A Characteristic Infra-red Absorption of the Triphenylmethyl Group.

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The spectra of 13 compounds which contain the triphenylmethyl group all show a medium-strength band at about 1185 cm.$^{-1}$ and a weak band at about 1280 cm.$^{-1}$ which seem to be characteristic of this group. These bands are assigned to the stretching modes of vibration of the C–Ph bonds.

IN connection with an investigation of rearrangements in the triphenylmethyl series a method was required by which this group could be easily identified. The infra-red spectra of a number of triphenylmethyl derivatives were therefore measured in the 800—1300 cm.$^{-1}$ region, and they all showed two bands, at 1179—1190 and 1270—1290 cm.$^{-1}$, which could not be attributed to any other group in these compounds, as seen by comparison with the spectra of similar substances not containing this group. It thus appears that these bands (see Table 1) are characteristic of the triphenylmethyl group. Besides the bands listed, the materials mentioned in Table 1 also show other bands in this region due to other parts of the molecule.

TABLE 1. *Position of* CPh_3 *bands in the* 1150—1300 *cm.*$^{-1}$ *region in various compounds.* (Cell thickness : 0·1 mm.; m = medium, w = weak.)

Compound	Concn.*	Bands (cm.$^{-1}$)	Compound	Concn.*	Bands (cm.$^{-1}$)
1. $CHPh_3$	0·20	1184 (m), 1290 (w)	8. $CPh_3{\cdot}CH_2{\cdot}CH_2Cl$	0·21	1187 (m), 1273 †
2. $CPh_3{\cdot}OH$	0·01 [a]	1179 (m), 1270 †	9. $CPh_3{\cdot}[CH_2]_3{\cdot}Cl$	0·19	1185 (m), 1286 (m)
3. $CClPh_3$	0·28	1184 (m), 1284 (w)	10. CPh_4	0·01 [a]	1186 (m), 1280 (w)
4. $CMePh_3$	0·27	1184 (m), 1282 (w)	11. $CPh_3{\cdot}CH_2{\cdot}CH_2Ph$	0·01 [a]	1186 (m), 1272 (w)
5. $CPh_3{\cdot}CH_2Cl$ ...	0·28	1185 (m), 1280 (w)	12. $CPh_3{\cdot}CHPh_2$	0·11	1187 (m), 1272 (w)
6. $CPh_3{\cdot}COCl$ ...	0·26	1190 (m), 1278 (w) [b]	13. $CPh_3{\cdot}CH(OH){\cdot}CHPh_2$	0·01 [a]	1184 (m), 1277 (w)
7. $CPh_3{\cdot}CH_2{\cdot}OEt$	0·15	1182 (m), 1279 (m)			

[a] A 2-mm. cell. [b] This band merges with a band at about 1265 cm.$^{-1}$.

* Concentrations are given in terms of g. per 1 c.c. of carbon disulphide. † Shoulder.

The infra-red absorption of triphenylmethane has been reported by Richards and Thompson (*Proc. Roy. Soc.*, 1949, *A*, **195**, 1) and Karagounis (*Helv. Chim. Acta*, 1951, **34**, 994), bands being recorded in this region at about 1190 and 1300 cm.$^{-1}$ for a carbon tetrachloride solution and at about 1179 cm.$^{-1}$ for the solid phase. Triphenyldeuteromethane in the same solvent also shows bands at about 1191 and 1283 cm.$^{-1}$ (Brown, Mighton, and Senkus, *J. Org. Chem.*, 1938, **3**, 62). For solid triphenylmethanol, Barnes, Gore, Liddel, and Williams ("Infra-red Spectroscopy," Reinhold Publ. Corp., New York, 1944, p. 59) report bands at about 1185 and 1280 cm.$^{-1}$. The spectra of *o*- and *m*-nitrotriphenylmethane ("Catalog of Infra-red Spectrograms," Sadtler & Son, Inc., Philadelphia; Nos. 1022, 1021) also show similar bands.

Sheppard (*Trans. Faraday Soc.*, 1950, **46**, 531) assigned the 1139—1159 cm.$^{-1}$ band, which appears in the spectra of *tert.*-butyl derivatives, to that mode of vibration which involves the symmetrical stretching of the C–Me bonds, and the 1230—1240 cm.$^{-1}$ band to the corresponding non-symmetrical mode of vibration. By analogy, the 1179—1190 cm.$^{-1}$ band in triphenylmethyl derivatives may be assigned to that mode of vibration in which all the phenyl groups move in phase in a stretching of the C–Ph bonds, and the 1270—1290 cm.$^{-1}$ band to a similar stretching vibration in which one phenyl group is out of phase. The relative intensity of these bands is in agreement with this assignment since, as with *tert.*-butyl derivatives, the symmetrical band is higher in intensity.

It is, however, noteworthy that, while the *tert.*-butyl halides show a decrease of about 50—70 cm.$^{-1}$ in the frequency of the first band and of about 10—20 cm.$^{-1}$ in that of the second band, relative to the values of these bands in the hydrocarbons (Simpson and Sutherland, *Proc. Roy. Soc.*, 1949, *A*, **199**, 169; 1200—1215 and 1250 cm.$^{-1}$), no such decrease was found in the triphenylmethyl compounds. A possible explanation may be that the mechanical coupling between the fourth substituent of the central carbon atom and the three $C{-}C_{ar.}$ bonds is not strong here and does not play a great part in determining the frequency of these bands as does the analogous coupling in the case of the *tert.*-butyl derivatives (especially in relation to the first mode of vibration, see Sheppard, *loc. cit.*).

It should also be mentioned that, although *neo*pentane does not show the first band, corresponding to the symmetrical mode of vibration, at about 1200 cm.$^{-1}$ as do other hydrocarbon derivatives of *iso*butane (Simpson and Sutherland, *loc. cit.*), yet its analogue tetraphenylmethane (No. 10 of Table 1) does show it very clearly. This mode of vibration is not infra-red active in *neo*pentane on account of its perfect symmetry: it is therefore interesting that in the spectrum of tetraphenylmethane this band does appear.

The rise in the frequencies of the bands when C–Ph bonds are substituted for the C–Me bonds, *e.g.*, in CPh_3Cl, seems to be due to the effect of the neighbouring (aromatic) double bonds which tend to strengthen the other bonds of the doubly-bound carbon atom (Walsh, *Trans. Faraday Soc.*, 1947, **43**, 60). This rise is especially significant since the greater mass of a phenyl group would, *per se*, be expected to decrease the frequency.

On further examination of the infra-red absorption of similar compounds which do not contain the triphenylmethyl radical it appears that, although some of these compounds also show bands which are in or near the ranges assigned to this group, yet in most cases these compounds do not show both of the bands in the correct places and of the right intensity. If the special cases of the polar compounds triphenylmethanol and triphenylacetyl chloride (Table 1, Nos. 2 and 6) and the first member of the series,[*] triphenylmethane, are ignored in setting the limits for the characteristic ranges of absorption, the narrower ranges 1182—1187 and 1272—1286 cm.$^{-1}$ are obtained. These are more characteristic for the triphenylmethyl derivatives as can be seen from Table 2, which gives the absorption bands in this region of a number of similar compounds from which the triphenylmethyl group is absent.

TABLE 2. *Absorption bands of some compounds related to those of Table* 1 *in the* 1150—1300 *cm.*$^{-1}$ *region.*

Compound	Concn.*	Cell thickness (mm.)	Bands (cm.$^{-1}$)
14. $CHPh_2{\cdot}CH_2Ph$	0·24	0·1	1156, 1239
15. $CHPh_2Br$	0·01	2	1149, 1179, 1258
16. $CPh_2{:}CHPh$	0·17	0·1	1155, 1176, 1245, 1269
17. $CPh_2{:}CPhCl$	0·11	0·1	1154, 1177, 1231, 1287 (v. w.)
18. $CBr(CH_2Ph)_3$	0·01	2	1154, 1178, 1227, 1274 †
19. $C(OH)(CH_2Ph)_3$	0·01	2	1154, 1170, 1194 (w), 1208 (w), 1246, 1270

* See footnote, Table 1. † See footnote, Table 1.

It is, however, fully justified to assume that any substance which does not show a band at about 1180—1190 cm.$^{-1}$ does not contain a triphenylmethyl group. As the other band at about 1280 cm.$^{-1}$ is usually weak, a similar conclusion about this band seems unsafe. Hexaphenylethane, for instance, was observed (Karagounis, *loc. cit.*) to possess a band at about 1191 cm.$^{-1}$ in carbon tetrachloride solution but not one at about 1280 cm.$^{-1}$. Care should also be taken in comparing results obtained with different solvents, for a change of solvent is liable to cause small shifts in wave-lengths (see, *e.g.*, Williams, Hastings, and Anderson, *Analyt. Chem.*, 1952, **24**, 1911).

Experimental.—The instrument used in these measurements was a Perkin–Elmer Infra-red Spectrophotometer, Model 12C, equipped with a sodium chloride prism.

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[*] In the *tert.*-butyl series also, the first member, *iso*butane, behaves somewhat differently from the other members and shows bands at 1173 and 1277 cm.$^{-1}$ (American Petroleum Institute, Research Project 44. National Bureau of Standards Catalogue of Infra-red Data, Curve No. 439).