

The Crystal Structure of 2,2,4,4-Tetramethyl-3-methylenecyclobutanone

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The crystal structure of 2,2,4,4-tetramethyl-3-methylenecyclobutanone ($C_9H_{14}O$) has been determined from three-dimensional X-ray diffraction data. The crystals are in orthorhombic space group $Pnma$, with $Z=4$ and $a=12.869$ (2), $b=9.966$ (2), $c=7.107$ (1) Å. Data were collected manually on a diffractometer using zirconium-filtered $Mo K\alpha$ radiation. 639 independent reflections were observed. The structure was solved by direct methods and refined by full-matrix least-squares calculations to yield a final R of 0.069. The results indicate a planar cyclobutane ring.

Introduction

The cyclobutane ring exists in both planar and puckered conformations in the solid state. Although the origin of these conformational differences among cyclobutanes is not very well understood, Bohn & Tai (1970) have suggested that the planar conformations are due to a dominance of crystal packing forces over intramolecular forces. Until recently (Shirrell & Williams, 1974a), simple cyclobutane compounds possessing planar rings have only been found in those molecules with a centrosymmetric arrangement of substituents. However, a centrosymmetric arrangement in itself is not sufficient to assure a planar ring.

To gain more information about the nature of these forces that influence the conformation of the cyclobutane ring, we have initiated a study of several exocyclic 1,3-double-bonded derivatives of 2,2,4,4-tetramethylcyclobutane. Previously, the structures of 2,2,4,4-tetramethyl-1,3-cyclobutanedithione (Shirrell & Williams, 1973), 2,2,4,4-tetramethyl-1,3-cyclobutanedione (Shirrell & Williams, 1974b), and 2,2,4,4-tetramethyl-3-thio-1,3-cyclobutanedione (Shirrell & Williams, 1974a) have been reported. We have also solved the structure of a 1:1 mixture of *syn* and *anti* 2,2,4,4-tetramethylcyclobutane 1,3-dioxime. All of these compounds possess planar rings.

We report here the structure of 2,2,4,4-tetramethyl-3-methylenecyclobutanone. This compound does not possess a centrosymmetric arrangement of substituents, but contains a planar ring.

Experimental

A sample of this compound was kindly provided by Dr D. H. Gibson and Mr J. Joseph, Department of Chemistry, University of Louisville. The crystals used in this study were grown by sublimation.

Approximate cell dimensions, systematic absences ($hk0$: h odd; $0kl$: $k+l$ odd), and orthorhombic symmetry were obtained from oscillation and Weissenberg photographs taken with nickel-filtered $Cu K\alpha$ radiation. The possible space groups are Pna_2 , and

$Pnma$. The centrosymmetric space group, $Pnma$, was initially chosen on the basis of a statistical analysis of the data and later confirmed by the successful structure determination.

The crystal used for accurate lattice constants and intensity data was a transparent polyhedron of approximate dimensions $0.30 \times 0.25 \times 0.50$ mm. It was mounted in a Lindemann capillary tube with the 0.5 mm axis (b) parallel to the walls of the capillary tube. Since the compound is extremely volatile, the crystals would either sublime and reform on the walls of the capillary tube or they would sublime sufficiently to allow them to become misoriented when exposed to the X-ray beam. This problem was overcome by taking the data at slightly below room temperature (18°C).

Using vanadium-filtered $Cr K\alpha$ radiation ($\lambda=2.2916$ Å), 14 reflection angles with high 2θ values were accurately measured. The lattice constants were determined by a least-squares fit (Williams, 1964) to these data using the extrapolation function of Nelson & Riley (1945). The values obtained are $a=12.869$ (2), $b=9.966$ (2), and $c=7.107$ (1) Å. The volume of the unit cell is 911.49 Å³, and the calculated density for four molecules of $C_9H_{14}O$ (F.W. 138.21) is 1.01 g cm⁻³. The observed density, measured by flotation in an aqueous solution of potassium iodide, was 1.00 g cm⁻³.

The intensities of 639 independent reflections (up to $2\theta=45^\circ$) were measured on a Siemens manual diffractometer using zirconium-filtered $Mo K\alpha$ radiation ($\lambda=0.7107$ Å). Intensities were measured using the $\theta-2\theta$ scan technique with a scan rate of 2° min⁻¹. In order to decrease the time of exposure of the crystal to the X-ray beam, the background was determined as a function of crystal setting. The take-off angle was 2.5° , and the receiving slit was 4×4 mm. A check of the intensities of several reflections showed them to remain constant within instrumental and statistical fluctuations during the data collection. The Lorentz and polarization corrections were made in the usual manner. For $Mo K\alpha$ radiation, the linear absorption coefficient for this compound is 0.71 cm⁻¹. No absorption correction was made. The standard deviation of each intensity measurement was estimated by the for-

mula: $\sigma^2(I) = CT + CB + (0.05CT)^2 + (0.05CB)^2$ where CT is the total counts and CB is the background counts. The error in the structure factor, $\sigma(F_o)$, was calculated from $\sigma(I)$ by the finite difference method (Williams & Rundle, 1964). If $CT < CB$ then F_o was set equal to zero. 45 reflections were observed to have F_o equal to zero. In the least-squares refinement the weight of each reflection was taken as $1/[\sigma(F_o)]^2$.

Structural determination

The structure factors were scaled by Wilson's (1942) method and were converted to normalized structure factors by FAME (Dewar, 1970) for use in the phase determination. 107 of these reflections with $E \geq 1.35$ were used in the computer program MULTAN (Germain, Main & Woolfson, 1970). The choice of the correctly phased set was unambiguous. The correct set had the best figures of merit. All 107 signs were determined, giving an E map in which all of the non-hydrogen atoms appeared as the ten highest peaks.

Isotropic least-squares refinement of these positions using a modification of the full-matrix program of Busing, Martin & Levy (1962) resulted in an R of 0.182 for all data. The function minimized in the least-squares calculations was $\sum(F_o - |F_c|/K)^2/\sigma^2(F_o)$. The scattering factors of Hanson, Herman, Lea & Skillman (1964) were used for oxygen and carbon.

After several least-squares cycles, using anisotropic temperature factors, R dropped to 0.112. A difference Fourier map then revealed the eight hydrogen atoms. The anisotropic temperature factors for all hydrogen atoms were set equal to the temperature factors of the carbon atom to which they are bonded. Their coordinates were varied in the least-squares refinement, but not their temperature factors. The scattering factors of Stewart, Davidson & Simpson (1965) were used for hydrogen. Six cycles of anisotropic full-matrix least-squares refinement were necessary before all param-

eters shifted less than 0.05σ and the final weighted R was 0.069. The final unweighted R was 0.071. A difference Fourier map was prepared from the final model. The values on this map varied in apparently random fashion from 0.175 to $-0.018 \text{ e } \text{\AA}^{-3}$.

The final atomic parameters are listed in Table 1 together with their estimated standard deviations.*

* The list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30655 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

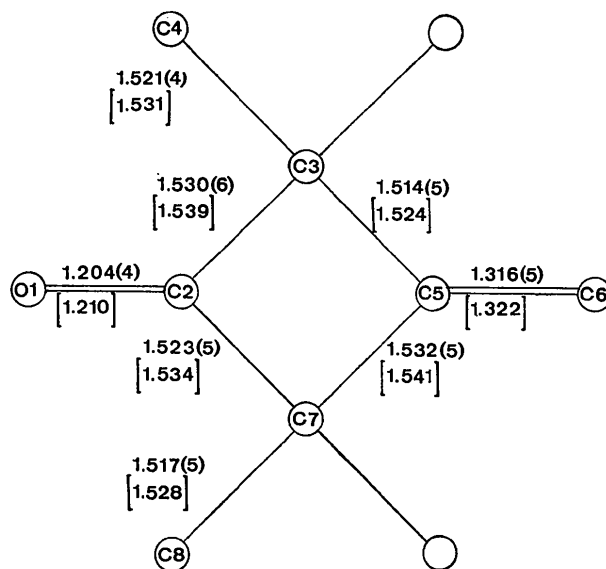


Fig. 1. Bond distances (Å) and their estimated standard deviations. The values enclosed in brackets are the thermally corrected distances; the remainder are the uncorrected distances.

Table 1. Final atomic parameters and anisotropic thermal vibrational parameters ($\times 10^4$) and their estimated standard deviations for 2,2,4,4-tetramethyl-3-methylenecyclobutanone

$$T = \exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)]$$

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
O(1)	-2567 (2)	2500	2888 (4)	68 (2)	273 (5)	385 (9)	0	48 (3)	0
C(2)	-1832 (3)	2500	1840 (6)	57 (3)	105 (4)	313 (12)	0	21 (4)	0
C(3)	-1722 (3)	2500	-304 (5)	56 (2)	120 (5)	252 (11)	0	-6 (4)	0
C(4)	-2159 (3)	3768 (4)	-1195 (6)	89 (3)	229 (6)	380 (10)	37 (3)	-21 (4)	59 (7)
H(4a)	-2921 (25)	3760 (33)	-1094 (41)			Same as C(4)			
H(4b)	-1953 (25)	3688 (36)	-2398 (51)			Same as C(4)			
H(4c)	-1784 (23)	4587 (34)	-346 (45)			Same as C(4)			
C(5)	-562 (3)	2500	50 (5)	51 (2)	91 (4)	233 (9)	0	6 (4)	0
C(6)	253 (3)	2500	-1067 (7)	69 (3)	174 (6)	255 (11)	0	5 (5)	0
H(6a)	905 (31)	2500	-462 (53)			Same as C(6)			
H(6b)	143 (27)	2500	-2520 (42)			Same as C(6)			
C(7)	-665 (3)	2500	2197 (5)	55 (2)	94 (4)	221 (9)	0	9 (4)	0
C(8)	-268 (3)	3758 (3)	3160 (5)	90 (2)	135 (4)	310 (9)	-8 (3)	4 (4)	-44 (5)
H(8a)	-582 (21)	4571 (27)	2442 (42)			Same as C(8)			
H(8b)	-604 (22)	3754 (29)	4329 (41)			Same as C(8)			
H(8c)	502 (23)	3761 (27)	3124 (35)			Same as C(8)			

Discussion

The bond distances, not corrected for thermal motion, are given in Fig. 1, and the bond angles in Table 2. The cyclobutane ring atoms are coplanar, lying on a crystallographic mirror plane. The bond distances were corrected for the effect of thermal motion according to the rigid molecular model of Cruickshank (1961). The screw tensor was assumed to be near zero. Fig. 1 shows the thermally corrected bond distances. The orientation of the thermal ellipsoids, as plotted by the computer program of Johnson (1965), is given in Fig. 2.

Table 2. Bond angles ($^{\circ}$) and their estimated standard deviations for 2,2,4,4-tetramethyl-3-methylenecyclobutanone

O(1)-C(2)-C(3)	133.5 (4)	C(3)-C(5)-C(6)	133.3 (4)
O(1)-C(2)-C(7)	132.2 (4)	C(3)-C(5)-C(7)	94.6 (3)
C(3)-C(2)-C(7)	94.3 (3)	C(6)-C(5)-C(7)	132.0 (4)
C(2)-C(3)-C(4)	112.4 (2)	C(2)-C(7)-C(5)	85.3 (3)
C(2)-C(3)-C(5)	85.7 (3)	C(2)-C(7)-C(8)	114.0 (2)
C(4)-C(3)-C(4')	112.4 (3)	C(5)-C(7)-C(8)	114.9 (2)
C(4)-C(3)-C(5)	115.7 (2)	C(8)-C(7)-C(8')	111.4 (3)

Fig. 2 also shows the observed approximately eclipsed conformation of the *gem* methyl hydrogens, corresponding to $H \cdots H$ non-bonded contacts of 2.51 and 2.37 Å. The shortest transannular $H \cdots H$ contact is 2.51 Å; the average methyl $H-C-H$ bond angle is 112.9° . The average methylene $C-H$ bond, uncorrected for thermal motion, is 0.99 Å.

Two of the cyclobutane ring angles, $C(7)-C(2)-C(3) = 94.3 (3)^{\circ}$ and $C(3)-C(5)-C(7) = 94.6 (3)^{\circ}$, are larger than usual for internal ring angles in simple four-membered rings (see Table 3, Shirrell & Williams, 1973). This would be expected owing to their sp^2 character. A comparison with the structure of 2,2,4,4-tetramethyl-1,3-cyclobutanedione shows that the internal ring angle involving the carbonyl carbon is within experimental error of the one observed in this compound. The bond lengths in the cyclobutane ring are slightly shorter than normal, but are consistent with those found in simple four-membered rings.

The 1,3-transannular distance, $C(2)-C(5) = 2.070 (5)$ Å, is of interest because of the possibility of π -interaction between the p -orbitals of the 1,3-transannular carbons.

This interaction would be affected by ring puckering of the cyclobutane ring. The possibility of ring puckering is decreased if the sizes of the exocyclic 1,3-atoms are increased. The π -interaction can be detected by observing the presence of: (1) splitting in the $n \rightarrow \pi^*$ absorption band (Ballard & Park, 1970); and (2) a shift to higher wavelengths of the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ absorption bands when compared to isolated double bonds (Labhart & Wagniere, 1959).

In the observed absorption spectra (Ballard & Park, 1970; Diebert, 1970) of several of the exocyclic 1,3-

double-bonded derivatives of 2,2,4,4-tetramethylcyclobutane, there are indications that as the van der Waals radii of the 1,3-exocyclic atoms increase, the π -interaction between the ' p ' orbitals of the 1,3-transannular carbons decreases. In 2,2,4,4-tetramethyl-3-methylenecyclobutanone, the van der Waals radius for the methylene group, 2.0 Å (Pauling, 1960), is much larger than that of oxygen, 1.40 Å. Thus, there would be a

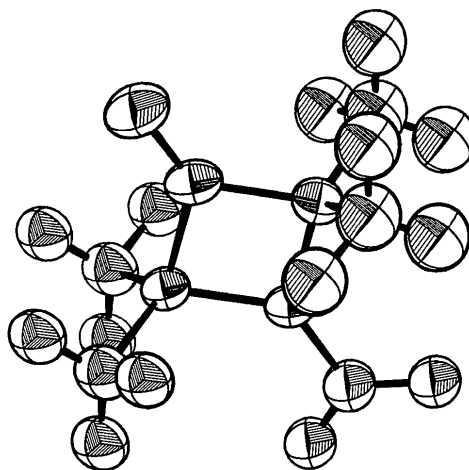


Fig. 2. The molecular structure. The thermal ellipsoids enclose a probability density of 0.30.

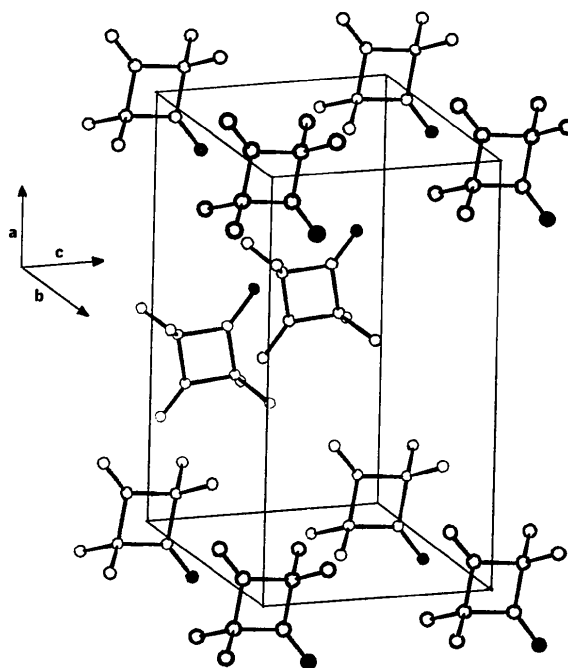


Fig. 3. The molecular packing in the crystal. The solid circles indicate oxygen atoms. The origin of the unit cell was chosen at the center of the molecule to aid in interpretation of the packing.

larger interaction between $\text{CH}_3 \cdots \text{CH}_2$ than between $\text{CH}_3 \cdots \text{O}$. This would tend to hold the methylene ring carbon, C(5), in a planar configuration and not allow its 'p' orbitals to overlap significantly with the 'p' orbitals of C(2), the carbonyl ring carbon.

The cyclobutane ring lies on a crystallographic mirror plane. This compound is only the second simple cyclobutane compound that is planar but which does not contain a centrosymmetric arrangement of substituents. By analysis of the intramolecular $\text{CH}_3 \cdots \text{CH}_2$ and $\text{CH}_3 \cdots \text{O}$ interactions, one would predict the cyclobutane ring to be planar. Thus, there can be no relief of eclipsing by making the ring non-planar in these substances. For simple cyclobutane compounds without endocyclic or exocyclic double bonds, Adman & Margulis (1969) and Margulis (1969) have proposed a rule for predicting the conformation of four-membered rings in the solid state: if the ring is not centrosymmetrically substituted, then the ring will be puckered.

The packing of the molecule is shown in Fig. 3. The symmetry-related molecules pack in sheets at $y=0.25$ and $y=0.75$. In each sheet the molecules pack in a face-centered arrangement. A central molecule is surrounded by eight other molecules, each of which is rotated 90° from the central molecule. The intermolecular distances all appear to be of the normal van der Waals type.

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