10. *The Basic Properties, Infrared Spectra, and Structures of Triphenylamine and Tri-*p*-tolylamine.*

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Complexes are formed between triarylamines and boron trichloride and boron tribromide. The preparations of these adducts and also of some triarylammonium salts are described. From a consideration of the infrared spectra of triphenylamine and tri-*p*-tolylamine it is considered that there is a planar or almost planar arrangement about the central nitrogen atom in these molecules.

It has generally been considered that triarylamines are almost non-basic since, apart from hydrofluoric [1] and perchloric [2] acids, they dissolve only in acids which oxidise them. In a recent publication [3] one of us has given preliminary details of the preparation of some triphenylammonium salts from non-aqueous solvents. We now give further details of these preparations and of the preparation of some tri-*p*-tolylammonium salts, and describe the preparation of some triarylamine complexes.

Triarylamine Complexes.—Triphenylamine and tri-*p*-tolylamine solutions in benzene become slightly coloured when Lewis acids such as boron trifluoride, stannic chloride, and antimony tribromide are added. It seems likely that some form of weak complex is being formed and these are under investigation. On addition of boron trichloride or tribromide to the triarylamine solutions there is immediate precipitation of dark-coloured solids. The

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[1] Weinland and Reischle, *Ber.*, 1908, **41**, 3617.
[2] Hofmann, Metzler, and Höbold, *Ber.*, 1910, **43**, 1080.
[3] Sharp, *Chem. and Ind.*, 1958, 1235.

triphenylamine–boron trichloride adduct was too unstable to be isolated at room temperature, but 1 : 1 adducts were prepared between triphenylamine and boron tribromide and between tri-*p*-tolylamine and boron trichloride. An adduct in which the molecular proportions are nearly 1 : 2 was formed between tri-*p*-tolylamine and boron tribromide. The 1 : 1 adducts are presumably straightforward co-ordination compounds but the 1 : 2 adduct recalls the 1 : 2 adducts formed between ethers and boron trifluoride[4] and between various amines and boron halides.[5] It is possible to write structures which contain tetrahalogenoborate ions for these adducts but Brown and his co-workers[5] consider that they probably contain halogen bridges. The infrared spectra of the 1 : 1 boron trichloride–tri-*p*-tolylamine adduct and the 2 : 1 boron tribromide–tri-*p*-tolylamine adduct prepared in the present work are both very similar and it must be concluded that the bonding to the amine in the two adducts is very similar. This is not conclusive evidence, however, for the type of bonding present in the rest of the molecule. The order of stability of the boron halide adducts ($BF_3 < BCl_3 < BBr_3$) is in accordance with the normal order of strengths of the boron halides as Lewis acids.[6]

Triarylammonium Salts.—The addition of traces of moisture to the solution of triphenylamine and boron trifluoride in benzene precipitates a pale green oil which rapidly crystallises and which we formulate as triphenylammonium fluoroborate. Hydrolysis of boron trifluoride gives some tetrafluoroboric acid by disproportionation of hydroxytrifluoroboric acid[7] or alternatively the reaction could proceed by disproportionation of a precipitate of triphenylammonium hydroxyfluoroborate. The infrared spectrum of the crystalline product shows no hydroxyl groups. Tri-*p*-tolylamine gave a similar oil but this would not crystallise. Passage of hydrogen halide through a solution of triarylamine and the appropriate metal halide gave other triarylammonium salts. Because of the insolubility of the boron trichloride and boron tribromide adducts in benzene solution it was not possible to prepare the tetrachloroborates or tetrabromoborates; hydrogen halide passed through a solution of tri-*p*-tolylamine and stannic halide in benzene gave a deep blue precipitate which was probably the aminium salt. The triarylammonium salts are extremely sensitive to moisture and must be handled in the dry-box. They slowly lose hydrogen halide at room temperature, and analysis and examination of physical properties must be carried out immediately after preparation. The salts are soluble in chloroform but they cannot be recovered and it is very doubtful whether they are stable in solution.

The formulation of these derivatives as triarylammonium salts is supported by their infrared spectra which, except for the fluoroborate, are almost identical over the range 2000—650 cm.$^{-1}$. The fluoroborate has the strong bands associated with the fluoroborate ion near 1000 cm.$^{-1}$ and at about 750 cm.$^{-1}$.[8] The 1000 cm.$^{-1}$ peak shows more splitting than is normally observed in fluoroborates and it is believed that this splitting and the occurrence of the normally infrared-inactive band at 750 cm.$^{-1}$ are due to strong hydrogen bonding between cation and anion. Over the range 1600—650 cm.$^{-1}$ the spectra are very similar to those of related tetrahedral molecules such as triphenylmethane and tri-*p*-tolylchloromethane (see Figure), the spectra providing further evidence in favour of the formulation of these salts as triarylammonium derivatives. Between 4000 and 2000 cm.$^{-1}$ the spectra depend on the anion. The normal aromatic C–H frequencies occur near 3000 cm.$^{-1}$ but the N–H frequencies are split and appear between 2900 and 2400 cm.$^{-1}$. The assignment of these bands has been confirmed by preparation of *N*-deuterotriphenylammonium fluoroborate, in which the corresponding N–D bands are observed between 2250 and 2050 cm.$^{-1}$. The position and appearance of these bands provides additional evidence for the presence of hydrogen bonding between cation and anion in all these salts.[9]

[4] Wirth, Jackson, and Griffiths, *J. Phys. Chem.*, 1958, **62**, 871.
[5] Brown, Stehle, and Tierney, *J. Amer. Chem. Soc.*, 1957, **79**, 2020.
[6] Brown and Holmes, *ibid.*, 1956, **78**, 2173.
[7] Wamser, *ibid.*, 1951, **73**, 409.
[8] Coté and Thompson, *Proc. Roy. Soc.*, 1952, *A*, **210**, 217.
[9] Nuttall, Sharp, and Waddington, unpublished observations.

It would have been useful to have been able to compare the spectra of the present triphenylammonium salts with the spectra of triphenylamine–hydrofluoric acid and triphenylamine–perchloric acid but we could not repeat the preparation of these latter adducts satisfactorily. Triphenylamine dissolves in anhydrous hydrogen fluoride to give a dark-blue solution but on removal of solvent the triphenylamine was recovered unchanged. Only unchanged triphenylamine could be recovered from aqueous hydrofluoric acid. Attempts to prepare the triphenylamine–perchloric acid adducts gave either unchanged triphenylamine or dark-coloured oxidised products. Triphenylamine is soluble in anhydrous hydrogen chloride to give a pale blue solution but once again only triphenylamine could be obtained at room temperature after removal of solvent. The blue solutions of triphenylamine in hydrogen fluoride and hydrogen chloride are presumably due to the presence of protonated species but it seems unlikely that the protonation is on the nitrogen only as triphenylammonium salts are colourless or pale green.

*Infrared Spectra and Structure of Triphenylamine and Tri-*p*-tolylamine.*—The present demonstration that triarylamines have some basic properties leads to reconsideration of the evidence for the structure of these amines. The dipole moment of triphenylamine is 0·65 D;[10] such a small value may not be significantly different from zero. From a study of the ultraviolet spectrum Jaffé[11] considers that there is extensive conjugation in the molecule. The chemical properties of triphenylamine are in accordance with a stable conjugated system. We have now shown that the ultraviolet spectrum of tri-*p*-tolylamine is similar to that of triphenylamine and this is also evidence of the extensive conjugation between the lone-pair of electrons on the central nitrogen atom and the aromatic ring systems. Normally, lone pairs make a finite contribution to the stereochemistry of a molecule but to explain the low dipole moment it seems likely that in the triarylamines the lone pair of electrons is absorbed into the overall conjugated system.

If the skeletal arrangement about the central nitrogen atom of triphenylamine is planar it would be expected, by analogy with the triphenylmethyl carbonium ion, that the molecule would be propeller-shaped having symmetry D_3.[12] If the molecule were slightly bent about the central nitrogen atom the highest possible symmetry would be C_3. Ideally it should be possible to decide between these two configurations by a simple process of counting the number of components into which known vibrations are split but, as discussed previously,[12] such a simple assessment is not possible for molecules of this complexity.

The Figure shows the spectra of the amines, the corresponding ammonium salts, triphenylmethane, and tri-*p*-tolylchloromethane, the corresponding carbonium salts, and triphenylboron and the tri-*p*-tolylaminium cation. The differences between the spectra of the amines and the spectra of molecules such as triphenylmethane and the triphenylammonium ion which must be tetrahedral are sufficiently marked, particularly near 1600 and 1300 cm.$^{-1}$, to make it unlikely that the triarylamines are fully tetrahedral. The strong bands at 1600 and near 1300 cm.$^{-1}$ are common to the amines, to the related carbonium ions, and to triphenylboron and the tri-*p*-tolylaminium ion and favour a planar skeletal arrangement in the amines although it could possibly be considered that these bands merely show the effect of the extensive conjugation in the molecules. The presence of only one absorption band in the C–H out-of-plane region of the spectrum of triphenylamine is anomalous since, even with a planar propeller-shaped structure, there should be two infrared-active components for this vibration;[12] an all planar configuration would only give one band in this region. It is unlikely for steric reasons that the molecule is all-planar and there are two bands in the corresponding region in tri-*p*-tolylamine, so it must be assumed that the two vibrations are accidentally degenerate in triphenylamine. Thus, whilst not conclusive, the infrared spectra of triphenylamine and tri-*p*-tolylamine

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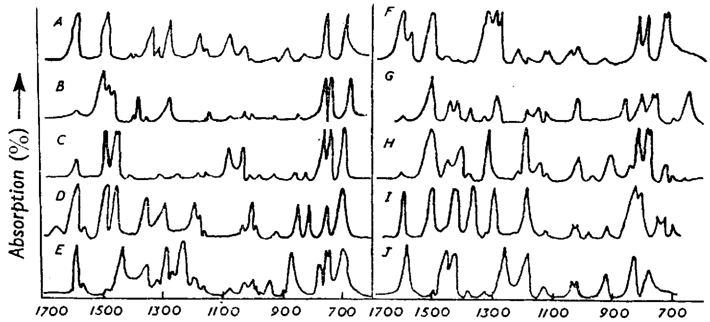
[10] Klages and Langpape, *Z. Elektrochem.*, 1959, **63**, 533.
[11] Jaffé, *J. Chem. Phys.*, 1954, **22**, 1430.
[12] Sharp and Sheppard, *J.*, 1957, 674.

agree with other evidence in favouring a planar, or almost planar, arrangement about the central nitrogen atom.

In having planar or near-planar structures, triarylamines, with conjugation between the lone pair of electrons on the nitrogen and π-electron systems of the aromatic rings, are very similar to trisilylamine, where the lone pair of electrons appears to be bonded to unfilled *d* orbitals on the silicon atoms.[13,14,15]

[*Added in proof.*] Recently Sasaki, Kimura, and Kubo [16] described electron diffraction measurements on triphenylamine. In the vapour at 200° the C–N–C bond angle is estimated to be 116 ± 2°. The authors comment that their values could be interpreted as involving a flat, trigonally-bonded nitrogen at equilibrium, the molecule appearing pyramidal because of thermal bending motions. They prefer, however, a non-planar molecule of C_3 symmetry. Since the infrared studies of the present work were carried out on the solid it is possible that a planar configuration is stabilised in that phase.

Infrared spectra of triarylamines and related compounds.



A, Triphenylamine; *B*, Triphenylammonium bromoantimonite; *C*, Triphenylmethane; *D*, Triphenylmethyl chlorostannate; *E*, Triphenylboron; *F*, Tri-*p*-tolylamine; *G*, Tri-*p*-tolylammonium chloroantimonite; *H*, Tri-*p*-tolylchloromethane; *I*, Tri-*p*-tolylmethyl hexafluoroniobate; *J*, Tri-*p*-tolylaminium hexafluorotantalate.

EXPERIMENTAL

Triphenylamine and tri-*p*-tolylamine in benzene gave dark-coloured products with boron trichloride and boron tribromide. These adducts were characterised by condensing excess of the halides on a solution of a known quantity of the amine in benzene or toluene, the whole experiment being carried out in a vacuum line. After allowing the solutions to warm, excess of reactants and solvent were removed *in vacuo* and the pale brown products weighed. The adducts are extremely sensitive to moisture and fume even in the dry-box. Analyses were made for halogen, the transfer to solution being made as quickly as possible. Although a solution of triphenylamine in benzene gave a dark-coloured precipitate with boron trichloride the product was unstable under vacuum at room temperature. We prepared *triphenylamine–boron tribromide* [1 mole of amine absorbs 0·9 mole of BBr_3. Found Br, 45·5. $(C_6H_5)_3N,BBr_3$ requires Br, 48·4%]; and *tri-*p*-tolylamineboron trichloride* [1 mole of amine absorbs 1·1 moles of BCl_3. Found: Cl, 23·4. $(C_7H_7)_3N,BCl_3$ requires Cl, 26·3%], and *tribromide* [1 mole of amine absorbs 1·8 moles of BBr_3. Found: Br, 55·0. $(C_7H_7)_3N,BBr_3$ requires Br, 44·6. $(C_7H_7)_3N,2BBr_3$ requires Br, 60·8%].

Triphenylammonium salts were prepared as previously described.[3] *N*-Deuterotriphenylammonium fluoroborate was prepared by shaking sodium-dried benzene with heavy water followed by passage of boron trifluoride through a solution of triphenylamine in the moist benzene. The following tri-*p*-tolylammonium salts were prepared by similar methods to those

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[13] Hedberg, *J. Amer. Chem. Soc.*, 1955, **77**, 6491.
[14] Ebsworth, Hall, MacKillop, McKean, Sheppard, and Woodward, *Spectrochim. Acta*, 1958, **13**, 202.
[15] Kriegsmann and Förster, *Z. anorg. Chem.*, 1959, **298**, 212.
[16] Sasaki, Kimura, and Kubo, *J. Chem. Phys.*, 1959, **31**, 477.

used for triphenylammonium salts [3] (tri-*p*-tolylammonium fluoroborate would not crystallise): *chloroantimonite* [Found: C, 44·3; H, 4·4; Cl, 24·4. $(C_7H_7)_3NHSbCl_4$ requires C, 45·7; H, 4·0; Cl, 25·7%], *bromoantimonite* [Found: C, 32·7; H, 3·4. $(C_7H_7)_3NHSbBr_4$ requires C, 34·5; H, 3·0%]. The passage of hydrogen halide through a benzene solution of tri-*p*-tolylamine and stannic chloride or stannic bromide gave a deep blue precipitate. Attempts were made to prepare perchlorates and fluorides as described in the literature.[1,2] In all cases, after removal of solvent, only unchanged amine or very dark oxidised products remained. Triphenylamine dissolved readily in anhydrous hydrogen fluoride to give a deep blue solution. On evaporation of the solvent in a stream of dry nitrogen unchanged triphenylamine remained. Triphenylamine dissolved in liquid hydrogen chloride to give a pale blue solution but again only triphenylamine remained on removal of solvent.

Ultraviolet spectra were recorded in methanol on a Unicam SP.500 spectrophotometer. The spectrum of triphenylamine was very similar to that recorded by Jaffé: [11] $\lambda_{\text{max.}}$ 296—298 mμ, $\varepsilon_{\text{max.}}$ 19,900. $\lambda_{\text{min.}}$ 249—250, $\varepsilon_{\text{min.}}$ 1600. That of tri-*p*-tolylamine had $\lambda_{\text{max.}}$ 298 mμ, $\varepsilon_{\text{max.}}$ 56,450; $\lambda_{\text{min.}}$ 252 mμ, $\varepsilon_{\text{min.}}$ 1470.

Infrared spectra were recorded on a Perkin-Elmer Model 21 spectrophotometer with rock-salt or fluorite optics. Mulls were prepared in Nujol or hexachlorobutadiene (in the dry-box if necessary).

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