J. Am. Chem. Soc. **2000,** *122,* 5075−5081

Solvent-Mediated Intramolecular Electron Transfer in U-Shaped Systems with Different "Bite Sizes"

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Received June 7, 1999. Revised Manuscript Received March 9, 2000

Abstract: The rate of photoinduced charge separation is measured as a function of solvent for four donor (D)−bridge−acceptor (A) systems: **DMN[10]DCV**, **DMN[10nb]DCV**, **DMN[10cy]DCV**, and **DMAN[10cy]DCV**. In the first three members of this series, the D/A pair is kept constant and contains the strong dimethoxynaphthalene (DMN) donor which enables detection of electron transfer over a wide range of solvent polarity. In the fourth member, DMN is substituted by a dimethoxyanthracene (DMAN) unit, which decreases the driving force for photoinduced charge separation by about 0.58 eV and thereby limits the occurrence of electron transfer to polar solvents. In all systems the bridge is held at a length of 10 σ bonds. The configuration of the bridge is, however, varied to increase its bending in the series, which leads to center-to-center D/A distances decreasing from 13.4 Å in the first system to 9.54 Å in the second, and 7.50 Å in the latter two. In **DMN[10nb]DCV**, the rate of intramolecular charge separation over 9.54 Å is always smaller than that over 13.4 Å in **DMN[10]DCV**, which is in line with a dominant through-bond mechanism that is more efficient via an extended array of σ bonds. However, in **DMN[10cy]DCV**, the rate is as high as or even higher than that in **DMN[10]DCV**. Although changes in the driving force are also important, as shown, for example, by the dramatic rate decrease in **DMAN[10cy]DCV** as compared to that of **DMN[10cy]DCV**, the high rates observed for **DMN[10cy]DCV** in polar aromatic solvents as well as in acetonitrile strongly indicate an important contribution of through-solvent interaction across the 7.5 Å D/A distance, which in principle allows the intercalation of a single solvent molecule in close contact with both D and A. At the longer distance of 9.54 Å in **DMN[10nb]DCV**, a smaller contribution of through-solvent interaction can still be detected for polar aromatic solvents but not for acetonitrile. The inherently discontinuous distance dependence of through-solvent interaction and its possible interesting dependence on molecular structure and temperature are discussed.

Introduction

The mechanism of long-range electron transfer remains a topic of active research and discussion. Donor (D)−bridge−acceptor (A) compounds in which the bridge maintains a well-defined donor−acceptor distance and relative orientation[1−4] have proven to be of great use in these studies. Especially in compounds where the bridge has an extended structure, it has been shown unequivocally that through-bridge electronic interaction plays a dominant role in mediating intramolecular electron transfer between D and A. While this is not unexpected in the case of π-conjugated bridges, the dominance of through-bridge interaction has been found to apply also when extended, rigid, saturated hydrocarbon bridges are used. In fact, the latter type of long-range electron transfer has provided some of the most sensitive and convincing tests of through-σ-bond interaction (TBI) and its structural dependence. Regarding the latter, especially the theoretical prediction[5] of optimal TBI across an all-trans array of σ bonds was confirmed repeatedly.[6−9] It was typically found that the decrease of the rate of electron transfer (k) with the number of bonds (n) in such an all-trans array can be described by an exponential ($k \sim \exp(-n\beta)$) with a damping factor $\beta = 0.9 \pm 0.1$ per σ bond under conditions where the changes in rate are thought to be determined mainly by the changes in electronic coupling (V), i.e., $k \sim V^2$. In one instance, we noted[8] that for an extended $n = 8$ bridge, removal of the internal all-trans configuration not only reduced the rate of electron transfer—as expected from the predicted reduction in V_{TBI}—but also led to a significantly stronger solvent dependence of that rate. We then tentatively proposed that this may be related to a relative increase in the contribution of through-solvent interaction (TSI).

Efforts have been made to determine the importance of TSI in intermolecular electron-transfer processes in rigid matrixes[10,11]

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10.1021/ja991895m CCC: $19.00

and lately also in liquid solution.[12,13] Evidently, competition between TBI and TSI could be studied by the construction of D−bridge−A systems containing a rigid but U-shaped bridge. Such a U-shape on one hand might diminish TBI by the absence of an all-trans coupling path and on the other hand should enhance TSI by reducing the direct D/A distance as compared to the through-bond distance. Recently, several D−bridge−A systems with a more or less pronounced U-shape have, indeed, been reported. The first types of U-shaped systems were multichromophoric ones.[14−17] Although through-solvent-mediated charge recombination and charge separation mechanisms were implicated, the presence of extra chromophores in the bridges complicates interpretation of the rate data. More recently, also several bichromophoric systems with a pronounced U shape and closer approach of D and A have been reported by Zimmt et al. Especially in two of these with respectively an 11-bond bridge[18] and a 9-bond bridge,[19−22] D and A are brought in a face-to-face orientation with a center-to-center separation across the “cleft” as close as 10.0 and 7.1 Å, respectively. From a study of the solvent and temperature dependence of the rates of photoinduced charge separation in these systems as well as from theoretical calculations, compelling evidence was found for significant TSI in electronegatively substituted aromatic solvents. These results were interpreted from a superexchange mechanism in which the electron affinity of the solvent plays a decisive role.[18]

In these studies, rather “weak” D/A pairs were employed that require significant solvation assistance to make charge separation thermodynamically feasible. This implies that the (Marcus) barrier to electron transfer is inherently high and rather steeply increases with a decrease of the solvent dielectric constant, thus severely limiting the range of solvent polarity in which charge separation occurs and also making its rate strongly limited by Franck−Condon factors.

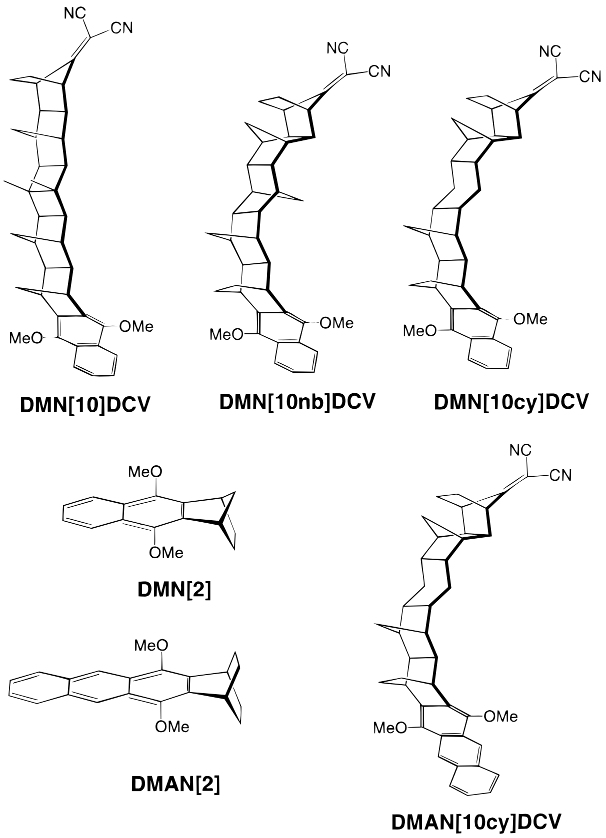

Figure 1. Structures of the bichromophores studied and of the model donors **DMN[2]** and **DMAN[2]**.

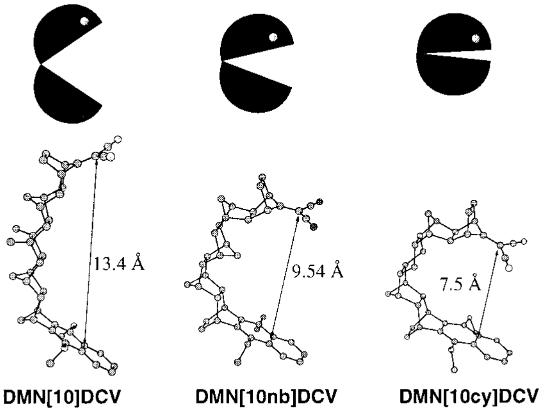

Figure 2. Perspective drawings of **DMN[10]DCV**, **DMN[10nb]DCV**, and **DMN[10cy]DCV** as modeled with the Sybyl force field (see Experimental Section) with R_c indicated (hydrogens omitted for clarity).

To reduce this problem, we have now studied the D−bridge−A systems **DMN[10]DCV**, **DMN[10nb]DCV**, and **DMN[10cy]DCV** (see Figure 1) containing the rather strong dimethoxynaphthalene (DMN)/dicyanovinyl (DCV) donor−acceptor pair. The latter two systems differ in that the hydrocarbon bridge of the former possesses a central norbornane group (nb) while the latter possesses a cyclohexane ring (cy). For comparison, also the **DMAN[10cy]DCV** system was studied which contains (see Figure 1) the less powerful 1,4-dimethoxyanthracene donor unit employed extensively by Zimmt et al.[18−22] Substitution of the 1,4-dimethoxyanthracene donor by 1,4-dimethoxynaphthalene enhances the driving force for photoinduced charge separation by about 0.6 eV because it increases the singlet energy from 3.00 to 3.78 eV while the ground-state oxidation potential increases much less, i.e., from 0.9 to 1.1 V (versus SCE). All D−bridge−A systems in Figure 1 contain a 10-bond bridge, but the curvature of it differs and leads to D/A distances of 13.4, 9.54, and 7.50 Å, respectively (see Figure 2). An X-ray structure of the ketone precursor to **DMN[10nb]DCV** (i.e., C=(CN)$_2$ replaced by C=O) revealed that this ketone recrystallized with one molecule of CH$_2$Cl$_2$ in a 1:1 stoichiometry with the CH$_2$Cl$_2$ molecule lying within the ketone’s molecular cavity.[23]

Results and Discussion

Table 1 compiles rates of photoinduced charge separation from the donor singlet excited state at room temperature in a wide range of solvents for the D−bridge−A systems of Figure 1.

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Table 1. Experimental Rate (k_{exp}) and Estimated Barrier ($\Delta G^{\#}$) of Photoinduced Charge Separation as a Function of Solvent at Room Temperature

solvent	dielectric constant (ϵ)	refractive index (n)	k_{exp} ($\times 10^8$ s^{-1}) [$\Delta G^{\#}$ (eV)]			
			DMN[10]DCV	**DMN[10nb]DCV**	**DMN[10cy]DCV**	**DMAN[10cy]DCV**
TIPB (1,3,5-triisopropyl benzene)	2.1 ± 0.1	1.4882	19 [0.111]	5.9 [0.039]	187 [0.005]	– [0.210]
benzene	2.28	1.5011	72 [0.093]	21.3 [0.033]	500 [0.004]	– [0.191]
DBE (di-*n*-butyl ether)	3.10	1.3992	35 [0.096]	8.0 [0.043]	49 [0.010]	– [0.175]
DEE (diethyl ether)	4.20	1.3524	51 [0.096]	7.5 [0.047]	49 [0.014]	0.07 [0.166]
EtAc (ethyl acetate)	6.02	1.3724	85 [0.080]	9.2 [0.038]	124 [0.011]	0.21 [0.147]
THF (tetrahydrofuran)	7.58	1.4072	120 [0.066]	18 [0.030]	110 [0.008]	0.27 [0.134]
ODCB (orthodichloro-benzene)	9.93	1.5515	141 [0.034]	65 [0.012]	665 [0.001]	2.0 [0.104]
BzCN (benzylcyanide)	19.0	1.521	103 [0.036]	58 [0.014]	221 [0.002]	1.3 [0.102]
PhCN (benzonitrile)	25.20	1.5282	*a* [0.035]	*a* [0.013]	*a* [0.002]	9.5 [0.100]
ACN (acetonitrile)	37.50	1.3441	24 [0.073]	7 [0.037]	141 [0.011]	0.3 [0.133]

[a] Total electron-transfer quenching of the DMN singlet occurs by this solvent.

As reported earlier,[24] the variation of rate with solvent is modest for the extended system **DMN[10]DCV**, notwithstanding the large changes in driving force predicted to be brought about by changing the solvent dielectric constant between $\epsilon \approx 2.2$ and 37. This is interpreted to indicate both a virtually solvent-independent electronic coupling of the TBI type (V_{TBI}) and an almost solvent independent Franck–Condon factor (see below).

It is well known that one should be careful with interpreting rates only in terms of changes in the total electronic coupling (V) because changing the solvent (and/or the distance) may also change the Franck–Condon factor. Within the framework of basic electron transfer theory, the latter translates into the Marcus barrier ($\Delta G^{\#}$), and the rate of nonadiabatic electron transfer can be written as

$$k = [2\pi^{3/2}V^2 \exp(-\Delta G^{\#}/k_{\mathrm{B}}T)]/(h^2\lambda k_{\mathrm{B}}T)^{1/2} \qquad (1)$$

In eq 1, h is Planck's constant, k_{B} Boltzmann's constant, and λ the reorganization energy.

Thus, not only changes in V but also changes in $\Delta G^{\#}$ have a dramatic influence on the rate and thereby frustrate extraction of V from electron-transfer rates. In principle, this can be remedied by determining $\Delta G^{\#}$ from temperature-dependent studies, but the interpretation of these has turned out to be complex due to the changes of the solvating properties of solvents with temperature.[25] It is therefore not amazing that, e.g., quite different V values are derived[26,27] from a single set of temperature-dependent rate data employing different solvation models.[28]

As we have pointed out before,[29] for each D/A combination there exists a unique distance ($R_{\mathrm{c}}^{\mathrm{opt}}$) at which $\Delta G^{\#}$ becomes zero, irrespective of the solvent dielectric constant, provided that the refractive index remains constant. For photoinduced charge separation in solvents with $n^2 = 2$, the condition under which this occurs is given,[29] to a good approximation, by

$$R_{\mathrm{c}}^{\mathrm{opt}} = 7.2/[E_{\mathrm{ox}}(\mathrm{D}) - E_{\mathrm{red}}(\mathrm{A}) - E_{00} + \lambda_{\mathrm{in}} + 6.81/r] \quad (2)$$

In eq 2, $E_{\mathrm{ox}}(\mathrm{D})$ and $E_{\mathrm{red}}(\mathrm{A})$ represent the one-electron redox potentials (in volts) of D and A as measured in a polar solvent such as acetonitrile, E_{00} the energy (in electronvolts) of the locally in D or A excited state, λ_{i} the internal reorganization energy (in electronvolts), and r (in angstroms) the average ionic radius.

For the DMN/DCV donor–acceptor pair, the values $E_{\mathrm{ox}}(\mathrm{D}) = 1.1$ V, $E_{00} = 3.78$ eV, $E_{\mathrm{red}}(\mathrm{A}) = -1.7$ V, $r = 4.5$ Å, and $\lambda_{\mathrm{in}} = 0.6$ eV apply.[24] Equation 2 then gives $R_{\mathrm{c}}^{\mathrm{opt}} = 6.35$ Å. This implies that electron transfer in **DMN[10cy]DCV** ($R_{\mathrm{c}} = 7.5$ Å) should be close to barrierless in all solvents. In Table 1, this is further illustrated by calculating the barrier explicitly in each solvent, taking into account its dielectric constant and its refractive index and employing the well-known dielectric continuum models[29] with again the average ionic radius set at 4.5 Å and a constant internal reorganization energy set at 0.6 eV.[24] For **DMN[10cy]DCV**, a very small barrier is then, indeed, estimated, irrespective of the solvent employed. Unavoidably, the barrier increases with R_{c} and at the same time becomes more solvent dependent in **DMN[10nb]DCV** and **DMN[10]DCV** (see Table 1).While in all three DMN/DCV systems the estimated barriers are quite small, it should be realized that even small barriers have a significant kinetic effect, which starts to exceed an order of magnitude for **DMN[10]DCV** upon going to low-polarity solvents. We stress that under such conditions the separation of barrier effects from electronic coupling effects in determining the rate of electron transfer (see eq 1) becomes progressively more difficult.

For the DMAN/DCV combination, eq 2 predicts that $R_{\mathrm{c}}^{\mathrm{opt}}$ is as small as 4.2 Å, and as can be seen from Table 1, the attenuation of the electron transfer by barrier effects must be very dramatic in all solvents (about 2 orders of magnitude in polar solvents and exceeding 3 orders of magnitude in low-polarity solvents) for **DMAN[10cy]DCV**, even at the short distance of 7.5 Å. In fact, charge separation is calculated to

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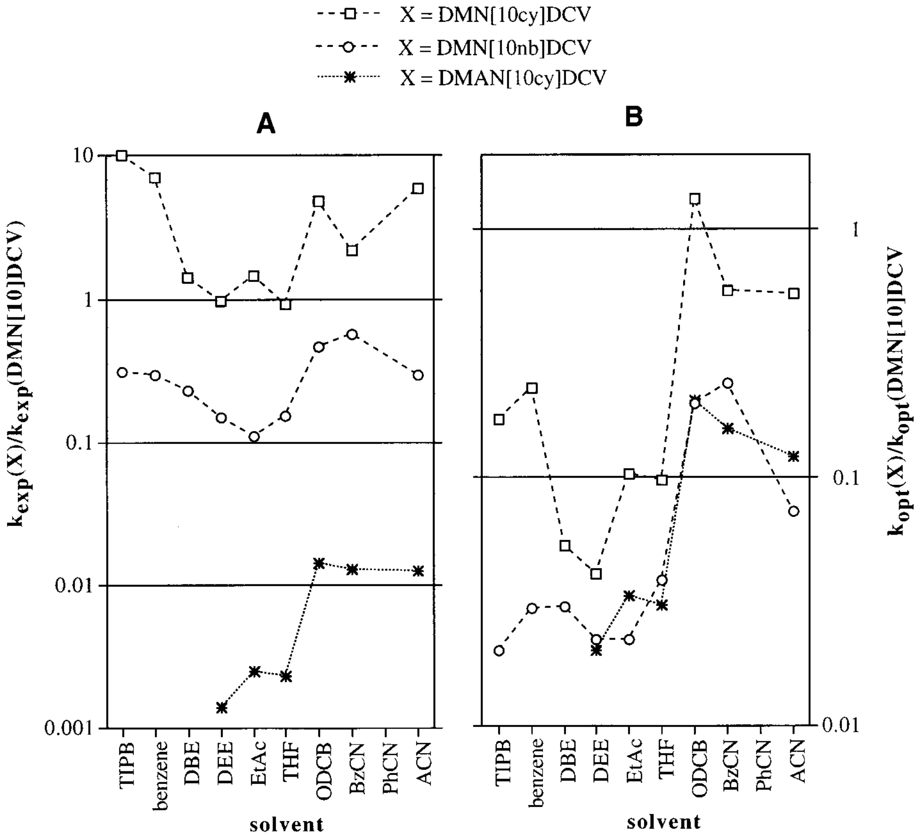

Figure 3. Rates of photoinduced charge separation in **DMN[10nb]DCV**, **DMN[10cy]DCV**, and **DMAN[10cy]DCV** relative to that in **DMN[10]DCV** as found experimentally, k_{exp} (A), and after correction to "zero barrier" conditions, k_{opt} (B).

become significantly endergonic for **DMAN[10cy]DCV** in low-polarity solvents, and experimentally we found it quite difficult to detect significant effects of electron transfer on the fluorescence in nonpolar solvents and were only able to estimate its rate with reasonable confidence in diethyl ether and in higher polarity media (see Table 1).

We now first qualitatively discuss the experimental rate data compiled in Table 1, and for this purpose we have plotted in Figure 3A the rates of the bent systems relative to that of **DMN[10]DCV** in each solvent (note that for the DMN/DCV systems, no rates in PhCN can be measured because this strongly electron-accepting solvent itself fully quenches the singlet excited state of DMN). Electron transfer in **DMN[10nb]DCV** ($R_c = 9.5$ Å) is always slower than that in **DMN[10]DCV** ($R_c = 13.4$ Å), despite the lower barrier that could give it a rate advantage of up to an order of magnitude. Clearly, in the extended system, the higher barrier must be overcompensated by a larger *V*, which undoubtedly can be attributed to the presence of an all-trans TBI pathway in that extended system. Whether in **DMN[10nb]DCV** the decrease of V_{TBI} is partly compensated by an eventual increase of V_{TSI} cannot be deduced with certainty from a qualitative inspection of the data, but this will be discussed in more detail below. We do, however, note already that the rate reduction is rather strongly solvent dependent and is especially less pronounced in the polar aromatic solvents ODCB and BzCN, although in such polar solvents the barrier reduction gained by reducing the distance from 13.4 to 9.54 Å must be relatively small (see Table 1).

In **DMN[10cy]DCV**, R_c is further reduced to 7.5 Å, and as compared to **DMN[10nb]DCV**, a dramatic rate increase occurs in all solvents, making electron transfer as fast as or in several cases even much faster than that for **DMN[10]DCV** (see Figure 3A). There is no reason[30] to assume that TBI in **DMN[10cy]DCV** should be more effective than that in **DMN[10nb]DCV**, but of course there is a significantly lower barrier in the former (see Table 1) that accounts for at least a part of the rate increase. This barrier-related effect should, however, be most pronounced in low-polarity solvents and decrease to a lower and almost constant effect at higher polarities. That is clearly not in line with the observations, and therefore an additional effect, such as a solvent-dependent contribution of V_{TSI}, may already be invoked for **DMN[10cy]DCV** from this inspection of the experimental rates. The experimental rates for **DMAN[10cy]DCV** are too low to draw any conclusion by direct comparison with the DMN/DCV systems and furthermore extend over a smaller polarity region, but again we note that the rate ratios plotted in Figure 3A show a strong solvent dependence that crudely resembles that of the other bent systems.

To reveal more quantitatively the eventual changes in *V* occurring as a function of structure and solvent, we have corrected the experimental rates to "zero barrier conditions". It should be stressed that these barriers are notoriously difficult to obtain experimentally, especially because changes in solvent parameters with temperature play such a complicating role in most common organic solvents employed here,[28,29] and that also upon calculational derivation of the barriers the solvation model employed as well as its parametrization[31] plays a critical role. The dielectric continuum model we employed here requires only a few parameters but has been found[25] to reproduce quite well the experimentally determined barrier in cases where the temperature-dependent behavior of the rate is uncomplicated. Of course, the dielectric continuum model does not take into account any specific solvent/solute interactions, and even so its outcome depends rather critically upon the choice of

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parameters, such as the average ionic radius and the internal reorganization energy. Therefore, the absolute value of "zero barrier rates" (k_{opt}) obtained even in the case of such relatively small barriers as those present in our DMN/DCV systems must, in our opinion, be taken with a grain of salt. Although we will return to the question of how large the V values actually are in our compounds, we therefore now only assume that in each solvent used the weaknesses inherent to the barrier corrections made apply equally to at least the three very closely related DMN/DCV systems. If so, the ratio of the "zero barrier rates" obtained for the three DMN/DCV systems in each solvent carries information about the eventual changes in the relative V^2 values as a function of solvent (note that an additional correction for the change of the reorganization energies as required by eq 1 is too small to be relevant within this context and has therefore been omitted). The outcome of this operation is extremely revealing, as shown in Figure 3B.

Again taking **DMN[10]DCV** as a reference, the strong relative rate enhancement shown by **DMN[10cy]DCV** in the low-polarity solvents benzene and TIPB as compared to that in medium-polarity solvents is now less extreme and should thus, to a large extent, be attributed to the increased importance of barrier-induced retardation for **DMN[10]DCV** at low polarity.[32] However, a clear solvent dependence of the rate ratio remains, and the ratio still reaches its highest values in both low-polarity and especially in high-polarity aromatic solvents as well as in acetonitrile, thus suggesting a significant increase of V^2 for **DMN[10cy]DCV** in these solvents. Interestingly, the "zero barrier" ratio exceeds unity only in ODCB (ratio = 1.32) and is significantly below unity in most other solvents. This implies that in most solvents, even at the short distance of $R_c = 7.5$ Å in **DMN[10cy]DCV**, the loss of TBI as compared to that in **DMN[10]DCV** ($R_c = 13.4$ Å) is not fully compensated by the gain in TSI!

The comparison of "zero barrier rates" for **DMN[10nb]DCV** with **DMN[10]DCV** yields similar but less pronounced effects for the polar aromatic solvents ODCB and BzCN, but much less pronounced indications for a significant enhancement of the relative V^2 in ACN or in low-polarity aromatic solvents are found.

Clearly, **DMN[10]DCV** is a rather poor reference for **DMAN[10cy]DCV**, and less value should therefore be attributed to the absolute position of the data points plotted in Figure 3B for the ratio of the k_{opt} values of these two compounds. In fact, the barrier correction to be applied to the ratio of the experimental rate of **DMAN[10cy]DCV** over that of **DMN[10]DCV** ranges from 1 order of magnitude in high- and medium-polarity solvents up to almost 2 orders of magnitude in nonpolar solvents. Nevertheless, the results obtained indicate that, for this system, ODCB, BzCN, and ACN behave similarly and, just as for **DMN[10cy]DCV**, enhance the V^2 for the bent system relative to that of the extended system as compared to the situation in the medium-polarity solvents.

There seems to be little doubt that the rate ratio modulations observed in Figure 3B must be attributed to a significant value and solvent dependence of V_{TSI} in the bent systems. Logically, this effect is more pronounced at $R_c = 7.5$ Å than at $R_c = 9.54$ Å, but it also appears that this increase in distance reduces the number of solvents capable of producing significantly enhanced TSI. Thus, not only the indications that for **DMN[10cy]DCV**, at $R_c = 7.5$ Å, TSI is slightly enhanced in TIPB and in benzene disappear at $R_c = 9.54$ Å for **DMN[10nb]DCV**, but especially also ACN seems to be much less effective in promoting TSI at the latter distance in comparison to the polar aromatic solvents. It is important to note that earlier results obtained by Zimmt et al. for DMAN/acceptor pairs appear to show this trend too. Thus, in a system with $R_c = 10$ Å, the value of V for ACN was concluded[18] to be only 14% of that in PhCN, but in a system with $R_c = 7.1$ Å it was found[20] to be 33%. Also for the $R_c = 7.5$ Å **DMAN[10cy]DCV** system we study here, acetonitrile appears to be "above average" in supporting TSI across such a small cleft.

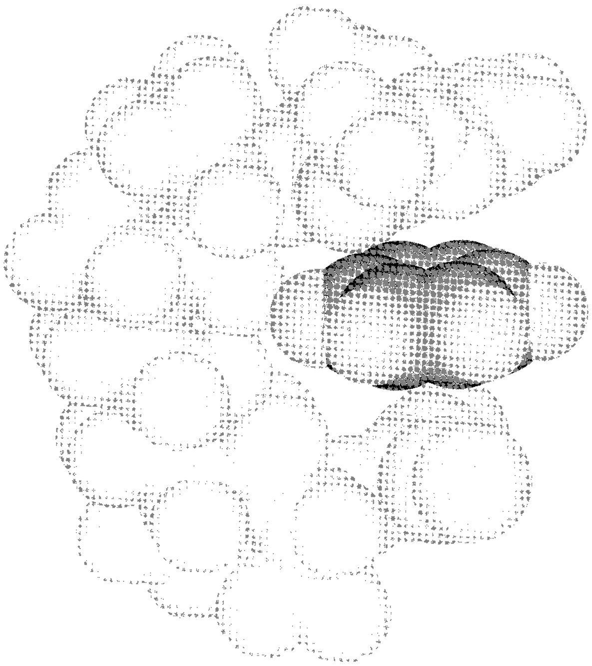

Figure 4. 3D model of a benzene molecule in the "jaws" of **DMN[10cy]DCV**.

In this relation, it should be realized that the distance dependence of TSI can, in principle,[2] be highly discontinuous and solvent structure dependent. Taking a van der Waals thickness of $T = 3.5$ Å for a typical π-system, the $R_c = 7.5$ Å cleft in **DMN[10cy]DCV** allows a rather tight fit of a single aromatic solvent molecule in that cleft (see Figure 4). For the 9.54 Å cleft in **DMN[10nb]DCV**, this fit would be very loose for one solvent molecule and extremely tight for two. The small number of solvent molecules interposed between D and A makes the decrease of TSI with distance, in principle, highly discontinuous with local maxima at distances that allow tight fit of one, two, three, etc. solvent molecules.

A crude prediction of the degree of discontinuity can be achieved by a simple superexchange pathway analysis.[3,33,34] In this model, the cleft is filled with the maximum number of solvent molecules that can be fitted in (N), leaving a total free space $F = R_c - T(N + 1)$, where the van der Waals thickness of D, A, and each of the solvent molecules is set at T.

If the fit is tight ($F = 0$), the superexchange via the stack of N solvent molecules may be written as $V_{TSI} = V_0(V_0/\Delta E)^N$, where V_0 stands for the resonance integral between nearest neighbors (assuming an equal value for solvent/solvent, D/solvent, and A/solvent contacts), while ΔE is the energy gap between the transition state for electron transfer from D to A and a virtual state in which charge is on one of the solvent

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[32] We are very grateful to one of the reviewers who pointed out how strongly "contaminated" by barrier effects the ratio of the uncorrected rate constants (Figure 3A) becomes at low polarity.

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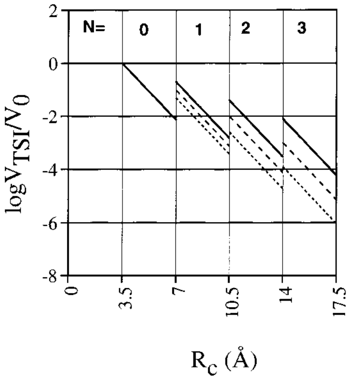

Figure 5. Distance dependence of V_{TSI} (in units V_0) as predicted by eq 3 for a molecular "thickness" $T = 3.5$ Å and assuming that the maximum number of molecules (N) is inserted between D and A. The curves drawn were calculated for a ratio $V_0/\Delta E = 0.05$ (dotted line), 0.1 (dashed line), and 0.2 (solid line).

molecules. It is assumed that this gap is the same for each solvent molecule in the cleft.

If the fit is not tight, the free spaces reduce the interaction between successive components. For this, an empirical through-space distance dependence is assumed with a high damping factor γ_F. In an earlier parametrization for electron pathway analysis in proteins, a value $\gamma_F = 1.7$ Å^{-1} was proposed,[35] which implies a decrease of electron-transfer rates through space with a damping factor of $2\gamma_F = 3.4$ Å^{-1}. Ab initio MO calculations[1] indicate that a smaller value for γ_F of 1.4 Å^{-1} is more appropriate. The expression for V_{TSI} then becomes

$$V_{TSI} = V_0(V_0/\Delta E)^N\,[\exp(-1.4F)]$$
$$= V_0(V_0/\Delta E)^N\,[\exp\{-1.4(R_c - T(N+1)\}] \quad (3)$$

It is important to note that, within this approximation, the distance dependence of V_{TSI} predicted by eq 3 is independent of how the total free space F is divided along the DS_NA array. Thus, solvent motions that do not change F should not influence the distance dependence of V_{TSI}, even though the absolute value of V_{TSI} is certainly strongly dependent on the orientation of the solvent molecules relative to D and A and to each other[3,19] because this influences V_0. In Figure 5, the dependence of V_{TSI} (in units of V_0) on R_c predicted by eq 3 is plotted for $T = 3.5$ Å and for the values of the ratio $V_0/\Delta E = 0.05$, 0.1, and 0.2. In the simple model underlying eq 3, it is then found (see Figure 5) that local maxima in coupling should result at R_c values that allow a tight fit of a whole number of solvent molecules, while beyond each of these R_c values the coupling drops steeply. Although the steep steps predicted will certainly be smoothed by solvent motions that modulate the total free space F, a rather strong discontinuity is expected to remain for small numbers of N under the constraint of well-defined cleft sizes in U-shaped D−bridge−A molecules.

We now return to the question of what determines the efficiency of a particular type of solvent molecule in mediating electron transfer in terms of the ΔE term from the simple superexchange model above (eq 3) that takes into account the energy gap between the transition state for charge separation and a state in which the negative charge is on the solvent and the positive charge on the donor ($D^+/S^-/A$). The energy required to put an electron from the donor on a solvent molecule is directly related to the ionization potential of the donor and the electron affinity of the solvent. The UB3LYP-calculated[36] ionization potential (IP = 7.24 eV) of **DMN[2]** differs little from that reported[18] for **DMAN** (IP = 7.4 eV), which should make DMN- and DMAN-based systems equally sensitive to the effects of TSI. The electron affinities of the solvents employed vary widely (e.g., EA = −1.12 eV for benzene,[37] −0.8 eV for BzCN,[18] and −2.8 eV for ACN[18]). ΔE decreases with increasing solvent electron affinity, and as a result, solvents with high electron affinity are expected to provide more efficient TSI. Therefore, the apparently strong V_{TSI} contribution in electronegatively substituted aromatic solvents such as BzCN as compared to that in benzene by itself comes as no surprise. However, the finding that at short range, i.e., at the $R_c = 7.5$ Å distance available in **DMN[10cy]DCV** as well as in **DMAN-[10cy]DCV** also in ACN, where ΔE should be 2 eV larger than that in BzCN and 1.68 eV larger than that in benzene, V_{TSI} seems to be important is surprising and clearly cannot be accounted for on the basis of ACN's electron affinity alone. Another aspect of solvent-mediated electron transfer in U-shaped systems may deserve attention in this connection. In fact, the situation where one or a few solvent molecules are intercalated between D and A, as modeled in Figure 4, should be considered as a distinct thermodynamic entity which is in equilibrium with an entity (or entities) lacking tightly intercalated solvent and in which electron transfer is thus probably much slower. The rate of electron transfer observed under fast solvent-exchange conditions is then a weighted average of that occurring in molecules possessing "solvent-filled" cavities and those having "solvent-free" cavities. This complication, if present, would have a number of interesting and far-reaching consequences, such as the following: (i) the overall rate would not be a direct measure of the solvent participation but rather the product of that participation and the affinity of the solvent to occupy the cleft; (ii) the temperature dependence of electron transfer would contain a contribution[20] of the change in the equilibrium constant between the filled and empty states, which can, in principle, give rise to an apparent (negative) activation energy of electron transfer that is, in fact, due to a change in electronic coupling V_{TSI}; (iii) under conditions of slow solvent exchange electron transfer can no longer be described by a single exponential and may even be limited by the rate at which a solvent molecule enters the cleft.

These aspects are presently under active investigation, but with respect to the unexpected efficiency of acetonitrile in mediating TSI across short distances, we already note that the small size, polar nature, and strongly solvating properties of this solvent have recently been found to allow it to enter quite effectively a narrow, π-system lined cavity.[38] Also, the rates of photoinduced ET in a tetrad, in which the terminal chromophores are separated by less than 7 Å, have been reported[17] to be the same in both benzonitrile and acetonitrile, and in view of the very long TBI pathway there is no doubt that, in that tetrad, ET should occur by a dominant TSI mechanism.

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Finally, we return briefly to the question of what the actual value of V is in our compounds. While we think that the variations in V^2 are reasonably well reflected by the plots provided in Figure 3B, we are, for reasons amply outlined above, hesitant to put too much value on the absolute values of V that can, in principle, be calculated readily from the data in Table 1 via application of eq 1. Nevertheless, it seems important to point out that, for **DMN[10]DCV**, a value of $V = 17.6\ \text{cm}^{-1}$ has been reported[39] that was determined not from kinetic data but independently from the radiative transition probability of the very weak charge-transfer fluorescence it displays in DBE. This V, therefore, should be related to the electronic coupling of the charge-separated state with the ground state rather than with the locally excited state. Nevertheless, it appears quite comforting to find that from the data in Table 1 and application of eq 1, a value $V = 21\ \text{cm}^{-1}$ in DBE is derived.

Concluding Remarks

The three DMN−bridge−DCV molecules depicted in Figures 1 and 2 have allowed us to investigate the possible role of through-solvent interaction (TSI)-mediated electron transfer over a wider solvent polarity range than that accessible for similar systems in which the strong DMN donor is substituted by the much weaker DMAN donor, such as in **DMAN[10cy]DCV**. Especially at the 7.5 Å distance present in **DMN[10cy]DCV**, through-solvent interaction is detectable for some polar as well as nonpolar solvents. Although a simple superexchange model predicts that the solvent electron affinity should be a decisive factor, acetonitrile, which has a very negative electron affinity (EA = −2.8 eV), appears to mediate TSI more effectively than, e.g., benzene (EA = −1.12 eV) across a 7.5 Å distance. At the longer distance of 9.54 Å found in **DMN[10nb]DCV**, however, acetonitrile largely loses its ability to mediate TSI, while in electronegatively substituted aromatic solvents TSI is still apparent. The "bite size" of the D−bridge−A system thus appears to have an effect on the relative efficiency of solvent molecules in mediating TSI across short ranges corresponding to one or two solvent molecule diameters, but it cannot yet be established whether this is the result of differences in the orientation of the various solvent molecules in the cleft between D and A or whether different affinities for residing in that cleft also play a role.

Finally, it should be noted that ab initio MO calculations on the charge-transfer-state geometry of several U-shaped D−bridge−A systems closely related to those studied here have revealed a strong tendency of such systems to undergo extensive conformational changes driven by the electrostatic attraction of the oppositely charged termini.[40] While until now these calculations have been restricted to the gas phase, it is well known from experiments on less rigidly bridged systems that such "harpooning" phenomena[41] also can be significant in low dielectric constant solvents.[42] Under such conditions, the ground-state conformation and the transition state of electron transfer may differ sufficiently to make the ground-state R_c an insufficient descriptor to estimate the electronic interaction involved in the actual electron-transfer process.

Experimental Section

Syntheses. The synthesis of **DMN[10]DCV** has been described earlier.[24] **DMN[10nb]DCV**, **DMN[10cy]DCV**, and **DMAN[10cy]DCV** were synthesized as described in the Supporting Information.

Charge separation rates were determined by time-resolved fluorescence spectroscopy employing time-correlated single-photon counting as described previously.[24] An excitation wavelength of 322 nm was employed for the DMN systems and 339 nm for the DMAN systems, and the decay of the DMN or DMAN fluorescence was detected at three wavelengths around the maximum. For the model system **DMN-[2]**, the (monoexponential) decay time (τ_{ref}) was determined in each solvent and varies between 5.9 ns in benzene and 7.5 ns in acetonitrile.[43] For the model **DMAN[2]**, the fluorescence lifetime appears more variable, i.e.: benzene, 22 ns; DBE, 15.6 ns; DEE, 13.1 ns; EtAc, 18.5 ns; THF, 21.8 ns; ODCB, 16.4 ns; BzCN, 23 ns; PhCN, 22.3 ns; and ACN, 20.7 ns. This is a serious problem because the experimental rate of charge separation is calculated from $k_{\text{exp}} = 1/\tau - 1/\tau_{\text{ref}}$, and the rate in **DMAN[10cy]DCV** is so low (see Table 1) that the actual value of τ_{ref} has a large influence. For the DMN/DCV bichromophores, the rates are, on the other hand, so high that the precise value of τ_{ref} plays little role, i.e., $k_{\text{exp}} = 1/\tau - 1/\tau_{\text{ref}} \approx 1/\tau$. It should be noted that, for the bichromophores, the decay in general contains, in addition to a major short component, a minor component with $\tau \approx \tau_{\text{ref}}$ due to small impurities that lack the DCV acceptor. This does not influence the accuracy of the rate determination as long as the two components can be separated reliably. For **DMAN[10cy]DCV**, this becomes quite problematic in low-polarity media (where charge separation is, in fact, calculated to be endergonic), and therefore no rate data in such media are given in Table 1.

Molecular Geometries. The molecular geometries shown in Figures 2 and 4 were determined employing the Sybyl force field in MacSpartan.[44] In the case of **DMN[10]DCV** and **DMN[10nb]DCV**, X-ray structural data are available for the precursor ketones (i.e., C═O instead of $C{=}C(CN)_2$)[45,23] that fully substantiate the validity of this approach. Thus, the X-ray structure of the ketone precursor to **DMN[10nb]DCV** gives a value of 9.5 Å for the distance between the center of the naphthalene unit and the carbonyl oxygen. Interestingly, this ketone recrystallized with one molecule of CH_2Cl_2 in a 1:1 stoichiometry with the CH_2Cl_2 molecule lying within the ketone's molecular cavity.

Quantum Chemical Calculations. Vertical IPs were calculated as the UB3LYP energy of the radical cation minus the B3LYP energy of the neutral, and the vertical EAs as the B3LYP energy of the neutral minus the UB3LYP energy of the radical anion. The 6-311G(d) and 6-311+G(d) basis sets were used for the IP and EA calculations, respectively. Geometries employed were HF/3-21G-optimized structures of the corresponding neutrals. All calculations were performed with Gaussian 94 (Revision B).[36]

Acknowledgment. This research has been financially supported by the Council for Chemical Sciences of The Netherlands Organization for Scientific Research (CW-NWO) and by the Australian Research Council (ARC). The award of an ARC Senior Research Fellowship to M.N.P.-R. is also gratefully acknowledged.

Supporting Information Available: Full experimental details for the synthesis of **DMN[10cy]DCV** (=**25**, **DMN[10nb]DCV** (=**26**), and **DMAN[10cy]DCV** (=**31**) (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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