parameters, and accounts for the similar spectroscopic properties (Bettinetti *et al.*, 1990). The molecular packing in the crystal of the title compound is illustrated in Fig. 2. Homochiral molecules are linked head-to-tail *via* O(12)—H(30)···O(10) bonds [2.755 (5) Å] forming polymer-like chains normal to **b**. Parallel chains of homochiral molecules are joined by hydrogen bonds O(10)—H(26)···O(12) [2.840 (5) Å], complemented by C(1)—H(13)···O(12) [3.507 (4) Å] contacts (Berkovitch-Yellin & Leiserowitz, 1984), while C(1)—H(13)···O(10) interactions [3.716 (4) Å] lie within the limits of the van der Waals radii. A similar situation is found in the molecular packing of the enantiomer. Paired chains alternate in the crystal lattice with analogous chains of molecules of the opposite chirality, with distances between equivalent atoms in the 4.4–7.4 Å range. This is considerably longer than the 4–5 Å range found in the enantiomer; the distance between the centres of cyclohexene rings of the title compound is 5.60 Å (4.32 Å in the enantiomer crystal). These weaker interchain forces are consistent with the lower melting point (404.8 *versus* 423.8 K) and the higher solubility (16.8 *versus* 11.3 g L^{-1} in water at 398 K).

This work was partially supported by a grant from CNR to GPB. The authors are grateful to Corvi SpA (Piacenza) for the supply of racemic *trans*-sobrerol.

References

Berkovitch-Yellin, Z. & Leiserowitz, L. (1984). *Acta Cryst.* B**40**, 159–165.
Bettinetti, G. P., Giordano, F., Fronza, G., Italia, A., Pellegata, R., Villa, M. & Ventura, P. (1990). *J. Pharm. Sci.* **79**, 470–475.
Busing, W. R., Martin, K. O. & Levy, H. A. (1962). *ORFLS*. Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee, USA.
Coppens, P. & Hamilton, W. C. (1970). *Acta Cryst.* A**26**, 71–83.
Giuseppetti, G., Tadini, C. & Bettinetti, G. P. (1992). *Acta Cryst.* C**48**, 148–150.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1980). *MULTAN*80. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
Nardelli, M. (1983). *Comput. Chem.* **7**, 95–98.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Roberts, P. & Sheldrick, G. M. (1975). *XANADU*. Program for crystallographic calculations. Univ. of Cambridge, England.

Acta Cryst. (1992). C**48**, 878–883

Structures of Partially Deuterated Sodium Trihydrogen Dimalonate and Sodium Hydrogen Malonate (a Reinvestigation) at 120 K

By Nicoline Kalsbeek

Department of Chemistry, University of Copenhagen, The H.C. Ørsted Institute, Universitetsparken 5,
DK-2100 Copenhagen Ø, Denmark

(*Received* 27 *August* 1991; *accepted* 17 *October* 1991)

Abstract. (1) $Na^+.C_3(H,D)H_2O_4^-.C_3(H,D)_2H_2O_4$, M_r = 230.11 (undeuterated), orthorhombic, $Pnma$, a = 8.484 (2), b = 6.859 (2), c = 14.950 (5) Å, V = 870.0 (7) Å^3, Z = 4, D_x = 1.757 g cm^{-3}, λ(Mo $K\bar{\alpha}$) = 0.71073 Å, μ = 1.951 cm^{-1}, F(000) = 472, T = 120 K, R = 0.031 for 1064 observed reflections. (2) $Na^+.C_3H_3O_4^-$, M_r = 126.04, monoclinic, $P2_1/c$, a = 6.671 (2), b = 7.390 (3), c = 9.359 (4) Å, β = 100.49 (3)°, V = 453.7 (5) Å^3, Z = 4, D_x = 1.845 g cm^{-3}, λ(Mo $K\bar{\alpha}$) = 0.71073 Å, μ = 2.363 cm^{-1}, F(000) = 256, T = 120 K, R = 0.025 for 1439 observed reflections. Partially deuterated sodium trihydrogen dimalonate is a superacid salt containing one malonic acid molecule and one hydrogen malonate ion. Three different asymmetric hydrogen bonds occur in this compound. The malonic acid molecule contains a short intramolecular hydrogen bond of length 2.532 (2) Å. One short [2.548 (2) Å] and one long [2.738 (2) Å] intermolecular hydrogen bond connect the malonic acid molecule and the hydrogen malonate ion forming infinite chains in the structure. A comparison is made with the crystal structure of sodium hydrogen malonate where the hydrogen malonate ions are connected by short asymmetric hydrogen bonds of length 2.5546 (9) Å forming infinite chains in the structure. In both compounds the Na ions are octahedrally coordinated by O atoms.

0108-2701/92/050878-06$06.00

Introduction. The crystal structure determinations of partially deuterated sodium trihydrogen dimalonate (1) and sodium hydrogen malonate (2) have been performed as a continuation of earlier studies of acid salts of malonic acid and succinic acid with special interest in the hydrogen bonding (Kalsbeek & Larsen, 1991; Kalsbeek, 1991). Acid salts of carboxylic acids and dicarboxylic acids have been extensively investigated structurally (Speakman, 1972) and spectroscopically (Hadži, 1965).

In the majority of the acid salts the anions are linked by short hydrogen bonds forming infinite chains in the structure. In order to investigate the isotope effect on the short hydrogen bond it was attempted to crystallize sodium hydrogen malonate from D_2O and H_2O. The isotope effect has been reviewed by Rundle (1964) for short O—H···O hydrogen bonds and discussed for several hydrogen oxalate salts and a hydrogen maleate salt by Tellgren & Olovsson (1971), Thomas (1972, 1973) and Hussain, Schlemper & Fair (1980).

From H_2O sodium hydrogen malonate crystallized in the space group $P2_1/c$ as previously reported by Rao & Parthasarathy (1974). When crystallizing the compound from D_2O only the acid H atom in the short hydrogen bond is substituted. However instead of crystallizing sodium deuterium malonate from D_2O sodium trihydrogen dimalonate formed. The phenomena that a superacid salt forms instead of the simple acid salt has also been observed by Soriano-Garcia & Parthasarathy (1978) and Currie (1972) in their attempt to crystallize the hydrogen malonate salts of lithium and potassium. The formation of an even more complicated superacid salt of malonic acid has been observed in the case of dirubidium tetrahydrogen trimalonate (Soriano-Garcia, Toscano, Villena-Iribe & Campero-Celis, 1986).

Compounds (1) and (2) were crystallized under identical conditions (from D_2O and H_2O), and still two different compounds formed indicating that the equilibrium conditions for forming the two salts are very similar. To be able to compare the two compounds as carefully as possible, results of the same accuracy are desirable, therefore the low-temperature results for sodium hydrogen malonate are presented with the results for the previously uncharacterized superacid salt.

Experimental. Equimolar amounts of malonic acid and NaOH were dissolved in D_2O and H_2O respectively. Suitable crystals for the diffraction studies were obtained by slow evaporation of these solutions yielding colourless crystals for both compounds. Both solutions were kept at room temperature and were not isolated from the atmospheric air. The crystals obtained from D_2O were not fully deuterated. The effect of deuteration is marginal in an X-ray experiment. From the neutron-diffraction study of a compound prepared in the same way as compound (1) (N. Kalsbeek, unpublished) the degree of deuteration was determined to *ca* 15%. It is supposed that the same deuteration was obtained for compound (1). In order to obtain virtually full deuteration it is required to keep the evaporating solution isolated from the air.

Table 1. *Crystal data and a summary of results from data reduction and structure refinements*

	Compound (1)	Compound (2)
Crystal size (mm)	0.15 × 0.20 × 0.30	0.07 × 0.35 × 0.35
Intensity data collection		
Max. $\sin\theta/\lambda$ (Å^{-1})	0.8061	0.8064
Range of *h*	−11–11	0–10
Range of *k*	0–13	−8–11
Range of *l*	−24–24	−15–14
Standard reflections	210, 020, 004	113, 011, 202
Type of scan	ω–2θ scan	ω–2θ scan
Number of measured reflections	6109	2982
Structure refinement		
Number of unique reflections	2037	1987
Number of reflections used in the refinement	1064	1439
Criterion for significance	$I/\sigma(I) > 2$	$I/\sigma(I) > 2$
Number of variables	110	85
Weights w^{-1}	$\sigma_{cs}^2(F) + 0.0004\|F\|^2$	$\sigma_{cs}^2(F) + 0.0004\|F\|^2$
R	0.031	0.025
wR	0.036	0.033
S	1.089	1.118
Max. shift/e.s.d.	0.01	0.001
Max. and min. in $\Delta\rho$ (e Å^{-3})	0.259, −0.365	0.410, −0.261

The data collection was performed at 120 K using an Enraf–Nonius CAD-4 diffractometer with graphite-monochromated Mo $K\bar{\alpha}$ radiation. Unit-cell dimensions were determined from a least-squares refinement of 22 reflections ($18.1 < \theta < 22.3°$) (1) and 18 reflections ($19.4 < \theta < 22.7°$) (2). Experimental conditions and results from refinements are summarized in Table 1. Data reduction included Lp correction. The remeasurement of three standard reflections every 10000 s showed no significant change in intensity during exposure time (−0.5%) for compound (1) and (−0.1%) for compound (2). No corrections for decay or absorption were performed. The symmetry equivalent reflections were averaged giving $R_{\rm int} = 0.029$ for compound (1) and $R_{\rm int} = 0.010$ for compound (2).

Both structures were solved by direct methods with the program *SHELXS*86 (Sheldrick, 1990) which provided coordinates for all non-H atoms. The H atoms were located from $\Delta\rho$ maps and the structures refined using the full-matrix least-squares method minimizing $\sum w(|F_o| - |F_c|)^2$. Except for H(1*a*) in compound (1) the positional and isotropic displacement parameters for the H atoms were included in the refinement. Refinement of the isotropic displacement parameter for H(1*a*) led to a physically unrealistic large value, consequently it was fixed. O(3*b*) in compound (1) is disordered in the space group *Pnma*. In order to place this atom in a general position in *Pnma* the occupancy has to be

0.50. Refinement in $Pn2_1a$ with O(3*b*) ordered was attempted. Two models with O(3*b*) in the two positions were tried, both led to higher residuals and no convergence. From this it was concluded that the structure is best described as disordered in the space group *Pnma*.

All calculations except the structure determinations were performed with the Enraf–Nonius *SDP* program system (Enraf–Nonius, 1985). Scattering factor values for all atoms were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV) and used as contained in the program system.

Discussion. The final positional parameters and equivalent isotropic displacement parameters are given in Tables 2 and 3.* Partially deuterated sodium trihydrogen dimalonate crystallizes in the orthorhombic space group *Pnma*. The crystal structure contains one Na ion, one malonic acid molecule and one hydrogen malonate ion in the asymmetric unit. The three residues are situated in the crystallographic mirror plane $y = 0.25$ with all non-H atoms except O(3*a*) and O(3*b*) in the mirror plane. This is in contrast to the corresponding lithium and potassium supersalts (Soriano-Garcia & Parthasarathy, 1978; Currie, 1972) where all residues are found in general positions.

In the structure of sodium hydrogen malonate the cation and anion are both found in general positions in agreement with Rao & Parthasarathy (1974). The differences in cell dimensions for sodium hydrogen malonate resulting from cooling to 120 K are 0.007 (*a* axis), −0.132 (*b* axis), 0.022 Å (*c* axis) and −0.02° (*β*). The strong interaction caused by the very short hydrogen bonds in the direction of the *a* axis is reflected in the insignificant change in the length of this axis on cooling. The only significant change is in the direction of the *b* axis perpendicular to the infinite hydrogen-bonded chains in the structure.

Table 2. *Final positional and equivalent isotropic displacement parameters* (Å^2) *for compound* (1)

H atoms were refined isotropically; the U value for atom H(1*a*) was not refined. $U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	Occupancy	x	y	z	U_{eq}
Na	0.50	0.67064 (8)	0.25000	0.62182 (4)	0.0134 (1)
O(1*a*)	0.50	0.77386 (15)	0.25000	0.35539 (9)	0.0271 (4)
O(2*a*)	0.50	0.59347 (15)	0.25000	0.46464 (8)	0.0219 (4)
O(3*a*)	1.00	0.27791 (12)	0.08871 (16)	0.36109 (6)	0.0234 (3)
C(1*a*)	0.50	0.62845 (20)	0.25000	0.38589 (12)	0.0166 (4)
C(2*a*)	0.50	0.50952 (19)	0.25000	0.31045 (11)	0.0181 (4)
C(3*a*)	0.50	0.34577 (20)	0.25000	0.34553 (11)	0.0162 (4)
H(1*a*)	0.50	0.847 (3)	0.305 (4)	0.401 (2)	0.025
H(2*a*)	1.00	0.528 (2)	0.366 (2)	0.275 (1)	0.032 (5)
O(1*b*)	0.50	0.15641 (15)	0.25000	0.71541 (8)	0.0237 (4)
O(2*b*)	0.50	0.40660 (14)	0.25000	0.67516 (8)	0.0222 (4)
O(3*b*)	0.50	0.01283 (17)	0.18950 (25)	0.45475 (10)	0.0156 (4)
O(4*b*)	0.50	−0.05591 (14)	0.25000	0.59645 (8)	0.0151 (3)
C(1*b*)	0.50	0.26805 (20)	0.25000	0.65425 (11)	0.0144 (4)
C(2*b*)	0.50	0.21845 (19)	0.25000	0.55786 (11)	0.0155 (4)
C(3*b*)	0.50	0.04389 (21)	0.25000	0.53638 (11)	0.0210 (4)
H(1*b*)	0.50	0.061 (3)	0.279 (7)	0.687 (2)	0.043 (9)
H(2*b*)	1.00	0.268 (2)	0.137 (2)	0.528 (1)	0.024 (4)
H(3*b*)	0.50	0.162 (5)	0.122 (7)	0.391 (3)	0.062 (14)

Table 3. *Final positional and equivalent isotropic displacement parameters* (Å^2) *for compound* (2)

H atoms were refined isotropically. $U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
Na	0.75541 (5)	0.04664 (5)	0.55929 (4)	0.00895 (6)
O(1)	0.06364 (9)	0.41006 (10)	0.71944 (8)	0.0147 (1)
O(2)	0.07650 (9)	0.18217 (9)	0.56424 (7)	0.0118 (1)
O(3)	0.69316 (9)	0.30616 (10)	0.68982 (7)	0.0122 (1)
O(4)	0.50983 (9)	0.39747 (10)	0.85438 (7)	0.0127 (1)
C(1)	0.15162 (11)	0.31761 (11)	0.62724 (8)	0.0084 (1)
C(2)	0.35091 (11)	0.39503 (12)	0.60246 (9)	0.0091 (1)
C(3)	0.53172 (11)	0.36271 (11)	0.72761 (9)	0.0079 (1)
H(1)	−0.054 (3)	0.365 (3)	0.719 (2)	0.042 (5)
H(2)	0.379 (2)	0.349 (2)	0.515 (2)	0.011 (3)
H(3)	0.334 (2)	0.521 (2)	0.593 (2)	0.019 (4)

In Table 4 the two malonate residues in compound (1) are denoted *a* and *b*. By inspecting the geometry of the four carboxy groups in compound (1) residue *a* can be identified as the hydrogen malonate ion with C(1*a*)—O(1*a*)—O(2*a*) the carboxylic acid group and C(3*a*)—O(3*a*)—O(3*a'*) the carboxylate group. Residue *b* contains two carboxylic acid groups and hence is the malonic acid molecule. The difference Fourier electron density maps showed H(1*a*) and H(1*b*) at bonding distance to O(1*a*) and O(1*b*) but problems arose in localizing the H atom which from carboxy group geometry would be expected to be found at O(3*b*). The final difference map showed electron density 1.10 Å from O(3*a*). From a structural chemistry point of view this does not make sense and furthermore it cannot be excluded that this density is lone-pair density on O(3*a*). Probably because of the disorder in the structure a definite localization of the last H atom is not possible.

In Fig. 1 the malonic acid molecule in compound (1) and the two hydrogen malonate ions in compounds (1) and (2) are represented illustrating the atom-numbering scheme and their stereochemistry. The two C—C distances to the ionized and unionized carboxy groups in most acid salts of dicarboxylic acids differ significantly, the shorter distance being to the carboxylic acid group. This is observed for example by Kanters, Kroon, Beurskens & Vliegenthart (1966), Derissen, Endeman & Peerdeman (1968), Schouwstra (1972) and Briggman & Oskarsson (1978). In this context compound (1) is anomalous. In the hydrogen malonate ion (residue *a*) the C—C distance to the carboxylate group is significantly shorter than to the carboxylic acid group [1.485 (2) compared to 1.513 (2) Å]. It cannot be

---

* Lists of observed and calculated structure factors, anisotropic displacement parameters and bond lengths and angles for the Na coordination have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54788 (33 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AB0248]

Table 4. *Bond lengths* (Å), *bond angles* (°), *torsional angles* (°) *and hydrogen-bond geometry* (Å, °)

	Compound (1)		
	Residue *a*	Residue *b*	Compound (2)
C(1)—O(1)	1.315 (2)	1.317 (2)	1.3191 (11)
C(1)—O(2)	1.214 (2)	1.216 (2)	1.2219 (10)
C(3)—O(3)	1.269 (1)	1.316 (2)	1.2643 (10)
C(3)—O(4)		1.234 (2)	1.2482 (11)
C(1)—C(2)	1.513 (2)	1.501 (2)	1.5037 (11)
C(2)—C(3)	1.485 (2)	1.515 (2)	1.5393 (10)
O(1)—C(1)—O(2)	124.43 (16)	121.12 (15)	123.20 (8)
O(1)—C(1)—C(2)	111.53 (14)	117.71 (14)	114.52 (7)
O(2)—C(1)—C(2)	124.04 (15)	121.17 (15)	122.26 (8)
O(3)—C(3)—O(4)*	121.38 (15)	122.51 (15)	125.94 (7)
O(3)—C(3)—C(2)	119.30 (8)	113.10 (14)	115.33 (7)
O(4)—C(3)—C(2)		121.08 (15)	118.70 (7)
C(1)—C(2)—C(3)	111.13 (14)	118.52 (14)	114.58 (7)

The Na ions

Compound (1)		Compound (2)	
Na—O(2*a*)	2.4395 (14)	Na—O(1^{i})	2.4196 (7)
Na—O($3a^{i}$)	2.3775 (11)	Na—O(2^{ii})	2.3575 (8)
Na—O($3a^{ii}$)	2.3775 (11)	Na—O(2^{iii})	2.4342 (8)
Na—O($1b^{iii}$)	2.4363 (14)	Na—O(3)	2.3511 (8)
Na—O(2*b*)	2.3778 (14)	Na—O(4^{i})	2.3494 (8)
Na—O($4b^{iv}$)	2.3509 (14)	Na—O(4^{iv})	2.3212 (7)
Average	2.3933		2.3722

	Compound (1)		
	Residue *a*	Residue *b*	Compound (2)
O(1)—C(1)—C(2)—C(3)	180	0	75
O(2)—C(1)—C(2)—C(3)	0	180	−106
O(3)—C(3)—C(2)—C(1)	−89	−160	133
O(4)*—C(3)—C(2)—C(1)	89	0	−49

D—H···*A*	*D*···*A*	*D*—H	H···*A*	*D*—H···*A*
Compound (1)				
O(1*a*)—H(1*a*)···O($3b^{v}$)	2.5475 (19)	1.00 (3)	1.61 (3)	153 (3)
O(3*a*)—H(3*b*)···O(3*b*)	2.7380 (18)	1.10 (4)	1.66 (4)	167 (3)
O(1*b*)—H(1*b*)···O(4*b*)	2.5315 (17)	0.94 (3)	1.69 (3)	148 (4)
Compound (2)				
O(1)—H(1)···O(3^{v})	2.5546 (9)	0.85 (2)	1.71 (2)	168 (2)

Symmetry operations for compound (1): (i) $-x+1, -y, -z+1$; (ii) $-x+1, y+\frac{1}{2}, -z+1$; (iii) $x+\frac{1}{2}, -y+\frac{1}{2}, -z+\frac{3}{2}$; (iv) $x+1, y, z$; (v) $x+1, -y+\frac{1}{2}, z$. Symmetry operations for compound (2): (i) $-x+1, y-\frac{1}{2}, -z+\frac{3}{2}$; (ii) $x+1, y, z$; (iii) $-x+1, -y, -z+1$; (iv) $x, -y+\frac{1}{2}, z-\frac{1}{2}$; (v) $x-1, y, z$.

* In compound (1) residue *a* O(4) = O(3′) where ′ is the symmetry operation ($x, -y+\frac{1}{2}, z$).

excluded that the anomalies are caused by slight disorder in the rest of residue *a*. In the malonic acid molecule (residue *b*) the C—C distances are expected to be roughly identical. The difference between the two C—C distances is indeed smaller than in the two hydrogen malonate ions, but they are not identical. In compound (2) the C—C distance to the carboxylic acid group is the shorter as previously reported (Rao & Parthasarathy, 1974).

The two carboxy groups in a malonate residue are generally planar and are either coplanar or significantly twisted with respect to each other. Usually hydrogen malonate residues containing an intramolecular hydrogen bond are planar while those involved in intermolecular hydrogen bonding are twisted. An exception is the virtually planar hydrogen malonate ion in potassium hydrogen malonate (Sime, Speakman & Parthasarathy, 1970).

The conformations of the malonate residues in compounds (1) and (2) are illustrated by the torsional angles given in Table 4. The carboxy group in the malonic acid molecule (residue *b*) in compound (1), containing the disordered O(3*b*), is relatively non-planar compared to the five other carboxy groups in the two compounds. Except for O(3*b*) this carboxy group is virtually planar. The two hydrogen malonate ions in compounds (1) and (2) respectively are twisted.

The packing in the two structures is illustrated by the stereo drawings given in Fig. 2. The malonic acid molecule in compound (1) contains a short asymmetric intramolecular hydrogen bond of length 2.5315 (17) Å between O(1*b*) and O(4*b*) (see Table 4). This is in contrast to the results found for the corresponding lithium and potassium superacid salts where the short intramolecular hydrogen bond is found in the hydrogen malonate ion. As observed in the crystal structures of the superacid lithium and potassium salts (Soriano-Garcia & Parthasarathy, 1978; Currie, 1972) two asymmetric intermolecular hydrogen bonds link the malonic acid molecule and the hydrogen malonate ion in compound (1) forming

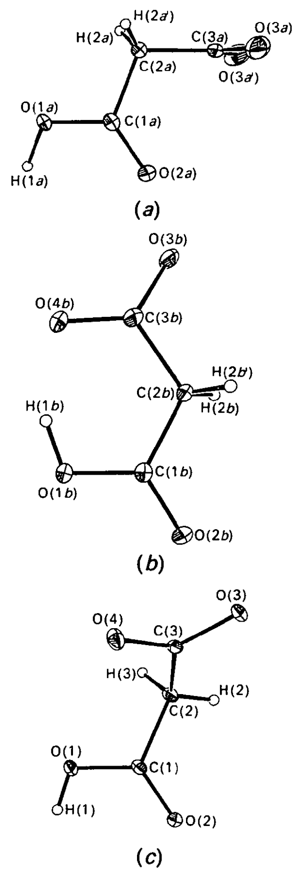
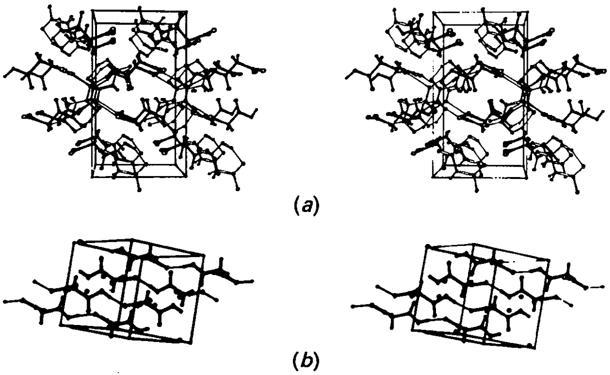


Fig. 1. *ORTEP* (Johnson, 1965) drawings of the malonate residues found in (*ab*) compound (1) and (*c*) compound (2) illustrating the atom-numbering schemes. The thermal ellipsoids inclose 50% probability and the H atoms are drawn as spheres with a fixed radius. H(3*b*) is not drawn. Symmetry code: (i) $x, -y+\frac{1}{2}, z$.

infinite chains in the structure. The hydrogen-bond lengths in compound (1) are 2.5475 (19) and 2.7380 (18) Å respectively.

Several occurrences of intramolecular hydrogen bonds in hydrogen malonate salts been reported recently; the benzylammonium and 4-picolinium salts (Djinović, Golič & Leban, 1990) and the guanidinium and potassium salts (the last salt crystallized from dimethyl sulfoxide) (Djinović, Golič, Hadži & Orel, 1988). In the case of the first three compounds the intramolecular hydrogen bond is asymmetric but very short: 2.430 (2), 2.493 (3) and 2.407 (3) Å respectively. The X-ray data for potassium hydrogen malonate crystallized from dimethyl sulfoxide are not presented in the work of Djinović *et al.* (1988) but the IR spectrum for guanidinium hydrogen malonate and potassium hydrogen malonate are virtually identical and very different from the IR spectrum for the known modification of potassium hydrogen malonate crystallized from water containing an intermolecular hydrogen bond. The reported intramolecular hydrogen bonds in the hydrogen malonate ions are all bent with the O—H···O angle in the range 153–159°. The intramolecular hydrogen bond in compound (1) is even more bent, the angle being 148 (4)°.

In the structure of compound (2) the hydrogen malonate ions are linked in infinite chains by an asymmetric short hydrogen bond of length 2.5546 (9) Å in the direction of the *a* axis in agreement with the previous description given by Rao & Parthasarathy (1974). Their hydrogen-bond length at room temperature is 2.556 (3) Å. An asymmetric short hydrogen bond linking the hydrogen malonate ions in infinite chains is also found in the magnesium and methylammonium acid salts of malonic acid (Briggman & Oskarsson, 1978; Djinović & Golič, 1991). The hydrogen-bond lengths are 2.589 (1) and 2.544 (1) Å respectively. In contrast the short hydrogen bonds in the acid malonic salts of ammonium, caesium and potassium are symmetric (in the ammonium and caesium salts two hydrogen bonds). These are all, as usually found, about 0.1 Å shorter than the asymmetric hydrogen bonds; in the range 2.459 (5) (potassium salt) to 2.488 (3) Å (ammonium salt) (Chapuis, Zalkin & Templeton, 1975; Soriano-Garcia, Toscano, Villena, Rodríguez & Campero-Celis, 1988; Currie & Speakman, 1970).


(*a*)

(*b*)

Fig. 2. Stereo drawing of (*a*) compound (1) and (*b*) compound (2). Compound (1) is seen along the *b* axis, the *a* axis is horizontal and the *c* axis vertical. Compound (2) is seen along the *c* axis, the *a* axis is horizontal and the *b* axis vertical. The hydrogen malonate ion in compound (1) is shown with filled bonds and the malonic acid molecule with open bonds.

In compounds (1) and (2) the Na ions are octahedrally coordinated by O atoms from the anions. From Table 4 it can be seen that both octahedra are slightly distorted. The mean Na—O distance in compound (1) is 2.39 compared to 2.37 Å in compound (2). This larger coordination octahedron is also reflected in the larger displacement parameter for Na in compound (1), 0.0134 (1) compared to 0.00895 (6) $Å^2$ in compound (2).

Mr Flemming Hansen is thanked for assisting in the experimental crystallographic work and Dr Sine Larsen for valuable discussions. Dr Rita Grønbæk Hazell is appreciated for assisting in the refinement of the neutron structure of partially deuterated sodium hydrogen succinate. The Danish Natural Science Research Council supported this research by financing the X-ray diffractometer (J.nr. 11-1837 to SL). The Carlsberg Foundation is thanked for financial support.

References

Briggman, B. & Oskarsson, Å. (1978). *Acta Cryst.* **B34**, 3357–3359.
Chapuis, G., Zalkin, A. & Templeton, D. H. (1975). *J. Chem. Phys.* **62**, 4919–4922.
Currie, M. (1972). *J. Chem. Soc. Chem. Commun.* pp. 972–973.
Currie, M. & Speakman, J. C. (1970). *J. Chem. Soc. A*, pp. 1923–1926.
Derissen, J. L., Endeman, H. J. & Peerdeman, A. F. (1968). *Acta Cryst.* **B24**, 1349–1354.
Djinović, K. & Golič, L. (1991). *Acta Cryst.* **C47**, 2367–2371.
Djinović, K., Golič, L., Hadži, D. & Orel, B. (1988). *Croat. Chem. Acta*, **61**, 405–412.
Djinović, K., Golič, L. & Leban, I. (1990). *Acta Cryst.* **C46**, 281–286.
Enraf–Nonius (1985). *Structure Determination Package.* Enraf–Nonius, Delft, The Netherlands.
Hadži, D. (1965). *Pure Appl. Chem.* **11**, 435–453.
Hussain, M. S., Schlemper, E. O. & Fair, C. K. (1980). *Acta Cryst.* **B36**, 1104–1108.
Johnson, C. K. (1965). *ORTEP.* Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
Kalsbeek, N. (1991). *Acta Cryst.* **C47**, 1649–1653.
Kalsbeek, N. & Larsen, S. (1991). *Acta Cryst.* **C47**, 1005–1009.
Kanters, J. A., Kroon, J., Beurskens, P. T. & Vliegenthart, J. A. (1966). *Acta Cryst.* **21**, 990–995.
Rao, S. N. & Parthasarathy, R. (1974). *J. Chem. Soc. Perkin Trans.* 2, pp. 683–685.
Rundle, R. E. (1964). *J. Phys.* (*Paris*), **25**, 487–492.
Schouwstra, Y. (1972). *Acta Cryst.* **B28**, 2217–2221.
Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.

SIME, J. G., SPEAKMAN, J. C. & PARTHASARATHY, R. (1970). *J. Chem. Soc. A*, pp. 1919–1923.
SORIANO-GARCIA, M. & PARTHASARATHY, R. (1978). *J. Chem. Soc. Perkin Trans.* 2, pp. 668–670.
SORIANO-GARCIA, M., TOSCANO, R. A., VILLENA, R., RODRÍGUEZ, A. & CAMPERO-CELIS, A. (1988). *J. Crystallogr. Spectrosc. Res.* **18**, 671–678.
SORIANO-GARCIA, M., TOSCANO, R. A., VILLENA-IRIBE, R. & CAMPERO-CELIS, A. (1986). *J. Crystallogr. Spectrosc. Res.* **16**, 207–216.
SPEAKMAN, J. C. (1972). *Struct. Bonding (Berlin)*, **12**, 141–199.
TELLGREN, R. & OLOVSSON, I. (1971). *J. Chem. Phys.* **54**, 127–134.
THOMAS, J. O. (1972). *Acta Cryst.* B**28**, 2037–2045.
THOMAS, J. O. (1973). *Acta Cryst.* B**29**, 1767–1776.

Acta Cryst. (1992). C**48**, 883–885

Structure of (*Z*,*Z*)-3,11-Diiodo-*N*,*N*-ditosyl-1,9-diazacyclohexadeca-3,11-diene

BY M. ANDERSON

Shell Research Ltd, Sittingbourne Research Centre, Kent ME9 8AG, England

T. GALLAGHER, M. F. MAHON AND K. C. MOLLOY

School of Chemistry, University of Bath, Claverton Down, Bath BA2 7AY, England

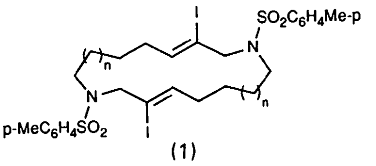
AND R. SHAW

Shell Research Ltd, Sittingbourne Research Centre, Kent ME9 8AG, England, and
School of Chemistry, University of Bath, Claverton Down, Bath BA2 7AY, England

(*Received* 20 *May* 1991; *accepted* 8 *October* 1991)

Abstract. $C_{28}H_{36}I_2N_2O_4S_2$, $M_r = 782.5$, orthorhombic, $P2_12_12_1$, $a = 11.153\ (4)$, $b = 14.833\ (3)$, $c = 19.332\ (5)$ Å, $V = 3198.0$ Å^3, $Z = 4$, $D_x = 1.62$ g cm^{-3}, $\lambda(\text{Mo}\ K\alpha) = 0.71069$ Å, $\mu = 21.03$ cm^{-1}, $F(000) = 1552$, room temperature, $R = 0.0776$ for 1582 unique reflections. The 16-membered diaza heterocycle has (*Z*) stereochemistry about each of the two double bonds; the two N atoms exhibit a more planar geometry than usually observed in sulfonamides.

Introduction. The iodine-mediated cyclization of *N*-sulfonyl allenic amines [ω-(4-toluenesulfonamido)-1,2-alkadienes] provides an efficient entry into functionalized medium-ring nitrogen heterocycles. In addition to monoaza heterocycles, the diaza derivatives (1) (n = 1–4) have also been synthesized in up to 40% yield (Shaw, Anderson & Gallagher, 1990). The structure of (1) (n = 1), (*Z*,*Z*)-3,11-diiodo-*N*,*N*-ditosyl-1,9-diazacyclohexadeca-3-11-diene, a 16-membered diaza macrocycle, is reported in this paper.



(1)

Experimental. The synthesis of the title compound has been reported previously (Shaw, Anderson & Gallagher, 1990). Crystals were obtained by recrystallization from benzene.

A diamond-shaped crystal of approximate dimensions 0.35 × 0.35 × 0.35 mm was selected and used for data collection. Data were measured at room temperature on a Hilger and Watts Y290 four-circle diffractometer in the range $2 < \theta < 24°$ using ω–2θ scans, covering the ranges $h\ 0\rightarrow12$, $k\ 0\rightarrow15$, $l\ 0\rightarrow20$. Cell dimensions were based on 12 accurately centred reflections with $13 < \theta < 16°$. 2815 reflections were collected of which 1582 were unique and observed with $I \geq 3\sigma(I)$. A standard reflection measured after every 50 reflections showed no systematic crystal decay throughout data collection. Data were corrected for Lorentz and polarization effects and also for absorption (Walker & Stuart, 1983). Absorption maximum and minimum: 1.06, 0.90. The structure was solved by conventional Patterson methods and refined using full-matrix least squares based on *F*, using the *SHELX* suite of programs (Sheldrick, 1976, 1986). Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). All non-H atoms were treated anisotropically; H atoms were included at calculated positions (C—H = 1.08 Å) with a common fixed thermal parameter ($U = 0.05$ Å^2).

0108-2701/92/050883-03$06.00