Triplet Excitation Transfer through the Walls of Hemicarcerands: Dependence of the Electronic Coupling on the Size of the Molecular Cage

Zinaida S. Romanova,[†,⊥] Kurt Deshayes,*[,†,§] and Piotr Piotrowiak*[,‡]

Contribution from the Department of Chemistry and Center for Photochemical Sciences, Bowling Green State University, Bowling Green, Ohio 43403, and Department of Chemistry, Rutgers University, Newark, New Jersey 07102

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Abstract: Triplet excitation transfer from biacetyl trapped inside three hemicarcerands of different size (**1**, **2**, and **3**) to acceptors in the surrounding medium was investigated. The largest hemiracerand **1** employs four butyl linkers and the intermediate hemicarcerand **2** four *o*-xylyl linkers. The smallest hemicarcerand **3** contains only three methylene linkers. Both neat liquid triplet acceptors and acceptors dispersed in solvents were used. The primary objective of this work was to determine the dependence of the energy transfer rate on the size and the electronic structure of the molecular cages. There is a pronounced, more than 10-fold, increase of triplet energy transfer rates with decreasing size of the cage. The corresponding electronic coupling, $|V|$, increases approximately by a factor of ∼3.5 from the largest hemicarceplex **1** to the smallest hemicarceplex **3**. This increase of the electronic interaction is similar to that observed in covalently bound systems when the distance between the triplet donor and the acceptor is reduced by one carbon−carbon σ-bond. The electronic structure of the hemicarcerand appears to be of secondary importance, at least when T_1 states of the donor and the acceptor are far from a resonance with the T_1 state of the cage. A very good agreement between the results obtained in neat acceptors and in solution was found, indicating that the association between the acceptors and the molecular cages is negligible, if at all present. An unexpectedly large interaction between the guest and the polarizable walls of the hemicarcerands manifested by emission red-shifts was observed in all cases. This suggests that the entrapment within the molecular cage gives rise to an environment considerably different from that of a single molecule in the gas phase. An interesting correlation between the magnitude of the phosphorescence spectral shift, $\Delta\nu_{0-0}$, and the guest-to-external acceptor electronic coupling, $|V|$, was found.

Introduction

In order to understand the role of unbound intervening medium in charge and excitation transfer processes, we[1] and others[2] have undertaken the study of excitation transfer reactions where a barrier between the donor and the acceptor is imposed by the encapsulation of one of the partners within Cram's closed surface hemicarcerand hosts. The earlier work has shown that the intervening wall of the hemicarceplex lowers the electronic coupling between the triplet donor guest (biacetyl) and the acceptors on the outside, so that the existence of the parabolic Marcus relationship between rate constant and driving force can be clearly demonstrated, despite the fact that the donor and the acceptor are not linked to one another and can freely diffuse. While our previous studies concentrated on the details of the $\Delta G°$ and the internal reorganization energy dependence of triplet excitation transfer,[3] the work reported here explores for the first time the correlation between the size of the hemicarcerand cage and the magnitude of the electronic coupling between the encapsulated guest and the outside environment (Figure 1). Changing the size of the cage is expected to play a role similar to varying the average distance between the donor and the acceptor. In accordance with the simple superexchange picture,[4] the overall donor−acceptor coupling in these systems can be viewed as a sequence of guest ↔ host and host ↔ solute interactions, and thus is proportional to the product of the coupling between the T_1 state of the incarcerated donor and the virtual triplet states of the cage, with the coupling between the cage and the T_1 state of the acceptor, i.e., $V_{total} \propto V_{guest-cage} \cdot V_{cage-acceptor}$. The interaction between the external surface of the cage and the acceptors in solution is most likely only weakly dependent on the size of the hemicarcerand. However, the time-averaged interaction between the guest and the internal surface of the cage, $V_{guest-cage}$, should be highly sensitive to the size of the molecular cavity, thus rendering the overall coupling V_{total} dependent on the size of the hemicarcerand.

The hemicarcerands employed in this study are shown in Figure 1. The host dimensions were varied by changing the butyl linking units found in **1** to *o*-xylyl fragments in **2**, and to

† Bowling Green State University.
‡ Rutgers University.
⊥ Current address: Department of Chemistry, Stanford University, Stanford, CA 94305-5080.
§ Current address: Genentech Inc., Department of Protein Engineering, 1 DNA Way, South San Francisco, CA 94080-4990.

(1) (a) Farrán, A.; Deshayes, K.; Matthews, C.; Balanescu, I. *J. Am. Chem. Soc.* **1995**, *117*, 9614. (b) Farrán, A.; Deshayes, K. *J. Phys. Chem.* **1996**, *100*, 3305.
(2) (a) Pina, F.; Parola, A. J.; Ferreira, E.; Maestri, M.; Armaroli, N.; Ballardini, R.; Balzani, V. *J. Phys. Chem.* **1995**, *99*, 12701. (b) Parola, A. J.; Pina, F.; Ferreira, E.; Maestri, M.; Balzani, V. *J. Am. Chem. Soc.* **1996**, *118*, 11610.
(3) Place, I.; Farrán, A.; Deshayes, K.; Piotrowiak, P. *J. Am. Chem. Soc.* **1998**, 120, 12626.
(4) Piotrowiak, P. Principles Methods and Techniques. In *Electron Transfer in Chemistry*; Balzani, V., Editor-in-Chief; Piotrowiak, P., Ed.; Wiley-VCH: Weinheim, 2001; Vol. 1, Part 1, Chapter 6, p 215.

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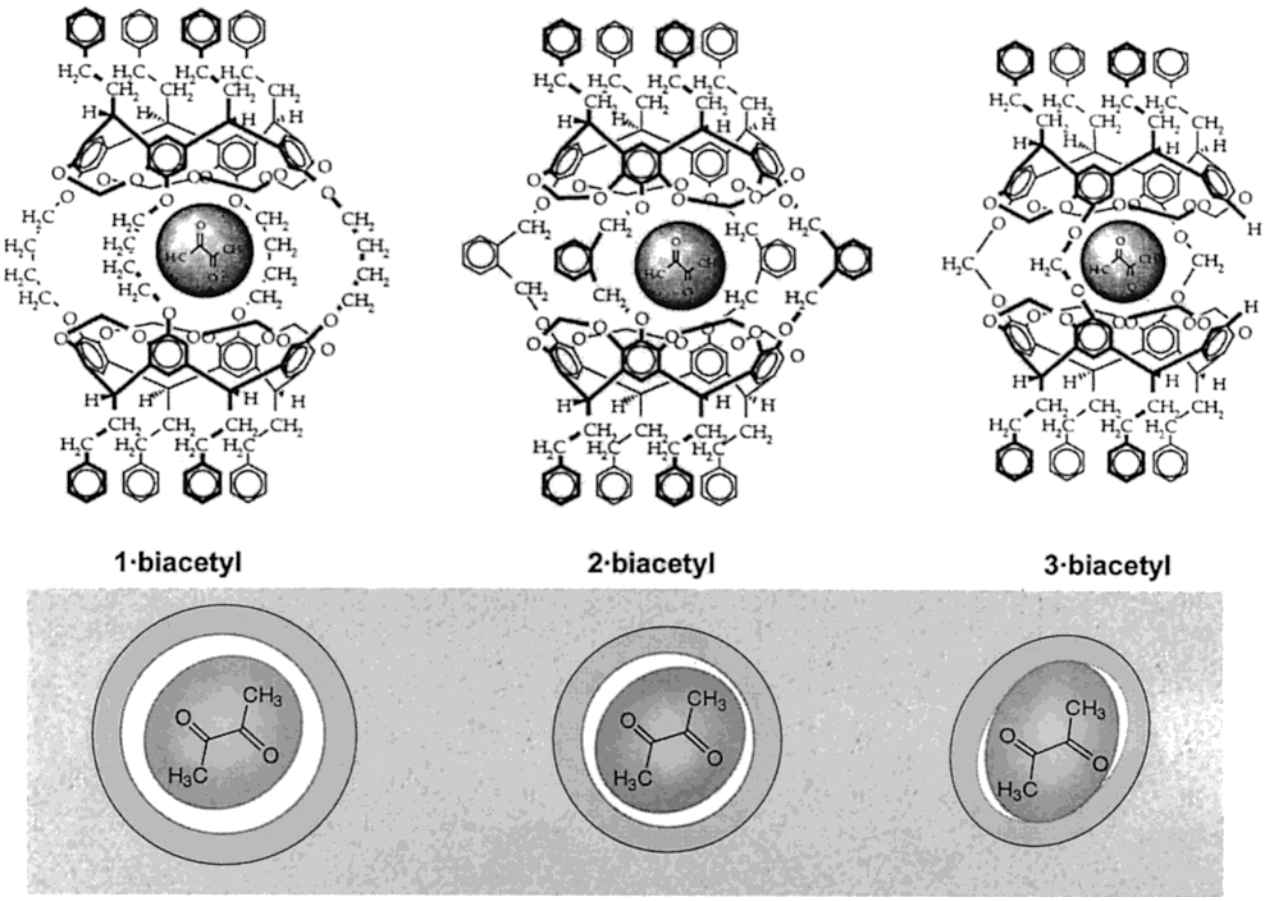

Figure 1. Hemicarceplexes employed in this study: **1**·biacetyl (four butyl linkers), **2**·biacetyl (four *o*-xylyl linkers), and **3**·biacetyl (three methylene linkers).

methylene groups in **3**. In the case of the smallest hemicarcerand **3**, one methylene bridge was removed to create a sufficiently large portal through which biacetyl could be exchanged into interior of **3**.[5] The hemicarceplexes were stable indefinitely at room temperature, in agreement with the behavior of similar complexes reported in the literature.[6] Since the encapsulation of biacetyl slows all triplet transfer rates by more than 2 orders of magnitude, the presence of any free biacetyl would lead to a sharply biexponential behavior, which would be readily detected in the phosphorescence quenching measurements. Free biacetyl was not detected in any of the excitation transfer experiments reported in this paper.[7] As in our previous studies,[1,3,8] in order to verify that the incarcerated biacetyl cannot come into direct contact with the acceptors and that the excitation transfer must be mediated by the hemicarcerand shell, triplet lifetime measurements in H-atom-donating solvent, 2-propanol, were performed. No quenching that could be attributed to hydrogen abstraction was observed for any of the host−guest assemblies.

Two sets of triplet energy transfer experiments were performed. In the first series the acceptors were, as in all preceding studies, dispersed in solution at millimolar concentrations. In the second series of measurements *neat liquid triplet acceptors* were used for the first time as solvents in which the cage molecules with the incarcerated donor were dissolved.[9] With the donor−acceptor electronic coupling greatly reduced by the presence of the hemicarcerand wall, such measurements are readily possible with standard nanosecond equipment (described in the Experimental Section). It was expected that by eliminating the diffusion step and measuring triplet transfer rates in neat acceptors, we will be able to probe the role (if any) of the possible adhesion of acceptors to the surface of the hemicarcerand and, at least qualitatively, asses the uniformity of the electronic coupling mediated by the cage. A detailed discussion is given in the body of the paper.

Experimental Section

Materials and Synthesis. All chemicals were purchased from Aldrich Chemicals, Fisher Scientific, and Lancaster. All solvents, except for spectroscopic grade methylene chloride and benzene, were additionally purified by methods described in the Supporting Information. The hosts were synthesized according to literature procedures.[10] Biacetyl was exchanged for one molecule of dimethyl acetamide (DMA) within the interior of each host (see Supporting Information) to give, after purification, the desired complexes as confirmed by mass spectrometry and proton NMR. The syntheses of **1**·biacetyl, **2**·biacetyl, and **3**·biacetyl

(5) The size of the empty cavity of hemicarcerand **1** is only slightly larger than that of **2**. However, the cage with four butyl links is far more flexible and can adapt to the size and shape of the guest much more readily than the cage with four *o*-xylyl fragments.

(6) Warmuth, R.; Yoon, J. *Acc. Chem. Res.* **2001**, *34*, 95 and references therein.

(7) This is a minor issue since the separation of two kinetic components corresponding to the incarcerated and free biacetyl would be extremely facile considering the large difference between the respective quenching rates.

(8) Romanova, Z. S.; Deshayes, K.; Piotrowiak, P. *J. Am. Chem. Soc.* **2001**, *123*, 2444.

(9) Naturally, there are examples of energy- and electron-transfer experiments in neat acceptors or donors which do not involve encapsulation of one of the partners in a molecular cage.

(10) The procedures for construction of hosts **1**−**3** follow in order: (a) Robbins, T. A.; Knobler, C. B.; Bellew, D. R.; Cram, D. J. *J. Am. Chem. Soc.* **1994**, 116, 111. (b) Cram, D. J.; Blanda, M. T.; Paek, K.; Knobler, C. B. *J. Am. Chem. Soc.* **1992**, *114*, 7765. (c) Cram, D. J.; Tanner, M. E.; Knobler, C. B. *J. Am. Chem. Soc.* **1991**, *113*, 7717.

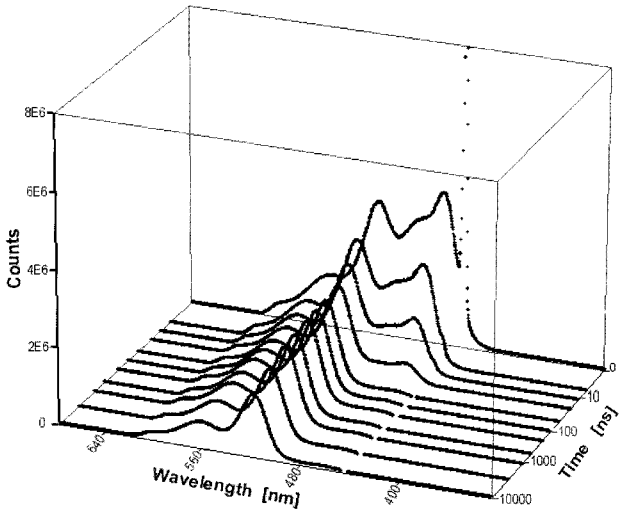

Figure 2. An example of simultaneously collected time-resolved fluorescence and phosphorescence spectra of biacetyl (degassed solution in CH_2Cl_2). The sharp 445 nm feature at $t = 0$ is the ~3 ns OPO excitation pulse.

are given in the Supporting Information, along with the ^{1}H NMR and FAB MS data. Synthesis of intermediate compounds was performed using the procedures initially developed by Cram et al.[11]

Static Emission Spectra. Emission and excitation spectra were measured on a SPEX 1680 Fluorolog double-monochromator spectrofluorimeter/phosphorimeter. The excitation wavelength was 430 nm. The measurements were performed in 1 cm path length quartz cuvette, and the range of concentrations was 0.2−1 mM. When needed, the samples were degassed by bubbling Ar for at least 15 min.

Time-Resolved Experiments. The measurements were carried out using a nanosecond Q-switched Nd:YAG laser (Continuum, NY61) equipped with a Surelite OPO (Continuum) and a MultiSpec 257 Spectrograph (Oriel) with an InstaSpec V intensified CCD detector (Andor). The excitation pulse had a wavelength of 445−450 nm, energy of 1.0−2.5 mJ, and duration of ~3 ns. The system was operated at 10 Hz repetition rate, and the number of averaged acquisitions was adjusted depending on the signal-to-noise ratio. The delay time between the laser pulse and the ICCD gate was varied from nanoseconds to milliseconds. Changing the duration of the gate from 4 ns for fluorescence to 500 ns−100 μs for phosphorescence allowed a clear discrimination between the emission from the S_1 and T_1 states, due to the several orders of magnitude difference in their lifetimes. In several instances, the concentration of the samples was limited by the solubility of the hemicarceplexes; however, the high intensity of the laser pulse allowed us to work in the 0.1−0.2 mM range. The solutions for the time-resolved measurements where degassed by at least four freeze−pump−thaw cycles.

Determination of Bimolecular Rate Constants in Solution. All aromatic compounds used as excitation quenchers were purified by recrystallization from alcohols. The lifetimes of biacetyl triplet were obtained by fitting the decay of emission with the single exponential. The samples were excited at 430 nm, and the emission was monitored at 528, 534, and 540 nm for **1**·biacetyl, **2**·biacetyl, and **3**·biacetyl, respectively. The quenching experiments were performed in spectroscopic grade methylene chloride and benzene. The range of concentrations was 0.25−5.0 mM, and the samples were prepared in a 1 cm quartz cell placed in a jacketed cell holder attached to a RM6 Lauda Brinkmann thermostatic bath with a Barnant 90 digital thermocouple thermometer. The temperature was stabilized at 25.8 °C to within ±0.1 °C. The pseudo-unimolecular rate constants k_{TT} were calculated using the Stern−Volmer equation, $1/\tau = 1/\tau_0 + k_{TT}[Q]$, where τ and τ_0 are the lifetimes measured with and without the quencher, and [Q] is the concentration of the quencher. The rate constants were determined from the slope of the $1/\tau$ versus [Q] plot. The correlation coefficients were better than 0.99 in all cases.

Determination of the Triplet Transfer Rates in Neat Acceptors. All organic acceptors used as a liquid medium for energy transfer studies were additionally purified as described in the Supporting Information. The purity was checked by monitoring the UV−vis absorption of the undiluted liquids at 430−450 nm. The hemicarceplexes dissolved in neat acceptors were excited by the laser pulse at 450 nm, and the phosphorescence was monitored at different delay times.[12] The intensity at the phosphorescence maximum was plotted against time, and the lifetimes were obtained from single-exponential fitting.

Results and Discussion

1. Interaction of the Guest with the Cage−Spectral Properties of Hemicarceplexes 1, 2, and 3. The static fluorescence and phosphorescence spectra of hemicarceplexes **1** (four butyl linkers), **2** (four *o*-xylyl linkers), and **3** (three methylene linkers) reveal the presence of a considerable interaction between the incarcerated biacetyl and the walls of the cage. Interestingly, for all studied cages the biacetyl emission origins are red-shifted not only in comparison with the gas-phase reference (Figure 3) but also with respect to the spectra of free biacetyl in methylene chloride, a polar and polarizable solvent, $\epsilon = 8.9$, $n = 1.42$. This result is somewhat unexpected and shows that while the guest within a hemicarcerand is effectively protected from contact with external reagents, its environment is not as similar to that of an isolated molecule in the gas phase as it is sometimes suggested.[13] Among the three hemicarceplexes, **1**·biacetyl, **2**·biacetyl, and **3**·biacetyl, the bathochromic shifts follow the expected trend and increase as the size of the hemicarcerand decreases (Table 1). As a consequence, the driving force for triplet energy transfer from the incarcerated biacetyl decreases slightly as the cage becomes smaller.

The characteristic negative ^{1}H NMR chemical shift of the incarcerated biacetyl caused by the shielding by the phenyl rings of the host exhibits a trend similar to that of the emission shifts, i.e., **3** ≈ **2** > **1** (see the Supporting Information). The presence of a single sharp biacetyl peak in the high-resolution ^{1}H NMR spectra indicates that in the two larger cages, **1** and **2**, the guest molecule is able to reorient. Naturally, even a very slow reorientation (~10^4 s^{-1}) is sufficient to average the chemical shifts resulting from the possible distribution of the guest orientations within the cage. Therefore, on the basis of the NMR spectra alone, it is not possible to conclude whether the position of the biacetyl donor remains static on the time scale of the triplet excitation transfer event. The biacetyl peak in the 400 MHz ^{1}H NMR spectrum of the smallest hemicarceplex **3** is split, indicating the presence of two distinct orientations of the guest within the cage with an exchange rate slower than ~10 s^{-1}.

At first it is tempting to ascribe the emission shifts to the coupling between the transition dipole of the guest chromophore and the polarizability tensor of the cage. However, the $T_1 \rightarrow S_0$ transition moment of biacetyl is orders of magnitude smaller

(11) (a) Sherman, J C.; Knobler, C. B.; Cram, D. J. *J. Am. Chem. Soc.* **1991**, *113*, 2194. (b) Kurdistani, S. K.; Helgeson, R. C.; Cram, D. J. *J. Am. Chem. Soc.* **1995**, *117*, 1659.

(12) Even after extensive purification, the neat acceptors exhibited a residual absorption as high as 0.1 in the 430−450 nm window. However, no emission was detected upon the excitation of the neat olefinic acceptors at 450 nm. In the case of the liquid derivatives of naphthalene, a strong emission at 410 and 400 nm (i.e., at a wavelength shorter than the excitation wavelength) with lifetimes of 7−8 ns was observed. It was tentatively ascribed to result from the multiphoton excitation followed by the formation of an exciplex. Thanks to the short lifetimes of this species and the more than 60 nm offset from the fluorescence of the hemicarceplexes, it was possible to avoid the interference with the emission from biacetyl.

(13) (a) Cram, D. J.; Tanner, M. E.; Thomas, R. *Angew. Chem., Int. Ed. Engl*. **1991**, *30*, 1024. (b) Warmuth, R. *Angew. Chem., Int. Ed. Engl*. **1997**, *37*, 1347.

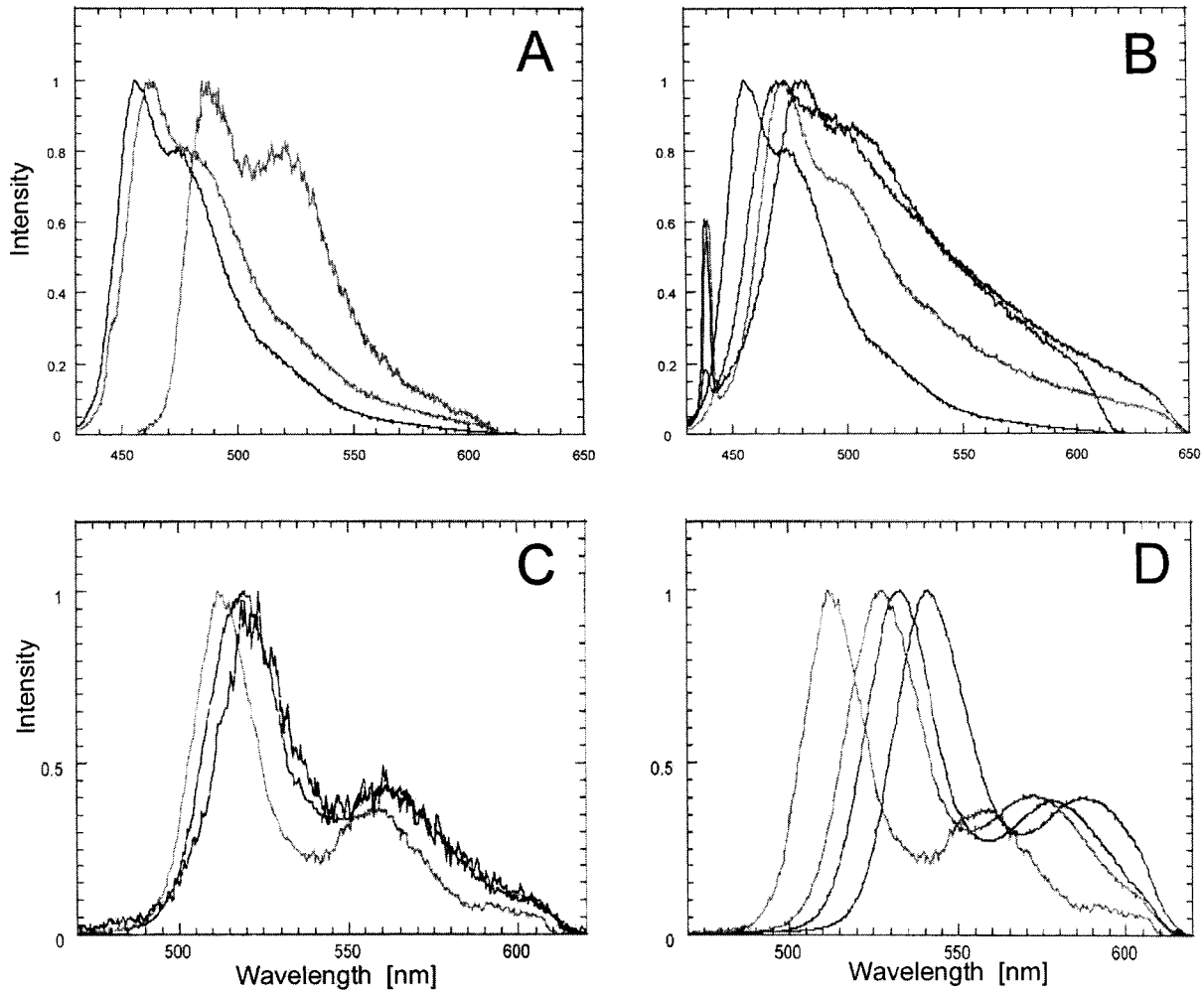

Figure 3. Normalized emission spectra of biacetyl in different environments: (a) from left to right, fluorescence in gas phase, solution in CH_2Cl_2, and neat liquid; (b) from left to right, fluorescence in gas phase, **1**·biacetyl, **2**·biacetyl, and **3**·biacetyl; (c) from left to right, phosphorescence in gas phase, solution in CH_2Cl_2, and neat liquid; (d) from left to right, phosphorescence in gas phase, **1**·biacetyl, **2**·biacetyl, and **3**·biacetyl.

Table 1. Spectral Characteristics of Biacetyl Emission in Different Environments

	fluorescence origin			$\Delta\nu_{0-0}$,	phosphorescence origin			$\Delta\nu_{0-0}$,	S_1-T_1 gap,	τ_{S1},	τ_{T1},
medium	nm	cm^{-1}	kcal/mol	cm^{-1}	nm	cm^{-1}	kcal/mol	cm^{-1}	cm^{-1}	ns	ms
gas phase	457	21 880	62.6	0	513	19 490	55.7	0	2390		
CH_2Cl_2	463	21 600	61.8	280	519	19 270	55.1	220	2230	8.5	
benzene	468	21 370	61.1	510	523	19 120	54.7	370	2250	11.5[a]	1.03[b]
neat biacetyl	488	20 490	58.6	1390	522	19 160	54.8	330	1330		
1·biacetyl	470	21 280	60.9	600	528	18 940	54.2	550	2340	10.1[c]	1.10[c]
2·biacetyl	473	21 140	60.5	740	533	18 760	53.7	730	2380	11.2[c]	0.88[c]
3·biacetyl	480	20 830	59.6	1050	541	18 480	52.9	1010	2350	10.8[c]	0.61[c]

[a] From: Murov, S. L.; Carmichael, I.; Hug, G. L. *Handbook of Photochemistry*; Marcel Dekker, Inc.: New York, 1997. [b] From: Sandros, K. *Acta Chem. Scand.* **1964**, *18*, 2355. [c] This work. The margin of error for the triplet lifetimes is ±10%, and that for the singlet lifetimes is ±20%.

than that of the allowed $S_1 \rightarrow S_0$ transition, yet the respective bathochromic shifts are nearly identical and thus cannot be explained in these terms. As a result of the parallel $S_1 \rightarrow S_0$ and $T_1 \rightarrow S_0$ shifts, the S_1-T_1 splitting of the incarcerated biacetyl remains remarkably independent of the size of the cage (Table 1). The magnitudes of the shifts suggest that the free space within even the largest hemicarceplex **1** is considerably smaller than the average voids in liquids under normal conditions. Consequently, it could be postulated that the "effective local pressure" experienced by biacetyl within the hemicarcerand must be higher than the ambient (naturally, the guest may be undergoing a more specific structural distortion, e.g., it may become increasingly nonplanar as the cavity becomes smaller). Indeed, it would be worthwhile to compare the emission spectra reported here with solution spectra obtained at elevated hydrostatic pressures. The triplet lifetime of the encapsulated biacetyl decreases quite rapidly as the hemicarcerand cage becomes smaller (Table 1), providing another confirmation that the perturbation increases with the diminishing size of the void.

It is worth mentioning that MO calculations indicate that the molecular volume of biacetyl does not increase upon formation of the T_1 state. This is a somewhat uncommon behavior, as most organic chromophores, particularly the aromatics and olefins, expand upon promotion to an excited state because of the population of the antibonding π^* orbital. In contrast, biacetyl is predicted to contract slightly upon the formation of the n $\rightarrow$

Table 2. Pseudo-Unimolecular Rate Constants of Intermolecular Triplet Energy Transfer from Biacetyl Incarcerated in **1**, **2**, and **3** to Acceptors in Solution (Benzene, $T = 25.5$ °C)

		1·biacetyl		**2**·biacetyl		**3**·biacetyl	
acceptor	E_T,[a] kcal/mol	$-\Delta G°$, kcal/mol	k^{sol},[b] s^{-1}	$-\Delta G°$, kcal/mol	k^{sol},[b] s^{-1}	$-\Delta G°$, kcal/mol	k^{sol},[b] s^{-1}
naphthalene	60.5	−6.3	2.4×10^2	−6.8	3.3×10^2	−7.6	4.6×10^2
naphthalene (ΔG corrected)		−6.3	2.4×10^2	−6.3	7.9×10^2	−6.3	4.8×10^3
9-bromoanthracene	41.3	12.9	8.2×10^5	12.4	1.3×10^6	11.6	1.7×10^7
9-bromoanthracene (ΔG corrected)		12.9	8.2×10^5	12.9	8.2×10^5	12.9	5.7×10^6
9,10-dibromoanthracene	40.2	14.0	4.2×10^5	13.5	8.0×10^5	12.7	1.1×10^7
9,10-dibromoanthracene (ΔG corrected)		14.0	4.2×10^5	14.0	5.0×10^5	14.0	3.1×10^6

[a] From: Murov, S. L.; Carmichael, I.; Hug, G. L. *Handbook of Photochemistry*; Marcel Dekker, Inc.: New York, 1997. [b] The rates carry an error of ±10%.

π^* triplet state.[14] This suggests that the perturbation of the ground state, rather than preferential stabilization of the excited state, is the likely source of the observed spectral and lifetime changes.

Finally, is also of interest to include in this comparison of the environment-dependent spectral shifts the emission spectra obtained in neat liquid biacetyl, which was expected to give particularly broad and strongly shifted bands. Quite surprisingly, the phosphorescence spectrum measured in neat biacetyl (Figure 3C) exhibits less of a bathochromic shift than those obtained for the hemicarceplexes. This indicates that the resonance coupling between the triplet states of molecules in neat liquids is weak, most likely because of the spin-forbidden-ness of the $T_1 \rightarrow S_0$ transition, which makes the usually dominant exciton coupling negligibly small. This leaves only the short-range exchange coupling, which can be substantial only between the nearest neighbors. On the other hand, the fluorescence spectrum of neat biacetyl (Figure 3A) exhibits the expected behavior, i.e., it is much more red-shifted and broadened than the spectra obtained from in hemicarceplex (or solvent), thus indicating the presence of a strong long-range exciton coupling between the allowed $S_1 \rightarrow S_0$ transitions of the molecular liquid (the sharp cutoff of the short-wavelength portion of the fluorescence spectrum in Figure 3A is due to strong reabsorption).

2. Triplet Energy Transfer to Acceptors in Solution. The rates of diffusional triplet energy transfers from biacetyl enclosed in hemicarcerands **1**, **2**, and **3** to acceptors in benzene solution were studied in order to elucidate how the effective electronic coupling $|V|$ between the guest and the external acceptors varies depending on the size of the molecular cage. Three triplet acceptors spanning the driving force range from −7 to +16 kcal/mol were employed in order to provide a more reliable picture of the size dependence of $|V|$.[15]

The measured transfer rates followed the expected trend and increased with the decreasing cage size for all studied acceptors, $k_3^{sol} > k_2^{sol} > k_1^{sol}$ (see Table 2). The average transfer rates for the smallest cage **3** are more than 10 times faster than those for the largest cage **1**. In all cases good monoexponential phosphorescence decays were obtained, indicating that the solution was homogeneous, free of aggregation between the hemicarceplexes and the acceptors. As emphasized in the Introduction, the possibility of a direct contact between the incarcerated biacetyl and the acceptors, particularly important in the case of the smallest methylene cage containing only three linkers, was excluded by running experiments in isopropyl alcohol, which effectively quenches the biacetyl triplet in free solution by hydrogen abstraction. The pseudo-unimolecular rate constants in Table 2 can be used to estimate the effective electronic couplings mediated by the cages using the standard "golden rule" expression,

$$k = \frac{2\pi}{\hbar}|V|^2(\mathrm{FCWD}) \qquad \text{or} \qquad |V| = \sqrt{\frac{\hbar}{2\pi}\frac{k}{(\mathrm{FCWD})}} \quad (1a,b)$$

where the Franck−Condon weighted density of states (FCWD) is expressed in terms of the driving force $\Delta G°$ and reorganization energy λ using either the classical or the semiclassical version of the Marcus theory. Since the hemicarceplex **2** has been already studied in detail by this group,[1,3,8] and the average magnitude of electronic coupling for freely diffusing aromatic acceptors, including the ones used in the present work, has been already established to be 0.26 cm^{-1},[3] the values of $|V|$ for hemicarceplexes **1** and **3** can be obtained by straightforward scaling,

$$k_i/k_2 = (V_i/V_2)^2 \qquad \text{or} \qquad V_i = V_2(k_i/k_2)^{1/2} \quad (2a,b)$$

provided that the Franck−Condon densities of states do not change from one hemicarceplex to another. Naturally, the triplet energies and reorganization energies of the acceptors in solution are independent of the size of the hemicarceplex. However, as discussed above, the triplet energy of the incarcerated biacetyl does decrease with the diminishing size of the host (Table 1). The corresponding reduction of the driving force influences the observed triplet transfer rates and distorts the recovered cage size dependence of $|V|$: in the case of the endoergic transfer to naphthalene the $\Delta G°$ shift significantly decreases the rates, i.e., it works against the increased electronic coupling; in the case of the highly exoergic transfer to bromoanthracene and dibromoanthracene, which takes place in the "inverted region", the $\Delta G°$ shift increases the rates, thus enhancing the influence of the growing $|V|$. To compensate for this effect, the pseudo-unimolecular rates for each acceptor can be renormalized to a constant value of $\Delta G°$.[16] The renormalized values are included in Table 2.

Since the confinement within the hemicarcerand affects the triplet energy of biacetyl, it is reasonable to expect that it may

(14) According to AM1 calculations, the volume of biacetyl shrinks by ~1% upon the $S_0 \rightarrow T_1$ transition. This is consistent with the exceptionally small internal reorganization energy of biacetyl and the $n\pi^*$ nature of the transition. The same calculations predict that most other organic compounds increase their volume by 1−3% upon the formation of the T_1 excited state.

(15) Acceptors that lie deep in the "normal" and "inverted" region were selected in order to separate the purely electronic effects from the changes in the Franck−Condon factors. However, unlike in the previous study (ref 3), it was not our objective to perform a detailed investigation of the $\Delta G°$ and reorganization energy dependence for each of the hemicarceplexes.

(16) For the sake of simplicity, we based the correction for the cage-dependent $\Delta G°$ shift on the classical Marcus equation, $k = (\pi/\hbar 2\lambda k_B T)^{1/2}|V|^2 e^{-(\Delta G° + \lambda)^2/4\lambda k_B T}$, with the average total reorganization energy of 6 kcal/mol taken from ref 3. For each acceptor, the rates for hemicarceplexes **2** and **3** were normalized to the $\Delta G°$ value of hemicarceplex **1**. The classical Marcus equation most likely overestimates the rate correction in the "inverted region" (9-bromoanthracene and 9,10-dibromoanthracene). However, this is not exceedingly important since the magnitudes of the cage-size-dependent electronic coupling extracted from the corrected and uncorrected rates are very similar.

Table 3. Rates of Triplet Energy Transfer from **1**·Biacetyl, **2**·Biacetyl, and **3**·Biacetyl to Neat Acceptors, k^{neat}

			1·biacetyl		**2**·biacetyl		**3**·biacetyl	
acceptor	E_T,[a] kcal/mol	mp,[b] °C	$-\Delta G°$, kcal/mol	k^{neat},[c] s^{-1}	$-\Delta G°$, kcal/mol	k^{neat},[c] s^{-1}	$-\Delta G°$, kcal/mol	k^{neat},[c] s^{-1}
Olefinic Acceptors								
cycloheptatriene	38.0	−79	16.2	2.6×10^5	15.7	3.3×10^5	14.9	1.6×10^6
cycloheptatriene (ΔG corrected)			16.2	2.6×10^5	16.2	3.8×10^5	16.2	2.3×10^6
Aromatic Acceptors								
1-methylnaphthalene	60.7	−22	−6.5	$>1.4 \times 10^3$	−7.0	$>1.2 \times 10^3$	−7.8	$>2.0 \times 10^3$
1-methylnaphthalene (ΔG corrected)			−6.5	$>1.4 \times 10^3$	−6.5	$>2.9 \times 10^3$	−6.5	$>2.1 \times 10^5$
1-chloronaphthalene	58.6	−2.5	−4.4	$>3.7 \times 10^3$	−4.9	$>2.7 \times 10^3$	−5.7	$>5.5 \times 10^3$
1-chloronaphthalene (ΔG corrected)			−4.4	$>3.7 \times 10^3$	−4.4	$>3.7 \times 10^3$	−4.4	$>4.0 \times 10^4$

[a] From: Murov, S. L.; Carmichael, I.; Hug, G. L. *Handbook of Photochemistry*; Marcel Dekker, Inc.: New York, 1997. [b] From: *Handbook of Chemistry and Physics*; CRC Press: Boca Raton, 1990. [c] The rates carry an error of ±10%.

also influence its reorganization energy, λ. Since the reorganization energy of biacetyl in solution is very small,[3,4] the overall value of λ_{total} is dominated by the contribution of the acceptor. Therefore, the small changes in $\lambda_{biacetyl}$ that could be induced by the hemicarcerand can be ignored in the analysis.

The average value of the cage-mediated electronic coupling $|V|$ extracted from the renormalized pseudo-unimolecular rate constants increases by a factor of 3.3 from the largest hemicarceplex **1** to the smallest hemicarceplex **3**. If the uncorrected rate constants are used, one obtains a slightly different average ratio of the coupling elements, $|V_3|/|V_1| = 3.7$. The small difference confirms that the increase in electronic coupling is a more important factor than the minor change of energetics. The individual values of $|V|$ are 0.20 cm^{-1} for **1**, 0.26 cm^{-1} for **2** (the reference point), and 0.66 cm^{-1} for **3**. If the uncorrected rate constants are used, the final results are very similar, with $|V_1| = 0.20$ cm^{-1}, $|V_2| = 0.26$ cm^{-1} (reference), and $|V_3| = 0.74$ cm^{-1}. The overall change of electronic coupling is comparable to that observed in covalently bound systems when the separation between the triplet donor and the acceptor is reduced by one carbon−carbon σ-bond.[5,17] Although this series of hemicarceplexes is too short to permit a decisive separation of the size and electronic structure effects, it appears that the size of the cage plays the dominant role, and no special amplification of coupling is observed in the case of hemicarcerand **2**, whose walls contain the aromatic *o*-xylyl linkers. The presence of aromatic groups could lead to enhanced superexchange coupling if the unpopulated "virtual states" of the cage were close to a resonance with either the relevant excited state of the donor, or the acceptor, or both. Since the T_1 state of the *o*-xylyl fragment is located well above (≥25 kcal/mol) the T_1 states of both biacetyl and the acceptors, the corresponding enhancement of coupling will be minor. A separate study addressing specifically the role of the electronic structure of the cage in mediating the energy transfer, and the possibility of stepwise transfer, will be reported shortly.

3. Energy Transfer to Neat Liquid Triplet Acceptors. As mentioned earlier, we decided to investigate energy transfer from the incarcerated donor to neat liquid triplet acceptors in order to eliminate the diffusional step of the process and to attempt to address two important issues: first, the possibility of adsorption of the acceptors on the surface of the hemicarceplex, and second, the uniformity of the electronic coupling propagated across the wall of the molecular cage. The existence of even weakly bound hemicarceplex−acceptor aggregates could distort the $\Delta G°$ dependence reported in the previous communication,[3] although the monoexponential phosphorescence decays and linear Stern−Volmer plots, which were obtained for all cage/acceptor combinations, provided strong evidence against this possibility. In the second case, if the electronic coupling mediated by the cage were highly inhomogeneous, different geometries of an encounter between the acceptor and the surface of the cage would lead to different efficiencies of triplet energy transfer. As a result, the triplet transfer rates measured in neat acceptors, where the entire surface of the cage is continuously in contact with the quenchers, should be faster than the properly scaled rates in solution, which correspond to the average of the distribution of the more and less efficient encounters. As a consequence, the straightforward comparison of the triplet transfer rates in liquid acceptors with the solution pseudo-unimolecular rate constants appropriately scaled by the molarity of neat acceptors can yield very valuable information about the nature of the interaction between the acceptor and the outer surface of the molecular cage.

There are only a few substances that are liquid at room temperature and whose T_1 states lie below that of biacetyl. In this study we used cycloheptatriene and two liquid derivatives of naphthalene, 1-methylnaphthalene and 1-chloronaphthalene. The T_1 states of the substituted naphthalenes are higher than that of biacetyl, and thus the fast back transfer poses a difficulty. While in the case of dilute solutions the problem of back transfer can be practically eliminated by the use of a secondary acceptor (typically oxygen),[18] this complication is more difficult to alleviate in the case of viscous neat acceptors. As a consequence, the quenching rates measured in liquid derivatives of naphthalene must be viewed only as the lower limits of the real forward triplet transfer rate.

The triplet energy transfer rates obtained in neat acceptors, k^{neat}, are presented in Table 3. It should be emphasized that here we report the overall *transfer rates*, and not pseudo-unimolecular *rate constants*, as we did in the case of triplet energy transfer in solution in Table 2. Representative examples of the phosphorescence decays obtained in neat cycloheptatriene and the monoexponential fits are given in Figure 4. As in the case of the solution results, the rates of triplet transfer to liquid acceptors increase with the decreasing size of the cage (Table 3). The only disagreement with this trend occurs for hemicarceplex **2** in naphthalene derivatives, but even this discrepancy disappears if the appropriate correction for the shift in $\Delta G°$ is introduced. The triplet transfer rates to neat cycloheptatriene are much less sensitive to the small changes of $\Delta G°$ because of the large reorganization energy of this compound ($\lambda \approx 23$ kcal/

(17) Closs, G. L.; Piotrowiak, P.; McInnis, J. M.; Fleming, G. R. *J. Am. Chem. Soc.* **1988**, *110*, 2652.

(18) The vastly different quenching rates of free and incarcerated triplet donors by O_2 have been used by us and others to prevent back-transfer (refs 1−3). In free solution the O_2 triplet quenching is usually faster than 10^9 M^{-1} s^{-1}, yet it slows to $\sim 10^4$ M^{-1} s^{-1} for encapsulated donors. Therefore, in nonviscous solvents the typical ∼1−2 mM concentration of O_2 is sufficient to completely quench triplet acceptors without affecting the lifetime of the incarcerated biacetyl.

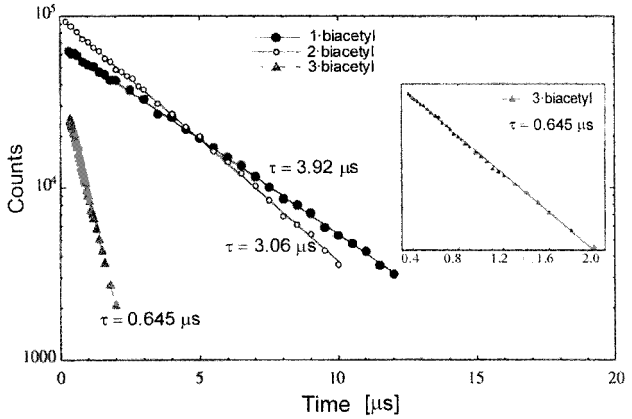

Figure 4. Triplet quenching of **1**·biacetyl, **2**·biacetyl, and **3**·biacetyl dissolved in neat cycloheptatriene. Note the excellent linearity. The traces were not normalized for the differences in the hemicarceplex concentration and the excitation pulse energy.

Table 4. Average Electronic Coupling between the T_1 State of Incarcerated Biacetyl and the Neat Liquid Cycloheptatriene

hemicarceplex	**1**·biacetyl	**2**·biacetyl	**3**·biacetyl
coupling, cm^{-1}	0.41	0.50	1.31

mol).[19] If we employ the same simple scaling approach as above (eq 2), the effective root-mean-square electronic coupling between the triplet state of the incarcerated biacetyl and the triplet states of the molecules of the liquid acceptor surrounding the cage can be obtained. The resulting values for liquid cycloheptatriene are listed in Table 4 (since the rates for liquid naphthalenes represent only the lower limits, it would not be meaningful to analyze them in a similar manner). Notably, the increase of the effective coupling with the decreasing size of the cage is nearly identical with that found in the case of diffusional triplet energy transfer from the same hemicarceplexes, with the $|V_3|/|V_1|$ ratio of 3.2, vs 3.3.

It is also very informative to compare the transfer rates measured for the same hemicarceplex in liquid acceptors and in dilute solutions. As it can be seen in Table 5, in the case of hemicarceplex **2**, the ratio of these rates, k^{neat}/k^{sol}, follows remarkably closely the molarity of the neat olefinic acceptors. This confirms that there is no association between the hemicarceplex and the acceptors in solution.

Finally, we would like to point out the interesting correlation of the magnitude of the electronic coupling mediated by the walls of hemicarcerands **1**, **2**, and **3** with the magnitude of the corresponding spectral shifts of the biacetyl phosphorescence. The present series of compounds is certainly too small to allow quantitative conclusions; nevertheless, if biacetyl in the gas phase serves as the reference point with $\Delta\nu_{0-0} = 0$ and $V = 0$, one obtains an approximately linear correlation between $|V|$ and $\Delta\nu$ (Figure 5). The existence of such correlation should not be entirely surprising, since, in accordance with the superexchange model of the propagation of the donor−acceptor coupling, the overall interaction should be proportional to the product of the coupling between the guest and the cage with the interaction between the cage and the acceptors, i.e., $V_{total} \propto V_{guest-cage} \cdot V_{cage-acceptor}$. The authors are aware that the phosphorescence spectral shift corresponds to the diagonal element and the donor−acceptor coupling to the off-diagonal element of the appropriate secular equation, and the observed quasi-linear relationship might be accidental. On the other hand, the first-order perturbation theory predicts that in the limit of weak coupling, $V \ll \Delta E$, the shift of the diagonal element is proportional to the square of the off-diagonal element scaled by the ΔE.[20] Therefore, we believe that the observed trend is not fortuitous; however, the limited number of data points precludes a meaningful attempt at distinguishing between a linear or quadratic relationship between V and $\Delta\nu_{0-0}$.

(19) Reorganization energy based on AM1 and ab initio MO calculations, reported in refs 3 and 4.

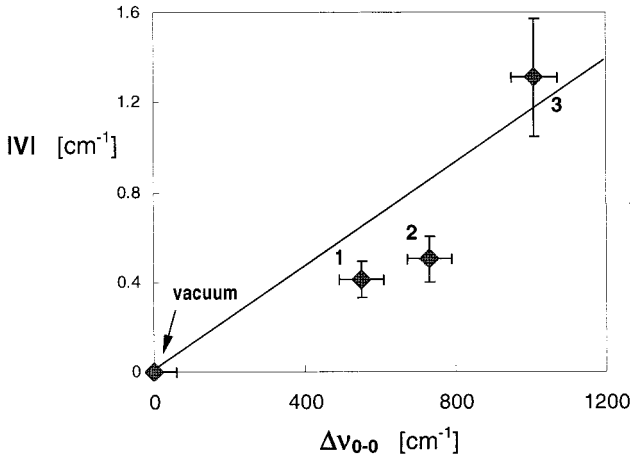

Figure 5. Correlation between the magnitude of the incarcerated biacetyl ↔ neat triplet acceptor (cycloheptatriene) electronic coupling and the red-shift of the phosphorescence origin for molecular cages **1**−**3**. The line is drawn only as a guide.

Conclusions

The presented work gives the first quantitative comparison of the magnitude of electronic coupling mediated by molecular cages of different size. We have found that the magnitude of coupling increases with the diminishing size of the cage, indicating that the interaction between the guest and the walls of the hemicarcerand becomes stronger (it is reasonable to assume that the interaction between the outside surface of the cage and an individual external acceptor molecule is, in principle, independent of the size of the cage). The triplet energy transfer accelerates by more that a factor of 10 upon transition from the largest to the smallest cage. The corresponding ~3.5-fold increase of the donor−acceptor electronic coupling is similar to that reported for covalently bound systems when the donor−acceptor separation is reduced by one carbon−carbon σ-bond.[17] The increased guest ↔ cage interaction is reflected not only in faster triplet energy transfer rates but also in pronounced shifts of the emission spectra, the magnitude of which approximately parallels the magnitude of the donor−acceptor coupling. The interesting question whether the guest within the hemicarcerand cavity experiences an increased but for the most part homogeneous "local pressure" rather than a more specific geometrical distortion will be further investigated.

It appears that, at least in this short series of hemicarceplexes, the details of the electronic structure of the exterior of the molecular cage, e.g., the presence or absence of the *o*-xylyl groups in the walls of the hemicarcerand, are less important than its size. The excitation transfer rates measured in neat olefinic triplet energy acceptors scale very well with the results obtained in solution, thus indicating that there is no significant aggregation of the acceptors on the walls of the cages. A more detailed study on the influence of the electronic structure of

(20) For example, see: Atkins, P. W.; Friedman, R. S. *Molecular Quantum Mechanics*; Oxford University Press: Oxford, 1997; Chapter 6, p 164.

Table 5. Correlation between the Rates of Triplet Transfer from **2**·Biacetyl to Neat Acceptors, k^{neat}, and the Pseudo-Unimolecular Rate Constants for Triplet Transfer to the Same Acceptors in Solution, k^{sol}

acceptor	k^{neat}, s^{-1}	k^{sol}, s^{-1}	k^{neat}/k^{sol}	molarity, mol/L	(k^{neat}/k^{sol})/molarity
cycloheptatriene[a]	3.3×10^5	3.4×10^4	9.7	9.6	1.01
1,3-cyclohexadiene[a]	7.4×10^5	6.7×10^4	11.0	10.5	1.05
naphthalene[b]	*$>1.2 \times 10^3$*	*3.3×10^2*	*>3.6*	*6.8*	*>0.53*

[a] Comparison between the uncorrected rates from Table 3 and pseudo-unimolecular rates from ref 3. [b] Comparison between the lower limit obtained for **2**·biacetyl in neat 1-methylnaphthalene and the pseudo-unimolecular rate in benzene solutions of **2**·biacetyl and naphthalene.

the hemicarcerand on the rate of excitation transfer will be reported shortly.

Since the molecular cage is not chemically bound either to the donor, or to the acceptor, there is a great similarity between electronic coupling mediated by the walls of a hemicarcerand with the coupling mediated by a solvent molecule separating the donor and the acceptor. In recent years, solvent-mediated electron transfer has been receiving increasing attention among experimentalists[21] and theoreticians alike,[22] with perhaps the most interesting insights provided by the "C-clamp" model systems which can accommodate a single reorienting solvent molecule between the donor and acceptor moieties.[23] The "C-clamp" enforces the donor−acceptor separation, while the solvent molecule provides the pathway for coupling. In our systems the hemicarcerand cage fulfills both roles simultaneously. Since the average thickness of the hemicarcerand wall is comparable with the diameters of typical organic solvent molecules, one can conclude on the basis of the presented results that even under the most favorable circumstances the solvent-mediated contribution to electronic coupling in triplet excitation transfer is unlikely to exceed 1 cm^{-1}.

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Supporting Information Available: Experimental details and characterization data (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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