

## ENERGY STORAGE IN ORGANIC PHOTOISOMERS\*

GUILFORD JONES, II, SHEAU-HWA CHIANG and PHAN THANH XUAN

Department of Chemistry, Boston University, Boston, Mass. 02215 (U.S.A.)

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### Summary

Criteria for the successful photochemical storage of solar energy as latent heat in organic materials are outlined. Photoisomerization reactions which have some potential for storage of photon energy in kinetically stable products are surveyed. Emphasis is placed on well-known internal cyclo-additions which display thermal reversibility, large storage capacities and high chemical and quantum efficiencies. Chemicals available on an industrial scale, which are known to undergo valence isomerization, are identified. Attempts to drive these reactions via exciplexes (complexes involving strong electron donor or electron acceptor sensitizers) are described. The sensitized isomerization of dimethylnorbornadiene-2,3-dicarboxylate (7) and a model compound, hexamethyldewarbenzene, are identified as *bona fide* exciplex isomerizations. Triplet sensitizers have been employed in the sensitization of 7 to visible light (to 500 nm). The potential importance of endothermic energy transfer in triplet sensitization (the upconversion of very low energy triplets) is discussed. The review includes developments by several research groups in the spectral sensitization of isomerizable substrates, the use of heterogeneous photosensitizers, and photocalorimetric techniques.

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### 1. Introduction

The potential for storage of radiant energy in chemical bonds was recognized as early as 1909 [1]. In this early reference Weigert pointed out the energy storage capability of anthracene photodimerization [2]. Organic photoreactions other than this prototype were not included in early surveys of photochemical conversion of solar energy [3 - 5]. Splitter and Calvin [6] were perhaps the first to note the possible use of light-derived small ring organic compounds in the conversion of radiant energy.

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TABLE 1

Requirements for organic photochemical conversion of solar energy

Imperative	Observation
	$A \xrightarrow{h\nu} B$ $B \longrightarrow A + \text{heat}$
(1) Reactant A must absorb or be sensitized to ultraviolet and visible light.	Useful range = 300 - 700 nm (40 - 90 kcal einstein <sup>-1</sup> ), about 50% of incident solar energy.
(2) Photoproduct B must not competitively absorb (or quench sensitizer).	Reaction A → B should be photochromic (decrease in the degree or continuity of unsaturation of A).
(3) The quantum yield for reaction A → B must be near unity.	Intramolecular reactions should be favored over intermolecular ones; luminescence should not be competitive.
(4) Reaction A → B must have a large positive ground state enthalpy.	Selected valence photoisomerizations with $\Delta H = 10 - 30 \text{ kcal mol}^{-1}$ are known; reactions should be selected in which small rings are generated and/or conjugation disrupted.
(5) Photoproduct B must be (kinetically) stable	Orbital topology restrictions for selected isomerizations inhibit B → A; reversions at 50 - 100 °C will be useful.
(6) A chemical control external to the cycle $A \rightleftharpoons B$ may be used to initiate B → A.	Metal or acid catalysts may be suitable.
(7) Reactant A (B) must be inexpensive	Availability on an industrial scale eventually required. Cost should be less than \$1.00 lb <sup>-1</sup>
(8) Materials must not be dangerous or difficult to handle.	Chemicals which are toxic or which require unusual atmospheres or pressure should be avoided.

A valuable assessment of organic photoreactions in the storage of solar energy was reported by Sasse at the previous meeting [7], and other recent papers [8, 9] have reviewed quantitative aspects of photon energy storage in organic materials. Part of this recent effort has focused on the storage of solar energy as latent heat. Conventional solar-thermal energy conversion devices, although generally effective, are limited by solar intermittency. An important goal in the development of advanced conversion systems is the identification of materials with "long term" storage capability (several days, perhaps weeks). Photoactive compounds which under solar irradiation give energy-rich yet stable reaction products are one promising class of latent heat storage materials. The economic and engineering requirements and advantages for a hypothetical photochemical solar-thermal transducer have been critically examined [10, 11]. The possibilities for organic photoelectrochemical energy conversion have not been evaluated as thoroughly, although the creation of photopotentials in a reversible organic system has been reported [12, 13].

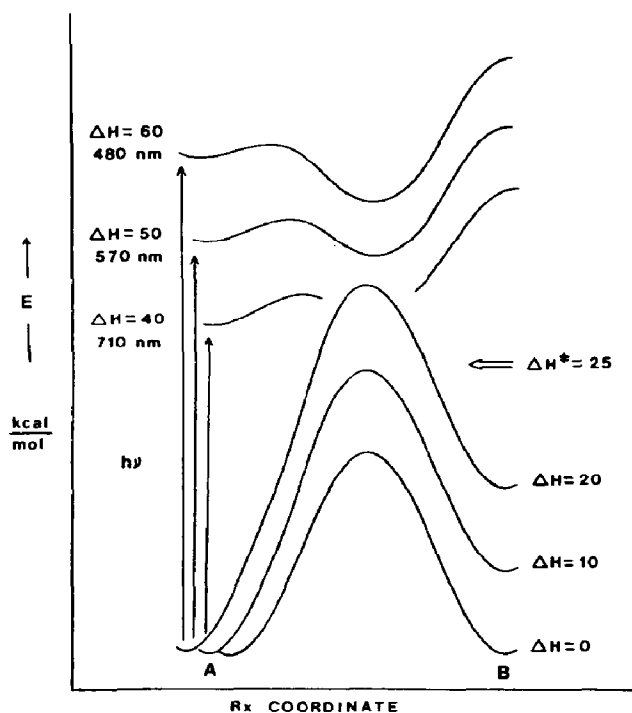


Fig. 1. The potential surface diagram for a hypothetical photochemical reaction with varying energies of excitation and storage in a kinetically stable product.

Criteria for the efficient photochemical conversion of solar energy and observations appropriate for cyclic organic heat storage systems are collected in Table 1. The requirements are most readily applied to the interconversion of isomers. Properly selected organic isomerization systems have significant storage enthalpies owing to the creation of bond angle strain in small rings or the loss of resonance energy in  $\pi$  systems. Thermodynamic instability can be blended with orbital topology or symmetry constraints which confer kinetic stability on photoproducts. This divergence of thermodynamic and kinetic driving forces offers a solution to the back reaction problem which inorganic systems display, but presents a new dilemma. As shown in Fig. 1, for reactions which store more energy in kinetically stable products and use longer wavelengths of light, photoreaction encounters a rising barrier generated by the ground state energy surface. Although the penalty for this type of surface interference is not known, it seems unlikely that low energy single photons ( $\lambda > 700$  nm) will efficiently drive a reaction with high storage capacity and a kinetically stable product. In short, deep seated molecular reorganizations exact a higher price in photochemical driving force (photon energy) compared with electron transfer reactions but they offer significant advantage in storage capability.

After a review of recent studies which are generally important to the development of efficient energy storing organic photoreactions, this paper

TABLE 2

Photocalorimetric heats of reaction (at 25 °C) [14]

Reaction	Excitation wavelength (nm)	$\phi^a$	$\Delta H$ (kcal mol <sup>-1</sup> )	$Q$ (%) <sup>b</sup>
Azobenzene ( <i>trans</i> → <i>cis</i> )	546	0.45	11.7 ± 1.3	10.0
Fe(C <sub>2</sub> O <sub>4</sub> ) <sub>3</sub> <sup>3-</sup> → Fe <sup>2+</sup>	446	0.98	-12.8 ± 0.7	19.6
Re <sub>2</sub> (CO) <sub>10</sub> + I <sub>2</sub>	336	0.49	-15.6 ± 2.0	5.9

<sup>a</sup>Quantum efficiency at excitation wavelength.<sup>b</sup>Calvert's  $Q$  value [3] modified for absolute values of stored enthalpy:  $Q = 100 \Delta H \phi / E_{hv}$ .

will focus on the status of reaction types, substrates and mechanisms from which useful chemical systems are likely to be selected. Special attention will be paid to potential methods of activation of modest chromophores to visible light.

## 2. Supporting studies

New developments in a technique for the determination of storage enthalpies of photochemical reactions have recently been reported [8, 9, 14]. In the more extensive study [14] of the method, called photocalorimetry [15], a number of light-induced reactions were examined for chemical heat effects. Heats absorbed or liberated on irradiation of a conventional calorimeter cell were measured with reference to a light-absorbing photoinactive standard. Several of the ground state enthalpy changes measured in this way are shown in Table 2 (including a storage enthalpy for an organic isomerization) along with  $Q$  values [3] which indicate the efficiency of conversion of light into chemical energy. The photocalorimetry technique requires relatively simple apparatus and should be of great value in obtaining thermodynamic data at ambient and other temperatures. Large storage enthalpies (exceeding 10 kcal mol<sup>-1</sup>) for quantum efficient photoreactions can be reliably determined (potentially useful reactions can be surveyed) without careful study of the back reaction.

Other ancillary developments involve the design of working chemical components of potential use in a solar-thermal photochemical transducer. A generally accepted plan for such a device which includes well-known engineering features is shown in Fig. 2. In an important series of studies prototype light-absorbing and catalytic components which would be necessary for activating and reversing a photochemical working fluid have been developed. Hautala *et al.* [16] have prepared a series of sensitizers bound to polymeric supports which act as light harvesting and energy transfer agents for the isomerization of norbornadiene to quadricyclene (1 → 2). Ketone chromophores (ArCOAr) attached to polystyrene have been

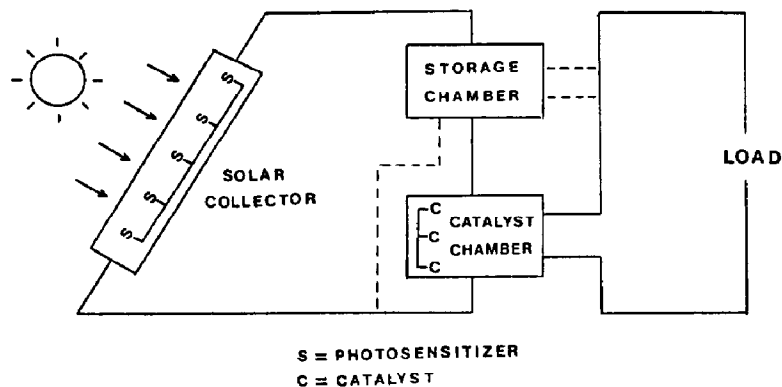
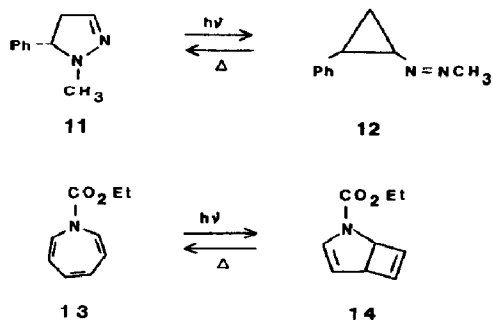
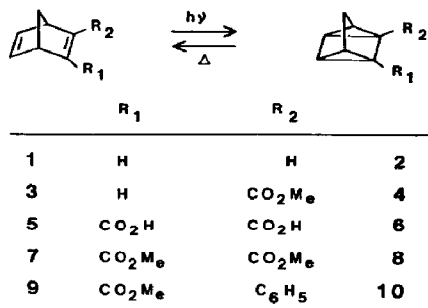


Fig. 2.

shown to drive the reaction  $1 \rightarrow 2$  efficiently through heterogeneous sensitization. An alternative silica-bound photosensitizer has been prepared and is now under evaluation [17]. The advantages of providing a durable stationary light absorbing system for photochemical energy storage are underscored in this work. In a collaborative effort King *et al.* [18] have extensively examined transition metal catalysts which induce and control the rate and chemical efficiency of the prototype back reaction  $2 \rightarrow 1$ .



### 3. Selection of reactions

Organic photoisomerizations which store latent heat may be considered by class. *Geometrical isomerizations* [19] are generally efficient reactions which can be driven by direct irradiation or by photosensitization. A variety of these isomerizations can be induced using visible absorbing sensitizers; several have been studied in great detail (e.g. the stilbenes PhCH=CHPh [19]). Unfortunately, energy differences for geometrical isomers are usually small (less than 10 kcal mol<sup>-1</sup>). The interconversion of azobenzene which stores photon energy moderately well (Table 2) deserves further study. Objectives for this system include modification of the unfortunate preference for the *trans* isomer at the photostationary state for direct [14] and sensitized [20] photoisomerization. Small storage enthalpies may be offset to a degree if exceptionally long wavelengths are utilized efficiently. An approach to the problem of spectral sensitivity involving the azobenzene geometrical isomerization has been reported by Dabrowiak and coworkers [21]. In this study the azobenzene unit was linked to a metalloporphyrin chromophore.

Higher storage enthalpies (above 10 kcal mol<sup>-1</sup>) are commonly found for *valence isomerizations*. These skeletal rearrangements are further classified as sigmatropic shifts [22], electrocyclic reactions and internal cycloadditions [23]. The first two of these categories have received little attention in terms of photon energy storage but are represented by a number of thermally reversible photochemical reactions. Sigmatropic contraction 11 → 12 [24] stores energy (amount unknown) through small ring formation. The important parameters for an electrocyclic interconversion have been measured (isomer pair 13, 14) [25]. The storage capacity is 63 cal g<sup>-1</sup>, thermal reversion occurs at useful temperatures and the forward reaction can be driven with visible light (458 nm) although the quantum yield is low ( $\phi = 0.01$ ).

Examples of energy storing photochemical cycloaddition include the valence isomerization of linked anthracenes [8, 26] and the internal cycloaddition of enone [9] and styrene [27] chromophores. The first highly efficient valence isomerization to break the "400 nm barrier" was the norbornadiene conversion (1 → 2). Important early developments of this system include (1) the first conversion of a derivative to the seemingly tortured photoisomer (5 → 6) [28], (2) an early example of photosensitization using 1 → 2 [29] and (3) extension to a host of substituted norbornadienes (e.g. 7 → 8, 9 → 10) showing near perfect generality for the reaction [30].

Important parameters for a selection of norbornadienes, including the storage enthalpies that are known, are shown in Table 3. The data include the recent finding by Hautala [16] that the 1 → 2 isomerization uses effectively a portion of visible light with sensitization by Michler's ketone and a polymer supported analog. The behavior of norbornadiene-copper(I) complexes has been studied by Kutal [31, 34, 35]. Two modes of "sensitization" have been identified: (1) excitation of ground state complexes (with

TABLE 3  
Isomerization of norbornadienes

Reaction	Sensitizing agent	Absorption edge (nm)	Quantum yield <sup>a</sup>	Storage enthalpy (kcal mol <sup>-1</sup> ) <sup>b</sup>
1 → 2	ArCOAr	420	0.7 [16]	26.7 [32]
	P-ArCOAr	420	0.6 [16]	
	CuCl	330	0.4 [31]	
	Cu(PPh <sub>3</sub> ) <sub>2</sub> BH <sub>4</sub>	330	0.2 [31]	
7 → 8		320	0.5 <sup>c</sup> [30]	18.5 [33]
9 → 10		360	0.6 <sup>d</sup> [30]	23.0 [7]

<sup>a</sup> At 313 nm except where noted; for sensitized reactions, high [norbornadiene] (e.g. 0.5M).

<sup>b</sup> From differential scanning calorimetry of the back reaction.

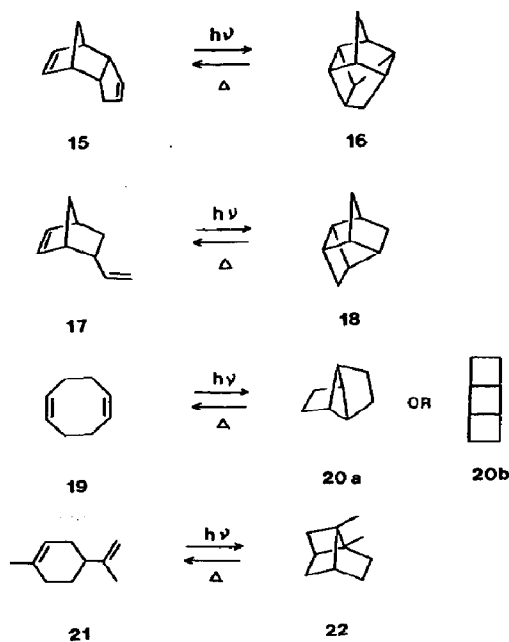
<sup>c</sup> Direct irradiation.

<sup>d</sup> Direct irradiation at 334 nm.

(CuX)) which show improved spectral sensitivity [31] and (2) activation of 1 via an excited complex (with Cu(PPh<sub>3</sub>)<sub>2</sub>BH<sub>4</sub>) (see later) [34]. Most encouraging is the effectiveness of widely different types of sensitization for the reaction of 1.

#### 4. Selection of substrates

Economic factors for latent heat storage include the cost of storage material and the number of energy storage cycles which can be achieved.



Previous estimates [8, 10, 11] show that cost considerations for development of a practical photochemical working fluid are severe (the storage chemical should cost less than \$1 lb<sup>-1</sup>). Although developmental work in an early stage should not be overly restricted by economic priorities, in any survey one should be mindful of chemicals which are abundant and inexpensive.

The number of industrial chemicals for which energy storing photo-reactions are known is quite small; several candidates deserve mention. Dicyclopentadiene (15) (\$0.12 lb<sup>-1</sup> in bulk [36]) is obtained in large quantities in the thermal cracking of gas oil and naphtha and is used in the preparation of resins and insecticides. It has a relatively low toxicity (toleration = 100 ppm) [37] and is stable to 120 °C, where its rate of reversible monomerization to cyclopentadiene is significant [38]. 1,5-Cyclooctadiene (19), a dimer of butadiene prepared by metal catalyzed oligomerization, is used as a rubber modifier and in the preparation of flame retardants. Limonene (21) is a terpene which occurs widely in nature (racemic mixture known as dipentene). It is found in large quantities in citrus fruits and is in fact an abundant waste product of the citrus industry. The principal industrial use of limonene is in the preparation of polyterpene tackifiers used in adhesives. It is non-toxic and non-carcinogenic [39] and is available in bulk at \$0.08 lb<sup>-1</sup>.

The availability of 15 and its interchangeable monomer, cyclopentadiene, makes possible large scale routes to the norbornadienes through Diels-Alder addition. The parent compound (1), the butadiene adduct 17 and the series 6, 7 (available through the cyclopentadiene-2-butyne diol adduct) are among the possibilities.

Valence photoisomerization of all of these presently or potentially abundant chemicals is known [23] (UV irradiation in the presence of a sensitizer typically required) with the exception of the reaction of limonene (21 → 22), for which there is precedent [40], and the isomerization, 19 → 20b, which remains undocumented. All of the isomerizations are of a common type,  $\pi^2 + \pi^2$ , and share the advantage of having a back reaction which is generally catalyzed by transition metals [18, 41]. Storage enthalpies for the suggested isomerizations, although expected to be large, are unknown (but see Table 3); a value for 15 → 16 ( $\Delta H = 16 \text{ kcal mol}^{-1}$ , 120 cal g<sup>-1</sup>) can be estimated, based on data for an analog [9]. Most of the isomerizable substrates are readily handled liquids of moderate volatility.

## 5. Selection of mechanisms

In the foregoing discussion chemicals suitable for large scale use in an energy storage system were readily identified. The proposed photochemistry is conventional, but the modesty of the chromophores of choice industrial chemicals offers a formidable mechanistic challenge in terms of utilization of visible light. In this section two mechanisms of photosensitization will



be discussed with reference to recent results from our laboratory. The mechanisms represent the classical perturbations of excited encounter complexes, electron transfer and energy transfer. The first involves exciplexes [42, 43] which exploit the powerful redox properties of excited states. The second involves exchange energy transfer in which advantage is taken of the long lifetime of triplet photosensitizers.

### 5.1. Isomerization involving exciplexes

Bond order changes in a substrate induced through partnership in an excited complex may lead to isomerization. A number of these *exciplex isomerizations* have been documented, including geometrical isomerization of conjugated dienes [44, 45] and cyclopropanes [46], and optical isomerization of sulfoxides [47]. The induction of isomerization may be viewed as a template effect resulting from electronic polarization. Important to this discussion are bonding changes in non-conjugated dienes due to perturbation by approaching electron donors or acceptors.

In a molecular orbital study of **1**, Hoffmann [48] showed that loss or gain of electron density in the diene leads to an increase in transannular bonding (a general result involving the population and symmetry of molecular orbitals). We have found in similar calculations on dienes perturbed by excited donors and acceptors (Fig. 3) significant increases (about 25%) in transannular  $\pi$  bond order [49]. An isomerization mechanism is concluded if further relaxation of a polarized, partially transannularly bonded electron donor-acceptor (EDA) exciplex leads to the valence isomer (Fig. 3).

The template effect is probably involved in the copper(I) sensitization of **1**  $\rightarrow$  **2** [31, 34]. That copper is acting as a specific complexing agent is indicated by the finding [50, 51] that electron acceptors in general drive the isomerization in the reverse direction (**2**  $\rightarrow$  **1**), no doubt the result of the superior reducing capability of **2** ( $IP_a = 8.4$  (**1**) and  $7.4$  (**2**) eV). This unusual

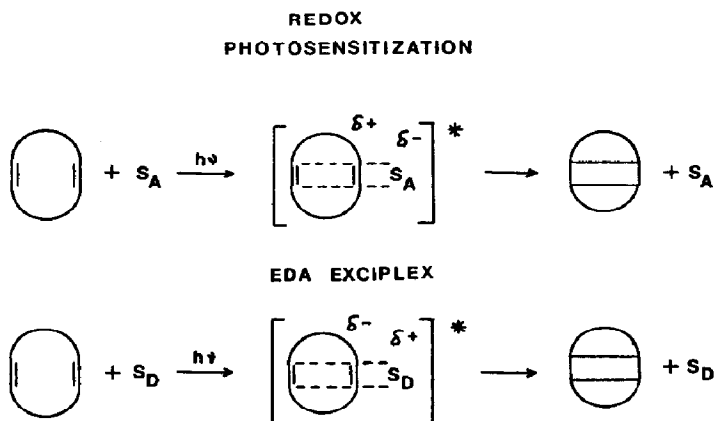


Fig. 3.

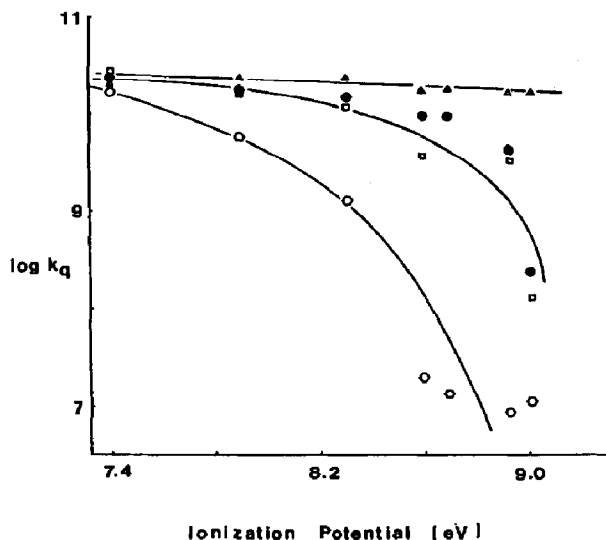


Fig. 4. Stern-Volmer constants for the quenching of aromatic nitriles vs. ionization potentials of diene quenchers. The sensitizers and their  $E_{\text{red}}$  values (against the SCE) are as follows:  $\Delta$ , 1,4-dicyanobenzene, 2.7 V;  $\bullet$ , 9,10-dicyanoanthracene, 2.1 V;  $\square$ , 1-cyanonaphthalene, 2.1 V;  $\circ$ , 9-cyanoanthracene, 1.4 V. Data for quadricyclene (2) (IP = 7.4 eV) are included.

participation by 2 in EDA exciplex isomerization is not expected for other cage photoisomers which are not exceptional electron donors (*e.g.*  $IP_V$  (20a) = 9.8 eV).

The first step in the evaluation of the "industrial dienes" is the demonstration that these rather modest substrates can efficiently intercept excited photosensitizers. A number of unsaturated compounds including 1, 15, 17, 19 and 21 were paired with a series of robust electron acceptors. The latter, a group of cyano-substituted aromatics, were selected for their range of electrochemical properties (reduction potentials,  $E_{1/2} = -0.82$  to  $-1.80$  V against the standard calomel electrode (SCE)) and their varied absorption ( $\lambda_{\text{max}} = 290 - 400$  nm). The interception of excited states by the dienes was assayed by the quenching of sensitizer fluorescence.

The quenching results (Fig. 4) show that the dienes intercept the fluorescent state of the acceptor sensitizers with a wide range of efficiencies. Quenching rate constants are clearly a function of the expected donor-acceptor interaction. For the most potent sensitizer, quenching rates are at a maximum (near the diffusion limit,  $k_q = 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ ). As the sensitizer acceptor potential (a function of ground state reduction potential and excitation energy,  $E(\text{red})^* = E_{1/2}(\text{red}) + E_{00}$ ) [52] becomes more modest, the sensitivity to diene donor ability (ionization potential) rises sharply. Importantly, all substrates acted as quenchers (albeit some slowly) regardless of the range of excitation energies used ( $E_{00} = 68 - 90 \text{ kcal mol}^{-1}$ ), *i.e.* low photon energy can be compensated to a degree by redox driving force in the binding of a substrate in an EDA exciplex.

Direct evidence for exciplex formation between donor dienes and acceptor sensitizers was obtained in experiments using a non-polar solvent. Quenching in cyclohexane resulted in the appearance of a new emission which was weaker and red shifted relative to sensitizer fluorescence. Structureless long wavelength emission commonly ascribed to exciplexes [42] was not observed for quenching in a polar solvent, acetonitrile. This familiar pattern of results is currently interpreted [53, 53] in terms of non-ionic and radiative dissociation of a polar exciplex in a non-polar solvent and the completion of electron transfer to give free radical ions (ionic photodissociation) in polar solvent. The solvent effect in fact separates two regimes of redox photosensitization [55] involving polar and truly ionic exciplex chemistry.

Although the desired complexation and polarization of donor substrates was achieved, the formation of photoisomers via exciplexes could not be confirmed (quantum efficiencies for formation of 16, 18 and 20a are less than 0.01). Further investigation, however, revealed that significant photochemistry resulted from irradiation of the cyano-aromatics and dienes. Direct involvement of photosensitizer was determined by isolation of an addition product for the 19-cyanonaphthalene pair. The concentration dependence of the quantum yield of photoaddition (Fig. 5) matched the Stern-Volmer quenching profile ( $i/s = k_q\tau_0$ ), consistent with a common origin for emission and reaction in singlet cyanonaphthalene. Sensitizer disappearance was also observed (limiting quantum efficiencies were high, about 0.5) for other nitrile-diene pairs. Exciplex photoaddition, which is preferred in this series over exciplex isomerization, has precedent in several combinations of aromatic nitriles with alkenes [56].

The opposite regime of EDA exciplex formation has also been examined. Electron acceptor substrates 7 and 9 were used as quenchers of fluorescent donor sensitizers having a range of redox and absorption properties. The results (Table 4), although short of the correlation obtained in the other series, are again consistent with EDA interaction for quenching (7 is expected to be the better acceptor). For the norbornadienes quenching did not lead to exciplex emission in polar or non-polar solvents.

TABLE 4

Rate constants ( $k_q, M^{-1} s^{-1}$ ) for quenching of donor sensitizer fluorescence by electron acceptors in cyclohexane

Sensitizer	Acceptor	
	7	9
2-Methoxynaphthalene	$6.4 \times 10^9$	$5.2 \times 10^{10}$ <sup>a</sup>
2,6-Dimethoxynaphthalene	$9.7 \times 10^9$	$9.6 \times 10^9$
1,4-Dimethoxyanthracene	$6.4 \times 10^9$	$1.9 \times 10^9$
9,10-Dimethylanthracene	$1.0 \times 10^9$	$0.8 \times 10^9$

<sup>a</sup> Acceptor absorption overlaps donor emission slightly; Forster energy transfer is likely.

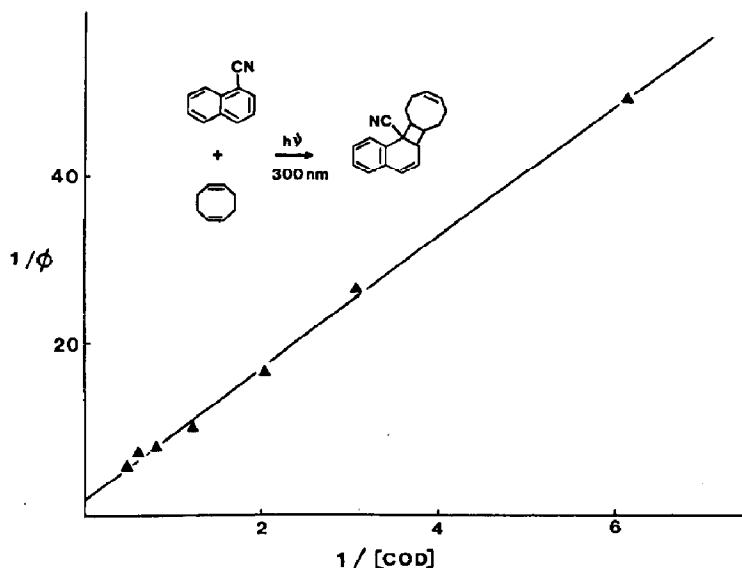


Fig. 5. The dependence of the quantum yield for the disappearance of 1-cyanonaphthalene on the concentration of 19 (solvent, cyclohexane; intercept  $1/\phi_{lim} = 1.7$ ).

Photochemical results (obtained so far only for 7) are more encouraging than the findings for the donor dienes. Isomerization of 7 in the presence of 2-methoxynaphthalene or 2,6-dimethoxynaphthalene is readily observed. According to the concentration profile for isomerization naphthalene singlets are responsible for photosensitization. Emission-reabsorption and the Forster energy transfer mechanism are ruled out for activation of 7 owing to the poor overlap of sensitizer emission and quencher absorption ( $\lambda_{max}(7)$ , 249 nm; Forster critical distance  $R_0$  and critical concentration [57] are 6.0 Å and 2.1 M respectively).

The efficiency of exciplex isomerization of 7 is respectable ( $\phi_{lim} \rightarrow 0.3$  for sensitization by 2-methoxynaphthalene), but the improvement in spectral sensitivity using the donor naphthalene sensitizers is modest. Unfortunately, exciplex isomerization does not accompany the quenching of the visible absorbing donor anthracenes. We suspect, but have not yet proved, that sensitizer addition may be important for these binary combinations of 7.

The demonstration that an energy storing isomerization can be driven via exciplexes is important and relates significantly to other sensitization strategies [31, 34, 35]. However, the more subtle requirements for the reaction (other than energetic criteria [52]), which would allow a wider choice of light absorbing agents, are not yet understood. Two features which are apparently important (for diene isomerization) are (1) the presence of reactive positions in the sensitizer which promote exciplex addition (over isomerization) and (2) the necessity for overlap of orbitals in diene substrates (greater in 7 than in 15 or in 19) for nascent transannular bonding within the lifetime of exciplexes (*i.e.* a requirement that the substrate

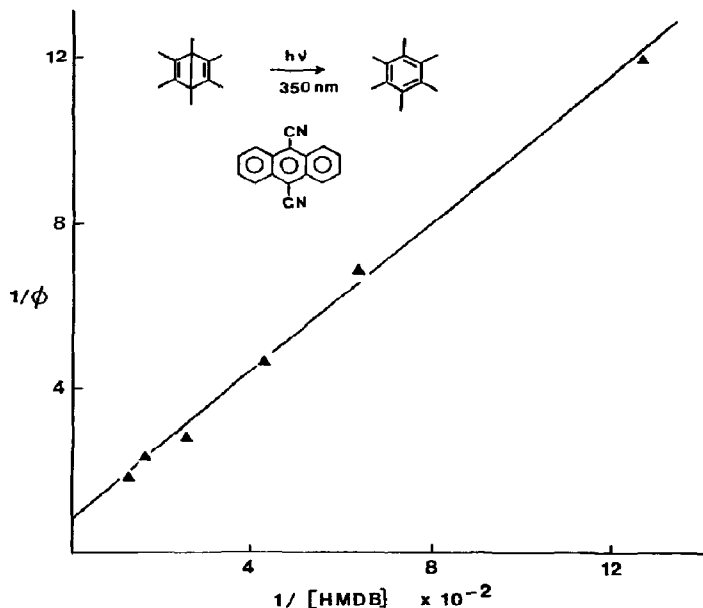


Fig. 6. The dependence of the quantum yield of isomerization on the concentration of HMDB (solvent, cyclohexane; irradiation at 350 nm).

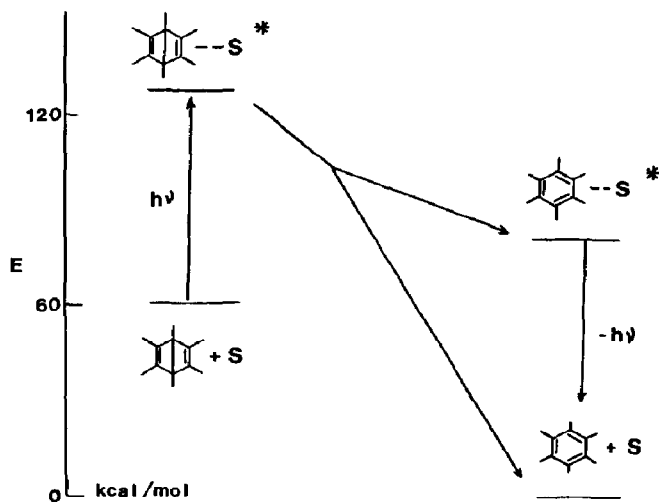


Fig. 7.

undergo only minor changes in geometry in reaching the isomeric product [44]).

A prototype exciplex isomerization has been studied in detail and the results are most informative. We have found that hexamethyldewarbenzene (HMDB) acts as a most effective quencher of aromatic nitrile fluorescence (Fig. 4, IP = 7.9 eV). Quenching is accompanied by molecular rearrange-

TABLE 5

Triplet sensitized isomerization of dimethyl-2,3-norbornadiene-dicarboxylate (7)<sup>a</sup>

Sensitizer	$E_T$ (kcal mol <sup>-1</sup> )	Wavelength (nm)	Quantum yield <sup>b</sup>
Benzophenone	68	366	0.6 (0.7)
Fluorenone	53	366	0.6
Camphorquinone	50	435	0.3
		480	0.3 (0.6)
Acridine orange	48	366	0.008 (0.2) <sup>c</sup>

<sup>a</sup>0.1 M 7 in benzene.<sup>b</sup>Values in parentheses are limiting quantum yields calculated by extrapolation ( $1/\phi$  vs.  $1/[\text{compound 7}]$ ) plots.<sup>c</sup>Values diminished by the low intersystem crossing yield (0.4) of the sensitizer.

ment, the quantum yield of which shows the necessary dependence of HMDB concentration (Fig. 6) (extrapolated quantum yields are near 1.0). Most unusual are the findings concerning exciplex emission which is observed on quenching 1-cyanonaphthalene (CN) and 1,4-dicyanobenzene (DCB). The new emission for these sensitizers paired with HMDB is identical to the exciplex fluorescence obtained on quenching the same sensitizers with hexamethylbenzene (24) ( $\lambda_{\text{max}}(\text{CN})$ , 373 nm;  $\lambda_{\text{max}}(\text{DCB})$ , 392 nm). Monitoring of HMB produced shows that trivial reabsorption-quenching is not responsible for the coincidence of spectra.

In a three-component experiment [58] in which 2,4-dimethyl-2,5-hexadiene (DMH) (a second electron donor) was used to quench exciplex emission, Stern-Volmer analysis revealed similar lifetimes for HMB and HMDB derived exciplex emission. Most importantly, CN-HMDB exciplex fluorescence could be quenched by DMH at concentrations where sensitized isomerization (HMDB  $\rightarrow$  HMB) was undiminished, showing that the emitting state could not be the source of rearrangement.

Our results are similar to those of Taylor [59] who examined the CN-HMDB pair in non-polar solvents and concluded that exciplex isomerization is adiabatic (*i.e.* that exciplex emission is a photoproduct (HMB exciplex) fluorescence). The mechanism (shown simply in Fig. 7) involves the partnership in an exciplex of the donor and acceptor which persists during molecular rearrangement of an excited surface! The results differ considerably from those reported by Evans [60] concerning exciplex isomerization of HMDB in a polar solvent (methanol). In this study exciplex emission was not observed and other evidence (limiting quantum yields greatly exceed 1) pointed to a light-induced chain mechanism for HMDB decomposition involving radical ions.

Relative yields of emission derived from HMDB and HMB and three acceptor sensitizers were determined. Data points at identical levels of sensitizer quenching gave relative yields for the adiabatic path (the portion of exciplex isomerization which "stores" energy!) Values ranged from 20 to

50% (highest for 1,4-dicyanoanthracene sensitizer) and appeared to depend more on the energy of the HMB exciplex (the adiabatic product) (determined from emission wavelength) than on  $E(\text{red})^*$  for the sensitizer (the redox driving force — exciplex binding). The behavior of HMDB exciplexes adds still more flavor to the continuing story of the adiabatic photochemistry of Dewar benzenes [61 - 63].

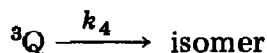
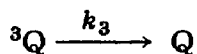
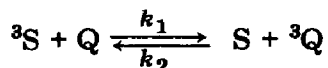
### 5.2. Triplet sensitized isomerization

The earliest studies [23, 39] of internal cycloaddition employed triplet photosensitizers to activate poorly absorbing substrates. Studies by Hammond and Murov [50] showed that the 1 → 2 isomerization could be driven by sensitizers with surprisingly low triplet energies (less than 60 kcal mol<sup>-1</sup>), albeit with diminished quantum efficiency. We have employed low energy sensitizers for the isomerization of 7 in order to show that the 500 nm absorption barrier can be crossed, *i.e.* that a significant portion of visible light can be used in driving a reaction with a large storage capacity (Table 3). Preliminary results are shown in Table 5 for photolysis in benzene. The effectiveness of sensitizers, camphorquinone and acridine orange, which absorb in the 400 - 550 nm region is most promising.

The norbornadienes constitute an interesting structure-reactivity series involving triplet sensitization. For the parent diene (1) sensitizer quenching rates and quantum yields for isomerization diminish for sensitizers below 65 kcal mol<sup>-1</sup> [16, 50] (equivalent to 440 nm light). The fall-off point for 3 appears to be about 58 kcal mol<sup>-1</sup> (equivalent to 498 nm light) according to a recent thorough study by Gorman and Rodgers [64]. Our results indicate that 7 can be driven with about 50 kcal mol<sup>-1</sup> of excitation energy and, in a formal sense, an effective use of 570 nm light. With camphorquinone as sensitizer the upper limit efficiency of storage of excitation energy ( $E_T = 50$  kcal mol<sup>-1</sup>) is 22% at the high quencher concentration limit. (For sensitizers with  $E_T \leq 50$  kcal mol<sup>-1</sup> quantum yields are sharply concentration dependent — see note to Table 5).

A feature of triplet sensitization which is potentially important for photon energy storage problems concerns the extent to which the transfer of excitation energy is endothermic. The energy of the lowest triplet of 1 and the other norbornadienes is not known (several rather high estimates — greater than 70 kcal mol<sup>-1</sup> — have been obtained) [65, 66]. Simple considerations of singlet-triplet separation for 1, 3 and 7 lead one to suspect that triplet levels for these substrates are not as low as 65, 58 and 50 kcal mol<sup>-1</sup> (near the fall-off regions previously noted). Since triplet exciplexes appear not to be involved in isomerization [63], it is most likely that norbornadiene rearrangement is a relatively efficient thermally activated process for a host of sensitizers having insufficient energy.

Significant amounts of thermal energy can in principle be used in triplet sensitization in order to boost sensitizer triplet levels. For kinetic analysis the classical energy transfer scheme [67] need only be modified to include a back transfer step:



The amount of energy which is allowed in endothermic transfer is readily computed according to Sandros [68] using the equation

$$\Delta E_T = \frac{\ln k_2/k_1}{RT}$$

where  $k_2$  is assumed to be the diffusion controlled rate constant (about  $10^{10} \text{ M}^{-1} \text{ s}^{-1}$ ).

Large energy separations are possible [68, 69] if fast reacting acceptor triplets limit the amount of back transfer ( $k_4 \gg k_2$ ) and if very long lived sensitizers permit low values of  $k_1$ . In the case where fast acceptor triplet reaction follows irreversible endothermic transfer (the internal cycloadditions may be a case in point) the energy separation takes an Arrhenius form identical to the Sandros equation above. Sensitizer lifetime and the concentration of the acceptor remain important representing competing sensitizer radiationless decay and biomolecular energy transfer quenching.

The *thermal upconversion of sensitizer triplets* could be an important strategy in efficient use of solar energy to drive isomerization reactions.  $\Delta E_T$  values range between 7 and 13 kcal mol<sup>-1</sup> for temperatures between 25 °C and 100 °C and  $\Delta \ln k$  values of 5 - 7. These energy differences with lower excitation energy requirements translate into large intrusions into the visible for photosensitizers absorbing in the 500 - 600 nm region. Thermal upconversion allows use of the large segment of the solar insolation spectrum which is not optically absorbed but heats the photoactive medium. The measurement of the temperature dependence of quantum yields of reactions driven by long lived low energy triplet sensitizers deserves considerable attention in order to determine to what extent the elevated temperatures of solar collectors can improve photochemical efficiencies.

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