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Optical and Thermal Electron Transfer in Rigid Difunctional Molecules of Fixed Distance and Orientation¹

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Abstract: Pulse radiolysis has been used to investigate intramolecular electron transfer in a series of molecules in which dimethoxynaphthalene (M₂N) and dicyanovinyl (DCV) groups are held at fixed distance and orientation by rigid saturated hydrocarbon bridges. Electron transfer from M₂N^{•-} to DCV is faster than $1 \times 10^9 \text{ s}^{-1}$ for compounds in which the two groups are separated by 4, 6, 8, 10, or 12 saturated carbon-carbon bonds. For the 4-, 6-, and 8-bond compounds, optical electron transfer bands are present in the visible-near-infrared absorption spectra of the anions. The positions shift to higher energies with increasing solvent polarity. Their intensities are large ($\epsilon \approx 2000 \text{ M}^{-1} \text{ cm}^{-1}$ for the 4-bond compound) and decrease rapidly as the length of the bridge increases. It is clear that exceptionally large, long-distance electronic coupling of the two π systems occurs through the saturated bonds of the bridge. These electronic couplings are 0.16, 0.06, and 0.03 eV across 4-, 6-, and 8-bond bridges. Even larger couplings have been observed previously by photoelectron spectroscopy, but not for such large π systems. With these large electronic couplings, long-distance electron transfer in the 4- and 6-bond compounds is expected to be adiabatic. Even for the 8-bond compound with a center-to-center distance of $\sim 12 \text{ \AA}$ the electron-transfer rate deduced from the optical electron-transfer absorption band is $>10^{12} \text{ s}^{-1}$.

During the last few years, measurements of intramolecular electron transfer have provided insights into the effects of distance, energy, and orientation on electron-transfer (ET) rates.²⁻³³ When electronic couplings, V , are small, the ET rate expression has the simple nonadiabatic form

$$k(r) = 2\pi/\hbar |V(r)|^2 \text{FCWD} \quad (1)$$

In eq 1, the rate is a product of an electronic factor $|V(r)|^2$, which is approximately proportional to overlap of donor and acceptor wave functions, and a Franck-Condon-weighted density of states (FCWD).

From photoelectron or electron transmission spectra,³⁴⁻⁴⁰ in which the electronic couplings appear as spectroscopic splittings, and from measurements of charge-transfer emissions,^{3-5,28} it has become apparent that through-bond interactions⁴¹⁻⁴⁵ can be the major source of electronic coupling in difunctional molecules containing two-electron donor/acceptor groups held apart by a rigid aliphatic bridge. Through-bond transmission of electronic interactions has also been examined by theoretical calculations of molecular electronic structure,⁴⁶⁻⁴⁹ and it has recently been found to enhance the rates of intramolecular electron-transfer reactions.^{3-6,28-33}

Very rapid electron transfer, probably due to through-bond interactions, has recently been observed²⁹⁻³² in the series of

molecules in Chart I in which a dimethoxynaphthalene group (M₂N) is separated from a dicyanovinyl (DCV) group by bridges

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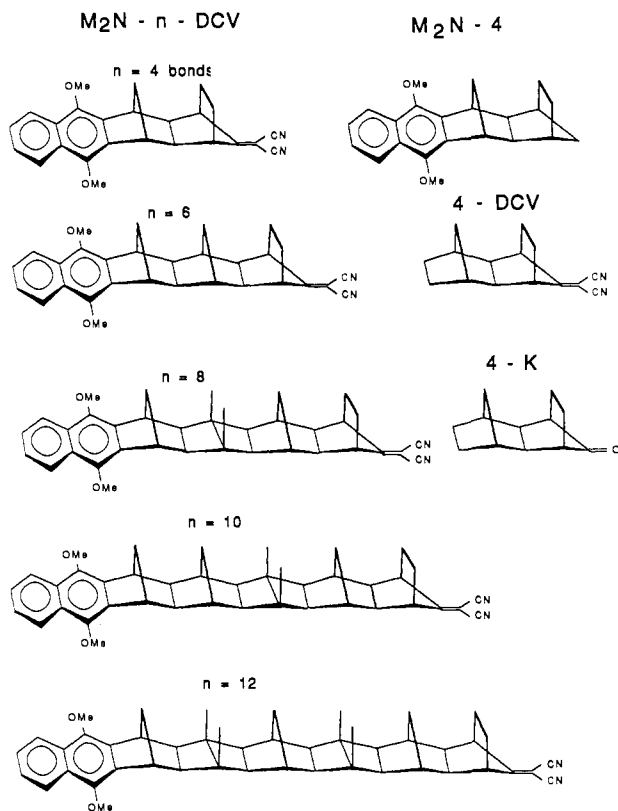
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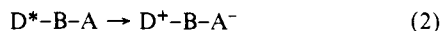
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Chart I



(B) having 4, 6, 8, 10, or 12 saturated bonds. Photoexcitation of these molecules provided evidence for rapid electron transfer²⁹⁻³²



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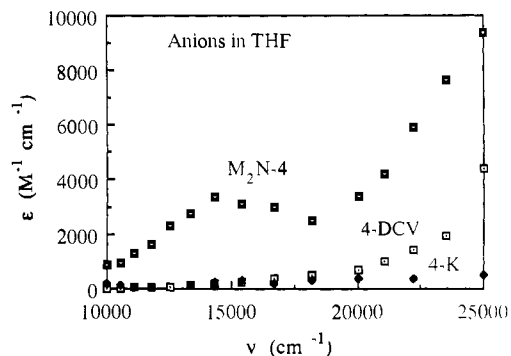


Figure 1. Absorption spectra taken 100 ns after pulse radiolysis of monofunctional compounds containing either the dimethoxynaphthalene (M_2N), the dicyanovinyl (DCV), or ketone (K) group. The spectra are due principally to radical anions of the parent compounds.

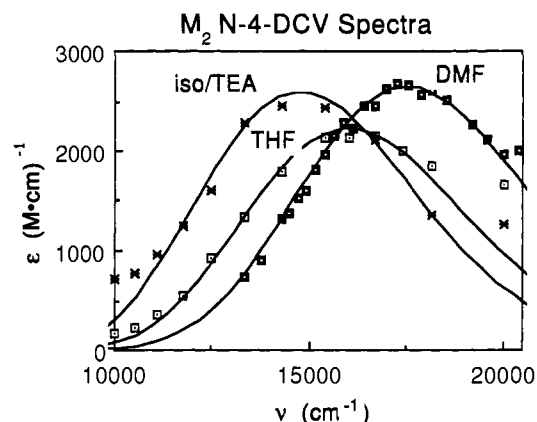


Figure 2. The strongly solvent-dependent optical absorption band of the anion of the 4-band compound M_2N -4-DCV recorded 100 ns after pulse radiolysis. The spectrum of the dicyanovinyl radical anion (see Figure 1) was subtracted from the spectra. The lines are a simulation of eq 4 with use of the reorganization parameters given in Table II.

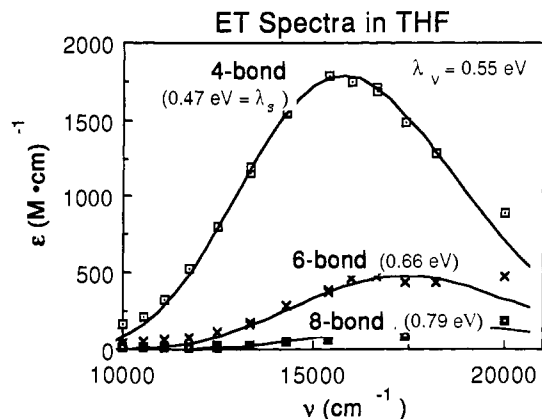


Figure 3. The intensity of the optical electron transfer band decreases rapidly with increasing number of σ bonds in bridging group. The spectra were obtained in 0.01 M solutions in THF of the compounds M_2N - n -DCV, where $n = 4, 6, 8$ bonds. The spectrum of 4-DCV⁻ (Figure 1) was subtracted from each, leading to substantial uncertainties in the 8-bond ET spectrum (see text).

The experiments measured fluorescence quenching of the donor (dimethoxynaphthalene) or microwave absorptions of the "giant

Table I. Optical Electron-Transfer Bands in M_2N -4-DCV as a Function of Solvent Polarity

solvent	$h\nu_{\max}$ (cm^{-1})	$\epsilon_{\text{op}}^{-1} - \epsilon_s^{-1}$	λ_s (calcd) ^b	λ_s (eV)	λ_v (eV)	D	V (eV)
DMF	1.74×10^4	0.464	0.62	0.68	0.55	5.2×10^3	0.24 ± 0.04
THF	1.50×10^4	0.373	0.50	0.50	0.55	5.9×10^3	0.22 ± 0.04
isooctane ^a	1.46×10^4	0.001	0.001 ^c	0.35	0.55	6.7×10^3	0.21 ± 0.04

change of λ_s with solvent polarity

^a Isooctane (2,2,4-trimethylpentane) containing 0.02 M triethylamine to scavenge positive charge. ^b Taking THF as a reference, λ_s for the other solvents was calculated with eq 6. ^c Calculated for pure isooctane, not taking into account the presence of 0.02 M TEA.

dipoles³⁰⁻³² created by reaction 2.

We report here the results of pulse radiolysis experiments in which electrons were attached to these molecules in solution to study the rates of reactions of the type



The rates of reaction 3 were found to be greater than the range of our measurements at present. The experiments revealed that the anions of molecules with 4, 6, or 8 bonds possessed new optical electron-transfer (intervalence) absorption bands which provide information on the strengths of the electronic couplings between the D and A groups and on the reorganization parameters, both of which are principal factors in electron-transfer processes.

Experimental Section

Procedures have been described previously.³³ Solutions of the difunctional compounds and corresponding monofunctional compounds were made in fused silica cells with use of purified solvents. The degassed solutions were then sealed off under vacuum. The solutions at 296 ± 2 K were subjected to 30-ps pulses of 20-MeV electrons from the Argonne electron linear accelerator to create radical anions of the solute molecules by attachment of solvated electrons formed by ionization of the solvent. Transient absorption from the anions was measured by using light from a pulsed xenon arc lamp or flash lamp, which was detected by either a photomultiplier, silicon photodiode, or biplanar photodiode and digitized by a Tektronix 7912 transient digitizer. The system risetime was 0.7 ns with the biplanar photodiode and 2–3 ns with the other detectors. Syntheses of the compounds have been described elsewhere.^{32,39}

Results

A. Spectra and Kinetics. Figure 1 shows absorption spectra of radical anions of the monofunctional model compounds. Estimates of the molar extinction coefficients were obtained by measuring the absorbance of biphenyl anion in each solvent under the same conditions. We assumed that $[\text{biphenyl}(1^-)] = [M_2N-4]^- = [4\text{-DCV}]^-$ when similar solutions of the appropriate solutes are radiolyzed with the same size pulse and that $\epsilon(\text{biphenyl}^-) = 1.2 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ at 650 nm.^{51,52} The extinction coefficients thus obtained are accurate to $\pm 20\%$. The same procedure was used for the spectra in Figures 2, 3, and 4.

Radical anions of the molecules M_2N - n -DCV ($n = 4, 6, 8, 10, 12$) in THF showed no evidence of absorption due to the radical anion of the dimethoxynaphthalene group (M_2N), indicating that rate constants and electron transfer from M_2N^- to DCV are greater than $1 \times 10^9 \text{ s}^{-1}$ in all five compounds. These very fast electron transfers through as many as 12 saturated carbon-carbon bands are consistent with fast electron-electron transfer observed

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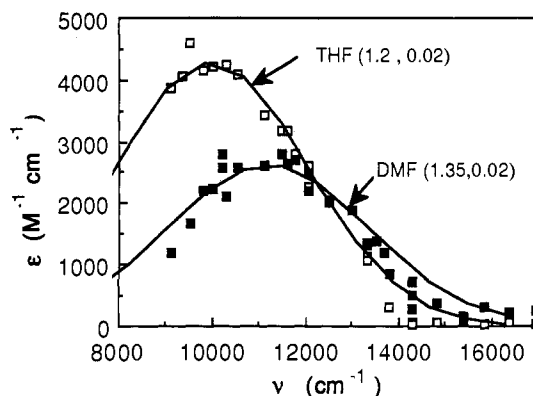


Figure 4. Optical electron-transfer spectra of the M_2N -4- K^- in which the dimethoxynaphthalene (M_2N) and aliphatic ketone (K) groups are separated by the 4-bond bridge. Spectra from a solution of a mixture of the monofunctional models M_2N -4 and 4- K were subtracted, to remove local absorptions of M_2N^- . Substantial uncertainties from this subtraction may distort the shape as well as the size of the optical electron-transfer bands.

for charge separation (reaction 2) in the same compounds^{11,29-32} and charge exchange ($k \gg 2 \times 10^9 \text{ s}^{-1}$) observed across ten saturated bonds in difunctional steroids.^{6,7,33}

The free energy change for electron transfer from M_2N^- to DCV measured electrochemically is $-1.01 \pm 0.03 \text{ eV}$ in THF, dioxane, acetonitrile, and Me_2SO solutions containing 0.1 M $\text{Et}_4\text{N}^+\text{ClO}_4^-$.⁵⁰ This is very close to the reorganization energies estimated from optical electron-transfer bands below, so these reactions are optimally exoergic and expected to be fast. Estimates of the rates, obtained from the optical electron-transfer bands, will be given below.

A simplifying feature of the pulse radiolysis technique is that it facilitates the study of reactions (e.g., reaction 3) in which an ion and a neutral species (D^- and A) react to form a neutral and an ion (D and A^-). When D and A are of similar sizes, the free energy change for such a reaction is almost independent of solvent polarity. It is also independent of reaction distance (work terms are negligible). For photoexcited reactions (e.g., reaction 2), changing the solvent polarity or the distance affects the free energy change.

B. Optical Electron-Transfer Bands. A mixture of the monofunctional model compounds M_2N -4 and 4-DCV, each at 0.01 M in THF, yielded a spectrum at $t > 100 \text{ ns}$ (not shown) nearly identical with that in 4-DCV alone, with no trace of M_2N^- absorption. This is expected because ET from M_2N -4⁻ to 4-DCV will be complete by 100 ns and the equilibrium constant for $\Delta G^\circ = -1.01 \text{ eV}$ is $\sim 10^{18}$. However, when the two groups are present in the same molecule, and are separated by 4 saturated bonds, a large new absorption band is present in the electronic spectrum of the corresponding radical anion (Figure 2). The band shifts to higher energies in more polar solvents, as expected for an optical electron-transfer (intervalence) absorption.

The intensity of the optical electron-transfer band, and to a lesser extent its position (energy), is a strong function of the separation, decreasing by a factor of ~ 4 for each additional two bonds between the M_2N and DCV groups (Figure 3). In Figure 3, the absorption in a solution of 4-DCV (see Figure 1) was subtracted to correct for local transitions of the DCV⁻ ion. The remaining spectra are plausibly due entirely to long-distance optical electron-transfer transitions. The small absorption for the 8-bond

Table II. Reorganization Energies and Electronic Couplings Used To Fit Optical Electron Bands in THF as a Function of Bridge Length for Compounds M_2N - n -DCV ($n = 4, 6, 8$)

bonds ^a n	R_{DA} , ^b Å	reorgan- ization energies ^c		$h\nu_{max}$ (cm^{-1})	D	V (eV)
		λ_v (eV)	λ_s (eV)			
4	5.9	0.55	0.47	1.58×10^4	4057	0.162 ± 0.02^d
6	8.8	0.55	0.66	1.67×10^4	954	0.060 ± 0.01
8	11.8	0.55	0.79	1.8×10^4	275	0.030 ± 0.01

^aNumber of saturated carbon-carbon bonds in the shortest path between the dimethoxynaphthalene (M_2N) and dicyanovinyl (DCV) groups. ^bCenter-to-center distance between the M_2N and DCV groups. ^cReorganization energies for high-frequency modes (λ_v) represented by one mode with a frequency of 1500 cm^{-1} and low-frequency (mainly solvent) modes (λ_s) described classically. ^dThis value is different from that in Table II because a different set of data was used. The difference reflects experimental uncertainty (see Results section).

compound, together with the uncertainties in subtraction, makes the extinction coefficients for M_2N -8-DCV⁻ relative to the 4- and 6-bond compounds uncertain to $\pm 35\%$ (in addition to the absolute uncertainty given above). Some additional uncertainty arises because two different batches of the 6-bond compound gave different bands of different intensities. The sum of the various sources of uncertainty is expressed where the electronic couplings, V , are reported in Table II. The intensities of the 4-bond ketone in THF are different in Figures 2 and 3. They come from two independent datasets taken on different days, and the differences are indicative of experimental uncertainties in determination of extinction coefficients.

Optical electron-transfer spectra for the 4-bond compound M_2N -4-K, in which a ketone group (K) replaces the DCV group, are shown in Figure 4. A solution of an equimolar mixture of M_2N -4 and 4-K gave a spectrum resembling that of M_2N -4⁻, but $\sim 2/3$ as intense, suggesting that the equilibrium constant for reaction 2 is $\approx 0.5 \pm 0.2$, when the acceptor is the ketone group. Thus, the ketone group is more difficult to reduce than the dimethoxynaphthalene group by 0.02 ± 0.01 eV. However, we have not observed the rate constant for this reaction, so it is not certain that the reaction is at equilibrium.

In Figure 4, the spectra of the mixture were subtracted from the spectra of M_2N -4-K⁻ to correct for local absorptions. These subtractions are very large and are clouded both by experimental uncertainties (e.g., is the reaction at equilibrium?) and by basic questions of whether the optical electron-transfer transitions and the local transitions are strictly additive.

Discussion

Optical Electron-Transfer Bands. The optical electron-transfer bands in these difunctional compounds display striking sensitivity to both solvent polarity (Figures 2 and 4) and separation of the donor and acceptor groups (Figure 3). These bands are the result of a light absorption act in which the photon removes an electron from one group (e.g., DCV⁻) and transfers it across the σ bonds of the bridge to the acceptor. These bands have been extensively studied for binuclear complexes of transition-metal ions,⁵³⁻⁵⁷ especially by Taube and co-workers. In metal complexes, they are usually called "intervalence bands",⁵⁸ because they occur in mixed valence complexes [e.g., Ru^{II} -bridge- Ru^{III}].

These bands have also been discussed in theoretical papers by Hush^{58,59} and recently by several groups⁶⁰⁻⁶³ who have investigated

quantum mechanical details crucial to understanding cases with very strong electronic coupling. The simplified theory reviewed recently by Hush⁵⁹ is adequate for the data here.

According to the theoretical treatments, the Franck-Condon envelopes giving the positions (photon energies), widths, and shapes of the bands are the same as those for thermal electron-transfer reactions and are governed by the same reorganization energies. The intensities of the bands are proportional to the squares of the electronic couplings, V , which are nearly the same as those for thermal electron transfer. Thus, we may expect to obtain information about electron-transfer rates from the optical electron-transfer absorption bands.

The shape of an optical electron-transfer band will be given approximately by eq 4. In eq 4, α is taken as 1.0, r_α is the

$$\epsilon(E) = \frac{707.6V^2\alpha^2R_{DA}^2}{(\lambda_s k_B T)^{1/2} h\nu_{max}} F(E) = DF(E) \quad (4)$$

center-to-center distance from the donor to acceptor group, λ_s is the solvent reorganization energy, and $F(E)$ is the relative Franck-Condon factor at photon energy E . The assumptions underlying this equation were recently discussed by Hush.⁵⁹ Here we modify Hush's approach to include bond length changes, which give rise to reorganization of a high-frequency mode, in addition to the low-frequency solvent modes. Then $F(E)$ is given by eq 5, which is based on nonadiabatic theories⁶⁴⁻⁶⁹ of electron transfer

$$F(E) = \sum_{w=0}^{\infty} (e^{-S} S^w / w!) \exp[-(E - \lambda_s - wh\nu)^2 / 4\lambda_s k_B T] \quad (5)$$

In eq 5, the reorganization energy of the high-frequency molecular vibration is $\lambda_v = Sh\nu$, where ν is the vibrational frequency. The sum is over the vibrational quantum number w in the products. For thermal electron transfer, $-\Delta G^\circ$ replaces E .

Equation 4 was used to fit the spectra in Figure 2. To obtain fits V , which controls the intensity, and the solvent reorganization energy, λ_s , was adjusted for each solvent, but λ_v was required to be independent of solvent and of the size of the bridge. Table I gives the parameters used in the fits and compares the solvent reorganization energies with the predictions of a simple calculation due to Marcus,⁶⁶ which treats the solvent as a dielectric continuum

$$\lambda_s = e^2(1/2r_D + 1/2r_A - 1/R_{DA})(1/\epsilon_{op} - 1/\epsilon_s) \quad (6)$$

In eq 6 r_D and r_A are the radii of the donor and acceptor groups (treated as spheres), R_{DA} is the center-to-center separation of the groups, and $\epsilon_{op} = n^2$ (n = refractive index) and ϵ_s are the optical and static dielectric constants of the solvent. Table II gives the variations of V and λ_s with donor/acceptor distance for the plots in Figure 3.

In Table II, we see that the variation of λ_s with distance in THF is in good accord with the predictions of eq 6. But when the solvent dielectric constant is varied, it is clear from Table I that the values of λ_s obtained from the fits to the spectra and the estimates of eq 6 are only in qualitative agreement. Taking THF as an arbitrary reference, the increase of λ_s going to DMF is larger than calculated by eq 6, and the decrease going to isooctane is much smaller than calculated. Because the errors are opposite in direction, they are not likely to be explained by a single error in

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Table III. Optical Electron-Transfer Bands in the Four-Bond Ketone Radical Anion, M_2N-4-K^-

solvent	$h\nu_{\max}$ (eV)	λ_s	λ_v	D	V (eV)
DMF	1.40	1.35	0.02	2.9×10^3	0.17
THF	1.22	1.20	0.02	4.4×10^3	0.19

eq 6 or its application. These "errors" may simply be a consequence of the triethylamine (TEA) which was added to scavenge positive ions.

Electron Coupling Interactions, V . The electron coupling interactions, V , reflect the mixing of donor and acceptor wave functions. Both the intensity of optical electron-transfer transition and rates of nonadiabatic thermal electron transfer are proportional to V^2 . The very large V 's found here indicate that *through-bond* interactions greatly enhance the couplings. Electron coupling interactions through disordered solvent (no through-bond contribution) were estimated from measurements of ET rates in MTHF glass.⁷⁰ For the distances in the 4-, 6-, and 8-bond compounds, V 's obtained from ET rates in the glass were 0.021, 0.006, and 0.0015 eV. For the 8-bond compound in the present work, the interaction is 20 times larger (rates or OET bands would be 400 times larger!) than that in the nonbonded case.

The interactions here are also larger than in other bonded systems. V in the 4-bond compound $M_2N-4-DCV$ is 6.2 times larger (V^2 38 times) than V in the 4-bond 1-biphenyl-3-naphthylcyclohexane ($V = 185 \text{ cm}^{-1} = 0.023 \text{ eV}$) studied by Closs and co-workers.³³ The larger V in the present compound is due in part to the two paths (a factor of 2) through the norbornyl framework in $M_2N-4-DCV$ and to the smaller size of the π system in DCV and the very large H MO coefficient (0.7) at the carbon which is attached to the bridge. These factors, relevant only for through-bond interactions, provide additional evidence that through-bond interactions dominate the electronic coupling. The effectiveness of the norborane-type bridge in transmitting electronic interactions has been demonstrated by Paddon-Row and co-workers: measurements of electronic couplings as large as 0.4 eV through four bonds have been found with photoelectron spectroscopy.³⁵⁻⁴⁰

The interactions in $M_2N-4-DCV$ are independent of solvent (Table I) within experimental uncertainty. V for the corresponding ketone M_2N-4-K^- (0.19 eV in THF, 0.17 eV in DMF) is similar to that in the DCV compound. This similarity is due to special circumstances. V for through-bond interactions is expected to be proportional to the MO coefficient on the atom of the π system which is attached to the σ bridge. If the excess electrons were distributed evenly over the six atoms of the DCV group, the coefficient would be $6^{-1/2}$ vs. $2^{-1/2}$ for the two atoms of the ketone group. But, according to Hückel calculations,³² the coefficient on the DCV group is $2^{-1/2}$, not $6^{-1/2}$, explaining the similar V 's.

V^2 decreases by a factor of 29 from the 4- to the 8-bond compound, or a factor of 2.3 ± 0.5 per bond. This is a weaker decrease than that found from electron-transfer rates across cyclohexane, decalin, and androstane bridges, where V^2 decreases by a factor of 3.0 per bond.

Estimates of Electron-Transfer Rates. The reorganization parameters and electronic couplings obtained from optical electron-transfer spectra, along with the free energy changes, provide the information needed to estimate the rates of thermal electron transfer. Table IV gives these estimates for the molecules $M_2N-n-DCV$ in THF.

Table IV. Estimates of Thermal Electron-Transfer Rates in THF, k , Calculated from Optical Electron-Transfer Spectra by Using Equations 7-10 and Parameters from Table II

n	$\bar{\nu}$ (cm^{-1})	$\bar{\nu}$ (s^{-1})	P_{12}°	κ	k (s^{-1})
4	1101	3.3×10^{13}	0.999	1.0	1.5×10^{13}
6	1011	3.03×10^{13}	0.60	0.75	1.1×10^{13}
8	972	2.9×10^{13}	0.20	0.34	4.0×10^{12}

Equation 1 is adequate only when electronic couplings are small (the nonadiabatic case). For large electronic couplings, V , as in the present compounds, the rates lose their strong dependence on V , eventually becoming independent of V , except for distortions of potential surfaces by very large interactions. In this situation, the solvent dynamics can become rate limiting, and the departure from simple nonadiabatic rate expressions is likely to depend on the free energy change as well as the reorganization parameters. In the absence of actual rates, we shall neglect the possible effects of solvent dynamics and roughly estimate the rates using semiclassical transition-state theory.^{59,68}

$$k = \bar{\nu} \kappa F(\Delta G^\circ) \quad (7)$$

where F is given by eq 5, $\bar{\nu}$ is an effective vibrational frequency,^{68,69} and κ is the electronic transmission factor. From a simple Landau-Zener treatment^{59,68,69}

$$\kappa = 2P_{12}^\circ / 1 + P_{12}^\circ \quad (8)$$

$$P_{12}^\circ = 1 - \exp \left[\frac{-V^2}{h\bar{\nu}} \left(\frac{\pi}{(\lambda_s + \lambda_v)k_B T} \right)^{1/2} \right] \quad (9)$$

$$\bar{\nu}^2 = \frac{\nu_v^2 \lambda_v + \nu_s^2 \lambda_s}{\lambda_s + \lambda_v} \quad (10)$$

where P_{12}° is the probability of remaining on the lower (adiabatic) potential energy surface.

According to the estimates in Table IV, thermal ET in the 4-bond is strongly adiabatic—the rate in this compound is not limited by electronic coupling. Only in the 8-bond compound is the reaction substantially nonadiabatic.

For the 10- and 12-bond compounds, the rates would be definitely nonadiabatic and would therefore decrease as V^2 . If V^2 continues to decrease by a factor of 2 to 2.7 per bond, as the OET spectra indicate for the 4-, 6-, and 8-bond compounds, then the thermal ET rates for the 12-bond compound would still be $\approx 10^{11} \text{ s}^{-1}$, much larger than our measured lower limit of 10^9 s^{-1} . This is true even if V^2 decreases by the factor of three per bond found for cyclohexane-type bridges.³³ In that case, the rate in the 12-bond compound would still be $4 \times 10^{10} \text{ s}^{-1}$. It is clear that the conclusion that the experimental observation that $k > 10^9 \text{ s}^{-1}$, even for the 12-bond compound, is consistent with predictions based on the optical ET bands.

Thermal electron transfer has been observed in the ps to ns time region after light excitation of the molecules $M_2N-n-DCV$ (reaction 1 and its reverse to the ground state).²⁹⁻³² The electronic couplings for reaction 1 are likely to be similar to those in the present study. If so, then the 8-bond compound would be expected to transfer electrons in subpicosecond times (see Table IV) at optimal exoergicity. Rates observable at times of 20 ps or longer would have to have very unfavorable since the charge separation reaction is weakly exoergic and the charge recombination reaction is very exoergic ($\approx 3.5 \text{ eV}$ in nonpolar solvent).

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