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ORGANIC PHOTOCHEMICAL STORAGE OF SOLAR ENERGY

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ABSTRACT

The prospects for driving endoergic reactions of simple, relatively abundant organic chemicals by photochemical means have been examined. Strategies for utilization of light of varying wavelength involve sensitization mechanisms which depend on the redox properties of energy storing substrates and photosensitizers. Of principal interest is valence isomerization which can be induced by electron donor-acceptor interaction between substrate and sensitizer in an excited complex or exciplex.

Completed photophysical studies show that potentially isomerizable substrates efficiently intercept redox photosensitizers. The quenching of emission of electron acceptor sensitizers by non conjugated hydrocarbon dienes is indeed a function of the reduction potential of the acceptors (a series of aromatics with varying absorption characteristics) and the oxidation potentials of the substrates. Electron deficient dienes have been shown alternatively to be efficient quenchers of excited donor sensitizers. That exciplexes are formed between isomerizable substrates and donor or acceptor sensitizers has been confirmed by emission spectroscopy. The rearrangement of hexamethyldewarbenzene to hexamethylbenzene, a model exciplex isomerization has been examined in some detail.

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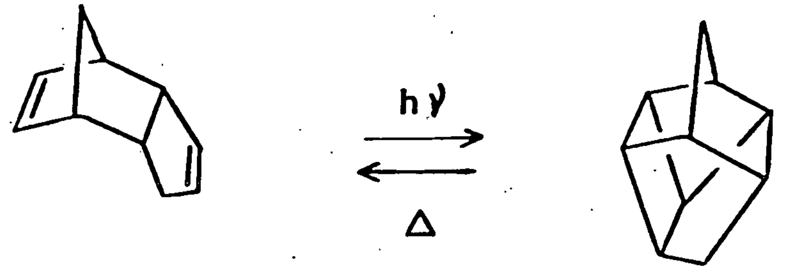
INTRODUCTION

Criteria for the use of organic chemicals in reversible photochemical systems which store radiant energy as latent heat have been previously described.[1] Applications of these light driven cyclic systems could be as modest as the development of inexpensive devices for the measurement of solar intensity (color test pyranometers) or as ambitious as the use of an organic fluid to collect and photochemically store solar energy on a large scale.[2] If the latter objective is to be met, efficient photochemical activity for some abundant chemical available on an industrial scale must be demonstrated. A principal objective of our work is the examination of potentially energy storing photoreactions of several inexpensive chemicals with emphasis on sensitization of the energy storage step to visible light.

Fundamental difficulties with choice industrial chemicals such as dicyclopentadiene (**1**) and cyclooctadiene (**3**) are their generally modest chemical properties and their lack of low lying excited states (e.g., isomerizations **1** → **2** and **3** → **4** have been shown to occur with short wavelength uv light only). An important goal is the development of new sensitization schemes not involving classical transfer of excitation energy. Such a mechanism was described in detail in our original proposal and is outlined in Scheme 1. The mechanism depends for driving force on the attractive interaction of an electron acceptor and a non-conjugated diene system. This polarization is expected to induce transannular bonding to give valence isomer. The norbornadiene-quadricyclene photoisomerization (**5** → **6**, R = H) which has been shown[3] recently to occur on complexation with transition metals may employ such a mechanism.



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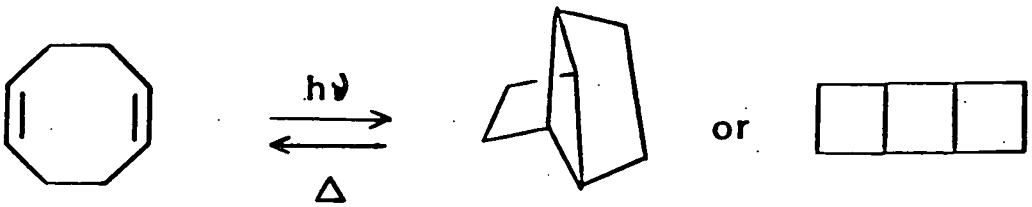
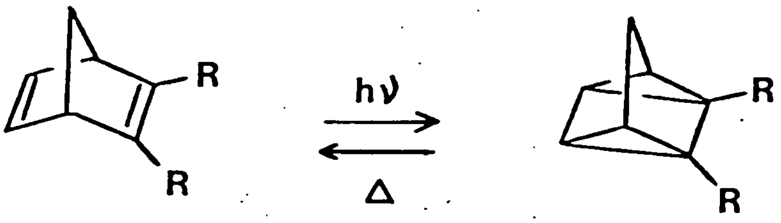
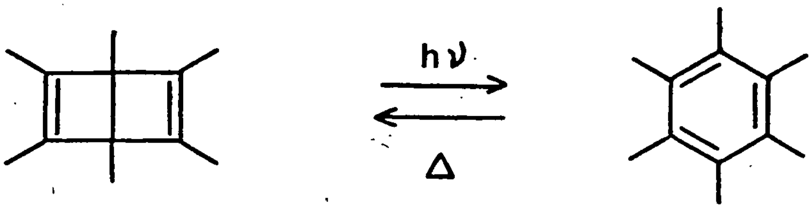


3 4a 4b

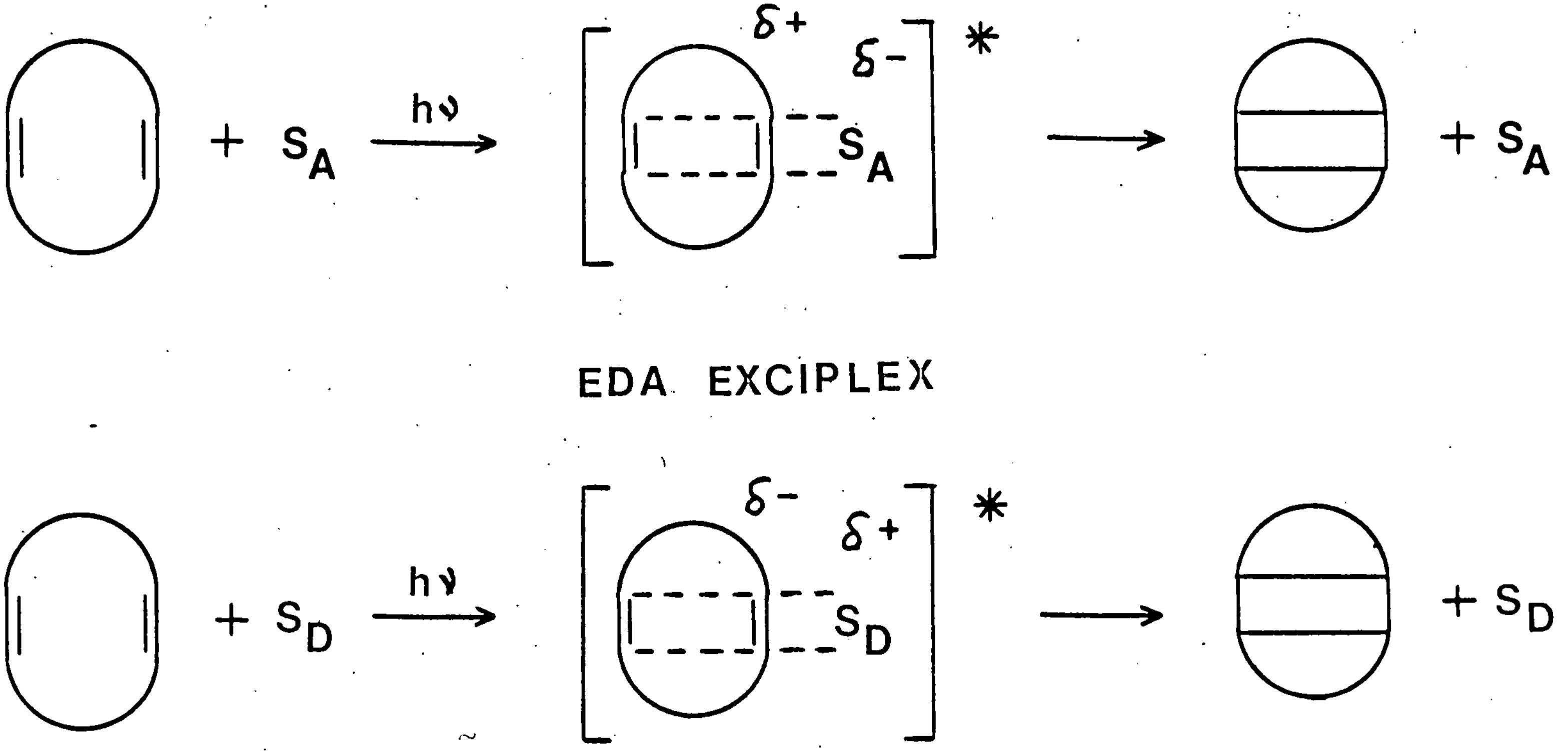


5 R = CO_2Me 6



7 8

SCHEME 1



PHOTOPHYSICAL MEASUREMENTS

Electron Donor Substrates. The first step in the evaluation of the industrial dienes and similar substrates is the demonstration that these rather unreactive chemicals can efficiently intercept excited photosensitizers. Several dienes capable of acting as modest electron donors 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 vs. SCE) and their varied use of ultraviolet and visible light (λ_{max} 290 - 400 nm). These sensitizers are also highly fluorescent so that the interception of excited states by the quencher dienes could be assayed spectrophotometrically. Substantial electron transfer in a donor-acceptor complex of sensitizers and substrates was judged to be favorable according to the Weller equation,[4]

$$\Delta G = E_{1/2}(ox) - E_{1/2}(red) - E_{00} - C$$

which relates the free energy for electron exchange within a complex to ground state redox properties, sensitizer excitation energy, and a solvent parameter.

Analysis of the quenching results (Table 1) shows that the dienes in fact intercept the fluorescent state of the acceptor sensitizers with moderate efficiency. The recorded values are quenching constants computed from the slopes of Stern-Volmer plots of relative emission yields and quencher concentration. The electron donor ability of the dienes is indicated by experimental ionization potentials and the electron acceptor ability of the sensitizers is given by ground state reduction potentials. The dependence of quenching rate on structure for substrate sensitizer pairs is illustrated in Figure 1. Clearly,

Table 1. Rate Constants (k_q, x 10^{-9} M^{-1} sec^{-1}) for Quenching of the Fluorescence of Electron Acceptor Sensitizers in Cyclohexane

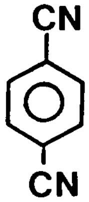
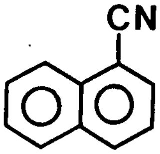
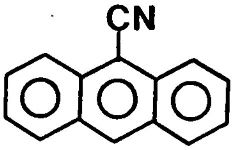
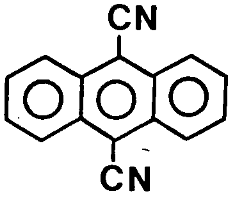
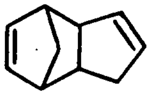
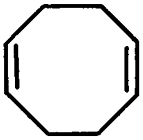
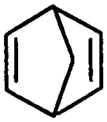
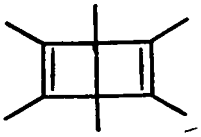
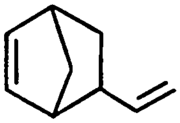
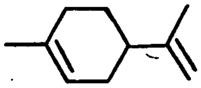
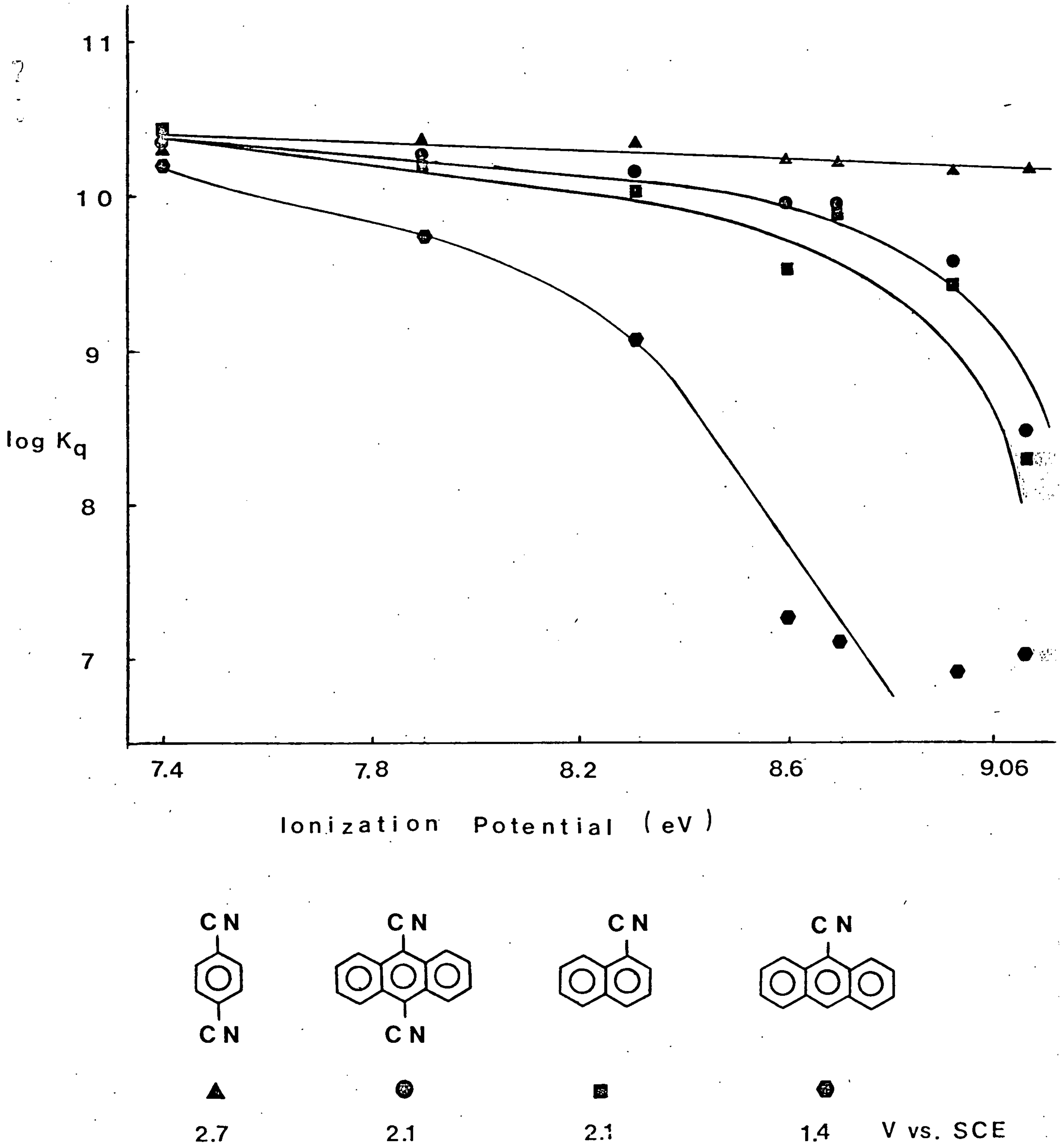
Substrate		Sensitizers			
(I.P., eV)					
 8.93	(**1**)	5.2	0.049	0.009	---
 9.06	(**3**)	5.9	0.009	---	---
 8.70	(**5**, R = H)	6.1	0.095	0.008	0.014
 7.90	(**7**)	10.8	4.79	0.12	7.33
 8.90		6.4	0.029	---	0.005
 8.60		6.8	0.18	0.027	0.010

FIGURE 1



$$E^{*}_{red} = E_{1/2}(red) + E_{o,o}$$

the quenching phenomenon involves the expected electron donor-acceptor interaction. Note that for the most potent sensitizers quenching rates are at a maximum (near the diffusion limit, $K_q \sim 10^{10}$ M^{-1} sec^{-1}) and that as sensitizer acceptor potential (a function of ground state reduction potential and excitation, $E(red)* = E_{1/2}(red) + E_{00}$) becomes more modest, the sensitivity to diene donor ability is revealed.

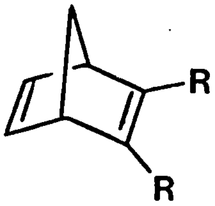
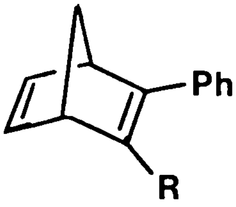
In addition to showing that the emission of acceptor sensitizers is quenched by isomerizable dienes, it is important to show that bona fide exciplexes (of the type proposed in Scheme 1) result from the quenching process. Direct evidence for diene-acceptor exciplexes has been obtained. The quenching of sensitizer fluorescence is accompanied by the appearance of new emission (broad structureless bands at longer wavelength). We assign these new emissions (Table 2) to exciplex fluorescence. Although exciplex emission has been observed with increasing regularity for organic systems,[5] our measurements are the first involving sensitizer complexes with substrates capable of isomerization.

Electron Acceptor Substrates. Two norbornadiene derivatives (e.g., $\underset{\sim}{5}$) have been synthesized and their ability as redox quenchers determined. A group of electron donor sensitizers was selected for quenching studies. These fluorophores represented a range of donor ability (oxidation potentials, $E_{1/2}(ox) = 0.9 - 1.4$ V vs. SCE) and again a range of light absorption capability (λ_{max} 320 - 450 nm). The results of emission quenching for the donor sensitizers and acceptor substrates are shown in Table 3. The quenching constants obtained by Stern-Volmer analysis are uniformly high indicating that sensitizer-substrate interaction is especially favorable. Emitting exciplexes were not observed for donor sensitizer quenching, suggesting that a rapid photochemical decay channel exists for these systems.

Table 2. Exciplex emission maxima for acceptor sensitizers and donor dienes in Cyclohexane Solution.

	Sensitizer (λ_{max}, nm)	
Diene	p-dicyanobenzene	1-cyanonaphthalene
dicyclopentadiene (**1**)	310	tail
cyclooctadiene (**3**)	370	394
hexamethyldewarbenzene (**7**)	393	363
hexmethylbenzene (**8**)	393	367
norbornadiene (**5**, R = H)	--	345
5-vinylnorbornene	--	345

Table 3. Rate Constants for Quenching of Electron Donor Sensitizers by Electron Acceptor Substrates in Cyclohexane.

	Donor (k_q, M^{-1} sec^{-1})	
Sensitizer	 R = CO_2Me	
2-methoxynaphthalene	6.4×10^9	5.2×10^{10}
2,6-dimethoxynaphthalene	9.7×10^9	9.6×10^9
1,4-dimethoxyanthracene	6.4×10^9	1.9×10^9
9,10-dimethylanthracene	1.0×10^9	0.8×10^9

Hexamethyldewarbenzene Isomerization. The quenching of acceptor sensitizer fluorescence by hexamethyldewarbenzene (**7**) gave unusual results and was studied in somewhat more detail. It appeared from photophysical measurements alone that exciplex isomerization occurs for this system. The exciplex emission from **7** - sensitizer pairs has an unusual feature - it is identical to the new emission which appears when sensitizers are quenched with hexamethylbenzene (**8**), the valence isomer of **7**!

We have shown independently that quenching by **7** in fact leads to **8**, a true redox sensitization. The results raise the novel possibility that exciplex formation induces ring opening of **7** to both ground and excited (still complexed) hexamethylbenzene.

Photochemical Studies. The valence isomers of all isomerizable substrates have been prepared by conventional ultraviolet photolysis or other means. Development of analytical methods for rapid and thorough assay of valence isomerization induced by redox sensitization is now underway.

CONCLUSIONS

An early objective of the program has been reached. Chemicals selected on the basis of their availability and photochemical energy storage potential have been shown to form complexes with photosensitizers having widely different light absorption properties. The binding of sensitizers and substrates appears to depend on electron donor-acceptor interaction (the redox properties of sensitizer-substrate pairs). The formation of exciplexes is efficient for both donor and acceptor substrates and all potentially isomerizable substrates have been complexed with one or more sensitizers in one of the two donor-acceptor regimes.

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(3) C. Kutal, D.P. Schwendiman, and P. Grutsch, *Solar Energy*, **19**, 651 (1977).

(4) D. Rehm and A. Weller, *Israel J. Chem*., **8**, 259 (1970).

(5) M.S. Gordon and W.R. Ware, Ed., "The Exciplex," Academic Press, New York, 1975.