

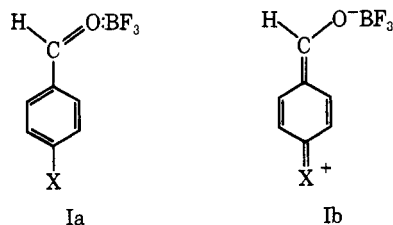
Boron Trifluoride Complexes of Aromatic Aldehydes. V. The CHO:BF₃ Pseudosubstituent¹

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Abstract: Boron trifluoride forms solid, stable 1:1 σ - σ complexes with aromatic aldehydes. The CHO:BF₃ pseudosubstituent proved to be an extremely strong electron-withdrawing group. The ir, uv, and nmr spectra of 17 such complexes were correlated with a new data matrix technique and compared with NO₂, CHO, and CHOH⁺ benzene derivatives.

In 1878 Landolf reported the formation of solid complexes when aromatic aldehydes are treated with boron trifluoride.² Almost 80 years later, Lombard and Stephan prepared a series of such complexes in an analogous manner and studied their thermal behavior.³ No attempt has been made to characterize these complexes and no structure was suggested. In 1965, Mhyre and coworkers isolated a stable complex of boron trifluoride and mesitaldehyde and studied its ir and uv spectra.⁴ The scarcity of information regarding these interesting complexes prompted us to start a detailed study of these compounds with a view to establishing their structure and ground- and excited-state properties. We thought that if these complexes would prove to be of a 1:1 composition, aldehyde:BF₃ and the boron trifluoride directly linked to the aldehyde function, the resulting group CHO:BF₃ might be considered as a pseudosubstituent, e.g., Ia. The formyl (CHO) substituent by itself is a strong electron-withdrawing group, and we expected that the CHO:BF₃ group would be a much stronger electron-withdrawing group. Such a pseudosubstituent would stabilize resonance forms favoring a high carbon-carbon π -bond character in the ground state, e.g., Ib. The first indication to this effect came from the nmr studies which demonstrated the relatively high barrier to rotation about the C_{aryl}-C_{formyl} bond.⁵ We



report the ground- and excited-state properties and the nature of bonding of these complexes and their relation to the parent free benzaldehydes.

This Study. We have prepared 17 complexes of substituted aromatic aldehydes and boron trifluoride and determined their ultraviolet, infrared, and nmr spectra. The absorption bands and extinction coefficients were

correlated with the respective properties of the free aldehydes, the protonated aldehydes (bearing the pseudosubstituent CHOH⁺), and the analogous nitrobenzene derivatives. The energy differences between the ground- and excited-state levels of the complexes, their electron-withdrawing properties, and the nature of complexation have been determined. The large volume of data accumulated in the present study prompted us to develop a new method for its rapid evaluation and for the correlation of our experimental results with other data taken from the literature (the data matrix); *vide supra*.

Experimental Section

Table I shows the uv spectral data of the 17 complexes and Table II shows some ground-state properties of these complexes in methylene chloride solution. The complexes are sensitive to humidity, and they have to be prepared and maintained under strict anhydrous conditions. All complexes except those derived from *p*-nitrobenzaldehyde and *p*-cyanobenzaldehyde can be prepared in a carbon tetrachloride solution of the aldehyde, by addition of boron trifluoride etherate. All these complexes are precipitated by the addition of boron trifluoride gas to the free aldehyde in carbon tetrachloride solution at room temperature. Regular crystals are obtained from methylene chloride solutions saturated with the complexes. The complexes can be preserved for long periods of time. Some of them, especially those bearing an electron-donating substituent, could be kept as solids for over 1 year in sealed ampoules. The only unstable complexes are the ones with an electron-withdrawing substituent. Some of the more stable complexes can be sublimed. Elementary analyses of the complexes were within experimental error and all complexes gave the ratio BF₃/aldehyde = 1. Nmr spectra were recorded at high settings of amplitude, and the purity of the complexes at low temperatures (lower than their exchange temperatures) was shown to be >99%, and no free aldehyde could be detected. We assume, therefore, that these are stable 1:1 boron trifluoride-aromatic aldehyde complexes. The spectra of both the isolated complexes and of the complexes prepared *in situ* (i.e., by passing gaseous boron trifluoride through the solution) are identical, although in the latter there is an excess of boron trifluoride.

The aromatic aldehydes were distilled twice *in vacuo* immediately before use. Methylene chloride of analytical grade was washed with concentrated sulfuric acid, distilled into a flask containing calcium hydride from which it was redistilled, and preserved with magnesium perchlorate (Anhydron). The uv spectra were determined in 1-cm pathway cells with the aid of a Unicam SP-800 spectrophotometer. The extinction coefficients of the free aldehydes were determined at two or more concentrations, and the difference between the two determinations was no greater than $\pm 2\%$. The extinction of the solution was determined before and after passage of gaseous boron trifluoride through the solution. Subsequently, a third measurement was obtained, by the addition of 1 drop of dilute ethanol, giving a spectrum which superimposed the original aldehyde. Solutions of the precipitated complex always showed the superimposed spectra of both the complex and the aldehyde. Therefore, dilutions were made in methylene chloride saturated with

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Table I. Spectral Data of Benzaldehydes and Their Boron Trifluoride Complexes

Substituent	B band				C band				A band		Transition energy difference, ΔE_T^B ΔE_T^C	
	λ_{\max} , nm ^a Complex	λ_{\max} , nm ^a Aldehyde	ϵ Complex ^c	ϵ Aldehyde ^d	λ_{\max} , nm ^b Complex	λ_{\max} , nm ^b Aldehyde	ϵ Complex ^e	ϵ Aldehyde	λ_{\max} Complex	ϵ Complex ^e		
1. 4-H	281.6	246.5	18,800	12,800	330 ^s	282 ~290 ^s	1330	1240			14.5	14.8
2. 4-OCH ₃	331.0	284.5 276.0 ^f	34,900	17,000 18,200 ^f		294 ^s			235 241 ^s	9,100	14.1	17.1
3. 4-CH(CH ₃) ₂	298.0	258.4 ^g	25,800	17,500		~291 ^s					14.7	
4. 4-CH ₃	285.7	251.2 ^g	18,300	12,400	339	295	3150	1850			13.7	12.6
5. 4-F	285.3	249.0	16,900	12,600		283 ^s 274 ^s ^f		800			14.6	
6. 4-Cl	298.5	257.8	23,600	18,100		290 ^s 281 ^s ^f		1300			15.1	
7. 4-Br	307.0	262.0	24,000	19,300		291 ^s 282 ^s ^f		~1700			16.0	
8. 4-CN	284.5	251.5 260.0 ^f	31,100	22,900 21,100 ^f	325 ^s	291 ^s 299 ^s ^f	~1600	1900 1700 ^f			13.3 9.5	11.3 8.5
9. 4-NO ₂	278.4	265	21,600	15,500	320 ^s	304	~3000	2450			5.0	7.4
10. 4-N(CH ₃) ₂	401 \pm 1 389 \pm 1 ^f	338.5 ^h		32,800					~265	<i>i</i>	13.2 10.8	
11. 4-N(C ₂ H ₅) ₂	404 \pm 1 ^f 392 \pm 1 ^f	343 ⁱ		35,500					268	<i>i</i>	12.6 10.4	
12. 3,5-CH ₃	294.5	256.4	18,400	12,300	342	299	1960	1670			14.4	12.0
13. 3,5-OCH ₃	320.0	269.9	10,800	7,600	391	325.5	2290	2750	237	17,500	16.6	14.7
14. 3,4,5-OCH ₃	368 \pm 1	287.5	17,600	12,100		~317 ^s			234	16,300	21.8	
15. 2,6-Cl	287.5 ^k	252.6 ^k	11,200	6,900	362	306	2940	1810			13.7	14.3
16. 2-OCH ₃	287.5	253.6	15,200	10,500	380	319	6020	4950			13.3	14.3
17. 2,4,6-CH ₃	305.4	265.7	24,800	14,400	347	299	3860	2160			14.0	13.2

^a ± 0.2 nm. ^b ± 1 nm. Superscript s denotes shoulder. ^c $\pm 5\%$. ^d $\pm 2\%$. ^e $\pm 10\%$. ^f Doublet. ^g Nonsymmetrical unresolved doublet. ^h Nonsymmetrical peak probably due to an absorption at 305 nm. ⁱ $\epsilon < 2500$. ^j Nonsymmetrical probably due to an absorption at 310 nm. ^k Nonsymmetrical toward higher wavelengths.

Table II. Ground-State Properties of Benzaldehydes and Their BF₃ Complexes

Substituent	Ir			Nmr				Ionization potential of aldehyde ^a
	$\nu_{C=O}$, cm ⁻¹ Aldehyde	$\nu_{C=O}$, cm ⁻¹ Complex	$\Delta\nu$, cm ⁻¹	δ , cps Aldehyde	δ , cps Complex	$\Delta\delta$, cps	J_{13C-H} , cps	
1. 4-NO ₂	1712	1642	70	1017.8	999.9	17.6	179.3	10.27
2. 4-CN	1711	1642	69	1011.4	992.2	19.2	178.9	
3. 2,6-Cl	1711	1631	80	1048.3	1022.2	26.1	187.7	
4. 3,5-OMe	1703.5	1622	81.5	988.5	956.9	31.6	175.5	
5. 4-Cl	1703.5	1627	76.5	1003.1	968.1	35	175.9	9.61
6. 4-Br	1703	1626	77	997.1	970.3	26.5	175.7	
7. 4-H	1703	1626	77	998.4	970.5	27.9	174.2	9.73
8. 4-F	1702	1627	75	997.3	966.1	31.2	175.1	
9. 4- <i>i</i> -Pr	1701.5	1625	76.5	993.4	957.8	35.6	173	
10. 3,5-Me	1698	1624	74	989.9	956.2	33.7	172.9	
11. 4-Me	1695	1619	76	992.1	955.7	36.4	173.1	9.33
12. 3,4,5-OMe	1692	1611	81	983.7	934.7	49.1	174.4	
13. 2-OMe	1690	1610	80	1038.3	994.9	43.4	180.3	
14. 4-OMe	1682	1598	84	987	934.6	52.4	172.3	8.60
15. 2,4,6-Me	1681	1596	85	1047	981.5	65.5	171.4	
16. 4-N(Me) ₂	1664	1588	76	976.9	869.7	107.2	168.1	8.25
17. 4-N(Et) ₂	1664	1590	74	964.4	863.7	100.6	167.5	

^a A. Foffani, S. Pignataro, B. Contone, and F. Grasso, *Z. Phys. Chem. (Frankfurt am Main)*, **42**, 221, 236 (1964).

boron trifluoride, and thus the spectra of the pure complexes were determined. The estimated error in these extinction coefficient measurements does not exceed $\pm 5\%$. The ir spectra were recorded with the aid of a Perkin-Elmer 621 spectrometer, in KBr cells in dry methylene chloride. The cells had to be polished after each measurement. Both the bands of the free and complexed aldehyde were obtained consistently. The only measurement described in the literature⁴ was erroneously assigned; it resulted in fact from the reaction of the cells and boron trifluoride. The nmr measurements were carried out on a Varian HA-100D spectrometer, at 94.077 and 100 MHz in dry methylene chloride.

The correlations were programmed with our Fortran IV program yovi. The input to this program consists of the data matrix; each row represents a different compound and each column represents a physical property derived from experiment (e.g., $\nu_{C=O}$, λ_{\max} , δ), from theoretical calculations (ground state, E_T (Hückel)), etc., or from the literature (ionization potentials, σ , σ^+ constants, etc.). Where necessary, logical transformations were made. There are three optional output modes. (a) Each pair of columns is correlated⁶ (according to standard equations) and the correlation

(6) H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953).

coefficient (CC), standard (STD) and specific deviations, as well as the slope and intercept are calculated and printed. (b) In the second mode the program automatically chooses the pairs of high correlation coefficients (*e.g.*, >0.96) and then the on-line Calcomp 656 plotter renders plots of the points and their best-fit line.⁷ (c) A printed graph is obtained from each possible pair in which each derivative is symbolized by a letter; thus a rapid visual impression of the character of each correlation is obtained (nonlinearity or deviation of a certain point from the line are sometimes meaningful). This program consumes a short computer time, and we feel that it can be of great help in rapid analysis of data and in isolating linearly dependent pairs. All calculations were performed on the CDC-6400 computer at the Computing Centre of the Hebrew University.

Results and Discussion

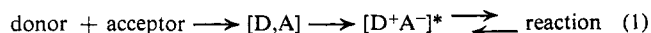
It is necessary to establish the nature of the boron trifluoride–aromatic aldehyde complexes (1:1) in order to be able to correlate the uv spectra of these compounds with the spectra of the free aldehydes or other benzenoid compounds.

In the uv absorption studies (Table I) we have used the band notation adopted by Moser and Kohlenberg.⁸ Appropriately substituted benzene derivatives should give rise to spectra in which displacement of all benzene bands occurs. Extensive studies of the correlation between the absorption and structure of benzene derivatives have been made by Doub and Vandenberg.⁹ The displaced benzene spectrum of substituted benzaldehydes has been demonstrated by Dreaden and Forbes,¹⁰ where they have shown that there are good correlations between the band displacement ($\Delta\lambda$) in substituted benzaldehydes, acetophenones, and nitrobenzenes. They have also demonstrated that the nitrobenzaldehydes should be considered as nitrobenzene rather than benzaldehyde derivatives.

We assume that the boron trifluoride acceptor is linked to the carbonyl oxygen donor. Other possible donors which were considered and excluded are (a) the aromatic moiety which because of its weak basicity has been shown to be an unlikely candidate,¹¹ and (b) basic substituents of the aromatic aldehydes such as a methoxy group which is known to form such complexes.¹² However, if this were true in our case, then it would be expected that such complexes should shift the wavelength of the absorption in the uv spectrum to shorter wavelengths (blue shifts).^{13,14} On the contrary, we find a marked red shift (Table I) for both the unsubstituted and substituted benzaldehyde complexes including those complexes bearing basic substituents. Furthermore, the nmr spectra of our complexes show the “normal” chemical shift attributed to the protons of methoxy and dialkylamino groups when they are attached to an aromatic ring. If boron trifluoride were linked to these groups, we would expect a considerable downfield shift. The nmr absorptions of the formyl protons of the BF_3 complexes (Table II) are shifted to higher field compared to those of the free aldehydes. This effect can be attributed

both to a change in the anisotropy of the carbonyl group and to the polarization of the carbon–hydrogen bond. Electron-releasing substituents (*e.g.*, methoxy, dialkylamino) shift the formyl proton to higher field compared with other substituents, both in the free and in the complexed aldehydes. The appearance of the ir complexed carbonyl absorption which appears at 70–80 cm^{-1} at lower wave numbers relative to the free aldehydes (Table II) proves that the boron trifluoride acceptor is linked to the carbonyl oxygen donor. These results are also in line with the enhanced polarity of the complexed carbonyl group as compared with the free aldehyde. Protonation of the carbonyl shows a red shift in the uv and a high-field shift in the nmr in an analogous manner to BF_3 complexation.^{15,16}

In the past, boron trifluoride complexes, *e.g.*, of aromatic esters, were described as charge-transfer complexes.¹⁷ If this were the case, we would expect the transition energy (E_T) of the complexes to correlate with the ionization potential of the free aldehydes; on the contrary, we find no such correlation. Secondly, if we were dealing with charge-transfer complexes, we would expect the boron trifluoride to be the acceptor even in the excited state and would anticipate a blue shift of the benzene bands, as well as new bands appearing in the visible region, according to the equation¹⁸



As mentioned previously, it is solely the red shift that we observed. Actually the above equation (1) which describes the charge transfer itself is inconsistent with the supposed VB formulation, according to which the complexes should have an additional negative charge on the carbonyl oxygen in the excited state. Kosower¹⁹ has shown a very good correlation between E_T values and Hammett constants in the case of charge-transfer complexes whose substituents are distant from the complexation site; we find at best a very poor correlation of E_T with σ , σ^+ , and σ_R constants.

On the basis of all the previous arguments, we now refer to the complexes of boron trifluoride and aromatic aldehydes as 1:1 stable σ – σ complexes in which the boron trifluoride is linked directly to the carbonyl oxygen.

Spectral Correlations

The correlation of the complex uv B-band absorption with that of the free aldehydes is shown in Figure 1. The line is a computed best-fit line, and the correlation, which is good (CC = 0.956), shows that the complexed aldehydes like the free aldehydes also manifest a displaced benzene spectrum. The correlation includes all the 17 aldehydes and complexes having substituents in the ortho, meta, and para positions which were prepared, and the correlation is presented in eq 2. If we exclude ortho- and meta-substituted

$$\lambda_{\text{max}}^{\text{complex}} = 1.36\lambda_{\text{max}}^{\text{aldehyde}} - 56.5 \text{ nm} \quad (2)$$

(CC = 0.956; STD = 12 nm)

- (7) C. Y. Ho, “Polyfit,” Share Program Library, SDA 3289.
 (8) C. M. Moser and A. I. Kohlenberg, *J. Chem. Soc.*, 804 (1951).
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 (17) M. Taillandier, J. Liquier, and E. Taillandier, *J. Mol. Struct.*, **2**, 437 (1968).
 (18) E. M. Kosower, “An Introduction to Physical Organic Chemistry,” Wiley, New York, N. Y., 1958, pp 179.
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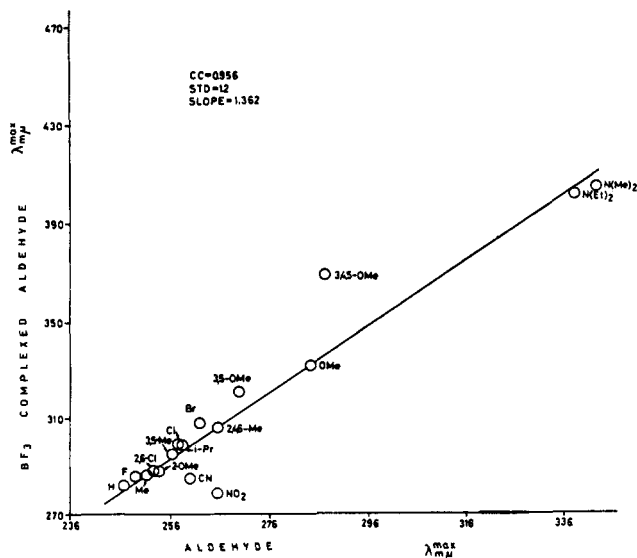


Figure 1. A computed best-fit line of the correlation of the complex uv B band with that of the free aldehydes for 17 benzaldehydes and their complexes. The numbers at the circles represent the position of the corresponding substituents; the unnumbered substituents represent para positions.

aldehydes and complexes, the correlation coefficient is even higher (0.979).

Since the nitro derivatives have a transition moment opposed to all other benzaldehydes,¹⁰ we obtain an even better correlation when we exclude *p*-nitrobenzaldehyde and its complex, as can be shown in eq 3.

$$\lambda_{\max}^{\text{complex}} = 1.29\lambda_{\max}^{\text{aldehyde}} - 38.0 \text{ nm} \quad (3)$$

(CC = 0.994; STD = 5.6 nm)

The slope of the line represented by eq 2 or 3 shows that by comparison to the free aldehydes, the sensitivity of the absorption to ortho and meta substituents is greater than to para substituents. It can also be seen that all ortho derivatives are on the line. It is clear that in the complexes, the ground state and the excited state are closer to each other. This can be rationalized either by a lowering of the excited level or a raising of the ground level or both (Table I). In those cases where the B-band displacement is appreciable, the C band appears only as a shoulder of the B band. This does not necessarily mean that the analogy to the benzene spectrum does not hold. There is a strong dependence of the planarity of the molecule on the appearance of the C band: the more planar the molecule, the weaker the band. The ratio λ_C/λ_B was not constant in our case either in the free or the complexed aldehyde. Forbes¹⁰ claims that an interplanar angle of 90° between the carbonyl and ring planes is the most probable for the transitions represented by the C band. We find that complex formation results in a smaller steric hindrance than that of the free aldehyde and that the energy barrier to rotation is higher in the complex. The C band is stronger in the mesitaldehyde complex than in the *p*-tolualdehyde or 3,5-dimethylbenzaldehyde complexes. The extinction coefficient ratio of the C band in the tolualdehyde complex to that of the free aldehyde is 1.7, while for the B band it is 1.47. The ratio of the C band in the mesitaldehyde complex to the free aldehyde is 1.80, and of the B band

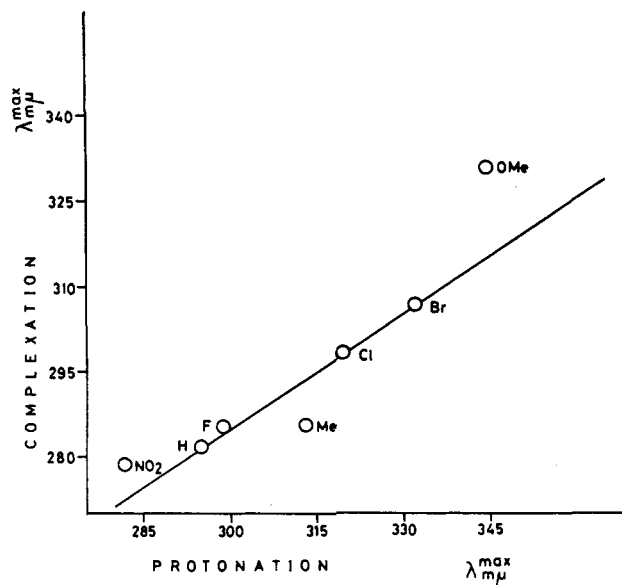


Figure 2. The absorption maxima (λ_{\max}) of para-substituted complexes vs. the λ_{\max} of the corresponding protonates. (The line is not a computed best-fit line.)

1.72. These results contradict Forbes' assumptions. In the infrared spectrum, the trend is as follows: in mesitaldehyde, the carbonyl absorbs at 1681 cm^{-1} ; in tolualdehyde, the carbonyl absorbs at 1695 cm^{-1} ; and the absorption of the complexes is at 1596 and 1619 cm^{-1} , respectively. Thus, the difference in absorption between the free aldehyde and the complex is not the same, implying that complexation of aldehydes plays an important role in lowering steric hindrance, a phenomenon to which we shall refer later. The Forbes theory of the origin of the C band is unacceptable also in the case of the *o*-methoxybenzaldehyde, since the intensity of the C band in the complex is smaller than the intensity of the same band of the free aldehyde.

We could not detect the $n \rightarrow \pi^*$ transition in the complexes, whereas in the free aldehydes this transition occurs at 320–330 nm, a region where the B band or the C band of the complexes appears. Moreover, this transition in the complex should be of a different nature since in the complex the character of the non-bonded electron is changed.

An analogous pseudosubstituent to $\text{CHO}:\text{BF}_3$ is the protonate, i.e., $\text{CHO}:\text{H}^+$. Protonation of benzaldehydes has been reported in the past.¹⁵ We attempted to correlate the B-band absorption of the complexes with that of the protonates. Figure 2 shows the plot of this absorption of the complexes vs. the B-band absorption of the protonates. The line is not a best-fit line; the low correlation coefficient may be rationalized by assuming that the strong interaction between the medium (H_2SO_4 , 98%) and the basic substituent of the benzaldehyde, e.g., nitro or methoxy, affects the absorption of the protonates. Comparison of the $\text{CHO}:\text{BF}_3$ pseudosubstituent with the strong electron-withdrawing nitro group led to the following conclusions. The uv spectra of substituted aromatic nitro compounds correlate well with both the free and the complexed benzaldehydes. The correlation of the B-band absorption is shown in eq 4 and 5.

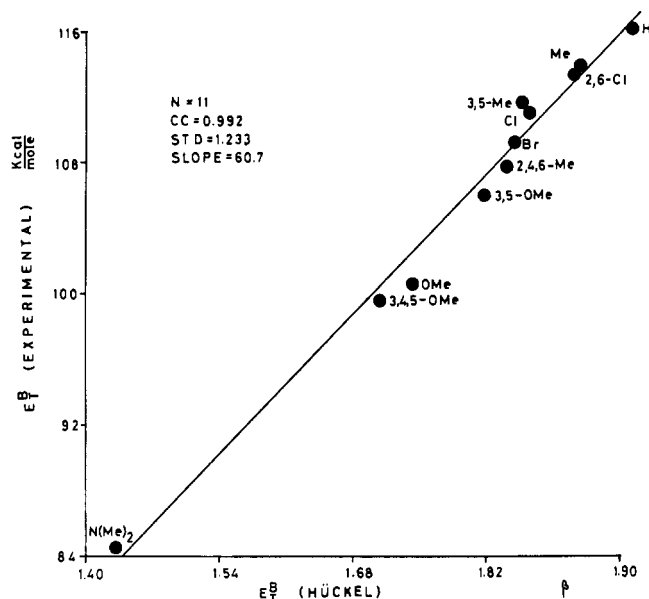


Figure 3. A computed best-fit line of the experimental transition energy to the second excited level (E_T^B) vs. the corresponding calculated transitions by the Hückel method. The numbers at the circles represent the positions of the corresponding substituents; unnumbered circles represent para positions.

$$\lambda_{\max}^{\text{NO}_2} = 1.1\lambda^{\text{complex}} - 54.3 \text{ nm} \quad (4)$$

$$(N = 10; \text{CC} = 0.994; \text{STD} = 6.1 \text{ nm}; \text{slope} = 1.1)$$

$$\lambda_{\max}^{\text{NO}_2} = 1.43\lambda^{\text{aldehyde}} - 97.0 \text{ nm} \quad (5)$$

$$(N = 10; \text{CC} = 0.990; \text{STD} = 8 \text{ nm}; \text{slope} = 1.43)$$

The slopes of the correlation lines show that the wavelength dependence on the substituent of the nitro compounds resembles that of the complexes (slope = 1.10); on the other hand, this slope is higher in the case of the free aldehydes (1.43). All the BF_3 complexes studied absorb at longer wavelengths than the corresponding nitro compounds. This red shift suggests that the pseudosubstituent $\text{CHO}:\text{BF}_3$ is a stronger electron-withdrawing substituent than the nitro group. Close inspection of Table I reveals that complex formation of the benzaldehydes results in an enhancement of the intensity of the B band. As the contribution of the dipolar structures in the ground state is greater in the complexes than in the corresponding free aldehydes, there arises the question as to whether this finding can be correlated with the above-mentioned enhancement of the band intensities. If complex formation of substituted benzaldehydes modifies only the electron-withdrawing properties of the formyl group, leaving all other factors that determine band intensity (transition probability) intact, it might be expected that the ratio $\gamma = \epsilon(\text{complex})/\epsilon(\text{aldehyde})$ would correlate with the electron-releasing properties of the substituent. The value of γ for benzaldehyde is 1.47; it is interesting to note (Table III) that the order of γ values in the halogen-substituted benzaldehydes is of the same order as expected for the electron-releasing properties of the substituents. This holds true also for the hyperconjugative effect of the alkyl-substituted benzaldehydes. It seems that when halogen and alkyl substituents are considered, this factor rather than the wavelength shift might determine the relative order of electron-releasing properties of these substituents. Table III

Table III. The Intensity Ratios (γ) of the Second Transition (B Band) between the BF_3 Complexed and Protonated Benzaldehydes and the Respective Free Benzaldehydes

Substituent on benzaldehyde	$\gamma = \epsilon(\text{complexed})/\epsilon(\text{non-complexed})^a$	$\gamma = \epsilon(\text{protonated})/\epsilon(\text{non-protonated})^b$	ΔE_T^B , kcal/mol, protonates
Benzaldehyde	1.47	1.92	19.1
<i>p</i> -Fluoro	1.35	1.77	19.2
<i>p</i> -Chloro	1.30	1.72	21.4
<i>p</i> -Bromo	1.25	1.49	23.2
<i>p</i> -Iodo		1.39	28.5
<i>p</i> -Methoxy	1.91	2.28	17.4
<i>p</i> -Methyl	1.47	1.95	22.5
2,4,6-Trimethyl	1.72	2.3	19.4
<i>p</i> -Nitro	1.39	1.3	6.3
<i>p</i> -Isopropyl	1.38		
3,4,5-Trimethoxy	1.46		
2,6-Dichloro	1.62		

^a In methylene chloride solutions. ^b The data of the protonated benzaldehydes in 98% H_2SO_4 are compared with free benzaldehydes in EtOH or 44% H_2SO_4 : K. Yates and R. Stewart, *Can. J. Chem.*, **37**, 664 (1959); A. Burawoy and A. R. Thompson, *J. Chem. Soc.*, 4314 (1956).

also gives the data taken from the literature^{15,20} of some substituted benzaldehyde protonates and their γ values. Here again the order of γ values for *p*-halogenobenzaldehydes shows that this factor is governed by the electron-releasing properties of the para substituents. Sterically hindered benzaldehydes show especially high γ values which might represent the diminution of the steric hindrance in the complex thus enhancing the conjugative effect mentioned previously.

Both complexes and protonates of benzaldehydes are perturbed systems that might shed light on the properties of the parent benzaldehydes. In order to have a better understanding of the benzaldehydes, we carried out a theoretical treatment of these systems. We wanted to find out the absolute values of the levels and the effect of the substituents on these values. The classical Hückel method²¹ and the $\omega\beta$ modification were employed for our calculations. These two semi-empirical methods²² gave an excellent correlation between experimental and theoretical transition energy values for the B band (E_T^B). The Hückel method is known to give such excellent correlations in some cases,^{23,24} especially when the parameters are carefully chosen.²⁵ The parameter set is taken from the literature.²⁶⁻²⁸ We carried out the calculations on 11 benzaldehydes. The regression obtained from the Hückel method is given by eq 6. The result obtained

$$E_T^B(\text{exptl}) = 60.7 \times$$

$$E_T^B(\text{Hückel } \beta \text{ units}) - 3.38 \text{ kcal/mol} \quad (6)$$

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Table IV. The Energies of the Highest Occupied Level and of the Second Excited Level (B) in a Series of Benzaldehydes

Substituent	Hückel, β units			$\omega\beta$, β units		
	E_T^B	Ground level	Second excited level	E_T^B	Ground level	Second excited level
Benzaldehyde	1.975	0.975	-1	1.958	0.967	-0.991
<i>p</i> -Methyl	1.920	0.920	-1	1.932	0.938	-0.995
<i>p</i> -Chloro	1.867	0.867	-1	1.904	0.892	-1.012
<i>p</i> -Bromo	1.851	0.851	-1	1.892	0.878	-1.014
<i>p</i> -Methoxy	1.744	0.744	-1	1.833	0.803	-1.030
<i>p</i> -Dimethylamino	1.431	0.431	-1	1.660	0.612	-1.047
2,6-Dichloro	1.914	0.836	-1.078	1.925	0.890	-1.035
2,4,6-Trimethyl	1.842	0.896	-0.946	1.885	0.922	-0.963
3,5-Dimethyl	1.859	0.913	-0.946	1.911	0.953	-0.958
3,5-Dimethoxy	1.819	0.685	-1.133	1.842	0.764	-1.077
3,4,5-Trimethoxy	1.710	0.577	-1.133	1.805	0.693	-1.112

($N = 11$; CC = 0.992; STD = 1.2 kcal/mol;
slope = 60.7)

from the $\omega\beta^{25}$ method after one iteration is represented by eq 7.

$$E_T^B(\text{exptl}) = 108 \times E_T^B(\text{in } \beta \text{ units}) - 95.14 \text{ kcal/mol} \quad (7)$$

($N = 11$; CC = 0.994; STD = 1.13 kcal/mol;
slope = 108)

Figure 3 shows the plot of experimental transition energy to the second excited level (E_T^B) vs. the corresponding calculated transition (by the Hückel method). Table IV shows the energy of the highest occupied level and of the second excited level.

The coefficients of the atomic orbitals of the second excited level show that in all cases they are almost identical and independent of the substituent (each equals ~ 0.5 for carbons 2, 3, 5, and 6 and zero for all other carbon atoms). This is a benzenoid transition and even a simplified approximation such as the Hückel method can predict the experimental values up to ± 2 nm over a region of 100 nm.

The slope of the regression line in Figure 3 is not incidental. The spectroscopic value of β is 60 kcal/mol and we get 60.7 kcal/mol. This is in agreement with the results of Wohl²⁹ and the classical results of Heilbronner and Murrel³⁰ for catacondensed hydrocarbons. Our system contains heteroatoms and yet shows an excellent agreement with these results.

The coefficients of the atomic orbitals in the first excited level show that all the atomic orbitals contribute to this molecular orbital (all C_i 's of the same order $\neq 0$). These calculations confirm that the substituents have an important role on the energy of the first excited level. This conclusion is in agreement with the classical works of Burawoy,¹⁵ Doub and Vandenbelt,⁹ and Forbes.³¹ No correlation was found between the transition energies of the first and third transitions and the theoretical results. This result is not surprising since the parameters for the heteroatoms were calculated from ground-state properties (e.g., electron affinities), and we can predict the excited-state levels

using these parameters, only if the excited state is independent of these parameters (which is the case of the B band).

The $\omega\beta^{25}$ method did not seem to be helpful for our system. The more iterations are processed the more the different aldehydes resemble one another. After one iteration the spectroscopic value of β obtained by this method was already 108 kcal/mol, and this value increased after further iterations. Apparently there is no justification for using the $\omega\beta$ method in molecules bearing heteroatoms, since the values of the parameters that have been chosen are drastically changed. The high correlation coefficient and the intercept³⁰ we get using the Hückel method demonstrate that in our case this classical method gives valuable information. According to the literature²² the intercept of the best-fit line in such calculations should be zero.

Finally, the electron-withdrawing character of the CHO:BF_3 pseudosubstituent was spectacularly revealed by the fluorine magnetic resonance spectrum of the *p*-fluorobenzaldehyde- BF_3 complex. It has been shown that intramolecular ^{19}F nmr shielding in the special case of para-substituted fluorobenzenes can be directly related to the π -electron charge density on the fluorine atom or its bonded carbon atom.³² Fluorine chemical shift is sensitive to the very small intramolecular perturbations in the fluorine atom π -charge density produced by a distant para substituent and this measurement has been shown by Taft³² to be the most sensitive probe available to investigate such interactions. The fluorine chemical shift of the *p*-fluoro derivatives substantiates the assumption that the CHO:BF_3 pseudosubstituent is an extremely strong electron-withdrawing group. The absorption of *p*-fluoronitrobenzene appears at 9.99 ppm and that of *p*-fluorobenzaldehyde at 9.42 ppm; the *p*-fluorobenzaldehyde complex absorbs at 20.93 ppm (CH_2Cl_2 relative to fluorobenzene). For comparison, *p*-fluoro- α,β,β -tricyanovinylbenzene with its highly strong electron-withdrawing group absorbs at 12.10 ppm (acetone relative to fluorobenzene). The value of the ^{19}F chemical shift of the BF_3 complex is of the order of the ^{19}F chemical shifts of *p*-fluoro-substituted carbonium ions.³³

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