1950, 2812; Brown and Reagan, *J. Amer. Chem. Soc.*, 1947, **69**, 1032; Remington, *ibid.*, 1945, **67**, 1838.

[4] Sherwood and Calvin, *ibid.*, 1942, **64**, 1350.

[5] Brown, *ibid.*, 1955, **77**, 6841.

[6] Kross and Fassel, *ibid.*, 1956, **78**, 4225.

[7] Francel, *ibid.*, 1952, **74**, 1265.

[8] Trotter, *Canad. J. Chem.*, 1959, **37**, 351.

[9] Francke, Hörman, and Schiebe, *Chem. Ber.*, 1957, **90**, 330.

[10] Wepster, *Rec. Trav. chim.*, 1957, **76**, 335; Van Veen, Verkade, and Wepster, *ibid.*, p. 801.

[11] Ramsay, *J. Amer. Chem. Soc.*, 1952, **74**, 72.

RESULTS

Ultraviolet Spectra.—The absorption curves consisted mainly of a single intense maximum lying in the range 210—280 mμ, with one or more inflexions on the long-wavelength side. For the interpretation of the results it was necessary to identify corresponding bands in the various

TABLE 1.

Compound	$\lambda_{max.}$ (mμ)	$\nu_{max.}$ (cm.$^{-1}$)	Peak intensity (l. mole^{-1} cm.$^{-1}$)
Nitrobenzene	269·0	37,180	7,700
o-Dinitrobenzene	<210·0	>47,600	—
m- ,,	242·0	41,300	16,580
p- ,,	265·0	37,740	14,400
o-Nitrotoluene	265·0	37,740	5,500
m- ,,	274·0	36,500	7,300
p- ,,	283·5	35,260	9,220
2,3-Dinitrotoluene	<210·0	>47,600	—
2,4- ,,	252·0	39,700	14,100
2,5- ,,	266·5	37,510	11,600
2,6- ,,	241·0	41,500	8,980
3,4- ,,	219·0	45,690	10,040
3,5- ,,	248·0	40,300	12,020
1,2,4-Trinitrobenzene	235·0	42,530	15,440
1,3,5- ,,	227·0	44,070	12,500
2,3,4-Trinitrotoluene	238·5	41,190	12,340
2,3,5- ,,	238·5	41,190	17,440
2,3,6- ,,	258·0	38,760	8,960
2,4,5- ,,	237·0	42,190	14,040
2,4,6- ,,	232·0	43,100	18,620
3,4,5- ,,	242·0	41,300	16,720

TABLE 2.

	Band frequencies (cm.$^{-1}$)		Integrated intensities per NO_2 group *		Band widths (cm.$^{-1}$)	
Compound	ν_a	ν_s	$10^{-4}I_a$	$10^{-4}I_s$	$\Delta\nu_a$	$\Delta\nu_s$
Nitrobenzene	1534	1348	2·72	1·86	11·4	8·0
o-Nitrotoluene	1530	1349	2·85	1·90	13·8	15·4
m- ,,	1535	1350	2·71	1·89	11·9	8·1
p- ,,	1527	1346	2·45	2·25	10·9	7·1
o-Ethylnitrobenzene	1531	1352	2·59	2·13	16·5	19·3
p- ,,	1522	1348	2·53	2·28	20·0	10·0
o-Nitrobiphenyl	1534	1360	3·00	1·32	15·6	21·4
o-Nitroaniline	1516	1346	2·44	1·92	13·3	10·5
p- ,,	1509	1336	2·84	3·74	17·7	10·1
o-Nitrobenzaldehyde	1536	1348	2·90	1·95	16·6	12·7
p- ,,	1537	1347	2·64	1·86	17·5	13·9
o-Chloronitrobenzene	1540	1358	2·70	1·76	15·4	22·9
3-Nitro-4-t-butylaniline	—	1372	—	—	—	16·6
o-Nitro-t-butylbenzene	—	1375	—	—	—	16·3
o-Dinitrobenzene	1546	1368, 1350	3·59	1·71	17·6	18·0, 15·4
m- ,,	1542	1347	2·34	1·79	13·3	8·4
p- ,,	1542	1340	2·46	1·92	11·0	11·5
2,3-Dinitrotoluene	1552	1364, 1346	2·95	1·45	16·4	17·3, 13·1
2,4- ,,	1540	1348	2·10	1·80	15·0	12·1
2,5- ,,	1550	1346	2·76	1·64	18·0	12·6
2,6- ,,	1540	1363, 1348	2·68	1·78	17·8	26·8, 20·0
3,4- ,,	1548	1360, 1346	2·99	1·70	17·6	22·9, 13·1
3,5- ,,	1546	1356, 1341	2·18	1·68	12·9	12·6, 8·4
2,4-Dinitro-1-t-butylbenzene	1539	1372, 1352	3·18	2·37	25·3	16·3, 16·3
1,2,4-Trinitrobenzene	1562	1348	2·33	1·06	17·1	13·0
1,3,5- ,,	1557	1344	2·39	1·48	12·8	8·6
2,3,4-Trinitrotoluene	1572, 1558	1360, 1347	3·47	1·26	12·0, 28·4	16·3, 13·5
2,3,5- ,,	1563, 1549	1354, 1344	2·72	1·08	17·3, 12·3	10·3, 9·8
2,3,6- ,,	1573, 1557	1358, 1351	3·05	1·31	15·4, 14·8	22·4, 9·1
2,4,5- ,,	1566	1371, 1348	3·02	1·28	24·6	13·3, 18·4
2,4,6- ,,	1558	1354	2·70	1·36	16·4	14·0
3,4,5- ,,	1579, 1567	1369, 1350	2·90	1·26	16·0, 12·3	20·8, 15·6
2,4,6-Trinitrophenol	1554	1347	2·23	1·69	29·4	13·2

* Calculated from the total intensity of the doublet in the cases where splitting occurs.

spectra. Following Vandenbelt,[1a] we considered only the most intense maxima, and these are assumed to correspond with his so-called " First Primary Band." Table 1 gives the wavelengths (mμ), frequencies (cm.$^{-1}$), and peak intensities of this band.

Infrared Spectra.—The frequencies (in wave-numbers) of the symmetric (ν_s) and asymmetric (ν_a) stretching modes of the nitro-group are collected in Table 2, cols. 2 and 3. Cols. 4 and 5 contain the mean value of the integrated intensity per nitro-group: these are calculated from the total intensity of the doublet in those cases where band-splitting occurs. The half-intensity band widths are shown in cols. 6 and 7 of Table 2.

DISCUSSION

Ultraviolet Spectra.—*Nitrobenzenes.* In the following discussion the ultraviolet band shifts are considered relative to those of nitrobenzene, which is regarded as the parent compound of the whole series.

The spectra of the polynitrobenzenes can be interpreted by considering the polar interaction of several nitro-groups with the ring. The extensive conjugation of the nitro-group with the aromatic system lowers the electron density at certain ring positions so that additional nitro-substituents must compete for the available electron density with a reduction in the conjugation of each, and an increase in the energy of the excited state to give a hypsochromic displacement of the absorption band, as shown by the results for the di- and tri-nitrobenzenes. The selective withdrawal of electrons from certain ring positions suggests that the reduction in conjugation of several nitro-groups depends on their relative orientation, and accounts for the spectral differences between the *m*- and *p*-dinitrobenzenes.

In the case of *o*-dinitrobenzene steric hindrance must be considered. A pair of adjacent nitro-groups cannot both simultaneously occupy the coplanar configuration necessary for conjugation with the benzene ring. There are two possibilities: (*a*) one group is coplanar, with the second twisted out-of-plane; (*b*) both nitro-groups are twisted out-of-plane simultaneously. The spectral consequences of these alternatives are as follows. For (*a*), the spectrum should resemble that of the *meta*- or *para*-dinitro-compound. For (*b*), with neither group coplanar, the conjugation of both substituents with the ring is almost zero and the absorption should approach that of benzene itself. The fact that *o*-dinitrobenzene possesses no band above 210 mμ favours the second alternative, at least in the excited state. The introduction of a third nitro-group carries the decrease in conjugation a stage further and the two trinitrobenzenes examined absorb at somewhat shorter wavelengths than the *m*- and *p*-dinitro-compounds. The 1,2,4-isomer has a pair of vicinal nitro-groups which by analogy with *o*-dinitrobenzene should both be non-coplanar and therefore unconjugated. Their combined inductive effects will however still operate to reduce the conjugation of the group in the 4-position and produce the observed hypsochromic shift.

Nitrotoluenes. The results for *m*- and *p*-nitrotoluene are consistent with the —*I* effect normally associated with the methyl group,[12] which tends to release electrons to the ring thereby enhancing conjugation of the nitro-group and resulting in the observed bathochromic displacements. In *o*-nitrotoluene this effect is more than neutralised by the steric effect which has been shown to occur between adjacent methyl and nitro-groups.[3,4] The steric effect is much less than that between vicinal nitro-groups and its influence on the spectrum is correspondingly smaller.

The discussion of the dinitrobenzenes and mononitrotoluenes suggests that the following factors are of importance in determining the ultraviolet characteristics of polynitro-aromatic compounds: (*a*) A pair or more of nitro-groups tend partially to reduce their conjugation by mutual competition between their mesomeric-plus-inductive effect, and the magnitude of the reduction is determined by their relative positions around the ring. (*b*) A pair of vicinal nitro-groups interfere sterically with one another so that neither can be coplanar with the ring. (*c*) Methyl groups enhance the conjugation of nitro-groups

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[12] Dewar, " The Electronic Theory of Organic Chemistry," Clarendon Press, Oxford, 1949, p. 52.

except when they are situated in the *ortho*-position: the latter circumstance introduces a small degree of steric hindrance.

The magnitude of these effects may be evaluated from the spectral data by considering the displacements ($\Delta\nu$) of the absorption maxima relative to nitrobenzene. These are given in Table 3. The significance of each $\Delta\nu$-value in terms of the factors (*a*), (*b*), and (*c*) described above is indicated in col. 4 by the appropriate symbol.

The six isomeric dinitrotoluenes may be regarded formally as composed of various combinations of the six disubstituted benzene derivatives. The factors (*a*), (*b*), and (*c*) being assumed to be additive, the values of $\Delta\nu$ in Table 3 enable the frequency shifts for the dinitrotoluenes to be calculated. For example, 2,6-dinitrotoluene contains the following structural features: (i) one pair of *meta*-oriented nitro-groups, $\Delta\nu = 4120$ cm.$^{-1}$; (ii) a methyl group *ortho* to two nitro-groups, $\Delta\nu = 2 \times 560 = 1120$ cm.$^{-1}$; Total $\Delta\nu = 5240$ cm.$^{-1}$. Similar calculations were carried out for all six isomers. Adding to each value of $\Delta\nu$ the frequency for nitrobenzene (37,180 cm.$^{-1}$) gives a set of calculated frequencies which are compared with the observed values in Table 4.

TABLE 3.

Compound	ν (cm.$^{-1}$)	$\Delta\nu$ (cm.$^{-1}$)	Effect	Compound	ν (cm.$^{-1}$)	$\Delta\nu$ (cm.$^{-1}$)	Effect
Nitrobenzene	37,180	—	—	*o*-Nitrotoluene ...	37,740	560	(*c*)
o-Dinitrobenzene	>47,600	>10,420	(*a*), (*b*)	*m*- ,, ...	36,500	−680	(*c*)
m- ,,	41,300	4,120	(*a*)	*p*- ,, ...	35,260	−1,920	(*c*)
p- ,,	37,740	560	(*a*)				

TABLE 4. *Dinitrotoluenes.*

	2,3	2,4	2,5	2,6	3,4	3,5
ν (calc.)	>47,480	39,940	37,620	42,420	>45,000	39,940
ν (obs.)	>47,600	39,700	37,510	41,500	>45,690	40,300

The assumption of the additivity of the effects cannot be more than an approximation and with this in mind the agreement between the calculated and observed band positions is very satisfactory. The largest deviation occurs for the 2,6-isomer for which the calculated position is some 900 cm.$^{-1}$ too high. This suggests that the total steric effect between a methyl group and a nitro-group on each side of it is much less than twice the effect for a single nitro-group.

Owing to their increased complexity, the trinitrotoluenes cannot be analysed in this way and the small departures from additivity observed for the dinitrotoluenes are expected to be enhanced by a further substituent. Qualitatively the spectra follow patterns similar to those noted above. The introduction of a methyl group has the expected effect of increasing the conjugation of the nitro-groups through its $-I$ effect and the trinitrotoluenes all absorb at wavelengths somewhat longer than those of the corresponding trinitrobenzene. No 1,2,3-trinitrobenzene could be prepared to complete the series of comparisons.

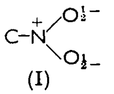
The absorption bands of the trinitrotoluenes cover a smaller spectral range than those of the dinitro-series, indicating that the effect of extensive nitro-group substitution is to equalise the energies within a series of isomers. The mutual reduction of conjugation is a useful concept for the interpretation of the spectra of this class of compound. The effect approaches a limit when three nitro-groups are present since the mean frequencies for the mono-, di-, and tri-nitro-compounds are 36,670, 41,760, and 41,970 cm.$^{-1}$, respectively.

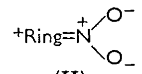
Infrared Spectra.—Band frequencies. The frequencies of the symmetric vibration of the nitro-group (Table 2, col. 3) exhibit little regularity with respect to the number and position of the nitro-substituents, probably owing to the interaction with the C–N vibration.[4,6] However, an empirical relation seems to exist between the incidence of steric effects and the shape of the band. In all compounds in which at least one nitro-group is strongly hindered the band splits into a doublet as shown in Table 2. In nearly all other cases the band is single. The reason for this is not clear as the asymmetric band does not behave in this way, but the effect may nevertheless find useful practical application in structural diagnosis.

The asymmetric frequencies (Table 2, col. 2) confirm the observations of other workers[5,6] that powerful electron-donor groups such as NH_2 lower the frequency of this band in the mononitro-series from around 1534 cm.$^{-1}$ towards 1500 cm.$^{-1}$. The important result emerges that the frequencies as a whole fall into three ranges corresponding to the mono-, di-, and trinitro-series: Mononitro: $\nu_a = 1509$—1540, *i.e.*, <1540 cm.$^{-1}$; dinitro: $\nu_a =$ 1539—1552 cm.$^{-1}$; trinitro: $\nu_a = 1554$—1567 cm.$^{-1}$. In some of the trinitro-compounds band splitting occurs but the range quoted is based on the lower-frequency component. Slight overlapping of the ranges occurs for the mono- and di-nitro-series, but in general the ranges are sufficiently distinct to be used as an indication of the degree of nitration of unknown compounds. The only serious discrepancies in the above correlations arise when a dinitro-compound also contains strong electron-donor groups such as NR_2; for example, *N*-methyl-2,4-dinitroaniline has $\nu_a = 1534$ cm.$^{-1}$, but this probably represents the maximum displacement of the dinitro-frequency into the mononitro-range.

The increased asymmetric frequency of the polynitro-compounds implies a high N–O bond order, and is consistent with the reduced conjugation of the nitro-groups in such compounds deduced from the ultraviolet spectra. With one exception (2,3,5-trinitrotoluene) the asymmetric band splits when three vicinal nitro-groups are present or when four substituents are in adjacent ring positions.

Integrated band intensities. The integrated band intensities per nitro-group (I_a and I_s) for the two stretching vibrations are shown in Table 2, cols. 4 and 5. The symmetrical band intensities show little regularity with the positions of the nitro-substituents although the values tend to fall as the number of nitro-groups increases. This is consistent with the ultraviolet data which indicate that several nitro-groups together are less fully conjugated than a single one. Structures (I) and (II) represent the charge distributions for the extreme cases of zero and full conjugation respectively. Reduced conjugation with the ring as in (I) should therefore lower the charge gradient and with it the band intensity, as observed.


(I)


(II)

Clearly, a number of factors will influence the band intensities in these compounds. The asymmetric intensities might also be expected to follow a similar trend but this is not observed. It is of interest however that the highest values occur for those compounds which contain two or three vicinal nitro-groups: for the five compounds of this class which were studied, I_a lies above $2{\cdot}9 \times 10^4$.

Half-intensity band widths. The asymmetric band widths (Table 2, col. 6) show no correlation with the structural features, but the symmetric band widths reveal an interesting relation. The band width of an isolated nitro-group is in the range 8—11 cm.$^{-1}$, but the presence of small hindering groups (Me, Et) progressively broadens the band to 19 cm.$^{-1}$, without changing the frequency. This effect may be related to that observed by Orr[13] in the case of the C–H deformation bands in sterically hindered *trans*-stilbenes. Large blocking groups (Bu^t), however, lead to intermediate band widths of about 16 cm.$^{-1}$ with an accompanying rise in frequency towards 1375 cm.$^{-1}$, both of which values are close to those of the unconjugated nitro-group in nitromethane.

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[13] Orr, *Spectrochim. Acta*, 1956, **8**, 218.