temperature factors are unusually high; this probably indicates that there is some disorder in these compounds.

In Table 6 some other compounds with β-K$_2$SO$_4$-like structures are listed. The structure of K$_2$ZnCl$_4$ is not yet known, but the agreement between the axes of this compound and orthorhombic K$_2$CoCl$_4$ suggests that the structures may be almost the same.

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Hydrogen-Bond Motifs of Carboxylic Acids: the α-Form of Monochloroacetic Acid

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Abstract. C$_2$H$_3$O$_2$Cl, monoclinic, $P2_1/c$; $a = 5\cdot380$ (1), $b = 19\cdot150$ (4), $c = 7\cdot860$ (2) Å, $\beta = 109\cdot14$ (10)°; $Z = 8$, $D_c = 1\cdot64$ g cm^{-3}. The structure consists of centrosymmetric tetramers formed by hydrogen bonding between carboxyl groups of the two independent molecules. Corresponding bond distances and angles involving non-hydrogen atoms of the independent molecules are very similar; their conformations differ: one molecule is planar, the other has a dihedral angle of 20·3°.

Introduction. C$_2$H$_3$O$_2$Cl exists in three distinct crystalline varieties (Aumeras & Minangoy, 1948). The α-form is the stable modification at ambient conditions with a m.p. of 64°C, the β- and γ-forms are metastable with m.p.'s of 54 and 51 °C respectively. From IR and Raman spectroscopy it was concluded that the metastable β-form crystallizes in the cyclic centrosymmetric hydrogen-bonded dimer type (Sinha, Katon & Jakobsen, 1975), whereas the results for the α-form are inconsistent with a dimer structure and strongly indicate a hydrogen-bond motif with a polymeric nature (Sinha, Katon & Jakobsen, 1974). The analysis of the α-form was performed to elucidate the hydrogen-bond motif.

Prismatic crystals were obtained by sublimation *in vacuo*. A crystal $0\cdot3 \times 0\cdot4 \times 0\cdot5$ mm was selected and

Table 1. *Fractional coordinates* ($\times 10^4$ *for* Cl, O *and* C; $\times 10^3$ *for* H) *and anisotropic thermal parameters* ($\times 10^4$) *of the non-hydrogen atoms*

The estimated standard deviations are given in parentheses and refer to the last decimal position of respective values. The anisotropic temperature factor is of the form exp $[-2\pi^2(a^{*2}h^2 U_{11} + \ldots + 2b^*c^*klU_{23})]$.

	x	y	z	U_{11} or B (Å^2)	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Molecule 1									
Cl	−379 (2)	6706 (1)	9904 (1)	722 (6)	560 (5)	498 (5)	−116 (4)	353 (4)	−107 (4)
O(1)	3057 (5)	6596 (1)	6272 (3)	625 (15)	415 (14)	541 (14)	−97 (11)	334 (12)	−61 (10)
O(2)	782 (5)	5806 (1)	7228 (4)	706 (16)	340 (11)	735 (17)	−110 (11)	454 (14)	−89 (11)
C(1)	1669 (6)	6384 (2)	7276 (4)	426 (15)	345 (15)	379 (15)	11 (12)	158 (13)	21 (12)
C(2)	1461 (9)	6961 (2)	8517 (5)	841 (29)	394 (18)	511 (21)	−71 (18)	373 (20)	−21 (15)
H(1)	322 (7)	713 (2)	925 (5)	3·8					
H(2)	62 (7)	730 (2)	786 (5)	3·8					
H(3)	302 (7)	631 (2)	549 (5)	3·7					
Molecule 2									
Cl	−6497 (2)	3409 (1)	6768 (1)	529 (5)	422 (4)	696 (6)	−115 (4)	274 (4)	−59 (4)
O(1)	−3047 (5)	5177 (1)	8216 (3)	596 (15)	518 (14)	589 (15)	−187 (12)	361 (12)	−190 (12)
O(2)	−2747 (5)	4434 (1)	6128 (3)	564 (14)	448 (13)	564 (14)	−96 (11)	350 (12)	−119 (11)
C(1)	−3783 (6)	4623 (2)	7186 (4)	369 (15)	396 (15)	402 (15)	−6 (12)	166 (13)	2 (12)
C(2)	−6106 (7)	4282 (2)	7501 (6)	499 (20)	396 (17)	659 (23)	−66 (15)	324 (18)	−70 (16)
H(1)	−611 (6)	430 (2)	873 (5)	3·6					
H(2)	−741 (7)	451 (2)	688 (5)	3·6					
H(3)	−157 (7)	546 (2)	806 (5)	3·9					

sealed in a capillary tube to prevent sublimation. The cell dimensions, obtained at room temperature with a Nonius CAD-4 computer-controlled diffractometer, agree with those reported by Weiss (1959). Intensities for 1748 independent reflexions ($\sin \theta/\lambda < 0.65$ Å^{-1}) were collected with an ω–2θ scan and Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å). 333 reflexions had an integrated intensity $< 2.5\sigma(I)$ and these were given zero weight in the refinement. After Lorentz and polarization corrections the data were placed on an approximate absolute scale by means of a Wilson plot. No correction was applied for absorption [μ(Mo $K\alpha$) = 8.0 cm^{-1}].

The structure was solved by an automatic symbolic procedure (Spek, 1975) based on 241 reflexions with $E \geq 1.45$. The resulting E map showed the location of all non-hydrogen atoms. Isotropic block-diagonal least-squares refinement followed by anisotropic refinement and a difference synthesis revealed the positions of the H atoms, which were assigned constant isotropic thermal parameters equal to those of the carrier atoms. Three more cycles of anisotropic full-matrix refinement resulted in a final R of 0.042 ($R = \sum\|F_o| - |F_c\|/\sum|F_o|$) and $R_w = 0.061$ $\{R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}\}$. The quantity minimized was $\sum w(|F_o| - |F_c|)^2$, with $w = \sigma^{-2}(F_o)$ determined by counting statistics. The shifts in the last cycle were less than 0.05σ; the goodness-of-fit, defined as $[\sum w(|F_o| - |F_c|)^2/(m - s)]^{1/2}$, where m is the number of observations and s the number of parameters refined, was 0.74. A final difference synthesis showed no peaks above 0.25 e Å^{-3}. The scattering factors of Cromer & Mann (1968) were used for Cl, O and C, and of Stewart, Davidson & Simpson (1965) for H. The final positional and thermal parameters are listed in Table 1.*

Discussion. The bond distances and angles of the two independent molecules (Table 2) compare well with those reported for the analogous fluoroacetic acid (Kanters & Kroon, 1972), hydroxyacetic acid (Pijper, 1971) and two modifications of bromoacetic acid (Leiserowitz & vor der Brück, 1975). As can be seen in Table 2, corresponding bond distances and angles involving non-hydrogen atoms of the two molecules do not differ significantly, whereas the conformation angles of the two molecules are different. The dihedral angle C(2)–C(1)–O(1)–O(2)/C(1)–C(2)–Cl is 0.8° in molecule 1 and 20.3° in molecule 2. Both molecules adopt the synplanar conformation commonly observed in crystals of substituted acetic acids (Kanters, Kroon, Peerdeman & Schoone, 1967; Leiserowitz, 1976). The C–C bond distances, 1.502 and 1.501 Å respectively, are appreciably shortened. This shortening has also been reported for crystals of acetic acid and its derivatives (Table 3).

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31926 (12 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

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

Estimated standard deviations are given in parentheses.

	Molecule 1	Molecule 2
C(2)–Cl	1.765 (5)	1.759 (4)
C(2)–C(1)	1.502 (5)	1.501 (5)
C(1)–O(1)	1.316 (5)	1.315 (4)
C(1)–O(2)	1.201 (4)	1.199 (5)
C(2)–H(1)	0.99 (3)	0.97 (4)
C(2)–H(2)	0.86 (3)	0.84 (3)
O(1)–H(3)	0.82 (4)	1.00 (4)
C(1)–C(2)–Cl	112.0 (3)	112.1 (3)
C(2)–C(1)–O(1)	109.8 (3)	110.4 (3)
C(2)–C(1)–O(2)	125.8 (4)	125.8 (3)
O(1)–C(1)–O(2)	124.3 (3)	123.8 (3)
H(3)–O(1)–C(1)	111 (3)	116 (3)
H(1)–C(2)–Cl	111 (2)	108 (2)
H(2)–C(2)–Cl	107 (3)	109 (2)
H(1)–C(2)–C(1)	111 (2)	115 (2)
H(2)–C(2)–C(1)	108 (3)	105 (3)
H(1)–C(2)–H(2)	109 (3)	107 (3)

Table 3. C–C *bond distances in acetic acid and some simple derivatives*

	C–C	Temperature*
Acetic acid[a]	1.482 (8) Å	5 °C
	1.478 (6)	−190
CH$_3$COONH$_4$.CH$_3$COOH[b]	1.488 (5)	−40
C$_6$H$_5$N$_2$Cl.CH$_3$COOH[c]	1.470 (16)	−10
FCH$_2$COOH[d]	1.46 (1)	
BrCH$_2$COOH[e], $P2_1/c$	1.490 (12)	
$Pccn$	1.496 (11)	
ClCH$_2$COOH[f], α-form	1.502 (5)	
	1.501 (5)	
CH$_3$COONH$_4$.ClCH$_2$COOH[g]	1.506 (4)	
HOCH$_2$COOH[h]	1.508 (3)	
	1.498 (3)	
CH$_3$CH$_2$COOH[i]	1.502 (10)	−95

(a) Nahringbauer (1970). (b) Nahringbauer (1969). (c) Rømming & Tjørnhom (1968). (d) Kanters & Kroon (1972). (e) Leiserowitz & vor der Brück (1975). (f) This work. (g) Ichikawa (1972). (h) Pijper (1971). (i) Strieter, Templeton, Scheuerman & Sass (1962).

* Where no temperature is given, the C–C distances of compounds refer to room-temperature structures.

The hydrogen-bond motif is shown in Fig. 1 (a projection of the structure down **a**). Eight molecules are arranged in two groups of four which each form a centrosymmetric hydrogen-bonded tetramer. This hydro-
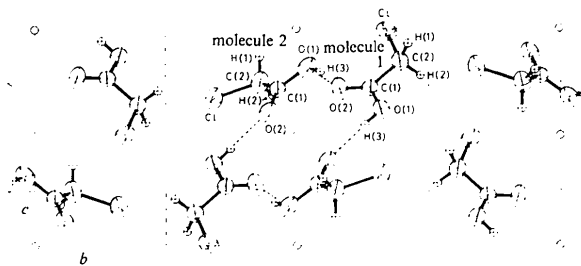

Fig. 1. Projection of the structure along **a**. Hydrogen bonds are denoted by dashed lines.

gen-bond motif is very different from that usually observed in crystals of carboxylic acids, *i.e.* the centrosymmetric hydrogen-bonded dimer motif. It is intriguing to observe that the dimer motif is present in crystals of the closely related fluoroacetic acid (Kanters & Kroon, 1972) and two modifications of bromoacetic acid (Leiserowitz & vor der Brück, 1975). The tetramer motif is also different from that observed in crystalline acetic acid (Nahringbauer, 1970) and formic acid (Holtzberg, Post & Fankuchen, 1953) which both adopt an approximately planar arrangement consisting of one molecule hydrogen-bonded to two neighbours *via* single O–H···O(carbonyl) bonds. This motif, for which the name catemer has been suggested (Berney, 1973; Leiserowitz, 1976), implies a rather short C(H) ···O(carbonyl) contact conferring in some degree a dimeric character on the catemer motif. In Fig. 2 the three motifs, cyclic dimer (I), catemer (II) and tetramer (III) are shown, and in Table 4 the planarity of these
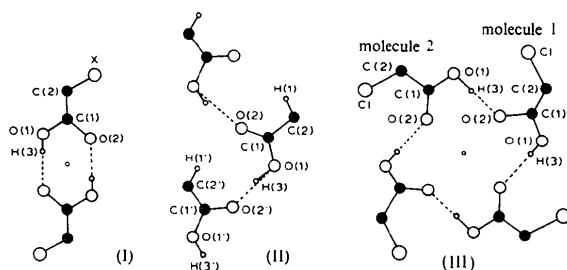
motifs in structures of acetic acid and some halogenated derivatives is represented. It is evident on geometrical grounds that the catemer motif (II) is very unlikely for chloroacetic acid because this would imply a short C–Cl···O(carbonyl) contact. However, this unfavourable interaction can be avoided by rotation of the molecule by 180° with respect to the O···O hydrogen-bond axis, thus converting (II) into (III). Though the cyclic dimer model I seems very reasonable for chloroacetic acid, particularly in regard to the dimer structures of fluoro- and bromoacetic acids, it has been shown to occur only in the metastable β-form (Kanters, Roelofsen & Feenstra, 1976).

The hydrogen-bond geometries of the two intermolecular hydrogen bonds in the α-form are very similar (Table 5). The donor angles appear to be smaller than those observed in dimer types (~113°), whereas the acceptor angles are larger than the corresponding angles in dimers (~123°) and these acceptor angles are close to those found in acetic acid (132°), which adopts a truly polymeric hydrogen-bond motif.

The X-ray results thus confirm the results from IR and Raman studies, from which it was concluded that the α- and β-forms of monochloroacetic acid have entirely different hydrogen-bond motifs, the α-form having a polymer type (Sinha, Katon & Jakobsen, 1974) and the β-form the cyclic dimer type (Sinha, Katon & Jakobsen, 1975). At the level of approximation of the applied oriented gas model of the structure, it appears that the spectroscopic results for the α-form are inconsistent with a hydrogen-bonded dimer type but consistent with either a tetramer or polymer structure (Katon, 1976).

Fig. 2. Hydrogen-bond motifs in carboxylic acids: (I) cyclic dimer, (II) polymer and (III) tetramer.

Table 4. *Deviations* (Å) *from least-squares planes*

The atoms constituting the planes in the hydrogen-bond modes are C(1), C(2), O(1), O(2) and symmetry-related atoms* in acetic acid, fluoroacetic acid and bromoacetic acid. The plane in chloroacetic acid is constituted by C(1), C(2), O(1) and O(2) of molecules 1 and 2 and their centrosymmetrically related atoms. The distances to the planes of X [X = H(1),F,Br] and H(3) are also given. See Fig. 2 for atomic numbering.

	C(1)	C(2)	O(1)	O(2)	X	H(3)	C(1')	C(2')	O(1')	O(2')	X'	H(3')
Acetic acid	0·027	−0·268	−0·065	0·379	−0·254	0·112	−0·015	−0·238	−0·071	0·251	0·251	0·053
Fluoroacetic acid	−0·003	0·009	−0·009	−0·009	0·005	−0·301						
Bromoacetic acid, $P2_1/c$	−0·001	−0·006	0·008	0·008	−0·254	−0·394						
$Pccn$	0·007	−0·005	0·001	0·001	−0·686	−0·050						

Chloroacetic acid, α-form	Molecule 1						Molecule 2					
	C(1)	C(2)	O(1)	O(2)	Cl	H(3)	C(1)	C(2)	O(1)	O(2)	Cl	H(3)
	−0·034	0·112	0·124	−0·288	−0·088	0·097	−0·036	0·220	−0·104	−0·129	−0·216	−0·239

* In acetic acid the molecules are related by a glide plane, whereas in the other acids the molecules are related by a centre of inversion.

Table 5. *Hydrogen-bond geometry*

Mole-cule 1	Mole-cule 2		Mole-cule 2	Mole-cule 1	
O(1)··········O(2^i)		2·697 (3) Å	O(1)··········O(2)		2·706 (4) Å
O(1)——H(3)···O(2^i)		175 (2)°	O(1)——H(3)···O(2)		168 (2)°
C(1)——O(1)···O(2^i)		105·9 (4)	C(1)——O(1)···O(2)		106·8 (4)
O(1)···O(2^i)——C(2^i)		140·2 (3)	O(1)···O(2)——C(1)		137·0 (3)

Symmetry code: Superscript (i) − x, 1 − y, 1 − z.

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Hydrogen-Bond Motifs of Carboxylic Acids: the β-Form of Monochloroacetic Acid

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Abstract. $C_2H_3O_2Cl$, monoclinic, $P2_1/c$; $a = 4·635$ (10), $b = 12·974$ (24), $c = 6·686$ (16) Å, $\beta = 107·93$ (19)°; $Z = 4$, $D_c = 1·647$ g cm^{-3}. The structure consists of cyclic dimers formed by hydrogen bonding across centres of symmetry.

Introduction. As part of a programme to study the monotropy of monochloroacetic acid, the structure of the stable α-form has been determined (Kanters & Roelofsen, 1976). The α-form exhibits a hydrogen-bond motif that has not so far been observed in carboxylic acids in the solid state (Leiserowitz, 1976). The motif consists of centrosymmetric hydrogen-bonded tetramers and may be looked upon as an intermediate form of the polymeric structure of acetic acid (Nahringbauer, 1970) and formic acid (Holtzberg, Post & Fankuchen, 1953) and the commonly observed cyclic dimer structure.

From IR and Raman studies of the metastable β-form of monochloroacetic acid (Sinha, Katon & Jakobsen, 1975) it was concluded that this modification adopts the usual cyclic hydrogen-bonded dimer type. This paper describes the determination of the crystal structure of the β-form.

Crystals were prepared by the method described by Aumeras & Minangoy (1948). This consists of heating the melt of the α-form (m.p. 64°C) to 75°C and keeping the melt at that temperature for 30 min to ensure that no traces of the stable α-form are present. After allowing the melt to cool slowly at a rate of 1°C/20 min, rapid crystallization of tablets of the β-form takes place at 54°C. Oscillation and Weissenberg photographs indicated that the crystals were monoclinic, with systematic absences $h0l$, $l = 2n + 1$ and $0k0$, $k = 2n + 1$, determining the space group as $P2_1/c$. It appeared that the crystals thus prepared were twinned.

Table 1. *Fractional coordinates* ($\times 10^4$ *for* Cl, C *and* O; $\times 10^3$ *for* H)
and anisotropic thermal parameters ($\times 10^4$) *of the non-hydrogen atoms*

The estimated standard deviations are given in parentheses and refer to the last decimal position of respective values. The anisotropic temperature factor is of the form $\exp[-2\pi^2(a^{*2}h^2U_{11} + \ldots + 2b^*c^*klU_{23})]$.

	x	y	z	U_{11} or B (Å²)	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cl	2007 (3)	3356 (1)	1156 (2)	479 (8)	662 (10)	414 (7)	−5 (7)	28 (6)	143 (6)
O(1)	−2634 (9)	4077 (3)	−4566 (6)	440 (23)	596 (25)	416 (20)	−146 (19)	6 (17)	97 (18)
O(2)	1832 (8)	4638 (3)	−2507 (6)	409 (21)	528 (23)	425 (19)	−96 (17)	72 (16)	53 (17)
C(1)	−457 (10)	4131 (4)	−2800 (7)	289 (25)	321 (23)	373 (24)	34 (18)	91 (19)	−44 (18)
C(2)	−1178 (13)	3509 (5)	−1108 (8)	407 (30)	522 (32)	378 (26)	−101 (24)	63 (22)	6 (23)
H(1)	−293 (12)	391 (4)	−63 (8)	3·3					
H(2)	−224 (12)	292 (4)	−160 (8)	3·3					
H(3)	−226 (13)	444 (4)	−536 (9)	3·7					