Table IV. Percentage Yields of Carbene-Derived Products Obtained by Photolysis of Diaryldiazomethanes (0.03 M) in Isooctane at 298 K

$Ar(Ar')CN_2$	$Ar(Ar')CH_2$ A	$(Ar(Ar')C)_2$ B	$(Ar(Ar')C{=}N)_2$ C	$Ar(Ar')CH_2$ D	yield of C/yield of (A + B + D)
$(I)N_2$	39	<1	39	29	0.64
$(II)N_2$	47	4	19	30	0.23
$(III)N_2$	57	14	5	24	0.05
$(IV)N_2$	15	85			0.00

a sensitive function of carbene structure (Table IV). The product yields show that diphenylcarbene readily abstracts hydrogen from the solvent, there being no detectable yields of the dimeric product tetraphenylethylene. By contrast, dimesitylcarbene gives high yields of olefin. As expected, the ratios for mesitylphenyl- and mesityl-*o*-tolycarbenes fall between these extremes. Clearly, the difference in activation energies for the hydrogen abstraction vs. dimerization reactions increases substantially with steric crowding in the carbene itself. Presumably, the dimerization reaction has a low activation energy for all of the carbenes investigated. The reduction in the rate of hydrogen abstraction for the more crowded carbenes may reflect a steric effect and/or an electronic stabilization. However, we are unable to discriminate between these possibilities or the strength of the available data.

Summary

The triplet–singlet energy gap in diarylcarbenes can be enhanced by substitution of methyl groups at the ortho positions of the aromatic rings. Substitution of this kind forces an expansion of the central C–C–C angle of the carbene which, in turn, leads to an increase in the triplet–singlet energy gap. The effect is manifest in both the EPR spectra of the carbenes and in their chemistry.

Registry No. I, 3129-17-7; II, 98678-48-9; III, 98678-49-0; IV, 85236-86-8; V, 883-40-9; VI, 61080-14-6; VII, 65231-75-6; VIII, 98678-50-3; MeOH, 67-56-1.

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(33) Hadel, L. M.; Platz, M. S.; Scaiano, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 2831.

Development of a Solar Energy Storage Process. Photoisomerization of a Norbornadiene Derivative to a Quadricyclane Derivative in an Aqueous Alkaline Solution

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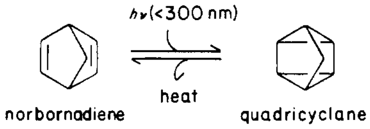
In an aqueous alkaline solution, the photoisomerization of norbornadiene derivatives **1** to quadricyclane derivatives **2** was investigated. Upon irradiation with sunlight, **1a–g** isomerized quantitatively to **2a–g** even in the presence of air, although the reaction medium was water which was usually reactive toward cyclopropane and cyclobutane rings of quadricyclane. In fact, **1h–j** gave undesirable compounds on irradiation under the same conditions. In order to increase solubility and the amount of heat being stored, we synthesized compounds **3** which had two norbornadiene chromophores in the same molecule. From analyses of the spectral data and the photoreactivities of **3**, we confirmed the same behavior as those of **1**, i.e., the two neighboring chromophores did not interfere. Since the reaction medium is water and the photoisomerization by sunlight is clean, these water-soluble norbornadiene derivatives **1a–g**, **1k–m**, and **3a–c** are promising for solar energy storage.[1]

Solar energy storage has received much attention from the viewpoint of solving today's energy problem.[2] Valence isomerization of norbornadiene and quadricyclane is one



of the most promising systems for solar energy storage, and many chemists have studied it for the last decade.[2,3] This system has an inherent disadvantage that norbornadiene cannot absorb sunlight by itself. To solve this problem, many improvements have been investigated; these are mainly classified into two categories: (i) use of sensitizers and (ii) introduction of chromophores. In the former, Kutal et al.[4] proposed an iridium complex ($\pi\pi^*$ exitation) as the sensitizer rather than acetophenone or benzophenone ($n\pi^*$ exitation) which easily reacted with norbornadiene and quadricyclane to give undesired adducts.[5]

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(1) In the system, sunlight conversion efficiency is much lower than a solar battery in actual use. However, the system has merits in the points that energy of sunlight is converted to the chemical energy and the chemical energy is able to be stored for future use.

(2) (a) Sasse, W. H. F. "Solar Power and Fuels"; Bolton, J. R., Ed.; Academic Press: New York, 1977; Chapter 8. (b) Laird, T. *Chem. Ind. (London)* **1978**, 186. (c) Jones, G., II; Chiang, S.; Xuan, P. T. *J. Photochem.* **1979**, *10*, 1. (d) Scharf, H.-D.; Fleischhauer, J.; Leismann, H.; Ressler, I.; Schlenker, W.; Weitz, R. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 652.

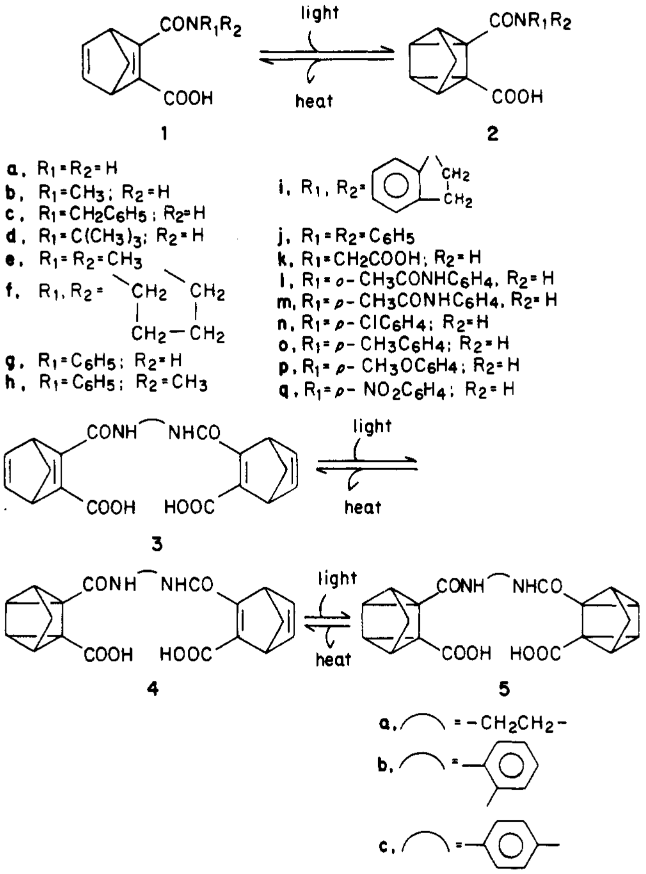
(3) (a) Hautala, R. R.; King, R. B.; Kutal, C. "Solar Energy; Chemical Conversion and Storage", The Humana Press: Clifton, NJ; 1979. (b) Philippopoulos, C.; Marangozis, J. *Ind. Eng. Chem. Prod. Res. Dev.* **1984**, *23*, 458. (c) Maruyama, K.; Tamiaki, H. *Kagaku Kogyo (Osaka)* **1984**, *58*, 319.

(4) (a) Kutal, C. *Adv. Chem. Ser.* **1978**, *168*, 158. (b) Grutsch, P. A.; Kutal, C. *J. Chem. Soc., Chem. Commun.* **1982**, 893.

(5) (a) Hammond, G. S.; Turro, N. J.; Feisher, A. *J. Am. Chem. Soc.* **1961**, *83*, 4674. (b) Hammond, G. S.; Wyatt, P.; DeBore, C. D.; Turro, N. J. *J. Am. Chem. Soc.* **1964**, *86*, 2532. (c) Gorman, A. A.; Leyland, R. L.; Rodgers, M. A. J.; Smith, P. G. *Tetrahedron Lett.* **1973**, 5085. (d) Hautala, R. R.; Little, J. *Adv. Chem. Ser.* **1978**, *184*, 1. (e) Hautala, R. R.; King, R. B.; Sweet, E. M.; Little, J. L.; Shields, A. W. *J. Organomet. Chem.* **1981**, *216*, 281.

0022-3263/85/1950-4742$01.50/0

Scheme I. Valence Isomerization in Water



In the latter, Maruyama et al.[6] and Mukai et al.[7] proposed introduction of several chromophores to one of the two double bonds of the norbornadiene molecule; these derivatives were easily synthesized, but the quantum yield of the photoisomerization was relatively low. Yoshida et al.[8] and Yonemitsu et al.[9] also proposed introduction of donor–acceptor chromophores to both of the double bonds of the norbornadiene molecule; in these cases the quantum yield of the photoisomerization was high, but the syntheses of these norbornadiene derivatives were difficult. In all of the above systems, an organic solvent was used as the reacting medium, which was disadvantageous to actual use. Therefore, we used water, safe and inexpensive, as the reaction medium. We report here the photoisomerization of a large number of norbornadiene derivatives to quadricyclane derivatives in an aqueous alkaline solution, as a step toward the practical storage of solar power in strained molecules.[10]

Results and Discussion

Norbornadiene cannot absorb light of wavelengths longer than 300 nm, so it is difficult for norbornadiene to isomerize to quadricyclane on irradiation with sunlight. To solve this problem and to use water as the reaction medium, we introduced carbamoyl and carboxyl groups into one of the two double bonds of the norbornadiene skeleton (Scheme I). Norbornadiene derivatives **1** were prepared with easy procedures and in high yields, which enabled us to synthesize **1** on a large scale.[11] Compounds **1a–q** were highly soluble in an aqueous alkaline solution because of their carboxyl groups. In the solution, **1a–q** had

Scheme II. Synthesis of Norbornadiene Derivatives

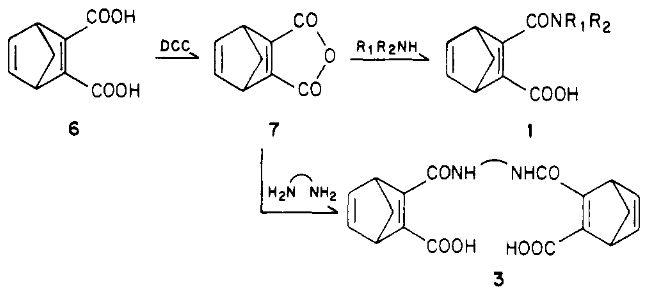
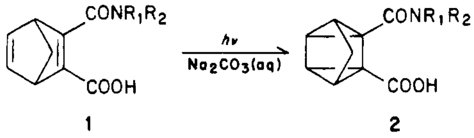
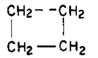
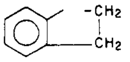


Table I. Photoisomerization of 1 to 2



	R_1	R_2	yield, %	$\Phi_{313\,\mathrm{nm}}$[a]	$\lambda_{\epsilon=1}$[b] nm
1a	H	H	100	0.59 ± 0.03	365
1b	CH_3	H	100	0.52 ± 0.01	365
1c	$CH_2C_6H_5$	H	100	0.59 ± 0.01	370
1d	$C(CH_3)_3$	H	100	0.54 ± 0.01	370
1e	CH_3	CH_3	100	0.45 ± 0.02	335
1f			100	0.50 ± 0.02	340
1g	C_6H_5	H	100	0.09 ± 0.01[c]	430
1h	C_6H_5	CH_3	70	0.31 ± 0.02[d]	360
1i			0		415
1j	C_6H_5	C_6H_5	0		405
1k	CH_2COOH	H	100	0.57 ± 0.02	365

[a] Quantum yield was determined by UV spectral kinetic analysis. [b] Error was within ±2 nm (in 0.1 M Na_2CO_3 (aq)). [c] See ref 15. [d] Determined by HPLC technique.

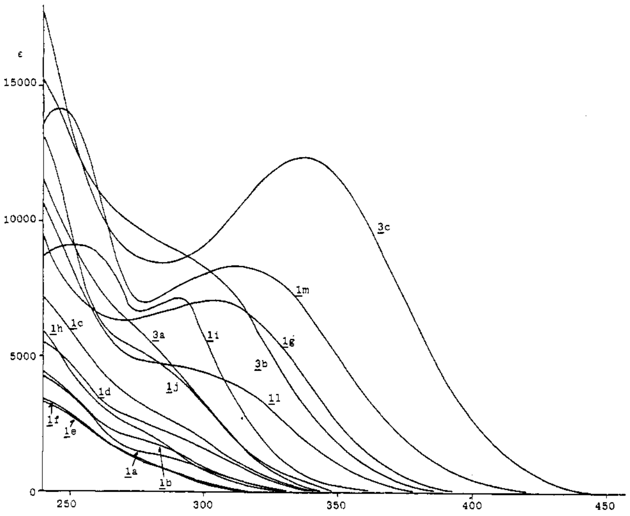


Figure 1. UV spectra of water-soluble norbornadiene derivatives in Na_2CO_3 (aq).

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(6) (a) Maruyama, K.; Terada, T.; Yamamoto, Y. *Chem. Lett.* **1981**, 839. (b) Maruyama, K.; Terada, T.; Yamamoto, Y. *J. Org. Chem.* **1981**, *46*, 5294.

(7) Toda, T.; Hasegawa, E.; Mukai, T.; Tsuruta, H.; Hagiwara, T.; Yoshida, T. *Chem. Lett.* **1982**, 1551.

(8) Yoshida, Z. *Heterocycles* **1984**, *21*, 331.

(9) Hirao, H.; Ando, A.; Hamada, T.; Yonemitsu, O. *J. Chem. Soc., Chem. Commun.* **1984**, 300.

(10) Preliminary report on this subject was already published in the following: Maruyama, K.; Tamiaki, H. *Chem. Lett.* **1982**, 1699.

(11) We synthesized **1b** (204 g, 1.1 mol) from **6** (360 g, 2.0 mol) in a yield of 53% without isolating **7**. For purification, the crude product was extracted with dichloromethane and recrystallized.

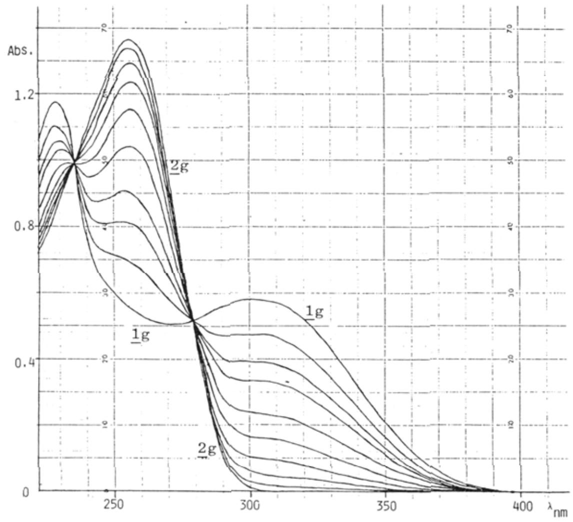

Figure 2. UV spectra of photoisomerization of **1g** to **2g** (1×10^{-4} M **1g** in 1×10^{-2} M $NaCO_3$ (aq) was irradiated with sunlight).

absorbance at wavelengths above 300 nm and were thus sensitive to sunlight (Figure 1). Table I lists the absorption edges, that is, the wavelength where the extinction coefficient is unity. It is seen that those of the nonsubstituted amide **1a** and *N*-alkyl amides **1b–d** are shifted to a longer wavelength than those of the *N*,*N*-dialkyl amides **1e**,**f** and that of the *N*-aryl amide **1g** is also shifted to a longer wavelength than those of the *N*-alkyl-*N*-aryl amides **1h**,**i** and *N*,*N*-diaryl amide **1j**. From a comparison of **1e** with **1f** or of **1h** with **1i**, however, it appears that the cyclized structure of the amido moiety works to weaken the extent of the hypsochromic shift. When the methyl group of the *N*-methyl amide **1b** was substituted by a benzyl group as in **1c**, or by a *tert*-butyl group as in **1d**, i.e., substitution by more bulky group, no effect was observed in the UV spectra. In the case of the *N*-aryl amides, **1g**, **1h**, and **1j**, substitution of the amido hydrogen of **1g** by a methyl group (**1h**) induced a larger hypsochromic shift in its absorption edge than that by a phenyl group (**1j**).[12] In the case of the *N*-methyl amides, **1b**, **1e**, and **1h**, the same behavior was also observed. Therefore, steric factors in the local vicinity around the amido nitrogen may affect mainly the wavelength of the absorption edges of water-soluble norbornadiene derivatives **1** in an aqueous sodium carbonate solution.

Table II. Oxygen Effect on Quantum Yield of 1 to 2

	conditn	$\Phi_{rel}{}^a$
1b	Ar	1
	air	1.00 ± 0.13
	O_2	0.99 ± 0.10
1g	Ar	1
	air	1.09 ± 0.06
	O_2	1.03 ± 0.04

[a] Φ_{rel} was the value of each quantum yield relative to the quantum yield under argon. Quantum yield of **1b** to **2b** was measured at 313 nm and that of **1g** to **2g** at 366 nm.

Table III. Quantum Yield Dependence upon Concentration

	concn, M	Φ^a
1b	1.0×10^{-1}	0.53 ± 0.02^c
	1.0×10^{-2}	0.51 ± 0.03^c
	1.0×10^{-3}	0.52 ± 0.01^b
1g	1.4×10^{-2}	0.034 ± 0.002^c
	1.1×10^{-3}	0.038 ± 0.006^b
	1.0×10^{-4}	0.032 ± 0.005^b

[a] Quantum yield of **1b** to **2b** was measured at 313 nm and that of **1g** to **2g** at 366 nm. [b] Determined by UV spectral kinetic analysis. [c] Determined by HPLC technique.

When aqueous sodium carbonate solutions of **1a–g** were irradiated with the light from a high pressure mercury arc lamp filtered through a Pyrex glass or with sunlight, **1a–g** isomerized to **2a–g** quantitatively. The photoisomerization proceeded in an aqueous alkaline solution, and in spite of the presence of a lot of water of hydroxide anion, the reaction was so clean that we could not detect the possible adducts of water or other decomposition compounds by means of HPLC and ^1H NMR.[13] The isosbestic point observed by following the UV spectral change in the reaction (Figure 2) was proof that the isomerization of **1** to **2** by sunlight was very clean. Even in open air the reaction was clean. From Table II, moreover, the quantum yields under air and under oxygen relative to the quantum yield under argon were nearly unity, so the presence of oxygen had no effect on the quantum yield of photoisomerization. At higher concentrations of **1**, we could observe no formation of the dimers of **1** or byproducts,[14] and no inhibition of the photoisomerization in the range of concentration from 10^{-1} to 10^{-4} mol/l (Table III). Thus, the present system is suitable for the photoisomerization reaction on a large scale, at a high concentration, and under mild conditions.

On the contrary, **1h** irradiated in an aqueous sodium carbonate solution (light: >300 nm) gave **2h** only in a yield of 70% accompanied with 30% of byproducts. Similarly **1i** and **1j** gave no **2i** and **2j** under the same conditions, but byproducts predominantly. Therefore, for our purpose, neither *N*-alkyl-*N*-aryl amides nor *N*,*N*-diaryl amides are suitable.

From Table I, the quantum yields of *N*-alkyl amides **1a–f** to **2a–f** are about 0.5 but that of *N*-aryl amide **1g** to **2g** is 0.09. Comparing **1g** with **1c** or **1h**, we find that the ability of the phenyl group to conjugate with the carbamoyl group of the water-soluble norbornadiene derivatives decreases the quantum yield. These facts indicate the general tendency that as the wavelength of the absorption edges of **1** increases, the quantum yields of **1** to **2** decrease.[15]

Which factor is the most important for efficient solar power collection, the absorption edge of a compound or its quantum yield?[2d] We examined these problems by using an actual device to undertake photoreaction of *N*-alkyl amide **1b** and *N*-aryl amide **1g** on irradiation with daylight. When 0.1 M solutions of **1b** and of **1g** in an aqueous sodium carbonate solution were irradiated respectively with sunlight in a hard glass cell for 1 day, the conversions of **1b** to **2b** and of **1g** to **2g** were measured. In spite of occasional adverse weather (in Kyoto, November 1984), the conversion of **1b** to **2b** was 2.2–2.7 times greater

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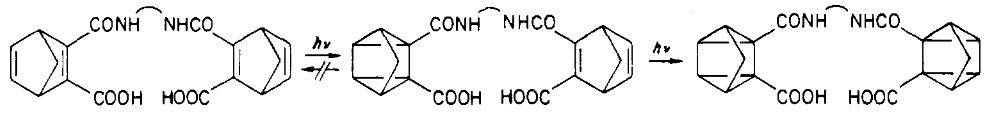
(12) Though it is accepted in general that a phenyl group is more bulky than a methyl group, in the disubstituted amides **1e**,**h**,**j**, a methyl group is likely to act more bulkily than a phenyl group because of the local vicinity around the amido nitrogen. A phenyl group has a plane structure and the steric hindrance may be overcome by rotation of the C–N bond. On the contrary, a methyl group has a spherical structure and the steric hindrance may not be avoided. For example, in the ortho-substituted biphenyl including pheny and methyl substituents, the same order of bulkiness was observed. See: Suzuki, H. *Bull. Chem. Soc. Jpn.* **1959**, *32*, 1350; **1960**, *33*, 109.

(13) (a) Jones, E. R. H.; Mansfield, G. H.; Whiting, M. C. *J. Chem. Soc.* **1956**, 4073. (b) Cristol, S. J.; Snell, R. L. *J. Am. Chem. Soc.* **1958**, *80*, 1950. (c) Smith, C. D. *Org. Synth.* **1971**, *51*, 133. (d) Behr, A.; Keim, W.; Thelen, G.; Scharf, H.-D.; Ressler, I. J. *Chem. Tech. Biotechnol.* **1982**, *32*, 627.

(14) Acton, N.; Roth, R. J.; Katz, T. J.; Frank, J. K. Maier, C. A.; Paul, I. C. *J. Am. Chem. Soc.* **1972**, *94*, 5446.

(15) Maruyama, K.; Tamiaki, H., Yanai, T. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 781.

Table IV. Photoisomerization of 3 to 4 and 4 to 5 in Na_2CO_3 (aq)



3 4 5

	$\Phi_{313\,nm}$	$\Phi_{366\,nm}$	$\lambda_{\epsilon=1}$,[a] nm
3a	0.58 ± 0.01[c]	[e]	370
4a	0.56 ± 0.03[d]	[e]	370
3b	0.16 ± 0.01[c]	0.045 ± 0.01[b]	430
4b	0.19 ± 0.02[d]	0.05 ± 0.005[d]	420
3c	0.035 ± 0.002[d]	0.004 ± 0.001[b,f]	475
4c	0.034 ± 0.002[d]	0.0034 ± 0.0004[d]	470
1g	0.09 ± 0.01[c,g]	0.035 ± 0.005[c,g]	430
1l	0.18 ± 0.01[c]	0.06 ± 0.01[c]	420
1m	0.07 ± 0.01[d]	0.007 ± 0.001[c]	460

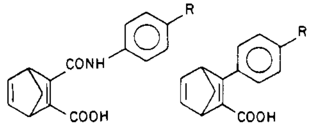
[a] Error was within ±2 nm (0.1 M Na_2CO_3 (aq)). [b] Determined by UV spectral analysis. [c] Determined by UV spectral kinetic analysis. [d] Determined by HPLC technique. [e] This compound had so small an absorbance that no photoisomerization was observed at 366 nm. [f] In $NaHCO_3$ (aq). [g] See ref 15.

than that of **1g** to **2g**. Therefore, a larger quantum yield is more effective for solar energy storage than enlargement in the absorption edge. In view of the facts described above, the nonsubstituted amide **1a** and alkyl amide **1b** could be better selections for a water-soluble solar energy storage system.[16]

To increase the solubilities of water-soluble norbornadiene derivatives in water, we introduced another carboxyl group. Photoreaction of **1k** to **2k** was as clean as that of **1b** to **2b** (Table I). Introduction of the second carboxyl group did not affect the photoreaction.[17] In order to increase the stored energy per unit weight,[18] we synthesized compounds **3**, which had two norbornadiene chromophores and two water-solubilizing carboxyl groups in the molecule. We then investigated the photochemical behavior of compounds **3**. Upon irradiation of aqueous sodium carbonate solutions of **3** with an appropriate light, **3** isomerized stepwise, first to **4** and then to **5** (Table IV). The reactions of **3** were as clean as those of **1**, and no intramolecular cyclization between one norbornadiene chromophore and the other was observed.[19] In the course of the photoisomerization, we did not observe the back reaction of **4** to **3** from analysis of the reaction by means of HPLC.

None of the pairs of chromophores, that is, norbornadiene chromophore and norbornadiene chromophore, norbornadiene chromophore and quadricyclane chromophore, or quadricyclane chromophore and quadricyclane chromophore, showed any interaction with each other in the ground state from analyses of their ^1H NMR and IR spectra (see Experimental Section). Moreover, the fact that there was no difference between the quantum yields of **3** to **4** and those of **4** to **5** (Table IV) indicated that these two chromophores did not interact with each other in the excited state. On irradiation with light of 366 nm, the quantum yield of the para isomer **3c** (0.004) was about 10 times smaller than that of the ortho isomer **3b** (0.045). The quantum yields of para isomers **3c** and **4c** were generally smaller than those of ortho isomers **3b** and **4b** at all the irradiating wavelengths (Table IV).

Table V. UV Spectra of Compounds Containing Para Substituents



	R	**1** $\lambda_{\epsilon=1}$,[a] nm	**8** λ_{max},[b] nm
g	H	430	284
n	Cl	435	294
o	CH_3	445	301
p	OCH_3	465	317
q	NO_2	470	327

[a] In 0.1 M Na_2CO_3 (aq). Error was within ±2 nm. [b] In 95% ethanol. See ref 21.

Considering the quantum yields of ortho isomer **1l** and para isomer **1m** ($\Phi_{1l\rightarrow 2l} > \Phi_{1m\rightarrow 2m}$, see Table IV), we realize that this fact is a substitution effect. As is the case in the photoreactions of **1** to **2**, an increase in the wavelength of the absorption edge also corresponded to a decrease in the quantum yield of the photoisomerization.[15] The quantum yield of **3b** to **4b** on irradiation with 313-nm light (0.16) was larger than that with 366-nm light (0.045). It was found that all the quantum yields of norbornadiene chromophores (**1**, **3**, **4**) to quadricyclane chromophores (**2**, **4**, **5**) were dependent upon the wavelength of irradiating light (Table IV).[15,20] The absorption edges of **1m** and **3c** (para isomers) were shifted to longer wavelengths than that of **1g**, but those of **1l** and **3b** (ortho isomers) were shifted to shorter wavelength than that of **1g** (Figure 1 and Table IV).

A red shift in the absorption edges was observed for the para-substituted derivatives **1** (in the order of the substituents: $NO_2 > OCH_3 > CH_3 > Cl > H$), and this order

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[16] While $\Delta H_{2g\rightarrow 1g}$ was 1.1 times larger than $\Delta H_{2b\rightarrow 1b}$, photoisomerization efficiency was more overwhelming for solar energy storage than the efficiency of stored energy which was released in the reverse isomerization.

[17] (a) Cristol, S. J.; LaLonde, R. T. *J. Am. Chem. Soc.* **1959**, *81*, 5417. (b) Dauben, W. G.; Cargill, R. L. *Tetrahedron* **1961**, *15*, 197.

[18] By assuming that both $\Delta H_{4\rightarrow 3}$ and $\Delta H_{5\rightarrow 4}$ are equal to $\Delta H_{2\rightarrow 1}$, the stored energy per unit weight of **5a** is 1.005 times larger than that of **2b** and that of **5b,c** is 1.18 times larger than that of **2g**. Further, an increase in solubility induces a greater increase of stored energy per unit saturated solution.

[19] Tanida, H.; Hata, Y.; Matsui, Y.; Tanaka, I. *J. Org. Chem.* **1965**, *30*, 2259.

[20] Quadricyclane derivative **2g** as a typical example absorbs none of the light at the irradiation wavelengths (313 and 366 nm) and induces no back-reaction and so the fact is independent of the reverse reaction. We may explain the behavior as follows. Since a decrease of the irradiation wavelength induces an increase in the quantum yield, the higher vibrational state of the excited norbornadiene derivative is more efficient to give the corresponding quadricyclane derivative. See: Turro, N. J.; Ramamurthy, V.; Cherry, W.; Farneth, W. *Chem. Rev.* **1978**, *78*, 125.

was quite the same as observed for the absorption maxima of the corresponding compounds **8** in which the aryl group possessed a greater degree of coplanarity with the double bond (Table V).[21] These facts indicate that the degree of conjugation between the phenyl group and the amido group determines the wavelength of absorption edge. In para isomers, the absorption edges of **2m** and **5c** as well as those of the corresponding norbornadiene derivatives **1m** and **3c** were shifted toward longer wavelengths to absorb sunlight. Upon irradiation with light of 313 nm, **2m** isomerized to **1m**, and **5c** to **4c**. Even under these conditions, **4c** did not back-isomerize to **3c** as noted above. The photoreaction was also clean, and there was a photostationary state between **1m** and **2m** or between **4c** and **5c** (Table VI). From Table VI, it is indicated that undesirable exothermic photoisomerization of quadricyclane derivatives **2m** and **5c** to norbornadiene derivatives **1m** and **4c** is more efficient than the desirable endothermic photoisomerization.[22] Therefore, a very large bathochromic shift of the absorption edge of the norbornadiene derivative should not be a supreme requisite for an efficient solar energy storagre system.

Experimental Section

Apparatus. All melting points were measured with a Yanagimoto micro melting point apparatus and were uncorrected. ^1H NMR spectra were recorded on a JEOL JMN-PS-100 instrument; chemical shifts (δ) are expressed in parts per million relative to tetramethylsilane. Infrared spectra were measured with a JASCO IRA-1 spectrometer. Ultraviolet and visible spectra were measured with a Shimadzu UV-200 spectrometer. Mass spectra were recorded with a JEOL JMS-DX-300 spectrometer. HPLC analyses were carried out with a Waters liquid chromatograph containing a μ-Bondpak C_{18} column. The elemental analyses were performed at the Microanalysis Center of Kyoto University.

Materials. Acetonitrile for photolysis was dried by standard techniques and distilled under nitrogen. Water for photolysis was deionized and distilled. For other purposes reagent-grade solvents were simply distilled except as otherwise noted. All acids, bases, and salts were commercially available and used without further purification. Norbornadiene-2,3-dicarboxylic acid (**6**),[23] 3-(phenylcarbamoyl)norbornadiene-2-carboxylic acid (**1g**),[6b,15] 3-[(*p*-chlorophenyl)carbamoyl]norbornadiene-2-carboxylic acid (**1n**),[15] 3-(*p*-tolylcarbamoyl)norbornadiene-2-carboxylic acid (**1o**),[15] 3-(*p*-anisylcarbamoyl)norbornadiene-2-carboxylic acid (**1p**),[6b,15] and 3-(phenylcarbamoyl)quadricyclane-2-carboxylic acid (**2g**),[6b,15] were synthesized by the literature procedures.

Synthesis of Norbornadiene-2,3-dicarboxylic Acid Anhydride (7). Dicyclohexylcarbodiimide (206 mg, 1.0 mmol) was dissolved in dry acetone (3 mL). Dry acetone (10 mL) solution of **6** (180 mg, 1.0 mmol) was added drop by drop with stirring at room temperature under argon. During addition, a white precipitate of dicyclohexylurea was formed. After the slow addition, the mixture was stirred overnight at room temperature under argon and then filtered. The filtrate was concentrated in vacuo, giving a yellowish green oil which was chromatographed on a short column of silica gel (Wakogel C-200) with benzene as an eluant. The first fraction was evaporated to give **7** as white crystals in a yield of 80% (130 mg), mp 86–89 °C (lit.[24] mp 88–89 °C). Recrystallization from ether gave a pure sample.

Synthesis of 3-Carbamoylnorbornadiene-2-carboxylic Acid (1a). An aqueous solution of ammonium hydroxide (25%, 2 mmol) was added dropwise to acid anhydride **7** (162 mg, 1 mmol) at 0 °C. After the solution was stirred for 10 min at 0 °C, the insoluble materials were removed by filtration. The filtrate was acidified by cold hydrochloric acid at 0 °C, and a white precipitate was filtered and dried. The yield was 75% (134 mg). Recrystallization from ethyl acetate gave an analytically pure sample: white needles; mp 212.5–214 °C; ^1H NMR (CD_3OD) δ 1.98–2.38 (m, 2 H), 4.02–4.18 (m, 2 H), 6.85–7.03 (m, 2 H); IR (KBr) 2860–3640 (br, COOH), 3190, 3340 (NH), 1650, 1695 cm^{-1} (C=O); UV (1×10^{-1} M Na_2CO_3 (aq)) λ_{max} 237.5 (ϵ 4510), 290 nm (1300, sh); MS, *m/e* 179 (M^+). Anal. Calcd for $C_9H_9NO_3$: C, 60.33; H, 5.06; N, 7.82. Found: C, 60.28; H, 5.07; N, 7.84.

Synthesis of 3-(Methylcarbamoyl)norbornadiene-2-carboxylic Acid (1b). In a manner similar to the synthesis of **1a**, the reaction of **7** with a commercially available aqueous solution of methylamine gave **1b** in a yield of 83%: white needles; mp 205.5 °C (from dry chloroform); ^1H NMR (D_2O-Na_2CO_3) δ 2.35–2.62 (m, 2 H), 3.25 (s, 3 H), 4.25–4.52 (m, 2 H), 7.4–7.56 (m, 2 H); IR (KBr) 2300–3700 (br, COOH), 3280 (NH), 1670 cm^{-1} (C=O); UV (1×10^{-3} M Na_2CO_3 (aq)) λ_{max} 228 (ϵ 5700), 285 nm (2000, sh); MS, *m/e* 193 (M^+). Anal. Calcd for $C_{10}H_{11}NO_3$: C, 62.17; H, 5.74; N, 7.25. Found: C, 62.46; H, 5.74; N, 7.48.

Synthesis of 3-(Benzylcarbamoyl)norbornadiene-2-carboxylic Acid (1c). From reaction of **7** with commercially available benzylamine, a reaction mixture was obtained in a manner similar to the synthesis of **1g** and chromatographed over silica gel to give **1c** in a yield of 95%: white needles; mp 167–169 °C (from dichloromethane and hexane); ^1H NMR ($CDCl_3$) δ 2.0–2.3 (m, 2 H), 3.8–3.95 (m, 1 H), 4.15–4.25 (m, 1 H) 4.48–4.65 (m, 2 H), 6.6–7.6 (br, 1 H), 6.76–7.0 (m, 2 H), 7.31 (s, 5 H); IR (KBr) 2900–3700 (br, COOH), 3300 (NH), 1680 cm^{-1} (C=O); UV (1×10^{-2} M Na_2CO_3 (aq)) λ_{max} 235.5 (ϵ 7310), 280 nm (3070, sh); MS, *m/e* 269 (M^+). Anal. Calcd for $C_{16}H_{15}NO_3$: C, 71.36; H, 5.61; N, 5.20. Found: C, 71.14; H, 5.62; N, 5.11.

Synthesis of 3-(*tert*-Butylcarbamoyl)norbornadiene-2-carboxylic Acid (1d). In a manner similar to the synthesis of **1c**, the reaction of **7** with commercially available *tert*-butylamine gave **1d** in a yield of 57%: white needles; mp 194–196 °C (from dichloromethane and hexane); ^1H NMR ($CDCl_3$) δ 1.45 (s, 9 H), 2.0–2.32 (m, 2 H), 3.79–3.9 (m, 1 H), 4.1–4.25 (m, 1 H), 6.2–6.5 (br, 1 H), 6.85–7.02 (m, 2 H); IR (KBr) 3200–3600 (br, COOH), 3300 (NH), 1680 cm^{-1}; UV (1×10^{-1} M Na_2CO_3 (aq)) λ_{max} 233.5 (ϵ 5600), 280 nm (2500, sh); MS, *m/e* 235 (M^+). Anal. Calcd for $C_{13}H_{17}NO_3$: C, 66.36; H, 7.28; N, 5.95. Found: C, 66.13; H, 7.14; N, 6.04.

Synthesis of 3-(Dimethylcarbamoyl)norbornadiene-2-carboxylic Acid (1e). In a manner similar to the synthesis of **1a**, the reaction of **7** with a commercially available aqueous solution of dimethylamine gave **1e** in a yield of 67%: white plates; mp 198.5–201 °C (from dichloromethane and hexane); ^1H NMR ($CDCl_3$) δ 2.05–2.2 (m, 1 H), 2.25–2.4 (m, 1 H), 3.0 (s, 6 H), 3.8–3.92 (m, 1 H), 4.02–4.14 (m, 1 H), 6.87–7.11 (m, 2 H), 10.2–10.5 (br, 1 H); IR (KBr) 2240–3220 (br, COOH), 1630, 1690 cm^{-1} (C=O); UV (1×10^{-1} M Na_2CO_3 (aq)) λ_{max} 234 (ϵ 4100), 275 nm (1300, sh); MS, *m/e* 207 (M^+). Anal. Calcd for $C_{11}H_{13}NO_3$: C, 63.76; H, 6.32; N, 6.76. Found: C, 63.68; H, 6.22; N, 6.78.

Synthesis of *N*-[(3-Carboxynorbornadien-2-yl)carbonyl]pyrrolidine (1f). In a manner similar to the synthesis of **1c**, the reaction of **7** with commercially available pyrrolidine gave **1f** in a yield of 88%: white needles; mp 167–169.5 °C (from dichloromethane and hexane); ^1H NMR ($CDCl_3$) δ 1.65–2.2 (m, 4 H), 2.05–2.36 (m, 2 H), 3.25–3.85 (m, 4 H), 3.95–4.2 (m, 2 H), 6.84–6.96 (m, 1 H), 7.03–7.16 (m, 1 H); IR (KBr) 2100–3260 (br, COOH), 1630, 1695 cm^{-1} (C=O); UV (1×10^{-1} M Na_2CO_3 (aq)) λ_{max} 234.5 (ϵ 4170), 270 nm (1600, sh); MS, *m/e* 233 (M^+). Anal. Calcd for $C_{13}H_{15}NO_3$: C, 66.94, H, 6.48; N, 6.00. Found: C, 66.68; H, 6.41; N, 6.10.

Synthesis of 3-(Methylphenylcarbamoyl)norbornadiene-2-carboxylic Acid (1h). In a manner similar to the synthesis of **1c**, the reaction of **7** with commercially available *N*-methylaniline gave **1h** in a yield of 78%: white plates; mp 187.5–189 °C (from dichloromethane and hexane); ^1H NMR ($CDCl_3$) δ 1.7–2.0 (m, 2 H), 3.06–3.24 (m, 1 H), 3.41 (s, 3 H), 3.88–4.06 (m, 1 H), 5.45–5.64 (m, 1 H), 6.62–6.75 (m, 1 H), 6.96–7.56 (m, 5 H); IR (KBr) 3100–3700 (br, COOH), 1700 cm^{-1} (C=O); UV (1×10^{-2} M Na_2CO_3 (aq)) 270 nm (ϵ 2600, sh); MS, *m/e* 269 (M^+). Anal. Calcd for $C_{16}H_{15}NO_3$: C, 71.36; H, 5.61; N, 5.20.

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(22) In organic solvents, we recognized the similar tendency that reverse photoisomerization was more rapid than desirable photoisomerization.[6b] In acetonitrile, for example, the quantum yield of **2g** to **1g** at 254 nm was about 4 times larger than that of **1g** to **2g**. The quantum yield of reverse photoisomerization in a organic solvent was estimated to be about 0.4 and nearly equal to that in an aqueous solution.

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Found: C, 71.06; H, 5.51; N, 5.10.

Synthesis of *N*-[(3-Carboxynorbornadien-2-yl)carbonyl]indoline (1i). *In a manner similar to the synthesis* of **1c**, the reaction of **7** with commercially available indoline gave **1i** in a yield of 80%: white needles; mp 202–204.5 °C (from dichloromethane and hexane); ^{1}H NMR ($CDCl_3$) δ 2.05–2.44 (m, 2 H), 3.05–3.3 (m, 2 H), 3.8–4.2 (m, 4 H), 6.9–7.4 (m, 4 H), 8.0–8.2 (br, 1 H), 9.2–10.2 (br, 1 H); IR (KBr) 3200–3700 (br, COOH), 1675 cm^{-1} (C=O); UV (1×10^{-2} M Na_2CO_3 (aq)) λ_{max} 251 (ϵ 9030), 292 nm (7180); MS, *m/e* 281 (M$^+$). Anal. Calcd for $C_{17}H_{15}NO_3$: C, 72.58; H, 5.37; N, 4.98. Found: C, 72.52; H, 5.28; N, 4.90.

Synthesis of 3-(Diphenylcarbamoyl)norbornadiene-2-carboxylic Acid (1j). In a manner similar to the synthesis of **1c**, the reaction of **7** with commercially available diphenylamine gave **1j** in a yield of 79%: white needles; mp 187–189 °C (from dichloromethane and hexane); ^{1}H NMR ($CDCl_3$) δ 1.85–2.05 (m, 2 H), 3.35–3.48 (m, 1 H), 3.9–4.03 (m, 1 H), 5.72–5.88 (m, 1 H), 6.56–6.7 (m, 1 H), 7.04–7.5 (m, 10 H); IR (KBr) 3200–3700 (br, COOH), 1710 cm^{-1} (C=O); UV (1×10^{-2} M Na_2CO_3 (aq)) 270 nm (ϵ 5500, sh); MS, *m/e* 331 (M$^+$). Anal. Calcd for $C_{21}H_{17}NO_3$: C, 76.12; H, 5.17; N, 4.23. Found: C, 76.34; H, 5.31; N, 4.13.

Synthesis of 3-[(Carboxymethyl)carbamoyl]norbornadiene-2-carboxylic Acid (1k). In a manner similar to the synthesis of **1a**, the reaction of **7** with commercially available glycine in tetrahydrofuran gave **1k** in a yield of 99%: white crystals; mp 241–242 °C (from water); ^{1}H NMR (D_2O–Na_2CO_3) δ 2.4–2.68 (m, 2 H), 4.28–4.56 (m, 2 H), 4.29 (s, 2 H), 7.44–7.53 (m, 2 H); IR (KBr) 2400–3600 (br, COOH), 3260 (NH), 1720, 1680 cm^{-1} (C=O); UV (1×10^{-3} M Na_2CO_3 (aq)) λ_{max} 232 (ϵ 5200), 285 nm (2200, sh); MS, *m/e* 237 (M$^+$). Anal. Calcd for $C_{11}H_{11}NO_5$: C, 55.70; H, 4.67; N, 5.90. Found: C, 55.53; H, 4.72; N, 5.98.

Synthesis of 3-[(*o*-Acetamidophenyl)carbamoyl]norbornadiene-2-carboxylic Acid (1l). 2-Aminoacetanilide was synthesized by the procedure below. *o*-Phenylenediamine (1.08 g, 10.0 mmol) was suspended in dichloromethane (10 mL). A dichloromethane (30 mL) solution of acetic anhydride (0.94 mL, 10.0 mmol) was added drop by drop with stirring at room temperature under nitrogen. After the slow addition, the mixture became a homogeneous yellow solution. Concentrated aqueous sodium hydroxide solution was added, and the resulting mixture was then extracted with dichloromethane. The extract was evaporated to give 2-aminoacetanilide; recrystallization from benzene gave white plates in a yield of 85% (1.28 g), mp 132 °C.

In a manner similar to the synthesis of **1c**, the reaction of **7** with 2-aminoacetanilide gave **1l** in a yield of 98%: pale yellow crystals; mp 202.5–204.5 °C (from acetonitrile); ^{1}H NMR (D_2O–Na_2CO_3) δ 2.5–2.8 (m, 2 H), 2.72 (s, 3 H), 4.36–4.64 (m, 2 H), 7.36–7.55 (m, 2 H), 7.75–7.92 (m, 3 H), 7.96–8.15 (m, 1 H); IR (KBr) 2900–3700 (br, COOH), 3280 (NH), 1690, 1660 cm^{-1} (C=O); UV (1×10^{-2} M Na_2CO_3 (aq)) 285 nm (ϵ 4800, sh); MS, *m/e* 312 (M$^+$). Anal. Calcd for $C_{17}H_{16}N_2O_4$: C, 65.38; H, 5.16; N, 8.97. Found: C, 65.37; H, 5.16; N, 8.88.

Synthesis of 3-[(*p*-Acetamidophenyl)carbamoyl]norbornadiene-2-carboxylic Acid (1m). In a manner similar to the synthesis of **1c**, the reaction of **7** with commercially available 4-aminoacetanilide gave **1m** in a yield of 89%: yellow needles; mp 235–237 °C (from acetonitrile); ^{1}H NMR (D_2O–Na_2CO_3) δ 2.36–2.45 (m, 2 H), 2.43 (s, 3 H), 4.4–4.64 (m, 2 H), 7.45–7.56 (m, 2 H), 7.83 (a half of AB q, *J* = 9 Hz, 2 H), 7.96 (a half of AB q, *J* = 9 Hz, 2 H); IR (KBr) 3000–3700 (br, COOH), 3250 (NH), 1690, 1660 cm^{-1} (C=O); UV (1×10^{-2} M Na_2CO_3 (aq)) λ_{max} 247 (ϵ 15500), 313 nm (8950); MS, *m/e* 312 (M$^+$). Anal. Calcd for $C_{17}H_{16}N_2O_4$: C, 65.38; H, 5.16; N, 8.97. Found: C, 65.60; H, 5.27; N, 9.00.

Synthesis of 3-[(*p*-Nitrophenyl)carbamoyl]norbornadiene-2-carboxylic Acid (1q). In a manner similar to the synthesis of **1c**, the reaction of **7** with commercially available *p*-nitroaniline in acetone gave **1q** in a yield of 48%: yellow plates; mp 222–227 °C (from ethanol); ^{1}H NMR (CD_3CN) δ 2.0–2.3 (m, 2 H), 4.05–4.3 (m, 2 H), 6.84–6.92 (m, 2 H), 7.74 (a half of AB q, *J* = 8 Hz, 2 H), 8.19 (a half of AB q, *J* = 8 Hz, 2 H), 10.3–10.5 (br, 1 H); IR (KBr) 2440–3660 (br, COOH, NH), 1685 cm^{-1} (C=O); UV (1×10^{-1} M Na_2CO_3 (aq)) λ_{max} 205 (ϵ 18800), 348 nm (21100); MS, *m/e* 300 (M$^+$). Anal. Calcd for $C_{15}H_{12}N_2O_5$: C, 60.00; H, 4.03; N, 9.33. Found: C, 60.19; H, 3.98; N, 9.20.

Synthesis of *N*,*N*′-Bis[(3-carboxynorbornadien-2-yl)carbonyl]ethylenediamine (3a). In a manner similar to the synthesis of **1c**, the reaction of 2 equiv of **7** with 1 equiv of commercially available ethylenediamine gave **3a** in a yield of 78%. All compounds **3**, **4**, and **5** were purified by reverse-phase liquid chromatography: white crystals; mp >300 °C; ^{1}H NMR (D_2O–$NaHCO_3$) δ 2.3–2.7 (m, 4 H), 3.85 (s, 4 H), 4.2–4.4 (m, 4 H), 7.3–7.5 (m, 4 H); IR (KBr) 3200–3700 (br, COOH), 3270 (NH), 1690 cm^{-1} (C=O); UV (1×10^{-2} M Na_2CO_3 (aq)) λ_{max} 231 (ϵ 12400), 280 nm (5400, sh); MS, *m/e* (relative intensity) 385 (M$^+$ + 1, 71), 384 (M$^+$, 100). Anal. Calcd for $C_{20}H_{20}N_2O_6$: C, 62.49; H, 5.24; N, 7.29. Found: C, 62.52; H, 5.12; N, 7.31.

Synthesis of *N*,*N*′-Bis[(3-carboxynorbornadien-2-yl)carbonyl]-*o*-phenylenediamine (3b). In a manner similar to the synthesis of **3a**, the reaction of **7** with commercially available *o*-phenylenediamine gave **3b** in a yield of 62%: pale yellow crystals; mp >300 °C; ^{1}H NMR (D_2O–Na_2CO_3) δ 2.38–2.7 (m, 4 H), 4.32–4.92 (m, 4 H), 7.3–7.5 (m, 4 H), 7.7–8.0 (m, 4 H); IR (KBr) 3100–3600 (br, COOH), 3290 (NH), 1690 cm^{-1} (C=O); UV (1×10^{-2} M Na_2CO_3 (aq)) 280 nm (ϵ 9500, sh); MS, *m/e* 432 (M$^+$). Anal. Calcd for $C_{24}H_{20}N_2O_6$: C, 66.66; H, 4.66; N, 6.48. Found: C, 66.41; H, 4.73; N, 6.35.

Synthesis of *N*,*N*′-Bis[(3-carboxynorbornadien-2-yl)carbonyl]-*p*-phenylenediamine (3c). In a manner similar to the synthesis of **3a**, the reaction of **7** with commercially available *p*-phenylenediamine in acetone gave **3c** in a yield of 80%: yellow crystals; mp >300 °C; ^{1}H NMR (D_2O–$NaHCO_3$) δ 2.3–2.6 (m, 4 H), 4.3–4.5 (m, 4 H), 7.3–7.4 (m, 4 H), 7.85 (s, 4 H); IR (KBr) 3100–3700 (br, COOH), 3320 (NH), 1680 cm^{-1} (C=O); UV (1×10^{-2} M Na_2CO_3 (aq)) λ_{max} 237 (ϵ 17800), 337.5 nm (12400); MS, *m/e* 432 (M$^+$). Anal. Calcd for $C_{24}H_{20}N_2O_6$: C, 66.66; H, 4.66; N, 6.48. Found: C, 66.37; H, 4.57; N, 6.43.

General Procedure for Synthesis of the Quadricyclane Derivative. Either an aqueous alkaline (Na_2CO_3 or $NaHCO_3$) solution or a dry acetonitrile solution of a norbornadiene derivative was prepared in Pyrex tubes and was irradiated with a 300-W high pressure mercury arc lamp through a filter of aqueous saturated copper sulfate solution. For the synthesis of **2m** and **5c**, an acetone solution filter was used in order to cut off light not useful for the photoreaction. The completion of the photoreaction was determined by TLC, NMR, UV, or HPLC techniques. For example, in 0.1 M solutions of **1a–h**,**k**,**l** and **3a**,**b** irradiation of about 2–6 h was required for the completion, and in 0.01 M solutions of **1m** and **3c** about 1–3 days. For the reaction in aqueous alkaline solutions, the solution was acidified, and resulting precipitates were filtered. The precipitates were reasonably pure quadricyclane derivatives. For the reaction in acetonitrile solutions, the solution was evaporated to give reasonably pure quadricyclane derivatives. For **2h**, the reaction mixture was chromatographed over silica gel with dichloromethane as an eluant. Compounds **4a–c** were separated from unreacted **3a–c** and further reacted to **5a–c** by the HPLC technique.

3-Carbamoylquadricyclane-2-carboxylic acid (2a): 100% yield; white crystals; mp 176–178 °C (from ethyl acetate); ^{1}H NMR (CD_3OD) δ 1.98–2.75 (m, 6 H); IR (KBr) 2320–3700 (br, COOH), 3330 (NH), 1650, 1690 cm^{-1} (C=O); MS, calcd for $C_9H_9NO_3$ *m/e* 179.0582, found *m/e* 179.0581 (M$^+$).

3-(Methylcarbamoyl)quadricyclane-2-carboxylic acid (2b): 100% yield; white crystals; mp 167–170 °C (from acetonitrile); ^{1}H NMR (D_2O–Na_2CO_3) δ 2.55–3.0 (m, 6 H), 3.2 (s, 3 H); IR (KBr) 2820–3260 (br, COOH), 3270 (NH), 1670 cm^{-1} (C=O); MS, calcd for $C_{10}H_{11}NO_3$ *m/e* 197.0740, found *m/e* 193.0752 (M$^+$).

3-(Benzylcarbamoyl)quadricyclane-2-carboxylic acid (2c): 100% yield; white needles; mp 143–144 °C (from dichloromethane and hexane); ^{1}H NMR ($CDCl_3$) δ 1.96–2.7 (m, 6 H), 4.3–4.5 (m, 2 H), 7.1–7.4 (m, 5 H), 8.1–8.6 (br, 1 H), 14.8–16.5 (br, 1 H); IR (KBr) 3000–3700 (br, COOH), 3280 (NH), 1680 cm^{-1} (C=O); MS, calcd for $C_{16}H_{15}NO_3$ *m/e* 269.1051, found *m/e* 269.1048 (M$^+$).

3-(*tert*-Butylcarbamoyl)quadricyclane-2-carboxylic acid (2d): 100% yield; white needles; mp 159–161 °C (from dichloromethane and hexane); ^{1}H NMR ($CDCl_3$) δ 1.34 (s, 9 H), 2.0–2.8 (m, 6 H); IR (KBr) 3000–3640 (br, COOH), 3250 (NH), 1680 cm^{-1} (C=O); MS, calcd for $C_{13}H_{17}NO_3$ *m/e* 235.1208, found *m/e* 235.1209 (M$^+$).

3-(Dimethylcarbamoyl)quadricyclane-2-carboxylic acid (2e): 100% yield; white crystals; mp 139–141 °C (from di-

Table VI. Photostationary State

			$\Phi_{Q\rightarrow N}/\Phi_{N\rightarrow Q}$	
	$\epsilon_{313\ \mathrm{nm}}$	$\Phi_{313\ \mathrm{nm}}$	obsd	calcd
1m (N)	9050	0.07 ± 0.01		
2m (Q)	350	0.35 [illegible] 0.04	5.0	4.9^{a}
4c (N)	10400	0.034 ± 0.002		
5c (Q)	5000	0.40 ± 0.04	11.8	11.8^{b}

[a] $[\mathbf{1m}]_{pss}/[\mathbf{2m}]_{pss} = 16/84$. [b] $[\mathbf{4c}]_{pss}/[\mathbf{5c}]_{pss} = 85/15$.

chloromethane and hexane); ^{1}H NMR ($CDCl_3$) δ 2.15–2.65 (m, 6 H), 2.9 (s, 6 H); IR (KBr) 2250–3240 (br, COOH), 1695 cm^{-1} (C═O); MS, calcd for $C_{11}H_{13}NO_3$ *m/e* 207.0895, found *m/e* 207.0900 (M^+).

***N*-[(3-Carboxyquadricyclan-2-yl)carbonyl]pyrrolidine (2f)**: 100% yield; white needles; mp 132–135 °C (from dichloromethane and hexane); ^{1}H NMR ($CDCl_3$) δ 1.68–2.08 (m, 4 H), 2.08–2.6 (m, 5 H), 2.84–2.96 (m, 1 H), 2.8–3.9 (m, 4 H), 14.5–15.2 (br, 1 H); IR (KBr) 3220–3650 (br, COOH), 1710 cm^{-1} (C═O); MS, calcd for $C_{13}H_{15}NO_3$ *m/e* 233.1052, found *m/e* 233.1050 (M^+).

3-(Methylphenylcarbamoyl)quadricyclane-2-carboxylic acid (2h): 70% yield; white needles; mp 181.5–184 °C (from dichloromethane and hexane); ^{1}H NMR ($CDCl_3$) δ 1.6–1.73 (m, 1 H), 1.8–2.04 (m, 2 H), 2.14–2.22 (m, 1 H), 2.24–2.44 (m, 2 H), 3.27 (s, 3 H), 7.0–7.5 (m, 5 H); IR (KBr) 3200–3650 (br, COOH), 1700 cm^{-1} (C═O); MS, calcd for $C_{16}H_{15}NO_3$, *m/e* 269.1051, found *m/e* 269.1028 (M^+).

3-[(Carboxymethyl)carbamoyl]quadricyclane-2-carboxylic acid (2k): 100% yield; white crystals; mp 239 °C; ^{1}H NMR (D_2O–Na_2CO_3) δ 2.45–3.04 (m, 6 H), 4.25 (s, 2 H); IR (KBr) 2300–3680 (br, COOH), 3250 (NH), 1730, 1680 cm^{-1} (C═O); MS, calcd for $C_{11}H_{11}NO_5$ *m/e* 237.0637, found *m/e* 237.0689 (M^+).

3-[(*o*-Acetamidophenyl)carbamoyl]quadricyclane-2-carboxylic acid (2l): 100% yield; white crystals; mp 168–169.5 °C (from acetonitrile); ^{1}H NMR (D_2O–Na_2CO_3) δ 2.8–3.22 (m, 6 H), 2.82 (s, 3 H), 7.8–8.08 (m, 4 H); IR (KBr) 3000–3700 (br, COOH), 3220 (NH), 1660, 1640 cm^{-1} (C═O); MS, calcd for $C_{17}H_{16}N_2O_4$ *m/e* 312.1109, found *m/e* 312.1180 (M^+).

3-[(*p*-Acetamidophenyl)carbamoyl]quadricyclane-2-carboxylic acid (2m): 100% yield; white crystals; mp 209–212 °C (from acetonitrile); ^{1}H NMR (D_2O–Na_2CO_3) δ 2.6–3.16 (m, 6 H), 2.68 (s, 3 H), 7.88 (a half of AB q, J = 9 Hz, 2 H), 8.02 (a half of AB q, J = 9 Hz, 2 H); IR (KBr) 3000–3700 (br, COOH), 3300 (NH), 1640–1660 cm^{-1} (C═O); MS, calcd for $C_{17}H_{16}N_2O_4$ *m/e* 312.1109, found *m/e* 312.1106 (M^+).

***N*-[(3-Carboxynorbornadien-2-yl)carbonyl]-*N′*-[(3-carboxyquadricyclan-2-yl)carbonyl]ethylenediamine (4a)**: white crystals; mp >300 °C; ^{1}H NMR (D_2O–Na_2CO_3) δ 2.2–2.95 (m, 8 H), 3.75 (s, 4 H), 4.1–4.4 (m, 2 H), 7.25–7.35 (m, 2 H); IR (KBr) 3200–3680 (br, COOH), 3270 (NH), 1690 cm^{-1} (C═O); UV (1×10^{-1} M Na_2CO_3 (aq)) 290 nm (ϵ 1790, sh); MS, calcd for $C_{20}H_{20}N_2O_6$ *m/e* 384.1320, found *m/e* 384.1318 (M^+).

***N*-[(3-Carboxynorbornadien-2-yl)carbonyl]-*N′*-[(3-carboxyquadricyclan-2-yl)carbonyl]-*o*-phenylenediamine (4b)**: pale yellow crystals; mp >300 °C; ^{1}H NMR (D_2O–Na_2CO_3) δ 2.4–3.1 (m, 8 H), 4.35–4.6 (m, 2 H), 7.4–7.56 (m, 2 H), 7.7–8.0 (m, 4 H); IR (KBr) 3100–3700 (br, COOH), 3260 (NH), 1690, 1640 cm^{-1} (C═O); UV (1×10^{-1} M Na_2CO_3 (aq)) 310 nm (ϵ 3400, sh); MS, calcd for $C_{24}H_{20}N_2O_6$ *m/e* 432.1320, found *m/e* 432.1323 (M^+).

***N*-[(3-Carboxynorbornadien-2-yl)carbonyl]-*N′*-[(3-carboxyquadricyclan-2-yl)carbonyl]-*p*-phenylenediamine (4c)**: yellow crystals; mp >300 °C; ^{1}H NMR (D_2O–Na_2CO_3) δ 2.34–3.05 (m, 8 H), 4.32–4.56 (m, 2 H), 7.3–7.44 (m, 2 H), 7.73–7.9 (m, 4 H); IR (KBr) 3000–3690 (br, COOH, NH), 1685 cm^{-1} (C═O); UV (1×10^{-1} M Na_2CO_3 (aq)) λ_{max} 260 (ϵ 15200), 315 nm (10400); MS, calcd for $C_{24}H_{20}N_2O_6$ *m/e* 432.1320, found *m/e* 432.1318 (M^+).

***N*,*N′*-Bis[(3-carboxyquadricyclan-2-yl)carbonyl]ethylenediamine (5a)**: 100% yield; white crystals; mp >300 °C; ^{1}H NMR (D_2O–$NaHCO_3$) δ 2.44–3.04 (m, 12 H), 3.85 (s, 4 H); IR (KBr) 3000–3700 (br, COOH), 3380 (NH), 1680 cm^{-1} (C═O); MS, calcd for $C_{20}H_{20}N_2O_6$ *m/e* 384.1320, found *m/e* 384.1323 (M^+).

***N*,*N′*-Bis[(3-carboxyquadricyclan-2-yl)carbonyl]-*o*-phenylenediamine (5b)**: 100% yield; white crystals; mp >300 °C; ^{1}H NMR (D_2O–Na_2CO_3) δ 2.6–3.2 (m, 12 H), 7.84–7.96 (m, 4 H); IR (KBr) 3000–3700 (br, COOH), 3360 (NH), 1650 cm^{-1} (C═O); MS, calcd for $C_{24}H_{20}N_2O_6$ *m/e* 432.1320, found *m/e* 432.1320 (M^+).

***N*,*N′*-Bis[(3-carboxyquadricyclan-2-yl)carbonyl]-*p*-phenylenediamine (5c)**: 100% yield; white crystals; mp >300 °C; ^{1}H NMR (D_2O–$NaHCO_3$) δ 2.5–3.1 (m, 12 H), 7.87 (s, 4 H); IR (KBr) 3000–3700 (br, COOH), 3420 (NH), 1680, 1640 cm^{-1} (C═O); MS, calcd for $C_{24}H_{20}N_2O_6$ *m/e* 432.1320, found *m/e* 432.1322 (M^+).

Isosbestic Points in UV Spectra on Photoisomerization of 1g to 2g. A 1×10^{-4} M solution of **1g** in 1×10^{-2} M Na_2CO_3 (aq) in a UV cell (1 cm length) was irradiated with sunlight (in Kyoto, July 15, 1982, a fine day, 1:30–2:00 pm). After appropriate time intervals, the cell was transferred into the UV spectrometer and the spectrum was recorded. The isosbestic points were seen at 235 and 279 nm. Under the above conditions, **1g** completely isomerized to **2g** on irradiation with clear daylight within 30 min.

Determination of Quantum Yield of Photoisomerization. A 300-W high pressure mercury projector lamp was used as a light source. A combination of Corning 7-54 glass filter, $NiSO_4$ aqueous solution filter, potassium hydrogen phthalate aqueous solution filter, and K_2CrO_4 aqueous solution filter was used for isolation of 313-nm light.[25] A combination of Corning 7-37 glass filter, $CuSO_4$ aqueous solution filter, and 2,7-dimethyl-3,6-diazacyclohepta-1,6-diene perchlorate aqueous solution filter was used for isolation of 366-nm light.[25] Light intensity was determined by potassium ferrioxalate actinometry.[25]

UV Spectral Analysis. The amount of the quadricyclane derivative produced was determined by measuring the amount of norbornadiene derivative before and after irradiation by means of UV spectrometer.

UV Spectral Kinetic Analysis. According to the method described by Kaupp and Prinzbach,[26] we measured the quantum yield more than 10 times in one series.

HPL Chromatogram Analysis. Amounts of norbornadiene derivative consumed and quadricyclane derivative produced were determined by measuring each area of the liquid chromatogram.

Each quantum yield was an average value of more than three experiments.

Oxygen Effect. Argon, air, and oxygen were bubbled through Na_2CO_3 aqueous solutions of **1** in Pyrex test tubes. These three solutions were irradiated with the filtered light on a merry-go-round apparatus. The quantum yields were determined by the HPLC technique described above.

Photoisomerization by Sunlight. Na_2CO_3 aqueous solutions (0.5 M) of 0.1 M **1b** and **1g** in a cell made of hard glass (5 cm × 5 cm × 1 mm) were irradiated with sunlight (in Kyoto, 1984 November) for 1 day under the same conditions. Each conversion was determined by the HPLC technique.

Photostationary State at 313 nm. Na_2CO_3 aqueous solutions of **1m** and **2m** were irradiated with 313-nm light. Before the conversion of each photoisomerization exceeded a few percentage, the irradiation was stopped and the quantum yields were determined by the HPLC technique. When the solution of **1m** was irradiated for a long enough time, the photostationary state was achieved; $[\mathbf{1m}]/[\mathbf{2m}] = 16/84$. When the solution of **2m** was irradiated, the same photostationary state was achieved. Using the equation that $\epsilon_{1m}[\mathbf{1m}]_{pss}\Phi_{1m\rightarrow 2m} = \epsilon_{2m}[\mathbf{2m}]_{pss}\Phi_{2m\rightarrow 1m}$[27] and the data (Table V), $\Phi_{2m\rightarrow 1m}/\Phi_{1m\rightarrow 2m} = 4.9$ was calculated. The calculated value was almost equal to the value (5.0) obtained by experiment. In the cases of **4c** and **5c**, a similar phenomenon was observed, and the calculated value (11.8) was equal to the observed value (11.8).

Registry No. **1a**, 98736-22-2; **1b**, 98736-23-3; **1c**, 98736-24-4; **1d**, 84328-13-2; **1e**, 98736-25-5; **1f**, 98736-26-6; **1g**, 78941-78-3; **1h**, 98736-27-7; **1i**, 98736-28-8; **1j**, 98736-29-9; **1k**, 98736-30-2; **1l**, 84293-19-6; **1m**, 84293-20-9; **1n**, 96627-81-5; **1o**, 96627-82-6; **1p**, 79632-15-8; **1q**, 98736-31-3; **2a**, 98736-32-4; **2b**, 90632-73-8; **2c**, 98736-33-5; **2d**, 88049-65-4; **2e**, 98736-34-6; **2f**, 98736-35-7; **2g**,

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78941-77-2; **2h**, 98736-36-8; **2k**, 98736-37-9; **2l**, 98736-43-7; **2m**, 98736-44-8; **3a**, 84293-23-2; **3b**, 84293-21-0; **3c**, 84293-22-1; **4a**, 98736-38-0; **4b**, 98736-39-1; **4c**, 98736-40-4; **5a**, 98736-41-5; **5b**, 98736-42-6; **5c**, 98759-92-3; **6**, 15872-28-3; **7**, 17397-31-8; $MeNH_2$, 74-89-5; $PhCH_2NH_2$, 100-46-9; *t*-$BuNH_2$, 75-64-9; Me_2NH, 124-40-3; MeNHPh, 100-61-8; Ph_2NH, 122-39-4; AcNH-*p*-$C_6H_4NH_2$, 122-80-5; *p*-$NO_2C_6H_4NH_2$, 100-01-6; AcNH-*o*-$C_6H_4NH_2$, 34801-09-7; *o*-$NH_2C_6H_4NH_2$, 95-54-5; $NH_2(CH_2)_2NH_2$, 107-15-3; *p*-$NH_2C_6H_4NH_2$, 106-50-3; pyrrolidine, 123-75-1; indoline, 496-15-1; glycine, 56-40-6.

Conformations of Hexahydropyridazine Cation Radicals

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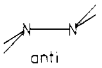
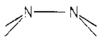
The variable temperature ESR spectra of the cations of 1,2-dimethylhexahydropyridazine (**3**) *cis*- and *trans*-1,2,3,6-tetramethylhexahydropyridazine (**4** and **5**), *trans*-3,4-dimethyl-3,4-diazabicyclo[4.4.0]decane (**6**), and 1,2,3,3,6,6-hexamethylhexahydropyridazine (**7**) are reported and demonstrate that these species exist in half-chair conformations. The 3,6-diaxial methyl form of 5^+ is about 1 kcal/mol stabler than its 3,6-diequatorial ring reversal form. The UV spectra of solutions containing these cations and those of three other hexahydropyridazine cation radicals are described.

Tetraalkylhydrazine cation radicals $R_4N_2^+$ have approximately sp^2-hybridized nitrogen atoms and hence a p-rich atomic orbital centered at each nitrogen. There is a strong electronic preference for coplanarity of these p-rich orbitals, producing π and π* MOs. The π MO is doubly occupied and the π* singly occupied, a situation which has been described as a "three-electron π bond".[1] Bending at N in $R_4N_2^+$ is unusually easy, and constricting the RNR and RNN bond angles by linking the R groups in rings has been shown to induce bending of the nitrogens at equilibrium, increasing the fraction of s hybridization in the π system. If the nitrogen lone pairs remain coplanar, bending at N can either cause the alkyl groups to be staggered, shown as anti, or to be eclipsed, as in syn. The


anti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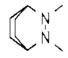
symmetries of the bonding π and antibonding π* orbitals change between syn- and anti-bent structures, which affects their spectroscopic properties because π and π* mix with the σ and σ* orbitals when the nitrogens are bent. A given amount of bend syn causes larger mixing than the same amount of bend anti, producing a larger increase in both the nitrogen ESR splitting constant a(N) and the wavelength for the π,π* transition in the $R_4N_2^+$ optical spectrum, λ_m.[2] Both steric and electronic effects favor anti bend in acyclic and *N,N*-cycloalkyl examples. In contrast, the *N,N'*-bicyclic cations 1^+ and 2^+ show relatively large a(N) values (13.9 and 16.0 G, respectively), which we have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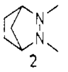
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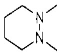
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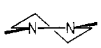
argued indicates they are syn bent at nitrogen.[2] Because their bicyclic structures hold the ring CNNC dihedral angle near 0°, anti bending forces twisting of the 3e-π bond, while syn bending allows it to remain untwisted, rationalizing syn bending of 1^+ and 2^+.

Table I. ESR Splitting Constants for Radical Cations of Hexahydropyridazines[a]

compd	temp, °C	a(2 N), a(2 CH_3)	other splittings	LW for simulation, G
3	−100	ca. 12.8	27.6 (2 H)	1.2
4	+60	13.65 (2 H)	ca. 13.65 (2 H)	
		12.62 (6 H)		0.3
	−100	ca. 12.9	27.5 (1 H)	1.5
5	+85	ca. 13.0	8.2 (2 H)	1.2
	−105	ca. 13.2_5	3.6 (2 H)	1.5
6	−105	ca. 12.7	23.2 (2 H), 4.2 (2 H)	1.2
7	+60	ca. 13.0		1.0
	−60	ca. 12.8		1.7

[a] Generated by $(4\text{-}BrC_6H_4)_3N^+SbCl_6^-$ oxidation in butyronitrile and reported in gauss = 0.1 mT. The a values reported are believed to be accurate to about 0.1 G.

The six-membered ring monocyclic compound, dimethylhexahydropyridazine **3**, might be expected to give a half-chair radical cation I if the nitrogens remained flat in the cation (ring CNNC angle about 0° again). We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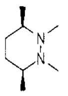
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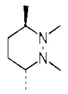
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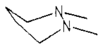
II

published room temperature ESR spectra 4^+ and 5^+ several years ago[3] with ring tertiary hydrogen splittings which did not agree with our predictions for I conformations of these species. We expected 5^+ to have pseudoequatorial C_3,C_6 methyl groups and hence pseudoaxial tertiary hydrogens. Since 4^+ would be rapidly equilibrating between equal energy I structures and pseudoaxial splittings are much larger than pseudoequatorial splittings, we expected a(2 H) for 5^+ to be much larger than a(2 H) for 4^+ if they were in half-chair conformations I. We observed the opposite, a(2 H) of 6.2 G for 5^+ and a(2 H) of 13 G for 4^+, and suggested that these cations were in boat conformations II. This paper reports low-temperature ESR and UV spectra of these and related cations which show that the assumption we made in 1971 that 5^+ would be stablest with

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