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DONOR–ACCEPTOR COMPLEXES OF QUINOLINE N-OXIDES WITH BORON TRIFLUORIDE

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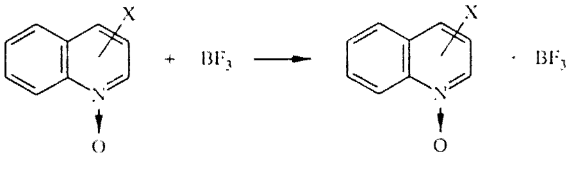
Molecular n – v complexes of quinoline N-oxides with BF_3 have been studied by electronic and IR spectroscopy. In most case the donor centre is the oxygen atom of the N-oxide group.

Aromatic N-oxides are known to be polydentate electron donors in reactions with various types of electron acceptors [1, 2]. The donor atom in these compounds may be the oxygen atom of the N-oxide group or the aromatic π-system. Moreover in N-oxides containing functional groups, other heteroatoms with unshared electron pairs may also be potential donor centers. In this connection it is interesting to study the nature of the complexes formed from the points of view of the structures of both the N-oxide and the acceptor. This is particularly true of polycyclic compounds in which the N-oxide is in direct resonance interaction with substituents which participate in intramolecular charge transfer.

The present work is a study of complexes of the quinoline and isoquinoline N-oxides IIa-h with a typical p-acceptor, boron trifluoride, which, according to literature data [3], effectively excludes the formation of complexes involving the π electrons of the aromatic system (Table 1).



I a–g

II a–g

It has been established that quinoline N-oxide forms complexes with p-acceptors exclusively via the oxygen atom [3]. It is necessary to elucidate which of the heteroatoms will form a bond with BF_3 in the case of substituted polycyclic N-oxides.

We have previously shown that electronic spectroscopy is a suitable method to study intramolecular charge transfer in a series of aromatic N-oxides [4]. We have now used this method to study intermolecular interactions in $CHCl_3$. This solvent was chosen because concurrent interaction between chloroform and BF_3 is not possible.

We distinguished two absorption regions for the N-oxides studied and their complexes with boron trifluoride in chloroform (1 and 2, Table 1). The first (a $\pi \rightarrow \pi^*$ transition, λ 250-300 nm) provided little information and is close to the cut off point for chloroform (245 nm). In the second region ($\lambda > 300$ nm) the absorption maximum, characteristic of quinoline N-oxides, is shifted to shorter wavelength in the spectra of complexes with boron trifluoride. This observation may be explained by coordination of the BF_3 molecule by the oxygen of the N-oxide group. Formation of the new O–B donor–acceptor bond disrupts the p,π conjugation with this oxygen atom which leads to a hypsochromic shift and a decrease in the extinction coefficient for the long wavelength absorption band. The small increase in ε for complex IIe is evidently caused by an increase in hyperconjugation of the methyl group. It was previously observed that the tendency for deprotonation of the methyl group in α-picoline was considerably increased in the presence of BF_3 [5].

In the case of isoquinoline N-oxide, which has a more complex electronic spectrum than quinoline N-oxide, formation of a complex with BF_3 led to changes for which the reasons are not obvious.

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TABLE 1. Electronic Spectra of Quinoline and Isoquinoline N-Oxides and Their Complexes with Boron Trifluoride in Chloroform

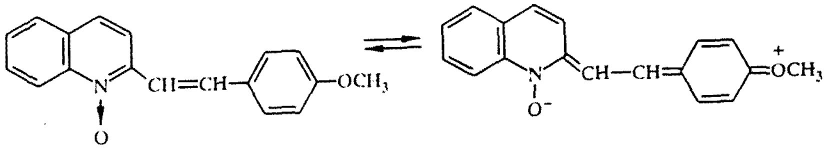
Compound	Substituent	N-oxide or BF_3 complex	λ_{max} (nm), lg ε	
			1	2
Ia	H	—	250 sh	325 sh (3,82), 335 (3,89), 350 sh (3,83)
IIa	H	BF_3	252 sh	312 sh (3,71), 322 (3,76), 355 sh (3,07)
Ib	4-OCH_3	—	256 (4,03)	352 (3,88)
IIb	4-OCH_3	BF_3	252 sh	308 sh (3,82), 314 (3,84), 330 sh
Ic	4-Cl	—	250 (4,15)	339 sh, 343 (4,04), 353 sh (4,00)
IIc	4-Cl	BF_3	250 sh	310 sh (3,74), 319 (3,81), 343 sh (3,73), 356 sh (3,45)
Id	4-SCH_2Ph	—	252 (4,09), 280 (3,59)	324 sh (4,43), 362 (4,61), 377 sh (4,51)
IId	4-SCH_2Ph	BF_3	251 sh (4,08), 295 sh	308 sh, 322 sh, 346 (4,16), 358 (4,16)
Ie	2-CH_3	—		330 (3,83), 341 (3,82)
IIe	2-CH_3	BF_3		310 (3,81), 321 (3,85), 343 sh (3,13)
If	2-$CH{=}CHC_6H_4(4'\text{-}OCH_3)$	—	248 sh	316 sh, 326 (4,56), 379 (4,41)
IIf	2-$CH{=}CHC_6H_4(4'\text{-}OCH_3)$	BF_3	257 (4,20)	316 (4,09), 326 sh, 408 (4,39)
Ig	4-NO_2	—	260 (4,26)	383 (4,12)
IIg	4-NO_2	BF3	260 (3,92)	383 (3,79)
Ih	Isoquinoline N-oxide	—	252 sh (4,14), 260 sh (4,23) 266 sh (4,26), 289 sh (3,88), 301 (4,03), 311 (3,98) 313 (3,98), 347 sh	
IIh	Isoquinoline N-oxide	BF_3	261 sh (3,48), 269 (3,56) 282 (3,55), 291 sh (3,47), 312 sh, 320 (3,45), 332 (3,52)	

In the case of complexes of the functionally substituted N-oxides II c-e, interaction of the π system with the substituents led to more complex spectra with more bands appearing as shoulders. It has been shown previously that (in the presence of heteroatoms) weak p → π^* transition bands appear as shoulders on high intensity intramolecular charge transfer bands in the long wavelength region.

Since the donor–acceptor bond in complexes between a p-donor and BF_3 and other group III metal halides is close to a normal covalent bond the O–B absorption band in compounds of this type should appear in the long wave region of the UV spectra according to literature data [3]. The necessary condition for the band to appear in the visible or near UV region is considered to be a not particularly strong interaction between the donor and acceptor [6].

However the UV spectrum of the hydrochloride IIIb is similar that of the corresponding complex with BF_3 IIb (see experimental). That N-oxides are undoubtedly protonated at the oxygen atom of the N → O bond [7] confirms that BF_3 is coordinated by the same atom.

In contrast to the electronic spectra of all the other compounds examined, the spectrum of the complex IIf shows a bathochromic shift of the absorption band in region 2. Two resonance forms arising from intramolecular charge transfer can be written for the original N-oxide If. The "quinoid" structure IV should be stabilised further in the complex with BF_3, which explains the red shift.



IV

TABLE 2. Characteristics of N-Oxides and Their Complexes*

Compound	m.p., °C	Bond*2 (ν, cm^{-1})	Stretching frequencies (ν, cm^{-1})		
			N—O	O—B	B—F
Ia	62	1270		—	
IIa	160...161	—	970	1090	1150
Ib	55...56	1290		—	
IIb	191...192	—	934	1095	1135
IIIb	151...153	—		1105	
Ic	133...135	1307		—	
IIc	100...102	—	910	1095	1150
Id	159...160	1300		—	1145
IId	235...236	—	920	1100	1145
Ie	77...78	1320		—	
IIe	114...116	—	915	1110	1145
If	142...143	1360 s, 1290 m	970 s	1030 s	1190
IIf	219...220	—	920	1100	1140 1160
Ig	152...154	1522 s, 1305 s, 1200 w	990	1135	1160 m
IIg	90 (decomp.)	1545 s 1265		1080	1120
Ih	105...106	1255		—	
IIh	226...228	—	965	1085	

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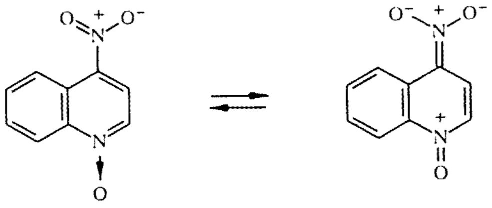
*Numbering of compounds corresponds to Table 1.

*2N=O ⇄ N → O bond.

The IR spectra also confirm the formation of n,ν-complexes of the N-oxides with BF_3. Bands characteristics of the N → O group appear in the 1310-1255 cm^{-1} region of the spectra of the aromatic N-oxides Ia-h. These bands disappear and new bands appear in the 1190-910 cm^{-1} region in the spectra of their complexes with BF_3 (Table 2). According to the literature absorption bands for the N → O in aliphatic N-oxides fall in the same region (970-950 cm^{-1}) [8]. In the present case the absorption bands occur in this region because the bond order of the N−O bond is decreased as a result of formation of the molecular complex. Moreover new absorption bands for B−F [9] and O−B bonds [4] should appear in this region (calculations gave a value of 1147 cm^{-1} for the O−B stretch).

As noted above, the UV spectrum of the complex of isoquinoline N-oxide with BF_3 (IIh) is uninformative. However the IR spectrum shows unambiguously that the donor−acceptor bond involves the oxygen atom just as in the complexes with quinoline N-oxides.

4-Nitroquinoline N-oxide (Ig) is unusual among the N-oxides studied since its structure is better described by the "quinoid" resonance structure V:



V

A structure of this type explains the color, for example, of 4-nitropyridine N-oxide [10] and also o- and p-nitro- and nitrosophenols and their ethers [11, 12]. Since the N-oxide bond in Ig has an order of close to 2, its absorption in the IR appears as a very strong band at 1522 cm^{-1} which corresponds to an N=O bond according to literature data and calculations. In its turn the N−O symmetrical stretch of the nitro group appears at 1305 cm^{-1}, slightly lower than for nitro groups in most aromatic nitro compounds (1357-1318 cm^{-1} [13]). This fact may also be explained by a decrease in the multiple bond order of the N−O bonds of the nitro group in resonance form V.

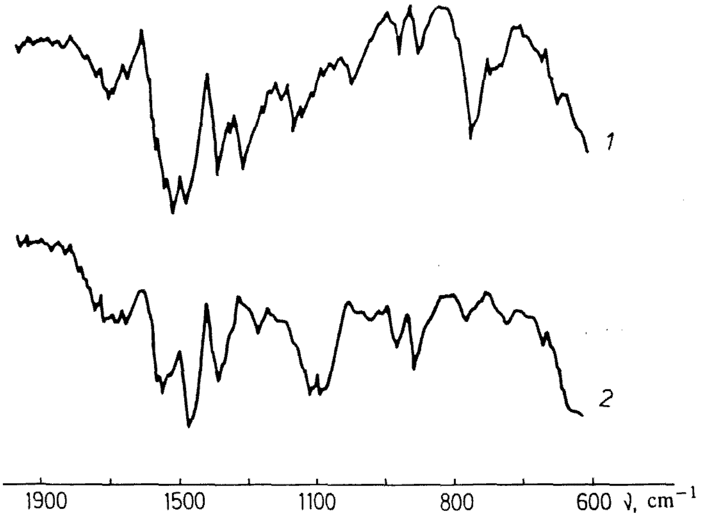
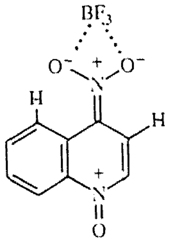


Fig. 1. IR spectra: 1) 4-nitroquinoline N-oxide (Ig) and 2) the complex of 4-nitroquinoline N-oxide with boron trifluoride (IIg).

Interestingly these effects are intensified in complex IIg. The N-oxide NO stretch now appears at 1545 cm^{-1}, while the NO stretch for the nitro group appears at 1265 cm^{-1} and the intensity of the latter is decreased somewhat (Fig. 1). These observations may be explained by coordination of the BF_3 to the oxygen atoms of the nitro group rather than the oxygen atom of the N-oxide.



IIg

Hence in this complex the multiplicity of the N−O bond in the N-oxide groups is increased while that of the N-O bonds in the nitro group is decreased.

No shift in the absorption maxima was observed in the electronic spectrum on forming the complex between 4-nitroquinoline N-oxide and boron trifluoride, but there was a considerable hypochromic effect. This is understandable in terms of the formation of complex IIg, which is similar to V, and should be characterized by coincidence of the absorption maxima. However it is known that steric factors which cause a quite small destruction of coplanarity in the conjugated system leave the positions of absorption maxima unchanged, but decrease their intensity [14-16] as was observed in this case.

In our view the formation of a complex of BF_3 with the nitro group of the N-oxide Ig is not unexpected. In particular, formation of similar complexes between nitrobenzene and $AlCl_3$ [17], nitromethane and $AlCl_3$ [18] and N_2O_4 and BF_3 [19] has been reported.

It is known that BF_3 is known to be a strong Lewis acid which does not form complexes with the π-systems of aromatic compounds [3]. In fact we have observed that it reacts with most of the quinoline N-oxides studied at the oxygen atom of the N → O group which is a hard donor centre. In the case of the N-oxide, complex IIg resonance conjugation leads to localization of the negative charge on the oxygen atoms of the nitro group and they interact with BF_3.

EXPERIMENTAL

IR spectra in Nujol were recorded with a UR-20 spectrometer and UV spectra of chloroform solutions with a UV-vi Specord spectrophotometer. Chloroform was washed with water, dried over anhydrous K_2CO_3, and redistilled.

Frequencies of stretching vibrations were calculated from the formula:

$$\nu = \frac{1}{2\pi c}\left(\frac{f}{\mu}\right)^{1/2},$$

where $f = 5 \cdot 10^5$ or $10 \cdot 10^5$ dyne.cm^{-1}, the force constants for single and double bonds respectively, and μ is the reduced mass

Synthesis of the Complex of Quinoline N-Oxide with BF_3 (IIa). Boron trifluoride etherate (0.15 ml) was added t a solution of quinoline N-oxide (0.145 g) in chloroform (2 ml). After 2 h the precipitate was centrifuged at 1500g, washed wit chloroform (2 × 0.5 ml) and ether (2 × 1 ml) and dried in the air, to give IIa as a white powder in quantitative yield, mp 160 161°C (mp 157.5-158.6°C [10].

The other N-oxide complexes were synthesised analogously (Table 2). In some cases 0.1-0.4 ml of absolute ether wa added to aid crystallization. The least stable complex, IIg, was not washed with ether.

4-Methoxyquinoline N-Oxide Hydrochloride (IIIb). Concentrated hydrochloric acid (1.12 ml) was added to saturated solution of 4-methoxyquinoline N-oxide (0.175 g) in ethanol. The solution was evaporated in vacuum and the mois crystals were dissolved in the minimum amount of n-butanol on heating. The solution was cooled to room temperature and the salt precipitated with ether to give a quantitative yield of IIIb as a white powder, mp 151-153°C. UV spectrum, λ_{max}, lgε: 24 sh, 309 sh (3.82), 320 (3.83), 332 sh, 353 nm (sh).

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