Boron Trifluoride Addition Compounds of Primary Aromatic Diamines

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The preparation and characterization of boron trifluoride addition compounds of the following diamines are described: *p*-phenylenediamine (IIIa), benzidine (IIIb), 3,3′-dimethylbenzidine (IIIc), 3,3′-dimethoxybenzidine (IIId), 3,3′-dichlorobenzidine (IIIe), α,α′-bi-*p*-toluidine (IIIf), and 1,8-naphthalenediamine (IIIg). These compounds are the first reported examples of boron trifluoride addition compounds of primary aromatic diamines. The infrared spectra offer strong support for the classical coördination structure of these addition compounds.

The ability of boron trifluoride to accept electron pairs from electron donors has long been recognized and is demonstrated by the existence of a great variety of boron trifluoride addition compounds.[1b] Attempting to prepare particularly stable coördination compounds and then investigate the nature of the bond between donor and acceptor, we have chosen to use amines for these investigations, since the coördination power of a donor atom is known to increase with decreasing atomic size. Furthermore, intending to add resonance energy to the stability of the compounds expected, we have aimed the present investigation at the synthesis of boron trifluoride addition compounds of primary aromatic carbocyclic and heterocyclic di- and polyamines. The coördination power of the latter has never before been examined.

Experimental[2]

Starting Materials.—The carbocyclic and heterocyclic di- and polyamines (I, VI, and VII) used for these investigations were purified by repeated recrystallizations until they appeared spectroscopically pure. Boron trifluoride was applied in the form of its diethyl ether addition compound (II). This was purified by vacuum distillation[3] and the fraction $n^{20}\text{D}$ 1.3443 was used for the investigations.

Synthesis of Boron Trifluoride Addition Compounds of Aromatic Diamines (III).—The addition of the diamines (I) to boron trifluoride ethyl etherate proceeds more or less vigorously and is modified advantageously by employing suitable solvents and low temperatures. It was found that, of various experimental modifications, the addition of I to II in ethyl ether as the diluent furnished the best results. The general procedure may be demonstrated on **boron trifluoride–benzidine addition compound (IIIb)**: A three-neck round-bottomed flask fitted with a reflux condenser, drying tube, thermometer, and addition funnel was charged with 28.4 g. of II (0.2 mole). While the temperature in the flask was maintained at 0 to +5°, a suspension of 18.4 g. (0.1 mole) of dry recrystallized benzidine (Ib) in 100 ml. of absolute ether was added dropwise. For this procedure it is advisable to use an addition funnel with a sufficiently wide bore in the stopcock to avoid clogging. The mixture was refluxed for 1 hr., suction filtered and the solid vacuum-dried over phosphorus pentoxide. There was obtained 31.9 g. of IIIb (quantitative yield), m.p. 335–336°.

Purification of Boron Trifluoride Addition Compounds of Aromatic Diamines (III).—The following addition compounds could be recrystallized (agent and crystalline form in parentheses): IIIc (water and activated charcoal; roseate clusters of needles); IIId (methanol and charcoal; beige needles in clusters); IIIf (water or isopropyl alcohol; colorless, fine long needles). Compounds IIIa, IIIb, IIIe, IIIg, VIII, and IX could not be purified by recrystallization, because upon boiling with solvents they changed into solids of ill-defined compositions. Therefore, in these cases the crude materials were repeatedly triturated with ethyl ether at room temperature and then dried *in vacuo* over phosphorus pentoxide. It is a well known fact in boron trifluoride chemistry that addition compounds with organic donor molecules oftentimes cannot be recrystallized, *e.g.*, in the case of *p*-toluidine[4] and polyfunctional organic amines,[5] and it is rather surprising that compounds IIIc, IIId, and IIIf possess such a high degree of stability which makes them capable of recrystallization from water without undergoing any reaction.

Triphenylborine Addition Compound of *p*-Phenylenediamine (V).—To a well cooled solution of 3.9 g. (0.016 mole) of recrystallized and dried triphenylborine (IV)[6] in 60 ml. of dry ether was added dropwise a suspension containing 0.9 g. (0.008 mole) of *p*-phenylenediamine (Ia) in 50 ml. of dry ether. While flushing the reaction vessel continuously with dry nitrogen, the reaction mixture was refluxed for 2 hr. and then allowed to cool. The white solid reaction product was isolated by suction filtration and weighed, vacuum-dried, 4.1 g. (yield 85.3%). By recrystallization from chloroform, V was obtained in the form of white needles melting at 148–149° (cor.).

Anal. Calcd. for $C_{42}H_{38}B_2N_2$: C, 85.15; H, 6.47; B, 3.65; N, 4.73. Found: C, 84.89; H, 6.62; B, 3.69; N, 5.08.

Results and Discussion

Boron trifluoride addition compounds (III) of aromatic diamines possessing a molar ratio of diamine/boron trifluoride = 1:2 were obtained from the boron trifluoride addition compound of diethyl ether (II) and the following diamines (I): *p*-phenylenediamine (Ia), benzidine (Ib), 3,3′-dimethylbenzidine (Ic), 3,3′-dimethoxybenzidine (Id), 3,3′-dichlorobenzidine (Ie), α,α′-bi-*p*-toluidine (If), and 1,8-naphthalenediamine (Ig). The reactions proceed according to equation 1 in which

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[1a] Paper presented at the 142nd National Meeting of the American Chemical Society in Atlantic City, New Jersey, September, 1962.

[1b] H. S. Booth and D. R. Martin, "Boron Trifluoride and Its Derivatives," John Wiley and Sons, Inc., New York, N. Y., 1949.

[2] All melting points are corrected. Analyses were carried out by Galbraith Laboratories Inc., Knoxville, Tennessee, and Spang Microanalytical Laboratory, Ann Arbor, Michigan.

[3] A. W. Laubengayer and G. R. Finlay, *J. Am. Chem. Soc.*, **65**, 884 (1943).

[4] S. Sugden and M. Waloff, *J. Chem. Soc.*, 1492 (1932).

[5] E. L. Muetterties, *Z. Naturforsch.*, **12B**, 264 (1957).

[6] E. Krause and R. Nitsche, *Ber.*, **55**, 1261 (1922); E. Krause, *ibid.*, **57**, 216 (1924).

Table I

Preparation of Boron Trifluoride Addition Compounds of Carbocyclic Aromatic Diamines $F_3B \cdot H_2N—R—NH_2 \cdot BF_3$ (III)

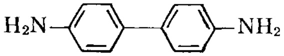
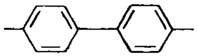
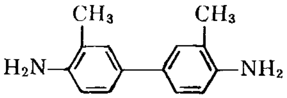
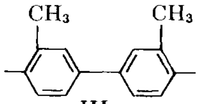
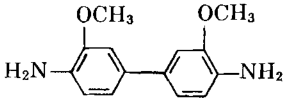
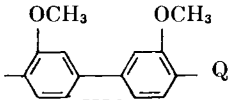
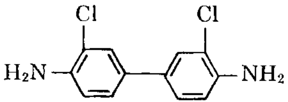
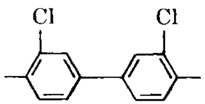
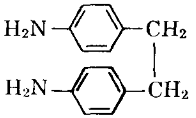
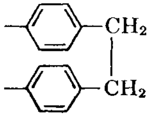
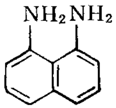
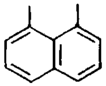
Amine I applied	Reaction Product III R =	Yield, %	M.p., °C. (cor.)	Empirical formula	Carbon, %		Hydrogen, %		Boron, %		Fluorine, %		Nitrogen, %	
					Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
 Ia	 IIIa	Quantitative	235–237	$C_6H_8B_2F_6N_2$	29.56	29.34	3.31	3.57	8.88	9.10	46.76	46.66	11.49	11.27
 Ib	 IIIb	Quantitative	335–336	$C_{12}H_{12}B_2F_6N_2$	45.06	44.81	3.78	3.99	6.76	6.93	35.64	35.31	8.76	8.67
 Ic	 IIIc	96.4	356–358	$C_{14}H_{16}B_2F_6N_2$	48.33	48.02	4.64	4.89	6.22	5.91	32.76	32.68	8.05	7.83
 Id	 IIId	Quantitative	288–290	$C_{14}H_{16}B_2F_6N_2O_2$	44.26	44.03	4.25	4.50	5.70	6.03	30.00	30.48	7.37	7.28
 Ie	 IIIe	Quantitative	308–310	$C_{12}H_{10}B_2Cl_2F_6N_2$	37.07	36.79	2.59	2.69	5.57	5.81	29.32	28.98	7.21	7.00
 If	 IIIf	93.9	249–251	$C_{14}H_{16}B_2F_6N_2$	48.33	48.12	4.64	4.75	6.22	6.30	32.76	32.66	8.05	7.81
 Ig	 IIIg	97.1	272–274	$C_{10}H_{10}B_2F_6N_2$	40.88	41.07	3.43	3.44	7.36	7.01	38.80	38.41	9.53	9.31

TABLE II

PROMINENT INFRARED ABSORPTION FREQUENCIES OF BF_3 ADDITION COMPOUNDS OF AROMATIC DIAMINES (III)

Compound	Asymmetrical NH stretching in cm.$^{-1}$	Symmetrical NH stretching in cm.$^{-1}$	NH deformation in cm.$^{-1}$	C—N stretching in cm.$^{-1}$	B—F stretching in cm.$^{-1}$
IIIa	3560	3220	1580	1330	1125
IIIb	3590	3200	1620	1320	1125
IIIc	3570	3220	1630	1290	1130
IIId	3490	3180	1600	1260	1135
IIIe	3500	3150	1590	1280	1110
IIIf	3590	3250	1580	1350	1120
IIIg	3570	3130	1610	1300	1100

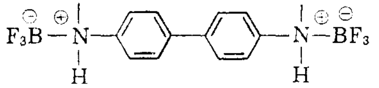
R represents a bivalent aromatic radical. Pertinent data referring to the preparation of III are summarized in Table I.

$$\underset{\text{I}}{H_2N—R—NH_2} + \underset{\text{II}}{2BF_3O(C_2H_5)_2} \longrightarrow \underset{\text{III}}{F_3BH_2N—R—NH_2BF_3} + 2O(C_2H_5)_2 \quad (1)$$

The nature of the boron–nitrogen bond formed by the donation of the lone electron pair of the nitrogen atom has never unequivocally been established. However, the formation of the bond may vary between two extremes, namely, incomplete sharing of the electron pair resulting in a very weak bond, and complete sharing involving transfer of one electronic charge to the acceptor atom and thereby giving rise to a strong bond. Consequently, various types of structures have been postulated, the most important ones of which are the normal coördination structure,[7,8] the ionic type,[9] and the π-complex.[10]

We have made an infrared investigation attempting to shed some light on the nature of the boron–nitrogen coördination bond in the new compounds III. On the basis of the infrared spectra, the ionic structure must be ruled out, because the latter would contain an ammonium vibrational element and, although the $NH_2^{\oplus}$ stretching mode is well known,[11] it is not observed with III.

Also excluded by infrared spectroscopy has been the π-complex structure. The latter would entail only one band in the NH stretching absorption region. However, spectra of III taken in hexachloro-1,3-butadiene or "Fluorolube MO-10"[12] as dispersing agents indicate two bands. The positions of prominent bands in III are summarized in Table II. The occurrence of two absorption bands in this range is to be interpreted as being due to the symmetrical and asymmetrical NH stretching mode of primary amines which, in turn, allows the conclusion that the primary amine structure of I has remained intact when being converted into III. The structure of the boron trifluoride addition compounds of primary aromatic diamines may thus best be presented as the normal coördination type III rather than as a π-complex type.



III

Of a primary amino grouping such as is present in structure III one would also expect a band at 1650–1590 cm.$^{-1}$ due to NH deformation vibrations[13] and another band between 1340–1250 cm.$^{-1}$ caused by C—N stretching vibrations of primary aromatic amines.[14] Both types have been observed with all compounds III and are also included in Table II. The last mentioned band in III had to be measured in a Nujol mull because of absorptions of Fluorolube in the same region. Another marked absorption between 1135–1100 cm.$^{-1}$ is also summarized in Table II and may be correlated to B—F stretching.[15]

Our chief argument in support of the normal coördination structure is a B—N adduct in which the boron atom does not carry halogen atoms so that the aforementioned type of π-complex formation becomes impossible. As a matter of fact, replacement of boron trifluoride by $B(C_6H_5)_3$ in IIIa leading to the corresponding triphenylborine addition compound leaves the pattern of the infrared spectrum set by the boron trifluoride addition compounds unaltered. The two NH stretching bands found at 3320 and 3220 cm.$^{-1}$ allow one to assign to the triphenylborine addition compound of *p*-phenylenediamine the normal coördination structure (V) also (equation 2).

Previous evidence to support the classical coördination structure of simple borine–amine compounds has been adduced by Raman investigations[7] and electrical conductivity measurements.[7,8] Assignment of the coördination structure to III entails a change of configuration on the boron trifluoride molecule from planar to tetrahedral upon

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[7] J. Goubeau, M. Rahtz, and H. J. Becher, *Z. anorg. allgem. Chem.*, **275**, 161 (1954).

[8] W. Gerrard, M. F. Lappert, and C. A. Pearce, *J. Chem. Soc.*, 381 (1957).

[9] C. A. Brown and R. C. Osthoff, *J. Am. Chem. Soc.*, **74**, 2340 (1952).

[10] W. Gerrard and E. F. Mooney, *J. Chem. Soc.*, 4028 (1960).

[11] R. A. Heacock and L. Marion, *Can. J. Chem.*, **34**, 1782 (1956).

[12] "Fluorolube MO-10" is a registered trade name applied by the Hooker Chemical Corp., Niagara Falls, New York, to an oil being essentially a polymer of chlorotrifluoroethylene.

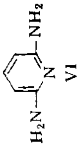
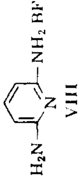
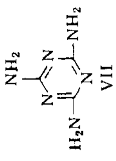
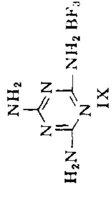
[13] G. B. B. M. Sutherland, *Discussions Faraday Soc.*, **9**, 274 (1950).

[14] R. B. Barnes, R. C. Gore, R. W. Stafford, and V. Z. Williams, *Anal. Chem.*, **20**, 402 (1948).

[15] T. D. Parsons, E. D. Baker, A. B. Burg, and G. L. Juvinall *J. Am. Chem. Soc.*, **83**, 250 (1961).

Table III

Preparation of Boron Trifluoride Addition Compounds of Heterocyclic Aromatic Polyamines

Amine applied	Reaction product	Yield, %	M.p., °C. (cor.)	Empirical formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Boron, % Calcd.	Boron, % Found	Fluorine, % Calcd.	Fluorine, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
 VI	 VIII	96.4	205–207	$C_5H_7BF_3N_3$	33.94	33.61	3.98	3.90	6.12	6.24	32.21	32.19	23.75	23.46
 VII	 IX	Quantitative	>420°	$C_3H_6BF_3N_6$	18.58	18.36	3.11	3.23	5.58	5.89	29.39	28.99	43.34	43.03

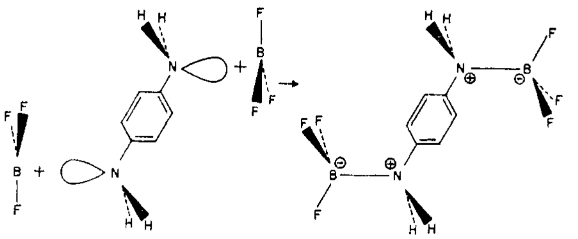
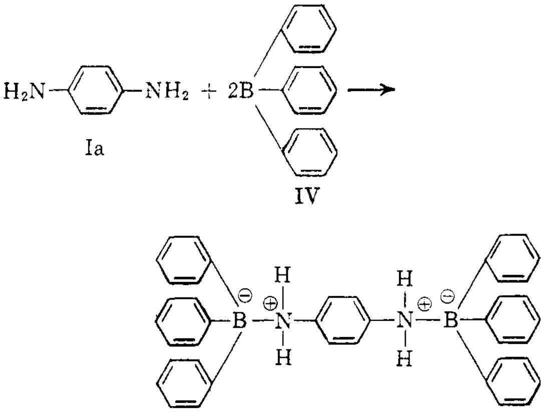


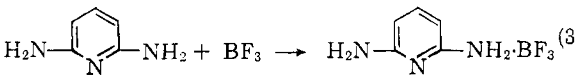
Fig. 1.—Configuration change in the formation of the B—N coördination bond.



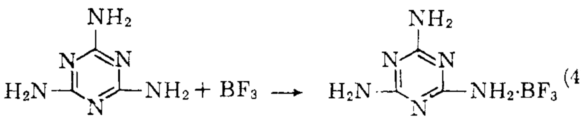
Ia IV V (2)

formation of the boron–nitrogen bond, while the amine applied already possesses tetrahedral configuration, as expressed in Fig. 1.

A different picture, however, is revealed in the heterocyclic di- and triamine series. As representatives of this compound type, 2,6-diaminopyridine (VI) and melamine (VII) were chosen. Although these compounds contain, respectively, two and three amino groups per mole, they give with boron trifluoride under the same experimental conditions as used in the carbocyclic series only addition compounds (VIII and IX) of a 1:1 molar ratio, as presented in equations 3 and 4 and Table III.



VI VIII (3)



VII IX (4)

This abnormal behavior of the electrophilic agent boron trifluoride toward VI and VII finds its parallel in the corresponding failure of the electrophiles nitrous acid and sulfonyl chloride to effect normal diazotization and sulfonation on 2,6-

diaminopyridine[16] and aminotriazines.[17] Clearly, the unshared electron pairs of the amino nitrogen atoms are not fully available for reactions of the electrophilic type. Similar unusual boron trifluoride adducts of a 3:1 molar ratio are also known in the aliphatic series.[18]

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[16] A. E. Tschitschibabin and O. A. Seide, *J. Russ. Phys. Chem. Soc.*, **46**, 1233 (1914); A. I. Titov, *J. Gen. Chem. USSR*, **8**, 1483 (1938).

[17] C. Broche, *J. prakt. Chem.*, [2] **50**, 116 (1894).

[18] E. L. Muetterties, *Z. Naturforsch.*, **12b**, 264 (1957).

Structure and Stability of Isomeric Fluorobromoethylenes. I. The Geometrical Isomers of 1-Bromo-2-fluoro- and 1,2-Dibromo-1-fluoroethylene

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The *cis-trans* isomeric forms of 1,2-dibromo-1-fluoroethylene have been prepared and their structures determined from the infrared spectra and dipole moments. These have been correlated with the corresponding data for the *cis-trans* isomeric 1-bromo-2-fluoroethylenes. Certain regularities in the series of the 1,2-dihalogenoethylenes are discussed.

In a recent publication,[1] the two known[2] *cis-trans* isomeric 1-bromo-2-fluoroethylenes (*cis:* b.p. 40°, dipole moment 1.9 D.; *trans:* b.p. 20°, dipole moment 0.3 D.) have been described in detail; the *cis* form is the more stable one, the equilibrium lying at 75% *cis* isomer. This equilibrium has been reached by heating of the pure isomers at 100° in the presence of acid.

In the framework of a larger project, the two above isomers were also studied in this laboratory some three years ago. The constants measured fully agree with those reported by Viehe[1]: *cis* isomer: b.p. 39.8° (760 mm.); dipole moment 1.95 D.. *trans* isomer: b.p. 19.8° (760 mm.), dipole moment ∼0. The infrared spectra observed in solution (Fig. 1a and 1b) agree with those published by Viehe,[1] which refer to the vapor phase. The *trans* compound is characterized by a lower intensity of the $C{=}C$ band and a smaller number of absorption bands[3]; furthermore, it shows the out-of-plane vibration of the C—H bond at 890 cm.$^{-1}$, while that frequency lies in the *cis* isomer at 730 cm.$^{-1}$. There is also a difference between the two isomers in the position of the C—F frequency: *cis*-1035, *trans*-1100 cm.$^{-1}$. This appears to be a more general effect; in the spectra published by Viehe,[1] one finds the following peaks for the C—F absorption of other 1-fluoro-2-halogenoethylenes studied: 1,2-Difluoroethylene: *cis* 1120 and 1140, *trans*-1168 and 1149 cm.$^{-1}$. 1-Chloro-2-fluoroethylene: *cis*-1073 and 1057, *trans*-1139 and 1125 cm.$^{-1}$. 1-Iodo-2-fluoroethylene: *cis*-1038 and 1027, *trans*-1102 and 1092 cm.$^{-1}$. The C—F frequency is always *lower* in the *cis* isomer, and the magnitude of the shift increases with the increase in atomic weight of the second halogen atom.

The infrared spectrum of the two isomeric 1-bromo-2-fluoroethylenes can be used to advantage for a study of their isomerizability. The *cis* isomer is fairly stable and can, therefore, be obtained very easily by distillation from the mixture of the isomers. In sealed glass ampoules, it can be kept at room temperature for several months without significant isomerization; transformation into the equilibrium mixture does take place but very slowly. The *trans* compound, on the other hand, polymerizes during distillation to oily and solid products and is much more easily isomerized; transformation into the equilibrium mixture (Fig. 1c) takes place within three to four days at room temperature (without added external catalyst). (This is somewhat at variance with the description of the isomerization given by Viehe.[1]) Both compounds isomerize more quickly in carbon tetrachloride solution than in the isolated state, as can be seen from the infrared spectrum of their solutions (Fig. 1d). At the same time, the compounds appear to add carbon tetrachloride to the double bond, as evidenced by the following observations (although we have not isolated the adduct): (a) While the C—H stretching frequency in the unsaturated compounds lies at 3120 cm.$^{-1}$, in the solution a peak gradually appears at 3020 cm.$^{-1}$, corresponding to that frequency in a *saturated* molecule. (b) The intensity of the $C{=}C$ band (1640 cm.$^{-1}$) decreases gradually. (c) A peak at 1260 cm.$^{-1}$ appears and increases gradually in intensity; it is also due to a C—H vibration of the saturated compound. (d) In the 1020–1150-cm.$^{-1}$ region the peaks become less clear, probably because of the appearance of new C—F vibrations—*viz.* those of saturated fluorine compounds.

These results have made it possible to arrive at

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[1] H. G. Viehe, *Ber.*, **93**, 1697 (1960).

[2] F. Swarts, *J. Chim. Phys.*, **20**, 49 (1923).

[3] H. J. Bernstein and J. Powling, *J. Am. Chem. Soc.*, **73**, 1843 (1951).