

799. *The Characteristic Infra-red Absorption Frequencies of Aromatic Nitro-compounds.*

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The characteristic infra-red absorption frequencies of aromatic nitro-groups in 23 compounds in the range 700—1800 cm^{-1} are considered and the average values shown to be : 1518 cm^{-1} for the antisymmetrical N—O stretching, 1349 cm^{-1} for the symmetrical N—O stretching, and 849 cm^{-1} for the C—N stretching vibrations.

A NUMBER of nitrobenzene and nitrodiphenyl derivatives have been examined as part of a programme on the investigation of the characteristic infra-red absorption frequencies of benzene derivatives. Before conclusions can safely be drawn about the benzene ring frequencies, it is necessary to recognize and discount characteristic frequencies of the aromatic nitro-group, and evidence on this topic is presented here.

The standard tables of characteristic frequencies (Thompson, *J.*, 1948, 328; Williams, *Rev. Sci. Instr.*, 1948, 19, 135) indicate infra-red absorption by nitro-groups in general in the ranges 1550—1600 and 1300—1350 cm^{-1} . The nitronaphthalenes measured by Hathway and Flett (*Trans. Faraday Soc.*, 1949, 45, 818) all show strong bands near 1345 cm^{-1} and the existence of the two frequencies is confirmed by studies of Raman spectra (see Landolt-Börnstein, "Tabellen," 1 Band, Atom- und Molekular-Physik, 2 Teil, Molekeln 1, Table 14145, XVII). These two characteristic frequencies are amply confirmed for aromatic compounds by the present work and seem to be strongly active in infra-red absorption. In view of the complete assignment of some simple nitroparaffins by Smith, Pan, and Nielsen (*J. Chem. Phys.*, 1950, 18, 706) the frequency at 1518 cm^{-1} must be assigned to the antisymmetrical and that at 1349 cm^{-1} to the symmetrical valency stretching mode of the nitro-group. Smith, Pan, and Nielsen also place the C—N stretching frequencies in the region 800—900 cm^{-1} . For the aromatic nitro-compounds there does seem to be a strong band at the centre of this range, and the table shows its exact position for each of the 23 compounds whose spectra have been measured; the table also shows the positions of the strong bands near 1518 cm^{-1} and 1349 cm^{-1} . In a few cases alternative bands are possible for the correlation and these are given in parentheses; in some cases alternative modes of vibration can be suggested for these frequencies, *e.g.*, the 837- cm^{-1} absorption of *p*-nitroaniline is probably due to the out-of-plane, umbrella vibration of the hydrogen atoms. Strong bands near 1330 cm^{-1} due to trifluoromethyl groups (Thompson and Temple, *J.*, 1948, 1432) are omitted from the table. Also given in the table are the mean frequency and standard deviation for each column. The final entries are the mean and standard deviation for the infra-red and Raman frequencies to be found in the literature (Hathway and Flett, *loc. cit.*; Landolt-Börnstein, *op. cit.*; Barnes, Gore, Liddel, and Williams, "Infra-red Spectroscopy," Reinhold, 1944; Randall, Fowler, Fuson, and Dangel, "Infra-red Determination of Organic Structures," van Nostrand, 1949); the numbers in parentheses are the numbers of compounds whose frequencies appear in the mean. For the 849- cm^{-1} frequency no infra-red figures were found in the literature and only Raman frequencies are included; if two doubtful attributions, *o*-nitrotoluene at 794 cm^{-1} and *m*-nitrophenol at 817 cm^{-1} , are excluded, the entry would read (8) 862 \pm 8, which is a more reasonable standard deviation.

The C—N stretching vibration is surprisingly constant in frequency and approximate intensity, since this mode might have been expected to be susceptible to interaction; 849 cm^{-1} must, therefore, be considered as a characteristic absorption frequency, and even if it is not by itself a clear indication of an aromatic nitro-group in compounds of unknown structure its presence would provide supporting evidence. It must also be recognized when other features of the spectrum are discussed when aromatic nitro-groups are known to be present, and in particular it must not be confused with the out-of-plane C—H deformation frequency of 1:3:5-trisubstituted benzenes. In two cases, *o*-nitroaniline at 848

4154 *Absorption Frequencies of Aromatic Nitro-compounds.*

cm.⁻¹ and 5-nitro-*o*-toluidine at 1333 cm.⁻¹, the absorption is decidedly weak, but there are no cases in the table where the frequencies fail to appear in the infra-red spectra.

Compound	Frequencies, in cm. ⁻¹ *		
Nitrobenzene	1534 vs	1353 vs	854 s
<i>o</i> -Trifluoromethylnitrobenzene.....	1539 vs	1356 vs	854 s
<i>p</i> - " "	1530 vs	1360 vs	837 vs
<i>o</i> -Nitroaniline	1513 s	1349 s	848 w
<i>o</i> -Nitroacetanilide	1500 s	1341 s	856 m
<i>m</i> -Nitroaniline	1522 s	1345 s	868 s
<i>m</i> -Nitroacetanilide	(1539 s) 1505 s	1346 s	840 m (824 s)
<i>p</i> -Nitroaniline	1525 s	1348 s	857 s (837 s)
<i>p</i> -Nitroacetanilide	1506 vs	1348 vs	848 vs
5-Nitro- <i>o</i> -toluidine (Me = 1)	1515 m	1333 w	827 s
5-Nitro- <i>o</i> -acetotoluidide (Me = 1)	(1534 s) 1506 vs	1345 vs	837 m (826 s)
2-Nitro-3-trifluoromethylaniline	1523 s	1351 s	851 m
2-Nitro-3-trifluoromethylacetanilide	1535 vs	1370 vs	850 m
4-Nitro-2-trifluoromethylaniline	1494 s	1341 m	832 m
4-Nitro-2-trifluoromethylacetanilide	1515 vs	1365 vs	850 m
4-Nitro-3-trifluoromethylaniline	1495 vs	1356 s	837 m
4-Nitro-3-trifluoromethylacetanilide	1519 vs	1335 vs	(861 m) 840 s
4-Nitrodiphenyl	1510 vs	1341 vs	854 vs
4-Nitro-3-trifluoromethyldiphenyl	1533 vs	1341 vs	(855 m) 850 s
2-Nitro-3'- "	1529 vs	1350 s	855 m
4-Nitro-3'- "	1510 s	1347 vs	857 s
4 : 4'-Dinitro-3-trifluoromethyldiphenyl	1529 dbl vs	1348 vvs	852 s 843 s
4 : 4'-Dinitro-3 : 3'-bistrifluoromethyldiphenyl ...	1529 vs	1348 vs	854 s 843 s
Mean and standard deviation	1518 ± 13	1349 ± 9	849 ± 9
" " literature	(25) 1527 ± 11	(38) 1346 ± 6	(10) 853 ± 26

(No. of compounds in parentheses)

* vs = Very strong, s = strong, m = medium, w = weak, dbl = double.

The compounds whose spectra are available do not form a carefully chosen set which would be required for a discussion of the influences affecting the exact frequencies; but inspection does indicate that factors, such as the existence of *p*-amino-groups or *p*-nitro-diphenyls, which lead to a larger contribution of the form $\text{>C=N}\begin{matrix} \text{O} \\ \diagdown \\ \text{O} \end{matrix}$ to the electronic structure, lead also to a lowering of the antisymmetrical stretching frequency at 1518 cm.⁻¹. When two nitro-groups are present the absorption bands are especially strong and broad, or even double.

Experimental.—The spectra measured were those of the pure liquids or solid films dispersed in a Nujol mull as observed with a Grubb-Parsons spectrometer with a rock-salt prism. The materials were commercial products recrystallized or redistilled, and acetylated where necessary, except for the trifluoromethyl derivatives, which were synthesized by Pettit and Tatlow (*J.*, 1951, 3459).

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