

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

A BS

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER Summary Report	2. GOVT ACCESSION NO. AD-103411	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) The Storage of Solar Energy in Small Rings	5. TYPE OF REPORT & PERIOD COVERED Technical, 5/1/74 - 10/31/76	
7. AUTHOR(s) Guilford Jones, II	6. PERFORMING ORG. REPORT NUMBER	
PERFORMING ORGANIZATION NAME AND ADDRESS Department of Chemistry Boston University Boston, Massachusetts 02215	8. CONTRACT OR GRANT NUMBER(s) N00014-67-A-0280-0003 ARPA Order-2721	
CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research 800 North Quincy Street Arlington, Virginia 22217	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS ARPA Order No. 2721/1-4-74 Program Code No. 4F10	
MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) Summary rept. 1 May 74 - 31 Oct 76	12. REPORT DATE April 15, 1976	
	13. NUMBER OF PAGES 12/24	
	15. SECURITY CLASS. (of this report) Unclassified	
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE	
DISTRIBUTION STATEMENT (of this Report) Reproduction in whole or in part is permitted for any purpose of the United States Government. Approved for public release; distribution unlimited		
DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) photochemical conversion of solar energy, valence isomerization, homogeneous catalysis, photo- and thermal chemistry		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) A number of valence photoisomerizations which can be driven by ultraviolet and visible light (300 - 500 nm) have been examined. These isomerizations have quantum efficiencies ranging as high as 0.4 and store as much as 10% of absorbed radiant energy as chemical potential energy (latent heat). The isomerizations can be reversed efficiently in thermal reactions at 40 - 180°. Luminescence and kinetics studies reveal factors which control the efficiencies of cyclically coupled photochemical and thermal reactions.		

AD A103411

LEVEL 1

DTIC ELECTED AUG 27 1981

X-2 TAB 19118

DD FORM 1473 1 JAN 73

EDITION OF 1 NOV 65 IS OBSOLETE S/N 0102-014-6601

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

COPY FILE DTC

401003

Joe

OFFICE OF NAVAL RESEARCH

Contract N00014-67-A-0280-003

Sponsored by the
Advanced Research Projects Agency
ARPA Order No. 2721

SUMMARY REPORT

The Storage of Solar Energy in Small Rings

by

Guilford Jones, II

Department of Chemistry
Boston University
Boston, Massachusetts 02215

April 15, 1976

Reproduction in whole or in part is permitted for any purpose
of the United States Government

Approved for public release; distribution unlimited

The views and conclusions contained in this document are those
of the authors and should not be interpreted as necessarily
representing the official policies, either expressed or implied,
of the Advanced Research Projects Agency of the U.S. Government.

TABLE OF CONTENTS

	<u>Page</u>
I. Introduction.....	1
II. Work Completed - Capsule Reports.....	3
III. Overview.....	11
IV. Appendix.....	16
V. References.....	19
VI. Publications and Presentations Citing ARPA Support.....	20

Accession For	
NTIS GRA&I	<input checked="" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A	

THE STORAGE OF SOLAR ENERGY IN SMALL RINGS

ABSTRACT

Criteria for and results concerning the use of organic materials in the photochemical conversion of solar energy are summarized. Target molecules are shown to generally undergo endoergic valence isomerization upon irradiation with near ultraviolet and visible light (300 - 500 nm). Photoisomers are kinetically stable but revert to starting materials under thermal activation with or without a catalyst. Considerable variation is found in the quantum efficiencies, light absorption properties, and ease of retrieval of stored energy for several valence isomeric pairs. In selected systems 5 - 10% of absorbed photon energy is stored as chemical potential energy.

Using emission and kinetics data for the isomerization systems, an evaluation of mechanism for energy storing photoreactions is presented. A useful generalization obtains: quantum efficiencies for reactions which store photon (radiant) energy in relatively stable products will be determined by the chemistry of intermediates formed after the absorption of light. Emphasis on this feature in the design of new and more efficient systems is called for.

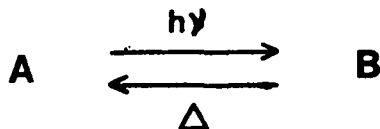
Other developments related to the study of organic isomerization systems are noted, including their application as photorefractive holographic materials to be used in optical memory devices.

I. INTRODUCTION

Studies directed to the application of organic photochemistry in the utilization of solar energy have been initiated. The object of the work is to assess organic materials for their ability to undergo efficient photochemical reaction on absorption of atmospherically filtered solar radiation. Such reactions, driven by near ultraviolet and visible light, should be significantly endoergic and should give a reasonably stable isomeric product which can be reverted in a controlled thermal reaction to the original photoactive substance. In this hypothetical cyclic system, electronic excitation (radiant) energy is stored as chemical potential energy (as latent heat). Unlike sensible heat storage, this kind of energy retention does not require insulation as a critical parameter of efficiency and offers the possibility of medium to long range (days, weeks) storage of solar energy. Studies on target molecules produce information (through efficiency monitoring and maximization) regarding the ideal photochemical reaction for energy conversion.

The plan is to produce a working substance for use in a solar-thermal energy conversion unit. Alternative smaller scale uses of reversible organic photoreactions include the wavelength-sensitive monitoring of solar flux (development of inexpensive color test pyranometers).

Below are listed well recognized¹ imperatives for the photochemical conversion of solar energy along with suggestions and observations relevant to applications in organic photochemistry. These generalizations are directed to the cyclic system:



Imperative

1. Reactant A must absorb most of the visible and ultraviolet (filtered) solar emission
2. Photoproduct B must not appreciably absorb solar emission.
3. The quantum yield for reaction $A \rightarrow B$ must be near unity.
4. The reaction $A \rightarrow B$ must have a large positive ground state enthalpy.
5. Photoproduct B must be thermally (kinetically) stable.

Observation

Monophotonic photochemistry at >700 nm is quite unlikely; the useful range = $300 - 700$ nm ($40 - 90$ kcal/Einstein), representing $\sim 50\%$ of total solar energy.

Reaction should be photochromic with a decrease in the degree or continuity of unsaturation in A.

Intramolecular reactions should be generally favored over intermolecular reactions; highly luminescent chromophores should be avoided.

Selected valence photoisomerizations with $\Delta H = 10 - 30$ kcal/mol are common; reactions should be selected in which small rings are generated and/or aromaticity disrupted; such reactions are usually photochromic.

(Geometric photoisomerizations store little energy and are not significantly photochromic.)

Orbital topology restrictions for selected isomerizations enhance $A \rightarrow B$ ($h\nu$) and inhibit $B \rightarrow A$ (thermal); the most useful temperature range for reversion = $50 - 100^\circ$.

- | | |
|--|--|
| 6. A chemical control external to the cycle $A \rightleftharpoons B$ may be used to initiate $B \rightarrow A$. | Metal or acid catalysis of isomerizations is well known, but efficiencies are not uniform and readily predictable. |
| 7. Reactants A (B) must be inexpensive. | Materials should be commercially available or prepared in short conventional syntheses; costs of manufacture are difficult to project; the program should not be overly limited by this criterion initially. |

It is important to understand the blend of factors which in principle enable organic materials to store electronic excitation energy more efficiently and more permanently than inorganic substances. Properly selected organic systems have significant storage enthalpies because bond angle strain energies (~ 25 kcal/mol per small ring generated) and resonance energies, potentially gained and lost, respectively, during photoisomerization, are large. Additionally, orbital topology factors, understood in terms of selection rules governing potentially concerted thermal reactions², quite commonly confer on photoproducts of extreme thermodynamic instability, surprising kinetic stability in the absence of an appropriate catalyst. Besides these special features for organic materials, other advantages which would accrue to a photochemical solar-thermal energy conversion system are lower solar collector cost and weight, cloudy-day effectiveness, smaller storage area and reduced insulation, and storage capability at room temperature.³

II. WORK COMPLETED

In view of the above imperatives and observations, a number of valence isomerizations were examined during the first eighteen months of operation. The

results concerning four classes of compounds are summarized in the following Capsule Reports. The results are organized under symbols P (photochromism and absorption properties), ϕ (quantum and chemical yield for photolysis), H (enthalpy change in the ground state, A \rightarrow B), T (temperature range and kinetic parameters for reversion), and \$ (availability of system, reflecting nominally the cost). A final assessment, of photon energy storage efficiency where sufficient data are available, is the calculation of "Q value" using a modification of the relationship suggested by Calvert^{1a}:

$$Q = \frac{\Delta H \times \phi \times 100}{E_{h\nu}}$$

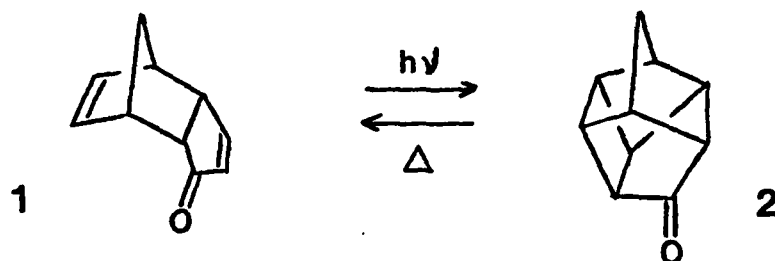
where ΔH is the ground state enthalpy change (A \rightarrow B) (kcal/mol), ϕ is quantum efficiency, and $E_{h\nu}$ is photon energy (kcal/Einstein) (an average value for useable wavelengths of light).

The first report describes the photoisomerization of a ketone derivative of dicyclopentadiene (1), the attractive feature of which was the previously measured⁴ sizeable storage enthalpy. Although 1 does not absorb in the visible, chromophore modification was a straightforward option, if a good quantum yield and a facility for the back reaction could have been demonstrated. The subject of the second report is 1-ethoxycarbonyl-1H-azepine (5), whose photochromic isomerization to a strained bicyclic derivative and its thermal reverse were reported in qualitative but not quantitative detail.⁵ The third report involves pleadiene (7), a hydrocarbon which absorbs strongly in the visible and which was reported as a product of thermal reaction from its strained valence isomer 8.⁶ Its photochemistry had not been previously examined.

The final report includes data for anthracene derivatives, a class of compounds about which there has been traditional speculation¹ concerning energy storage capability. Our new approach to this system was to link anthracene

moieties into a single molecule in various ways in order to improve the quantum efficiency for photo-cycloaddition of the anthracene units, to raise the endothermicity of the photochemical step through the formation of new small rings required by the linkage, and to enhance absorption in the visible by enforcing chromophore interaction. Reports concerning such system have appeared⁷, but quantitative data have not been available.

CAPSULE REPORT I (For details see Technical Report No. 1)



P $\lambda_{\max} (1) = 330 \text{ nm}$, $\lambda_{\max} (2) = <300 \text{ nm}$; useful range = 300 - 380 nm.

ϕ $\phi = 0.40$ in solution (330 - 380 nm); >99% chemical yield.

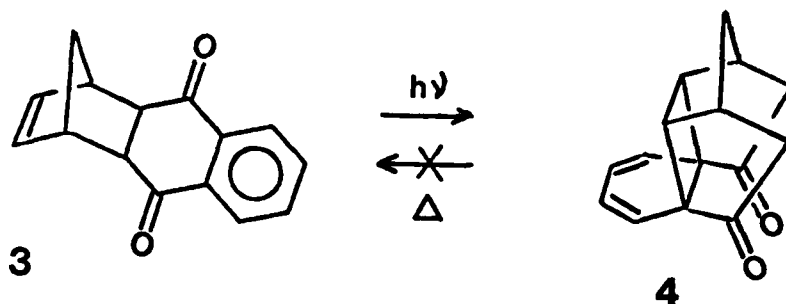
H $\Delta H = 16.4 \text{ kcal/mol}$, measured by heat of combustion.⁴

T 2 stable to 295°; reversion catalyzed by Rh(I) complexes.

(140 - 180°); good yield for catalyzed reversion but catalysts degrade on cycling.

\$ Two-step preparation of 1 from dicyclopentadiene; similar chemical available on industrial scale at \$0.50/lb.

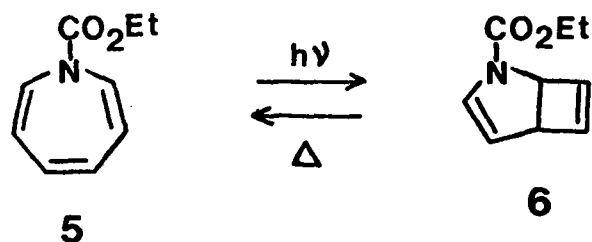
Assessment. P, ϕ , H, \$ and the stability of 2 encourage an extension to a similar system absorbing in the visible. Q = 8%, which compares favorably with inorganic photochemical storage systems^{2a}. However, metal catalysts are unsuited for the reversion reaction and acid catalysts examined so far are also not sufficiently effective. A similar photoisomerization system ($3 \rightarrow 4$) which shows remarkable quantum efficiency ($\phi = 1.0$ ⁸), was investigated; reversion $4 \rightarrow 3$ could not be affected cleanly on heating with or without catalyst.



Basic research contributions. The kinetics of Rh(I) catalysis were examined in detail⁹, resulting in a ranking of transition metal complexes for reactions of the type $2 \rightarrow 1$. The rate of catalyzed isomerization of 2 was compared with other "cage" compounds. The catalyzed exothermic opening of small rings was shown to be less facile than previously expected, with 2 representing a substrate limit for catalyzed reversion.

The photochemical kinetics of $1 \rightarrow 2$ were examined.¹⁰ Quenching studies showed that the lifetime for the reactive triplet excited state of 1 is extremely short and temperature dependent. To accommodate lifetime and quantum yield data a mechanism is required in which an intermediate is interposed between triplet 1 and 2 . It is partitioning of this transient species which determines quantum yield.

CAPSULE REPORT II (For details, see Technical Report No. 2)



P $\lambda_{\text{max}} (\overset{\sim}{5}) = 330 \text{ nm}$ (tails to 500 nm, orange in color); $\overset{\sim}{6}$ absorbs at $<300 \text{ nm}$; useful range = 300 - 460 nm.

\emptyset $\emptyset = 0.013$ in solution (330 - 380 nm); chemical yield $>97\%$.

H 10.4 kcal/mol, measured by differential scanning calorimetry.

T Uncatalyzed reversion occurs cleanly at 113 - 143°;

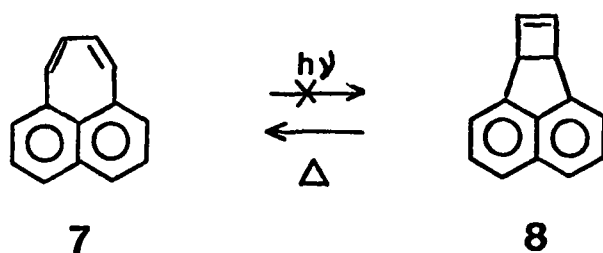
$E_a = 28.7 \text{ kcal/mol}$.

\$ One-step preparation of $\overset{\sim}{5}$ from benzene and ethyl azidoformate.

Assessment. System displays suitable photochromism and can be driven readily on a small scale with sunlight or with laser emission (458 nm). The uncatalyzed reversion requires suitable temperatures and the system can be cycled in sequential photolysis - pyrolysis steps. However, the quantum efficiency is unacceptable; $Q = 0.21\%$. Also, some system degradation occurs over ten energy storage cycles.

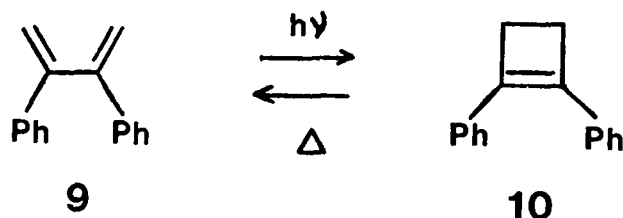
Basic research contributions. The excited state responsible for isomerization $\overset{\sim}{5} \rightarrow \overset{\sim}{6}$ was identified as the $n, \pi\pi^*$ singlet. Excited triplet states of $\overset{\sim}{5}$ are unreactive. On the basis of absorption, sensitization, and quenching data and in the absence of luminescence from $\overset{\sim}{5}$, energies of the low lying excited states were determined ($S_1 = 60 \pm 1 \text{ kcal/mol}$, $T_1 = 55 \pm 1 \text{ kcal/mol}$). A mechanism is proposed in which an intermediate is involved for both photolysis of $\overset{\sim}{5}$ and pyrolysis of $\overset{\sim}{6}$.¹¹

CAPSULE REPORT III

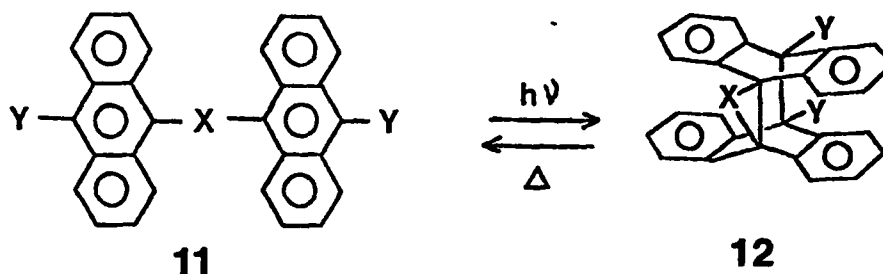


- P λ absorbs strongly at 300 - 520 nm (red in color),
 λ absorbs at <320 nm (colorless).
- ϕ $\phi = <0.01$ (in benzene, 330 - 380 nm).
- H unknown, estimated 10 - 20 kcal/mol by comparison with similar systems.
- T 200°, high yield.⁶
- \$ Three-step preparation from acenaphthalene and maleic anhydride; procedure somewhat tedious.

Assessment. Photoisomerization could not be affected under several sets of conditions. Although absorption and thermal parameters for the system are acceptable, a strategy for promoting the photoreaction is not obvious. A survey of isomerizations of aromatic hydrocarbons reveals that quantum efficiencies are generally low. For example, the endoergic, thermally reversible¹² isomerization $9 \rightarrow 10$ was brought about by irradiation at 254 nm, but $\phi = 0.025$. A low triplet energy is expected for 9 , but visible absorbing and other photosensitizers did not promote valence isomerization.



CAPSULE REPORT IV



- a: X = CH₂CH₂, Y = H
- b: X = CH₂CH₂, Y = CH₃
- c: X = CH₂, Y = H
- d: X = CHO, Y = H
- e: X = CH₂CH₂, Y = CH₂CH₂

P 11a - 11d absorb strongly at 350 - 420 nm (yellow in color), 11e absorbs strongly at 400 - 450 nm (tailing to 520 nm, orange in color), 12 absorb at <300 nm (colorless).

Ø see table for isomerization and fluorescence quantum yield data (benzene solution); chemical yields for photoisomerization are >99%.

H see table for enthalpy values (kcal/mol) determined by DSC for thermal back reaction in the solid state.

T see table for temperature ranges for back reaction ($\tau_{1/2}$ = 30 - 120 min).

§ Typical syntheses require 3 - 4 steps for anthracene, anthraquinone, or anthrone starting materials (yields good to excellent).

Table I. Photo-thermal Data for Isomerizations $11 \rightleftharpoons 12$

	ϕ_{isom}	ϕ_{flr}	ΔH	Q(%)	T(°C)
a	0.26	0.16	14.6	5.4	120-135
b	0.05	0.14			
c	0.15	0.06	17.3	3.7	130-150
d	0.29	0.02			
e	0.36	< 0.001	8.5	5.1	60-70

Assessment. The reactions $11 \rightarrow 12$ are nicely photochromic and $11e$ absorbs significantly in the visible. The linking of the anthracene units was successful in enhancing quantum efficiencies for cycloaddition (for comparison, $\phi = 0.1$ is the maximum efficiency for intermolecular cycloaddition of 9-methylanthracene and, for this model, fluorescence is more competitive, $\phi = 0.5$). Storage enthalpies are good but somewhat lower than anticipated on the basis of the strain energy gained and aromaticity lost in photoisomerization (for more details, see Other New Developments, part 1). (Q values are shown in Table I.) Reversion reactions occur cleanly at reasonable temperatures without a catalyst present. The systems may be cycled moderately well; generally after thirty successive photochemical and thermal steps, decomposition is significant. Relatively low solubility of 11 and 12 in common solvents is a disadvantage for the system. On the other hand, solvent can be avoided since anthracenes 11 can be incorporated in polymeric films. In early experiments this solid state alternative appears promising; $11d$ has been shown to efficiently and reversibly photoisomerize in polymethyl methacrylate.

Basic research contributions. The most complete set of photophysical and photochemical data concerning linked aromatic systems has been provided for the

anthracenes in our study. Fluorescence quantum yield and lifetime measurements point to an unusually rapid decay of singlet excited states for 11 . This decay channel which is fostered by the linking of anthracene chromophores is more likely the result of intramolecular photochemical reaction than the result of introduction of a new or enhanced mode of unreactive radiationless decay (e.g., a higher rate of intersystem crossing). This reactive decay channel cannot involve direct formation of photoisomer since the quantum efficiency of isomerization is <1 . A mechanism involving formation of an intermediate following excitation is consistent with the results. Partitioning of this intermediate between 11 and 12 determines quantum efficiency for the system.

III. OVERVIEW

Principal Findings. All of the organic isomerization systems studied so far satisfy at least two of the five criteria for solar energy conversion: absorption and photochromism (P), quantum efficiency (ϕ), storage enthalpy (H), back reaction suitability (T), and material availability ($\$$). Systems $1,2$ and $3,4$ meet three of the requirements (ϕ , H, and $\$$) quite well, could be modified in order to utilize more of the solar spectrum (satisfying criterion P), but are principally deficient in not having a clean back reaction under catalysis conditions. System $5,6$ shows promise on bases other than its quantum efficiency. The most successful systems to date are the linked anthracenes (11 , 12). System $11e,12e$ is the best of these, meeting to a significant degree all five criteria. Where cycling experiments could be performed ($5,6$ and $11,12$), an order of magnitude for fatigue of the systems has been established: 10 - 30 cycles are practical; as many as 100 cycles appears unachievable for the isomerizations examined so far.

Photon energy conversion efficiencies (Q values) determined from experimental data for $1,2$ (8%) and for selected systems, 11 , 12 (~5%) and estimated for $3,4$ (25%) compare favorably with values calculated for inorganic photochemical storage

systems.^{1a} This result is due principally to the comparatively large storage enthalpies which properly selected organic systems display. A most encouraging aspect of our findings is that this extreme thermodynamic instability in photo-products is matched with good kinetic stability (relatively high temperatures required for back reactions); i.e., a significant fraction of radiant energy can be almost indefinitely stored as chemical potential energy. Although this feature of organic isomerization systems has been known for some time and is theoretically understood², the growing number of examples for which the phenomenon is experimentally verified warrants further investigation in terms of its application.

Mechanistic studies, completed as an ancillary part of the program, have been valuable (note Basic research contributions in the Capsule Reports). A mechanistic pattern has developed which will aid in designing new systems (see Appendix for details). In particular, our findings point to the partitioning of intermediates formed after absorption of radiation (and not to the partitioning of an initially formed excited state) as the factor which determines quantum efficiency of isomerization.

Prospectus. Some further development of the linked anthracene systems(11, 12) is anticipated. Experiments will be directed to achieving greater use of visible light in driving photoisomerizations and to finding a catalyst which will allow a cleaner back reaction (but still at a useful temperature) and less fatigue.

Our initial purpose was to conduct a broad survey of organic isomerizations. A more convincing demonstration of energy conversion, than that achieved in systems examined so far, may be found in other isomerizations which employ different light absorbing units and somewhat different reaction schemes. We will extend our survey to systems which employ the biacetyl, quinone, and thione chromophores (expected photoactivity in the 450 - 500, 500 - 550, and 550 - 650 nm regions, respectively). The aforementioned generality concerning isomerization mechanisms (see Appendix) which evolved from our early work, will be an important aspect of design for the new systems. Catalysis of the back reaction, important for controlling energy

retrieval and reducing any energy expenditure involved in recovering stored heat, will be emphasized.

In light of our early experience it is prudent to update our perspective on the application of organic isomerizations in the photochemical conversion of solar energy:

How much of the solar spectrum can be employed to drive efficiently (with single photons) an endoergic isomerization?

Probably 40% (on an energy basis) (300 - 600 nm). Modestly efficient use of the 300 - 500 range already demonstrated.

How much of absorbed solar energy can be stored?

Half of absorbed photon energy (avg., 55 kcal/Einstein) probably can be stored (27 kcal/mol). Storage enthalpies in the 10 - 20 kcal/mol range already documented.

What is the energy density of organic photoproducts?

See Table II for a comparison of heat storage systems. Note that organic systems so far examined deliver heat at 50 - 150°.

What level of system fatigue will be acceptable?

From the crude comparison of Table II, >100 cycles is a reasonable goal. This level of material survival has not yet been achieved. Somewhat lower operating temperatures for the back reaction may be required.

What cost of the organic storage material will be acceptable?

Must be <\$1.00/lb. Material cost of reversible storage of 10^6 Btu = <\$4,000.

Table II. Energy Storage Capacities of Materials

MATERIAL	KCAL/MOL	CAL/G	BTU/LB
SENSIBLE HEAT STORAGE			
WATER ($\Delta T = 50^{\circ}\text{C}$)	0.9	50	91
ROCK, METAL ($\Delta T = 50^{\circ}\text{C}$)		10	18
LATENT HEAT STORAGE			
METHANE (COMBUSTION)	210	13,100	23,600
GLAUBER'S SALT ^a (1 CYCLE)	11	60	108
(100 CYCLES)		6,000	10,800
ORGANIC VALENCE ISOMER (1 CYCLE)	20	100	180
(MW 200) (100 CYCLES)		10,000	18,000

^aSodium sulfate decahydrate, a phase change heat of fusion material which absorbs on melting and delivers heat (at $\sim 30^{\circ}$) on crystallization. Potential and problems for use of this material in solar energy conversion are described in ref. 13.

Other New Developments.

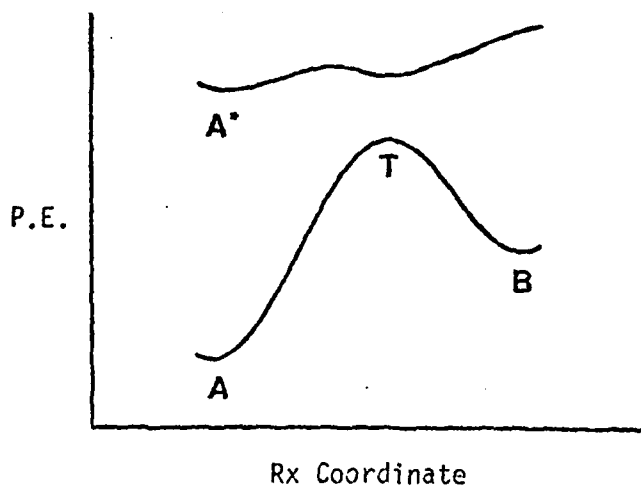
(1) Photocalorimetry. In connection with several problems encountered with measuring storage enthalpies, we have made approaches to the development of a new photochemical technique (the direct calorimetric measurement of ground state enthalpy absorbed or liberated as a result of photochemical reaction). We observed that storage enthalpies measured as solid-solid transitions for $\lambda_2 \rightarrow \lambda_1$ by differential scanning calorimetry were less than half that estimated on the basis of bond energy and other data. We reasoned that a more reliable measure of heat absorbed by the system as the result of irradiation in solution could be obtained by irradiating samples directly in dewar flasks equipped with sensitive thermistors under controlled optical conditions. Our measurements are not as yet sufficiently precise, but they do indicate a significantly higher storage enthalpy than that determined by DSC for-back reaction in the solid state. If our instrumentation can be improved the technique will be important for determination of a wide range of photo-thermochemical properties.

(2) Applications for optical memories. In connection with our collaboration with a group at Battelle Laboratories in the preparation of energy storing polymeric films, a number of experiments have been carried out in order to assess reversible photorefractive behavior. We have in mind the potential development of one or more of the organic isomerization systems (e.g., λ_1, λ_2) as a holographic recording material.¹⁴ We have so far shown that the system λ_1, λ_2 can be driven in both directions photochemically, and the photochromism observed for the system in a polymethyl methacrylate film is substantial. The required¹⁴ significant change in refractive index upon irradiation is expected. Using these and other similar materials, experiments will be directed now to the development of phase holograms with the capability of recording, reading, and erasing information.

IV. APPENDIX

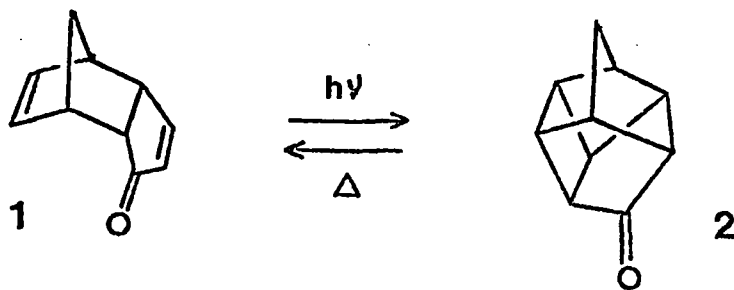
The Importance of Intermediate Partitioning
In Energy Storing Photoreactions

The problem which is central to the observation of significant photoreactivity using low energy (single) photons (practically speaking, the visible portion of solar radiation) is illustrated in the figure below. The objective of one energy conversion scheme is to drive a starting material A to photoproduct B, which is energy-rich, reasonably kinetically stable, and revertible to A. Quantum efficiency will depend largely on the extent to which A^* avoids a sizeable ground state potential energy barrier. In selecting materials which absorb increasingly toward the red, a point is reached at which A^* has insufficient energy to mount the thermal surface, and photoreactivity will cease unless special mechanisms are employed (e.g., significant thermal activation of A^* , tunneling, etc.). We



have examined several systems for which the excitation energy ($A - A^*$) exceeds the thermal barrier ($A - T$) by no more than 20 kcal/mol. The data permit the generalizations that kinetically identifiable intermediates are important for endoergic photoisomerizations which give stable products, and that it is the partitioning of these intermediates (and not competitive decays of the initial excited species) which determine quantum efficiencies.

The case for intermediate partitioning is illustrated for dienone **1**. Quenching studies show that the lifetime of reactive triplet λ is extremely short and temperature dependent ($k_{\text{decay}} = 1.1 - 3.5 \times 10^{10} \text{sec}^{-1}$, 4 - 51°C).¹⁰ Normal (unreactive) radiationless decay for cyclic enones is no faster than 10^8sec^{-1} . A fast reactive decay channel for triplet λ appears responsible for the short lifetime, but direct formation of **2** without competition is ruled out by the observed quantum efficiency ($\phi = 0.36$, 320 - 380 nm). The required mechanism involves one or more intermediates (e.g., λ_3), formation of which from triplet λ is lifetime limiting and partitioning of which (to λ and to λ_2) determines the quantum yield.





13

A similar pattern of kinetics and quantum yields is found for linked anthracenes λ (Capsule Report 4). Should this pattern of intermediate partitioning be even more general? Current theory regarding reactive radiationless decay affirms the trend.¹⁵ The systems selected, for which kinetic stability and thermodynamic instability in photoproduct are compatible, exhibit weakly avoided surface crossings (normally S_0 and S_2). At some near mid-point along the reaction coordinate, excited and ground surfaces will be close lying for facile radiationless transition and minima in S_1 and T_1 will be provided. From this diradical and biradicaloid geometry (corresponding, in the cycloadditions presented, to structures with one bond made and the other left incomplete, e.g., 13) excited molecules funnel to product and back to reactant. Anticipation of electronic factors which control partitioning (for example, the introduction of dipolar character¹⁶ in the intermediate through appropriate substitution which would favor product formation as the result of electrostatic attraction of centers which must bond in the final step) should be valuable in designing energy storing systems which can be driven with high quantum efficiency.

V. REFERENCES

- (1) a. See J. G. Calvert, in "Introduction to the Utilization of Solar Energy," A. M. Zarem, Ed., McGraw-Hill Book Co., N.Y., 1963 chp 9;
b. F. Daniels, "Direct Use of the Sun's Energy," Yale University Press, New Haven, 1964 chp 17;
c. R. J. Marcus, Science, 123, 399 (1956).
- (2) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, N.Y., 1970.
- (3) S. G. Talbert, D. H. Friesling, J. A. Eibling, and R. A. Nathan, Solar Energy, 17, 367 (1975).
- (4) R. C. Cookson, E. Crundwell, R. R. Hill, and J. Hudec, J. Chem. Soc., 3062 (1964).
- (5) L. A. Paquette and J. H. Barrett, J. Amer. Chem. Soc., 88, 1718 (1966).
- (6) a. J. E. Shields, D. Gabrilovic, J. Kopecky, W. Hartmann, and H. G. Heine, J. Org. Chem., 39, 515 (1974);
b. J. Meinwald, G. E. Samuelson, and M. Ikeda, J. Amer. Chem. Soc., 92, 7604 (1970).
- (7) a. R. Livingston and K. S. Wei, J. Amer. Chem. Soc., 89, 3098 (1967).
b. N. M. Weinshenker and F. D. Greene, ibid., 90, 506 (1963).
- (8) N. Filipescu and J. M. Menter, J. Chem. Soc. (B), 616 (1969).
- (9) G. Jones, II and B. R. Ramachandran, J. Org. Chem., 41, 798 (1976).
- (10) G. Jones, II and B. R. Ramachandran, J. Photochem., in press.
- (11) G. Jones, II and L. J. Turbini, J. Photochem., 5, 61 (1976).
- (12) M. A. Battiste and M. E. Burns, Tetrahedron Lett., 523 (1966).
- (13) M. Telkes, ASHRAE Journal, 38, September, 1974.
- (14) W. J. Tomlinson, et al., Applied Optics, 11, 533 (1972); (b) W. J. Tomlinson ibid., 11, 823 (1972).
- (15) J. Michl, Fortschritte der Chem. Forschung, 46, 1 (1974).
- (16) L. Salem and C. Rowland, Angew Chem. Int. Ed., 11, 92 (1972).

VI. PUBLICATIONS AND PRESENTATIONS CITING ARPA SUPPORT

- (1) "Catalytic Activity in the Reversion of an Energy Storing Valence Photoisomerization," G. Jones, II and B. R. Ramachandran, J. Org. Chem., 41, 798 (1976).
- (2) "Excited State Energy Barriers: Photokinetics of an Intramolecular Enone Cycloaddition," G. Jones, II and B. R. Ramachandran, J. Photochem., in press.
- (3) "Valence Photoisomerization of 1-Ethoxycarbonyl-1H-azepine: Excited State Energies and Multiplicity," G. Jones, II and L. J. Turbini, J. Photochem., 5, 61 (1976).
- (4) "Valence Photoisomerization of 1-Ethoxycarbonyl-1H-azepine and Its Thermal Reversion. Quantitative Aspects Including Energy Surface Relationships," G. Jones, II and L. J. Turbini, J. Org. Chem., in press.
- (5) "Reversible Photochemical Fixation of Solar Energy in Organic Materials," presented by G. Jones, II, NSF-RANN Workshop - The Current State of Knowledge of Photochemical Formation of Fuel, Osgood Hill Conference Center, North Andover, Massachusetts, September 23-24, 1974.
- (6) "Photochemical Storage of Solar Energy through Valence Isomerization of Organic Molecules," G. Jones, II, 8th International Conference on Photochemistry, Edmonton, Alberta, Canada, August 7 - 13, 1975, abstract N2
- (7) "Photochemical Conversion of Solar Energy," G. Jones, II, 2nd Annual Chemistry Symposium, Department of Chemistry, University of Rhode Island, March 27, 1976.
- (8) "The Importance of Intermediate Partitioning in Energy Storing Photoreactions," G. Jones, II, 12th Informal Conference on Photochemistry, National Bureau of Standards, Gaithersburg, Maryland, June 28, 1976, abstract accepted.