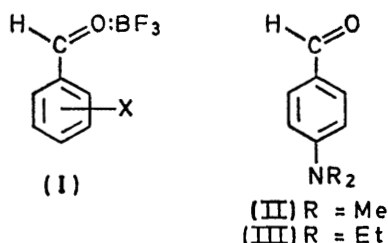


Boron Trifluoride Complexes. Part VI.¹ The Complexes and Conjugate Acids of *p*-Dimethyl- and -Diethylaminobenzaldehyde²

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Boron trifluoride forms three different complexes with *p*-dialkylaminobenzaldehyde, two 1:1 complexes (IV) and (V) and one 2:1 complex (VI). The structure of these complexes has been elucidated from their spectral properties. The strong electron-withdrawing pseudo-substituent $\text{BF}_3\text{:NR}_2$ is discussed and compared with the analogous H:NR_2 function. The kinetically controlled formation of (IV) and the thermodynamically controlled formation of (V) are discussed and compared with the behaviour of the conjugate acids.

AROMATIC aldehydes form stable complexes (I) with boron trifluoride.³ We have shown that these are σ - σ complexes, and that the boron trifluoride acceptor is linked to the carbonyl oxygen donor.⁴ The formation of these complexes is deduced from the basicity of the formyl group. The CHO:BF_3 group was referred to as a



pseudo-substituent, and we have studied its electron-withdrawing properties.^{1,4}

Substituted benzene derivatives bearing a basic substituent such as a methoxy- or dialkylamino-group are also known to form boron trifluoride complexes.⁵ In the case of anisaldehyde, only a 1:1 complex with boron trifluoride has been obtained, with the Lewis acid linked to the carbonyl, and not to the methoxy-group.⁴

We describe here the reaction between boron trifluoride and *p*-dimethyl- and -diethylaminobenzaldehyde (II) and (III). Neither complexes nor conjugate acids of these aldehydes have been reported in the literature. Aromatic aldehydes bearing two basic groups should in theory be able to form three different boron trifluoride complexes and acids. We observed three types of BF_3 complexes but only two types of the corresponding conjugate acids. Two of these complexes are 1:1 complexes in which the boron trifluoride is linked either to the carbonyl oxygen or to the dialkylamino-nitrogen atom. The third is a 1:2 complex in which two boron trifluoride molecules are linked to the aromatic aldehyde, one to the oxygen and the other to the nitrogen atom. Of the protonated species formed, one has a 1:1 and the other, a 1:2

composition. We regard the groups CHO:BF_3 , $\text{F}_3\text{B:NR}_2$, CHO:H^+ , and $\text{H}^+:\text{NR}_2$, as pseudo-substituents and this paper deals with their properties.

EXPERIMENTAL

The Table shows the u.v., carbonyl i.r., and formyl n.m.r. data of the various types of the complexes and the protonates of *p*-dimethyl- and -diethylaminobenzaldehyde. The 1:1 complexes in which the boron trifluoride is linked to the formyl group were prepared as described previously^{1,4} by the addition of either boron trifluoride gas or ether complex to the solution of the free aldehyde in carbon tetrachloride.[†] The precipitate was then filtered off under nitrogen. These complexes have to be prepared and maintained under anhydrous conditions, and they can be preserved as solids for long periods of time (over one year when kept in a sealed tube). When a solution of the 1:1 complex is allowed to stand for one week and then evaporated under anhydrous conditions a second 1:1 complex is obtained. The 1:2 complexes, in which two BF_3 molecules are linked to the aldehyde, could not be isolated. N.m.r. spectra were recorded on a Varian HA-100D spectrometer at high settings of amplitude and at low temperatures (below the exchange temperature of the complexes). These recordings showed a purity of >99% and no free aldehyde could be detected. The parent aldehydes were twice recrystallized from cyclohexane. Methylene chloride of analytical grade (Matheson, Coleman, and Bell) was dried and stored over magnesium perchlorate (anhydrous). The u.v. spectra were determined in 1 cm cells with a Unicam SP 800 spectrometer. The i.r. spectra were recorded on a Perkin-Elmer 621 spectrometer, in KBr cells, in dry methylene chloride as described previously.^{1,4} The correlations were programmed with our Fortran IV program YOFI,¹ and performed on the CDC 6400 computer at the computing centre of the Hebrew University.

We use the notation of Moser and Kohlenberg for benzenoid u.v. spectra.⁶ The transition ${}^1E_{2u} \leftarrow {}^1A_{1g}$ is referred to as the A band, the high intensity band of benzene at 200 nm resulting from the transition ${}^1B_{1u} \leftarrow {}^1A_{1g}$ as the B band, and the benzene band at 256 nm resulting from the transition ${}^1B_{2u} \leftarrow {}^1A_{1g}$ as the C band.

[†] The composition of the complexes (IV) and (V) was shown by microanalysis of C, H, and F to be 1:1 (within experimental error). The m.p.s of (IV) and (V) are 125 and 170 °C respectively. The n.m.r. spectra of (IV) and (V) at -60 °C showed a very weak formyl band of the free aldehyde.

¹ Part V, M. Rabinovitz and A. Grinvald, *J. Amer. Chem. Soc.*, 1972, **94**, 2724.

² For a preliminary report of this work see M. Rabinovitz and A. Grinvald, *Tetrahedron Letters*, 1971, 4325.

³ (a) M. Landolf, *Compt. rend.*, 1878, **86**, 671; (b) R. Lombard and J. P. Stephan, *Bull. Soc. chim. France*, 1957, 1369; (c) 1958, 1458.

⁴ M. Rabinovitz and A. Grinvald, *Tetrahedron Letters*, 1971, 641.

⁵ A. A. Palko, R. M. Healy, and L. London, *J. Chem. Phys.*, 1958, **28**, 214.

⁶ C. Moser and A. I. Kohlenberg, *J. Chem. Soc.*, 1951, 804.

RESULTS AND DISCUSSION

The nature of the 1:1 BF_3 -aromatic aldehyde complexes in which the BF_3 is linked to the carbonyl group has already been established.^{1,4} In all carbonyl complexes there is a marked red shift. Conversely, the BF_3 1:1 complexes in which the BF_3 is linked to the dialkylamino-group should give a blue shift due to breaking of p - π conjugation (as observed in the case of the anisole- BF_3 complex).⁵ When the complexes are prepared as described and dissolved in dry methylene chloride, a complicated u.v. spectrum is obtained. In

the solution was left for several days a new absorption at δ 10.07 appeared, while the absorption at δ 8.73 decreased. Both these bands showed however, an integration equivalent to one proton. This low-field absorption is typical of aromatic aldehydes bearing a strong electron-withdrawing group (p -nitrobenzaldehyde absorbs at δ 9.99) and is therefore assigned to the complex (V; R = Me). This assignment was confirmed by the spectrum of the isolated complex (V). The n.m.r. spectrum of a solution of the complex (IV; R = Me) in CH_2Cl_2 containing an excess of the free aldehyde,

p-Dimethyl- and -diethyl-aminobenzaldehyde (*p*- $\text{XC}_6\text{H}_4\text{Y}$) amino- and carbonyl complexes

Y	X	Compound	$\lambda_{\text{max.}}/\text{nm}$ (ϵ)		$\Delta E_{\text{T}}^a/$ kcal mol ⁻¹	$\nu_{\text{C=O}}/\text{cm}^{-1}{}^b$	δ (CHO) $^c, d$
			B Band	C Band *			
NMe ₂	CHO	(II)	338.5 (32,800)			1664	9.760
NEt ₂	CHO	(III)	343.0 (35,500)			1664	9.644
NMe ₂	CHO:BF ₃	(IV)	401		13.2	1588	8.697
			388				
NEt ₂	CHO:BF ₃	(IV)	404		12.6	1590	8.637
			392				
Me ₂ N:BF ₃	CHO	(V)	238.2 (17,000)	277 (1400)	-35.6	1713	10.108
				287 (1200)			
Me ₂ N:H ⁺	CHO	(VIII)	242 (13,000)	279 (1290)	-36.9 ^e		
				290s			
Et ₂ N:BF ₃	CHO	(V)	239.5 (21,000)	278 (1900)	-36.0	1713	10.078
				288 (1700)			
Et ₂ N:H ⁺	CHO	(VIII)	243 (15,800)	279 (1670)	-37.7 ^e		
				290s			
Me ₂ N:BF ₃	CHO:BF ₃	(VI)	267.5 ^f	315s	-22.4		
Me ₂ N:H ⁺	CHO:H ⁺	(VII)	279 (8750)	325s (705)	-21.3 ^e		
Et ₂ N:BF ₃	CHO:BF ₃	(VI)	268 (11,000)	315s	-23.3		
Et ₂ N:H ⁺	CHO:H ⁺	(VII)	280 (12,300)	325s (1150)	-22.0 ^e		

* s = Shoulder.

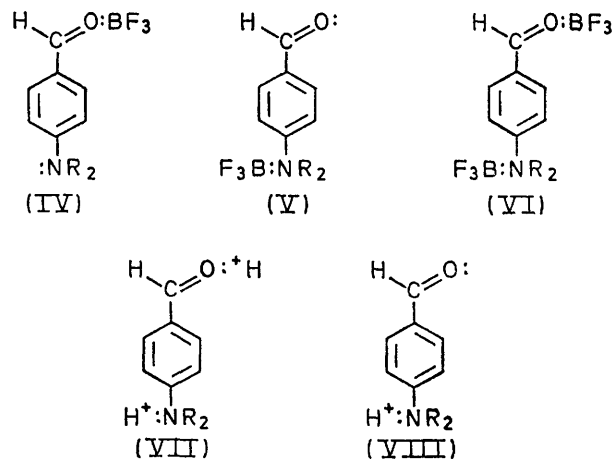
^a Transition energy difference from parent compound. ^b Perkin-Elmer 621 spectrometer. ^c Varian HA-100 D spectrometer.

^d Tetramethylsilane internal reference, at probe temperature. ^e Relative to $\lambda_{\text{max.}}$ of parent compound in 3% H_2SO_4 . ^f Sparingly soluble, ϵ is meaningless.

such a spectrum two strong bands are observed, one at *ca.* 240 and the other at *ca.* 400 nm. Addition of dilute ethanol increases the intensity of the short wavelength band (*ca.* 240 nm) and decreases that of the long wavelength band (*ca.* 400 nm). Addition of more ethanol causes the spectrum to revert to that of the parent *p*-dialkylaminobenzaldehyde. A change in the intensity of the blue-shifted band (which occurs at even shorter wavelengths than the B band of the parent aldehyde) occurred at the expense of the red-shifted one, when the solution of the complexes was left for some time. We conclude that the red-shifted band represents the B band of the carbonyl complex with the pseudo-substituent CHO:BF_3 (IV), and the blue-shifted band represents the B band of the aldehyde bearing the pseudo-substituent $\text{F}_3\text{B:NR}_2$ (V). The spectra of complexes (IV) and (V) when isolated proved this conclusion.

In the n.m.r. spectrum, the formyl proton of *p*-dimethylaminobenzaldehyde (II) appeared at δ 9.69 for a solution in methylene chloride. For a BF_3 complex, the formyl proton shifted to higher field and in the case of the complex of (II) [(IV; R = Me)] appears at δ 8.73. This high-field shift is common in all aromatic aldehyde carbonyl- BF_3 complexes. The absorption at δ 8.73 was the only one observed in this region for freshly prepared complexes. When

showed all three species (II), (IV), and (V) below the exchange temperature. Preparation of complexes by the addition of an excess of BF_3 gas to a solution of the



free aldehyde, a procedure which is very effective for normal benzaldehyde complex formation, gave a new species. In the u.v. spectrum, there was only one band at 267.5 nm (ϵ 11,000) in the case of *p*-diethylaminobenzaldehyde (III), and at 268 nm in the case of *p*-dimethylaminobenzaldehyde (II). This absorption is

similar to that of the BF_3 complex of *p*-nitrobenzaldehyde (λ_{max} , 265 nm),¹ which is a molecule bearing two strong electron-withdrawing groups ($\text{CHO}:\text{BF}_3$ and NO_2). The absorption at this wavelength suggests the presence of a 2 : 1 complex (VI) involving the carbonyl and dialkylamino-groups bearing the respective pseudo-substituents $\text{CHO}:\text{BF}_3$ and $\text{F}_3\text{B}:\text{NR}_2$.

Addition of dilute ethanol to this complex caused the appearance of only one band for the blue-shifted complex (V) (B band at 238 nm; $\text{F}_3\text{B}:\text{NR}_2$ complex).

The complexes (IV) and (V) may also be characterized by their carbonyl stretching frequencies. In complex (IV; $\text{R} = \text{Et}$) this absorption appeared at 1590 cm^{-1} while in the free aldehyde (III) it appeared at 1664 cm^{-1} (Table). Such a shift of *ca.* 70 cm^{-1} to lower wavenumbers which is common to all carbonyl oxygen complexes,^{1,4} can be rationalized by the enhancement of the electron-withdrawing character of the $\text{CHO}:\text{BF}_3$ pseudo-substituent (relative to the free CHO group). On the other hand, one should expect that a benzaldehyde with an electron-withdrawing pseudo-substituent will show the opposite trend, *i.e.*, a shift of the carbonyl absorption to higher wavenumbers. This is the case with *p*-nitrobenzaldehyde, in which the carbonyl function absorbs at 1711 cm^{-1} (Table). For complex (V; $\text{R} = \text{Me}$ or Et) in which the boron trifluoride is linked to the nitrogen, the carbonyl absorbs at 1713 cm^{-1} (the pseudo-substituent $\text{F}_3\text{B}:\text{NR}_2$ is a strong electron-withdrawing group). From the absorptions in the u.v. and i.r. spectra of complex (V) we assume that not only the *p*- π conjugation to the ring is affected, but that this complex behaves like a benzaldehyde derivative with an electron-withdrawing

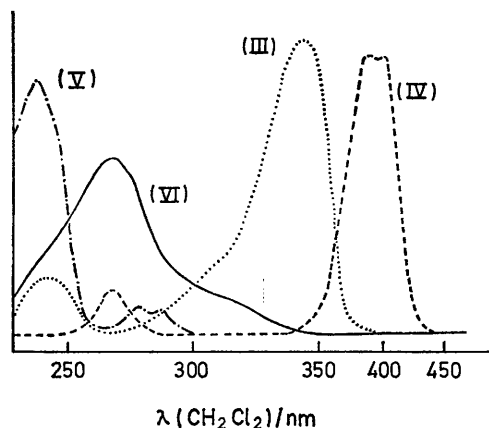


FIGURE 1 Superimposed u.v. spectra of (III)–(VI)

substituent comparable with the nitro group in *p*-nitrobenzaldehyde. In Nujol the i.r. spectrum of the 1 : 1 complex corresponds to the carbonyl complex only. The i.r. absorption of the 2 : 1 complex (VI) could not be measured since the excess of BF_3 attacks the windows of the i.r. cells. The superimposed u.v. spectra of the free *p*-diethylaminobenzaldehyde and its two 1 : 1

and 2 : 1 BF_3 complexes are shown in Figure 1. The superimposed i.r. spectra of the two 1 : 1 BF_3 complexes are shown in Figure 2.

The conjugated acids of *p*-dialkylaminobenzaldehyde have not been reported previously. In 98% sulphuric

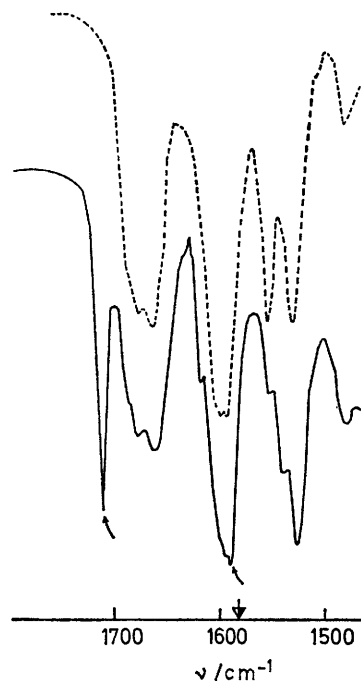


FIGURE 2 Superimposed i.r. spectra of a mixture of (II) and (IV) ····, and of a mixture of (II), (IV), and (V) —

acid there is a single band in the u.v. spectrum at 279 nm which we assign to the 2 : 1 protonated species, *i.e.*, the product (VIII) of protonation of both the carbonyl oxygen and the dialkylamino-group (Table). U.v. spectra for various concentrations of sulphuric acid did not show an absorption that could be assigned to 1 : 1 carbonyl protonated species, but in 5% sulphuric acid (v/v) in water the blue-shifted absorption of the 1 : 1 species (VII) was observed at 243 nm (ϵ 15,000). The free aldehyde was observed only in very high optical density at 338.5 nm (ϵ 32,800) for *p*-dimethylaminobenzaldehyde (II) and at 343 nm (ϵ 35,500) for *p*-diethylaminobenzaldehyde (III). These results show that in the case of the protonated species the *N*-species is much more likely to be formed and is more stable than the *O*-species. The formation of the oxygen- BF_3 complex must be the kinetically controlled process for the following reasons. (a) In the 1 : 1 complexes the oxygen- BF_3 linkage *viz.* (IV) is formed first. (b) The nitrogen- BF_3 1 : 1 complex (V) is formed either from (IV) by the addition of ethanol or alternatively after prolonged standing. (c) Addition of ethanol to (VI) (2 : 1 complex) converts the latter to the 1 : 1 nitrogen- BF_3 complex (V). The 1 : 1 $\text{N}:\text{BF}_3$ complex is also more resistant to alcohol, is the more stable product, and should be considered as the thermodynamically controlled product.

Of the 1 : 1 protonated species only the 1 : 1 nitrogen-proton complex is formed, probably due to the lack of steric factors (F strain). From the n.m.r. spectrum, a freshly prepared complex consists of > 99% of the 1 : 1 carbonyl oxygen-BF₃ complex. Lewis bases catalyse the formation of the N -complexes. The effect on the n.m.r., i.r., and u.v. spectra is the same if ethanol or the free aldehyde is added; the appearance of the N -complex is observed [in the n.m.r. spectrum all three species, free aldehyde complex (IV), and complex (V) can be observed below -70°C]. The fact that in the u.v. spectrum a mixture of the two 1 : 1 complexes is detected, can be attributed to slight amounts of moisture present in the dilute solutions employed for the u.v. measurements. The 2 : 1 complex is more dependent on the concentration of boron trifluoride and is readily formed when an excess of BF₃ is present.

The $R_2N:BF_3$ Pseudo-substituent.—We have previously shown that the 1 : 1 carbonyl complexes of a series of benzaldehydes (with the pseudo-substituent $CHO:BF_3$) have a displaced benzenoid spectrum.¹ This was demonstrated by the good correlation (r 0.956) of the complex B band absorption with that of the free aldehydes^{1,4} [equation (1)]. The question now arises whether a benzaldehyde derivative with the strong-electron withdrawing pseudo-substituent $R_2N:BF_3$ belongs to the benzaldehyde series or, as in the case of *p*-nitrobenzaldehyde, to another series.⁷ If a benzaldehyde with the pseudo-substituent $R_2N:BF_3$ [1 : 1 complex (V)] is considered as a member of the noncomplexed substituted benzaldehyde series, bearing a strong electron-withdrawing group $R_2N:BF_3$ then the 2 : 1 complex (VI), with BF₃ molecules on both carbonyl and dialkyl-amino-groups, should be considered as a member of the corresponding carbonyl-BF₃ complexed series. In this case, equation (1) should hold and predict the absorption maximum of the 'complexed' benzaldehyde (VI).

$$\lambda_{\text{max}}^{\text{complex}} = 1.36\lambda_{\text{max}}^{\text{aldehyde}} - 56.5 \text{ nm} \quad (1)$$

($N = 17$; r 0.956; s 12 nm)

Substitution of the value of the absorption of the 'free' aldehyde (V) bearing the pseudo-substituent $R_2N:BF_3$, into equation (1) gives the values 269.3 and 270.9 nm for the 2 : 1 complexes of *p*-dimethyl- and -diethyl-aminobenzaldehyde respectively. The deviation is much smaller than the standard deviation, and demon-

strates the ability of equation (1) to predict the absorptions of new compounds. In equation (2) the two new pseudo-substituents $Me_2N:BF_3$ and $Et_2N:BF_3$ together with another 15 substituents are included. The best fit of this computed correlation is shown in Figure 3

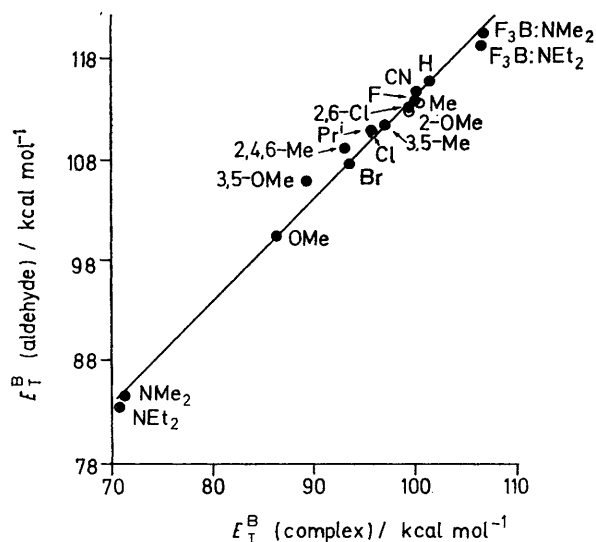


FIGURE 3 Correlation of the u.v. energy B band of the free aldehydes *vs.* the complexed aldehydes for 17 aldehydes and complexes including compounds (V and VI; $R = \text{Me}$ or Et). The unnumbered substituents refer to *para*-positions

and the high correlation coefficient (0.995) shows beyond doubt that there is a linear dependence between the transition energies of the complexes and the free aldehydes, and that the complexes are *not* charge transfer complexes, and that the group $R_2N:BF_3$ forms a pseudo-substituted compound which clearly belongs to the benzaldehyde series.

$$E_T^B(\text{complex}) = 0.98E_T^B(\text{aldehyde}) - 11.9 \text{ kcal mol}^{-1} \quad (2)$$

($N = 17$; r 0.995; s 1.09 kcal mol⁻¹)

Thus, the two new pseudo-substituents presented here, $R_2N:H^+$ and $R_2N:BF_3$ have extremely strong electron-withdrawing character.

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⁷ J. C. Dearden and W. F. Forbes, *Canad. J. Chem.*, 1958, **36**, 1362.