J. Org. Chem. **1987**, *52*, 2639–2644

fashion, 910 (58%) were judged observed ($F_o \geqslant 3\sigma(F_o)$) after correction for Lorentz, polarization, and background effects.[25] A phasing model was found without difficulty by using a multisolution tangent formula approach.[25] All non-hydrogen atoms were easily located on the initial E synthesis. Hydrogen atoms were located on a ΔF synthesis after partial refinement of the non-hydrogen positions and thermal parameters. Block-diagonal least-squares refinements with anisotropic non-hydrogen atoms and isotropic hydrogens converged to a crystallographic residual of 0.0369 (R_w = 0.0461) for the observed data. Further results of the crystallographic experiments are available and are described in the supplementary material paragraph.

Acknowledgment. The Cornell NMR facility is supported by the National Science Foundation Instrumentation Program (NSF CHE-7904825). Chemical Abstracts Service is thanked for their assistance with nomenclature.

Registry No. 3, 108058-71-5; **4**, 108058-70-4; **5**, 108058-73-7; **7**, 108058-72-6.

Supplementary Material Available: Tables of fractional coordinates and thermal parameters, anisotropic thermal parameters, interatomic distances and angles, and torsional angles for ketone **3** (5 pages). Ordering information is given on any current masthead page.

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(25) All crystallographic calculations were done on a PRIME 9955 computer operated by the Cornell Chemistry Computing Facility. Principle programs employed were the following: REDUCE and UNIQUE, data reduction programs by M. E. Leonwicz, Cornell University, 1978; MULTAN 78, MULTAN 80, and RANTAN 80, systems of computer programs for the automatic solution of crystal structures from X-ray diffraction data (locally modified to perform all Fourier calculations including Patterson syntheses) written by P. Main, S. E. Hull, L. Lessinger, G. Germain, J. P. Declercq, and M. M. Woolfson, University of York, England, 1978 and 1980; DIRDIF, written by P. T. Beurskens et al., University of Nijmegen, Netherlands, 1981; MITHRIL, an automatic solution package written by C. J. Gilmore, University of Glasgow, Scotland, 1983; BLS78A, an anisotropic block diagonal least-squares refinement written by K. Hirotsu and E. Arnold, Cornell University, 1980; PLUTO78, a crystallographic illustration program by W. D. S. Motherwell, Cambridge Crystallographic Data Centre, 1978; and BOND, a program to calculate molecular parameters and prepare tables written by K. Hirotsu, Cornell University, 1978.

Synthesis, Conformation, and Structure of 8,11-Bis(methoxycarbonyl)[6]paracyclophane

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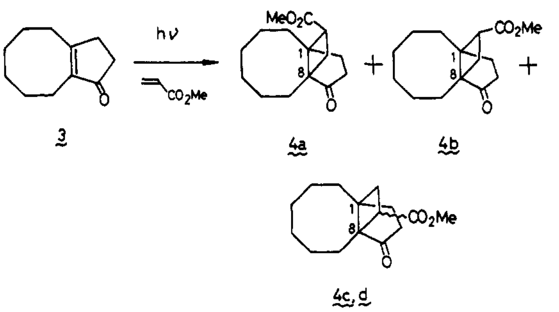
8,11-Bis(methoxycarbonyl)[6]paracyclophane (**1c**), a crystalline derivative of the smallest bridged paracyclophane system with two ester groups at the para position of the aromatic nucleus, has been successfully synthesized by utilizing thermal valence isomerization of its Dewar benzene-type isomer, [6.2.2]propelladiene (**2c**). The rate retardation observed in the above isomerization relative to those of the hydrocarbon **2a** and the monoester **2b** was attributed to development of steric repulsion between the ester groups and the benzyl hydrogens in the transition state. From the dynamic ^{1}H NMR behavior, it has been deduced that **1c** occurs preferentially in conformer A rather than B (20:1 ratio) in solution and ΔG^{*}_{c} for the inversion of the bridge has been estimated to be 12.9 kcal/mol (−24 °C). The X-ray analysis of **1c** not only confirmed the preference of conformer A but also revealed the remarkable deformation imposed on the benzene ring and the methylene bridge. The out-of-plane bending angle of the para carbon (C(7)) is 19.4°, and that of the benzyl carbon (C(1)) is 20.2°. While the bond lengths of the bridge are normal, the bond angles of C(2) and C(3) are remarkably expanded (116.8°) from the normal angle. On the basis of the short nonbonded distance between O(1) and H(11) (2.43 Å), it is deduced that the remarkable conformational bias in favor of conformer A over B is due to the severe nonbonded repulsion between the carbonyl oxygens and the benzyl hydrogens in the latter.

Recently, increasing interest has been focused on the chemistry of small-bridged [*n*]cyclophanes.[1] In the series of [*n*]paracyclophanes so far isolated,[2] the smallest bridged [6]paracyclophane (**1a**) was first synthesized by Jones and co-workers in 1974[3a] and a few years later by Jones and Bickelhaupt et al.[3b] More recently, we have developed a more convenient access route to the parent hydrocarbon **1a** and the 8-substituted derivative such as **1b** by taking advantage of the thermal valence isomerization of the corresponding Dewar benzene-type valence isomers, [6.2.2]propelladienes (**2a** and **2b**).[4] At the same time, Tochtermann and co-workers have explored a different route to 8,9-disubstituted derivatives such as **1d** using the reductive deoxygenation of the bridged oxepine derivatives.[5b] With successful access to this system, we and they have been investigating the structure, especially the out-of-plane bending of the benzene ring (ca. 20°), conformational behavior, and reactivities associated with the de-

Scheme I



[†] Department of Applied Fine Chemistry.

[‡] Department of Applied Chemistry.

(1) For a recent review: Rosenfeld, S. M.; Choe, K. A. In *Cyclophanes*; Keehn, P. M., Rosenfeld, S. M., Eds.; Academic: New York, 1983; Vol. I, Chapter 5.

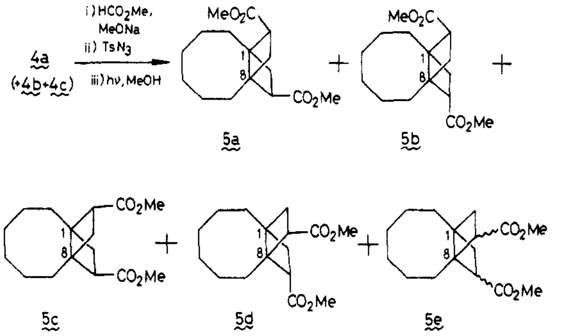
0022-3263/87/1952-2639$01.50/0 © 1987 American Chemical Society

Table I. Kinetic Data for Valence Isomerization of 2a–2c and 7a–7c in Hexane

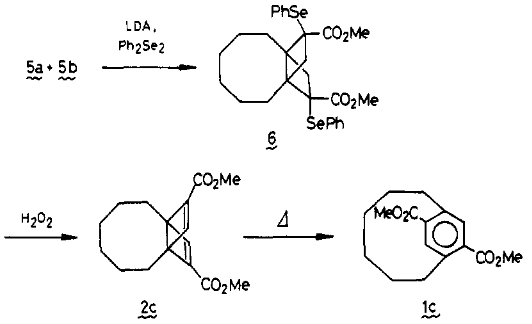
compd	T, °C	10^5k, s^{-1}	k_{rel}	E_a, kcal/mol	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, cal/deg mol
2a[a,b]	40.1	0.61				
	44.9	1.18				
	50.0	1.69	1.0	21.7	21.0	−15.3
	55.1	3.21				
2b[c]	50.0	8.67	5.1	24.9	24.3	−2.2
2c[a]	40.0	0.195				
	45.0	0.440				
	50.0	0.824	0.49	29.0	28.3	5.8
7a[a]	39.9	2.11				
	44.9	3.32				
	50.0	6.64	(1.0)	22.9	22.3	−9.0
7b[d]	50.0	35.2	(5.3)	23.3	22.6	−4.4
7c[e]	50.0	5.74	(0.86)	25.9	25.3	0.3

[a] This work. [b] The reported data (E_a = 19.9 kcal/mol, log A = 9.3)[3b] are almost consistent with ours. [c] Reference 4. [d] Reference 7b. [e] Reference 7c. The rate constant is an extrapolated value. The other kinetic data are those at 30.0 °C.

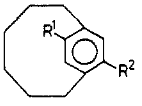
Scheme II



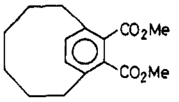
Scheme III



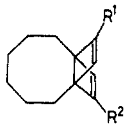
formation of this ring system.[4,5] As an extension of our work, in order to clarify the electronic and steric effect of the ester substituents on the aromatic nucleus, we report here the synthesis, conformation, and structure of 8,11-bis(methoxycarbonyl)-substituted derivative **1c**.



1a $R^1 = R^2 = H$
1b $R^1 = H, R^2 = CO_2Me$
1c $R^1 = R^2 = CO_2Me$



1d



2a $R^1 = R^2 = H$
2b $R^1 = H, R^2 = CO_2Me$
2c $R^1 = R^2 = CO_2Me$

The synthesis of **1c** was carried out in a straightforward manner using the thermal valence isomerization of the Dewar benzene isomer **2c** as the key step as outlined in Schemes I–III. First, photocycloaddition of the bicyclic enone **3** with methyl acrylate gave head to tail endo adduct **4a**, head to tail exo **4b**, and head to head adducts **4c** and **4d** (stereochemistry undetermined) in a ratio of 6:1:1 (**4c** + **4d**) in 49% combined yield (Scheme I). The h-t/h-h regiochemistry was determined on the basis of the chemical shift difference between the central quaternary carbons (C(1) and C(8)) in the ^{13}C NMR spectra (see the Experimental Section). The endo/exo stereochemical assignment of **4a** and **4b** was based on the configuration of the ring-contracted diesters **5a** (exo,endo) and **5b** (endo,endo) derived from **4a**. A mixture of the photoadducts containing mainly **4a** was subjected to ring contraction via (i) α formylation, (ii) diazo transfer, and (iii) Wolff photorearrangement to afford head to tail exo,endo diester **5a** and head to tail endo,endo **5b** (ca. 2:3) as the major products along with small amounts of head to tail exo,exo **5c**, head to head exo,endo **5d**, and a symmetrical head to head diester **5e** (stereochemistry uncertain) in 35% overall yield (Scheme II). The h-t/h-h regiochemistry was elucidated on the basis of the ^{13}C NMR chemical shift of the central quaternary carbons. The stereochemistry of **5a–c** was determined on the basis of the symmetry in the ^{13}C NMR spectra and the spectral and chromatographic similarities of exo,exo **5c** with those of the corresponding dimethyl [5.2.2]propellanedicarboxylates whose configuration was unambiguously established[6] (see the Experimental Section). Phenylselenenylation of **5a** and **5b** with an excess of LDA and diphenyl diselenide gave the bisselenide **6** [mp 168–171 °C; 32% yield], and the subsequent oxidation yielded the Dewar benzene **2c** [mp 60–62 °C; 73% yield] (Scheme III). As expected, thermal valence isomerization of **2c** took place smoothly to afford the crystalline cyclophane **1c** [mp 94–96 °C; 90% yield] after chromatography.

In order to elucidate the effect of the ester substituents on the [6.2.2]propelladiene → cyclophane valence isomerization, the isomerization rates of **2c** to **1c** were measured by means of UV spectroscopy. For comparison the isom-

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(2) The lowest homologues, [5]paracyclophanes, have been characterized at low temperature but have not yet been isolated: Jenneskens, L. W.; de Kanter, F. J. J.; Kraakman, P. A.; Turkenburg, L. A. M.; Koolhaas, W. E.; de Wolf, W. H.; Bickelhaupt, F.; Tobe, Y.; Kakiuchi, K.; Odaira, Y. *J. Am. Chem. Soc.* **1985**, *107*, 3716. Tobe, Y.; Kaneda, T.; Kakiuchi, K.; Odaira, Y. *Chem. Lett.* **1985**, 1301. Kostermans, G. B. M.; de Wolf, W. H.; Bickelhaupt, F. *Tetrahedron Lett.* **1986**, *27*, 1095.

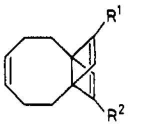
(3) (a) Cane, V. V.; Wolf, A. D.; Jones, M., Jr. *J. Am. Chem. Soc.* **1974**, *96*, 2643. (b) Kammula, S. L.; Iroff, L. D.; Jones, M., Jr.; van Straten, J. W.; de Wolf, W. H.; Bickelhaupt, F. *Ibid.* **1977**, *99*, 5815.

(4) Tobe, Y.; Ueda, K.; Kakiuchi, K.; Odaira, Y.; Kai, Y.; Kasai, N. *Tetrahedron Symposia-in-Print* **1986**, *42*, 1851 and references cited therein.

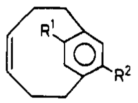
(5) (a) Günther, H.; Schmitt, P.; Fischer, H.; Tochtermann, W.; Liebe, J.; Wolff, C. *Helv. Chim. Acta* **1985**, *68*, 801. (b) Liebe, J.; Wolff, C.; Krieger, C.; Weiss, J.; Tochtermann, W. *Chem. Ber.* **1985**, *118*, 4144 and references cited therein.

(6) Unpublished results of our laboratories.

erization rate of hydrocarbon **2a** to **1a** was also determined under similar conditions. Table I lists the kinetic data for the isomerization of **2a–c** together with those of the [6.2.2]propellatrienes **7a–c**[6,7] to the (*Z*)-[6]paracycloph-3-enes **8a–c**[7] having a *Z* double bond in the bridge. As can be clearly seen, in both series, almost the same tendency in the difference of the isomerization rates and the kinetic parameters is observed while the difference is smaller in the propellatriene series **7a–c**. In general, the isomerization rates of monoesters **2b** and **7b** are fastest while those of diesters **2c** and **7c** are the slowest in each series. On the other hand, the activation energy and enthalpy increase remarkably with increasing ester substitution. Since (i) this tendency is in disagreement with that observed for the isomerization of halogen-sustituted Dewar benzenes[8] and (ii) the ester group is located rather apart from the central bond to be cleaved, the electronic effect of the ester substituents on the isomerization might be unimportant. On the other hand, it has been well documented that the steric strain that will arise in the benzene ring causes stabilization of the corresponding Dewar benzene isomers.[9] Consequently, it seems likely that the increase of the activation enthalpy with an increasing number of ester groups is due to the devlopment of steric repulsion between the ester group and the benzyl hydrogens in the transition state of isomerization of the mono- and diesters. Such interaction is supposed to be less important in the propellane framework but has appeared to be substantial in the resultant cyclophane system as described later. The increase of the activation entropy observed with an increasing number of ester groups, which compensates for the activation enthalpy, may be ascribed to the solvent release[8] on the following basis: (i) The transition state would be less polar than the starting Dewar benzene system because of the increase of the planarity of the π system along the reaction coordinate, although the resulting benzene ring is still highly bent. (ii) This polarity decrease would be greater with an increasing number of ester groups.



7a $R^1 = R^2 = H$
7b $R^1 = H, R^2 = CO_2Me$
7c $R^1 = R^2 = CO_2Me$



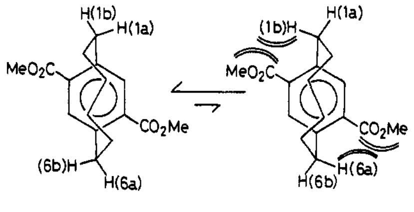
8a $R^1 = R^2 = H$
8b $R^1 = H, R^2 = CO_2Me$
8c $R^1 = R^2 = CO_2Me$

In analogy with other [6]paracyclophanes,[3-5] **1c** [λ_{max} (hexane) 350 nm (log ϵ 3.2), 270 (3.8), 230 (4.3)] showed considerable red shift in its UV absorption (ca. 50 nm for the longest wavelength band) compared with that of dimethyl 2,5-dimethylterephthalate,[10] indicating severe deformation of the benzene ring in this system.[11] It should be noted that the wavelength of the absorption maximum of **1c** is about 20 nm longer than those of monoester **1b** (λ_{max} 327 nm in hexane)[4] and the ortho diester **1d** (λ_{max} 329 nm in EtOH).[5b] This implies extensive π delocalization in **1c** due to the coplanarity of the two carbonyl and benzene π systems as indicated by the X-ray analysis (see below).

Table II. Selected Interatomic Bond Distances and Angles in 8,11-Bis(methoxycarbonyl)[6]paracyclophane (1c)

	Bond Distances, Å		
C(1)–C(2)	1.574 (13)	C(1)–C(7′)	1.515 (10)
C(2)–C(3)	1.545 (13)	C(3)–C(3′)	1.525 (18)
C(7)–C(8)	1.414 (7)	C(7)–C(9′)	1.388 (8)
C(8)–C(9)	1.395 (7)	C(8)–C(13)	1.489 (8)
O(1)–C(13)	1.206 (8)	O(2)–C(13)	1.330 (7)
O(2)–C(14)	1.468 (10)		
	Bond Angles, deg		
C(2)–C(1)–C(7′)	106.0 (7)	C(1)–C(2)–C(3)	116.8 (8)
C(2)–C(3)–C(3′)	116.8 (8)	C(8)–C(7)–C(1′)	121.2 (5)
C(1′)–C(7)–C(9′)	117.2 (5)	C(8)–C(7)–C(9′)	117.4 (5)
C(7)–C(8)–C(9)	118.3 (5)	C(7)–C(8)–C(13)	121.7 (5)
C(9)–C(8)–C(13)	119.2 (5)	C(8)–C(9)–C(7′)	120.2 (5)
O(1)–C(13)–C(8)	124.4 (6)	O(1)–C(13)–O(2)	122.6 (6)
O(2)–C(13)–C(8)	112.9 (5)	C(13)–O(2)–C(14)	116.3 (6)

It has been shown that [6]paracyclophanes **1a**, **1b**, and **1d** exhibited dynamic behavior in the ^1H NMR spectra from which the $\Delta G^\ddagger$ for the inversion of the hexamethylene bridge was estimated to be 13.3–13.9 kcal/mol.[3a,4,5a,12] Similarly, the para diester **1c** showed temperature-dependent NMR: at room temperature ($CDCl_3$, 25 °C), the methylene protons appeared as broad multiplets centered at δ −0.47, 0.79, 1.14, 1.59, 2.19, and 3.70 with equal intensities, and the aromatic protons at δ 7.92, as a singlet. At temperatures below −50 °C, the methylene signals that appeared at δ −0.69 (m), 0.52 (m), 1.24 (m), 1.67 (m), 2.13 (ddd, J = 12, 12, 6 Hz), and 3.76 (dd, J = 12, 4 Hz) moved and sharpened, and the aromatic protons split into two singlets at δ 7.92 and 8.04 with an intensity ratio of 20:1. This implies that **1c** occurs preferentially in either conformer A or B. The methylene signals of the minor conformer were concealed under those of the major one except for a low-intensity multiplet observed at δ 2.8–3.0. As the temperature was increased, the signals for the aromatic protons coalesced from which $\Delta G^\ddagger_c$(−24 °C) = 12.9 kcal/mol for the inversion of the bridge was estimated. At higher temperatures (Me_2SO-d_6, 150 °C), the methylene protons appeared at δ −0.25 (m, 2 H), 0.96 (m, 4 H), 1.52 (m, 2 H), 2.34 (d, J = 12, 12, 6 Hz, 2 H), and 3.58 (ddd, J = 12, 6, 4 Hz, 2 H), with the benzyl protons (H(1a), H(1b), H(6a), H(6b)) becoming sharper again. Taking into account the unambiguous assignment of the protons for the ortho diester **1d**,[5a] the above coupling constants and the chemical shifts for the benzyl protons of **1c** clearly indicate that it occurs predominantly in conformer A. This is consistent with the structure of **1c** in the crystal state shown by the X-ray analysis.



A B

Since monoester **1b** was shown to occur in two conformations in a ratio of ca. 4:1,[4] the conformational bias is enhanced markedly by the introduction of the second ester group at the position para to the first one. This result is

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(7) (a) Tobe, Y.; Ueda, K.; Kakiuchi, K.; Odaira, Y. *Angew. Chem.* **1986**, *98*, 364; *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 369. (b) Tobe, Y.; Kaneda, T.; Kakiuchi, K.; Odaira, Y. *Chem. Lett.* **1986**, 1217. (c) Tobe, Y.; Ueda, K.; Kaneda, T.; Kakiuchi, K.; Odaira, Y.; Kai, Y.; Kasai, N. *J. Am. Chem. Soc.* **1987**, *109*, 1136.

(8) Breslow, R.; Napierski, J.; Schmidt, A. H. *J. Am. Chem. Soc.* **1972**, *94*, 5906.

(9) For reviews see: van Tamelen, E. E. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 738; *Acc. Chem. Res.* **1972**, *5*, 186. Scott, L. T.; Jones, M., Jr. *Chem. Rev.* **1972**, *72*, 181.

(10) Cachia, M.; Wahl, H. *Bull. Soc. Chim. Fr.* **1958**, 1418. Gray, R.; Boekelheide, V. *J. Am. Chem. Soc.* **1979**, *101*, 2128.

(11) Allinger, N. L.; Sprague, J. T.; Liljefors, T. *J. Am. Chem. Soc.* **1974**, *96*, 5100.

(12) van Straten, J. W. Thesis, Vrije University, Amsterdam, 1978.

attributed to the steric repulsion between the ester groups and the benzyl hydrogens H(1b) and H(6a) in conformer B, strongly disfavoring this conformation relative to A. This steric interaction is also responsible for the relatively slow rate of valence isomerization of **2c** to **1c** relative to monoester **2b** as described above.

In order not only to clarify the deformation of the benzene ring and the methylene bridge of this system but also to make clear the predominant conformation of **1c**, X-ray crystallographic analysis of **1c** was undertaken.[13] Selected bond distances and angles are listed in Table II. As shown in Figure 1, the structure of **1c** has a crystallographic C_2 symmetry and it occurs as conformer A. Although in solid state, the above result confirms that conformational preference for conformer A over B in solution as deduced from the NMR study.

The distortion imposed on the benzene ring and the methylene bridge deserves discussion. The out-of-plane bending angle (α) of the carbon para (C(7)) from the plane of the other benzene carbons (C(8), C(9), C(8′), C(9′)) is 19.4°, and that (β) of the benzyl carbon (C(1′)) from the plane of C(8)–C(7)–C(9′) is 20.2°. The total bent angle ($\alpha + \beta$) is 39.6°. These bent angles are in good agreement with those observed for the ortho diester **1d** ($\alpha_{av} = 19.5°$, $\beta_{av} = 19.9°$, $\alpha + \beta = 39.4°$).[5b] By analogy, the deformation of the bridging chain of **1c** is similar to that of **1d** within the limits of accuracy. Namely, the bond lengths of the chain, C(1)–C(2) (1.574 Å), C(2)-C(3) (1.545 Å), and C-(3)–C(3′) (1.525 Å), are almost normal; the corresponding lengths of **1d** are 1.559 (av), 1.541, and 1.554 (av) Å.[5b] On the other hand, the bond angles of the bridge are contracted or expanded from the normal tetrahedral angle of 109.5°. The bond angle of the benzyl carbon, C(2)–C-(1)–C(7′) (106.0°), is contracted while those of C(1)–C-(2)–C(3) (116.8°) and C(2)–C(3)–C(3′) (116.8°) are considerably expanded from the normal; the corresponding angles of **1d** are 106.5° (av), 118.0° (av), and 117.1° (av), respectively.[5b] Apparently, the influence of the substituents on the deformation of the benzene ring and the bridge is rather small. However, the structure of **1c** would reflect that of the parent hydrocarbon **1a** better than of **1d**, in which a zigzag chain slightly tilts toward the direction opposite to the ester groups,[5b] because of its C_2 symmetry.

As shown in Figure 1, the two ester carbonyl planes are almost coplanar with the base plane of the benzene ring; the dihedral angle between planes O(1)–C(13)–O(2) and C(8)–C(9)–C(8′)–C(9′) is 8.3°. As a result of the extension of the π system, **1c** exhibits the aforementioned remarkable bathochromic shift in the UV spectrum relative to the ortho **1d**, in which one of the ester groups is almost orthogonal to the benzene plane due to the steric repulsion between the ester groups.[5b] Even in this conformation (conformer A), the nonbonded distance between O(1′) and H(11) is 2.43 (5) Å, which is shorter than the sum of van der Waals radii of oxygen and hydrogen (2.60 Å). It is reasonable to deduce that, in conformer B, the corresponding distance is shorter than that in conformer A. The other nonbonded distances between the ester group and the bridge hydrogens of **1c** are longer; i.e., C(13′)···H(11) = 2.86 (5) Å, C(13′)···H(21) = 3.00 (5) Å, O(1′)···H(21) = 3.27 (5) Å. Consequently, the nonbonded repulsion between the carbonyl oxygen O(1) and the benzyl hydrogen H(11) plays a crucial role in determining the relative stabilities of conformers A and B.

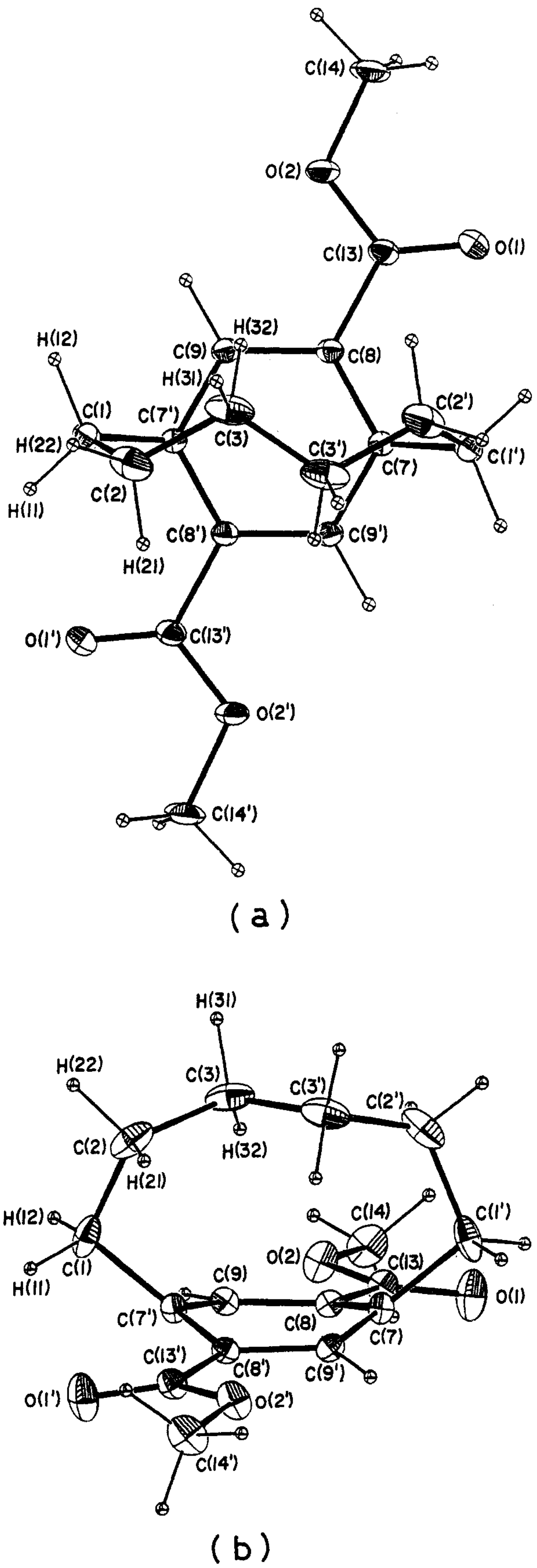

Figure 1. Molecular structure of 8,11-bis(methoxycarbonyl)-[6]paracyclophane (**1c**): (a) top view; (b) side view.

Experimental Section

Melting points were measured with a Yanagimoto micro melting point apparatus and are uncorrected. ^{1}H NMR spectra were

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[13] For the discussion on the X-ray structure of **1c**, the numbering of atoms in Figure 1 is used.

[14] For example: Sakai, Y.; Toyotani, S.; Ohtani, M.; Matsumoto, M.; Tobe, Y.; Odaira, Y. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1474. Tobe, Y.; Yonezawa, T.; Kakiuchi, K.; Odaira, Y. *Ibid.* **1982**, *55*, 3362.

obtained with a JEOL JNM-PS-100 spectrometer in CCl_4 unless otherwise noted, and ^{13}C NMR spectra, with a JEOL JNM-FX-60S spectrometer in $CDCl_3$ with Me_4Si as an internal standard. Mass spectra were measured on a Hitachi RMU-6E spectrometer. Infrared spectra were recorded on a Hitachi 260-10 spectrometer as liquid films unless otherwise stated. Analytical GLC was conducted with a Hitachi 163 gas chromatograph, and preparative GLC separation, on a Varian Aerograph 920 chromatograph with a 10% FFAP column.

Photocycloaddition of Enone 3 with Methyl Acrylate. A solution of enone 3 (4.96 g, 30.2 mmol) and methyl acrylate (27.0 mL, 300 mmol) in 30 mL of ether in a Pyrex reactor under nitrogen was irradiated with a 500-W high-pressure mercury lamp (HALoS, Eikosha). During irradiation, an additional 13.5 mL of the acrylate and 10 mL of dichloromethane were added four times at 3–5-h intervals, and irradiation was continued for 17 h. The contents of the reactor were transferred to a flask with hot acetone, and the solvent was evaporated. The residual polymer mass was extracted well with ether. The combined extracts of two runs were evaporated, and the residue was chromatographed on silica gel. Elution with 13% ether/petroleum ether afforded fractions I–V.

Fraction I: 0.18 g (1.2%); a mixture of head to head adducts **4c** and **4d** (3:1 ratio by ^{13}C NMR).

Fraction II: 2.42 g (16%); a mixture of **4c**, **4d**, and head to tail adduct **4a**.

Fraction III: 3.28 g (22%); head to tail endo **4a**.

Fraction IV: 0.60 g (4.0%); a mixture of **4a** and head to tail adduct **4b**.

Fraction V: 0.88 g (5.8%); head to tail exo **4b**.

The ratio of **4a**:**4b**:(**4c** + **4d**) was estimated by a combination of GLC and ^{13}C NMR spectra to be about 6:1:1. The h-t/h-h regiochemical assignment was made on the basis of the ^{13}C NMR chemical shift difference for the central quaternary carbons (C(1) and C(8)). The head to tail adducts **4a** and **4b** showed $\Delta\delta$ of 0 and 3.1 ppm, while the head to head **4c** and **4d** showed 11.6 and 12.6 ppm, respectively. Moreover, the endo/exo stereochemistry of **4a** and **4b** was elucidated on the basis of those of the ring-contracted diesters **5a**–**5c**: Since **4a** gave exo,endo **5a** and endo,endo **5b** in a ratio of 3:2, **4a** should have an endo ester group and therefore **4b** should be the exo isomer.

4a (head to tail endo): IR 1730, 1725, 1195, 1170 cm^{-1}; MS, *m/e* (rel intens) 250 (M^+, 4), 164 (100), 149 (39), 135 (38); ^1H NMR δ 0.8–3.0 (m, 19 H), 3.65 (s, 3 H); ^{13}C NMR δ 220.1 (s), 173.6 (s), 52.4 (s), 51.4 (q), 49.3 (s), 44.8 (d), 36.8 (t), 34.7 (t), 30.9 (t), 30.1 (t), 26.0 (t), 25.3 (t), 25.1 (t), 44.5 (t), 24.2 (t). Anal. Calcd for $C_{15}H_{22}O_3$: C, 71.97; H, 8.86. Found: C, 71.90; H, 8.93.

4b (head to tail exo): IR 1730, 1720, 1195, 1170 cm^{-1}; MS, *m/e* (rel intens) 250 (M^+, 2), 164 (100), 149 (41), 135 (40); ^1H NMR δ 0.8–3.0 (m, 19 H, contains t at δ 2.87, J = 9 Hz), 3.63 (s, 3 H); ^{13}C NMR δ 221.1 (s), 172.8 (s), 51.3 (s), 50.9 (q), 43.5 (d), 35.5 (t), 29.5 (t), 28.7 (t), 28.3 (t), 25.0 (t), 24.4 (t), 23.5 (t). Anal. Calcd for $C_{15}H_{22}O_3$: C, 71.97; H, 8.86. Found: C, 72.04; H, 8.99.

4c + **4d** (head to head, stereochemistry undetermined, 3:1 mixture): IR 1735, 1725, 1200, 1170 cm^{-1}; MS, *m/e* (rel intens) 250 (M^+, 18), 164 (100), 149 (75), 135 (87); ^1H NMR δ 0.6–3.0 (m, 19 H), 3.56, 3.63 (ca. 3:1, s, 3 H); ^{13}C NMR for major component **4c**, δ 220.6 (s), 172.4 (s), 56.8 (s), 51.7 (q), 45.2 (s), 41.9 (d), 37.7 (t), 35.5 (t), 32.2 (t), 30.1 (t), 29.3 (t), 25.5 (t), 25.2 (2 C, t), 23.7 (t); ^{13}C NMR for minor component **4d**, δ 221.9 (s), 173.5 (s), 55.4 (s), 51.4 (q), 42.8 (s), 40.0 (d).

Ring Contraction of Head to Tail Endo Adduct 4a. Ring contraction of a fraction containing mainly **4a** (3.17 g, 12.7 mmol) was carried out as described previously,[7c] and the subsequent chromatography of silica gel (10% ether/petroleum ether) gave fractions VI–IX.

Fraction VI: 21 mg (0.6%); head to head exo,endo diester **5d**.

Fraction VII: 248 mg (7.0%); a mixture of **5d** and head to tail diesters **5a** and **5b**.

Fraction VIII: 808 mg (23%); a mixture of head to tail exo,endo **5a** and head to tail endo,endo **5b** (2:3 by ^{13}C NMR).

Fraction IX: 171 mg (4.8%); a mixture of head to tail exo,exo **5c** and head to head symmetrical **5e** (2:3 by ^{13}C NMR).

The minor products **5c**, **5d**, and **5e** might be derived from **4b** and **4c** (or **4d**), which were contaminants in the adduct **4a** used. Again, the h-t/h-h regiochemistry of the diesters **5a**–**5e** was determined by the presence or absence of symmetry and the chemical shift difference of the central quaternary carbons (C(1) and C(8)) in the ^{13}C NMR spectra. The symmetrical head to tail diesters **5b** and **5c** showed eight lines with signals of the quaternary carbons at δ 48.7 and 47.3, respectively, and unsymmetrical, hence exo,endo, head to tail **5a** at δ 51.2 and 49.8. On the other hand, symmetrical head to head **5e** (stereochemistry undetermined) exhibited 12 peaks with the central carbons at δ 53.4 and 43.4 and unsymmetrical head to head exo,endo isomer **5d** at δ 54.9 and 43.7, respectively. The endo,endo or exo,exo stereochemistry of the symmetrical head to tail isomers **5b** and **5c** was assigned on the basis of (i) the similarity in the ^1H and ^{13}C NMR spectra of exo,exo **5c** with those of the corresponding *exo*,*exo*-dimethyl [5.2.2]propellanedicarboxylate whose configuration was unambiguously established[6] and (ii) the general tendency that endo esters are eluted more rapidly than exo esters on column and gas chromatography in the series of [*n*.2.2]propellanecarboxylates.

5a (head to tail exo,endo) + **5b** (head to tail endo,endo) (2:3 mixture): IR 1740, 1730, 1170 cm^{-1}; MS, *m/e* (rel intens) 280 (M^+, 3), 248 (80), 161 (64), 165 (100), 105 (100); ^1H NMR δ 1.0–3.4 (m, 18 H), 3.61, 3.63 (s, 6 H); ^{13}C NMR for **5a**, δ 174.1 (s), 173.6 (s), 51.2 (3 C, 2 q+s), 49.9 (s), 47.0 (d), 46.3 (d), 31.8 (t), 30.9 (t), 28.7 (2 C, t), 25.9 (t), 24.6 (t), 23.9 (t), 22.9 (t); ^{13}C NMR for **5b**, δ 174.1 (s), 51.2 (q), 48.7 (s), 41.3 (d), 34.8 (t), 28.7 (t), 24.6 (t), 22.9 (t). Anal. Calcd for $C_{16}H_{24}O_4$: C, 68.55; H, 8.63. Found: C, 68.36; H, 8.67.

5c (head to tail exo,exo) + **5e** (symmetrical head to head, stereochemistry undetermined) (2:3 mixture): IR 1740, 1730, 1170 cm^{-1}; MS, *m/e* (rel intens) 280 (M^+, 3), 248 (71), 161 (73), 105 (90), 91 (100); ^1H NMR δ 1.3–2.0 (m, 12 H), 2.1–3.3 (m, 6 H, contains t at δ 2.09, J = 12 Hz, and dd at δ 3.13, J = 11, 8 Hz), 3.55, 3.63 (3:2, s, 6 H); ^{13}C NMR for **5c**, δ 173.5 (s), 51.2 (q), 47.4 (s), 41.3 (d), 32.9 (t), 29.0 (t), 25.1 (t), 23.5 (t); ^{13}C NMR for **5e**, δ 173.5 (s), 53.4 (s), 50.9 (2 C, q), 43.4 (s), 41.6 (2 C, d), 35.2 (t), 32.9 (3 C, t), 25.5 (t), 24.6 (2 C, t), 23.8 (t). Anal. Calcd for $C_{16}H_{24}O_4$: C, 68.55; H, 8.63. Found: C, 68.68; H, 8.71.

5d (head to head exo,endo): IR 1735, 1725, 1170 cm^{-1}; MS, *m/e* (rel intens) 280 (M^+, 1), 248 (78), 161 (76), 105 (94), 91 (100); ^1H NMR δ 1.3–1.8 (m, 12 H), 1.81 (dd, J = 12, 8 Hz, 1H), 2.08 (dd, J = 8, 2 Hz, 1 H), 2.3–2.7 (m, 2 H), 3.22 (t, J = 8 Hz, 1 H), 3.26 (dd, J = 12, 8 Hz, 1 H), 3.61, 3.65 (s, 6 H); ^{13}C NMR δ 173.9 (2 C, s), 54.8 (s), 51.2 (2 C, q), 43.7 (s), 41.1 (d), 40.2 (d), 33.0 (t), 32.5 (t), 31.7 (t), 28.2 (t), 25.1 (t), 24.4 (t), 23.7 (t), 23.0 (t). Anal. Calcd for $C_{16}H_{24}O_4$: C, 68.55; H, 8.63. Found: C, 68.70; H, 8.68.

Bisphenylselenylation of Head to Tail Diesters 5a and 5b. To a solution of LDA prepared from 0.574 mL (4.1 mmol) of diisopropylamine and 2.67 mL of 1.5 N butyllithium (4.0 mmol) in 10 mL of tetrahydrofuran (THF) was added a solution of 280 mg (1.0 mmol) of a mixture of **5a** and **5b** (fraction VIII) in 1.5 mL of THF at −78 °C. After the mixture was stirred at that temperature for 30 min, a solution of 1.25 g (4.0 mmol) of diphenyl diselenide and 0.69 mL (4.0 mmol) of hexamethylphosphoramide in 3 mL of THF was added dropwise. The solution was stirred at −78 °C for 1 h and then gradually warmed up to room temperature. Usual workup followed by chromatography on silica gel (10% ether/petroleum ether) gave 127 mg (29%) of a mono(phenylselenide) (stereochemistry uncertain) and 191 mg (32%) of the bis(phenylselenide) **6**. The stereochemistry of **6** was assigned tentatively on the basis of (i) the symmetry in the ^1H NMR spectrum, (ii) the general tendency that the atack of an electrophile to the enolate derived from [*n*.2.2]propellanecarboxylates takes place preferentially from the endo side to afford an endo selenide,[4,6] and (iii) the difference in the chemical shift between the cyclobutane methylene protons ($\Delta\delta$ = 0.37 ppm for **6**) in the ^1H NMR spectrum; in general, the observed $\Delta\delta$ for endo selenides are ca. 0.4 whereas for exo they are 0.7–0.8 ppm, respectively.[4]

Monoselenide: IR 1730, 1270, 1220, 1200, 1145, 740, 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.2–2.2 (m, 12 H), 1.96 (d, J = 15 Hz, 1 H), 2.30 (d, J = 10 Hz, 2 H), 2.84 (d, J = 15 Hz, 1 H), 3.38 (t, J =

10 Hz, 1 H), 3.59 (s, 3 H), 3.64 (s, 3 H), 7.2–7.6 (m, 5 H).

6: mp 168–171 °C (from ether); IR (KBr) 1725, 1250, 1090, 725, 690 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.6–2.2 (m, 12 H), 2.31 (d, J = 16 Hz, 2 H), 2.68 (d, J = 16 Hz, 2 H), 3.56 (s, 6 H), 7.1–7.6 (m, 10 H). Anal. Calcd for $C_{28}H_{32}O_4Se_2$: C, 56.88; H, 5.43. Found: C, 56.96; H, 5.46.

9,11-Bis(methoxycarbonyl)[6.2.2]propella-9,11-diene (2c). To a solution of 310 mg (0.53 mmol) of **6** and 0.17 mL (2.1 mmol) of pyridine in 3.3 mL of dichloromethane was added a mixture of 0.3 mL of 30% hydrogen peroxide (2.6 mmol) and 0.3 mL of water. The mixture was stirred at room temperature for 1.5 h and then heated at 40 °C for 1.5 h. Usual workup followed by flash chromatography (15% ether/petroleum ether) gave 107 mg (73%) of the Dewar benzene **2c**: mp 60–62 °C (from petroleum ether); IR (KBr) 1715, 1580, 1100, 780 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.2–1.7 (m, 8 H), 2.0–2.2 (m, 4 H), 3.70 (s, 6 H), 7.28 (s, 2 H); ^{13}C NMR δ 163.1 (s), 155.2 (d), 145.7 (s), 61.5 (s), 51.6 (q), 26.5 (t), 25.0 (t), 24.7 (t).

8,11-Bis(methoxycarbonyl)[6]paracyclophane (1c). A degassed solution of 97 mg (0.35 mmol) of **2c** in 100 mL of hexane was sealed in ampules and heated at 50 °C for 95 h. The solvent was evaporated, and subsequent flash chromatography (20% ether/petroleum ether) gave 87 mg (90%) of cyclophane **1c** as white solid. Crystals suitable for X-ray analysis were obtained by recrystallization from cyclohexane.

1c: mp 94–96 °C (from hexane); IR (KBr) 1710, 1265, 1245, 1195, 790, 745, 675 cm^{-1}; MS, m/e (rel intens) 276 (M$^+$, 25), 217 (38), 205 (100); ^{1}H NMR (CDCl$_3$, 26 °C) δ −0.7 to +0.1 (m, 2 H), 0.5–1.4 (m, 4 H), 1.5–1.9 (m, 2 H), 1.9–2.4 (m, 2 H), 3.6–3.9 (m, 2 H), 3.92 (s, 6 H), 7.91 (s, 2 H); ^{13}C NMR δ 167.1 (s), 146.5 (s), 136.5 (d), 133.6 (s), 52.2 (q), 37.0 (t), 35.0 (t), 27.0 (t); UV (hexane) [λ_{max}, nm (log ϵ)] 350 (3.2), 270 (3.8), 230 (4.3). Anal. Calcd for $C_{16}H_{20}O_4$: C, 69.54; H, 7.30. Found: C, 69.32; H, 7.33.

Measurement of Valence Isomerization Rates of 2a, 2c, and 7a. The rate of thermal isomerization of **2c** to **1c** was determined by UV spectroscopy,[4] in which the appearance of absorption at 350 nm in degassed hexane (3.4 × 10^{-4} M) was measured. For the measurement of isomerization rates of **2a** and **7a**, a degassed hexane solution of **1a**[4] or **8a**[7] (1.4 × 10^{-3} M) was irradiated with a low-pressure mercury lamp at 0 °C for 2–3 h to yield a photostationary mixture of **1a** and **2a** or **7a** and **8a** (ca. 1:1), and the rates were determined by measuring the increase of absorption at 300 and 310 nm, respectively.

X-ray Crystal Structure Analysis of 1c. Crystal data: $C_{16}H_{20}O_4$, M_r = 276.3, monoclinic, space group $C2/c$, a = 19.415 (4) Å, b = 6.975 (1) Å, c = 11.811 (2) Å, β = 112.16 (1)°, V = 1481.4 (4) Å^3, Z = 4, D_c = 1.239 g cm^{-3}, μ(Cu Kα) = 8.4 cm^{-1}, F(000) = 592.

The X-ray diffraction data were collected on a Rigaku automated four-circle diffractometer with Ni-filtered Cu Kα radiation. The crystal with dimensions of 0.3 × 0.25 × 0.2 mm was used for the data measurement. The integrated intensities were measured by the θ–2θ scan technique with background countings at each end of the scan range for 5 s. The scan range was determined as $\Delta 2\theta = (2.0 + 0.3 \tan \theta)°$. The total number of reflections was 1087, among which 948 were observed reflections [$|F_o| > 3\sigma(F_o)$]. Three monitor reflections were measured for each block of 61 reflections to check for radiation damage and for any change of the crystal orientation of the crystal. No radiation damage of the crystal was observed. The measured intensities were corrected for Lorentz and polarization effects but not for absorption, because of the relatively small absorption effects of the compound for Cu Kα radiation. The crystal structure was solved by the direct method (MULTAN 78)[15] and was refined by full-matrix least squares (XRAY SYSTEM).[16] All the hydrogen atoms were searched for on the difference Fourier maps calculated after the anisotropic refinements of non-hydrogen atoms. The weighting scheme applied was $w = [\sigma^2(F_o) + 0.003(F_o)^2]^{-1}$. The final R index defined by $R = \sum(|F_o| - |F_c|)/\sum|F_o|$ was 0.112 for observed reflections. The weighted R index defined by $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ was the rather large value of 0.198. All computations were carried out on an ACOS-850S computer at the Crystallographic Research Center, Institute for Protein Research, Osaka University.

Supplementary Material Available: Tables of fractional atomic coordinates, anisotropic thermal parameters for non-hydrogen atoms, and interatomic bond distances and angles including hydrogen atoms (3 pages). Ordering information is given on any current masthead page.

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Synthesis and Properties of Tricyclo[5.3.0.0^{2,8}]deca-3,5-dien-9-one. A New Entry to the $C_{10}H_{10}$ Manifold

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Starting from 3,8-cyclodecadiene-1,6-dione bis(ethylene acetal) (**4**) a 10-step synthesis is described which leads to the title compound **18**. It is found that **18** rearranges to tricyclo[5.3.0.0^{2,10}]deca-3,5-dien-9-one (**33**) at room temperature. The pyrolysis and photolysis of the tosylhydrazone of **18** and **19** yields the cycloheptatriene derivatives **41** and **42**. From the mesylate of the corresponding alcohol of **18** two dihydroazulenes (**38** and **39**) could be isolated and characterized. In carrying out the Shapiro reaction with **19** we obtained tricyclo[5.3.0.0^{4,8}]deca-2,5,9-triene (**35**). MNDO calculations concerning the possible reaction path of tricyclo[5.3.0.0^{2,8}]decatriene (**2**) to **35** suggest a radical mechanism and isobullvalene (**34**) as an intermediate.

Introduction

Some time ago we investigated by means of MO calculations the through-bond interaction of two perpendicular π-systems via a four-membered ring system.[1] Evidence for the relay properties of the four-membered ring was found by studying the electronic absorption spectrum of tricyclo[3.3.0.0^{2,6}]octadiene[2] and of tetrabenzotricyclo[5.5.0.0^{2,8}]dodeca-3,5,9,11-tetraene[3] as well as the He I

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