The Characteristic Infrared Absorption Frequencies of Aromatic Trifluoromethyl Compounds.

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The characteristic frequencies of the C–F stretching vibrations of aromatic trifluoromethyl compounds are considered, and the symmetrical vibration shown to absorb strongly near 1321 cm.$^{-1}$ and the antisymmetrical vibrations near 1179 cm.$^{-1}$ and probably near 1140 cm.$^{-1}$.

The recent review of characteristic absorption frequencies by Bellamy ("The Infrared Spectra of Complex Molecules," Methuen, 1954) has shown that knowledge of the frequencies of the CF_3 group is fragmentary. Since the spectra of 21 compounds containing an aromatic CF_3 group prepared by Pettit and Tatlow (*J.*, 1951, 3459; 1954, 1071) had been measured in another connection, they were examined for evidence relating to the CF_3 group frequencies.

The most useful guide to the spectral region where the frequencies are most likely to be found is the assignment of 1 : 4-bistrifluoromethylbenzene by Ferguson, Mikkelson, Nielsen, and Smith (*J. Chem. Phys.*, 1953, **21**, 1731), who placed the symmetrical frequency at 1320 cm.$^{-1}$ and the antisymmetrical modes at 1180 and 1137 cm.$^{-1}$ in the infrared spectrum. These frequencies are in agreement with the comments of Thompson and Temple (*J.*, 1948, 1432) who found strong bands near 1330 and 1150 cm.$^{-1}$ in such compounds.

The second column of the Table shows the frequencies of the very strong infrared absorptions near 1321 cm.$^{-1}$ of the compounds listed; in the compounds containing also a nitro-group the band was distinct from that near 1349 cm.$^{-1}$ of this group (Randle and Whiffen, *J.*, 1952, 4153). There can be little doubt about the assignment of these bands to the symmetrical C–F stretching vibrations.

Compound	Frequencies (cm.$^{-1}$)		
	Symm.	Antisymmetrical	
Trifluoromethylbenzene (*a*)	1326	1176	1127
m-Fluorotrifluoromethylbenzene (*a*)	1333	1174	1135
p- ,, ,, (*b*)	1335	1175	1150
p-Bistrifluoromethylbenzene (*a*)	1320	1180	1137
2 : 5-Difluorotrifluoromethylbenzene (*a*)	1325	1190	1149
o-Nitrotrifluoromethylbenzene	1305	1181	1136
m- ,, ,,	1312	1172	1143
p- ,, ,,	1319	1181	1150
o-Trifluoromethylacetanilide	1316	1167	1158
m- ,, ,,	1318	1173	1129
p- ,, ,,	1332	1180	1152
2-Nitro-3-trifluoromethylaniline	1308	1185	1136
4-Nitro-3- ,, ,,	1326	1190	1145
4-Nitro-2- ,, ,,	1319	1181	1145
2-Nitro-3-trifluoromethylacetanilide	1326	1181	1136
4-Nitro-3- ,, ,,	1314	1172	1142
4-Nitro-2- ,, ,,	1315	1181	1135
4-Nitro-3-trifluoromethyldiphenyl	1314	1181	1141
4′- ,, ,,	1328	1172	1136
2′- ,, ,,	1337	1170	1130
4-Amino-3- ,, ,,	1319	1179	1152
4-Acetamido-3- ,,	1324	1190	1141
4 : 4′-Dinitro-3-trifluoromethyldiphenyl	1312	1185	1149
4 : 4′-Dinitro-3 : 3′-bistrifluoromethyldiphenyl	1330	1190	1154
4 : 4′-Diacetamido-3-trifluoromethyldiphenyl	1313	1181	1132
2 : 4′-Diamino-4 : 2′-bistrifluoromethyldiphenyl	1335	1172	1128
Mean and standard deviation	1321 ± 9	1179 ± 7	1140 ± 9

(*a*) A.P.I. project 44. Catalogue of Infrared Spectra. (*b*) Thompson and Temple, *loc. cit.*

Although for an isolated CF_3 group the antisymmetric stretching vibrational mode is degenerate, the aromatic ring will lift this degeneracy and lead to two orthogonal vibrations with changes of dipole moment vector parallel and perpendicular to the ring. The two vibrations will differ only slightly in frequency and, in view of the strongly polar nature of the C–F link, should both be strong in infrared absorption. In agreement with the work of the authors cited above, strong bands were found in the range 1100—1200 cm.$^{-1}$ whose intensities were greater than is common for the in-plane aromatic C–H deformation absorptions usually found in this range. The highest frequency of the observed intense absorptions lies near 1179 cm.$^{-1}$ in each case, whereas the nearest in-plane C–H deformation frequency given by Randle and Whiffen (" Molecular Spectroscopy," Report on the conference held in London in October, 1954, by the Institute of Petroleum) is slightly lower for some substitution types such as *ortho* (band at 1159 ± 7 cm.$^{-1}$), 1 : 2 : 3 (1160 ± 5 cm.$^{-1}$), 1 : 2 : 4 (1151 ± 8 cm.$^{-1}$), although for others, including mono- (1177 ± 8 cm.$^{-1}$), *meta* (1165 ± 6 cm.$^{-1}$), and *para* (1179 ± 7 cm.$^{-1}$), these C–H deformation frequencies overlap the proposed CF_3 range. Of the 26 compounds in the Table, for 11, which include all the 1 : 2 : 3, 1 : 2 : 4, and all but one of the *ortho* cases, the strong band is outside the normal range (taken as twice the standard deviation) of the C–H deformation frequencies of the substitution types involved, and in the remaining 15 cases the frequency is higher than the average value. Together with the strength of the bands and the fact that there are usually other bands which could be the C–H deformation frequencies, this evidence suggests that one of the antisymmetrical vibration frequencies has been correctly located near 1179 cm.$^{-1}$. The second antisymmetrical frequency must lie close to this, and all the compounds show strong absorption between 1170 and 1100 cm.$^{-1}$, but the existence of C–H deformation frequencies in this range makes choice of the CF_3 frequencies difficult. Indeed, it is not certain that only one of the bands involves appreciable C–F stretching, since the vibrational mode which is symmetrical to the plane of the benzene ring may interact with the C–H deformations so that the vibrations are mixed in type and, in particular, the weaker C–H deformations may borrow intensity from the stronger C–F stretchings. Another explanation of the number of strong bands assumes that some of them are sum-and-difference tones involving the very low CF_3 internal rotation frequency. The most satisfactory average frequency seemed to be 1140 cm.$^{-1}$ as given in the table, but a value nearer 1112 cm.$^{-1}$ is also possible.

Experimental.—The spectra are those of solid films obtained by using the Nujol technique with a Grubb–Parsons single-beam spectrometer with a rock-salt prism.

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