

- DUCHAMP, D. J. & MARSH, R. E. (1969). *Acta Cryst.* B25, 5.
 FLORENCIO, F. & SMITH, P. (1970). *Acta Cryst.* B26, 659.
 FORNIÉS MARQUINA, J. M. (1969). Ph.D. Thesis, Univ. de Zaragoza.
 GÓMEZ BELTRÁN, F. & FORNIÉS MARQUINA, J. M. (1965). *Combustibles*, XXIV.
 GONZÁLEZ SÁNCHEZ, F. (1956). Ph.D. Thesis, Univ. de Zaragoza.
 LONG, R. E. (1965). UCLA Dissertation. Parts II and III.
 NOWACKI, W. & JAGGI, U. (1957). *Z. Kristallogr.* 109, 272.
 ROLLETT, J. S. & SPARKS, R. A. (1960). *Acta Cryst.* 13, 273.
 PEDONE, C., BENEDETTI, E. & ALLEGRA, G. (1970). *Acta Cryst.* B26, 933.
 SIM, G. A., ROBERTSON, J. M. & GOODWIN, T. H. (1955). *Acta Cryst.* 8, 157.

Acta Cryst. (1972). B28, 1677

The Crystal and Molecular Structure of δ -Pyrazincarboxamide

BY GISLE RØ AND HARALD SØRUM

Institutt for Røntgenteknikk, Universitetet i Trondheim, Norges Tekniske Høgskole, N 7034 Trondheim-NTH, Norway

(Received 29 November 1971)

δ -Pyrazincarboxamide crystallizes in the space group $P\bar{1}$ with unit-cell dimensions $a=5.728$ (2), $b=5.221$ (3), $c=9.945$ (6) Å, $\alpha=96.81$ (5), $\beta=97.27$ (4), $\gamma=106.22$ (4)°. The structure was first solved on the basis of a three-dimensional Patterson synthesis and later confirmed by the method of symbolic addition. Refinement was achieved by means of the full-matrix least-squares method, including anisotropic temperature factors and the use of a weighting scheme. The final value of the R_1 index is 0.061. The molecules are closely planar and connected by hydrogen bonds across the centres of symmetry to form dimers, which are held together in the lattice by van der Waals forces.

Introduction

Pyrazincarboxamide is known to appear in four different crystalline modifications, namely α -, β -, γ - and δ -pyrazincarboxamide (hereafter abbreviated α -, β -, γ - and δ -PCA) respectively, as shown by Tamura, Kuwano & Sasada (1961). The crystal structure of α -PCA was solved and refined by Takaki, Sasada & Watanabe (1960), and a report on a structure determination for β -PCA has recently been given by Rø & Sørurn (1972). While the molecular structures of these two forms show relatively small differences only, distinct differences are found in the molecular packing and especially in the intermolecular hydrogen bonds. Some preliminary results on the γ and δ forms were given by Tamura & Kuwano (1962), by comparing the infrared absorption spectra of the four crystalline modifications. Takaki (1965) used an ellipsoid-model approach to the determination of the crystal structure of γ -PCA, but no detailed structure determination has yet appeared for the γ and the δ forms of PCA. The present paper reports the results of a structure determination of δ -PCA.

Experimental

Crystals of δ -PCA were obtained by recrystallization of commercial PCA in a mixture consisting of one

part of hexane and one part of absolute ethanol. The crystals were transparent plates showing a pronounced cleavage plane identified later as the (012) plane. The crystal chosen for the structure determination was a rectangular plate having the dimensions $0.12 \times 0.20 \times 0.04$ mm. The crystallographic a axis was mounted along the φ axis of a Picker FACS-1 four-circle automatic diffractometer and the cell dimensions together with the calculating matrix were refined by the method of least squares using Busing and Levy's notation. Twelve strong reflexions at high 2θ values were used in the refinement. The crystallographic data are:

δ -pyrazine-2-carboxamide;
 $C_5H_5N_3O$; F.W. 123.11; m.p. 188°C;
 Triclinic; $Z=2$; $\lambda(\text{Cu } K\alpha_1)=1.5405$ Å;

$$\begin{aligned} a &= 5.728 \pm 0.002 \text{ \AA} \\ b &= 5.221 \pm 0.003 \\ c &= 9.945 \pm 0.006 \\ \alpha &= 96.81 \pm 0.05^\circ \\ \beta &= 97.27 \pm 0.04 \\ \gamma &= 106.22 \pm 0.04. \end{aligned}$$

Volume of the unit cell $V=279.58$ Å³;
 Density, calculated with $Z=2$: $D_x=1.462$ g.cm⁻³;
 Absorption coefficient for $\lambda(\text{Cu } K\alpha)$ ($=1.5418$ Å):
 $\mu=9.25$ cm⁻¹.
 Space group $P\bar{1}$. $F(000)=128$.

The collection of intensity data was based on the application of the $2\theta/\theta$ scan method using the symmetrical A setting with an upper limit of $2\theta=128^\circ$. The complete data set thus obtained consisted of 928 independent reflexions. The 100 and 012 reflexions were used as standards and were remeasured after every 20 reflexions. They both showed a linear decrease in intensity of about 13% during the time used for the data collection. The structure factors were derived from the measured intensities by means of a data reduction program, which also corrected for the reduction in the integrated intensities of the standards, and introduced the Lorentz and polarization factor corrections simultaneously. The value of μR_{\max} is 0.11 and no absorption corrections were made.

E statistics strongly indicate a centric unit cell, as may be seen from a comparison of the following values.

	δ -PCA	Centric	Acentric
$\langle E \rangle$	0.758	0.798	0.886
$\langle E^2 - 1 \rangle$	1.110	0.968	0.736
$\langle E ^2 \rangle$	1.038	1.00	1.00
$ E > 3.0\%$	1.62	0.27	0.01
$ E > 2.0\%$	4.53	4.55	1.83
$ E > 1.0\%$	25.36	31.73	36.79

Determination of the structure

The structure of β -PCA was conveniently solved by using the symbolic addition procedure, and attempts were therefore first made to solve the structure of δ -PCA by the application of the same method. The E statistics showed a fairly high degree of symmetry which is considered to be favourable for the sign deter-

mination. 123 structure factors with $|E| > 1.5$ were selected, and 6 of these having a suitable value of $|E|$ and many Σ_2 relations were given a sign or a letter symbol as follows:

h	k	l	Chosen sign or symbol	$ E $ value	Final sign
2	$\bar{3}$	6	+	4.30	-
3	2	$\bar{5}$	+	2.98	-
5	$\bar{2}$	$\bar{2}$	+	4.92	+
5	$\bar{1}$	0	+A	4.87	+
6	$\bar{3}$	$\bar{4}$	+B	2.20	+
3	1	$\bar{1}$	+C	2.20	+

Using the program *SYMBOL* and the probability formula according to Cochran & Woolfson (1955)

$$P_+(h) \simeq \frac{1}{2} + \frac{1}{2} \tanh(\sigma_3 \cdot \sigma_2^{-3/2} |E_{\bar{h}}| \sum_k E_{\bar{k}} \cdot E_{\bar{h}-\bar{k}})$$

and rejecting all signs with $P_+ < 0.97$ gave a symbol, letter or combination of letters for 114 additional structure factors. The letter distribution indicated

$$+A = + \text{ or } -, +B = + \text{ or } - \text{ and } +C = - \text{ or } +.$$

Nine different models, including an attempt to determine the sign of the $0\bar{2}\bar{4}$ reflexion by means of the Σ_1 relation, were tried. None of the initially chosen sign combinations led, however, to a reasonable structure in this case, and this way of approach was consequently abandoned. Instead a three-dimensional Patterson map along the b axis was calculated. The interpretation of this map was based on the assumption of the existence of dimers in the structure, having dimeric contacts of approximately 2.90 Å across the centres of symmetry,

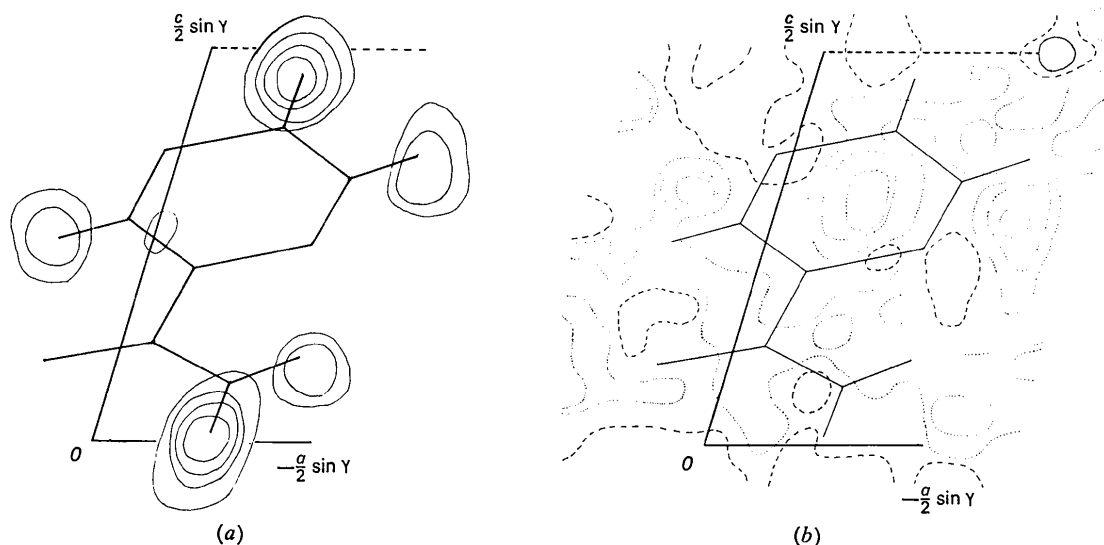


Fig. 1. Difference maps for δ -PCA. (a) Shows the difference map calculated at the stage of refinement where $R_1 = 8.5\%$ for the determination of the hydrogen positions. Heights of maxima are: H(3) 0.369, H(5) 0.616, H(6) 0.347, H(8') 0.376 and H(8'') 0.529 e.Å⁻³. (b) Shows the final difference map. The zero contour is shown by dashed lines, negative contours by dotted lines and positive contours by full lines at intervals of 0.07 e.Å⁻³, and represents average values of the three Fourier map sections closest to the atom in question.

as already found in the structure of α - and β -PCA. A set of maxima corresponding to interatomic vectors in the (012) plane was then easily interpreted, and a complete trial structure, comprising all atoms except the hydrogen atoms, was derived. This trial structure showed satisfactory convergence on refinement.

It has been verified after the structure determination was completed, that the chosen sets of reflexions and sign combinations, which were initially tried for the symbolic addition procedure, were not favourable ones. Another starting set (see final sign in the Table above) could now be found which led unequivocally to the same structure as that derived from the Patterson map. This may give an additional confirmation of the structure obtained.

Refinement of the structure

The structure of δ -PCA was refined by means of a full-matrix least-squares refinement program minimizing the function $\sum w(|F_o| - K|F_c|)^2$. The atomic scattering factors for C, N and O were those given by Doyle & Turner (1968), and for H by Stewart, Davidson & Simpson (1965). In the first stages of the least-squares refinement the atomic scattering factor of carbon was used for all the heavier atoms. The first three refinement cycles lowered the R_1 index from $R_1 = 55.0\%$ to $R_1 = 38.2\%$, the R_1 index being defined, as usual, by $\sum ||F_o| - K|F_c|| / \sum |F_o|$. A sharpened Fourier synthesis based on 129 structure factors with $|E| > 1.5$ gave only slight changes of the atomic positions. Before continuing the least-squares refinement all the unobserved reflexions and also those corresponding to $\sigma(F_o) > 0.5$ were removed from the data set, reducing the number of reflexions included from 928 to 595. In the following refinement cycle the R_1 index was reduced to $R_1 = 20.2\%$. Refinement of atomic coordinates and isotropic temperature factors of all atoms except hydrogen

simultaneously converged at a value of $R_1 = 18.0\%$. It was possible at this stage to distinguish between the heavier atoms by an inspection of the B values, and refinement with individual scattering factors for C, N and O gave a value R_1 of 14.9% . The following introduction of anisotropic temperature factors resulted in a further reduction to a value of $R_1 = 8.5\%$.

A difference map was calculated at this stage, and the positions of the five hydrogen atoms appeared in this map as dominant maxima, having peak densities ranging from 0.37 to 0.62 e.Å⁻³. The refinement of all atomic coordinates and thermal vibration parameters, including those of the hydrogen atoms, lowered the R_1 index to a value of $R_1 = 6.2\%$. The strongest reflexion 012 was omitted during this refinement because the difference $F_o - F_c = -8.50$ indicated a strong influence of extinction for this reflexion. A final cycle of refinement was carried out using the weighting scheme proposed by Cruickshank (1965):

$$w_1 = (0.0051|F_o|^2 - 0.057|F_o| + 1.16)^{-1} \text{ for } |F_o| < 10$$

and

$$w_2 = (0.022|F_o| + 0.84)^{-1} \text{ for } |F_o| \geq 10.$$

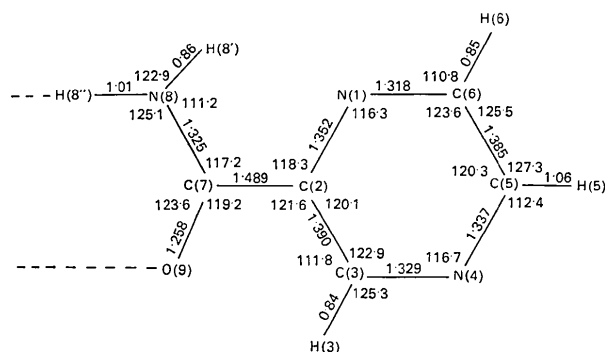


Fig. 2. Bond lengths (Å) and bond angles (°) in δ -PCA.

Table 1. Atomic coordinates and thermal vibration parameters of δ -PCA

The thermal vibration parameters are defined by the expression:

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

The atomic coordinates and β values for the non-hydrogen atoms are multiplied by 10^4 and the atomic coordinates for the hydrogen atoms by 10^3 .

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
N(1)	3414 (6)	5757 (9)	-2513 (5)	128 (13)	512 (24)	138 (7)	146 (14)	53 (7)	141 (10)
C(2)	1116 (8)	4882 (10)	-2221 (5)	177 (15)	297 (22)	84 (6)	57 (15)	30 (8)	32 (9)
C(3)	-742 (8)	5810 (11)	-2824 (6)	110 (16)	450 (28)	129 (8)	109 (17)	36 (9)	106 (12)
N(4)	-375 (7)	7570 (9)	-3694 (5)	173 (13)	505 (25)	131 (6)	152 (15)	55 (7)	132 (10)
C(5)	1910 (8)	8460 (11)	-3962 (5)	231 (19)	438 (28)	110 (7)	145 (18)	65 (9)	111 (12)
C(6)	3760 (9)	7535 (13)	-3360 (6)	158 (16)	587 (32)	143 (8)	162 (19)	72 (9)	174 (14)
C(7)	638 (8)	2885 (10)	-1262 (5)	206 (16)	280 (21)	96 (6)	39 (15)	29 (8)	53 (9)
N(8)	2539 (8)	2153 (10)	-719 (5)	226 (16)	388 (23)	119 (6)	109 (15)	112 (9)	32 (8)
O(9)	-1510 (5)	1990 (7)	-1006 (4)	171 (12)	392 (17)	134 (5)	71 (11)	55 (6)	98 (8)
	x	y	z	$B(\text{Å}^2)$					
H(3)	-210 (12)	510 (12)	-258 (6)	6.7 (1.7)					
H(5)	206 (7)	985 (8)	-466 (4)	2.2 (0.9)					
H(6)	510 (12)	819 (8)	-365 (6)	6.8 (1.7)					
H(8')	381 (13)	279 (13)	-108 (7)	7.1 (1.9)					
H(8'')	245 (9)	76 (10)	-9 (5)	3.9 (1.1)					

The final value of the R_1 index is 6.1%. A reduction of the 'square fit' from a value of 1.26 to 1.14, with simultaneous reductions in the standard deviations, especially for the hydrogen atoms was observed in the final refinement cycle.

A plot of the difference maps is shown in Fig. 1. The atomic coordinates and thermal vibration parameters for δ -PCA are given in Table 1 together with their estimated standard deviations. The observed and calculated structure factors are listed in Table 2.

Table 2. Observed and calculated structure factors for δ -PCA

The columns are $k, l, |F_o|$ and F_c .

Table with multiple columns containing numerical data for structure factors. The columns are labeled k, l, |F_o|, and F_c. The data is organized into several sections, some with headers like '***** HZ *****' and '***** HZ A *****'. The values range from approximately -10 to 10 for k and l, and from -10 to 10 for |F_o| and F_c.

Discussion

Molecular structure

The values of the bond lengths and bond angles of δ -PCA with their estimated standard deviations are given in Table 3, and shown schematically in Fig. 2. All bond lengths between the heavier atoms except those involving N(8) or O(9) were corrected for thermal motion using the libration correction method proposed by Cruickshank (1956).

Table 3. Bond lengths and bond angles of δ -PCA

The standard deviation is set three times higher than the e.s.d. value.

	Uncorrected	Corrected
N(1)–C(2)	1.348 Å	1.352 (3) Å
C(2)–C(3)	1.387	1.390 (3)
C(3)–N(4)	1.328	1.329 (4)
N(4)–C(5)	1.333	1.337 (3)
C(5)–C(6)	1.382	1.385 (3)
C(6)–N(1)	1.317	1.318 (4)
C(2)–C(7)	1.488	1.489 (4)
C(7)–N(8)	1.325 (3)	
C(7)–O(9)	1.258 (3)	
C(3)–H(3)	0.84	
C(5)–H(5)	1.06	
C(6)–H(6)	0.85	
N(8)–H(8')	0.86	
N(8)–H(8'')	1.01	
H(8'')–N(8)–H(8')	122.9°	
H(8'')–N(8)–C(7)	125.1	
H(8')–N(8)–C(7)	111.2	
O(9)–C(7)–N(8)	123.6 (3)	
N(8)–C(7)–C(2)	117.2 (4)	
C(2)–C(7)–O(9)	119.2 (4)	
C(7)–C(2)–N(1)	118.3 (4)	
C(7)–C(2)–C(3)	121.6 (4)	
N(1)–C(2)–C(3)	120.1 (3)	
C(2)–C(3)–N(4)	122.9 (4)	
C(2)–C(3)–H(3)	111.8	
H(3)–C(3)–N(4)	125.3	
C(3)–N(4)–C(5)	116.7 (4)	
N(4)–C(5)–C(6)	120.3 (3)	
N(4)–C(5)–H(5)	112.4	
H(5)–C(5)–C(6)	127.3	
C(5)–C(6)–N(1)	123.6 (4)	
C(5)–C(6)–H(6)	125.5	
H(6)–C(6)–N(1)	110.8	
C(6)–N(1)–C(2)	116.3 (4)	
C(5)–C(2)–C(7)	179.2 (4)	

The average value of the C–N bonds within the pyrazine ring of δ -PCA is 1.334 Å, agreeing with the value, also 1.334 Å, found in β -PCA. There is, however, a distinct difference between the δ and the β -form regarding the C–N bonds of the ring. In β -PCA the spread of the values for individual C–N bonds from the average value is at most 0.001 Å, which is considered to be insignificant. In δ -PCA, on the contrary, the individual bonds have values ranging from 1.318 Å for the C(6)–N(1) bond to 1.352 Å for the N(1)–C(2) bond (see below), and they compare well with the corresponding bond lengths found in α -PCA by Takaki *et al.* (1960), with the exception of the C(6)–N(1)

bond, which is found to be 1.356 Å in α -PCA. The average value of the C–C bond lengths within the pyrazine ring is found to be 1.388 Å and slightly longer than the corresponding values for α -PCA and β -PCA: 1.383 and 1.385 Å respectively.

It is of interest to compare the bond lengths of the amide group of δ -PCA with those found previously for α -PCA, β -PCA and picolinamide (Takano, Sasada & Kakudo, 1966). The amide bond lengths for these four compounds are as follows.

	C(2)–C(7)	C(7)–N(8)	C(7)–O(9)
δ -PCA	1.489 Å	1.325 Å	1.258 Å
α -PCA	1.503	1.312	1.244
β -PCA	1.513	1.327	1.231
picolinamide	1.515	1.330	1.241

It may be seen from these values that there are distinct differences between δ -PCA and β -PCA as regards the C(2)–C(7) and the C(7)–O(9) bonds, and that these differences are even more pronounced than in the case of α -PCA and β -PCA. Rø & Sørurn (1972) assumed in comparing the bond lengths of α -PCA and β -PCA that the shorter C(2)–C(7) bond and longer C(7)–O(9) bond of α -PCA could indicate that the resonance between the amide group and the pyrazine ring, giving some double bond character of the C(2)–C(7) bond, is stronger in α -PCA than in β -PCA. On this assumption the bond lengths obtained for δ -PCA seem to indicate an enhanced resonance between the amide group and the pyrazine ring in the structure of δ -PCA compared with that of α -PCA. It is furthermore likely that the observed spread in the values of the C–N bond lengths, and partly also for the C–C bonds (mentioned above), is related to this apparent resonance system. Thus, it may be seen from Fig. 2. that the C(2)–N(1) bond (1.352 Å) adjacent to the C(7)–C(2) bond is somewhat lengthened, compared with the average C–N bond value of the ring (1.334 Å), whereas the next nearest bond C(6)–N(1) is shortened (1.318 Å). The same effect may be present, but less pronounced, for the other branch, where the nearest bond C(2)–C(3) is slightly longer (1.390 Å) than the average C–C distance (1.388 Å), while the next nearest bond C(3)–N(4) is a little shorter (1.329 Å) than the average C–N distance of the pyrazine ring. The observations of Tamura & Kuwano (1962) on the infrared absorption spectra of the four modifications of PCA, showing that the C=O bonds have a different construction in these modifications, lend some support to this explanation of the differences in the bond lengths. The C(7)–N(8) bond length of δ -PCA is probably significantly longer than that in α -PCA, and agrees better with the values found for β -PCA and picolinamide. The value of 1.325 Å for the C(7)–N(8) bond is also in good agreement with that found in cyclopropancarboxamide by Long, Maddox & Trueblood (1969) (1.328 Å) and in acetamide by Hamilton (1965) (1.334 Å).

The C–H and the N–H bond lengths in δ -PCA are

on average 0.92 and 0.94 Å respectively, and these values are not significantly different from the corresponding values for α -PCA and β -PCA. The mean values of the C–N–C and the N–C–C bond angles of the pyrazine ring found for δ -PCA are 116.5 ± 0.4 and $121.7 \pm 0.4^\circ$ respectively, which are close to those found in α -PCA (115.8 and 122.1°) and in β -PCA (116.2 and 121.9°). Chatar Singh (1965) found a value of $115.7 \pm 0.2^\circ$ for the C–N–C angle as a weighted mean value for six-membered heterocyclic compounds without extra-annular attachment to the ring nitrogen. Sasada, Takano & Kakudo (1964) report a mean value of 121.1° for seven N–C–C bond angles of pyridine rings. There is a close resemblance between corresponding individual values of the bond angles in the α , β and δ modifications of PCA. This applies also to the bond angles found in the amide group of the three different forms.

The C(7) carbon atom of the carboxamide group of δ -PCA lies very close to the plane of the pyrazine ring, since the value of the angle C(5)–C(2)–C(7) is found to be $179.2 \pm 0.4^\circ$. Thus, the plane of the carboxamide group deviates only 0.8° from that of the pyrazine ring. This angle of deviation was found to be 3.2° in β -PCA and 5° in α -PCA. The best plane through the whole molecule calculated according to Blow (1960) is given by:

$$0.09038x + 0.63402y + 0.76802z + 0.09119 = 0.$$

The distances of the heavier atoms from this plane are rather small – 0.016 Å for the N(1), N(8) and O(9) atoms – being considerably smaller for the other atoms. The carboxamide group is slightly twisted around the C(2)–C(7) bond out of the molecular plane.

Crystal structure

The crystal structure of δ -PCA is shown in projection along the crystallographic b axis in Fig. 3. The molecules lie closely parallel to the (012) plane having a spacing of $d_{012} = 3.22$ Å. This plane is also a pronounced cleavage plane of the δ -PCA crystals. A feature common to the other forms of PCA and to other compounds containing a carboxamide group, is also easily recognized in the present case, namely the formation of dimers by hydrogen bond across the centres of symmetry. The hydrogen bond in question N(8)–H(8'')–O(9) has in δ -PCA a value of 2.90 Å, as compared to 2.92 Å in β -PCA and 2.90 Å in α -PCA. There appears, however, to be no strong hydrogen bond linking the dimers together in the crystal lattice of δ -PCA, similar to those found in the structures of α -PCA and β -PCA. The distance from the oxygen atom of one dimer to the nitrogen atom of the carboxamide group of the nearest neighbour dimer is 3.480 Å in δ -PCA, and can hardly be considered as a hydrogen bond. The contacts N(1) (x, y, z)–C(3) ($1+x, y, z$) and C(6) (xyz)–N(4) ($1+x, y, z$) are closely parallel to the a

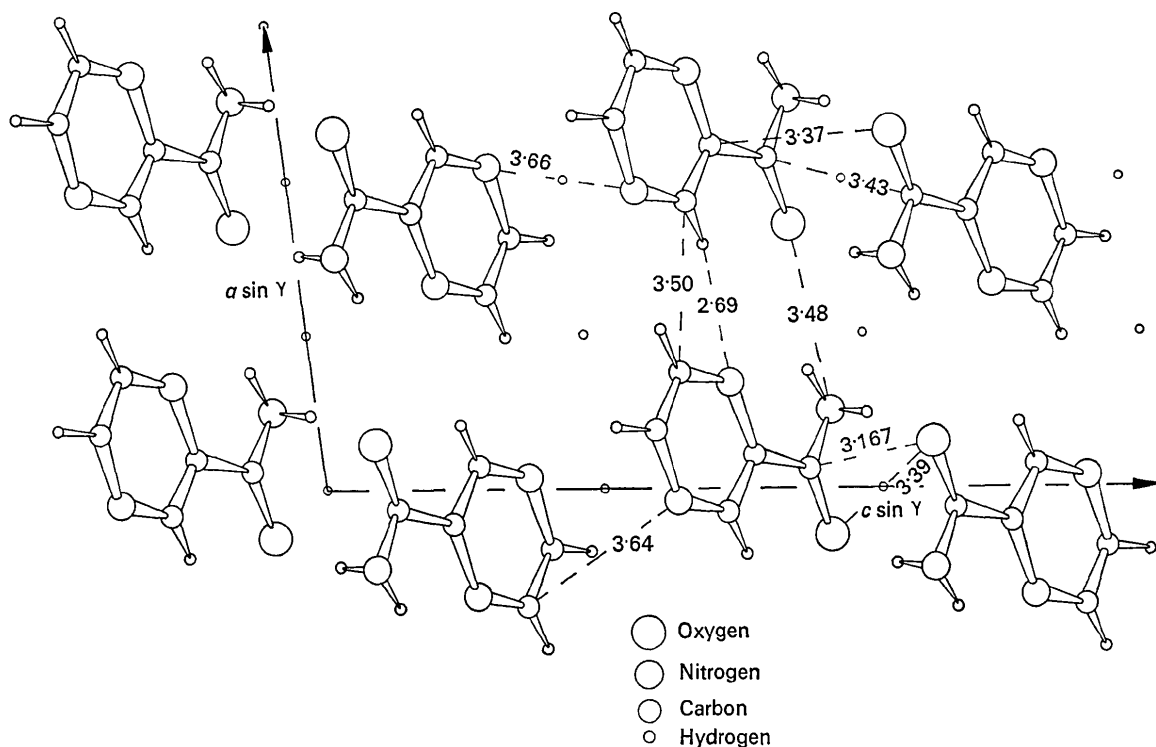


Fig. 3. Molecular packing in the crystal structure of δ -PCA viewed down the b axis. Dashed lines indicate some of the shortest interdimer atomic distances.

axis and to the N(8) (x, y, z)-O(9) ($1+x, y, z$) bond and have the values of 3.393 and 3.413 Å respectively. These values are not significantly different from those found for corresponding contacts in the structure of β -PCA. The hydrogen atoms of the same contacts in δ -PCA are found at the following distances H(8') (x, y, z)-O(9) ($1+x, y, z$), 2.82 Å; N(1) (x, y, z)-H(3) ($1+x, y, z$), 2.69 Å and H(6) (x, y, z)-N(4) ($1+x, y, z$), 2.71 Å. A close approach of 3.167 Å is found between C(7) of one molecule and O(9) of the nearest molecule along the b axis, and this feature may be related to the twisting of the carboxamide group around the C(2)-C(7) bond.

All other C-C, C-N, C-O or O-N intermolecular distances have normal values. Considering the intermolecular contact distances mentioned above the dimers are apparently linked together in the (012) plane, as well as across this plane, by van der Waals forces. The structure of δ -PCA differs in this respect from those of α -PCA and β -PCA, as a hydrogen bond N(8) \cdots H(8')-N'(1) of 3.14 Å was found in α -PCA between neighbour dimers, and in the structure of β -PCA an interdimeric hydrogen bond of 3.17 Å was found between neighbouring carboxamide groups.

Thermal motion

The translational and rotational vibration tensors **T** and **L** are given in Table 4. The thermal motions of the molecules in δ -PCA are somewhat more pronounced than in β -PCA and more comparable to those found in α -PCA.

Table 4. Values of T_{ij} (in 10^{-2} Å²) and L_{ij} (in deg²) of δ -PCA

$$\mathbf{T} = \begin{pmatrix} 5.33 & 0.00 & 0.84 \\ & 3.42 & 0.26 \\ & & 0.73 \end{pmatrix}$$

$$\mathbf{L} = \begin{pmatrix} 1.9 & & 0.5 \\ & -3.1 & 0.9 \\ & 23.9 & 1.8 \end{pmatrix}$$

The oscillations around the C(2)-C(5) axis, b axis and c axis in these three modifications may be compared as follows.

	C(2)-C(5) axis	b axis	c axis
α -PCA	5.7°	2.6°	1.2°
β -PCA	3.8	2.2	1.0
δ -PCA	4.9	1.4	1.3

The thermal vibration parameters given in Table 1 have been transformed to the corresponding u_{ij} values, which refer to a new set of molecular orthogonal axes m_1 , m_2 and m_3 defined in such a way that m_1 passes through C(2)-C(5), the transverse axis m_2 passes through C(2) and lies in the molecular plane, while m_3 passes through C(2) but is perpendicular to the plane of the molecule. In Table 5, the u_{ij} values obtained in this way are compared to u_{ij} values calculated from the translational and rotational vibration tensors T_{ij} and L_{ij} . The average deviation in observed u_{ij} 's is 0.38, standard deviation in calculated u_{ij} 's 0.83 and average deviation between calculated and observed values 0.70. The thermal motions of the N(8) and O(9) atoms do not seem to follow the rigid body assumption, and these atoms were therefore not included.

The agreement between observed and calculated values is reasonable, and the rigid body assumption thus appears to apply fairly well in this case. The thermal motions are, however, in contrast with those found in the structures of α -PCA and β -PCA, strongly anisotropic, having the largest vibration amplitudes along the m_1 axis, average values along the m_2 axis and rather small amplitudes along the m_3 axis.

The following programs were used on a UNIVAC 1108 computer:

DATRED (1970), a program for deriving $|F|$ values from observed intensities.

SCALIN (1970), a program for conversion of F values to the corresponding E values.

SIGMA2, a program listing all possible Σ_2 relations. *SYMBOL* (1969), a program for iterative use of Σ_2 relations.

These programs were all written by J. A. Hjortås of this Institute.

FOUFU1, a Fourier summation program.

LSFIV4, a full-matrix least-squares program based on the Oak Ridge program *ORFLS* (TM-305) by Busing, Martin & Levy.

PAFV01, a function and error program based on the Oak Ridge program *ORFFE* (TM-306) by Busing, Martin & Levy.

BEPLA1, a program for calculating best planes.

These four programs were written by O. Borgen & B. Mestvedt, the first one in cooperation with J. Finjord (Technical Reports 52, 45, 47 and 40 from Institute of Physical Chemistry, N.T.H.)

Table 5. Observed and calculated u_{ij} values for δ -PCA (in 10^{-2} Å²)

	u_{11}		u_{22}		u_{33}		u_{12}		u_{13}		u_{23}	
	obs	calc	obs	calc	obs	calc	obs	calc	obs	calc	obs	calc
N(1)	8.49	6.89	3.64	3.60	1.47	2.44	0.05	0.08	0.71	-0.63	0.19	0.37
C(2)	4.01	6.09	3.62	3.42	2.72	1.53	0.44	0.26	0.03	0.62	0.13	0.00
C(3)	7.34	6.85	3.94	3.54	1.38	1.41	0.11	0.03	0.30	0.70	0.36	0.32
N(4)	8.09	7.33	3.65	3.57	2.16	1.86	0.01	-0.06	0.74	0.55	0.05	0.43
C(5)	6.76	7.28	3.13	3.43	3.11	2.44	0.18	0.22	0.90	0.20	-0.10	0.14
C(6)	9.66	8.56	3.34	3.51	1.92	3.03	0.28	0.69	0.88	1.15	-0.20	-0.06
C(7)	4.70	6.04	3.24	3.50	3.29	3.34	0.44	0.28	-0.28	0.69	0.55	-0.23

We are indebted to Mr Th. Mortenson for the supply of crystalline material of δ -PCA, to Mr J. Mastad for making the drawings and to Mr F. Mo and Mr J. A. Hjortås for valuable discussions.

References

- BLOW, D. N. (1960). *Acta Cryst.* **13**, 168.
 CHATAR SINGH (1965). *Acta Cryst.* **19**, 861.
 COCHRAN, W. & WOOLFSON, M. M. (1955). *Acta Cryst.* **8**, 1.
 CRUICKSHANK, D. W. J. (1956). *Acta Cryst.* **9**, 754.
 CRUICKSHANK, D. W. J. (1965). In *Computing Methods in Crystallography*. Edited by J. S. ROLLETT, p. 114. New York: Pergamon Press.
 DOYLE, P. A. & TURNER, P. S. (1968). *Acta Cryst.* **A24**, 390.
 HAMILTON, W. C. (1965). *Acta Cryst.* **18**, 866.
 LONG, R. E., MADDOX, H. & TRUEBLOOD, K. N. (1969). *Acta Cryst.* **B25**, 2083.
 RØ, G. & SØRUM, H. (1972). *Acta Cryst.* **B28**, 991.
 SASADA, Y., TAKANO, T. & KAKUDO, M. (1964). *Bull. Chem. Soc. Japan.* **37**, 940.
 STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175.
 TAKAKI, Y., SASADA, Y. & WATANABE, T. (1960). *Acta Cryst.* **13**, 693.
 TAKAKI, Y. (1965). *Mem. Osaka Gakuhei Univ.* **B14**, 39.
 TAKANO, T., SASADA, Y. & KAKUDO, M. (1966). *Acta Cryst.* **21**, 514.
 TAMURA, C. & KUWANO, H. (1962). *Nippon Kagaku Zasshi.* **83**, 971.
 TAMURA, C., KUWANO, H. & SASADA, Y. (1961). *Acta Cryst.* **14**, 693.

Acta Cryst. (1972). **B28**, 1684

Hydrogen Bond Studies. LVII.* The Crystal Structure of Picrylsulphonic Acid Tetrahydrate, $\text{H}_5\text{O}_2^+\text{C}_6\text{H}_2(\text{NO}_2)_3\text{SO}_3^-\cdot 2\text{H}_2\text{O}$

BY JAN-OLOF LUNDGREN

Institute of Chemistry, University of Uppsala, Box 531, S-751 21 Uppsala 1, Sweden

(Received 13 September 1971)

The crystal structure of picrylsulphonic acid tetrahydrate has been determined from three-dimensional single-crystal X-ray diffraction data recorded at room temperature using a Stoe four-circle diffractometer. The crystals are triclinic, space group $P\bar{1}$, with two formula units in a cell of dimensions: $a = 8.346$ (1), $b = 11.367$ (1), $c = 8.065$ (2) Å, $\alpha = 97.77$ (2), $\beta = 109.32$ (1), $\gamma = 83.22$ (1)°. A full-matrix least-squares refinement based on F gave a final weighted R value of 0.042. The structure comprises H_5O_2^+ ions, picrylsulphonate ions and water molecules. The H_5O_2^+ ions, water molecules and sulphonate groups are hydrogen bonded together to form layers. The $\text{O}\cdots\text{O}$ distance within the H_5O_2^+ ion is 2.429 (2) Å. Other $\text{O}\cdots\text{O}$ hydrogen bond lengths are in the range 2.61 to 2.88 Å.

Introduction

This work is part of a series of systematic studies of solid hydrates of strong acids currently in progress at this Institute. The crystal structures of the hydrates of two other sulphonic acids, 2,5-dibromobenzenesulphonic acid trihydrate and 2,5-dichlorobenzenesulphonic acid trihydrate, have been reported earlier (Lundgren, 1972; Lundgren & Lundin, 1972). References to several papers describing crystal structures of hydrates of strong inorganic acids can be found in the paper by Lundgren (1972). The structure determination of picrylsulphonic acid tetrahydrate reported in the present paper is based on single-crystal X-ray diffraction data collected at room temperature.

Crystal data

2,4,6-Trinitrobenzenesulphonic acid tetrahydrate (picrylsulphonic acid tetrahydrate),

$\text{C}_6\text{H}_2(\text{NO}_2)_3\text{SO}_3\text{H}\cdot 4\text{H}_2\text{O}$. F. W. 365.231. Triclinic, $a = 8.346$ (1),* $b = 11.367$ (1), $c = 8.065$ (2) Å, $\alpha = 97.77$ (2), $\beta = 109.32$ (1), $\gamma = 83.22$ (1)°, $V = 713.2$ Å³ at 22°C. $Z = 2$, $D_x = 1.701$ g.cm⁻³. Space group $P\bar{1}$.

Experimental

Picrylsulphonic acid is commercially available. Well-shaped parallelepipedal crystals of the tetrahydrate are easily grown from an aqueous solution of the acid by slow evaporation at room temperature. The crystals show a tendency to lose some of their water when exposed to the atmosphere for a few days. Crystals of suitable dimensions were therefore mounted and sealed in thin-walled glass capillaries.

The intensity data were recorded at room temperature using a crystal of dimensions $0.19 \times 0.23 \times 0.51$ mm. The measurements were made on a Stoe four-

* Numbers in parenthesis here and throughout this paper are the estimated standard deviations in the least significant digits.

* Part LVI: *Acta Chem. Scand.* (1972). In the press.