135. *Complex Fluorides. Part VIII.*[1] *The Preparation and Properties of Salts of the Triphenylmethyl Cation : The Infrared Spectrum and Configuration of the Ion.*

By D. W. A. SHARP and N. SHEPPARD.

Salts of the triphenylmethyl cation with anions of the complex fluoro-acids can be prepared by the ionic reaction between chlorotriphenylmethane and the appropriate silver salt in organic solvents. Some properties of these salts are discussed. The infrared spectra of the complexes provide direct evidence for the ionic nature of the salts in most cases. The detailed spectra have been considered in relation to likely configurations for the cation, namely the all-planar (D_{3h}), the propeller-like (D_3), and an unsymmetrical structure. The infrared spectra favour the D_3 configuration in the crystalline state.

IN previous papers [1] it has been shown that the hypothetical complex fluoro-acids of formulæ HMF_4 and HMF_6 form a series of very strong acids, whose salts are completely ionised in the solid state. In view of their well-characterised properties, the anions corresponding to these acids provide an ideal series for the study of properties of salts, and are now applied to the salts of the triphenylmethyl cation.

Silver fluoroborate is soluble in ether ; [2] the following salts are also soluble in this solvent : silver hexafluoro-phosphate, -arsenate, -antimonate, -niobate, and -tantalate, and fluorosulphonate. The interaction of these ethereal solutions with chlorotriphenylmethane in ether gives a yellow precipitate containing equivalent proportions of the triphenylmethyl salt and silver chloride. Ether is preferable to toluene as a solvent as the silver salts are far more soluble, and the triphenylmethyl salts comparatively insoluble, in ether, and aromatic hydrocarbons form fairly stable complexes with the silver salts so that excess of hydrocarbon is difficult to remove. Using this method, we have now prepared triphenylmethyl fluoroborate, hexafluoro-phosphate, -arsenate, -antimonate, -niobate, and -tantalate, and fluorosulphonate. In addition the new covalent compound, triphenylmethyl trifluoroacetate, has been prepared. The method is an extension of that employed by Mackenzie and Winter [3] to prepare acetyl perchlorate solutions and by Burton and Praill [4] for the preparation of acetyl and benzoyl perchlorates from acetyl and benzoyl chlorides and silver perchlorate in nitromethane. Schmeisser [5] prepared some solid perchlorates by this method but it is believed that this is the first time that carbonium salts have been thus prepared.

Solid salts which have been supposed to contain the triphenylmethyl cation have long been known. Chlorotriphenylmethane forms addition compounds with many acidic or inorganic acid chlorides (for references see Schmidlin [6]), classifiable as complex chlorides, *i.e.*, triphenylmethyl salts of the appropriate complex chloro-acids ; in the present work it has been shown that these salts contain the triphenylmethyl cation. Triphenylmethyl perchlorate has previously been prepared [7] as a yellow crystalline solid, and has a high conductivity in liquid sulphur dioxide.[8] Triphenylmethyl fluoroborate has earlier been prepared from chlorotriphenylmethane and acetyl fluoroborate in acetic anhydride,[9] or by addition of boron trifluoride to fluorotriphenylmethane ; [10] it is dissociated in nitrobenzene solution.[10]

[1] Parts VI and VII, Sharp and Sharpe, *J.*, 1956, 1855, 1858.
[2] Sharpe, *J.*, 1952, 4538.
[3] Mackenzie and Winter, *Trans. Faraday Soc.*, 1948, **44**, 171.
[4] Burton and Praill, *J.*, 1950, 2034.
[5] Schmeisser, *Angew. Chem.*, 1955, **67**, 493.
[6] Schmidlin, " Das Triphenylmethyl," Enke, Stuttgart, 1914, p. 111.
[7] Hofmann and Kirmsreuther, *Ber.*, 1909, **42**, 4856.
[8] Hofmann, Kirmsreuther, and Thal, *Ber.*, 1910, **43**, 186.
[9] Seel, *Z. anorg. Chem.*, 1943, **250**, 331.
[10] Witschonke and Kraus, *J. Amer. Chem. Soc.*, 1947, **69**, 2472.

It must be assumed that, since the solid silver salts are ionised,[1] ion-pairs exist in ethereal solution. In view of the rapidity of the precipitation (apparently instantaneous) of the mixture of triphenylmethyl salt and silver chloride, it is probable that chlorotriphenylmethane is appreciably dissociated also in polar solvents. Bentley, Evans, and Halpern [11] showed that chlorotriphenylmethane exists, to a proportion of 0·032%, as ion-pairs in nitromethane; however, they measured the concentration of carbonium ions spectrophotometrically by comparison with a solution of triphenylmethanol in concentrated sulphuric acid, this being used as a standard solution containing only carbonium ions.[12] This method neglects the possibility of effects on the absorption due to solvation by the nitromethane, which is a more ready electron donor than sulphuric acid. It was further observed that chloride-ion exchange in such a solution was very fast, a result recently confirmed by bromide-ion exchange in solutions of bromotriphenylmethane in acetone.[13] The importance of solvation in the splitting of a link, $R_3C{:}X \rightleftharpoons R_3C^+ + {:}X^-$, has been discussed by many authors. Gelles, Hughes, and Ingold [14] have shown the high reactivity of chlorotriphenylmethane in the presence of nucleophilic reagents which solvate the cation. Even such a weak donor as benzene can solvate the triphenylmethyl ion; [15] that the present reactions can be carried out by using benzene or toluene as solvent, the precipitation again being instantaneous, supports this.

Triphenylmethyl salts are very soluble in such nucleophilic solvents as acetone and acetonitrile, giving yellow solutions at room temperature. The salts have been reported to be insoluble in ether but in fact triphenylmethyl fluoroborate is slightly soluble in this solvent to give a colourless solution, the yellow ion presumably being solvated by the ether. On evaporation of the solution yellow triphenylmethyl fluoroborate is deposited. Fairbrother [16] reports that a mixture of arsenic tribromide and bromotriphenylmethane in benzene gives a colourless solution, yet, on removal of the solvent, an orange compound is deposited. This evidence for the ready solvation of the triphenylmethyl cation may again explain the comparatively low apparent ionisation of certain of the salts when measured spectroscopically.[16] Yellow solutions of triphenylmethyl fluoroborate in acetonitrile or acetone–chloroethylene when cooled nearly to freezing become colourless. This can be explained by the more complete formation of the triphenylmethyl–solvent complex at low temperatures. Further work is necessary on these solutions, which we hope to report later.

The pure salts decompose on melting and, if dissolved in acetone–chloroethylene, the salts of the heavier anions tend to be precipitated as oils when pentane is added, as does fluorotriphenylmethane when treated with aluminium chloride; [17] the composition of such oils is unknown. The salts are stable in dry air, darkening slightly when kept. In moist air they decompose rapidly to the methanol.

The complex fluoro-acids are ideal for the study of purely ionic salts since any covalent-bond formation between anion and cation will result in gross distortion of the fluoro-anion, which is readily detected by infrared spectroscopy through a splitting of absorption bands as the high symmetry of the anion is destroyed. In the present series all the salts of the complex fluoro-acids have absorption peaks characteristic of the undistorted fluoro-anions where these occur in the region investigated, *viz.*, 4000—650 cm.$^{-1}$ (see p. 681 where the observed frequencies are compared with those found in the spectra of simple alkali and silver salts [1]). In addition to the few strong bands due to the anions a much more complex pattern of absorption bands is observed owing to the triphenylmethyl cations (see Figure). The fact that these spectra are almost identical in

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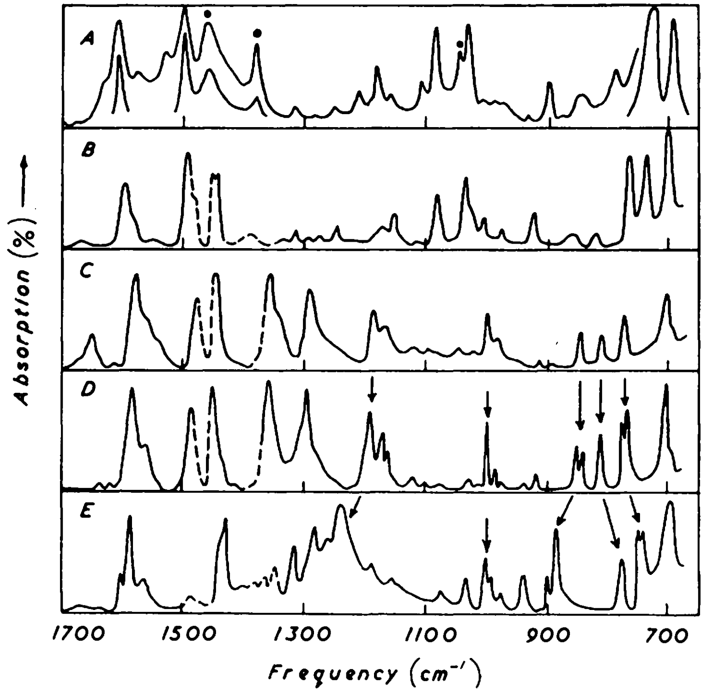
[11] Bentley, Evans, and Halpern, *Trans. Faraday Soc.*, 1951, **47**, 711.
[12] Anderson, *J. Amer. Chem. Soc.*, 1935, **57**, 1673.
[13] de la Mare and Hughes, *J.*, 1956, 845.
[14] Gelles, Hughes, and Ingold, *J.*, 1954, 2918.
[15] Swain and Kreevoy, *J. Amer. Chem. Soc.*, 1955, **77**, 1122.
[16] Fairbrother, *J.*, 1945, 503.
[17] Blicke, *J. Amer. Chem. Soc.*, 1924, **46**, 1515.

each case confirms the evidence from the anion spectra that complete ionisation has occurred. Furthermore the general pattern of absorption bands due to the cation can readily be distinguished from that obtained from molecules in which the triphenylmethyl group is tetrahedral, *e.g.*, triphenylmethane (see Figure), chlorotriphenylmethane, etc.

The addition compounds $Ph_3C{\cdot}Cl,SnCl_4$ and $Ph_3C{\cdot}Cl,SbCl_5$ have also been prepared; as they also show the characteristic infrared spectrum of the triphenylmethyl cation they may now definitely be formulated as the ionic complex chlorides $Ph_3C^+,SnCl_5^-$ and $Ph_3C^+,SbCl_6^-$. The apparently unusual co-ordination of tin in the former compound is known in other complexes, *e.g.*, phosphorus pentachloride–stannic chloride.[18]

With oxy-salts co-ordination may occur between the oxygen atom of the anion and the cation to give partial covalent character to the salt. Two compounds of this type have been studied. The infrared spectrum of triphenylmethyl fluorosulphonate is completely characteristic of an ionic salt, but that of the trifluoroacetate shows it to be more accurately described as covalent. Thus the C=O frequency occurs at 1785 cm.$^{-1}$, identical with the value reported by Haszeldine [19] for trifluoroacetic esters, and differs very considerably from the corresponding frequency (1695 cm.$^{-1}$) found in the spectra of ionic salts.[19] Furthermore the pattern of absorption bands due to the aromatic portion of the complex is much nearer that characteristic of a tetrahedral triphenylmethyl group than to that characteristic of the carbonium ion. Only the considerable strength of the band at 1365 cm.$^{-1}$ suggests some degree of ionic character (see following section).

Infrared spectra of the triphenylmethyl cation, triphenylboron, and related molecules.



A, PhMe (liquid film; ● denotes absorption band due to methyl group); *B*, $Ph_3C{\cdot}H$; *C*, $Ph_3C^+SnCl_5^-$; *D*, $Ph_3C^+TaF_6^-$; *E*, Ph_3B (full line, spectrum of a Nujol mull; broken line: spectrum of a hexachlorobutadiene mull).

The Infrared Spectrum and Structure of the Triphenylmethyl Cation.—The Figure illustrates the typical infrared spectrum of the triphenylmethyl cation as obtained from

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[18] Payne and Groeneveld, Proc. Symposium on Co-ordination Chemistry, Copenhagen, 1953, p. 146.
[19] Haszeldine, *Nature*, 1951, **168**, 1028.

the crystalline salts with TaF_6^- and $SnCl_5^-$ anions. The spectra of toluene, triphenylmethane, and triphenylboron are shown for comparison. The frequency range illustrated is from 1700 to 650 cm.$^{-1}$ as the absorption bands in this region are likely to be sensitive to the configuration of the cation. The anions chosen do not absorb in this region.

It is generally considered that the carbonium ion is stabilised by resonance between canonical forms in which the positive charge is located either on the central carbon atom or alternatively on the *ortho* and the *para* carbon atoms in the benzene rings.[20] As in the triphenylmethyl radical,[21, 22] this type of resonance stabilisation is expected to be greatest for an all-planar configuration of the ion (symmetry class D_{3h}). However, as Lewis, Magel, and Lipkin have pointed out,[23] such a configuration would give rise to great steric hindrance between the *ortho* hydrogen atoms of adjacent benzene rings. It is therefore much more probable that the structure is distorted out of the plane by rotation of one or more benzene rings about the central bonds, which would relieve the steric strains but would not necessarily greatly inhibit conjugation between the separate benzene rings, the valence bonds to the central carbon atom remaining co-planar. The relative insensitivity of the ultraviolet spectrum of this type of ion to the presence of bulky *ortho*-substituents on the benzene rings [24] also supports the idea that the triphenylmethyl cation itself is non-planar.

The most symmetrical structure of this type is propeller-like in shape with symmetry D_3; in this, each benzene ring is rotated from the coplanar position in the same sense about a central C–C bond so as to relieve the steric strain. Lewis and his colleagues [23] have very successfully explained the existence of isomers of the cation of crystal-violet [4 : 4′ : 4″-tri(dimethylamino)triphenylmethyl chloride] in terms of this structure and a variant in which one benzene ring is rotated out of the original plane in the opposite direction to the others. The second isomeric configuration has no symmetry elements.

In more recent studies of the ultraviolet spectra of the triphenylmethyl cation and related ions Newman and Deno,[24] Deno, Jaruzelski, and Schriesheim,[25] and Branch and Walba [26] all prefer unsymmetrical configurations of the parent ion. Deno and his co-workers conclude from the close similarity between the ultraviolet spectra of the ions R_3C^+, R_2CH^+, and R_2CMe^+ (R = *p*-chlorophenyl), and other observations, that the conjugation in the triphenylmethyl ion extends across only one or two of the benzene rings. They appear to have in mind a structure in which the plane of at least one benzene ring makes a large angle with the planes of the other two, *i.e.*, a rather more distorted form of the second configuration proposed by Lewis *et al.* On the other hand, from ultraviolet spectra of the triphenylmethyl cation and related compounds, Chu and Weissman [27] prefer a structure with a 3-fold axis which is closely related to the D_3 propeller-like configuration. They [27] consider the spectra of the triphenylmethyl free radical and assign to it a structure of symmetry C_3 corresponding to a slight non-coplanarity of the central C–C bonds as indicated by paramagnetic-resonance studies.[28] They also interpret the spectrum of the carbonium ion in terms of C_3 symmetry by analogy, but, quite apart from the smallness of the non-planarity assumed for the free radical, *i.e.*, the slightness of the deviation from D_3 symmetry, it is not certain that the same effect should occur with the ion. As C^+ is isoelectronic with boron there are stronger reasons for expecting that the " sextet " of bonding electrons, in the sense used by Sidgwick,[29] should lead to coplanar C^+–C or B–C valencies.

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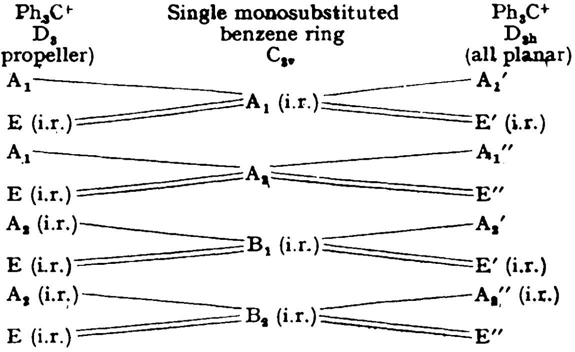
[20] Wheland, " Resonance in Organic Chemistry," Wiley, New York, 1955, p. 364.
[21] Pauling and Wheland, *J. Chem. Phys.*, 1933, **1**, 362.
[22] Dewar, *Proc. Camb. Phil. Soc.*, 1949, **45**, 638.
[23] Lewis, Magel, and Lipkin, *J. Amer. Chem. Soc.*, 1942, **64**, 1774.
[24] Newman and Deno, *ibid.*, 1951, **73**, 3644.
[25] Deno, Jaruzelski, and Schriesheim, *J. Org. Chem.*, 1954, **19**, 155.
[26] Branch and Walba, *J. Amer. Chem. Soc.*, 1954, **76**, 1564.
[27] Chu and Weissman, *J. Chem. Phys.*, 1954, **22**, 21.
[28] Weissman and Sowden, *J. Amer. Chem. Soc.*, 1953, **75**, 503; also personal communication.
[29] Sidgwick, " Chemical Elements and their Compounds," Oxford Univ. Press, 1950, 543.

Infrared spectroscopy provides in principle another means of distinguishing between the D_{3h}, D_3, and unsymmetrical configurations of the ion as discussed above. Karagounis[30] has considered the analogous problem of the determination of the configuration of the triphenylmethyl free radical, and has listed the number of vibration frequencies allowed in the infrared spectra for various assumed symmetries of the nuclear framework. The majority of vibration frequencies of the ion correspond to coupled vibrations of the three benzene rings. For each vibration of a single monosubstituted benzene ring, an ion with a 3-fold symmetry axis (D_{3h} or D_3) would have two different frequencies (one consisting of a doubly degenerate pair) whereas an unsymmetrical ion would have three different frequencies. In the latter case all three frequencies will be infrared active, in the case of D_3 symmetry both frequencies will be active for some vibrations, but for D_{3h} symmetry in every case only one will be allowed in the infrared spectrum. The more detailed relation between the symmetry species for the vibrations of a monosubstituted benzene ring, and the analogous coupled vibrations of the ion under D_{3h} and D_3 symmetries are summarised below.



(i.r.) denotes infrared activity.

It might be inferred from the above that the three likely configurations of the ion could be distinguished by a simple assessment of the total number of absorption bands in the infrared spectrum; on this basis Karagounis has assigned the symmetry D_{3h} to the free radical.[30] However, we do not consider this method reliable as the number of bands observed in a complex spectrum such as this may be much less than the number predicted theoretically for several reasons. Thus, the couplings between the vibrational motions of the separate benzene rings may be so weak that separate absorption bands corresponding to a number of frequencies of the ion are not resolved. Furthermore, since many of the allowed frequencies in the spectrum of a typical monosubstituted benzene such as toluene are weak, the analogous ones of the ion may not be observed. Such factors are liable to give an artificially simple spectrum and this is well exemplified by comparison of the spectra of toluene and triphenylmethane (see Figure). The three benzene rings of the latter molecule are disposed at three corners of a tetrahedron with the " methane " carbon atom in the centre. Whatever their relative orientations about the C–C single bonds, more than twice the number of frequencies are allowed in the spectrum as in that of toluene, and yet the overall complexity of the observed spectrum is not notably greater than that of the smaller molecule.

A more reliable procedure for deducing the symmetry of the ion from its infrared spectrum is to take into account the number of components into which well-defined absorption bands of a single aromatic ring split in the spectrum of the ion. In the spectrum of toluene the strongest bands in the region illustrated are those at 1605, 1497, 728, and

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[30] Karagounis, *Helv. Chim. Acta*, 1951, 34 894

694 cm.$^{-1}$; of these only the third is clearly split into components in the spectrum of the ion. A very similar pattern is observed in the spectrum of triphenylboron. The band at 728 cm.$^{-1}$ in the spectrum of toluene is well known to correspond to the vibration in which all five aromatic C–H bonds bend out of the plane of the benzene ring in unison (symmetry class B_2), and this frequency is rather sensitive to structural changes. In the spectrum of the triphenylmethyl cation this band is replaced by two well-separated components near 810 and 770 cm.$^{-1}$ (774 and 747 cm.$^{-1}$ for triphenylboron); the lower-frequency band is further split into a close-lying doublet separated by 5 cm.$^{-1}$ in some but not all of the spectra of the ion (see Figure). A third neighbouring band near 840 cm.$^{-1}$, although often of considerable intensity, is clearly to be assigned to another type of vibration as it shifts in the opposite direction on passing from the triphenylmethyl cation to triphenylboron (see Figure and p. 680).

The main splitting of 38 cm.$^{-1}$ is undoubtedly caused by interaction of the benzene rings within the cation, and as there are commonly only two components it may be concluded that the ionic symmetry is D_3 (see earlier discussion). The D_{3h} structure would have only one infrared active band and is definitely excluded, while the unsymmetrical configuration might have been expected to give three. In the spectra of crystals further band splittings may occur either through interaction of separate ions or molecules in the unit cell or because a vibration which is degenerate for a free ion may be slightly split owing to unsymmetrical surroundings in the crystal, *i.e.*, the ion may be located on a lattice site of lower symmetry than itself. As either of these causes depend on interionic rather than valence-type forces they usually give rise to splittings of only a few cm.$^{-1}$ in magnitude in the spectra of aromatic compounds.[31] The subsidiary splitting of the band near 772 cm.$^{-1}$ is probably due to one or other of these causes; the split-degeneracy explanation seems the more likely as the two components are of similar intensity. It is very unlikely that this splitting is caused by a lower ionic symmetry than D_3 as it should then have been observed in all the spectra.

A number of other qualitative features of the observed spectrum can also readily be accounted for in terms of D_3 symmetry for the ion with resonance interaction between the central carbon atom and the three benzene rings:

(1) The spectrum of triphenylmethane, with its pyramidal configuration of the aromatic groups, has a very similar overall appearance to that of toluene. The spectra of triphenylmethyl ion and triphenylboron are also closely similar to each other but considerably different from those of the other two molecules, the analogies and differences being particularly marked in the region 1100—900 cm.$^{-1}$. They point to a considerable change of configuration from triphenylmethane to the triphenylmethyl cation such as from a pyramidal to a planar configuration of the valency bonds about the central carbon atom. It would be very surprising if the B–C bonds were not coplanar with trigonal symmetry, and there can be no doubt from the spectral similarities that the boron compound and the cation have the same configuration.

(2) In the spectra of the cation, absorption bands near 1580, 1360, and 1300 cm.$^{-1}$ are all much stronger than, and considerably shifted from, the corresponding bands of triphenylmethane or toluene. The first and last bands are also strong in the triphenylboron spectrum. As absorption bands occurring in this region of the spectra of monosubstituted benzenes are mostly caused by skeletal stretching vibrations of the benzene rings[32] the enhanced intensity means that this type of vibration of the ion gives rise to much greater dipole changes than for triphenylmethane. This is readily explicable if the changes in ring shape during the vibrations cause the net positive charge on the ion to move from one type of location to another across the ring system.

(3) The mean value of the two out-of-plane CH frequencies of the ion discussed above

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[31] Pimentel and McClellan, *J. Chem. Phys.*, 1952, **20**, 270.

[32] Randle and Whiffen, "Molecular Spectroscopy," Institute of Petroleum, London, 1955, p. 111; Whiffen, *J.*, 1956, 1350.

is *ca.* 790 cm.$^{-1}$, as compared with the value of 728 cm.$^{-1}$ for toluene. It is well known [33, 34] that electrophilic substituents such as nitro-groups and carboxylic acid or ester groupings cause well marked increases in this type of frequency. The observed value of the bands in the spectrum of the ion is therefore consistent with an interaction of the π electron system of the benzene rings with the formally vacant p orbital of the central carbon atom. The lower charge on the nucleus of boron than of carbon should lead to a less pronounced electron withdrawal in the former case; in agreement with this the mean frequency of the main bands in triphenylboron is only 760 cm.$^{-1}$.

It is important to note that both of the out-of-plane CH frequencies in the spectrum of the cation are at much higher frequencies than the single band in toluene. This implies that all benzene rings are participating in the resonance. Had one of these not been concerned, as visualised by some supporters of the unsymmetrical structure for the ion, then at least one band would have been expected in the vicinity of 730 cm.$^{-1}$.

(4) The bands near 1190 and 845 cm.$^{-1}$ in the spectrum of the ion move to 1240 cm.$^{-1}$ and 885 cm.$^{-1}$ in that of triphenylboron. These undoubtedly correspond to two of the well-known X-sensitive vibrations of mono-substituted benzene rings of formula PhX.[32, 35] They correspond to coupled C–X and aromatic-ring bond stretching vibrations. In simpler single-ring compounds the higher frequency increases with decreasing electronegativity of X,[35] and the observed frequency shift is therefore in the expected direction.

It may be concluded that the evidence from the infrared spectra is strongly in favour of the D_3 propeller-like structure for the triphenylmethyl cation in the crystalline state. It is very probable that at least a considerable fraction of the ions in solution in non-solvating solvents have this shape also, although some of them may adopt the unsymmetrical configuration under these conditions.[23]

EXPERIMENTAL

All operations with triphenylmethyl salts were conducted with rigid " dry-box " techniques. Filtrations were made through sintered-glass funnels with use of a hand pressure bulb. Ether was distilled over sodium and kept in the " dry-box " before use, acetone was stored over calcium chloride and distilled before use. *n*-Pentane was stored over sodium. Commercial chlorotriphenylmethane and triphenylboron were used as supplied; after a sample had been opened it was kept, as far as possible, in the " dry-box " over phosphoric oxide.

Silver salts were prepared as previously described.[1] Silver trifluoroacetate was prepared from sodium trifluoroacetate and silver nitrate [36] and stored over phosphoric oxide for two months before use.

Triphenylmethyl fluoroborate was precipitated from ethereal solutions of silver fluoroborate and chlorotriphenylmethane, and dissolved in acetone–chloroethylene, the solution was filtered to remove silver chloride, and treated with pentane, to precipitate the salt which was collected and washed successively with ether and pentane. It had m. p. 202° (decomp.) (Found: C, 69·4. Calc. for Ph_3C,BF_4: C, 69·1%). The equivalent weight was determined by adding excess of silver fluoroborate solution to a weighed amount of chlorotriphenylmethane in ether. Silver chloride was dissolved in aqueous ammonia, filtered free from organic material, and precipitated with nitric acid (Found: equiv. of silver chloride precipitated per equiv. of chlorotriphenylmethane, 1·01). A further sample of triphenylmethyl fluoroborate was prepared by Witschonke and Kraus's method [10] and had an infrared absorption spectrum identical with that of a sample prepared by precipitation. Other triphenylmethyl salts tended to give oils when purification was attempted by the above method. Purification could be effected by dissolving in acetonitrile and evaporating off excess of solvent but, since the equivalent weights were satisfactory and the infrared absorption spectra of the mixtures of the salt and silver

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[33] Bellamy, *J.*, 1955, 2818.

[34] Kross, Fassel, and Margoshes, *J. Amer. Chem. Soc.*, 1956, **78**, 1332.

[35] Kross and Fassel, *ibid.*, 1955, **77**, 5858.

[36] Haszeldine, *J.*, 1951, 584.

chloride showed the presence of the required ions, this was not generally attempted. Microanalysis of the complex fluorides is very difficult, the free fluoride tending to pass through any catalyst.

Other triphenylmethyl salts were therefore characterised as follows (all equivs. as AgCl precipitated per equiv. of chlorotriphenylmethane) : *hexafluorophosphate*, m. p. 115° (decomp.) (equiv., 0·99) ; *hexafluoroarsenate* (equiv., 0·99) ; *hexafluoroantimonate* (equiv., 0·99) ; *hexafluoroniobate* (equiv., 1·00) ; *hexafluorotantalate* (equiv., 0·98) ; *fluorosulphonate* (equiv., 0·98) ; *trifluoroacetate* purified as for the fluoroborate, m. p. 106° (decomp.) (Found : C, 71·1 ; H, 4·4. $Ph_3C,C_2O_2F_3$ requires C, 70·8 ; H, 4·2%).

Triphenylmethyl chlorostannate was prepared by condensing excess of stannic chloride on a benzene solution of chlorotriphenylmethane [16] and removing excess of reactants and solvent *in vacuo* (Found : Cl, 32·9. Calc. for $Ph_3C,SnCl_5$: Cl, 32·9%). Triphenylmethyl chloroantimonate was prepared similarly, excess of antimony pentachloride being removed by washing with ether and pentane (Found : Cl, 33·8. Calc. for $Ph_3C,SbCl_6$: Cl, 32·8%). On exposure to moist air triphenylmethyl fluoroborate decomposed to the methanol (Found : C, 87·3 ; H, 6·5. Calc. for $Ph_3C{\cdot}OH$: C, 87·6 ; H, 6·2%). Solubilities of triphenylmethyl salts were tested with dried solvents.

Infrared spectra were measured in suspension in Nujol and hexachlorobutadiene mulls (prepared and kept in the " dry-box ") on a Perkin-Elmer Model 21 spectrometer with rock-salt optics. Mulls of triphenylboron were prepared, in the " dry-box," under nitrogen.

Infrared Peaks Characteristic of Anions.—The following infrared peaks (cm.$^{-1}$) occur in addition to the characteristic spectrum of the triphenylmethyl ion. Positions are approximate as the ions tend to give broad peaks, which when superimposed on the background spectrum are difficult to locate exactly. $Ph_3C^+BF_4^-$; 1050, 1097 (cf. KBF_4 ; 1032, 1058 [37]) : $Ph_3C^+PF_6^-$; 850 (cf. KPF_6 ; 845,[1]) : $Ph_3C^+AsF_6^-$; 700 (cf. $RbAsF_6$; 700 [1]) : $Ph_3C^+SO_3F^-$; 710m, 1070s, 1289m, 1336w, 1643w, 2320w (cf. KSO_3F ; 732s, 972vw, 1073s, 1277s, 1299s, 1656w, 2347w).

Infrared Spectra.—Detailed infrared spectra recorded are given below. These figures are representative of those obtained for various compounds containing the triphenylmethyl cation, all other salts studied giving almost identical spectra. Data for triphenylmethane and toluene are given for comparison only. All figures are in cm.$^{-1}$, and letters have their usual significance.

$Ph_3C^+BF_4^-$: 661w, 703s, 770s, 811s, 850w, 918w, 952w, 985w, 1000w, 1040m, 1058s, 1097s, 1172w, 1195w, 1299s, 1313w, 1364m, 1454s, 1490s, 1565w, sh, 1587s, 2850w, 2910w, 3080w.

$Ph_3C^+TaF_6^-$: 704s, 770s, 775m, 810m, 840m, 850m, 920w, 940w, 976w, 985w, 1000m, 1032w, 1164m, sh, 1172m, 1190s, 1297s, 1359s, 1415w, sh, 1452s, 1485s, 1560m, sh, 1583s, 1620w, 1635w, 2860w, 2950w.

$Ph_3C^+SnCl_5^-$: 646w, 702s, 770m, 807m, 842m, 915w, 955w, sh, 980w, 997m, 1025w, 1046w, 1100w, 1166w, 1185m, 1293s, 1355s, 1406w, sh, 1448s, 1480s, 1577s, 1649m,* 2920w, 3040w, 3330m.*

$Ph_3C^+SbCl_6^-$: 648w, 702s, 773s, 810m, 842m, 916w, 980w, 997m, 1022w, 1166w, 1186m, 1296s, 1359s, 1410w, 1451s, 1483s, 1582s, 2950m.

$Ph_3C{\cdot}O_2C{\cdot}CF_3$: 620m, 704s, 744w, sh, 760s, sh, 769s, 844m, 890w, 907w, 923w, 935w, 960m, 1007w, 1035w, 1088w, 1150s, sh, 1159s, sh, 1166s, 1192w, sh, 1227s, 1331w, 1365s, 1450s,1495m, 1785s, 3040w, 3450w.

Ph_3B : 697s, 742m, 749m, 774m, 885s, 900w, 938m, 976w, 990w, 1000m, 1032m, 1075w, 1158w, sh, 1189w, sh, 1240s, 1263w, 1280s, 1315s, 1350m, 1430s, 1492w, 1565w, sh, 1588s. 1600w, sh, 3050w.

Ph_3CH : 660m, 700s, 735s, 760s, 822w, 853w, 860w, 920m, 975w, 1005w, 1034m, 1080m, 1155w, 1179w, 1248w, 1278w, 1296w, 1315w, 1336w, 1390w, 1445s, 1452s, 1494s, 1595s.

$Ph{\cdot}CH_3$ [38] : (650—1650 cm.$^{-1}$) 694s, 728s, 786m, 844m, 872w, 896m, 930w, 966w, 982w, 1003w, 1030s, 1042m, 1081s, 1107w, 1156m, 1179m, 1211w, 1250w, 1282w, 1314w, 1333w, 1379s, 1460s, 1497s, 1527w, sh, 1575w, 1605w.

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* These peaks are attributed to traces of moisture.

[37] Coté and Thompson, *Proc. Roy. Soc.*, 1951, *A*, **210**, 217.

[38] American Petroleum Institute, Infra-red spectrogram No. 308, submitted by U.S. Naval Research Lab., Washington, D.C.

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UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE. [*Received, July 24th*, 1956.]