

Fig. 3. Molecular packing of *N*-acetyl anthranilic acid.

those along the *b* direction are between C(2) and C(2<sup>III</sup>) at 3.186 Å and C(2) and C(3<sup>III</sup>) at 3.418 Å (see Table 2 for symmetry code). A drawing of the molecular crystal packing is shown in Fig. 3.

The crystal structure has interesting features relating to the possible mechanism of its TL. As is often the case for triboluminescent materials (Zink, 1975), it crystallizes in a polar noncentrosymmetric space group. The mechanism of TL emission proposed by Zink & Kaska (1973) suggests that TL can arise from excited molecular states populated by mechanical stress. If this mechanism can be applied to this com-

pound, its symmetry and crystal structure certainly are appropriate for the building of large dipole moments due to mechanical stress.

The crystal structure is consistent with its strong optical birefringency, as the average molecular plane is close to (100), as can be seen in Fig. 3.

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### Structure of the *D* Form of DL- $\alpha$ -Amino-*n*-butyric Acid

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**Abstract.** C<sub>4</sub>H<sub>9</sub>NO<sub>2</sub>, monoclinic, *I*2/a, *a* = 9.88 (2), *b* = 4.79 (1), *c* = 24.21 (4) Å,  $\beta$  = 102.3 (1)°, *V* = 1119.4 Å<sup>3</sup>, *D*<sub>c</sub> = 1.22 Mg m<sup>-3</sup>, *Z* = 8. The crystal structure of the high-temperature *D* form was refined by block-diagonal least-squares calculations to *R* = 0.083 for 922 visually estimated reflections. The terminal methyl group is statistically distributed in equal proportions over two positions, *trans* and *gauche* II to the N atom.

**Introduction.** Ichikawa & Iitaka (1968) have reported the crystal structure of the *A* form of the title compound. Akimoto & Iitaka (1972) found that crystals of the *A* form undergo a solid-phase transformation at 201 K to the low-temperature *C* form. Recently, Nakata, Takaki & Sakurai (1980) found that the *A* form undergoes another reversible solid-phase trans-

formation at about 337 K accompanied by characteristic diffuse scattering during the transition. In this paper we deal with the structure determination of the high-temperature *D* form, as part of an X-ray study of the phase transformation between the *A* and *D* forms.

Crystals of the *D* form were prepared from those of the *A* form by heating in a thermostat at 353 K for 2 d. Since thermal hysteresis was too large, cell dimensions and intensity data for the *D* form could be obtained at room temperature. All the crystals examined gave diffraction patterns showing various degrees of streaking along *c*\* on Weissenberg photographs. The intensities of diffuse streaks along row lines *hk*ζ with *h* + *k* odd varied from specimen to specimen, whereas those of diffuse streaks with *h* + *k* even were weak but unchanged. Therefore, a crystal showing very weak streaks with *h* + *k* odd was selected for the data

collection. The cell dimensions were determined from photographs taken with a Buerger back-reflection Weissenberg camera of which the camera constant was calibrated using Ag as a standard. Intensity data were collected from equi-inclination Weissenberg photographs for  $k = 0$  to 3 with Ni-filtered Cu  $K\alpha$  radiation. Intensities of 922 independent reflections were measured visually and corrected for Lorentz and polarization factors. No correction for absorption was applied.

Since the cell dimensions of the *D* form are very similar to those of the *A* form ( $P2_1/a$ ) except for the doubling of  $c$  and a small increase in  $\beta$ , and in addition the intensity distribution of the  $h0l$  reflections is approximately the same as that of the *A* form, the positional parameters derived from those of the *A* form were used as the starting parameters for the refinement. The atomic parameters for the non-hydrogen atoms except for the  $C_\gamma$  atom were refined by block-diagonal least-squares calculations (*HBL5 V*; Ashida, 1973). Subsequent Fourier and difference syntheses indicated that the  $C_\gamma$  atom is located in equal proportions at the two positions corresponding to *trans* (*T*) and *gauche* II (*GII*) to the N atom. Further refinements reduced  $R$  to 0.12 with the weighting scheme of the type  $w = 1 - \exp(-20s^2)$  with  $s = \sin \theta/\lambda$ . Five of the nine H atoms were then located on a difference map and were included in the least-squares calculations with fixed positional parameters and temperature factors of

$B = 3.0 \text{ \AA}^2$ . The final  $R$  value was 0.083. The atomic parameters are listed in Table 1† and bond lengths and angles in Table 2. All computations were carried out on an ACOS System 800 computer of the Computation Center of Osaka University.

**Discussion.** Molecules in a crystal of the *D* form show statistical disorder of the terminal  $C_\gamma$  atom at the two positions, *T* and *GII*. The averaged structure viewed down  $b$  is shown in Fig. 1. It consists of alternate stacking along  $c$  of two layers,  $Q$  and  $\bar{Q}$ , where  $\bar{Q}$  is related to  $Q$  by the translation  $\frac{1}{2}(a + b)$ . Within a layer, molecules are linked together by three types of  $\text{NH}\cdots\text{O}$  hydrogen bonds, of 2.82, 2.87 and 2.78 Å, to form a two-dimensional network. The very short inter-layer contacts  $C_\gamma(T) - C_\gamma(T)$  of 2.63 Å and  $C_\gamma(GII) - C_\gamma(GII)$  of 3.03 Å suggest that these contacts do not exist between stacks of layers. Moreover, the occurrence of the weak diffuse streaks along  $c^*$  indicates that the disorder in the positioning of the terminal  $C_\gamma$  atom is one-dimensional and hence each layer has an ordered arrangement of the  $C_\gamma$  atom.

A fundamental difference between the crystal structures of the *A* and *D* forms concerns the arrangement of layers along  $c$ . As described above, the *D* form consists of two layers  $Q$  and  $\bar{Q}$  with a stacking sequence  $Q\bar{Q}Q\bar{Q}\dots$ , while the *A* form consists of a layer, *P*, with a sequence  $PPP\dots$ . The structures of layers *P* and  $Q$  are essentially the same except that in layer  $Q$  the terminal  $C_\gamma$  atom is located in equal proportions at the two positions *T* and *GII*, while in layer *P* it is located at the three positions *T*, *G1* and *GII* with proportions 0.40, 0.36 and 0.24 respectively (Ichikawa & Iitaka, 1968). By comparing the structures of the *A* and *D* forms, the phase transformation from the *A* to the *D* form may be explained in terms of the translation  $\frac{1}{2}(a + b)$  of every second layer and

Table 1. Fractional atomic coordinates with e.s.d.'s

	<i>x</i>	<i>y</i>	<i>z</i>
O(1)	-0.262 (2)	-0.198 (3)	0.164 (3)
O(2)	-0.083 (2)	0.064 (2)	0.204 (2)
N	0.103 (2)	-0.307 (3)	0.186 (2)
C(1)	-0.136 (2)	-0.139 (3)	0.176 (3)
C(2)	-0.040 (2)	-0.332 (4)	0.152 (3)
C(3)	-0.040 (4)	-0.247 (8)	0.090 (4)
$C_\gamma(T)^*$	-0.163 (12)	-0.279 (20)	0.049 (12)
$C_\gamma(GII)^*$	0.037 (19)	-0.371 (21)	0.058 (16)
H(N1)	0.165†	-0.473	0.175
H(N2)	0.151	-0.111	0.180
H(N3)	0.105	-0.345	0.230
H(2)	-0.083	-0.532	0.161
H(3)	-0.039	-0.089	0.064

\* Occupancy factor 0.5.

† Average standard deviation of the H atom positions is 0.039.

Table 2. Bond lengths (Å) and angles (°)

O(1)–C(1)	1.253 (4)	C(2)–C(1)–O(1)	116.2 (3)
O(2)–C(1)	1.242 (4)	C(2)–C(1)–O(2)	117.8 (3)
N–C(2)	1.488 (4)	O(1)–C(1)–O(2)	126.0 (3)
C(1)–C(2)	1.526 (5)	C(3)–C(2)–C(1)	109.8 (4)
C(2)–C(3)	1.543 (9)	N–C(2)–C(1)	109.4 (3)
C(3)– $C_\gamma(T)$	1.401 (22)	C(3)–C(2)–N	108.6 (4)
C(3)– $C_\gamma(GII)$	1.333 (22)	$C_\gamma(T)$ –C(3)–C(2)	118.2 (10)
		$C_\gamma(GII)$ –C(3)–C(2)	123.9 (11)

† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34898 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

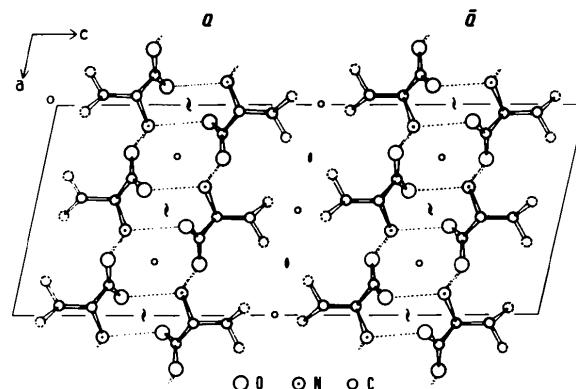


Fig. 1. The packing arrangement of layers  $Q$  and  $\bar{Q}$  viewed down  $b$ .

repositioning of the methyl groups, mainly from *G*I to *G*II.

It is very interesting that the *C* form (Akimoto & Iitaka, 1972) has the same space group (*I*2/*a*) as that of the *D* form and similarly consists of two layers, *R* and  $\bar{R}$ , with a stacking sequence  $R\bar{R}R\bar{R}\dots$  along *c*, where  $\bar{R}$  is related to *R* by the translation  $\frac{1}{2}(\mathbf{a} + \mathbf{b})$ . The structures of layers *Q* and *R* are also very similar to each other except that all the *C*<sub>γ</sub> atoms in layer *R* are at the positions corresponding to *trans T* to the N atom.

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**The disordered crystal structure of pentachlorothiophenol.** By G. WOJCIK, *Instytut Chemii Organicznej i Fizycznej, Politechnika Wrocławska, Wybrzeże Wyspińskiego 27, 50370 Wrocław, Poland* and G. P. CHARBONNEAU,\* Y. DELUGEARD and L. TOUPET, *Groupe de Physique Cristalline, ERA au CNRS n° 015, Université de Rennes, campus de Beaulieu, 35042 Rennes CEDEX, France*

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### Abstract

$C_6HCl_5S$ , monoclinic,  $P2_1/c$ ,  $a = 8.16$  (2),  $b = 3.85$  (1),  $c = 16.65$  (3) Å,  $\beta = 116.7$  (3)°,  $Z = 2$ ,  $D_c = 2.01$  Mg m<sup>-3</sup>,  $\mu(\text{Mo } K\alpha) = 1.686$  mm<sup>-1</sup>. The structure was refined to an *R* value of 0.061 for 1193 reflexions. The molecules are situated on centres of symmetry in the unit cell. The substituents of the benzene ring are equivalent and were represented in the refinement by pseudo-atoms with scattering factors  $f_{\text{sub}}$  equal to  $(5f_{\text{Cl}} + f_{\text{S}})/6$ .

### Introduction

Many penta- and hexasubstituted benzenes exhibit disordered structures in the crystalline state at room temperature (Tulinsky & White, 1958; Charbonneau, 1968; Fourme, Renaud & André, 1972; Messager & Blot, 1971). This work was conducted as part of an extensive study of disorder of substituted benzenes.

Pentachlorothiophenol (PCTP) was investigated by Brot & Darmon (1966) by means of NMR and dielectric methods. They found two types of reorientation movements in solid PCTP: reorientation of the proton in the SH group active above 100 K and reorientation of the whole molecule about its pseudo-hexagonal axis, active above 150 K. On the

other hand, PCTP displays the presence of a weak  $\lambda$  anomaly of the  $C_p$  curve in the temperature range 200–250 K (Radomska, 1978). Moreover, it is known that PCTP and the high-temperature phase of pentachlorophenol (Wojcik & Rohleder, 1976) form solid solutions over the whole concentration range (Radomski, Gola & Radomska, 1975). All this suggests that the high-temperature phase of PCTP may be disordered in a similar manner to that of pentachlorophenol. Commercial PCTP was purified by repeated sublimation under vacuum and by crystallization from CCl<sub>4</sub>. Pale-yellow single crystals were grown by slow evaporation from a CCl<sub>4</sub> solution. A needle of approximate dimensions 0.10 × 0.10 × 5 mm was used for data collection. The lattice constants and space group were determined from Weissenberg photographs. Intensity data were collected on an Enraf–Nonius three-circle automatic diffractometer with Zr-filtered Mo  $K\alpha$  radiation (scan range: 1.20°). Two control reflexions were measured after every 50 reflexions and their intensities showed no unusual fluctuations or decay with time. Absorption effects were neglected but corrections for the change in the column of the crystal bathed by the X-ray beam were applied to the measured intensities; 1193 independent reflexions were used in the structure determination.

Space-group requirements fix the positions of the two molecules at centres of symmetry, resulting in the apparent centrosymmetry of the molecules and the equivalence of the six substituents of the benzene. Since PCTP is isomorphous with dichlorodurene (Messager & Blot, 1971) these coordi-

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