

Table 4. *Principal axes of librational tensors (direction cosines relative to a, b and c*)*

Complete molecule				<i>p</i> -Benzoquinone nucleus			
Value	Direction cosines			Value	Direction cosines		
32 (°) ²	+0.098	+0.540	+0.836	44 (°) ²	-0.219	+0.143	+0.965
17	+0.947	+0.208	-0.245	30	+0.795	+0.600	+0.091
6	+0.306	-0.815	+0.491	8	+0.566	-0.787	+0.244
	$\left(\frac{\sum \Delta U_{ij}^2}{m-n}\right)^{\frac{1}{2}} = 0.004 \text{ \AA}^2$				$\left(\frac{\sum \Delta U_{ij}^2}{m-n}\right)^{\frac{1}{2}} = 0.003 \text{ \AA}^2$		

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The Crystal and Molecular Structure of Azobisisobutyronitrile, C₈H₁₂N₄

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Azobisisobutyronitrile (AIBN, C₈H₁₂N₄) crystallizes in the monoclinic space group *P*2₁/*c* with two molecules in the unit cell of dimensions *a* = 5.506, *b* = 8.236, *c* = 10.995 Å and β = 96.07°. The structure has been determined by Patterson synthesis and refined by the full-matrix least-squares method with anisotropic thermal parameters for the non-hydrogen atoms, to *R* = 0.11. All hydrogen atoms were located by difference Fourier synthesis. The molecule has a centre of symmetry at the mid-point of the N(1) = N(1') double bond. All atoms except those of the methyl groups are planar with a maximum deviation of 0.01 Å. This plane serves as a non-crystallographic mirror plane of the molecule. The methyl groups do not rotate and conform to the mirror plane of the molecule with a mean deviation of 0.05 Å. Thus, the symmetry of the molecule is nearly 2/*m*. The most important interatomic distances are N=N 1.221, C-N 1.490, C-CN 1.470, C-CH₃ 1.530, C≡N 1.144 Å and the mean value C-H is 0.97 Å.

Introduction

AIBN is applied as an initiator in radical polymerization. The kinetics of its decomposition in the solid state have recently been investigated in the authors' institute (Boros-Gyevi & Tüdös, 1969). The present crystal-structure determination is an extension of the previous work.

Experimental

Technical AIBN was crystallized three times from a mixture of chloroform and light petroleum at a temperature of about 3°C. In this way colourless, slightly opaque crystals were obtained in the form of small needles. From a well shaped needle an approximately cubic sample with a cross section of about 0.5 mm was

cut and used for X-ray diffraction. In open air the crystals decompose. To prevent decomposition the sample was sealed in a glass capillary. The capillary was then mounted properly on a special goniometer head (Kálmán, 1967), where all three crystal axes could be brought one by one into favourable positions for taking Weissenberg photographs. Thus, all crystal and intensity data were collected on the same specimen.

The lattice parameters were determined from Buerger precession X-ray photographs around the crystallographic axes using Cu K α radiation. The density was measured by a pycnometer. The summarized crystal data are as follows:

$$\begin{array}{ll} a = 5.506 \pm 0.004 \text{ \AA} & M.V. = 164.13 \\ b = 8.236 \pm 0.008 & D_m = 1.08 \text{ g.cm}^{-3} \\ c = 10.995 \pm 0.008 & D_x = 1.099 \text{ g.cm}^{-3} \\ \beta = 96.07 \pm 0.04^\circ & Z = 2 \\ F(000) = 176 & \mu(\text{Cu K}\alpha) = 5.7 \text{ cm}^{-1} \\ & (\lambda = 1.5418 \text{ \AA}) \\ V = 495.75 \text{ \AA}^3 & \text{Space group } P2_1/c. \end{array}$$

The monoclinic space group $P2_1/c$ has been determined from the systematic absences, reflexions $0k0$ absent for k odd and $h0l$ absent for l odd. As in the unit cell two molecules are present, the molecule has a centre of symmetry.

Intensities of the reflexions were recorded with a STOE equi-inclination Weissenberg camera using the multiple-film technique on 0 to 5, 0 to 3 and 0 to 1 layers about the a , b and c crystallographic axes, respectively. The intensities were eye-estimated using calibrated intensity scales. A total, of 1023 independent reflexions were collected of which 274 were unobserved. Reflexions with zero intensity were taken with a value of $I_0 = \frac{1}{3} I_{\min}$.

The intensities originating from different films were brought to a common scale by multiple-film scaling and by interlayer scaling after applying L_p factors. No absorption corrections were made ($\mu R = 0.3$). The absolute scale and approximate overall temperature

factor were determined from all three-dimensional data by the Wilson plot method.

Determination of the structure

For the structure determination from all reflexions, the three-dimensional Patterson function was calculated, using the program of Albano, Domenicano & Vaciago (1966) on the ICT 1905 computer. Considering that the molecule has a center of symmetry at the midpoint of the N(1)=N(1') double bond, it was easy to pick up the inversion peak corresponding to the interatomic vector of N(1')=N(1) (Fig. 1) close to the origin of the Patterson map. This peak gives the vector $(2x, 2y, 2z)$ of the crystal lattice, where (x, y, z) are the coordinates of the N(1) atom. Thus, in the crystal lattice, we could fix one atom and an interatomic vector of the molecule, which gave a starting point for picking up two more interatomic vectors of the molecule determining the sites of C(1) and C(3) atoms. Considering the tetrahedral coordination to these three atoms, the sites of the tetrahedral coordinated C(2) and C(4) atoms could be generated geometrically.

Table 1. *Final fractional coordinates of atoms in the asymmetric unit.*

The e.s.d.'s are given in parentheses and refer to the least significant digits. In the notation of hydrogen atoms the first digit refers to the corresponding carbon atom.

	x	y	z
N(1)	-0.0166 (3)	0.0731 (2)	-0.0050 (2)
N(2)	0.4683 (5)	0.0054 (3)	0.2184 (2)
C(1)	0.1481 (4)	0.1754 (3)	0.0797 (2)
C(2)	0.3267 (4)	0.0770 (3)	0.1564 (2)
C(3)	-0.0152 (5)	0.2675 (3)	0.1601 (3)
C(4)	0.2813 (6)	0.2903 (3)	-0.0005 (2)
H(31)	-0.117 (10)	0.333 (6)	0.110 (5)
H(32)	0.066 (8)	0.349 (5)	0.216 (4)
H(33)	-0.090 (8)	0.180 (5)	0.204 (4)
H(41)	0.179 (8)	0.343 (5)	-0.056 (4)
H(42)	0.359 (10)	0.382 (6)	0.050 (5)
H(43)	0.380 (8)	0.221 (5)	-0.056 (4)

Table 2. *Anisotropic thermal parameters of the nitrogen and carbon atoms and isotropic parameters of the hydrogen atoms*

The e.s.d.'s are in parentheses.

The b_{ij} are given, as defined by:

$$T = \exp [-10^{-4}(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)]$$

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
N(1)	281 (6)	108 (2)	80 (1)	-18 (6)	-57 (5)	-14 (3)
N(2)	363 (8)	202 (4)	121 (2)	38 (9)	-106 (8)	56 (5)
C(1)	271 (7)	110 (3)	72 (2)	-10 (7)	-44 (6)	-17 (3)
C(2)	281 (7)	129 (3)	83 (2)	-15 (6)	-15 (6)	-3 (4)
C(3)	355 (9)	169 (4)	114 (2)	47 (10)	2 (8)	-81 (5)
C(4)	448 (10)	151 (4)	95 (2)	-118 (10)	-21 (8)	31 (5)
H(31)			5.03 (128) \AA^2			
H(32)			3.15 (99)			
H(33)			3.05 (100)			
H(41)			4.73 (118)			
H(42)			2.73 (98)			
H(43)			3.28 (97)			

The approximate atomic coordinates of these five atoms with an overall isotropic factor of B=3.705, taken from the Wilson plot, gave a structure-factor agreement of R=0.57 for all reflexions. A three-dimensional Fourier synthesis, using all reflexions, then gave the coordinates of the still missing N(2) atom and improved the coordinates for the former five atoms, expressed in the Fourier function. The

coordinates of all non-hydrogen atoms of the molecule resulted in an R value of 0.30. From this point on, the refinement of the structure was carried out by full-matrix least-squares methods using the Albano et al. (1966) program on the ICT 1905 computer, minimizing

the function $\Phi = \sum_h w_h (F_{oh} - \frac{1}{G} |F_{ch}|)^2$ where G is the weighting factor. The weighting factor of Cruickshank

Table 3. Observed and calculated structure factors (10 F)

* Unobserved reflections.

Table with 16 columns of hkl indices and 16 columns of intensity values (Fo, Fc). Rows correspond to different reflections, with some marked as unobserved (*). The table lists observed and calculated structure factors for various reflections.

(1961a), $w_h = 1/(a + b \cdot F + cF^2)$ was used with $a = 2.0$, $b = 1$ and $c = 0.03$. Three cycles with isotropic temperature factors and three cycles with anisotropic temperature factors reduced the R values for all reflexions to 0.189 and 0.133, respectively.

After least-squares refinement of the heavy atoms, a three-dimensional $F_o - F_c$ difference Fourier function was calculated, removing all heavy atoms of the molecule. In this way all hydrogen atoms of the molecule could be located. The inclusion of the hydrogen atoms in the structure-factor calculation reduced the R value to 0.114. The hydrogen parameters were then refined by isotropic least-squares methods using only reflexions with $0.3 \leq \sin \theta \leq 0.7$ ($Cu, K\alpha$) and starting with the overall isotropic temperature factor originating from the Wilson plot. After three cycles the agreement factor decreased 2% for the reflexions used in the refinement. Finally, only the non-hydrogen atoms were refined once more by anisotropic least-squares methods using all reflexions. After three cycles the shift of the parameters was less than 0.1σ and the final agreement factor for the observed and all reflexions was 0.097 and 0.110, respectively.

Final atomic parameters with their estimated standard deviations are given in Tables 1 and 2. The structure factors calculated from these parameters are listed in Table 3. The atomic scattering factors for all atoms were taken from *International Tables for X-ray Crystallography* (1962).

Geometry of the molecule

In the AIBN molecule (Fig. 1) all atoms except those of the methyl groups are planar. The plane constants of the best plane of these atoms, referred to the orthogonalized axial system, are given in Table 4. The deviations from the best plane for atoms forming the plane range from 0.001 to 0.012 Å. The atoms of the two methyl groups are not in this plane. They belong to the same asymmetric part of the molecule and relate, in good approximation, in pairs with the best plane as the mirror plane. The mean deviations from this mirror plane symmetry are 0.016 Å for carbon atoms and 0.07 Å for hydrogen atoms. Thus, the symmetry of the molecule including the hydrogen atoms, is $2/m$ within the experimental error.

Interatomic distances and bond angles of the molecule are given in Table 5.

Thermal motion analysis

The root-mean-square amplitudes and the vectors of the principal axes of the thermal-vibration ellipsoids for the non-hydrogen atoms of the molecule were calculated from the anisotropic thermal parameters (Table 2) and are listed in Table 6. With the aid of these data the molecule was drawn in orthogonal projection along the crystallographic a axis (Fig. 2), where the heavy atoms are represented by their thermal-vibration ellipsoids.

The thermal motion of the AIBN molecule has also been analysed as a rigid body, including all heavy atoms of the molecule. This analysis was made on the basis of Cruickshank's (1961b) procedure using the program of Schomaker & Trueblood (1968). The U tensors of the individual atoms calculated from rigid-

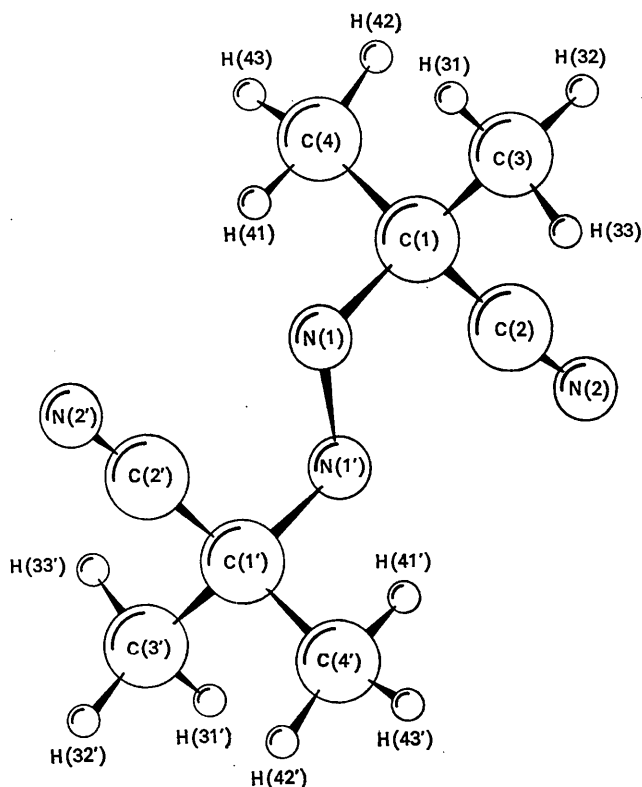


Fig. 1. Perspective view of the AIBN molecule with identifications of the atoms.

Table 4. *Least-squares plane formed by atoms of the molecule excluding those of the methyl groups and distances, to this plane for all asymmetric atoms of the molecule*

Plane is referred to crystal axes and coordinates are considered in Å.

$$\text{Plane equation: } 0.7150x + 0.0587y - 0.7684z = 0$$

Asymmetric atoms	Distances (Å)			
N(1), N(2), C(1), C(2)	0.012,	-0.006,	0.001,	0.002
C(3), H(31), H(32), H(33)	-1.2833,	-1.2285,	-1.3984,	-1.9931
C(4), H(41), H(42), H(43)	1.2515,	1.3441,	1.1746,	2.0719

Table 5. Bond lengths and bond angles with their e.s.d.'s in parentheses

	Distances (Å)		Angles (°)		Mean (°)
N(1)-N(1')	1.221 (3)	N(1')-N(1)-C(1)	115.2 (2)		
N(1)-C(1)	1.490 (3)	N(1)-C(1)-C(2)	111.9 (2)	}	108.4
N(2)-C(2)	1.144 (3)	N(1)-C(1)-C(3)	106.6 (2)		
C(1)-C(2)	1.470 (3)	N(1)-C(1)-C(4)	106.6 (2)	}	110.5
C(1)-C(3)	1.528 (4)	C(2)-C(1)-C(3)	109.9 (2)		
C(1)-C(4)	1.532 (4)	C(2)-C(1)-C(4)	109.8 (2)	}	110.1
C(3)-H(31)	0.919 (34)	C(3)-C(1)-C(4)	111.9 (2)		
C(3)-H(32)	0.988 (34)	C(1)-C(2)-N(2)	177.5 (2)	}	110.1
C(3)-H(33)	0.983 (32)	H(31)-C(3)-H(32)	100.2 (41)		
C(4)-H(41)	0.899 (34)	H(31)-C(3)-H(33)	118.0 (41)	}	109.1
C(4)-H(42)	1.003 (34)	H(32)-C(3)-H(33)	112.1 (37)		
C(4)-H(43)	1.027 (34)	C(1)-C(3)-H(31)	107.8 (32)	}	108.3
		C(1)-C(3)-H(32)	116.5 (26)		
		C(1)-C(3)-H(33)	103.0 (26)	}	110.4
		H(41)-C(4)-H(42)	102.0 (41)		
		H(41)-C(4)-H(43)	101.5 (36)	}	110.4
		H(42)-C(4)-H(43)	121.5 (39)		
		C(1)-C(4)-H(41)	112.8 (27)	}	110.4
		C(1)-C(4)-H(42)	110.3 (30)		
		C(1)-C(4)-H(43)	108.2 (24)		

body thermal motion (U_{calc}) and derived from structure analysis (U_{obs}) are in fairly good agreement (Table 7), supporting the rigid-body assumption.

Table 6. Principal axes of the thermal-vibration ellipsoids for the asymmetric atoms of the molecule given by their lengths and coordinates of their end points (in fractions) referred to crystal axes

The origins of principal axes are considered to be at the site of the corresponding atoms.

	<i>i</i>	$(u^2)^{\dagger}$ (Å)	<i>x</i>	<i>y</i>	<i>z</i>
N(1)	1	0.247	-0.043	0.072	0.012
	2	0.197	-0.032	0.094	-0.010
	3	0.176	-0.039	0.062	-0.015
N(2)	1	0.308	0.492	-0.007	0.196
	2	0.264	0.490	0.034	0.216
	3	0.196	0.496	-0.002	0.229
C(1)	1	0.235	0.122	0.171	0.095
	2	0.198	0.133	0.197	0.076
	3	0.175	0.127	0.166	0.069
C(2)	1	0.236	0.306	0.078	0.174
	2	0.212	0.318	0.102	0.153
	3	0.106	0.310	0.073	0.151
C(3)	1	0.293	-0.003	0.288	0.140
	2	0.229	0.025	0.267	0.168
	3	0.209	-0.010	0.247	0.150
C(4)	1	0.288	0.242	0.306	0.010
	2	0.229	0.259	0.291	-0.019
	3	0.209	0.266	0.268	0.003

The translational T and librational ω tensors of the rigid body are given in Table 8. The principal axes of the T and ω tensor ellipsoids are given in Table 9 in which their lengths and directional cosines are referred to the orthogonalized axial system. The last two columns show the angles of principal axes to the non-crystallographic mirror plane of the molecule and to the direction of the N(1)-C(1) bond, respectively.

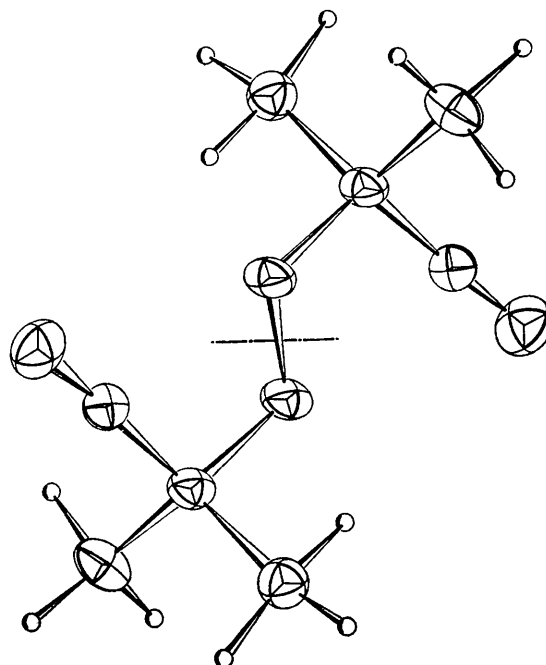


Fig. 2. Perspective view of the AIBN molecule. The atoms are represented by their thermal vibration ellipsoids.

From these data it can be seen that the principal axis with greatest libration (5.9°) is almost parallel (1.7°) to the non-crystallographic mirror plane as well as to the N(1)-C(1) bond (2°). The next greatest principal axis is nearly rectangular to the same plane (73.1°).

Discussion of the structure

In the AIBN molecule all atoms except those of the methyl groups form a plane. The greatest deviation from this plane (0.012 \AA) shows the N(1) atom (Table 4), which is in double bond with its *meso* related pair

N(1') with a bond length of 1.221 Å (Table 5). This agrees within 1σ with the value 1.218 ± 0.005, reported for *p*-azoxyanisole (Krigbaum, Chatani & Barber, 1970). The C–N= bond length with its value of 1.490 Å is exactly the same as was found for nitromethane (Tannenbaum, Johnson, Myers & Gwinn, 1954) and shorter within about 1σ than the value, 1.496 ± 0.005 Å, found in *p*-azoxyanisole (Krigbaum *et al.*, 1970). The C–CN bond length is found to be 1.470 Å and agrees within 2σ with the value 1.474 ± 0.002 Å determined for propionitrile (Lerner & Dailey, 1957), (*sp*³–*sp* C–C single bond). The mean C–CH₃ bond length of 1.530 Å agrees within 1.5σ with the values of 1.534 and 1.525 ± 0.004 Å reported for ethane (Allen & Plyler, 1959) and for DL-*N*-chloroacetylalanine (Cole, 1970) respectively. The C≡N bond length of 1.144 Å agrees with the mean values 1.144 ± 0.010 and 1.143 ± 0.004 Å reported for hydrogen cyanide tetramer (Penfold & Lipscomb, 1961) and 1,4-bis(dicyanomethylene)cyclohexane (Iwasaki & Aihara, 1970), respectively. The C–H bond lengths vary over a range of 1.5σ (± 0.05 Å) with a mean value of 0.97 Å.

All hydrogen atoms of the molecule could unambiguously be located from the *F*_o–*F*_c difference Fourier synthesis with fairly good C–H bond lengths (Table 5). From this fact we conclude that the methyl

groups do not rotate. Comparing the r.m.s. displacements of the thermal-vibration ellipsoids of the different atoms in the molecule (Table 6), it turns out that the methyl carbon and the CN nitrogen atoms have the greatest thermal vibration, but it cannot be assumed that the thermal motion of the methyl group is conspicuously large. Thus, this occurrence of the methyl groups is very similar to that in DL-*N*-chloroacetylalanine (Cole, 1970).

The part of the molecule forming the non-crystallographic mirror plane has an *S* shaped conformation with three different kinds of bond angles: N(1')–N(1)–C(1), N(1)–C(1)–C(2) and C(1)–C(2)–N(2) with values of 115.2, 111.9 and 177.5°, respectively. The three consecutive atoms forming the last angle and containing the CN radical are almost on a straight line. Calculating the angles N(1)–C(2)–C(1) and N(1)–C(2)–N(2), both are in the same plane and give a sum of 182.5°. From this we can conclude that the CN radical is tilted out of the *S* curve towards the methyl groups.

The bond angles around the C(1) atom [N(1)–C–C and C–C–C type of angles] average 108.4 and 110.5°, respectively; they have a maximum deviation of 2σ and approximate the tetrahedral angle (Table 5). The bond angles in the methyl groups show greater deviations, but considering the mean values of groups, they

Table 7. Observed and calculated components of *U* tensors of the individual atoms in the asymmetric part of the molecule, referred to the orthogonalized axial system in 10⁻² Å²

	<i>U</i> ₁₁		<i>U</i> ₂₂		<i>U</i> ₃₃		<i>U</i> ₁₂		<i>U</i> ₁₃		<i>U</i> ₂₃	
	Obs	Calc	Obs	Calc	Obs	Calc	Obs	Calc	Obs	Calc	Obs	Calc
N(1)	4.55	4.08	3.70	3.74	4.84	4.75	-0.18	0.41	-1.39	-0.82	-0.31	0.19
N(2)	6.01	6.03	6.95	6.44	7.32	6.59	0.30	-0.02	-2.40	-2.79	1.29	0.56
C(1)	4.36	4.58	3.77	4.04	4.37	4.99	-0.07	0.07	-1.13	-0.75	-0.40	-0.05
C(2)	4.43	4.61	4.45	5.08	5.03	5.05	-0.17	-0.11	-0.77	-1.22	-0.06	0.17
C(3)	5.52	5.51	5.80	5.43	6.89	7.21	0.73	0.52	-0.70	-0.60	-1.85	-1.92
C(4)	7.01	6.98	5.18	5.05	5.75	5.55	-1.43	-1.62	-0.93	-1.13	0.71	0.47

Table 8. The translational *T*(10⁻² Å²) and librational *ω*(10⁻² rad²) tensors of the molecule as rigid-body referred to the orthogonalized axial system.

The e.s.d.'s are given in parentheses.

$$\mathbf{T} = \begin{pmatrix} 3.87 (17) & 0.39 (13) & -0.70 (14) \\ & 3.74 (15) & 0.18 (13) \\ & & 4.56 (16) \end{pmatrix} \quad \omega = \begin{pmatrix} 0.46 (4) & 0.34 (3) & 0.26 (3) \\ & 0.39 (4) & 0.28 (4) \\ & & 0.55 (4) \end{pmatrix}$$

Table 9. The principal axes of the translational *T* and librational *ω* tensor ellipsoids of the molecule as a rigid body, and the directional cosines (unit-vector components) of the amplitudes referred to the orthogonalized axial system.

The last two columns give the angles of the principal axes to the non-crystallographic mirror plane of the molecule and to the direction of the N(1)–C(1) bond, respectively.

	<i>i</i>	(<i>μ</i> ²) [†] (Å ²)	<i>x</i> _{<i>u</i>}	<i>y</i> _{<i>u</i>}	<i>z</i> _{<i>u</i>}	Angle to plane (°)	Angle to bond (°)
<i>T</i>	1	0.224	0.539	0.045	-0.841	76.9	101.8
	2	0.201	0.468	0.814	0.344	8.1	21.9
	3	0.177	0.700	-0.579	0.418	10.1	81.3
<i>ω</i>	1	0.103 (rad ²)	-0.581	-0.551	-0.600	1.7	2.0
	2	0.052	-0.546	-0.283	0.789	73.1	88.0
	3	0.027	-0.604	0.785	-0.136	16.9	88.2

approximate the tetrahedral angle within a value of less than 1σ .

The packing of the molecules in the crystal lattice is given by two orthogonal projections in Fig. 3. This packing conforms with the molecular close-packing. The outmost atoms of the molecule are N and H and

the neighbouring molecules contact through these. The intermolecular N-H and H-H distances shorter than 3.0 \AA are given in Table 10. Both mean values of the shortest intermolecular N-H and H-H distances are greater than the sums of the corresponding van der Waals radii, but the deviation is much less in the case

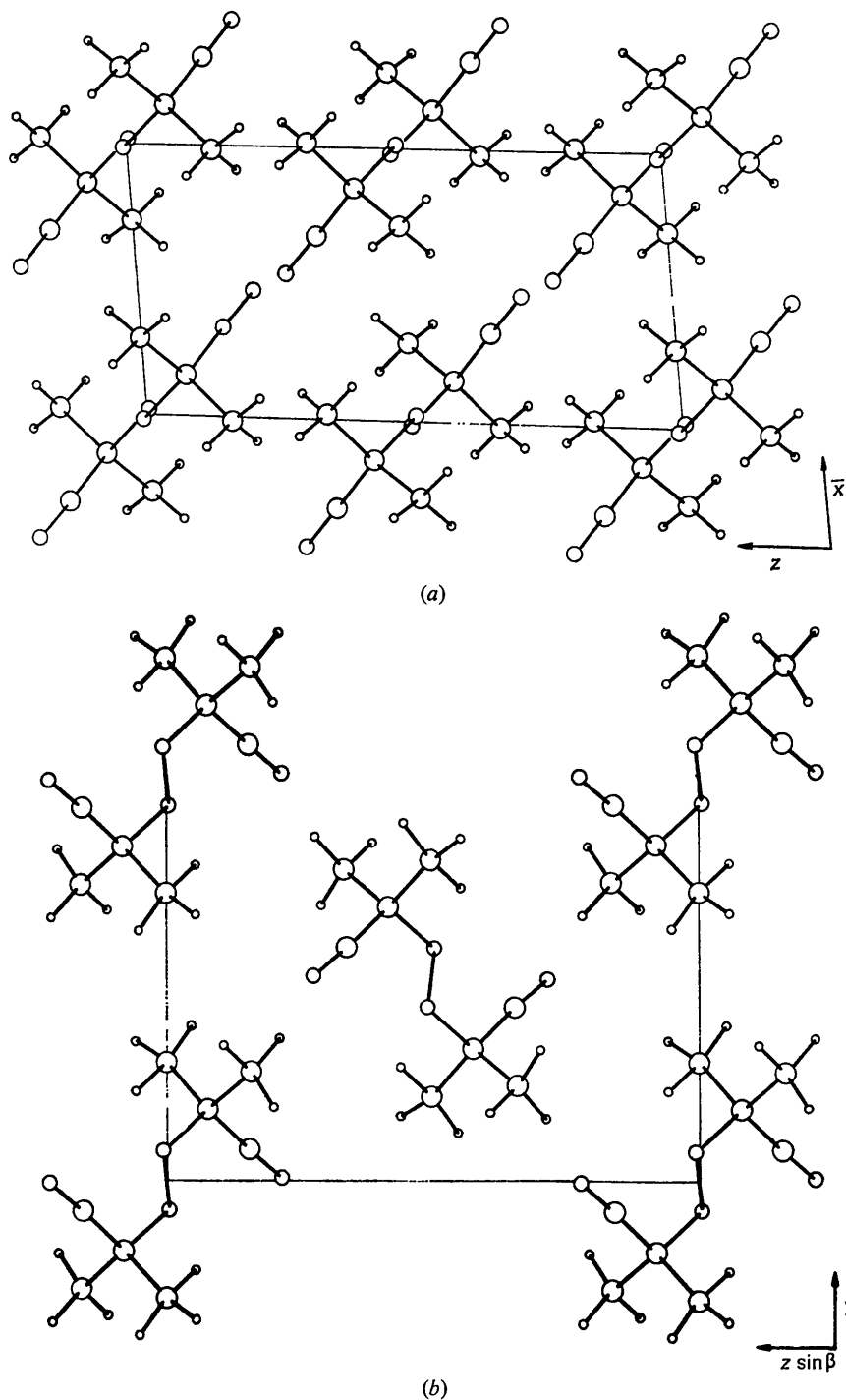


Fig. 3. Structure of AIBN in two orthogonal projections, (a) on the (010) plane, (b) on the (100) plane.

Table 10. *The shorter intermolecular N-H and H-H distances*

The atoms in the first column belong to the reference molecule at (x,y,z) corresponding to the data in Table 1.

From	To	In molecule at			Distance (Å)	
N(2)	H(32)	1-x	-½+y	½-z	2.891	Mean: 2.831 Å
N(2)	H(33)	1+x	y	z	2.845	Min: 2.776
N(2)	H(42)	1-x	-½+y	½-z	2.814	
N(2)	H(43)	1-x	-y	-z	2.776	
H(31)	H(41)	-x	1-y	-z	2.741	
H(31)	H(42)	-1+x	y	z	2.922	
H(32)	H(33)	-x	½+y	½-z	2.858	Mean: 2.872 Å
H(32)	H(41)	x	½-y	½+z	2.975	Min: 2.741
H(32)	H(43)	x	½-y	½+z	2.949	
H(33)	H(32)	-x	-½+y	½-z	2.858	
H(33)	H(41)	x	½-y	½+z	2.888	
H(42)	H(42)	1-x	1-y	-z	2.789	

of N-H distances. Thus, the degree of close-packing of the molecules in the crystal is determined most probably by the shortest N-H distance, which is 2.776 Å. This corresponds to the hydrogen van der Waals radius of 1.27 Å, derived from the structure of C₁₂H₂₀ (Sasvári & Löw, 1965), if we accept the van der Waals radius of 1.50 Å for nitrogen (Pauling, 1960). Under the same condition, the shortest N-H distance of 2.776 Å is greater than the sum of the van der Waals radii if the van der Waals radius of hydrogen is considered to be 1.17 Å as determined by Kitaigorodskii (1961).

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