stepped out to +2.0 V vs. SCE and held for a period of 45–60 min. Solutions were analyzed by GLC vs. internal standard. Conversions of 30–40% to the cage isomer **4** were observed.

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**Registry No. 3**, 1076-13-7; **4**, 704-02-9; **3·5** (R = H), 84415-05-4; **3·5** (R = $CO_2Et$), 84415-06-5; **3·5** (R = $CF_3$), 84415-07-6; **3·6**, 84415-08-7; **3·5** (R = CN), 84471-47-6.

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# Photoisomerization of Charge-Transfer Complexes of Hexamethyl(Dewar benzene). Contrasting Paths for Rearrangement Involving Adiabatic Reaction and Ionic Photodissociation

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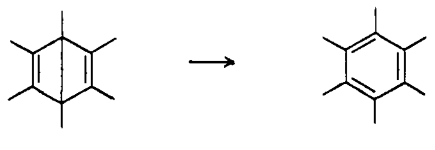
**Abstract:** The charge-transfer (CT) complexes of hexamethyl(Dewar benzene) (HMDB) with electron acceptors, fumaronitrile, diethyl 1,2-dicyanofumarate, and 1,2,4,5-tetracyanobenzene, have been characterized and compared to similar complexes of hexamethylbenzene (HMB). Irradiation of HMDB CT bands in the 313–435-nm region under a variety of conditions leads to HMDB → HMB isomerization. The quantum yield of rearrangement in a nonpolar solvent is low (e.g., 0.06), although the relative yield of adiabatic isomerization, monitored by emission from excited complexes of HMB, is high (0.72). Quantum efficiencies for isomerization of complexes in polar media generally exceed unity, consistent with a radical-ion chain mechanism for ring opening. The quantum chain reaction depends on the polarity of the solvent, the reduction potential of the acceptor, the extent of conversion, and the wavelength of irradiation. The wavelength effect is associated with excitation to upper vibrational levels of a CT band with enhancement of ionic photodissociation. Comparison of the quantum yield results for excited CT complexes with the findings for rearrangement of HMDB via exciplexes reveals generally different patterns of reactivity.

Dewar benzene and its derivatives have been the focus of extensive investigation since the first synthesis of the parent compound by van Tamelen and Pappas in 1963.[1] The kinetics,[2] thermochemistry,[3] and mechanistic detail[4] for the highly exothermic ring opening to benzene valence isomers have been studied. The reactivity of Dewar benzenes with electrophilic agents has been investigated,[5] with particular attention to hexamethyl(Dewar benzene) (HMDB), the most readily accessible of the simple derivatives.[6] This structure claims the longest known C–C bond ($C_1$–$C_4$) (1.63 Å),[7] and it liberates 60 kcal/mol on isomerization to its valence isomer **2**.[2a,3c] Reaction of HMDB with acids,[8] cycloaddition reagents,[9] other conventional electrophiles,[10] and metals[11] has been widely studied. A number of theoretical investigations of Dewar benzenes have been carried out,[12] including the mapping of the potential surfaces for ring opening to the aromatic isomer.[13] Photoelectron spectra have been employed in the assignment of molecular orbital energy levels for several Dewar benzene derivatives; the data predict a relatively high reactivity for HMDB as an electron donor (vertical ionization potential = 7.8 eV).[14]



HMDB HMB

Dewar benzenes were initially of photochemical interest as precursors to prismanes.[15] More recently, attention has turned to the large exothermicity of ring opening and its consequences in terms of thermal generation of electronically excited molecules.

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Table I. Absorption Properties and Physical Constants for Charge-Transfer (CT) Complexes of Hexamethyl(Dewar benzene) (HMDB) and Hexamethylbenzene (HMB)

| | donor | solvent | CT absorption maximum, nm | wavelength observed,[a] nm | $K_{CT}$, M$^{-1}$ | $\epsilon$, M$^{-1}$ cm$^{-1}$ |
|---|---|---|---|---|---|---|
| fumaronitrile, *t*-CNCCH=CHCN (FUM) | HMDB | $C_3H_7OC_3H_7$ | ~300 | 334 | <0.01 | |
| | HMB | $C_3H_7OC_3H_7$ | 308 | 334 | 0.33 | 142 000 |
| diethyl 1,2-dicyanofumarate, *t*-$EtO_2C(CN)C{=}C(CN)CO_2Et$ (DDF) | HMDB | $CH_2Cl_2$ | ~380 | 390 | <0.01 | |
| | HMB | $CH_2Cl_2$ | 450 | 450 | 0.47 | 2 700 |
| 1,2,4,5-tetracyanobenzene, (TCNB) | HMDB | $CH_2Cl_2$ | *b* | 340 | <0.01 | |
| | HMB[c] | $CH_2Cl_2$ | 340 | 340 | 0.079 | 17 400 |
| | | | 425 | 425 | | |

[a] Wavelength at which absorbances were obtained for calculation of $K_{CT}$ and $\epsilon$. [b] Tail to 460 nm. [c] Dual complexes observed (see ref 52).

Indeed, ring opening of the parent Dewar benzene is weakly chemiluminescent.[16] In addition, the unusually skewed potential surfaces for valence isomerization permit adiabatic photochemical ring opening (excited state → excited-state rearrangement)[17] as shown for Dewar benzene[18] and its naphthalene and anthracene analogues.[19]

The most intriguing of the photoreactions of HMDB involves isomerization to HMB, which is induced in the presence of sensitizers that are good electron acceptors. The first of several unusual features was reported by Evans and his co-workers[20] who noted an exceptionally high quantum yield (e.g., $\phi = 80$) for valence isomerization that accompanied the quenching of naphthalene fluorescence by HMDB in a polar solvent. A mechanism (vide infra) involving electron transfer and a chain reaction of HMDB radical cation was proposed.[20] Taylor[21] found a contrasting situation for fluorescence quenching by HMDB in nonpolar solvents. Emission of exciplexes of HMB was observed and assigned to an adiabatic exciplex isomerization, the only current example of an exciplex → exciplex rearrangement.

We were attracted to the HMDB → HMB isomerization as part of an investigation of photosensitization mechanisms that involve electron-donor-acceptor (EDA) interaction.[22] In earlier publications,[23] further study of the adiabatic exciplex isomerization of HMDB in a nonpolar solvent was reported. The yield of excited product on sensitization by a series of electron-acceptor aromatics was shown to be a function of the amount of excitation energy that is maintained in the HMB exciplex. The principal steps leading to "adiabatic emission" are shown in Scheme I. Sensitized ring opening proved also to be driven most efficiently by singlet sensitizers and to be sensitive to substitution of the Dewar benzene structure.[23]

**Scheme I**

$$\text{Sens}^* + \text{HMDB} \rightarrow [\text{Sens–HMDB}]^*$$

$$[\text{Sens–HMDB}]^* \rightarrow [\text{Sens–HMB}]^*$$

$$[\text{Sens–HMDB}]^* \rightarrow \text{Sens} + \text{HMB} + h\nu_f$$

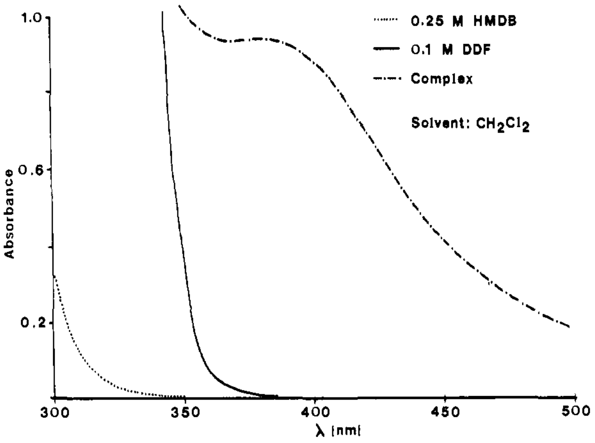

**Figure 1.** Absorption spectrum of the CT complex of HMDB and DDF and of the components alone (at the same concentration).

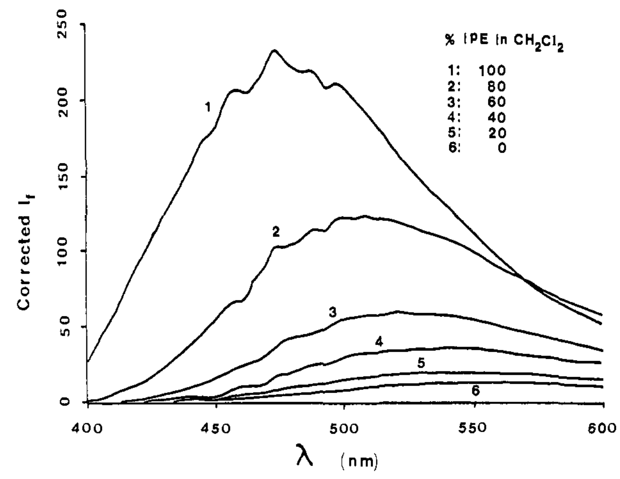

**Figure 2.** Corrected fluorescence spectra of the complex of FUM and HMB in isopropyl ether (IPE) and in mixtures with dichloromethane at room temperature (excitation 334 nm).

The sensitization of isomerization reactions on quenching excited states through EDA interaction is relatively well-known.[24] A recent modification of this form of electron-transfer sensitization[25] involves interaction of a sensitizing agent with an isomerizable substrate in the ground state, and irradiation of the resultant charge-transfer (CT) complex.[24c,26] In the present paper, we wish

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**Table II.** Quantum Efficiencies for Photoisomerization (HMDB → HMB) of CT Complexes HMDB[a]

| | | | excitation wavelength,[b] nm | | | | |
|---|---|---|---|---|---|---|---|
| acceptor | solvent | $\lambda_{max}$ (CT), nm | 436 | 405 | 366 | 334 | 313 |
| FUM | acetonitrile | 310 | | | 1.1 | 2.3 | 5.5 |
| | acetonitrile[c] | 310 | | | 0.38 | 0.72 | 2.1 |
| | dichloromethane | 300 | | | 0.22 | 0.41 | 0.87 |
| | isopropyl ether | 300 | | | 0.063 | 0.064 | 0.041 |
| DDF | acetonitrile | 380 | 0.94 | 3.2 | 17 | | |
| | dichloromethane | 380 | 0.34 | 1.2 | 11 | | |
| TCNB | dichloromethane | d, e | | | 8.5 | 15.0 | 31[f] |

[a] Nitrogen-purged samples, 0.25 M in HMDB and 0.1 M in acceptor (except where noted), 25 °C, 1.0 ± 0.5% conversion. [b] Monochromator band-pass = 9.6 nm. [c] Inverse complex [HMDB] = 0.06, [acceptor] = 0.73 M. [d] Tail beyond TCNB band to 460 nm. [e] For CT mode, [TCNB] = 0.007-0.18 M and [HMDB] = 0.5 M (334, 366 nm). [f] TCNB excitation, fluorescence quenching mode; [TCNB] = 0.008 M, [HMDB] = 0.25.

to report on the photochemistry of CT complexes of HMDB.[27] In this study we have found (for nonpolar solvent) yet another adiabatic HMDB isomerization and (for polar media) a significant wavelength effect on isomerization yield that provides an insight to the dynamics of ionic photodissociation of complexes.

## Results

**Absorption and Emission of CT Complexes.** Addition of HMDB or HMB (oxidation potentials = 1.58 and 1.62 V, respectively, vs. SCE, acetonitrile)[20] to solutions of electron acceptors, fumaronitrile (FUM), diethyl 1,2-dicyanofumarate (DDF), and 1,2,4,5-tetracyanobenzene (TCNB) (reduction potentials = −1.29,[26e] −0.32, and −0.66[28] V, respectively, vs. SCE, acetonitrile), resulted in new absorption bands as shown in Figure 1 (additional spectra, ref 27). Other absorption data for HMDB complexes are presented in Table I, along with equilibrium constants for complex formation that were calculated by using an iterative weighted curve fitting of a general concentration–absorption relationship similar to the procedure reported by Carta and his co-workers.[29,30] Calculated equilibrium constants for HMDB complex formation were invariably small (<0.1) and in the range that is subject to significant error (intercepts of $A_0/A$ vs. $1/D_0$ plots ~0),[31] so that $K$ and $\epsilon$ values could not be reliably determined.

Fluorescence emission was not observed for HMDB or HMB complexes at room temperature in polar solvents. However, solubilities of the components allowed examination of the HMB/FUM pair in isopropyl ether (IPE) ($\epsilon$ 3.9) and in solvent mixtures with $CH_2Cl_2$ ($\epsilon$ 8.9) (Figure 2). The trends of decreased emission yield and a broadening and shift of the spectrum to longer wavelengths with increased solvent polarity are similar to trends found for other CT complexes.[32] The data suggest a relative stabilization of a large dipole moment for the excited CT state[33] and an increase in rate of nonradiative decay in polar solvent[34] (vide infra). Emission from both HMB and HMDB complexes with FUM could be obtained in a nonpolar glass at 77 K (Figure 3). The slight red shift and reduced intensity in the HMDB band is similar to the trend found for the emission of cyanonaphthalene exciplexes of HMDB and HMB at low temperature noted by Taylor.[21] The observation of a discrete CT-state emission from HMDB complexes in a glass in which diffusion for donor and acceptor components is limited suggests that these weak associates are not "contact" CT species, although the small size of $K_{CT}$ (apparent from experiments at room temperature) is in the limiting range suggested for the contact type.[35]

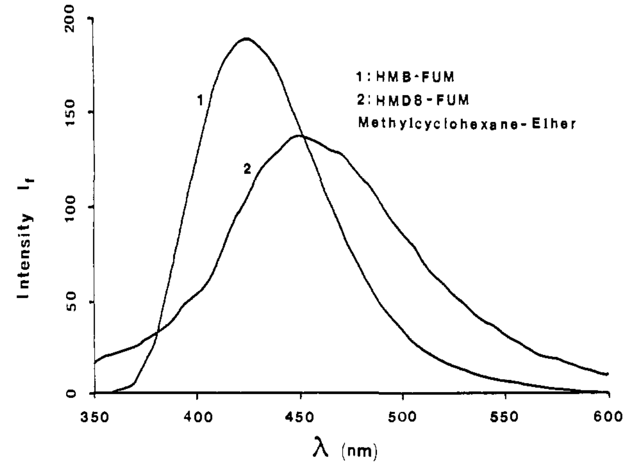

**Figure 3.** Fluorescence of CT complexes of FUM with HMB and HMDB in a glass at 77 K (excitation at 334 nm). Accurate relative yields of emission were not determined although conditions were comparable.

One further comparison was made of the emission of the HMB/FUM system under CT conditions with the spectrum obtained by quenching the fluorescence of HMB with FUM in IPE solvent. Thus, the emission of HMB centered at ~300 nm (excitation at 275 nm) was nearly completely quenched on addition of 0.01 M FUM, a concentration of acceptor that gave no evidence of absorption by the CT complex ($\lambda_{max}$ 308 nm). The emission produced on HMB fluorescence quenching was identical with the emission (Figure 2, spectrum 1, $\lambda_{max}$ ~470 nm) obtained on irradiation at 320 nm of the complex generated on combining 0.01 M HMB and 0.10 M FUM in IPE. A range of concentrations of FUM was inspected (0.01–0.10 M), all resulting in the same emission profile on appropriate irradiation at 280 or 320 nm.

**Quantum Yields of HMDB Isomerization—Nonpolar Solvent.** Irradiation of the HMDB/FUM complex in IPE resulted in clean conversion to HMB. Quantum yields for rearrangement on photolysis at several wavelengths measured on a monochromator/light pipe/quantum counter apparatus are shown in Table II. Fluorimeter excitation (λ 334 nm) of HMDB/FUM at room temperature in IPE gave rise to an emission that was virtually identical with the fluorescence observed on irradiation of the HMDB/FUM complex (Figure 4). The spectrum is assigned to HMB/FUM fluorescence, an emission that could not be accounted for by any build up of HMB during fluorimeter irradiation

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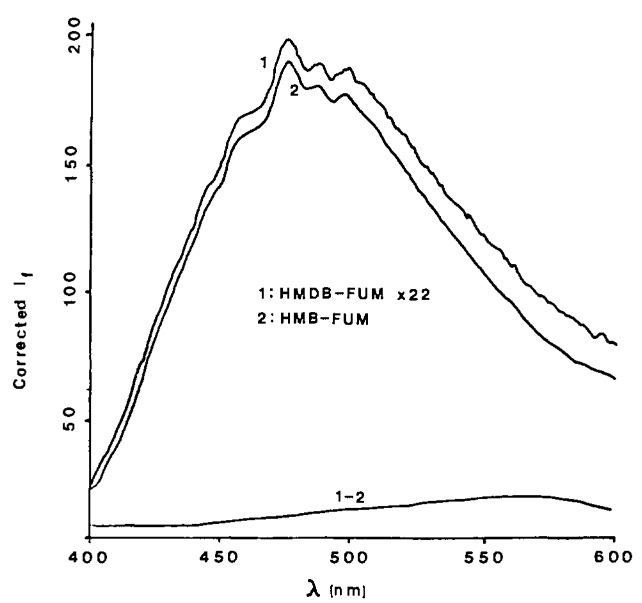

**Figure 4.** Fluorescence spectra for CT complexes of FUM with HMDB and HMB from which relative yields of emission were obtained (isopropyl ether solvent, excitation at 334 nm, room temperature).

of HMDB/FUM (the difference spectrum (Figure 4) is possibly a residual HMDB/FUM fluorescence[21]).

The identity of emission spectra from HMDB and HMB complexes is consistent with the imposition of a rearrangement that connects excited complexes of HMDB and HMB, an adiabatic isomerization analogous to the exciplex rearrangement observed previously.[21,23] A modification, suitable for the CT system, of the exciplex mechanism (Scheme I) for adiabatic and diabatic isomerization is shown in Scheme II (A = acceptor).

**Scheme II**

$\mathrm{A + HMDB \rightleftarrows A\text{-}HMDB}$ CT complex formation ($K_{CT}$)

$\mathrm{A\text{-}HMDB \xrightarrow{h\nu} {}^1[A\text{-}HMDB]}$ CT excitation

$\mathrm{{}^1[A\text{-}HMDB] \rightarrow A\text{-}HMDB}$ CT* decay ($k_1$)

$\mathrm{{}^1[A\text{-}HMDB] \rightarrow A\text{-}HMB}$ CT* isomerization ($k_2$)

$\mathrm{{}^1[A\text{-}HMDB] \rightarrow {}^1[A\text{-}HMB]}$ adiabatic isomerization ($k_3$)

$\mathrm{{}^1[A\text{-}HMB] \rightarrow A + HMB + } h\nu$ product complex emission

$\mathrm{{}^1[A\text{-}HMB] \rightarrow A + HMB}$ product complex decay

The yield of adiabatic isomerization [$P = k_3/(k_2 + k_3)$] was evaluated by comparing yields of fluorescence of A–HMDB and A–HMB complexes under conditions of equal absorbance at the exciting wavelength (334 nm). After factoring in the quantum yield of ring opening at 334 nm, the adiabatic yield was obtained from several experiments (0.1 M, FUM, 0.16 H HMDB):[36]

$$P = \frac{I_f(\mathrm{HMDB})}{0.064 I_f(\mathrm{HMB})} = 0.72 \pm 0.03$$

HMDB and HMB complexes gave rise to different emission on irradiation in a glass at 77K (vide supra, Figure 3), indicating that adiabatic ring opening is not important at low temperature.

In view of the "double isomerization" observed on irradiation of stilbene–FUM complexes,[26d] the appearance of maleonitrile (MAL) was monitored for photolysis of HMDB/FUM complexes in IPE. However, geometrical isomerization FUM ⇄ MAL did not accompany ($\phi < 0.005$) CT valence photoisomerization of HMDB under these conditions. In addition, photolysis of the complex generated on combination of HMDB and MAL ($\lambda_{max}$ 280 nm) led to valence isomerization ($\phi \sim 0.04$, IPE), but again no geometrical isomer could be detected. Overall disappearance of isomer components (GLC vs. internal standard) was examined in light of the recently reported photoaddition reactions of HMDB and triplet aldehydes.[37,38] With FUM and HMDB in IPE, disappearance other than valence isomerization was negligible ($\phi$ < 0.01).

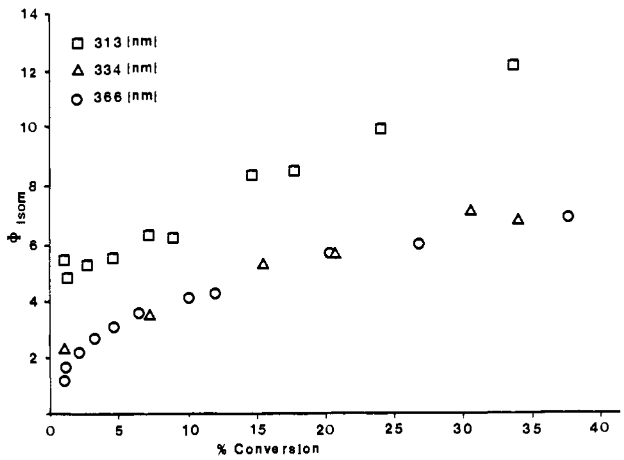

**Figure 5.** Dependence of quantum yield for valence isomerization of the CT complex of FUM and HMDB on wavelength and on the extent of conversion to HMB in acetonitrile.

**Quantum Yields of HMDB Isomerization—Polar Solvent.** Quantum efficiencies measured for rearrangement of HMDB complexes in relatively polar media are shown in Table II. For each acceptor at certain wavelengths and with a sufficiently polar solvent, quantum yields exceeded unity. The results are consistent with a mechanism involving ionic photodissociation of complexes and chain reaction (Scheme III) of radical cations as deduced by Evans[20] for isomerization via fluorescence quenching or electrochemical oxidation of HMDB.

**Scheme III**

initiation $\mathrm{A\text{-}HMDB \xrightarrow{h\nu} A^{-}\cdot + HMDB^{+}\cdot}$

propagation $\mathrm{HMDB^{+}\cdot \rightarrow HMB^{+}\cdot}$

$\mathrm{HMB^{+}\cdot + HMDB \rightarrow HMB + HMDB^{+}\cdot}$

termination

$\mathrm{A^{-}\cdot + HMB^{+}\cdot\ (HMDB^{+}\cdot) \rightarrow A + HMB\ (HMDB)}$

A dependence of apparent quantum efficiency on the extent of conversion (irradiation time) proved to be another complicating feature in quantum yield measurement. This effect results from the greater complexing ability of HMB vs. HMDB coupled with a greater tendency of HMB complexes to dissociate to chain-carrying HMB cations. For example, absorbance ratios for FUM complexes (identical concentrations of HMB and HMDB in $CH_2Cl_2$) are 6.8, 8.8, and 7.1 for 313, 334, and 366 nm. HMB complexes with TCNB are again the more potent absorbers with ratios of 20 and 19 for 334 and 366 nm. Time (conversion) dependences of quantum yields were determined for FUM and DDF complexes for photolysis of HMDB–DDF at 405 nm, efficiencies of 3.2 and 13 were measured at 1.1% and 3.1% conversion, and a value of 2.3 was obtained on extrapolation to zero time. A similar display of data is shown in Figure 5 for irradiation of HMDB–FUM in acetonitrile at three wavelengths. The data presented in Table II are quantum efficiencies measured at very

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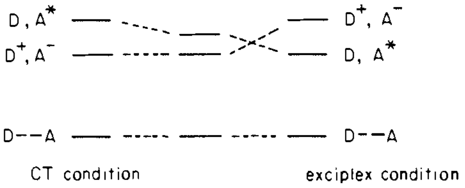
(36) A reduction in the emission yield was observed at >0.2 M HMDB similar to the exciplex quenching by excess HMDB noted previously.[21,23]

(37) Carless and Trivedi[38] noted that aromatic aldehyde and ketone sensitizers brought about HMDB → HMB isomerization along with photoaddition (no quantum efficiencies reported). In our previous study[23] using biacetyl as sensitizer, ring opening was not efficient ($\phi < 0.01$), although a reaction with sensitizer was apparent.

(38) Carless, H. A. J.; Trivedi, H. S. *J. Chem. Soc., Chem. Commun.* **1981**, 950.

Scheme IV



low conversion (~1%) of HMDB.[39]

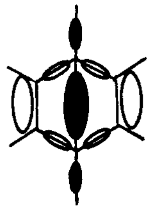
A dependence on the initial concentration of HMDB was expected on the basis of the findings of Evans[20] concerning the efficiency of the chain process in methanol. In fact, irradiation of an "inverse" complex (excess of the acceptor FUM) using minimal HMDB led to lower yields (Table II). The TCNB acceptor offered yet another comparison: isomerization via CT excitation or fluorescence quenching. The emission of TCNB at 330 nm was readily quenched at low concentrations of HMDB (Stern–Volmer constant, $k_q\tau = 77$ M$^{-1}$, $CH_2Cl_2$). With a measured lifetime of 5 ns for TCNB singlets,[40] a quenching contant $k_q = 1.5 \times 10^{10}$ M$^{-1}$ s$^{-1}$ could be calculated. At 313 nm, the absorption of TCNB was dominant (>95%), and at 0.25 M HMDB, TCNB singlet quenching was nearly complete (>95%); on the other hand, the CT complex with HMDB was preferentially excited at longer wavelengths. Thus, quantum yields under CT irradiation (344 and 366 nm) and under sensitizer fluorescence quenching (313 nm) conditions could be determined accurately with proper adjustment of concentrations. The observed enhancement of isomerization yield for the shorter CT wavelength (344 nm) parallels the findings for the other acceptors, but note that the true enhancement is probably greater since different [HMDB] were required for proper adjustment of absorbances (see Table I).

As a basis for further comparison, quantum yield experiments under fluorescence quenching conditions were conducted with a very polar solvent, similar to the experiment of Evans[20] in which rearrangement of HMDB was sensitized by naphthalene in methanol. The fluorescence of 1-cyanonaphthalene (used previously for sensitization in cyclohexane with limiting $\phi \sim 1.0$[23]) was readily quenched by HMDB in acetonitrile ($k_q\tau = 147$ M$^{-1}$). Under these conditions (0.27 M HMDB, 98% fluorescence quenching), quantum yields for isomerization were exceedingly large (as high as 220) and not very reproducible even at 1–2% conversion of HMDB, indicating that radical-ion chains can be relatively long.

## Discussion

The dependences of isomerization yield shown in Table II involving the strength of acceptor and medium polarity clearly point to a competition among (1) photoionization of complexes to radical ions capable of rearrangement via a chain mechanism, (2) a residual isomerization in nonpolar solvent, and (3) other nonradiative decay paths. The analysis is conveniently divisible in terms of the behavior in nonpolar medium, where the novel feature is the adiabatic photoreaction, and in polar solvents, for which unusual wavelength effects on isomerization yield have been observed.

The common feature for acceptor-induced modes of rearrangement is the shift of electron density from HMDB that is anticipated for bimolecular encounter in a quench complex or through CT excitation. Both interactions result in loss of electron density in the highest occupied molecular orbital for HMDB (HOMO). The assignment of HOMO to an orbital of $a_1$ symmetry displaying significant $\sigma/\pi$ mixing is consistent with semiempirical calculations and with the observed photoelectron spectrum for HMDB (broad band for first ionization at 7.8 eV).[14] According to this analysis, shift of electron density from HOMO to an acceptor orbital results in weakening of the central $C_1C_4$ bond.[41]



**Rearrangement in Nonpolar Solvent: Adiabatic Isomerization and a Comparison of Excited CT Complexes and Exciplexes.** The low yields of HMDB rearrangement in nonpolar solvent (FUM complexes in isopropyl ether) are striking when compared to the limiting quantum efficiencies ($\phi \sim 1.0$) for ring opening induced on quenching the fluorescence of a series of aromatic sensitizers, which are electron acceptors but for which ground-state absorption by complexes is absent (e.g., 1-cyanonaphthalene, 9,10-dicyanoanthracene).[21,23] Since neither FUM geometrical isomerization nor cycloaddition of FUM and HMDB appear to play a significant role, another facile mode of nonradiative decay for the CT system must be important.

In the preceding paper,[22a] a mechanism was proposed for valence isomerization that proceeds on quenching singlet sensitizers in nonpolar media. The important elements include the aforementioned donor–acceptor interaction (orbital perturbation), which results from intimate encounter of sensitizer and isomerizable substrate. This collisional interaction induces bond-order changes in substrate and allows progress along the reaction coordinate for isomerization. A critical feature for product formation involves the sharing of excitation energy by the sensitizer and substrate, which facilitates nonradiative decay at the approximate midpoint of reaction (perycylic minimum, biradicaloid geometry; Figure 4, ref 22a). The appropriate potential energy surfaces for ring opening of uncomplexed HMDB have been calculated,[13] and the options available for the partitioning of a biradicaloid species for Dewar naphthalene isomerization have been discussed.[19c]

The important distinction for fluorescence quenching vs. CT complex irradiation experiments has to do with the extent of charge resonance vs. excitation resonance for the appropriate excited complexes. The configurational composition of excited complexes derives from the theory of Mulliken[41] in which wave functions for dative and locally excited "resonance forms" are employed. For our purposes, consider combination of an electron donor D and an electron acceptor A in an excited complex (EC) as follows:

$$\psi_{EC} = c_1\psi(A^-,D^+) + c_2\psi(A^+,D^-) + c_3\psi(A,{}^*D) + c_4\psi(AD^*)$$

Beens and Weller[42] recognized at an early stage that excited complexes could exhibit a wide range of charge separation and excitation resonance. Although there have been suggestions that both exciplexes (obtained via fluorescence quenching) and excited charge-transfer complexes are essentially contact ion pairs, a growing list of experimental[43,44] and theoretical[45] findings indicates

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[39] In the quantum yield analysis, the role of a ring opening of HMDB CT complexes not involving ionization but coupled with secondary photolysis to produce a high yield of chain carrying ions cannot be completely eliminated. For example, the absorbance of solutions increased by 20% after photolysis of HMDB–TCNB to 2% conversion, signaling the onset of HMB–TCNB absorption. However, for a significant contribution at conversion levels around 1%, the nonionic ring opening would have to be very efficient (not indicated for CT photolysis in nonpolar medium) and the chain lengths originating from HMB photoionization would have to be exceptionally long (not indicated for higher conversion runs in which HMB complexes principally absorb, see Figure 5).

[40] The lifetime of TCNB (0.009 M in dichloromethane) was obtained by single photon counting. We are grateful to Professor A. M. Halpern for making this measurement.

[41] Mulliken, R. S.; Person, W. B. "Molecular Complexes"; Wiley-Interscience: New York, 1969; Chapter 2.

[42] (a) Beens, H.; Weller, A. *Acta Phys. Pol.* **1968**, *4*, 593. (b) Weller, A. In "The Exciplex"; Gordon, M., Ware, W. R., Eds.; Academic Press: New York, 1975; p 23. (c) Beens, H.; Weller, A. In "Organic Molecular Photophysics"; Foster, R., Ed.; Wiley: New York, 1975; Vol. 2.

[43] For discussions of exciplex absorption spectra, see: (a) Mataga, N.; Ottolenghi, M. In "Molecular Association"; Foster, R., Ed.; Academic Press: New York, 1979; Vol. 2. (b) Fujiwara, H.; Nakashima, N.; Mataga, N. *Chem. Phys. Lett.* **1972**, *47*, 185. (c) Orbach, N.; Ottolenghi, M. *Ibid.* **1975**, *35*, 175.

that the more general result will be that exciplex intermediates generated in a medium of low polarity show a moderate charge separation short of full electron transfer.

The array of excited species and their relative energies is shown simply in Scheme IV, in which the dominant zeroth order configurations are depicted. The ideal CT condition (Weller's type I complexation[42]) results from combination of strong donor and acceptor and the absence of low-lying local excited states. With a large weighting, $c_1$, the excited state is an ion pair.[32a] For this system the appearance of a CT band to the red of the absorption of the components will be the important spectral feature. For the exciplex condition (Weller's type II complex[42]), interaction of donor and acceptor is moderate, and the low-lying excited species is the locally excited state. At this extreme, binding in the ground state is negligible (light absorption by uncomplexed species dominates) and a bimolecular quenching step is required for excited complex formation. A less well-defined intermediate range, in which both dative and locally excited configurations are low lying, is also potentially important. In this situation absorption by CT complexes and monomeric species will not be resolved and the nature of the excited species generated on irradiation will depend in a subtle way on the concentrations of donor and acceptor components, the extinction coefficients of complexed and uncomplexed species, and the extent of configuration interaction between CT and local states for excited complexes at a particular geometry.

The photochemical consequences of configuration identity and state mixing are striking. The components of an ideal excited CT complex are strongly bound by coulombic attraction and need only transfer an electron with minimal nuclear displacement in order to return to the ground state. Flash photolysis data[45] support the notion of an especially short lifetime for excited CT states and, in fact, low quantum efficiencies for fluorescence and photochemical reaction appear to be a general result for CT systems. Our data (Table II) for irradiation of FUM–HMDB in isopropyl ether are consistent with this trend. Under fluorescence quenching conditions, the system (employing acceptors such as 1-cyanonaphthalene or 9,10-dicyanoanthracene, which are either weaker electron acceptors or which have very low-lying locally excited states) does not contend with the contact ion pair and its unproductive decay. Instead, bimolecular encounter permits a more leisurely interaction,[48] the exploration of a number of geometries for mutual polarization of donor and acceptor and, ultimately, for systems capable of isomerization, the transfer of excitation energy (to the donor) as part of a reactive radiationless decay.

An economical interpretation of our results is that the two extremes of reactivity for excited complexes (ionic CT* vs. polar but nonionic exciplex) are well represented in the quantum yield data for HMDB isomerization in nonpolar solvents and that substantial mixing of configurations for low-lying states of the respective systems is not indicated. Notably, the exciplex condition that was inspected, encompasses quenching rates which are relatively robust (rate constants for fluorescence quenching, $k_q$ = 4–13 × $10^9$ $M^{-1}$ $s^{-1}$, for the series of cyano-substituted aromatic sensitizers[23]). These data suggest that excitation resonance is an important if not dominant contributor to the stability of exciplexes in nonpolar media even where donor–acceptor interaction is appreciable. At the other extreme, the appearance of a resolved CT absorption is indicative of a low-lying ionic state that is most readily populated by excitation within the CT band. However, our emission results for HMB–FUM and other similar data[43a,44c] suggest that this ion-pair CT excited state is also sampled (is in fact not avoided) when the same donor–acceptor pair are combined in a fluorescence quenching experiment. Apparently, the clear resolution of a CT absorption band from local excitation of the components assures a state separation for which substantial configuration interaction is not required; i.e., a relatively high "purity" of the low-lying (ion-pair) state results. The valence isomer systems[22] such as HMDB–HMB provide a unique chemical probe of configurational identity for the respective excited complexes that are employed for sensitizing rearrangement. This probe results from the sensitivity of these electron donors to the type of perturbation (the presence or absence of ionic species, vide infra) as opposed to the strength of donor–acceptor interaction, which is more commonly indicated by redox potentials.

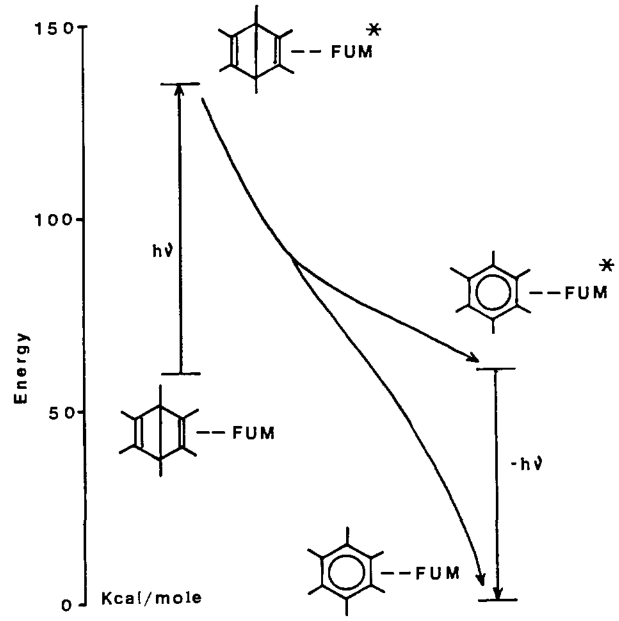

**Figure 6.** Energy diagram for the isomerization of complexes of FUM and HMDB showing both adiabatic and diabatic components (see text). The relative energies for the complexes are assumed to be approximately reflected in the energy difference for HMDB and HMB (60 kcal/mol, ref 3); excitation energies were estimated from absorption and emission data for the complexes. A pathway for diabatic rearrangement involving dissociation to the components is not included.

A second comparison for the HMDB–FUM system in IPE involves the high value for the adiabatic yield (0.72), the portion of rearrangement that occurs on an excited surface. In contrast, *P* values obtained for HMDB isomerization sensitized by cyanoaromatics ranged from 0.20 to 0.50. The highest yield (sensitizer = 9,10-dicyanoanthracene) was associated with the system having the lowest energy for the product (HMB) exciplex (57 kcal/mol)[23] (i.e., a systematic trend showing a dependence on the degree to which ground- and excited-state surfaces must be separated in the latter stages of rearrangement). Low values for the adiabatic yield were also obtained by Taylor[21] for rearrangement in the fluorescence-quenching mode. The trend in adiabatic yield is not readily extended to HMDB–FUM for which the energy of the excited product complex is ~70 kcal/mol.

A higher yield for CT* vs. exciplex systems is again consistent with the notion of fundamentally different electronic structures for the exciplex and CT* species. The competition between rearrangement pathways is shown in Scheme V and the energetics of CT ring opening induced by FUM depicted in Figure 6. Notably, the diabatic portion of exciplex isomerization is *disso-*

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(44) For discussions of the issues of exciplex polarity, configuration interaction, and multiple excited states for donor–acceptor pairs, see: (a) Sadovskii, N. A.; Babaev, S. M.; Kuzmin, M. G. *Chem. Phys. Lett.* **1981**, *80*, 427. (b) Thomas, M. M.; Krickamer, H. G. *J. Chem. Phys.* **1981**, *74*, 3198. (c) Dresner, J.; Prochorow, J. *J. Lumin.* **1981**, *24/25*, 539. (d) Itoh, M.; Furuya, S.; Okamoto, T. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 2509. (e) Lewis, F. D.; Simpson, J. T. *J. Am. Chem. Soc.* **1980**, *102*, 7593. (f) Marcondes, M. E. R.; Toscano, V. G.; Weiss, R. G. *Ibid.* **1975**, *97*, 4485. (g) Labianca, D. A.; Taylor, G. N.; Hammond, G. S. *Ibid.* **1972**, *94*, 3679.

(45) (a) Eaton, D. F.; Pensak, D. A. *J. Phys. Chem.* **1981**, *85*, 2760. (b) Tavares, M. A. F. *J. Chem. Phys.* **1980**, *72*, 44.

(46) For review of the photochemistry of CT complexes, see ref 43a and: (a) Masuhara, N.; Mataga, N. *Acc. Chem. Res.* **1981**, *14*, 312. (b) Ottolenghi, M. *Ibid.*, **1973**, *6*, 153. (c) Davidson, R. S., in ref 32a. (d) Kimura, K. *Rev. Chem. Intermed.* **1979**, *2*, 321.

(47) The reduction in quantum yield for HMDB–FUM in IPE at 313 nm may be due to enhanced decay from an upper vibrational level within the CT band.[46b]

(48) From an experiment in which exciplex isomerization was quenched by a secondary donor, the lifetime of the 1-cyanonaphthalene—HMDB exciplex was estimated at ~1 ns (25 °C, cyclohexane).[23]

*ciative*, whereas complexation may be sustained for rearrangement via the CT state. Furthermore, the force that binds donor and acceptor is enhanced for CT* (electrostatic attraction, the enthalpy of an ionic bond) so that partnership of donor–acceptor pairs is more likely to be maintained on the excited surface. The difference thus involves an entropy-controlled partitioning that favors the diabatic path for exciplex isomerization vs. an enthalpy-controlled adiabatic rearrangement for the excited CT system. To the extent that, for the CT system, electron transfer is complete and remains so along the adiabatic path, the pericyclic process involves the interconversion of two doublet radical cations.[49]

**Scheme V**

exciplex isomerization

$$\begin{aligned}[\text{A–HMDB}]^* &\rightarrow [\text{A–HMB}]^* \\ &\rightarrow \text{A} + \text{HMB}\end{aligned}$$

CT* isomerization

$$\begin{aligned}[\text{A}^-\text{–HMDB}^+]^* &\rightarrow [\text{A}^-\text{–HMB}^+]^* \\ &\rightarrow [\text{A–HMB}] \\ &\rightarrow \text{A} + \text{HMB}\end{aligned}$$

**Rearrangement in Polar Solvent: Wavelength Effects on Ionic Photodissociation.** The principal trends in isomerization efficiency (Table II) involve regular increases in quantum yield with increases in acceptor strength, solvent polarity, and excitation frequency. This profile is most readily understood in terms of variation in the yield of radical cations, which is "amplified" through an electron-transfer relay mechanism (Scheme III). The dependence on excitation wavelength is a most compelling result, since bona fide wavelength effects involving the selective photochemistry of different vibronic levels remain relatively rare.[51] The trends for HMDB complexes cannot be ascribed to (1) differences in light intensity (see Experimental Section), (2) the concentration of complex components (particularly HMDB), (3) differential absorbance of complexes at the exciting wavelengths, or (4) extent of conversion (vide supra). Also, no evidence was obtained from the spectral data for the existence of different types of HMDB complexes that could adsorb at different wavelengths or for more than one transition for a given complex.[52] It would be most unlikely that these artifacts could be repeated for complexes involving three acceptors absorbing in different regions. In addition, the enhancement of yield at shorter wavelengths is absent for isomerization in nonpolar solvent (HMDB–FUM in IPE), suggesting that the principal influence is not a general mechanism of vibrational excitation of the Dewar benzene molecule itself, an important effect for ring opening of Dewar naphthalene.[19a,c]

Ionic dissociation of a Franck–Condon state of the CT complex (for which there is some precedent[34,46a,55]) must compete at least modestly with usually fast vibrational relaxation (and possibly intersystem crossing,[46b] vide infra). The primary ion yield for photolysis of HMDB complexes in polar solvent is not yet known, since chain lengths for radical-cation propagation have not been determined. However, other results[34,55] concerning ionic photodissociation of CT complexes suggest that ion yields are quite low (<5%). The much higher HMDB isomerization yields obtained under fluorescence-quenching conditions (naphthalene[20] and 1-cyanonaphthalene sensitizers) tend to confirm this result for the present system. For our CT examples, the production of ions in bulk solution appears to range over a factor of about 20, depending on the acceptor and excitation wavelength (FUM, 366 nm vs. DDF, 366 nm), if it is assumed that chain lengths are independent of acceptor.

With TCNB as sensitizer, solvent of moderate polarity ($CH_2Cl_2$) is suitable for ionic photodissociation and chain reaction. For this system a comparison can be made between irradiation of a CT complex and fluorescence quenching involving the same electron acceptor (TCNB). We note that the efficiency of rearrangement (i.e., the yield of ionic photodissociation) for irradiation at shorter wavelengths (CT excitation) approaches, but does not surpass, the yield found for irradiation of uncomplexed TCNB.

For this behavior we adopt the model that the quenching of TCNB fluorescence in a relatively polar solvent results in formation of solvent separated ion pairs due to "long-range" electron transfer,[57] in lieu of the collisional mechanism (vide supra) that drives the reaction with high efficiency in a nonpolar solvent (e.g., cyclohexane).[23] Dissociation of the solvent-separated species into free ions competes with rapid singlet recombination. The solvent separated intermediate may in turn be generated indirectly by evolution by contact ion pairs produced on irradiation of the corresponding ground-state CT complex. Irradiation of CT complexes at shorter wavelengths populates a series of vibronic levels, some of which are dissociative with respect to ion separation and an accompanying dielectric relaxation.[27,57]

Notably, the discovery of wavelength effects for isomerization driven by CT excitation has not been restricted to the HMDB example and is, therefore, not readily reconciled in terms of the hyperactivity of a particular isomerization substrate. The additional cases include CT-induced isomerization of quadricyclene to norbornadiene[26a] and rearrangement of 1,4,4a,5,8,8a-hexahydro-1,4,5,8-*endo*,*endo*-dimethanonaphthalene[58] (note accompanying paper[22a]). A wavelength dependence that persists for the present system at higher conversion of HMDB (Figure 5) (where HMB complexes are the principal absorbing species) must also be included in the pattern of photoionization reactivity. In the accompanying paper,[22a] we describe the other isomerization systems that have been examined.

The absence of rearrangement of FUM to its geometrical isomer in the face of some precedent for "double isomerization" (the stilbene–FUM CT system)[26c] deserves some final comment. For nonpolar medium, a mechanism of intersystem crossing of complexes followed by the decay of triplet complexes to triplet fumaronitrile is feasible.[26b,g,59] On the other hand, internal conversion of CT* may be prohibitively fast for intersystem crossing to compete (the facile HMDB rearrangement is barely competitive, vide supra). For a polar medium, "triplet recombination" of radical

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(49) The electrochemical[20] and photochemical results for HMDB are consistent with a much reduced barrier for ring opening of the radical cation vs. the neutral parent molecule (slow at 105 °C, $E_a = 37$ kcal/mol[2a]), consistent with reduced orbital symmetry requirements for pericyclic reactions of open-shell systems.[50] For the reaction induced on fluorescence quenching, by way of the excitation transfer mechanism, a barrier exists between the biradicaloid minimum and the excited state of product (the adiabatic path) (see Figure 4, ref 22a), a barrier that may be substantially reduced for the CT* (ion-pair) rearrangement.

(50) (a) Haselbach, E.; Bally, T.; Lanyiova, Z. *Helv. Chim. Acta* **1979**, *62*, 577. (b) Haselbach, E.; Bally, T.; Lanyiova, Z.; Baertschi, P. *Ibid.* **1979**, *62*, 583. (c) Bauld, N. L.; Cessac, J. *J. Am. Chem. Soc.* **1977**, *99*, 23.

(51) (a) Turro, N. J.; Ramamurthy, V.; Cherry, W.; Farneth, W. *Chem. Rev.* **1978**, *78*, 125. (b) Schuster, D. A.; Eriksen, J. *J. Org. Chem.* **1979**, *44*, 4254.

(52) Multiple absorption bands have in fact been reported for HMB–TCNB (our data, Table I) and ascribed to different unoccupied acceptor orbitals.[53] One could imagine similar dual transitions for HMDB complexes involving excitation of electrons in $a_1$ (HOMO) and $b_2$ orbitals of HMDB (0.5-eV separation). However, oscillator strengths for transition involving originating orbitals of different symmetry would not necessarily be similar.

(53) Iwata, S.; Tanaka, J.; Nagakura, S. *J. Am. Chem. Soc.* **1966**, *88*, 894.

(54) (a) Egawa, K.; Nakashima, N.; Mataga, N.; Yamanaka, C. *Chem. Phys. Lett.* **1971**, *8*, 108; (b) *Bull. Chem. Soc. Jpn.* **1971**, *44*, 3287.

(55) (a) Masuhara, H.; Saito, T.; Maeda, V.; Nataga, J. *Mol. Struct.* **1978**, *47*, 243. (b) Hinatu, J.; Yoshoda, F.; Masuhara, H.; Mataga, N. *Chem. Phys. Lett.* **1978**, *59*, 80.

(56) Laser flash photolysis experiments were carried out in an effort to directly observe the formation of radical ions from CT complexes. The apparatus provided by Professor G. B. Schuster consisted of a nitrogen laser that emits at 337 nm with a pulse duration of ~10 ns. For the systems HMDB–FUM, HMB–FUM, and HMB–TCNB in acetonitrile, transient absorption was not observed in the 350–500-nm range and within the 0.1–1.0-μs time regime ($TCNB^-$ absorbs at 462 nm[55a]). For a related fluorescence quenching experiment involving 1,4-dicyanonaphthalene, transient absorption at 500 nm was readily observed (G. B. Schuster and N. Peacock, unpublished results).

(57) Jones, G., II; Chiang, S.-H.; Becker, W. G.; Welch, J. A. *J. Phys. Chem.* **1982**, *86*, 2805.

(58) Jones, G.; II; Becker, W. G.; Chiang, S.-H. *J. Photochem.* **1982**, *19*, 245.

(59) Lim, B. T.; Okajima, S.; Chandra, A. K.; Lim, E. C. *Chem. Phys. Lett.* **1981**, *79*, 22.

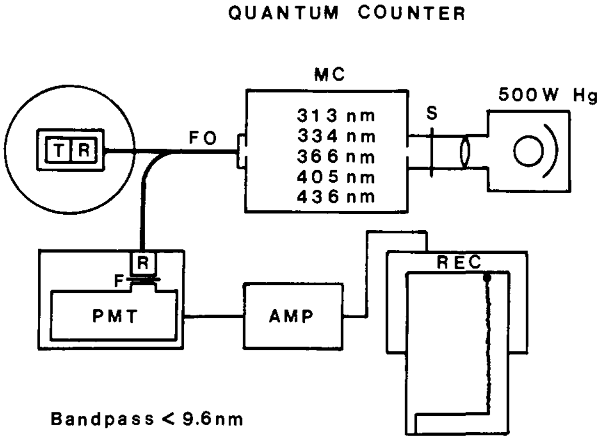

**Figure 7.** Photolysis apparatus for the determination of quantum yields, including lamp, monochromator (calibrated wavelengths indicated), photomultiplier, amplifier, and recorder (FO = fiber optic light pipes, R and T = front and back irradiation cells, R′ = rhodamine dye fluorescence cell).

ions[24d,e,60] could result in formation of FUM triplets. The energies of either HMDB–FUM or HMB–FUM ion pairs (~65 kcal/mol, from the CT absorption data) are in fact placed above the energy level for FUM triplets (59 ± 2 kcal/mol).[61] However, a low yield of ions coupled with a modest yield of triplet recombination would go undetected. The quantum efficiency for FUM geometrical isomerization from stilbene complexes in benzene is indeed quite low,[26b,g] and CIDNP results are not consistent with a significant yield of FUM triplets for photolysis of the same system in a polar solvent.[24e]

## Experimental Section

HMDB (Aldrich) was purified by preparative GLC (>99% purity achieved) on column A (column temperature 90 °C). HMB (Aldrich) was recrystallized three times from ethanol (mp 165 °C). Fumaronitrile (FUM) (Aldrich) was recrystallized three times from hexane/chloroform and obtained free of its geometrical isomer (>99%, GLC). Maleonitrile (MAL)[62] was prepared by irradiation of a 0.15 M acetonitrile solution of FUM for 15 h, employing a standard Hanovia immersion apparatus and a Vycor filter. A photostationary mixture of the two isomers was reached (~40% MAL); solvent removal in vacuo and preparative GLC on column A (150 °C) provided MAL that was nearly free of FUM (98%).

Diethyl dicyanofumarate (DDF) (Fluka) was recrystallized three times from ethanol (samples were also purified by vacuum sublimation). 1,2,4,5-tetracyanobenzene (Pfaltz and Bauer) was first passed through a column of Florisil (60/100 mesh) (elution with acetone) to remove colored impurities. The white solid obtained was twice recrystallized from ethanol. The resulting sample in $CH_2Cl_2$ was transparent to wavelengths >330 nm.

Reagent-grade isopropyl ether was treated for peroxides by partitioning with an aqueous ferrous salt solution, dried over $MgSO_4$, and twice distilled from sodium under nitrogen (middle cut). MCB Omnisolv (distilled in glass) acetonitrile was shaken with $CaH_2$ until there was no further liberation of hydrogen. The liquid was decanted and distilled, first from fresh calcium hydride $CaH_2$ (middle cut) and then from $P_2O_5$ under a positive nitrogen pressure. Spectrophotometric-grade dichloromethane (Aldrich) was used without further purification.

Preparative GLC was carried out on a Varian A-90-P3 instrument equipped with column A: 1 m × $^3/_8$ in. 15% OV-225 on Anakrom 70/80. Analytical GLC was performed on a Varian 3700 instrument (FID) equipped with the following columns (helium carrier gas). Column B: 50 m × 0.5 mm SP2100 glass capillary (support-coated open tubular column); retention time, HMDB and HMB, 5.1 and 14.7 min (T program, 70–160 °C). Column C: 50 mm × 0.25 mm OV-17 stainless steel (wall-coated open tubular column) (Universal Scientific); ret time, FUM and MAL, 5.8 and 7.7 min, 140 °C). GLC peak areas were determined by digital integration on a Hewlett Packard 3380A electronic integrator. Cyclic voltammetry (Bioanalytical Systems instrument) was utilized to obtain the reduction potential for DDF in dry acetonitrile (0.1 M tetraethylammonium perchlorate supporting electrolyte; Pt auxiliary electrode; saturated calomel reference electrode). The reduction potential $E_{red}$ = −0.28 V vs. SCE was obtained as $[E_p(ox) + E_p(red)]/2$.

Emission spectra were recorded on a Perkin-Elmer MPF-44A fluorescence spectrophotometer equpped with a differential-corrected spectra unit and a cryostat assembly for low-temperature measurement. Samples were undegassed and recorded at room temperature or at 77K (liquid nitrogen); reagent-grade methylcyclohexane was the glass-forming solvent.

**Photolysis Apparatus.** The light source was either a Bausch and Lomb SP200 (Osram HB0200 W lamp) or an Oriel Model 6183 (Oriel 500 W lamp) superpressure mercury lamp housing. The monochromator was a Bausch and Lomb high-intensity model (1350 grooves/mm); entrance slit = 2.68 mm, exit slit = 1.50 mm, maximum spectral band-pass = 9.6 nm. Two optical-fiber light pipes (Schott Optical Glass, Inc.) were positioned with a stainless steel fitting to the monocromator exit slit and focused either on a quantum counter (2 × 250 mm light pipe) or on a brass sample holder (4 × 250 mm light pipe) constructed for two cuvettes (photolysis sample and a back cell for measurement of transmitted light) (Figure 7). The quantum counter[63] consisted of a cell for a fluorescent dye (rhodamine B in 5% ethylene glycol), a RCA IP 28 PMT, a high-impedance operational amplifier, and recorder. The apparatus was calibrated with the ferrioxalate actinometer, noting recent recommendations[64] and utilizing four samples, each with different photolysis duration. The relative intensities were 0.42 (313 nm), 0.25 (334 nm), 1.0 (366 nm), 0.68 (405 nm), and 1.02 (436 nm). Standard deviation of the calibration constants was ≤1.8%. Intensities were sensitive to factors such as lamp alignment and focus so that recalibration was required on lamp replacement; intensities were also checked periodically. A typical value for intensity at 366 nm was $1.8 \times 10^{18}$ photons $min^{-1}$. The absorbance of photolysis samples was normally >2; with samples of lower optical density, transmitted light was measured with ferrioxalate actinometry (note back cell, Figure 7).

Isomerization quantum yields were obtained by using GLC analysis for the appearance of product at low conversion (areas corrected for molar response). Integrated light intensities for total photolysis time were obtained from the quantum counter recorder tracings. Photolysis samples were magnetically stirred during irradiation. Recorded quantum efficiencies are typically the average of three runs with average deviations of ±10% ($\phi < 4$) or ±30% ($\phi > 4$).

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**Registry No.** HMDB·FUM, 84303-77-5; HMDB·DDF, 84303-78-6; HMDB·TCNB, 84303-79-7; HMB·FUM, 78689-02-8; HMB·DDF, 84303-80-0; HMB·TcNB, 7431-47-2.

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