Boron Trifluoride Complexes. Part VII.[1] Ground-state Properties of Complexes of Aromatic Aldehydes

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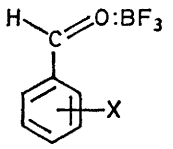
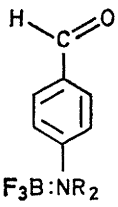
Aromatic aldehydes form stable σ–σ complexes with boron trifluoride. The i.r., ^1H n.m.r., ^{13}C n.m.r., ^{19}F n.m.r., and dynamic n.m.r. spectra of a series of such complexes establish the $CHO{:}BF_3$ group as a pseudo-substituent. Very good correlations were observed between the i.r. carbonyl frequencies and the ^1H n.m.r. chemical shifts of the formyl proton with the respective Brown σ^+ substituent constants emphasizing the dependence of these quantities on the charge density on the carbonyl carbon atom of the complexes. The positive charge densities in the formyl carbon atom of the BF_3 complexes were found to be significantly higher than in the respective free aldehydes.

AROMATIC aldehydes have been shown to form stable σ–σ 1 : 1 complexes (I) with boron trifluoride. Valuable information on their properties has been derived from correlations of the u.v. spectra of the complexes and of the corresponding free aldehydes.[2a] In order to shed light upon the ground-state properties of the complexes we have studied in detail their i.r. and n.m.r. spectra.[2b] The $CHO{:}BF_3$ pseudo-substituent proved to be a strong electron-withdrawing group with a substantial effect on the aromatic ring. On the other hand, the parent carbonyl group itself may serve as an internal probe for the study of the effect of complex formation. Our main interest was to study the nature of the formyl group in the complexes *vis à vis* the free aldehydes. We have paid special attention to the carbonyl absorption in the i.r., the chemical shifts of the formyl carbon, and hydrogen atoms, and the ^{13}C–H coupling constant. Furthermore we have studied the dynamic n.m.r. spectra † of these complexes as a probe for the π character of the C_{aryl}–C_{formyl} bond.



(I)



(II)

EXPERIMENTAL

The complexes were prepared either *in situ* or isolated as previously described.[2a] The i.r. spectra were recorded with a Perkin-Elmer 621 spectrometer for methylene chloride solutions in KBr cells. The cells are attacked by boron trifluoride and therefore had to be polished after each recording. The i.r. spectrum of each complex always contained the carbonyl bands of both the free and complexed aldehyde.‡ Our experimental method enabled us to trace the formation of the free aldehyde at the expense of the complex. The ^1H n.m.r. spectra were recorded on a Varian HA-100 spectrometer in methylene chloride or deuteriochloroform. The ^1H n.m.r. study was performed either (at low temperatures) below exchange temperatures or at the probe temperature, in the presence of an excess of BF_3 gas (in order to prevent exchange). The ^{13}C–H coupling constants of the free aldehydes were determined in highly concentrated solutions. These solutions were also used to determine the purity (>99%) of the aldehydes or the complexes. All ^1H spectra were recorded in the HA mode locked to Me_4Si or to CH_2Cl_2. Theoretical n.m.r. spectra were simulated with a LAOCN-3 program.[4] ^{13}C N.m.r. spectra were recorded on a Varian FT XL-100 spectrometer. Our data correlation matrix program was used and the correlations were carried out on the CDC-6400 computer at the computing centre of the Hebrew University.

RESULTS AND DISCUSSION

(A) *I.r. Spectra*.—The carbonyl bands of the free aldehydes correlate well with Brown's σ^+ constants,[5] as indicated in equation (1). With Hammett's σ constants

$$\nu_{C=O}^{\text{aldehyde}} = 19\sigma^+ + 1700{\cdot}6\ \text{cm}^{-1} \qquad (1)$$

(No. of points *n* 13; correlation coefficient *r* 0·965; standard deviation *s* 3·15 cm^{-1}; slope 19)

the correlation was poor (*r* 0·846). The fact that only σ^+ and not σ correlates well, indicates that there is a strong interaction between the formyl group and the electron-releasing substituents. This is the case in nucleophilic reactions. The i.r. carbonyl absorptions of the complexed aldehydes appear 69—81 cm^{-1} lower than those of the free aldehydes (Table 1). This shift is intermediate between those of the complexes of aliphatic and aromatic ketones.[6] The band intensities of the complexes are also larger which shows a larger conjugative effect.[7]

The correlation of the complexes' carbonyl absorption with Brown's σ^+ substituent constants is indicated in

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† For details of dynamic n.m.r. see G. Binsch, in 'Topics in Stereochemistry,' eds. E. L. Eliel and N. L. Allinger, vol. 3, 1967, Interscience, New York, p. 97 *et seq.*

‡ The i.r. absorption of the only complex described[3] was erroneously identified. The absorption reported resulted from the reaction of the cells with BF_3.

[1] Part VI, M. Rabinovitz, and A. Grinvald. *J.C.S. Perkin II*, 1973, 514.

[2] (*a*) M. Rabinovitz and A. Grinvald, *J. Amer. Chem. Soc.*, 1972, **94**, 2724; (*b*) for a detailed study of Lewis acid adducts see B. P. Susz and K. Weber, *Helv. Chim. Acta*, 1970, **53**, 2085.

[3] P. C. Myhre, C. D. Fisher, A. T. Nielsen, and W. M. Schubert, *J. Amer. Chem. Soc.*, 1965, **87**, 29.

[4] A. A. Brothner-By and S. M. Castelano, LAOCN 3, QCPE catalogue No. 111, Indiana University, 1971.

[5] H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, 1958, **80**, 4979.

[6] P. Chalandon and B. P. Susz, *Helv. Chim. Acta*, 1958, **41**, 697.

[7] L. J. Bellamy, *J. Chem. Soc.*, 1955, 4221.

equation (2) (see Figure 1). In this case, as a result of

$$\nu_{C=O}^{\text{complex}} = 20{\cdot}6\sigma^{+} + 1625{\cdot}7\ \text{cm}^{-1} \qquad (2)$$

(n 12; r 0·983; s 2·6 cm^{-1}; slope 20·6)

complex formation and a higher electron demand the substituents correlate with σ^{+} even better than in the case of free aldehydes. Here again, the correlation with Hammett's σ constants is poor (r 0·892). The slopes of the regression lines of both equations (1) and (2) are very close (19·0 and 20·6) and the $\Delta\nu_{C=O}$ values are almost constant (in nine cases the value is 75 ± 1 cm^{-1}) and thus are not influenced by the substituent (Table 1). We conclude that when a very strong electron-withdrawing group (CHO⁚BF$_3$) is present its effect is predominant and the substituent effect on $\Delta\nu$ (carbonyl stretching frequency) becomes secondary. The shifts of the *ortho*-substituents are greater than expected. We attribute this fact to the contraction of the formyl group as a result of complex formation which releases some of the steric strain. A similar effect has also been observed in the u.v. spectrum.[2a]

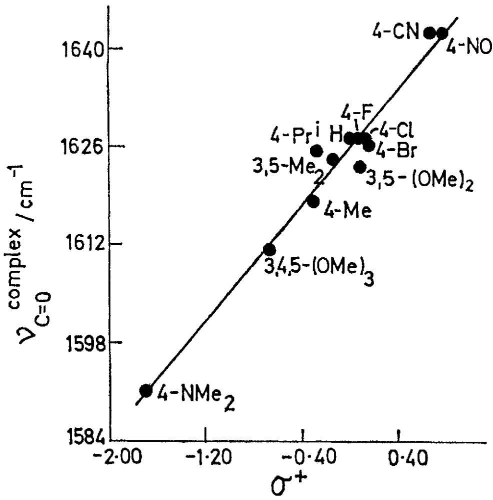

FIGURE 1 A computed best-fit line of the correlation of the stretching frequency of the complexed carbonyl group with Brown σ^{+} substituent constants for 12 BF$_3$ complexes of benzaldehydes (r 0·983; s 2·6 cm^{-1}; slope 20·6)

TABLE 1

I.r. frequencies (ν/cm^{-1}) of aromatic aldehydes and their BF$_3$ complexes

No.	Substituent	$\nu_{C=O}$[a]	$\nu_{C=O}$[b]	$\Delta\nu_{C=O}$	$\nu_{C=O}$[a]	$\nu_{C=C}$[b]	$\Delta\nu_{C=C}$	ν_{C-CHO}[b,c]
1	4-NO$_2$	1642	1711	−69	1601	1606	5	810 849
2	4-CN	1642	1711	−69	1608	1608	0	827
3	4-Cl	1627	1703·5	−76·5	1586	1596	10	833
4	4-F	1627	1702	−75	1586	1597·5	11·5	832
5	4-H	1627	1703	−76	1584	1597	13	826
6	4-Br	1626	1703	−77	1586	1591	5	833 830
7	4-Pr^i	1625	1702	−77	1598	1608	10	841 862
8	4-Me	1618	1694	−76	1594	1601	7	833 853
9	4-OMe	1596	1683	−87	1589	1599	10	832
10	4-NMe$_2$	1591	1664	−73		1593		832
11	4-NEt$_2$	1590	1664	−74		1594		838
12	3,5-Me	1624	1698	−74	1593	1610	17	855
13	3,5-(OMe)$_2$	1623	1703	−78	1593	1607	15	831 848
14	3,4,5-(OMe)$_3$	1611	1693	−82	1573	1586	13	832
15	2,6-Cl$_2$	1631	1712	−81	1578	1578	0	844 857
16	2-OMe	1610	1690	−80	1598	1601	3	834
17	2,4,6-Me$_3$	1596	1682	−84		1608		854
18	4-F$_3$B⁚NMe$_2$		1712·5	+48·5		1605		
19	4-F$_3$B⁚NEt$_2$		1713	+49		1606		

[a] Boron trifluoride complex [b] Free aromatic aldehyde. [c] Hydrogen deformation.

We have already seen[8] that aromatic aldehydes bearing two basic groups, *e.g.* *p*-dialkylaminobenzaldehyde, also form, besides the carbonyl complex, another 1 : 1 complex in which the boron trifluoride is linked to the nitrogen. These compounds bearing the F$_3$B⁚NR$_2$ linkage, *e.g.* (II), represent pseudo-substituted benzene rings. In the case of (II) the carbonyl group should absorb nearly in the same wavelength as *p*-nitrobenzaldehyde, a benzaldehyde bearing a strong electron-withdrawing group. In fact the absorptions are 1712·5 cm^{-1} for (II; R = Me) and 1713 cm^{-1} for (II; R = Et), while *p*-nitrobenzaldehyde absorbs at 1711 cm^{-1}.

When the i.r. spectra of the precipitated 1 : 1 complexes of BF$_3$ and *p*-dimethylaminobenzaldehyde were measured in Nujol, the only observable spectrum was that of the carbonyl complex (I; X = *p*-NMe$_2$). It is only in solution that these two complexes equilibrate.[8] After addition of ethanol both complexes can be observed. From Table 1 it can also be seen that the C=C ring absorptions in the BF$_3$–nitrogen linked complex (II) are almost identical with those of *p*-nitro- and -cyanobenzaldehyde. In the oxygen–BF$_3$ linked complexes

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[8] M. Rabinovitz and A. Grinvald, *Tetrahedron Letters*, 1971, 4325.

(I), the C=C frequency is lower than in the corresponding free aldehydes. This means that the bond orders in the ring weaken and the aromatic ring donates charge to the complexed formyl group. The i.r. spectra of various Lewis acid complexes of other carbonyl compounds were previously studied by Susz.[2b]

TABLE 2

N.m.r. data * for the formyl proton in free and complexed aldehydes

No.	Substituent	δ_F [a,b]	δ_F [b,c]	$\Delta\delta$ [b]	$J_{C^{13}-H}$ [a]	$J_{C^{13}-H}$ [c]	$\Delta J_{C^{13}-H}$
1	4-NEt_2	863·7	964·4	100·7	177·0	167·5	9·5
2	4-NMe_2	872·6	969·3	96·7	177·0	168·1	8·9
3	4-OMe	930·5	982·1	52·4	180·7	172·3	8·4
4	3,4,5-$(OMe)_3$	934·7	983·8	49·1	181·2	174·4	6·8
5	4-Me	955·7	987·3	36·4	182·0	173·1	8·9
6	3,5-Me_2	956·2	989·9	33·7	181·9	172·9	9·0
7	3,5-$(OMe)_2$	956·9	988·5	31·6	183·6	175·5	8·1
8	i Pr	957·8	993·4	35·6	181·9	173	8·9
9	4-F	966·1	997·3	31·2	184·1	175·1	9·0
10	4-Cl	968·1	998·6	30·5	183·2	175·9	7·3
11	4-Br	970·3	997·1	26·8	183·0	175·7	7·3
12	4-H	970·5	998·4	27·9	183·2	174·2	9·0
13	4-CN	992·2	1011·4	19·2	184·0	178·9	5·1
14	4-NO_2	999·9	1017·8	17·9	185·5	179·3	6·2
15	2,4,6-Me_3	981·5	1046·9	65·4	176·6	171·4	5·2
16	2-OMe	994·9	1038·3	43·4	185·8	180·3	5·5
17	2,6-Cl	1022·2	1048·5	26·3	189·5	187·7	1·8
18	4-$F_3B\!:\!NMe_2$		1007·8	−38·5			
19	4-$F_3B\!:\!NEt_2$		1010·8	−46·4			

* In Hz from internal Me_4Si; δ_F = C*H*O chemical shift.

[a] Complex. [b] Below exchange temperature (low temperature −60 to −95°). [c] Free aldehyde.

(B) *N.m.r. Spectra.*—A variety of factors may influence the chemical shift of the formyl hydrogen of the aromatic aldehydes. The electron-withdrawing carbonyl oxygen atom polarizes the C–H bond of the formyl group and thus should shift the absorption to low field. The same shift is also expected as a result of the anisotropies of the aromatic ring and the carbonyl group. The aromatic ring itself should shift the absorption to high field and this effect is linked directly to the properties and location of the ring substituents. We have already shown that the substituent constant σ^+ correlates very well with the i.r. carbonyl absorptions. If this holds also for the correlation with the formyl proton chemical shift then the substituents would be expected to influence both the anisotropy of the carbonyl group and the polarization of the C–H bond. In the free aldehydes, the formyl protons correlate with σ and σ^+ constants but the correlation with the latter is better [equations (3) and (4)]. The better correlation with

$$\delta_{formyl}{}^{aldehyde} = 29{\cdot}95\sigma + 993{\cdot}9\ \mathrm{Hz} \qquad (3)$$
$$(n\ 10;\ r\ 0{\cdot}960;\ s\ 3{\cdot}87\ \mathrm{Hz};\ \mathrm{slope}\ 23{\cdot}9)$$

$$\delta_{formyl}{}^{aldehyde} = 18{\cdot}02\sigma^+ + 999{\cdot}9\ \mathrm{Hz} \qquad (4)$$
$$(n\ 10;\ r\ 0{\cdot}979;\ s\ 2{\cdot}81\ \mathrm{Hz};\ \mathrm{slope}\ 18{\cdot}02)$$

σ^+ [equation (4)] shows that the influence of the charge of the carbonyl carbon is in the same direction as the anisotropic effect.

Complex formation causes a shift of the formyl proton to high field (Table 2). All the factors already mentioned should also exist in the complexes. From the i.r. spectra we concluded that the effect of complex formation is nearly the same for all *meta*- and *para*-substituted benzaldehydes, except *para*-nitro and *para*-cyano. Figure 2 shows a plot of the chemical shift of the formyl proton against the σ^+ constants in the free and complexed aldehydes. The slopes of the curves also indicate that the chemical shift of the formyl proton of the complexed aldehydes is more sensitive to substituent effects than the corresponding free aldehydes. Equation (5) shows the connection between Brown's σ^+ constants and the chemical shift of the formyl protons of the complexes. Here again the complexes correlate

$$\delta_{formyl}{}^{complex} = 48{\cdot}1\sigma^+ + 963{\cdot}9\ \mathrm{Hz} \qquad (5)$$
$$(n\ 13;\ r\ 0{\cdot}987;\ s\ 6{\cdot}35\ \mathrm{Hz};\ \mathrm{slope}\ 48{\cdot}1)$$

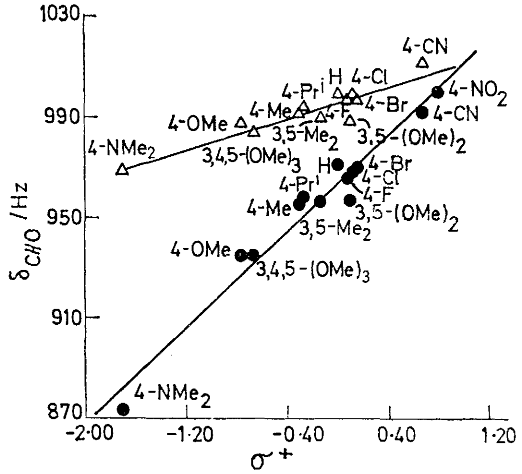

FIGURE 2 Computed best-fit lines of the correlation of the formyl proton chemical shifts of free (Δ; *n* 12; *r* 0·934; *s* 3·8 Hz; slope 15·8) and BF_3 complexed (●; *n* 13, *r* 0·981; *s* 6·35 Hz, slope 48·1) benzaldehydes with Brown σ^+ substituent constants

better with σ^+ than the free aldehydes. However, the correlation with σ in the case of the complexes is lower than in the case of the free aldehydes (r 0·865). These results emphasize the strong relationship between the charge on the carbonyl carbon and the chemical shifts of the formyl proton of the free and even more so of the complexed aldehydes.

The value of the carbon–proton coupling constant shows the expected additivity relationship with the substituent.[9] The value of ^{13}C–H coupling constant increases with the increase in the electronegativity of the substituents.[10] Table 2 shows that the ^{13}C–H coupling constants of the complexes are 6—9·5 Hz larger than those of the free aldehydes. In the free aldehydes the s character of the C–H bond is 33·5—35·7%, while in the complexes it is 35—37%. The analysis of the experimental results shows that there is a good correlation between $J_{^{13}\text{C-H}}$ and the chemical shift of the formyl proton as well as with the σ and σ^+ [equation (6)] constants. It is noteworthy that unlike the

$$J_{^{13}\text{C-H}}{}^{\text{complex}} = 3{\cdot}17\sigma^+ + 182{\cdot}9 \text{ Hz} \qquad (6)$$

(n 13; r 0·969; s 0·53 Hz; slope 3·5)

complexes, the $J_{^{13}\text{C-H}}$ values of the free aldehydes correlate better with Hammett's σ than with Brown's σ^+ constants. However, the good correlation of σ^+ of both free and complexed aldehydes with the chemical shifts of the formyl proton (Figure 3) shows that the magnitude of the anisotropic effect is constant in the aldehydes and complexes and that it is mainly the charge on the carbonyl carbon atom that causes the shifts of the formyl proton.

Table 2 also shows unexpected high values for $J_{^{13}\text{C-H}}$ of *o*-methoxybenzaldehyde and 2,6-dichlorobenzaldehyde. However, the corresponding values of their complexes are in line with those of all other complexes. This fact as reflected in their $\Delta J_{^{13}\text{C-H}}$ values can be explained in terms of a ' release ' of steric hindrance in the corresponding complexes due to 'compression' compared with the sterically hindered free aldehydes.

In the theoretical spectra of the BF_3 complex of benzaldehyde[4] the chemical shift of the *para*-hydrogen is at 802·9 Hz while in the free aldehyde this hydrogen absorbs 50 Hz to higher field. The withdrawal of charge from the ring by the pseudo-substituent is also demonstrated by the low field shift of the other complexes, *e.g.*, *p*-methoxybenzaldehyde complex: *ortho*-protons $\Delta\delta$ 37 *meta*-protons $\Delta\delta$ 14; *p*-diethylaminobenzaldehyde complex: *ortho*-protons $\Delta\delta$ 13 *meta*-protons $\Delta\delta$ 10; 3,5-dimethoxybenzaldehyde complex: *ortho*-protons $\Delta\delta$ 27·5 *para*-protons $\Delta\delta$ 30·8; 3,4,5-trimethoxybenzaldehyde complex: *ortho*-protons $\Delta\delta$ 28·6; *para*-nitrobenzaldehyde: $\Delta\delta$ 40 Hz for *ortho*-protons. These results lead to the conclusion that the $CHO{:}BF_3$ group should be considered as more strongly electron withdrawing than the nitro-group.

The nature of the $CHO{:}BF_3$ group is also reflected in the dynamic n.m.r. spectra of the complexes as compared with those of the free aldehydes. The expected higher barriers to rotation about the C_{aryl}–C_{formyl} bond due to a partial π character of this bond were evaluated by this technique. The heights of the barriers were found to be substituent dependent and significantly higher than those of the free aldehydes.[11] *p*-Dimethylaminobenzaldehyde, *p*-anisaldehyde, 3,4,5-trimethoxybenzaldehyde, *p*-tolualdehyde, and 3,5-dimethylbenzaldehyde complexes showed ΔG^* values of 16·0, 14·2, 12·8, 11·2, and 10·8 kcal mol^{-1} respectively. In the BF_3 complex of 2,4,6-trimethylbenzaldehyde two methyl signals appear at δ 2·48 and 2·73 (probe temperature; integration ratio 1 : 2 respectively). At —90° three methyl signals appeared at δ 2·48, 2·71, and 2·75 (integration 1 : 1 : 1) showing that the two methyl groups at positions 2 and 6 are non-equivalent. This is because of the slow rotation (on the n.m.r. time scale) about the C_{aryl}–C_{formyl} bond.

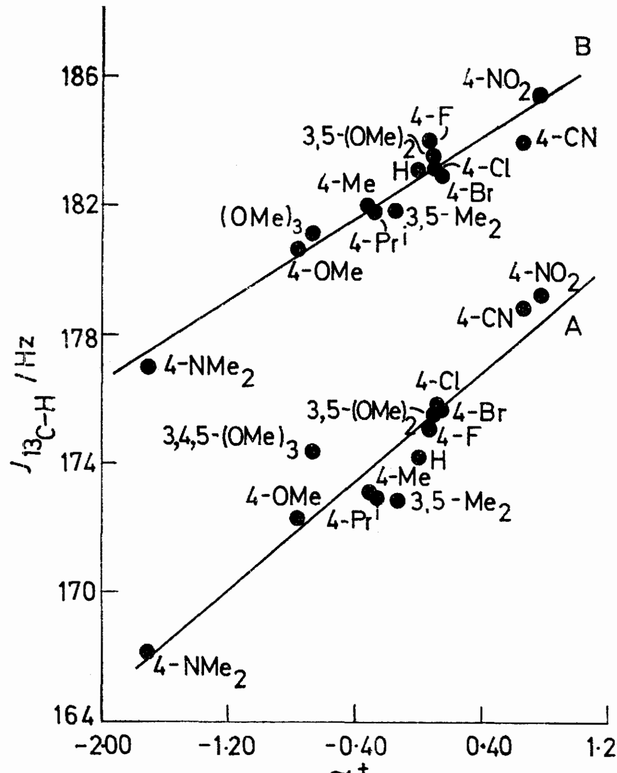

FIGURE 3 Computed best-fit lines of the correlation of carbon-hydrogen coupling constants of the formyl proton of A, free (n 13; r 0·940; s 1·02 Hz; slope 4·24) and B, BF_3 complexed (n 13; r 0·969; s 0·5 Hz; slope 3·1) benzaldehydes with Brown σ^+ substituent constants

^{13}C and ^{19}F n.m.r. substantiate our conclusions on

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[9] N. Muller and D. E. Pritchard, *J. Chem. Phys.*, 1959, **31**, 768, 1471.

[10] (*a*) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, 'High Resolution NMR Spectroscopy,' Pergamon Press, 1966, p. 1019; (*b*) E. R. Malinowski, L. Z. Pollara, and J. P. Larmann, *J. Amer. Chem. Soc.*, 1962, **84**, 2649; (*c*) N. Muller, *J. Chem. Phys.*, 1962, **36**, 359.

[11] A. Grinvald and M. Rabinovitz, *Chem. Comm.*, 1969, 642.

the nature of the CHO:BF$_3$ group. *p*-Fluoronitrobenzene and *p*-fluorobenzaldehyde show ^{19}F resonances at 9·99 and 9·42 p.p.m., respectively (CH$_2$Cl$_2$; relative to fluorobenzene) and the *p*-fluorobenzaldehyde–BF$_3$ complex absorbs at 22·93 p.p.m. (acetone; relative to fluorobenzene) (for comparison *p*-fluoro-αββ-tricyanovinylbenzene with its highly electron-withdrawing group absorbs at 12·10 p.p.m.[12]) thus showing that CHO:BF$_3$ is a stronger electron-withdrawing group than the nitro group. Finally, ^{13}C n.m.r. measurements strengthen our conclusion that the positive charge density at the formyl carbon atom of the BF$_3$ complex is higher than in the respective free aldehyde. In the free benzaldehyde the ^{13}C resonance of the formyl group appears at 191·8 p.p.m. but at 199·8 p.p.m. in the complex (CH$_2$Cl$_2$; relative to Me$_4$Si).

We thank Varian AG, Zug, Switzerland, for Fourier transform ^{13}C n.m.r. spectra. The Central Research Fund of the Hebrew University of Jerusalem is thanked for financial support.

[3/417 *Received, 22nd February,* 1973]

[12] W. A. Sheppard and R. M. Henderson, *J. Amer. Chem. Soc.*, 1967, **89**, 4446.