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Structure of 2,3,4-Trichloro-1-naphthaleneglyoxylic Acid

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Abstract. $C_{12}H_5Cl_3O_3$, monoclinic, $P2_1/a$, $a = 17.199$ (10), $b = 6.094$ (4), $c = 12.057$ (9) Å, $\beta = 106.10$ (8)°, $Z = 4$, $D_c = 1.66$, $D_o = 1.681$ (1) g cm⁻³ (by flotation in aqueous KI solution); $R = 0.053$ for 1848 reflections. The roughly planar glyoxylic acid group is rotated 60° out of the naphthalene plane. The compound crystallizes as hydrogen-bonded dimers between carboxylic acid groups about a center of symmetry. The α -CO does not participate in the hydrogen bonding in this crystal structure.

Introduction. Colorless, elongated needle crystals were grown from CCl_4 by slow evaporation. The crystals sublimed readily and X-ray data were obtained using a quartz capillary and Zr-filtered Mo $K\alpha$ ($\lambda = 0.71069$ Å) radiation. A single crystal of approximate dimensions $0.15 \times 0.20 \times 0.10$ mm was used. From indexed Weissenberg photographs the systematic absences $0k0$, k odd, and $h0l$, h odd uniquely determined the space group to be $P2_1/a$.

Three-dimensional intensity data were collected on a Picker FACS-1 diffractometer equipped with a scintillation counter and pulse-height analyzer. In total 2382 reflections out to $55^\circ 2\theta$ were measured using the θ - 2θ scan mode. Of these, 1848 had $I > \sigma(I)$ and were used in subsequent calculations. No absorption corrections were made.

The structure was determined using *MULTAN* (Main, Woolfson & Germain, 1971). Only the empirical formula was known before the structure determination. The parent ion was not observed in the mass spectra, but the isotopic distribution indicated the presence of three Cl atoms per molecule. The structure was refined using difference Fourier maps and full-

matrix least-squares methods. The quantity minimized was $\sum w(|F_o| - |F_c|)^2$ where the weight w applied to each observation was taken to be $1/\sigma^2(F)$. The $\sigma(F)$ values were obtained from counting statistics (Stout & Jensen, 1968). C, O and Cl atoms were allowed to

Table 1. Fractional atomic coordinates ($\times 10^4$, for H $\times 10^3$) and isotropic thermal parameters

The standard deviations are given in parentheses. The isotropic temperature factors for non-hydrogen atoms were obtained from the anisotropic parameters by the relationship $B = (B_{11}B_{22}B_{33})^{1/3}$, where $B_{11} = 4b_{11}/(a^*)^2$, $B_{22} = 4b_{22}/(b^*)^2$, and $B_{33} = 4b_{33}/(c^*)^2$ (Stout & Jensen, 1968).

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å ²)
Cl(2)	3558 (1)	9741 (1)	1584 (1)	4.67 (3)
Cl(3)	1722 (1)	10516 (2)	354 (1)	5.32 (3)
Cl(4)	422 (1)	7459 (2)	859 (1)	5.17 (3)
O(1)	4351 (1)	4253 (4)	3130 (3)	5.58 (4)
O(2)	5217 (1)	7898 (4)	4041 (2)	4.64 (4)
O(3)	4088 (1)	8916 (4)	4492 (2)	4.08 (4)
C(1)	3097 (2)	6260 (5)	2622 (3)	2.99 (5)
C(2)	2846 (2)	7996 (5)	1878 (3)	3.35 (5)
C(3)	2009 (2)	8364 (5)	1310 (3)	3.31 (5)
C(4)	1443 (2)	6967 (5)	1528 (3)	3.60 (5)
C(5)	1097 (2)	3642 (6)	2508 (3)	4.61 (6)
C(6)	1341 (3)	1909 (6)	3225 (4)	5.46 (6)
C(7)	2175 (3)	1548 (6)	3768 (3)	4.92 (6)
C(8)	2739 (2)	2924 (6)	3579 (3)	4.10 (6)
C(9)	2518 (2)	4772 (5)	2834 (3)	2.43 (5)
C(10)	1671 (2)	5148 (5)	2287 (3)	3.37 (5)
C(11)	3994 (2)	5922 (5)	3187 (3)	3.74 (5)
C(12)	4445 (2)	7775 (5)	3969 (3)	3.34 (5)
H(5)	52 (2)	390 (6)	213 (3)	4.8 (8)
H(6)	96 (3)	96 (8)	329 (4)	8.8 (14)
H(7)	239 (2)	48 (6)	432 (3)	5.4 (9)
H(8)	323 (2)	272 (6)	391 (3)	5.0 (9)
H(2)	551 (3)	931 (9)	466 (5)	11.2 (15)

refine anisotropically. The H atoms were given isotropic temperature factors and fixed initially. The H atoms were located from a difference Fourier map. During the

Table 2. Selected intermolecular distances (Å)

Distances are given which are less than or close to the sum of the van der Waals radii for the individual atoms (Pauling, 1960).

		Symmetry
Cl(2)···O(1) next cell	3.386 (6) Å	x, y, z
Cl(3)···C(2)	3.420 (5)	$-x, -y, -z$
O(1)···H(6)	3.752 (5)	$\frac{1}{2} + x, \frac{1}{2} - y, z$
Cl(2)···C(3)	3.346 (5)	$\frac{1}{2} - x, \frac{1}{2} + y, -z$
O(2)···H(6)	2.907 (5)	$\frac{1}{2} - x, \frac{1}{2} + y, -z$
O(3)···H(8) next cell	2.674 (6)	x, y, z
Cl(3)···C(2)	3.420 (5)	$-x, -y, -z$

Table 3. Selected torsion angles (°) with their standard deviations

O(1)–C(11)–C(1)–C(9)	53.8 (4)
O(1)–C(11)–C(1)–C(2)	–124.7 (4)
O(1)–C(11)–C(12)–O(2)	32.9 (4)
O(1)–C(11)–C(12)–O(3)	–144.2 (4)
O(2)–C(12)–C(11)–C(1)	–152.8 (4)
O(3)–C(12)–C(11)–C(1)	30.2 (4)
C(12)–C(11)–C(1)–C(2)	61.1 (4)
C(12)–C(11)–C(1)–C(9)	–120.4 (4)
O(3)–C(12)–O(2)–H(2)	–1.8 (6)

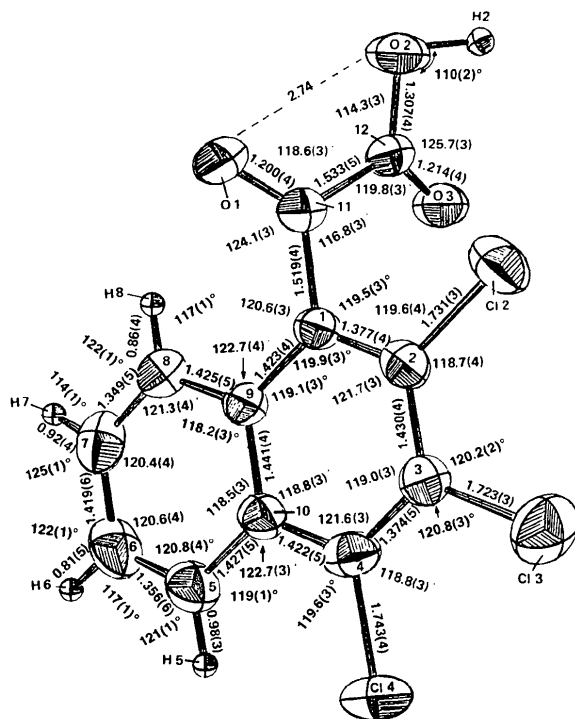


Fig. 1. ORTEP drawing of the molecule; the thermal ellipsoids are at 50% probability for C, O, and Cl and at 10% probability for H atoms. The C atoms are numbered while the O, H, and Cl atoms are designated and numbered. All distances (Å) and angles (°) including H are given with their standard deviations.

last four cycles of refinement the H coordinates were permitted to vary and during the last two cycles the H isotropic temperature factors were allowed to vary also. The final refinement results gave a conventional R value, $\sum |F_o| - |F_c| / \sum |F_o|$, of 0.053 and a weighted R value, $[\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$, of 0.053. The standard deviation in an observation of unit weight was 1.58.

There were no significantly large positive or negative electron density peaks in a final difference Fourier synthesis; the largest positive region was $0.4 \text{ e } \text{Å}^{-3}$ and the largest negative region was $0.3 \text{ e } \text{Å}^{-3}$.

The atomic scattering factors of C, O and Cl were taken from Cromer & Mann (1968) and for H from Stewart, Davidson & Simpson (1965). Anomalous-scattering corrections taken from *International Tables for X-ray Crystallography* (1968) were introduced for Cl atoms for the final stage of refinement. In addition to local programs for the IBM 370/165 computer, the programs used in this determination were *FORDAP* (Zalkin, 1974), *ORFLS* and *ORFFE* (Busing, Martin & Levy, 1962, 1964), *ORTEP* (Johnson, 1970), *PLANES* (Smith, 1964) and *MULTAN* (Main, Woolfson & Germain, 1971). The results are presented in Tables 1, 2 and 3, and in Fig. 1.*

Discussion. The average C–C bond length in the naphthalene ring is 1.399 Å with no bond more than one standard deviation from the mean. The naphthalene ring is essentially planar with the greatest deviation of a ring C atom being 0.01 Å. The α -CO group is rotated $61.1(4)^\circ$ from the naphthalene plane, as given by the torsion angle C(2)–C(1)–C(11)–C(12) and shown by Fig. 2, a view down the a axis. The α -CO group has a torsion angle of $32.9(4)^\circ$ between the two approximately *cis* (synperiplanar) carbonyl O atoms. Parthasarathy, Ohrt, Horeau, Vigneron & Kagan (1970) report an angle of 104° between the carbonyl O atoms for the glyoxylate group in (–)-menthyl *p*-bromophenylglyoxylate. This gives an angle of 76° between the α -CO group and the carboxylate plane. An angle of 75° was reported by Oehme & Schellenberger (1968) for the two carbonyl O atoms of ethyl phenylglyoxylate. Both of these torsion-angle values for the α -CO O atoms to the carboxyl plane are in good agreement with the value reported for this structure. The dihedral angle reported for the angle between the carboxyl plane and the α -CO group of pyruvic acid is $57.6(5)^\circ$ (Dyllick-Brenzinger, Bauder & Günthard, 1977).

The molecule packs in dimer pairs situated about a center of symmetry, as shown by Fig. 3 which is a view

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36429 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

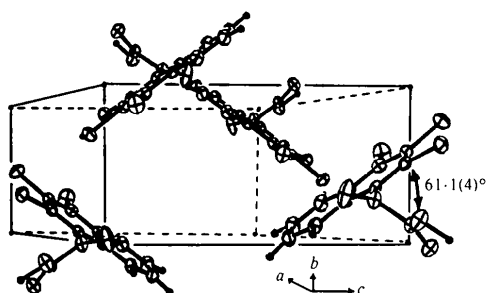


Fig. 2. ORTEP drawing down the long axis, *a*. This view shows the torsion angle [61.4 (4)°] of the glyoxylate group with respect to the naphthalene-ring part of the molecule.

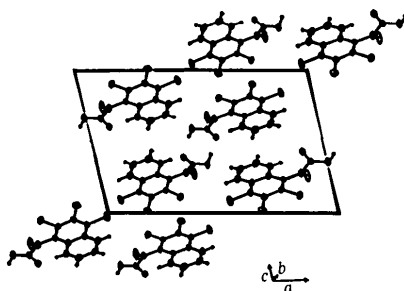


Fig. 3. ORTEP drawing of the unit cell down the short axis, *b*. The hydrogen bonding, forming dimers about a center of symmetry, is shown by this view.

of the molecular packing down *b*, the short axis. The α -CO is not involved in hydrogen bonding in this crystal structure, as it was for pyruvic acid (Dyllick-Brenzinger *et al.*, 1977) (microwave spectra). Hirota & Shinazaki (1969) reported spectral evidence for intramolecular hydrogen bonding for phenylglyoxylic acid in *n*-hexane, methylene chloride, and chloroform. Intramolecular hydrogen bonding was reported in α -keto and α -alkoxy carboxylic acids by Michinori & Minoru (1961) from infrared studies in CCl_4 solutions. Preliminary spectral studies of the reported compound in our laboratory with visible-UV and IR do not show evidence for hydrogen bonding involving the α -CO. The results of this work will be reported elsewhere. Intramolecular hydrogen bonding would be favored by *trans* carbonyl O atoms for the α -CO and carboxyl groups, which would result in a *cis* hydroxyl to α -CO conformation. The barriers for internal rotation may not be very large for rotation about the C-C and C-O bonds and the results for solution or gaseous spectra may thus exhibit intramolecular hydrogen bonding while the formation of dimers is favored in crystals.

Potential-energy minima should be computed for rotation of the hydroxyl and for rotation of the α -CO groups in this molecule. Once the dimer is formed the hydroxyl group is oriented away from the α -CO oxygen and thus prevents hydrogen bonding of this type.

There are no unusual bond distances or angles in this structure, but the torsion angles involving the α -CO group are of interest and the torsion angle between the two carbonyl O atoms within the glyoxylate group may indicate a potential minimum near the 30° angle.

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