

statistics,  $w = 1/\sigma^2(F_o)$ ;  $\Delta/\sigma$  (max.) = 0.101; largest peaks on final difference map +0.210 and -0.200 e Å<sup>-3</sup>. All calculations were made with the NRC VAX *Crystal Structure System* (Gabe, Lee & Le Page, 1985). Atomic scattering factors from *International Tables for X-ray Crystallography* (1974).

**Discussion.** Final atomic coordinates are given in Table 1;\* Fig. 1, which contains the atomic numbering, has been prepared from the output of *ORTEPII* (Johnson, 1976), and Fig. 2 from the output of *PACKER*, part of the NRC VAX *Crystal Structure System* (Gabe, Lee & Le Page, 1985). Table 2 contains selected bond lengths and bond angles. The molecule has the chair conformation with one S=O bond axial and the other equatorial. The S=O bond lengths are similar to those in dimethyl sulfoxide [1.47 (4) Å] and dimethyl sulfone

\* Lists of structure amplitudes and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44436 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

[1.44 (3) Å] (Allen & Sutton, 1950) and there are no unusual bond lengths involving carbon. It appears that this is the first determination of the crystal structure of a cyclic dithiane dioxide.

The crystal packing is shown in Fig. 2. All intermolecular contacts are normal.

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## Low- and High-Temperature Structure of (*E*)-2,2'-Dimethylstilbene

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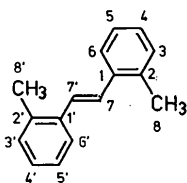
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**Abstract.** C<sub>16</sub>H<sub>16</sub>,  $M_r = 208.29$ , monoclinic,  $P2_1/n$ ,  $Z = 2$ ,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å,  $F(000) = 224$ . At 296 K:  $a = 10.886$  (2),  $b = 6.698$  (2),  $c = 8.683$  (1) Å,  $\beta = 98.53$  (1)°,  $V = 626.1$  (2) Å<sup>3</sup>,  $D_x = 1.105$  Mg m<sup>-3</sup>,  $\mu = 0.0577$  mm<sup>-1</sup>,  $R = 0.047$  for 892 independent

reflections. At 118 K:  $a = 10.784$  (2),  $b = 6.622$  (1),  $c = 8.565$  (1) Å,  $\beta = 97.78$  (1)°,  $V = 606.0$  (2) Å<sup>3</sup>,  $D_x = 1.142$  Mg m<sup>-3</sup>,  $\mu = 0.0596$  mm<sup>-1</sup>,  $R = 0.045$  for 1319 independent reflections. The molecule is centrosymmetric in the crystal. The length of the ethylenic

bond is 1.280 (4) Å at 296 K and 1.325 (2) Å at 118 K. The torsion angle of the C—Ph bond is 11.7(4)° at 296 K and 18.5(2)° at 118 K. The C—C bond lengths and angles at 118 K were fairly well reproduced by molecular-mechanics calculations except for the length of the ethylenic bond and the angles in which the bond is involved. The results for 296 K perfectly agree with the recent results for 299 K [Tirado-Rives, Fronczek & Gandour (1985). *Acta Cryst. C* **41**, 1327–1329].

**Introduction.** The length of the ethylenic bond in the title compound was recently found to be 1.284 (4) Å at 299 K on the basis of X-ray diffraction (Tirado-Rives, Fronczek & Gandour, 1985). To our and their surprise, this bond, which is conjugated with the benzene rings, is shorter than an isolated C=C double bond, of which the standard length is 1.337 (6) Å (*International Tables for X-ray Crystallography*, 1968). Examination of this unusual result is one of the main purposes of the present study, in which X-ray diffraction of the title compound has been measured at 296 and 118 K.



**Experimental.** Experimental details are summarized in Table 1. The solvent for recrystallization was isopropyl alcohol. 20 (40) reflections used for measuring lattice parameters at 296 K (118 K). Structure solved with *MULTAN78*, refined on *F*. H atoms located on difference Fourier map, refined isotropically for 296 K data and anisotropically for 118 K data.  $w = (0.00143|F_o|^2 - 0.01709|F_o| + 0.11516)^{-1}$  for 296 K data and  $w = (0.00191|F_o|^2 - 0.00560|F_o| + 0.07703)^{-1}$  for 118 K data. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). Atomic parameters are listed in Table 2\* and selected geometrical parameters are given in Table 3. *ORTEP* drawings of the molecule are shown in Fig. 1.

**Discussion.** Our results for 296 K perfectly agree with the recent results for 299 K (Tirado-Rives *et al.*, 1985). In both the results, all the thermal parameters are normal and the final difference Fourier synthesis gave no residual atoms. That is, no disorder was found in either crystal.

\* Lists of H-atom coordinates, anisotropic thermal parameters and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44512 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Experimental details of the X-ray diffraction study of (E)-2,2'-dimethylstilbene*

	296 K	118 K
<b>Data acquisition parameters</b>		
Crystal dimensions (mm)	0.3 × 0.3 × 0.4	0.13 × 0.64 × 0.40
Diffractometer used	Rigaku AFC-4	Rigaku AFC-5
Radiation	Mo <i>K</i> α	Mo <i>K</i> α
Scan mode	ω-2θ	ω-2θ
Scan speed (° min <sup>-1</sup> )	4.0	3.0
Range of <i>hkl</i>	-14 ≤ <i>h</i> ≤ 14 0 ≤ <i>k</i> ≤ 8 0 ≤ <i>l</i> ≤ 11	-19 ≤ <i>h</i> ≤ 19 -11 ≤ <i>k</i> ≤ 0 -15 ≤ <i>l</i> ≤ 15
Max. 2θ (°)	55	80
Standard reflections	200, $\bar{1}$ 13, 015	200, $\bar{1}$ 13, 015
Intensity variation of standards (%)	2.5	10*
Criterion for observed reflections	<i>F</i> <sub>o</sub>   ≥ 3σ(  <i>F</i> <sub>o</sub>  )	<i>F</i> <sub>o</sub>   ≥ 2.5σ(  <i>F</i> <sub>o</sub>  )
Measured reflections	1017	3992
Unique reflections	892	1931
Unobserved reflections	640	1999
<b>Structural determination parameters</b>		
Number of variables	105	146
<i>R</i>	0.047	0.045
<i>wR</i>	0.041	0.045
<i>S</i>	0.3511	0.3866
Max. Δ/σ in final cycle	0.319	0.328
Residual density (e Å <sup>-3</sup> )	-0.180 to 0.135	-0.237 to 0.540
Computer programs used	<i>MULTAN78</i> † <i>UNICS3</i> ‡	<i>MULTAN78</i> † <i>UNICS3</i> ‡

\* All of the intensity data were corrected on the basis of the intensity variation of the standard reflections.

† Main, Hull, Lessinger, Germain, Declercq & Woolfson (1978).

‡ Sakurai & Kobayashi (1979).

When the temperature was lowered to 118 K, all of the cell lengths and β were reduced by ca 1% retaining the same crystal system and space group as 296 K. The thermal parameters at 118 K are, naturally, much smaller than those at 296 K. The final difference Fourier synthesis gave no residual atom, but clearly exhibited the peaks of the bonding electrons at the centers of all of the C—C bonds, which were not observed at 296 K.

There is no intermolecular interatomic distance shorter than the sum of the relevant van der Waals radii at both temperatures.

The observed molecular structure has the following features. (1) The molecule is centrosymmetric. (2) The length of the ethylenic bond is 1.280 (4) Å at 296 K and 1.325 (2) Å at 118 K. (3) The C—C bonds of the benzene rings at 118 K are slightly longer (at least 0.009 Å longer) than those at 296 K. (4) The lengths of single bonds C1—C7 and C2—C8 at 118 K are nearly equal to those at 296 K. (5) All the C—C—C bond angles except C1—C7—C7' do not change on lowering temperature. (6) Torsion angle C7'—C7—C1—C6 is 11.7 (4)° at 296 K and 18.5 (2)° at 118 K.

Since atomic positions determined by X-ray diffraction are those averaged by thermal vibrations, their accuracy and precision are higher at the lower temperature. As shown in Table 3, except for the ethylenic bond, the observed C—C bond lengths at 118 K are in fair agreement (within a deviation of 0.006 Å) with the calculated ones obtained by the

Table 2. Final coordinates ( $\times 10^4$ ) and equivalent isotropic thermal parameters for (*E*)-2,2'-dimethylstilbene, with *e.s.d.*'s in parentheses

	296 K				118 K			
	<i>x</i>	<i>y</i>	<i>z</i>	$B_{eq}^*(\text{\AA}^2)$	<i>x</i>	<i>y</i>	<i>z</i>	$B_{eq}^*(\text{\AA}^2)$
C1	1559 (2)	1359 (3)	-73 (2)	4.2	1583 (1)	1369 (2)	-55 (1)	1.4
C2	2813 (2)	960 (3)	491 (2)	4.2	2849 (1)	947 (2)	515 (1)	1.3
C3	3710 (2)	2263 (3)	110 (2)	4.9	3776 (1)	2243 (2)	107 (1)	1.5
C4	3409 (2)	3913 (4)	-806 (3)	5.7	3482 (1)	3927 (2)	-843 (1)	1.8
C5	2184 (2)	4325 (4)	-1348 (3)	5.9	2233 (1)	4367 (2)	-1381 (1)	1.8
C6	1271 (2)	3064 (3)	-972 (2)	5.2	1298 (1)	3100 (2)	-982 (1)	1.7
C7	575 (2)	13 (4)	295 (3)	5.2	583 (1)	37 (2)	360 (1)	1.9
C8	3190 (2)	-820 (4)	1507 (3)	5.7	3211 (1)	-851 (2)	1558 (1)	1.8

$$* B_{eq} = \frac{1}{3}(a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + 2ab\beta_{12}\cos\gamma + 2ac\beta_{13}\cos\beta + 2bc\beta_{23}\cos\alpha).$$

Table 3. Geometrical parameters for (*E*)-2,2'-dimethylstilbene

	X-ray		MMP2	
	296 K*	118 K	$\pi$ -bond order	
<b>Bond lengths (\AA)</b>				
C7-C7'	1.280 (4)	1.325 (2)	1.353	0.9432
C1-C7	1.471 (3)	1.473 (2)	1.478	0.2391
C1-C2	1.405 (2)	1.414 (1)	1.410	0.6435
C2-C3	1.386 (3)	1.398 (2)	1.399	0.6746
C3-C4	1.373 (3)	1.391 (2)	1.396	0.6608
C4-C5	1.375 (3)	1.394 (2)	1.394	0.6676
C5-C6	1.380 (4)	1.390 (2)	1.396	0.6672
C6-C1	1.393 (3)	1.404 (2)	1.404	0.6499
C2-C8	1.504 (3)	1.508 (2)	1.512	
<b>Bond angles (<math>^\circ</math>)</b>				
C1-C7-C7'	128.5 (2)	126.1 (1)	124.9	
C7-C1-C2	120.6 (2)	120.2 (1)	120.5	
C7-C1-C6	120.9 (2)	120.9 (1)	120.9	
C1-C2-C3	118.7 (2)	118.8 (1)	119.7	
C2-C3-C4	121.9 (2)	121.6 (1)	121.2	
C3-C4-C5	119.7 (2)	119.6 (1)	119.4	
C4-C5-C6	119.5 (2)	119.5 (1)	119.8	
C5-C6-C1	121.6 (2)	121.5 (1)	121.4	
C6-C1-C2	118.5 (2)	118.9 (1)	118.5	
C1-C2-C8	121.5 (2)	121.4 (1)	121.6	
C3-C2-C8	119.9 (2)	119.8 (1)	118.7	
<b>Torsion angles (<math>^\circ</math>)</b>				
C1'-C7'-C7-C1	180	180	180	
C7'-C7-C1-C6	11.7 (4)	18.5 (2)	25.6	

\* The listed bond lengths, angles and torsion angles, observed at 296 K, agree with those observed at 299 K (Tirado-Rives *et al.*, 1985) within deviations of 0.008 \AA, 0.3 $^\circ$  and 1.0 $^\circ$ , respectively.

molecular-mechanics method using the MMP2 program (Allinger, 1982; Allinger & Flanagan, 1983) and systematically reflect the variance of the  $\pi$ -bond orders of the C-C bonds. This fact clearly demonstrates the high reliability of the results for 118 K.

Does the ethylenic bond have really the abnormally short length at room temperature? If it does, the basic relation between bond order and bond length would break down for this bond. If it does not, that is, if the observed short length is only apparent, careful consideration would be necessary for the interpretation of X-ray crystallographic data in some instances.

Probably the latter is the case. The apparent short length may be ascribed to the neglect of anharmonic oscillation in the data analysis. The fact that on

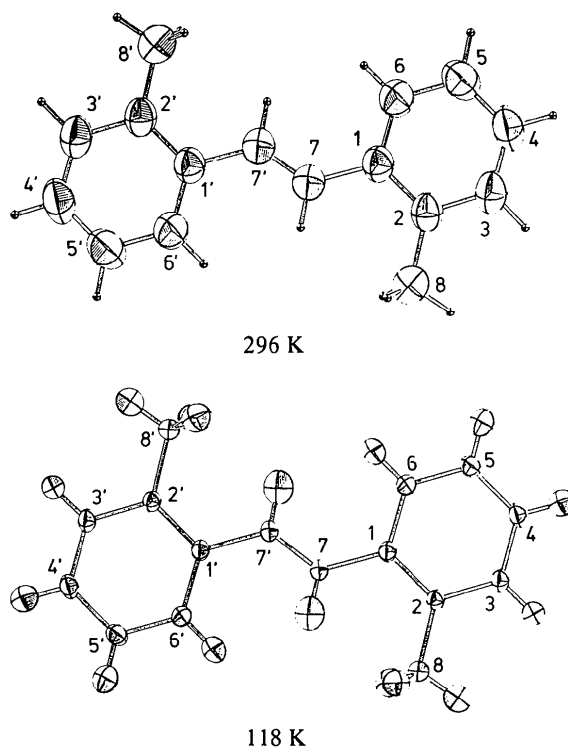


Fig. 1. ORTEP drawings (Johnson, 1965) of (*E*)-2,2'-dimethylstilbene at 296 and 118 K. For 296 K, C atoms are represented by thermal ellipsoids with 50% probability and H atoms by spheres with a diameter of 0.1 \AA. For 118 K, both C and H atoms are represented by thermal ellipsoids with 50% probability.

lowering temperature the distance between C1 and C1' remains almost unchanged [3.871 (4) \AA at 296 K and 3.878 (2) \AA at 118 K], while the distance between C7 and C7' and bond angles C1-C7-C7' and C1'-C7'-C7 are significantly changed may suggest that anharmonicities are considerably involved in the bending motions around C7 and C7'. Their contributions may be smaller at the lower temperature. As a result, the lower the temperature, the longer the observed length of the ethylenic bond may be. The fact that it is still shorter than an isolated C=C double bond at

118 K may be ascribed to the anharmonicities which still remain at this temperature.

On lowering the temperature, an increase in the torsion angles of the C—Ph bond was observed. This is expected to be accompanied by the shortening of the ethylenic bond since its bond order is increased by the twisting of the C—Ph bond. But, in fact, a lengthening of the ethylenic bond was observed on lowering the temperature. This result may be explained by the assumption that on lowering temperature the shortening of the bond caused by the increase of the torsion angle of the C—Ph bond was outweighed by the lengthening due to the decrease of the above-mentioned anharmonicity.

The present study demonstrates that X-ray crystallographic data which apparently seem to be normal may not always give fully reliable geometry for a molecule and that the molecular structure may be changed without phase transition in a crystal on varying the temperature.

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### Structure of 3-Isoadenosine

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**Abstract.** 3-β-D-Ribofuranosyladenine, C<sub>10</sub>H<sub>13</sub>N<sub>5</sub>O<sub>4</sub>, *M<sub>r</sub>* = 267.25, orthorhombic, *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>, *a* = 13.470 (4), *b* = 16.054 (6), *c* = 5.141 (2) Å, *V* = 1111.8 (7) Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* = 1.596 g cm<sup>-3</sup>, λ(Mo *K*α) = 0.71073 Å, μ = 1.18 cm<sup>-1</sup>, *F*(000) = 560, *T* = 298 K, *R* = 0.043, *wR* = 0.042 for 1136 reflections. The tautomeric form present in the crystal is 6-NH<sub>2</sub>. The adenine moiety is nearly planar and the torsional angle of the glycosidic linkage O(4')—C(1')—N(3)—C(4) is -161.5°. All N and O atoms except N(3) and O(4') participate in a three-dimensional hydrogen-bonding system.

**Introduction.** 3-Isoadenosine (Leonard & Laursen, 1963, 1965) is an isomer of adenosine in which the D-ribofuranosyl moiety is attached to N(3) of adenine. Because of the close spatial relationship between these two compounds (Leonard, Cruickshank, Groziak, Clauson & Devadas, 1986), the determination of the structure of 3-isoadenosine is desired in order to furnish information concerning the preferred tautomeric form

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in the crystal, the orientation of the ribose ring, and the intermolecular hydrogen-bonding pattern, and to compare its structure with adenosine (Lai & Marsh, 1972) and other known N(3)-substituted adenines (Petersen & Furberg, 1975; Kistenmacher, Urmev & Rossi, 1977).

**Experimental.** The title compound was recrystallized from water as transparent, colorless acicular crystals of dimensions approximately 0.1 × 0.2 × 0.8 mm; *D<sub>m</sub>* was not measured. The X-ray data were measured with a Syntex P2<sub>1</sub> automated four-circle diffractometer using graphite-monochromatized Mo *K*α radiation. The lattice parameters were refined using 15 reflections with 2θ values between 17.8 and 19.5°; 1448 unique reflections were measured (+*h*, +*k*, +*l*) to the limit of 2θ < 54.0° using the ω/2θ scan technique, scan rate 2.0–15.0° min<sup>-1</sup>, scan range 1.7° with a scan-to-background ratio of 0.25, 1136 reflections with *I* > 2.58σ(*I*), σ(*F*<sub>o</sub><sup>2</sup>) based on counting statistics plus the term 0.02*F*<sub>o</sub><sup>2</sup>. Anomalous-dispersion, Lorentz, and polarization corrections were applied. Three standard intensities monitored per 100 reflections showed no

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