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Supramolecular Photochemistry and Photophysics. Biacetyl Imprisoned in a Hemicarcerand

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When biacetyl is imprisoned into Cram's hemicarcerand **1**, its absorption, fluorescence, and phosphorescence maxima are red shifted compared to the values obtained for solutions of free biacetyl in any solvent. Furthermore, the lifetime of the T_1 excited state of imprisoned biacetyl is unaffected by solvent nature and presence of dioxygen. These results show that inclusion into the hemicarcerand (i) shields biacetyl from interaction with the solvent molecules and (ii) prevents deactivation of its long-lived T_1 excited state by energy transfer to dioxygen. The perturbation provided by the cavity on the spectroscopic properties of biacetyl is much smaller than that provided by even the most "innocent" solvent. The consequent picture is that of a biacetyl molecule which is contained in a not-too-tight cavity where no specific host−guest interaction takes place. The peculiar spectroscopic and excited-state behavior of biacetyl imprisoned in hemicarcerand **1** supports Cram's view that the inner phase of carcerands and hemicarcerands is to be considered as a new phase of matter.

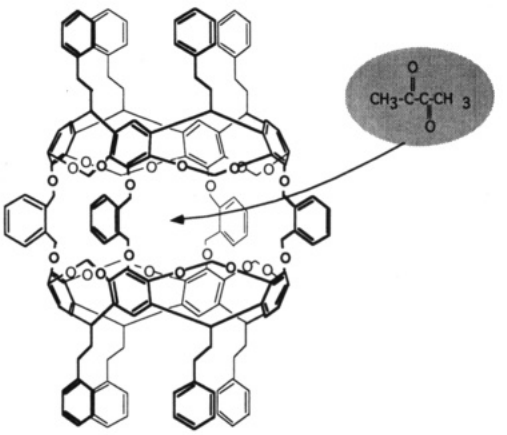
Carcerands and hemicarcerands are rigidly hollow hosts synthesized by Cram and co-workers.[2,3] Carcerands are spherical-type molecular cavities where small molecules (particularly, solvent molecules) can be irreversibly imprisoned when the two halves of the structure are covalently linked by proper bridges in the last step of the synthesis. Hemicarcerands are cage-type molecules with larger voids and with "portals" through which a variety of molecules can enter at high temperatures and then remain imprisoned at room temperature for a more-or-less long period of time ("constrictive" binding).[4] Carcerands and hemicarcerands play an important role in the development of supramolecular chemistry[5] since they offer the opportunity to study the excited-state behavior of guest molecules isolated in an environment constituted of a specific, discrete molecular inner phase.[6,7] Starting from the pioneering work of Turro and Cline Love,[8] several studies on the photochemical and photophysical properties of molecules enclosed in constrained media,[9,10] particularly in cyclodextrins,[11] and zeolites[12] have already been reported.

Continuing our investigations in this field,[7] we have studied the changes taking place in the absorption, fluorescence, and phosphorescence spectra, and the lifetime and reactivity toward dioxygen of the lowest excited state of biacetyl (2,3-butanedione) when this molecule is imprisoned into the hemicarcerand **1** (Scheme 1). In comparison with the hemicarcerand previously used to imprison 9-cyanoanthracene,[7] **1** is characterized by smaller portals and interior cavity.[13] This makes it suitable for encapsulation of relatively small molecules.

Biacetyl was chosen as a guest of hemicarcerand **1** because of its size, which was expected to fit well the cavity of **1**, and its well-known spectroscopic properties.[14] Furthermore, biacetyl absorbs and emits in the visible spectral region, with no interference with absorption and emission by the host.

The most important feature in the absorption spectrum of biacetyl is a weak band (λ_{max} = 420 nm, ϵ_{max} = 22 M^{-1} cm^{-1} in CH_2Cl_2) assigned to a spin-allowed n−π^* transition. The maximum of this band is slightly solvent dependent (λ_{max} = 422 nm in benzene and 405 nm in water). Biacetyl exhibits a weak and broad fluorescence band (λ_{max} = 463 nm in CH_2Cl_2) and a much stronger and structured phosphorescence band (λ_{max} = 518 nm in CH_2Cl_2), both of n−π^* origin. In the following we will mostly concentrate our attention on the strong phosphorescence emission which originates from the lowest triplet excited state T_1. Its energy position is solvent dependent (Figure 1), and its lifetime (which is intrinsically very long, millisecond time scale) is strongly affected by the presence of dioxygen (the bimolecular quenching constant, k_q, is 8 × 10^9 M^{-1} s^{-1} in benzene).[15] Actually, the phosphorescence band cannot be observed in air-equilibrated solutions. In carefully deaerated solutions the lifetime of the T_1 excited state is 0.43 ms in CH_2Cl_2 and 0.50 ms[16] in benzene.

SCHEME 1



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When biacetyl is imprisoned into hemicarcerand **1**,[17] its spectroscopic and excited-state properties do not depend on the

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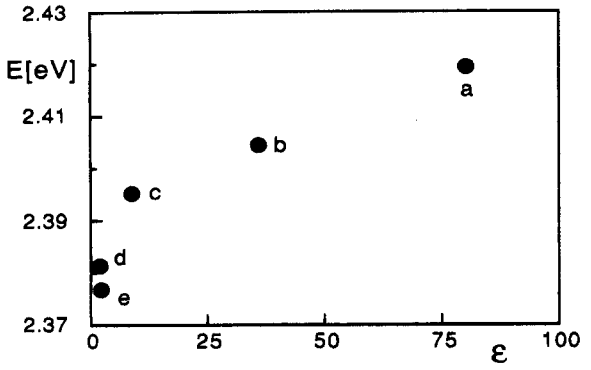

Figure 1. Energy of the maximum of the biacetyl phosphorescence band vs the dielectric constant (ϵ) of the solvents used: (a) water; (b) acetonitrile; (c) dichloromethane; (d) benzene; (e) cyclohexane.

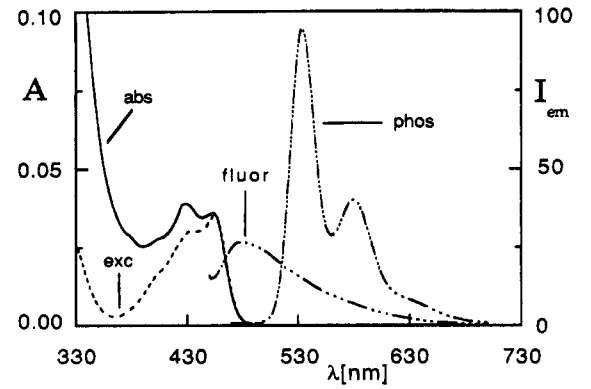

Figure 2. Absorption (abs), fluorescence (fluor), phosphorescence (phos), and excitation (exc) spectra of the hemicarceplex made of **1** and biacetyl in CH_2Cl_2 at room temperature.

solvent nature. Figure 2 shows the absorption, emission, and excitation spectra of the hemicarceplex in CH_2Cl_2. The absorption, fluorescence, and phosphorescence maxima lie at 429, 480, and 533 nm, respectively, i.e., they are red shifted compared to the values obtained for solutions of free biacetyl in any solvent. Furthermore, the lifetime of the T_1 excited state of biacetyl in the hemicarceplex (0.84 ms) is unaffected by solvent nature and presence of dioxygen. Taking into consideration the uncertainty caused by experimental errors, an upper limit of 10^4 M^{-1} s^{-1} can be established for the quenching constant of dioxygen on the phosphorescent excited state of the imprisoned biacetyl molecules, a value about 10^6 times smaller than that obtained for free biacetyl in the same solvent. The excitation spectrum of the hemicarceplex is similar to that of biacetyl, indicating that excitation of the host is not followed by energy transfer to the guest. Lack of energy transfer from an aromatic moiety to a 1,2-diketone was also observed for benzenecycloalkanediones.[19]

The results obtained show that inclusion into hemicarcerand **1** (i) shields biacetyl from interaction with the solvent molecules and (ii) prevents deactivation of its long-lived T_1 excited state by energy transfer to dioxygen. The former result is not surprising since CPK molecular models show that neither CH_2Cl_2 nor benzene solvent molecules can penetrate into the cavity when it is occupied by biacetyl. The smaller size of dioxygen, however, should at least allow the O_2 molecules to contact biacetyl through the portals. The lack of quenching, in fact, shows that the formation of an encounter complex of suitable distance/geometry to allow efficient energy transfer is prevented.

Since imprisoned biacetyl molecules are shielded from interaction with the solvent, their spectroscopic and excited state properties must reflect the environment constituted by the internal cavity of the hemicarceplex. Comparison of the position of the phosphorescence maximum for the imprisoned molecules (533 nm, 2.33 eV) with the values obtained in a variety of solvents (Figure 1) suggests that the perturbation provided by the cavity is much smaller than that provided by even the most "innocent" solvent. This is confirmed by the lifetime of the T_1 excited state, which for the imprisoned molecules is longer than that found in any solvent. The consequent picture is that of a biacetyl molecule which is contained in a not-too-tight cavity where no specific host–guest interaction takes place. This picture is fully consistent with NMR results which indicate that biacetyl is free to rotate inside the cavity of **1**,[20] as well as with the lack of sensitization of biacetyl phosphorescence upon excitation of the hemicarcerand (Figure 2). Interestingly, however, the lifetime of the T_1 excited state imprisoned in the hemicarcerand is much shorter than the reported lifetime in the gas phase at room temperature (1.8 ms).[21] A reason for this behavior has likely to be found in the great number of collisions experienced by the T_1 excited state with the walls of the hemicarcerand cage. In the gas-phase experiments it has indeed been observed that the lifetime of the T_1 excited state of biacetyl *decreases* with decreasing diameter of the cell. Surprisingly, however, in the gas phase the phosphorescence band shows its maximum at about 510 nm, i.e., blue shifted compared to the maximum of the hemicarceplex and close to that found in CH_3CN and CH_2Cl_2.

In conclusion, the peculiar spectroscopic and excited-state behavior of biacetyl imprisoned in hemicarcerand **1** supports Cram's view that the inner phase of carcerands and hemicarcerands is to be considered as a new phase of matter. From the applicative viewpoint, the lack of oxygen quenching on the strong and long-lived phosphorescence of incarcerated biacetyl could open the way to a new family of luminescent labels, particularly for immunoassay.[22]

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References and Notes

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(17) Hemicarcerand **1** was obtained by the method described by Cram and co-workers.[4] Under such conditions, one molecule of the solvent (namely, *N,N*-dimethylacetamide) remains encapsulated in the interior of the cage at room temperature. The species so obtained was characterized by ^{1}H NMR and elemental analysis. Inclusion of biacetyl in **1** was obtained following the procedure given by Cram and co-workers[4] to prepare hemicarceplexes of guests of similar size (e.g., 2-butanone). The isolated compound was purified by silica gel chromatography and characterized by ^{1}H NMR ($CDCl_3$) on a Bruker ARX 400 spectrometer. The hemicarceplex of biacetyl is soluble in CH_2Cl_2 and benzene at room temperature, and under such conditions it is stable for months. Absorption spectra, luminescence (emission and excitation) spectra, and excited-state lifetimes were obtained by using equipment and procedures previously described.[18]

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