Comparison of the Photoinduced Electron Transfer Reaction in a Rigid Cyclophane and Its Corresponding Bimolecular Donor/Acceptor Complex

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The back electron transfer following photoexcitation of the bimolecular charge-transfer complex between 1,4-dimethoxybenzene (DMB) and 7,7-dicyanobenzoquinone methide (DCBM) is compared to the dynamics observed for the corresponding spatially constrained cyclophanes. In a recent letter (*J. Phys. Chem.* **1999**, *103*, 2740), we reported that the back electron transfer dynamics for two structurally related cyclophanes of DMB and DCBM were identical and that these data provided direct evidence for the through-bond mechanism of electron transfer in this bridged organic donor/acceptor systems. The study of the noncovalent bimolecular system herein enables us to experimentally determine the through-space electron transfer rate for this charge transfer pair. We find that the rate of back electron transfer is faster in the cyclophane than in the bimolecular complex. This difference in reaction rates can be accounted for quantitatively using the Bixon−Jortner equation for the electron transfer reaction rate, if the difference in driving force for the two systems is taken to be the energy difference between the absorption maxima of the corresponding charge transfer bands. Using the same approach for determining the relative driving force for the two cyclophane structures studied, we find that that the experimental data requires a common reaction distance, despite the fact that the center-to-center distance between the donor and acceptor molecules is increased by 25%. These data provide convincing evidence that the reaction process in the cyclophanes occurs by a through-bond mechanism. The origin of the different driving forces among the two cyclophanes and the noncovalent bimolecular complex is attributed to conformational changes in the donor and acceptor moieties that result from the constraints imposed by the alkyl spacers.

Introduction

There have been many recent studies that focus on understanding how the distance and orientations between donor and acceptor groups affects electron transfer rates.[1−27] Many of these adjust the length of a spacer between the donor and acceptor groups. Two commonly discussed electron transfer mechanisms are the "through-bond" and "through-space" mechanism. In the former, the electron tunnels along the covalent bonds of the molecule, and so the distance between the donor and acceptor is given by the sum of the distances of the covalent bonds linking the two moieties. In the through-space mechanism, the electron tunnels through the surrounding medium, and so the distance between the donor and acceptor is approximated by the spatial separation between the two species. The relative importance of through-bond and through-space electron transfer is generally determined from the dependence of the electron transfer on distance. The applicability of a particular mechanism has relied mostly on the comparison of distant-dependent experimental data to that predicted by the theoretical expressions. Specifically, for a nonadiabatic electron transfer reaction,[28] the rate constant is generally described by eq 1,

$$k_{ET} = (4\pi^2/h)\,|V|^2\mathrm{FC} \tag{1}$$

where V is the electronic coupling matrix element and FC is the Franck−Condon weighted density of states. Because V depends on the spatial overlap of the molecular orbitals associated with the donor and acceptor moieties, it is sensitive to distance and is commonly modeled by[28]

$$|V|^2 = |V_0|^2 \exp(-\beta r_{DA}) \tag{2}$$

where V_0 and β are a constants and r_{DA} is the distance between the donor and acceptor. Because the orbital overlap differs for through-bond and through-space electron transfer pathways, the difference in reaction rate is manifested by a change in the value of β. Experimental studies of rigidly spaced donor/acceptor systems imply that β is on the order of 2.8 Å^{-1} for "through-space" electron transfer[28d] and 1.1 Å^{-1} for "through-bond" electron transfer.[1,27] Thus, evidence in support of a particular model is often tied to the observed value of β and its interpretation.

One notable exception to the above approach for determining the relative importance of these two mechanisms is a recent study by Meyer and co-workers.[26b] In that study, the back electron transfer following photoexcitation of chromophores that were covalently attached to a helical oligoproline structure was examined. By varying the experimental conditions, the helix could be converted between a proline-I and proline-II helix, which in turn affected the through-space distance (1850 and

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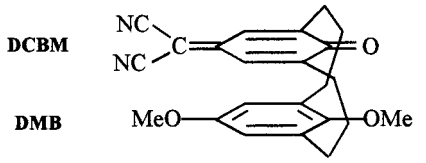
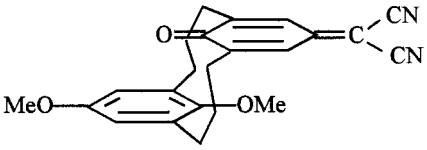
SCHEME 1: Structure of Cyclophanes I and II



Cyclophane I



Cyclophane II

1150 pm) between the chromophores involved in the back electron transfer. The through-bond distance, however, remained constant. The observed electron transfer rates for the two helical structures were identical within experimental error, arguing convincingly in favor of a through-bond mechanism.

We recently reported a similar type of study for a pair of cyclophane molecules.[20] The structures of the two cyclophanes are shown in Scheme 1. Each system contains the same donor (1,4-dimethoxybenzene, DMB) and acceptor (7,7-dicyanobenzoquinone methide, DCBM), with the donor and acceptor rigidly positioned relative to one another by alkyl linkers. Taken together, these two cyclophane structures have the unique feature that the through-bond distance between any pair of atoms is held constant, while the spatial distance between the donor and acceptor is changed. We reported that following excitation of the charge transfer band, the half-life for the back electron transfer reaction is 12 ± 2 ps for both cyclophanes.[20] In addition, the reaction dynamics are independent of both excitation wavelength and solution temperature and independent of solvent (CD_3CN, CH_3CN, methanol, chloroform).[20] From these observations, we concluded that the electron transfer process takes place in the so-called "Marcus inverted region" and that the mechanism occurred by a through-bond electron transfer process. Compared to the systems studied by Meyer and coworkers,[26b] the through-space distances in the cyclophanes studied herein were considerably smaller (~25% of that of the oligoproline molecule, 360 pm for I and 470 pm for II), and at these shorter distances, a through-space and through-bond process could be expected to compete to a greater extend than at greater donor acceptor distances. Despite this, our experimental results for these cyclophanes showed that the through-bond mechanism can remain the dominant reaction pathway at short donor−acceptor distances as well.

In this paper, we compare the photo-induced back electron transfer for the cyclphanes to that exhibited by the noncovalently bonded donor−acceptor complex. The comparison between the cyclophane and the noncovalent bimolecular complex enables us to explore the dynamics of electron transfer for this single charge transfer pair, but in one case either (or both) a through-bond and through-space mechanism could be operative (cyclophane) and in the other only a through-space electron transfer can occur (noncovalent bimolecular complex). In addition, we examine the dynamics from a theoretical viewpoint, demonstrating that the observed changes in reaction dynamics can be accounted for by taking advantage of the insights afforded by the change transfer absorption properties of these complexes.

Experimental Section

The electron transfer dynamics were measured by performing femtosecond pump−probe absorption experiments. The experimental apparatus consists of a regeneratively amplified titanium: sapphire laser system (Spectra Physics, 1 kHz repetition rate). The output pulses from this device are 80 fs in duration, 1 mJ in energy, and have a center wavelength of 800 nm. This laser beam pumps an optical parametric amplifier (OPA, Spectra Physics), which can be tuned throughout the visible and UV region of the optical spectrum. The OPA output was split into two beams using a glass plate to create a pump beam (95% of the incident pulse intensity) and a probe beam (5% of the incident light intensity). The two beams then traveled different paths and were recombined on the sample. The path length of one arm was controlled using a computer controlled delay stage. After propagating through the sample, the intensity of the probe beam was measured by a photodiode. The diode output was directed to a lock-in amplifier, which was referenced to a mechanical chopper located in the path of the pump beam and interafces to the PC controlling the delay stage.

The electron-transfer reaction dynamics for the cyclophanes were examined in acetonitrile, deuterated acetonitrile, and dichloromethane solutions. The bimolecular complex was examined in acetonitrile. The concentration of the cyclophanes was on the order of 10^{-5} M, and no evidence of bimolecular complexes was manifested in the absorption spectrum. Degenerate pump−probe absorption measurements for the cyclophane and the bimolecular DCBM/DMB complex in acetonitrile were recorded for wavelengths between 480 and 540 nm. No wavelength-dependent dynamics were observed. The temperature of the water-jacketed sample cell was controlled to within $\pm 1°$ C.

The compound 7,7-dicyanobenzoquinone methide (DCBM) was synthesized from 1,4-cyclohexanedione and malononitrile following the four-step procedure reported by Hyatt.[29] 1,4-Dimethoxybenzene was purchased from Aldrich Chemical Co. and used without further purification.

Results and Discussion

Figure 1 shows plots of the absorption spectra of bimolecular DCMB/DMB complex and cyclophane I in acetonitrile. The cyclophane charge transfer absorption band peaks at 478 nm ($\epsilon = 3860$ M^{-1} cm^{-1}). The charge-transfer absorption band for the noncovalent bimolecular complex has a maximum absorbance at 496 nm, red-shifted by 760 cm^{-1} from that of the cyclophane. Using the method of Keefer and Andrews,[30] the molar absorptivity of the bimolecular charge-transfer band was determined to be 190 ± 20 M^{-1} cm^{-1}, significantly lower than that reported for the cyclophane (see Table 1).

Following excitation of the charge-transfer band of either cyclophane, we see an instrument-limited bleach followed by a recovery of the absorption signal. The transient absorption data for the cyclophanes and bimolecular complex were well described by single-exponential decays; see Figure 2. Both cyclophanes show a back electron transfer half-life of $\tau_{et} = 12 \pm 2$ ps.[20] The bimolecular complex reveals, on the other hand, a back electron transfer half-life of $\tau_{et} = 34 \pm 5$ ps.

As stated above, from a comparison of two different cyclophanes that employ DMB−DCMB coupling, we concluded that the reaction occurs by a through-bond mechanism. This conclusion suggests that a through-space electron transfer is kinetically noncompetitive. When the bridging alkyl linkers are removed, one would expect that the back-electron transfer rate constant would then decrease because only a through-space mechanism could occur. This is consistent with the experimental observations. However, this comparison is not quite valid because the

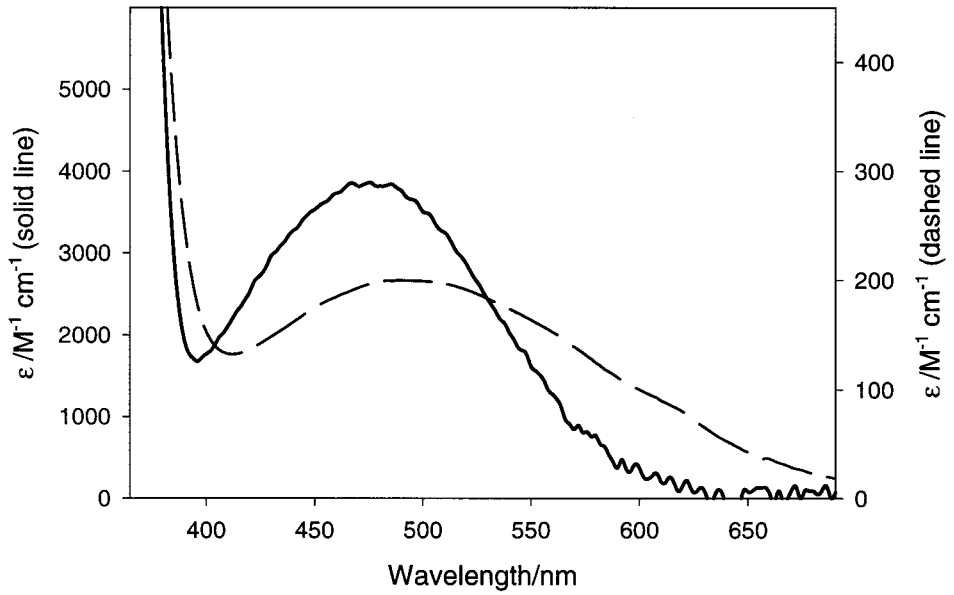


Figure 1. Absorption spectrum of cyclophane I (solid line) and the DMB/DCBM bimolecular complex (dashed line) in acetonitrile solution at room temperature.

TABLE 1: Parameters Describing the Charge-Transfer Band Observed in the Absorption Spectra for the Two Complexes[a]

parameter	stacked cyclophane	unstacked cyclophane	bimolecular complex
$\epsilon_{max}/M^{-1}\,cm^{-1}$	3860	6025	200
υ_{max}/cm^{-1}	20920 (478 nm)	21368 (468 nm)	20161 (496 nm)
$\Delta\upsilon_{1/2}/cm^{-1}$	6890	6890	5560

[a] The fwhm for each band, $\Delta\upsilon_{1/2}$, was determined using a Gaussian line shape, and ϵ_{max} for the bimolecular complex was calculated as described in the text.

charge transfer spectra indicate that the driving force for the cyclophane and the bimolecular complex are different. We will now show that this difference in reaction rate can be understood in terms of a change in reaction driving force. We will then use the spectroscopic data for the bimolecular complex to calculate the corresponding through-space rate for the driving force of cyclophane I. This will show that the through-bond and through-space rates for cyclophane I actually differ by a factor of 700, demonstrating that the through-space mechanism is kinetically noncompetitive in the cylophane molecule.

There are several theoretical formalisms that expand upon the general idea embodied by eqs 1 and 2 and thereby derive an expression for the rate constant in terms of molecular parameters. The Bixon−Jortner equation has met with significant success in treating the dynamics of electron-transfer reactions in the Marcus inverted region, and we will use this formalism for our present analysis. The Bixon−Jortner equation[31] is a quantum mechanical equation that models the electron transfer process in terms of a vibrationally assisted tunneling process. The rate constant, k_{et}, is expressed as

$$k_{et} = e^{-s}|V|^2\left(\frac{4\pi^3}{h^2\lambda_s k_B T}\right)^{1/2}\sum_{j=0}\left(\frac{s^j}{j!}\right)(1+H_j)^{-1}\times \exp\left(\frac{-(\Delta G^\circ+\lambda_s+jh\upsilon_v)^2}{4\lambda_s k_B T}\right) \quad (3)$$

where $s = \lambda_v/h\upsilon_v$, $H_j = 8\pi^2F_j|V|^2\tau_L/(h\lambda_s)$, and $F_j = e^{-s}s^j/j!$. In this expression, the Gibbs energy of reaction is denoted by ΔG° and the reorganization energy, λ, is partitioned into solvent (λ_s) and vibrational (λ_v) components, ($\lambda = \lambda_s + \lambda_v$). Figure 3 shows a schematic potential energy diagram that indicates the meaning of λ and ΔG° for an electron transfer reaction in the Marcus inverted region.

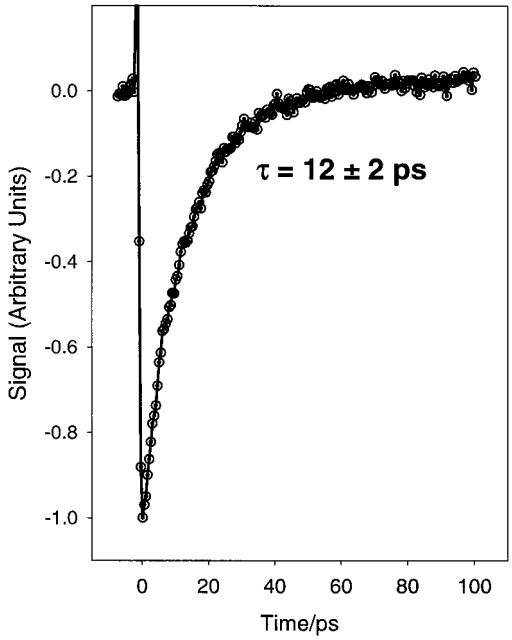


Figure 2. Degenerate pump/probe dynamics at 480 nm recorded following excitation of the charge-transfer band of cyclophane I in acetonitrile solution at room temperature. The circles are the experimental data. The solid line is a single-exponential recovery with a time constraint of 12 ± 2 ps. Similar dynamics are observed for cyclophane II.

There has been great success in modeling the coupling of the ground and excited states by one characteristic vibration, usually taken to be a C−C skeletal mode, ca. 1500 cm^{-1}.[32] There are recent studies that indicate that a lower frequency mode, ca. 100 cm^{-1}, may be important for quantitative modeling.[33] For simplicity, we will assume a single mode at 1500 cm^{-1}, thereby reducing the summation over vibrational modes, j, and leaving us only to determine $|V|$, λ, and ΔG° in order to calculate k_{et}.

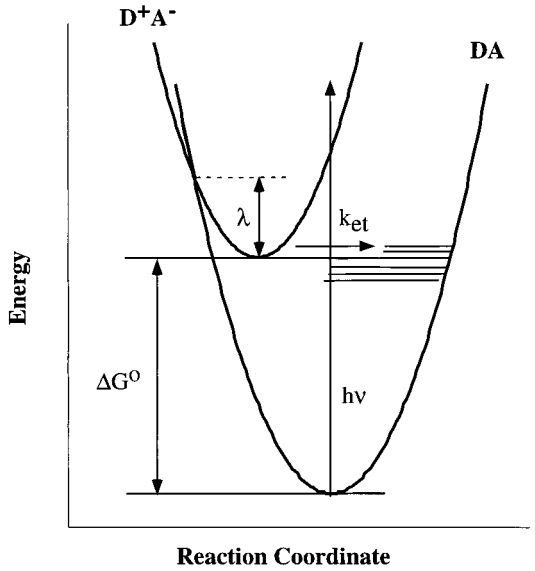


Figure 3. Schematic potential energy diagram for an electron-transfer reaction in the Marcus inverted region. The reorganization energy, λ, and driving force, $\Delta G°$, are labeled. Excitation of the charge-transfer band of the donor−acceptor complex DA directly produces D^+A^-. Back-electron transfer, indicated by k_{et}, occurs by tunneling to high-lying vibrational levels of the DA complex.

Further, we will assume that the relative values of $\Delta G°$ for these electron transfer reactions can be deduced from the observed shifts in the charge transfer absorption spectra. If we take the charge transfer absorption band of the cyclophane I as our reference point, then the absorption band for the bimolecular complex is red-shifted by 760 cm^{-1}. It is important to note that the cyclophane structure clearly constrains many degrees of freedom that are accessible to the bimolecular complex. In addition, we cannot reliably determine the donor−acceptor distance for the bimolecular case, and therefore, as a starting point for the calculations, we will assume that the center-to-center distance remains equal to that calculated for cyclophane I (360 pm). For the analysis presented below, it is important to note that the relationship between k_{et} and the reaction driving force is determined by the differences between $\Delta G°$ and λ, not by the absolute values for either.

Using the reported electrochemical data for this particular system, $E°_{ox} = -1.09$ V for DMB[34] and $E°_{red} = 0.12$ V for DCBM,[35] and taking the center-to-center donor−acceptor separation for cyclophane I to be 360 pm,[20] we calculate that $-\Delta G° = 1.10$ eV for cyclophane I. If we take the energy difference in the absorption maxima for the charge-transfer band to reflect of the change in driving force for the reaction, then the driving force for the bimolecular system is $-\Delta G° = 1.01$ eV. For an electron transfer reaction in the Marcus inverted region, such a decrease in driving force suggests that the rate constant for the bimolecular complex will be greater than that of cyclophane I. However, examination of eq 3 shows that the rate also depends quadratically on the electronic coupling matrix element $|V|$ and there is no reason to assume that this remains unchanged when the alkly linkers are removed, vide infra.

To quantify the difference in rate constants using Bixon−Jortner theory, we need to determine λ_s and λ_v, the solvent and vibrational components of the reorganization energy, and $|V|$, the coupling matrix element. While it is difficult to determine these quantities precisely, λ_s and $|V|$ can be estimated. Because we are comparing two cases that use the same donor and acceptor, errors in these calculations should affect both cases similarly. Thus, it should prove to be instructive to use estimates of these quantities in the Bixon−Jortner expression to see if the difference in reaction rates can be accounted for in terms of the change in reaction driving force reflected by the charge transfer absorption spectra.

Continuum models for the solvation component of the reorganization energy depend on the donor−acceptor separation and the effective molecular volume of the two moieties. The simplest expression relating λ_s to these quantities is given by[36]

$$\lambda_s = \frac{e^2}{4\pi\epsilon_0}\left(\frac{1}{\epsilon_{op}} - \frac{1}{\epsilon_s}\right)\left(\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{r}\right) \qquad (4)$$

where ϵ_{op} and ϵ_s are the optical and solvent dielectric constants respectively, a_1 and a_2 are the radii of spheres with volumes equivalent to the molecular volumes of the donor and acceptor, and r is the donor−acceptor separation. Ab initio calculations were performed using HF/STO-3G (SPARTAN) determining that both DMB and DCBM have molecular volumes on the order of 1.4×10^5 pm^3. Using the calculated volumes, we find $\lambda_s = 0.275$ eV. Once again if we start by assuming a constant center-to-center distance for cyclophane I and the bimolecular complex, the value of λ_s will be the same for both cases.

The rate constant k_{et} depends quadratically on the matrix coupling element, $|V|$. Small changes in $|V|$ can therefore significantly alter the reaction rate. Clearly, the donor−acceptor geometry affects the magnitude of $|V|$. In addition, Hynes and co-workers have shown that in certain cases $|V|$ is strongly dependent on solvent properties,[37] and therefore we shall focus on comparing the cyclophanes and the bimolecular complex in a single solvent, acetonitrile. Experimental determination of $|V|$ remains a difficult problem; however, there are approaches for estimating the value of $|V|$ from the measured charge-transfer spectrum. To try and gain some insight into the value of $|V|$ for the systems studies herein, we will analyze the charge-transfer absorption band using the Hush−Mulliken equation.[38]

$$|V|\ (cm^{-1}) = (0.00206/r\ (nm))(\epsilon_{max}\nu_{max}\Delta\nu_{1/2})^{1/2} \qquad (5)$$

Using the values shown in Table 1, we calculate $|V| = 0.53$ eV for cyclophane I and $|V| = 0.10$ eV for the bimolecular complex. The value of $|V|$ changes significantly despite the fact that the two electron-transfer systems have the same donor and acceptor molecules.

Calculation of the rate for electron-transfer now requires estimation of the vibrational reorganization energy, λ_v. This is the only parameter in the Bixon−Jortner model that we are unable to estimate from experimental data. Thus, we will determine the value of λ_v needed to quantitatively account for the electron transfer half-life for cyclophane I (12 ps)[20] and then use that value to calculate the rate constant for the bimolecular complex. Because the donor and acceptor moieties are the same in all cases, it is reasonable to assume that the value of λ_v will be essentially the same for both cases.

Combining the above calculated values and using the observed rate constant gives a value for λ_v of 0.12 eV for cyclophane I. This value is in reasonable agreement with those determined for similar complexes.[4] In addition, $-\Delta G°$ (=1.10 eV) > $(\lambda_v + \lambda_s) = (0.4$ eV), which must be true for the reaction to occur in the Marcus inverted region. If we now take the parameters for the bimolecular complex ($-\Delta G° = 1.01$ eV, $|V| = 0.11$ eV) and assume that λ_v and λ_s are the same for the bimolecular complex and the cyclophane, then $\tau_{et} = 43$ ps, which is excellent quantitative agreement with the experimental value (34 ps).

Before addressing the origin of the change in driving force between the cyclophane and bimolecular complex, it is interesting to ask the following question: "What would be the time constant for the bimolecular reaction be if we set the reaction exothermicity to that of cyclophane I?" Under those conditions, the calculated reaction half-life is 8.3 ns, which is a factor of over 700 greater than that observed. Within the assumptions made above, this calculated time constant is an estimate of the rate of the through-space electron transfer process for the cyclophane, and thus supports our earlier conclusion that the through-space mechanism of electron transfer is not operative in these molecules. Furthermore, let us assume, as is generally the case, that the dominant contribution to the through-bond and through-space mechanisms for the cyclophane is reflected by the difference in the electronic coupling $|V|$. In this case, if we take $r = 360$ pm and β to be 2.8 $Å^{-1}$ for through-space and 1.1 $Å^{-1}$ for through-bond electron transfer, then we predict that the rate of through-bond electron transfer will be faster than a through-space transfer by a factor of 450 (eqs 1 and 2). This is also consistent with the above conclusion.

We now recall that the electron transfer dynamics are identical for the two cyclophanes, even though there is a change in the center-to-center distance between the two chromophores. The charge-transfer absorption band of cyclophane **II** is blue-shifted by 450 cm^{-1} from that of cyclophane I, and is characterized by a larger extinction coefficient (see Table 1). If we take the shift in the absorption spectrum to reflect a change in reaction driving force (as done above for the bimolecular complex), then $-\Delta G° = 1.15$ eV for cyclophane II. If we now take the center-to-center distance for cyclophane II to be 470 pm,[12] calculate $|V|$ and λ_s from eqs 5 and 4, respectively, and use the same value for λ_v (=0.12 eV) that we estimated previously for cyclophane I, then we calculate a reaction half-life of 2.5×10^{-9} ps. This value is clearly unreasonable. However, if we only adjust the distance parameters in this set of equations to obtain agreement between the calculated and experimental value of 12 ps, then we find that this distance must be 363 pm. This distance is within 1% of that used to calculate the kinetics for cyclophane I. This result strongly suggests that the electron transfer in both cyclophanes "senses" the same distance, which is consistent with a through-bond mechanism.

We now try to address the origin of the change in driving force for this reaction, as reflected by the charge transfer band, given that the donor and acceptor moieties are the same in all cases. The driving force depends on the oxidation and reduction potentials of the chromophores, as well as on a dielectric term that, to a first approximation, scales with the intermolecular distance between these chromophores. If we take this latter contribution to the driving force to be $e^2/4\pi\epsilon_0\epsilon_s r$,[36] then the distance between the donor/acceptor in bimolecular complex would have to be approximately 200 pm in order to account for the reduced driving force. In addition, the intermolecular distance in cyclophane II would need to be 680 pm, which is about 50% greater than the constrained distance of 470 pm. Thus, it seems unreasonable to attribute the observed changes in driving force (on the order of 0.1 eV) to this dielectric term.

We therefore attribute the change in driving force predominantly to changes in the electrochemical behavior of the donor/acceptor moieties in the three cases examined. To explore this possibility we have used simple ab initio calculations (Spartan, STO-3G basis set) to calculate the HOMO energy for DMB allowing for the geometry to be optimized, as well as the cases where the molecular framework of DMB is constrained to that characteristic of the optimized geometry for both cyclophanes. For both cyclophanes, geometry optimized calculations show that the rings of both the donor and acceptor moieties deviate significantly from planarity. This is also revealed in the X-ray crystal structure of cyclophane I.[39] In contrast, geometry optimized calculations of DMB show that the aromatic ring is planar, as expected, and the energy of the HOMO is −7.09 eV. If we constrain DMB to have the geometry of that found for cyclophane I, then the HOMO energy changes to −6.25 eV. For cyclophane II, the HOMO energy is −6.31 eV. This comparison shows that distortion of the DMB moiety imposed by the cyclophane structure can result in substantial change (10%) in the energy of the HOMO. Similar effects are calculated for the LUMO of the DCMB moiety. Specifically, the LUMO of the DCMB for the geometry optimized molecule and constrained structures calculated for cyclophane I and II are 2.50, 2.52, and 2.60 eV, respectively. These calculations suggest that it is reasonable to attribute the differences in reaction driving forces for the bimolecular complex and the cyclophanes to changes in the electronic structure that arise from geometrical constraints imposed by the molecular architecture of the different systems.

The above discussion points out that the difference between the electron transfer kinetics for the cyclophanes and the corresponding bimolecular complex can be reasonably accounted for by a change in driving force that accompanies a change in molecular geometry. An important aspect of this analysis is that the same donor and acceptor groups are used in the three cases (two cyclophanes, one bimolecular complex). Many biological electron transfer reactions occur between pigments that are embedded in a protein matrix that specifies an orientation and distance between the two redox-active molecules.[25] In some cases, the protein is known to distort the conformation of the embedded chromophores.[6] The present study shows that small changes in molecular geometry imposed by external constraints can alter the driving force for the reaction and thereby the rate. These effects should be considered, for example, when comparing electron transfer rates between wild-type and mutant proteins. In these cases, mutation in the vicinity of the chromophore may not only affect the redox properties of the pigment due to changes in the local electrostatic environment but may also affect the kinetics of the reaction by causing small changes in the structure of the chromophore.

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