

Structure of Dimethylmalonic Acid, A Redetermination

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Abstract. $C_5H_8O_4$, $M_r = 132.12$, tetragonal, $I4_1/acd$, $a = 12.662$ (2), $c = 16.234$ (4) Å, $V = 2603$ (1) Å³, $Z = 16$, $D_m = 1.349$ (2), $D_x = 1.349$ g cm⁻³, $\lambda(Mo K\alpha) = 0.71069$ Å, $\mu = 1.11$ cm⁻¹, $F(000) = 1119.9$, $T = 293$ K, final $R = 0.047$, wR (on $|F_o|^2$) = 0.065 for 509 unique observed reflections. The previous determination [Haas & Brenner (1966). *Acta Cryst.* **20**, 709–711] is confirmed and improved with location of all H atoms. Pertinent parameters for the doubly hydrogen bonded

pair of carboxyl groups, $-C(=O)\cdots O=C-$, related by a crystallographic diad are: C–O 1.307 (3), C=O 1.207 (3), O \cdots O 2.662 (5) Å, O–C=O 123.7 (2), and C–O \cdots O=C 12.3 (4)°.

Experimental. Colourless transparent crystal 0.44 × 0.40 × 0.20 mm, D_m by flotation in *n*-hexane/CCl₄, mean $\mu_r = 0.02$, Nicolet R3m diffractometer, cell parameters from 2θ values of 21 reflections with $10 \leq 2\theta \leq 20^\circ$ (Sparks, 1976), ω - 2θ scan at 2.02–8.37° min⁻¹, scan range 1° below $K\alpha_1$ to 1° above $K\alpha_2$, stationary background counts for one-half of scan time at each end, $2\theta_{max} = 54^\circ$, $0 \leq h \leq 11$, $0 \leq k \leq 16$, $0 \leq l \leq 20$ with $h \leq k$, intensities of two standards monitored every 125 data measurements were within $\pm 1\%$, 623 independent reflections measured, profile fitting of raw intensities (Diamond, 1969), 509 observed with $|F_o| < 3\sigma(|F_o|)$, empirical absorption correction based on ψ scans of ten strong reflections (North, Phillips & Mathews, 1968; Kopfmann & Huber, 1968), transmission factors 0.895–0.935. The structure was refined from the previous model (Haas & Brenner, 1966), weighting function $w = [\sigma^2(|F_o|) + 0.0008|F_o|^2]^{-1}$, C and O atoms anisotropic, all H atoms appeared on difference map and refined with isotropic temperature factors, isotropic extinction parameter $g = 1.1(1) \times 10^{-6}$ where correction for calculated structure amplitude given by $|F_c|_{corr} = |F_c|[(1 + g|F_c|^2)/\sin 2\theta]^{-1/4}$, final R (59 variables) = 0.047, wR (on $|F_o|^2$) = 0.065, $S = 1.594$, $(\Delta/\sigma)_{max} = 0.001$, extrema in final difference map +0.25 to -0.14 e Å³, atomic scattering factors from *International Tables for X-ray Crystallography* (1974),

calculations on Data General Nova 3/12 minicomputer using *SHELXTL* program system (Sheldrick, 1982). The atomic parameters are reported in Table 1,† and bond distances and angles in Table 2. The atom-numbering scheme is shown in Fig. 1.

Related literature. The previous structural determination (Haas & Brenner, 1966) by the symbolic addition method with 342 observed $Cu K\alpha$ data attained $R = 0.098$ for unit weights; standard deviations on bond distances and angles were 0.010 Å and 0.5°, respectively.

† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 43025 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional atomic coordinates and thermal parameters (Å² × 10⁴ for C and O, × 10³ for H)

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq} or U_{iso}^*
O(1)	0.1278 (2)	0.3291 (1)	0.0170 (1)	685 (7)†
O(2)	0.1860 (1)	0.2526 (1)	0.1311 (1)	573 (6)†
C(1)	0.1856 (2)	0.2607 (2)	0.0571 (1)	425 (7)†
C(2)	$\frac{1}{2}$	0.1904 (2)	0	478 (9)†
C(3)	0.3270 (3)	0.1230 (3)	0.0502 (2)	745 (11)†
H(1)	0.087 (2)	0.363 (2)	0.054 (2)	83 (9)
H(3A)	0.366 (2)	0.081 (2)	0.017 (2)	72 (8)
H(3B)	0.288 (3)	0.075 (2)	0.080 (2)	98 (10)
H(3C)	0.379 (3)	0.164 (3)	0.086 (2)	134 (16)

* Exponent of the isotropic temperature factor takes the form: $-8\pi^2 U_{iso} \sin^2 \theta / \lambda^2$.

† U_{eq} calculated as one-third of the trace of the orthogonalized U tensor.

Table 2. Bond distances (Å), bond angles (°) and selected torsion angles (°)

C(1)–O(1)	1.307 (3)	C(1)–O(2)	1.207 (3)
C(1)–C(2)	1.522 (2)	C(2)–C(3)	1.530 (3)
O(1)⋯O(2)	2.662 (5)		
O(1)–C(1)–O(2)	123.7 (2)	O(1)–C(1)–C(2)	112.6 (2)
O(2)–C(1)–C(2)	123.7 (2)	C(1)–C(2)–C(3)	110.1 (1)
C(1)–C(2)–C(1 ^h)	108.3 (2)	C(1)–C(2)–C(3 ^h)	108.0 (1)
C(3)–C(2)–C(3 ^h)	112.2 (3)		
O(1)–C(1)–O(2)⋯O(1 ^h)	–3.8 (3)	O(1)–C(1)–C(2)–C(3)	172.1 (2)
C(1)–O(2)⋯O(1 ^h)–C(1 ^h)	12.3 (4)		

Symmetry code: (i) $-\frac{1}{2} + y, \frac{1}{2} + x, \frac{1}{2} - z$; (ii) $\frac{1}{2} - x, y, -z$.

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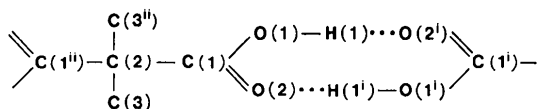


Fig. 1. Numbering scheme and hydrogen bonding between carboxyl groups across a twofold axis. A second independent twofold axis passes through C(2).

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Structure of *N*-(4-Amino-3-furazanyl)-2,2,2-trichloro-*N'*-methoxyacetamide

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Abstract. $C_4H_6Cl_3N_4O_2$, $M_r = 248.48$, monoclinic, $P2_1/c$, $a = 9.287$ (1), $b = 9.493$ (1), $c = 13.208$ (2) Å, $\beta = 108.47$ (1)°, $V = 1104.5$ (3) Å³, $Z = 4$, $D_x = 1.494$ Mg m⁻³, $\lambda(\text{Cu } K\alpha) = 1.54178$ Å, $\mu = 7.653$ mm⁻¹, $F(000) = 500$, $T = 295$ K, final $R = 0.047$, $wR = 0.060$ for 1400 independent observed reflections. The furazan ring is planar, while the adjacent primary and secondary amine groups deviate from the ring-atoms least squares plane by only 0.10 and 0.13 Å, respectively. In addition the acetamide moiety is planar to within 0.04 Å, except for its three chlorine substituents. Intermolecular hydrogen bonding occurs between the secondary amine and ring nitrogen N(2).

Table 1. Atom coordinates ($\times 10^4$) and temperature factors ($\text{Å}^2 \times 10^3$)

Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Cl(1)	10972 (1)	-3638 (1)	3684 (1)	74 (1)
Cl(2)	8459 (1)	-3377 (1)	1751 (1)	75 (1)
Cl(3)	8518 (1)	-5596 (1)	3237 (1)	81 (1)
O(1)	7273 (3)	1809 (2)	4102 (2)	49 (1)
C(4)	6396 (3)	48 (3)	3053 (2)	37 (1)
O(9)	6413 (2)	-2326 (2)	4397 (2)	47 (1)
N(6)	8729 (3)	-1478 (3)	3820 (2)	42 (1)
N(5)	6038 (3)	1324 (3)	3254 (2)	46 (1)
N(2)	8359 (3)	763 (3)	4430 (2)	44 (1)
C(3)	7852 (3)	-301 (3)	3797 (2)	35 (1)
C(7)	8169 (3)	-2843 (3)	3667 (2)	35 (1)
N(8)	7022 (3)	-3334 (3)	3879 (2)	39 (1)
C(11)	8986 (4)	-3829 (3)	3118 (3)	45 (1)
N(12)	5530 (3)	-733 (3)	2218 (2)	47 (1)
C(10)	5113 (5)	-2859 (5)	4601 (4)	75 (2)

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Experimental. A clear 0.28 × 0.18 × 0.43 mm data crystal was provided by C. Coon of Lawrence Livermore Laboratory. Automated Nicolet R3m diffractometer with incident-beam graphite monochromator, 25 centered reflections within $40 \leq 2\theta \leq 60^\circ$ used for determining lattice parameters. $(\text{Sin}\theta/\lambda)_{\text{max}} = 0.55$ Å⁻¹, range of hkl : $0 \leq h \leq 10$, $0 \leq k \leq 10$, $-13 \leq l \leq 14$. Standards 406, 040, 006, monitored every 60 reflections with linear variation of 3.1% over data collection, $\theta/2\theta$ mode, scan width $(2.0 + \Delta_{\alpha 1\alpha 2})^\circ$,

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

Cl(1)–C(11)	1.767 (3)	Cl(2)–C(11)	1.767 (4)
Cl(3)–C(11)	1.752 (3)	O(1)–N(5)	1.403 (3)
O(1)–N(2)	1.383 (3)	C(4)–N(5)	1.306 (4)
C(4)–C(3)	1.435 (4)	C(4)–N(12)	1.360 (4)
O(9)–N(8)	1.396 (4)	O(9)–C(10)	1.411 (5)
N(6)–C(3)	1.377 (4)	N(6)–C(7)	1.387 (4)
N(2)–C(3)	1.301 (4)	C(7)–N(8)	1.272 (4)
C(7)–C(11)	1.525 (5)		
N(5)–O(1)–N(2)	110.2 (2)	N(5)–C(4)–C(3)	108.7 (2)
N(5)–C(4)–N(12)	123.1 (3)	C(3)–C(4)–N(12)	128.0 (3)
N(8)–O(9)–C(10)	110.6 (3)	C(3)–N(6)–C(7)	124.3 (3)
O(1)–N(5)–C(4)	105.7 (2)	O(1)–N(2)–C(3)	106.0 (2)
C(4)–C(3)–N(6)	128.7 (3)	C(4)–C(3)–N(2)	109.4 (3)
N(6)–C(3)–N(2)	121.6 (2)	N(6)–C(7)–N(8)	127.7 (3)
N(6)–C(7)–C(11)	115.0 (3)	N(8)–C(7)–C(11)	117.2 (3)
O(9)–N(8)–C(7)	110.8 (2)	Cl(1)–C(11)–Cl(2)	108.7 (2)
Cl(1)–C(11)–Cl(3)	108.4 (2)	Cl(2)–C(11)–Cl(3)	109.1 (2)
Cl(1)–C(11)–C(7)	110.2 (2)	Cl(2)–C(11)–C(7)	108.6 (2)
Cl(3)–C(11)–C(7)	111.7 (3)		
Hydrogen bonds			
N...H	2.29 (4)	N...N	3.03 (1)
N...H–N	152.4 (2.8)		