Polarities and Directional Polarisabilities of Trimethylamine Adducts of Boron Trihydride and Boron Trihalides. Stereospecific Solute–Solvent Interactions

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Molar Kerr constants are reported for the boron trihydride and the boron trihalide adducts of trimethylamine as solutes in dioxan and benzene. The anisotropic electron polarisabilities of the adduct molecules are derived from the measurements in dioxan. The changes in polarisability on co-ordination are discussed. Estimates of the polarisability parameters for a tetrahedrally disposed BX_3 (X = H, F, Cl, Br, and I) are derived. The molar Kerr constant data in benzene are interpreted in terms of stereospecific solute–solvent interactions.

THE refractivity (and therefore mean polarisability) of a system is markedly reduced by the development of strong polarity within it.[1] The anisotropy of such diminutions is usually unknown. The molecules $Me_3N,-BX_3$ ($X = H$, F, Cl, Br, or I), formed from their constituent pairs with polarity increments of three or more debye units and refractivity contractions beyond prob-

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[1] R. J. W. Le Fèvre, in 'Advances in Physical Organic Chemistry,' ed. V. Gold, Academic Press, London and New York, 1965, vol. 3, pp. 30, 64.

able errors of observations,[1,2] are convenient for study since their structures are axially symmetric and their polarisability ellipsoids should be ones of revolution.

Accordingly we have made the measurements, here reported, of molar Kerr constants, dipole moments, *etc.*, of these complexes in dioxan or benzene, and from them (*a*) computed principal polarisabilities for each solute, and (*b*) estimated overall and anisotropic changes in the polarisability resulting from co-ordination. A further analysis provides group polarisabilities for the tetrahedrally disposed BX_3 species. Interpretation of the data for the adducts is in favour of stereospecific adduct–benzene interactions.

EXPERIMENTAL

Materials and Apparatus.—The solutes were prepared by published procedures:[2-4] trimethylamine–borane, sublimed, m.p. 92—94 °C, trimethylamine–boron trifluoride, vacuum sublimed, m.p. 146—147 °C, trimethylamine–boron trichloride, white needles (from dry ethanol), m.p. 238—239 °C, trimethylamine–boron tribromide, white needles (dry ethanol), m.p. 232—234 °C, and trimethylamine–boron tri-iodide, white powder (dry chloroform–light petroleum), m.p. *ca.* 200 °C (decomp.). All solutes were prepared in a dry nitrogen atmosphere and their purity was checked by microanalysis (C, H, and halogen) and i.r. and n.m.r. spectra.

TABLE 1

	ε_1	d_1	$(n_1)_D$	10^7B_1	$10^{12}{}_sK_1$
Dioxan	2·2090	1·0280	1·4202	0·068	0·0116
Benzene	2·2725	0·87378	1·4973	0·410	0·0756

TABLE 2

Polarisations, refractions, dipole moments, and molar Kerr constants of adducts Me_3N,BX_3 (X = H, F, Cl, Br, and I) (from observations on solutions at 25 °C) *

X	Solvent	Range of 10^6w_2	$\alpha\varepsilon_1$	β	γ	δ	$_\infty P_2$/cm³	R_D/cm³	μ/D [a]	$10^{12}({}_mK_2)$
H	Dioxan	199—1679	36·1	−0·465	−0·013	42·5	462	25·6	4·62	22·7
F	Dioxan	72—258	32·9	0·162	—	37·5	717	23·8 [b]	5·81	33·4 [f]
Cl	Dioxan	110—509	28·3	0·212	0·034	−48·7	861	38·6	6·33	−126
Br	Dioxan	306—1099	17·7	0·511	0·045	−123	945	47·5	6·61	−472
I	Dioxan	197—539	$13·2_5$	0·624	0·054	−227	1031	59·5	6·88	−1219
H	Benzene	451—1417	$31·4_5$ [c]	−0·211 [c]	−0·073 [c]	−25·9	462	—	4·62 [e]	−217
F	Benzene	122—457	28·5 [d]	0·132 [d]	—	−46·9	713	—	5·81 [e]	−571 [f]
Cl	Benzene	409—1265	24·7 [d]	0·359 [d]	—	−31·5	846	—	6·29 [e]	−565 [f]
Br	Benzene	611—1905	15·3 [c]	0·543 [c]	0·037 [c]	−29·5	938	—	6·60 [e]	−849
I	Benzene	207—525	10·3	0·692	0·061	−42·2	922	—	6·50 [e]	−1592

* The coefficients were derived from the observed quantities $\Delta\varepsilon$, Δd, Δn, and ΔB (the incremental changes in dielectric constant, density, refractive index, and Kerr constant, respectively, for solutions having solute weight fractions w_2) by use of the following relations: $\alpha\varepsilon_1 = \Sigma\Delta\varepsilon/\Sigma w_2$; $\beta = \Sigma\Delta d/d_1\Sigma w_2$; $\gamma = \Sigma\Delta n/n_1\Sigma w_2$, and $\delta = \Sigma\Delta B/B_1\Sigma w_2$.

[a] Calculated on the basis of $_DP = 1·05R_D$. [b] Calculated value, determined as follows: $R_D(Me_3N,BF_3) = R_D(Me_3N\colon) + R_D(BF_3) + R_D(N{-}B)$, where $R_D(Me_3N\colon) = 20·2$ cm³ (R. J. W. Le Fèvre and P. Russell, *Trans. Faraday Soc.*, 1947, **43**, 374), $R_D(BF_3) = 6·0$ cm³ [R. Gillis, *Rev. Pure Appl. Chem.* (*Australia*), 1960, **10**, 21] and $R_D(N{-}B) = -2·3_5$ (the mean value determined from data concerning the chloride and bromide; see text). [c] Coefficients calculated from data in ref. 3. [d] Coefficients calculated from data in ref. 2. [e] Determined using the refractions at the Na-D line, listed for dioxan as solvent. The moment of the iodide adduct in dioxan is considered to be more accurate as experimental difficulties were encountered with the benzene solutions. [f] $10^{12}{}_\infty({}_mK_2)$ derived neglecting contributions from γ terms.

Apparatus, techniques, symbols used, and methods of calculation have been described,[5-8] with the exception that the refractive indices for the dioxan solutions were determined using a Wild precision spectrometer. The split-beam method for calculating *n* was employed.[9] The data of Table 1 apply at 25 °C for the solvents used. The measurements are summarised in Table 2.

Previous Measurements.—The following dipole moment estimates are recorded in the literature (which contains no value for Me_3N,BI_3): $\mu(Me_3N,BH_3) = 4·62$ (C_6H_6),[3] 4·72 (C_6H_6), 4·66 ($C_4H_8O_2$);[10] $\mu(Me_3N,BF_3) = 5·81$ (C_6H_6);[2] $\mu(Me_3N,BCl_3) = 6·29$ (C_6H_6);[2] $\mu(Me_3N,BBr_3) = 6·60$ (C_6H_6).[3] The molar Kerr constants have not previously been measured.

DISCUSSION

Dioxan was chosen as a non-interacting solvent environment. The chemical shifts of the sensor protons in these adducts in dioxan were of similar magnitude to those recorded in ' inert ' solvents such as chloroform[11] and dichloromethane.[12] No resonance was observed for free trimethylamine at 139·5 Hz downfield from tetramethylsilane. The possibility of dissociation of the adduct, with dioxan acting as a competing base for the borane and boron trihalides, is thus excluded. Carbon tetrachloride was precluded as a solvent by solubility limitations.

Molecular Polarisabilities of the Adducts.—Each adduct is assumed to have a tetrahedral disposition of valencies

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[2] G. M. Phillips, J. S. Hunter, and L. E. Sutton, *J. Chem. Soc.*, 1945, 146.

[3] C. M. Bax, A. R. Katritzky, and L. E. Sutton, *J. Chem. Soc.*, 1958, 1258.

[4] E. L. Muetterties, *J. Inorg. Nuclear Chem.*, 1960, **15**, 182.

[5] C. G. Le Fèvre and R. J. W. Le Fèvre, *Rev. Pure Appl. Chem.* (*Australia*), 1955, **5**, 261.

[6] R. J. W. Le Fèvre, ' Dipole Moments,' Methuen, London, 3rd edn., 1953.

[7] R. J. W. Le Fèvre and G. L. D. Ritchie, *J. Chem. Soc.*, 1963, 4933.

[8] C. G. Le Fèvre and R. J. W. Le Fèvre, in ' Physical Methods of Organic Chemistry,' ed. Weissberger, Interscience, New York, 3rd edn., vol. 1, ch. 36, p. 2459.

[9] L. C. Martin, ' Optical Measuring Instruments,' Blackie, London, 1924.

[10] J. R. Weaver and R. W. Parry, *Inorg. Chem.*, 1966, **5**, 713.

[11] J. M. Miller and M. Onyschuk, *Canad. J. Chem.*, 1963, **41**, 2898.

[12] A. G. Massey and A. J. Park, *J. Organometallic Chem.*, 1966, **5**, 218.

about the nitrogen and boron atoms when it exists as a solute in an inert solvent environment. Structure analyses support this supposition.[13,14] The polarisability ellipsoid associated with each of the molecules Me_3N,BX_3 is one of revolution with $b_1 \neq b_2 = b_3$, where b_1 is the electro-optical polarisability in the direction of the molecular three-fold symmetry axis and b_2 and b_3 are the electro-optical polarisabilities perpendicular to this axis. In each case the permanent electric moment is located along b_1, so that $\mu_1 = \mu$(observed), $\mu_2 = \mu_3 = 0$.

TABLE 3

Proton magnetic resonance measurements (chemical shifts) * of the methyl protons in Me_3N,BX_3, in different solvent media

X	Dioxan	Chloroform [11]	Dichloromethane [12]
H	153·5	159·5	155
F	152	157·3	156
Cl	175·5	180·2	182
Br	186·5	190·8	189
I	197·5	—	201

* The spectra were determined on a Varian A60 spectrometer. The solution concentrations were of the order of 1—2%. Tetramethylsilane was taken as internal reference, and the data recorded is the upfield chemical shift in Hz.

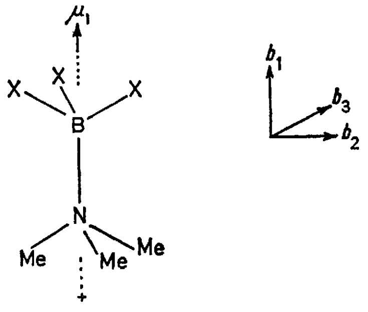

FIGURE 1

The molecular quantities b_i and μ_i may be related to the electronic polarisation ${}_{\mathrm{E}}P$ and the molar Kerr constant by wav of the Lorentz–Lorenz and Langevin–Born equations which, for the molecules Me_3N,BX_3 simplify to (1) and (2). The terms ${}_{\mathrm{E}}P$, ${}_{\mathrm{D}}P$, N, k, and T refer, in

$$ {}_{\mathrm{E}}P = 4\pi N\,(b_1 + 2b_2)/9 \qquad (1)$$

$$ {}_{\mathrm{m}}K = 4\pi N\,\{{}_{\mathrm{D}}P(b_1 - b_2)^2/kT\,{}_{\mathrm{E}}P + \mu_{\mathrm{obs}}{}^2(b_1 - b_2)/k^2T^2\}/405 \qquad (2)$$

turn, to the electron polarisation, distortion polarisation, the Avogadro constant, the Boltzmann constant, and the absolute temperature. In the absence of refractivity dispersion data ${}_{\mathrm{E}}P$ cannot be directly evaluated and we assume in the calculations that ${}_{\mathrm{E}}P = 0{\cdot}95R_{\mathrm{D}}$ and the ratio ${}_{\mathrm{D}}P : {}_{\mathrm{E}}P = 1{\cdot}1$. Substitution in equations (1) and (2) of the μ_{obs} and ${}_{\infty}({}_{\mathrm{m}}K_2)$ values of Table 2 (which were obtained from measurements in dioxan) leads to the molecular polarisability semi-axes * in Table 4. The measured values in benzene were not used in the calculations since solute–benzene associations are known to occur.

TABLE 4

Polarisability semi-axes of the molecules Me_3N,BX_3

X	b_1	$b_2\ (= b_3)$	b_1/b_2	Σb_i
H	$9{\cdot}71_5$	9·62	1·01	28·95
F	9·02	8·93	1·01	26·88
Cl	$14{\cdot}32_5$	14·61	0·98	$43{\cdot}54_5$
Br	17·23	18·21	0·95	53·65
I	20·85	23·18	0·90	67·21

Changes in Polarisability on Co-ordination.—The refractions (at the Na-D line) of trimethylamine (20·2 cm^3) and boron trichloride (20·9 cm^3) † or boron tribromide (29·5 cm^3) † together exceed those measured for the compounds Me_3N,BCl_3 (38·6 cm^3) or Me_3N,BBr_3 (47·5 cm^3) respectively. The refractivity contraction is *ca.* 2·5 cm^3 for the chloride and *ca.* 2·2 cm^3 for the bromide. Experimental data are not available for computation of refraction changes for the hydride, fluoride, and iodide. The overall reduction in refractivity, and hence polarisability, is better appreciated from the directional polarisability variations on formation of the N–B bond. The following approach was necessitated to account for the contribution of the lone pair of electrons to the trimethylamine group polarisabilities. Tolkmith[15] estimated the nitrogen lone-pair refraction to be 2·6 cm^3. It being assumed that ${}_{\mathrm{E}}P = 0{\cdot}95R_{\mathrm{D}}$ for the nitrogen lone pair, the sum of the semi-axes, b_i for trimethylamine, excluding the lone pair contribution, is extracted from the difference ${}_{\mathrm{E}}P(Me_3N\colon)$‡ $-\ {}_{\mathrm{E}}P(N\colon)$, by use of equation (1). From Kerr constant measurements of $Me_3N\colon$ in

$$ b_1{}^{\mathrm{Me_3N}} + 2b_2{}^{\mathrm{Me_3N}} = 20{\cdot}06 \qquad (3)$$

cyclohexane[16] as solvent, the nitrogen lone pair being assumed to be isotropically polarisable, equation (4) is obtained. Solution of equations (3) and (4) gives the

$$ b_1{}^{\mathrm{Me_3N}} - b_2{}^{\mathrm{Me_3N}} = -0{\cdot}27 \qquad (4)$$

'true' semi-axes for the Me_3N group (without the lone pair), $b_1 = 6{\cdot}51$, $b_2 = b_3 = 6{\cdot}78$. It is now possible to derive values for $\Delta b_i{}^{\mathrm{Me_3N,BX_3}} = b_i(\mathrm{obs})^{\mathrm{Me_3N,BX_3}} - \{b_i{}^{\mathrm{Me_3N}} + b_i{}^{\mathrm{BX_3}}\}$, which will indicate the directional changes in polarisability consequent upon co-ordinate-bond formation. Results are in Table 5. On formation of the N–B bond in these adducts there is an increase in polarisability along the bond and a decrease in polarisability perpendicular to the bond. This is consistent with a decrease in the angle subtended by $b_{\mathrm{L}}{}^{\mathrm{B-X}}$ with b_1 and an increase in the angle subtended by $b_{\mathrm{T}}{}^{\mathrm{B-X}}$ and $b_{\mathrm{V}}{}^{\mathrm{B-X}}$ with b_1 ($b_{\mathrm{L}}{}^{\mathrm{B-X}} > b_{\mathrm{T}}{}^{\mathrm{B-X}} = b_{\mathrm{V}}{}^{\mathrm{B-X}}$; refer to Table 7). Attempts to estimate the bond anisotropy of the N–B

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* The polarisability semi-axes of bonds or groups, b_{L}, b_{T}, or b_{V} or of molecules b_1, b_2, or b_3 are quoted throughout in Å^3 units.

† These values were calculated by use of the Cauchy relationship, from refractive index data tabulated in Landolt–Bornstein 'Physikalisch-Chemische Tabellen,' Springer, Berlin, 4th edn., 1912, p. 1021.

‡ Extrapolated from $R_{\mathrm{C}} = 19{\cdot}791$ and $R_{\mathrm{G}} = 20{\cdot}406$ to give ${}_{\mathrm{E}}P = 19{\cdot}34$ cm^3 (*cf.* A. I. Vogel, *J. Chem. Soc.*, 1952, 514).

[13] P. S. Bryan and R. L. Kuczkowski, *Inorg. Chem.*, 1971, **10**, 200.

[14] P. H. Clippard, R. C. Taylor, and J. C. Hanson, *J. Cryst. Mol. Structure*, 1971, **1**, 363.

[15] H. Tolkmith, *Ann. N.Y. Acad. Sci.*, 1959, **79**, 187.

[16] R. S. Armstrong and K. R. Skamp, unpublished results.

link were unsuccessful, because of the apparent near-zero refraction of this bond.[17] However assuming the B–X polarisability parameters are invariant in progressing from the 'isolated' BX_3 molecules to the co-ordinated BX_3 species, then we can obtain the longitudinal bond polarisability, b_L^{N-B}, by resolution: $b_1^{Me_3N,BX_3} = b_1^{Me_3N} + 3b_L^{B-X}\cos^2 70\tfrac{1}{2}° + 3b_T^{B-X}\sin^2 70\tfrac{1}{2}° + b_L^{N-B}$. Thus b_L^{N-B} emerges as 0·53 (fluoride adduct), $1{\cdot}22_5$(Cl), 1·53(Br), and 1·23(H, assuming $b_L^{B-H} = b_T^{B-H} = b_V^{B-H} = 0{\cdot}61$; see below).* The gradual increase in b_L^{N-B} is associated with the polarity increments in these adducts and a decrease in the N–B bond distance[13,14] in progressing from the fluoride to the iodide. The nitrogen lone pair thus appears to retain its isotropy to a greater degree in the fluoride, relative to the bromide. This apparent deformation of the lone pair is in line with the trends in the electron-pair acceptor properties of the BX_3 molecules.[18]

TABLE 5

Computation of directional polarisability changes arising from the formation of the adducts Me_3N,BX_3

X	$b_1(BX_3)$ [a]	$b_2(= b_3)(BX_3)$ [a]	b_1 (calc.) [b]	$b_2(= b_3)$ (calc.) [b]	Δb_1	$\Delta b_2(= b_3)$
F	1·71 [c]	2·57 [c]	8·22	9·35	+0·80	−0·42
Cl	5·92	8·99	12·43	15·77	$+1{\cdot}89_5$	−1·16
Br	7·98	13·08	14·49	19·86	+2·74	−1·65

[a] R. S. Armstrong, M. J. Aroney, A. Hector, and R. J. W. Le Fèvre, *J. Chem. Soc.* (*B*), 1968, 1203. [b] Calculated assuming the constituent molecules are isolated, *i.e.*, $b_i^{calc} = b_i(Me_3N) + b_i(BX_3)$, where b_1 lies along the 3-fold symmetry axis of Me_3N and BX_3. [c] Determined using approximate link polarisabilities for $b_L^{B-F} \approx 1{\cdot}14$, $b_T^{B-F} \approx 0{\cdot}57$ (ref. *a*).

TABLE 6

Tetrahedral BX_3 group polarisabilities compared with values derived from structurally similar situations

	BX_3, tetrahedral (in Me_3N,BX_3)			BX_3, tetrahedral [a] (in $C_4H_8O_2,BX_3$)			BX_3, tetrahedral [b] (calculated)			CX_3, tetrahedral [c]		
X	b_1	$b_2 = b_3$	Σb_i	b_1	$b_2 = b_3$	Σb_i	b_1	$b_2 = b_3$	Σb_i	b_1	$b_2 = b_3$	Σb_i
F	$1{\cdot}13_5$	1·14	$3{\cdot}41_5$	1·3	1·9	5·1	1·92	2·44	6·80	2·00	2·18	6·36 [d]
Cl	6·44	6·82	20·08	7·0	7·6	22·2	6·60	8·65	23·90	6·28	8·25	22·78 [e]
										6·43	8·33	23·09
Br	$9{\cdot}34_5$	10·42	$30{\cdot}18_5$				9·11	12·51	34·13	8·46	11·93	32·32 [f]
I	$12{\cdot}96_5$	15·39	$43{\cdot}74_5$							15·25	17·20	49·65 [f]

[a] See ref. *a* Table 5. [b] Calculated assuming b_i^{B-X} remains invariant when the hybrid state of boron changes from sp^2 to sp^3. [c] Extracted from data in refs. *d*, *e*, and *f*. Comparisons involving values determined from solution measurements in benzene are complicated by known solute–solvent interactions, *viz.*, ref. *e*. [d] R. J. W. Le Fèvre and C. G. Le Fèvre, *J. Chem. Soc.*, 1954, 1577; gaseous state data, CCl_3F and CHF_3. [e] R. J. W. Le Fèvre, D. V. Radford, G. L. D. Ritchie, and P. F. Stiles, *J. Chem. Soc.* (*B*), 1968, 148; carbon tetrachloride solution data, $HCCl_3$ and H_3CCCl_3. [f] R. J. W. Le Fèvre and G. L. D. Ritchie, *J. Chem. Soc.*, 1963, 4933; benzene solution data, $HCBr_3$ and HCI_3.

Group Anisotropy of the Tetrahedral Species BX_3.—For bond anisotropies inaccessible *via* the Kerr effect, Le Fèvre[19,20] predicted a quantity $Q = (1/r_{AB})^2(b_L^{AB}/\bar{M})^{\frac{1}{2}}$, where r_{AB} is the internuclear distance of the bond AB, b_L^{AB} the longitudinal polarisability of AB, $\bar{M}$ is the reduced mass, and Q is empirically related to the i.r. stretching frequency ν_{AB}, by $\nu = 9273Q - 254$. For the B–H link, utilising data for ν^{10}B–H, ν^{11}B–H,[21] the r_{BH} distance,[22] and assuming the B–H link to be isotropic, we find $b_L^{B-H} = b_V^{B-H} = b_T^{B-H} = 0{\cdot}61$. Approximating these bond polarisabilities to the tetrahedral BH_3 situation, the semi-axes b_i for the 'Me_3NB' moiety are b_i('Me_3NB') $= b_i(Me_3N,BH_3) - b_i(BH_3)$ so that $b_1 = 7{\cdot}88_5$, $b_2 = b_3 = 7{\cdot}79$. Table 6 contains the values thus derived for the b_i's of the BX_3 group and also compares them with the appropriate calculated and experimental values for tetrahedral BX_3, isolated BX_3 molecules, and the analogous tetrahedral CX_3 group. The etherate species of BF_3 and BCl_3 represent a structurally and electronically similar situation to those of the trimethylamine adducts. Agreement is best in this case. In all instances the value for $\Sigma b_i^{BX_3}$ extracted from the adducts are smaller than those from the isolated molecules and this may be caused by loss of p_π–p_π bonding[18] in the B–X link and a change in the hybrid state of boron consequent upon co-ordination. Further analysis of the BX_3 group anisotropy, by resolving B–X bond polarisabilities, exemplifies these two changes. The longitudinal polarisability of the B–X link is markedly reduced in the adduct, relatively to the free boron trihalides, and this is characteristic when such a variation in charge distribution occurs (*cf.* Table 7). These calculations are based on the assumption that the N–B anisotropy is invariant with X. It has been shown above that this may not necessarily be the case, particularly when X = F.

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* Estimates have been made for b_L^{N-B} in the adducts Me_3N,BX_3, by use of the 'infrared rule' (see Discussion section), from values of ν(N–B) (*cf.* R. L. Amster and R. C. Taylor, *Spectrochim. Acta*, 1964, **20**, 1487) and the N–B distances.[13,14] They lie between 1·1 and 1·4 (X = H, F, Cl, and Br).

[17] M. J. Aroney, R. J. W. Le Fèvre, and J. D. Saxby, *Austral. J. Chem.*, 1965, **18**, 253, and references therein.

[18] T. D. Coyle and F. G. A. Stone, in 'Progress in Boron Chemistry,' ed. H. Steinberg and A. L. McCloskey, Pergamon Press, London, New York, 1964, vol. 1, ch. 3 (and references therein).

[19] R. J. W. Le Fèvre, *Proc. Chem. Soc.*, 1959, 363.

[20] R. J. W. Le Fèvre, *Austral. J. Chem.*, 1961, **14**, 312.

[21] W. Gordy, H. Ring, and A. B. Burg, *Phys. Rev.*, 1950, **78**, 512.

[22] G. W. Bethke and M. K. Wilson, *J. Chem. Phys.*, 1957, **26**, 1118.

Solute–Solvent Interactions.—Variation in the magnitude of the Kerr constant of a solute measured in different solvents is a sensitive probe of solute–solvent interactions (see ref. *e*, Table 6). The molar Kerr constants in Table 2 point to benzene being an interacting solvent with these adducts. In each case the $_{\infty}({}_{m}K_2)$ in benzene is algebraically more negative than in the inert solvent dioxan. That this association is electrostatic is inferred when the dipole moment of the adduct is related to the difference in the upfield chemical shift of the methyl protons in the n.m.r. spectra of benzene solutions relatively to dioxan solutions $(\Delta\delta^{\text{Dioxan}}_{\text{Benzene}} = \delta^{\text{Dioxan}} - \delta^{\text{Benzene}})$. This relationship is approximately linear, as has been shown for other systems where a dipole–induced dipole mechanism is operating.[23]

TABLE 7

The B–X bond polarisability semi-axes

X	b_L^{B-X}	$b_T^{B-X}(= b_V^{B-X})$	$\frac{b_L}{b_T}$	Σb_i	b_L^{B-X}	$b_T^{B-X}(= b_V^{B-X})$	$\frac{b_L}{b_T}$	Σb_i
	Derived from adducts Me_3N,BX_3				Derived from isolated BX_3 molecules, see ref. *a*, Table 5			
H	0·61	0·61	1·00	1·83	—	—	—	—
F	0·38	0·38	1·00	1·14	1·14	0·57	*ca.* 2	2·27
Cl	2·49	2·10	1·19	6·69	4·02	1·97	2·04	7·96
Br	4·07	$2·99_5$	1·36	10·06	6·06	2·66	2·28	11·38
I	6·48	4·05	1·60	14·58	—	—	—	—

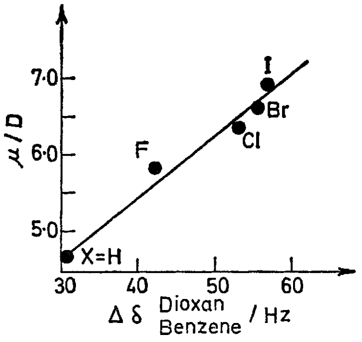

FIGURE 2

TABLE 8

Chemical shift and dipole moment data for Me_3N,BX_3 molecules *

X	$\Delta\delta^{\text{Dioxan}}_{\text{Benzene}}$	μ/D
H	30·5	4·62
F	42	5·81
Cl	53	6·33
Br	55·5	6·61
I	57	6·88

* Refer to footnote, Table 3.

As suggested by Armstrong *et al.*[24] the most favoured 1 : 1 solute–solvent collision complex would have the configuration which is favoured by (*a*) attraction of the positive end of the Me_3N,BX_3 dipole and the nucleophilic π-system of the benzene ring and (*b*) repulsive interaction between the benzene π-electrons and the lone pairs of the X atoms. A comparison of the calculated ${}_{m}K^{c}$ for the hypothetical 1 : 1 complex with the experimentally observed value implies that there is a probable equilibrium mixture of the type $Me_3N,BX_3 + C_6H_6 \rightleftharpoons Me_3N,BX_3,C_6H_6$. Finally trimethylamine–borane shows stereospecific interactions with the solvent benzene, at both ends of the molecule, as the deshielding of the borane sensor protons illustrates:[25] δ (in Hz) (solvent), $-99(F_2ClCCCl_2F)$; $-98·4(CDCl_3)$; $-97·2$(1,4-dioxan); $-97·2$(MeCN); $-127·8(C_6H_6)$. In the present work it was found that δ = −138 Hz for a *ca.* 3% benzene solution. As the molar Kerr constant is still negative such an association can be sterically less important than that previously mentioned although the sign does suggest that the orientation of benzene molecules around the borane protons may be other than perpendicular to the

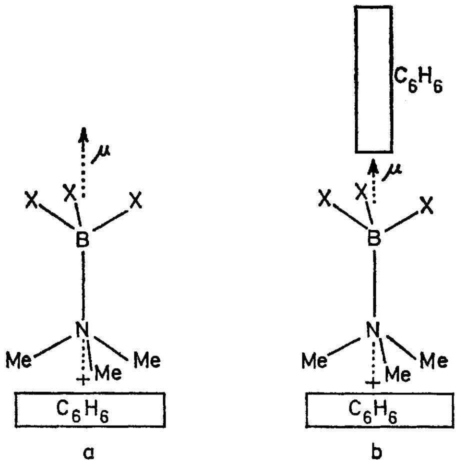

FIGURE 3

TABLE 9

Comparison of calculated molar Kerr constants for hypothetical 1 : 1 collision complexes Me_3N,BX_3,C_6H_6, $10^{12}{}_{m}K^{c}{}_{\text{calc}}$, with experimentally derived molar Kerr constants, $10^{12}{}_{\infty}({}_{m}K_2)$

X	$10^{12}{}_{m}K^{\text{calc}}$	$10^{12}{}_{\infty}({}_{m}K_2)$
H	−852	−217
F	−1346	−571
Cl	−1745	−565
Br	−2254	−849
I	−3158	−1592

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[23] T. L. Brown and K. Stark, *J. Amer. Chem. Soc.*, 1965, **69**, 2679.

[24] R. S. Armstrong, M. J. Aroney, R. J. W. Le Fèvre, R. K. Pierens, J. D. Saxby, and C. J. Wilkins, *J. Chem. Soc.* (*A*), 1969, 2735.

[25] C. W. Heitsch, *Inorg. Chem.*, 1965, **4**, 1019.

dipole moment direction (see Figure 3b). A cluster of benzene molecules could be so orientated about the BH_3's as to allow deshielding of these hydrogens whilst only partly offsetting the anisotropic contribution of the C_6H_6 molecules at the positive end of the dipole.

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