

NEW MOLECULAR ENERGY STORAGE SYSTEMS*

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Summary

In order to find an outstanding molecular energy storage system A/B composed of a cycle of reactions including a direct sunlight-induced endoergic process and an energy-releasing reverse process, the photochemical valence isomerization of new organic compounds leading to highly strained systems was investigated on the basis of new concepts. Metal complex catalysis for the energy-releasing process was also studied using homogeneous and heterogeneous catalysts. Consequently we found an excellent system ("DONAC"). A bench-scale test plant was constructed to examine the practical application of the energy-releasing process from donor-acceptor quadricyclane to donor-acceptor norbornadiene.

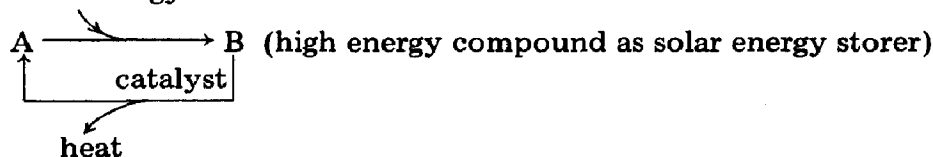
1. Introduction

Fossil resources (petroleum, natural gas and coal) are very important not only as fuels for mankind, but also as organic raw materials for chemical industries. However, these resources may be exhausted in the near future as it is impossible to regenerate them. If they did become exhausted, man could not live on the Earth. Therefore new ways of obtaining energy which is inexhaustive, plentiful and clean must be established before fossil resources are exhausted. Solar energy is inexhaustive, plentiful and clean but has drawbacks such as (1) high energy distribution in the visible region (a maximum at around 500 nm) rather than in the UV region, (2) low energy density on the Earth and (3) changes in the light intensity with time (in particular, no irradiation at night).

Thus it is necessary to store solar energy in the long term and in concentrated form so that it can be used continuously including at night. If a new compound could be found which could perform such a function ($A + \text{sunlight} \rightarrow B$) and which could control the cycloreversion process with a catalyst ($B + \text{catalyst} \rightarrow A + \text{heat}$), heat could be obtained continuously even at night. This sort of system is termed a molecular energy storage system for solar energy:

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solar energy



Molecular energy storage systems are the most direct way of obtaining controllable heat energy and should have the merits of long-term storage of solar energy and repeated generation of heat if a suitable system can be found. The most promising candidate for use as a molecular energy storage system is a "direct" photochemical valence isomerization system involving the formation of a highly strained molecule B. A photosensitized isomerization system could also be suitable if we could settle various inevitable problems (*e.g.* side reactions) arising from the sensitizer. In this paper we should like to deal with the former system.

2. What are the requirements of a molecular energy storage system?

A molecular energy storage system is composed of a cycle of reactions including (1) an endoergic process (an uphill reaction), leading to a highly strained molecule, and (2) the reverse exoergic process (cycloreversion) with a catalyst:



On the basis of function analysis for molecular energy storage systems we have pointed out [1] that the following seven conditions must be simultaneously satisfied in a molecular energy storage system for sunlight.

(a) Reactant A must absorb sunlight in the UV and the visible region. The absorption band of A should be broad towards the visible region and should have a low absorption coefficient ($\epsilon \approx 10^2$).

(b) The reaction $A \rightarrow B$ should be photochromic, and the photoproduct (valence isomer B) must not absorb sunlight.

(c) The quantum yield for the reaction $A \rightarrow B$ must be approximately unity even in the presence of oxygen.

(d) The reaction $A \rightarrow B$ must have a large positive ground state enthalpy (high energy storage). The energy stored must be greater than 100 kcal kg^{-1} .

(e) The photoproduct B must be stable and must bear the long-term storage at ambient temperatures.

(f) The reaction $B \rightarrow A$ must be controlled with a heterogeneous catalyst.

(g) Reactions $A \rightarrow B$ and $B \rightarrow A$ must proceed quantitatively.

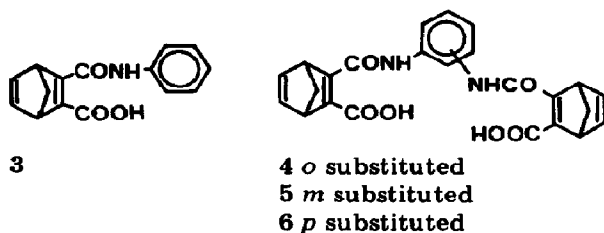
TABLE 1

Absorption characteristics and isomerization quantum yield of norbornadienes

Norbornadienes	λ (nm) at $\epsilon = 35$	Quantum yield (at 366 nm)
3	396	0.09
4	410	0.03
5	420	0.03
6	460	0.004

It seemed to be quite impossible to obtain compounds A and B which satisfied all seven conditions. Although we know of various photovalence isomerization systems (A/B), they occur only with direct UV (200 - 300 nm) irradiation (which does not satisfy condition (a)) or with sensitized irradiation. It might be possible to absorb a limited part of the UV (of wavelength greater than 300 nm) and visible region of sunlight with sensitized irradiation by choosing a suitable sensitizer; however, the reaction system could become contaminated on repetition of processes (1) and (2) because of side reactions (*e.g.* the generation of singlet oxygen and/or the reaction of A with the sensitizer). One such example is the benzophenone-photosensitized isomerization of norbornadiene 1 to quadricyclane 2.

The introduction of the usual chromophore group(s) gives rise to a bathochromic shift, but it reduces the quantum yield and decreases the amount of energy stored because of the increase in molecular weight as exemplified by the work on the direct photovalence isomerization of norbornadienes (3 - 6) to quadricyclanes [2] (Table 1):



A similar tendency is also observed for the photovalence isomerization of tri-*t*-butylisoquinolines 7 to the corresponding valenes 8 [3].

Therefore in order to design a functional molecule A which satisfies condition (a) without any sacrifice of the other conditions it is necessary to introduce a new concept of colour development which is not accompanied by a large increase in molecular weight. We succeeded in solving this extremely difficult problem using a quite new concept (*i.e.* control of the distance and angle between the donor olefin and acceptor olefin parts of molecule A which are bound in a non-conjugated manner, and a change in the nature of the donor and acceptor groups). Then, we investigated the problem with respect to condition (b) that A absorbs the UV (wavelengths

greater than 300 nm) and visible regions of sunlight and B does not. Eventually, we found a solution to this problem by the skeletal reorganization of coloured molecule A (π system) to colourless molecule B (σ system). As exemplified above, the quantum yields for the usual organic photochemical reactions are very low (about 10^{-3} - 10^{-2}) even in the absence of molecular oxygen which is responsible for a further decrease in the quantum yield. Therefore it should be extremely difficult to solve the problem for condition (c). We succeeded in solving this problem by designing a rigid structure (e.g. a cage structure) for A so that σ -type interaction of π electrons should be possible between both the donor olefin part and the acceptor olefin part of molecule A. Then the solution of the problem for condition (d) was examined. We expressed [4] the energy stored ES (kcal mol⁻¹) in solution as follows:

$$ES = -\left(\sum^B \Delta h_i - \sum^A \Delta h_i\right) + (SE^B - SE^A) - (RE^B - RE^A) - (LE^B - LE^A) \quad (3)$$

In this equation, $\sum^A \Delta h_i$ and $\sum^B \Delta h_i$ are the sum of the energies of disappearing bonds and the sum of the energies of newly forming bonds by photovoltage isomerization respectively, SE^B and SE^A are the strain energy of B and the strain energy of A respectively, RE^B and RE^A are the resonance energy of B and the resonance energy of A respectively, and LE^B and LE^A are the solvation energy for B and the solvation energy for A respectively. The first term of the right-hand side in eqn. 3 becomes always negative (exothermic) but constant for a given valence isomerization pair (A/B). Also the difference in solvation energies should be small in most cases. Therefore the amount of energy stored is largely governed by both the strain energy difference (the second term) and the resonance energy difference (the third term). In practice, the amount of energy stored in kilocalories per kilogram (or calories per gram) is more important than that quoted in kilocalories per mole. In the molecular design of the A/B pair we took these points into account. In relation to the problem for condition (e), it is necessary that compounds A and B are stable enough to sunlight, oxygen and heat (at least at about 100 - 150 °C). In addition, it is essential that the A/B pair has an appropriate energy barrier in its potential energy surface, as is shown in Fig. 1, to prevent thermal cycloreversion (B \rightarrow A) both during storage and during the energy-storing process (1).

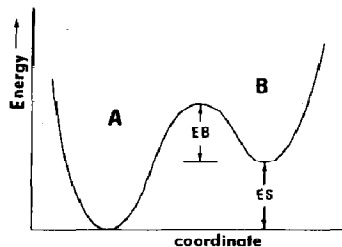


Fig. 1. Potential surface diagram for the A/B pair: EB, energy barrier; ES, energy stored.

We succeeded in solving these problems by experimental and theoretical approaches. We investigated various catalysts for the energy-releasing cycloreversion process (2) from the point of view of the specific interaction of Brønsted acids, Lewis acids and transition metal complexes with the bent σ bonds of B, because we had already clarified [5] that the bent σ bond characteristic of strained systems has an electron-donating nature between that of the lone pair and that of the ordinary σ bond. In the investigation of catalysts, it is important to find active but still reaction-controllable catalysts. If the catalytic activity is too high, this may lead to a violent reaction due to the additional thermal cycloreversion with generated heat. Another important point is that there must be no side reactions due to the catalyst. To make the cycle of processes (1) and (2) possible, it is necessary to prepare an immobilized catalyst with the above properties. As a result of various investigations, we found particular metal complexes that satisfied the above requirements. As for the problem with respect to condition (g), we checked the cleanliness of the cycle of reactions (1) and (2) experimentally using compounds A and B synthesized on the basis of the above results.

3. New molecular energy storage system based on new concepts

According to the principle of function synthesis we repeated (1) the better molecular design for solar energy storage systems, (2) its synthesis and (3) a check of the above seven requirements in order to obtain compounds A and B which satisfy all the conditions. Finally (1979 - 1981) we made the discovery that the donor-acceptor (DA) norbornadienes (A) and the corresponding quadricyclanes (B) formed an extremely good molecular energy storage system for solar energy [6 - 8]. The simplest model which represents the present author's new concept for the molecular design of A is shown in Fig. 2.



Fig. 2. Non-conjugatively bound donor olefin and acceptor olefin (---, plural σ bonds).

This sort of system is generally colourless if both olefin parts are colourless. However, we thought that colour could be made to appear by controlling the distance and the angle θ between the olefins in the non-conjugated system. We proved this concept to be correct by examining the absorptions of DA bicyclo[2.2.*n*]alkadienes 9 and DA cyclohexa-1,4-diene 10:

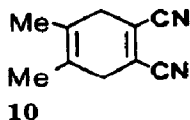
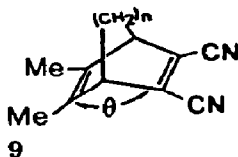


TABLE 2

New absorption band which appeared in the non-conjugatively bound donor olefin and acceptor olefin

System	n	Trend of increasing θ	New absorption band		
			λ_{\max} (nm)	Trend of increasing λ	ϵ_{\max}
10	Non-bridged	↑	283	↓	496
	3		305		178
9	2		306		162
	1		338		200

Some examples are shown in Table 2.

The new absorption band is ascribed to the charge transfer transition from the donor olefin (highest occupied molecular orbital (HOMO)) to the acceptor olefin (lowest unoccupied molecular orbital (LUMO)) by molecular orbital calculations [9]. In Table 2 it is shown that the bathochromic shift of the new band increases with decreasing n or decreasing dihedral angle θ and reaches a maximum in DA norbornadiene ($n = 1$). Another feature of this charge transfer band is that it is broad and has low intensity, which also satisfies condition (a). We examined the features of this new band by changing the partial structure of DA norbornadiene. For example, if one of the double bonds of DA norbornadiene (donor, Me (Me \equiv methyl); acceptor, CO₂Me) is saturated, the characteristic colour due to charge transfer transition disappears as shown in Fig. 3.

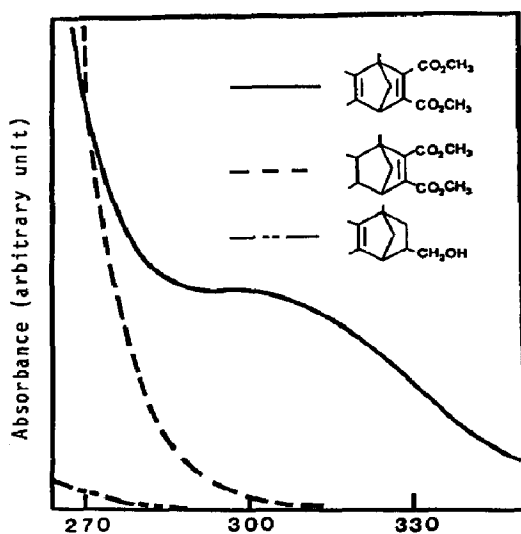


Fig. 3. Longest wavelength absorption for substituted bicyclo[2.2.1]alkadiene and bicyclo[2.2.1]alkenes in acetonitrile.

Another example of colour appearance in the much longer wavelength region is 1,2,3-trimethyl-5,6-dicyanonorbornadiene **11** ($\lambda_{\max} = 334$ nm; $\epsilon_{\max} = 212$; absorption end (λ at $\log \epsilon = 0$) = 430 nm). The DA norbornadiene **11** has also a characteristic very broad band with low intensity (10^2) which is suitable as a solar energy storage system. Its absorption is shown in Fig. 4 together with the absorptions for dicyanonorbornadiene **12** and norbornadiene **1**. This figure clearly indicates that the present author's concept is extremely useful for the development of colour in the non-conjugated system.

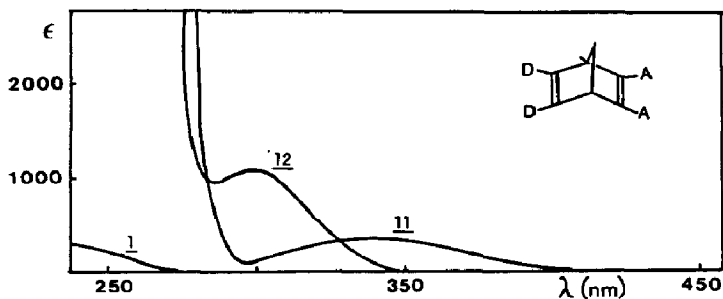


Fig. 4. Electronic spectra of norbornadienes (solvent, MeCN): **11**, D \equiv Me, A \equiv CN; **12**, D \equiv H, A \equiv CN; **1**, A \equiv D \equiv H.

The colour of DA norbornadiene (generally DA bicyclo[2.2.*n*]alkadiene) can be shifted to longer wavelengths with an increase in the electron-donating nature (*i.e.* in the control of the HOMO in the molecule) of the donor olefin part and in the electron-withdrawing nature (*i.e.* in the control of the LUMO in the molecule) of the acceptor olefin part, as is shown in Fig. 5. By mixing such DA norbornadienes the absorption spectrum of the mixture can be brought close to the solar spectrum. The effect of the solvent on the characteristic charge transfer band of DA norbornadienes is also interesting. For example, from an examination of the relationship between the wavenumber ($1/\lambda_{\max}$) of the charge transfer band for **11** and **12** *versus* the dielectric constant *D* of the solvent it is shown that the charge transfer band of DA norbornadiene shows a red shift. This is an example of solvato-

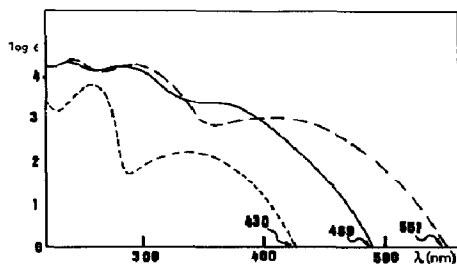
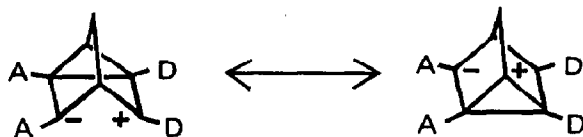


Fig. 5. The characteristic charge transfer spectra of DA norbornadienes in MeCN (Ar \equiv *p*-MeOC₆H₄-) (- · - ·, D \equiv Me, A \equiv CN; —, D \equiv Ar, A \equiv CO₂Me; - - -, D \equiv Ar, A \equiv CN).

chromism. Therefore the colour of our compounds (A) can be shifted to the longer wavelength region by using a suitable solvent.

The X-ray structure of 11 as an example of DA norbornadiene [10] is close to that of the parent norbornadiene with respect to the skeleton. This indicates that the charge transfer interaction at the ground state is negligibly small. From the X-ray data and the effect of the solvent on the charge transfer band, it is concluded that the dipolar structure



does significantly contribute to the excited singlet state of DA norbornadiene. The ionization potentials of 11 (DA norbornadiene) obtained by photoelectron spectroscopy are different from those of 1 (norbornadiene) and 12 (dicyanonorbornadiene) as shown in Table 3.

TABLE 3

Vertical ionization potentials (IPs) of norbornadienes

Compound		IP (eV)		
		First	Second	Third
D = A = H	1 ^a	8.69	9.55	11.26
D = H; A = CN	12	9.60	10.40	11.90
D = Me; A = CN	11	8.90	9.92	11.40

^aRef. 11.

It is indicated in this table that the first ionization potential, for example, corresponding to the HOMO is increased by the introduction of a cyano group to 13, but approaches that of the parent norbornadiene 1 when a methyl group is introduced to 12. From a comparison (Table 4) of the oxidation (corresponding to ionization potential) and reduction (corresponding to electron affinity) potentials for 11, 12 and 1 it can be said that the ionization potential of 11 is close to that of the parent 1 and that the electron affinity of 11 is close to that of the dicyano-substituted norbornadiene 12. This is a feature of DA norbornadienes.

We observed that solar insolation on DA norbornadiene afforded quantitatively the corresponding DA quadricyclane, which has no absorption in the wavelength region longer than 300 nm (*i.e.* it is colourless):

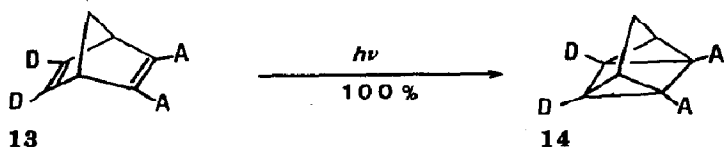


TABLE 4

Half-wave oxidation and reduction potentials of norbornadienes^a

Compound	Solvent	$E_{1/2}^{\text{red}}$ (V)	$E_{1/2}^{\text{ox}}$ (V)	$E_{1/2}^{\text{ox}}$ (V) (calculated) ^b
D ≡ A ≡ H 1	MeCN	—	2.0	1.8
	CH ₂ Cl ₂	-2.5	2.0	
D ≡ H; A ≡ CN 12	MeCN	-1.4	—	2.5
	CH ₂ Cl ₂	-1.5	—	
D ≡ Me; A ≡ CN 11	MeCN	-1.5	2.0	2.0
	CH ₂ Cl ₂	-1.6	2.1	

^aCyclic voltammetry on a platinum electrode, (*n*-Bu)₄NClO₄ (Bu ≡ butyl) (0.1 M) in MeCN or CH₂Cl₂ solution versus Ag/AgCl.

^bObtained from the ionization potentials using $E_{1/2}^{\text{ox}} = 0.827 \times \text{ionization potential} - 5.40 \text{ V}$ [12].

The quantum yield (Φ for 313 nm) of this energy-storing process is exemplified in Table 5.

As is seen in Table 5 the quantum yields are close to unity even in the presence of oxygen for DA norbornadiene. The quantum yields of DA norbornadiene 11 remained almost the same when the wavelength of the light was changed (for 313 nm, 334 nm and 366 nm). In contrast, the quantum yield for 12 (acceptor norbornadiene) was 0.59 in the absence of oxygen. It is noteworthy that photochemical valence isomerization for DA norbornadiene by lower energy photons occurs with a high quantum yield (close to unity). The solvent polarity does not substantially affect the quantum yield for DA norbornadiene (solvent: *n*-heptane, benzene, acetonitrile, chloroform, *i*-PrOH (Pr ≡ propyl)).

DA quadricyclanes are stable in the solid state. Their stability in solution changes with the substituents as shown in Table 6. The use of an aryl group as the donor decreases the thermal stability of DA quadricyclanes, which could be improved by introducing some substituents at the bridgehead position(s).

The values of $t_{1/2}$ at 33.5 °C indicate the usefulness of these DA quadricyclanes as solar energy storage systems. These DA quadricyclanes do not decompose with sunlight, molecular oxygen or heat (at about 100 - 150 °C). The amounts of energy stored are estimated from the heat of reversion for DA quadricyclanes, as is shown in Table 7. It is of interest that the amount ($-\Delta H$) of energy stored for quadricyclanes is almost the same with a change of substituents. Thus we obtain the DA quadricyclane with an energy storage value of about 120 - 130 kcal kg⁻¹. We also investigated the catalyst for the cycloreversion process for DA quadricyclane to DA norbornadiene (eqn. (4)) (Q ≡ quadricyclane; NBD ≡ norbornadiene):

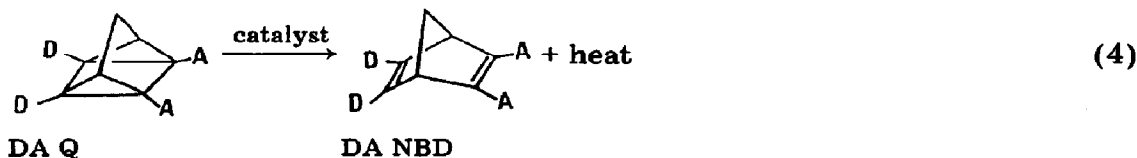
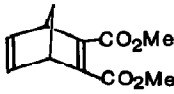
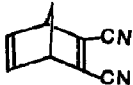
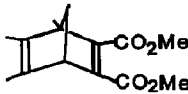
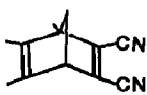
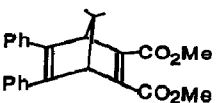



TABLE 5

Quantum yields for the photoisomerization of norbornadienes to quadricyclanes^a

Norbornadienes	Φ (degassed)	Φ (non-degassed)
	0.45 ^b	
	0.59 ^c	0.52 ^c
	0.87	0.85
	0.96	1.01
 ^d	1.06	0.97
 ^d	0.95	0.97

^aHigh pressure mercury lamp irradiation in benzene through coupled solution filters ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (250 g l^{-1}) + $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ (120 g l^{-1}) + K_2CrO_4 (0.27 g l^{-1})); path length, 0.5 cm; Valerophenone actinometer ($\Phi = 0.33$ [13]), except where otherwise noted.

^bRef. 14.

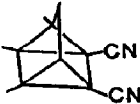
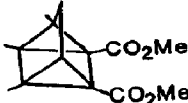
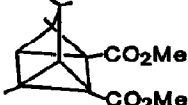
^cIn acetonitrile.

^dBecause of the thermolability of the corresponding quadricyclanes, the apparent values of Φ for their formation were very low at a tractable temperature. Here, thermal cycloreversion was taken into account to obtain plausible values of Φ , employing an equation $dQ/dt = I\Phi - kQ$ where I (einstein $\text{l}^{-1} \text{s}^{-1}$) is the incident light intensity and k (s^{-1}) is the first-order kinetic constant for thermal cycloreversion at the conditions employed.

For example we observed that Lewis acids (*e.g.* $\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$) and Brønsted acids (*e.g.* $\text{CF}_3\text{SO}_3\text{H}$, H_2SO_4 , 2,4-dinitrobenzenesulphonic acid, *m*-nitrobenzenesulphonic acid and *p*-toluenesulphonic acid) show catalytic effect on the cycloreversion of 1,2,3-trimethyl-5,6-dicyanoquadricyclane 14, but they are not good catalysts because of side reactions (*e.g.* cationic oligomerization). Although various transition metal complexes are reported to have catalytic activity for the isomerization of quadricyclane to norbornadiene, most of them have only poor catalytic activity for quadricyclanes with high ionization potentials such as DA quadricyclanes. We found that not only silver

TABLE 6

Half-life times $t_{1/2}$ for the thermal reversion of donor-acceptor quadricyclanes

Quadricyclane	Solvent	$t_{1/2}$ at 33.5 °C ^a
	Xylene	124 days
	Xylene	4.3 years
	Xylene	38 years

^a Estimated using the kinetic parameters E_a and $\ln A$ obtained by Arrhenius plots for the temperature range 80 - 135 °C.

TABLE 7

Heat of reversion for donor-acceptor quadricyclanes

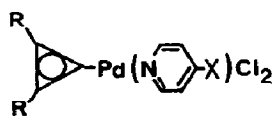
Donor	Acceptor	Solvent	Catalyst	Reaction temperature (°C)	$-\Delta H$ (kcal mol ⁻¹)
Me	CO ₂ Me	Neat	None	DSC	19 ^a
Me	CN	MeCN	AgO ₃ SCF ₃	30	21 ^b
		C ₆ H ₅ Cl	None	DSC	21 ^a
H	H	C ₆ H ₆	Rh ₂ (NOR) ₂ Cl ₂	30	22 ^b

DSC, differential scanning calorimetry.

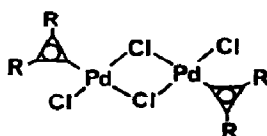
^a Determined on a Mettler TA 3000 system.

^b Determined on an LKB microcalorimetry batch system.

ions but also cyclopropenylidene palladium(II) complexes (15, 16) (R ≡ *t*-Bu, phenyl, (*i*-Pr)₂N)



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have catalytic effect for reaction (4) and clarified the mechanism of the catalysis.

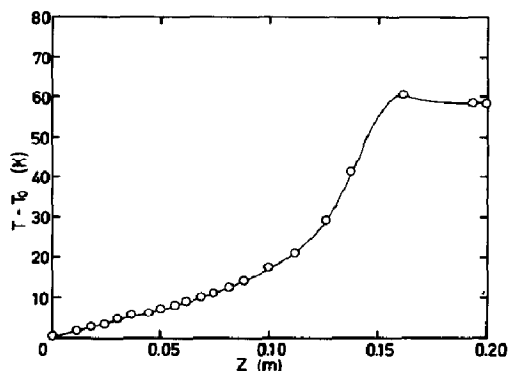
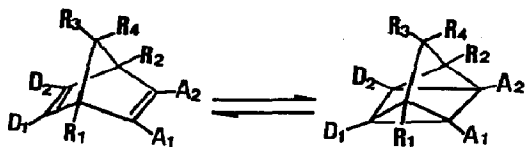


Fig. 6. Temperature distribution in the axial direction of the reactor ($V = 1.78 \times 10^{-7} \text{ m}^3 \text{ s}^{-1}$; $C_0 = 1.09 \times 10^3 \text{ mol m}^{-3}$; $T_0 = 293.85 \text{ K}$).

We also examined the catalytic function of transition metal complexes with planar ligands (*e.g.* the porphyrin cobalt complex) for the cycloreversion process (eqn. (4)). Consequently we found that although the porphyrin cobalt(I) complex did not show the catalytic function for reaction (4), the porphyrin cobalt(II) and cobalt(III) complexes catalysed this reaction. Of the cobalt(II) and cobalt(III) complexes the cobalt(III) complex has the higher catalytic activity for the conversion of quadricyclane to norbornadiene, but the reaction becomes contaminated. In contrast, the cobalt(II) complex can control this reaction for the various quadricyclanes without any by-product and the introduction of an electron-withdrawing group into tetraphenylporphyrin cobalt(II) complex increases its catalytic activity.

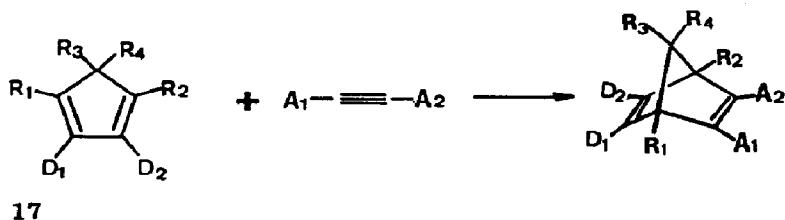
For practical application of the catalyst for this purpose, the catalysts must be immobilized and used repeatedly with high activity. We prepared various immobilized catalysts of this kind. The bench-scale test showed that the immobilized catalyst (Ag^+ -anchored polymer catalyst) catalyses smoothly the cycloreversion process to generate heat (eqn. (4)) and is able to control reaction (4) as shown in Fig. 6.

Thus, the (DA norbornadiene)/(DA quadricyclane) system mentioned above satisfies all seven conditions required for a molecular energy storage system for solar energy. The author terms this A/B system DONAC ($D_1, D_2 \equiv$ donor; $A_1, A_2 \equiv$ acceptor; $R_1, R_2, R_3, R_4 \equiv$ H or alkyl etc.):



DA norbornadienes (DONAC) are very easily synthesized by the Diels–Alder reaction of donor groups possessing cyclopentadiene derivatives 17 with acceptor groups possessing acetylene derivatives. The biggest problem in the synthesis of DA norbornadienes was to find a short path (one or two steps) by which 17 could be synthesized; until now this has been impossible.

Recently, we have found such a method of synthesizing 17 which can be applied on a large scale. Using this method, for example, 17 ($R_1, D_1, D_2 \equiv \text{Me}$; $R_2, R_3, R_4 \equiv \text{H}$) can be synthesized in one step:



4. Outlook

Our new molecular energy storage system for solar energy is expected to have wide applications, *e.g.* for cooling and/or warming of houses, buildings and vehicles etc., for use in agriculture (*e.g.* in greenhouses), for melting snow, for cultivating the desert and, eventually, for generating electricity. At present, a chemical company is able to produce DONAC and a construction company is investigating its practical application. It must be emphasized that fossil resources are distributed only in very few countries on the Earth, but that the Sun illuminates all the countries of the world, regardless of whether they are rich or poor. Thus our new molecular energy storage system is expected to make an extremely large contribution to the life of mankind.

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