Figure 5. Relationship between hydronium ion catalytic coefficients for enolization (△) and ketonization (O) and pK_E for simple aldehydes and ketones in aqueous solution at 25 °C.

rings.[37] The origin of the alternation in enol content in going from the 5- to the 6- to the 7-membered-ring system is less clear. A similar alternation has been found in the keto–enol equilibrium of α-carbomethoxycycloalkanones,[38] and also in the exo–endo double bond isomerization of isopropylidenecycloalkanes to 1-isopropylcycloalkenes,[39] but not in the similar isomerization of methylenecycloalkanes to 1-methylcycloalkenes, for which $K_{endo/exo}$ decreases regularly from 5- to 6- to 7-membered-ring systems.[40]

This alternating ring-size effect appears also in both of the rate constants that make up K_E. The data of Table I show that rates of enolization of the cyclic ketones fall in the order $6 > 5 \approx 7$

and that there is a converse relationship, $5 \approx 7 > 6$, for rates of ketonization. The reactivity order $6 > 5 \approx 7$ has also been observed for enolization in a different solvent,[41] and the ketonization order $5 \approx 7 > 6$ is similar to that found for hydrolysis of the corresponding ethyl vinyl ethers.[42]

The converse nature of the reactivity orders shown by enolization and ketonization in these systems indicates that structural effects on the keto–enol equilibria are expressed in a complementary fashion in the forward and reverse reactions. Such sharing of structural effects extends to the other keto–enol systems of Table III. Figure 5 shows that both the enolization rate constants and the ketonization rate constants correlate in these systems with the equilibrium constants; the slopes of the two correlations, moreover, are of opposite sign, indicating that the relationships are converse.[43]

The forward and reverse reactions, however, do not share the structural effects equally. Ketonization is considerably more sensitive to structural changes than is enolization, as shown by the greater absolute magnitude of its correlation slope, 0.83 ± 0.06, in comparison to that for enolization, 0.17 ± 0.06.

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Observation of a Remarkable Dependence of the Rate of Singlet–Singlet Energy Transfer on the Configuration of the Hydrocarbon Bridge in Bichromophoric Systems

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Abstract: Intramolecular singlet energy transfer can be detected in a series of rigid bichromophoric molecules (1(n)) where a dimethoxynaphthalene chromophore and a carbonyl chromophore are separated by extended all-trans arrays of up to eight C–C σ bonds (1(8)). In the series of compounds 2(n) "kinks" are introduced in the array of σ bonds of the saturated hydrocarbon system, which bridges the chromophores. Singlet energy transfer is then much less efficient (i.e. in 2(6)) or even absent (i.e. in 2(8)), which supports the earlier interpretation of the energy transfer mechanism in 1(n) as being mainly mediated by through-bond exchange interaction and furthermore explains the virtual absence of such interaction in more flexible systems where the chromophores are linked by polymethylene bridges.

Transfer of electronic energy between chromophores, located in different molecular entities or covalently connected to a single

(macro)molecular framework, plays a vital role in many photophysical and photochemical processes, including such widely

Chart I. Structures of the Bichromophoric Molecules 1(n) and 2(n) Studied, as Well as the "Isolated" Chromophore Models 3 and 4
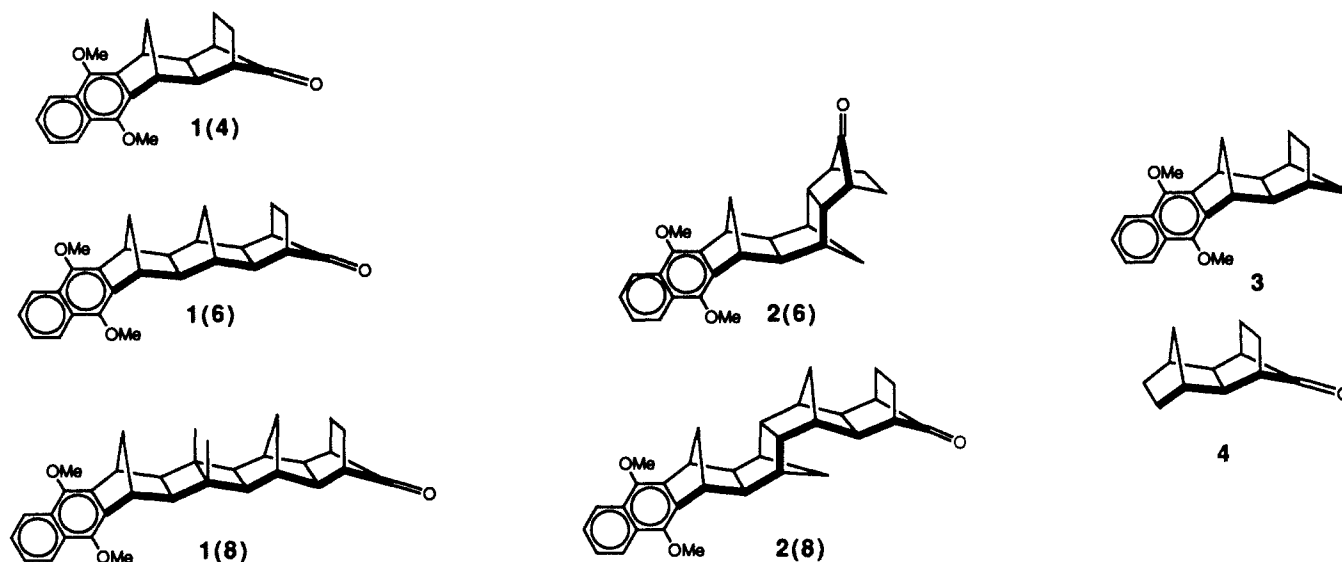

different areas as photographic sensitization and the intricate light harvesting antenna systems found in natural photosynthesis.[2]

Although an indirect mechanism may be followed (i.e. emission/reabsorption), direct energy transfer is now considered to be possible by either of two mechanisms.[3] At short chromophore–chromophore distances and/or for energy transfer between states that are not coupled by significant radiative transition probability (e.g. for triplet–triplet energy transfer), the overlap-dependent Dexter exchange mechanism prevails. For energy transfer between states of identical multiplicity and which are coupled by significant radiative transition probability, the Förster dipole–dipole coupling mechanism can operate. Because the latter mechanism is not overlap dependent, it tends to prevail for singlet–singlet energy transfer between chromophores that are separated by distances in excess of the sum of their van der Waals radii. At such distances Dexter-type transfer may still be detected for triplet–triplet energy transfer, but at a rate that would make it undetectable on the time scale of singlet lifetimes.

We were therefore surprised to find[4] that singlet–singlet energy transfer, from the π–π^* excited naphthalene chromophore to the n–π^* state of the carbonyl chromophore in the series of molecules 1(n) (see Chart I), occurred with rates that were too high and that gave a rate/distance dependence that was too strong to be accounted for by an exclusive Förster mechanism even if the dipole moment orientation factor is assumed to have its maximum value (see ref 4 for a discussion of this orientation factor in the present compounds). We tentatively explained these results in terms of a Dexter-type mechanism resulting from long-range through-bond (TB) coupling between the two chromophores and the hydrocarbon bridge in 1(n). Furthermore we proposed that a direct relation exists between the exchange interaction matrix elements of the Dexter mechanism, obtained for the series 1(n), and the electron-coupling integrals for photoinduced-electron-transfer processes in molecules structurally similar to 1(n) but having a dicyanovinyl group[5] instead of the carbonyl group.

However, our conclusion that long-range Dexter-type energy transfer was taking place in the series of molecules 1(n) was recently criticized by Speiser and Rubin[6] on the grounds that their

energy transfer rate data, obtained[7] for less rigid molecules such as 5, gave a distance dependence that cannot be reconciled with a Dexter-type mechanism acting over distances significantly beyond diirect chromophore–chromophore contact. Since Speiser and Rubin could find no explanation for the apparently disparate
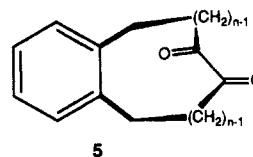
behavior of 1(n) and 5 toward energy transfer, they were led to question our interpretation of the data obtained for 1(n). However, their reasoning is based on the implicit assumption that the rate of intramolecular energy transfer between a pair of chromophores is *independent of the nature of the hydrocarbon bridge connecting the chromophores*. This assumption is almost certainly incorrect since it has been convincingly demonstrated[5,8,9] that various hydrocarbon bridges play a very important role in mediating long-range intramolecular electron transfer (via a through-bond coupling mechanism) and that the rate of electron transfer is markedly effected by the nature and configuration of the bridge.[10-12] Given that a Dexter energy-transfer mechanism may be visualized in terms of two electron-transfer processes,[3,4,13] then one should expect strong dependence of the Dexter-type energy transfer on the nature and geometry of the hydrocarbon bridge.

The main purpose of this paper is to present additional experimental evidence in support of our belief that a Dexter-type mechanism governs intramolecular singlet energy transfer in 1(n). Specifically, we demonstrate the remarkably strong dependence of singlet energy transfer dynamics on the bridge configuration, through comparison of the rates for 1(n), in which the highlighted bonds of the bridge have an all-trans configuration, with those

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Table I. Fluorescence Lifetime (τ in Picoseconds), Fluorescence Quantum Yield (ϕ in Percent) and Calculated Rate of Intramolecular Energy Transfer k (10^6 s^{-1}) As Calculated by Using Eq 2 and Eq 1 (in Parentheses)

	3		1(4)			1(6)			1(8)			2(6)			2(8)		
solvent	τ	ϕ	τ	ϕ	k eq 2 (eq 1)	τ	ϕ	k eq 2 (eq 1)	τ	ϕ	k eq 2 (eq 1)	τ	ϕ	k eq 2 (eq 1)	τ	ϕ	k eq 2 (eq 1)
n-hexane	9900		85		11660	3400		193	7600		31	8600		15	10000		0
cyclohexane	9600	35	80	0.42	12400 (8580)	3100	11	218 (227)	7100	27	37 (31)	8300	31	16 (13)	9700	35	0 (0)
benzene	5900		263		3630	3700		101	5400		16	5600		9	5900		0
di-n-butyl ether	7600	33	100	0.77	9870 (5510)	3400	15	163 (158)	6300	31	27 (8)	6800	31	15 (8)	7700	31	0 (8)
diethyl ether	7500	27	125	0.67	7870 (5240)	3900	14	123 (124)	6500	24	21 (17)	6900	27	12 (0)	7400		0
ethyl acetate	6400	40	270	1.40	3550 (4310)	4400	27	71 (75)	6000	38	10 (8)	6100	38	8 (8)	6500		0
tetrahydrofuran	6100	24	265	1.60	3610 (2300)	4100	17	80 (68)	5800	27	8 (0)	5850	23	7 (7)	6000	24	0 (0)
acetonitrile	7500	33	1200	4.90	700 (765)	6500	30	21 (13)	7650	33	0 (0)	7400	34	2 (0)	7600		0

for 2(n), in which one (in 2(6)) or two (in 2(8)) trans arrangements of bonds have been converted into cis (or gauche) alignments. We also show how our results of this study nicely explain why the Dexter mechanism predominates for 1(n), but is unimportant for 5. Finally, we compare the singlet energy transfer rate data reported herein with rates of photoinduced electron transfer obtained by us on related molecules. This comparison complements the recent elegant studies of Closs et al.,[13] who delineated an important quantitative relationship between rates of electron transfer and the corresponding rates of triplet–triplet energy transfer.

Results and Discussion

Detection of Intramolecular Energy Transfer via Time-Resolved Emission Spectroscopy.

In our first paper[4] on the dynamics of long-range singlet–singlet energy transfer in 1(n) the rate constants k_{11} were calculated from eq 1 by comparison of the fluorescence quantum yields (ϕ) for 1(n) with that for the model donor chromophore 3. This procedure is rather error-prone because

$$k_{11} = [\phi(3)/\phi - 1]/\tau(3) = (Q - 1)/\tau(3) \qquad (1)$$

of the general problems in determining accurate quantum yields, which consequently have a relative uncertainty ranging from 15% for the more strongly fluorescent systems to about 20% for the very weakly fluorescent 1(4). Thus at low quenching ratios ($Q \approx 1$) the uncertainty in k_{11} as determined by using eq 1 is about 20% of $1/\tau(3)$, which sets a lower limit of about 20×10^6 (in s^{-1}) to k_{11} values that are detectable. At high quenching ratios even minor impurity fluorescence may lead to significant underestimation of Q and therefore of k_{11}. Furthermore, it should be pointed out that the absolute values of our previous rate data based on eq 1 turned out to be in error through use of an inaccurate value of the fluorescence lifetime of the model donor $\tau(3)$. The latter had been obtained by using picosecond-time-correlated single-photon-counting equipment with a laser pulse repetition frequency of 94 MHz and by applying a background correction for the overshooting of fluorescence created by laser pulse i into the time domain following pulse $i + 1$. We since found that this correction cannot adequately cope with fluorescence lifetimes ≥ 4 ns. Consequently, we have now redetermined such lifetimes with use of equipment adapted to measure lifetimes in the ≥ 3-ns domain (see Experimental Section).

The redetermined lifetimes for 3, in a series of solvents, are given in Table I, together with fluorescent lifetimes for 1(n) and 2(n). The fluorescence spectra of 1(n) and 2(n) are identical with that for the model system 3. For all compounds, satisfactory monoexponential fluorescence decay curves were obtained with the exception of 1(4), which required biexponential fitting revealing, in addition to the major picosecond component (see Table I), a component with a lifetime in the nanosecond range attributable to minor impurity. Also shown in Table I are the fluorescence quantum yields determined for 2(n), together with those determined previously for 3 and 1(n).

The availability of fluorescence lifetimes now allows us to calculate rates of singlet energy transfer by using eq 2, and these are also listed in Table I, together with those obtained by using eq 1.
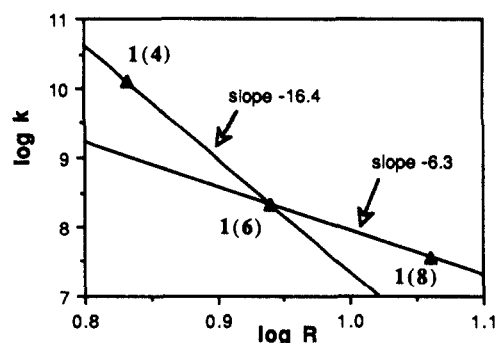
$$k_{11} = 1/\tau - 1/\tau(3) \qquad (2)$$

Figure 1. Double logarithmic plot of the rate (k) of intramolecular energy transfer in series 1(n) as a function of the center-to-center distance[4] (R in Å) between the chromophores (rate data refer to cyclohexane and are calculated by using eq 2; see Table I).

In the high range of k_{11}, application of eq 2 is not thwarted by the impurity fluorescence problems typical for eq 1, the uncertainty in k_{11} now arising only from that in τ, which is in the order of 5%. In the low range of k_{11} the uncertainties in τ and $\tau(3)$ add to set a lower limit of about 7×10^6 (in s^{-1}) on k_{11} for detectability, i.e. about 3 times below that achievable via eq 1.

Inspection of Table I shows that the k_{11} values obtained with eq 1 and 2 agree to within the limits of experimental uncertainty, while optimal agreement is, as expected, obtained for 1(6) that features a moderate quenching ratio. The enhanced accuracy achieved by using the present lifetime measurements, (via eq 2) compared to that using the quenching ratio determination inherent in eq 1, enables the detection of energy transfer to be made even under circumstances in which it is too slow to influence significantly the fluorescence quantum yield (e.g. for 1(8) in polar solvents and for 2(6)). Furthermore the comparison indicates that, as expected, impurity fluorescence leads to an underestimation of k_{11} for 1(4) if eq 1 is applied. In the remainder of this publication we will therefore limit our discussion to rate data obtained via time-resolved measurements by using eq 2.

Effect of Solvent and Bridge on the Rate of Energy Transfer.

For all bichromophoric systems the data of Table I reveal a gradual drop in the rate of energy transfer with increasing solvent polarity. As we have discussed previously,[4,14] this effect corresponds quantitatively with the decrease in the spectral overlap between the donor fluorescence and the acceptor absorption with increasing solvent polarity. This observation thus strongly supports the singlet energy transfer mechanism of the additional decay channel which operates in 1(n) and 2(n), but which is absent in 3.

In our earlier publication[4] we noted that the distance dependence of the rate of energy transfer in series 1(n) differs strongly from that expected on the basis of a pure Förster-type dipole–dipole interaction mechanism, which requires[3] the rate to be proportional to the inverse sixth power of the distance. By using the more accurate rate data now obtained, this can be demonstrated even more clearly as exemplified for cyclohexane in Figure 1, although the same picture emerges in all solvents studied. Thus in none of the solvents studied, the distance dependence of k_{11} in series

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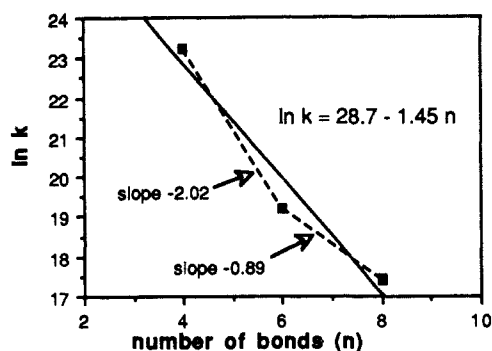
Figure 2. Exponential plot of the rate (k_{11}) of intramolecular energy transfer in series 1(**n**) as a function of the number (n) of σ bonds between the chromophores (rate data refer to cyclohexane and are calculated by using eq 2, see Table I).

1(n) can be fitted to a single inverse power law. Instead the rate decreases very much more steeply than predicted by the Förster mechanism from 1(4) to 1(6). While the decrease in rate from 1(6) to 1(8) seems not incompatible with that predicted by the Förster mechanism, we stipulated before[4] that even for 1(8) the absolute value of k_{11} is about 1 order of magnitude larger than can be calculated to result from this mechanism.

It was, in fact, these observations that led us to conclude that a Dexter-type exchange process is the major contributor to the energy transfer for 1(**n**) although, admittedly, additional dipole–quadrupole and quadrupole–quadrupole mechanisms might in principle also be invoked to explain the steep decrease of the energy-transfer rate with distance.

As exemplified for cyclohexane in Figure 2, a better fit can be obtained if the energy-transfer rate in series 1(n) is expressed via an exponential dependence on the number of bonds (n) separating the chromophores although a certain curvature is indicated, that pertains in all solvents.

Compounds 2(n) differ from 1(n) mainly with respect to the configuration of the hydrocarbon bridge. In 1(**n**) these bridges always possess all-trans arrays of σ bonds, but in 2(**n**) these arrays contain gauche and s-cis components. From X-ray studies[11,15] we know that this has only a minor effect on the spatial separation of the chromophores, bringing these slightly closer together in 2(**n**) compared to those in the corresponding molecules 1(n). Thus, also taking orientation factors into account, only a minor change in the rates is expected for Förster type energy transfer. Similar arguments would apply to the effect of the bridge configuration on Dexter-type energy transfer if the exchange interaction between the chhromophores were mediated by through-space overlap. Through-bond interaction, however, has been predicted to be maximized across all-trans arrays of σ bonds and to decrease rather drastically if "kinks" are introduced in the coupling path.[16,17,18] This prediction has been tested at various levels of theory and has been substantiated experimentally by one of us using photoelectron spectroscopy and electron transmission spectroscopy of bridged dienes.[19] More recently the utility of this concept has been demonstrated[10–12] to achieve modulation of rates of intramolecular electron transfer.

Inspection of the data in Table I clearly reveals that the rate of intramolecular energy transfer decreases quite dramatically upon going from 1(n) to 2(**n**). Thus no significant energy transfer could be detected in 2(8) while its rate in 2(6) is about 1 order of magnitude smaller than in 1(6) thereby making it even slightly slower than in 1(8)!

These results convincingly demonstrate that the efficient energy transfer observed in compounds 1(**n**) must result mainly from through-bond exchange interaction across the all-trans arrangement of σ bonds comprising the hydrocarbon bridges. The dramatic decrease in the rate of energy transfer for 2(**n**) is not only consistent with this interpretation but also provides a straightforward explanation for the apparent inconsistency[6] of our results in series 1(n) and the earlier results of Speiser and Rubin,[7] who found that intramolecular Dexter-type singlet energy transfer cannot be detected if the chromophores are moved apart beyond direct contact. In the compounds like 5, studied by Speiser and Rubin, the chromophores are interconnected by two "parallel" polymethylene chains. Depending on the number of methylene groups these molecules adopt one or more conformations. However, according to the published conformational analyses,[20] these never provide an all-trans array of σ bonds. The present data for 2(n) show that under such circumstances the rate of Dexter-type energy transfer is indeed minor when direct chromophore/chromophore overlap is avoided, which is fully consistent with the results of Speiser and Rubin.

Comparison with Electron Transfer. We have pointed out before[4] that the exchange interaction responsible for Dexter-type energy transfer across the bridges in 1(n) is related to the through-bond electronic interaction, and this allows fast electron transfer to take place across such bridges. On this basis we proposed that, upon structural variation of the bridge, a quadratic relation might hold between the rate of electron transfer (k_{et}) and the rate of Dexter-type singlet–singlet energy transfer (k_{11}) according to eq 3. This view was independently put forward by

$$k_{11} \propto (k_{et})^2 \tag{3}$$

Closs et al.,[13a] who also provided experimental verification for such a quadratic relation by studying both thermal electron transfer and triplet–triplet energy transfer (k_{33}) across a series of saturated hydrocarbon bridges and later[13b] refined eq 3 by making use of the product of electron- and hole-transfer rates. Comparison of the ratios of the energy transfer rates in series 1(n) and 2(n) for the same value of n, with such ratios obtained recently by us for photoinduced electron transfer across the same bridges[10,11] could in principle provide a direct test of the validity of eq 3 for singlet energy transfer. For $n = 8$ this is, however, thwarted by the fact that the energy transfer in 2(8) is too slow to be detected. For $n = 6$ the ratio of the energy transfer rates 1(6)/2(6) is in the range 13.6–10 over the whole range of solvents studied (see Table I). Unfortunately electron-transfer rates across the all-trans six-bond bridge are too fast to be determined very reliably and until now only a rather crude estimate has been obtained in more polar media. In such media the ratio of the electron transfer rates across the bridges incorporated in 1(6) and 2(6), respectively, is in the order of 6 ± 2, the high uncertainty being mainly due to the problems in determining the exceptionally fast rate for electron transfer across the all-trans array of six σ bonds.[11] From this crude estimate a ratio of 36 ± 20 for the rates of energy transfer is predicted by using eq 3. It may thus be tentatively concluded that, in contrast to the results obtained by Closs et al.[13] for triplet–triplet energy transfer, eq 3 overestimates the effect of changes in the degree of through-bond interaction on the rate of singlet–singlet energy transfer. A plausible explanation is that the effect of changes in exchange interaction on the experimental ratio of singlet energy transfer for 1(6)/2(6) is damped by the occurrence of additional Förster-type mechanisms (i.e. dipole–dipole and higher order), a complication not occurring in the study of triplet–triplet energy transfer. This explanation is consistent with the curvature noted in the exponential plot given in Figure 2. Interestingly, by using the same type of all-trans bridges, such plots have been found to be fairly linear for electron transfer with a slope close to unity.[5,21] As indicated by the dashed lines in Figure 2 the quadratic behavior

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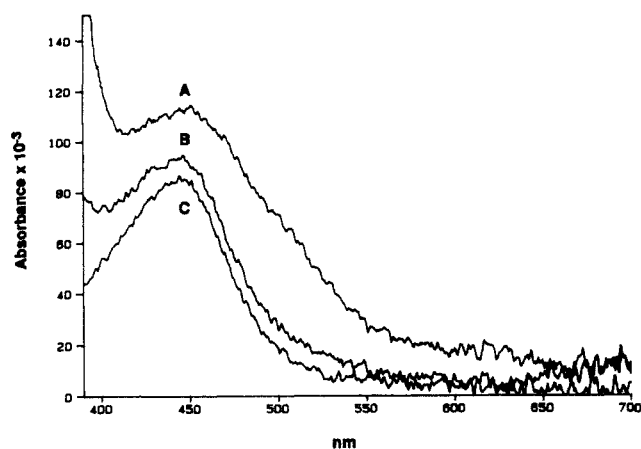
Figure 3. Transient absorption spectra following 308-nm excitation (pulsewidth ~7 ns) of 1(6) in cyclohexane. The time window of the spectra is 5 ns and is delayed by 10, 20, and 30 ns from the start of the laser pulse for curves A, B, and C, respectively.

demanded by eq 3 thus seems to be obeyed going from $n = 4$ to $n = 6$, but not at larger separations, again supporting the onset of a mixed mechanism.

Transient Absorption Studies. As we have argued before,[4,14] the relatively weak electron acceptor capacity of the carbonyl chromophore seems to rule out any significant contribution of electron transfer to the quenching of the naphthalene fluorescence occurring in the bichromophoric systems studied here. In order to confirm this absence of electron transfer experimentally, transient absorption spectra of some of the bichromophoric molecules were recorded, since it is known that the radical cation of the donor shows strong characteristic absorption bands in the visible (590 nm) and near UV region (410 nm) which are readily detected in the transient absorption spectra of compounds where the carbonyl group is substituted by a more powerful electron acceptor.[22] As is evident from the spectra displayed in Figure 3 the transients formed upon excitation of the present bichromophoric systems lack these absorptions, instead in all cases a band around 450 nm is present, known[22] to be characteristic for the triplet state of the dimethoxynaphthalene donor chromophore. For 1(6) and 1(8) a spectrum taken within a time window partially overlapping the laser pulse (curve A in Figure 3) furthermore shows absorption around 500 nm, attributable to donor $S_1 \rightarrow S_n$ absorption, which is not observed for 1(4). The rapid and efficient population of the local donor triplet in compounds where the donor singlet is depopulated almost exclusively via singlet–singlet energy transfer (i.e. especially in 1(4)) points toward indirect formation via triplet–triplet energy transfer (k_{33} in Figure 4) from an n–π* triplet of the acceptor populated by efficient intersystem crossing (k_{isc}) of the latter. This order of events has been observed before in bichromophoric systems containing a combination of aromatic and carbonyl chromophores[23–25] and furthermore the results of Closs et al.[13] provide a direct rationale for the apparently high rate of triplet–triplet energy transfer in the present systems.

Concluding Remarks

The present comparison of singlet–singlet energy transfer in the all-trans systems 1(n) with that in the bent systems 2(n) provides convincing evidence for the operation of a through-bond exchange mechanism in the former systems up to a chromophore separation of eight σ bonds. It should be stressed that our detection of through-bond mediated energy transfer was predecessed by various other studies, involving a smaller number of bonds in the coupling path. Thus in 1975 Amrein and Schaffner[23] already reported conformationally dependent through-bond triplet energy
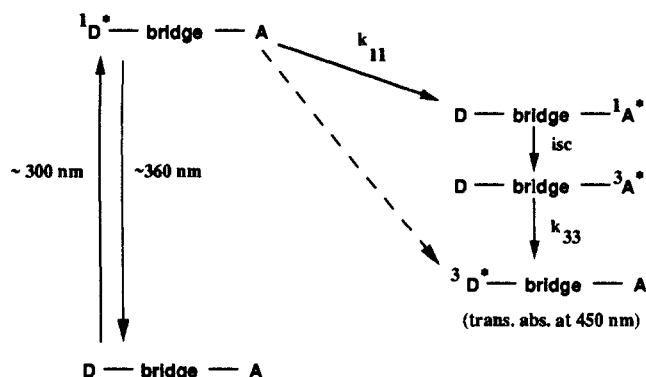

Figure 4. Term scheme for the bichromophoric compounds showing the main pathways leading to population of the donor triplet. The dashed arrow indicates direct intersystem crossing of the donor, which may become significant at low values of k_{11}.

transfer across three σ bonds. In 1980 Zimmerman et al.[24] provided strong evidence for through-bond mediated singlet energy transfer across a bicyclooctane spacer constituting a coupling path of five σ bonds, and in 1983 Schippers et al.[26] similarly identified through-bond singlet energy transfer in diketones across four σ bonds. While the recent studies of Closs et al.[13] confirm the generality of a through-bond mechanism for triplet energy transfer across extended arrays of σ bonds, its scope as a mechanism for singlet energy transfer appears more limited. Although our present results show a through-bond exchange mechanism to be feasible for intramolecular singlet energy transfer over eight σ bonds (i.e. in 1(8)), they also indicate that this puts severe conformational requirements on the bridging group and even so the rate falls off quite steeply with the number of intervening bonds. This and the additional possibility of singlet energy transfer via a Förster-type mechanism make it therefore unlikely that a through-bond exchange mechanism could be detected for singlet energy transfer across more than eight σ bonds.

Experimental Section

Synthesis, purification and structure elucidation of the compounds 1(n), 2(n), 3, and 4 have been described elsewhere.[5a,27,28]

Corrected emission spectra were obtained with use of a SPEX Fluorolog-2 spectrofluorimeter. Fluorescence quantum yields were determined by electronic integration of the emission spectra for carefully deoxygenated solutions with an absorbance ≤0.2 at the excitation wavelength (300 nm) using 9,10-diphenylanthracene as a reference (Φ = 0.9 in cyclohexane[29]). Fluorescence lifetimes in the picosecond range were obtained by time-correlated single-photon counting with use of the equipment described extensively before[5a] (excitation wavelength 303 nm).

For fluorescence lifetimes ≥3 ns a setup was used which employs single-shot decay measurements.[30] The sample solution is excited by the 308-nm pulse (~7 ns fwhm) of a Lambda Physik EMG-101 XeCl-excimer laser. The emerging fluorescence is detected by an RCA 1P28 photomultiplier, wired for fast response, via a Zeiss MQII monochromator. The signal of the photomultiplier is fed into a Tektronix 11302 500-MHz oscilloscope triggered by the laser light via a photodiode. A Tektronix DCS01 camera system is used to digitize the oscilloscope trace, which is then analyzed with a homewritten program on the basis of iterative reconvolution.

Transient absorption spectra were obtained by using the same EMG-101 excimer laser as the excitation source (energy ~40 mJ/pulse) and a 450-W high-pressure Xe arc as the probe light, pulsed with a Müller Elektronik MSP05 pulser to enhance its brightness during the observation time gate of the detector. The probe light, after passing through the sample cell, is dispersed via a spectrograph (EG&G model 1234) equipped with a 150 g/mm grating and a 250-μm slit, resulting in a 6-nm spectral resolution. This is coupled to a gated, intensified diode array

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detector (EG&G model 1421) forming part of an EG&G OMA-III data handling system. For the spectra shown in Figure 3 the detector gate width was set at 5 ns, while the delay of the gate pulse was incremented in steps of 10 ns with respect to the laser pulse.

π-Facial Selectivity in Catalytic Osmylation Reactions of Chiral C1-Oxygenated Allylic Silanes
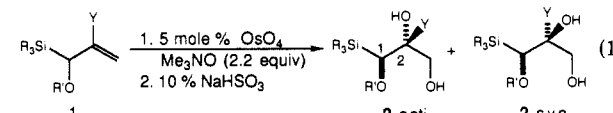
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Abstract: Oxygen-substituted allylic and crotyl silanes undergo vicinal hydroxylations with unprecedented levels of diastereofacial selectivities in the presence of catalytic amounts of osmium tetroxide to predominantly form 1,2-anti-1,2,3-triol units. The magnitude of face selectivity was influenced by two factors: the steric bulk of the silicon group and the type of substituent on the C1-oxygen. As the size of the silicon group increased [$Me_3Si- \rightarrow Et_3Si- \rightarrow PhMe_2Si- \rightarrow {}^tBuMe_2Si- \rightarrow Ph_2MeSi-$] the anti selectivity improved. Allylic silanes containing ethers and esters gave moderate to good anti selectivity. (*E*)-crotylsilanes gave higher selectivities than the corresponding *Z* stereoisomers. When a hydroxyl group is present the vicinal hydroxylation proceeded with virtual face specificity for the allylic and (*E*)-crotylsilanes producing the triol products with anti/syn selectivities reaching 147:1. Lower but still significant selectivities were obtained for the *Z* stereoisomers. These experiments present evidence supporting the notion that the steric effects of trialkyl silyl group are as important as σ donor effects in these electrophilic addition reactions.

Studies on electrophilic addition reactions to π systems adjacent to stereogenic carbon atoms have been the subject of considerable experimental and theoretical interest.[1] A fascinating aspect of this chemistry is the manner by which the asymmetric center can alter the relative rates of additions to either face (k_{anti}/k_{syn}) of the π system. It has been well-documented that chiral allylic metals can promote and direct the regio- and stereochemical outcome of many addition reactions.[2] Initial investigations by Kishi and co-workers[3] have shown that chiral allylic alcohols and ethers undergo diastereoselective osmylation reactions preferentially away from the oxygen function. This pattern has been confirmed in conformationally rigid systems.[4a] More recently Vedejs[4c] and Fleming[2g,h] have reported that allylic silanes par-

Table I. Diastereoselective Vicinal Hydroxylations of Chiral C1-Oxygenated Allylic Silanes[a]

chiral silane	R′	R₃Si	Y	ratio 2 anti/syn[b]	% yield[c,d]
1a	Ac	SiMe₃	H	6.5:1	57
1b	Ac	SiEt₃	H	7.5:1	67
1c	Ac	SiMe₂Ph	H	7.0:1	70
1d	Ac	Si^{t}BuMe₂	H	11.3:1	70
1e	Ac	SiPh₂Me	H	11.5:1	58
1f	SiEt₃	SiMe₂^{t}Bu	H	12.6:1	36
1g	PhCO	SiMe₃	H	4.0:1	75
1h	Ac	SiMe₃	CH₃	3.5:1	63
1i	H	SiMe₃	CH₃	>97:3	65[e]

[a] The osmylation reactions were run in acetone/water [8:1; 5.0 mol % OsO₄; Me₃NO (2.2 equiv)] 0.2–0.5 M in substrate. [b] All products were isolated as anti/syn diastereomers, and ratios were determined by integration of the C1 methine protons at 93.94 KG (400 MHz NMR) or by capillary GC analysis after acetylation (Ac₂O, NEt₃, catalyst DMAP, CH₂Cl₂). [c] All products exhibited the expected ¹H NMR (400 MHz), IR, and mass spectral characteristics. [d] All yields are based on pure materials isolated by chromatography on SiO₂. [e] Crude yield.

ticipate in vicinal hydroxylation reactions with useful levels of selectivity. Here we disclose our results of a study to determine the *influence of a geminally substituted alkoxy-trialkylmetal center* on the π-facial selectivity in catalytic osmylation reactions. Our experiments present evidence supporting the notion that the steric influence[4] of the silicon group is as important as σ donor effects.[5a] The oxygen-substituted allylic silanes undergo vicinal hydroxylations with very high levels of diastereofacial selectivities

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