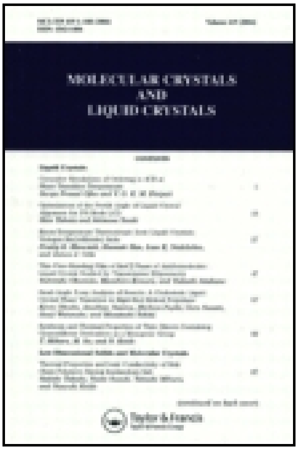

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Structure and Elastic Properties of Dibenzyl at 293 k and 110 k

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Structure and Elastic Properties of Dibenzyl at 293 k and 110 k

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An investigation of dibenzyl by X-ray diffraction and Brillouin scattering from 293 down to 10 K showed no tendency toward phase transition on cooling. Molecular structures at 293 and 110 K are essentially the same. The space group is monoclinic, $P\,2_1/a$ with a centrosymmetric molecule. The 13 elastic constants were determined from Brillouin scattering spectra at room temperature. The maximum sound velocity coincides with the molecular long axis as opposed to the short axis as has been previously reported. Temperature dependence of the sound velocity from 293 down to 10 K did not exhibit any anomaly which could indicate a phase transition.

INTRODUCTION

The crystal structure of dibenzyl was reported by Robertson[1] and Jeffrey.[2] The molecule possesses a center of symmetry and the central bond CH_2—CH_2 is inclined at about 70° to the plane of the benzene rings. However, a molecule with non-parallel rings is suggested from a far-infrared and laser Raman analysis by Mathur and Tabisz.[3] Teslenko,[4] measuring the wave propagation velocities in dibenzyl, reported that the direction of greatest compression coincides with that of the major axis of the molecule. On the other hand, Ryzhenkov[5] found a minimal thermal expansion in the same direction.

Some of the above reported results being obviously contradictory invited an independent investigation. The X-ray analysis of Robertson and Jeffrey appeared basically sound. However, an examination of X-ray data at room temperature leads to isotropic temperature factors of about 6 Å^2 for the carbon atoms. Such a large value is a characteristic feature of disordered struc-

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tures, especially when this disorder is not taken into account in the refinement. Therefore, an eventual phase transition must be considered which might explain the non-centrosymmetric molecule suggested by Mathur and Tabisz.

In the first part of this paper, we report the refinement of the crystal structure at 293 and 110 K. In the second part, we determine experimentally the elastic properties obtained by Brillouin scattering, from 293 down to 10 K. This then may clarify the contradiction between sound velocities and thermal expansion measurements.

CRYSTAL STRUCTURE AT 293 AND 110 K

Refinement

Crystals of dibenzyl from methanol are colorless prisms, elongated along the b axis. A crystal of approximate dimensions 0.3 × 0.3 × 0.4 mm was sealed in a Lindemann capillary tube and used at 293 and 110 K for data collection on an Enraf-Nonius CAD-4 diffractometer (graphite-monochromator MoK$_\alpha$ radiation, $\lambda = 0.71073$ Å). The unit-cell parameters, which are reported in Table I, were determined by a least-squares analysis of the setting angles of 25 reflections. During the data collection, three reflections were recorded periodically, but their intensities did not vary significantly. Of 1663 reflections measured by the θ–2θ scan technique with $2\theta_{\max} = 60°$ only 494 were observed above background with $I > 2\sigma(I)$ and used for the refinement. At 110 K, with the same limit $2\theta_{\max} = 60°$, 1024 reflections had $I > 2\sigma(I)$ and were treated as observed. The refinement by full-matrix least-squares method started with the C atoms coordinates given by Robertson. All the H atoms were then located from a difference electron density map and refined isotropically together with anisotropic temperature factors for the C atoms. The refinement converged to $R = 0.076$ and

TABLE I

Crystal Data

	293 K	110 K
Formula	C_6H_5—CH_2—CH_2—C_6H_5	
M_r	182.26	
a(Å)	12.802(3)	12.550(5)
b	6.148(2)	6.120(3)
c	7.724(2)	7.468(4)
β(°)	116.06(2)	114.77(4)
V(Å^3)	546.1	520.7
Space group	P 2_1/a	P 2_1/a
Z	2	2

$$R_w = \Sigma\, w^{1/2} \Big| |F_0| - |F_c| \Big| / \Sigma\, w^{1/2} |F_0| = 0.087$$

with $w^{-1} = \sigma^2(I) + (0.04\, I)^2$. At 110 K with $w^{-1} = \sigma^2(I) + (0.07\, I)$,^{2} the final agreement factors were $R = 0.055$ and $R_w = 0.068$. Positional parameters† are given in Table II.

DISCUSSION

The atom numbering is shown in Figure 1. The bond lengths and angles given in Tables III and IV show that the high temperature factors at room tempera-

TABLE II

Atom coordinates and equivalent isotropic temperature factors

	x	y	z	$B_{eq}(\text{Å}^2)$
293 K				
C(1)	0.0274(3)	0.0938(7)	−0.0285(6)	6.6(1)
C(2)	0.1468(3)	0.1520(6)	0.1208(5)	4.63(9)
C(3)	0.1686(3)	0.3356(6)	0.2349(5)	5.8(1)
C(4)	0.2776(4)	0.3901(7)	0.3660(6)	6.8(1)
C(5)	0.3709(3)	0.2634(7)	0.3856(6)	6.4(1)
C(6)	0.3505(3)	0.0791(7)	0.2762(6)	6.1(1)
C(7)	0.2420(3)	0.0247(6)	0.1456(5)	5.3(1)
H(1)	−0.026(4)	0.205(8)	−0.083(6)	11.1(13)
H(2)	0.002(3)	0.047(8)	−0.159(6)	10.5(13)
H(3)	0.106(3)	0.419(6)	0.232(5)	8.1(11)
H(4)	0.292(3)	0.502(6)	0.439(4)	7.5(10)
H(5)	0.445(3)	0.300(6)	0.491(4)	7.4(10)
H(6)	0.417(3)	−0.010(6)	0.290(5)	7.6(11)
H(7)	0.224(2)	−0.095(5)	0.065(4)	5.6(8)
110 K				
C(1)	0.0240(1)	0.1025(3)	−0.0262(2)	2.39(3)
C(2)	0.1464(1)	0.1587(2)	0.1207(2)	1.85(2)
C(3)	0.1684(1)	0.3430(2)	0.2379(2)	2.27(3)
C(4)	0.2819(1)	0.3963(3)	0.3701(2)	2.67(3)
C(5)	0.3745(1)	0.2637(3)	0.3862(2)	2.63(3)
C(6)	0.3535(1)	0.0788(3)	0.2729(2)	2.38(3)
C(7)	0.2405(1)	0.0260(2)	0.1412(2)	2.02(3)
H(1)	−0.032(2)	0.231(4)	−0.035(3)	4.5(5)
H(2)	0.024(2)	0.084(3)	−0.157(3)	3.9(4)
H(3)	0.105(2)	0.441(3)	0.229(2)	2.8(4)
H(4)	0.293(2)	0.532(3)	0.447(2)	3.1(4)
H(5)	0.450(2)	0.307(3)	0.468(2)	3.3(4)
H(6)	0.416(1)	−0.015(3)	0.279(2)	2.8(4)
H(7)	0.228(1)	−0.102(3)	0.063(2)	2.6(4)

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†A list of structure factors and anisotropic thermal parameters may be obtained from the authors.

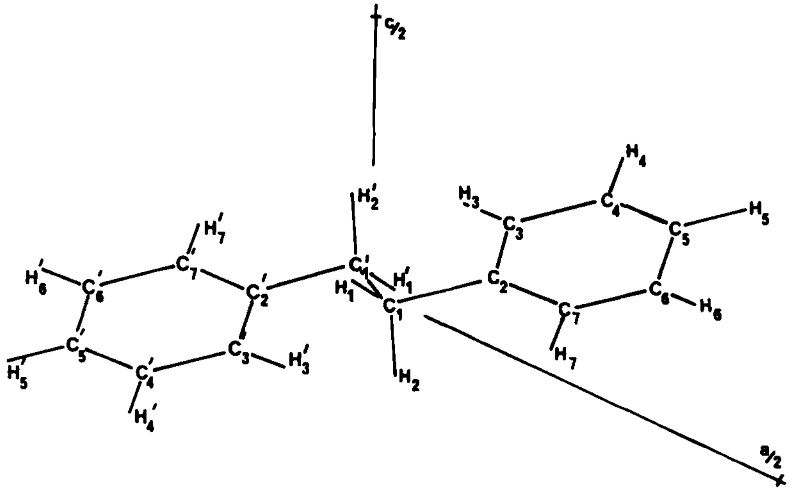

FIGURE 1 The crystal structure of dibenzyl molecule projected along **b**.

ture are not the result of a structural disorder. Both structures at 293 and 110 K are similar, the planes defining the two benzene rings are parallel, but not coplanar. With a maximum deviation from the mean plane of 0.02 Å at 293 K and 0.01 Å at 110 K the equations of the least-squares planes of the benzene ring are:

at 293 K $-0.1265\,x - 0.5370\,y + 0.8340\,z = 0.6508$

at 110 K $-0.1287\,x - 0.5273\,y + 0.8399\,z = 0.6244$

TABLE III

Bond lengths (Å) with e.s.d.'s in parentheses

	293 K	110 K
C'(1)—C(1)	1.513(6)	1.519(2)
C(1)—C(2)	1.498(4)	1.507(2)
C(2)—C(3)	1.383(4)	1.389(2)
C(3)—C(4)	1.357(4)	1.390(2)
C(4)—C(5)	1.378(4)	1.383(2)
C(5)—C(6)	1.368(4)	1.377(2)
C(6)—C(7)	1.352(4)	1.384(2)
C(1)—H(1)	0.93(4)	1.03(2)
C(1)—H(2)	0.96(4)	0.98(2)
C(3)—H(3)	0.95(4)	0.98(2)
C(4)—H(4)	0.86(3)	0.99(2)
C(5)—H(5)	0.96(3)	0.92(2)
C(6)—H(6)	0.98(3)	0.96(2)
C(7)—H(7)	0.92(2)	0.96(2)

TABLE IV

Bond angles (°) with e.s.d.'s in parentheses

	293 K	110 K
C′(1)—C(1)—C(2)	113.9(0.3)	113.3(0.1)
C(1)—C(2)—C(3)	122.5(0.3)	121.3(0.1)
C(2)—C(3)—C(4)	122.0(0.3)	120.97(0.1)
C(3)—C(4)—C(5)	120.0(0.3)	119.7(0.1)
C(4)—C(5)—C(6)	118.6(0.3)	119.8(0.1)
C(5)—C(6)—C(7)	121.4(0.3)	120.4(0.1)
C(6)—C(7)—C(2)	121.0(0.3)	120.7(0.1)
C(3)—C(2)—C(7)	116.9(0.3)	118.4(0.1)
C(1)—C(2)—C(7)	120.5(0.3)	120.3(0.1)

Although there is good agreement for the C—C bond lengths, significant differences exist for C(3)—C(4) and C(6)—C(7). Jeffrey also found unusually short bonds in the phenyl ring. The new 110 K results indicate that thermal motion might be responsible for this effect. Jeffrey and Robertson found a shorter C′(1)—C(1) bond (1.48 Å) than C(1)—C(2) (1.50 Å) which is in opposition to the present study. The angle between the central C—CH_2—CH_2—C plane and the plane of the phenyl ring is 73.4° (67.1° at 110 K). Similar values are found in dimethyl-4,4′-methylene bis (phenyl carbamate),[6] in triphenyl ethane,[7] in tetraphenylethane[8] and in 4,4′-dimethyldibenzyl.[9] However, the dihedral angle is 89° in 0,0′ dibromodibenzyl [1,2-Bis(2-bromophenyl)-ethane)],[10] which is probably due to packing interactions. In the structure proposed by Mathur and Tabisz the planes defining the two benzene rings are inclined at an angle to each other. It then appears that the assignments for the characteristic frequencies leading to this conclusion should be reconsidered.

ELASTIC PROPERTIES

Brillouin scattering

The elastic properties of dibenzyl have been investigated through Brillouin scattering. The Brillouin formula relates the lineshift ν to sound velocity v and refractive indices in the crystal. It is well known that

$$\nu = \pm v(n_i^2 + n_s^2 - 2n_in_s\cos\theta)^{1/2}/\lambda_0.$$

where λ_0 and θ are the laser wave length and the scattering angle, n_i and n_s the refractive indices for the incident and scattered beams.

The spectrometer used was a stabilized triple-pass Fabry Perot[11] equipped with an Argon ion laser.

The study of the elastic properties by Brillouin scattering requires the knowledge of the refractive indices at the working laser line. The principal values given below have been measured at 4880 Å with a prism deviation method and their ratios recorded by Brillouin backscattering.

$$n_\alpha = 1.535 \pm 0.008;\ n_b = 1.637 \pm 0.003;\ n_\gamma = 1.762 \pm 0.015$$

These data are very similar to those given by Wynchell[12] at 5890 Å:

$$n_\alpha = 1.529;\ n_b = 1.629;\ n_\gamma = 1.757$$

Moreover the slight difference is proportional to the effect of dispersion. The principal directions α and γ are in the (a, c) plane while n_γ is obtained for a polarization at +40° from **a**, which direction coincides roughly with the molecular long axis as shown in the Figure 2.

Crystals used throughout the experiments were grown from the melt by a Bridgman technique. Several slab shaped samples were cut along the crystallographic axes **a**, **b**, **c*** and along the principal optical axes α, **b**, γ with typical dimensions $5 \times 4 \times 2$ mm^3.

Room temperature elastic constants

Brillouin scattering spectra usually yield two or three sound velocities for each propagating direction. As dibenzyl belongs to a monoclinic symmetry group, 13 elastic constants have to be determined; at least an equal number of sound velocities are required. Sound velocities were measured along 7 nonequivalent directions, either in a right angle or in a backscattering geometry, producing 19 velocities. These data are collected in Table V for comparison with the previously obtained values by Teslenko. The agreement is good except for the [101] direction where the values obtained by the ultrasonic method show a better agreement with those found for the $[10\bar{1}]$ direction. This discrepancy

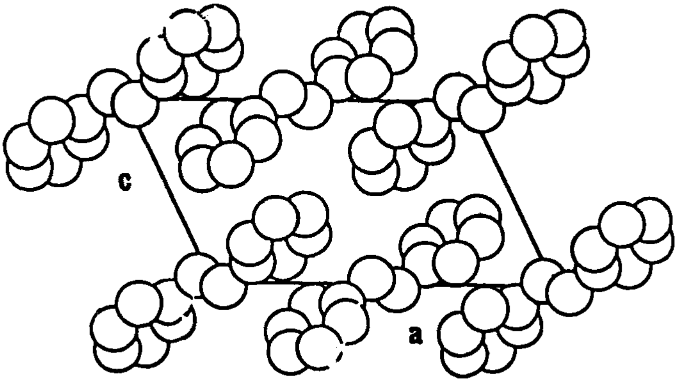

FIGURE 2 Packing of the dibenzyl molecules viewed down **b**.

TABLE V

Dibenzyl sound velocities measured by Brillouin scattering and ultrasonic method

Phonon		V m/s	
Direction	Polarization	Brillouin	Ultrasonic[3]
[100]	[100]	3138	3040
[100]	[010]	1241	1280
[100]	[001]	1568	1540
[010]	[010]	2567	2490
[010]	$[\alpha 0 \beta]$	1884	1830
[010]	$[\bar{\alpha} 0 \beta]$	—	1400
[001]	[001]	2700	2560
[001]	[010]	1755	1670
[001]	[100]	1552	1500
[101]	[101]	3416	2290
[101]	$[01\underline{0}]$	—	1820
$[10\underline{1}]$	$[10\underline{1}]$	1367	1380
$[10\underline{1}]$	[101]	2400	—
$[10\underline{1}]$	[010]	1778	—
[101]	[101]	1400	—
[011]	[011]	3005	2680
[011]		1609	1600
[011]		1142	1080
[110]	[110]	2945	2840
[110]		1728	1600
[110]		1237	1260

also propagates into the elastic constant set in the form of an opposite sign for the C_{15}, C_{25}, C_{35} and C_{46} constants. Table VI then compares the elastic constants previously obtained with those resulting from our study, through a least squares analysis of the sound velocities. In the last column of this table we have added the elastic compliance constants related to our C_{ij}.

From these constants it is possible to compute the sound velocities in any direction inside the crystal. Figure 3 displays on polar diagrams the variation of these velocities in the (a, c), (a, b) and (b, c) planes. It may be noticed that in the (a, c) plane diagram drawn by Teslenko the direction of maximum longitudinal sound velocity lies along the *c* axis. Could it possibly be that the crystal was turned over during Teslenko's experiment, changing **b** to −**b** and [101] to $[10\bar{1}]$?

Temperature dependence of the Brillouin spectra

The elastic properties provide a good way to detect the occurrence of phase transitions. The variation of the sound velocities versus temperature may exhibit different kinds of anomalies.[13] In our attempt to find any phase transition in dibenzyl at low temperature we selected two particular phonon directions:

TABLE VI

Elastic constants and compliance moduli of dibenzyl from Brillouin scattering and ultrasonic methods

$C_{ij}\cdot 10^{-9}$ N/m^2	Brillouin	Ultrasonic[3]	$S_{ij}\cdot 10^{10}$ m^{2}N^{-1}
c_{11}	9.81	9.45	2.26
c_{22}	7.37	6.80	2.48
c_{33}	8.06	7.20	2.29
c_{44}	3.24	3.10	3.34
c_{55}	2.72	2.55	5.88
c_{66}	2.62	2.60	4.14
c_{12}	4.48	3.95	−0.62
c_{23}	4.78	3.35	1.15
c_{13}	4.25	4.15	−0.75
c_{15}	2.91	−2.4	−2.14
c_{25}	0.92	−0.8	−0.01
c_{35}	0.27	−0.7	0.97
c_{46}	−0.81	0.8	1.03

α and γ along whose elastic vibrations might be coupled to different hypothetical molecular reorientations.

Based on the velocity variations being typical examples of an anharmonic stiffening (Figure 4) the result of these measurements is negative, as far as phase transitions are concerned. The relative velocity variation between room and liquid helium temperature may however reach a considerable value. This is due to room temperature being not far from the melting point (52°C).

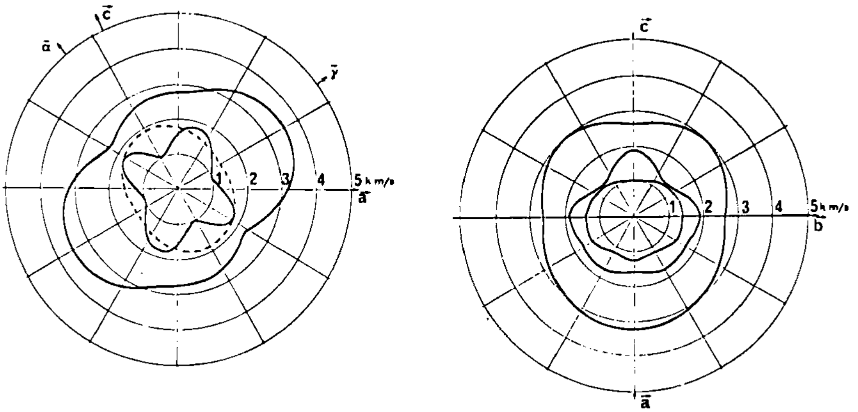

FIGURE 3 Sound velocity polar diagrams in the (a, c) plane (left) and in the (a, b) and (b, c) planes (right). The dashed curve in the (a, c) plane is related to the true transverse mode.

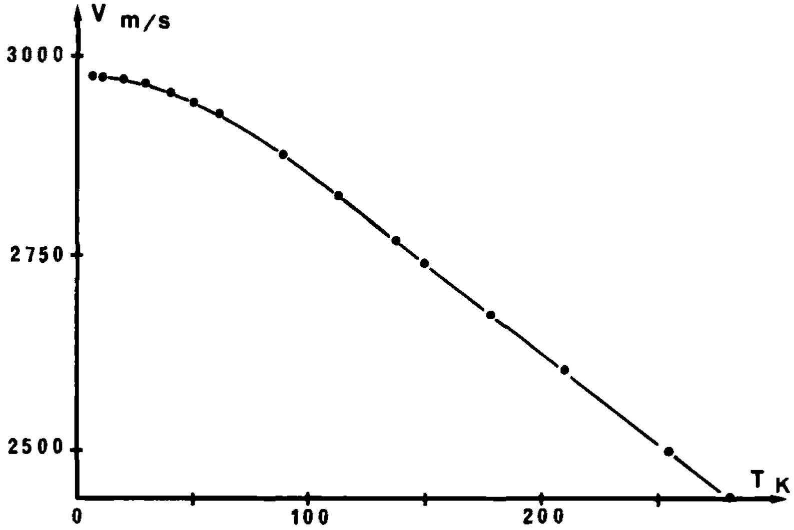

FIGURE 4 Variation of the quasi longitudinal sound velocity versus temperature for the mode propagating along α.

DISCUSSION

The largest sound velocity coincides with the molecular long axis. A similar situation is found in polyphenyls and is explained by a very simple chain model where the crystal structure is considered as parallel rows of aromatic rings coupled by intra and inter molecular forces. The related force constants differing by two orders of magnitude, it is not surprising to find the maximum longitudinal sound velocity along the molecular long axis. Shown on the diagrams of the (a, b) and (b, c) planes is a more isotropic variation of the longitudinal sound velocities, which agrees with a maximum velocity in the direction of the length of the molecule.

If we now compare the spatial variations of the thermal expansion with the linear compressibility tensors we find a great similarity. The principal values in the (a, c) plane of the thermal expansion tensors α_3 and α_1 shown by Ryzhenkov are nearly in the same ratio (3.6) as the one obtained from our linear compressibility principal values β_3 and β_1 (3.7). In both cases the largest values are found within 10° along the c direction which is roughly perpendicular to the molecular long axis. This shows that in such crystals the thermal strain has the same anisotropy as the strain created by an hydrostatic pressure. This similarity previously observed in other crystals like anthracene, thiourea[14] has not received, to our knowledge, any plausible theoretical explanation.

Acknowledgments

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