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Abstract

Isolation of the unstable 1:1 complex of 4-nitrosoanisole with $NO^+PF_6^-$ allows its precise X-ray structural characterization. The charge-transfer crystal is formed *via* strong N ··· N coordination [the distance of 1.938(5) Å corresponding to a σ-bond order of ≈0.2] in the mean plane of the planar 4-nitrosoanisole donor. Thorough analysis of its molecular geometry in terms of valence

resonance and MO schemes reveals a strong charge polarization with a local negative charge localized on the nitroso group and a local positive charge distributed over the adjacent *p*-methoxybenzyl moiety. Such a charge distribution accommodates the well-known passivation of nitrosoarenes to multiple nitrosation and explains the ease of demethylation of the complex. Comparison of a variety of nitroso- and nitroarene structures has shown that the nitrosoarene experiences a much stronger quinoidal distortion of the aromatic ring as compared with the latter. This indicates a stronger electron-withdrawing effect of the nitroso group relative to that of the nitro group. The weakened aromatic resonance in the nitrosoarenes could be responsible for the observed slower rate and the measurable isotope effect in electrophilic nitrosation as opposed to nitration.

Introduction

Electrophilic nitrosation of arene donors (**ArH**) bears direct mechanistic similarities to the more common aromatic nitration. In each case, a simple cationic species, nitrosonium (NO^+) or nitronium (NO_2^+), is the active electrophile [1] [reaction (1)]. However, there are some striking differences in the course of electrophilic substitution—foremost of which are the large rate diminution and measurable kinetic isotope effect in nitrosation compared with nitration.[2] These facets have been attributed to the relatively slow deprotonation of the Wheland intermediate leading to significant reversibility [reaction (2)], where B is a Brønsted base.[3] Indeed, electrochemical (redox) studies demonstrate that nitrosoarenes are significantly better electron donors and hence stronger bases than the corresponding nitroarenes. Even more striking is the fact that nitrosoarenes are significantly better donors (by 5 to 20 kcal mol^{-1}) than the arene donors from which they are derived! [3] Despite this favorable electronic change, it is noteworthy that multiple electrophilic nitrosations of the aromatic ring do not occur. As such, we conclude that a deeper understanding of electrophilic nitrosation requires a detailed structural analysis of nitrosoarenes as electron donors (bases).

$$\mathrm{ArNO} \xleftarrow[(-\mathrm{H}^+)]{\mathrm{NO}^+} \mathrm{ArH} \xrightarrow[(-\mathrm{H}^+)]{\mathrm{NO_2}^+} \mathrm{ArNO_2} \quad (1)$$

$$\mathrm{ArH} + \mathrm{NO}^+ \rightleftharpoons \mathrm{Ar}^+\!\!<^{\mathrm{H}}_{\mathrm{NO}} \xrightarrow{\mathrm{B}} \mathrm{ArNO} + \mathrm{H(B)}^+ \quad (2)$$

Results and discussion

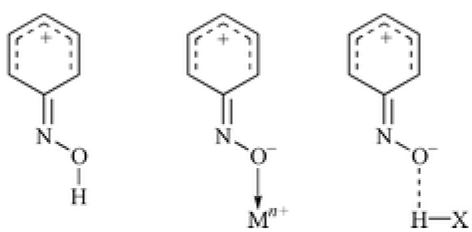
Direct experimental observation of nitrosoarenes as electron donors (bases) derives from the appearance of coloured complexes in the course of electrophilic nitrosation with nitrosonium salts.[3] For example, spectral titration of nitrosoanisole in acetonitrile indicates a 1:1 complex that absorbs at λ_{max} = 422 nm (ε_{max} 25 000 M^{-1} cm^{-1}) with an enhanced formation constant of K_{assoc} > 40 000 M^{-1} [equilibrium (3)].

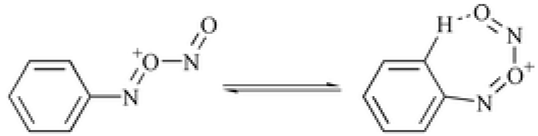
A recent reevaluation of the formation constant by Moodie and coworkers in acidic media (sulfuric and trifluoroacetic acids) confirms the strong complex formation of nitrosoanisole and other nitrosoarenes with NO^+.[4]

$$ArNO + NO^+ \overset{K_{assoc}}{\rightleftharpoons} [ArNO, NO^+] \quad (3)$$

1

The electronic spectrum of **1** unfortunately does not reveal at which of several potential sites of the multifaceted aromatic donor the acid–base interaction occurs with the nitrosonium acceptor (acid), viz., σ-bonding to either a nitroso or methoxy oxygen center, or to one of the ring carbons (including the ipso positions) or π-bonding to the delocalized aromatic centroid. Previous studies of nitrosoarenes with other acceptors (acids) such as those involved in complete proton transfer,[5] metal coordination [6] or even hydrogen bond formation [7] have consistently shown the acid–base interaction to occur always at the terminal oxygen atom, typically anti to the benzene ring. It was thus reasonable to assign the linear structure to the addition product of NO^+ to nitrosoarenes.[10] The alternative syn rotamer (involving an intramolecular hydrogen bond) was favored later to accommodate the increased barrier to rotation [equilibrium (4)].[4]





(4)

In order to resolve this and other ambiguities, we carefully grew single crystals of the 1∶1 complex from a mixture of 4-nitrosoanisole and nitrosonium hexafluorophosphate. X-Ray crystallography of the highly unstable brown crystals of **1** at −150 °C reveals the 1∶1 complex to have the unprecedented structure shown by the ORTEP diagram in Fig. 1. The electrophilic nitrosonium cation thus interacts with the lone electron-pair of the (nitroso) nitrogen atom and not the partial negative charge localized on the terminal oxygen atom, nor with any of the ring carbon centers (vide supra). Importantly, the complexation of the NO^+ moiety to nitrosoanisole does not result in the convenient formation of a single σ-bond. Instead, the observed N ··· N distance of 1.938(5) Å falls in between the standard 1.45 Å for a N–N single bond [11] and 3.10 Å for a van der Waals contact.[12] Our estimate based on Pauling's bond distance–order relationship [13] gives a bond order of 0.2 for this unique N ··· N interaction. Such a partial bond leads to a discrete ("locked") conformation in which (a) the NO^+ moiety is well situated in the mean plane of the nitrosoarene entity (which also maintains its almost flat conformation characteristic of the uncomplexed donor [14]) and (b) the O ··· O distance between the nitroso group and the nitrosonium moiety is much shortened to 2.511(4) Å which is significantly less than the equilibrium separation of 3.04 Å expected for a van der Waals pair of oxygens.[13]

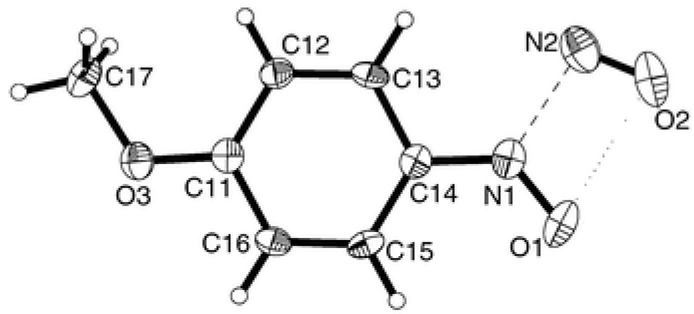


Fig. 1 Projection of the cation entity of the complex **1** onto its mean plane showing the numbering of non-hydrogen atoms; the thermal displacement ellipsoids are drawn at the 50% probability level.

The structure of the [ArNO, NO^+] complex can be qualitatively represented in valence-bond (resonance) terms as a combination of non-bonded (**A**) and bonded contributions (**B** and **C**), as shown in Chart 1, in which bonded structures **B** and **C** contribute a total of ≈20%. This partial bonding is expected to also result in some elongation (≈0.01 and 0.02 Å, based on Pauling's relationship [13]) of the N–O distances in the nitroso and nitrosonium moieties, respectively. Indeed, the N–O bond distance of 1.120(4) Å observed for the NO^+ moiety is elongated by 0.03 Å relative to those previously measured in the charge-transfer (π) complexes of NO^+ with weak donors such as toluene [1.093(3) Å] [15] and bicumene [1.092(6) Å].[16]

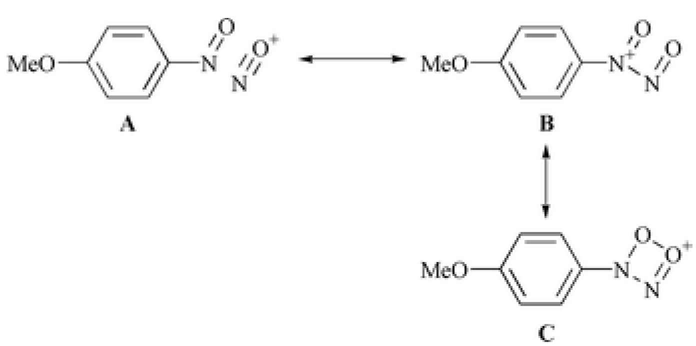


Chart 1

The unique partially bonded structure of the [ArNO, NO^+] complex in Fig. 1, as established by X-ray crystallography, provides considerable insight into several important facets of electrophilic aromatic nitrosation. First, the complexation of nitrosoarenes with the "soft" NO^+ electrophile at the nitrogen center indicates that the HOMO of nitrosoarene (as an electron donor) resides on the nitroso substituent and not on the aromatic ring.[17] This conclusion accounts for the fact that multiple substitution is not observed during electrophilic nitrosation, despite the fact that the nitrosoarene product is a better donor than the arene from which it is derived. Second, complexation of NO^+ at the nitrogen and not the oxygen center derives from the charge-transfer nature of the interaction of the nitrosoarene donor with the NO^+ acceptor in which the electrons from the donor's HOMO are donated to one of the two degenerate π*-LUMOs of the acceptor [18] (see Chart 2). Both interacting orbitals lie in the mean plane of **1** and are more localized over the corresponding nitrogen atoms than over the oxygens which themselves are subject to the same (albeit weaker) orbital overlap, as illustrated in Chart 2.[18] This dative interaction results in a more compact spatial localization of the lone pair of the nitroso nitrogen and is reflected in an unusually open value of the opposite C–N O bond angle of 127°.[19]

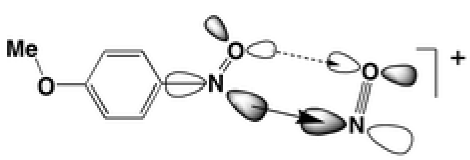


Chart 2

The coordination of the cationic acceptor NO^+ to the nitroso functionality confers some additional positive charge onto the aromatic ring.[21] Such an enhanced charge polarization is detected by additional shortening of the C(Ar)–NO bond to 1.353(5) Å; [20] the contraction can be a composite result of (1) an inductive effect via overlap of the HOMO of the 4-nitrosoanisole (basically the n-orbital of the nitroso group situated in the coordination plane) with the unfilled π*-orbital of the NO^+ cation to result in a relief of its antibonding effect onto the C(Ar)–NO σ-bond (see Chart 2) and (2) a mesomeric effect via π-conjugation of the second unfilled π*(z)-orbital (orthogonal to the coordination plane) of the NO^+ cation with the π-system of the 4-nitrosoanisole molecule (see Chart 3).

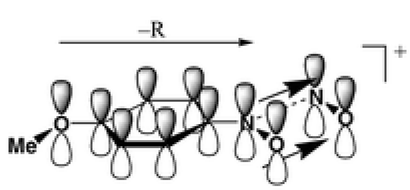


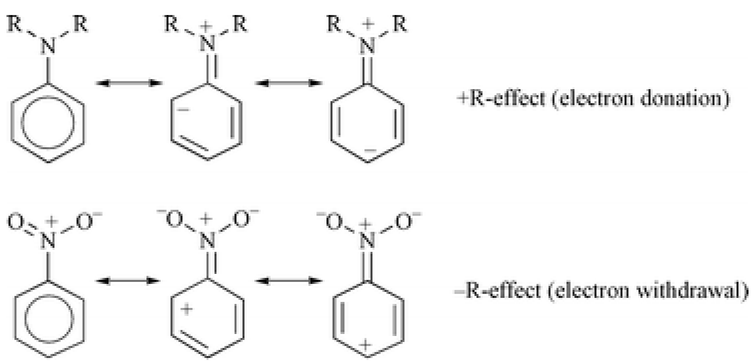
Chart 3

We believe that this enhanced charge polarization with substantial participation of the electron-donating 4-methoxy group [23] is responsible for the hydrolytic demethylation of the p-methoxybenzyl group that often accompanies electrophilic nitrosation.[24] Complexation of NO^+ in the manner illustrated in Charts 2 and 3 may also be accommodated in the high rotation barriers [25] reported by Moodie and coworkers.[4]

Comments on electrophilic aromatic nitrosation versus nitration

The ability of nitrosoanisole to strongly coordinate the cationic NO^+ acceptor accords with its unusually enhanced total donor strength as measured electrochemically (vide supra). The complexation of NO^+ however is largely centered around the nitroso functionality (as established in Fig. 1), but it is not obvious how the NO substituent affects the donor properties of the aromatic ring itself. Since the latter will relate directly to the ease of deprotonation of the Wheland intermediate (i.e. base strength) in nitrosation vis á vis nitration, let us compare the effects of the nitroso and nitro groups on the structural (and thus electronic) properties of the aromatic ring.

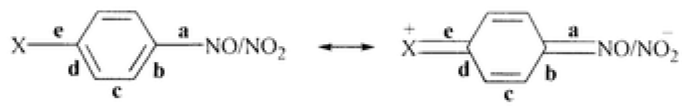
Resonance effects of substituents on an aromatic ring (also called conjugation or mesomeric effects) are a well-known type of electronic effect [26] which cause observable structural distortions in the aromatic moiety [27] due to contribution of quinoidal polarized resonance structures.



The molecular polarization and corresponding structural changes are largely amplified in o- and p-substituted arenes containing chemical groups with opposed (captodative) resonance effects.[26]

In these systems, the degree of quinoidal distortions of the benzene ring is very sensitive to changes in the donor–acceptor strengths of the substituents and thus it can be used as a criterion for comparing relative resonance effects [22] of different chemical groups onto a benzene ring. Accordingly, let us compare some known structures of nitro- and nitroso-substituted arenes to ascertain the difference between these two chemical groups by their effect onto the adjacent benzene moiety (Table 1).

Table 1 Relative degree of quinoidal distortions in p-substituted nitroso- and nitroarenes [a]



X	a (-NO/-NO_2)	b (-NO/-NO_2)	c (-NO/-NO_2)	d (-NO/-NO_2)	e (-NO/-NO_2)
H-	1.418/1.465	1.400/1.386	1.359/1.383	1.379/1.388	—/—
RO-	1.318[c]/1.468	1.399/1.381	1.369/1.376	1.407/1.388	1.335/1.356
Me_2N-	1.368/1.421	1.407/1.383	1.357/1.369	1.429/1.407	1.332/1.355
^{-}O-	1.349/1.421	1.425/1.397	1.361/1.373	1.443/1.426	1.270/1.289

[a] Geometrical parameters **a** through **e** are given in Å with typical precision of better than 0.5 pm. Note also that **b**, **c** an variations are significantly less than the quinoidal distortion. [b] An estimate (%) of the degree of quinoidal distortion t between arbitrary values **a** = 1.47 and **c** = 1.39 Å for **Q** = 0% (a pure benzenoid structure) and **a** = 1.30 and **c** = 1.33 Å f structure). [c] Imprecise data.[14]

The structural data for a variety of related molecules have unexpectedly shown that the degree of quinoidal distortions of the benzene ring is always much higher in nitroso-substituted compounds as compared with their nitro-substituted analogs. The difference grows with increase of +R-effect of a donor p-substituent (in a series −H < −OR < $-NR_2$ < $-O^-$) that indicates a larger −R-effect of the NO-substituent than that of the NO_2-substituent. Thus the nitroso group is much more capable of acquiring a partial negative charge than the nitro group. In other words, the nitroso-substituent is a better electron-acceptor than the nitro-substituent, and as such it induces a larger effective positive charge over the benzene ring! [35]

This finding does not contradict the fact that as a whole the nitrosoarenes are much stronger donors than the parent arenes and nitroarenes.[3] Their total donor strength is determined only by a strong excess of the local donor properties acquired by the nitroso group, whereas the local properties of the benzene ring appear to be strongly accepting in the nitroso-substituted arenes, especially, when compared with the nitro-substituted analogs. Moreover, it may explain the different rate of deprotonation of the corresponding Wheland intermediates.[2]

The Wheland intermediates in nitrosation and nitration are metastable owing to loss of the original aromatic resonance energy of the arene substrates (see Chart 4), but the energy of the aromatic resonance can be restored either by elimination of the electrophile (NO^+ or NO_2^+) or by deprotonation. As a result of the −R-effect of the nitroso and nitro groups on the benzene ring, the recovery of the aromatic resonance energy via deprotonation (a) should be incomplete in both cases but (b) should be much less for nitroso derivatives as compared with nitro derivatives. This is shown by a predominant quinoidal distortion for the nitroso product relative to the predominant benzenoid structure for the nitro product in Chart 4. This combination should lead to a higher probability for reverse elimination of the electrophile (NO^+) and a lower rate of deprotonation of the nitroso (Wheland) intermediate as compared with the corresponding nitro (Wheland) intermediate.

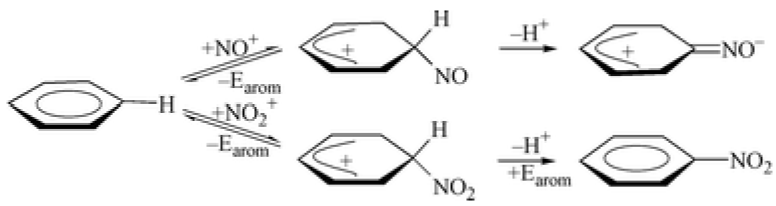


Chart 4

Summary and conclusions

The excess donor properties of the nitrosoarenes (as compared with the parent arenes) [3] are almost localized at their nitroso group as demonstrated by the structure of the complex of 4-nitrosoanisole with NO^+ (Fig. 1). The intermolecular N ⋯ N interaction (bond order ≈0.2) in the complex has a strong charge-transfer character with a partially localized σ-bond. The charge transfer results in an enhanced electron deficiency of the benzene ring that is particularly favorable to demethylation of the corresponding 4-nitrosoanisole complex,[4] and in general inhibits any further electrophilic substitution of the benzene ring.

The structures of the nitrosoarenes altogether exhibit a much stronger degree of quinoidal distortions as compared with the corresponding nitroarenes (Table 1). As such they are less stabilized by the energy of the aromatic resonance and their formation from the corresponding Wheland intermediates during nitrosation should be less efficient than analogous formation of more “benzenoid” nitroarenes (Chart 4). This conclusion accords well with the known slower rate and significant kinetic isotope effects in nitrosation as compared with nitration.[2]

Experimental

Materials

4-Nitrosoanisole was available from an earlier study.[3] Nitrosonium hexafluorophosphate (Strem) was stored in a Vacuum Atmospheres HE-493 glovebox kept free of moisture, oxygen and solvent vapors. Dichloromethane (Mallinckrodt analytical reagent) was repeatedly stirred with fresh aliquots of sulfuric acid (≈20% by volume) until the acid layer remained clear. After separation, it was washed successively with water, aqueous sodium bicarbonate, water, and aqueous sodium chloride and dried over calcium chloride. The dichloromethane was distilled twice from P_2O_5 under an argon atmosphere and stored in a Schlenk flask fitted with a Teflon valve fitted with Viton O-rings. Toluene (Fisher, ACS certified) was refluxed over sodium for 12 hours, distilled under an argon atmosphere, and stored in a Schlenk flask as described for dichloromethane. All glassware was dried in an oven at 140 °C for 12 hours and cooled in vacuo prior to use.

Crystallization of the nitrosonium complex of 4-nitrosoanisole
Nitrosonium hexafluorophosphate (31.0 mg, 0.18 mmol) was placed in a dry Schlenk flask under an atmosphere of argon and the flask then sealed with a rubber septum. Anhydrous dichloromethane (5 ml) was added with the aid of a cannula and the flask cooled to −78 °C in a dry ice–acetone bath under a positive pressure of argon. A solution of 4-nitrosoanisole (28.8 mg, 0.21 mmol) in dichloromethane (1 ml) was prepared in a separate Schlenk flask under an argon atmosphere. This flask was cooled to −78 °C and the cold solution transferred into the flask containing the nitrosonium salt with the aid of a cannula. The resultant mixture was stirred at −78 °C for 45 minutes. During this time the solution first became bright yellow and then progressively darker until a dark golden-brown solution was formed. The solution was left to stand undisturbed for an hour at −78 °C and then cold (−78 °C) toluene (5ml) was carefully added with the aid of a cannula. The toluene formed a clear layer above the dark brown solution. The flask was maintained at −78 °C for three days after which time dark golden-brown crystals had formed. The solvents were then carefully removed from the flask with the aid of a cannula using a positive argon pressure.

Crystal structure determination of the complex 1

The dark brown crystals were placed in small portions onto a glass slide positioned directly on an X-ray diffractometer under a cold nitrogen gas stream (at about −30 °C over the surface of the slide). Under these conditions, the crystals decompose (losing their color) in a less than minute. (Under ambient conditions the decomposition of the crystals takes 2–3 s.) After a few abortive attempts, a small crystal (showing significant surface decomposition) was successfully mounted on the diffractometer and kept at −150 °C during the data collection.

The X-ray diffraction measurements were carried out with a SMART 1K CCD diffractometer (Mo-Kα radiation) equipped with an LT-2 nitrogen gas stream low temperature device.† The structure solution (direct methods) and least squares refinement (against F^2 on all data) were performed with SHELXTL software.[36]

Crystal data.. $C_7H_7N_2O_3^+ \cdot PF_6^- \cdot C_7H_8$, M = 404.25, T = 123(2) K, triclinic, space group $P\bar{1}$ (No. 2), a = 7.508(1), b = 10.775(1), c = 11.358(1) Å, α = 89.38(1), β = 72.05(1), γ = 79.25(1)°, U = 857.7(1) $Å^3$, Z = 2, D_x = 1.565 g cm^{-3}, λ = 0.71073 Å, μ = 0.239 mm^{-1}, 7704 reflections (4084 unique) with 2θ ≤ 56°, 237 variables refined to R = 0.077 [3745 data, I ≥ 2σ(I)], wR(F^2) = 0.139, $\Delta\rho_{min/max}$ = −0.34/0.47 e $Å^{-3}$. Hydrogen atoms were localized objectively in a difference Fourier synthesis but were put into refinement using a riding/rotating geometrical model that provided better results. A solvate toluene molecule is present in the crystal of **1** (see Fig. 2) which provides some additional stabilization of the structure by formation of a weaker π-electron donor–acceptor complex with the 4-nitrosoanisole–nitrosonium entity. The interplanar distance is ≈3.3 Å within the donor–acceptor couple and ≈3.5 Å between them. Selected geometrical parameters of the complex **1** are represented in the Table 2.

Table 2 Selected geometrical parameters (Å; deg) of structure **1**

Bonds		Bond angles	
a Mean planes: A through N(1),N(2),O(1),O(2) (av. deviation 0.010 Å); B through N(1)O(1)C(14); C through C(11),C(12),C(13),C(14),C(15), C(16) (av. deviation 0.003 Å); D through O(3),C(11),C(17); E through C(1),C(2),C(3),C(4),C(5),C(6) (toluene benzene ring, av. deviation 0.004 Å).			
N(1) ··· N(2)	1.938(5)	N(2)–N(1)–O(1)	108.2(3)
N(1)–O(1)	1.211(4)	N(2)–N(1)–C(14)	124.8(3)
N(1)–C(14)	1.353(5)	O(1)–N(1)–C(14)	127.0(3)
N(2)–O(2)	1.120(4)	O(2)–N(2)–N(1)	100.0(3)
O(1) ··· O(2)	2.511(4)	C(11)–O(3)–C(17)	118.9(3)
O(3)–C(11)	1.320(4)	C(12)–C(11)–C(16)	121.2(3)
O(3)–C(17)	1.454(5)	N(1)–C(14)–C(13)	116.1(3)
C(11)–C(12)	1.407(5)	N(1)–C(14)–C(15)	122.6(3)
C(11)–C(16)	1.420(5)		
		Dihedral angles	
C(12)–C(13)	1.362(5)		
C(15)–C(16)	1.351(5)	A/B	1.9(3)
C(13)–C(14)	1.431(5)	B/C	3.0(3)
C(14)–C(15)	1.413(5)	C/D	1.9(2)
		C/E	3.3(1)

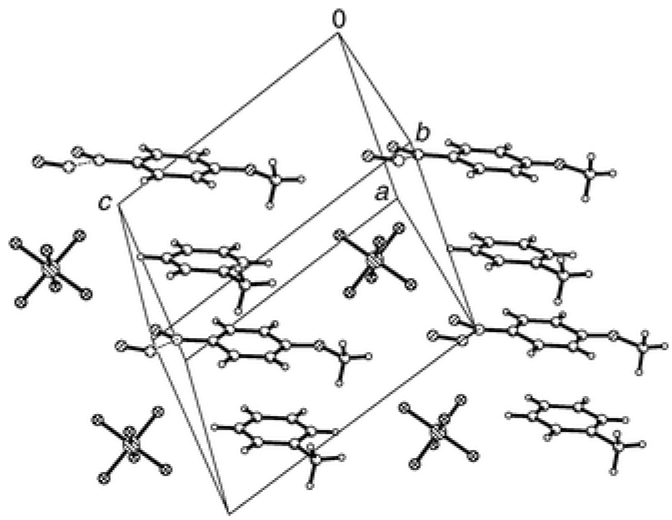


Fig. 2 Crystal structure of the complex **1** to illustrate the position of the toluene solvate.

Acknowledgements

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