The Nuclear Magnetic Resonance Spectra of Aromatic Aldehyde–Boron Trifluoride Complexes

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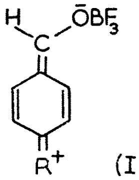
HIGH-RESOLUTION n.m.r. spectroscopy has been used in the estimation of the barriers to rotation about σ-bonds in systems in which this bond possesses some π-character.[1] Amides and related derivatives have received most attention,[2] but aromatic aldehydes were also investigated and estimates for the barriers to rotation have been presented.[3]

An increase of the energy barriers to rotation of protonated amides or boron trihalide–amide complexes over that for the free amides has been shown.[4] Benzaldehydes also form relatively stable 1 : 1 molecular complexes with boron trifluoride[5,6] and presumably the lone pair of the oxygen is involved in bonding to the boron halide.[6b] We have studied the effect of complex formation with BF_3 on n.m.r. spectra in a series of benzaldehydes, and the parameter E_a, for internal rotation about the C–C bond. Protonation and complex formation at the oxygen atom would stabilize



(I)

TABLE

Chemical shifts[a] of aromatic aldehyde–boron trifloride complexes

Aldehyde	Substituent protons	Aromatic protons	Formyl proton	Δδ Substituent[b]	Δδ Aromatic[c] hydrogens	Δδ Formyl[d] hydrogen	T_c[e]
Anisaldehyde	242	460[f]	573	− 8[g]	−12[f]	+23	−17°
Trimethoxybenzaldehyde ..	246[g] 234[h]	443	569	−12[g] − 2[h]	−13	+26	−28°
p-Tolualdehyde	149	470[f]	576	− 5[g]	−17[f]	+23	−41°
3,5-Dimethylbenzaldehyde ..	141[h]	466[i]	578	− 3[h]	−23[i]	+13	−47°

[a] In Hz. Varian 60 MHz. A-56/60 n.m.r. instrument. [b] Chemical shift difference of the substituent proton in the free aldehyde and in the complex. [c] Chemical-shift difference of aromatic proton in the free aldehyde and in the complex. [d] Chemical-shift difference of the formyl proton in the free aldehyde and in the complex. [e] Coalescence temperature ±5°. [f] A_2B_2 centre. [g] *para*-Substituent. [h] *meta*-Substituent. [i] *ortho*-Protons.

resonance forms favouring a higher π-bond character of the C–C bond [*cf.* (I)] as could be shown by the chemical shift of the formyl hydrogen in the aldehyde–boron trifluoride complex as compared with that of the free aldehyde (Table).

The Table shows that the chemical shifts of the *para*-substituent and the formyl proton in the free aldehydes compared with their complexes justifies the suggestion of the stabilization of the more polar structure in the complex. The difference of the chemical shift of the formyl proton in the aldehyde and complex is of the order of 20 Hz. It can be seen that the formyl hydrogen is most sensitive to polar interactions in the aldehyde molecule (either intra- or intermolecular).[7] The difference in chemical shifts of the *para*-substituent protons, when this substituent is a methyl or a methoxy-group, shows that the boron trifluoride does not form a complex with the methoxy-group. In boron trifluoride-complexed ethers, this difference should be of the order of 1 p.p.m.[8] The fact that the change in chemical shift of the *meta*-substituents is less pronounced than that of the *para*-substituents again shows that the dipolar structure plays a more important role in the complex and that this is facilitated by *para*-electron-releasing substituents. The same phenomenon was observed in the u.v. and i.r. spectra.[6b] The possibility of a complex between the aromatic moiety and boron trifluoride had been excluded.[9]

The temperature dependence of the n.m.r. spectra‡ can be demonstrated by the comparison of both 3,4,5-trimethoxybenzaldehyde and its boron trifluoride complex (Figure, b). In both compounds the two aromatic protons show a sharp singlet, while at low temperature the difference between them is striking. The free aldehyde aromatic protons show only broadening of the singlet at −70°, the aldehyde complex showing a classical AB spectrum at −40° (which is about 30° below coalescence temperature). The reported coalescence temperature (T_c) for anisaldehyde is −99°† (in vinyl chloride) which corresponds to ΔF^* of 9·2 kcal./mole, and T_c the complex (in methylene chloride) is −17°§ which corresponds to an approximate ΔF^* of 14·2 kcal./mole. This shows a higher π-bond character in the C–C bond of the complex compared with that of the free aldehyde. The ACBB′ spectrum which the anisaldehyde complex shows below T_c (Figure, a) is similar to that of *p*-methoxy-$\alpha\alpha'$-di-t-butylbenzyl alcohol at low temperatures.[10]

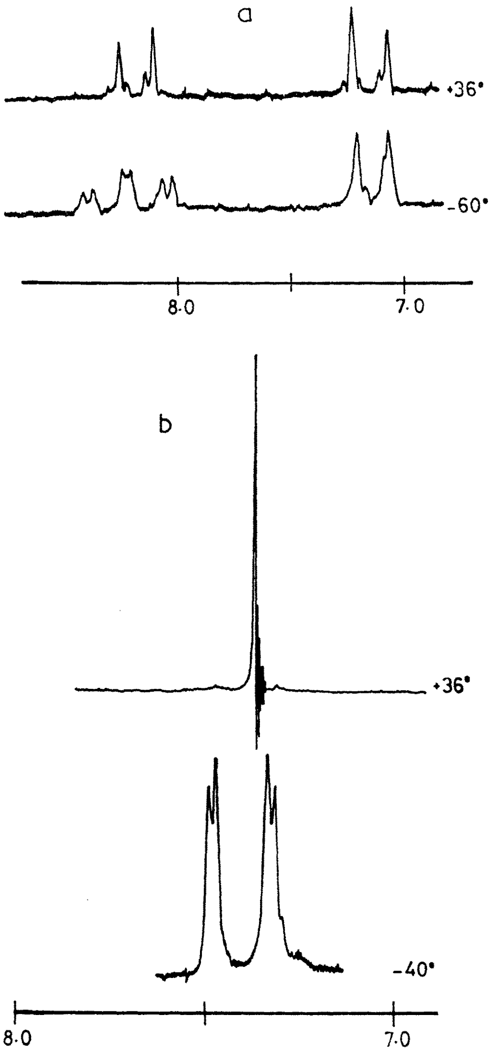


FIGURE. *Boron trifluoride complexes of anisaldehyde* (a)†,§ *and* 3,4,5-*trimethoxybenzaldehyde* (b)‡ *at room temperature and below coalescence temperature.*

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† (a) 60 MHz. Spectrometer.
‡ Varian 100 MHz. Spectrometer, HA-100 D.
§ 60 MHz. Spectrometer, Varian A-56/60.

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