Novel bis-arene (Sandwich) Complexes with NO\textsuperscript{+} Acceptor. Isolation, X-ray Crystallography and Electronic Structure

Sergiy V. Rosokha  
*University of Houston*

Sergey V. Lindeman  
*Marquette University, sergey.lindeman@marquette.edu*

Jay K. Kochi  
*University of Houston*

Sergey V. Lindeman was affiliated with the University of Houston at the time of publication.
Novel Bis-Arene (Sandwich) Complexes with NO$^+$ Acceptor. Isolation, X-ray Crystallography and Electronic Structure

S. V. Rosokha
Department of Chemistry, University of Houston, Houston, Texas

S. V. Lindeman
Department of Chemistry, University of Houston, Houston, Texas

J. K. Kochi
Department of Chemistry, University of Houston, Houston, Texas

Abstract
The unusual charge-transfer complexes of various arene donors (ArH) with the nitrosonium cation (NO$^+$) resulting from bimolecular [1 : 1] associations can be extended at suitably high ArH concentrations to termolecular processes leading to the analogous [2 : 1] complexes. Spectral analyses of the intense color changes accompanying the arene interaction with NO$^+$ provide optimum conditions for the isolation of pure crystalline ternary complexes. Single crystal X-ray crystallographic determinations establish the unique sandwich
structure consisting of the NO moiety interposed (parallel) between a pair of cofacial arene donors—reminiscent of the well-known transition metal sandwich complexes with aromatic ligands. The electronic structure associated with the arene binding to NO in the ternary complex is analyzed by the application of the semi-empirical LCAO molecular-orbital methodology and the Mulliken (charge-transfer) formulation of the electronic (UV–VIS–NIR) transitions. The resultant evaluation of the electronic coupling (matrix) elements $H_{ab}$ indicates strong donor/acceptor interactions of the frontier orbitals of the arene donor (HOMO) and nitrosonium acceptor (LUMO) that are only slightly less than those extant in the corresponding binary [1 : 1] complexes.

Introduction

Various aromatic hydrocarbons from benzene through to hexamethylbenzene, naphthalene and anthracene derivatives, etc. readily form a wide array of molecular complexes with the nitrosonium cation. Especially notable are the complete spectrum of vivid colors that characterize these molecular associations as they arise from charge-transfer interactions of the arene donors (ArH) with the nitrosonium acceptor (NO$^+$). Although Mulliken developed charge-transfer (CT) theory primarily for simple [1 : 1] complexes, the possibility of ternary [2 : 1] complexes has been of increasing interest. However, the structural characterization of such higher-order complexes has not been so straightforward since they are generally weaker than their binary analogues, and thus much more difficult to isolate in pure crystalline form for X-ray crystallographic analysis. Moreover, the spectral characterization of ternary complexes is often beset by the overlapping absorption bands of the binary complexes.

Our continuing interest in nitrosonium charge-transfer complexes stems from their unusual electronic structure, which in the case of arene donors is characterized by complete electron delocalization arising from strong donor/acceptor interactions. Viewed in this way, they are closely akin to transition-metal coordination compounds with arene ligands. Indeed the parallel may also bear on their structural resemblance, since the “open-face” sandwich structure I of the binary complex can be extended to the (putative) sandwich structure II of the ternary bis-arene complex.

![Chart 1](image)

Sandwich structures such as II can be considered as a link between different types of arene coordination to main-group analogues and transition metal complexes. Thus our objectives in this study are the isolation and X-ray structural analysis of the [2 : 1] bis-arene complexes of the nitrosonium acceptor, their unambiguous spectral assignment, and most importantly, the electronic formulation of the arene/NO$^+$ binding that characterizes these interesting (coordination) complexes.
Results

Spectral changes accompanying arene association with nitrosonium cation are generally characterized by an intense absorption band centered near 340 nm and a much weaker band in the region around 430–510 nm. Quantitative UV–VIS spectrophotometry coupled with isolation and X-ray crystallography establish the formation of the [1 : 1] complex according to eqn. (1).

\[
\text{ArH} + \text{NO}^+ \overset{K_1}{\rightleftharpoons} [\text{ArHNO}]^+ \tag{1}
\]

Spectral characterization of the [2 : 1] bis-arene complex with NO

Absorption spectra of the ternary complexes were elucidated at relatively high arene concentrations. For example, if the arene concentration was less than 0.05 M, the general shapes of the absorption spectra obtained upon the addition of various amounts of arene donor to a dichloromethane solution of nitrosonium salt were rather invariant as shown in Fig. 1(A) (spectra 1–3). Furthermore, the shapes of spectra were essentially invariant in the temperature range from 200 to 300 K. On the other hand, at the higher range of arene concentrations from 0.05 to 0.1 M (and greater), the UV–VIS spectra showed significantly different behavior. In particular, the absorbance in 450–550 nm region grew faster than that in the 330–350 nm region with increasing additions of arene, as shown in Fig. 1(A) (spectra 5–7). Finally, at very high arene concentrations of >1 M, the opposite trend in absorbance change near 500 nm \((A_{500})\) and 340 nm \((A_{340})\) was unmistakable, and highly indicative of the growth of new species that were substantially different from the [1 : 1] molecular association. This conclusion is also supported by the temperature dependence of the spectral changes. Thus at high arene concentrations, dramatic (non-proportional) changes of the absorbance were observed at different wavelengths as the temperature was progressively decreased from 20 to −90 °C, as shown in Fig. 1(B). In fact, under certain conditions the temperature variation resulted in a reversible (absorbance) interchange of the 340 and 500 nm bands to evoke a clear isosbestic point (Fig. 1(B)). Finally, in the limits of very high arene concentrations and at very low temperatures, the high-energy band essentially disappeared (Fig. 2).

Fig. 1 (A) Spectral changes attendant upon the incremental addition of toluene to 0.001 M solutions of nitrosonium cation in dichloromethane, at 22 °C. The concentration of toluene (in M): 0.001 (1), 0.003 (2), 0.01 (3), 0.03 (4), 0.1 (5), 1 (6), 3 (7). (B) Temperature modulation of UV–VIS absorption spectra of nitrosonium/toluene dyads (concentration of nitrosonium is 0.5 mM concentration of toluene is 0.5 M in dichloromethane). Temperature: 20 °C (1), 0 °C (2), −20 °C (3), −40 °C (4), −50 °C (5), −60 °C (6), −70 °C (7), −77 °C (8), −84 °C (9) −90 °C (10).
UV–VIS spectra of nitrosonium complexes with p-xylene for (nitrosonium concentrations of 1.2 mM in dichloromethane): [ArH,NO]+ (concentration of p-xylene is 0.05 M, 22 °C) and [(ArH)_2,NO]+ (concentration of p-xylene is 0.8 M, −85 °C).

Based on these spectral changes, the new species were considered to be the ternary complex resulting from the complexation of a second arene onto the [1∶1] complex according to eqn. (2).

\[ [\text{ArH,NO}^+] + \text{ArH} \rightleftharpoons [\text{ArH}_2,\text{NO}^+] \]  

(2)

Such ternary complexes were all characterized by an intense band around 460–530 nm. The molar absorptivity for the principal band of the ternary benzene complex with a spectral maximum at $\lambda_T = 455$ nm was evaluated as $2.5 \times 10^3$ dm$^3$ mol$^{-1}$ cm$^{-1}$ based on the concentration-dependent spectral changes at various temperatures. Similarly, the molar absorptivities for the related ternary complexes of toluene, xylene, and mesitylene are included in Table 1, together with that of 1,3,5-tri-tert-butylbenzene. The bathochromic trend in the Mulliken correlation of $h\nu$ with the increasing donor ability of the alkylbenzene expectedly followed that of the low-energy band in the corresponding binary complexes.

Table 1 Spectral characteristics and formation constants for 1∶1 and 1∶2 complexes of nitrosonium cation with aromatic donors

<table>
<thead>
<tr>
<th>Aromatic donor</th>
<th>$E^{\text{ox}}_{\text{ArH}}$</th>
<th>Binary complex</th>
<th>Ternary complex</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$V$ vs. SCE</td>
<td>$\lambda_B$</td>
<td>$\epsilon_B$</td>
</tr>
<tr>
<td>BEN</td>
<td>2.7</td>
<td>336</td>
<td>1.6</td>
</tr>
<tr>
<td>TOL</td>
<td>2.42</td>
<td>338</td>
<td>3.5</td>
</tr>
<tr>
<td>o-XY</td>
<td>2.13</td>
<td>336</td>
<td>3.6</td>
</tr>
<tr>
<td>p-XY</td>
<td>2.06</td>
<td>332</td>
<td>4.0</td>
</tr>
</tbody>
</table>

$^a$ In dichloromethane solution, at 22 °C, wavelength $\lambda$ in nm, molar absorptivity $\epsilon$ in $10^3$ dm$^3$ mol$^{-1}$ cm$^{-1}$. $^b$ From ref. 8.
The formation constants $K_2$ for the ternary complexes were determined over a wide range of arene concentrations by fitting the absorbance ratios at the band maxima of the binary and ternary complexes $A_{340}/A_{500}$ to the experimental values according to eqn. (3),

$$A_{340}/A_{500} = \left(\varepsilon_{340} + K_2[ArH] \varepsilon_{340}\right)/\left(\varepsilon_{500} + K_2[ArH] \varepsilon_{500}\right)$$

(3)

where $[ArH]$ is the arene concentration, $\varepsilon_{340}$ and $\varepsilon_{500}$ are the molar absorptivities of the binary complex, $\varepsilon_{340}$ and $\varepsilon_{500}$ are those of the ternary complex, and $K_2$ is the formation constant of the ternary complex. The validity of eqn. (3) was shown by the coincidence of the calculated values to the experimental data, and it is confirmed by the fit of the curved line over the entire span of arene concentrations from $10^{-4}$ M to $7$ M (see Experimental section). It is notable that the $K_2$ values in Table 1 are consistently lower than the corresponding $K_1$ values, as also observed previously in other types of binary and ternary charge-transfer complexes.

The relative magnitudes of the spectral parameters for the binary and ternary complexes of arene donors with nitrosonium acceptor, as listed in Table 1, are particularly informative. Thus, at low arene concentrations of up to $0.01$ M, the magnitude of $K_2[ArH]$ is very small and eqn. (3) predicts the charge-transfer spectra to be dominated by the contribution of the binary complex, since the absorbance ratio $A_{340}/A_{500}$ is simply equal to $\varepsilon_{340}/\varepsilon_{500}$ [and the same is generally true at other (monitoring) wavelengths]. On the other hand, at high arene concentrations, the numerator terms became comparable to the denominator terms in eqn. (3) and increasing arene concentrations (that lead to increasing values of $K_2[ArH]$) result in the shift of the absorbance ratio $A_{340}/A_{500}$ from values characteristic of the binary complex to those of the ternary complex. The same effect is achieved by lowering of the temperature, which leads to the increase of $K_2$.

Isolation and X-ray structure of the ternary complex

Spectral measurements established by eqn. (3) indicated that either increasing the arene concentration or lowering the temperature will allow the charge-transfer equilibrium to be deliberately shifted from the binary to the ternary complex, and vice versa. Indeed, the simultaneous variation of both concentration and temperature was particularly helpful for the isolation of different types of crystalline complexes. For example, the dark-red crystals grown at high arene concentrations (near 1 M) at low temperature (near −80 °C) consisted of the ternary complex [(ArH)$_2$NO$^+$]X$^-$ (see Experimental section for details). On the other hand, crystallization from dichloromethane solutions containing equimolar amounts of arene and nitrosonium salt at a moderately low temperature (about −20 °C) by the slow diffusion of hexane led to pure brown crystals of the binary complex.

The successful isolation of crystalline ternary NO$^+$ complexes of toluene, o-xylene and mesitylene allowed us to establish their molecular structure by X-ray diffraction analysis (see Experimental section) and to compare their structural parameters with those of the corresponding [1 : 1] complexes in Table 2. All these ternary complexes are characterized by the general structure (Chart 2) in which the nitrosonium moiety is sandwiched between a
pair of cofacial arene donors (see Figs. 3 and 4), much like that for the well-known transition-metal bis-arene complexes.\textsuperscript{9,10} Their \textit{inner-sphere} character is established by the intermolecular (arene/NO) separation of $\sim 2.5$ Å, which is significantly less than the sum of the van der Waals radii of 3.25 Å.\textsuperscript{19} In the toluene and \textit{o}-xylene complexes, the NO moiety is symmetrically located between the arene planes, but in the mesitylene complex, NO is substantially closer to one ring at a distance of 2.16 Å which approximates that in the binary complex.\textsuperscript{12} Most importantly, the complexation of NO$^+$ leads to a significant lengthening of the N–O bond to 1.08–1.14 Å, which is intermediate between that of the reduced nitric oxide (1.15 Å) and that of uncomplexed NO$^+$ (1.06 Å).\textsuperscript{12,20} Such a N–O bond elongation is diagnostic of extensive electron delocalization between the arene donor and nitrosonium acceptor, and the comparison of the bond lengths in Table 2 (column 8) indicates that the degree of charge transfer in the ternary complex, \textit{i.e.}

$$[[\text{ArH}]_2, \text{NO}^+] \leftrightarrow [[\text{ArH}]_2^+, \text{NO}^-]$$

is more or less comparable to that previously measured in the binary complexes.\textsuperscript{12} It is also important to note that the gross structure of the binary complex is similar to the lower-half of the ternary complex, as compared in Figs. 3 and 4.
Fig. 4 Molecular structures of (left) the binary [1 : 1] complex and (right) the ternary [2 : 1] complex of mesitylene with the nitrosonium acceptor.

Table 2 Selected bond lengths, bond angles and distances for the binary and ternary complexes of aromatic donors with nitrosonium acceptor

| Aromatic  | Complex | Bond length and distances in Å (± 0.005 Å) and angles in degrees (± 0.2°) unless indicated otherwise. For the notation of bond distances and in the ternary complexes see Chart 2. The internal angles α₁ and α₂ relate to the NO orientation to l₁ and l₂ respectively, and ϕ is the tilt angle of the arene ligand. In the binary complexes l represents the distance between nitrogen atom and aromatic plan and α is the angle between N–O bond and perpendicular to aromatic plane. | TOL | 2.498 | 2.510 | 98.7 | 98.9 | 25.1 | 1.14 |
|-----------|---------|---------------------------------------------------------------|-----|--------|--------|--------|--------|--------|--------|--------|
| o-XY      | Ternary | 2.62 | 2.65 | 92 | 93 | 26 | 1.084 |
|           | Binary  | 2.155 | 157.0 | – | 1.084 |
| MES       | Ternary | 2.158 | 2.691 | 153.5 | 165.5 | 20.5 | 1.089 |
|           | Binary  | 2.185 | 149.1 | – | 1.081 |

Discussion

Molecular structure and electronic transitions in ternary [(ArH)₂,NO⁺] complexes

The novel molecular structures of the ternary complexes of arene donors with the nitrosonium acceptor as depicted in Chart 2 (and Figs. 3 and 4), are characterized by intense electronic (VIS–NIR) absorptions at λ₁ ≈ 450–500 nm (ε₁ = 2500–8000 dm³ mol⁻¹ cm⁻¹) that lead to their dark-red (charge-transfer) colors. The spectral parameters listed in Table 1 bear a rather close relationship to the (very weak) low-energy band of the corresponding binary complex and this similarity presents an unusual opportunity to compare them quantitatively.
The electronic (or charge-transfer) structure of the binary complex of arene donors with the nitrosonium acceptor has been successfully treated within the framework of Mulliken (valence bond or molecular-orbital) theories. To describe the inner-sphere complex quantitatively, the mutual interaction of the donor/acceptor molecular orbital is considered according to the basic LCAO methodology in which only the frontier orbitals of the arene (HOMO) and nitrosonium (LUMO) are explicitly taken into account. The accompanying orbital diagram for the donor/acceptor interaction of benzene and NO$^+$ is represented in Chart 3, in which the linear combination of donor/acceptor orbitals leads to a new bonding orbital $\Psi_+ = C_{\text{NO}}\psi_{\text{NO}} + C_{\text{ArH}}\psi_{\text{ArH}}$ and a new antibonding orbital $\Psi_- = C'_{\text{NO}}\psi_{\text{NO}} + C'_{\text{ArH}}\psi_{\text{ArH}}$ with the mixing coefficients normalized. The absorption band $(h\nu_B)$ listed in Table 1 is assigned to the electronic transition from the bonding to the antibonding molecular orbitals $(\Psi_+ \rightarrow \Psi_-)$ of the binary complex, the transition energy of which is expressed as shown in eqn. (4).

$$h\nu_B = (\Delta_{AB}^2 + 4H_{AB}^2)^{1/2}$$  \hspace{1cm} (4)

The resonance integral: $H_{AB} = \int \psi_{\text{NO}} \psi_{\text{ArH}}$ in eqn. (4) represents the donor/acceptor interaction energy. The HOMO–LUMO gap is $\Delta_{AB}$ which is represented by the difference of the Coulomb integrals: $\varepsilon_{\text{ArH}} = \int \psi_{\text{ArH}} \psi_{\text{ArH}}$ and $\varepsilon_{\text{NO}} = \int \psi_{\text{NO}} \psi_{\text{NO}}$ corresponding to the donor and acceptor orbitals, respectively. [Note that $\Delta_{AB}$ is evaluated in solution as the difference in the oxidation potential $E^0_{\text{ox}}$ of the arene donor and the reduction potential $E^0_{\text{red}}$ of the nitrosonium acceptor].

The low-energy weak band (due to symmetry reasons) corresponds to the electronic transition from the non-interacting arene orbital to antibonding orbital of binary complex.

The ternary complex consisting of two arene donors with a single NO$^+$ acceptor can be treated by an analogous procedure, and the corresponding molecular-orbital diagram is presented in Chart 4.
Based on the semi-empirical LCAO MO methodology (see Experimental section for details), the energies of the bonding, non-bonding, and the antibonding orbitals in the ternary complex are expressed as follows in eqns. (5)–(7),

\[
\varepsilon_+ = \frac{1}{2}(\varepsilon_{NO} + \varepsilon_{ArH}) - \frac{1}{2} (\Delta_{AB}^2 + 8H_{AB}^2)^{1/2}
\]

(5)

\[
\varepsilon_{NB} = \varepsilon_{ArH}
\]

(6)

\[
\varepsilon_- = \frac{1}{2}(\varepsilon_{NO} + \varepsilon_{ArH}) + \frac{1}{2} (\Delta_{AB}^2 + 8H_{AB}^2)^{1/2}
\]

(7)

where the notations \(\Delta_{AB}\) and \(H_{AB}\) are the same as those expressed above. The transition from bonding to antibonding MO (\(\Psi_+ \rightarrow \Psi_-\)) is symmetry forbidden in ternary complexes, and the corresponding absorption band is very weak. Therefore, the principal band in these compounds, \(h\nu_T\), corresponds to the non-bonding to antibonding MO (\(\Psi_{NB} \rightarrow \Psi_-\)) transition, and its energy is expressed as in eqn. (8),

\[
\hbar\nu_T = \frac{1}{2} (\Delta_{AB}^2 + 8H_{AB}^2)^{1/2} + \frac{1}{2} \Delta_{AB}
\]

(8)

The oscillator strength of band \(h\nu_T\) is predicted to be 1.5 to 2 times greater than the principal band \(h\nu_B\) in the corresponding binary complex, and this is confirmed experimentally in Fig. 2.

The marked difference in the spectral shapes of the charge-transfer bands in ternary and binary complexes as shown in Fig. 2 depends in large measure on the magnitude of the donor/acceptor electronic coupling (interaction) energy \(H_{AB}\) as given by the resonance integral \(\int \psi_{NO} H \psi_{ArH} \)..

(i) For the binary complex the values of \(H_{AB}\) in Table 3 (column 4) are computed for various alkylbenzenes according to eqn. (4) from the HOMO–LUMO gap \(\Delta_{AB}\) (column 2) together with the experimental data for the principal band (\(h\nu_B\)) in column 3.
Table 3 Comparison of the donor/acceptor electron interaction term ($H_{AB}$) for binary and ternary complexes as evaluated from the corresponding spectral data and the oxidation potential of arenes

<table>
<thead>
<tr>
<th>Aromatic donor</th>
<th>Binary complex $\Delta_{AB}$/eV</th>
<th>Binary complex $h\nu_{B}$/eV</th>
<th>Ternary complex $H_{AB}$/eV</th>
<th>Ternary complex $h\nu_{T}$/eV</th>
<th>Ternary complex $H_{AB}$/eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>BEN</td>
<td>1.21</td>
<td>3.70</td>
<td>1.75</td>
<td>2.73</td>
<td>1.44</td>
</tr>
<tr>
<td>TOL</td>
<td>0.93</td>
<td>3.67</td>
<td>1.77</td>
<td>2.51</td>
<td>1.41</td>
</tr>
<tr>
<td>o-XY</td>
<td>0.64</td>
<td>3.69</td>
<td>1.82</td>
<td>2.46</td>
<td>1.5</td>
</tr>
<tr>
<td>p-XY</td>
<td>0.57</td>
<td>3.74</td>
<td>1.85</td>
<td>2.32</td>
<td>1.42</td>
</tr>
<tr>
<td>MES</td>
<td>0.62</td>
<td>3.66</td>
<td>1.80</td>
<td>2.48</td>
<td>1.52</td>
</tr>
<tr>
<td>CUM</td>
<td>0.8</td>
<td>3.66</td>
<td>1.78</td>
<td>2.39</td>
<td>1.39</td>
</tr>
</tbody>
</table>

*a* Calculated from the difference of the redox potentials of the arene donor (Table 1) and nitrosonium acceptor (1.48 V vs. SCE). *b* From ref. 8. *c* Calculated via eqn. (4) from $\Delta_{AB}$ and $h\nu_{B}$. *d* Calculated via eqn. (8) from $\Delta_{AB}$ and $h\nu_{T}$. *e* Cumene.

(ii) For the ternary complex the values of $H_{AB}$ in column 6 are calculated from eqn. (8) for the same arene donors from the experimental spectral data for the principal band $h\nu_{T}$ in column 5 and $\Delta_{AB}$ in column 2.

Since the magnitudes of $H_{AB}$ for both the ternary and the binary complexes are substantially larger than the HOMO–LUMO gap, the energy of the bonding orbital is appreciably lower than the non-bonding arene orbital; and this results in large differences in the high and low energy bands according to MO diagrams in Charts 3 and 4. It then follows that the large bathochromic shift of the principal absorption bands on proceeding from the binary to ternary complex, as illustrated in Fig. 2, is simply given by the energy difference: $h\nu_{B} - h\nu_{T}$. The magnitude of the bathochromic shift is 7800 cm$^{-1}$ for the benzene complex, and rises to 9500 cm$^{-1}$ for the mesitylene complex.

Molecular structures and relative binding of arene/NO$^+$ dyads in ternary and binary complexes

The X-ray-based structural parameters listed in Table 2 indicate that N–O lies nearly parallel to the arene planes of toluene and o-xylene. The placement of NO equidistant from both arene planes describes a nearly symmetrical (sandwich) structure for the ternary complex. By contrast, the intermolecular arene/NO distance in the binary-o-xylene complex is approximately 0.4 Å closer, and it thus represents a somewhat contracted version in an “open-face” sandwich configuration. The increase in the donor/acceptor separation in the ternary complexes relative to that in the binary analogue follows the trend in the $H_{AB}$ values (Table 3) to indicate a diminished electronic interaction between the arene donor and NO$^+$ in the ternary complex. The same conclusion applies to the relative values in Table 1 for the formation constants $K_{f}$ and $K_{i}$ in eqns. (1) and (2), respectively. Both of these then follow the charge-transfer trends for the ternary complexes relative to the binary complexes that are predicted theoretically.

Conclusions

Exceptional charge-transfer interactions of common arenes like benzene, toluene, and xylene (ArH) with the nitrosonium acceptor (NO$^+$X$^-$) are characterized by vivid red colors of ternary [(ArH)$_2$NO$^+$X$^-$] complexes. Isolation of the dark red [2 : 1] crystals and X-ray structural analyses establish the unusual sandwich structure (Chart 2) in which the NO$^+$ moiety is intercalated between a pair of cofacial arene donors—much like the well-known bis-
arene complexes of transition metals. Quantitative analysis of electronic (UV–NIR) spectra with the aid of semi-empirical LCAO molecular orbital methodology traces the strong intermolecular ArH/NO+ interactions to Mulliken charge-transfer forces involving sizeable magnitudes of the electronic coupling elements $H_{AB} \approx 1.4$ eV.

**Experimental**

**Materials**

Nitrosonium hexachloroantimonate was prepared from SbCl5 and NOCl according to the literature procedure. The alkylbenzenes (Aldrich): [benzene (BEN), toluene (TOL), o-xylene (o-XY), p-xylene (p-XY), mesitylene (MES), 1,3,5-tri-tert-butylbenzene (TBB) and cumene (CUM)], dichloromethane (Merck), and hexane (Merck) were purified according to standard laboratory procedures and were stored in the Schlenk flasks under an argon atmosphere.

**General procedure for the preparation arene/nitrosonium complexes**

For the preparation of the ternary complexes, a 50 mL flask fitted with a Schlenk adapter was charged with nitrosonium salt (0.05–0.1 mmol NO+SbCl6−), together with the large excess of the aromatic donor in anhydrous dichloromethane (10 ml) under an argon atmosphere. The dark-red solution was carefully layered with dry hexane (30 ml) and then very slowly cooled to −77 °C. During the course of 3–7 days, dark-red crystals of the complex [(ArH)2,NO]+SbCl6− were observed and these were always handled at low temperatures. Crystal data for the ternary complexes are presented below. In order to prepare the binary complexes, a 50 mL flask fitted with a Schlenk adapter was charged with nitrosonium salt (0.05–0.1 mmol), and an equimolar solution of the aromatic donor in anhydrous dichloromethane (10 ml) was added under an argon atmosphere. The brown solutions were layered with dry hexane (30 ml) and very slowly cooled to −20 °C. During the course of 3–7 days, dark-brown crystals of the complex [ArH,NO]+SbCl6− were deposited.

**X-Ray crystallography**

The intensity data for all the compounds were collected with a Siemens SMART diffractometer equipped with a 1K CCD detector using Mo-Kα radiation ($\lambda = 0.71073$ Å) at −150 °C. The structures were solved by direct methods and refined by full matrix least-squares procedure with IBM Pentium and SGI O2 computers. [Note that the X-ray structure details of various compounds mentioned here are on deposit and can be obtained from Cambridge Crystallographic Data Center, UK.]

- ([Toluene]$_2$,NO+]SbCl6−. Formula: C$_{14}$H$_{16}$Cl$_6$NOSb, M 548.73, orthorhombic, Pnma, $a = 11.215(2)$, $b = 15.911(3)$, $c = 11.501(2)$ Å, $V = 2052.3(7)$ Å$^3$, $D_c = 1.776$ g cm$^{-3}$, $Z = 4$. The total number of reflections measured were 25541 of which 4945 reflections were symmetrically non-equivalent. Final residuals were $R_1 = 0.0610$ and $wR_2 = 0.0828$ for 2234 reflections with $I > 2\sigma(I)$.

- ([o-Xylene]$_2$,NO+]SbCl6−. Formula: C$_{16}$H$_{20}$Cl$_6$NOSb, M 576.78, monoclinic P2$_1$/c, $a = 11.666(2)$, $b = 16.482(3)$, $c = 23.254(4)$ Å, $V = 4470(1)$ Å$^3$, $D_c = 1.714$ g cm$^{-3}$, $Z = 8$. The total number of reflections measured were 47115 of which 4802 reflections with $2\theta < 45^\circ$ were symmetrically non-equivalent. Final residuals were $R_1 = 0.0930$ and $wR_2 = 0.2419$ for 4519 reflections with $I > 2\sigma(I)$.

- ([Mesitylene]$_2$,NO+]SbCl6−. Formula: C$_{18}$H$_{24}$Cl$_6$NOSb, M 604.83, monoclinic, Cm, $a = 12.502(1)$, $b = 10.516(2)$, $c = 9.852(2)$ Å, $\beta = 109.46(5)^\circ$, $V = 1221.2(4)$ Å$^3$, $D_c = 1.645$ g cm$^{-3}$, $Z = 2$. The total number of reflections measured were 8122 of which 4169 reflections were symmetrically non-equivalent. Final residuals were $R_1 = 0.0310$ and $wR_2 = 0.0629$ for 3559 reflections with $I > 2\sigma(I)$.

Crystal data for the binary complexes were reported previously.
Spectral measurements

The UV–VIS absorption spectra were recorded on a HP 8453 diode-array spectrometer. Low-temperature studies were carried out with the aid of a low-temperature Dewar equipped with quartz windows for UV–VIS measurements. All operations were performed in an inert (argon) atmosphere with Teflon-capped cuvettes (0.1–1.0 cm) equipped with side arms.

The spectral characteristics and equilibrium constants for the 1 : 1 complexes were described previously. Recent measurements confirm that the higher order complexes can be neglected at the low arene concentrations (≤ 0.01 M) used in the previous work.

Spectral characteristics of [2 : 1] complexes were determined at high (1 M) concentrations of arene at low temperature, under conditions in which the nitrosonium acceptor was fully associated with the aromatic donor. From the mass balance: \[\text{[ArH,NO]}^+ + \text{[(ArH)\text{2},NO]}^+ = \text{[NO]}^0\], the molar absorptivities of the ternary complexes could be determined from the spectral changes of the binary complex into the ternary complexes as the temperature was lowered. The \(\varepsilon\) values obtained were verified by their calculation directly from the absorbance data (under conditions in which the equilibrium was shifted completely to the ternary complex).

Equilibrium constants of [2 : 1] complexes were determined from the dependence of the absorbance ratio \(A_{340}/A_{500}\) on the arene concentration (Fig. 5). The absorbance at the wavelength \(\lambda\) can be presented as the sum of the absorption of binary and ternary complexes (the absorbance of an uncomplexed ArH and NO\(^+\) in the UV–VIS range studied can be neglected): \(A_{\lambda} = \varepsilon_{\lambda}^B\text{[ArH,NO]}^+ + \varepsilon_{\lambda}^T\text{[(ArH)\text{2},NO]}^+\), (where \(\varepsilon_{\lambda}^B\) and \(\varepsilon_{\lambda}^T\) are extinction coefficients at wavelength \(\lambda\) of binary and ternary complexes). Therefore: \(A_{340}/A_{500} = \{\varepsilon_{340}^B\text{[ArH,NO]}^+ + \varepsilon_{340}^T\text{[(ArH)\text{2},NO]}^+\}/\{\varepsilon_{500}^B\text{[ArH,NO]}^+ + \varepsilon_{500}^T\text{[(ArH)\text{2},NO]}^+\} = \{\varepsilon_{340}^B + \{(\text{[(ArH)\text{2},NO]}^+)/\text{[ArH,NO]}^+\}\} \times \varepsilon_{340}^T/\varepsilon_{500}^T + \{(\text{[(ArH)\text{2},NO]}^+)/\text{[ArH,NO]}^+\}\varepsilon_{500}^T\). From the eqns. (1) and (2) it follows that: \([\text{ArH,NO]}^+ = K_1[\text{ArH}][\text{NO}^+]\) and \([\text{[(ArH)\text{2},NO]}^+] = K_2[\text{ArH}][\text{NO}^+]K_1[\text{ArH}][\text{NO}^+]\). Therefore, \([\text{ArH,NO]}^+ \text{[ArH]} = K_2[\text{ArH}][\text{NO}^+]\), substituting the ratio of binary/ternary concentrations by \(K_2[\text{ArH}]\), we obtained \(A_{340}/A_{500} = \{\varepsilon_{340}^B + K_2[\text{ArH}][\text{NO}^+]\} / \{\varepsilon_{500}^B + K_2[\text{ArH}]\varepsilon_{500}^T\} \) (i.e., eqn. (3)). In this expression, all values except \(K_2\) are known. Therefore, \(K_2\) can be determined by minimizing (variation of \(K_2\)) the sum of the squares of the difference between the experimental and the calculated values of \(A_{340}/A_{500}\) at different arene concentrations, \(\Delta = \sum((A_{340}/A_{500})_{\text{exp}} - (A_{340}/A_{500})_{\text{calc}})^2\). The values of \(K_2\) obtained in such a way for systems with different arene donors (at room temperature) are presented in Table 1. The curved lines in the Fig. 5 represent the calculated dependencies of \(A_{340}/A_{500}\) ratio on the arene concentration at room and low temperatures (based on eqn. (3) and data from Table 1). Coincidence of the calculated values to the experimental data over the entire span of arene concentrations from \(10^{-4}\) M to 7 M confirms the validity of this approach. Since the magnitude of \(K_2[\text{ArH}]\) is very small, at low arene concentrations (up to 0.01 M), the absorbance ratio: \(A_{340}/A_{500}\) is equal to \(\varepsilon_{340}^B/\varepsilon_{500}^B\) and the charge-transfer spectra are dominated by the binary complex. The increase of arene concentrations leads to increasing values of \(K_2[\text{ArH}]\) and gradually the terms \(K_2[\text{ArH}]\varepsilon_{500}^T\) in numerator and denominator became comparable to \(\varepsilon_{500}^B\). The result is a shift of the absorbance ratio \(A_{340}/A_{500}\) from values characteristic of the binary complex to those of ternary complex. It should be also noted that \(K_2\) values calculated from low-temperature are (expectedly) higher than those at room temperature (e.g., for complexes with \(p\)-xylene, \(K_2\) are 0.6 and 0.17 M\(^{-1}\) at −77 and 22 °C, respectively). Therefore, lowering the temperature leads to the increase of the \(K_2[\text{ArH}]\), and also results in the shift of the absorbance ratio \(A_{340}/A_{500}\) from values characteristic of the binary complex to those of ternary complex (provided \([\text{ArH}]\) is not too small, Fig. 6).
Fig. 5 Dependence of the absorbance ratio at 340 and 500 nm of the nitrosonium/p-xylene mixture in dichloromethane upon the concentration of p-xylene at 22 °C (●) and −77 °C (△) temperatures. Lines represent best fit based on eqn. (3). Note: at low arene concentrations the ratio $A_{340}/A_{500}$ is the same both at room and low temperatures, while at high arene concentrations these ratios at low temperature are increasingly decreased.

Fig. 6 Dependence of the absorbance ratio at 340 and 500 nm on temperature for the p-xylene/nitrosonium dyads in dichloromethane (1 mM NO$^+$) with concentration of p-xylene 0.002 M (♦) and 0.2 M (▲).
MO formulation for ternary complexes
According to the basic MO methodology as applied to intermolecular interactions, the molecular orbitals of the complex ($\Psi$), can be expressed as the linear combination of the frontier orbitals of the reacting species, i.e. the HOMO of two benzenes (denoted as $\psi_{\text{ArH}}$ and $\psi_{\text{ArH'}}$) and the LUMO of nitrosonium ion (denoted as $\psi_{\text{NO}}$): $\Psi = C_{\text{NO}}\psi_{\text{NO}} + C_{\text{ArH}}\psi_{\text{ArH}} + C_{\text{ArH'}}\psi_{\text{ArH'}}$. Taking into account the interaction between neighboring atoms only, and assuming the electronic interaction ($\Delta$) of nitrosonium with both arenes to be the same; the energies of these orbital are given as: $\varepsilon = [\Psi^\text{HH}\Psi]/[\Psi^2] = (C_{\text{NO}}^2\varepsilon_{\text{NO}} + C_{\text{ArH}}^2\varepsilon_{\text{ArH}} + C_{\text{ArH'}}^2\varepsilon_{\text{ArH'}} + 2C_{\text{NO}}C_{\text{ArH}}\varepsilon_{\text{ArH}} + 2C_{\text{NO}}C_{\text{ArH'}}\varepsilon_{\text{ArH'}})/(C_{\text{NO}}^2 + C_{\text{ArH}}^2 + C_{\text{ArH'}}^2 + 2C_{\text{NO}}C_{\text{ArH}}\varepsilon_{\text{ArH}} + 2C_{\text{NO}}C_{\text{ArH'}}\varepsilon_{\text{ArH'}})$. The solution of the secular equation (taking $S_{\text{ab}} = 0$) results in three molecular-orbital wavefunctions with the energies given by eqns. (5)–(7). The expressions for these wavefunctions (taking into account the normalization: $C_{\text{NO}}^2 + C_{\text{ArH}}^2 + C_{\text{ArH'}}^2 = 1$) are: $\Psi_a = (1/(a^2 + 2\Delta_{\text{ab}}^2))^{3/2}((H_{\text{ab}}\psi_{\text{ArH}} + a\psi_{\text{NO}} + H_{\text{ab}}\psi_{\text{ArH'}}))$, $\Psi_{\text{ib}} = (1/(b^2 + 2\Delta_{\text{ab}}^2))^{3/2}((H_{\text{ab}}\psi_{\text{ArH}} + b\psi_{\text{NO}} + H_{\text{ab}}\psi_{\text{ArH'}}))$, and $\Psi_{\text{ib}} = (1/\Delta_{\text{ab}} - (\Delta_{\text{ab}}^2 + 8H_{\text{ab}}^2))^{3/2}$. These wavefunctions are used to simplify the wave-function presentation.

Acknowledgements
We thank the R.A. Welch Foundation and National Science Foundation for financial support.

References
12(a) E. K. Kim and J. K. Kochi, J. Am. Chem. Soc., 1991, 113, 4962 ; (b) hereinafter the SbCl₆⁻ counterion will be omitted for clarity.
13(a) Due to limited solubility, especially at low temperatures, we were able to study the association of only a few alkyl-substituted benzenes in the high-concentration range; (b) for the quantitative analyses of the spectral dependence on concentration and temperature, see Experimental section.
14The nitrosonium salt NOSbCl₆ was used in the 0.2 to 5.0 mM concentration range. The spectral shapes did not depend on its concentration.
15The absorbances $A_{340}$ and $A_{500}$, and molar absorptivities $\varepsilon_{340}$ and $\varepsilon_{500}$ refer to the high (340) and low energy (500) bands, respectively, in all complexes.
16For spectral changes previously observed during the formation of the ternary complexes, see refs. 5 and 6.
17(a) This suggestion is confirmed unambiguously by the isolation and X-ray structural characterization of [2 : 1] complexes; (b) the energy of the principal band in [2 : 1] complexes is close to that of the low-energy band in [1 : 1] complexes. Due to partial spectral overlapping with the much more intense (high-energy) principal band of the binary complex, it was necessary for the low-energy bands of the [1 : 1] complexes.
nitrosonium complexes with different aromatic donors to be characterized via numerical deconvolution of the spectra of the complexes into the gaussian components. The wavelengths of low-energy absorption bands for the binary \([\text{ArH},\text{NO}]^+\) complexes are (in nm): 425 (BEN), 445 (TOL), 466 (\(o\)-XY), 486 (\(p\)-XY), 484 (MES), 508 (TBB)\(^{18}\).

18For the derivation of eqn. (3), see Experimental section.


20Infrared spectra of the NO changes were not measured owing to the thermal lability of the ternary complexes.

21The accompanying changes in the bond lengths of the ring carbons arising from partial conversion to arene cation radicals were within the precision of the X-ray diffraction data.

22Previous studies also noted that the electronic spectra of ternary complexes were generally similar to their binary counterparts. The presence of higher order species was usually detected only as a deviation of the optical density from the concentration dependence of binary complexes\(^{16}\).


26(a) Benzene is characterized by two degenerate HOMO.\(^{24c,25b}\) Due to symmetry restrictions, only one of them participates in molecular bonding with nitrosonium,\(^{24f}\) while the energy of the second HOMO of the complexed arene is essentially the same as that of the free arene. Note: the aromatic donor HOMO and nitrosonium acceptor LUMO, which do not participate in bonding, are identified in Charts 3 and 4 as dashed lines; (b) alkyl substitution splits the degeneracy of the aromatic HOMO (e.g. the first and second ionization potentials of TOL are 8.83 and 9.36 eV, for \(p\)-XY they are 8.67 and 9.15\(^{25b}\)). Such a splitting, though it is not taken explicitly into account in the simplified MO description presented here (i) represents the difference (~0.5 eV) between the calculated and the observed energy of low-energy band in binary complexes\(^{8}\) and (ii) is responsible for the presence of additional components in the UV–VIS spectra of the ternary complexes\(^{28}\).

27Both bonding and antibonding orbitals in the ternary complexes are centrosymmetric (see Experimental section for their expression as the linear combination of arene and nitrosonium HOMO), and the transitions between such orbitals are symmetry forbidden (see, e.g. R. S. Drago, *Physical Methods in Chemistry*, W. B. Saunders Company, Philadelphia, 1977.) It should be noted that in nitrosonium complexes with cofacial polyaromatic donors,\(^{29}\) the rigid donor structure results in distortion of the chromophore symmetry. This removes the forbidden character of the bonding-to-antibonding transition and leads to an increased intensity of the corresponding (high-energy) absorption bands (S. V. Rosokha, S. V. Lindeman, R. Rathore and J. K. Kochi, manuscript under preparation).
28 Transition from the non-interacting arene HOMO to the antibonding MO is also expected to take place in the same energy range, but with much less intensity (similar to those in the corresponding 1:1 complexes). Indeed, the careful examination of the spectra of the [2:1] complexes reveals that the low-energy bands are composed of (at least) two close-lying bands.


31 G. M. Sheldrick, SHELX-86, Program for Structure Solution; University of Göttingen, Germany, 1986.

32 These crystallographic data are the same as those obtained originally by Brownstein et al., but the use of the modern CCD detector allowed a data set with better resolution to be obtained. This was sufficient to clearly resolve the earlier partial disorder of NO⁺ and to provide the improved geometric parameters listed in Table 2 (CCDC reference number 181218. See http://www.rsc.org/suppdata/p2/b2/b202323g/ for crystallographic files in .cif or other electronic format).


34 All the [1:1] and [2:1] arene complexes with nitrosonium were prepared in dichloromethane solution, as single crystals suitable for X-ray crystallography. However, the [2:1] complex with o-xylene was comprised of a heavily twinned modulated phase, despite numerous attempts under various conditions and temperatures. This unfortunately allowed only general structural features to be established. However, we finally found 1-nitropropane to be a highly desirable solvent for the crystallization of the [2:1] o-xylene complex with nitrosonium at −65 °C at high concentrations of NO⁺SbCl₆⁻ (50 mmol) and o-xylene (> 1000 mmol). The substantially improved quality of the red crystals allowed conventional X-ray structure determination albeit with somewhat limited precision (see Table 2).