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Conformational Aspects of *meso*-Tartaric Acid. VI. Structure of (–)-α-Methylbenzylammonium Hydrogen *meso*-Tartrate, $C_8H_{12}N^+.C_4H_5O_6^-$

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Abstract. $M_r = 271{\cdot}27$, monoclinic, $P2_1$, $a = 6{\cdot}471$ (2), $b = 13{\cdot}74$ (1), $c = 7{\cdot}585$ (6) Å, $\beta = 108{\cdot}87$ (6)°, $V = 638{\cdot}2$ (8) Å^3, $Z = 2$, $D_x = 1{\cdot}412$ Mg m^{-3}, $T = 295$ K, λ(Mo $K\bar{\alpha}$) = 0·7107 Å, μ(Mo $K\bar{\alpha}$) = 0·123 mm^{-1}, $F(000) = 288$. $R = 0{\cdot}036$ for 2946 significant [$I \geq 2{\cdot}5\sigma(I)$] reflections. The molecular conformation of the *meso*-tartrate anion is nearly centrosymmetric and thus clearly different from the specific dissymmetric conformation found in previously studied *meso*-tartaric acid compounds. The ammonium group of the base molecule is hydrogen bonded to the *meso*-tartrate anions. The carboxyl coupling in this acid salt occurs *via* a short asymmetric H bond.

Introduction. The conformation of *meso*-tartaric acid molecules and anions found in crystals of the free acid as well as of salts appears to be synperiplanar around the terminal C–C bonds and synclinal around the central C–C bond (paper I: Kroon, Peerdeman & Bijvoet, 1965; paper II: Bootsma & Schoone, 1967; paper III: Kroon & Kanters, 1972; paper IV: Kroon & Kanters, 1973; paper V: Kroon, 1982). Thus in these centrosymmetric crystals the conformational antipodes of *meso*-tartaric acid, occurring in equal proportions, constitute in fact a racemic mixture. Overwhelming evidence has been obtained that in solution amongst the three staggered conformations about the central C–C bond to be envisaged the conformations found in crystals are predominant (Kroon, 1982, and references therein). This preference for the specific dissymmetric conformation suggests that it should be feasible to convert *meso*-tartaric acid into one of its enantiomers by means of cocrystallization with an optically active base. Then, to observe the possible racemization reaction, the crystals obtained may be dissolved at some suitable temperature.

This paper describes the structure determination of a crystalline 1:1 complex of *meso*-tartaric acid with (–)-α-methylbenzylamine.

Experimental. The specimen used was an extremely well diffracting irregular prismatic fragment with longest dimension no greater than 0·5 mm; Enraf–Nonius CAD-4 diffractometer, Zr-filtered Mo $K\alpha$ radiation, cell constants from a least-squares analysis of 2θ, φ, ω and κ settings of 25 reflections, intensity data collected in $\omega/2\theta$ scan mode, no systematic fluctuations in standard reflections 212 and $\bar{2}0\bar{1}$, 3570 independent reflections, $2\theta \leq 75{\cdot}9°$, h 0–11, k –12–12, l 0–23, 2946 considered to be observed and used in the subsequent analysis. Corrections for average change in intensity of reference reflections and for Lp corrections, no correction for absorption.

The structure was solved by direct methods. The phasing procedure used consists of the reduction of a redundant set of linear equations of phases that represent triple-phase structure invariants (see Fortier, DeTitta, Fronckowiak, Smith & Hauptman, 1979). The method has successfully been applied to centrosymmetric structures (Fortier *et al.*, 1979; Fortier, Duffy-Fronckowiak, Smith, Hauptman & DeTitta, 1980). In our institute this procedure has recently been extended to non-centrosymmetric structures and both its general description and application to the structure determination of the title compound are described in full detail elsewhere (Pontenagel, 1983). The phasing procedure was followed by a tangent refinement and the resulting E map revealed the *meso*-tartrate anion in the ten highest peaks. One subsequent Fourier synthesis was sufficient to locate the non-H atoms of the cation; H atoms were located from a difference synthesis.

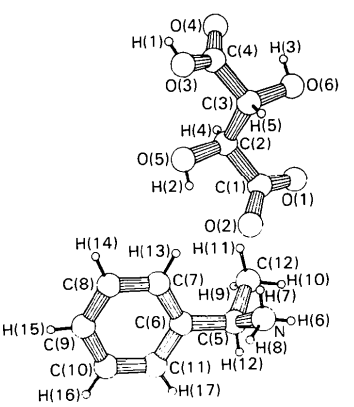

Fig. 1. Perspective view of the complex molecules, showing the atom labelling.

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Table 1. *Fractional atomic coordinates and isotropic thermal parameters* (Å²)

For non-H atoms $U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	*y*	*z*	U_{eq}
O(1)	0·7282 (1)	0·5556	0·5377 (1)	0·0359 (2)
O(2)	1·0794 (1)	0·5777 (1)	0·6966 (1)	0·0370 (2)
O(3)	0·8223 (1)	0·6075 (1)	1·2559 (1)	0·0355 (2)
O(4)	0·4944 (1)	0·5483 (1)	1·0936 (1)	0·0344 (2)
O(5)	1·0432 (1)	0·5219 (1)	1·0150 (1)	0·0356 (2)
O(6)	0·5153 (1)	0·6363 (1)	0·7810 (1)	0·0368 (2)
N	0·2727 (1)	0·5087 (1)	0·4212 (1)	0·0298 (2)
C(1)	0·8874 (1)	0·5593 (1)	0·6869 (1)	0·0245 (2)
C(2)	0·8438 (1)	0·5363 (1)	0·8694 (1)	0·0239 (2)
C(3)	0·7116 (1)	0·6180 (1)	0·9243 (1)	0·0243 (2)
C(4)	0·6659 (1)	0·5876 (1)	1·1025 (1)	0·0241 (2)
C(5)	0·2649 (2)	0·3998 (1)	0·4078 (1)	0·0351 (3)
C(6)	0·4177 (2)	0·3546 (1)	0·5843 (1)	0·0314 (2)
C(7)	0·3779 (2)	0·3624 (1)	0·7541 (2)	0·0374 (3)
C(8)	0·5192 (3)	0·3196 (1)	0·9143 (2)	0·0448 (4)
C(9)	0·6984 (3)	0·2684 (1)	0·9057 (2)	0·0511 (4)
C(10)	0·7403 (3)	0·2603 (1)	0·7397 (3)	0·0543 (5)
C(11)	0·5996 (2)	0·3025 (1)	0·5789 (2)	0·0430 (4)
C(12)	0·0286 (2)	0·3661 (1)	0·3639 (2)	0·0528 (4)
H(1)	0·783 (3)	0·597 (2)	1·339 (2)	0·046 (6)
H(2)	1·130 (3)	0·536 (1)	0·969 (2)	0·033 (5)
H(3)	0·420 (3)	0·607 (2)	0·820 (2)	0·040 (6)
H(4)	0·761 (2)	0·479 (1)	0·855 (2)	0·027 (5)
H(5)	0·782 (2)	0·684 (1)	0·937 (2)	0·020 (4)
H(6)	0·207 (3)	0·536 (2)	0·329 (2)	0·039 (6)
H(7)	0·211 (3)	0·529 (1)	0·501 (2)	0·030 (5)
H(8)	0·423 (3)	0·530 (2)	0·475 (3)	0·043 (6)
H(9)	0·020 (4)	0·298 (2)	0·336 (3)	0·065 (8)
H(10)	−0·054 (3)	0·393 (2)	0·246 (3)	0·050 (6)
H(11)	−0·026 (4)	0·389 (2)	0·475 (4)	0·064 (7)
H(12)	0·323 (3)	0·378 (2)	0·317 (2)	0·041 (6)
H(13)	0·248 (3)	0·398 (2)	0·763 (3)	0·048 (6)
H(14)	0·485 (4)	0·331 (2)	1·029 (3)	0·047 (6)
H(15)	0·793 (4)	0·234 (2)	1·002 (3)	0·062 (7)
H(16)	0·874 (3)	0·226 (2)	0·747 (3)	0·056 (7)
H(17)	0·623 (3)	0·302 (2)	0·464 (2)	0·044 (6)

Table 2. *Bond distances* (Å), *bond angles* (°), *selected torsion angles* (°) *and hydrogen-bond geometry*

C(1)–O(1)	1·261 (1)	C(5)–N	1·499 (2)
C(1)–O(2)	1·247 (1)	C(5)–C(6)	1·516 (2)
C(1)–C(2)	1·532 (1)	C(5)–C(12)	1·528 (2)
C(2)–O(5)	1·415 (1)	C(6)–C(7)	1·397 (2)
C(2)–C(3)	1·548 (2)	C(7)–C(8)	1·393 (2)
C(3)–O(6)	1·402 (1)	C(8)–C(9)	1·376 (2)
C(3)–C(4)	1·532 (1)	C(9)–C(10)	1·376 (3)
C(4)–O(3)	1·300 (1)	C(10)–C(11)	1·391 (2)
C(4)–O(4)	1·216 (1)	C(11)–C(6)	1·390 (2)

C(2)–C(1)–O(1)	117·8 (1)	N–C(5)–C(6)	110·5 (1)
C(2)–C(1)–O(2)	117·4 (1)	N–C(5)–C(12)	109·1 (1)
O(1)–C(1)–O(2)	124·8 (1)	C(12)–C(5)–C(6)	112·9 (1)
C(1)–C(2)–O(5)	110·2 (1)	C(5)–C(6)–C(7)	121·4 (1)
C(1)–C(2)–C(3)	111·9 (1)	C(5)–C(6)–C(11)	120·1 (1)
O(5)–C(2)–C(3)	109·6 (1)	C(7)–C(6)–C(11)	118·5 (1)
C(2)–C(3)–O(6)	111·3 (1)	C(6)–C(7)–C(8)	120·5 (1)
C(2)–C(3)–C(4)	108·7 (1)	C(7)–C(8)–C(9)	120·0 (1)
O(6)–C(3)–C(4)	110·4 (1)	C(8)–C(9)–C(10)	120·2 (2)
C(3)–C(4)–O(3)	114·6 (1)	C(9)–C(10)–C(11)	120·1 (2)
C(3)–C(4)–O(4)	120·3 (1)	C(10)–C(11)–C(6)	120·6 (1)
O(3)–C(4)–O(4)	125·1 (1)		

C(1)–C(2)–C(3)–C(4)	177·4 (1)	O(4)–C(4)–C(3)–O(6)	27·0 (2)
O(1)–C(1)–C(2)–O(5)	166·6 (1)	N–C(5)–C(6)–C(7)	67·2 (1)
O(2)–C(1)–C(2)–O(5)	−11·4 (2)	C(12)–C(5)–C(6)–C(7)	−55·2 (2)
O(3)–C(4)–C(3)–O(6)	−152·9 (1)		

Hydrogen-bonding geometry (distances in Å, angles in deg)

	O–H	H···O	O···O	O–H···O
O(3)–H(1)···O(1^{i})	0·77 (2)	1·75 (2)	2·508 (1)	169 (3)
O(5)–H(2)···O(4^{ii})	0·78 (2)	2·24 (2)	2·808 (1)	130 (2)
O(6)–H(3)···O(2^{iii})	0·86 (2)	2·14 (2)	2·801 (1)	133 (2)
N–H(6)···O(5^{iv})	0·79 (2)	2·28 (2)	2·962 (1)	145 (2)
N–H(7)···O(2^{iii})	0·87 (2)	2·05 (2)	2·918 (1)	177 (2)
N–H(8)···O(1^{v})	0·97 (2)	1·91 (2)	2·863 (1)	167 (2)

Symmetry code: (i) *x*, *y*, 1 + *z*; (ii) 1 + *x*, *y*, *z*; (iii) −1 + *x*, *y*, *z*; (iv) −1 + *x*, *y*, −1 + *z*; (v) *x*, *y*, *z*.

Full-matrix refinement on *F* of positional and thermal parameters (non-H atoms anisotropic, H atoms isotropic) performed with a locally adapted version of the *XRAY* system (Stewart, 1976) converged at $R = 0{\cdot}036$, $R_w = 0{\cdot}048$, $S = 1{\cdot}47$; $w = (\sigma_F^2 + 0{\cdot}0006|F_o|^2)^{-1}$, scattering factors for the non-hydrogen atoms from Cromer & Mann (1968), for H the *f* curve of Stewart, Davidson & Simpson (1965); no significant shift/error values in the final least-squares cycle, final difference-map features in the range −0·20 to 0·36 e Å^{-3}, the highest peaks residing in the neighbourhood of bond centres.

Discussion. Final parameters are listed in Table 1.* The data on the molecular geometry, involving non-hydrogen atoms only, may be found in Table 2, while the numbering system appears in Fig. 1.

As can be inferred from the selected torsion angles in Table 2 the *meso*-tartrate anion adopts a nearly centrosymmetric conformation. Thus far only dissymmetric conformations of the *meso*-tartaric acid molecule are found in various centrosymmetric crystals, whereas in the necessarily dissymmetric crystal of the title compound the *meso*-tartaric anions choose a nearly centrosymmetric form in a dissymmetric environment. As a consequence the present attempt to chiralize *meso*-tartaric acid by cocrystallizing it with the asymmetric base turned out to be unsuccessful. The carboxyl groups are rotated from the C–C(α)–O(H) planes by 13 and 27° respectively. Such twists that are greater than normally found in α-hydroxyacetic acid moieties (Kroon, 1982) are sufficient to avoid short intramolecular contacts: O(1)···O(6) and O(3)···O(5) are 2·860 (2) and 2·908 (2) Å respectively.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39029 (27 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

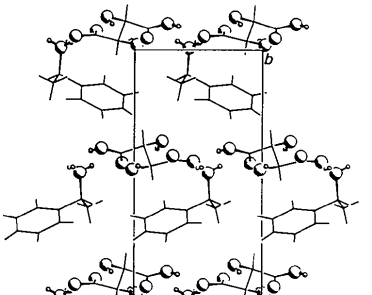

Fig. 2. Packing diagram projected down **a**; for clarity only the non-carbon atoms with H atoms bonded to them are represented by open circles.

A view of the structure along **a** is given in Fig. 2. The structure is characterized by a strong hydrogen-bonded network, details of which are given in Table 2.

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Structure of DL-Selenomethionine, $C_5H_{11}NO_2Se$

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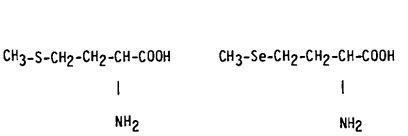
Abstract. $M_r = 196{\cdot}1$, monoclinic, $P2_1/a$, $a = 9{\cdot}893\ (1)$, $b = 4{\cdot}713\ (2)$, $c = 17{\cdot}082\ (4)$ Å, $\beta = 101{\cdot}63\ (1)°$, $V = 780{\cdot}0\ (7)$ Å^3, $Z = 4$, $D_m = 1{\cdot}67$, $D_x = 1{\cdot}76$ g cm^{-3}, λ(Cu $K\alpha$) $= 1{\cdot}5418$ Å, $\mu = 61{\cdot}8$ cm^{-1}, $F(000) = 392$, $T = 294$ K. Final $R = 0{\cdot}079$ for 1391 observed reflections. The crystal structure is found to be isomorphous to that of the α-form of DL-methionine. The two Se–C bond lengths are 1·938 (4) and 1·907 (8) Å, and the C–Se–C angle is 98·9 (3)°, slightly smaller than the C–S–C angle.

Introduction. Selenium is an important component of several biologically important macromolecules and is essential in trace amounts, though it is toxic in large quantities. For example, selenium is found to be a component of several enzymes, some proteins whose role in biological systems is not yet known and some bacterial aminoacyl transfer nucleic acids (Stadtman, 1980). Formate dehydrogenase, glycine reductase, nicotinic acid hydroxylase, xanthine dehydrogenase and glutathione peroxidase are some of the naturally occurring selenoproteins. Glutathione peroxidase is a selenium-dependent enzyme found in mammalian cells; this enzyme contains selenium in the form of selenocysteines (Forstrom, Zakowski & Tappel, 1978). Recently, there has been some evidence for the occurrence of selenium as selenomethionine in *Clostridium kluyveri* (Hartmanis & Stadtman, 1982). Naturally, the question arises, why is selenium preferred over sulfur in these proteins? This preference may be due to differences in the chemical and stereochemical properties of amino acids that contain selenium instead of sulfur. Some possible chemical reasons for the preference to selenium over sulfur in biological catalysts are (Stadtman, 1980): (i) At biological pH, selenols (*R*SeH), in contrast to thiols (*R*SH) are largely ionized in enzymes and are charged. (ii) Selenols have lower redox potentials than thiols (*e.g.* selenocysteine *vs* cysteine); this may be the reason for the occurrence of selenols in redox catalysts, *e.g.* formate dehydrogenase and glycine reductase which are found in anaerobic bacteria. (iii) Seleno-organic compounds are generally more reactive than the corresponding sulfur compounds. (iv) Selenols are good nucleophiles and serve as good leaving groups. A comparison of the stereochemical features of the biologically active molecules containing sulfur with those containing selenium will throw some light on the question: What stereochemical feature (if any) favors the selection of selenium over sulfur in some proteins? In this context, we decided to compare the crystal structures and conformation of methionine (I) with selenomethionine (SeM) (II).



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