Photochemical [2 + 2] Dimerization of [6](1,4)-Anthracenophane

Yoshito Tobe,* Tohru Takahashi, Kazuya Kobiro,[1] and Kiyomi Kakiuchi

Contribution from the Department of Applied Fine Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565, Japan. *Received November 21, 1990.*
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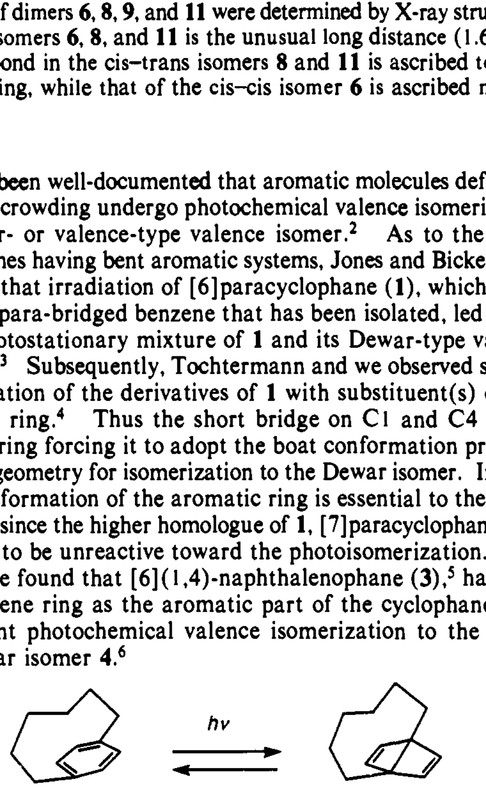
Abstract: Irradiation of [6](1,4)-anthracenophane (**5**) through a solution filter ($\lambda > 350$ nm) gave five kinds of cyclobutane dimers **6–10** conjoined at the C1 and C2 of the anthracene core. Neither valence isomerization to the Dewar isomer nor [4 + 4] dimerization at C9 and C10 was observed. The absence of remarkable effect of concentration or solvent polarity on the product distribution suggests that the dimerization of **5**, at least leading to the major isomer **9**, proceeds through an excited triplet state. Irradiation of **5** through a Pyrex filter afforded dimer **11** as the major product which was derived from the cis–trans dimer **8**. This was accomplished by intramolecular hydrogen abstraction from the bridge methylene by the bridgehead double bond of the lower vinylnaphthalene unit followed by transannular coupling of the diradical intermediate. The molecular structures of dimers **6**, **8**, **9**, and **11** were determined by X-ray structure analyses. The most remarkable structural feature of the head-to-head isomers **6**, **8**, and **11** is the unusual long distance (1.62–1.64 Å) of the cyclobutane bond a (C7–C38). The elongation of this bond in the cis–trans isomers **8** and **11** is ascribed to steric repulsion between the methylene groups across the cyclobutane ring, while that of the cis–cis isomer **6** is ascribed mainly to "through-bond" interaction.

It has been well-documented that aromatic molecules deformed by steric crowding undergo photochemical valence isomerization to Dewar- or valence-type valence isomer.[2] As to the paracyclophanes having bent aromatic systems, Jones and Bickelhaupt reported that irradiation of [6]paracyclophane (**1**), which is the smallest para-bridged benzene that has been isolated, led to the clean photostationary mixture of **1** and its Dewar-type valence isomer **2**.[3] Subsequently, Tochtermann and we observed similar isomerization of the derivatives of **1** with substituent(s) on the aromatic ring.[4] Thus the short bridge on C1 and C4 of the benzene ring forcing it to adopt the boat conformation provides an ideal geometry for isomerization to the Dewar isomer. Indeed, severe deformation of the aromatic ring is essential to the isomerization since the higher homologue of **1**, [7]paracyclophane, was reported to be unreactive toward the photoisomerization.[3] Recently, we found that [6](1,4)-naphthalenophane (**3**),[5] having a naphthalene ring as the aromatic part of the cyclophane, also underwent photochemical valence isomerization to the hemi-1,4-Dewar isomer **4**.[6]



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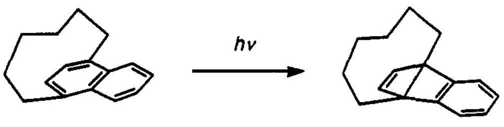

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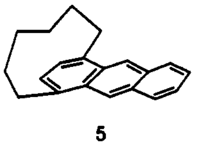

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On the contrary, we have found that irradiation of [6](1,4)-anthracenophane (**5**),[5] an anthracene homologue of **1** and **3**, did not lead to its valence isomer but to the cyclobutane dimers **6–11** in high efficiency. Particularly noteworthy is that (i) the photochemical behavior of **5** is not in line with those of **1** and **3** and (ii) **5** gave [2 + 2] photodimers conjoined at C1 and C2 of the anthracene core instead of giving [4 + 4] dimers connected at C9 and C10, which are the common products of the photochemistry of anthracene and its derivatives.[7] This is, to our knowledge, the first example of photochemical [2 + 2] cycloaddition that takes place at C1–C2 of an anthracene derivative.[8] Moreover, the relationship between the structure and the relative geometry of the cyclobutane ring of the dimers **6–11** would be of interest in connection with the chemistry of [2 + 2] dimers of aromatic molecules which has been the subject of intensive synthetic and theoretical studies.[9] In this context, the X-ray crystallographic structure analyses of the dimers **6**, **8**, **9**, and **11** have been undertaken to reveal that they possess unusually long cyclobutane bonds probably due to the steric repulsion and/or "through-bond" interaction.

In this paper, we disclose the photoreaction of **5** leading to the [2 + 2] photodimers **6–11** and the molecular structures of the dimers **6**, **8**, **9**, and **11**.

Results and Discussion

When a solution of **5** in cyclohexane (4×10^{-2} M) was irradiated at room temperature through a solution filter of 1,4-diphenylbutadiene (0.12 M in tetrahydrofuran), which cuts off wavelengths shorter than 350 nm, five dimers **6–10** were obtained. The relative ratio of **6–10** determined by HPLC (UV detector with detection wavelength of 254 nm) was 5%, 11%, 18%, 45%, and 21%, respectively. The major and least soluble isomer **9** was isolated by washing out the other isomers with ether. The remaining products were isolated by repeated chromatography on silica gel. The isolated yields were 1.6%, 1.6%, 10%, 34%, and 10%, respectively (Scheme I).

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[1] Present address: Niihama National College of Technology, 7-1 Yagumo-cho, Niihama, Ehime 792, Japan.

[2] (a) Bryce-Smith, D.; Gilbert, A. *Tetrahedron* **1976**, *32*, 1309. (b) Yoshida, Z.; Miki, S. *Kagaku no Ryoiki* **1978**, *32*, 775.

[3] Kammula, S. L.; Iroff, L. D.; Jones, M., Jr.; van Straten, J. W.; de Wolf, W. H.; Bickelhaupt, F. *J. Am. Chem. Soc.* **1977**, *99*, 5815.

[4] (a) Liebe, J.; Wolff, C.; Krieger, C.; Weiss, J.; Tochtermann, W. *Chem. Ber.* **1985**, *118*, 4144. (b) Tobe, Y.; Ueda, K.; Kakiuchi, K.; Odaira, Y.; Kai, Y.; Kasai, N. *Tetrahedron* **1986**, *42*, 1851.

[5] Tobe, Y.; Takashaski, T.; Ishikawa, T.; Yoshimura, M.; Suwa, M.; Kobiro, K.; Kakiuchi, K.; Gleiter, R. *J. Am. Chem. Soc.* **1990**, *112*, 8889.

[6] Tobe, Y.; Takahaski, T.; Kobiro, K.; Kakiuchi, K. *Chem. Lett.* **1990**, 1587.

[7] Trecker, D. J. *Organic Photochemistry*; Chapman, O. L., Ed.; Marcel Dekker: New York, 1969; Vol. 2, pp 85–86.

[8] Unsymmetrical [4 + 4] dimerization at C1–C4 and C9–C10 of an anthracene derivative has been reported: Felix, G.; Lapauyade, R.; Bouas-Laurent, H.; Clin, B. *Tetrahedron Lett.* **1976**, 2277.

[9] Benzene dimers: Gleiter, R.; Gubernator, K.; Grimme, W. *J. Org. Chem.* **1981**, *46*, 1247. Yang, N. C.; Hrnjez, B. J.; Horner, M. G. *J. Am. Chem. Soc.* **1987**, *109*, 3158. Yang, N. C.; Noh, T.; Gan, H.; Halfon, S.; Hrnjez, B. J. *Ibid.* **1988**, *110*, 5919. Schriver, G. W.; Gerson, D. J. *J. Am. Chem. Soc.* **1990**, *112*, 4723. Naphthalene dimer: Tobe, Y.; Hirata, F.; Nishida, K.; Fujita, H.; Kimura, K.; Odaira, Y. *J. Chem. Soc., Chem. Commun.* **1981**, 786.

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Scheme I

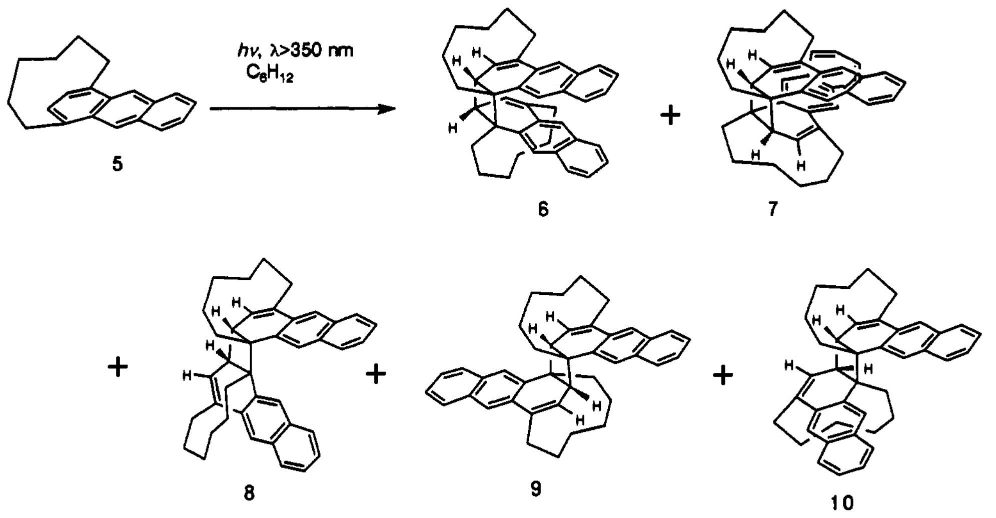
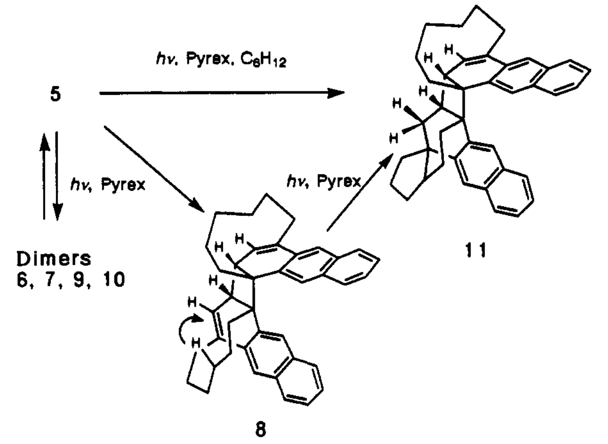


Table I. Product Distribution in the Photodimerization of **5**[a]

solvent	concn, M	6	7	8	9	10
		product ratio,[b] %				
cyclohexane	4×10^{-2}	5	11	18	45	21
	4×10^{-3}	5	10	16	43	25
benzene	1×10^{-2}	9	5	17	49	21
CH_2Cl_2	8×10^{-3}	16	4	14	45	21
	1×10^{-3}	17	5	15	44	20
CH_3CN	1×10^{-2}	24	9	9	41	18

[a] Irradiation through a solution filter of 1,4-diphenylbutadiene (λ > 350 nm). [b] The ratio was determined by HPLC (ODS column, UV detector with detection wavelength of 254 nm).

Scheme II



That the products **6–10** are the cyclobutane dimers fused at C1 and C2 of the anthracene ring was elucidated by the presence of vinyl and the methine protons which couple each other in the ^{1}H NMR spectra. Of the five dimers **6–10**, only **8** exhibits signals due to the two kinds of successively aligned vinyl (δ 6.12 (d, J = 7.0 Hz) and 6.35 (d, J = 3.3 Hz)) and methine protons (δ 3.19 (dd, J = 12.1, 7.0 Hz)) and 3.32 (dt, J = 12.1, 3.3 Hz)), indicating clearly that **8** has a cis–trans stereochemistry around the cyclobutane ring. The relative configuration of **8** was determined by the X-ray analysis to be cis–trans/head to head/syn as described later. Since the remaining dimers **6**, **7**, **9**, and **10** exhibit only one kind of vinyl and methine protons, their cyclobutane ring should have cis–cis configuration. The vinyl and the methine protons of the dimers **7** and **9** appear as sharp doublets which couple one another (J = 7.5 Hz). On the other hand, those protons of the dimers **6** and **10** appear as multiplets due to the long-range coupling between the vinyl and the remote methine protons. These results indicate that the dimers **6** and **10** have head-to-head configuration while **7** and **9** have head-to-tail arrangement in which the long-range coupling is not feasible. Since the structures of **6** and **9** were finally established by the X-ray analysis to be cis–cis/head to head/syn and cis–cis/head to tail/anti, respectively, it is reasonable to assume that **7** and **10** are cis–cis/head to tail/syn and cis–cis/head to head/anti isomers, respectively.

The distribution of the dimers is not affected by the concentration (10^{-2}–10^{-3} M) of **5** in the photoreaction, nor does the polarity of the solvent affect the product ratio remarkably as shown in Table I. While the ratio of **6** increased slightly with increasing solvent polarity, that of **9** remained constant. These results coupled with the entire lack of stereoselectivity in the cycloaddition suggest that the dimerization, at least to the major isomer **9**, proceeds via an excited triplet state of **5**.[10] It has been documented that the photochemical valence isomerization of benzene to the Dewar isomer takes place through its excited singlet state.[2a,11] Similarly, [4 + 4] dimerization of anthracenes is well-known to proceed via the excited singlet state.[10b] Since **5** did not undergo the valence isomerization or [4 + 4] dimerization, it seems likely that the population of the excited singlet state of **5** is small relative to its triplet state, probably due to facile intersystem crossing. The reasons for this are not fully understood. On the other hand, it is also possible to explain the anomalous reactivity of **5** in terms of the structural features of the anthracene core. Namely, the lack of **5** toward isomerization to the Dewar-type isomer is explained by a smaller charge density at C1 and C4 of LUMO of anthracene than those of naphthalene and benzene.[12] Also the enhanced reactivity of **5** toward [2 + 2] photodimerization[13] is probably due to the higher double bond character of the C1–C2 bond of anthracene, which is deformed severely by the short bridge, than to those of naphthalene and benzene.[14] This is in accord

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(10) (a) Reference 7, pp 96–101 and 107–110. (b) Turro, N. J. *Modern Molecular Photochemistry*; Benjamin/Cummings: Menlo Park, CA, 1978; pp 456–458.

(11) Reference 10b, pp 499–503.

(12) Coulson, C. A.; Streitwieser, A., Jr. *Dictionary of π-Electron Calculations*; Pergamon Press: Oxford, 1965; p 39 and references cited therein.

(13) [2 + 2] photocyclodimerization of bridgehead enones, which is one of the typical reactions of the excited triplet of α,β-enones, has been reported: House, H. O.; DeTar, M. B.; VanDerveer, D. *J. Org. Chem.* **1979**, *44*, 3793. House, H. O.; Sieloff, R. F.; VanDerveer, D. *Ibid.* **1981**, *46*, 4639.

(14) According to the MNDO calculations done for bent benzene, naphthalene, and anthracene with a bent angle of 20° at C1 and C4 and another 20° at H1 and H4, the π bond order of the C1–C2 bond of the bent benzene decreases with slight increase in the π bond order of the C2–C3 bond, which is in accord with ab initio calculations of the STO-3G level.[15] On the contrary, the π bond orders of C1–C2 bonds of the bent naphthalene and bent anthracene increase with a remarkable decrease of the π bond order of the C1–C8a bond of the former and the C1–C9a bond of the latter hypothetical molecules, respectively (Tobe, Y., unpublished results).

Table II. Crystal Data and Selected Refinement Parameters for X-ray Analysis of Dimers **6**, **8**, **9**, and **11**

compd	**6**	**8**	**9**	**11**
recryst solvent	CH_2Cl_2–petroleum ether	CH_2Cl_2–Et_2O	CH_2Cl_2	MeOH
formula	$C_{40}H_{40}$	$C_{40}H_{40}\cdot CH_2Cl_2$	$C_{40}H_{40}$	$C_{40}H_{40}$
cryst system	monoclinic	monoclinic	monoclinic	triclinic
space group	$C2/c$	$P2_1/n$	$P2_1/n$	$P\bar{1}$
cell const				
a, Å	18.788 (2)	27.631 (2)	14.159 (4)	11.724 (2)
b, Å	28.401 (2)	7.223 (1)	7.872 (3)	12.888 (2)
c, Å	10.886 (1)	16.613 (2)	13.689 (3)	11.576 (2)
α, deg				113.00 (2)
β, deg	100.05 (1)	104.06 (1)	111.79 (2)	119.30 (1)
γ, deg				79.01 (2)
V, Å^3	5720.1 (9)	3216.2 (6)	1416.9 (7)	1404.2 (4)
Z	8	4	2	2
d_{calc}, g cm^{-3}	1.232	1.251	1.221	1.228
no. of data collected	4252	4754	2102	4167
no. of unique data	3603	4044	1843	3547
R	0.084	0.138	0.073	0.075
R_w	0.134	0.216	0.120	0.123

with the unusual reactivities of **5** in its thermal reactions with dienophiles.[16]

Irradiation of **5** in cyclohexane through a Pyrex filter gave a complex mixture of products due to further photochemical reactions of the initial products **6**–**10** having a vinylnaphthalene chromophore. Purification of the major product, however, was achieved by chromatography followed by recrystallization to afford a new dimer **11** at 32% yield. The NMR spectra of **11** indicate that it is unsymmetric and possesses only one vinyl group. This means one of the double bond in **6**–**10** is lost by further photoreaction. Control experiments on individual irradiation of the dimers **6**–**10** revealed that the cis–cis dimers **6**, **7**, **9**, and **10** gave the monomer **5** via cycloreversion along with unidentified products. On the other hand, cycloreversion was not observed for the cis–trans isomer **8** which gave the new dimer **11**. The structure of **11** was established by X-ray analysis. The formation of **11** is explained in terms of the intramolecular hydrogen abstraction from the methylene bridge by the bridgehead double bond of the lower vinylnaphthalene unit with a trans junction of the 6–4 fused system (Scheme II). This reaction offers one of the relatively rare examples of intramoelcular hydrogen abstraction from π,π^* excited states.[17]

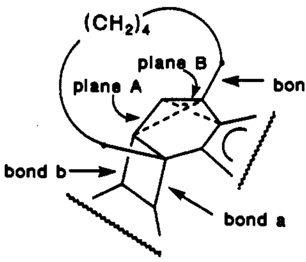
In order not only to determine the stereochemistry of the cyclobutane ring of the dimers but also to elucidate the structural feature around the cyclobutane and the bridgehead double bonds, single-crystal X-ray structure analyses of the dimers **6**, **8**, **9**, and **11** were undertaken. Table II lists the crystal data and selected refinement parameters and Figure 1 illustrates their ORTEP[18] views. In the case of the dimer **8**, the data are somewhat less reliable than that of the others due to the large thermal factors of the solvent molecule (CH_2Cl_2) in the crystal.

The structural features of the dimers are summarized in Table III. These include (i) the bond length of the cyclobutane ring for bonds a (C7–C38) and b (C20–C39), (ii) the average pucker angle (ϕ) of the cyclobutane ring, (iii) the dihedral angle (θ) between planes A and B which represents the torsion angle of the bridgehead double bond, (iv) the angle (χ) between the plane B and bond c which indicates the pyramidalization of the bridgehead double bond, (v) the dihedral angle (α) between the mean planes of two naphthalene rings, and (vi) the angle (β) between the naphthalene plane and the cyclobutane bond a (C7–C38). In the case of cis–cis/head to tail/anti isomer **9**, because of the presence of a symmetry center in the center of the cyclobutane ring, the lower half of the molecule is symmetrical with respect to the upper half. In the case of the others, the structural factors θ, χ, and β are determined for both the upper and the lower halfs of the molecules.

Table III. Selected Structural Parameters for Dimers **6**, **8**, **9**, and **11**

	compd			
parameter	**6**	**8**	**9**	**11**
bond length, Å				
bond a	1.637 (5)	1.622 (8)	1.584 (8)	1.639 (5)
bond b	1.543 (6)	1.515 (10)		1.545 (7)
av pucker angle				
ϕ, deg	16.4	40.5	0	38.7
deformation angles				
θ, deg (upper unit)	8.2	4.6	14.8	17.3
θ, deg (lower unit)	25.4	1.4		
χ, deg (upper unit)	10.2	11.3	17.3	9.7
χ, deg (lower unit)	14.1	3.7		
α,[a] deg	60.6	80.9	0	105.0
β,[b] deg				
upper unit	53.9	56.0	57.6	47.2
lower unit	64.1	42.5		26.1

[a] Dihedral angle between naphthalene rings. [b] Angle between bond a and the naphthalene ring.



The most important of the structural feature of the head-to-head dimers **6**, **8**, and **11** is the unusual long distance (1.62–1.64 Å) of the cyclobutane bond a. The corresponding bond of the head-to-tail isomer **9** is normal. In general, the C1–C2 bond in *cis*-1,2-diarylcyclobutanes is stretched due to steric repulsion between the aromatic rings and/or "through-bond" interaction between the π orbitals of the aromatic rings and the strained cyclobutane σ bond.[19] As shown in Table III, the dihedral angles (α) between two naphthalene rings in the cis–trans dimers **8** and **11** are nearly 90°, indicating that two naphthalene ring units are almost orthogonal to one another with a face-to-edge arrangement. Moreover, the angles (β) between the naphthalene ring and the cyclobutane bond a in the lower units of **8** and **11** are considerably small compared with those in cis–cis isomer **6**. In spite of these unfavorable geometries for the "through-bond" interaction, the

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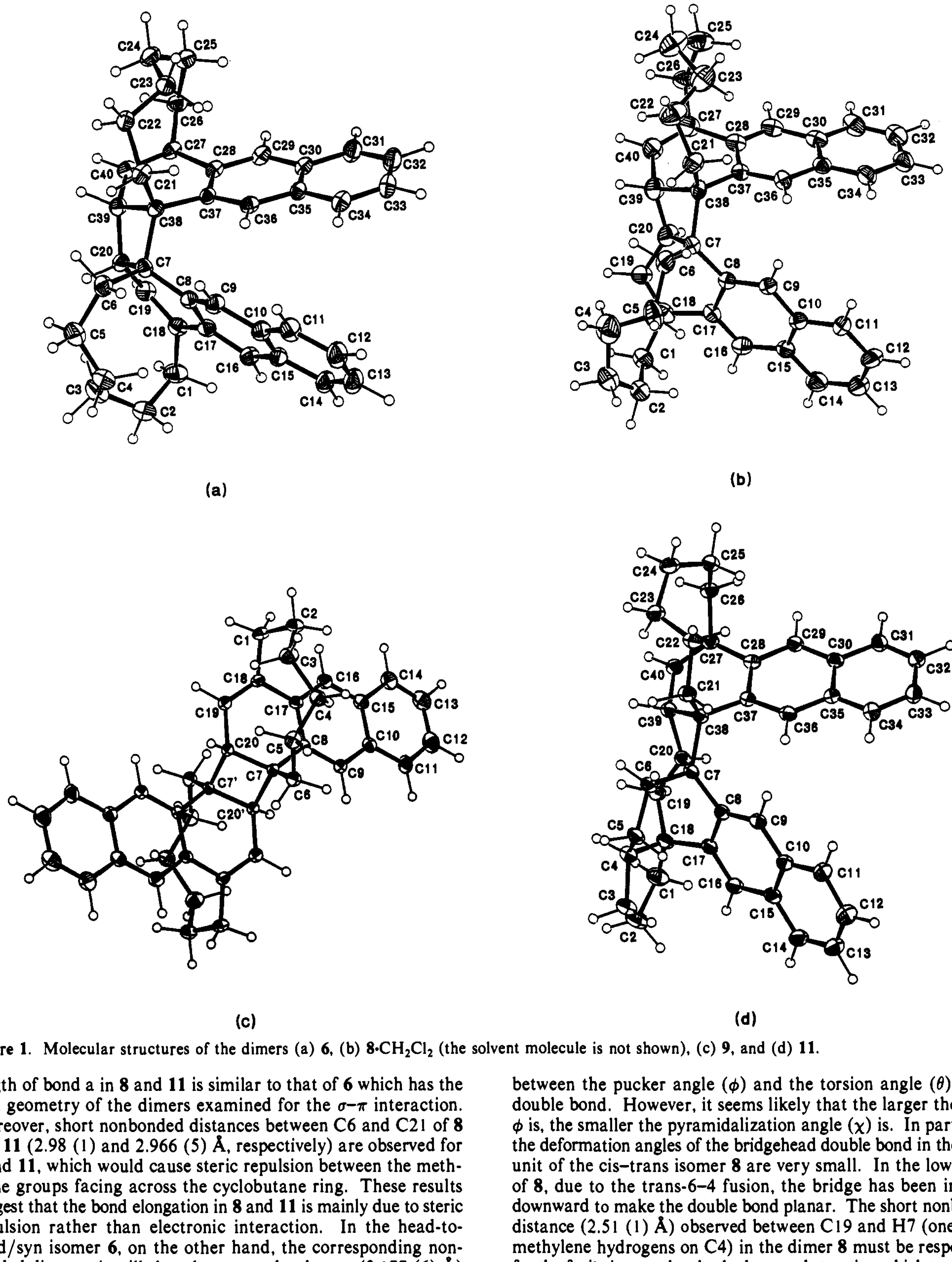
(15) Gready, J. E.; Hambley, T. W.; Kakiuchi, K.; Kobiro, K.; Sternhell, S.; Tansey, C. W.; Tobe, Y. *J. Am. Chem. Soc.* **1990**, *112*, 7537.

(16) Tobe, Y.; Takahashi, T.; Kobiro, K.; Kakiuchi, K. *Tetrahedron Lett.* **1991**, *32*, 359.

(17) Reference 10b, pp 402–404.

(18) Johnson, C. K. *ORTEP II. Report ORNL*-5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.

(19) Harano, K.; Ban, T.; Yasuda, M.; Ōsawa, E.; Kanematsu, K. *J. Am. Chem. Soc.* **1981**, *103*, 2310. Ōsawa, E.; Ivanov, P. M.; Jaime, C. *J. Org. Chem.* **1983**, *48*, 3990.



(a)

(b)

(c)

(d)

Figure 1. Molecular structures of the dimers (a) **6**, (b) **8**·CH_2Cl_2 (the solvent molecule is not shown), (c) **9**, and (d) **11**.

length of bond a in **8** and **11** is similar to that of **6** which has the best geometry of the dimers examined for the σ–π interaction. Moreover, short nonbonded distances between C6 and C21 of **8** and **11** (2.98 (1) and 2.966 (5) Å, respectively) are observed for **8** and **11**, which would cause steric repulsion between the methylene groups facing across the cyclobutane ring. These results suggest that the bond elongation in **8** and **11** is mainly due to steric repulsion rather than electronic interaction. In the head-to-head/syn isomer **6**, on the other hand, the corresponding nonbonded distance is still short but somewhat longer (3.177 (6) Å) than those of **8** and **11**. Consequently, it is reasonable to deduce that the stretching of bond a in dimer **6** is mainly due to "through-bond" interaction although there must be considerable contribution of steric interaction as well. Indeed, the fact that, of the dimers **6**–**11**, only **6** underwent clean thermal cycloreversion to the monomer **5** upon heating at its melting point is consistent with the above deduction.

The cis–trans isomers **8** and **11** have large pucker angles of the cyclobutane ring which is one of the largest observed in fused cyclobutane systems.[20] There seems to be no apparent relationship between the pucker angle (ϕ) and the torsion angle (θ) of the double bond. However, it seems likely that the larger the angle ϕ is, the smaller the pyramidalization angle (χ) is. In particular, the deformation angles of the bridgehead double bond in the lower unit of the cis–trans isomer **8** are very small. In the lower unit of **8**, due to the trans-6–4 fusion, the bridge has been inclined downward to make the double bond planar. The short nonbonded distance (2.51 (1) Å) observed between C19 and H7 (one of the methylene hydrogens on C4) in the dimer **8** must be responsible for the facile intramolecular hydrogen abstraction which took place between these atoms upon photoexcitation of **8**.

Experimental Section

Irradiation of 5 through a Solution Filter. A solution of 494 mg (1.90 mmol) of **5** in 50 mL of cyclohexane was irradiated with a 500-W high-pressure mercury lamp under nitrogen atmosphere through a solution filter of 1,4-diphenylbutadiene (0.12 M) in tetrahydrofuran at room

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[20] Moriarty, R. M. *Topics in Stereochemistry*; Eliel, E. L., Allinger, N. L., Eds.; Wiley: New York, 1974; Vol. 8, pp 271–421.

temperature for 50 min. The residue obtained by evaporation of the solvent was washed with ether and filtered. The insoluble solid (162 mg) was almost pure **9**. The filtrate was concentrated and then chromatographed on silica gel. By the repeated chromatography with 3% benzene–petroleum ether as the eluent, the following products were obtained in the order of elution: dimer **10**, 49 mg (10%); dimer **9**, 3 mg (total yield 34%); dimer **7**, 8 mg (1.6%); dimer **8**, 51 mg (10%); dimer **6**, 8 mg (1.6%). Irradiation was done in different solvents and the product ratio was analyzed by HPLC (ODS column, CH_3CN eluent, UV detector with detection wavelength of 254 nm). The results are summarized in Table I.

6: mp 209–210 °C dec (recrystallized from ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 7.7 Hz, 2 H), 7.37 (s, 2 H), 7.26 (s, 2 H), 7.2–7.1 (m, 6 H), 5.79 (m, 2 H), 3.83 (m, 2 H), 3.0–2.9 (m, 2 H), 2.4–2.2 (m, 2 H), 2.2–2.0 (m, 4 H), 1.9–0.6 (br m, 14 H), 0.16 (br m, 2 H); IR (KBr) 1620, 1590, 950, 890, 750 cm^{-1}; MS, *m/z* (rel intensity) 520 (M$^+$, 8), 260 (100), 217 (65). HR MS calcd for $C_{40}H_{40}$ 520.3130, found 520.3120.

7: mp 237–238 °C (recrystallized from ether–petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, J = 8.0 Hz, 2 H), 7.35 (s, 2 H), 7.20 (ddd, J = 8.1, 6.6, 1.5 Hz, 2 H), 7.16 (br d, J = 7.7 Hz, 2 H), 7.10 (ddd, J = 8.1, 6.6, 1.5 Hz, 2 H), 6.63 (s, 2 H), 6.20 (d, J = 7.5 Hz, 2 H), 2.97 (d, J = 7.5 Hz, 2 H), 2.83 (br d, J = 12.8 Hz, 2 H), 2.20 (m, 2 H), 1.72 (m, 4 H), 1.6–0.9 (br m, 14 H), 0.47 (br m, 2 H); IR (KBr) 1630, 1590, 885, 745, 735 cm^{-1}; MS, *m/z* (rel intensity) 520 (M$^+$, 3), 260 (100), 217 (25). HR MS calcd for $C_{40}H_{40}$ 520.3130, found 520.3112.

8: mp 255–257 °C dec (recrystallized from ether–CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (s, 1 H), 8.11 (s, 1 H), 7.95 (d, J = 8.1 Hz, 1 H), 7.71 (d, J = 8.1 Hz, 1 H), 7.7–7.5 (m, 2 H), 7.60 (s, 1 H), 7.56 (s, 1 H), 7.49 (ddd, J = 8.1, 8.0, 1.1 Hz, 1 H), 7.39 (ddd, J = 8.1, 8.0, 1.1 Hz, 1 H), 7.3–7.2 (m, 2 H), 6.35 (d, J = 3.3 Hz, 1 H), 6.12 (d, J = 7.0 Hz, 1 H), 3.32 (dt, J = 12.1, 3.3 Hz, 1 H), 3.19 (dd, J = 12.1, 7.0 Hz, 1 H), 3.10 (br d, J = 13.2 Hz, 1 H), 2.94 (br d, J = 13.9 Hz, 1 H), 2.4–2.2 (m, 3 H), 2.2–1.9 (m, 3 H), 1.7–1.1 (m, 14 H), 0.79 (br m, 1 H), 0.6–0.4 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.9 (s), 142.3 (s), 138.7 (s), 137.2 (s), 136.4 (s), 135.8 (s), 132.4 (s), 132.0 (s), 131.9 (s), 131.8 (s), 129.5 (d), 129.2 (d) 128.0 (d), 127.3 (d, 2 C), 127.2 (d), 126.8 (d), 125.8 (d), 125.3 (d, 2 C), 125.1 (d), 124.5 (d), 123.5 (d), 120.7 (d), 58.4 (s), 57.3 (s), 42.3 (d), 39.5 (d), 36.7 (t), 35.5 (t), 34.7 (t), 29.4 (t), 28.6 (t), 28.1 (t), 25.8 (t + br t), 21.7 (t), 20.0 (t) (four methylene signals are probably overlapping at δ 25.8); IR (KBr) 1620, 1590, 945, 890, 885, 870, 740 cm^{-1}; MS, *m/z* (rel intensity) 520 (M$^+$, 65), 273 (31), 260 (100), 217 (42). Anal. Calcd for $C_{40}H_{40}.CH_2Cl_2$: C, 81.30, H, 6.99. Found: C, 81.89; H, 6.96.

9: decomposed at ca. 300 °C without melting (recrystallized from CH_2Cl_2–benzene); ^{1}H NMR (600 MHz, $CDCl_3$, 44 °C) δ 7.79 (br d, J = 8.2 Hz, 4 H), 7.69 (s, 2 H), 7.66 (s, 2 H), 7.40 (m, 4 H), 6.09 (d, J = 7.5 Hz, 2 H), 3.69 (d, J = 7.5 Hz, 2 H), 3.26 (br d, J = 12.2 Hz, 2 H), 2.31 (m, 2 H), 1.78 (m, 4 H), 1.7–0.7 (br m, 14 H), 0.36 (br m, 2 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 140.0 (s), 134.2 (s), 133.9 (s), 132.9 (s), 132.4 (s), 128.0 (d), 127.1 (d), 125.7 (d), 125.4 (d), 125.2 (d), 125.1 (d), 120.3 (d), 47.1 (s), 39.3 (br d + t), 35.3 (t), 30.0 (t), 27.5 (t), 24.3 (t), 23.9 (t); IR (KBr) 1625, 1590, 1040, 945, 885, 875, 735, 730 cm^{-1}; MS, *m/z* (rel intensity) 520 (M$^+$, 5), 260 (100), 217 (41). Anal. Calcd for $C_{40}H_{40}$: C, 92.26; H, 7.74. Found: C, 91.87; H, 7.70.

10: decomposed at ca. 295 °C without melting (recrystallized from CH_2Cl_2–ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.8–7.9 (m, 4 H), 7.76 (s, 4 H), 7.4–7.5 (m, 4 H), 5.98 (m, 2 H), 3.13 (dt, J = 13.2, 3.3 Hz, 2 H), 2.75 (m, 2 H), 2.4–0.6 (br m, 20 H), 0.21 (br m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.6 (br s), 138.0 (s), 135.6 (s), 132.3 (2s), 130.0 (br d), 127.8 (d), 127.7 (d), 127.4 (d), 125.5 (d), 125.4 (d), 121.7 (d), 56.1 (br s), 43.9 (br d), 40.9 (t), 35.5 (t), 29.7 (br t), 27.6 (br t), 24.8 (br t) (one methylene signal is probably overlapping with the broad triplet at δ 27.6); IR (KBr) 1620, 1590, 950, 940, 880, 845, 740, 735 cm^{-1}; MS, *m/z* (rel intensity) 520 (M$^+$, 2), 260 (100), 217 (31). Anal. Calcd for $C_{40}H_{40}$: C, 92.26; H, 7.74. Found: C, 92.19; H, 7.75.

Irradiation of 5 through a Pyrex Filter. A solution of **5** (95 mg, 0.37 mmol) in 5 mL of cyclohexane was irradiated in a Pyrex tube as described before for 1.5 h. The solvent was evaporated and the residue was chromatographed on silica gel with 1% ether–petroleum ether as the eluent. The fraction containing the major product (46 mg) was collected and was recrystallized from CH_2Cl_2–petroleum ether to give 30 mg (32%) of the dimer **11**: mp 248–250 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (s, 1 H), 8.09 (s, 1 H), 7.86 (d, J = 8.1 Hz, 1 H), 7.76 (d, J = 7.7 Hz, 1 H), 7.63 (t, J = 7.7 Hz, 2 H), 7.53 (s, 1 H), 7.40 (ddd, J = 8.1, 7.0, 1.1 Hz, 1 H), 7.36 (s, 1 H), 7.33–7.27 (m, 3 H), 6.08 (d, J = 7.3 Hz, 1 H), 3.1–3.0 (br d, J = ca. 11 Hz, 1 H), 3.03 (dd, J = 11.3, 7.3 Hz, 1 H), 2.42–2.18 (m, 5 H), 2.10 (dd, J = 12.8, 9.2 Hz, 1 H), 2.0–1.2 (m, 16 H), 1.02 (br m, 1 H), 0.7–0.6 (m, 1 H), 0.23 (ddd, J = 15.6, 12.8, 5.1 Hz, 1 H); ^{13}C NMR (150 MHz, $CDCl_3$, 50 °C) δ 145.5 (s), 141.5 (br s), 140.2 (s), 137.8 (s), 136.1 (s), 132.2 (s, 2 C), 131.7 (s), 131.2 (s), 130.8 (br d), 127.6 (d), 127.5 (d), 127.4 (d), 127.0 (d), 126.9 (d), 125.4 (d, 2 C), 125.3 (d), 124.7 (d), 124.5 (d), 122.9 (d), 121.0 (d), 58.2 (s), 56.8 (s), 54.8 (d), 50.8 (s), 45.6 (br d), 42.3 (d), 39.2 (t), 38.3 (t), 37.5 (t), 35.7 (t), 32.9 (t), 29.7 (t), 29.1 (t), 29.0 (t), 27.0 (br t), 25.4 (t), 22.9 (t) (one methylene signal is probably overlapping with the broad triplet at δ 27.0); IR (KBr) 1625, 1585, 1035, 940, 880, 870, 735, 720 cm^{-1}; MS, *m/z* (rel intensity) 520 (M$^+$, 100), 285 (38), 287 (36). HR MS calcd for $C_{40}H_{40}$ 520.3130, found 520.3124.

X-ray Analysis of Dimers 6, 8, 9, and 11. The X-ray diffraction data were collected on a Rigaku automated four-circle diffractometer with Ni-filtered Cu Kα radiation. The integrated intensities were measured by the θ–2θ scan technique up to $2\theta = 120°$. The structure was solved by the direct method (MULTAN-78)[21] and refined by the full-matrix least-squares (X-RAY SYSTEM)[22] on independent reflections with $|F_o| > 3\sigma(F)$. The non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined isotropically. The crystal data and selected refinement parameters are listed in Table II. The interatomic bond distances and angles, fractional atomic parameters, and anisotropic thermal parameters are given in the Supplementary Material.

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Supplementary Material Available: Tables of interatomic bond distances and angles, fractional atomic coordiantes, and anisotropic thermal parameters for non-hydrogen atoms for **6**, **8**, **9**, and **11** (18 pages). Ordering information is given on any current masthead page.

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