

**Molecular Recognition of NO/NO<sup>+</sup> via Multicenter (Charge-Transfer) Binding to Bridged Diarene Donors. Effect of Structure on the Optical Transitions and Complexation Thermodynamics**

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Bridged diarenes form very strong [1:1] complexes with nitrosonium/nitric oxide in which the NO moiety is optimally sandwiched in the cleft between a pair of cofacial aromatic rings which act as a molecular "Venus flytrap". The spectral features of these associates are generally similar to those for [1:1] and [2:1] nitrosonium complexes with mononuclear alkyl-substituted benzenes, and they are appropriately described within the LCAO molecular-orbital methodology and the Mulliken (charge-transfer) formulation of donor/acceptor electronic transitions. The thermodynamics study indicates that the efficient binding is determined by (i) the close matching of the donor/acceptor redox potentials and (ii) the ability of bridged diarenes for multicentered interactions with a single NO moiety. The best fit of the electronic and structural parameters is provided by a calixarene host that allows the interacting centers to be arranged in a manner similar to those extant in [2:1] nitrosonium complexes with analogous (nonbridged) aromatic donors; this results in its very strong noncovalent binding with nitrosonium/nitric oxide with the formation constant of  $K_B \approx 10^8 \text{ M}^{-1}$  and free-energy change of  $-\Delta G^\circ = 45 \text{ kJ mol}^{-1}$ . Such strong, selective, and reversible bindings of nitrosonium/nitric oxide by (cofacial) aromatic centers thus provide the basis for the development of efficient NO sensors/absorbents and also suggest their potential relevance to biochemical systems.

**Introduction**

Supramolecular associations via the noncovalent bonding of various guests to different hosts have drawn increased attention due to their role in molecular recognition, transport, catalysis, sensors, and other nanomolecular devices.<sup>1,2</sup> Such relatively weak bindings generally depend on electrostatic and hydrophobic forces, hydrogen-bond formation, and charge-transfer interactions in which the activation barriers for intermolecular association are essentially nil; as a result, a host capable of multicenter interactions with the guest is often required to ensure maximum selectivity/sensitivity. To consider the latter in the design of supramolecular receptors based on charge-transfer interactions, we now turn to different aromatic hosts for appropriate coordination sites (and their optimal arrangement) to bind various nitrogen oxide guests.

The importance of nitric oxide (NO<sup>•</sup>) in a variety of biochemical systems has resulted in a growing interest

in the kinetics/thermodynamics of binding and release of this small paramagnetic molecule and of its oxidized form, the nitrosonium cation (NO<sup>+</sup>).<sup>3</sup> However, most of the studies heretofore have dealt with transition-metal complexes while the question of the reversible, specific, and efficient binding of NO<sup>•</sup> by organic receptors generally remains open.<sup>4,5</sup>

A suitable entry into this problem was revealed by studies of [1:1] nitrosonium/arene (charge-transfer) complexes [ArH,NO]<sup>+</sup>,<sup>6,7</sup> which showed complete electron

(1) (a) Lehn, J.-M. *Supramolecular Chemistry: Concepts and Perspectives*; VCH: New York, 1995. (b) *Comprehensive Supramolecular Chemistry*; Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Vogtle, F., Lehn, J.-M., Eds.; Pergamon: Oxford, 1996.

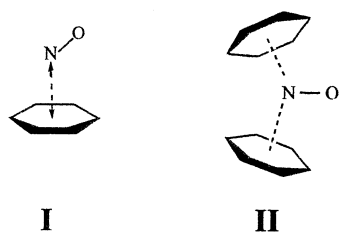
(2) (a) Schneider, H.-J.; Mohammad-Ali, A. K. Receptors for Organic Guest Molecules: General Principles. In *Comprehensive Supramolecular Chemistry*; Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Vogtle, F., Lehn, J.-M., Eds.; Pergamon: Oxford, 1996; Vol. 2, p 69. (b) Whitlock, B. J.; Whitlock, H. W. The Role of the Cavity in the Design of High-efficiency Hosts. In *Comprehensive Supramolecular Chemistry*; Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Vogtle, F., Lehn, J.-M., Eds.; Pergamon: Oxford, 1996; Vol. 2, p 309.

(3) For some recent studies, see: (a) Laverman, L. E.; Ford, P. C. *J. Am. Chem. Soc.* **2001**, *123*, 11614. (b) Laverman, L. E.; Wanat, A.; Oszajca, J.; Stochel, G.; Ford, P. C.; van Eldik, R. *J. Am. Chem. Soc.* **2001**, *123*, 9780. (c) Wolak, M.; Zahl, A.; Schneppensieper, T.; Stochel, G.; van Eldik, R. *J. Am. Chem. Soc.* **2001**, *123*, 285. (d) Andersen, J. F.; Ding, X. D.; Balfour, C.; Shokhireva, T. K.; Champagne, D. E.; Walker, F. A.; Montfort, W. R. *Biochemistry*, **2000**, *39*, 10118. (e) Adachi, H.; Sonoki, H.; Hoshino, M.; Wakasa, M.; Hayashi, H.; Miyazaki, Y. *J. Phys. Chem.* **2001**, *105*, 392. (f) Note that the complete (thematic) issue of *Chemical Reviews* (*Chem. Rev.* **2002**, *102*, 857) is devoted to nitric oxide chemistry.

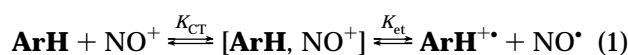
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## CHART 1



delocalization in intermolecular complexes in the half-sandwich structure **I** (Chart 1) due to strong electronic donor/acceptor interactions.<sup>7b</sup> Thus, they are formed (barrierless) either by the binding of nitrosonium cation with various aromatic donors (as delineated by  $K_{CT}$ ) or by nitric oxide with the corresponding aromatic cation radical (as delineated by  $K_{et}$ ) in a set of reversible (coupled) equilibria



where the overall equilibrium constant is  $K_{ET} = K_{CT}K_{et}$  and the Nernst relationship defines the overall free-energy change:  $\Delta G_{ET} = F(E^{\circ}_{ox} - E^{\circ}_{red})$ .<sup>7,8</sup> Moreover, the corresponding [2:1] complexes  $[(\text{ArH})_2, \text{NO}^+]$  were recently found at very high arene concentrations, and X-ray crystallography reveals their overall sandwich structure **II** with the NO moiety interacting with two cofacial arene rings, as illustrated in Chart 1.<sup>9</sup>

Thus, aromatic compounds in which the ability for noncovalent bonding has already been used in the development of a variety of supramolecular hosts<sup>10</sup> appear to be suitable coordinating sites for the binding of nitric oxide/nitrosonium, and the inter-rim connection of several arene groups with a molecular bridge will optimize the chelate effect for effective host/guest interaction. This study was undertaken to clarify the spectral properties of nitrosonium complexes with polynuclear aromatic donors and, most importantly, to determine the structural and electronic factors that control the intermolecular binding.<sup>11</sup> The donor ability of the polynuclear (bridged diarene) donors in Chart 2 was modulated by different

(6) (a) Reents, W. D., Jr.; Freiser, B. S. *J. Am. Chem. Soc.* **1980**, *102*, 271. (b) Brownstein, S.; Gabe, E.; Lee, F.; Tan, L. *J. Chem. Soc., Chem. Commun.* **1984**, 1566. (c) Brownstein, S.; Gabe, E.; Lee, F.; Piotrowski, A. *Can. J. Chem.* **1986**, *64*, 1661. (d) Brownstein, S.; Gabe, E.; Louie, B.; Piotrowski, A. *Can. J. Chem.* **1987**, *65*, 1661. (e) For a recent review, see: Borodkin, G. I.; Shubin, V. G. *Russ. Chem. Rev.* **2001**, *70*, 211.

(7) (a) Kim, E. K.; Kochi, J. K. *J. Am. Chem. Soc.* **1991**, *113*, 4962. (b) Rosokha, S. V.; Kochi, J. K. *J. Am. Chem. Soc.* **2001**, *123*, 8985.

(8) Note that the reduction potential of  $\text{NO}^+$  in dichloromethane is 1.49 V vs SCE.<sup>7b</sup>

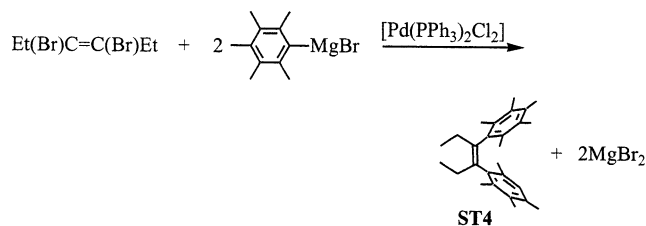
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(10) (a) Hof, F.; Craig, S. L.; Nuckolls, C.; Rebek, J., Jr. *Angew. Chem., Int. Ed.* **2002**, *41*, 1488. (b) Pochini, A.; Ungaro, R. Calixarene and Related Host. In *Comprehensive Supramolecular Chemistry*; Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Vogtle, F., Lehn, J.-M., Eds.; Pergamon: Oxford, 1996; Vol. 2, p 103. (c) Hayashida, O.; Shivanyuk, A.; Rebek, J., Jr. *Angew. Chem., Int. Ed.* **2002**, *41*, 3423. (d) Dougherty, D. S. Cyclophane Hosts: Binding of Lipophilic and Cationic Guests. In *Comprehensive Supramolecular Chemistry*; Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Vogtle, F., Lehn, J.-M., Eds.; Pergamon: Oxford, 1996; Vol. 2, p 195. (e) Odashima, K.; Koga, K. Cyclophane and Related Synthetic Hosts for Recognition and Discrimination of Nonpolar Structures in Aqueous Solutions and at Membrane Surfaces. In *Comprehensive Supramolecular Chemistry*; Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Vogtle, F., Lehn, J.-M., Eds.; Pergamon: Oxford, 1996; Vol. 2, p 143.

numbers of methyl substituents and by varying the dihedral angle  $\varphi$ , in which  $\varphi$  varies from  $\sim 120^\circ$  in the dihydroanthracene analogue **MEA**,  $\varphi \approx 60^\circ$  for the stilbene derivatives **ST1–4**, and  $\varphi \approx 0^\circ$  for the 1,3-alternate calixarene **CAL**.

## Results

The bridged (cofacial) diarenes used in this and related studies<sup>11</sup> were conveniently synthesized in high yields utilizing the palladium-catalyzed cross coupling of readily available 1,2-dibromoalkenes with the desired Grignard reagent, e.g.



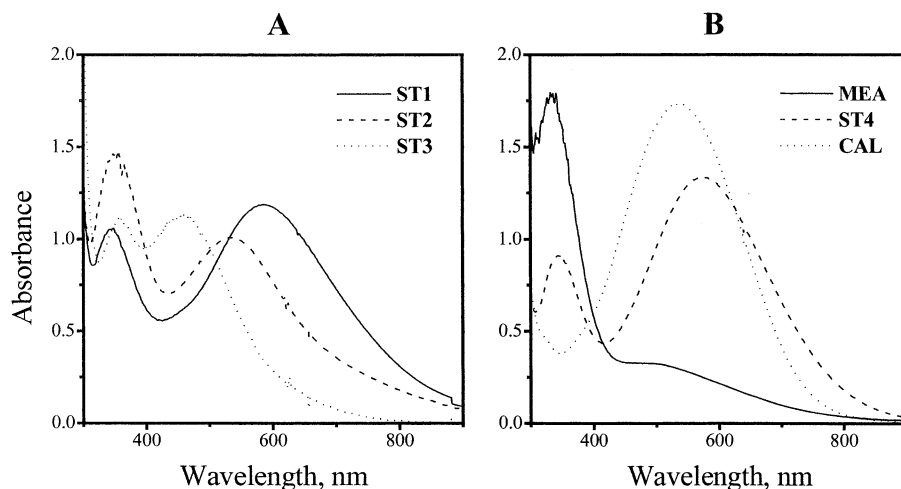
which is based on a versatile process originally described by Kochi and co-workers<sup>12</sup> (for additional details see the Experimental Section).

**1. Spectral (UV–vis) Characterization of  $\text{NO}^+/\text{NO}$  Associations with Various Bridged Diarenes.** Addition of the diarene donors (**Ar<sub>2</sub>** in Chart 2) to 0.1–1.0 mM solutions of the nitrosonium salt  $\text{NO}^+\text{SbCl}_6^-$  in dichloromethane resulted in intense (red-to-violet) colorations. Spectrophotometric analysis revealed the appearance of a pair of absorption bands (Figure 1) with energies similar to those previously observed in cationic nitrosonium complexes with mononuclear alkylbenzenes.<sup>7,9</sup> Two spectral features shown in Figure 1 are especially noteworthy. First, more or less invariant (high-energy) bands were observed in the region  $\lambda_{\text{max}} = 340\text{--}350$  nm. By contrast, the bathochromic shift of the low energy band from  $\lambda_{\text{max}} = 456$  nm (**ST3**), to 535 nm (**ST2**), and to 590 nm (**ST1**) as observed in (Figure 1A) paralleled the increasing donor strengths of the aromatic moieties (see the trend of the oxidation potentials in Table 1).<sup>13</sup> Second, the relative (absorbance) intensity of the high and low energy bands in (Figure 1B) depended on the donor structure and on the relative concentrations of  $\text{NO}^+$ /diarene. For solutions of the stilbenoids **ST1–ST4** containing a large excess of nitrosonium cation (see the dashed spectra in Figure 2), the bands near 340 nm were more intense than those at 500–600 nm (these spectra were quite similar to those previously observed<sup>7</sup> in [1:1] nitrosonium complexes with monoarenes [**ArH**,  $\text{NO}^+$ ]). With increasing concentrations of the diarenes, the absorbance in the 450–550 nm region ( $A_{500}$ ) grew

(11) (a) For a preliminary communication, see: Rosokha, S. V.; Kochi, J. K. *J. Am. Chem. Soc.* **2002**, *124*, 5621. (b) Rathore, R.; Kochi, J. K. *J. Org. Chem.* **1998**, *63*, 8630. (c) Rathore, R.; Lindeman, S. V.; Kochi, J. K. *Angew. Chem., Int. Ed.* **1998**, *37*, 1585.

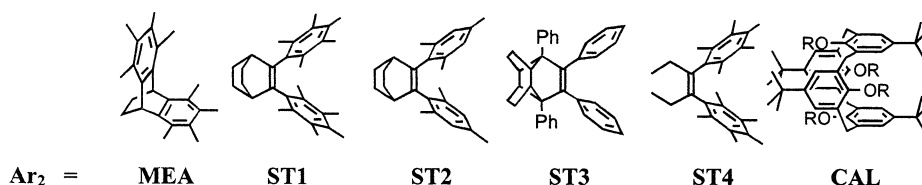
(12) See: (a) Rathore, R.; Kochi, J. K. *Can. J. Chem.* **1999**, *77*, 913 (b) Rathore, R.; Lindeman, S. V.; Kumar, A. S.; Kochi, J. K. *J. Am. Chem. Soc.* **1998**, *120*, 6012. (c) Sun, D.; Lindeman, S. V.; Rathore, R.; Kochi, J. K. *J. Chem. Soc., Perkin Trans. 2* **2001**, 1585. (d) Rathore, R.; Weigand, U.; Kochi, J. K. *J. Org. Chem.* **1996**, *61*, 5246. (e) See also: Rathore, R.; Deselnicu, M. I.; Burns, C. L. *J. Am. Chem. Soc.* **2002**, *124*, 14832.

(13) Mulliken, R. S.; Person, W. B. *Molecular Complexes*; Wiley: New York, 1969.



**FIGURE 1.** UV-vis spectra of various nitrosonium complexes from  $\sim 1$  mM bridged diarenes (as indicated) and  $\sim 0.2$  mM  $\text{NO}^+\text{SbCl}_6^-$  in dichloromethane at  $22^\circ\text{C}$ .

### CHART 2



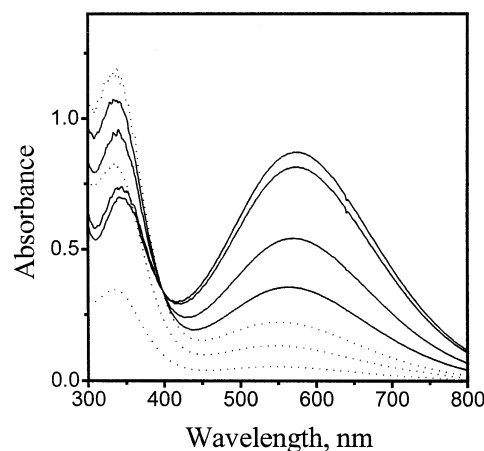
**TABLE 1.** Spectral Data and Equilibrium Constants<sup>a</sup> for  $[\text{Ar}_2\text{NO}]^+$  Complexes

diarene donor	$E_{\text{ox}}^{\circ}$ , V vs SCE	$\lambda$ , nm ( $\epsilon$ , $10^3 \text{ M}^{-1} \text{ cm}^{-1}$ ) <sup>b</sup>	$K_{\text{B}}$ , $\text{M}^{-1}$ <sup>c</sup>	$K_{\text{et}}$ , $\text{M}^c$	$K_{\text{ET}}$	$\nu_{\text{NO}}$ , $\text{cm}^{-1}$ <sup>d</sup>
MEA	1.46	334 (7.8) 510 (1.5)	$1.3 \times 10^6$	$1.7 \times 10^{-6}$	2.1	1900
ST1	1.35	345 (4.6) 590 (5.3)	$1.3 \times 10^7$	$1.3 \times 10^{-5}$	170	1885
ST2	1.45	350 (6.6) 535 (4.5)	$5.0 \times 10^5$	$6.5 \times 10^{-6}$	3.3	1925
ST3	1.55	360 (5.0) 460 (5.1)	<i>e</i>	<i>e</i>	<i>e</i>	1990
ST4	1.47	345 (4.0) 575 (5.8)	$5.0 \times 10^7$	$3.0 \times 10^{-8}$	1.5	<i>e</i>
CAL	1.45	538 (8.5)	$2.0 \times 10^8$	$1.6 \times 10^{-8}$	3.2	1958

<sup>a</sup> In dichloromethane at  $22^\circ\text{C}$ . <sup>b</sup> In parentheses: extinction coefficient ( $\epsilon \pm 0.2 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ ). <sup>c</sup>  $\pm 30\%$ . <sup>d</sup> Stretching frequency. <sup>e</sup> Not measured.

faster than that in the 330–350 nm region ( $A_{340}$ ).<sup>14</sup> Moreover, when the relative concentrations of the reagents were within the range  $1/2[\text{NO}^+]_0 \leq [\text{Ar}_2]_0 \leq [\text{NO}^+]_0$ , the opposite trend in absorbance changes near 500 and 340 nm was observed with increasing diarene concentrations (with a clear isobestic point established in Figure 2). Finally, when the diarene concentration was higher than the nitrosonium concentration ( $[\text{Ar}_2]_0 \geq [\text{NO}^+]_0$ ), the shape of spectra remained rather invariant with further additions of diarene donor (or with temperature variation). As such, the  $A_{340}/A_{500}$  ratio dropped sharply with increasing diarene concentrations from  $A_{340}/A_{500} \approx 7$  at  $[\text{Ar}_2] \ll [\text{NO}^+]$  to  $A_{340}/A_{500} \approx 1$  (when the  $\text{NO}^+$  and diarene concentrations became nearly equimolar), and then the absorbance ratio remained more or less constant (Figure 3).

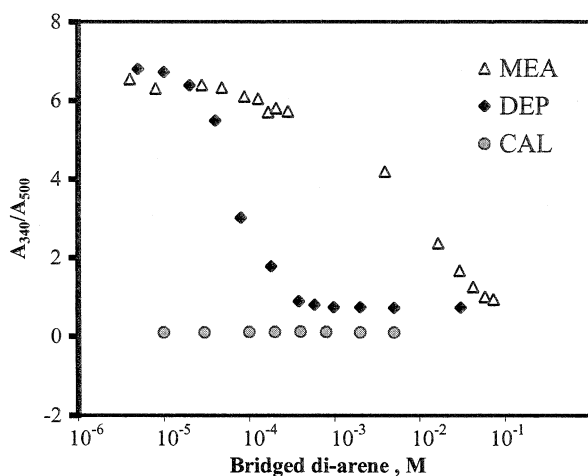
For dichloromethane solutions containing the diarene donors MEA and CAL, the spectral characteristics observed upon changing the relative concentrations of the reagents differed from those obtained with the stilbenoid



**FIGURE 2.** Spectral changes attendant upon the successive addition of the stilbenoid donor ST4 (bottom to top: 0.02, 0.05, 0.08, 0.1, 0.12, 0.13, 0.15 mM) to 0.2 mM  $\text{NO}^+\text{SbCl}_6^-$  in dichloromethane at  $22^\circ\text{C}$  showing the relative (absorbance) increase of the low energy band.

donors ST1–ST4. For example, the decreased (relative) intensity of the high energy band ( $A_{340}/A_{500}$ ) with increas-

(14) For clarity, the absorbances ( $A_{340}$  and  $A_{500}$ ) and extinction coefficients ( $\epsilon_{340}$  and  $\epsilon_{500}$ ) refer to the high (340) and low energy (500) bands, respectively, in all complexes (although the actual maxima of the corresponding bands varied somewhat).



**FIGURE 3.** Dependence of the relative intensity of the high energy and low energy bands ( $A_{340}/A_{500}$ ) on the concentration of various diarenes (as indicated) in dichloromethane solutions containing 0.2 mM of  $\text{NO}^+\text{SbCl}_6^-$  at 25 °C. [Note that the absorbance at 340 nm was taken as that of the high-energy band for  $[\text{CAL}, \text{NO}]^+$  (not observed)].

ing concentrations of the diarene was not as precipitous for the **MEA**/ $\text{NO}^+$  system as that observed with the stilbenoids (see the slopes in Figure 3). By strong contrast, the spectra of the **CAL**/ $\text{NO}^+$  system contained only a single (intense) band at  $\lambda = 538$  nm (Figure 1), and its shape (Figure 3) did not vary with the relative amounts of the reagents (at all concentrations studied).

Since the oxidation potentials of the diarenes (Table 1) are lower than the reduction potential of nitrosonium,<sup>8</sup> their oxidation to the corresponding cation radicals is energetically favorable, and electron transfer was expected to be facile. However, the UV-vis spectra of diarene mixtures with  $\text{NO}^+$  (contained in tightly closed cuvettes) revealed no signs of the presence of cation radicals,<sup>15</sup> and the systems were ESR silent. Moreover, when nitric oxide was deliberately bubbled into solutions of the diarene cation-radical (e.g., **CAL**<sup>+</sup> and **ST4**<sup>+</sup> prepared in situ by the oxidation with  $\text{PbO}_2$ ), the spectral bands of the cation-radicals immediately disappeared, and the spectrum of the resulting solution was the same as that formed by the interaction of nitrosonium and the bridged diarene (in excess).

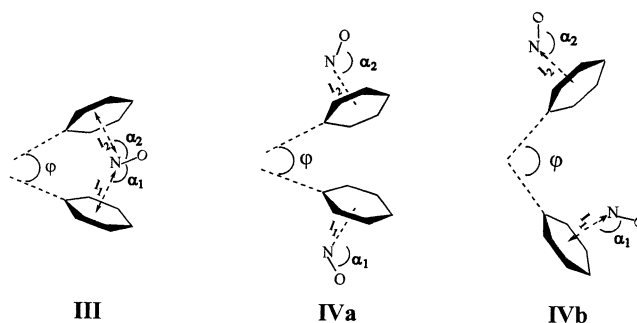
## II. X-ray Crystallography of Diarene Associates with Nitrosonium Acceptor

Spectral characteristics shown in Figures 1 and 2 indicated that (at least) two new species resulted from the interaction of diarenes with nitrosonium. To structurally elucidate these spectral changes, single crystals were grown by the slow diffusion of hexane into dichloromethane solutions containing various amounts of both reagents (see the Experimental Section for details), as follows:

(A) In solutions containing excess diarene, X-ray crystallographic analysis showed that [1:1] complexes of

(15) (a) For example, the stilbenoid cation radicals are characterized by spectral bands with maxima in nm (in parentheses, extinction coefficients in  $10^3 \text{ M}^{-1} \text{ cm}^{-1}$ ): **ST1**<sup>+</sup>, 426 (9.9), 740 (5.7), and 1162 (7.4); **ST2**<sup>+</sup>, 410 (10.1), 681 (4.9), and 1100 (5.4);<sup>12a</sup> **CAL**<sup>+</sup>, band at 450 nm<sup>+</sup>.<sup>15b</sup> (b) Rathore, R.; Lindeman, S. V.; Rao, K. S.; Sun, D.-L.; Kochi, J. K. *Angew. Chem. Int. Ed.* **2000**, *39*, 2123.

**CHART 3**



**TABLE 2.** Selected Bond Lengths, Bond Angles, and Distances for Bis- and Mono-coordinated Complexes of Nitrosonium with Diarenes<sup>a</sup>

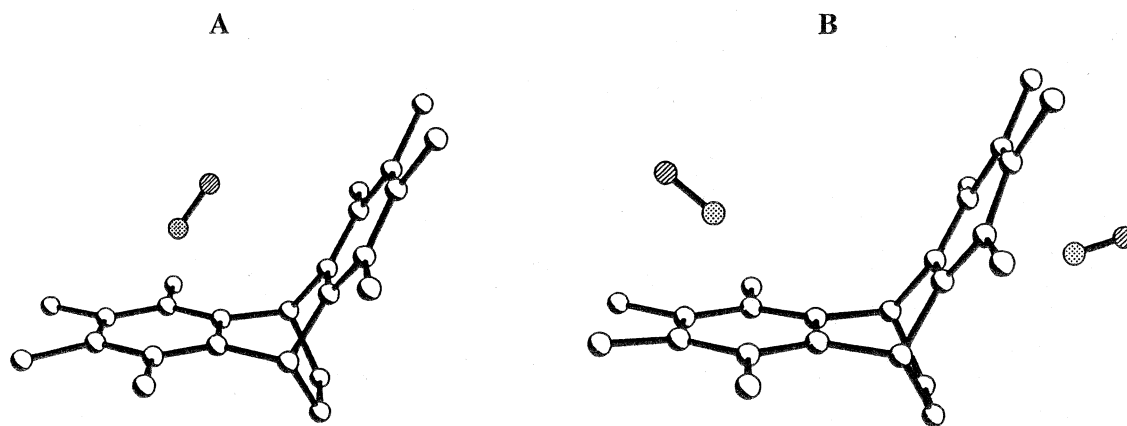
complex	$l_1$	$l_2$	$\alpha_1$	$\alpha_2$	$d_{\text{NO}}^b$	$\varphi$
<b>[MEA, NO]</b> <sup>+c</sup>	2.146	3.104	144.3	84.1	1.098	119.6
<b>[MEA, (NO)<sub>2</sub>]</b> <sup>2+d</sup>	2.106	2.10	138.8	132	1.132, 1.134	117.5
<b>[ST1, NO]</b> <sup>+e</sup>	2.238	2.703	117.8	89.4	1.112	61.1
<b>[ST2, (NO)<sub>2</sub>]</b> <sup>2+f</sup>	2.119	2.119	41.9	41.9	1.108, 1.108	60.0
<b>[ST3, NO]</b> <sup>+g</sup>	2.247	2.751	137.2	89.5	1.087	68.6
<b>[ST4, NO]</b> <sup>+i</sup>	2.901	2.149	87.6	124.4	1.118	63.2
<b>[ST4, (NO)<sub>2</sub>]</b> <sup>2+g</sup>	2.081	2.071	132.7	136.2	1.095, 1.106	68.0
<b>[CAL, NO]</b> <sup>+j</sup>	2.076	2.10 <sup>f</sup>	137.2	134 <sup>h</sup>	1.116, 1.11 <sup>h</sup>	54.8
	2.552	2.552	84.2	84.2	1.084	11.6

<sup>a</sup> Bond length and distances in Å and angles in degrees. For notation of the bond distances and angles, see Chart 3. <sup>b</sup> NO bond length. <sup>c</sup> From ref 11b. <sup>d</sup> Structure **IVb** in Chart 3. <sup>e</sup> From ref 11c. <sup>f</sup> Structure **IVa** in Chart 3. <sup>g</sup> Two units. <sup>h</sup> Disordered. <sup>i</sup> From ref 11a. <sup>j</sup> From ref 15b.

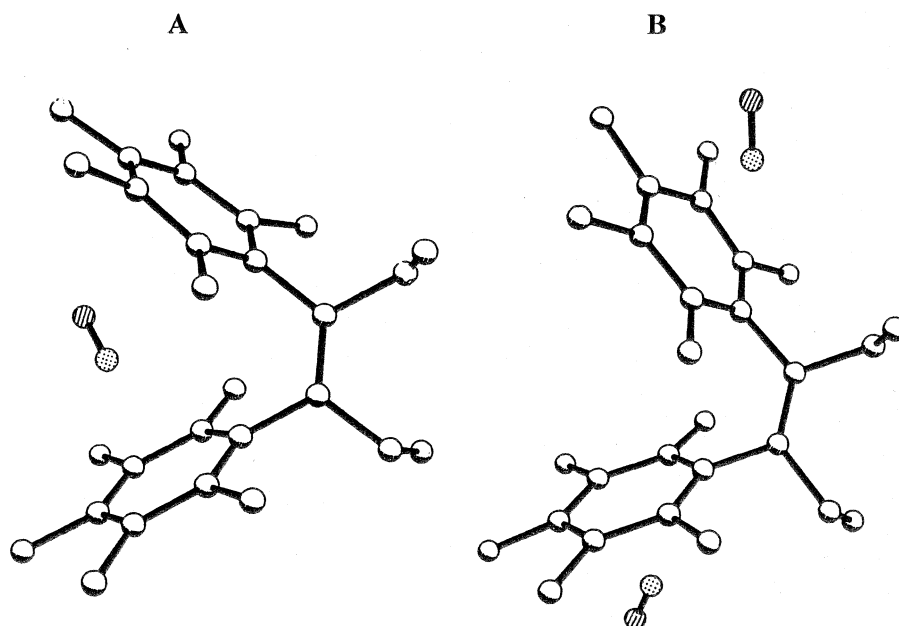
diarene and nitrosonium were formed. In these associates (see Figures 4A and 5A), the NO moiety lies within the narrow cleft formed by a pair of cofacial aromatic rings (see structure **III** in Chart 3). Selected distances and angles characterizing these complexes are presented in Table 2.

In **[MEA,NO]**<sup>+</sup>, the NO moiety sits at an oblique (bent) orientation to one ring and parallel to the other ring at interplanar separations of 2.15 and 3.10 Å, respectively, as illustrated in Figure 4A. With increasing cofacial orientation of the phenyl moieties (e.g., Figure 5A), the distance from the (bent) NO to the benzenoid chromophore is increased in stilbenoids **ST1–4**, but the (parallel) distance to the second ring decreased significantly (see Table 2). In the 1,3-alternate conformer of the *tert*-butyl calix[4]arene (**CAL**), the NO is tightly sandwiched between two parallel rings at a single distance of 2.55 Å, and the flexible angular requirement for NO binding to the aromatic donor allowed its complete encapsulation between the two more or less parallel aromatic rings.<sup>15b</sup>

Complexation of  $\text{NO}^+$  led to significant lengthening of the N–O bonds to lie in the range  $d = 1.09–1.12$  Å, which is intermediate between that of the reduced nitric oxide (1.15 Å) and that of uncomplexed  $\text{NO}^+$  (1.06 Å).<sup>7</sup> We interpret such an N–O bond elongation as diagnostic of extensive electron delocalization between the arene donor and the nitrosonium acceptor, and this conclusion is confirmed by IR spectroscopy. Thus, the energies of the N–O stretching vibrations (Table 1), which are diagnostic of the charge residing on the N–O moiety,<sup>7</sup> are much closer to that of the reduced nitric oxide (1876  $\text{cm}^{-1}$ ) than to that of uncomplexed  $\text{NO}^+$  (2272  $\text{cm}^{-1}$ ),<sup>7</sup> to indicate a



**FIGURE 4.** Molecular structures of the [1:1] bis-coordinated (A) and [1:2] mono-coordinated (B) complexes of nitrosonium with MEA.



**FIGURE 5.** Molecular structures of the [1:1] bis-coordinated (A) and [1:2] mono-coordinated (B) complexes of nitrosonium with ST4.

substantial degree of charge transfer from the aromatic donor to the nitrosonium acceptor.

(B) X-ray structure analysis of crystals obtained from cooled dichloromethane solutions containing a *large excess of the nitrosonium* salt indicated that another type of complex was formed. In these compounds, two nitrosonium cations are bonded to a single diarene donor, with each aromatic ring coordinating one NO group (see Figures 4B and 5B). The position of the nitrosonium cation relative to aromatic rings differed depending on the diarene used (see  $\text{Ar}_2$  structures **IVa** and **IVb** in Chart 3). In the case of MEA (characterized by the largest dihedral angle  $\varphi$  between the aromatic moieties), one of the NO was located inside and the other outside the diarene cleft (Figure 4B). In the complexes with more cofacial aromatic rings, both nitrosonium moieties were located outside the cleft. The structural characteristics of these complexes are also presented in the Table 2. Most interestingly, the calixarene donor yielded only complexes in which the NO group was situated between two benzene

rings (see structure **III**), despite all efforts to obtain type **IVa** and **IVb** complexes.

### III. Spectral and Structural Identification of Different Types of Nitrosonium Complexes with Bridged Diarenes. Equilibrium Constants for Their Formation

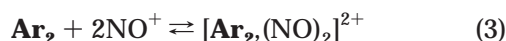
X-ray crystallographic analysis indicated that basically two types of nitrosonium complexes with bridged diarenes ( $\text{Ar}_2$ ) were formed. One of them is the complex in which the NO moiety is situated within the diarene cleft and is bonded to *two* aromatic rings, and such complexes containing a bis-coordinated nitrosonium will be hereafter designated as  $[\text{Ar}_2\text{NO}]^+$ . Structurally, these complexes are reminiscent of the [2:1] complexes of nitrosonium with monoarenes (see structure **II** in Chart 1).<sup>9</sup> Importantly, solid-state electronic spectroscopy (see Figure S1 in the Supporting Information) indicates that bridged diarene complexes with bis-coordinated nitro-

nium are characterized by a high (relative) intensity of the low-energy band (which is also characteristic of [2:1] complexes with mono-arenes<sup>9</sup>). Since such [1:1] diarene complexes  $[\text{Ar}_2, \text{NO}]^+$  were successfully crystallized from solutions containing excess diarene, together with the fact that the spectral features of such solutions corresponded to the solid-state spectra of  $[\text{Ar}_2, \text{NO}]^+$ , we conclude that the prevailing process in those systems with  $[\text{Ar}_2]_0 \geq [\text{NO}^+]_0$  is accurately described by eq 2



where  $K_B$  is the association constant of the diarene donor. Under these conditions, the spectral shape was not affected by either a change in the relative concentration of the reagents (vide supra) or decreasing temperature (from +20 °C to -75 °C) and the absorption intensity depended linearly on the nitrosonium concentration. These observations are consistent with the conclusion that (i) only one type of complex determines the solution absorption, namely  $[\text{Ar}_2, \text{NO}]^+$ , and (ii) the concentration of this complex is essentially equal to the initial concentration of nitrosonium cation,  $[\text{NO}^+]_0$ . As such, the extinction coefficients could be calculated directly from the absorbance intensity and the equilibrium constants of their formation,  $K_B$  (in eq 2), could be determined by the competition method (Table 1, see the Experimental Section for details.)

When the relative concentrations were  $[\text{Ar}_2]_0 < [\text{NO}^+]_0$ , the spectral shapes depended on the relative concentration of reagents (vide supra). In particular, the ratios of the intensities of the high and low energy bands rose with increasing ratios of  $[\text{NO}^+]_0 / [\text{Ar}_2]_0$ . Finally, at  $[\text{NO}^+]_0 \gg [\text{Ar}_2]_0$ , the spectra became similar to those of the [1:1] complexes of monoarenes.<sup>7</sup> Since X-ray crystallographic analysis indicated that two nitrosonium cations are coordinated to the diarene (with each nitrosonium being connected only to one aromatic ring), the acceptor in such complexes will hereinafter be described as monocoordinated nitrosonium and the complex will be designated as:  $[\text{Ar}_2, (\text{NO})_2]^{2+}$ . In addition to the process described by eq 2, there is also the possibility of complex formation in which one nitrosonium is coordinated to one aromatic ring of the diarene (eq 3), and this process will prevail in solutions containing a large excess of nitrosonium salt.



These experimental results indicate that the molecular (X-ray) and electronic (UV-vis) structures of both (aromatic ring/nitrosonium cation) fragments in  $[\text{Ar}_2, (\text{NO})_2]^{2+}$  complexes are similar to those previously measured in [1:1] complexes of nitrosonium with monoarenes.<sup>7</sup> The clear spectral distinction between  $[\text{Ar}_2, (\text{NO})_2]^{2+}$  and  $[\text{Ar}_2, \text{NO}]^+$  allowed us to estimate the equilibrium constants for binding of one nitrosonium with one aromatic ring of the diarene. [Note that highly accurate calculations were precluded owing to the possibility of several variants for coordination; see the Experimental Section for details]. Multiwavelength regression analysis of the spectral changes at different (reagent) concentrations indicated that the formation constants for one-ring coordination are of the order  $10^5 \text{ M}^{-1}$  in the case of the stilbenoid donors

**ST1** and **ST4** as well as **MEA**. In the case of the calixarene donor **CAL**, only two-ring coordination of nitrosonium was observed, vide supra.

## Discussion

To elucidate the specific nitrosonium complexes of various bridged diarenes and the thermodynamics of their formation, let us first consider their diagnostic optical spectra in the light of the analogous characteristics of nitrosonium complexes with monoarenes that were examined previously.

### I. Electronic Structure and Optical Transitions in Nitrosonium Complexes with Bridged Diarenes.

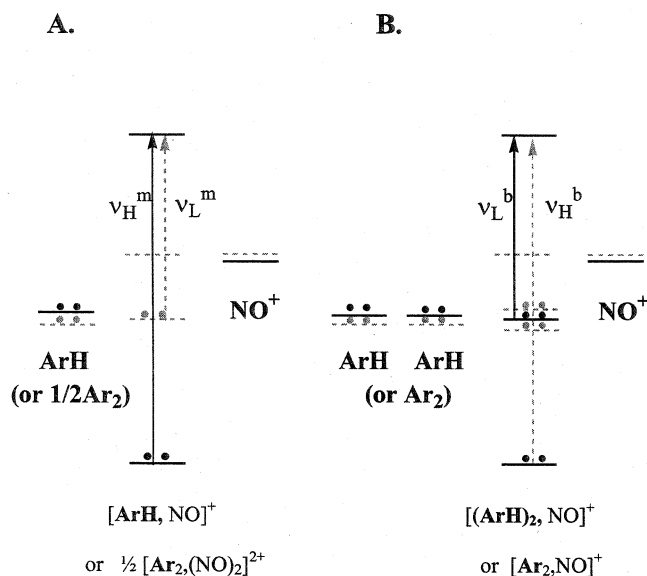
Spectral characteristics of diarene complexes with mono- and bis-coordinated nitrosonium can be theoretically elucidated with the aid of the semiempirical LCAO molecular orbital methodology that was successfully applied previously to [1:1] and [2:1] nitrosonium complexes of monoarenes.<sup>7b,9,16</sup>

The nitrosonium coordination in  $[\text{ArH}, \text{NO}]^+$  and in  $[\text{Ar}_2, (\text{NO})_2]^{2+}$  results from the donor/acceptor interaction of the frontier orbitals, i.e., the HOMO of the arene and the LUMO of  $\text{NO}^+$ , as qualitatively illustrated in the molecular orbital diagrams in Figure 6 (see the Supporting Information for details).<sup>17</sup> The intense high-energy band ( $\nu_{\text{H}}^{\text{m}}$ ) corresponds to the transition from the bonding-to-antibonding molecular orbitals shown in Figure 6A. The second, low energy band ( $\nu_{\text{L}}^{\text{m}}$ ) recognizes the fact that the arene HOMO is degenerate. Due to symmetry reasons, the second HOMO does not strongly interact with  $\text{NO}^+$ , and the spectral intensity of the electronic transition from the noninteracting to antibonding orbital ( $\nu_{\text{L}}^{\text{m}}$ ) is relatively low.<sup>7</sup>

The [2:1] nitrosonium complexes with monoarenes  $[(\text{ArH})_2, \text{NO}]^+$  and diarene complexes with bis-coordinated nitrosonium  $[\text{Ar}_2, \text{NO}]^+$  result from the interaction of the nitrosonium LUMO with the arene HOMOs of the two aromatic rings,<sup>9</sup> which leads to the three types of molecular orbitals (bonding, nonbonding, and antibonding) presented in Figure 6B. As a result, there are two electronic transitions that are labeled ( $\nu_{\text{L}}^{\text{b}}$ ) for nonbonding-to-antibonding and ( $\nu_{\text{H}}^{\text{b}}$ ) for bonding-to-antibonding. The energies of these transitions are similar to those of the corresponding bands in [1:1] complexes  $[\text{ArH}, \text{NO}]^+$ .<sup>9</sup> It should be noted, however, that different symmetry restrictions leads to different relative intensities of the low and high energy absorption bands in [1:1] and [2:1]

(16) (a) Hückel, E. *Grundzüge der Theorie ungesättigter and Aromatischer Verbindungen*; Verlag Chemie, G.m.b.H.: Berlin, 1938. (b) Flurry, R. L., Jr. *Molecular Orbital Theories of Bonding in Organic Molecules*; Marcel Dekker: New York, 1968. (c) Jorgensen, W. L.; Salem, L. *The Organic Chemist's Book of Orbitals*; Academic Press: New York, 1973. Dewar, M. J. S.; Dougherty, R. C. *The PMO Theory of Organic Chemistry*; Plenum Press: New York, 1975. (e) Carroll, F. A. *Perspectives on Structure and Mechanism in Organic Chemistry*; Brooks/Cole Publishing Co.: New York, 1998. (f) Rauk, A. *Orbital Interaction Theory of Organic Chemistry*; Wiley: New York, 1994. For the application of LCAO molecular orbital methodology to charge-transfer complexes, see: (g) Flurry, R. L. *J. Phys. Chem.* **1965**, *69*, 1927. (h) Flurry, R. L. *J. Phys. Chem.* **1969**, *73*, 2111. (i) Flurry, R. L. *J. Phys. Chem.* **1969**, *69*, 2787.

(17) (a) Fleming, I. *Frontier Orbitals and Organic Chemical Reactions*; Wiley: New York, 1976. (b) Traven, V. F. *Frontier Orbitals and Properties of Organic Molecules*; Ellis Horwood: New York, 1992. (c) Klopman, G. *J. Am. Chem. Soc.* **1968**, *90*, 223. (d) Fukui, K. *Acc. Chem. Res.* **1971**, *4*, 57. (e) Fukui, K. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 801.



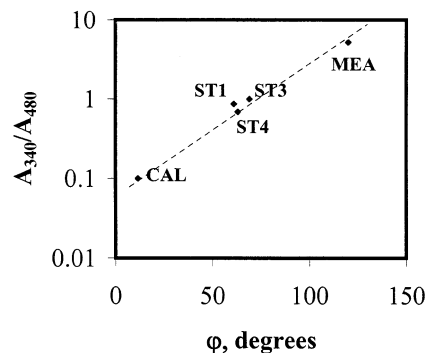
**FIGURE 6.** Molecular-orbital diagrams for the charge-transfer complexes of (A) mono-coordinated ( $[\text{ArH}, \text{NO}]^+$  and  $[\text{Ar}_2, (\text{NO})_2]^{2+}$ ) and (B) bis-coordinated ( $[(\text{ArH})_2, \text{NO}]^+$  and  $[\text{Ar}_2, \text{NO}]^+$ ) nitrosonium complexes showing the interactions of the arene HOMO and nitrosonium acceptor LUMO. Note: Orbitals that do not participate in the CT interactions and the forbidden electronic transitions (for symmetry reasons) are shown in gray.

charge-transfer complexes of monoarenes.<sup>9,18</sup> The same restrictions also apply to bridged diarene complexes with mono- and bis-coordinated nitrosonium. Let us first take the intense high energy bands in [1:1]  $[\text{ArH}, \text{NO}]^+$  complexes (labeled  $\nu_{\text{H}}^{\text{m}}$  in Figure 6A) as the basis for comparison and then consider the intensities of the low and high energy bands ( $\nu_{\text{L}}^{\text{b}}$  and  $\nu_{\text{H}}^{\text{b}}$  in Figure 6B) in complexes with bis-coordinated nitrosonium [i.e.,  $[(\text{ArH})_2, \text{NO}]^+$  and  $[\text{Ar}_2, \text{NO}]^+$ ] relative to those of  $\nu_{\text{H}}^{\text{m}}$ . [Note that the low energy band  $\nu_{\text{L}}^{\text{m}}$  in  $[\text{ArH}, \text{NO}]^+$  is weak relative to  $\nu_{\text{H}}^{\text{m}}$ , vide supra]. There is no symmetry restriction for the nonbonding-to-antibonding electronic transition in complexes with bis-coordinated nitrosonium  $[(\text{ArH})_2, \text{NO}]^+$ <sup>9</sup> since this originates from the molecular orbitals of the complex formed by nitrosonium and arene orbitals with appropriate (interaction) symmetries. Therefore, the intensity of low-energy bands in the complexes with bis-coordinated nitrosonium (see  $\nu_{\text{L}}^{\text{b}}$  in Figure 6B) were previously estimated<sup>9,18</sup> to be similar (or somewhat higher) in energy relative to those of  $\nu_{\text{H}}^{\text{m}}$ . Experimental measurements confirm such a prediction both in [2:1] complexes of monoarenes  $[(\text{ArH})_2, \text{NO}]^+$ <sup>9</sup> and in diarene complexes with bis-coordinated nitrosonium  $[\text{Ar}_2, \text{NO}]^+$ .

The high energy band  $\nu_{\text{H}}^{\text{b}}$  in bis-coordinated nitrosonium  $[\text{Ar}_2, \text{NO}]^+$  and  $[(\text{ArH})_2, \text{NO}]^+$  corresponds to the bonding-to-antibonding transition (Figure 6B), and it is symmetry forbidden in centrosymmetric ternary complexes.<sup>18a,19</sup> Therefore, the  $\nu_{\text{H}}^{\text{b}}$  is predicted to be very weak

(18) (a) Buduka, M. F.; Sokolov, N. D. *Spectrochim. Acta Part A* **1995**, *51*, 2379. (b) In complexes with bis-coordinated nitrosonium, there are also transitions from the noninteracting orbitals of the arene to the antibonding molecular orbital; but they are expected to be much less intense (similar to the low-energy bands  $\nu_{\text{L}}$  in 1:1 complexes) and are overshadowed by the nonbonding-to-antibonding transition.

(19) Drago, R. S. *Physical Methods in Chemistry*; W. B. Saunders Co.: Philadelphia, 1977.

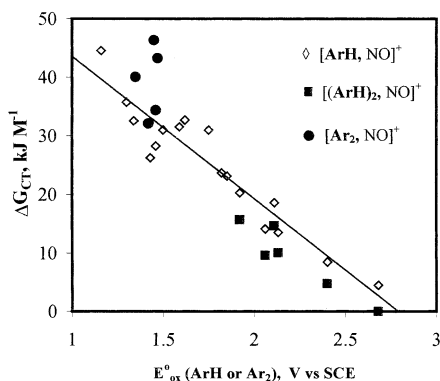


**FIGURE 7.** Correlation of the of the relative extinction coefficient of the high and low energy bands  $A_{340}/A_{500}$  and the dihedral angle between aromatic rings in bis-coordinated nitrosonium complexes with diarenes [for **CAL**, the absorbance near 340 nm was taken as the high-energy band (not observed)].

relative to  $\nu_{\text{H}}^{\text{m}}$  (and to  $\nu_{\text{L}}^{\text{b}}$ ). Accordingly, only the intense band around 500 nm is experimentally observed in [2:1] complexes of nitrosonium with monoarenes,  $[(\text{ArH})_2, \text{NO}]^+$ .<sup>9</sup> Of the diarene complexes with bis-coordinated nitrosonium  $[\text{Ar}_2, \text{NO}]^+$ , only the spectrum of  $[\text{CAL}, \text{NO}]^+$  (with one intense band near 530 nm) is similar to the spectra of  $[(\text{ArH})_2, \text{NO}]^+$ . In complexes of the other diarenes (**ST1–ST4** and **MEA**) with bis-coordinated nitrosonium  $[\text{Ar}_2, \text{NO}]^+$ , the intensity of  $\nu_{\text{H}}^{\text{b}}$  is comparable to that of  $\nu_{\text{L}}^{\text{b}}$  (Table 1).

The ratio of the intensities of the high to low energy bands is closely related to the dihedral angle  $\varphi$  between the aromatic rings—the increase of  $\varphi$  being accompanied by a corresponding increase in the relative intensity of the high-energy band as seen in Figure 7. This leads to the conclusion that two symmetry-related factors determine the spectral features of the  $[\text{Ar}_2, \text{NO}]^+$  in the following way: First, the low-energy bands  $\nu_{\text{L}}^{\text{b}}$  are intense, since they are allowed in [2:1] charge-transfer complexes. Second, although the high energy bands  $\nu_{\text{H}}^{\text{b}}$  are forbidden in the [2:1] centrosymmetric complexes, their increased intensities in the structurally similar  $[\text{Ar}_2, \text{NO}]^+$  are related to the weakening symmetry restrictions with the distortion of the chromophore as determined by the geometric characteristics of relatively rigid diarene (see the structural features in Table 2). Thus, in  $[\text{CAL}, \text{NO}]^+$ , the nitrosonium is situated between nearly parallel aromatic rings with the same nitrosonium-to-ring separations. Accordingly, the chromophore is practically centrosymmetric, the bonding-to-antibonding transition is forbidden, and the intensity of the high energy band is negligible. The angular increase between the aromatic rings in **ST1–ST3** and **MEA** results in the distortion of the chromophore symmetry and in the intensity increase of  $\nu_{\text{H}}^{\text{b}}$ .

**II. Chelate Effect in Charge-Transfer Complexes of Nitrosonium with Aromatic Donors.** Complex formation of bridged diarenes with nitrosonium leads to exceptionally high  $K_{\text{B}}$  constants (Table 1) that are a characteristic of the equilibrium in eq 2. The values of  $K_{\text{B}} = 10^6$ – $10^8 \text{ M}^{-1}$  are several orders of magnitude higher than those observed for charge-transfer complexes of mono-arenes with nitrosonium with  $K_{\text{CT}} = 10^1$ – $10^5 \text{ M}^{-1}$



**FIGURE 8.** Dependence of the free-energy change ( $\Delta G_{CT}$ ) for complex formation on the oxidation potential of the aromatic donor ( $E_{ox}^{\circ}$ ) for various types of arene/ $\text{NO}^+$  complexes (as indicated).

<sup>7</sup> and other organic acceptors with  $K_{CT} = 10^0\text{--}10^2 \text{ M}^{-1}$ .<sup>20</sup> To understand how such strong bindings of nitrosonium with diarenes occur (and to determine principal factors affecting such a binding), let us compare the free-energy change of this process relative to that for the nitrosonium complexation of monoarenes.<sup>21</sup> (The choice of the abscissa in Figure 8 is determined by the fact that the oxidation potential of monoarenes is a critical factor affecting the stability of nitrosonium complexes.<sup>7</sup>)

The equilibrium constants for the formation of [2:1] complexes of nitrosonium with the alkylbenzenes are 4–7 times smaller than the corresponding values for [1:1] complexes with the same donors.<sup>9</sup> [Such a behavior also corresponds to previously published data for other types of donor/acceptor complexes.<sup>22</sup>] Figure 8 shows that the free energy change  $-\Delta G_{CT}$  for [2:1] complexes is decreased by roughly 1 kcal/mol relative to those of [1:1] complexes with the same donor. In other words, the binding of the second monoarene to nitrosonium is energetically unfavorable relative to the first. Such an unfavorable coordination of the second arene is related to loss of entropy associated with the three-particle complexation, which is not fully compensated by the enthalpy gain.<sup>23</sup> On the other hand, the equilibrium constants for complex formation of nitrosonium with diarenes are substantially higher (up to several orders of magnitude) than those for structurally similar [1:1] complexes. For the appropriate comparison of nitrosonium coordination of mono- and diarenes, the oxidation potential of the donors should be taken into account. The

effect of the presence of two connected coordination centers is most clear when nitrosonium coordination with bridged diarenes is considered relative to the trend line (showing the dependence of  $-\Delta G_{CT}$  on  $E_{ox}^{\circ}$ ) established for the coordination of monoarenes. Figure 8 shows that the coordination of nitrosonium with diarenes is generally more favorable (up to 4 kcal mol<sup>-1</sup> for **CAL**) than the [1:1] complexation with monoarenes. It is noteworthy that the equilibrium constant for nitrosonium coordination to one ring of the diarene donor affords values of the same order,  $K_{CT} = 10^5 \text{ M}^{-1}$ , as the [1:1] complexation of a monoarene with a similar oxidation potential. Thus, the free energy gain for diarene complexation with (bis-coordinated) nitrosonium  $[\text{Ar}_2, \text{NO}]^+$  is substantially higher than that for [2:1] complexes with monoarenes (with similar structural and electronic properties). This conclusion supports the importance of the chelate effect—as manifested both in the enthalpy gain from multibond formation as well as the entropy loss from one-ligand coordination.<sup>24</sup>

**III. Thermodynamic and Structural Criteria for Nitric Oxide/Nitrosonium Molecular Recognition by the Cofacial Disposition of Aromatic Groups in Bridged Diarenes.** The experimental results indicate that  $[\text{Ar}_2, \text{NO}]^+$  complexes are spontaneously formed via the binding of nitrosonium with arene donors or the equivalent binding of nitric oxide with their cation radicals owing to coupled equilibria in eq 4



which is similar to that of monoarenes depicted in eq 1, where the overall equilibrium constant is  $K_{ET} = K_B K_{et}$ . The linear plot in Figure 8 shows the direct relationship of the free-energy change ( $-\Delta G_{CT}$ ) for complex formation with the oxidation potential ( $E_{ox}^{\circ}$ ) of various monoarene donors. Most importantly, consideration of the three-state equilibria in eqs 1 and 4 indicates that those systems with weak arene donors ( $E_{ox}^{\circ} > 1.5 \text{ V}$ ) favor the diamagnetic reagents (**ArH** and  $\text{NO}^+$ ). By contrast, the relatively electron-rich donors ( $E_{ox}^{\circ} < 1.5 \text{ V}$ ) favor the equilibrium shift to the paramagnetic species (**ArH**<sup>•+</sup> and  $\text{NO}^{\bullet}$ ), and the charge-transfer complex is only observed at low temperatures.<sup>25</sup> Complex formation is optimized at the isergonic point, and this has been theoretically confirmed by the LCAO molecular orbital description of the charge-transfer complex showing the occurrence of maximum electronic (donor/acceptor) coupling when  $E_{ox}^{\circ}(\text{arene}) \approx E_{red}^{\circ}(\text{NO}^+) = 1.5 \text{ V vs SCE}$ .<sup>7</sup> Thus, the best choice for nitrosonium/nitric oxide complexation based solely on *electronic* factors lies with aromatic donors having  $E_{ox}^{\circ} \approx 1.5 \text{ V}$ , and this requirement is satisfied by the bridged

(20) (a) Foster, R. *Organic Charge-Transfer Complexes*; Academic: New York (b) Briegleb, G. *Electronen-Donator-Acceptor Komplexe*; Springer: Berlin, 1961. (c) Andrews, L. J.; Keefer, R. M. *Molecular Complexes in Organic Chemistry*; Holden-Day: San-Francisco, 1964. (d) For a recent update on aromatic donors, see: Rosokha, S.; Kochi, J. K. In *Modern Arene Chemistry*; Astruc, D., Ed.; VCH—Wiley: New York, 2002; Chapter 13, pp 435 ff.

(21) Note that the free energy change for complex formation ( $\Delta G_{CT} = -RT \ln K$ ) is considered instead of the equilibrium constant to allow direct comparison with different donor/acceptor stoichiometries.

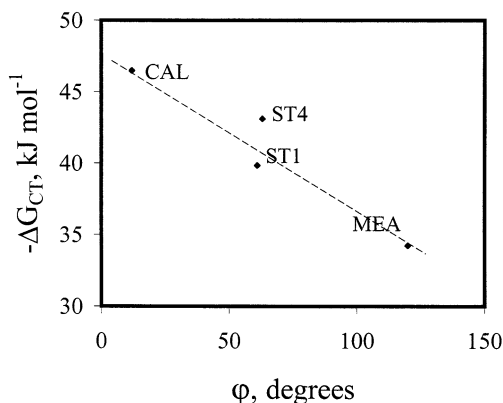
(22) (a) Gribaudo, M. L.; Knorr, F. J.; McHale, J. L. *Spectrochim. Acta* **1985**, *41A*, 419. (b) Dodson, B.; Foster, R.; Bright, A. A. S.; Foreman, M. I.; Gorton, J. *J. Chem. Soc. B* **1971**, 1283. (c) Merriam, M. J.; Rodriguez, R.; McHale, J. L. *J. Phys. Chem.* **1987**, *91*, 1058.

(23) The energy (enthalpy) gain of [1:1] and [2:1] complexes is mainly connected with the relocation of *two* electrons initially residing on the donor orbital to lower-lying molecular orbitals of the complex. The second electron pair in [2:1] complexes resides on the nonbonding orbital.

(24) For the thermodynamics of the chelate effect, see: Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley: New York, 1988.

(25) (a) Note that similar to monoarene systems,<sup>7b</sup> if the diarene is characterized by a relatively low oxidation potential, the equilibrium in eq 4 is shifted (at room temperature) to the aromatic cation radical and nitric oxide. Complex formation is favored only at low temperatures. For example, the addition of nitric oxide to the stilbenoid donor similar to **ST1** but with two 1,4-dimethoxy-3-methylphenyl aromatic rings ( $E^{\circ} = 1.0 \text{ V vs SCE}$ ) results at room temperature in the formation of the cation radical (with  $\lambda_{max} = 460 \text{ nm}$ ). Cooling the solution to  $-80 \text{ }^{\circ}\text{C}$  leads to an equilibrium shift toward the nitrosonium complex (with  $\lambda_{max}$  at 380 and 780 nm). (b) For the **ST1** and **ST4** systems, the equilibrium in eq 4 can be shifted to the cation radical simply by the removal of  $\text{NO}^{\bullet}$  in vacuo.





**FIGURE 9.** Dependence of free-energy change for complex formation on the dihedral angle  $\varphi$  between aromatic ring planes in diarene complexes  $[\text{Ar}_2\text{NO}]^+$ .

diarenes in Table 1. Since Figure 8 shows that the free-energy gain upon complex formation is much higher with diarenes than those with monoarenes of comparable  $E^\circ_{\text{ox}}$ , it is clear that *structural* factors must also be evaluated.

Previously published results indicate that the presence of bulky aromatic substituents (which prevent the optimal approach of nitrosonium to the donor) decreases the efficiency of the arene/nitrosonium complexation.<sup>7</sup> Diarenes provide aromatic moieties that are efficient for coordination, but in order to maximize the chelating effect the multidentate ligand must also be organized in such a way that the coordinating (NO) center is encapsulated with minimal (distortional) penalty. We thus note that NO lies within the undistorted calixarene complex  $[\text{CAL}, \text{NO}]^+$  equidistant from the cofacial aromatic planes at a distance of  $d = 2.55 \text{ \AA}$ . Such a distance is close to those established by the X-ray structures of the [2:1] complexes of toluene ( $d = 2.5 \text{ \AA}$ ) and *o*-xylene ( $d = 2.6 \text{ \AA}$ ),<sup>9</sup> where the arrangement of both donors is not restricted by the connecting bridge or steric hindrance. Thus, the relatively flexible structure of calixarene allows a nearly optimal arrangement of coordinating sites, and as a result, **CAL** forms the most stable NO complex (Table 1). In the other diarene complexes, the dihedral angle  $\varphi$  is not optimum and the two distances are nonequivalent, indicating that the second bond provides some additional free-energy gain, but the rather rigid structures of the stilbenoid ligands (**ST1–4**) as well as that of the dihydroanthracene analogue **MEA** do not allow optimal placement of the aromatic ring for NO binding. (For example,  $d = 2.15$  and  $3.10 \text{ \AA}$  in  $[\text{MEA}, \text{NO}]^+$ ,  $d = 2.24$  and  $2.70 \text{ \AA}$  in  $[\text{ST1}, \text{NO}]^+$ , and  $d = 2.15$  and  $2.90 \text{ \AA}$  in  $[\text{ST4}, \text{NO}]^+$  shown in Table 2.) Therefore, complexes of these diarenes with nitrosonium are weaker, as illustrated in Figure 9.

The nearly ideal fit of the bridged diarenes to the  $\text{NO}/\text{NO}^+$  requirements (both from the electronic and structural points of view) ensure the specific molecular recognition of the guest by the cofacial aromatic host,<sup>26</sup> as well as their strong noncovalent binding with free-energy gains of up to  $45 \text{ kJ/mol}$ . Since the oxidation potentials of diarenes are close to the reduction potential of nitrosonium, nearly the same free energy gain takes place at complex formation starting from either the nitrosonium/diarene dyad or the nitric oxide/cation radical dyad. Selective (tight) binding, together with the distinctive and intense coloration of resulting complexes,

allows an NO sensor to be designed on the basis of the coupled equilibria in eq 4. For example, colorless (dichloromethane) solutions of either **CAL** or **ST4** with some added oxidant (e.g.,  $\text{PbO}_2$  or  $\text{Et}_3\text{OSbCl}_6$ ) persist unchanged for prolonged periods.<sup>11d,27</sup> However, immediately upon the exposure to nitric oxide (gas), the colorless solutions take on an intense purple coloration (Figure S2A in the Supporting Information) diagnostic of the diarene complexes (Figure S3 in the Supporting Information). The same color change is observed in the solid state with a mull prepared as an intimate mixture of **CAL** and  $\text{PbO}_2$ . Exposure of such a coated (pale gray) alumina plate to nitric oxide produces the dramatic color change (Figure S2B in the Supporting Information) that is completely reversible simply by NO entrainment with a mild air stream or upon evacuation.

### Summary and Conclusion

Cofacial (polynuclear) aromatic compounds form strong and highly colored complexes with nitrosonium in which the acceptor is coordinated to one or two aromatic rings (depending on the reactants ratio). The spectral features of such complexes are described by the same LCAO molecular orbital methodology used for the [1:1] and [2:1] nitrosonium complexes with alkyl-substituted benzenes, when the distortion of chromophore (symmetry) effects from the relatively rigid structure of the di-arene is specifically taken into account. The study of the thermodynamics of nitrosonium/nitric oxide complexation with aromatic compounds allows us to conclude that several factors are important for the most efficient donor/acceptor complexation, namely (a) the oxidation potential of the aromatic donor should be close to the reduction potential of the acceptor, (b) the chelation coordination sites consist mononuclear aromatic donors without numerous bulky substituents, and (c) the chelation via multicentered binding provides additional energy gain in complexation, the most efficient allowing the suitable arrangement of coordination sites as those extant in (similar) nonconnected ligands. Bridged diarenes (especially **CAL** with the requisite flexibility to allow optimal bis-coordination) satisfy these requirements and result in strong noncovalent binding between  $\text{ArH}/\text{NO}^+$  and  $\text{ArH}^+/\text{NO}^\bullet$  dyads. Such a strong and selective host/guest interaction together with distinct and intense coloration of the resulting complexes allows an NO sensor to be designed on the basis of the coupled equilibria in eq 4. Strong and reversible binding of  $\text{NO}^+/\text{NO}^\bullet$  by cofacial arene centers (comparable to those in transition-metal coordination complexes<sup>3</sup>) auger well for their consideration in biochemical systems.

### Experimental Section

**Materials.** Nitrosonium hexachloroantimonate was prepared from  $\text{SbCl}_5$  and  $\text{NOCl}$  according to the literature

(26) Note that no noticeable complex formation between diarene and other acceptors (such as tetracyanoethylene, tetracyanoquinodimethane, dichlorodicyanobenzquinone) are known.<sup>20</sup> The problem is related to the apparent mismatch of the diarene cavity to the requirements of the guest.

(27) (a) Particularly in nonaqueous solutions. (b) Note that this procedure circumvents the kinetic lability of arene cation radicals. (c) From the results in Table 1 (eq 2), we estimate the intrinsic NO sensitivity to be  $\sim 1 \mu\text{M}$  on the basis of a spectrophotometric resolution of 0.01 in the optical density; but for a solid-state device, the practical sensitivity will depend on its design, particularly for application to an aqueous environment.

procedure.<sup>7a</sup> Hexamethylbenzene was purified by repeated recrystallization from ethanol. The synthesis of the stilbenoids **ST1–ST4** and the 1,3-alternate conformer of *tert*-butylcalix-[4]arene methyl ether were described previously<sup>12,15b,28</sup>. The permethylated 9,10-dihydro-9,10-ethanoanthracene<sup>29a</sup> donor **MEA** was obtained by repeated bromomethylation<sup>29b</sup> followed by hydrodebromination with lithium aluminum hydride: yield 92%; mp 211–213 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.79 (br s, 4H), 2.28 (s, 12H), 2.49 (s, 12H), 5.11 (s, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 15.5, 16.7, 25.6, 36.9, 127.4, 131.7, 140.1; GC–MS *m/z* 318 (M<sup>+</sup>), 318 calcd for C<sub>24</sub>H<sub>30</sub>. Anal. Calcd for C<sub>24</sub>H<sub>30</sub>: C, 90.51; H, 9.49. Found: C, 90.32; H, 9.21. Dichloromethane, hexane, and acetonitrile were purified according to standard laboratory procedures<sup>30</sup> and were stored in Schlenk flasks under an argon atmosphere. UV–vis, FT-IR, and NMR spectrometers used as well as electrochemical apparatus and the procedure for the determination of the oxidation potentials have been described elsewhere.<sup>7</sup> All operations were performed in an inert atmosphere box in Teflon-capped cuvettes equipped with a sidearm.

**General Procedure for the Preparation of Nitrosonium Complexes with Bridged Diarenes.** For the preparation of the diarene complexes with bis-coordinated nitrosonium [Ar<sub>2</sub>,NO]<sup>+</sup>, a 50-mL flask fitted with a Schlenk adapter was charged with nitrosonium salt (0.05–0.1 mmol NO<sup>+</sup>SbCl<sub>6</sub><sup>-</sup>), together with the slight 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 –70 °C. During the course of 3–7 days, dark red-violet crystals of the complex [Ar<sub>2</sub>,NO]<sup>+</sup>SbCl<sub>6</sub><sup>-</sup> were formed. Crystal data for these complexes are presented below. To prepare the diarene complexes with monocoordinated nitrosonium, [Ar<sub>2</sub>(NO)]<sup>2+</sup>, a 50-mL flask fitted with a Schlenk adapter was charged with nitrosonium salt (0.1–0.2 mmol) and then anhydrous dichloromethane (10 mL) was added under an argon atmosphere. After dissolution of nitrosonium, the solution was cooled to –30 or –40 °C, and the solution of the aromatic donor (0.01–0.02 mmol) was added. The brown solutions were layered with dry hexane (30 mL) and very slowly cooled to –70 °C. During the course of 3–7-days, dark brown crystals of the complex [Ar<sub>2</sub>(NO)<sub>2</sub>]<sup>+</sup>(SbCl<sub>6</sub><sup>-</sup>)<sub>2</sub> were deposited.

**X-ray Crystallography.** The intensity data for all the compounds were collected with the aid of a Siemens SMART diffractometer equipped with a CCD detector using Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) at –150 °C, unless otherwise specified. The structures were solved by direct methods<sup>31</sup> and refined by full-matrix least-squares procedures with IBM Pentium and SGI O<sub>2</sub> computers. (Note that the X-ray structure details of various compounds mentioned here are on deposit and can be obtained from Cambridge Crystallographic Data Centre, Cambridge, U.K., and are also available in CIF format in the Supporting Information.) [**MEA**,(NO)<sub>2</sub>]<sup>2+</sup>(SbCl<sub>6</sub><sup>-</sup>)<sub>2</sub> CH<sub>2</sub>Cl<sub>2</sub>: formula C<sub>25</sub>H<sub>32</sub>Cl<sub>14</sub>N<sub>2</sub>O<sub>2</sub>Sb<sub>2</sub>, MW 1132.33, triclinic *P*-1, *a* = 10.8602(5) Å, *b* = 13.1116(6) Å, *c* = 14.8897(6) Å,  $\alpha = 77.221(1)^\circ$ ,  $\beta = 83.298(1)^\circ$ ,  $\gamma = 81.585(1)^\circ$ , *V* = 2037.6(1) Å<sup>3</sup>, *D<sub>c</sub>* = 1.846 g cm<sup>-3</sup>, *Z* = 2,  $\mu = 2.272$  mm<sup>-1</sup>. The total number of reflections measured were 28 321 of which 17 207 reflections were independent (*R*<sub>int</sub> = 0.0276). Final residuals were *R*1 = 0.0397 and *wR*2 = 0.0902 for 11 406 reflections with *I* > 2 $\sigma$ (*I*). [**ST2**, (NO)<sub>2</sub>]<sup>2+</sup>(NO<sup>-</sup>)<sub>2</sub>(SbCl<sub>6</sub><sup>-</sup>)<sub>4</sub>: formula C<sub>28</sub>H<sub>36</sub>Cl<sub>28</sub>N<sub>4</sub>O<sub>4</sub>-Sb<sub>4</sub>, MW 1972.21, monoclinic *C2/c* [regular twin (–100 010

001)], *a* = 10.870(2) Å, *b* = 20.407(2) Å, *c* = 28.548(5) Å,  $\beta = 90.000(4)^\circ$ , *V* = 6333(2) Å<sup>3</sup>, *D<sub>c</sub>* = 2.068 g cm<sup>-3</sup>, *Z* = 4,  $\mu = 2.906$  mm<sup>-1</sup>. The total number of reflections measured were 33 265 of which 9937 reflections were independent (*R*<sub>int</sub> = 0.1572). Final residuals were *R*1 = 0.0716 and *wR*2 = 0.1820 for 6520 reflections with *I* > 2 $\sigma$ (*I*). [**ST3**, NO]<sup>+</sup>SbCl<sub>6</sub><sup>-</sup> 1.5CH<sub>2</sub>Cl<sub>2</sub>: formula C<sub>37.5</sub>H<sub>35</sub>Cl<sub>9</sub>NOSb, MW 956.47, monoclinic *C2/c* at 93 K, *a* = 36.694(4) Å, *b* = 11.897(1) Å, *c* = 21.742(2) Å,  $\beta = 124.507(2)^\circ$ , *V* = 7821(1) Å<sup>3</sup>, *D<sub>c</sub>* = 1.624 g cm<sup>-3</sup>, *Z* = 8,  $\mu = 1.353$  mm<sup>-1</sup>. The total number of reflections measured were 49 923 of which 17 775 reflections were independent. Final residuals were *R*1 = 0.0523 and *wR*2 = 0.1219 for 11 552 reflections with *I* > 2 $\sigma$ (*I*). [**ST4**,(NO)<sub>2</sub>]<sup>2+</sup>(SbCl<sub>6</sub><sup>-</sup>)<sub>2</sub> 0.5CH<sub>2</sub>Cl<sub>2</sub>: formula C<sub>28.5</sub>H<sub>41</sub>Cl<sub>13</sub>N<sub>2</sub>O<sub>2</sub>Sb<sub>2</sub>, MW 1147.98, monoclinic *P2<sub>1</sub>/n*, *a* = 19.4836(8) Å, *b* = 13.9952(6) Å, *c* = 32.784(1) Å,  $\beta = 98.837(1)^\circ$ , *V* = 8833.3(6) Å<sup>3</sup>, *D<sub>c</sub>* = 1.726 g cm<sup>-3</sup>, *Z* = 8,  $\mu = 2.039$  mm<sup>-1</sup>. The total number of reflections measured were 126 267 of which 40 613 reflections were independent. Final residuals were *R*1 = 0.0486 and *wR*2 = 0.0995 for 20945 reflections with *I* > 2 $\sigma$ (*I*). The crystal data for [CAL, NO]<sup>+</sup>,<sup>15b</sup> [ST1, NO]<sup>+</sup>,<sup>11c</sup> [MEA, NO]<sup>+</sup>,<sup>11b</sup> and [ST4, NO]<sup>+</sup><sup>11a</sup> were published previously.

**Spectral Characterization and the Determination of the Equilibrium Constant of CT Complexes.** (a) In solutions containing an excess of diarene ([Ar<sub>2</sub>] > [NO<sup>+</sup>]), a linear dependence of the optical density with the concentration of nitrosonium cation was found. The shape of the spectra did not depend on the ratio of the reactant concentration and the temperature. Such a correlation indicates that practically all the nitrosonium ions were associated with the diarene, and the concentration of the complexes was thus equal to the initial concentration of the nitrosonium cation. The extinction coefficients of the absorption bands of such complexes were accordingly determined directly from the absorbance (Table 1). The spectral data in Table 1 were typically measured at [NOSbCl<sub>6</sub>]<sub>0</sub> = 0.2–1.0 mM and [Ar<sub>2</sub>] = 0.2–20 mM in 0.1–1.0 cm quartz cuvettes at 22 °C under an argon atmosphere.

The equilibrium constants *K<sub>B</sub>* in Table 1 were determined by competition methods. (Owing to high values of *K<sub>B</sub>*, the direct determination of the equilibrium constant is difficult.) The calculations were based on a series of (reversible) spectral changes ( $\Delta A_i$ ) observed upon incremental additions of the alkylbenzenes (usually hexamethylbenzene, **HMB**) to the solution of the nitrosonium complexes with diarene (and vice versa). Such an addition resulted in the decreasing intensity of the [Ar<sub>2</sub>,NO]<sup>+</sup> band and the increase of intensity near 340 nm, corresponding to [HMB,NO]<sup>+</sup>.<sup>7</sup> Spectral changes indicated that some nitrosonium cations were associated with **HMB**. Similarly, the incremental addition of the di-arene to the solution of [HMB,NO]<sup>+</sup> resulted in the reverse spectral change, and this confirmed the quantitative (reversible) interchange of nitrosonium cation between diarene and **HMB** (see Figure 10).

The ratio of equilibrium concentrations of the complexes with di-arene and mono-arene was determined by the product of ratios of the corresponding equilibrium constants and the equilibrium concentration of donors in solution.

$$[\text{Ar}_2, \text{NO}]^+ / [\text{ArH}, \text{NO}]^+ = (K_B / K_{CT}) \times ([\text{Ar}_2] / [\text{ArH}]) \quad (5)$$

Therefore, *K<sub>B</sub>* is expressed as in eq 6 (see the Supporting Information for details)

$$K_B = K_{CT} [(C^0 - \Delta C) / \Delta C] \{ ([\text{ArH}]^0 - \Delta C) / ([\text{Ar}_2]^0 - C^0 + \Delta C) \} \quad (6)$$

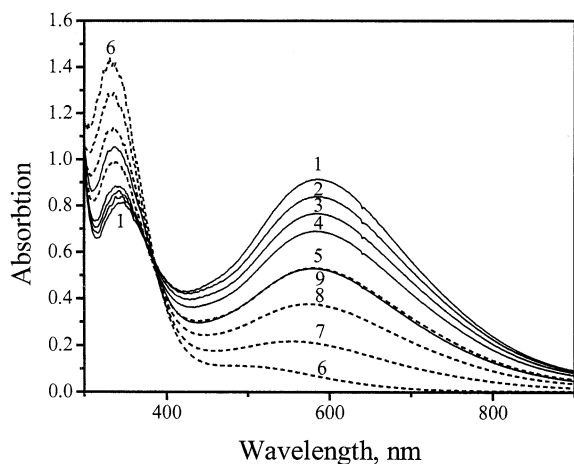
where *C*<sup>0</sup>, [Ar<sub>2</sub>]<sup>0</sup>, and [ArH]<sup>0</sup> were initial concentrations of nitrosonium, diarene, and hexamethylbenzene, respectively, and  $\Delta C = \Delta A_i / \Delta \epsilon_i$  (where  $\Delta \epsilon_i$  is the difference of extinction coefficients of nitrosonium ions complexes with donors Ar<sub>2</sub> and ArH at wavelength  $\lambda$ ). Thus, *K<sub>B</sub>* in Table 1 were calculated on the basis of the known equilibrium constant *K<sub>CT</sub>* = 6.0 × 10<sup>5</sup>

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**FIGURE 10.** Spectral changes attendant upon the incremental addition of (a) **HMB** to a 0.2 mM solution of  $[\text{ST4},\text{NO}]^+$  (solid lines, spectra 1–5) and (b) diarene **ST4** to a 0.2 mM solution of  $[\text{HMB},\text{NO}]^+$  (dashed lines, spectra 6–9) showing the interchange between the nitrosonium complexes with diarene and monoarene with variation of relative concentration of donors. Concentration (in mM): solid lines,  $[\text{ST4}]_0 = 1.0$  for all spectra and **HMB**, 1 = 0, 2 = 2.5, 3 = 5.5, 4 = 10, 5 = 20; dashed lines,  $[\text{HMB}]_0 = 5.0$  for all spectra and **ST4**, 6 = 0, 7 = 0.05, 8 = 0.15, 9 = 0.25 (dichloromethane,  $[\text{NO}^+\text{SbCl}_6^-]_0 = 0.2$  mM and  $T = 295$  K for all systems).

$M^{-1}$ ,<sup>7b</sup> as the average values of constants obtained from spectral changes  $\Delta A_\lambda$  (measured at the absorption maxima of the nitrosonium complexes with diarene and **HMB**) at different ratios of initial donor concentration.

(b) In systems containing an excess of nitrosonium ( $[\text{NO}^+] > [\text{Ar}_2]$ ), the spectral shape depended substantially on the concentration of the reactant. Spectral characteristics of solutions under such conditions were determined by the mixture of complexes in which nitrosonium was coordinated to both aromatic rings (spectral characteristics presented in Table 1) and to one aromatic ring (with spectral characteristics similar to those in [1:1] complexes with monoarene), i.e.,  $A^\lambda = C_b \epsilon_B^\lambda + C_m \epsilon_M^\lambda$ , where  $A^\lambda$  was the absorption at wavelength  $\lambda$  and  $C_b$ ,  $C_m$ ,  $\epsilon_B^\lambda$ , and  $\epsilon_M^\lambda$  were concentrations and extinction coefficients (at wavelength  $\lambda$ ) of complexes with bis- and mono-coordinated nitrosonium, respectively. Thus, the concentration of the different types of complexes (and therefore the equilibrium constant of their formation) can be determined from the multiwavelength analysis of the spectra obtained at different ratios of reactants (similar to the procedure used for the calculation of the corresponding parameters in [2:1] nitrosonium complexes with alkylbenzenes<sup>9</sup>). However, the quantitative consideration of nitrosonium complex formation with diarenes was complicated by the fact that, in addition to  $[\text{Ar}_2, \text{NO}]^+$  and  $[\text{Ar}_2, (\text{NO})_2]^{2+}$ , there also existed the possibility of complexes in which one nitrosonium was coordinated to the diarene via interaction with one aromatic ring (as the first step in formation of  $[\text{Ar}_2, (\text{NO})_2]^{2+}$ ). As such,  $C_m \epsilon_M^\lambda$  should be

substituted by the sum of several products referring to different modes of complexes with mono-coordinated nitrosonium. The presence of several unknown formation constants and extinction coefficients makes their calculation via minimization of the difference between the experimental and the calculated values of  $A_{340}/A_{500}$  at different arene concentrations (by variation of these parameters as previously described for [2:1] complexes with monoarenes<sup>9</sup>) very unreliable. Therefore, to estimate the equilibrium constant for mono-coordination of nitrosonium to the diarene, we assumed that the coordination of the two nitrosonium to two aromatic rings are independent: (a) the equilibrium constant for the mono-coordination of the first nitrosonium to the aromatic ring ( $K_M$ ) is equal to the equilibrium constant for mono-coordination of nitrosonium to the second aromatic ring of the complex (formed at first stage), and the equilibrium constant of process in eq 3 is  $K_M^2$ ; and (b) the extinction coefficients of both (NO/ring) fragments in the complex were equal to half of the extinction coefficient for  $[\text{Ar}_2, (\text{NO})]^{2+}$  and did not depend on the coordination of the nitrosonium to the other fragment. Then, the ratio of the absorption  $A_{340}/A_{500}$  could be expressed as (see the Supporting Information for details):

$$A_{340}/A_{500} = [(K_M + 2K_M^2[\text{NO}^+])\epsilon_M^{340} + K_B\epsilon_B^{340}] / [(K_M + 2K_M^2[\text{NO}^+])\epsilon_M^{500} + K_B\epsilon_B^{500}] \quad (7)$$

Thus, the spectral characteristics and formation constants of  $[\text{Ar}_2, (\text{NO})]^{2+}$  ( $K_B$ ,  $\epsilon_B^{340}$ , and  $\epsilon_B^{500}$ ) determined independently in the solutions with excess diarene (vide supra) and the ratio  $\epsilon_M^{340}/\epsilon_M^{500}$  determined at  $[\text{NO}^+]_0 \gg [\text{Ar}_2]_0$  (this ratio was nearly constant) allowed us to estimate the value of  $K_M \approx (3/10) \times 10^5 M^{-1}$  for complexes with stilbenoids and **MEA** from the dependence of  $A_{340}/A_{500}$  on concentration of  $\text{Ar}_2$  (Figure 3). The spectral characteristics of nitrosonium/**CAL** solutions corresponded to the spectrum of  $[\text{CAL}, \text{NO}]^+$  at all concentrations of reagents, and the ratio of  $K_M/K_B$  was too low and precluded accurate estimates of  $K_M$  to be made.

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**Supporting Information Available:** Determination of the equilibrium constants of bis- and mono-coordination of nitrosonium to the bridged diarene ( $K_B$  and  $K_M$ ). Details of the LCAO molecular-orbital formulation of [1:1] and [2:1] nitrosonium complexes with aromatic donors. Solid-state spectra of  $[\text{ST4}, \text{NO}^+][\text{SbCl}_6^-]$  and  $[\text{CAL}, \text{NO}^+][\text{SbCl}_6^-]$  (Figure S1). Color changes of  $\text{Ar}_2/\text{oxidant}$  systems in solution and in the solid state (Figure S2) and the corresponding spectral changes (Figure S3) attendant upon exposure of these systems to the nitric oxide. ORTEP diagrams for the diarene complexes  $[\text{ST3}, \text{NO}^+][\text{SbCl}_6^-]$  (Figure S4) and  $[\text{ST2}, (\text{NO})_2]^{2+}(\text{SbCl}_6^-)_2$  (Figure S5). X-ray crystallographic data (in CIF format) for **MES**, **ST2**, **ST3**, and **ST4**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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