Interaction of anisole and thioanisole with the nitrosonium cation: π- *vs.* n-complex formation

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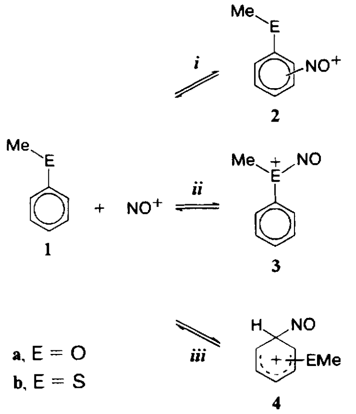
^{1}H, ^{13}C and ^{15}N NMR studies and the results of MINDO/3 calculations show the interaction between anisole, thioanisole and the nitrosonium cation to result in the formation of π- and n-complexes, respectively.

While the intermediacy of n- and π-complexes has often been postulated in the nitrosation reaction of arenes bearing heteroatom substituents[1] there is as yet no irrefutable evidence for the existence of such complexes in solution (*cf.* refs. 2–7).

In this work we have prepared complexes of compounds PhEMe (E = O, S) with the nitrosonium cation under long-life conditions and studied them by NMR spectroscopy.

The interaction of anisole with $NO^+AlCl_4^-$ in SO_2–CD_2Cl_2 at −70 °C results in formation of the π-complex **2a** (Scheme 1), as determined from the ^{1}H and ^{13}C NMR spectra (Tables 1 and 2), particularly from the relatively small down-field shifts of the signals of the methyl and phenyl groups (*cf.* refs. 3, 7–11).



Scheme 1

It should be noted that the chemical shifts for σ-complexes of type **4** are expected to be much larger (*cf.* ref. 12). The equivalence of 2- and 6-H, 3- and 5-H as well as C-2 and -6, -3 and -5 atoms observed in the ^{1}H and ^{13}C NMR spectra of the π-complex **2a** may be explained by the fast (on the NMR time scale) rotation of the MeO group and by the fast inter- or intra-molecular migration of the NO^+ group from one position of the phenyl ring to another (*cf.* refs. 8–10).

Additional evidence for the formation of π-complex **2a** has been obtained by ^{15}N NMR spectroscopy. When anisole is added at −70 °C to a solution of the labelled salt $Na^{15}NO_2$ (mole ratio PhOMe:$Na^{15}NO_2$ = 1:1) in FSO_3H–SO_2, the ^{15}N NMR spectrum no longer shows the signal of $^{15}NO^+$ (δ = 2.6) (*cf.* ref. 10), but contains the signal at 78.6 ppm at lower field from external CH_3NO_2. This value is very close to those for π-complexes of 1-methyl- and 1,3-dimethyl-naphthalene with NO^+ ($\delta_{-70\,°C}$ are 75.8 and 76.6, respectively).[10]

Interestingly, in contrast to anisole the interaction of thioanisole with $NO^+AlCl_4^-$ (SO_2–CD_2Cl_2, −70 °C) results in formation of the n-complex **3b** (Scheme 1). This is indicated by the ^{1}H and ^{13}C NMR data (Tables 1 and 2), particularly by the significant down-field shifts of the signals of the methyl group in the ^{1}H and ^{13}C NMR spectra and the high-field shift of the signal of C-1 in comparison with corresponding shifts for thioanisole. The latter evidently results from attraction of π-electron density to C-1 by electron-acceptor substituent Me–S$^+$–NO (*cf.* ref. 12). It is rather interesting that a similar effect is observed for the related sulfonium ions RS$^+$MePh (R = H,[13] CH$_3$[14]).

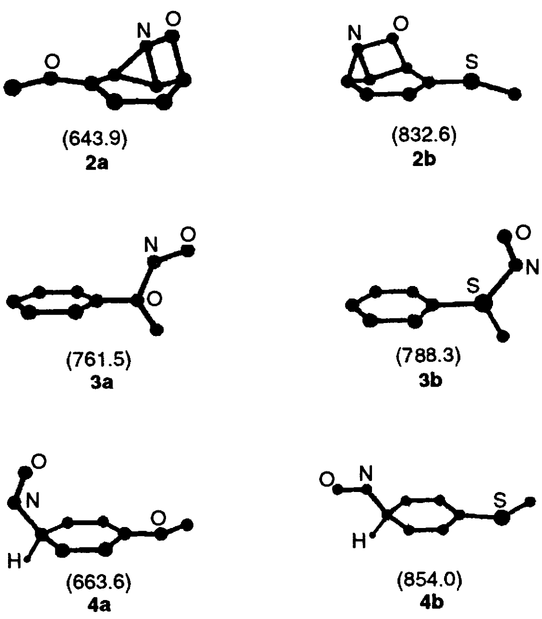


Fig. 1 MINDO/3 optimized structures for the complexes of anisole and thioanisole with nitrosonium cation and their heats of formation (in parentheses, Δ_fH kJ mol^{-1})

We have obtained further evidence of the n-complex character of the cation **3b** using ^{15}N NMR spectroscopy. Addition of thioanisole to a solution of the labelled salt $Na^{15}NO_2$ (mole ratio PhSMe:$Na^{15}NO_2$ = 1:1) in FSO_3H–SO_2 results in the formation of a complex whose ^{15}N chemical shift ($\delta_{-70\,°C}$ = 291.6) is rather close to that for the complex Me_2S with NO^+ prepared under the same conditions ($\delta_{-70\,°C}$ = 258.6).

When the PhEMe:$NO^+AlCl_4^-$ ratio, medium and temperature are varied, the chemical shifts change only slightly (Tables

Table 1 ^{1}H NMR data for the complexes **2a** and **3b** and the neutral precursors **1a, b**

Compound	T/°C	Anion	Solvent	Mole ratio, PhEMe:NO$^+$	δ^a CH$_3$	2,6-H	3,5-H	4-H
1a	−50	—	SO$_2$–CD$_2$Cl$_2$	—	3.72	6.88	7.30	6.98
2a	−70	AlCl$_4^-$	SO$_2$–CD$_2$Cl$_2$	1:1	4.01	7.34	7.73	7.56
2a	−50	AlCl$_4^-$	SO$_2$–CD$_2$Cl$_2$	1:1	4.05	7.45	7.90	7.76
2a	−50	AlCl$_4^-$	SO$_2$–CD$_2$Cl$_2$	1:4	4.05	7.44	7.89	7.76
2a	−30	AlCl$_4^-$	SO$_2$–CD$_2$Cl$_2$	1:1	4.03	7.31	7.73	7.63
2a	−50	SO$_3$F	FSO$_3$H–SO$_2$	1:1	4.12	7.34	7.71	7.54
1b	−50	—	SO$_2$–CD$_2$Cl$_2$	—	2.35	7.13	7.37	7.23
3b	−70	AlCl$_4^-$	SO$_2$–CD$_2$Cl$_2$	1:1	3.16	7.70	7.28	7.70
3b	−50	AlCl$_4^-$	SO$_2$–CD$_2$Cl$_2$	1:1	3.40	7.80	7.40	7.80
3b	−50	AlCl$_4^-$	SO$_2$–CD$_2$Cl$_2$	1:4	3.38	7.79	7.38	7.79
3b	−30	AlCl$_4^-$	SO$_2$–CD$_2$Cl$_2$	1:1	3.32	7.77	7.40	7.77
3b	−50	SO$_3$F$^-$	FSO$_3$H–SO$_2$	1:1	3.33	7.8	7.6	7.8

^{a} From internal CH$_2$Cl$_2$ (δ 5.33). CH$_3$ group signals are singlets, those of 2,6-H, 3,5-H and 4-H are multiplets.

Table 2 ^{13}C NMR data for the complexes **2a** and **3b** and the neutral precursors **1a, b**

Compound	T/°C	Anion	Solvent	Mole ratio, PhEMe:NO$^+$Y$^-$	δ^a CH$_3$	C-1	C-2,6^b	C-3,5^b	C-4
1a	−50	—	SO$_2$–CD$_2$Cl$_2$	—	54.9	159.5	114.8	130.7	122.0
2a	−70	AlCl$_4^-$	SO$_2$–CD$_2$Cl$_2$	1:1	56.4	166.0	121.0	137.0	129.2
2a	−50	AlCl$_4^-$	SO$_2$–CD$_2$Cl$_2$	1:1	56.6	166.4	121.2	137.1	129.5
2a	−30	AlCl$_4^-$	SO$_2$–CD$_2$Cl$_2$	1:1	56.8	166.6	121.4	137.2	129.6
2a	−50	SO$_3$F$^-$	FSO$_3$H–SO$_2$	1:1	57.8	163.3	120.3	135.8	129.2
1b	−50	—	SO$_2$–CD$_2$Cl$_2$	—	13.6	135.9	125.9	129.7	126.3
3b	−70	AlCl$_4^-$	SO$_2$–CD$_2$Cl$_2$	1:1	18.1	129.6	130.8	128.4	133.2
3b	−50	AlCl$_4^-$	SO$_2$–CD$_2$Cl$_2$	1:1	18.3	129.8	130.9	128.5	133.3
3b	−30	AlCl$_4^-$	SO$_2$–CD$_2$Cl$_2$	1:1	18.8	129.7	130.9	128.6	133.7
3b	−50	SO$_3$F$^-$	FSO$_3$H–SO$_2$	1:1	20.7	131.1	131.5	130.4	135.1

^{a} From internal CD$_2$Cl$_2$ (δ 53.6). ^{b} The shifts of C-2,6 and C-3,5 may be reversed.

1 and 2), indicating a virtually complete shift of the equilibrium *i* or *ii* (Scheme 1) towards the complexes **2a** and **3b**, respectively (*cf.* refs. 7, 10, 11).

The results of the MINDO/3 calculations[15] of the complexes of NO$^+$ with anisole and thioanisole are in agreement with experimental data. Fig. 1 represents key geometrical features, heats of formation of the most stable n-, π- and σ-complexes. In the case of anisole the π-complex is more favourable than the isomeric σ- or n-complex while in the case of thioanisole the n-complex is found to be more stable.

The above results show the nature of heteroatom E in the substituent ER to be decisive for the type of interaction between compounds PhER and the nitrosonium cation (π- *vs.* n-co-ordination). Two main factors are probably responsible for the observed difference in complex formation of anisole and thioanisole with NO$^+$: greater p,π-conjugation between the aromatic ring and the CH$_3$O rather than the CH$_3$S group,[16] and the smaller electronegativity of the S atom than the O atom.

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