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The Crystal Structure of Two Crystalline Polymorphs of *N*-(*p*-Methoxyphenyl-3-propyl)-*p*-bromobenzamide

Noritake YASUOKA, Nobutami KASAI and Masao KAKUDO

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamada-kami, Suita, Osaka

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The crystal structure analysis of *N*-(*p*-methoxyphenyl-3-propyl)-*p*-bromobenzamide was carried out by means of X-rays. This compound crystallizes in two crystalline polymorphs, both belonging to the monoclinic system.

α-form: $a = 14.59_2$, $b = 9.57_2$, $c = 11.24_2$ Å, $\beta = 94.2_6°$; $Z = 4$; space group $P2_1/c$.

β-form: $a = 11.94_0$, $b = 10.01_9$, $c = 6.57_7$ Å, $\beta = 90.5_6°$; $Z = 2$; space group $P2_1$.

A little difference in structure is observed between the molecules in the two polymorphs, while the conformations of the carbon-carbon bonds in the 3-aminopropyl group are of the *trans* form. In both forms, belts of molecules parallel to the *b* axis are formed by hydrogen bonds between the amide groups of the molecules related by the twofold screw axis. These belts are packed anti-parallel in the α-form, but parallel in the β-form.

The first step in the interpretation of an X-ray fiber diagram is, generally, to build up a plausible model which accounts for the observed fiber period.

In the X-ray structure analysis of a series of polyamides prepared by the condensation of 1,2-bis-[*p*-(3-aminopropyl)phenoxy]ethane and adipic acid or its homologues,[1] the fiber periods of all these polyamides have been observed to be shorter by 3—4 Å than the calculated values, assuming the ordinary bond lengths and bond angles in the calculation, and the *trans* conformations for all the single bonds in the polymer chains. This "shortening" of the observed fiber periods suggests the presence of conformations other than *trans*, or of bond lengths or angles different from the normal ones.

These polyamides, $[\mathrm{NHCH_2CH_2CH_2C_6H_4O{\text -}(CH_2)_nOC_6H_4CH_2CH_2CH_2NHCO(CH_2)_mCO}]_p$ ($n = 1,2,3,4,5,6$ $m = 4,8$), have very complicated repeating units. In addition, these polyamides are poorly crystalline and the diffraction data available from these fibers are not sufficient to build up a model of a molecular skeleton which accounts for the "shortening" of the observed fiber periods. In these cases it is effective to carry out the complete crystal structure analysis of some simple compounds containing the important parts of the polymer chain and to deduce the chain structure of the polymer on the basis of the determined conformations of the parts along the chain.

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[1] T. Ando, N. Yasuoka and S. Kuribayashi, *Nippon Kagaku Zasshi* (*J. Chem. Soc. Japan, Pure Chem. Sect.*), **87**, 536 (1966).

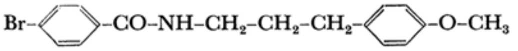
From these considerations, we undertook crystal structure analyses of a series of compounds with the formula of $XC_6H_4O(CH_2)_nOC_6H_4X$ (n=2,3 or 4, X=H, Cl or Br) to determine the conformation of methylene groups between phenoxy groups. The structures of *p,p'*-dichlorodiphenoxy-1,2-ethane (n=2 and X=Cl) and 1,2-diphenoxyethane (n=2 and X=H) have already been determined and reported,[2,3] and it has been found that the OCH_2-CH_2O groups are of the *gauche* form.

Next, the crystal structure analysis of *N*-(*p*-methoxyphenyl-3-propyl)-*p*-bromobenzamide was carried out in order to determine what the detailed structure of the $-C_6H_4CH_2CH_2CH_2NH-$ group is in the crystalline state. In addition, the finding of the polymorphism of this substance prompted us to make a complete crystal structure analysis and to ascertain what the difference is between two polymorphic forms.

Experimental

The two crystalline polymorphs of *N*-(*p*-methoxyphenyl-3-aminopropyl)-*p*-bromobenzamide were found to be stable at room temperature. Preliminary X-ray work revealed that both forms belong to the monoclinic system, but to different space groups: one is $P2_1/c$ and the other $P2_1$. The crystal of the $P2_1/c$ space group is named the α-form, and that of the $P2_1$ space group, the β-form. The crystal data of both polymorphs are summarized in Table 1.

TABLE 1. CRYSTAL DATA OF *N*-(*p*-METHOXYPHENYL-3-PROPYL)-*p*-BROMOBENZAMIDE



	α-form	β-form
a =	14.592 ± 0.007	11.940 ± 0.007 Å
b =	9.572 ± 0.005	10.019 ± 0.006 Å
c =	11.242 ± 0.006	6.557 ± 0.004 Å
β =	94.26 ± 0.03	90.56 ± 0.03°
V =	1565.9	784.4 Å^3
Z =	4	2
D_x=	1.476	1.474 g cm^{-3}
	$P2_1/c$	$P2_1$

Crystals of the α-form were obtained by slowly evaporating an ethanol solution saturated with this substance. After the α-form crystals had been picked up, the mother liquor was left to vaporize. When it was dried up, crystals of a different behavior from those of the α-form were obtained, these were later found to be the β-form.

The unit cell dimensions and reflection intensities were measured with a General Electric XRD-5 goniostat using zirconium-filtered Mo$K\alpha$ radiation within a range of $\sin\theta/\lambda$ less than 0.59 (2θ=50°). Each independenet reflection intensity was measured by the stationary-crystal stationary-counter technique at a counting time of 20 sec. 2743 reflections were collected in the case of the α-form and 1474 in the case of the β-form. The crystals used had the dimensions of $0.10\times0.15\times0.15$ mm^3 and $0.10\times0.15\times0.20$ mm^3 for the α- and β-forms respectively. No correction was made for the absorption, while the corrections for Lorentz and polarization factors were made in the usual way.

The infrared absorption spectra were measured in a KBr disk with a Hitachi EPI-1 spectrometer.

Structure Determination

α-Form. The three-dimensional Patterson function was synthesized, and the position of the bromine atom was easily obtained from it. Then the structure was solved by the minimum function method by superposing four sets of three-dimensional Patterson maps with coordinates of the bromine atoms at the four equivalent positions of the $P2_1/c$ space group. Significant peaks appeared on the minimum function map, and the coordinates of all the atoms except hydrogen could be read off. The structure factors were calculated with these atoms, and the three-dimensional electron density distribution was computed. The peak height of each atom was reasonable considering the chemical constitution of this compound.

Then the structure was subjected to least-squares refinement using the block-diagonal matrix approximation. After six cycles the discrepancy index decreased from 0.313 to 0.136. In the refinement, 2743 measured reflections were used. At this stage, the difference Fourier function was synthesized. Several residual peaks with heights of from 0.4 to 0.8 e.Å^{-3} appeared, most of them were found at sites where hydrogen atoms were expected to be present. All the hydrogen atoms with isotropic temperature factors were included in the refinement thereafter. The final discrepancy index is 0.124 for 2421 non-zero reflections, and 0.143 for all reflections.

The atomic scattering factors used in the calculations were taken from those of Hanson and his co-workers.[4] In the least-squares refinement the weight assigned for each reflections was 1.00 for most of them, but 0.25 for the few weakest ones. The computations throughout this work were done on a NEAC 2200 computer in this University and on a HITAC 5020 computer in the University of Tokyo, using programs written by Dr. Tamaichi Ashida of the Institute for Protein Research of this University.

The final atomic and thermal parameters are listed in Table 2. Tables of the observed and

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2) N. Yasuoka, T. Ando and S. Kuribayashi, This Bulletin, **40**, 256 (1967).

3) N. Yasuoka, T. Ando and S. Kuribayashi, *ibid.*, **40**, 270 (1967).

4) H. P. Hanson, F. Herman, J. D. Lea and S. Skillamn, *Acta Cryst.* **17**, 1040 (1964).

calculated structure factors are preserved by the Chemical Society of Japan.[*1] The three-dimensional electron density map is shown in Fig. 1.

β-Form. From the Patterson projection on (101), the x and z coordinates of the bromine atom were obtained. Since the y coordinate of one atom could be chosen arbitrarily in the $P2_1$ space group, that of the bromine atom was chosen as 0.0. The

TABLE 2. ATOMIC PARAMETERS OF α-FORM

(a) Atomic coordinates (in fraction of cell edges) and their standard deviations (in 10^{-3} Å)

Atom	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$
Br	1.2890	1	0.2829	1	0.6991	1
O(1)	1.0572	6	0.6293	6	0.2386	7
O(2)	0.4558	7	0.1207	7	−0.1152	7
N	0.9701	7	0.4362	7	0.2306	8
C(1)	1.2114	10	0.3523	9	0.5670	8
C(2)	1.1197	10	0.3098	9	0.5572	9
C(3)	1.0657	9	0.3594	9	0.4600	10
C(4)	1.0990	8	0.4510	8	0.3801	9
C(5)	1.1911	10	0.4898	9	0.3914	10
C(6)	1.2487	9	0.4363	10	0.4852	10
C(7)	1.0419	9	0.5133	9	0.2764	10
C(8)	0.9099	9	0.4965	10	0.1343	11
C(9)	0.8289	9	0.3968	10	0.1017	10
C(10)	0.7697	11	0.4594	10	−0.0048	10
C(11)	0.6884	9	0.3684	9	−0.0365	9
C(12)	0.6052	10	0.3861	10	0.0150	9
C(13)	0.5306	10	0.3042	10	−0.0098	10
C(14)	0.5358	8	0.1977	9	−0.0953	9
C(15)	0.6154	10	0.1782	10	−0.1516	9
C(16)	0.6897	9	0.2630	9	−0.1226	9
C(17)	0.4591	10	0.0042	11	−0.1966	11

(b) Temperature factors in form of $\exp(-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{13}hl+\beta_{23}kl))$

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Br	0.0081	0.0153	0.0115	0.0002	−0.0047	0.0027
O(1)	0.0062	0.0099	0.0155	−0.0004	−0.0049	0.0004
O(2)	0.0065	0.0169	0.0128	−0.0022	−0.0004	−0.0027
N	0.0049	0.0090	0.0151	−0.0020	−0.0033	0.0003
C(1)	0.0080	0.0080	0.0075	0.0040	−0.0016	−0.0004
C(2)	0.0071	0.0121	0.0096	−0.0047	0.0040	0.0028
C(3)	0.0061	0.0108	0.0108	0.0008	0.0019	0.0010
C(4)	0.0040	0.0090	0.0103	−0.0003	0.0012	−0.0036
C(5)	0.0061	0.0083	0.0124	−0.0012	−0.0001	0.0018
C(6)	0.0051	0.0130	0.0120	0.0026	−0.0008	0.0038
C(7)	0.0059	0.0074	0.0121	0.0024	0.0013	0.0001
C(8)	0.0044	0.0130	0.0147	−0.0013	−0.0030	0.0066
C(9)	0.0049	0.0118	0.0128	0.0009	−0.0025	0.0035
C(10)	0.0078	0.0121	0.0117	−0.0021	−0.0060	0.0035
C(11)	0.0062	0.0095	0.0091	0.0020	−0.0028	0.0058
C(12)	0.0068	0.0132	0.0084	−0.0005	−0.0013	−0.0002
C(13)	0.0072	0.0126	0.0110	−0.0014	0.0022	−0.0016
C(14)	0.0052	0.0107	0.0105	−0.0023	−0.0047	0.0029
C(15)	0.0061	0.0146	0.0093	0.0007	−0.0007	−0.0012
C(16)	0.0063	0.0120	0.0093	0.0006	0.0001	0.0010
C(17)	0.0066	0.0155	0.0142	−0.0072	−0.0025	−0.0076

[*1] The complete data of the F_o-F_c table are kept as Document No. 6901 at the office of the Bulletin of the Chemical Society of Japan. A copy may be secured by citing the document number and by remitting, in advance, ¥300 for photoprints. Pay by check or money order, payable to: The Chemical Society of Japan.

(c) Atomic coordinates and isotropic temperature factors for the hydrogen atoms

Atom	x	y	z	B
H(1)	1.081	0.246	0.614	3.6
H(2)	0.994	0.331	0.463	3.7
H(3)	1.221	0.565	0.338	3.3
H(4)	1.319	0.451	0.496	3.6
H(5)	0.958	0.350	0.259	3.6
H(6)	0.947	0.508	0.059	2.9
H(7)	0.886	0.583	0.162	5.4
H(8)	0.779	0.396	0.177	3.4
H(9)	0.858	0.315	0.061	4.4
H(10)	0.809	0.489	−0.074	4.7
H(11)	0.752	0.572	0.011	3.5
H(12)	0.599	0.470	0.081	2.0
H(13)	0.464	0.277	0.051	3.5
H(14)	0.618	0.120	−0.239	4.8
H(15)	0.747	0.259	−0.161	4.5
H(16)	0.512	0.045	−0.258	6.0
H(17)	0.499	−0.046	−0.145	5.9
H(18)	0.405	−0.040	−0.193	2.4

three-dimensional electron density distribution was then computed using all the observed reflections, with phases assigned by the bromine atom only. Atoms of the benzene ring to which the bromine atom attached and those of the amide group could be found easily, but it did not seem possible to assign those of the *p*-methoxyphenylpropyl group without error. The second Fourier synthesis was carried out on the basis of phases assigned by the Br, C(1) to C(7), N, and O(1) atoms. The coordinates of other non-hydrogen atoms could thus be obtained.

The atomic parameters were then refined by the least-squares method. The refinement was carried out with all the measured reflections. After 7 cycles the discrepancy factor was reduced from 0.233 to 0.081. The difference Fourier function was synthesized. Several peaks were found at sites where hydrogen atoms were expected to be present. All the hydrogen atoms with isotropic temperature factors were then included in the refinement. After two cycles, some hydrogen atoms were shifted in such a way that the bond distances to the attached atoms were rather long. The parameters of these shifted atoms were, therefore, restored to their original positions, after which two cycles of refinements were carried out with hydrogen atoms fixed in their original positions. The final discrepancy index is 0.070 for 1332 non-zero reflections, and 0.089 for all reflections.

The final atomic and thermal parameters are listed in Table 3. Tables of the observed and calculated structure factors are preserved by the Chemical Society of Japan. The three-dimensional electron density map is shown in Fig. 2.

Discussion

The bond lengths and bond angles in the molecules of the α- and β-form calculated from the final atomic coordinates are shown in Figs. 3 and 4 respectively. The estimated standard deviations of the bond lengths are from 0.010 to 0.015 Å in the α-form and from 0.012 to 0.030 Å in the β-form. Those of the bond angles are from 0.73 to 0.82°

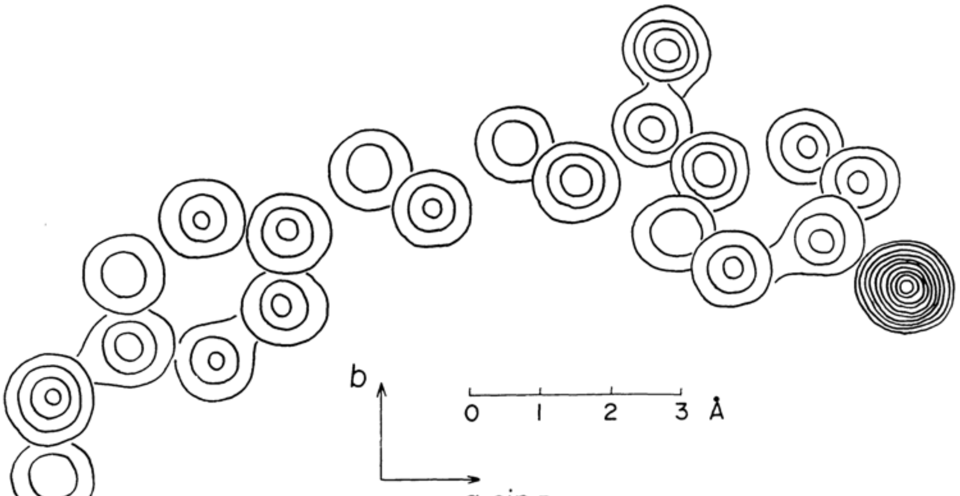


Fig. 1. The final electron density distribution of α-form. Composite diagram of sections parallel to (001) plane. Contours are at intervals of 2 e.Å^{-3}, beginning with the 2 e.Å^{-3} contour. For Br, contours are at intervals of 5 e.Å^{-3} beginning with 10 e.Å^{-3}.

TABLE 3. ATOMIC PARAMETERS OF β-FORM

(a) Atomic coordinates (in fraction of cell edges) and their standard deviations (in 10^{-3} Å)

Atom	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$
Br	0.2332	1	0.0000	4	1.3365	1
O(1)	0.4526	10	0.3483	11	0.5382	9
O(2)	1.0444	11	−0.1778	12	−0.3723	11
N	0.5315	12	0.1497	12	0.4633	12
C(1)	0.3035	15	0.0676	15	1.1025	12
C(2)	0.3959	11	−0.0042	26	1.0269	11
C(3)	0.4489	12	0.0495	14	0.8514	12
C(4)	0.4079	13	0.1649	14	0.7586	12
C(5)	0.3139	16	0.2285	16	0.8374	14
C(6)	0.2560	14	0.1764	17	1.0052	14
C(7)	0.4660	14	0.2306	15	0.5804	13
C(8)	0.5923	14	0.2082	16	0.2959	13
C(9)	0.6762	14	0.1079	16	0.2107	13
C(10)	0.7443	14	0.1701	15	0.0347	13
C(11)	0.8177	13	0.0737	15	−0.0743	13
C(12)	0.9242	15	0.0523	16	−0.0019	14
C(13)	0.9986	14	−0.0327	16	−0.1028	14
C(14)	0.9629	15	−0.0967	15	−0.2797	13
C(15)	0.8535	14	−0.0796	17	−0.3510	13
C(16)	0.7839	11	0.0054	27	−0.2457	11
C(17)	1.0129	24	−0.2468	22	−0.5475	16

(b) Temperature factors in form of $\exp(-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{13}hl+\beta_{23}kl))$

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Br	0.0090	0.0177	0.0207	−0.0045	0.0098	0.0032
O(1)	0.0109	0.0116	0.0237	0.0034	0.0137	0.0023
O(2)	0.0102	0.0141	0.0324	0.0058	0.0147	0.0024
N	0.0093	0.0070	0.0309	−0.0020	0.0149	−0.0008
C(1)	0.0098	0.0104	0.0159	−0.0074	0.0054	−0.0064
C(2)	0.0066	0.0109	0.0229	−0.0022	0.0002	−0.0097
C(3)	0.0063	0.0106	0.0162	−0.0006	0.0030	0.0001
C(4)	0.0069	0.0076	0.0171	−0.0002	0.0047	−0.0038
C(5)	0.0099	0.0093	0.0258	0.0007	0.0109	−0.0001
C(6)	0.0076	0.0125	0.0260	0.0012	0.0112	−0.0014
C(7)	0.0071	0.0100	0.0219	−0.0004	0.0081	0.0004
C(8)	0.0073	0.0112	0.0188	0.0013	0.0079	0.0053
C(9)	0.0086	0.0115	0.0212	0.0030	0.0163	0.0059
C(10)	0.0080	0.0099	0.0201	0.0005	0.0087	0.0033
C(11)	0.0072	0.0106	0.0235	0.0002	0.0136	0.0027
C(12)	0.0090	0.0117	0.0248	−0.0021	0.0031	−0.0049
C(13)	0.0084	0.0118	0.0283	0.0038	−0.0054	−0.0049
C(14)	0.0090	0.0091	0.0188	−0.0012	0.0096	−0.0013
C(15)	0.0077	0.0140	0.0206	0.0020	0.0064	−0.0023
C(16)	0.0060	0.0139	0.0205	−0.0043	0.0078	0.0006
C(17)	0.0167	0.0116	0.0259	0.0061	0.0169	−0.0114

(c) Atomic coordinates and isotropic temperature factors for the hydrogen atoms

Atom	x	y	z	B	Atom	x	y	z	B
H(1)	0.427	−0.093	1.104	3.5	H(5)	0.527	0.045	0.477	4.3
H(2)	0.523	0.002	0.787	3.6	H(6)	0.616	0.318	0.346	4.3
H(3)	0.269	0.325	0.798	4.5	H(7)	0.535	0.239	0.177	4.0
H(4)	0.168	0.213	1.042	4.6	H(8)	0.641	0.007	0.189	4.3

H(9)	0.732	0.074	0.331	3.6	H(14)	0.804	−0.153	−0.447	3.7
H(10)	0.789	0.254	0.084	4.0	H(15)	0.703	0.004	−0.303	5.3
H(11)	0.688	0.216	−0.073	4.0	H(16)	0.975	−0.188	−0.667	4.0
H(12)	0.951	0.103	0.139	4.0	H(17)	0.925	−0.274	−0.532	4.0
H(13)	1.083	−0.050	−0.038	4.0	H(18)	1.090	−0.280	−0.633	4.0

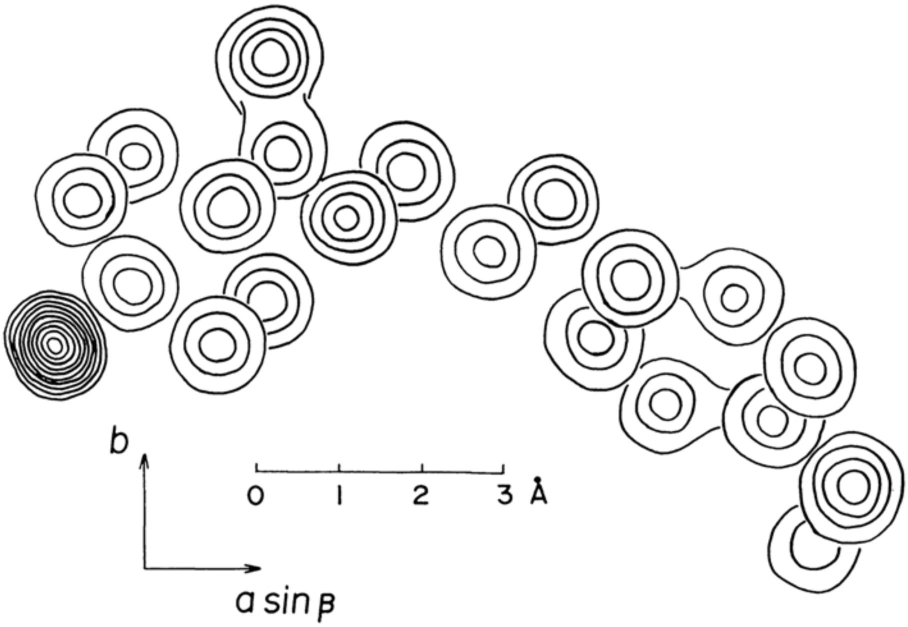


Fig. 2. The final electron density distribution of β-form.

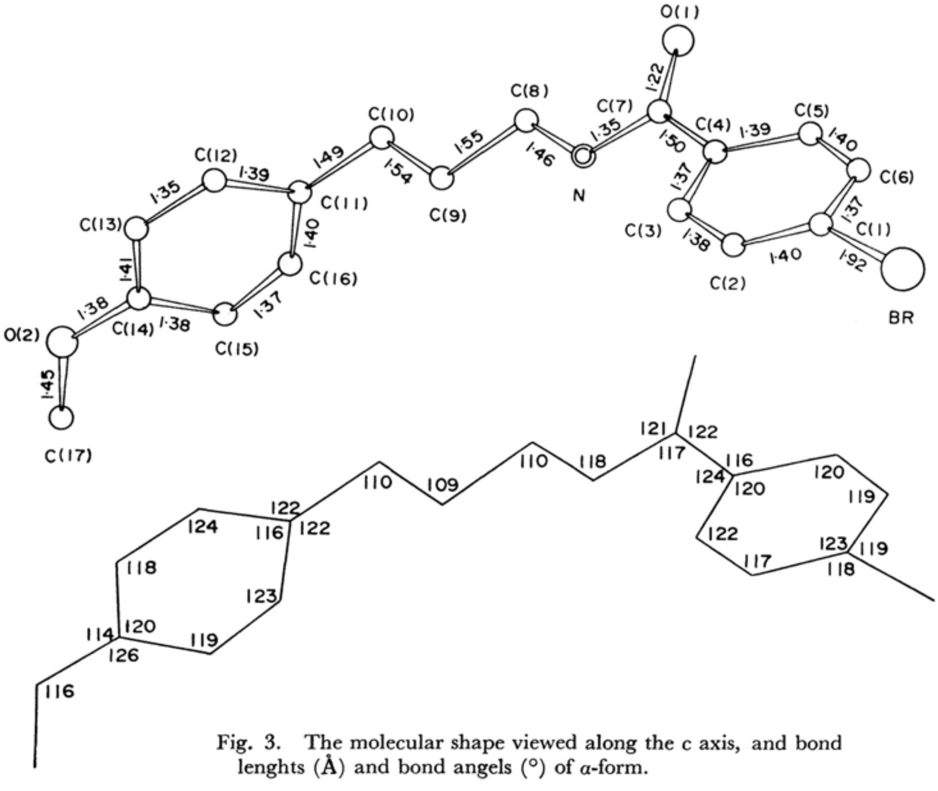


Fig. 3. The molecular shape viewed along the c axis, and bond lenghts (Å) and bond angels (°) of α-form.

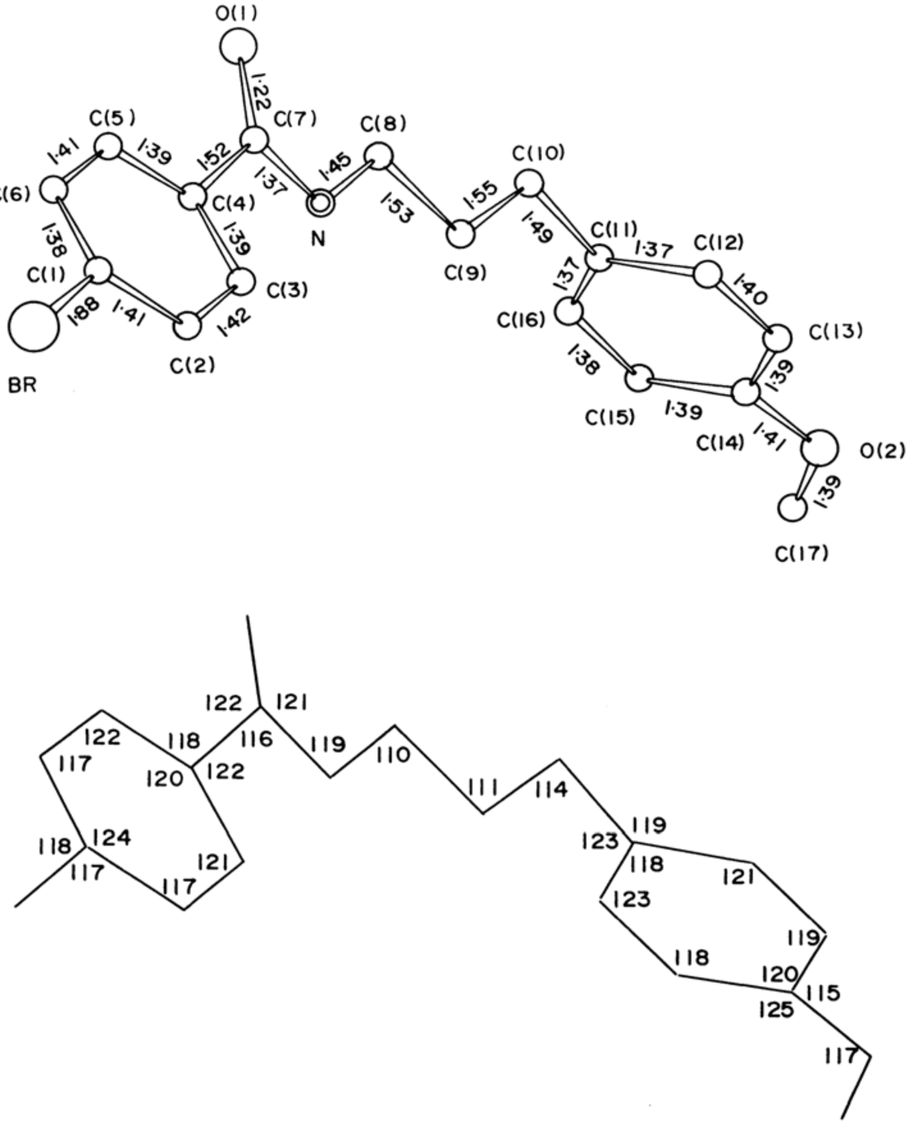


Fig. 4. The molecular shape viewed along the c axis, and bond lengths (Å) and bond angels (°) of β-form.

and from 1.01 to 1.81° in the α- and β-forms respectively. The smaller values of the estimated standard deviations in the α-form than in the β-form are considered to be due to the greater quantity of reflection data (2743 to 1474).

The atomic distances of the corrresponding bonds in the molecules of the two forms give very similar values. The differences of 0.05 Å in C(12)–C(13) and of 0.06 Å in C(17)–O(2) are not significant.

Concerning the 3-aminipropyl group, however, the internal rotation angles are slightly different from each other. Figure 5 illustrates a part of the molecule of each form projected on the best plane of the amide group. The values of the internal rotation angles are listed in Table 4. In Table 4, the internal rotation angles for a bond are defined as follows: looking from the right atom to the left, the clockwise rotation is taken as + and exact *trans* conformation, as 0°. The conformations of the propyl group in two forms are all *trans* in principle, but they show slight differences. First, the internal rotation angles about the C(4)–C(7) bond show a difference of 8.1°, the different inclination angle of the benzene ring to the amide plane

Table 4. Internal rotation angles

	C(4)—C(7)	——N	——C(8)	——C(9)	—C(10)	—C(11)
α-form	29.4	−3.4	− 4.2	−3.2	−2.0	89.6
β-form	21.3	2.3	−10.6	1.4	7.4	88.0

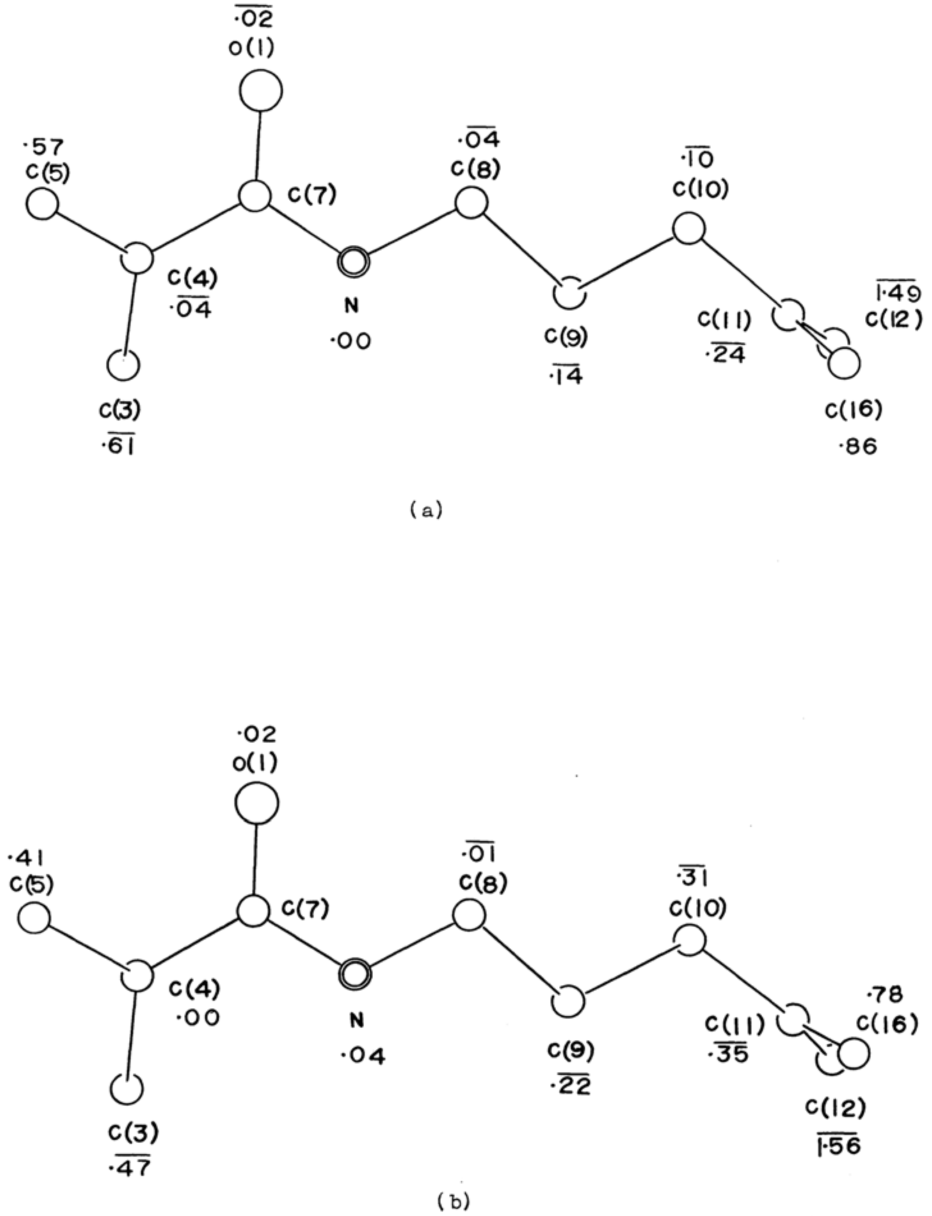
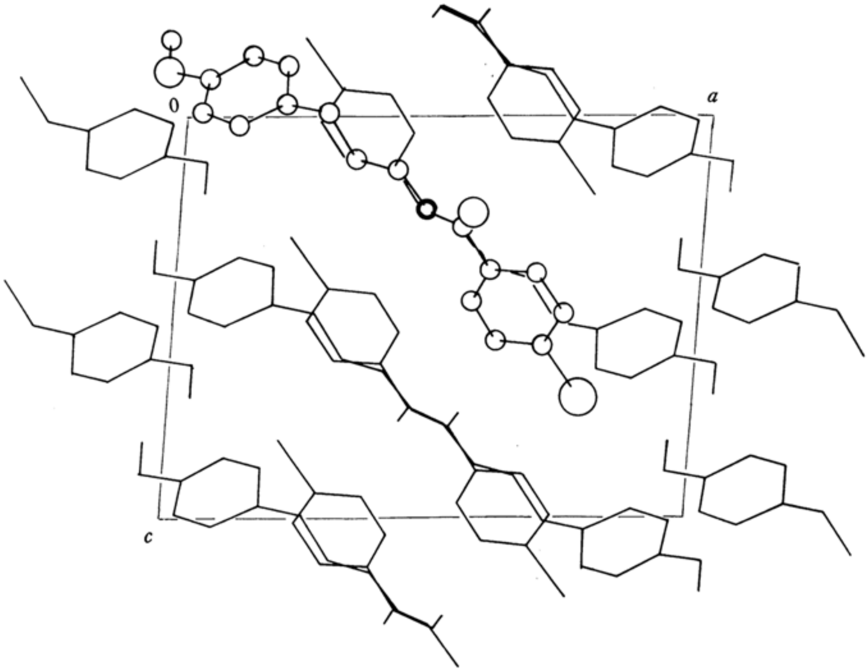


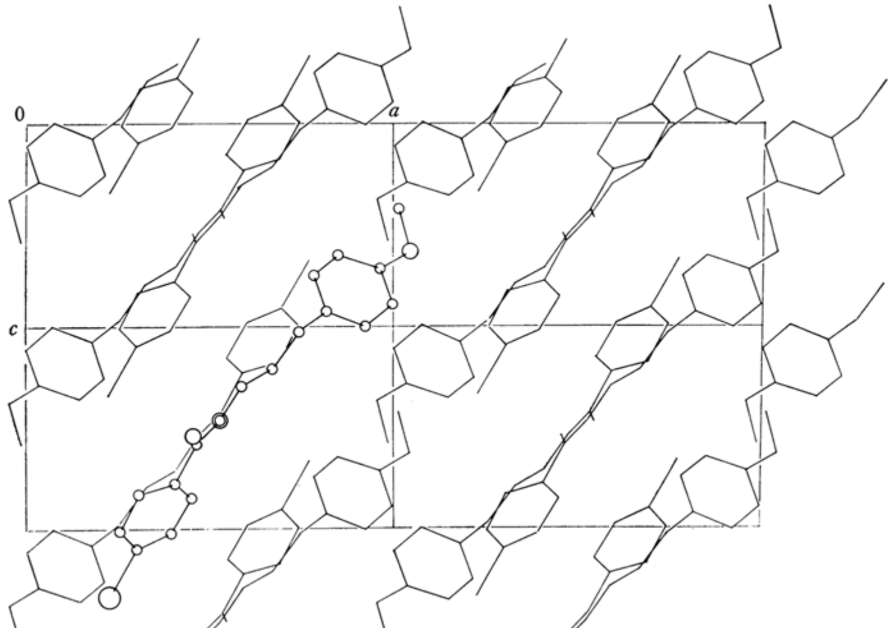
Fig. 5. The parts of the molecule projected on the best plane of the amide group.
(a) α-form; (b) β-form.
The figures on the names of atoms show the deviations from the plane.

results from this. Secondly, those about the N–C(8) and C(8)–C(9) bonds are different by some degrees. Therefore, the deviation of C(10) from the amide plane is different, as may be seen in Fig. 5. The angle about the C(9)–C(10) bond is different by 9.4° and somewhat releases the difference in the deviation of C(11) from the amide plane. Such a difference in the conformations of the two forms is considered to be due to interactions between adjacent molecules in the crystal.

The crystal structures of both forms projected along the *b* and *c* axes are shown in Figs. 6 and 7 respectively. In both forms the amide group of a molecule forms the hydrogen bond with that of the molecule related by the twofold screw axis parallel to the *b* axis. Thus, the belts of the molecules are formed by the hydrogen bonds. In the β-form the belts are packed together parallel to the *b* axis, but in the α-form the belts are packed antiparallel in the *b* direction. This difference is

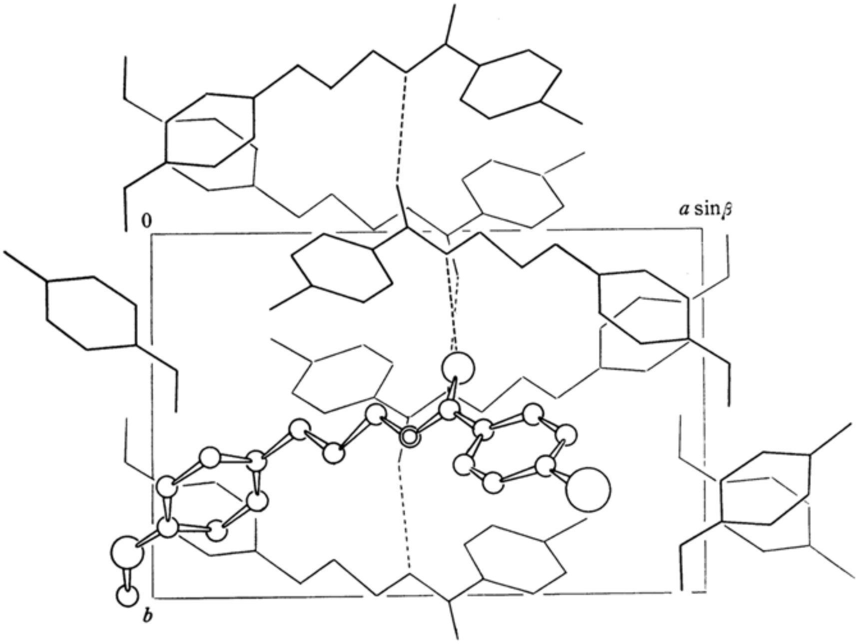


(a) α-form

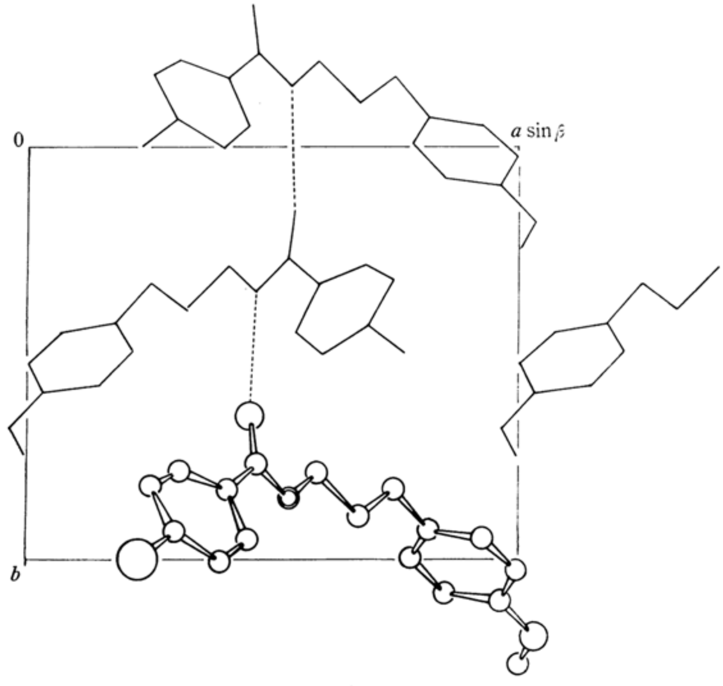


(b) β-form

Fig. 6. Arrangement of the molecules viewed along the *b* axis.



(a) α-form



(b) β-form

Fig. 7. Arrangement of the molecules viewed along the *c* axis.

TABLE 5. CLOSE CONTACTS OF ATOMS IN NEIGHBORING MOLECULES (Å)

α-form			β-form
	Equiv. 2		
O(1)–N	2.99	O(1)–N	3.03
O(1)–C(3)	3.53	O(1)–C(3)	3.47
O(1)–C(7)	3.95	O(1)–C(7)	4.03
O(1)–C(8)	3.81	O(1)–C(8)	3.81
O(1)–C(9)	3.48	O(1)–C(9)	3.45
C(5)–C(9)	3.91	C(5)–C(9)	3.82
C(5)–C(16)	3.99	C(5)–C(16)	4.04
C(6)–C(14)	4.14	C(6)–C(14)	3.92
C(6)–C(15)	3.50	C(6)–C(15)	3.59
C(6)–C(16)	3.57	C(6)–C(16)	3.69
C(8)–C(2)	3.70	C(8)–C(2)	3.58
C(8)–C(3)	3.66	C(8)–C(3)	3.59
C(10)–Br	3.85	C(10)–Br	4.12
C(10)–C(1)	3.84	C(10)–C(1)	4.12
	Equiv. 3		
C(11)–C(17)	3.79	C(11)–C(17)	3.68
C(12)–C(17)	3.80	C(12)–C(17)	3.66
C(13)–C(17)	3.83	C(13)–C(17)	3.67
C(14)–C(17)	3.76	C(14)–C(17)	3.70
C(15)–C(17)	3.68	C(15)–C(17)	3.76
C(16)–C(17)	3.68	C(16)–C(17)	3.74
	Equiv. 4		
O(1)–C(3)	3.95	Br–N	3.95
N–C(2)	3.71	Br–C(4)	3.83
C(2)–C(7)	3.55	Br–C(7)	3.94
C(2)–C(8)	3.99	N–C(16)	3.83
C(3)–O(1)	3.95	C(1)–N	3.68
C(3)–C(3)	3.46	C(1)–C(8)	3.92
C(3)–C(4)	3.60	C(2)–N	3.62
C(3)–C(7)	3.66	C(2)–C(8)	3.61
		C(2)–C(9)	3.72
		C(3)–C(8)	3.72
		C(3)–C(9)	3.62
		C(3)–C(10)	3.91
	Equiv. 5		
C(12)–C(12)	3.76	C(10)–O(2)	3.67
C(12)–C(13)	3.56	C(12)–O(2)	3.67
C(13)–C(13)	3.86		
	Equiv. 6		
O(1)–C(2)	3.63	O(1)–C(2)	3.67
	Equiv. 7		
Br–C(5)	3.74		
Br–C(6)	3.92		
C(2)–N	3.84		
C(12)–C(15)	3.79		
	Equiv. 8		
Br–O(2)	3.46		
Br–C(17)	3.77		

Designation of equivalent positions

	α-form	β-from
Equiv. 2	$2-x,\ 1/2+y,\ 1/2-z$	$1-x,\ 1/2+y,\ 1-z$
Equiv. 3	$1-x,\ 1/2+y,\ -1/2-z$	$2-x,\ 1/2+y,\ -1-z$
Equiv. 4	$2-x,\ 1-y,\ 1-z$	$x, y,\ 1+z$
Equiv. 5	$1-x,\ 1-y,\ -z$	$2-x,\ 1/2+y,\ -z$
Equiv. 6	$2-x,\ -y,\ 1-z$	$1-x,\ 1/2+y,\ 2-z$
Equiv. 7	$x,\ 1/2-y,\ 1/2+z$	
Equiv. 8	$1+x, y,\ 1+z$	

due to the absence or presence of the glide plane normal to the *b* axis in the β-form or α-form crystal respectively. The intermolecular approaches less than 4 Å are summarized in Table 5. These values are shown as the distances from the original molecule (x, y, z) to the equivalent molecule (*e. g.*, $\bar{x}, \bar{y}, \bar{z}$) related by the space group symmetry. The intermolecular contacts shown as Equiv. 2 in Table 5 are those between molecules related by the twofold screw axis (Fig. 7). The corresponding distances are all shown. Very similar contact distances are seen in two polymorphic forms.

The hydrogen bond distances are listed in Table 6 with estimated standard deviations and also with infrared absorption frequencies of the NH stretching band. It is well established that the stretching frequencies are lowered by the presence of hydrogen bonds and that the frequency shift is monotonic and approximately a linear function of the hydrogen bond distance. Though the difference between the two hydrogen bond distance is not fully significant, the lower frequency of the α-form corresponds to the shorter hydrogen bond distance, and *vice versa* in the β-form. This is in good agreement with Nakamoto's results.⁵⁾

TABLE 6. NH STRETCHING FREQUENCY AND HYDROGEN BOND DISTANCE

	ν(NH)	N···O distance
α-form	3323 cm^{-1}	2.988 ± 0.011 Å
β-form	3345 cm^{-1}	3.026 ± 0.014 Å

On the basis of the conformations of the 3-aminopropyl group determined above, and of those of the $-OCH_2CH_2O-$ group already reported,²,³⁾ a possible chain structure of the polyamide obtained by the condensation of 1,2-bis-[*p*-(3-aminipropyl)-phenoxy]ethane and adipic acid has been proposed.⁶⁾ The fiber period per repeating unit of this structure model is 26.4 Å, a value which agrees well with the observed value of 26.3 Å.

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