

## Structure of Dicyclohexylammonium Hydrogen Maleate

BY SEIK WENG NG

*Institute of Advanced Studies, University of Malaya, 59100 Kuala Lumpur, Malaysia*

AND WAI-HING YIP, RU-JI WANG AND THOMAS C. W. MAK\*

*Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong*

(Received 26 March 1990; accepted 30 May 1990)

**Abstract.**  $C_{12}H_{24}N^+ \cdot C_4H_3O_4^-$ ,  $M_r = 297.44$ , monoclinic,  $Cc$ ,  $a = 16.364$  (3),  $b = 9.766$  (2),  $c = 11.144$  (1) Å,  $\beta = 105.06$  (1)°,  $V = 1719.8$  (3) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.149$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å,  $\mu = 0.76$  cm<sup>-1</sup>,  $F(000) = 648$ ,  $T = 294$  K,  $R = 0.059$  for 1182  $|F_o| \geq 4\sigma|F_o|$  reflections. The cation forms donor H bonds to the anions which result in a polymeric chain parallel to the  $c$  axis.

**Introduction.** The [OC(O)CH=CHC(O)O] anion has been studied in the  $NH_4$  (Golic & Leban, 1982), primary  $RNH_3$  (Golic, Leban, Detoni, Orel & Hadzi, 1985), tertiary  $R_3NH$  (James & Williams, 1971, 1974) and quarternary  $R_4N$  (Drobez, Golic & Leban, 1985) ammonium, and iminium (Hsu & Schlemper, 1980; Hussain, Schlemper & Fair, 1980; James & Matsushima, 1976) hydrogen maleates. The present compound is a secondary ( $R_2NH_2$ ) ammonium hydrogen maleate.

**Experimental.** The title compound resulted from the unsuccessful synthesis of a triorganostannate by heating ( $c\text{-}C_6H_{11}$ )<sub>2</sub>NH, [( $n\text{-}C_4H_9$ )<sub>3</sub>Sn]<sub>2</sub>O and HO<sub>2</sub>CCH=CHCO<sub>2</sub>H (2:1:2 molar ratio), following a previous procedure (Ng, Kumar Das, Hossain, Goerlitz & van der Helm, 1990). Analysis: Found, C 64.80, H 9.40, N 4.77%; calculated for C<sub>16</sub>H<sub>27</sub>NO<sub>4</sub>, C 64.65, H 9.09, N 4.71%. Crystals suitable for X-ray diffraction were grown from evaporation of an ethanolic solution of the compound.

A crystal measuring  $0.18 \times 0.44 \times 0.48$  mm was used for the study. Cell dimensions were obtained from 25 strong ( $14.5 \leq 2\theta \leq 22.0^\circ$ ) reflections. Raw intensities collected on a Nicolet R3m/V four-circle diffractometer at room temperature (294 K) were processed with a profile-fitting procedure (Diamond, 1969) and corrected for absorption by using the  $\psi$ -scan data (Kopfmann & Huber, 1968). The maximum  $2\theta$  angle was  $50^\circ$ , with the  $hkl$  ranges being  $h$  0 to 20,  $k$  0 to 12 and  $l$  -14 to 14; 1567 reflections

were collected, with 1182 obeying  $|F_o| \geq 4\sigma|F_o|$ . Two standard reflections (31 $\bar{3}$ , 532) monitored after every 125 data showed an intensity variation of  $\pm 1\%$ . The transmission factors are 0.955 to 0.991. Direct phase determination yielded the positions of all non-H atoms, and they were subjected to anisotropic refinement. The carboxyl H atom in the hydrogen maleate anion could not be derived from a difference Fourier synthesis and was instead fixed at midway between the O(2) and O(3) atoms. The other H positions were generated geometrically (C—H bonds fixed at 0.96 and N—H bonds at 0.90 Å) and allowed to ride on their respective parent C or N atoms; all H atoms were assigned appropriate isotropic temperature factors and included in the structure-factor calculations. Computations were performed by using the *SHELXTL-Plus* program package (Sheldrick, 1985) on a DEC MicroVAX-II computer. Analytical expressions of atomic scattering factors were employed, and anomalous-dispersion corrections were incorporated (*International Tables for X-ray Crystallography*, 1974, Vol. IV, pp. 55, 99, 149). The final least-squares cycle was calculated with 188 variables;  $w = [\sigma^2(F_o) + 0.0006|F_o|^2]^{-1}$ . The residuals are  $R = 0.059$ ,  $wR = 0.069$  and  $S = 1.472$ ; residual extrema in the final difference map ranged from  $+0.19$  to  $-0.26$  e Å<sup>-3</sup>. Fractional coordinates are given in Table 1† and bond distances and angles in Table 2.

**Discussion.** Fig. 1 shows the crystal structure of dicyclohexylammonium hydrogen maleate, the atom-labeling scheme and the H bonds between the cation and anion. In the anion, an H atom is shared by two carboxyl groups to form a seven-membered ring; the O(2)···O(3) distance of 2.417 (7) Å is similar to dis-

† Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53259 (9 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

\* Author to whom correspondence should be addressed.

Table 1. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic temperature factors ( $\text{\AA}^2 \times 10^3$ )

$U_{eq}$  is defined as one third of the trace of the orthogonalized  $U$  tensor.

	$x$	$y$	$z$	$U_{eq}$
N	2500	813 (3)	2500	40 (1)
C(11)	1727 (4)	43 (5)	1859 (5)	47 (1)
C(12)	1431 (5)	-891 (6)	2739 (6)	77 (1)
C(13)	636 (5)	-1623 (7)	2106 (7)	98 (1)
C(14)	-79 (5)	-642 (8)	1483 (7)	98 (1)
C(15)	220 (5)	318 (7)	646 (7)	92 (1)
C(16)	1034 (4)	1048 (6)	1291 (6)	69 (1)
C(21)	3288 (4)	15 (5)	3101 (5)	44 (1)
C(22)	3545 (4)	-853 (6)	2137 (5)	60 (1)
C(23)	4375 (5)	-1630 (7)	2750 (7)	89 (1)
C(24)	5050 (4)	-687 (7)	3411 (7)	92 (1)
C(25)	4776 (5)	199 (7)	4321 (6)	94 (1)
C(26)	3981 (4)	977 (5)	3737 (6)	63 (1)
O(1)	2867 (4)	7783 (4)	5469 (4)	64 (1)
O(2)	2876 (3)	6297 (3)	4009 (4)	72 (1)
C(31)	2340 (4)	3370 (5)	4541 (5)	48 (1)
C(32)	2301 (4)	4247 (5)	5621 (5)	56 (1)
C(33)	2474 (4)	5554 (5)	5813 (5)	58 (1)
C(34)	2755 (4)	6618 (5)	5058 (5)	45 (1)
O(3)	2594 (4)	3878 (3)	3680 (4)	81 (1)
O(4)	2102 (3)	2171 (3)	4538 (4)	59 (1)

Table 2. Bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ )

$(c\text{-C}_6\text{H}_{11})_2\text{NH}_2$ cation			
N—C(11)	1.485 (6)	N—C(21)	1.507 (5)
C(11)—C(12)	1.508 (9)	C(11)—C(16)	1.510 (8)
C(12)—C(13)	1.491 (9)	C(13)—C(14)	1.53 (1)
C(14)—C(15)	1.49 (1)	C(15)—C(16)	1.516 (9)
C(21)—C(22)	1.511 (8)	C(21)—C(26)	1.502 (7)
C(22)—C(23)	1.551 (9)	C(23)—C(24)	1.479 (9)
C(24)—C(25)	1.49 (1)	C(25)—C(26)	1.501 (9)
C(11)—N—C(21) 118.4 (3)			
N—C(11)—C(16) 109.0 (4)			
C(11)—C(12)—C(13) 111.7 (5)			
C(13)—C(14)—C(15) 109.8 (7)			
C(11)—C(16)—C(15) 111.4 (5)			
N—C(21)—C(26) 109.9 (4)			
C(21)—C(22)—C(23) 109.6 (5)			
C(23)—C(24)—C(25) 112.6 (6)			
C(21)—C(26)—C(25) 110.5 (5)			
C(11)—N—C(12) 111.8 (4)			
C(12)—C(11)—C(16) 109.4 (6)			
C(12)—C(13)—C(14) 112.7 (5)			
C(14)—C(15)—C(16) 112.9 (5)			
N—C(21)—C(22) 109.7 (4)			
C(22)—C(21)—C(26) 111.8 (5)			
C(22)—C(23)—C(24) 111.7 (5)			
C(24)—C(25)—C(26) 112.3 (5)			
C(32)—C(31)—O(3) 119.1 (4)			
O(3)—C(31)—O(4) 123.1 (5)			
C(32)—C(33)—C(34) 132.3 (5)			
O(1)—C(34)—C(33) 118.5 (5)			
C(32)—C(31)—O(4) 117.8 (5)			
C(31)—C(32)—C(33) 129.6 (6)			
O(1)—C(34)—O(2) 121.9 (5)			
O(2)—C(34)—C(33) 119.5 (4)			

## Hydrogen bonds

N...O(1 <sup>a</sup> )	2.842 (6)	N...O(4)	2.848 (6)
O(2)...O(3)	2.417 (7)		

Symmetry transformation: (a)  $x, 1 - y, -\frac{1}{2} + z$ .

tances found in other hydrogen maleates (Olovsson & Olovsson, 1984). The cation forms donor hydrogen bonds with the O atoms from two hydrogen maleate anions (which are related by the  $c$  glide) [N...O(1) 2.842 (6), N...O(4) 2.848 (6)  $\text{\AA}$ ]; the

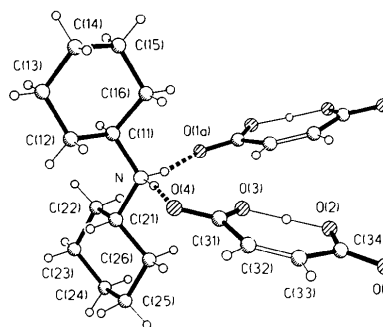
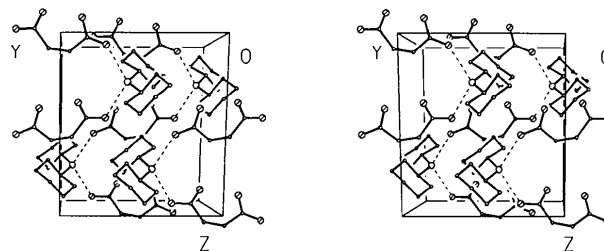


Fig. 1. Perspective view showing the atom-numbering scheme. Symmetry code is given in Table 3.

Fig. 2. Stereoview of the crystal structure of the title adduct parallel to the  $a$  axis. The origin of the unit cell lies at the upper right corner, with  $b$  pointing from right to left,  $c$  downwards, and  $a$  towards the reader.

C—N—C angle is opened to  $118.4 (3)^\circ$  as a result of the steric bulk of the cyclohexyl ring, as has been also observed in an organostannate (Ng *et al.*, 1990). Conversely, each hydrogen maleate anion forms acceptor H bonds with two neighboring cations. As shown in Fig. 2, the cations and anions are connected alternately by the H bonds to form zigzag chains along the  $c$  direction, and the  $C$ -centering operation relates them to the crystal packing.

We thank the Kuala Lumpur Rotary Research Foundation, the University of Malaya (Vote F PJP286/89) and Dr Ma Pui Han (grant No. 183902000) for supporting this work.

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*Acta Cryst.* (1991). **C47**, 400–402

## Structure of a Potential Steroid Intermediate – C<sub>15</sub>H<sub>20</sub>O<sub>2</sub>

BY N. SUKUMAR AND VASANTHA PATTABHI\*

*Department of Crystallography and Biophysics,† University of Madras, Guindy Campus, Madras-600 025, India*

(Received 21 March 1990; accepted 1 June 1990)

**Abstract.** 3-(2-Ethynyl-2-hydroxy-1-methylcyclohexyl)cyclohex-2-en-1-one, C<sub>15</sub>H<sub>20</sub>O<sub>2</sub>, *M<sub>r</sub>* = 232.29, monoclinic, *C2/c*, *a* = 30.206 (4), *b* = 6.686 (1), *c* = 13.412 (1) Å, *β* = 107.87 (1)°, *V* = 2578.1 (6) Å<sup>3</sup>, *Z* = 8, *T* = 295 K, *D<sub>m</sub>* = 1.201, *D<sub>x</sub>* = 1.197 g cm<sup>-3</sup>, Cu *Kα*, *λ* = 1.5418 Å, *μ* = 6.2 cm<sup>-1</sup>, *F*(000) = 1008, *R*(*F*) = 0.056, *wR* = 0.079 for 1870 observations with *I<sub>net</sub>* > 3.0σ(*I*). The hydroxyl and methyl groups attached to ring *A* are in axial orientations, while ring *B* is in an equatorial position. Ring *A* is in the most favoured chair conformation. The packing of the molecule is stabilized by O—H...O hydrogen bonds.

**Introduction.** Oxy-Cope moieties like hexa-1,5-diene (Fig. 1*a*) are capable of undergoing a Cope rearrangement. An anionic oxy-Cope rearrangement is a 3,3-sigmatropic shift in which an oxygen (as an alkoxide) attached to either of the carbon atoms numbered 1 in Fig. 1(*b*) undergoes rearrangement. However, when the vinyl groups are attached to the ring, the product will be a ring-enlarged carbonyl compound (Fig. 1*d*).

The title compound (I) and its reduction product (II) contain an oxy-Cope moiety. Compound (II) easily undergoes the oxy-Cope rearrangement to give the tricyclic compound (III) – a potential steroid intermediate (Satyamoorthi, Thangaraj, Srinivasan & Swaminathan, 1989). It is presumed that a *cis* orientation of the two double bonds (Fig. 2) in cyclic compounds will be highly conducive to a concerted rearrangement (Gadwood & Lett, 1982). In the present investigation it has been established that an anionic oxy-Cope rearrangement can occur even when the two vinyl moieties are in a 1,2-diequatorial orientation (*i.e.* *trans*).

\* To whom correspondence should be addressed.

† Contribution No. 756.

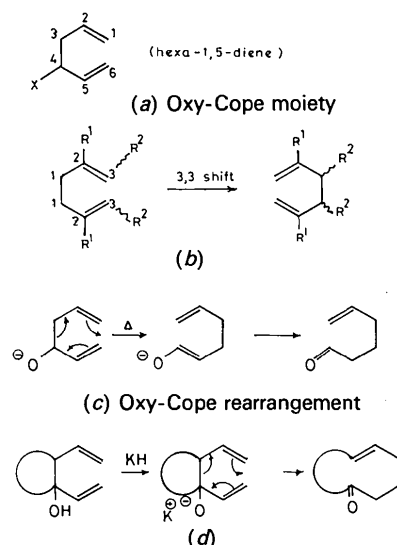


Fig. 1. Schematic representation of a molecule undergoing oxy-Cope rearrangement: (a) oxy-Cope moiety; (b), (c) oxy-Cope rearrangement; (d) oxy-Cope rearrangement involving a vinyl group attached to a ring.

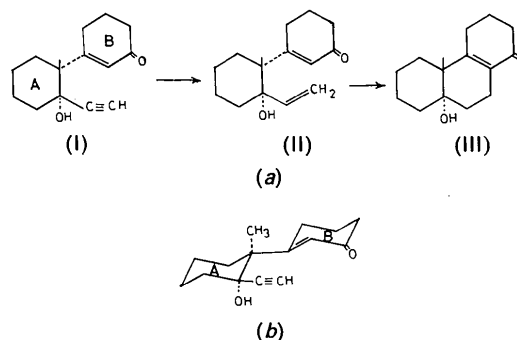


Fig. 2. Schematic diagram of the molecule and its reduction products: (a) proposed stereochemistry; (b) observed stereochemistry.