

Tetra-*n*-butylammonium Hydrogen Dichloromaleate*

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Abstract. $C_{16}H_{36}N^+ \cdot C_4HCl_2O_4^-$, $M_r = 426.4$, triclinic, $P\bar{1}$, $Z = 2$, $a = 8.950(2)$, $b = 10.516(4)$, $c = 13.116(4)$ Å, $\alpha = 99.50(3)$, $\beta = 97.19(4)$, $\gamma = 99.53(2)^\circ$, $V = 1185.9$ Å³, $D_m = 1.20(5)$ (floatation), $D_x = 1.194$ Mg m⁻³, $\mu(Cu K\alpha) = 2.650$, $\mu(Mo K\alpha) = 0.299$ mm⁻¹, at 293 (1) K. The structure contains tetra-*n*-butylammonium cations and hydrogen dichloromaleate anions and an extremely short intramolecular O...H...O hydrogen bond with an average distance of 2.20 (3) Å confirmed by the two independent diffractometer data sets obtained from the two different crystals. The correction due to thermal vibration gave an average value of 2.25 (3) Å. R and R_w values were 0.082 and 0.120 (Cu $K\alpha$, 1830 observed reflexions) and 0.075 and 0.101 (Mo $K\alpha$, 1337 observed reflexions) respectively. The moderate accuracy of the structure determination is because of a high degree of thermal disorder in the hydrogen dichloromaleate residue.

Introduction. As part of an investigation of acid salts of some dibasic acids, in search of short hydrogen bonds, crystals of tetra-*n*-butylammonium hydrogen dichloromaleate were prepared. The infrared spectra of the title compound and potassium hydrogen dichloromaleate, $KHC_4Cl_2O_4$, in solution indicate an intramolecular hydrogen bond. However, solid $KHC_4Cl_2O_4$ has intermolecular hydrogen bonds of 2.449 Å, linking the dichloromaleate residues into one-dimensional arrays (Golič, Detoni, Hadži & Orel, 1976). On the other hand, solid potassium hydrogen maleate and chloromaleate (Peterson & Levy, 1958; Ellison & Levy, 1965) have discrete monoanions with strong intramolecular hydrogen bonds of 2.437 and 2.403 Å respectively. The present X-ray analysis of the title compound was undertaken in order to confirm the intramolecular hydrogen bond suggested by the infrared spectroscopy.

The compound crystallizes from water as transparent prisms. The reciprocal lattice was explored by oscillation and Weissenberg photographs. Cell dimensions were obtained by least squares from the 2θ values of 30 moderately high-order reflexions measured on a CAD-4 diffractometer [Cu $K\alpha$, $\lambda = 1.54051$ Å]. The

centrosymmetric distribution of $|E|$ values ($\langle E^2 \rangle = 1.000$; $\langle |E^2 - 1| \rangle = 1.037$; $\langle |E| \rangle = 0.769$) indicated the space group $P\bar{1}$.

Two sets of data were collected on the diffractometer with two different crystals and two different radiations (Cu $K\alpha$ with Ni filter; Mo $K\alpha$ with graphite monochromator). Details of the data collection and reduction are given in Table 1. The data were corrected for variations in reference reflexions and Lorentz-polarization effects, but not for absorption.

The structure was solved with *MULTAN* 74 (Main, Woolfson, Lessinger, Germain & Declercq, 1974) from the Cu $K\alpha$ data. An E map with the highest combined figure of merit CFOM (2.74) obtained with the unit weighting of ABSFOM (1.025), ψ_o (410) and RESID (22.22) computed with 300 phases ($|E| > 1.68$) gave the initial coordinates for all the heavy atoms. Both sets of data were refined by least squares, minimizing $\sum w(|F_o| - k|F_c|)^2$, where the weighting function was determined empirically to keep $\sum w(\Delta F)^2$ uniform over the ranges of $(\sin \theta)/\lambda$ and $|F_o|$. The variables were divided into three separate blocks. Because of the low accuracy of the structure determination, no attempt

Table 1. *Data-collection summary*

Temperature (K)	293 (1)	
Diffractometer	CAD-4 automatic, four-circle	
Scan method	$\omega-2\theta$	
2θ scan width ($^\circ$)	0.8 + 0.2 tan θ	
Aperture (mm)	2.4 + 0.9 tan θ	
Reference reflexions	12 $\bar{3}$; $\bar{1}23$; $1\bar{1}3$	
Background	$\frac{1}{4}$ of the scan time at each of the scan limits	
Radiation (Å)	Cu $K\alpha$ ($\lambda = 1.5418$) Mo $K\alpha$ ($\lambda = 0.7107$)	
Size of crystal (mm)	0.29 × 0.37 × 0.33 0.35 × 0.42 × 0.38	
Scan rate ($^\circ$ min ⁻¹)		
Minimum	2.5	1.8
Maximum	20.1	20.1
Maximum scan time (s)	30	40
$2\theta_{max}$ ($^\circ$)	110	60
Intensity decrease (%)	8	7
Measured reflexions	6354 ($\pm h, \pm k, \pm l$)	7209 ($\pm h, \pm k, +l$)
Averaged reflexions	2980	6869
Mean discrepancy on I (%)	2.6	—
Observed reflexions $ I > 2\sigma(I)$	1830	1337
Unobserved reflexions	1150	5532
$\sigma(I)$ based on	Counting statistics	
μ (mm ⁻¹)	2.650	0.299

* For a preliminary account see Golič & Purkeljc (1976).

was made to locate the H atoms. Apart from the acidic H atom, the remaining H atoms were included at calculated positions with fixed isotropic temperature factors, assuming C—H = 1.09 Å and a staggered conformation. A final difference map was featureless. Final refinement parameters are given in Table 2. Scattering factors for Cl, O, N and C were those of Cromer & Mann (1968) and for H of Stewart, Davidson & Simpson (1965).

All calculations were performed on the CDC Cyber 172 computer at RRC Ljubljana with XRAY 72 (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). Table 3 lists the final coordinates.*

Discussion. Table 3 shows that there are no essential differences between the structures obtained from the Mo *K*α and Cu *K*α X-ray data and therefore only the Cu *K*α structure will be discussed. The criterion for this choice was the better variable-to-parameter ratio and consequently smaller e.s.d.'s of the fractional coordinates.

The structure is composed of separate tetra-*n*-butylammonium cations and hydrogen dichloromaleate anions (Fig. 1). The dichloromaleate residues exhibit extremely high thermal parameters; on the other hand, the vibrational parameters for the atoms in the cations are reasonable even for terminal C atoms.

Interatomic distances and angles are listed in Table 4. The cation is in the normal *trans* (staggered) conformation with average C—N and C—C distances of 1.519 (3) and 1.514 (3) Å and average C—N—C, N—C—C and C—C—C angles of 109.5 (2), 115.8 (2) and 111.2 (2)° respectively. These values are comparable to those found in other tetra-*n*-butylammonium derivatives. Each of the four *n*-butyl chains is planar to within 0.04 Å.

* Lists of structure factors and anisotropic thermal parameters from both data sets have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35088 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Refinement summary*

Final refinement cycle	Cu <i>K</i> α data	Mo <i>K</i> α data
Scale factor (<i>k</i>)	1.046	1.039
$R = \sum \Delta F / \sum F_o $	0.082	0.075
$R_w = [\sum w(\Delta F)^2 / \sum w F_o^2]^{1/2}$	0.120	0.101
Average shift/error	0.209	0.359
Maximum shift/error	0.876	1.400
Data (<i>m</i>)-to-variable (<i>n</i>) ratio	7.50	5.48
$[\sum w(\Delta F)^2 / (m - n)]^{1/2}$	0.399	0.450
Number of reflexions	1830	1337
Final difference map	0.39	0.24
Maximum $\Delta\rho$ (e Å ⁻³)		

The dichloromaleate residue is shown in Fig. 2. The most striking feature of this group is an extremely short intramolecular hydrogen bond of 2.221 (14) Å. Correction for bond shortening due to thermal vibrations,

Table 3. *Final fractional coordinates with e.s.d.'s in parentheses*

Coordinates are multiplied by 10⁴ for non-hydrogen and by 10³ for H atoms. $U_{eq} = (U_{11} \cdot U_{22} \cdot U_{33})^{1/3}$. Upper numbers: Cu *K*α data, lower numbers: Mo *K*α data.

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq} (Å ² × 10 ³)
Cl(1)	5554 (4)	388 (2)	1533 (2)	125 (2)
	5554 (5)	387 (3)	1533 (3)	123 (3)
Cl(2)	7665 (4)	2237 (5)	652 (2)	184 (3)
	7662 (5)	2237 (6)	654 (3)	185 (4)
O(1)	4373 (13)	1257 (12)	3269 (8)	189 (8)
	4386 (16)	1288 (15)	3256 (10)	183 (10)
O(2)	5665 (9)	3292 (10)	3744 (5)	133 (5)
	5672 (11)	3315 (13)	3727 (7)	133 (7)
O(3)	7063 (12)	4799 (8)	3073 (9)	144 (6)
	7025 (17)	4792 (11)	3074 (11)	148 (9)
O(4)	8345 (10)	4873 (11)	1672 (10)	192 (9)
	8342 (14)	4861 (14)	1664 (12)	194 (11)
N	7198 (4)	3812 (4)	7341 (3)	49 (2)
	7210 (6)	3820 (5)	7344 (4)	49 (3)
C(1)	5293 (10)	2193 (11)	3167 (7)	99 (6)
	5310 (13)	2219 (16)	3152 (10)	100 (8)
C(2)	6078 (7)	2014 (6)	2176 (5)	69 (3)
	6087 (9)	2025 (8)	2174 (6)	68 (5)
C(3)	6978 (7)	2803 (7)	1764 (5)	80 (4)
	6981 (9)	2811 (10)	1768 (7)	79 (5)
C(4)	7543 (10)	4371 (12)	2211 (13)	120 (8)
	7542 (14)	4381 (16)	2213 (17)	119 (11)
C(5)	7191 (6)	4634 (5)	6492 (4)	54 (3)
	7206 (8)	4649 (7)	6496 (5)	53 (4)
C(6)	8690 (7)	5576 (5)	6505 (4)	63 (3)
	8692 (9)	5570 (7)	6504 (6)	62 (5)
C(7)	8514 (8)	6369 (7)	5647 (5)	77 (4)
	8513 (10)	6364 (8)	5642 (6)	72 (5)
C(8)	9991 (8)	7267 (6)	5599 (6)	83 (4)
	9996 (11)	7270 (9)	5606 (8)	83 (5)
C(9)	7741 (6)	4655 (5)	8426 (4)	55 (3)
	7739 (9)	4655 (7)	8425 (5)	53 (4)
C(10)	6858 (7)	5740 (6)	8714 (5)	69 (4)
	6852 (10)	5728 (8)	8706 (6)	66 (5)
C(11)	7586 (10)	6566 (8)	9776 (5)	87 (4)
	7589 (13)	6569 (10)	9781 (7)	89 (7)
C(12)	6685 (11)	7556 (10)	10178 (7)	109 (6)
	6662 (14)	7521 (13)	10192 (8)	107 (8)
C(13)	8309 (6)	2871 (5)	7151 (4)	55 (3)
	8316 (8)	2866 (7)	7141 (5)	52 (4)
C(14)	8359 (6)	1894 (6)	7871 (5)	66 (3)
	8345 (9)	1883 (7)	7876 (6)	64 (4)
C(15)	9466 (8)	987 (7)	7598 (5)	86 (4)
	9475 (11)	991 (9)	7606 (7)	80 (6)
C(16)	9520 (11)	-19 (9)	8279 (8)	118 (6)
	9481 (14)	-25 (11)	8291 (9)	113 (8)
C(17)	5587 (6)	3067 (5)	7290 (4)	55 (3)
	5576 (8)	3054 (7)	7291 (5)	51 (4)
C(18)	4934 (6)	2037 (5)	6312 (4)	57 (3)
	4943 (8)	2035 (7)	6311 (5)	53 (4)
C(19)	3254 (6)	1521 (6)	6317 (5)	67 (4)
	3249 (8)	1529 (7)	6323 (6)	60 (5)
C(20)	2599 (8)	408 (7)	5399 (6)	83 (4)
	2599 (10)	400 (9)	5404 (8)	77 (6)

Table 3 (cont.)

	<i>x</i>	<i>y</i>	<i>z</i>		<i>x</i>	<i>y</i>	<i>z</i>
H(1)	692	397	574	H(19)	798	232	635
	692	398	574		798	232	634
H(2)	629	521	658	H(20)	946	346	724
	632	524	659		947	344	723
H(3)	899	624	726	H(21)	873	242	867
	901	624	726		869	241	868
H(4)	959	501	638	H(22)	721	131	780
	959	500	638		720	129	779
H(5)	815	570	490	H(23)	911	48	679
	816	569	489		915	49	679
H(6)	764	696	579	H(24)	1061	158	768
	764	695	578		1062	159	772
H(7)	1036	794	635	H(25)	987	49	909
	1035	794	636		981	47	911
H(8)	1086	667	545	H(26)	837	-61	819
	1087	668	547		833	-62	818
H(9)	986	784	498	H(27)	1031	-67	808
	987	784	499		1029	-66	809
H(10)	764	401	899	H(28)	558	257	796
	764	401	899		557	255	796
H(11)	894	511	847	H(29)	483	378	735
	894	511	847		481	376	736
H(12)	688	636	813	H(30)	505	247	562
	687	635	812		507	248	562
H(13)	567	531	874	H(31)	556	123	629
	567	529	874		556	122	629
H(14)	770	591	1033	H(32)	313	116	704
	774	592	1033		312	119	705
H(15)	872	708	971	H(33)	262	232	627
	871	711	971		262	232	627
H(16)	658	821	962	H(34)	272	76	467
	652	817	964		273	74	467
H(17)	555	704	1024	H(35)	323	-39	545
	554	698	1026		323	-39	546
H(18)	721	815	1095	H(36)	139	4	540
	718	812	1095		139	4	541

applied on the basis of the rigid-body TLS analysis [Schomaker & Trueblood (1968); computer program written by Filippini & Gramaccioli (1969)], gave the value 2.275 Å, which is still very unusual. For this reason, the whole crystal structure analysis was repeated with Mo $K\alpha$ data and the value obtained for O(2)···O(3) was 2.166 (18) Å. However, this value, as

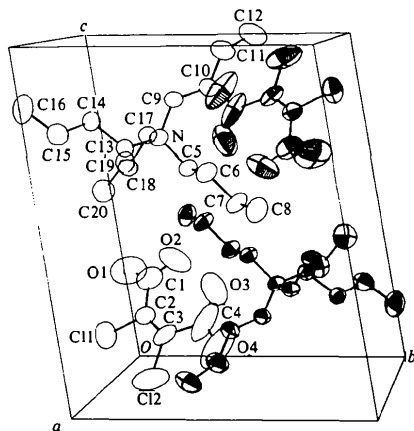


Fig. 1. A view of the structure along [100].

well as all the others in the dichloromaleate residue, is strongly affected by the high degree of thermal disorder; therefore, the values are not exact and will not be discussed in detail. The atomic groups (I): O(1), O(2), C(1), C(2); (II): O(3), O(4), C(3), C(4) and (III): Cl(1), Cl(2), C(2), C(3), are planar to within 0.008 for (I), 0.007 for (II) and 0.010 Å for (III). The dihedral angles (I),(III) and (II),(III) are 7.2 and 1.5°; thus the dichloromaleate residue is almost planar. The average

Table 4. Bond distances (Å) and angles (°), Cu $K\alpha$ data

N(<i>n</i> -C ₄ H ₉) ₄ ⁺ cation				
N—C(5)	1.519 (7)	C(5)—N—C(9)	111.9 (4)	
N—C(9)	1.522 (6)	C(5)—N—C(13)	108.5 (4)	
N—C(13)	1.528 (7)	C(5)—N—C(17)	108.4 (4)	
N—C(17)	1.511 (6)	C(9)—N—C(13)	107.8 (4)	
C(5)—C(6)	1.526 (7)	C(9)—N—C(17)	109.3 (4)	
C(6)—C(7)	1.515 (9)	C(13)—N—C(17)	111.0 (4)	
C(7)—C(8)	1.506 (9)	N—C(5)—C(6)	115.6 (4)	
C(9)—C(10)	1.516 (9)	C(5)—C(6)—C(7)	110.4 (5)	
C(10)—C(11)	1.519 (8)	C(6)—C(7)—C(8)	112.1 (5)	
C(11)—C(12)	1.488 (14)	N—C(9)—C(10)	115.2 (4)	
C(13)—C(14)	1.508 (9)	C(9)—C(10)—C(11)	109.9 (6)	
C(14)—C(15)	1.520 (10)	C(10)—C(11)—C(12)	113.5 (7)	
C(15)—C(16)	1.495 (14)	N—C(13)—C(14)	115.6 (5)	
C(17)—C(18)	1.519 (7)	C(13)—C(14)—C(15)	111.3 (5)	
C(18)—C(19)	1.513 (8)	C(14)—C(15)—C(16)	112.9 (7)	
C(19)—C(20)	1.514 (9)	N—C(17)—C(18)	116.6 (4)	
		C(17)—C(18)—C(19)	109.9 (5)	
		C(18)—C(19)—C(20)	111.3 (5)	
C ₄ HCl ₂ O ₄ ⁻ anion				
		Corrected*		
Cl(1)—C(2)	1.736 (6)	1.779	Cl(1)—C(2)—C(1)	109.0 (5)
Cl(2)—C(3)	1.708 (8)	1.751	Cl(1)—C(2)—C(3)	117.4 (5)
C(1)—O(1)	1.211 (15)	1.241	C(1)—C(2)—C(3)	133.5 (6)
C(1)—O(2)	1.241 (13)	1.271	Cl(2)—C(3)—C(2)	120.5 (6)
C(4)—O(3)	1.297 (19)	1.329	Cl(2)—C(3)—C(4)	114.3 (7)
C(4)—O(4)	1.191 (19)	1.219	C(2)—C(3)—C(4)	125.2 (8)
C(1)—C(2)	1.552 (11)	1.592	O(1)—C(1)—O(2)	128.1 (10)
C(2)—C(3)	1.291 (10)	1.321	O(1)—C(1)—C(2)	116.2 (9)
C(3)—C(4)	1.628 (14)	1.668	O(2)—C(1)—C(2)	115.6 (8)
O(2)···O(3)	2.221 (14)	2.275	O(3)—C(4)—O(4)	133.9 (11)
			O(3)—C(4)—C(3)	114.5 (10)
			O(4)—C(4)—C(3)	111.5 (12)

* Values corrected for rigid-body librations.

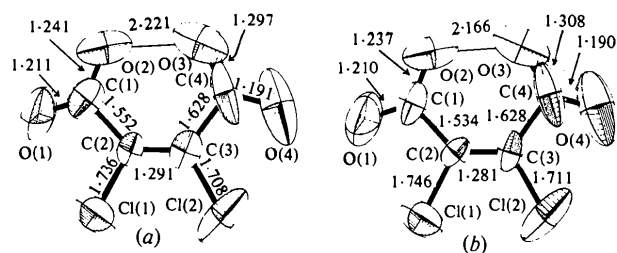


Fig. 2. A hydrogen dichloromaleate residue viewed along the normal to the mean plane. The atoms are represented by thermal ellipsoids drawn at the 50% probability level (Johnson, 1965). (a) Cu $K\alpha$ data, (b) Mo $K\alpha$ data.

deviation of the ten atoms from the mean plane is 0.05 Å, with extremes of -0.12 for O(1) and 0.13 Å for O(2).

Further work is being carried out in order to obtain data at low temperature.

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Structure d'un Nouvel Alcaloïde Bisindolinique: Complexe Moléculaire 1:1 Sungucine–Acétone

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Abstract. $C_{42}H_{42}N_4O_2 \cdot C_3H_6O$, $M_r = 634.8 (+58.1)$, orthorhombic, $P2_12_12_1$, $a = 13.779 (5)$, $b = 24.516 (6)$, $c = 10.640 (4)$ Å, $V = 3594.3$ Å³, $Z = 4$, $D_c = 1.28$ Mg m⁻³, $\mu = 0.643$ mm⁻¹, Cu $K\alpha$ radiation, final $R = 0.05$ (3394 reflexions). Sungucine represents a new type of bisindolinic alkaloid with an unusual C(23)–C(5') bond between the two parts of the molecule, which have the same stereochemistry. Ring D (and D') is almost in a boat conformation and C(2)–C(16) is *cis*. There are only van der Waals interactions in the crystals.

Introduction. La sungucine (Fig. 1) est un nouvel alcaloïde extrait des racines de *Strychnos icaja* Baill.;

ces dernières sont utilisées en Afrique centrale pour la préparation des poisons de flèche et d'épreuve. La nouvelle substance a été étudiée par UV, IR, spectrométrie de masse et RMN, mais une analyse radio-cristallographique a été nécessaire pour établir sa structure moléculaire originale (Lamotte, Dupont, Dideberg, Kambu & Angenot, 1979). C'est l'objet du présent article.

Les cristaux ont été obtenus à partir d'une solution d'acétone.

Les données ont été collectées au moyen d'un diffractomètre à quatre cercles Hilger & Watts. Sur 3607 réflexions mesurées, 3439 ont été considérées comme observées [$I > 2\sigma(I)$].

La structure a été déterminée par méthodes directes avec le programme *MULTAN 77* (Main, Lessinger, Woolfson, Germain & Declercq, 1977). L'affinement a © 1980 International Union of Crystallography

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