The two ring conformations of CYCLAM, designated *C(3)* and *C(33)*, are similar to that in 1-amino-1-cyclopentanecarboxylic acid monohydrate. Both rings have approximately C_s (envelope) symmetry. The ratio of the conformations was refined to 63% *C(3)* and 37% *C(33)*. C(2) was found to deviate by 0·53 Å from the plane formed by the other four ring atoms, and is on the same side of the plane as the carboxamide C atom [C(5)–C^2-*endo*]. In the *C(3)* conformation C(4) is on the opposite side to C(0) [C(5)–C^4-*exo*] and deviates from the plane by 0·62 Å. The two conformations are shown in Fig. 2.

The carboxamide group is almost orthogonal to the plane of the cyclopentane ring. Fig. 3 shows the molecular packing.

The N atom of the amide group forms two strong hydrogen bonds, N–H(1)···O^i ($\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$) = 2·93 and N–H(2)···$O^{ii}$ ($x, -y, \frac{1}{2} + z$) = 2·86 Å. The angles are 178·4 (i) and 177·7° (ii).

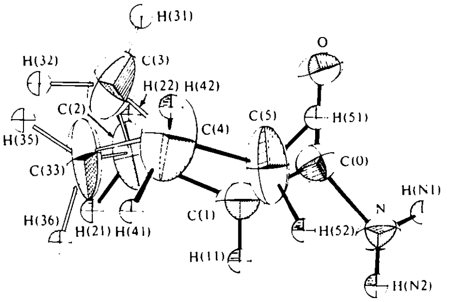

Fig. 2. The two conformations of CYCLAM.

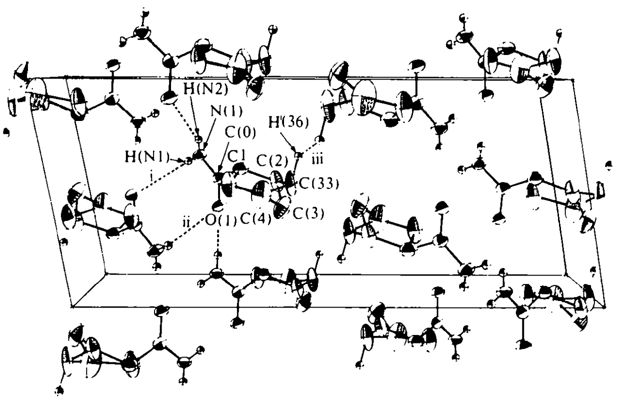

Fig. 3. Molecular packing.

All contact distances exceed the sum of the van der Waals radii, with the exception of an interaction between H(36) and H(36^{iii}) ($1 - x, y, \frac{3}{2} - z$).

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Hydrogen Bond Studies. A Neutron Diffraction Study of the Structures of Succinic Acid at 300 and 77 K

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Abstract

A neutron diffraction study of succinic acid has been carried out at 77 and 300 K. Both unit cells are monoclinic, space group $P2_1/c$. The cell dimensions are: $a = 5·519\ (2)$, $b = 8·862\ (6)$, $c = 5·101\ (2)$ Å, $\beta = 91·59\ (4)°$, $V = 249·39$ Å^3 at 300 K and $a = 5·464\ (1)$, $b = 8·766\ (3)$, $c = 5·004\ (1)$ Å, $\beta = 93·29\ (3)°$, $V = 239·31$ Å^3 at 77 K. Position parameters and anisotropic temperature factors of all the atoms of half the molecule were refined by a least-squares method. The final agreement factors for the

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1143 reflexions at 77 K and the 609 reflexions at 300 K are respectively 0·027 and 0·033. The molecule is quite planar and forms linear chains *via* hydrogen bonds in the crystal. The motions of the atoms are highly correlated because the translation parameter in the chain is constant. No significant disorder of the H atom in the hydrogen bond has been found. An oscillatory motion of the molecule around its minimal inertial axis has been shown.

Introduction

A precise study at different temperatures of crystalline adipic acid by polarized infrared radiation has revealed an anomalous feature of the hydrogen-bond bands (Auvert & Marechal, 1979). At low temperature the polarization of the ν_s band ($\mathrm{O{-}\overrightarrow{H}\cdots O}$) is not constant and varies by about 15° between the low- and high-frequency sides. The same feature occurs in succinic acid. This has been explained by assuming that the low-frequency modes are anharmonically coupled so strongly that the mode which modulates the ν_s band should be seen as a curvilinear vibration than an ordinary linear vibration. An interpretation of this phenomenon is given by the hypothesis of disorder of the H atom in the hydrogen bond as found in $KHCO_3$ crystals by Thomas, Tellgren & Olovsson (1974*a*).

The stretching motion ν_s of the H atom of the hydrogen bond is coupled to low-frequency hydrogen-bond modes and particularly to the stretching motion ν_σ ($\mathrm{\vec{O}{-}H\cdots\overleftarrow{O}}$) of the hydrogen bond. Because the ν_σ frequency is about 180–200 cm^{-1} (≃ 250–280 K) (Jakobsen, Mikawa & Brasch, 1967), a temperature dependence of the ν_σ frequency, and consequently a variation of the ν_s band (Leviel & Marechal, 1979), should be expected.

To solve these problems, a neutron diffraction study of succinic acid has been performed at 77 and 300 K.

Experimental

Pure succinic acid was obtained by successive crystallization in water of the commercial product. Large single crystals were grown by slow evaporation of the aqueous solution at room temperature. The single crystal described in Fig. 1 was used for the neutron diffraction study.

The measurements were carried out at 77 and 300 K on the D8 four-circle diffractometer situated at the High Flux Beam Reactor of the Institut Laue–Langevin. The cryostat used was a closed-loop refrigerator with helium as cooling fluid.

The cell parameters determined by least-squares refinement are given in the *Abstract*. The room-temperature cell agrees with that determined by Broadley, Cruickshank, Morrisson, Robertson & Shearer (1959) within 3σ.

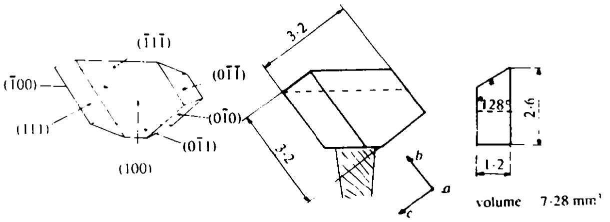

Fig. 1. The shape of the $(CH_2COOH)_2$ crystal used for the neutron data collection, with assigned faces. Dimensions are in mm.

Table 1. *Experimental data and summary of data treatment*

Temperature (K)	77	300
Wavelength (Å)	0·8963	0·8963
Scan mode	ω 2θ step scan	30 points peak 5 points background
Scan width	0 16 30 40 50	
angle θ (°)	2·5 2 2·6 3·4 4·2	
θ range (°)	0–45	0 40
Standard reflexions	352	352
Interval between standards	30 reflexions	30 reflexions
Detector aperture (mm)	14	14
Crystal to-detector distance (mm)	350	350
Number of reflexions measured	1235	763
Number of reflexions used in refinement (n_o)	1143	609
Maximum and minimum absorption coefficients (mm^{-1})	0·169 0·124	0·168 0·125
Number of parameters (n_p)	65	65
$R = \sum\lvert F_o - \lvert F_c\rvert\rvert/\sum F_o$	0·027	0·033
Goodness of fit, $s = [\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2]^{1/2}/(n_o - n_p)$	0·99	1·8

The experimental conditions for data collection are summarized in Table 1.

Data processing

The step-scan-recorded profile was reduced to structure factors according to the Lehmann & Larsen (1974) method which separates the peak and the background in such a way that $\sigma(I)/I$ is minimized. I is the integrated intensity and $\sigma(I)$ its c.s.d. based on counting statistics.

The absorption corrections were made before refinement using numerical integration over the volume of the crystal (Coppens, Leiserowitz & Rabinovich, 1965). The absorption coefficient had been experimentally determined using several crystals of different thickness at room temperature only. A correction proportional to the variation of the cell parameters was applied to determine the absorption coefficient at 77 K. The mean value μ = 0·21 (4) mm^{-1} (300 K) agrees with the calculated one assuming that the absorption arises entirely from the incoherent scattering of the H atoms. Information on the data treatment is given in Table 1.

Structure refinements

The neutron scattering lengths were taken from Bacon (1972). The refinements were performed on F^2 with a weighting scheme equal to $1/\sigma^2$ using the XRAY system of programs (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). Isotropic secondary extinction was introduced in both cases. The X-ray parameters determined by Broadley *et al.* (1959) were used as the starting point. Information about the refinements is presented in Table 1.*

Results

The atomic parameters obtained from refinement of both temperature data sets are presented in Table 2. In both cases the molecules are arranged in chains oriented along the [10$\bar{1}$] direction. The molecules are inclined out of this direction by an angle of 0·45 (5)° at 300 K and 0·38 (3)° at 77 K. Mean distances and angles at both temperatures are gathered in Table 3. Except for the two hydrogen atoms H(1), H(2), the molecule is quite planar, the COO plane being twisted by only $\simeq$ 10° from the carbon-skeleton plane around the chain axis. The high- and low-temperature structures present few differences. However, the bond lengths surprisingly decrease, some significantly, when the temperature increases. Nevertheless, both the cell dimensions and the volume increase with temperature. The translation parameter of the molecule in the chain remains exactly the same [7·619 (2) and 7·619 (6) Å]. An increase of the spacing between the succinic acid chain [3·583 (4) to 3·694 (7) Å] associated with a decrease in the β angle [93·29 (3) to 91·59 (4)°] explains the increase with temperature of the volume of the cell.

We have looked for the symmetrical position of the H atoms in the hydrogen bond as found by Thomas, Tellgren & Olovsson (1974*b*) in $KHCO_3$ crystals. A refinement of the population of an H atom statistically distributed in the two possible sites of the hydrogen

Table 2. *Positional parameters and equivalent isotropic thermal parameters* (Å^2) *for* $(CH_2COOH)_2$

$$U_{eq} = (U_1 U_2 U_3)^{1/3}.$$

	x	y	z	U_{eq}
Low temperature (77 K, LT)				
C(1)	0·0828 (1)	−0·0675 (1)	−0·0256 (1)	0·0910 (4)
C(2)	0·2614 (1)	−0·0344 (1)	−0·2355 (1)	0·0855 (7)
O(1)	0·2499 (1)	0·0780 (1)	−0·3815 (1)	0·0977 (8)
O(2)	0·4318 (1)	−0·1407 (1)	−0·2475 (1)	0·1018 (9)
H(1)	−0·0250 (3)	−0·1678 (1)	−0·0947 (3)	0·1523 (17)
H(2)	0·1876 (3)	−0·1040 (2)	0·1565 (2)	0·1537 (16)
H(3)	0·5436 (3)	−0·1193 (2)	−0·3958 (2)	0·1404 (11)
Room temperature (300 K, HT)				
C(1)	0·0808 (2)	−0·0664 (1)	−0·0277 (2)	0·1613 (8)
C(2)	0·2599 (2)	−0·0345 (1)	−0·2364 (2)	0·1539 (8)
O(1)	0·2528 (3)	0·0775 (2)	−0·3760 (3)	0·1826 (11)
O(2)	0·4240 (3)	−0·1395 (2)	−0·2570 (3)	0·1899 (12)
H(1)	−0·0253 (6)	−0·1635 (3)	−0·0924 (6)	0·2260 (20)
H(2)	0·1816 (6)	−0·1035 (4)	0·1466 (5)	0·2302 (17)
H(3)	0·5355 (6)	−0·1189 (3)	−0·4025 (5)	0·2112 (15)

Table 3. *Bond lengths* (Å) *and angles* (°) *before and after librational correction* (*all atoms included*)

	77 K	300 K	77 K (corrected)	300 K (corrected)
C(1) C′(1)	1·520 (1)	1·508 (2)	1·528 (1)	1·523 (2)
C(1) C(2)	1·503 (1)	1·499 (2)	1·503 (2)	1·504 (3)
C(1) H(1)	1·102 (2)	1·087 (3)	1·112 (2)	1·105 (2)
C(1) H(2)	1·096 (2)	1·087 (3)	1·099 (2)	1·107 (3)
C(2) O(1)	1·227 (1)	1·222 (2)	1·233 (2)	1·241 (3)
C(2) O(2)	1·321 (1)	1·305 (2)	1·325 (1)	1·318 (2)
O(2) H(3)	1·005 (2)	0·995 (4)	1·005 (3)	0·998 (5)
O′(1) O(2)	2·672 (1)	2·678 (2)	2·673 (2)	2·687 (3)
O(1) H(3)	1·670 (2)	1·687 (3)	1·670 (3)	1·693 (3)
C′(1) C(1) C(2)	112·45 (4)	112·47 (10)	112·23 (3)	112·38 (10)
C(1) C(2) O(1)	123·96 (5)	123·78 (11)	123·99 (6)	123·83 (9)
C(1) C(2) O(2)	112·55 (4)	113·28 (10)	112·23 (5)	112·61 (10)
O(1) C(2) O(2)	123·49 (5)	122·93 (13)	123·77 (5)	123·56 (14)
C(2) O(2) H(3)	111·26 (9)	111·99 (22)	110·93 (10)	111·29 (25)
H(1) C(1) H(2)	105·85 (11)	105·58 (25)	105·73 (13)	105·73 (25)
O(2) H(3) O′(1)	174·27 (12)	173·72 (29)	174·24 (13)	173·62 (28)
C(2) C(1) H(1)	106·95 (9)	107·13 (20)	106·99 (9)	107·25 (22)
C(2) C(1) H(2)	107·95 (9)	107·80 (20)	107·98 (10)	107·76 (20)

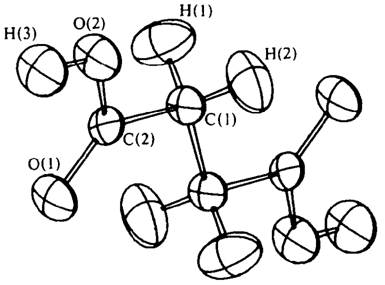

Fig. 2. A view of a molecule of succinic acid. Atoms are drawn with 50% probability ellipsoids.

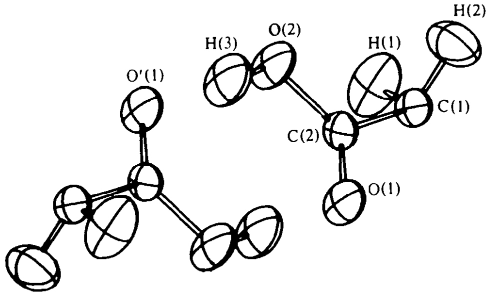

Fig. 3. A view of the carboxylic ring.

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* Lists of structure factors and anisotropic thermal parameters obtained at both temperatures have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36081 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 4. *R.m.s. thermal displacements and orientation with respect to the main inertia axes (I_x: approximately along chain direction; I_y: perpendicular to the plane of the molecule)*

	77K					300 K				
	R.m.s. thermal displacement (Å)	Angle with inertia system (°)*			Distance (Å) to I_x axis (minimal inertia axis)	R.m.s. thermal displacement (Å)	Angle with inertia system (°)†			Distance (Å) to I_x axis (minimal inertia axis)
		I_x	I_y	I_z			I_x	I_y	I_z	
	0·0757 (4)	11	86	79		0·1191 (8)	12	86	78	
C(1)	0·1096 (5)	82	24	67	0·530 (1)	0·2087 (9)	89	23	67	0·525 (3)
	0·0908 (3)	82	66	25		0·1689 (7)	77	68	26	
	0·0721 (6)	12	86	78		0·1162 (7)	10	88	79	
C(2)	0·0984 (9)	81	33	59	0·070 (2)	0·1871 (10)	84	43	47	0·062 (3)
	0·0881 (5)	82	57	34		0·1678 (8)	82	47	44	
	0·0775 (8)	23	86	67		0·1276 (10)	16	85	75	
O(1)	0·1282 (7)	87	5	86	1·272 (1)	0·2572 (12)	86	6	87	1·259 (4)
	0·0938 (9)	67	87	23		0·1854 (11)	75	87	15	
	0·0808 (10)	6	86	86		0·1297 (12)	2	89	88	
O(2)	0·1388 (8)	86	6	85	0·858 (3)	0·2777 (13)	89	4	86	0·848 (6)
	0·0942 (9)	87	85	6		0·1902 (11)	88	86	4	
	0·1475 (16)	11	84	81		0·1977 (20)	38	65	64	
H(1)	0·1191 (19)	80	38	54	1·480 (4)	0·1768 (22)	52	54	58	1·467 (10)
	0·2011 (15)	86	52	38		0·3302 (19)	87	47	43	
	0·1523 (15)	20	88	70		0·1839 (17)	37	76	57	
H(2)	0·1946 (14)	83	27	64	1·474 (4)	0·3166 (18)	88	22	67	1·463 (11)
	0·1224 (18)	71	63	34		0·2096 (15)	54	73	41	
	0·1079 (11)	8	89	82		0·1531 (16)	4	89	86	
H(3)	0·1793 (10)	88	3	88	0·445 (2)	0·2810 (14)	89	2	88	0·446 (9)
	0·1430 (13)	82	88	8		0·2190 (15)	86	88	4	

* The average error is ~1 on the last digit.
† The average error is ~2 on the last digit.

Table 5. **T** *and* **L** *matrices*

	Matrix	From atoms of the molecular plan			From all atoms		
		69 (3)	58 (4)	67 (6)	146 (10)	578 (14)	48 (11)
77 K	**T**		−7 (5)	−12 (4)		98 (12)	48 (10)
	(×10⁻⁴ Å²)			4 (5)			4 (11)
		28 (2)	4 (3)	3 (4)	42 (6)	4 (7)	14 (8)
77 K	**L**		6 (3)	−5 (5)		−1 (5)	23 (9)
	(deg²)			(3)			−2 (7)
		167 (9)	268 (6)	280 (8)	218 (11)	305 (12)	283 (10)
300 K	**T**		−27 (8)	−11 (9)		−23 (11)	−15 (9)
	(×10⁻⁴ Å²)			41 (7)			39 (12)
		84 (9)	8 (6)	5 (8)	107 (15)	6 (9)	4 (8)
300 K	**L**		9 (8)	−9 (7)		11 (8)	−8 (7)
	(deg²)			1 (9)			1 (6)

bond has shown that the occupancy of the second site is less than 1%, with an error of 1%.

Moreover, an examination of the Fourier difference maps and the application of the Dieterich, Paul & Curtin (1974) criterion lead to the same result: the H atom occupies one and only one site in the hydrogen bond. The existence of two isomers in crystalline succinic acid cannot be put forward to interpret the anomalous feature of the ν_s band in the IR spectroscopy study.

Figs. 2 and 3 represent a drawing of the succinic acid molecule with 50% thermal ellipsoids. It is clearly evident that the molecule has an oscillational motion, the existence of which is confirmed by the orientations of the r.m.s. components of the thermal displacement compared to the directions of the main inertia axes (Table 4).

For every atom in the plane of the molecule the largest r.m.s. component is perpendicular to the plane and its length increases with the distance from the I_x axis (which is approximately in the chain direction). This indicates an oscillation motion of the molecule around the minimal inertia axis I_x. A decrease of the apparent distance of the atoms from the axis of rotation

Table 6. *Distances* (Å) *to the I_x axis after correction for librational motion* (*all atoms included*)

	77 K		300 K	
	Without correction	Correction	Without correction	Correction
C(1)	0·530 (1)	0·535	0·525 (3)	0·534
C(2)	0·070 (2)	0·071	0·062 (3)	0·062
O(1)	1·272 (1)	1·278	1·259 (4)	1·277
O(2)	0·858 (3)	0·864	0·848 (6)	0·865
H(1)	1·480 (4)	1·495	1·467 (10)	1·507
H(2)	1·474 (4)	1·479	1·463 (11)	1·489
H(3)	0·445 (2)	0·449	0·446 (9)	0·457

corresponds to the increase in libration motion of the molecule with temperature as has already been seen by Paul & Pryor (1972) in $NaNO_3$ and Becka & Cruickshank (1963) in hexamethylenetetramine. We have corrected the atom positions for thermal motion by using the rigid-body-analysis method of Schomaker & Trueblood (1968). Two calculations were performed: in the first only the atoms in the plane of the molecule were taken as the rigid body, and in the second all atoms were included.

The symmetry restriction imposed by the centrosymmetric crystallographic point group implies that the screw tensor vanishes. The matrices **L** and **T** were determined from the atomic parameters described in the inertia-axes system and are given in Table 5.

As expected, the largest component of the libration matrix is L_{11}, corresponding to an oscillation of the molecule around the I_x inertia axis. This corresponds to an angle of libration of 5·4° at 77 K (6·5° with the second assumption) and 9·2° (and 10°) at room temperature. The distances of the atoms from the inertial axis I_x are reported in Table 6, together with the corresponding distances corrected for librational motion. The corrected distances now increase with temperature.

A set of corrected interatomic distances and angles is given in Table 3. The largest correction occurs in the C(1)–C′(1) bond distances which become equal within 1σ when the temperature varies. The only remaining shortening affects the C(2)–O(2) and H(3)–O′(1) distances. Because the translation along the chain is kept constant, the motions localized around the O(2) atom are highly correlated and may be due to the motion of this atom inside the carboxylic ring when the temperature increases. The atom H(3) goes into the carboxylic ring like O(2) when the temperature increases but this motion is perturbed by the hydrogen bond. This preferential orientation of the motions of the two atoms O(2) and H(3) indicates anisotropy of vibrating motion in the corresponding direction. This strongly suggests that the mode which couples anharmonically to the ν_s vibration is not the pure ν_σ stretching mode of an O–H···O bond but, rather, one of its low-frequency bending modes.

Conclusion

The main result of this study is the absence of disorder of the H atom in the hydrogen bond at both temperatures. The molecules are arranged in chains, the orientation of which corresponds to the main inertia axis. An oscillation motion around this axis has been shown and the angle of rotation increases with temperature. The fact that the translation parameter of the molecules in the chain is constant with temperature implies that the different motions of the atoms in the molecule are correlated, particularly around the O(2) atom.

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