Basicity of the Carbonyl Group. Part 6.[1] Calorimetric and Spectrometric Study of Complexation of *para*-substituted *N*-Ammoniobenzamidates by Boron Trifluoride

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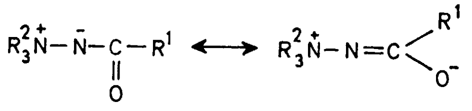
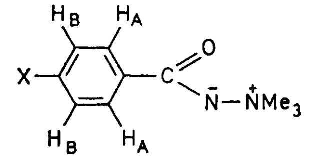
The complexation of 8 *para*-substituted *N*-ammoniobenzamidates by boron trifluoride has been studied by i.r. and ^1H n.m.r. spectroscopy, as well as by calorimetry. The formation of 1 : 1 addition compounds is demonstrated except for the *p*-cyano-compound (8) which complexes more than 1 mol. equiv. of boron trifluoride; this is attributed to the ability of the cyano-group to complex weakly with boron trifluoride. Spectroscopic evidence is presented which demonstrates that the complexation site is the carbonyl oxygen of the amidate function. The enthalpies of complexation correlate well with the linear free energy parameter $\sigma_p{}^0$ indicating that through conjugation effects in the free and complexed substrate are similar and rather small; the possible origin of these effects is discussed.

N-AMMONIOAMIDATES (1) are characterised by two charges of opposite sign on the vicinal nitrogen atoms. The negative charge is largely delocalised onto the adjacent carbonyl group thereby increasing its basicity. However previous work has shown that *N*-trimethylammonioamidates are protonated on nitrogen,[2] whereas the situation is less clear cut for amides [3] and it has been claimed that amides are protonated preferentially on oxygen at least in concentrated acids. Numerous examples exist of *O*-co-ordination of amide by Lewis acids or hydrogen bond donors in aprotic solvents.



(1a) (1b)

In view of their unique structure, and the lack of systematic and quantitative information about their basicity, in particular their Lewis basicity, we have undertaken a study of the complexation of a series of *N*-trimethylammoniobenzamidates (TAB), (2)—(9) by boron trifluoride. We have investigated the site of complexation by i.r. and ^1H n.m.r. spectroscopy. The thermodynamic aspect has been studied by the calorimetric measurement of the enthalpies of complexation.



(2) X = OMe
(3) X = Me
(4) X = H
(5) X = F
(6) X = Br
(7) X = CF_3
(8) X = CN
(9) X = NO_2

RESULTS AND DISCUSSION

Stoicheiometry of Complex Formation.—The stoicheiometry was determined with an accuracy >95%. The results (Table 1) show good evidence for the formation of 1 : 1 addition compounds apart from the case of (8) where we failed to obtain the expected sharp break in the calorimetric titration curve.[4] This anomaly is

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[1] M. Azzaro, G. Derrieu, L. Elegant, and J. F. Gal, *J. Org. Chem.*, 1975, **40**, 3155.

[2] M. Liler and D. G. Morris, *J.C.S. Chem. Comm.*, 1975, 93; *J.C.S. Perkin II*, 1977, 909; W. H. Beck, M. Liler, and D. G. Morris, *ibid.*, 1977, 1876.

[3] For a short review of the problem of *O*- or *N*-protonation of amides, see for example, C. J. Giffney and C. J. O'Connor, *J.C.S. Perkin II*, 1975, 706; A. J. Kresge, P. H. Fitzgerald and Y. Chiang, *J. Amer. Chem. Soc.*, 1974, **96**, 4698; M. Liler, *Adv. Phys. Org. Chem.*, 1975, **11**, 267.

[4] M. Durand, C. Jouanny, G. Jugie, L. Elegant, and J. F. Gal, *J.C.S. Dalton*, 1977, 57.

attributed to the partial complexation of the cyano-group. Nitriles are relatively weak Lewis bases as shown by their donor number,[5] for example. A ^{19}F n.m.r. study by Taft's group[6] shows that the boron trifluoride complex of *p*-fluorobenzonitrile is appreciably dissociated under similar conditions of solvent, temperature, and concentration to the present work. Complexes of boron trifluoride with various toluonitriles, isolated as solids, dissociate above 310 K.[7] The dissociation of the $2(BF_3):1$ (8) complex causes a curvature in the titration curve that prevents attainment of a precise stoicheiometry as with strong bases.[4]

TABLE 1

Stoicheiometry of complexes between $p\text{-}XC_6H_4CO\overset{-}{N}\overset{+}{N}(CH_3)_3$ and BF_3

X	$\frac{\text{mole } BF_3}{\text{mole ylide}}$
OCH_3	1.01
CH_3	0.98
H	1.04
F	0.99
Br	0.98
CF_3	0.96
CN	1.41 *
NO_2	0.99

* Anomaly due to complexation on the cyano-group.

TABLE 2

I.r. spectra of compounds $p\text{-}XC_6H_4CO\overset{-}{N}\overset{+}{N}(CH_3)_3$ free (F) and complexed by BF_3 (C) (0, 1M; CH_2Cl_2; regions studied: 2 300—1 450, 1 400—1 300, 1 250—1 100, 1 000—900, and 880—800 cm^{-1})

X	State										
OCH_3	(F)	1 610,1 600(s)	1 557,1 560(ms)	1 507(m)	1 488(m)	1 394(w)	1 340(s)	1 180,1 170(m)			855(sh),845(m)
	(C)	1 610,1 600(s)	1 562(ms)	1 518(m)	1 488(m)		1 367(s)	1 180(m)	1 105(br,s)	976,935(m)	878(ms),855,840(m)
CH_3	(F)	1 598(s)	1 555(s)		1 488(m)	1 394(w)	1 340(s)	1 176(w)			
	(C)	1 600(s)	1 560(m)		1 487(m)		1 370(s)	1 186(w)	1 105(br,vs)	980,935(m)	876,855,840(m)
H	(F)	1 602(s)	1 563(s)		1 488(m)	1 394(w)	1 338(s)				
	(C)	1 604(s)	1 570(s)		1 488(m)		1 367(s)		1 100,1 115(br,vs)	978,934(s)	875,852(s)
F	(F)	1 612,1602(s)	1 570(s)	1 502(s)	1 485(m)	1 392(w)	1 347(s)	1 150(m)			
	(C)	1 605(s)	1 575(s)	1 510(m)	1 485(m)		1 363(s)	1 160(m)	1 100(br,vs)	975,930(s)	875,855,842(s)
Br	(F)	1 600(s)	1 558(s)		1 489,1 480(m)	1 397(w)	1 335(s)	1 170(w)			
	(C)	1 600(s)	1 556(m)		1 485(m)		1 365(s)		1 100(br,vs)	975,930(m)	872,854,837(m)
CF_3	(F)	1 608(s)	1 570(s)		1 489(m)	1 395(w)	1 325(s)	1 168(s)	1 125(s)	970(m),950(w)	865(m)
	(C)	1 612(s)	1 570(s)		1 488(m)		1 373(m)		1 120(br,vs)	978(ms),934(m)	878,860,850(s)
CN	(F) *	1 602(s)	1 556(m)		1 487(m)		1 337(ms)				860(m)
	(C) *	1 610(s)	1 555(m)		1 488(m)		1 368(ms)		1 110,1 125(vs,br)	975(ms),930(m)	876,860,845(s)
NO_2	(F)	1 618(m)	1 585(s)	1 520(ms)	1 488(m)	1 350(w)	1 333(s)	1 317(s)			873(w),850(m)
	(C)	1 620(m)	1 585(s)	1 525(ms)	1 488(m)		1 350(s)		1 107(br,vs)	976,930(m)	880(sh on solvent peak),850(s)

* v(CN) (F) 2 228; v(CN) (C) 2 233 cm^{-1}.

I.r. Spectra.—The i.r. absorption bands of significant intensity which are not obscured by the solvent are reported in Table 2. The complexes between TAB and boron trifluoride show new bands in the region 1 100—1 120 (one or two very broad and intense bands) and 980—840 cm^{-1} (four or five bands of medium or strong intensity). The origin of the two bands at 1 100 ± 100 cm^{-1}, arising from ν_{asym} (B–F) of the complexed $^{10}BF_3$ and $^{11}BF_3$ group is well established.[8-12] Two of the remaining low frequency bands probably arise from ν_{asym} (B–F) (two isotopic varieties), but the overlap with bands of the TAB and the large variation of frequencies quoted in the literature for complexes with boron trifluoride precludes a straightforward attribution. The somewhat weak band at *ca.* 1 170—1 180 cm^{-1} can be attributed to the C–H in-plane deformation mode of the 1,4-disubstituted benzene ring.[13a] The band at 1 485—1 488 cm^{-1} which is almost independent of substitution and complexation is assigned to a deformation mode of the quaternary methyl, $\overset{+}{N}\text{–}CH_3$.[13b,14] In the region 1 620—1 555 cm^{-1} appear two bands characteristic of an aromatic ring linked to a carbonyl group.[13c] Unfortunately the stretching frequency of the carbonyl group cannot be distinguished, due to the pronounced conjugation which probably lowers the frequency below 1 600 cm^{-1}. The proximity of this frequency with those of the aromatic ring presumably gives rise to a strong coupling.

The most salient feature in the 1 600 cm^{-1} region is the very weak effect of boron trifluoride complexation in the anticipated region of carbonyl absorption. If complexation occurred at the formally negative nitrogen, one would expect the observation of a new carbonyl stretching frequency at *ca.* 1 700 cm^{-1} by analogy with protonation;[2] similarly the *N*-complexation of urea brings about a new brand at 1 725 cm^{-1}.[15] The absence of such an absorption is strong evidence for *O*-complexation by boron trifluoride. As in the present case the complexation by boron trifluoride of the oxygen of tetramethylurea causes a small shift of the Amide I band;[16a] this is explained by the contribution of other modes of vibration

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[5] V. Gutmann, 'Coordination Chemistry in Non-Aqueous Solutions,' Springer-Verlag, Vienna, 1968.

[6] R. W. Taft and J. W. Carter, *J. Amer. Chem. Soc.*, 1964, **86**, 4199.

[7] H. C. Brown and R. B. Johannensen, *J. Amer. Chem. Soc.*, 1950, **72**, 2934.

[8] P. H. Laswick and R. C. Taylor, *J. Mol. Structure*, 1976, **34**, 197 and references therein.

[9] M. T. Forel, M. Fouassier, and M. Tranquille, *Spectrochim. Acta*, 1970, **26A**, 1761 and references therein.

[10] T. C. Waddington and F. Klanberg, *J. Chem. Soc.*, 1960, 2339.

[11] A. R. Katritzky, *J. Chem. Soc.*, 1959, 2049.

[12] B. P. Susz and P. Chalandon, *Helv. Chim. Acta*, 1958, **41**, 1332.

[13] L. J. Bellamy, 'The Infrared Spectra of Complex Molecules,' Methuen, London, 1958, 2nd. edn., (*a*) p. 81; (*b*) p. 258; (*c*) pp. 71—74.

[14] L. J. Bellamy, 'Advances in Infrared Group Frequencies,' Chapman and Hall, London, 1968, p. 11.

[15] R. B. Penland, S. Mizushima, C. Curan, and J. V. Quagliano, *J. Amer. Chem. Soc.*, 1957, **79**, 1578.

[16] J. S. Hartman and G. J. Schrobilgen, *Canad. J. Chem.*, (*a*) 1972, **50**, 713. (*b*) 1973, **51**, 99.

to the so-salled ν(C=O) vibration. The same phenomenon is also observed in the complexation of amides by boron halides.[17,18]

In line with the previous arguments and by analogy with amides, the band situated at *ca.* 1 340 cm^{-1} and shifted towards higher frequency by *ca.* 30 cm^{-1} upon complexation is tentatively assigned to the $\nu(\mathrm{C{-}\bar{N}})$ mode. The increase in frequency is consistent with the contribution from (Ib) expected in the adduct, as in tetramethylurea [16a] and amides.[18]

TABLE 3

^{1}H N.m.r. spectra of compounds p-$\mathrm{XC_6H_4C\bar{O}\overset{+}{N}N(CH_3)_3}$ free (F) and complexed by $\mathrm{BF_3}$ (C) (0.25M; $\mathrm{CH_2Cl_2}$; p.p.m. from $\mathrm{Me_4Si}$)

X	State	Aromatic 2-H [a]	Aromatic 3-H [b]	$J_{2.3}$Hz	$\overset{+}{\mathrm{N}}(\mathrm{CH_3})_3$	X	Remarks
$\mathrm{OCH_3}$	(F)	7.83	6.78	9	3.39	3.75	
	(C)	7.78	6.90	9	3.47	3.82	
$\mathrm{CH_3}$	(F)	7.76	7.08	8.5	3.42	2.32	Ar$\mathrm{C}H_3$ coupled with 3-H (but not resolved)
	(C)	7.68	7.22	8.5	3.49	2.45	
H	(F)	~7.9	~7.3		3.41	$\delta_{\mathrm{X}} \sim \delta_{3\text{-H}}$	Approximate values due to the complexity of the spectra
	(C)	~7.8	~7.4		3.47		
F	(F)	7.90	6.96	8.5	3.42		$^4J_{\mathrm{F,\,2\text{-}H}}$ 5.5; $^3J_{\mathrm{F,\,3\text{-}H}}$ 9 Hz
	(C)	7.82	7.10	8.5	3.49		$^4J_{\mathrm{F\,\,2\text{-}H}}$ 5.5; $^3J_{\mathrm{F,\,3\text{-}H}}$ 9 Hz
Br	(F)	7.78	7.43	8.5	3.40		
	(C)	7.65	7.53	8.5	3.48		
$\mathrm{CF_3}$	(F)	8.05	7.57	8.5	3.43		
	(C)	7.90	7.67	8.5	3.49		
CN	(F)	8.01	7.58	8.0	3.40		
	(C)	7.88	7.71	8.0	3.52		
$\mathrm{NO_2}$	(F)	8.08			3.42		
	(C)	7.98	8.18	8.5	3.53		

[a] *ortho* to X. [b] *meta* to X.

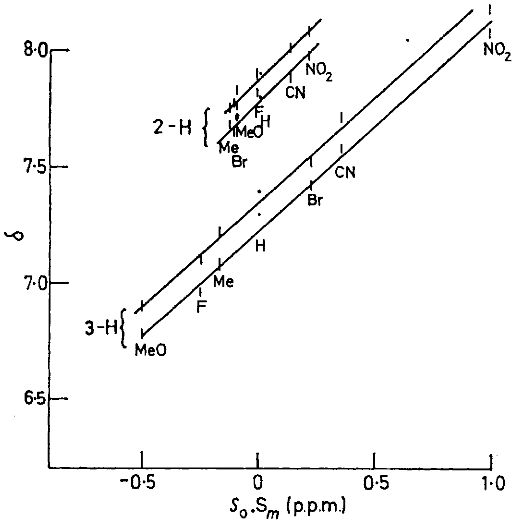

FIGURE 1 Plot of ^{1}H chemical shifts for 2- and 3-H (Table 3) in compounds (2)—(9) in free and complexed forms *versus* S_o and S_m values of Diehl [19]

^{1}H *N.m.r. Spectra.*—The results are shown in Table 3. For the sake of simplicity the aromatic part of the spectra has been analysed as an AB type. The assignments are supported by the good correlations obtained between the chemical shifts and the substitution increments, S_o and S_m of Diehl [19] (see Figure 1). We note that the protons *ortho* to the amidate function are shielded by complexation, whereas *meta*-protons are deshielded. In general deshielding of the aromatic signals would be anticipated because of the increased electron demand by the complexed amidate function. However other observations (*vide infra*) suggest that the function, at least in complexed form, is not truly conjugated with the benzene ring; thus other effects, such as changes in magnetic anisotropy and/or in the conformation of the ammonioamidate group caused by formation of the co-ordinative bond, can become important.

On the other hand the $\overset{+}{\mathrm{N}}$–$\mathrm{CH_3}$ protons are deshielded by 0.06—0.12 p.p.m. on complexation. Comparison with many literature examples of boron trifluoride complexation [20] shifts indicates that co-ordination of TAB takes place rather far from the proton under study. Thus mean values of complexation shifts for protons separated by three, four, and five bonds respectively from the carbonyl oxygen of ketones are 0.60, 0.25, and 0.10 p.p.m.[21–23] For alkylureas, corresponding values of 0.20 and 0.15 p.p.m. are noted for protons four and five bonds removed from oxygen. Comparison of these values (obtained in the same solvent, $\mathrm{CH_2Cl_2}$) with the observed 0.09 ± 0.03 p.p.m. for TAB is a good indication of a complexation site removed by five bonds from the *N*-methyl protons, *i.e.* the carbonyl oxygen.

Enthalpies of Complexation.—The enthalpies of complexation of TAB (Table 4) are considerably more

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[17] E. L. Muetterties and E. G. Rochow, *J. Amer. Chem. Soc.*, 1953, **75**, 490.

[18] W. Gerrard, M. F. Lappert, H. Pyszora, and J. W. Wallis, *J. Chem. Soc.*, 1960, 2144.

[19] P. Diehl, *Helv. Chim. Acta*, 1961, **44**, 829.

[20] A. Fratiello and C. S. Stover, *J. Org. Chem.*, 1975, **40**, 1244 and references therein.

[21] P. N. Gates and E. F. Mooney, *J. Inorg. Nuclear Chem.*, 1968, **30**, 839.

[22] R. J. Gillespie and J. S. Hartman, *Canad. J. Chem.*, 1968, **46**, 2147.

[23] G. Derrieu, Thesis, Université de Nice, 1973.

negative than those of other aromatic carbonyl compounds studied previously with boron trifluoride.[24-26] However the observed substituent effect is much lower in the present series of TAB than in previous work; for instance the variation in ΔH^0 between p-NO$_2$ and p-OMe is 25.8 for benzaldehydes and 9.2 kJ mol^{-1} for TAB.

TABLE 4

Enthalpy of complex formation between BF$_3$ and p-XC$_6$H$_4$CO$\overset{-}{\mathrm{N}}\overset{+}{\mathrm{N}}$(CH$_3$)$_3$ (CH$_2$Cl$_2$; 0.25M; 298.15 K)

X	$-\Delta H^0$/kJ mol^{-1} *	n †
OCH$_3$	117.57 ± 0.40	7
CH$_3$	116.90 ± 0.57	7
H	115.96 ± 0.31	8
F	113.36 ± 0.44	8
Br	113.14 ± 0.42	8
CF$_3$	112.86 ± 0.37	7
CN	110.83 ± 0.41	9
NO$_2$	108.34 ± 0.58	8

* Quoted errors are 95% confidence level.
† Number of measurements.

This substituent effect has been expressed quantitatively for the series of *para*- and *meta*-substituted benzaldehydes[24] and acetophenones[26] by ρ^+–σ^+ correlations. In the present work we have found significantly better correlations by the use of $\sigma_p{}^0$ (and to lesser extent σ_p) than $\sigma_p{}^+$ (Table 5 and Figure 2). In addition the standard deviation of the fit with $\sigma_p{}^0$ scale compares well with the precision of the data (Table 5). This finding signifies that contrary to the behaviour of substituted benzaldehydes and acetophenones, through conjugation between M^+ substituents and the N-ammonioamidate function is unimportant, at least in complexed TAB.

TABLE 5

Parameters of the equation $\Delta H^0 = \rho\sigma^{\mathrm{i}} + b$ (kJ mol^{-1})

σ^{i}	ρ	s_ρ [a]	$-b$	r [b]	s [c]	n [d]
$\sigma_p{}^+$ [e]	5.24	1.02	114.31	0.9026	1.45	8
σ_p [f]	7.57	1.04	115.36	0.9472	1.08	8
$\sigma_p{}^0$ [g]	8.89	0.54	115.88	0.9908	0.50	7
$\sigma_p{}^0$ [h]	8.42	0.81	115.96	0.9737	0.77	8

[a] Standard deviation of the slope ρ. [b] Correlation coefficient. [c] Standard deviation of the fit. [d] Number of data points. [e] From H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, 1958, **80**, 4979. [f] From D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, 1958, **23**, 420. [g] From Y. Yukawa, Y. Tsuno, and M. Sawada, *Bull. Chem. Soc. Japan*, 1972, **45**, 119. No value for CF$_3$ available from this source. [h] Footnote g plus the CF$_3$ value from A. J. Hoefnagel and B. M. Wepster, *J. Amer. Chem. Soc.*, 1973, **95**, 5357.

Two explanations may be offered for this absence of through conjugation: (a) a lack of coplanarity between the amidate function and the aromatic ring; (b) the supremacy of the negatively charged nitrogen in stabilising the complexed carbonyl, as compared to the π contribution of the aromatic ring.

In connection with hypothesis (a) the carbonyl group of TAB is slightly twisted by 17° from the plane of the aromatic ring at least in the solid state,[27] as compared with a corresponding angle of 3.5—6° found in acetophenones by electron diffraction.[28] However in the complex the bulkiness of the complexed function may force it to rotate away from the plane of the aromatic ring. Approach of boron trifluoride is made difficult in direction (1) of the Scheme by the synplanar relationship of the amidate function, approach in direction (2) of the Scheme may induce a steric compression with the *ortho*-hydrogens which in turn produces a rotation around the bond between the ring and the complexed carbonyl carbon.

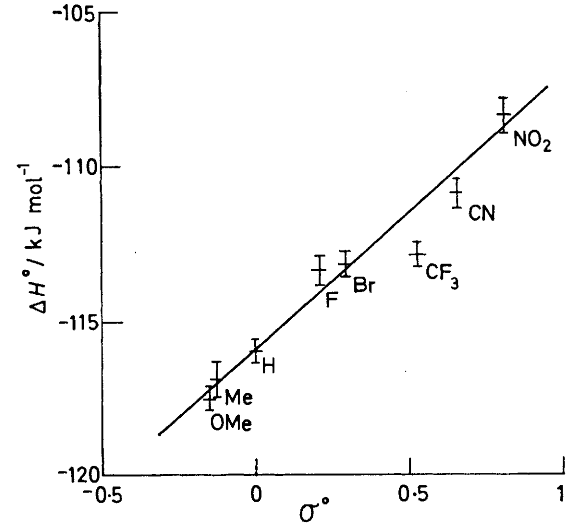
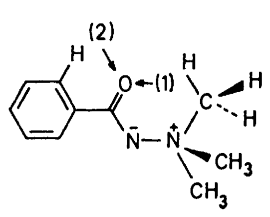


FIGURE 2 Correlation of enthalpies of complexation of compounds (2)—(9) against σ^0



SCHEME

However some arguments can be put in favour of (b); as the amidate function bears a negative charge the reaction between TAB and boron trifluoride is similar to the ionisation reaction of benzoic acids; a better correlation with σ than with σ^+ is therefore expected. Further the equilibrium constant for ion-pair formation between benzoic acids and 1,3 diphenylguanidine in benzene correlates with σ^0 values.[29] Here the proton is

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[24] J. F. Gal, L. Elegant, and M. Azzaro, *Bull. Soc. Chim. France*, 1973, 1150.

[25] J. F. Gal, L. Elegant, and M. Azzaro, *Bull. Soc. chim. France*, 1974, 411.

[26] J. F. Gal, L. Elegant, and M. Azzaro, Abstracts, 3rd I.U.P.A.C. Conference on Physical Organic Chemistry, La Grande Motte, 1976, p. 18.

[27] A. F. Cameron, N. J. Hair, D. G. Morris, and D. M. Hawley, *J.C.S. Perkin II*, 1972, 1072.

[28] M. P. Gupta, S. M. Prasad, and S. R. P. Yadav, *Current Sci.* 1974, **43**, 509; Y. Tanimoto, H. Kobayashi, S. Nakagura, and Y. Saito, *Acta Cryst.*, 1973, **B29**, 1822.

[29] M. M. Davis and H. B. Hetzer, *J. Res. Nat. Bureau Standards*, 1959, **60**, 569.

not completely transferred to the base, giving a complex where there exists some but not total charge development as is the case in ionisation. To this extent this reaction resembles complex formation between TAB and boron trifluoride.

Ellul and Moodie,[30] in their study of the equilibrium constant of complexation (K) between substituted benzamides and boron trifluoride in tetrahydrofuran, have shown that log K correlates better with σ than σ^+. This result has been taken as evidence that it is the nitrogen electron pair rather than the π electrons of the benzene ring which enters into conjugation with the carbonyl group. A similar conclusion is in order from analogous measurements with zinc dichloride and boron trifluoride in ether.[31]

In the present work the σ^0 correlation can be interpreted in terms of an even more powerful conjugating effect of the formally negative nitrogen, thereby inhibiting completely conjugation between the aromatic ring and the carbonyl group. The conjugative power of the amidate nitrogen is possibly reduced by the vicinal quaternary nitrogen; a parallel effect has been observed in *N*-alkylbenzamides which bear a strong electron-withdrawing group on nitrogen.[32] However the amidate nitrogen in TAB bears *two* electron pairs which indicates that conjugation is always possible.

In conclusion we note that hypotheses (a) and (b) are not irreconcilable, since a lack of conjugation between the amidate function and the aromatic ring facilitates rotation of one relative to the other.

EXPERIMENTAL

The preparation of the *N*-ammonioamidates and their physical and spectroscopic properties are reported in ref. 33.

All measurements were made in methylene chloride as solvent. Methylene chloride was purified by treatment with concentrated H_2SO_4,[34] distilled from P_2O_5, and stored in dark bottles over Linde 4 Å molecular sieves.

I.r. spectra were recorded on a Perkin-Elmer grating spectrophotometer, at 0.1M concentration, in a cell with KBr windows and a path length of 0.1 mm. Due to absorption of the solvent above 2 200 and in the regions 1 450—1 400, 1 350—1 300, 900—880, and 800—650 cm^{-1} and attack on the window by BF_3 giving absorptions at 1 100—1 000 and 535—525 cm^{-1} only regions indicated in Table 2 have been studied. By comparison with the polystyrene spectrum, the precision obtained is estimated to be ± 3 cm^{-1}.

^{1}H N.m.r. spectra were recorded on a Varian A-60 spectrometer at normal probe temperature (35 °C), the solvent peak being the internal reference and the chemical shifts converted to the tetramethylsilane scale by adding 5.30 p.p.m. Previous work [23-26] and some spectra run with tetramethylsilane have shown that the solvent peak is not shifted more than 1 Hz at the concentrations used, a value of the same order as the spectrometer accuracy. In the incompletely complexed solution, or in solution of complexes where we have added free TAB, the signals corresponding to the free and complexed TAB are observed, with relative intensities equal to the ratio of their respective concentrations. This indicates a slow exchange (on the n.m.r. time scale) of BF_3 between the free and complexed TAB. We have observed that the $\overset{+}{N}$–Me signals are less separated than the difference of their shifts in the solution as pure species, suggesting that the temperature of the spectrometer is just below the coalescence temperature.

For the less basic ketones [25,35] the coalescence temperature for this intermolecular exchange of BF_3 is well below −50 °C,[20,22,25] but for the alkylureas it is about room temperature.[16] This is in accord with the correlation observed between the enthalpy of complexation and the activation enthalpy of intermolecular exchange of $SbCl_5$ between various carbonyl compounds.[36]

The reversibility of the complex formation was shown in the following manner; the solution of complex, treated with an equal volume of 5% aqueous sodium hydroxide, shaken for 1 min, washed with water, and dried over 4 Å molecular sieves for 24 h gives a ^{1}H n.m.r. spectrum identical with those of the free TAB.

The stoicheiometry of the complexes was determined by the method of the calorimetric titration curve, as described in ref. 4. In the case of (8) the two complexation steps are in fact well separated, the only imprecise point being that which determines the stoicheiometry. Here the titration curve concerning the heat evolved $Q = f(\text{added } BF_3)$ has the following features. At acid : base ratios $\leqslant 0.9$ there is a straight line, slope ΔH, indicating a very stable 1 : 1 complex. At higher ratios (>1.0) the slope of the titration curve decreases monotonically; the heat evolved is no longer proportional to the number of moles of BF_3 added to the solution, thus indicating that the 2 : 1 complex is dissociated under our experimental conditions. The 1 : 1 complex which has high stability, an enthalpy of formation similar to other TAB complexes, and which exhibits a good fit in the correlations is thus considered unreservedly to be co-ordinated at the amidate function.

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