968. *Complex Fluorides. Part XI.* The Preparation and Infrared Spectra of Tri-*p*-tolylaminium Salts.*

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Tri-*p*-tolylaminium salts, $(C_7H_7)_3N^{\cdot +}$, of complex fluoro-acids can be prepared by oxidation of tri-*p*-tolylamine with a mixture of iodine and the silver salt of the complex fluoro-acid. The deep blue free-radical aminium salts are fairly stable to hydrolysis. The infrared spectra of tri-*p*-tolylaminium salts of both complex fluoro-acids and perchloric acid show no sign of covalent bonding between the cation and the anion. The spectrum of the tri-*p*-tolylaminium cation has been compared with the spectra of the triphenylmethyl carbonium ion and the tri-*p*-tolylmethyl carbonium ion and favours the crystalline aminium salts' having a D_3, propeller-like, configuration.

Sidgwick[1] lists two main types of aryl-nitrogen free radicals, the type depending upon the arrangement of valency electrons. Free radicals of nitrogen arise either by homolytic fission of an N–N bond or by oxidation, involving the removal of one electron, of the lone-pair in a nitrogen compound. The formation of the diaryl-nitrogen compound by dissociation of the tetra-arylhydrazines[2] is an example of the first type of reaction, and the oxidation of tri-*p*-tolylamine to the tri-*p*-tolylaminium cation of the second.

The nature of the aminium salts, first prepared by Wieland,[3] was elucidated by Weitz and Schwechten,[4] who showed that the deep blue products of the action of oxidising agents upon tri-*p*-tolylamine were salts of the tri-*p*-tolylaminium cation, $(CH_3\cdot C_6H_4)_3N^{\cdot +}$. In particular, it was shown that tri-*p*-tolylamine reacts with the solution resulting from the action of iodine upon silver perchlorate in ether to give tri-*p*-tolylaminium perchlorate. This solution was supposed to contain the chlorine tetroxide radical, but subsequent work[5] showed that the solution contains iodine perchlorate, the solvated iodine cation

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* Part X, *J.*, 1957, 4132.

[1] Sidgwick, " The Chemical Elements and their Compounds," Oxford Univ. Press, 1950.

[2] Wieland and Gambarjan, *Ber.*, 1906, **39**, 1500.

[3] Wieland, *Ber.*, 1907, **40**, 4263.

[4] Weitz, *Angew. Chem.*, 1922, **39**, 1193; Weitz and Schwechten, *Ber.*, 1926, **59**, 2307; 1927, **60**, 545.

[5] Haszeldine and Sharpe, *J.*, 1952, 993.

being an extremely powerful oxidising and iodinating agent. Sharpe [6] demonstrated that silver fluoroborate and iodine in ether gave a very similar solution containing iodine fluoroborate [7] and we have now shown that solvated iodine cations are formed by many silver salts of complex fluoro-acids, since the iodine cation, in each case, will oxidise tri-*p*-tolylamine to the tri-*p*-tolylaminium cation. Ethereal solutions containing positive iodine are extremely unstable; in the absence of tri-*p*-tolylamine the solvent is immediately iodinated.[5] Since the reaction proceeds by way of this oxidation the failure of triphenylamine to give similar aminium salts is understandable. Oxidation of triphenylamine may momentarily produce the appropriate free radical but there is immediate intermolecular attack through the highly activated *para*-positions with formation of tetraphenylbenzidine.[7] The stability of tri-*p*-tolylaminium salts to attack at the *para*-position is further enhanced by their great insolubility in ether and their removal from the possibility of further reaction.

Using the above reaction we prepared tri-*p*-tolylaminium fluoroborate, hexafluorophosphate, hexafluoroarsenate, hexafluoroniobate, hexafluorotantalate, and fluorosulphate. In addition, the hexafluoroantimonate was prepared and characterised by its infrared spectrum. This salt does not give consistent analytical results and it seems probable that antimony pentafluoride, which is presumably evolved on ignition, prevents complete combustion to carbon dioxide. Salts of complex fluoro-acids are often extremely difficult to analyse because of such interference.

We tried to prepare tri-*p*-tolylaminium trifluoroacetate since Haszeldine and Sharpe [5] have shown that iodine and silver trifluoroacetate react in ether to give a solution which contains a strong iodinating agent, presumably the solvated iodine cation, but were unsuccessful; addition of silver trifluoroacetate to a solution containing tri-*p*-tolylamine and iodine gave the deep blue colour characteristic of the aminium salts, but this rapidly faded to give a brown sludge of unknown composition. There are two possible causes of this decomposition: the tri-*p*-tolylaminium trifluoroacetate could be soluble in ether and thus react further with the active products present, or, by analogy with triphenylmethyl trifluoroacetate the aminium trifluoroacetate being formed might be expected to have predominantly covalent character; [8] the resulting nine valency electrons about the central nitrogen atom would cause great instability.

The infrared spectra of tri-*p*-tolylaminium perchlorate, chloroantimonate, and perbromide were described by Otting and Kainer,[9] who detected differences between their spectra and concluded that only in the perchlorate was the bonding purely ionic. Such covalent bonding cannot occur [10] in the salts of many complex fluoro-acids, whose infrared spectra should thus be those of the complex fluoro-anions superimposed on the spectra of the cations. Accordingly, the spectra of tri-*p*-tolylaminium salts of complex fluoro-acids showed a constant background due to the cation and the peaks corresponding to absorption by the anions occurred at positions expected for the completely free anions. The cation spectra now recorded are closely similar to Otting and Kainer's for tri-*p*-tolylaminium chloroantimonate but differ from their spectrum of the perchlorate. A repetition of the infrared spectrum of tri-*p*-tolylaminium perchlorate showed that, in fact, the spectrum of the aminium cation in this substance is identical with that obtained for the tri-*p*-tolylaminium cations in salts of complex fluoro-acids. The spectrum also contains rather diffuse bands which are characteristic of the perchlorate ion. We conclude that in no tri-*p*-tolylaminium salt so far examined is there evidence for anion–cation interaction. In Otting and Kainer's work there was possibly some decomposition in the potassium bromide disc and it may be significant that their spectrum of tri-*p*-tolylaminium perchlorate is fairly closely similar to that of tri-*p*-tolylamine, thus indicating possible decomposition to the latter.

[6] Sharpe, *J.*, 1952, 4538.

[7] Wieland, *Ber.*, 1913, **46**, 3301; Madelung, Reiss, and Herr, *Annalen*, 1927, **454**, 36.

[8] Sharp and Sheppard, *J.*, 1957, 674.

[9] Otting and Kainer, *Chem. Ber.*, 1954, **87**, 1205.

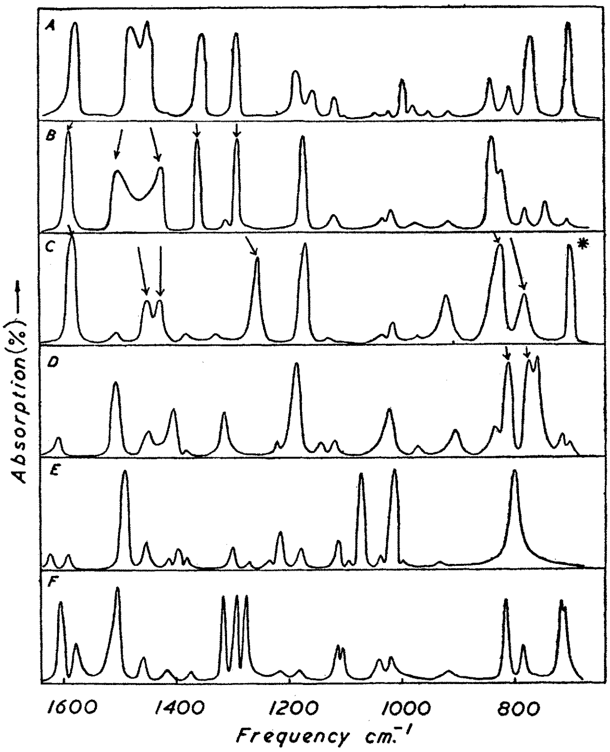
[10] Sharp and Sharpe, *J.*, 1956, 1855, 1858.

The infrared peaks characteristic of the anions now studied (cm.$^{-1}$) were as follows, with figures for potassium salts (except for AsF_6, rubidium salt) for comparison:

Anion =	BF_4	PF_6	AsF_6	SO_3F	ClO_4
$(C_7H_7)_3N\cdot$	1075 (diffuse)	845 s	698 s	710 m, 1065 s, 1283 s	1092 s, 1122 m
K or Rb	1032, 1058 [11]	845 [12]	700 [10]	732 s, 1073 s, 1277 s [13]	1075 s, 1122 s [14]

*The Infrared Spectrum and Structure of the Tri-*p*-tolylaminium Ion.*—The Figure shows infrared spectra of three ions and three reference compounds in the region likely to show absorption sensitive to the configuration of the cation. Except for tri-*p*-tolylaminium hexafluoroarsenate the anions do not absorb in this region.

The problem of the structure of the tri-*p*-tolylaminium ion is similar to that of the triphenylmethyl carbonium ion, the difference in the electronic structures of the tri-*p*-tolylmethyl carbonium ion and the tri-*p*-tolylaminium ion being the presence of one extra electron in the latter. The identity of tri-*p*-tolylaminium perchlorate as a free radical has been established from the paramagnetic susceptibility.[15] Thus the tri-*p*-tolylaminium ion is isoelectronic with the tri-*p*-tolylmethyl radical and hence a knowledge of the structure of the aminium ion will be very strong evidence for the structure of the carbon free radicals.



A, $Ph_3C^+SnCl_5^-$; *B*, $(p\text{-}C_7H_7)_3C^+NbF_6^-$; *C*, $(p\text{-}C_7H_7)_3N^+AsF_6^-$; *D*, $(p\text{-}C_7H_7)_3CCl$; *E*, $p\text{-}C_7H_7Br$; *F*, $(p\text{-}C_7H_7)_3N$.

* Absorption due to the AsF_6^- ion.

The triphenylmethyl carbonium ion is, from its infrared spectrum, probably planar, propeller-like in structure.[8] Many factors, particularly those relating to the steric effects of bulky aromatic rings, which influence the structure of carbonium ions are also important in the structure of the aminium salts. However, the configuration about the central

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[11] Coté and Thompson, *Proc. Roy. Soc.*, 1951, *A*, **210**, 217.
[12] de Lattre, *J. Chem. Phys.*, 1951, **19**, 1610.
[13] Sharp, *J.*, 1957, 3761.
[14] Miller and Wilkins, *Analyt. Chem.*, 1952, **24**, 1253.
[15] Rumpf and Trombe, *Compt. rend.*, 1938, **206**, 671.

nitrogen atom may be influenced by the extra electron in the latter ion. From molecular-orbital theory, Walsh concludes that the methyl radical should be pyramidal [16] but, from spectra, Herzberg and Shoosmith conclude that it is only slightly bent in its ground state and planar in an upper state.[17] For the aminium ion or for the triphenylmethyl free radical, resonance stabilisation will be a maximum for an all-planar configuration of the ion.[18, 19, 20] Swarc has pointed out that steric effects between the *ortho*-hydrogen atoms would make a completely planar structure impossible for the triphenylmethyl free radical [21] but the strain could be relieved by rotation of one or more aromatic rings about the central bonds. As for the triphenylmethyl cation, this rotation would not necessarily inhibit conjugation between the separate rings as the valency bonds to the central carbon atom would remain coplanar.

Little evidence exists for the structure of the tri-*p*-tolylaminium cation. Otting and Kainer [9] discussed its infrared spectrum in terms of an all-planar structure of symmetry D_{3h}, basing their evidence on Karagounis's [22] work on the triphenylmethyl radical which was also considered to have symmetry D_{3h}. However, the latter work is based on doubtful assumptions [8] and Otting and Kainer's discussion must be reconsidered. For the structures of the isoelectronic carbon free radicals there is more evidence, although it is not very definite. Chu and Weissman [23] have discussed the absorption and luminescent spectra of the triphenylmethyl free radical in terms of a structure of symmetry C_3 and consider that paramagnetic resonance supports this conclusion.[24] However, studies of the stabilisation of the triphenylmethyl radical in solid solutions of planar molecules such as fluorene suggest that the radical itself is planar.[25] Brown and Dodson [26] suggest that the entry of an electron into trimesitylboron, to form the trimesitylboron anion free radical, is into a non-localised orbital. The most readily envisaged stereochemical form of such a free radical, isoelectronic with the aminium salts and the carbon free radicals, is planar about the central boron atom.

For an entity as complicated as the tri-*p*-tolylaminium ion we cannot completely assign all the observed infrared bands to decide definitely the symmetry of the ion. Such a decision can be made only by comparing the infrared spectrum with those of compounds of known structure. From comparison with the spectrum of triphenylboron, the triphenylmethyl carbonium ion probably has a planar arrangement of the bonds about the central atom.[8] The infrared spectra of the triphenylmethyl carbonium ion, the tri-*p*-tolylmethyl carbonium ion, and the tri-*p*-tolylaminium ion show well-marked resemblance, between each other, but are completely distinct from those of compounds such as chlorotri-*p*-tolylmethane where a planar structure is not possible. These resemblances are particularly well marked in the spectra of the three cations near 1580, 1480, 1445, and 1300 cm.$^{-1}$, the bands being much stronger than those of *p*-bromotoluene and chlorotri-*p*-tolylmethane. For triphenylmethyl and tri-*p*-tolylmethyl salts there is a strong band near 1360 cm.$^{-1}$, but this is weak for tri-*p*-tolylaminium salts; however, it is also very weak in the spectrum of triphenylboron [8] and must be very sensitive to changes in substituents. These bands are all associated with skeletal stretching vibrations of the aromatic rings [27] and the enhanced intensity of this type of vibration is due to the greater dipole changes over the conjugated system than those over the aromatic systems of the

[16] Walsh, *J.*, 1953, 2296.
[17] Herzberg and Shoosmith, *Canad. J. Phys.*, 1956, **34**, 523.
[18] Pauling and Wheland, *J. Chem. Phys.*, 1933, **1**, 362.
[19] Hückel, *Z. Physik*, 1933, **83**, 632.
[20] Dewar, *Proc. Cambridge Phil. Soc.*, 1949, **45**, 638.
[21] Swarc, *Discuss. Faraday Soc.*, 1947, No. 2, 42.
[22] Karagounis, *Helv. Chim. Acta*, 1951, **34**, 994.
[23] Chu and Weissman, *J. Chem. Phys.*, 1954, **22**, 21.
[24] Weissman and Sowden, *J. Amer. Chem. Soc.*, 1953, **75**, 503, and personal communication.
[25] Aston, Fritz, and Seki, *J. Amer. Chem. Soc.*, 1957, **79**, 1000.
[26] Brown and Dodson, *ibid.*, p. 2302.
[27] Randle and Whiffen, "Molecular Spectroscopy," Institute of Petroleum, London, 1955, p. 111; Whiffen, *J.*, 1956, 1350.

simpler derivatives. The constancy of the pattern shows that all the ions have similar, presumably planar, arrangements about their central atoms. Tri-*p*-tolylamine also has a very strong band at about 1600 cm.$^{-1}$; this is not the same band that is enhanced in intensity at 1580 cm^{-1} in the carbonium and aminium salts, the latter band also occurring at about 1580 cm^{-1} in tri-*p*-tolylamine but being only of medium intensity.

The resemblance between the spectra of the three cations is continued over the range 1300—900 cm.$^{-1}$. The enhanced intensity of the δ_3 vibration at about 1180 cm.$^{-1}$ [28] is not especially characteristic of the spectra of planar radical ions as has been claimed by Otting and Kainer,[9] since this band is also very strong in chlorotri-*p*-tolylmethane.

Apart from the extra band at about 1360 cm.$^{-1}$ in the spectra of triphenylmethyl and tri-*p*-tolylmethyl salts the only major differences between the spectra of the three cations come in the region 900—700 cm.^{1}, this being the region most sensitive to ring substitution. Spectra of tri-*p*-tolylmethyl salts and tri-*p*-tolylaminium salts remain fairly similar, except that one additional peak of medium intensity occurs near 900 cm.$^{-1}$ in that of the aminium salt. The strong band near 800 cm.$^{-1}$ in *para*-substituted benzenes corresponds to the C–H out-of-plane vibration. In *p*-bromotoluene this vibration belongs to the symmetry class B_2 and hence, in accordance with the selection rules given for the triphenylmethyl carbonium ion,[8] should split into three components in a unsymmetrical planar structure, two in a D_3 propeller-like structure, and remain as one in a planar D_{3h} structure. This band is clearly split into two components in the spectra of both tri-*p*-tolylmethyl carbonium salts and tri-*p*-tolylaminium salts and, although not giving a completely definite decision since one component may possibly not be resolved, this splitting favours a planar, propeller-like structure for both these salts. The spectrum of chlorotri-*p*-tolylmethane also shows a similar splitting and, in this case, the lower band appears further split into a close-lying doublet. This subsidiary splitting does not occur in the spectra of fluorotri-*p*-tolylmethane or tri-*p*-tolylmethanol and, although it may be due to the symmetry of the molecule in chlorotri-*p*-tolylmethane, it is more likely due to intermolecular interactions or split degeneracy, the molecule being on a site of lower symmetry than itself.[8]

The mean values of the C–H out-of-plane frequencies of the tri-*p*-tolylmethyl carbonium ion and the tri-*p*-tolylaminium ion are 834 and 804 cm.$^{-1}$ respectively. Electrophilic substituents markedly increase the frequencies of this type of vibration [30, 31] and the value for the tri-*p*-tolylmethyl cation shows the effect of the interaction of the π-electron system of the aromatic rings with the formally vacant *p* orbital of the central carbon atom. The spectrum of the tri-*p*-tolylaminium ion does not show such a shift and the orbital containing the one unpaired electron cannot have a pronounced electron-withdrawing effect on the aromatic system.

EXPERIMENTAL

Silver salts of complex fluoro-acids were prepared with bromine trifluoride as described previously.[10] Silver perchlorate was prepared by the action of excess of silver carbonate on aqueous perchloric acid. The solution was evaporated to dryness and the last traces of water removed at 130° (Found: Ag, 51·6. Calc. for $AgClO_4$: Ag. 51·9%).

Tri-*p*-tolylamine was prepared by standard methods; *p*-toluidine and its hydrochloride were heated to produce di-*p*-tolylamine,[32] which was converted with *p*-iodotoluene into tri-*p*-tolylamine. Recrystallised from glacial acetic acid,[32] it had m. p. 117° (Wieland [33] records 117°).

For the preparation of *tri-*p*-tolylaminium salts*, tri-*p*-tolylamine was dissolved in anhydrous ether and a solution of iodine in ether added. On addition of the silver salt dissolved in ether, silver iodide and the deep blue aminium salt were precipitated. The aminium salt was extracted with the minimum quantity of chloroform and the solvent removed in a stream of dry air.

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[28] Kohlrausch and Paulsen, *Monatsh.*, 1939, **72**, 268.
[29] Bellamy, " The Infrared Spectra of Complex Molecules," Methuen, London, 1954.
[30] *Idem, J.*, 1955, 2818.
[31] Kross, Fassel, and Margoshes, *J. Amer. Chem. Soc.*, 1956, **78**, 1332.
[32] Rumpf, *Bull. Soc. chim. France*, 1940, **7**, 643.
[33] Wieland, *Ber.*, 1907, **40**, 4260.

The salts are slowly hydrolysed by atmospheric moisture but, with fast work, can be handled in the open. They are stable for months in a sealed tube. Owing to their intense colour, m. p.s could not be determined exactly [Found: C, 67·6; H, 5·9. $C_{21}H_{21}N,BF_4$ requires C, 67·4; H, 5·6. Found: C, 57·8; H, 4·9. $C_{21}H_{21}N,PF_6$ requires C, 58·3; H, 4·85. Found: C, 52·5; H, 4·6. $C_{21}H_{21}N,AsF_6$ requires C, 53·0; H, 4·4. Found: C, 50·8; H, 4·7. $C_{21}H_{21}N,NbF_6$ requires C, 51·1; H, 4·3. Found: C, 42·3; H, 3·6; Ta, 30·8. $C_{21}H_{21}N,TaF_6$ requires C, 43·3; H, 3·6; Ta, 31·3 (Ta was determined as Ta_2O_5 after ignition of the aminium salt). Found: C, 65·5; H, 5·6. $C_{21}H_{21}N,SO_3F$ requires C, 65·3; H, 5·4. Found: C, 65·4; H, 5·3. Calc. for $C_{21}H_{21}N,ClO_4$: C, 65·2; H, 5·5%]. The hexafluoroantimonate, prepared similarly, had the infrared spectrum expected for an aminium salt but could not be consistently analysed.

Chlorotri-*p*-tolylmethane was prepared from the carbinol (m. p. 94°) [prepared according to Mothwurf[34] from *p*-tolylmagnesium iodide and methyl *p*-toluate (Mothwurf records m. p. 96·5°)] which was converted by distillation with acetyl chloride[35] and recrystallising from light petroleum (b. p. 60—80°) into the chloro-derivative, m. p. 178° (Hey *et al.*[35] give m. p. 180°). Tri-*p*-tolylmethyl *salts* were prepared and characterised similarly to triphenylmethyl salts[8] (all equivs. as AgCl precipitated per equiv. of chlorotri-*p*-tolylmethane. Found: for the fluoroborate 1·01, hexafluorophosphate 0·99, hexafluoroniobate 0·99). They are yellow, crystalline solids, similar in every respect to triphenylmethyl carbonium salts. Their infrared spectra are that of the complex fluoro-anion superimposed on the background spectrum of the tri-*p*-tolylmethyl carbonium ion, the latter being the same for all the salts.

Fluorotri-p-*tolylmethane* was prepared similarly to fluorotriphenylmethane[36] by adding excess of anhydrous hydrogen fluoride to chlorotri-*p*-tolylmethane, allowing the excess to evaporate, and recrystallising the product from light petroleum. It had m. p. 115° (Found: C, 86·7; H, 6·8. $C_{22}H_{21}F$ requires C, 86·9; H, 6·9%).

Infrared spectra were measured in suspension in Nujol and hexachlorobutadiene mulls on a Perkin-Elmer Model 21 spectrometer with rock-salt optics. Mulls of tri-*p*-tolylmethyl carbonium salts were prepared and kept in the " dry box."

Detailed infrared spectra (cm.$^{-1}$) are given below. These figures are representative of those obtained with salts containing the tri-*p*-tolylmethyl carbonium and tri-*p*-tolylaminium ions, all the other salts studied and containing the same cation giving almost identical spectra.

$Ph_3C^+SnCl_5^-$: 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*.

$(p\text{-}C_7H_7)_3C^+NbF_6^-$: 710w, 746m, 780m, 823m, 839s, 919w, 975w, 1017m, 1030w, 1120w, 1185s, 1294s, 1314w, 1362s, 1427s, 1503s, 1595s, 2590w, 2860m, 2930m, 2970m.

$(p\text{-}C_7H_7)_3N^+AsF_6^-$: 700s†, 782m, 827s, 920m, 1019m, 1037w, 1127w, 1177s, 1257s, 1327w, 1385w, 1428s, 1454s, 1507w, 1582s, 1645w, 1920w, 2920m, 3060w.

$(p\text{-}C_7H_7)_3N^+ClO_4^-$: 700w, 777m, 822s, 915m, 1017w,sh, 1040w, 1092s, 1122w, 1169s, 1262s, 1320m, 1382w, 1429m, 1452m, 1505w, 1581s, 1642w, 2920w, 3050m, 3200w.

$(p\text{-}C_7H_7)_3N^+SbF_6^-$: 660s, 704m, 781s, 826s, 920m, 970w, 1017m, 1034m, 1128w, 1175s, 1220w, 1256s, 1328w, 1430m, 1450m, 1508w, 1583s, 1641w, 1925w, 1383w, 2610w, 2745w, 2870w, 2940m, 3080w.

$(p\text{-}C_7H_7)_3CCl$: 676w, 704w, 715w, 768s, 776s, 811s, 833m, 904m, 969w, 1018s, 1115w, 1144w, 1185s, 1204w, 1312m, 1380w, 1405m, 1450w, 1506s, 1608w, 1940w, 2860m, 2900s, 3020s.

$p\text{-}C_7H_7Br$: 799s, 932w, 955w, 1013s, 1037w, 1071s, 1092w, 1112m, 1178w, 1212m, 1231w, 1270w, 1300w, 1381w, 1396w, 1411w, 1452m, 1490s, 1592w, 1621m, 1774w, 1887m, 2920m, 3020w.

$(p\text{-}C_7H_7)_3N$: 640w, 714m, 781w, 815s, 920w, 1038w, 1113m, 1175w, 1216w, 1280s, 1297s, 1324s, 1380w, 1424w, 1457w, 1510s, 1585w, 1619m, 2900m, 2960m, 3060m.

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* These peaks are attributed to traces of moisture.

† Absorption due to AsF_6^- ion.

[34] Mothwurf, *Ber.*, 1904, **37**, 3155.

[35] Davies, Hey, and Williams, *J.*, 1956, 4401.

[36] Blicke, *J. Amer. Chem. Soc.*, 1924, **46**, 1515.