

## References

- BARTLETT, M. W. (1972). *BLKLS*. A crystallographic block-diagonal least-squares program. ETH Zürich (Switzerland).
- FELCHT, U. & REGITZ, M. (1975). *Chem. Ber.* **108**, 2040–2054.
- JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
- MAIN, P., WOOLFSON, M. M., LESSINGER, L., GERMAIN, G. & DECLERCQ, J. P. (1974). *MULTAN 74. A Computer Program for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univ. of York, England.
- OLOVSSON, J. & JÖNSSON, P.-G. (1976). *The Hydrogen Bond*, Vol. II, edited by P. SCHUSTER, G. ZUNDEL & C. SANDORFY, pp. 391–456. Amsterdam: North-Holland.

*Acta Cryst.* (1980). **B36**, 502–504

## *N*-Acetylanthranilic Acid (*o*-Acetamidobenzoic Acid), a Strongly Triboluminescent Material

BY Y. P. MASCARENHAS, V. N. DE ALMEIDA\* AND J. R. LECHAT

*Instituto de Física e Química de São Carlos, CP 369, 13560 São Carlos, SP, Brazil*

AND N. BARELLI

*Instituto de Química de Araraquara, CP 174, 14800 Araraquara, SP, Brazil*

(Received 5 July 1979; accepted 9 October 1979)

**Abstract.**  $C_9H_9NO_3$ , orthorhombic, *Fdd2*,  $a = 10.845$  (9),  $b = 30.204$  (7),  $c = 10.575$  (4) Å,  $V = 3464$  Å<sup>3</sup>,  $D_x = 1.378$ ,  $D_m = 1.36$  Mg m<sup>-3</sup> (by flotation),  $Z = 16$ . The final  $R = 0.064$  for 799 reflexions and 118 variables. The molecules are interbonded by hydrogen bonds through the O(1) of the carboxyl group and O(3<sup>1</sup>) of the acetamide group forming chains on alternating planes approximately parallel to (301) and (301).

**Introduction.** The strong triboluminescence (TL) of *N*-acetylanthranilic acid and of many other compounds was observed by Zink, Hardy & Sutton (1976). From their experience they suggest that the presence or absence of TL is probably a function of the crystal structure. The crystal structure determination of the title compound was undertaken to provide the necessary information needed to test such a possibility.

*N*-Acetylanthranilic acid was obtained by refluxing anthranilic acid and acetic anhydride with subsequent hydrolysis. Colorless platelets of single crystals with melting point 461–462 K were obtained by recrystallization from a solution of acetic acid and water. The *b* direction is perpendicular and the *a* and *c* directions are parallel to the flat surface of the platelets. The optical study was carried out on a polarizing microscope and

the refractive indices, determined by the immersion method, are:

$$\begin{array}{ll} n_\alpha = 1.449 & 2V = 30^\circ \\ n_\beta = 1.726 & \text{optical character} = \text{biaxial } (-) \\ n_\gamma = 1.775 & \text{birefringency} = \alpha - \gamma = 0.32, \end{array}$$

where the  $\alpha$ ,  $\beta$  and  $\gamma$  directions correspond respectively to the crystal *b*, *a* and *c* directions. Intensities were measured at room temperature on an Enraf–Nonius CAD-4 diffractometer with the  $\theta$ – $2\theta$  scan technique up to  $\theta = 75^\circ$ , using graphite-monochromatized Cu  $K\alpha$  radiation and a scintillation counter. Systematic absences were found when the following conditions were not obeyed:  $hkl$ :  $h + k, k + l, (l + h) = \text{even}$ ;  $0kl$ :  $k + l = 4n$  ( $k, l = 2n$ );  $h0l$ :  $l + h = 4n$  ( $l, h = 2n$ );  $hk0$ :  $h, k = 2n$ ;  $h00$ :  $h = 4n$ ;  $0k0$ :  $k = 4n$ ;  $00l$ :  $l = 4n$ , from which the space group *Fdd2* was inferred. Of the 866 measured independent reflections, 799 with  $I > 3\sigma(I)$  were considered as observed, where  $\sigma(I)$  is the standard deviation of the intensity on the basis of counting statistics. As the crystal used was a triangular platelet with a largest dimension of 0.3 mm,  $\mu = 0.888$  mm<sup>-1</sup>, no absorption or extinction correction was made. The structure was solved with *MULTAN* (Germain, Main & Woolfson, 1971). Scattering factors were from Cromer & Waber (1974) for C, O, N and H. The coordinates of all atoms, except hydrogens, and the respective anisotropic temperature factors were refined by full-matrix least-squares minimization of

\* Present address: Instituto de Matemática e Física, Universidade Federal de Goiás, Caixa Postal 597, 74000 Goiânia, GO, Brazil.

$\sum w(F_o - F_c)^2$  with constant unit weight for all reflections up to an  $R$  ( $= \sum ||F_o| - |F_c|| / \sum |F_o|$ ) equal to 0.100. The coordinates of the hydrogens of the benzene ring and of the carboxyl and acetamide groups were calculated assuming trigonal geometry and  $X-H = 1.00$  Å; they were assigned the thermal parameters of the atoms to which they are attached. The H atoms were included in the calculations but not refined, giving a final  $R = 0.071$  for all reflections and  $R = 0.064$  for the observed reflections only. A difference Fourier map was calculated to locate the methyl H atoms, but no significant peaks were found. Final positional parameters are listed in Table 1;\* intramolecular bond lengths and angles are shown respectively in Figs. 1 and 2.

All atoms, except the methyl hydrogens lie on three planes whose equations, of the form  $AX + BY + CZ =$

\* Lists of structure factors, H atom positional parameters and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34838 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional atomic coordinates ( $\times 10^4$ ) with their e.s.d.'s in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>
O(1)	650 (5)	794 (1)	6252 (1)
O(2)	1138 (5)	1372 (1)	5052 (5)
O(3)	2531 (5)	1207 (2)	668 (4)
N	1902 (5)	1216 (2)	2712 (5)
C(1)	1424 (5)	640 (2)	4232 (5)
C(2)	1369 (6)	191 (2)	4554 (6)
C(3)	1666 (6)	-137 (2)	3698 (6)
C(4)	2010 (6)	-13 (2)	2482 (6)
C(5)	2092 (6)	427 (2)	2139 (6)
C(6)	1812 (6)	759 (2)	2998 (5)
C(7)	1069 (6)	976 (2)	5194 (6)
C(8)	2298 (6)	1415 (2)	1635 (6)
C(9)	2408 (7)	1907 (2)	1736 (7)

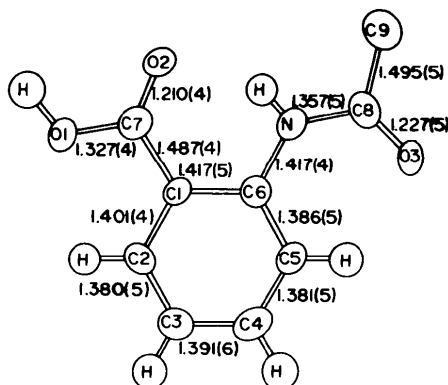


Fig. 1. Intramolecular bond lengths (Å) for *N*-acetyl-anthranilic acid with their e.s.d.'s in parentheses.

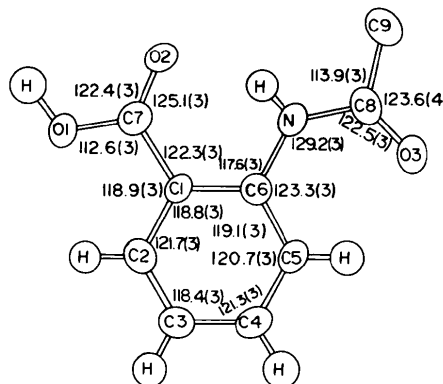


Fig. 2. Interatomic bond angles ( $^{\circ}$ ) for *N*-acetyl-anthranilic acid with their e.s.d.'s in parentheses.

$D$  (referred to the usual orthogonalized coordinates), are:

(1) The plane through atoms C(1), C(2), C(3), C(4), C(5), C(6), with  $A = -0.954$ ,  $B = -0.026$ ,  $C = -0.300$ ,  $D = -2.875$  Å.

(2) The plane through the atoms N, C(8), C(9) and O(3) of the acetamide group, with  $A = -0.948$ ,  $B = 0.101$ ,  $C = -0.301$ ,  $D = -2.451$  Å.

(3) The plane through the atoms C(7), O(1), and O(2) of the carboxyl group, with  $A = -0.928$ ,  $B = 0.011$ ,  $C = -0.372$ ,  $D = -3.088$  Å.

Planes (1) and (2) are planar within the largest standard deviation (0.008 Å). The dihedral angles between these three planes are (1)-(2), 7.3, (1)-(3), 4.9 and (2)-(3), 6.6°. The programs used in data reduction and refinement were *MULTAN* and those from Enraf-Nonius (1976). For the calculations of bond distances and angles a program written by Shiono (1971) was used and all the calculations were carried out on a PDP 11/45 computer.

**Discussion.** The hydrogen-bonding scheme consists of O(1)-H...O(3<sup>i</sup>) intermolecular bonds, forming molecular strips that run across alternating planes roughly parallel to the crystallographic planes (301) and (3̄01), and an intramolecular bond N-H...O(2). The corresponding distances and angles are given in Table 2. The closest intermolecular distances between parallel chains along the *c* direction are between N and O(3<sup>ii</sup>) at 3.436 Å and O(3<sup>ii</sup>) and C(8) at 3.399 Å, and

Table 2. Hydrogen-bonding distances (Å) and angles ( $^{\circ}$ ) with their e.s.d.'s in parentheses

<i>i</i>	<i>j</i>	<i>k</i>	$d_{ij}$	$d_{jk}$	$d_{ik}$	$\angle ijk$
O(1)	H(1)	O(3 <sup>i</sup> )	1.04	1.57	2.613 (4)	178
N	H(2)	O(2)	0.84	1.92	2.652 (4)	146

Symmetry code: (i)  $-\frac{1}{2} + x, \frac{1}{2} - y, \frac{3}{4} + z$ ; (ii)  $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{4} + z$ ; (iii)  $-x, -y, z$ .

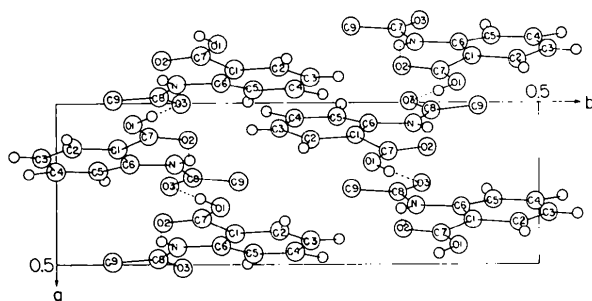


Fig. 3. Molecular packing of *N*-acetyl anthranilic acid.

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.

This work was supported by CNPq, FAPESP and FINEP.

#### References

- CROMER, D. T. & WABER, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, Table 2.2.B. Birmingham: Kynoch Press.
- Enraf-Nonius (1976). *Structure Determination Package*. Enraf-Nonius, Delft, Holland.
- GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* **A27**, 368–376.
- SHONO, R. (1971). Technical Report No. 49. Crystallography Department, Univ. of Pittsburgh, Pittsburgh, Pennsylvania, USA.
- ZINK, J. I. (1975). *Inorg. Chem.* **14**, 555–558.
- ZINK, J. I., HARDY, G. E. & SUTTON, J. E. (1976). *J. Phys. Chem.* **80**, 248–249.
- ZINK, J. I. & KASKA, W. C. (1973). *J. Am. Chem. Soc.* **95**, 7510–7512.

*Acta Cryst.* (1980). **B36**, 504–506

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

BY KAZUAKI NAKATA, YOSHITO TAKAKI AND KIICHI SAKURAI

*Department of Physics, Osaka Kyoiku University, Tennoji, Osaka 543, Japan*

(Received 6 September 1979; accepted 9 November 1979)

**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