

Crystal and Molecular Structure of (*E*)-1,1'-Bitetralinylidene

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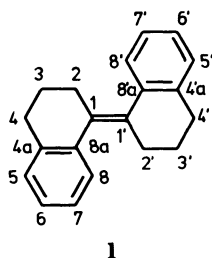
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(Received September 8, 1987)

The crystal structure of the title compound was determined by X-ray diffraction. The crystals have monoclinic symmetry with $a=13.481(5)$, $b=8.285(5)$, $c=13.092(3)$ Å, $\beta=96.24(3)^\circ$, and space group $P2_1/n$ with $Z=4$. The final R -factor was 0.065 for 2191 independent reflections. The torsion angles of the C-Ph bonds are $47.4(4)$ and $44.4(4)^\circ$. The cyclohexene rings have approximate twist-boat conformations. The molecular structure in the crystal is compared with that in the solution phase, that of (*E*)-stilbenes, and the results of the molecular mechanics calculations. It is also discussed in relation to the molecular packing.

In connection with our continuing studies of the geometry of stilbene systems,^{1,2} the molecular structure of the title compound (*E*)-1,1'-bitetralinylidene (**1**) is of interest, because **1** has the (*E*)-stilbene skeleton that is geometrically fixed by two methylene chains. Electronic absorption spectroscopic study of **1** has revealed that the torsion angle of the C-Ph bonds substantially deviates from 0° in the fluid and the glassy solution.² Molecular mechanics study using MMP1³ has shown that the torsion angle of the C-Ph bonds is 54° and that the cyclohexene rings have approximate twist-boat conformations in the isolated molecule.⁴ The purpose of the present study is to investigate the geometry of this molecule in the crystalline state and to compare it with that in the solution phase, with the geometry of (*E*)-stilbenes, and with the results of the molecular mechanics calculations.



Experimental

The sample of **1** was prepared by the method described in literature.⁴ Single crystals were recrystallized from isopropyl alcohol.

Crystal Data. $C_{20}H_{20}$, $M=260.36$. Monoclinic, $a=13.481(5)$, $b=8.285(5)$, $c=13.092(3)$ Å, $\beta=96.24(3)^\circ$, $V=1454(1)$ Å³ (by least-squares refinement on 20 reflections with $18 \leq 2\theta \leq 20^\circ$, $\lambda=0.71073$ Å), space group $P2_1/n$, $Z=4$, $D_x=1.190$ g cm⁻³, D_m not determined. The crystal used was a colourless plate. Approximate dimensions $0.8 \times 0.4 \times 0.2$ mm, $\mu(\text{Mo } K\alpha)=0.0622$ mm⁻¹. $F(000)=560$. $T=296$ K.

Data Collection and Processing. The integrated inten-

sities were collected on a Rigaku AFC-4 automated four-circle diffractometer using graphite-monochromatized Mo $K\alpha$ radiation. The ω - 2θ scan technique was employed at an ω rate of 4.0° min⁻¹. $2\theta_{\text{max}}=55^\circ$, collection range $h=-17$ to 17, $k=0$ to 10, $l=0$ to 16. Three standard reflections $\bar{1}21$, 710, and 264 were measured every 100 reflections, intensity variation $\leq 2.1\%$. 2419 reflections with $|F_o| > 3\sigma(F_o)$ were obtained. The intensities were corrected for Lorentz and polarization effects but not for absorption. 2191 reflections were unique and were used for refinement. 1298 reflections were unobserved.

Structure Analysis and Refinement. Structure was solved by direct methods with MULTAN78⁵ and was refined by full-matrix least squares minimizing $\sum w(|F_o|^2 - |F_c|^2)^2$, $w=(0.00462|F_o|^2 - 0.06153|F_o| + 0.68041)^{-1}$. 16 H atoms were obtained by the difference Fourier synthesis and 4 H atoms were located by standard bond lengths and angles. Isotropic temperature factors were assigned to all of the H atoms. 261 parameters consisting of 120 positional parameters, 120 anisotropic temperature factors, 20 isotropic temperature factors, and a scale factor were refined. In the final least squares refinement, $R=0.072$, $wR=0.083$, $S=1.1696$, and $(\Delta/\sigma)_{\text{max}}=0.790$. The maximum and the minimum height in the final difference Fourier synthesis were $+0.441$ and -0.658 e Å⁻³, respectively. For the structure at this stage (structure A), it was found that the temperature factors of C3 and C4 were exceptionally large ($B_{\text{eq}}=9.9$ Å² for C3 and $B_{\text{eq}}=7.0$ Å² for C4).

Therefore, further refinement was carried out on the basis of a disorder model constructed as follows. New atoms C3+ and C3- were located on the normal to the plane through C2, C3, and C4, which passes through C3, 0.25 Å above and below the plane, respectively. In a similar way, new atoms C4+ and C4- were located above and below the plane through C3, C4, and C4a. Then C3, C4, and hydrogen atoms attached to these atoms were deleted. Hydrogen atoms attached to the new carbon atoms were located by molecular mechanics calculations. Multiplicities of all of the new atoms were fixed to 0.5. For this model, 295 parameters consisting of 138 positional parameters, 132 anisotropic temperature factors, 24 isotropic temperature factors, and a scale factor were refined by full-matrix least squares minimizing $\sum w(|F_o| - |F_c|)^2$, $w=(0.00314|F_o|^2 - 0.04503|F_o| + 0.55851)^{-1}$. In the final least squares refinement, $R=0.065$, $wR=0.063$, $S=0.9538$, and $(\Delta/\sigma)_{\text{max}}=0.007$. The maximum and the minimum height in final difference Fourier synthesis were $+0.342$ and -0.249 e Å⁻³,

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respectively.

Atomic scattering factors were taken from the International Tables for X-Ray Crystallography.⁶⁾ Crystallographic calculations were performed on FACOM M-380 and M-780 computers at the Institute and on FACOM M-360 at the University of Tokyo using UNICSIII program system.⁷⁾ The molecular mechanics calculations were performed using the MMP2 program⁸⁾ on a HITAC M-682H computer of the Computer Centre of the University of Tokyo.

Results and Discussion

The final atomic parameters are listed in Table 1^{†††} and the geometrical parameters in Table 2. A perspective view of the molecule is shown in Fig. 1.

Table 2 and Fig. 1 show that the observed structure is asymmetric. However, in a rough approximation, it has a C_2 axis perpendicular to the ethylenic plane, in sharp contrast with (*E*)-stilbene (ES) and (*E*)- α,β -dimethylstilbene (E $\alpha\beta$ DMS), which have an inversion center (see Table 3).

The (*E*)-2-butene skeleton C8a-C1-C1'-C8'a holds the planar geometry. The double bond C1-C1' has a normal length 1.347 Å. It is nearly equal to the length of the ethylenic double bond of E $\alpha\beta$ DMS and is a little longer than that of ES. Absolute values of the torsion

Table 1. Final Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Thermal Parameters^{a)} for (*E*)-1,1'-Bitetralinylidene, with Estimated Standard Deviations in Parentheses

Atom	x	y	z	$B_{eq}/\text{\AA}^2$
Cl	3484(1)	1442(2)	1122(2)	2.9
C2	2990(2)	3101(3)	1163(2)	3.9
C3+	1870(5)	3101(8)	1264(5)	3.3
C3-	2078(6)	2923(13)	1773(9)	6.4
C4+	1388(6)	1590(1)	1557(6)	4.0
C4-	1670(5)	1536(9)	1910(5)	3.1
C4a	1818(2)	153(3)	1099(2)	4.1
C5	1142(2)	-1068(4)	800(3)	5.3
C6	1403(2)	-2318(4)	181(2)	5.3
C7	2344(2)	-2348(3)	-164(2)	4.6
C8	3022(2)	-1134(3)	132(2)	3.7
C8a	2782(2)	124(2)	780(2)	3.0
C1'	4452(1)	1186(2)	1454(1)	2.8
C2'	4907(2)	-506(3)	1590(2)	3.5
C3'	5733(2)	-656(3)	2480(2)	5.1
C4'	5716(2)	705(3)	3254(2)	4.7
C4'a	5789(2)	2303(3)	2708(2)	3.4
C5'	6442(2)	3531(3)	3061(2)	4.2
C6'	6488(2)	4946(3)	2509(2)	4.4
C7'	5888(2)	5151(3)	1591(2)	4.3
C8'	5231(2)	3937(3)	1230(2)	3.7
C8'a	5155(1)	2506(2)	1794(2)	2.9

$$a) B_{eq} = \frac{4}{3}(a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + 2ab\beta_{12}\cos\gamma + 2ac\beta_{13}\cos\beta + 2bc\beta_{23}\cos\alpha).$$

^{†††} List of H-atom coordinates, anisotropic temperature factors, and observed and calculated structure factors are deposited as Document No. 8784 at the Office of the Editor of Bull. Chem. Soc. Jpn.

angles of the C-Ph bonds of **1** are much larger than those of ES, but are significantly smaller than those of E $\alpha\beta$ DMS, in accordance with the results of our UV study.²⁾

Another (*E*)-2-butene skeleton C2-C1-C1'-C2' deviates from the planarity as shown by its torsion angle, and C2 and C2' atoms, as well as other sp^3 carbon atoms, are placed on a same side of the ethylenic plane (C8a-C1-C1'-C8'a). The two cyclohexene rings have approximate twist-boat conformations as shown in Fig. 2.

These results are essentially consistent also with the results of molecular mechanics calculations using MMP2. The most stable molecular structure obtained by the calculations is nearly C_2 symmetric and has the following geometrical parameters (cf. Table 2): Bond length C1-C1', 1.361 Å; torsion angles C1'-C1-C8a-C8, -49.3° ; C1-C1'-C8'a-C8', -49.4° ; C2-C1-C1'-C2', 157.1° ; C2-C1-C1'-C8'a, -10.4° ; C2'-C1'-C1-C8a, -10.5° .

One of the most interesting features of the X-ray structure is that there is a disorder in C3 and C4 but not in C3' and C4'. This may be explained in terms of the intermolecular nonbonding interactions in the crystal as follows.

The crystal structure is shown in Fig. 3. In a unit cell, there are 28 intermolecular nonbonding atom pairs whose distances (2.64–2.87 Å for C...H and 2.12–2.39 Å for H...H) are slightly shorter than the sum of the relevant van der Waals radii (2.90 Å for

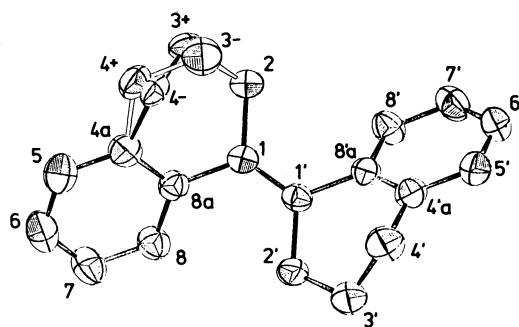


Fig. 1. Perspective view of (*E*)-1,1'-bitetralinylidene, drawn by ORTEP.⁹⁾

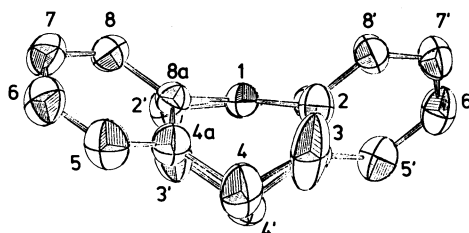


Fig. 2. End view of (*E*)-1,1'-bitetralinylidene. For the clarity, structure A is drawn.

Table 2. Geometrical Parameters for (*E*)-1,1'-Bitetralinylidene

Bond length/Å ^{a)}			
C1-C2	1.530(3)	C1'-C2'	1.533(3)
		C2'-C3'	1.527(4)
		C3'-C4'	1.518(4)
		C4'-C4'a	1.513(4)
C4a-C5	1.389(4)	C4'a-C5'	1.391(3)
C5-C6	1.384(4)	C5'-C6'	1.383(4)
C6-C7	1.393(4)	C6'-C7'	1.384(4)
C7-C8	1.385(4)	C7'-C8'	1.388(3)
C8-C8a	1.404(3)	C8'-C8'a	1.406(3)
C4a-C8a	1.408(3)	C4'a-C8'a	1.404(3)
C1-C8a	1.482(3)	C1'-C8'a	1.483(3)
C1-C1'	1.347(3)		
Bond angle/° ^{a)}			
		C1'-C2'-C3'	114.4(2)
		C2'-C3'-C4'	112.7(2)
		C3'-C4'-C4'a	109.2(2)
		C4'-C4'a-C5'	123.7(2)
		C4'-C4'a-C8'a	116.3(2)
C4a-C5-C6	120.6(3)	C4'a-C5'-C6'	120.6(2)
C5-C6-C7	120.2(3)	C5'-C6'-C7'	120.2(2)
C6-C7-C8	119.5(3)	C6'-C7'-C8'	119.5(2)
C7-C8-C8a	121.3(2)	C7'-C8'-C8'a	120.8(2)
C8-C8a-C4a	118.2(2)	C8'-C8'a-C4'a	118.5(2)
C1-C8a-C8	123.3(2)	C1'-C8'a-C8'	123.0(2)
C1-C8a-C4a	118.5(2)	C1'-C8'a-C4'a	118.5(2)
C8a-C1-C1'	123.1(2)	C8'a-C1'-C1	123.1(2)
Torsion angle/°			
C1-C2-C3+-C4-	31.7(5)	C1'-C2'-C3'-C4'	18.7(3)
C1-C2-C3--C4+	-46.1(9)		
C2-C3+-C4--C4a	-71.0(5)	C2'-C3'-C4'-C4'a	-56.6(3)
C2-C3--C4+-C4a	24.9(11)		
C3+-C4--C4a-C8a	61.0(5)	C3'-C4'-C4'a-C8'a	47.3(3)
C3--C4+-C4a-C8a	-7.2(9)		
C4--C4a-C8a-C1	-6.9(4)	C4'-C4'a-C8'a-C1'	1.9(3)
C4+-C4a-C8a-C1	14.1(5)		
C4a-C8a-C1-C2	-37.3(3)	C4'a-C8'a-C1'-C2'	-41.6(3)
C8a-C1-C2-C3+	22.8(4)	C8'a-C1'-C2'-C3'	29.5(3)
C8a-C1-C2-C3-	50.3(5)		
C8a-C1-C1'-C8'a	179.8(2)		
C1'-C1-C8a-C8	-44.4(3)	C1-C1'-C8'a-C8'	-47.4(3)
C2-C1-C1'-C2'	169.1(2)		
C2-C1-C1'-C8'a	-6.2(3)	C2'-C1'-C1-C8a	-4.9(3)

a) The bond lengths and angles related to the disordered atoms, C3± and C4±, are not listed in this table, because they are not reliable. They will be approximately equal to the corresponding ones in which C3' and/or C4' are involved.

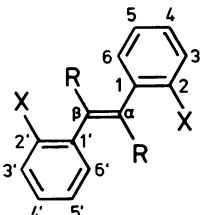
C...H and 2.40 Å for H...H) as shown in Table 4,¹²⁾ where parts of the molecule are designated as follows. A half of the molecule that has the atom numbers without primes in Fig. 1 is designated as *n*. Another half that has atom numbers with primes in Fig. 1 is designated as *n'*. An atom of the methylene groups and an atom of the benzene ring in the half *n*(or *n'*) are designated as *M* (or *M'*) and *B* (or *B'*), respectively.

The fact that all of the 28 van der Waals contact atom pairs involve the half of the molecule *n'* shows that it is sterically more crowded than the another half *n*. The fact that 4 van der Waals contact atom pairs involve atoms *M* while 16 van der Waals contact pairs involve atoms *M'* shows that the methylene groups of the cyclohexene ring for which the disorder was

observed are sterically much less crowded than those of the cyclohexene ring for which the disorder was not observed. The fact that there are 25 van der Waals contact atom pairs in which atoms of the benzene rings are involved shows that the benzene rings are sterically more crowded than the cyclohexene rings. Thus, the difference between the packing of the two halves of the molecule results in the asymmetrical molecular structure in the crystal.

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Table 3. Comparison of Geometrical Parameters for (*E*)-1,1'-Bitetralinylidene and (*E*)-Stilbenes


Compound	ES ^a R=X=H	I ^b R=X=(CH ₂) ₃	EαβDMS ^c R=CH ₃ , X=H
Bond length/Å			
α-β	1.326(2)	1.347(3)	1.341(19)
α-1	1.471(2)	1.482(3)	1.549(8)
β-1'	1.471(2)	1.483(3)	1.549(8)
Bond angle/°			
1-α-β	126.4(1)	123.1(2)	114.7(9)
1'-β-α	126.4(1)	123.1(2)	114.7(9)
Torsion angle/°			
1-α-β-1'	180.0	179.8(2)	180.0
6-1-α-β	5.3(2)	-44.4(3)	66.2
6'-1'-β-α	-5.3(2)	-47.4(3)	-66.2

a) Ref. 10. b) Data for structure **B** in this work.
c) Ref. 11.

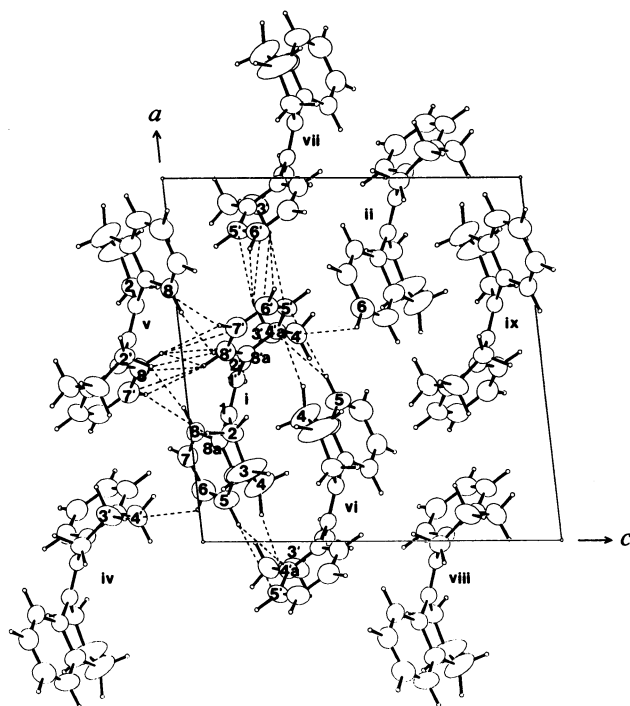


Fig. 3. The crystal structure of (*E*)-1,1'-bitetralinylidene viewed along the *b* axis. Dotted lines indicate van der Waals contact atom pairs. Molecules (structure **A**) generated by the following symmetry operations are drawn: (i) x, y, z ; (ii) $x, \bar{y}+0.5, z+0.5$; (iii) $x+0.5, \bar{y}-0.5, z+0.5$; (iv) $x-0.5, \bar{y}+0.5, z-0.5$; (v) $\bar{x}+1, \bar{y}+1, \bar{z}$; (vi) $\bar{x}+0.5, y+0.5, \bar{z}+0.5$; (vii) $\bar{x}+1.5, y+0.5, \bar{z}+0.5$; (viii) $x-0.5, \bar{y}+0.5, z+0.5$; (ix) $\bar{x}+1, \bar{y}+1, \bar{z}+1$. Molecule iii is hidden by molecule ii.

Table 4. Van der Waals Contact^a Atom Pairs in a Unit Cell

Class <i>n, n</i>	0 pairs		
Class <i>n, n'</i>	14 pairs		
Subclass	Atom 1 ^b	Atom 2 ^b	Distance/Å
<i>M, M'</i>	H(C4-) ¹ⁱ	H(C3') ^{2vi}	2.32(6)
<i>M, M'</i>	H(C3') ²ⁱ	H(C4-) ^{1vi}	2.32(6)
<i>M, B'</i>	H(C2) ²ⁱ	H(C7') ^v	2.22(5)
<i>M, B'</i>	H(C7') ⁱ	H(C2) ^{2v}	2.22(5)
<i>B, M'</i>	C4' ⁱ	H(C6) ³ⁱⁱⁱ	2.86(4)
<i>B, M'</i>	C4' ^{ai}	H(C5) ^{vi}	2.70(3)
<i>B, M'</i>	H(C6) ⁱ	C4' ^{iv}	2.86(4)
<i>B, M'</i>	H(C6) ⁱ	H(C3') ^{iv}	2.12(6)
<i>B, M'</i>	H(C8) ⁱ	H(C2') ^{2v}	2.34(4)
<i>B, M'</i>	H(C2') ²ⁱ	H(C8) ^v	2.34(4)
<i>B, M'</i>	H(C3') ²ⁱ	H(C6) ³ⁱⁱ	2.12(6)
<i>B, B'</i>	C5' ⁱ	H(C5) ^{vi}	2.85(3)
<i>B, B'</i>	H(C5) ⁱ	C4' ^{ai}	2.70(3)
<i>B, B'</i>	H(C5) ⁱ	C5' ^{vi}	2.85(3)

Class <i>n', n'</i>	14 pairs		
Subclass	Atom 1 ^b	Atom 2 ^b	Distance/Å
<i>M', M'</i>	H(C2') ²ⁱ	H(C2') ^{2v}	2.39(5)
<i>M', B'</i>	C5' ⁱ	H(C3') ^{1vi}	2.85(4)
<i>M', B'</i>	C6' ⁱ	H(C3') ^{1vii}	2.64(4)
<i>M', B'</i>	H(C3') ¹ⁱ	C5' ^{vii}	2.85(4)
<i>M', B'</i>	H(C3') ¹ⁱ	C6' ^{vii}	2.64(4)
<i>M', B'</i>	H(C3') ¹ⁱ	H(C6') ^{vii}	2.25(5)
<i>M', B'</i>	H(C6') ⁱ	H(C3') ^{1vii}	2.25(5)
<i>B', B'</i>	C7' ⁱ	H(C8') ^v	2.87(3)
<i>B', B'</i>	C8' ⁱ	H(C8') ^v	2.82(3)
<i>B', B'</i>	H(C7') ⁱ	H(C8') ^v	2.15(4)
<i>B', B'</i>	H(C8') ⁱ	C7' ^v	2.87(3)
<i>B', B'</i>	H(C8') ⁱ	C8' ^v	2.82(3)
<i>B', B'</i>	H(C8') ⁱ	H(C7') ^v	2.15(4)
<i>B', B'</i>	H(C8') ⁱ	H(C8') ^v	2.18(4)

a) Following van der Waals radii were used: H, 1.20; C, 1.70 Å.¹³ b) Symmetry codes are given in the caption of Fig. 3.

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12) The data given in Table 4 are based on the crystal structure of the disorder model. The crystal structure shown in Fig. 3 is, however, based on molecular structure **A** for the clarity, because a figure of the crystal structure of the disorder model is too much complicated for the indication of the van der Waals contact atom pairs.

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