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BORON TRIFLUORIDE COMPLEXES OF AROMATIC ALDEHYDES.[1]

THE CHO : BF_3 PSEUDOSUBSTITUENT

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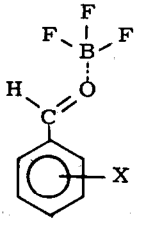
Although boron trifluoride complexes of aromatic aldehydes I have been known since 1878,[2] there is very little information about their spectral and chemical properties.[3,4] They are stable 1 : 1 solid complexes which are readily formed by treating a CCl_4 or CH_2Cl_2 solution of the free aldehyde with boron trifluoride gas or etherate. The complexes are sensitive to moisture and to Lewis bases but they can be preserved under anhydrous conditions for long periods of time (they may be purified by sublimation and preserved under anhydrous conditions). We have previously described the effect of complex formation on nmr spectra and hindered rotation about the C_{aryl}-C_{formyl} bond.[5] We now report that the bonding in these complexes, as inferred from the uv, ir and nmr spectra, is of a σ-σ and not a charge-transfer type,[6] and that the group CHO : BF_3 is a strong electron-withdrawing (pseudo) substituent.



I

The Table summarizes some spectral data of boron trifluoride complexes of aromatic aldehydes. Such complexes were previously described as charge transfer complexes.[6] If this were true we would expect the transition energy E_T to correlate with the ionization potential of the free aldehydes; on the contrary, we find no such correlation. In the uv, only a red shift is observed and no new bands appear in the visible region (Table). These data eliminated the possibility of a charge-transfer complex, and suggest molecular interactions of a σ-σ type. A correlation does exist between the uv band absorption of the free and complexed aldehydes.[7,8,9] This correlation is good (CC = 0.956) for 17 benzaldehydes and the best-fit line shown in Figure 1 shows that the complexed aldehydes manifest a displaced benzenoid spectrum like the free aldehydes, and establishes the -CHO : BF_3 group as a pseudosubstituent of the aromatic ring. The correlation for the para substituted derivatives only is better and is represented in equation (1).

$$\lambda_{max}^{complex} = 1.29\,\lambda_{max}^{aldehyde} - 38\ m\mu \qquad (1)$$

$$\cdot(N = 10;\ CC = 0.994;\ STD = 5.6\ m\mu;\ Slope = 1.29)$$

In the case of the para-dialkylaminobenzaldehydes, the 1 : 1 BF_3 complexation (in contrast to 1 : 1 protonation) occurs at the carbonyl oxygen rather than at the nitrogen. This conclusion is based on the following evidence: (a) As in all other benzaldehydes studied here, BF_3 complexation (as well as protonation)[13] shows a red shift in the uv spectra. Complexation at the nitrogen would require a blue shift as was indeed observed in the 1 : 1 protonation of the para-dialkylaminobenzaldehydes.[13] (b) The nmr absorption of the formyl protons in the 1 : 1 BF_3 complexes of these -NR_2 derivatives is shifted to higher field, while protonation, which occurs at the nitrogen, shows the opposite effect. Protonation of benzaldehyde[14] shifts the absorption of the formyl proton to higher field, in an anlogous manner to BF_3 complexation.

It appears that the CHO : BF_3 pseudosubstituent is an extremely strong electron withdrawing group. A good correlation is obtained between the uv spectra of our complexes and the respective nitrobenzene derivatives, while the correlation with the free aldehydes is poor. This conclusion is substantiated by the F^{19} chemical shift[10] of the para-fluoro derivatives. While the absorption of p-fluoronitrobenzene and p-fluorobenzaldehyde appears at 9.99 and 9.42 ppm respectively (CH_2Cl_2, relatively to fluorobenzene), the p-fluorobenzaldehyde-BF_3 complex absorbs at 22.93 ppm (for comparison p-fluoro-α,β,β-tricyanovinyl-benzene with its highly strong electron withdrawing group absorbs at 12.10 ppm[11](acetone, relative to fluorobenzene).

TABLE: Some Spectral Data of Boron Trifluoride Complexes of Benzaldehydes

Benzaldehyde	UV[9] λ_{max} (ϵ)*	IR[12] ν cm^{-1}**		NMR[10] δ cps***	
	Complex	Complex	Aldehyde	Complex	Aldehyde
Benzaldehyde	281.6 (18,800)	1626	1703	970	998
p-Anisaldehyde	331 (34,900)	1598	1682	935	987
p-Tolualdehyde	285.7 (18,300)	1619	1695	955	992
p-Fluoro-	285.3 (16,900)	1627	1702	966	997
p-Chloro-	298.5 (23,600)	1627	1703	968	1003
p-Bromo	307 (24,000)	1626	1703	970	997
p-*iso*-Propyl	298 (25,800)	1625	1701	958	993
p-Dimethylamino	401	1588	1664	869	976
p-Diethylamino	404	1590	1664	863	964

* Strongest band. ** Carbonyl frequency. *** Formyl proton at 100 MHz (TMS as reference)

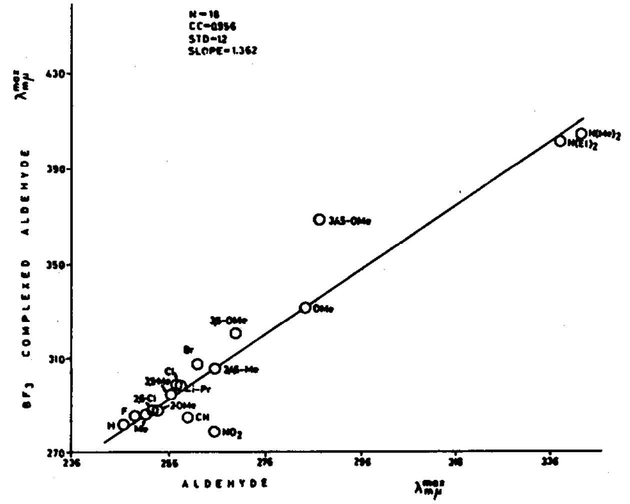


FIGURE 1: The correlation of λ_{max} of the strong band of the free aldehydes vs. λ_{max} of the strong band of the complexed aldehydes for 17 benzaldehydes and complexes. Each circle represents one benzaldehyde and its complex. The unmarked circles refer to the <u>para</u>-substituted derivatives while those which are numbered represent the positions of the substituents. Only <u>para</u>-cyano, <u>para</u>-nitro and 3.4.5-trimethoxy substituted compounds are not on the line.

Finally, the ir absorption[12] of the carbonyl group of the complexed aldehydes appears at 70-80 cm^{-1} in lower wavenumbers relative to the free aldehydes (Table). This effect is in line with the assumption of an enhanced polarity of the complexed carbonyl group as compared with the free aldehyde.

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