

The Crystal and Molecular Structure of 1,4-Bis(dicyanomethylene)cyclohexane

BY FUJIKO IWASAKI AND ARIYUKI AIHARA

Department of Materials Science, The University of Electro-Communications, Kojima-cho, Chofu-shi, Tokyo, Japan

(Received 27 March 1969)

Crystals of 1,4-bis(dicyanomethylene)cyclohexane, $C_6H_8[C(CN)_2]_2$ are monoclinic with $a=10.625$, $b=7.073$, $c=7.250$ Å, $\beta=92.3^\circ$ and $Z=2$, space group $P2_1/n$. The structure was deduced from a three-dimensional sharpened Patterson synthesis with visually estimated Cu $K\alpha$ data. Positional and anisotropic thermal parameters were refined by the block-diagonal least-squares method, the final R index being 0.079 for 924 observed reflexions. The molecule has a centre of symmetry and the six-membered ring takes a chair conformation, in spite of a fairly large dipole moment, 2.4 D, as has been observed in dioxane solutions. The observed interatomic distances 1.530, 1.496, 1.434 and 1.346 Å correspond well to those of $-CH_2-CH_2-$ (sp^3-sp^3), $-CH_2-C$ (sp^3-sp^2), $=C-C\equiv$ (sp^2-sp) and $>C=C<$ ($\sigma\pi-\sigma\pi$) respectively.

The mean value of the $-C\equiv N$ bonds is found to be 1.143 Å.

Introduction

There are three molecular conformations conceivable for 1,4-bis(dicyanomethylene)cyclohexane. They are the chair form [Fig. 1(a)], the boat form [Fig. 1(b)] and the twisted boat form [Fig. 1(c)]. The dipole moment of this substance observed in dioxane solutions is fairly high (~ 2.4 D) and moreover it depends markedly on temperature. It is suggested that the molecular conformation in solution is of the flexible twisted boat form (Aihara, Kitazawa & Iwasaki, 1968). The twisted boat form of the cyclohexane ring has indeed been observed in the molecule of cyclohexane-1,4-dione both in solution (Aihara, Chitoku & Higasi, 1962; Allinger, Blatter & Freiberg, 1966) and in crystals (Mossel & Romers, 1964; Groth & Hassel, 1964). The conformation of cyclohexane-1,4-dione in the crystal is described in terms of a twisted boat with an angle between the two C-O bonds of 155° . It is the aim of the present investigation to determine the molecular conformation

of 1,4-bis(dicyanomethylene)cyclohexane in crystals. A three-dimensional X-ray analysis was carried out.

Experimental

A sample of 1,4-bis(dicyanomethylene)cyclohexane was kindly supplied by Professor H. Mikawa of the Osaka University. Crystals suitable for X-ray work were grown from acetone as colourless prisms. The cell dimensions were obtained from zero level Weissenberg photographs (Cu K , $\bar{\alpha}=1.54178$, $\alpha_1=1.54051$, $\alpha_2=1.54433$ and $\beta=1.39217$ Å) about [010] and [001]. Copper powder diffraction lines were superposed on the films for calibration purposes.

Crystal data

1,4-bis(dicyanomethylene)cyclohexane, $C_{12}H_8N_4$

M.W. 208.22

Monoclinic

$a=10.625 \pm 0.002$ Å

$b=7.073 \pm 0.002$

$c=7.250 \pm 0.002$

$\beta=92.31 \pm 0.02^\circ$

$Z=2$

$V=544.44$ Å³

$D_x=1.270$ g.cm⁻³, $D_m=1.28$ g.cm⁻³

Systematic absences $h0l$ $h+l=2n+1$

$0k0$ $k=2n+1$

Space group $P2_1/n$ (No. 14, C_{2h}^5)

Intensity data were collected for six layers $h0l-h5l$ about the b axis and six layers $hk0-hk5$ about the c axis from approximately cylindrical crystals having an average radius of 0.15 mm. The multiple-film equi-inclination Weissenberg photographs were taken with Cu $K\alpha$ radiation. The intensities were estimated visually by comparison with a standard scale. Of the 1150 inde-

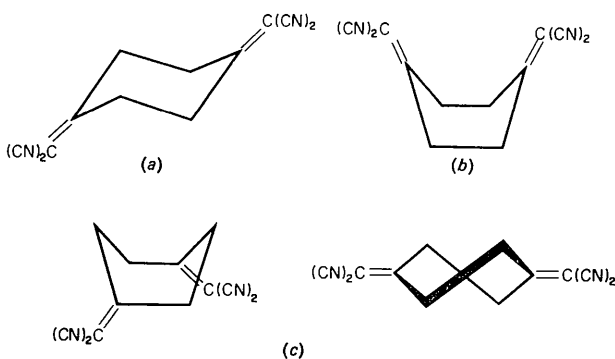


Fig.1. Possible molecular conformations 1,4-bis(dicyanomethylene)cyclohexane. (a) chair form, $\mu=0$, (b) boat form, $\mu \sim$ large, (c) twisted boat form, $\mu > 0$.

pendent reflexions within the effective copper limiting sphere ($\sin \theta = 0.997$), 924 non-zero reflexions were observed. The usual Lorentz and polarization and the Phillips spot shape corrections were applied, but no absorption correction was made. During the refinement extinction corrections were found to be necessary for strong reflexions; they were corrected according to: $I_o = I_{corr} \exp(-gI_{corr})$. The constant g was estimated graphically. The structure factors obtained from various sets of layer line photographs were put on the same scale by the least-squares method. They were placed on an approximately absolute scale by Wilson's method.

Structure determination

The crystals belong to the space group $P2_1/n$ and there are only two molecules in the unit cell. Therefore the molecules are required to have a centre of symmetry and the cyclohexane ring must take a chair conformation. A three-dimensional, sharpened Patterson map showed three partly resolved peaks at distances of 1.4–1.5 Å from the origin which were ascribed to images of C–C and C–N bonds. The orientation of the cyclohexane ring and the dicyanomethylene group in the structure was deduced by inspection of these peaks.

Five cycles of the block-diagonal least-squares refinement with the three-dimensional reflexions led to an R value of 0.195. Anisotropic thermal parameters were introduced and the R value came down to 0.146 after two cycles. Hydrogen atoms were located from a difference Fourier synthesis (Fig. 2) and were included in the structure factor computation. The R value decreased to 0.132. After correction for extinction for nine reflexions, three more cycles of least-squares refinement were carried out with anisotropic temperature factors for carbon and nitrogen atoms and with isotropic temperature factors for hydrogen atoms. The R value dropped to 0.079 for all the observed reflexions. The atomic scattering factors used were those listed in *International Tables for X-ray Crystallography* (1962a) and the quantity $\sum w(kF_o - F_c)^2$ was minimized

where w is the weight function and k is the scale factor. At the final stage of the refinement the following weighting scheme was employed: $w = 4F_{min}/|F_o|$ if $|F_o| > 4F_{min}$, $w = 1$ if $4F_{min} \geq |F_o| \geq F_{min}$ and $w = 0.2$ if $|F_o| < F_{min}$, where $F_{min} = 1.2$.

The final atomic parameters are listed in Table 1. A comparison of the observed and calculated structure factors is given in Table 2.

Results and discussion

The molecule has a centre of symmetry and the six-membered ring takes a chair conformation. Half of the cyclohexane ring and the dicyanomethylene group lie almost in one plane. The least-squares plane defined by the atoms, C(1), C(2), C(3), C(4), C(5) and C(6), is

$$-0.3358X - 0.2624Y + 0.9174Z = -0.5620,$$

where X , Y and Z are the coordinates in Å referred to the crystal axes a , b and c . The deviations of atoms from this plane are listed in Table 3.

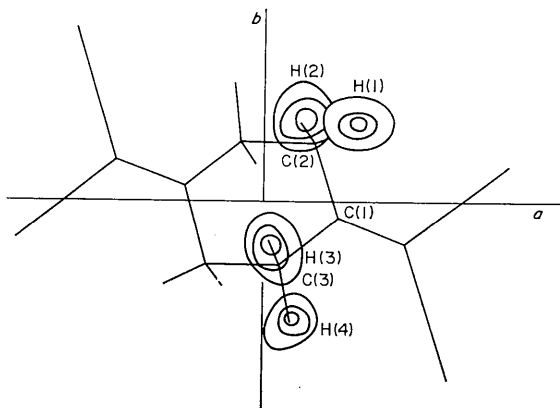


Fig. 2. Sections of the three-dimensional difference Fourier synthesis through the atomic centres parallel to (001). The contours are at intervals of 0.2 e.Å⁻³, starting with 0.2 e.Å⁻³.

Table 1. *The final atomic parameters and their estimated standard deviations*

The anisotropic temperature factors ($\times 10^4$) are of the form:

$$\exp \{ -(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl) \}.$$

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	0.1299 (2)	-0.0422 (4)	-0.0259 (4)	58 (2)	132 (5)	130 (5)	-13 (3)	-08 (3)	10 (4)
C(2)	0.0915 (3)	0.1571 (4)	0.0081 (4)	60 (2)	117 (5)	189 (6)	-10 (3)	-17 (3)	11 (5)
C(3)	0.0299 (3)	-0.1659 (4)	-0.1146 (4)	62 (2)	157 (6)	199 (6)	-10 (3)	-13 (3)	-37 (5)
C(4)	0.2468 (2)	-0.1061 (4)	0.0167 (4)	58 (2)	132 (5)	128 (5)	-06 (3)	00 (3)	-02 (4)
C(5)	0.3429 (3)	0.0104 (4)	0.1030 (4)	56 (2)	180 (6)	156 (6)	07 (3)	-07 (3)	-17 (5)
C(6)	0.2825 (3)	-0.2980 (4)	-0.0159 (4)	68 (2)	166 (6)	166 (6)	09 (3)	05 (3)	-17 (5)
N(1)	0.4192 (3)	0.0996 (5)	0.1740 (5)	74 (3)	270 (8)	269 (8)	-16 (4)	-22 (3)	-74 (6)
N(2)	0.3113 (3)	-0.4527 (5)	-0.0407 (5)	110 (3)	187 (7)	295 (8)	23 (4)	31 (4)	-39 (6)
H(1)	0.160 (3)	0.224 (5)	0.082 (5)	2.4 (7) Å ²					
H(2)	0.073 (3)	0.221 (5)	-0.110 (5)	2.2 (7)					
H(3)	0.009 (3)	-0.110 (5)	-0.238 (5)	2.3 (7)					
H(4)	0.060 (4)	-0.303 (6)	-0.127 (6)	3.3 (9)					

Table 3. *The deviations of the atoms from the mean plane*

C(1)	0.005 Å	N(1)	0.039 Å
C(2)	-0.002	N(2)	0.021
C(3)	0.001	H(1)	0.12
C(4)	-0.010	H(2)	-0.84
C(5)	0.005	H(3)	-0.85
C(6)	0.002	H(4)	0.06

The bond distances and angles, except those involving hydrogen atoms, are shown in Fig. 3 and Table 4. The standard deviations of the bond distances are 0.004 Å and those of the angles 0.2°, on the average. The distance C(2)–C(3') (1.530 Å) is significantly longer than C(1)–C(2) and C(1)–C(3) (1.491, 1.501 Å). These values can be accounted for by assuming an sp^3-sp^3 bond for C(2)–C(3') and an sp^3-sp^2 bond for C(1)–C(2) and C(1)–C(3) (Stoicheff, 1962). The bond angles C(1)C(2)C(3') (111.3°) and C(1)C(3)C(2') (110.9°) are slightly larger than the tetrahedral value. The angle C(2)C(1)C(3) (115.4°) is larger than the other angles of the cyclohexane ring, presumably owing to the effect of the C(1)–C(4) double bond (1.346 Å). There is a flattening of the six-membered ring from the perfect chair conformation. These dimensions of the cyclohexane ring are similar to the corresponding distances

and angles found in the molecules of cyclohexane-1,4-dione (Mossel *et al.*, 1964; Groth *et al.*, 1964) and cyclohexane-1,4-dioxime (Groth, 1968) (Table 5), although the cyclohexane rings of these molecules have a twisted boat form.

The length of the C(1)–C(4) bond (1.346 Å) is the normal C–C double bond length and those of C(4)–C(5) (1.436 Å) and C(4)–C(6) (1.432 Å) are normal values for an sp^2-sp C–C single bond (1.435 Å). The lengths of C(5)–N(1) and C(6)–N(2) (mean value 1.143 Å) are close to the C≡N bond length (1.16 Å) (*International Tables for X-ray Crystallography*, 1962b).

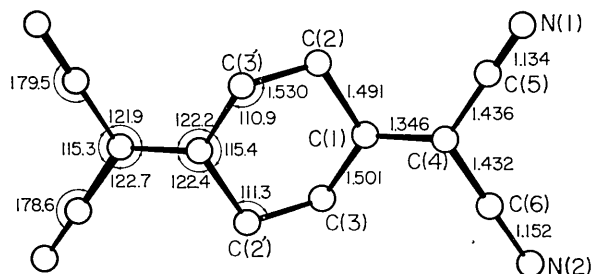


Fig. 3. Bond distances and angles in the 1,4-bis(dicyanomethylene)cyclohexane molecule.

Table 4. *Bond lengths and angles*

C(1)–C(2)	1.491 (4) Å	C(2)–C(1)–C(3)	115.4 (2)°
C(1)–C(3)	1.501 (4)	C(1)–C(2)–C(3')	111.3 (2)
C(2)–C(3')	1.530 (4)	C(1)–C(3)–C(2')	110.9 (2)
C(1)–C(4)	1.346 (4)	C(2)–C(1)–C(4)	122.4 (2)
C(4)–C(5)	1.436 (4)	C(3)–C(1)–C(4)	122.2 (2)
C(4)–C(6)	1.432 (4)	C(1)–C(4)–C(5)	122.7 (3)
C(5)–N(1)	1.134 (4)	C(1)–C(4)–C(6)	121.9 (2)
C(6)–N(2)	1.152 (4)	C(5)–C(4)–C(6)	115.3 (2)
		C(4)–C(5)–N(1)	178.6 (3)
		C(4)–C(6)–N(2)	179.5 (3)

Table 5. *Comparison of the mean bond lengths and angles of the cyclohexane rings*

	Present work	Cyclohexane-1,4-dione		Cyclohexane-1,4-dioxime
		M. & R.	G. & H.	
–CH ₂ –C=	1.496 Å	1.512 Å	1.504 Å	1.500 Å
–CH ₂ –CH ₂ –	1.530	1.536	1.554	1.532
CH ₂ –CH ₂ –C	111.1°	112.2°	111.4°	110.9°
CH ₂ –C–CH ₂	115.4	116.3	117.4	117.8

M. & R. Mossel & Romers (1964).

G. & H. Groth & Hassel (1964).

Table 6. *Interatomic distances and angles for the hydrogen atoms and their estimated standard deviations*

C(2)–H(1)	1.00 (4) Å	C(1)–C(2)–H(1)	110 (2)°
C(2)–H(2)	0.98 (4)	C(1')–C(2)–H(2)	110 (2)
C(3)–H(3)	0.99 (4)	C(3')–C(2)–H(1)	109 (2)
C(3)–H(4)	1.03 (4)	C(3')–C(2)–H(2)	106 (2)
C(4)···H(1)	2.56 (4)	H(1)–C(2)–H(2)	111 (3)
C(4)···H(4)	2.61 (4)	C(1)–C(3)–H(3)	106 (2)
C(5)···H(1)	2.46 (4)	C(1)–C(3)–H(4)	112 (2)
C(6)···H(4)	2.47 (4)	C(2')–C(3)–H(3)	106 (2)
		C(2')–C(3)–H(4)	111 (2)
		H(3)–C(3)–H(4)	111 (3)

These dimensions of the dicyanomethylene group are compared with those of tetracyanoquinodimethane in which C=C is 1.374, C-C 1.441 and C≡N 1.140 Å on the average (Long, Sparks & Trueblood, 1965). Interatomic distances and angles involving hydrogen atoms of the cyclohexane ring are listed in Table 6 with their estimated standard deviations.

The projections of the structure along the *b* and *c* axes are shown in Figs. 4 and 5 respectively, and the intermolecular distances less than 3.7 Å are listed in

Table 7. The molecules are found to lie nearly perpendicular to the *c* axis. All contacts between molecules are of the van der Waals type. The shortest intermolecular approach occurs between C(1)⋯N(2) (3.290 Å).

Table 7. Intermolecular distances less than 3.7 Å

1	x	y	z	5	$\frac{1}{2}-x$	$\frac{1}{2}+y$	$-\frac{1}{2}-z$
2	x	$1+y$	z	6	$\frac{1}{2}-x$	$-\frac{1}{2}+y$	$\frac{1}{2}-z$
3	$1-x$	$-y$	$-z$	7	$-\frac{1}{2}+x$	$\frac{1}{2}-y$	$-\frac{1}{2}+z$
4	$\frac{1}{2}-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$	8	$-\frac{1}{2}+x$	$-\frac{1}{2}-y$	$-\frac{1}{2}+z$

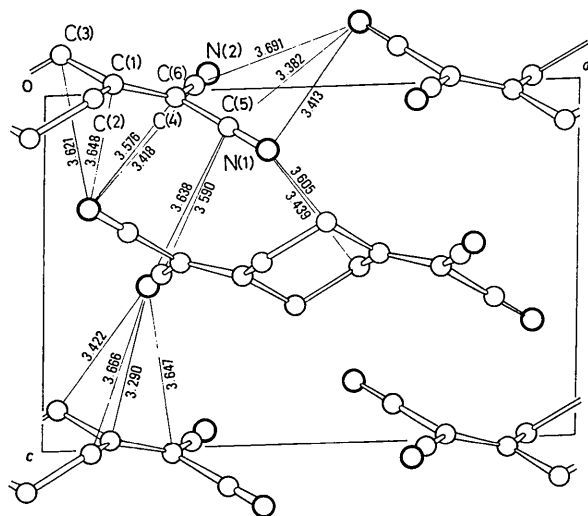


Fig. 4. Projection of the structure along the *b* axis. Intermolecular distances less than 3.7 Å are shown.

Atom (in molecule 1)	To atom	In molecule	<i>d</i>
C(1)	N(1)	6	3.648 Å
C(1)	N(2)	5	3.290
C(2)	N(2)	2	3.642
C(2)	N(2)	5	3.666
C(2)	N(1)	7	3.439
C(3)	N(1)	8	3.605
C(3)	N(1)	6	3.621
C(3)	N(2)	5	3.422
C(4)	N(1)	6	3.576
C(4)	N(2)	5	3.647
C(5)	C(6)	4	3.590
C(5)	N(1)	3	3.382
C(5)	N(2)	4	3.638
C(6)	N(1)	3	3.691
C(6)	N(1)	6	3.418
N(1)	N(2)	2	3.691
N(1)	N(1)	3	3.413

The root-mean-square vibrational amplitudes and the direction cosines of the principal axes of the thermal ellipsoids are presented in Table 8. It can be seen from

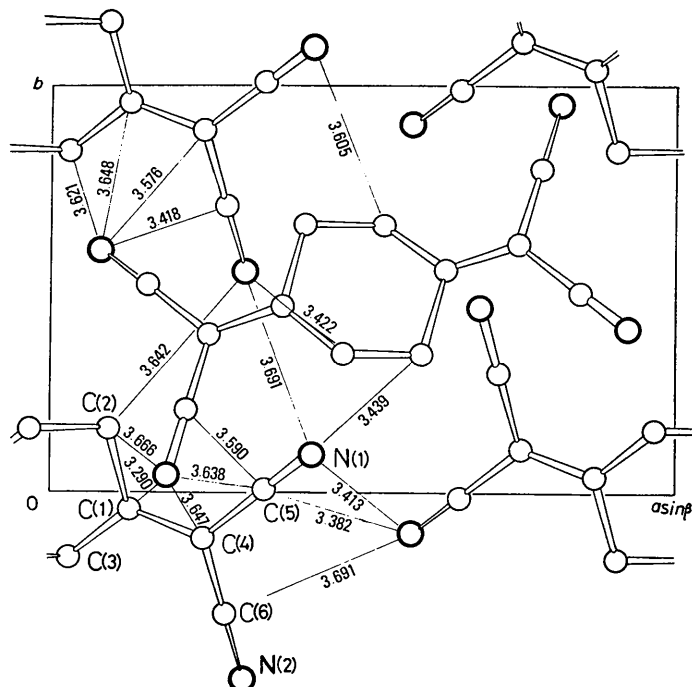


Fig. 5. Projection of the structure along the *c* axis.

this Table that the thermal motions of the C(1) and C(4) atoms are nearly isotropic, while those of the other atoms are significantly anisotropic. Fig. 6 shows the ellipsoids of thermal vibration. It is evident that the thermal motion is predominantly a libration about the long axis of the molecule. The directions of the largest vibration of the C(2) and C(3) atoms were found to lie near the normal of the mean plane formed by the six-membered ring. This fact implies that the six-membered ring has a tendency to a puckering motion and that the chair conformation in crystals may change to the flexible twisted boat form when the crystals are dissolved, in accord with the fairly large dipole moment and its temperature dependence, as described in the beginning of this paper.

Table 8. *The direction cosines (l_1, l_2, l_3) of the principal axes of anisotropic temperature factors relative to the crystal axes and the root-mean-square vibrational displacements*

	R.m.s.d.	l_1	l_2	l_3
C(1)	0.1668 Å	0.7584	0.5880	0.2507
	0.1776	-0.1766	0.6008	-0.7719
	0.2050	0.6275	-0.5416	-0.5842
C(2)	0.1663	0.5279	0.8442	0.0721
	0.1809	-0.7383	0.5105	-0.4107
	0.2338	-0.4198	0.1637	0.9089
C(3)	0.1694	0.6887	0.5823	0.4039
	0.2023	-0.6921	0.7056	0.1798
	0.2429	-0.2162	-0.4037	0.8970
C(4)	0.1747	0.7194	0.6161	0.2916
	0.1854	-0.0400	0.4974	-0.8643
	0.1885	0.6932	-0.6115	-0.4090
C(5)	0.1751	0.9347	-0.0718	0.3101
	0.1975	0.2314	-0.6202	-0.7583
	0.2231	0.2697	0.7812	-0.5735
C(6)	0.1881	0.7161	-0.6108	-0.3665
	0.2028	-0.6610	-0.4383	-0.5820
	0.2193	-0.2239	-0.6595	0.7260
N(1)	0.1854	0.8105	0.3809	0.4120
	0.2432	-0.5755	0.6592	0.5068
	0.2994	-0.1090	-0.6483	0.7573
N(2)	0.1968	-0.4498	0.8369	0.3298
	0.2565	-0.8409	-0.5145	0.2016
	0.2887	0.3010	-0.1868	0.9223

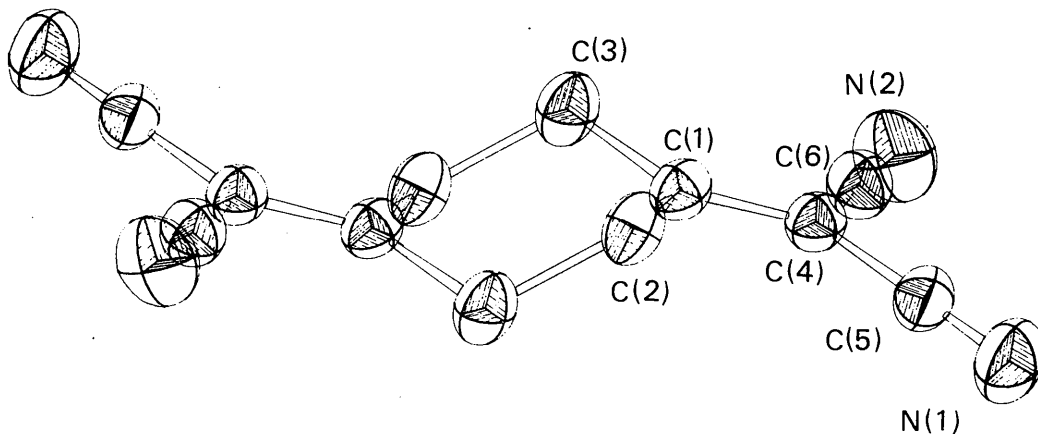


Fig. 6. A perspective drawing of 1,4-bis(dicyanomethylene)cyclohexane molecule showing the ellipsoids of thermal motion with a probability of 50 per cent.

It is interesting that the conformation of this molecule in the crystal is different from those of the cyclohexane-1,4-dione and cyclohexane-1,4-dioxime molecules, which take flexible twisted boat forms both in solution and in the crystalline state. The rigid chair conformation in the 1,4-bis(dicyanomethylene)cyclohexane crystal may be due to the presence of highly polar and bulky dicyanomethylene groups. The fact that the melting point of 1,4-bis(dicyanomethylene)cyclohexane (217°C) is higher than that of cyclohexane-1,4-dione (78.5°C) indicates a stronger molecular interaction in this crystal.

Computation

The main part of the calculations was performed on the HITAC 5020E computer of the Computer Centre of the University of Tokyo. The reduction of the original data was achieved with the program *FFLP* written by one of the authors (F.I.) and the block-diagonal least-squares refinement was carried out by the use of the program *HBL5-4* written by T. Ashida. The remaining calculations were made by the use of the universal crystallographic computation program system 5020 *UNICS* (*The Universal Crystallographic Computation Program System*, 1967). Fig. 6 was drawn with a plotter from the direct output of the CDC 3600 computer at C. Ito Electronic Computing Service Co., Ltd, using the program *ORTEP* (Johnson, 1965).

We wish to thank Professor Yoshihiko Saito of the University of Tokyo for valuable discussions. This work was supported in part by a Scientific Research Grant of the Ministry of Education.

References

- AIHARA, A., CHITOKU, K. & HIGASI, K. (1962). *Bull. Chem. Soc. Japan*, **35**, 2057.
 AIHARA, A., KITAZAWA, C. & IWASAKI, F. (1968). *Bull. Chem. Soc. Japan*, **41**, 1034.

- ALLINGER, N. L., BLATTER, H. M. & FREIBERG, L. A. (1966). *J. Amer. Chem. Soc.* **83**, 5028.
 GROTH, P. (1968). *Acta Chem. Scand.* **22**, 128.
 GROTH, P. & HASSEL, O. (1964). *Acta Chem. Scand.* **18**, 923.
International Tables for X-ray Crystallography (1962a). Vol. III, p. 202. Birmingham: Kynoch Press.
International Tables for X-ray Crystallography (1962b). Vol. III, p. 276. Birmingham: Kynoch Press.
- JOHNSON, C. K. (1965). *ORTEP*. Oak Ridge National Laboratory.
 LONG, R. E., SPARKS, R. A. & TRUEBLOOD, K. N. (1965). *Acta Cryst.* **18**, 932.
 MOSSEL, A. & ROMERS, C. (1964). *Acta Cryst.* **17**, 1217.
 STOICHEFF, B. P. (1962). *Tetrahedron*, **17**, 135.
The Universal Crystallographic Computation Program System, 5020 UNICS (1967). The Crystallographic Society of Japan.

Acta Cryst. (1970). B26, 97

The Crystal Structure of *p*-Azoxyanisole

BY W. R. KRIGBAUM, YOZO CHATANI* AND PATRICK G. BARBER

Department of Chemistry, Duke University, Durham, North Carolina 27706, U.S.A.

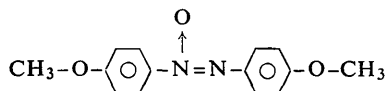
(Received 8 April 1968 and in revised form 4 August 1969)

The stable crystalline form of *p*-azoxyanisole is assigned to space group $P2_1/a$ (C_{2h}^5) with four molecules in the unit cell having parameters $a=15.776$, $b=8.112$, $c=11.018$ Å and $\beta=114.57^\circ$. The crystal structure was refined by full-matrix least-squares to a final R value of 0.091 using 2507 reflections measured with a manually operated single-crystal diffractometer. The molecules are arranged in the unit cell with their long axes approximately perpendicular to the (100) plane. The angle between the normals to the two benzene rings is 22.6° , and the $-N=N-$ bond conformation departs from the planar *trans* position by approximately 4.2° .

Introduction

Bernal & Crowfoot (1933) observed that despite the numerous studies of the mesomorphic behavior of liquid crystals, rather little attention had been paid to the crystalline structures of these compounds. They reported the analysis of several mesomorphic compounds, such as *p*-azoxyanisole, *p*-azoxyphenetole, 1,5-di(*p*-methoxybenzylideneamino)naphthalene, and several cinnamate compounds. Their studies, however, were performed over thirty years ago and provided structures which accounted for the optical properties but only qualitatively for the X-ray intensities. A knowledge of the complete crystal structure would obviously be of considerable assistance in interpreting diffraction studies performed upon the mesophase, which can exhibit interesting physical properties. For example, Falgueirettes (1959) and Kosterin & Chistyakov (1968) have studied the nematic liquid crystalline phase aligned by a magnetic or electric field.

Among the substances which melt to form a nematic mesophase, *p*-azoxyanisole:



has been most frequently selected for study. Bernal & Crowfoot (1933) noted the existence of two crystalline

modifications of this compound, a stable yellow form and an unstable white polymorph. More recently, Robinder & Poirier (1968) have demonstrated the existence of two monotropic crystalline phases of *p*-azoxyanisole in addition to the form which is stable at room temperature. This paper reports the refinement and crystal structure of the stable form of *p*-azoxyanisole.

Experimental

Single crystals of *p*-azoxyanisole were obtained as prisms by slow evaporation of an *n*-heptane solution. All measurements were performed using a manual Picker diffractometer, nickel-filtered copper radiation, and a scintillation counter with a pulse-height analyzer. The unit-cell parameters are: $a=15.776 \pm 0.012$, $b=8.112 \pm 0.005$, $c=11.018 \pm 0.009$ Å and $\beta=114.57^\circ \pm 0.04^\circ$ using $\text{Cu } K\alpha_1=1.5405$ and $\text{Cu } K\alpha_2=1.5443$ Å. Systematic absences of $h0l$ for h odd, and of $0k0$ for k odd, indicate the space group is $P2_1/a$ (C_{2h}^5). The density calculated for four molecules per unit cell is 1.337 g.cm^{-3} , which is in reasonable agreement with 1.348 g.cm^{-3} observed by Würstlin (1934). Transformation of the unit-cell parameters reported by Bernal & Crowfoot (1933), and by Würstlin (1934) to our convention permits the comparison shown in Table 1. Our parameters agree closely with those of Bernal & Crowfoot. The unit cell of Würstlin has a volume twice as large as ours, and we were unable to find the additional reflections reported by Würstlin which would require the larger unit cell.

* Present address: Faculty of Science, Osaka University, Osaka, Japan.