The Crystal and Molecular Structure of Benzanilide

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The crystal structure of benzanilide has been determined from Weissenberg photographs using Cu *Kα* radiations and refined to an *R* value of 0.075 for 766 independent reflections. The crystals are monoclinic, space group C2/c, $Z=4$, with $a=24.34(4)$, $b=5.325(3)$, $c=8.012(8)$ Å, $\beta=107.2(3)°$, $D_m=1.32$ and $D_x=1.321$ g cm^{-3}. Dihedral angle between the benzene rings is 62.6°, and each benzene ring makes dihedral angle of 31.3 and 31.6° with the plane of amido group as found in Kevlar and Nomex polymers. The molecules related by a ***b***-translation are linked together by N–H···O hydrogen bond [N···O 3.112(6), H···O 2.03 Å, N–H···O 157°] to form a chain along ***b***. The chains are held together primarily by dipole forces of carbonyl groups of the molecules related by inversion centers to form a sheet parallel to the *bc* plane. The sheets are stacked along ***a*** with disorder by van der Waals interactions.

The present work forms a part of studies on the relationship between molecular conformation and crystal structure of aromatic compounds containing amido group.[1)] One particular interest is in a comparison of the compounds in which two benzene rings are separated by two bonding atoms. Another aspect is of a model compound of the polymer chains in poly(*p*-phenyleneterephthalamide) (Kevlar) and poly(*m*-phenyleneisophthalamide) (Nomex). Their conformations have been explained to be governed primarily by torsion about the exocyclic bonds.[2—4)]

Experimental

Crystals were grown from an ethanol solution by slow evaporation as hexagonal plates with developed (100) and bounded by {001} and {011}. Systematic absences were *hkl* with $h+k$ odd, and *h*0*l* with *l* odd, hence the space group was Cc or C2/c. During the analysis Cc was ruled out. The density was measured by flotation in aqueous KI solution.

Crystal Data: Benzanilide, $C_{13}H_{11}NO$, $Mr=197.2$, mp 161—162 °C, monoclinic, space group C2/c, $a=24.34(4)$, $b=5.325(3)$, $c=8.012(8)$ Å, $\beta=107.2(3)°$, $V=992(3)$ Å^3, $D_m=1.32$, $D_x=1.321$ g cm^{-3}, $Z=4$, $\mu(\text{Cu }K\alpha)=6.89$ cm^{-1}, $F(000)=416$.

Intensity data were collected on Weissenberg photographs for the layers *h*0*l* to *h*4*l* by using a specimen of dimensions 0.3 × 2.0 × 0.4 mm. The intense reflections, particularly 002, were accompanied by diffuse streaks elongated along *a**. Intensities of 766 independent reflections were visually estimated and corrected for Lorentz and polarization factors and for spot shape. Inter-layer scaling was made according to the exposure time (about 40 h for each layer). Wilson's plot gave $B=6.99$ Å^2. Distribution of *E*-values preferred to centrosymmetrical space group.

Structure Determination and Refinement

The structure was solved from a Patterson map and refined by block-diagonal least-squares calculations. Analysis based on the space group Cc gave extraordinary values of bond lengths and angles even at the stage of *R* value of 0.087. Therefore the space group C2/c was adopted by assuming the disorder with occupancy factor 0.5 about the twofold rotation axis. A difference Fourier map (Fig. 1) at the stage of $R=0.10$ revealed the H atoms. For further refinements the H atoms were included with their thermal parameters ($B=6.99$ Å^2) and fixed positional parameters deduced from the geometry of the molecule. The weighting scheme used was: $w=1.0$ for $0<|F_o|\leq5.0$, $w=(5.0/|F_o|)^2$ for $|F_o|>5.0$. The final *R* value was 0.075 for 766 non-zero reflections.

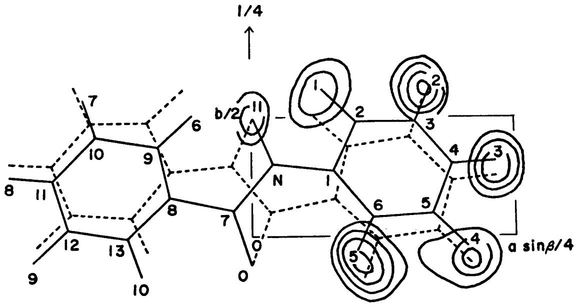

Fig. 1. Difference Fourier map at the stage of $R=0.10$. Contours are depicted for positive *x* region, at intervals of 0.1 *e* Å^{-3} starting at 0.1 *e* Å^{-3}. The molecular frames are based on the final positional parameters.

TABLE 1. THE FINAL POSITIONAL PARAMETERS (× 10^4) OF THE NON-HYDROGEN ATOMS WITH STANDARD DEVIATION IN PARENTHESES

For all the atoms the occupancy factor is 0.5.

	x	*y*	*z*
C(1)	771(2)	2764(10)	2581(6)
C(2)	985(3)	4802(11)	1826(7)
C(3)	1540(3)	4834(14)	1881(9)
C(4)	1901(2)	3029(12)	2742(7)
C(5)	1718(2)	1036(10)	3547(6)
C(6)	1140(2)	843(10)	3461(6)
C(7)	−175(2)	1083(11)	2435(7)
C(8)	−778(2)	1640(10)	2377(7)
C(9)	−904(2)	3817(9)	3197(6)
C(10)	−1497(2)	4215(11)	3132(7)
C(11)	−1906(2)	2396(12)	2224(8)
C(12)	−1757(3)	283(12)	1433(9)
C(13)	−1196(2)	−58(11)	1494(8)
N	188(2)	3020(9)	2533(6)
O	0	−1197(6)	2500

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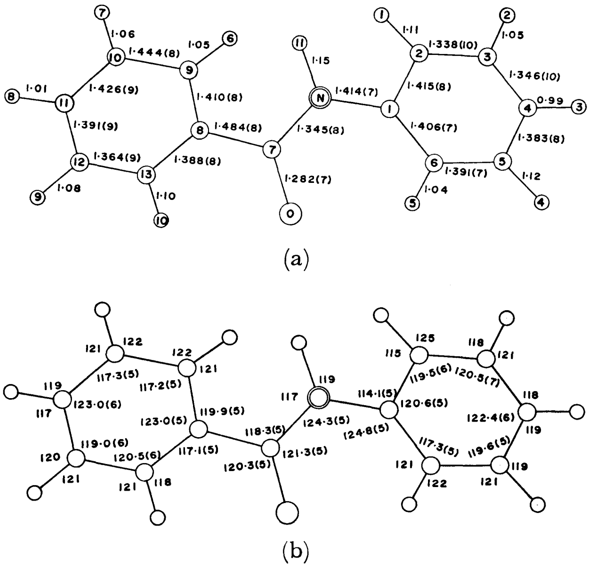
TABLE 2. THE POSITIONAL PARAMETERS ($\times 10^3$) OF THE HYDROGEN ATOMS

	x	y	z
H(1)	66	617	109
H(2)	169	633	128
H(3)	231	317	281
H(4)	204	−38	428
H(5)	99	−58	409
H(6)	−57	504	388
H(7)	−163	575	378
H(8)	−232	258	219
H(9)	−208	−104	75
H(10)	−106	−167	84
H(11)	0	500	250

Atomic scattering factors were taken from International Tables for X-Ray Crystallography.[5] The computations were carried out on an NEAC 2200-500 computer at the Okayama University Computer Center. The programs used were HBLS-5 and DAPH.[6] The final atomic parameters are listed in Tables 1 and 2.[7]

Results and Discussion

Molecular Structure. Bond lengths and angles are given in Fig. 2. The least-squares planes of the benzene rings and the amido group and the displacement of the atoms from the planes are listed in Table 3. The dihedral angles of two benzene ring-planes with respect to the amido group plane are 31.3 and 31.6°. These values are close to those in Kevlar and Nomex and consistent with the value calculated from the π-bond energy and the steric interaction.[4]



(a)

(b)

Fig. 2. The molecular structure: (a) bond lengths (Å) and numbering of atoms, (b) bond angles (°).

TABLE 3. THE LEAST-SQUARES PLANES AND DISPLACEMENTS (Å) OF THE ATOMS FROM THE PLANES $X=ax+cz\cos\beta$, $Y=by$, $Z=cz\sin\beta$.

(I) Amido group			
$0.0447X-0.0016Y-0.9992Z+1.9276=0$			
C(1)[a]	0.0083	H(11)	−0.0145
N[a]	−0.0182	C(2)	0.6152
C(7)[b]	0.0205	C(6)	−0.6317
O[a]	−0.0094	C(9)	−0.6525
C(8)[a]	−0.0008	C(13)	0.6319
(II) Benzene ring (1)			
$0.0626X-0.5203Y-0.8517Z+2.3766=0$			
C(1)[a]	0.0075	C(5)[a]	−0.0133
C(2)[a]	−0.0209	C(6)[a]	0.0098
C(3)[a]	0.0180	N	−0.1203
C(4)[a]	−0.0007	C(7)	0.4270
(III) Benzene ring (2)			
$0.1099X+0.5173Y-0.8488Z+1.3545=0$			
C(8)[a]	−0.0076	C(13)[a]	0.0091
C(9)[a]	0.0036	C(7)	−0.0390
C(10)[a]	−0.0008	N	0.5250
C(11)[a]	0.0018	O	−0.6643
C(12)[a]	−0.0059		

Dihedral angles (°) between the planes

(I) and (II)	(I) and (III)	(II) and (III)
31.3	31.6	62.6

a) Atoms used for the calculation of the planes.

It is interesting to compare the competitive interactions between the resonance effect of the benzene ring and the steric hindrance of attached atoms to the ring. Table 4 lists the torsion angles about the exocyclic bonds in the series of compounds, p-R–Ph–XY–Ph–R′-p, where the central part XY is such as CH=N, N=N, CH=CH (these are isoelectronic), and so on, and the substituents R and R′ are confined to relatively small groups for the sake of brevity A survey of the crystal structures of this series shows that the molecules in the crystals are classified into either centrosymmetrical or non-centrosymmetrical group, the present one belonging to the latter The former is visualized only when X and Y are identical or isoelectronic and R and R′ are also identical. The torsion angles are in general very small, suggesting the electronic delocalization extended over the central part between benzene rings. Large torsion angles occur only when X and Y are attached by bulky substituents (*e.g.* CN) or of sp^3 hybrid type missing conjugation. Even in this case parallelism of two benzene rings is maintained.

On the other hand, when X and Y or R and R′ are different the two benzene rings lose the parallelism and make in general large dihedral angle near 60°. In the non-centrosymmetrical group the torsion angles about each exocyclic bond differ greatly from each other in general. The disordered structure is, however, observed only when these torsion angles are similar to each other as in the present compound.

It is of interest to note that N-(p-chlorobenzylidene)-p-chloroaniline shows dimorphism where the Pccn form[8] belongs to the non-centrosymmetrical group while $P\bar{1}$ form[9] belongs to the centrosymmetrical one. They are conformational dimorphs, showing disorder about twofold rotation axis and inversion center respectively.

Crystal Structure. The crystal structure viewed along $\boldsymbol{c}$ is illustrated in Fig. 3. The four possible cells

TABLE 4. MOLECULAR CONFORMATIONS OF THE SERIES OF COMPOUNDS, *p*-R-Ph-XY-Ph-R′-*p*

The torsion angles (°) about X-C (aromatic) and Y-C (aromatic) bonds are denoted by $\widehat{XPh}$ and $\widehat{YPh}$ respectively, and the dihedral angles (°) between the benzene rings are by $\widehat{PhPh}$. The values were calculated based on the atomic coordinates in the literatures

Compound	R	XY	R′	Space group	*Z*	Disordered about	$\widehat{XPh}$	$\widehat{YPh}$	$\widehat{PhPh}$
Centrosymmetrical group									
(I)	Cl	CH=N	Cl	$P\bar{1}$	1	$\bar{1}$	0.1	−0.1	0
(II)	Cl	N=N	Cl	$P2_1/c$	2		1.0	−1.0	0
(III)	Br	CH=N	Br	$P2_1/a$	2	$\bar{1}$	2.2	−2.2	0
(IV)	Br	N=N	Br	$P2_1/c$	2		1.5	−1.5	0
(V)		CH=CH		$P2_1/a$	4[a]	$\bar{1}$	2.8	−2.8	0
							6.6	−6.6	0
(VI)	Me	CH=N	Me	$P2_1/c$	2	static positional disorder	3.5	−3.5	0
							6.6	−6.6	0
(VII)		N=N		$P2_1/a$	4[a]	$\bar{1}$	5.8	−5.8	0
(VIII)	Br	CF=CF	Br	Pccn	4		9.0	−9.0	0
(IX)	Me	N=N	Me	$P2_1/a$	2	1	11.2	−11.2	0
(X)		C(CN)=C(CN)		C2/c	4		25.2	−25.2	0
(XI)	Me	CH_2-CH_2	Me	I2/a	4		71.8	−71.8	0
(XII)		CH_2-CH_2		$P2_1/a$	2		72.7	−72.7	0
(XIII)		CF_2-CF_2		$P2_1/a$	2		85.1	−85.1	0
Non-centrosymmetrical group									
(XIV)	EtOOC	NO=N	COOEt	$P\bar{1}$	2		−1.5	1.5	0.4
(XV)	EtO	N=N	OEt	$P2_1/c$	4		6.7[b]	8.8[b]	2[b]
(XVI)	O_2N	CH=N	NMe_2	$P2_1/c$	4		−4.2	8.9	5.1
(XVII)	MeO	NO=N	OMe	$P2_1/a$	4		3.6	20.1	22.6
(XVIII)	Me_2N	NO=N		$P2_1/c$	4		2.1	31.3	32.6
(XIX)	Cl	CH=N	Cl	Pccn	4	2	26.5	26.5	49.6
(XX)	Me_2N	CH=N	NO_2	$P\bar{1}$	4[a]		10.3	41.4	52.9
							5.2	50.7	56.3
(XXI)		CO-O		$P2_1/c$	4		65.1	−9.8	55.7
(XXII)	MeO	CH_2-CO	OMe	$P2_1/c$	4		63.6	−0.8	62.2
(XXIII)		CO-NH		C2/c	4	2	29.4	37.3	62.6
(XXIV)		CH=N		$P2_1/c$	4		9.9	56.8	65.5
(XXV)	Me	CH=N	NO_2	$P2_1/c$	4		6.3	53.4	59.0
(XXVI)	HOOC	CH=N		$P2_1/c$	4		13.8	41.4	54.6

(I) *N*-(*p*-Chlorobenzylidene)-*p*-chloroaniline (metastable form).[9] (II) *trans*-*p*,*p*′-Dichloroazobenzene.[10] (III) *N*-(*p*-Bromobenzylidene)-*p*-bromoaniline.[11] (IV) *trans*-*p*,*p*′-Dibromoazobenzene.[12] (V) *trans*-Stilbene.[13] (VI) *N*-(*p*-Methylbenzylidene)-*p*-methylaniline (form III).[14] (VII) *trans*-Azobenzene.[15] (VIII) *p*,*p*′-Dibromo-α,α′-difluorostilbene[16] (IX) *p*-Azotoluene.[17] (X) *trans*-α,β-Dicyanostilbene.[18] (XI) 4,4′-Dimethyldibenzyl.[19] (XII) Dibenzyl.[20] (XIII) 1,2-Diphenyltetrafluoroethane.[21] (XIV) Ethyl *p*-azoxybenzoate.[22] (XV) 4,4′-Azodiphenetole.[23] (XVI) *p*-Nitrobenzylidene-*p*-dimethylaminoaniline.[24] (XVII) *p*-Azoxyanisole.[25] (XVIII) β-*p*-Dimethylaminoazoxybenzene.[26] (XIX) *N*-(*p*-Chlorobenzylidene)-*p*-chloroaniline (stable form).[8] (XX) *p*-Dimethylaminobenzylidene-*p*-nitroaniline.[24] (XXI) Phenyl benzoate.[27] (XXII) Deoxyanisoin.[28] (XXIII) Benzanilide (this work). (XXIV) Benzylidenaniline.[29] (XXV) *p*-Methylbenzylidene-*p*-nitroaniline.[29] (XXVI) Benzylideneaniline-*p*-carboxylic acid.[29]

a) The unit cell contains two kinds of molecules. b) Dihedral angles reported in the literature.

TABLE 5. FOUR POSSIBLE CELLS

Space group	Mode of sheet formation	Resulting sheet	Short contacts (Å) in the sheet C···H	Energy of dipole interactions (kcal/mol)	Mode of sheet stacking	Short contacts(Å) between the sheets		Interaction energy[a] (kcal/mol)
						H···H	C···H	
$P2_1/n$	$\bar{1}$	*A*	2.73, 2.76	−2.9	2_1	2.52	3.13	−32.1
$C\bar{1}$	$\bar{1}$	*A*			$\bar{1}$	2.39	3.02	−32.0
$P2_1/c$	*c*-glide	*B*	2.51, 2.54	−2.0	2_1	2.52	3.13	−31.5
Cc	*c*-glide	*B*			*n*-glide	2.39	3.02	−31.5

a) Intermolecular interaction energy for twelve nearest neighbors calculated by assuming the universal potential of Kitaigorodsky[30] for the intermolecular contacts smaller than 10 Å.

TABLE 6. CHARACTERISTIC FEATURES OF THE CHAINS OF AMIDO GROUPS RELATED BY A TRANSLATION

Compound	Space group	Dimension (Å) of axis along which the chain extends	N···O hydrogen bond length (Å)	Dihedral angle (°) between the amido group and benzene ring
(I)	$C2/c$	$b=5.325$	3.112	31.3
(II)	$P1$	$c=5.27$	—	30
(III)	$P2_1/n$	$b=5.19$[a]	—	30
(IV)	$P2_12_12_1$	$c=4.972$	2.868	39.8
(V)	Cc	$b=4.83$	2.954	42.4
(VI)	$P2_1$	$c=4.66$	3.050	46.4

(I) Benzanilide (this work). (II) Nomex.[4] (III) Kevlar.[4] (IV) 4-Chloro-dipropylacetanilide. (V) 2-Acetyl aminofluorenone (Haisa *et al.*, unpublished data). (VI) Phenylurea.[32]

a) The first setting is chosen.

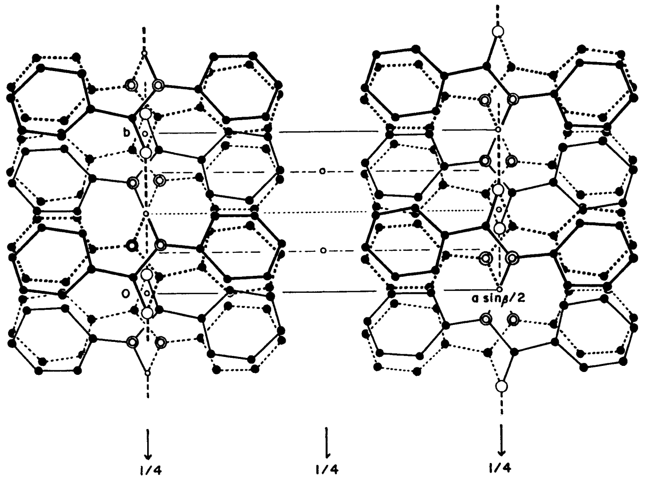
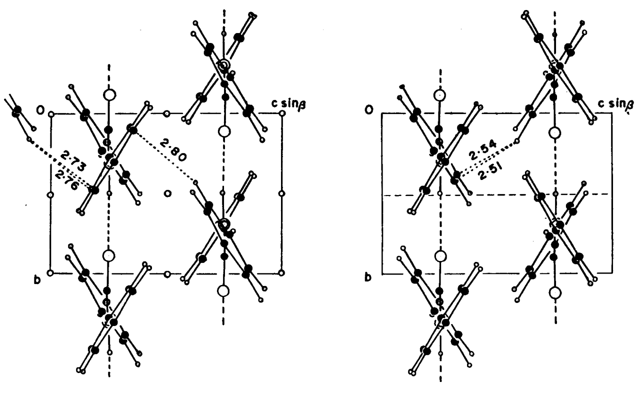


Fig. 3. The crystal structure viewed along ***c***. Arrangement of the molecules shown by solid lines corresponds to that in the $P2_1/n$ cell. The disordered molecules about twofold rotation axis are shown by dotted lines.



SHEET A SHEET B

Fig. 4. Two possible arrangements of the chains in the sheets. Short intermolecular contacts are shown by dotted lines, and hydrogen bonds by broken lines.

which generate the apparent space group $C2/c$ by adding the symmetry operation 2 for disordering are listed in Table 5. In the cells, the molecules related by a ***b***-translation are linked together by N–H···O hydrogen bond [N···O 3.112(6), H···O 2.03 Å, N–H···O 157, H···O=C 161°] to form a chain along ***b***. The chains are held together primarily by dipole interactions of the carbonyl groups of the molecules related by inversion centers or *c*-glide plane to form a sheet *A* or *B* parallel to the *bc* plane. Packing arrangement of the chains in the sheets is illustrated in Fig. 4. The sheets are stacked along ***a*** by van der Waals forces.

As seen from Table 5 and Fig. 4, the sheet *A* seems to prefer to the sheet *B* from the viewpoint of the molecular interactions. Concerning to the inter-sheet interactions, there are no significant differences among the stacking modes.

Disordered Structure. Disordering in the chain is not plausible, because it would result in an unexpectedly short intermolecular C···C contact of 3.03 Å. The disorder can be explained by a random stacking of the sheets *A* by two kinds of operations, 2_1 and $\bar{1}$, with an equal probability. In fact, the continuous streaks are elongated along a^* and no doubling of cell dimension *a* is observed.

The disordering of the present compound and the Pccn form of *N*-(*p*-chlorobenzylidene)-*p*-chloroaniline is similar in the axis about which disorder occurs, and the torsion angles around the central bond, but in the latter the disordering occurs by random arrangement of the molecular units.

Comparison of the Crystal Structure with the Related Compounds. The chains of amido groups related by a translation have been observed also in the related compounds as shown in Table 6. The dimension of the axis along which the chain extends becomes smaller with increasing the dihedral angle between the amido group and benzene ring. It is noted that the arrangement of the chains in the sheet (Fig. 4) is similar to that of Kevlar,[4] irrespective of the difference in the symmetry operation relating the chains.

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