

Monomethyl Succinate

BY J. A. KANTERS, H. M. DOESBURG AND T. KOOPS

Structural Chemistry Group, Rijksuniversiteit Utrecht, Transitorium 3, Padualaan 8, Utrecht, The Netherlands

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Abstract. $C_5O_4H_8$, monoclinic, $P2_1/a$, $a = 9.768$ (3), $b = 5.688$ (1), $c = 12.411$ (3) Å, $\beta = 111.4$ (2)°, $D_x = 1.37$ g cm⁻³. The structure consists of centrosymmetric dimers formed by hydrogen bonds between carboxyl groups of adjacent molecules. The conformation of the C chain of the monomethyl ester differs from that of the acid by rotation about the central C—C bond, which turns the planar C chain into a non-planar flexed one. In contrast to the ester group, the C ^{β} —C ^{α} —C=O arrangement of the carboxyl group deviates from the ideal synplanar form.

Introduction. The present study was undertaken to examine the effect of esterification of one of the carboxyl groups in a dicarboxylic acid. This is the first crystal structure report on a monomethyl ester of a saturated dicarboxylic acid and a comparison of conformational tendencies with monomethyl esters of two α,β -unsaturated dicarboxylic acids is presented.

Prismatic, colourless crystals of monomethyl succinate were obtained by slow evaporation from a solution in isobutanol. The crystals are hygroscopic, so were sealed in a capillary glass tube. Preliminary cell parameters and the space group ($P2_1/a$) were determined from photographs. From a crystal (0.6 × 0.5 × 0.2 mm) accurate cell dimensions and 2186 intensities were collected with a CAD-3 Nonius diffractometer [$\lambda(\text{Cu } K\alpha) = 1.54178$ Å] by the ω - 2θ scan technique. The upper limit for $\sin \theta/\lambda$ was 0.60. After application of the Lorentz-polarization correction, equivalent reflexions were averaged to give 1140 independent reflexions. Of these 966 had $I > 3\sigma(I)$. The data were placed on an approximate absolute scale by means of a Wilson plot; no correction was applied for absorption [$\mu(\text{Cu } K\alpha) = 10.5$ cm⁻¹].

The structure was solved by direct methods (Karle & Hauptman, 1956), based on 187 reflexions with $E > 1.40$. An E map showed all C and O atoms. Block-diagonal least-squares refinement of the positions and isotropic thermal parameters of the C and O atoms, followed by anisotropic thermal refinement and a difference synthesis, revealed the positions of all H atoms, which were assigned constant isotropic thermal factors equal to those of the carrier atom. Because of extinction the 200 reflexion was eliminated at this stage ($F_o - F_c = -17.08$). The function minimized was

Table 1. Fractional coordinates ($\times 10^4$ for C and O; $\times 10^3$ for H)

The estimated standard deviations are given in parentheses and refer to the last decimal position.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
C(1)	3980 (3)	742 (5)	6027 (2)	
C(2)	3109 (3)	1201 (6)	6769 (3)	
C(3)	3204 (3)	3733 (6)	7203 (3)	
C(4)	4698 (3)	4339 (5)	8056 (2)	
C(5)	6101 (5)	7280 (8)	9327 (4)	
O(1)	4400 (3)	-1449 (4)	6038 (2)	
O(2)	4258 (2)	2270 (4)	5439 (2)	
O(3)	4696 (2)	6421 (4)	8555 (2)	
O(4)	5757 (2)	3110 (4)	8288 (2)	
H(1)	478 (4)	-182 (6)	554 (3)	4.9 Å ²
H(21)	341 (3)	4 (5)	743 (2)	4.2
H(22)	206 (3)	84 (5)	625 (2)	4.2
H(31)	297 (3)	489 (5)	657 (2)	4.1
H(32)	245 (3)	398 (5)	761 (2)	4.1
H(51)	656 (4)	632 (6)	1002 (3)	6.1
H(52)	678 (4)	744 (6)	895 (3)	6.1
H(53)	599 (4)	864 (7)	978 (3)	6.1

Table 2. Interatomic distances (Å) and angles (°)

Estimated standard deviations are given in parentheses.

C(1)—C(2)	1.488 (5)	C(1)—C(2)—C(3)	114.1 (3)
C(2)—C(3)	1.529 (5)	C(2)—C(3)—C(4)	112.6 (2)
C(3)—C(4)	1.497 (4)	O(1)—C(1)—O(2)	122.9 (3)
C(1)—O(1)	1.310 (4)	O(1)—C(1)—C(2)	114.1 (3)
C(1)—O(2)	1.227 (4)	O(2)—C(1)—C(2)	123.0 (3)
C(4)—O(3)	1.337 (4)	O(3)—C(4)—O(4)	123.7 (2)
C(4)—O(4)	1.193 (4)	O(3)—C(4)—C(3)	111.5 (2)
C(5)—O(3)	1.443 (4)	O(4)—C(4)—C(3)	124.9 (3)
C(2)—H(21)	1.01 (3)	C(4)—O(3)—C(5)	116.5 (3)
C(2)—H(22)	1.01 (3)	C(1)—O(1)—H(1)	117 (2)
C(3)—H(31)	0.99 (3)	O(3)—C(5)—H(51)	114 (2)
C(3)—H(32)	1.04 (3)	O(3)—C(5)—H(52)	112 (2)
C(5)—H(51)	0.98 (4)	O(3)—C(5)—H(53)	111 (2)
C(5)—H(52)	0.95 (4)	C(1)—C(2)—H(21)	109 (2)
C(5)—H(53)	0.99 (4)	C(1)—C(2)—H(22)	104 (2)
O(1)—H(1)	0.85 (4)	C(3)—C(2)—H(21)	111 (2)
O(1)···O(2')	2.656 (4)	C(3)—C(2)—H(22)	109 (2)
(1 - <i>x</i> , - <i>y</i> , 1 - <i>z</i>)		C(2)—C(3)—H(31)	112 (2)
H(1)···O(2')	1.81 (4)	C(4)—C(3)—H(31)	107 (2)
		C(2)—C(3)—H(32)	109 (2)
		C(4)—C(3)—H(32)	108 (1)
		H(51)—C(5)—H(52)	108 (3)
		H(51)—C(5)—H(53)	92 (3)
		H(52)—C(5)—H(53)	117 (3)
		O(1)—H(1)···O(2')	173 (3)

Table 3. Dihedral angles of the monomethyl ester of succinic acid and the corresponding values of β -succinic acid

Plane through	Plane through	Dihedral angle		Conformation about
		Monomethyl succinate	β -Succinic acid	
C(1)C(2)O(1)O(2)	C(1)C(2)C(3)	26.9°	10.5°	C(1)–C(2)
C(3)C(4)O(3)O(4)	C(2)C(3)C(4)	9.0	10.5	C(3)–C(4)
C(4)O(3)C(5)	O(3)C(4)O(4)	6.4	—	C(4)–O(3)
C(1)C(2)C(3)	C(2)C(3)C(4)	68.5	0.0	C(2)–C(3)

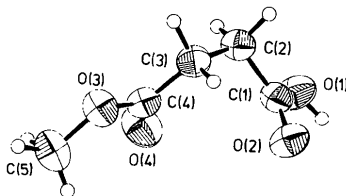
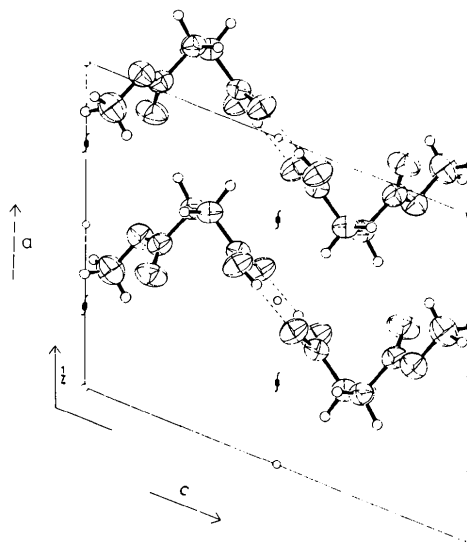


Fig. 1. Molecular conformation and atomic numbering in monomethyl succinate. The C and O atoms are represented by thermal ellipsoids at the 50% level.

$\Sigma w(|F_o| - |F_c|)^2$. In the final stage weights $w = \sigma^{-2}(F_o)$ were introduced. Block-diagonal anisotropic least-squares refinement followed by anisotropic full-matrix refinement resulted in a final R of 0.058 ($R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$) and $R_w = 0.066$ ($R_w = [\Sigma w(|F_o| - |F_c|)^2 / w F_o^2]^{1/2}$). The goodness-of-fit was 4.63; the maximum shift/error ratio was 0.11 for C and O parameters and 0.23 for H. A final difference map showed no electron density above 0.20 e \AA^{-3} . Tabulations of atomic scattering factors were used for C and O (Cromer & Mann, 1968) and H (Stewart, Davidson & Simpson, 1965). The final positional parameters are listed in Table 1.*

Discussion. Bond lengths and angles are given in Table 2, atomic numbering in Fig. 1. The length of the central C–C bond (1.529 \AA) is in good agreement with that accepted for an sp^3 – sp^3 bond (1.533 \AA ; Lide, 1962). C(1)–C(2) and C(3)–C(4) are slightly shorter than the value suggested for an sp^2 – sp^3 bond (1.505 \AA ; Lide, 1962), the respective values being 1.488 and 1.497 \AA . In contrast to the molecular conformation about the central C–C bond in β -succinic acid (Broadley, Cruickshank, Morrison, Robertson, Shearer & Shearer, 1959) where the molecular symmetry ($\bar{1}$) imposes an antiplanar arrangement, the conformation of methyl succinate is synclinal. This twisted C(1)–C(4) chain conformation is also found in the dimethyl ester of

meso-tartaric acid (Kroon & Kanters, 1973), DL-methylsuccinic acid (Schouwstra, 1973) and KH DL-methylsuccinate (Schouwstra, 1972). Dihedral angles are given in Table 3 with corresponding values for β -succinic acid. Esterification of one of the carboxyl groups results in a rotation of 68.5° about C(2)–C(3). In the ester group the C–O and C=O distances are 1.34 and 1.19 \AA respectively; the corresponding values in the carboxyl group are 1.31 and 1.23 \AA . The bond angles C–C–O (112°) and C–C=O (125°) in the ester part also differ from those in the carboxyl group, being 114 and 123° respectively. These systematic trends have been noticed before (Kroon & Kanters, 1973; Kanters, Kroon, Peerdeman & Schoone, 1967). The torsion angle C^β – C^α –C=O in the carboxyl group is -27.5° ; the corresponding value in the ester part is 8.0° . From these values it can be seen that though the arrangement in the carboxyl group has been twisted, it is still close to synplanar. This synplanar C^β – C^α –C=O arrangement is adopted in all saturated carboxylic acids and their ester groups (Leiserowitz, 1976). The hypothetical antiplanar C^β – C^α –C=O arrangement is

Fig. 2. A view of the molecular packing in monomethyl succinate down b . Hydrogen bonds are denoted by dashed lines.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32378 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

unfavourable because of the shorter non-bonding $C(2) \cdots O$ and $H(21) \cdots O$ distances and because of the preference for a staggered rather than an eclipsed disposition of bonds, if one regards a double bond as being decomposed into two bent bonds (Dunitz & Strickler, 1968). In α, β -unsaturated acids, where the *syn* form implies eclipsing of double bonds, some acids have either the *anti* form or show orientational *anti-syn* disordering, indicating a delicate balance between the two factors mentioned above. In monomethyl *trans,trans*-muconate (Rabinovich & Schmidt, 1967) the orientation of the methoxycarbonyl group is synplanar, while the carboxyl group shows the antiplanar conformation and exhibits no disorder, in contrast to monomethyl fumarate (Leiserowitz & Tang, 1977) where the conformations of ester and acid groups are identical to that in monomethyl *trans,trans*-muconate, though the acid group shows some orientational disorder. The difference in the $C=O$ and $C-O(H)$ distances, agreeing well with the mean reported for carboxyl groups without orientational disorder in 16 acids (Leiserowitz, 1976), and the well-defined position of the $O(H)$ H atom indicate absence of orientational disorder in the carboxyl group of monomethyl succinate. The dihedral angle $C(1)-C(2)-O(1)-O(2)/C(3)-C(4)-O(3)-O(4)$ is 82.2° . The distance of $C(5)$ from the best plane through $C(3), C(4), O(3)$ and $O(4)$ is 0.11 \AA . The H atoms of the methyl group are in the *anti* position, while in dimethyl *meso*-tartrate an approximately equal distribution of the *syn* and *anti* forms is present.

The molecules are hydrogen-bonded across centres of symmetry, thus forming cyclic centrosymmetric dimers. The $O-H \cdots O$ angle is close to linear (172.5°) with an $O \cdots O$ distance of 2.66 \AA . The deviation of

$H(1)$ from the plane of $C(1), O(1)$ and $O(2)$ is 0.11 \AA . The carboxyl groups forming the dimer are not coplanar; the displacement between them is 0.17 \AA , which agrees well with the average value reported for a number of centrosymmetric dimers (Jeffrey & Sax, 1963). The stacking of the dimers is determined by van der Waals interactions; no short distances except the hydrogen bond are present. The structure consists of two stacks of hydrogen-bonded pairs of molecules, centred at $(0,0,\frac{1}{2})$ and $(\frac{1}{2},0,\frac{1}{2})$, which are related by the *a* glide plane. The molecular packing is shown in Fig. 2.

References

- BROADLEY, J. S., CRUICKSHANK, D. W. J., MORRISON, J. D., ROBERTSON, J. M., SHEARER, F. R. S. & SHEARER, H. M. (1959). *Proc. Roy. Soc. A* **251**, 441–457.
 CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–323.
 DUNITZ, J. D. & STRICKLER, P. (1968). *Structural Chemistry and Molecular Biology*, edited by A. RICH & N. DAVIDSON, pp. 595–602. San Francisco: Freeman.
 JEFFREY, G. A. & SAX, M. (1963). *Acta Cryst.* **16**, 430.
 KANTERS, J. A., KROON, J., PEERDEMAN, A. F. & SCHOONE, J. C. (1967). *Tetrahedron*, **23**, 4027–4033.
 KARLE, J. & HAUPTMAN, H. (1956). *Acta Cryst.* **9**, 635–651.
 KROON, J. & KANTERS, J. A. (1973). *Acta Cryst.* **B29**, 1278–1283.
 LEISEROWITZ, L. (1976). *Acta Cryst.* **B32**, 775–802.
 LEISEROWITZ, L. & TANG, C.-P. (1977). To be published.
 LIDE, D. R. (1962). *Tetrahedron*, **17**, 125–134.
 RABINOVICH, D. & SCHMIDT, G. M. J. (1967). *J. Chem. Soc. (B)*, pp. 286–289.
 SCHOUWSTRA, Y. (1972). *Acta Cryst.* **B28**, 2217–2221.
 SCHOUWSTRA, Y. (1973). *Acta Cryst.* **B29**, 1–4.
 STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Acta Cryst. (1977). **B33**, 1288–1290

1-Benzotriazoleacetic Acid

BY F. GIORDANO AND A. ZAGARI

Istituto Chimico, Università di Napoli, Via Mezzocannone 4, Napoli, Italy

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Abstract. $C_6H_4N_3CH_2COOH$, $M_r = 177.2$, monoclinic, $P2_1/c$, $a = 13.26(4)$, $b = 4.53(1)$, $c = 15.18(4) \text{ \AA}$, $\beta = 113.1(2)^\circ$, $Z = 4$, $V = 838 \text{ \AA}^3$, $D_c = 1.41 \text{ g cm}^{-3}$, $F(000) = 368$. The compound crystallized from ethanol solution. The radiation used was $Mo K\alpha$. The structure was solved by direct methods. Least-squares refinement with 846 observed reflexions converged at R

$= 0.044$ for 146 parameters. The benzotriazole residue is planar. Strong $O-H \cdots N$ hydrogen bonds, 2.69 \AA in length and arranged across a glide plane, link the molecules together to form infinite chains running parallel to the *c* axis.

Introduction. A prismatic crystal ($0.16 \times 0.18 \times 0.5$