

Structure of Pyridinium Trihydrogen Dimalonate

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Abstract. $C_5H_6N^+ \cdot C_6H_7O_8^-$, $M_r = 287.22$, monoclinic, $P2_1/c$, $a = 17.250$ (2), $b = 7.759$ (1), $c = 9.721$ (1) Å, $\beta = 105.2$ (1)°, $V = 1255.6$ (5) Å³, $Z = 4$, $D_m = 1.52$ (2), $D_x = 1.519$ g cm⁻³, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 1.235$ cm⁻¹, $F(000) = 600$, $T = 293$ (2) K, final $R = 0.037$, $wR = 0.050$ for 1582 observed reflections. The non-planar malonate groups are connected in a two-dimensional network by asymmetric hydrogen bonds [2.508 (2), 2.643 (2) and 2.698 (2) Å]. A bifurcated hydrogen bond links the malonate and pyridinium groups [2.508 (2), 2.827 (2) Å].

Introduction. In potassium trihydrogen dimalonate (Currie, 1972), and in lithium trihydrogen dimalonate (Soriano-Garcia & Parthasarathy, 1978) one short asymmetrical intramolecular hydrogen bond and two intermolecular hydrogen bonds are found. Here we present the crystal and molecular structure of the title compound, in which only asymmetrical intermolecular hydrogen bonds exist, similar to the situation in dirubidium tetrahydrogen trimalonate (Soriano-Garcia, Toscano & Villena-Irbe, 1986).

Experimental. Crystals of pyridinium trihydrogen dimalonate were prepared from an acetonitrile solution containing equimolar portions of malonic acid and pyridine. Density determined by flotation. Space group from Weissenberg films. Unit-cell parameters and intensity data obtained on an Eraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo $K\alpha$ radiation. Crystal size: $0.30 \times 0.27 \times 0.44$ mm. Cell dimensions refined by least-squares fitting of 25 centred reflections monitored in the range $9 < \theta < 15^\circ$ using Mo $K\alpha$ radiation. Data-collection parameters: ω - 2θ scan, max. scan time 60 s, scan width $(0.8 + 0.3\tan\theta)^\circ$, aperture width $(2.4 + 0.9\tan\theta)$ mm; 12 068 reflections measured to $[(\sin\theta)/\lambda]_{\max} = 0.6608$ Å⁻¹, $-22 \leq h \leq 22$, $-10 \leq k \leq 10$, $-12 \leq l \leq 12$. Orientation control monitored ever 300 reflections, standard reflections (821, 832, 423) measured every 7500 s of scanning time did not show any significant change in intensity (-1.7%). Of 3249 unique reflections, 1582 were considered as

observed [$I > 3.0\sigma(I)$], R_{int} after merging for space group $P2_1/c$ was 0.019.

The structure was solved by direct methods using MULTAN80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). Positions of all non-H atoms revealed from the E map with the highest CFOM (2.84). Non-H atoms were refined with anisotropic thermal parameters. Positions of pyridinium and methylene H atoms calculated and included in structure-factor calculations as fixed-atom contributions. H atoms taking part in hydrogen bonds revealed from difference Fourier maps and refined with isotropic temperature factors, using XRAY76 (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976). Empirical weighting function $w = 8.0W_fW_s$, where $W_f(|F_o| < 0.01) = (|F_o|/0.01)^{1.0}$, $W_f(|F_o| > 8.0) = (8.0/|F_o|)^{1.2}$, $W_f(0.01 \leq |F_o| \leq 8.0) = 1.0$, $W_s(\sin\theta < 0.39) = [(\sin\theta)/0.39]^{1.5}$, $W_s(\sin\theta > 0.42) = [0.42/(\sin\theta)]^{1.4}$, $W_s(0.39 \leq \sin\theta \leq 0.42) = 1.0$, applied to keep $\sum w(\Delta F)^2$ uniform over ranges of $(\sin\theta)/\lambda$ and $|F_o|$. Refinement converged to $R = 0.037$ and $wR = 0.050$ for 197 parameters and 1955 contributing reflections including observed and less-thans for which $|F_o| > |F_c|$. Max. shift/e.s.d. = 0.085, average shift/e.s.d. = 0.008, $S = 0.97$, excursions in final difference Fourier map within 0.24 and -0.28 e Å⁻³.

Atomic scattering factors for H atoms were taken from Stewart, Davidson & Simpson (1965) and for other neutral atoms from Cromer & Mann (1968), and dispersion corrections were from Cromer & Liberman (1970). All calculations were performed on a DEC-10 computer at RCU-Ljubljana.

Discussion. The structure consists of two partially ionized malonate groups (A , B) and a pyridinium ion. The final fractional coordinates and U_{eq} values (Hamilton, 1959) are listed in Table 1.† The principal dimensions are presented in Table 2. Fig. 1 shows the

† Lists of structure factors, anisotropic thermal parameters, H-atom parameters, least-squares-planes equations and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54795 (16 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. Atom coordinates ($\times 10^4$ for non-H atoms, $\times 10^3$ for H atoms) and equivalent isotropic temperature factors ($\text{\AA}^2 \times 10^4$ for non-H atoms, $\text{\AA}^2 \times 10^2$ for H atoms) with e.s.d.'s in parentheses

	U_{eq} defined according to Hamilton (1959).			
	x	y	z	U_{eq}
O(11)	1932 (1)	4460 (2)	5547 (1)	404 (7)
O(12)	1108 (1)	4589 (2)	3380 (1)	467 (8)
O(13)	-623 (1)	3063 (2)	3617 (2)	521 (9)
O(14)	162 (1)	826 (2)	3511 (2)	445 (8)
C(11)	1278 (1)	4098 (2)	4626 (2)	291 (8)
C(12)	701 (1)	2985 (3)	5191 (2)	347 (9)
C(13)	9 (1)	2316 (2)	4032 (2)	325 (8)
O(21)	2967 (1)	5938 (2)	4571 (1)	404 (7)
O(22)	3846 (1)	5468 (2)	6653 (1)	440 (7)
O(23)	5609 (1)	6969 (2)	6294 (2)	561 (9)
O(24)	4828 (1)	9162 (2)	6520 (2)	510 (9)
C(21)	3666 (1)	6072 (2)	5452 (2)	300 (8)
C(22)	4257 (1)	7047 (3)	4829 (2)	357 (9)
C(23)	4975 (1)	7695 (2)	5957 (2)	338 (9)
N	2114 (1)	-104 (3)	3477 (2)	568 (12)
C(1)	2756 (2)	922 (4)	3881 (2)	592 (14)
C(2)	3114 (1)	1122 (3)	5296 (3)	527 (12)
C(3)	2815 (1)	266 (3)	6273 (2)	471 (11)
C(4)	2156 (1)	-768 (3)	5834 (3)	569 (13)
C(5)	1809 (1)	-957 (3)	4409 (3)	583 (14)
H(6)	191 (2)	-20 (5)	256 (4)	8 (1)
H(11)	-28 (2)	47 (4)	286 (4)	7 (1)
H(21)	254 (2)	532 (5)	499 (4)	10 (1)
H(22)	528 (2)	953 (4)	711 (3)	7 (1)

Table 2. Interatomic distances (\AA), valence angles ($^\circ$) and hydrogen-bond geometry (\AA , $^\circ$) with e.s.d.'s in parentheses

Malonate group A				
C(11)—O(11)	1.275 (2)	O(11)—C(11)—O(12)	124.2 (2)	
C(11)—O(12)	1.230 (2)	O(11)—C(11)—C(12)	114.4 (1)	
C(11)—C(12)	1.525 (3)	O(12)—C(11)—C(12)	121.4 (1)	
C(12)—C(13)	1.503 (2)	C(11)—C(12)—C(13)	113.0 (1)	
C(13)—O(13)	1.208 (2)	O(13)—C(13)—O(14)	123.2 (2)	
C(13)—O(14)	1.317 (2)	O(13)—C(13)—C(12)	123.7 (2)	
		O(14)—C(13)—C(12)	113.1 (2)	
Malonate group B				
C(21)—O(21)	1.288 (2)	O(21)—C(21)—O(22)	124.3 (2)	
C(21)—O(22)	1.221 (2)	O(21)—C(21)—C(22)	112.7 (2)	
C(21)—C(22)	1.517 (3)	O(22)—C(21)—C(22)	123.0 (1)	
C(22)—C(23)	1.509 (2)	C(21)—C(22)—C(23)	112.6 (2)	
C(23)—O(23)	1.197 (2)	O(23)—C(23)—O(24)	123.7 (2)	
C(23)—O(24)	1.316 (3)	O(23)—C(23)—C(22)	124.0 (2)	
		O(24)—C(23)—C(22)	112.3 (2)	
Pyridinium group				
N—C(1)	1.336 (4)	C(1)—N—C(5)	122.6 (2)	
N—C(5)	1.336 (4)	N—C(1)—C(2)	119.2 (3)	
C(1)—C(2)	1.361 (3)	C(1)—C(2)—C(3)	119.5 (3)	
C(2)—C(3)	1.367 (4)	C(2)—C(3)—C(4)	120.2 (2)	
C(3)—C(4)	1.365 (3)	C(3)—C(4)—C(5)	119.2 (2)	
C(4)—C(5)	1.365 (4)	C(4)—C(5)—N	119.3 (2)	
Hydrogen bonds				
D—H...A	D—H	H...A	D...A	\angle D—H...A
O(14)—H(11)...O(12)	0.90 (3)	1.75 (3)	2.643 (2)	174 (3)
O(24)—H(22)...O(22 ⁱⁱⁱ)	0.89 (3)	1.81 (3)	2.698 (2)	174 (3)
O(21)—H(21)...O(11)	1.05 (4)	1.46 (4)	2.508 (2)	178 (3)
N—H(6)...O(11 ⁱⁱ)	0.87 (4)	2.04 (4)	2.827 (2)	148 (4)

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

asymmetric unit; the unit-cell contents and the hydrogen-bonding scheme of malonate moieties are shown in Fig. 2.

Bond distances and angles in both compounds are within the expected ranges. The conformations of the

A and B species are similar to those in malonic acid (Goedkoop & MacGillavry, 1957), ammonium hydrogen malonate (Chapuis, Zalkin & Templeton, 1975) and dirubidium tetrahydrogen trimalonate (Soriano-Garcia *et al.*, 1986), where the two carboxyl groups are approximately perpendicular to each other.

The crystal structure is highly stabilized by a network of O...O and O...N hydrogen bonds (Table 2). The O(11) atom acts as an acceptor in a bifurcated hydrogen bond, linking the malonate and pyridinium groups [2.508 (2), 2.827 (2) \AA] (Fig. 2). The pyridinium cation and the hydrogen malonate group form an asymmetric hydrogen bond of 2.827 (2) \AA , which is longer than the corresponding hydrogen bonds in complexes between oxalate and pyridinium groups [2.716 (1), 2.792 (2) \AA] (Newkome, Theriot & Fronczek, 1985, 1986).

Considering the length and symmetry of the O...O hydrogen bonds, it can be observed that the three acid H atoms are equally shared by the two malonate groups, while the fourth H atom is bonded to pyridine. Since the degree of ionization of groups A and B is approximately the same, it is not reasonable to treat one as a hydrogen malonate and the other as a malonic acid molecule. The A and B moieties are

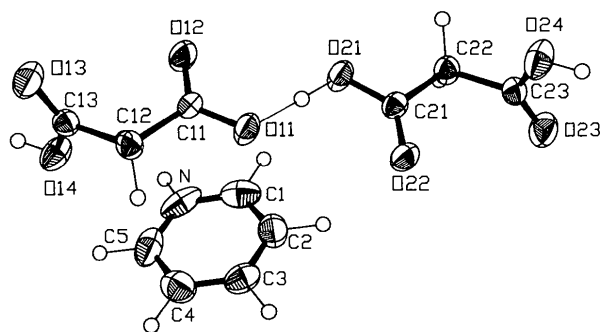


Fig. 1. ORTEP (Johnson, 1965) perspective view of the asymmetric unit showing the atomic labelling scheme with the anisotropic displacement parameters for the non-H atoms scaled to 50% probability.

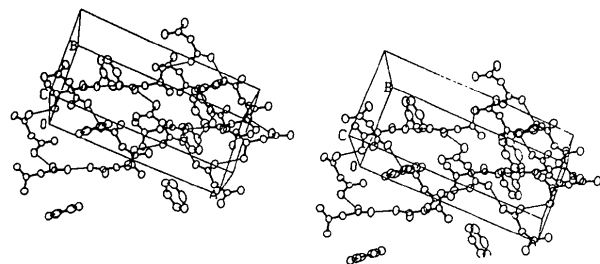


Fig. 2. Stereoscopic view presenting the unit-cell contents and hydrogen-bonding scheme of the malonate and pyridinium moieties.

mutually connected by asymmetric intermolecular hydrogen bonds giving rise to a network of chains parallel to the [111] direction.

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Structure of *N*-Nitroso-*r*-2,*c*-7-diphenylhexahydro-1,4-diazepin-5-one

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Abstract. $C_{17}H_{17}N_3O_2$, $M_r = 295.34$, orthorhombic, $P2_12_12_1$, $a = 7.659$ (1), $b = 12.741$ (1), $c = 15.095$ (1) Å, $V = 1473.19$ (2) Å³, $Z = 4$, $D_m = 1.33$, $D_x = 1.32$ Mg m⁻³, $\lambda(\text{Cu K}\alpha) = 1.5418$ Å, $\mu = 0.68$ mm⁻¹, $F(000) = 624$, $T = 295$ K, $R = 0.031$ for 1549 unique observed reflections with $I > 2.5\sigma(I)$. The seven-membered heterocyclic ring adopts a boat conformation flattened at the nitroso end of the ring. The substituent phenyl rings occupy pseudo-axial positions and the nitroso group is coplanar with the C(2), N(1), C(7) plane of the central ring. The crystal structure is stabilized by intermolecular N—H \cdots O and weak C—H \cdots O hydrogen bonds.

Introduction. Ever since the first demonstration of carcinogenicity in *N*-nitroso compounds (Magee & Barnes, 1956), there have been extensive biochemical and physicochemical studies on their structure–activity relationships (Lijinsky, 1984; Druckrey, Preussmann, Ivankovic & Schmahl, 1967; Magee,

Montesano & Preussman, 1976; Preussman, 1984). There is, however, little information on the detailed geometries of *N*-nitroso compounds although several solution NMR spectroscopic investigations have been carried out (Fraser & Grindley, 1975; Forrest, Hooper & Ray, 1974; Ellis, Jones & Papadopoulos, 1974). We have undertaken the synthesis (Senthilkumar, Jeyaraman, Murray & Singh, 1992) and structure analysis of a series of cyclic nitrosamines. The crystal structure analysis of *N*-nitroso-*r*-2,*c*-7-diphenylhexahydro-1,4-diazepin-5-one (I) is reported here.

Experimental. Colourless parallelepiped crystals obtained by slow evaporation from ethanol solution. Density measured by flotation in a chlorobenzene–bromobenzene mixture. Cell dimensions were obtained from 20 reflections ($6.5 < \theta < 34.2^\circ$), on an Enraf–Nonius CAD-4 diffractometer. Intensity data were collected up to $(\sin\theta)/\lambda = 0.626$ Å⁻¹, with $\omega - 2\theta$