Ultrafast Electron Transfer in Optically Prepared "Simple" Ion Pairs: The Mechanism at High Donor Concentration

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The ultrafast spectroscopy of the charge-transfer band of the benzene/Br atom electron donor-acceptor EDA complex and related complexes of various alkylated benzenes with Br atoms (arene/Br) have been investigated in several solvents at high donor concentrations. The excited state of the complex, a contact ion pair, is observed to decay (by charge recombination) with non-first-order kinetics on several time scales. Various aspects of the transient spectroscopy are investigated in detail. The previously described enhancement of the recombination rate at high donor concentration is observed to be general. Even donors with sterically bulky substituents show the rate enhancement at high concentration, precluding dimer cations as intermediates. The paper also reports observations of coherent vibrational motion in the mesitylene/Br complex ground state, initiated by impulsive excitation of the charge-transfer band. Finally, *ab initio* calculations of the computationally accessible complex benzene/Cl are reported, indicating that the equilibrium geometry has C_s symmetry with the Cl atom positioned over the C-C bond, i.e., a π complex. A σ complex of comparable energy is also observed. The various results are discussed in relation to the charge-recombination mechanism of the contact ion pair of the arene/Br complexes.

Introduction

Recent ultrafast pump-probe experiments on electron donoracceptor complexes (EDA) of benzene and methylated benzenes (arene donors) with a Br atom (acceptor) have led to important information on the dynamics of the excited state of the complex, a nominal contact ion pair, arene⁺/Br⁻.¹⁻³ In particular, the companion article in this issue,³ which we denote as HJB, describes the ultrafast spectroscopy of various arene/Br chargetransfer complexes at low arene concentration. The relationship of the ultrafast arene/Br research to the extensive background literature on EDA complexes in general and to EDA complexes with halogen acceptors in particular is discussed in HJB. The ground-state-return kinetics of arene⁺/Br⁻ is essentially a chargerecombination process (eq 1).

arene/Br
$$\stackrel{hv}{\underset{k_{\rm cr}}{\longleftrightarrow}}$$
 arene⁺/Br⁻ (1)

EDA complexes with aromatic moieties have been observed to exist as 1:1 DA and 2:1 D₂A complexes depending on the donor concentration.⁴ The same situation may occur in the case of the arene/Br complexes (eq 2).

arene/Br + arene
$$\stackrel{K_{2:1}}{\longleftrightarrow}$$
 arene₂/Br (2)

Obviously, at low donor concentration the observed ultrafast kinetics must be completely due to the 1:1 complex. Furthermore, there is insufficient time during the recombination process for diffusion of a second arene molecule to the 1:1 contact ion pair which might lead to enhanced recombination. The situation of low donor concentration was extensively investigated in HJB. Multiexponential kinetics with three components on the ~1-, 10-, and ~1000-ps time scales with comparable amplitudes were observed. The presence of the multiexponentiality was ascribed to multiple isomers of the arene/Br complex which, despite the

small geometric variations, exhibit dramatically different chargerecombination rates.

The present paper, in contrast, is concerned with how the recombination process is altered at high donor concentration. For the case of the Br complex with benzene, Bz/Br, recent papers have shown that the average recombination rate is greatly accelerated at high donor concentration,^{1,2} presumably due to specific complexation in the contact ion pair involving a second donor (benzene) molecule, as portrayed in eq 3.

$$Bz + Bz^{+}/Br^{-} \rightarrow Bz(Bz^{+}/Br^{-}) \xrightarrow{\sim} Bz(Bz/Br)$$
(3)

Spectroscopic evidence was presented that the interaction of the additional benzene actually leads to the formation of a benzene dimer cation, Bz_2^+ , in the ion pair. The benzene dimer radical cations is a well-studied species in solution,⁵ in the matrix,⁶⁻¹¹ and in the gas phase.¹²⁻¹⁷ In the present paper we continue to examine the possibility of an arene dimer cation intermediate in more detail by studying donors which should suppress dimer formation, such as tri-*tert*-butylbenzene. Alternatively, in an attempt to enforce dimer cation formation at low concentration, we study a donor that involves a synthetically tethered benzene dimer, namely, [2.2]paracyclophane.

Acceleration of the charge recombination has been observed for a number of EDA complexes of aromatic donors with 9,10dicyanoanthracene.¹⁸ The more charge-transfer character the first excited state of the complex has and the higher the energy of formation of the aromatic dimer radical cation is, the more efficient is the interception of the contact ion pair by excess donor. Formation of dimer radical cations has also been observed in several other examples of EDA complexes.^{5,19–21}

In the course of these investigations, oscillations were observed in the pump-probe spectroscopy of the mesitylene/ Br (Ms/Br) charge-transfer complex. These oscillations are assigned to impulsive excitation of ground-state vibrations of the complex. Some evidence suggests that the oscillations are due to the Ms-Br stretching coordinate and that the oscillations are, surprisingly, due to non-Condon effects on the absorption spectrum.

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Figure 1. Bleach recovery observed at 550 nm after 550-nm excitation of the Ms/Br complex in methanol at various Ms concentrations.

An additional focus of this paper is *ab initio* calculations on the Bz/Cl charge-transfer complex, which is more theoretically accessible than Bz/Br. The theoretical results strongly support the existence of multiple (at least two) ground-state isomers. In addition, the different isomers are shown to have vastly different electronic structure in their ground states and especially in their excited states.

Experimental Methods

All experimental methods are analogous to those described in HJB.³

Results and Discussion

Recombination Kinetics of Ms/Br at High Donor Concentration. The charge-recombination kinetics of the arene/ Br complex (see eq 1) is reflected in the bleach-recovery dynamics of the charge-transfer band. As mentioned in the Introduction, the recombination kinetics are non-first-order, exhibiting recovery on roughly three time scales. For example, consider the pump-probe dynamics of the Ms/Br complex excited at 550 nm in the charge-transfer band and probed at the same wavelength, as shown in Figure 1 for various Ms concentrations in methanol. Each transient has been fit with a convolution of the instrument response function with a model three-exponential decay. The best-fit parameters are listed in Table 1.

At the lowest concentrations the kinetics are insensitive to Ms concentrations, as described in HJB,³ and the fractional amplitude of each component apparently reflects the intrinsic kinetics of the Ms/Br complex, i.e., the Ms^+/Br^- recombination dynamics.

On the other hand, at much higher concentrations, effects due to additional Ms interactions are apparent. Perhaps the most obvious is the shortening of the lifetime of the longest kinetic component. This is assigned to two effects. First, as reported

TABLE 1: Best-Fit Parameters of Pump-Probe Transientsof the Ms/Br Complex in Methanol at DifferentConcentrations c and Probe Wavelengths λ_{probe}^{a}

λ _{probe} / nm	c/M	τ_1/ps	τ ₂ /ps	τ₃/ps	τ _{avg} / ps
390	0.5		16 (0.57)	100 (0.76)	
550	7.2 (neat)	1.0			1.0
	6.5	1.4			1.4
	5.0	1.2 (0.87)	8.3 (0.13)		2.1
	3.6	1.2 (0.79)	10.0 (0.21)		3.0
	2.0	1.2 (0.72)	11.8 (0.28)		4.2
	1.5	1.1 (0.66)	8.4 (0.18)	47 (0.16)	9.8
	1.0	1.1 (0.59)	9.8 (0.25)	59 (0.16)	12.5
	0.5	1.1 (0.60)	11.9 (0.18)	101 (0.22)	25.0
600	7.2 (neat)	1.0		. ,	
	0.5	0.6 (0.64)	10.2 (0.16)	100 (0.19)	
79 0	7.2 (neat)	$0.5(-0.48)^{b}$	1.1 (0.47)	9.6 (0.05)	
	2.0	$0.4 (-0.49)^{b}$	1.4 (0.41)	8.7 (0.10)	
	0.5	0.3 (-0.50)	1.0 (0.50)		

^{*a*} Transients were fitted to one, two, or three exponentials with relaxation times τ_1 , τ_2 , and τ_3 . The numbers in parentheses indicate the relative amplitudes A of the respective kinetic components. Negative amplitudes indicate a rising ΔOD component. τ_{avg} was calculated as $(A_1\tau_1 + A_2\tau_2 + A_3\tau_3)/(A_1 + A_2 + A_3)$. ^{*b*} Due to the similarity of τ_1 and τ_2 and the associated fitting problems, these amplitudes may be inaccurate.

earlier for the Bz/Br complex,² there is a diffusion-controlled "quenching" of Ms^+/Br^- by an additional Ms molecule. The quenching mechanism is associated with charge delocalization over Ms molecules in the collision complex and/or other effects (see below) that dramatically accelerate the instantaneous recombination rate of the collision complex of Ms and Ms^+/Br^- . Second, ground-state reequilibration (eq 4)

$$Ms + Br \stackrel{k_{dif}}{\longleftarrow} Ms/Br$$
 (4)

is also expected to be rapid and may play a role in the slow bleach-recovery dynamics if the equilibration rate is diffusioncontrolled, which is the case.²² The ground-state reequilibration, however, cannot account for the recovery dynamics alone. This was demonstrated by studying concentrated Ms solutions in methanol or cyclohexane for which the equilibrium ratio of Ms/Br to Ms + Br is >95%. Pump-probe experiments on these solutions with sufficient pump powers to significantly deplete the total ground state population of Ms/Br still show complete bleach recovery. If ground-state reequilibration were alone responsible for the apparent quenching effect, the bleach recovery would only be partial. Thus, ground-state recovery must be accelerated at high Ms concentration to explain these results.

At very high Ms concentration the amplitude of the fastest kinetic component increases significantly, and only one component can be observed at the highest concentration. Aside from the above-mentioned diffusion-controlled quenching of the ion pair by excess Ms, formation of ground-state 2:1 complexes may become possible (see Introduction). Thus, it is possible that the observed kinetics are not only due to a 1:1 complex but also due to a 2:1 contact ion pair formed by excitation of ground-state 2:1 complexes. The structures of such 2:1 complexes are unknown.

The equilibrium constant for formation of a Ms₂Br complex has been estimated²³ to be 0.11 M⁻¹, which would lead to significant amounts of 2:1 complexes at the higher Ms concentrations. For example at 3.6 M Ms \approx 30% of the complex would be in the 2:1 form.

Recombination Kinetics of Other Arene/Br Complexes at High Donor Concentration. Based on the results in the previous section, the increase in the charge recombination rate of Ms⁺/Br⁻ could be ascribed to both static and dynamic quenching by additional Ms. The static quenching involves preexisting 2:1 complexes. The question remains why an additional Ms molecule enhances the recombination rate of Ms^+/Br^- . For the case of Bz, we have previously assigned the rate enhancement to charge delocalization between the two benzene molecules which, in turn, was assumed to dramatically lower the energy gap to the ground state.¹ The large reduction in the energy gap was further assumed to accelerate the recombination process. The charge recombination is technically in the inverted regime, and the rate is therefore expected to follow an inverted energy gap law.24-26 In particular, the vibrational reorganization energy, λ_{vib} , can be estimated from calculations on the benzene cation, i.e., $\lambda_{vib} = 0.17 \text{ eV}.^{27,28}$ The solvent reorganization energy λ_{solv} can be estimated as ≤ 0.04 eV for nonpolar solvents.^{24,29} Finally, the long-wavelength edge of the charge-transfer band gives a rough measure of ΔG , i.e., ≈ -1.55 eV. Since $\lambda_{solv} + \lambda_{vib} + \Delta G$ is significantly negative, this reaction is in the inverted regime.

On the basis of spectroscopic (see below) and quenching data of the type shown above for Ms, it has been proposed that the charge delocalization in benzene actually leads to a fully formed benzene dimer cation, Bz_2^+ . For free benzene cations the process of dimer cation formation (eq 5) is highly favorable in

$$Bz^{+} + Bz \rightarrow Bz_{2}^{+} \tag{5}$$

the gas phase, in solution, and in a matrix. In the gas phase the enthalpy for reaction 5 is $\Delta H^{\ominus} = -20.6$ kcal mol^{-1,12} Formation of the aromatic dimer radical cations has been observed in studies of other EDA complexes.^{5,19,20}

In an attempt to further evaluate this type of intermediate in the charge recombination, we have explored the recombination dynamics of sterically hindered donors, which might be expected to exhibit less facile formation of dimer cations; i.e., we compared Bz/Br complexes with *tert*-butylbenzene/Br complexes. In a related study on EDA complexes of aromatic donors with NO⁺, no dimer cation formation was observed when *tert*-butylbenzene was the donor.²⁰ Furthermore, in a study on aromatic dimer radical cations the authors were unsuccessful at obtaining the dimer radical cation of *p-tert*-butyltoluene.⁸

Figure 2 compares the ground-state-recovery kinetics of concentrated solutions of *tert*-butylbenzene and benzene. Despite the bulky substituent group, the *tert*-butylbenzene system shows very efficient ground-state recovery, actually very similar to Bz and Ms. Figure 3 shows the ground-state recovery of an even bulkier donor, tri-*tert*-butylbenzene. Both of these bulky donors are not expected to form dimer cations, due to steric congestion. Yet, quenching is clearly observed. This demonstrates that formation of a dimer cation is not necessary for efficient quenching of the ion pair.

The data in Figure 4 portray the early-time dynamics of tritert-butylbenzene/Br complexes in MeOH and cyclohexane. The results are very similar to measurements at the lower concentration on the less bulky Ms and the less substituted benzene. This suggests that the charge-recombination kinetics and the mechanism of the different donors are analogous.

In an attempt to enforce dimer cation stabilization on the ion pair, we examined the ground-state-recovery dynamics of the [2.2]paracyclophane⁺/Br⁻ ion pair. [2.2]Paracyclophane has two closely spaced benzene rings and might serve as a model for an aromatic dimer. We have studied paracyclophane/Br complexes at sufficiently low concentrations that the 2:1 complex and diffusional quenching of the ion pair can be neglected. Due to limited solubility of [2.2]paracyclophane, our



Figure 2. Bleach recovery observed at 550 nm after 550-nm excitation of the Bz/Br (top panel) and the *tert*-butylbenzene/Br complex (bottom panel) in methanol. Donor concentration was 90% in both cases.

Figure 3. Comparison of the 550-nm bleach recovery of Bz/Br (top panel) and tri-*tert*-butylbenzene/Br (lower panel) in cyclohexane. Donor concentration was 2 M in both cases.

studies were constraint to the two solvents ethyl methyl ketone and CCl₄. The results are shown in Figure 5. Despite the possibility that a dimer-cation-like structure could be formed in the excited state due to the paracyclophane structure, the results are very similar to the low-concentration data on Ms/Br, even to the point of showing the special suppressing effect of CCl₄ on the ~1-ps component, which is demonstrated in Figure 6. In other words, no evidence is found to support the existence of special quenching due to the "built-in donor dimer" structure. However, it should be noted that the spacing of the benzene rings in [2.2]paracyclophane (3.1 Å) is somewhat smaller than the calculated ring spacing for the benzene dimer sandwich (3.5 Å).³⁰ Furthermore, the two benzene rings in [2.2]paracyclophane are not perfectly planar but rather have a boatlike configuration.³⁰

For Bz/Br another form of evidence that supported the benzene dimer cation intermediate was a transient absorption signal in the near-IR, which appeared soon after exciting the

Figure 4. The 550-nm bleach recovery on the 7-ps time scale of *tert*butylbenzene/Br in methanol (top panel) and tri-*tert*-butylbenzene/Br in cyclohexane (bottom panel). Donor concentrations were 90% for *tert*-butylbenzene and 2 M for tri-*tert*-butylbenzene.

Figure 5. Transient bleach recovery observed at 550 nm of the [2.2]paracyclophane/Br complex in methyl ethyl ketone and in CCl₄. Paracyclophane concentration was 0.01 M.

Bz/Br charge-transfer band of Bz/Br in neat benzene.¹ Subsequent experiments on charge-transfer complexes with stronger donors, such as Ms, have made that assignment of the transient in the near-IR to the dimer cation ambiguous. The stronger donors have a much greater charge-transfer complex formation constant. As a result, it is possible to study these at low enough concentration that 2:1 complexes and diffusional quenching can be suppressed, as described in HJB. Despite the absence of donor dimers, the low-concentration solutions still exhibit transient absorption signals at early times in the near-IR. Very similar transients are observed at high donor concentrations. For example, the 790-nm transient of Bz/Br at high benzene concentration shows an absorption feature (Figure 7). While there is nothing that rules out the original interpretation of this absorption as being due to the benzene dimer cation, the presence of a similar absorption for Ms at very low concentration makes a benzene dimer cation unnecessary to explain the results.

Figure 6. Transient bleach recovery on the 5-ps time scale of the [2.2]-paracyclophane/Br complex in methyl ethyl ketone and in CCl₄ observed at 550 nm. Paracyclophane concentration was 0.01 M.

Figure 7. Transient absorption of the Bz/Br complex in methanol at 2 M benzene concentration observed at various wavelengths.

There are further spectroscopic effects in the UV region of the spectrum. For the Br/Bz complex in 2 M benzene in methanol the 395-nm transients show an absorption due to a π - π * transition of the contact ion pair. The absorption has a delayed appearance time of 1.7 ps and a decay kinetics that follows the long-time tail of the bleach recovery dynamics of the 550-nm transient. The delayed absorption has been interpreted as an overlapping transient bleach associated with vibrational relaxation effects on the blue edge of the chargetransfer band.¹ The early-time dynamics at the three probe wavelengths in Figure 7 is, however, completely analogous to the kinetics of Ms/Br at very low concentration, i.e., a delayed appearance of the 395-nm absorption, a fast recovery component of the 550-nm bleach, and a short-lived transient at 790 nm. Thus, these effects can be partly, if not mostly, associated with the fast decay kinetic component of the Bz/Br 1:1 complex at moderate and low arene concentrations. In this interpretation both the 395-nm and the 790-nm transients contain contributions due to vibrational relaxation of the ground-state 1:1 complex (see HJB).

The question remains, however, what the correct interpretation of the transients is for highly concentrated donor solutions and, in particular, Br complexes in pure donor solvents. Under these conditions the 550-nm transients show the \approx 1-ps bleach recovery exclusively and no slower components. The 790-nm transients are prominent, and a typical example is given in Figure 7. No 395-nm absorption is observed. Thus, in pure donor solvents the entire contact ion pair population decays due to charge recombination with a \approx 1-ps lifetime, and the spectral features are consistent with a \approx 1-ps ground-state recovery and simultaneous vibrational excitation and relaxation on the blue and red edges of the charge-transfer band.

Why encounter of a donor molecule with the contact ion pair leads to very rapid charge recombination is not well understood at this point. While dimer cation formation is a possibility for donors with small substituents, this explanation becomes inadequate for the case of the sterically crowded donors. The similarity of the data for tri-tert-butylbenzene, Bz, and Ms actually suggests that the same mechanism is valid for all investigated donors. Also, the very similar results on [2.2]paracyclophane, a preformed dimer system, further suggests that the benzene dimer cation may not be involved at all. The situation might be quite complex. Subtle $\pi - \pi$ interactions of the donor with the contact ion pair could lead to a variation of the contact ion pair geometry and/or to charge delocalization and consequently to the observed acceleration of the charge recombination. Actually, $\pi - \pi$ interactions are believed to be responsible for the lack of the \approx 1-ps component in the charge recombination of the arene/Br complexes in CCl₄ (see HJB). Small alterations of the arene/Br geometry may significantly affect the electronic properties of the contact ion pair and in turn also the charge-recombination rate. This is supported by the results of ab initio calculations on the Bz/Cl complex which are described below.

Vibrational Coherence in the Pump–Probe Transients. Figure 8 shows a pump–probe transient of Ms/Br at moderate Ms concentrations in methanol with particularly high signalto-noise ratio. Superimposed on the bleach-recovery dynamics of the complex, an oscillatory component is observed. The oscillatory component becomes more obvious after subtracting from the observed signal a convolution of the instrument response function of the apparatus with a biexponential model decay. The difference signal clearly shows a complex oscillatory response, as shown in the top of Figure 8. A Fourier transform of the oscillatory part of the signal is displayed in Figure 9. The response is dominated by a 120-cm⁻¹ band. Nearly the same oscillations with the same phase and Fourier transform are observed with 620-nm probing.

The coherent oscillatory response of Ms/Br is similar to several recent examples of coherent vibrational responses in pump-probe spectroscopy in resonance with vibronic transitions of various molecules.³¹⁻³⁵ Generally speaking, the oscillations are due to resonant impulsive stimulated Raman scattering (RISRS). The pump pulse creates a coherent ground state vibrational wave packet due to two interactions of the pump pulse. For thermally excited modes the wave packet is partially associated with vibrational hole burning in certain cases. The RISRS phenomenon is complex, and its manifestation depends on the duration and spectral content of the pump and probe

Figure 8. Lower line: raw data of transient bleach of Ms/Br at 1 M mesitylene concentration in methanol observed at 550 nm after 550 nm excitation with a 70-fs pump pulse. Upper line: residuals of a fit of a convolution of a biexponential with the instrument response function to the raw data.

Figure 9. Fourier transform of oscillatory components on the bleach recovery of Ms/Br in 1 M mesitylene in methanol observed at 550 and 620 nm.

pulses, as well as the relative frequency of the pulse to the vibronic band.^{33,34} Only ground-state vibrational modes are observed in the RISRS case where the probe exclusively monitors the ground-state absorption, i.e., when no overlapping excited-state absorption or stimulated emissions are in resonance with the probe light. This is the situation for Ms/Br. The high-frequency cutoff of the RISRS oscillatory response is controlled by the duration of the pump pulse. Simply speaking, impulsive excitation does not occur when the duration of the pump pulse is much longer than the vibrational frequency of the mode.

For some systems the RISRS oscillations are strongest at the red and blue band edges of the band due to the nature of the wave packet produced from Raman-active modes.³³ The possibility of generating the second harmonic of the vibrational mode by pumping and probing at the band maximum has been discussed.³⁵ The usual Franck—Condon model for optical transitions leads to the prediction that the most active oscillatory modes should be the most active Raman modes in the frequency region capable of impulsive excitation; however, more complex effects can be observed.

For the Ms/Br example the oscillatory response is primarily at 120 cm⁻¹, which does not apparently correspond to a strong mode of Ms. Based on analogy to the Raman spectra of other EDA complexes, the 120-cm⁻¹ mode may be associated with a Ms-Br stretch. It is interesting that the oscillations are as strong and have the same phase at the band maxima as at a somewhat red-shifted wavelength (620 nm). This suggests that the RISRS mechanism for Ms/Br may differ partly from the usual Franck-Condon model. The strong oscillatory response at the center of the spectrum with no apparent wavelength dependence may be due to a non-Condon contribution to the signal. In detail, if the electronic part of the total absorption cross section is strongly dependent on the Ms/Br stretching coordinate, the complete absorption spectrum would be expected to oscillate in amplitude, in addition to the usual RISRS effect which involves a change in shape and position of the spectrum. More experimental data are necessary to evaluate whether the non-Condon effect is indeed operating for the Ms/Br complex. Unfortunately, the present experiments are at the limits of current technology due to the limited signal-to-noise of the Ms/Br pump-probe signal, the two major problems being low Ms/Br concentration and small amplitude of the oscillatory component.

Ab Initio Calculations on the Structure of the Bz/Cl Complex. A key component of the arene/Br ultrafast dynamics is strong dependence of the electronic structure of the ground and ion pair state on the Br-arene coordinates. In order to further explore this aspect of the arene/Br complexes, we set out to study EDA complexes by *ab initio* electron structure calculations. Unfortunately, even the Bz/Br complex is beyond the capabilities of *ab initio* calculations due to the large number of electrons, spin-orbit effects, complications due to spin contamination for radicals, and the general difficulty of obtaining suitable basis sets for bromine. In order to bring the calculation within reach of our computational resources, we examined the Bz/Cl system which has fewer electrons. This is, of course, a gas-phase calculation, and conclusions about the complex in solution must be drawn with great care.

There has been considerable debate as to the nature of the Bz/Cl complex. It has been speculated to be a π complex by some³⁶⁻⁴¹ and a σ complex by others.⁴²⁻⁴⁵ The possibility of both types of complexes being simultaneously present has also been discussed.^{42,43} The structure of the Bz/Cl π complex was speculated to have the halogen atom positioned directly above the center of the benzene ring ($C_{6\nu}$ symmetry).^{38,41} In theoretical and experimental studies the van der Waals complex of the argon atom with benzene has been found to possess $C_{6\nu}$ symmetry.⁴⁶⁻⁴⁸ In contrast, in complexes of Ag⁺ and Cu⁺ with aromatic molecules, the cation is located above and between two adjacent carbons.⁴⁹⁻⁵¹ The IR spectra of Bz/Br and Bz/I complexes in argon and nitrogen matrices indicate that the Bz/ Br complex has C_s symmetry⁵² whereas the Bz/I complex has $C_{6\nu}$ symmetry.⁵³ Another study also supports $C_{6\nu}$ symmetry for Bz/I.38

We have investigated the Bz/Cl complex structure with *ab initio* MO calculations using the GAUSSIAN 92 suite of programs installed on an IBM RISC6000 Model 560. For the ground state of the Bz/Cl complex two types of calculation were made, both employing a 3-21G* basis set, i.e., (i) geometry optimization with spin-unrestricted open-shell Hartree—Fock (UHF) followed by second-order Møller—Plesset calculations (MP2) and (ii) single-point calculations using fourth-order Møller-Plesset calculations (MP4). Unfortunately, the expectation value of the total spin operator $\langle S^2 \rangle$ in the UHF calculations were found to deviate from the expected value of 0.75 for some of the stationary points, indicating high spin contamination of

Figure 10. Two stable isomers of the Bz/Cl complex according to *ab initio* calculations.

the calculated electronic wave functions. The spin contamination can distort the potential energy hypersurface, and the optimized geometries, binding energies, etc., may be highly inaccurate. Reasonable estimates of the true energy at the stationary points can be obtained by using the formalism developed by Schlegel to project out the spin contamination.⁵⁴ Therefore, the energies of the stationary points were determined by MP4SDQ calculations which include a PMP calculation to project out the spin contamination. Stabilization energies were determined by comparing these spin-projected energies with the spin-projected energy of a Bz/Cl supermolecule where the distance of the chlorine atom and the benzene moiety is 9 Å. Zero-point energies were estimated at the MP2/3-21G* level.

If the geometry of the Bz/Cl is constrained to C_{6v} structure, the minimum-energy geometry at HF/3-21G* level has the Cl positioned of the center of the ring at 3.7 Å. This geometry, however, is not a stable minimum but a second-order saddle point. This should be contrasted to the Ar/Bz van der Waals complex which has a stable minimum C_{6v} structure. If the C_{6v} symmetry is relaxed to C_s symmetry and additional structure optimization at the MP2/3-21G* level is carried out, two stable minima are obtained. The structures of these two minima are shown in Figure 10 and are denoted as π and σ .

One of the stable minima is a π complex structure with the symmetry plane passing through the midpoints of two C-C bonds and with the chlorine atom positioned slightly outside of the benzene ring at a 101° angle to the plane of the ring. The distance between the Cl atom and the center of the C-C bond is 2.7 Å, which corresponds to a 3.2-Å distance between the Cl atom and the center of the benzene ring. Spin contamination in this case was negligible ($\langle S^2 \rangle = 0.756$ instead 0.75). Natural bond order (NBO) analysis of the structure indicates no bond formation between benzene and chlorine. All the carbon atoms in benzene essentially maintain their sp² character. Fermi contact and atomic spin density analysis also indicate the unpaired electron to be mostly confined to the chlorine atom in the complex. The spin-projected stabilization energy of this complex is -4.1 ± 0.5 kcal mol⁻¹ using the 3-21G* basis set. In order to determine the basis set dependence of the stabilization energy, a structural optimization using the $6-31+G^*$ basis was carried out. Subsequent spin projection on the PMP2/6- $31+G^*$ level gave a vey similar stabilization energy (-4.2 kcal mol⁻¹). The zero-point-energy difference between the π complex and benzene is estimated to be $0.5 \text{ kcal mol}^{-1}$.

The σ complex, also known as the chlorocyclohexadienyl radical, has the C_s symmetry plane passing through the C_1 and

Figure 11. Calculated stabilization energies of the Bz/Cl complex upon approach of a Cl atom to a benzene ring in different directions. In structures a, b, and c the distance is taken as the spacing between the Cl atom center and the plane of the benzene ring. In the planar structures d and e the distance is measured between the center of the benzene ring and the center of the Cl atom.

C₄ atoms of the benzene rings. The stationary point was found to have a geometry where the distance between the chlorine and the C_1 atom is 1.9 Å and the angle between the plane of the ring and the C-Cl bond is 119°. Unfortunately, the spin contamination for this calculation was quite high ($\langle S^2 \rangle = 1.2$). NBO analysis confirms the formation of a single bond between the Cl and the C₁ atoms. The C₁ atoms shows a sp^3 -type bonding whereas the other carbon atoms essentially maintain their sp² character. Fermi contact and atomic spin density analysis indicate that the unpaired electron is mostly confined to the five sp²-hybridized carbon atoms. The spin-projected stabilization energy was found to be -7.5 ± 0.5 kcal mol⁻¹ with the 3-21G* basis. As with the π complex, we investigated the basis set dependence of the stabilization energy. At the PMP2/6-31+G* level, the stabilization energy is again very similar (-7.75 kcal mol⁻¹). An estimate of the zero-pointenergy difference gave 1.3 kcal mol⁻¹. Interestingly, the stabilization energy is very similar to the estimated energy value of 7.2 \pm 2 kcal mol⁻¹ for the σ complex based on thermodynamical data.42 Considering the uncertainty in both calculation methods, the agreement might be coincidental.

In order to verify the stationary points located by the calculations described above, the potential energy surface for the interaction between Cl and benzene was explored along various directions with respect to the benzene plane. Single-point MP4SDQ calculations, which include spin projection (PMP4), were performed with the 3-21G* basis set. The position of the Cl atom was varied along different directions toward the benzene molecule as shown in Figure 11. In all calculations the benzene geometry ($R_{CC} = 1.407$ Å, $R_{CH} = 1.087$ Å) was kept rigid. Figure 11 shows the calculated stabilization energies obtained for various Bz-Cl geometries. Clearly, also in this higher-level calculation the complex with $C_{6\nu}$ symmetry is not the global minimum.

The major result of the calculations is that the Bz/Cl complex has two different stable isomers that have vastly different electronic structures but comparable stabilization energies. In order to obtain a rough idea of the excited states of the σ and

 TABLE 2: Properties of Excited-State Transitions of the

 Two Stable Bz/Cl Complexes Obtained from

 Single-Excitation CI Calculations after Optimization on the

 MP2/6-31+G* Level

	excitatio	on energy	oscillator	charge	
transition	in eV	in nm	strength	on $Cl(e)$	
π complex					
1-A"	0.768	1614	0.000	0.032	
2-A'	0.823	1507	0.000	0.049	
3-A''	3.299	376	0.001	-0.136	
4-A'	3.845	322	0.183	-0.985	
5-A''	4.221	294	0.003	-0.632	
6-A'	4.892	253	0.007	-0.090	
σ complex					
1-A"	4.865	254	0.008	-0.147	
2-A'	5.790	214	0.005	-0.111	
3-A''	5.893	210	0.049	-0.003	
4-A'	5.989	207	0.000	0.372	
5-A"	6.125	202	0.023	0.272	
6-A'	6.283	197	0.010	-0.556	

 π complexes, we calculated (CIS/6-31+G*) the energies, oscillator strengths, and atomic charges of the vertically excited states of the two complexes; see Table 2. Although such calculations are known to give poor energies, the results do give some qualitative information about the electronic structure of the two complexes. The excited states of the π complex can be assigned to a charge-transfer state, locally excited states on the benzene, and locally excited states on the Cl, just as expected for a π complex with EDA character. On the other hand, the σ -complex shows a complex set of transitions and oscillator strengths that are completely different from the π complex and the expectation for an EDA complex.

It is difficult to estimate the errors in the present calculations due to the several sources of error such as spin contamination, basis set superposition error, etc., and because of the lack of obvious simpler model systems. The actual magnitude of the stabilization energy of the π and σ complexes and even their relative stability may be in error. On the other hand, the results indicate that the electronic structure of the Bz/Cl complex is a very strong function of the Cl-Bz coordinates and in particular the position of the Cl atom with respect to the carbon atoms of Bz. It is likely that these results also apply to some extent to other arene/halogen complexes, including the Br/Bz complex. Although based on the spectroscopic evidence, and thermodynamics data on the arene/halogen complexes, σ -bonding interactions are probably less important for the Bz/Br complex than Bz/Cl complex.⁴² Nevertheless, the calculations suggest that also in the Bz/Br case small geometry variations could lead to very different electronic structures even though the potential energy changes only slightly. This would indicate that specific interactions with solvents play an important role in determining the electronic structure of the complex and consequently affect the charge-recombination rate of the Bz⁺/Br⁻ contact ion pair significantly.

Conclusions and Summary

In summary, we have reported an extensive investigation on the influence of excess donor molecules on the chargerecombination of photoexcited arene/Br EDA complexes. A broad variety of aromatic donors in numerous solvents were studied. Diffusion-controlled quenching of the contact ion pair by donor molecules was observed. In neat donor solvents the observed lifetime was on the order of 1 ps. While in the case of benzene and methylated benzene derivatives it is possible to ascribe the quenching effect to formation of intermediate 2:1 complexes, this explanation fails for the donors with bulky substituents. The similarity of the data for the sterically crowded, the less substituted arenes, and [2.2]paracyclophane actually suggests that the same mechanism for quenching is operative in all cases. This mechanism might involve specific $\pi-\pi$ interactions, causing slight geometric variations in the contact ion pair which might dramatically alter the charge-recombination rate.

We have also presented the results of *ab initio* calculations on the Bz/Cl complex. The results indicate two stable minima with comparable energies but completely different electronic properties, namely, a π - and a σ -type complex. The results were used to discuss the situation in the Bz/Br case and were supportive of the above-proposed quenching mechanism.

Finally, we have observed an oscillatory component in the bleach recovery of the Ms/Br complex. The 120-cm⁻¹ oscillation was assigned to vibrational motion, possibly the Ms-Br stretching motion, in the ground state initiated by resonant impulsive stimulated Raman scattering. The lack of a phase shift of the oscillation at two different wavelengths and the fact that the oscillation seems most prominent at the maximum of the charge-transfer band suggests that a non-Condon effect is responsible for the oscillatory behavior.

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