

## ISOMERIZATION OF DEWAR BENZENES INVOLVING ELECTRON DONOR-ACCEPTOR EXCIPLEXES

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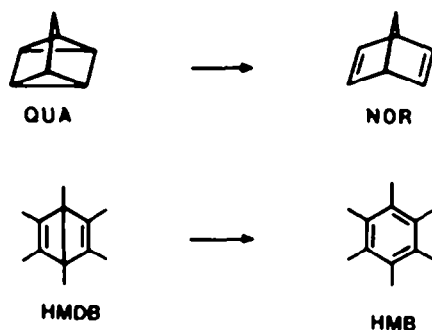
(Received in USA April 1981)

**Abstract**—Valence photoisomerization of hexamethyl (Dewar benzene) (HMDB) is sensitized by aromatic singlet photosensitizers 1,4-dicyanobenzene, 1-cyanonaphthalene, 9-cyanoanthracene, and 9,10-dicyanoanthracene with a limiting quantum efficiency of 1.0 in cyclohexane solvent. Quenching of the fluorescence of the aromatic sensitizers leads to exciplex emission which is identical to that obtained by quenching with the isomer, hexamethylbenzene (HMB). The emission is identified as HMB exciplex emission on the basis of relative lifetime and dual quenching experiments. The relative yield of HMDB-derived ("adiabatic") emission is 20–50% depending on the excitation energy of the HMB exciplex product. Neither biacetyl singlet or triplet nor 1-cyanonaphthalene triplet photosensitization is successful in bringing about isomerization of HMDB. Dimethyl 1,4,5,6-tetramethylbicyclo[2.2.0]hexa-2,5-diene-2,3-dicarboxylate undergoes valence isomerization on quenching electron donor fluorophores, with a quantum efficiency of 0.2. The aromatic valence isomer is not produced in an excited state in this case. Factors which govern the efficiency of adiabatic and diabatic isomerization of the Dewar benzenes are discussed, including sensitizer redox properties, configuration, and multiplicity, the excitation energy and binding characteristics of exciplexes, and the Dewar benzene substituent pattern.

Since the first reports by Hammond *et al.*<sup>1</sup> of an unusual mechanism for photosensitized valence isomerization of quadricyclene (QUA) to norbornadiene (NOR), a number of studies have focused on the role of excited complexes in driving molecular rearrangements. Solomon *et al.*<sup>2</sup> provided support for the view that electron transfer (as opposed to energy transfer) properties of the "sensitizer" and the isomerizable substrate are important. In the extreme, excited state quenching by outright electron transfer and subsequent isomerization of radical ions may be involved, as shown recently for the sensitized isomerization of QUA,NOR in polar solvents.<sup>3</sup>

Examples of the exciplex isomerization now include ring closure of nonconjugated dienes,<sup>4</sup> isomerization of alkenes and cyclopropanes,<sup>5</sup> and racemization of sulfoxides.<sup>6</sup> The more detailed discussions of mechanism have focused on the appearance of radical ion pairs,<sup>3,5a-c</sup> exciplex intersystem crossing,<sup>3d-h</sup> and the conversion of electronic into vibrational energy,<sup>1,5j</sup> any of which make isomerization via exciplexes possible. Irradiation of ground state (CT) complexes of isomerizable substrates provides yet another entry for molecular rearrangement.<sup>4a,5a,7</sup> The potential role of excited complexes in driving isomerization reactions which reversibly store energy has been pointed out.<sup>4b,8</sup>

Two early reports concerning the photosensitized conversion of HMDB to HMB described an exciplex isomerization which has displayed perhaps the most unusual features. Evans *et al.*<sup>9</sup> reported that the isomerization which results from quenching the fluorescence of aromatics by HMDB in polar solvents has a quantum efficiency well exceeding unity. A chain reaction involving radical ions which result from electron transfer quenching was proposed. Taylor<sup>10</sup> found, on the other hand, that fluorescence quenching by HMDB in a nonpolar solvent results in isomerization with a more typical quantum yield. He also showed that the emission, which accompanies ring opening, is identical to HMB exciplex fluorescence. The latter observation, consistent with the imposition of



an exciplex  $\rightarrow$  exciplex rearrangement,<sup>10</sup> constitutes the only current example of *adiabatic* exciplex isomerization.

Mechanistic features which permit adiabatic photochemistry (the formation of electronically excited products) have received considerable attention.<sup>11</sup> In our preliminary report concerning HMDB exciplex isomerization,<sup>12</sup> the adiabatic reaction was firmly established, and factors controlling the selection of adiabatic reaction vs non-adiabatic paths were identified. These findings are discussed more fully here, including dependences of exciplex isomerization on sensitizer configuration and multiplicity and on substituent patterns for Dewar benzene quenchers.

### RESULTS

**Fluorescence quenching.** The addition of HMDB or HMB to cyclohexane solutions of aromatic nitriles resulted in quenching of the emission of the aromatic compounds. Stern-Volmer analysis resulted in values for  $k_q\tau$  from which rate constants for quenching were extracted (Table 1) using known sensitizer lifetimes ( $\tau$ ) (Table 2). Values for  $k_q$  followed the trend expected for a quenching mechanism involving EDA interaction,<sup>4b,13</sup> reflecting the similar oxidation potentials of HMDB and HMB ( $E_{1/2}(ox) = 1.58$  and 1.62 V vs SCE, respectively)

Table 1. Photochemical and photophysical data for HMDB (HMB) quenching and isomerization\*

Sensitizer	$k_q(\text{HMDB})$ ( $\times 10^{-9} \text{sec}^{-1}$ )	$k_q(\text{HMB})$ ( $\times 10^{-9} \text{sec}^{-1}$ )	$\phi_{11m}^b$	$k_q \tau$ ( $\text{M}^{-1}$ ) <sup>c</sup>	$1/s$ ( $\text{M}^{-1}$ ) <sup>d</sup>	$\lambda_f(\text{exc})(\text{nm})^e$
1,4-dicyanobenzene (DCB)	10.4	13.2	(1.0)			392
1-cyanonaphthalene (CN)	3.2	4.4	0.98	84.0	85.6	373
9,10-dicyanoanthracene (DCA)	7.3	8.7	0.98	112.	119.	500
9-cyanoanthracene (CA)	0.13	2.6	(1.0)			450 <sup>f</sup>

\*Cyclohexane solution, room temperature. <sup>b</sup>Limiting quantum yields of HMDB  $\rightarrow$  HMB exciplex isomerization; irradiations were carried out using monochromator for DCB (288 nm) and CN (313 nm). <sup>c</sup>Stern-Volmer slopes from fluorescence quenching data for HMDB. <sup>d</sup>Intercept/slope ratios from quantum yield double reciprocal plots (Figures 1 and 2). <sup>e</sup>Wavelength maxima for HMB (HMDB) exciplex emission. <sup>f</sup>Emission detectable only for CA-HMB.

Table 2. Singlet sensitizer properties, HMB exciplex-excitation energies, and preference for adiabatic HMDB rearrangement

Sensitizer	$\tau_f$ (ns) <sup>a</sup>	$E_{1/2}^*(\text{red})(\text{V})^b$	$E_{00}(\text{exc})$ (kcal/mol)	Percent Adiabatic (P)
CN	26	2.1	77	20 $\pm$ 2
DCB	13	2.7	73	32 $\pm$ 2
CA	9	1.4	64	
DCA	15	2.1	57	50 $\pm$ 3

<sup>a</sup>Fluorescence lifetimes in hydrocarbon solvents from the literature: M. Yoshida, H. Sakuragi, I. Tanaka, K. Tokumaru, and N. Mirikawa, *Bull. Chem. Soc. Japan*, **48**, 2399 (1975); M. E. R. Marcondes, V. G. Toscano and R. G. Weiss, *J. Am. Chem. Soc.* **97**, 4485 (1975); E. Vander Donckt, M. R. Barthele, N. Antheunis, and M. Swinnen, *Mol. Photochem.* **8**, 121 (1977); Ref. 2. <sup>b</sup> $E_{1/2}^*(\text{red}) = E_{1/2}(\text{red}) + \text{sensitizer singlet energy}$ ; sensitizer ground state reduction potentials (vs. SCE, CH<sub>3</sub>CN) are reported; E. A. Chandross and J. Ferguson, *J. Chem. Phys.* **47**, 2557 (1967); D. R. Arnold and A. J. Maroulis, *J. Am. Chem. Soc.* **98**, 5931 (1976).

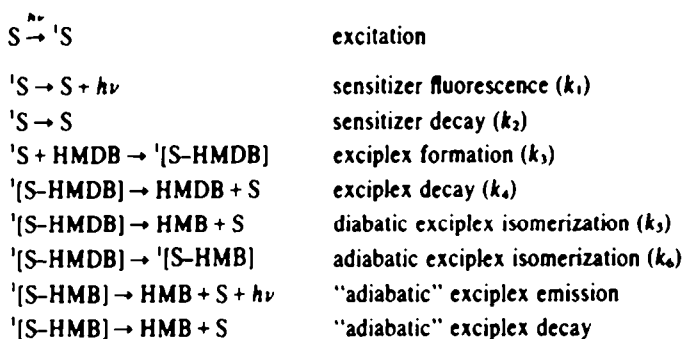
and the varied excited state reduction potentials,  $E_{1/2}^*(\text{red})$  (Table 2), of the fluorophores. The rate of fluorescence quenching was somewhat faster (2-3 fold) in acetonitrile solvent.<sup>14</sup>

**Quantum yields of HMDB isomerization.** Fluorescence quenching was accompanied by efficient rearrangement of HMDB. Quantum yields for HMDB  $\rightarrow$  HMB isomerization

in cyclohexane were concentration dependent, and the trend paralleled the emission quenching results. A mechanism for singlet sensitization is shown in Scheme 1.

The quantum yield expression consistent with the mechanism of Scheme 1 is as follows:

$$\frac{1}{\phi_{100m}} = \frac{k_4 + k_5 + k_6}{k_5 + k_6} + \frac{k_1 + k_2(k_4 + k_5 + k_6)}{k_3(k_5 + k_6)[\text{HMDB}]}$$



Scheme 1.

For CN and DCA sensitizers double reciprocal plots of quantum efficiency for isomerization and HMDB concentration (Figs. 1 and 2) were linear as expected and intercept/slope ratios ( $i/s$ ) closely matched  $k_4\tau$  values obtained from fluorescence quenching (Table 1) (i.e.  $i/s = k_3/k_1 + k_2 = k_4\tau$ ). Limiting quantum yields of  $\text{HMDB} \rightarrow \text{HMB}$  rearrangement ( $1/i$ , Fig. 1 and 2) were near unity (Table 1). Concentration dependence plots were regular but not linear for DCB and CA sensitizers (intercepts  $\sim 1$ ). DCB and HMDB were competitive absorbers, even at a favorable wavelength (288 nm), and CA underwent

competitive photodecomposition (dimerization,<sup>15</sup> which could be followed by the reduction in CA absorption) especially at low [HMDB].

**Exciplex/emission.** The quenching of aromatic nitrile fluorescence by HMDB and HMB in cyclohexane led to a new emission consistent with the results of Taylor concerning CN quenching.<sup>10</sup> The long wavelength fluorescence resulting from HMDB quenching was weaker but clearly superimposed on the emission obtained on HMB quenching (see Figs. 1, 3 and 4, Ref. 12). Fluorescence maxima for other exciplexes are

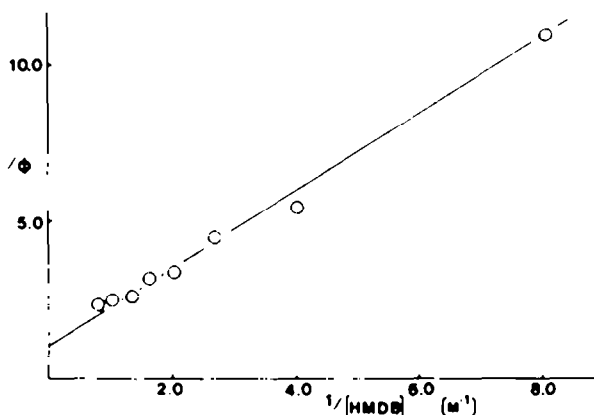


Fig. 1. The dependence of quantum yield on quencher concentration for CN sensitized isomerization of HMDB.  $[\text{CN}] = 1.3 \times 10^{-3} \text{ M}$ .

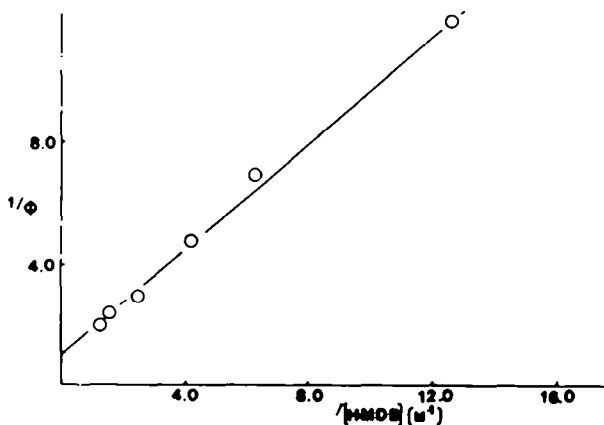


Fig. 2. The dependence of quantum yield on quencher concentration for DCA sensitized isomerization of HMDB.  $[\text{DCA}] = 7.5 \times 10^{-3} \text{ M}$ .

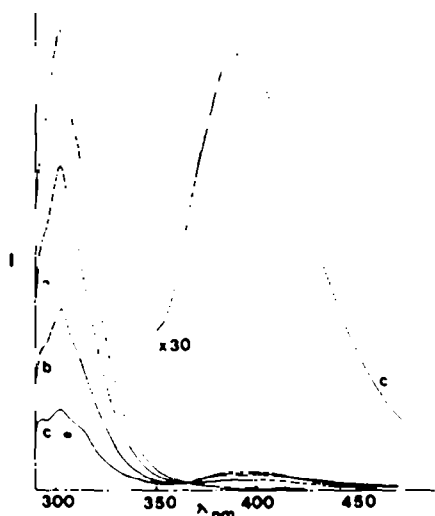


Fig. 3. The quenching of DCB fluorescence by HMDB in cyclohexane solution. (a,  $3.5 \times 10^{-3}$  M, b,  $1.2 \times 10^{-2}$  M, c,  $3.0 \times 10^{-2}$  M).

shown in Table 1. The emission from CA-HMB was very weak and poorly resolved, and the corresponding fluorescence of CA-HMDB was not observed.

To insure the origin of exciplex emission, samples were analyzed by glc before and after the measurement of fluorescence. For these experiments, purified samples of HMDB showed no HMB (<0.5%), a result which remained unchanged after fluorimeter irradiation. Given the similarity of quenching rate for HMDB and HMB (Table I), the portion of the observed exciplex emission resulting from HMDB addition, which is due to competitive HMB quenching, must have been negligible.

Additional evidence for the identity of the emitting exciplex was sought through three component quenching experiments, from which relative lifetimes of CN exciplexes derived from HMDB and HMB quenching could be obtained. An electron donor, 2,5-dimethyl-2,4-hexadiene (DMH), was the most effective exciplex quencher among several examined. DMH quenched CN-HMB fluorescence with Stern-Volmer constant,  $k_q\tau = 59 \text{ M}^{-1}$ . A complication was encountered in a similar experiment in which the emission from CN-HMDB was quenched by DMH. HMDB was a relatively effective quencher of CN-HMB fluorescence ( $k_q\tau = 35 \text{ M}^{-1}$ ) (Incremental addition of HMDB to CN results first in the appearance of

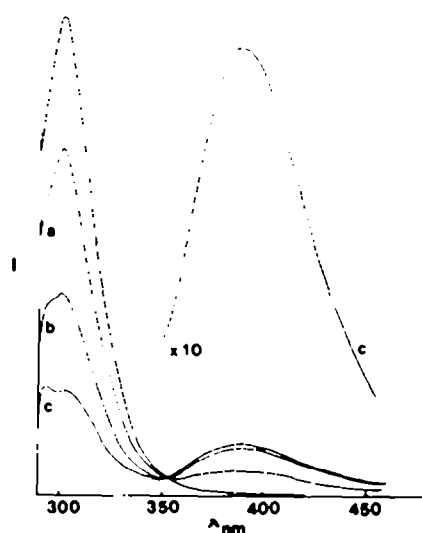


Fig. 4. The quenching of DCB fluorescence by HMB in cyclohexane solution. (a,  $2.4 \times 10^{-3}$  M, b,  $7.9 \times 10^{-3}$  M, c,  $1.7 \times 10^{-2}$  M HMB).

exciplex fluorescence which is reduced in intensity on further addition of HMDB; note Taylor's similar findings<sup>10</sup>). Stern-Volmer slopes for DMH quenching of the exciplex emission from CN-HMDB were 8.1, 23 and  $49 \text{ M}^{-1}$  at  $[\text{HMDB}] = 0.43, 0.22, \text{ and } 0.035 \text{ M}$ . These values extrapolated to  $k_q\tau = 60 \text{ M}^{-1}$  at  $[\text{HMDB}] = 0$ <sup>16</sup> in good agreement with the value obtained for CN-HMB exciplex quenching. This comparison showed an identity within experimental error for the lifetime of the emitting exciplex from CN-HMDB and CN-HMB.

In order to provide further evidence for the adiabaticity of exciplex rearrangement, it was important to show that the exciplex derived from a sensitizer and HMDB is not a precursor to isomerization having, coincidentally, spectral properties and lifetime similar to exciplexes of HMB. Another three-component quenching experiment, showed this clearly. The quenching of CN sensitized exciplex isomerization (overall yield of  $\text{HMDB} \rightarrow \text{HMB}$ ) was compared with quenching of exciplex emission (Fig. 5). Relative yields were corrected for direct quenching of CN singlets by DMH for which  $k_q\tau = 127 \text{ M}^{-1}$ . The results for exciplex fluorescence and isomerization quenching ( $k_q\tau = 23$  and  $5.3 \text{ M}^{-1}$ , respectively) demon-

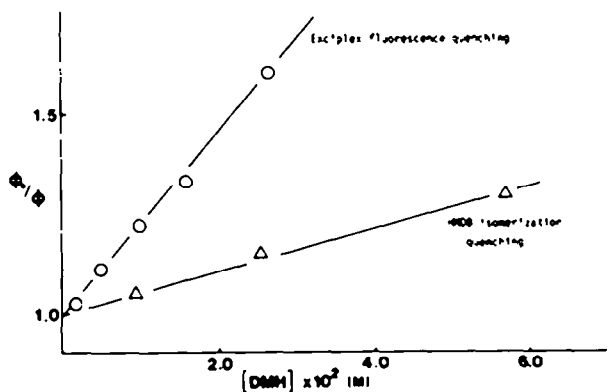


Fig. 5. Stern-Volmer plots for the quenching of the emission derived from CN-HMDB and CN sensitized isomerization of HMDB to HMB, both by DMH in cyclohexane solution.

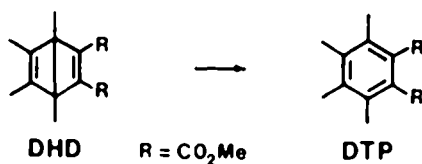
strate that the emitting species and the isomerizing species cannot be the same. The reacting CN-HMDB exciplex does appear to be interceptable; Taylor obtained spectroscopic evidence for this species in an emission study at low temperatures.<sup>10</sup> If DMH exciplex quenching proceeds at a rate comparable to CN quenching ( $k_q = 5 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$ ), then the lifetime of the rearranging CN-HMDB exciplex at room temperature is about 1 nsec.

The portion of exciplex isomerization which takes the adiabatic path ( $P = k_1/k_1 + k_6$ , Scheme 1), was determined from relative emission yields. The ratio of exciplex/monomer emission was recorded as a function of % of monomer sensitizer emission quenched by HMDB or HMB. At five levels of sensitizer quenching, for each of three sensitizers, the fraction,  $P$  (Table 2) was computed ( $P = I_{exc}/I_{mon}(\text{HMDB})/I_{exc}/I_{mon}(\text{HMB})$ ), where  $I_{exc}$  and  $I_{mon}$  represent maximum intensities of exciplex and sensitizer emission. For this procedure the residual sensitizer fluorescence served as an internal standard for the relative yield of exciplex emission.

*Investigation of other exciplex components.* The suitability of other types of sensitizers for exciplex isomerization was investigated. HMDB quenching of biacetyl (an "n,  $\pi^*$ " sensitizer) phosphorescence<sup>17</sup> (Fig. 6) and (at higher concentrations) fluorescence<sup>18</sup> did not lead to sensitized HMDB isomerization ( $\theta < 0.01$ ) under circumstances where polar exciplexes are implicated. A slow disappearance of biacetyl ( $\theta \approx 0.1$  at  $[\text{HMDB}] = 0.01 \text{ M}$ ) was observed. Aromatic nitrile triplets appeared also not to play a role in sensitized isomerization. Nitrogen purged samples of CN and HMDB did not give HMB on photolysis at concentrations of HMDB insufficient to quench CN fluorescence ( $\theta_{\text{CN}} < 0.01$  at  $0.001 \text{ M}$  HMDB). Under these conditions a good yield of CN triplets ( $\theta_{\text{CN}} = 0.3^{19}$ ) and HMDB quenching were expected. HMDB was indeed an effective quencher of CN phosphorescence ( $k_{q7} = 4.7 \times 10^5 \text{ M}^{-1}$ ), an emission (bands at 504, 543 and 585 nm) which was monitored at room temperature in dibromoethane following procedures required for observation of naphthalene phosphorescence.<sup>20</sup>

Substituent effects on exciplex isomerization were also probed. Dewar phthalate DHD and its valence isomer DTP were good quenchers of electron donating (but not electron accepting) aromatic sensitizers in cyclohexane (1,4-dimethoxyanthracene, 1,4-DMA,  $k_{q7} = 87$  and  $34$ ; 9,10-dimethylantracene,  $k_{q7} = 38$  and  $5.9 \text{ M}^{-1}$ , respec-

tively). DHD  $\rightarrow$  DTP isomerization was sensitized by the donor fluorophores in cyclohexane or benzene solution. The reaction, which was relatively slow, was most conveniently monitored by NMR with reference to changes in upfield Me group absorptions. The quantum yield of DHD isomerization was 0.16 at  $0.16 \text{ M}$  DHD, a concentration at which 93% of 1,4-DMA singlets are quenched (fluorescence measurement). Some disappearance of sensitizer during photolysis was again observed. An exciplex emission was observed on quenching 1,4-DMA with DTP ( $\lambda_{\text{max}} = 460 \text{ nm}$ ), but no new fluorescence was found on addition of DHD to 1,4-DMA. The relative yield of DHD-derived exciplex emission (conservatively) can be no more than 10%, representing less than half of the adiabatic ( $P$ ) fraction found for the least efficient HMDB (CN) pair (Table 2).



#### DISCUSSION

The evidence concerning isomerization of HMDB, which occurs on quenching the fluorescence of aromatic sensitizers in non-polar solvents, clearly favors a mechanism of rearrangement (in part) on an excited surface. At some stage along the reaction coordinate partitioning occurs to give HMB exciplexes and the ground state of products. This basic scheme and the energetics involved are shown in Fig. 7.

The adiabatic portion of exciplex rearrangement is revealed in the emission from S-HMDB combinations which is identical to HMB exciplex emission in terms of spectral features and lifetime. The fluorescent state resulting from HMDB quenching cannot be a precursor to rearrangement, since the emission can be quenched under conditions where the HMDB isomerization proceeds. As pointed out previously,<sup>12</sup> the most important determinant of adiabatic yield is the excitation energy of HMB exciplexes. The function,  $P$ , correlates better with exciplex energy than with the excited state reduction potential for the sensitizers (Table 2). In terms of the potential energy surfaces proposed by Michl<sup>21</sup> for Dewar naphthalene ring opening, the preference for forming

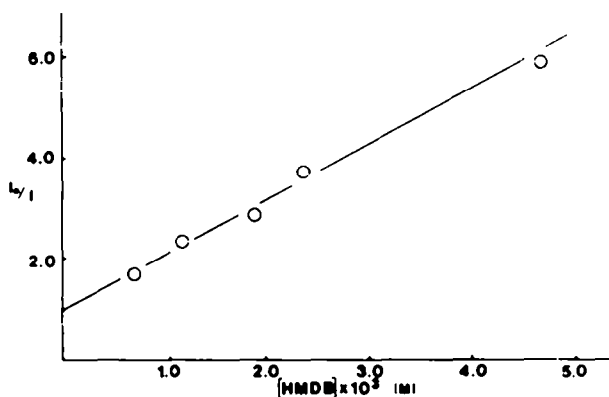


Fig. 6. Stern-Volmer plot for the quenching of biacetyl phosphorescence by HMDB in cyclohexane solution.

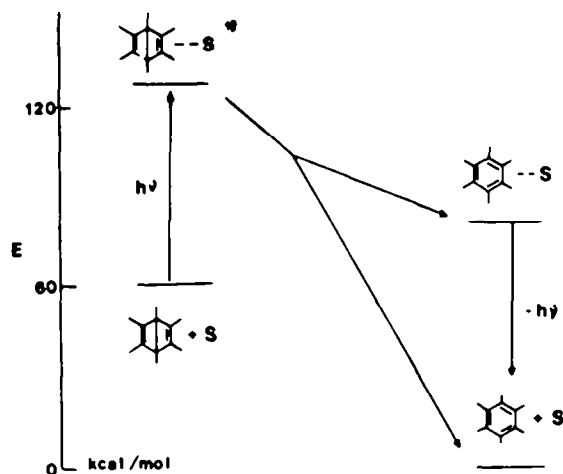
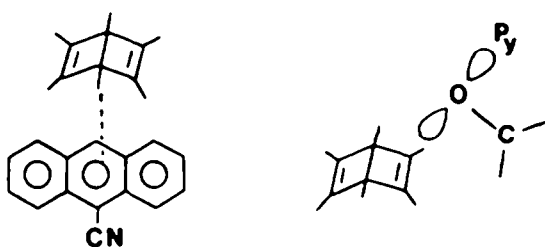


Fig. 7. Energy diagram for exciplex isomerization of hexamethyl (Dewar benzene) (the diffusive encounter step is omitted). For HMDB  $\rightarrow$  HMB ground state energetics, see Ref. 31. HMB exciplex excitation energies are found in Table 2; HMDB exciplex energies are estimated.

lower energy HMB exciplexes most likely results from adjustment of the small barrier separating the pericyclic minimum (approximate midpoint of reaction) and exciplex product on the adiabatic surface.<sup>†</sup>

The mechanism by which HMDB exciplex isomerization operates is not readily extended to sensitizers other than those which have  $\pi$ ,  $\pi^*$  singlet activity, suggesting a dependence of an otherwise facile rearrangement on exciplex configuration (geometry) and multiplicity. Several influences which are likely to be important can be identified. The failure of biacetyl singlets to drive the reaction may relate to exciplex geometry differences (an edge to face vs face to face<sup>22</sup> approach of pi moieties and/or an "endo" vs "exo" arrangement for  $n$ ,  $\pi^*$  and  $\pi$ ,  $\pi^*$  sensitizers, respectively; see below). The ineffectiveness of sensitizer triplets may result from the inherent lower energies of sensitizers and reduced EDA perturbation.



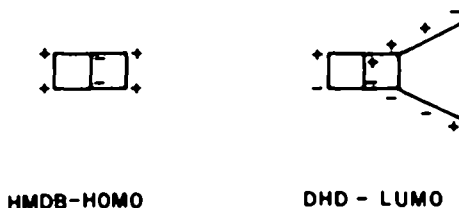
Two factors may reduce the yield of exciplex isomerization of the "reverse polarity" substrate, DHD, relative to HMDB. The  $\sigma$ - $\pi$  through-bond coupling which is important for the HOMO of HMDB<sup>23</sup> leads to

<sup>†</sup>As previously discussed,<sup>12</sup> we do not favor a mechanism for ring opening in cyclohexane involving "tight" ion-pair formation, rearrangement of HMDB radical cation, and ion recombination. Recent studies<sup>14b</sup> of ground state (charge transfer) complexes of HMDB and acceptors show that the dominant path in non-polar solvent for deactivation of ion pairs formed directly on CT excitation is non-radiative decay (back electron transfer) without rearrangement.

<sup>‡</sup>This factor may be part of a more general substituent influence on orbital symmetry restrictions for rearrangement.<sup>24</sup>

reduced  $C_1$ - $C_4$  bond order on electron donation to sensitizer. In fact, this perturbation is probably the most important influence in promoting ring opening. In contrast, electron donation to the LUMO is important in the exciplex binding of DHD. Ring opening is not so readily induced in this case ( $C_1$ - $C_4$  antibonding character is not so readily introduced) due to the heavy weighting of the LUMO on the maleate moiety<sup>‡</sup> (see below). Secondly, stabilization of the adiabatic route will depend on the preservation of exciplex binding during rearrangement. That HMB is at least as good a binding agent as HMDB (reflected in fluorescence quenching constants, Table 1) whereas DTP is less effective than DHD in attracting sensitizer, may be the determining factor in discouraging adiabatic rearrangement for the latter pair.

Our studies of the unusual features of HMDB-HMB isomerization are continuing with special attention to the photochemistry of ground state (CT) complexes of HMDB and the radical-ion chemistry<sup>9</sup> which is important in polar solvents.



#### EXPERIMENTAL

**General.** Spectrophotometric grade solvents were used without further purification in quantum yield and emission experiments except where noted. Commercially available sensitizers were purified by recrystallization: DCB from benzene, CA from glacial acetic acid, DCA from chloroform, and 1,4-DMA from cyclohexane. CN was sublimed twice *in vacuo*. Biacetyl was distilled under nitrogen. Hexamethylbenzene was recrystallized from EtOH.

HMDB was obtained on a small scale using a modification of the large scale procedure of Schafer<sup>25</sup> (the 2-butyne starting material is no longer available in quantity). Other samples of HMDB were generously supplied by Profs. C. C. Wamser and P. M. Maitlis. HMDB was purified by glc using a 10 ft.  $\times$  3/8 in. column (20% SF-96 on chromosorb W). DHD was prepared

following the procedure of Koster, Timmermans, and Bekkum,<sup>28</sup> and DTP was obtained by pyrolysis of the Dewar isomer according to a reported procedure.<sup>27</sup>

**Quantum yield measurements.** The photolysis apparatus consisted of a Rayonet RPR-204 photochemical reactor fitted with either RUL 3500 (330–390 nm) or RUL 3000 (280–330 nm) lamps and a merry-go-round attachment for simultaneous irradiation of N<sub>2</sub> purged 15 × 1.5 cm Pyrex cylindrical tubes. The procedures have been described previously including correction for differential absorption by sensitizers and actinometer.<sup>28</sup> The conversion of valerophenone to acetophenone ( $\phi = 0.33$ , 0.1 M valerophenone in benzene)<sup>29</sup> was used as actinometer. Gc analysis was performed on an OV-101 (3% on Chromosorb W) column with dodecane internal standard. Photolysis of CN and HMDB was carried out using a B and L—light pipe—quantum counter (rhodamine B) apparatus calibrated with potassium ferrioxalate<sup>30</sup> (light intensity =  $1.3\text{--}1.6 \times 10^{14}$  quanta/sec at  $313 \pm 4$  nm). DHD and 1,4-DMA were similarly irradiated at  $366 \pm 4$  nm in benzene ( $2.0\text{--}2.8 \times 10^{14}$  quanta/sec).

The isomerization of HMDB to HMB was monitored by gc using an OV-17 column (3% on Chromosorb P) at 120° and dodecane as internal standard. Conversion of HMDB was limited to <5%. The DHD–DTP isomerization was followed by NMR (characteristic Me group absorptions) with conversion limited to 20–25%. Slopes and intercepts for double reciprocal quantum yield plots were obtained by a linear least squares treatment of the data.

**Emission measurements.** Fluorescence and phosphorescence spectra were obtained using a Perkin–Elmer MPF-44A fluorescence spectrophotometer. For fluorescence measurements samples were degassed. Biacetyl phosphorescence was recorded for N<sub>2</sub> purged  $5.1 \times 10^{-3}$  M cyclohexane soles. The degassing procedure and method of analysis are described in another paper,<sup>17</sup> including a procedure for determination of lifetime. The data for biacetyl quenching by HMDB are (Fig. 6):  $k_q\tau = 1.0 \times 10^5 \text{ M}^{-1}$ ;  $\tau = 135 \mu\text{sec}$ ; and  $k_q = 7.7 \times 10^4 \text{ M}^{-1} \text{ sec}^{-1}$ .<sup>17</sup> A procedure reported by Turro *et al.*<sup>30</sup> for the observation of room temp. fluid solution phosphorescence of naphthalene was used for obtaining emission from triplet CN. A degassed  $2.1 \times 10^{-4}$  M solution of CN in the heavy atom solvent, 1,2-dibromoethane, gave rise to an emission with principal bands at 504, 543, and 585 nm. The intensity of emission at 504 nm was monitored as a function of HMDB concentration in independently prepared and degassed samples, and the quenching of phosphorescence observed. The slope of the linear Stern–Volmer plot was,  $k_q\tau = 4.7 \times 10^5 \text{ M}^{-1} \text{ sec}^{-1}$ .

**Acknowledgements**—This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences. We thank Profs. P. M. Maitlis and C. C. Wamser for providing samples of hexamethyl (Dewar benzene).

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