Identification and Structure of 2-Methyl-5-ethylpyridinium Tetrachlorophthalate
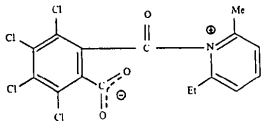
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Abstract. $C_{16}H_{13}Cl_4NO_4$, F.W. 425·1, triclinic, space group $P\bar{1}$, $a = 8·807$ (4), $b = 10·125$ (4), $c = 12·728$ (5) Å, $\alpha = 93·39$ (2), $\beta = 91·81$ (1), $\gamma = 129·56$ (2)°, $V = 869·94$ Å^3, $Z = 2$, $D_m = D_x = 1·62$ g cm^{-3}, $F(000) = 432$. The structure was solved by direct methods and refined by block-diagonal least squares to an R of 0·081. Two tetrachlorophthalate and two pyridinium ions are linked together by hydrogen bonds to form centrosymmetric dimeric units.

Introduction. The quaternization reaction of pyridines by phthalic anhydrides gives a betaine-like compound (Nagy, private communication):

Among several proposed structures, the captation product by water of this intermediate was assigned the structure of 2-methyl-5-ethylpyridinium tetrachlorophthalate on the basis of the present X-ray structure determination.

The cell constants were determined by least squares from 2θ values of 12 reflexions. Intensities of 2778 reflexions were measured on a Picker semi-automatic diffractometer with Ni-filtered Cu $K\alpha$ radiation ($\lambda = 1·54242$ Å) and the ω-2θ scan method ($\Delta 2\theta = \pm 1·1°$, $2\theta_{max} = 125°$); 2436 were included in the refinement, their intensities being greater than $2·5\sigma$.
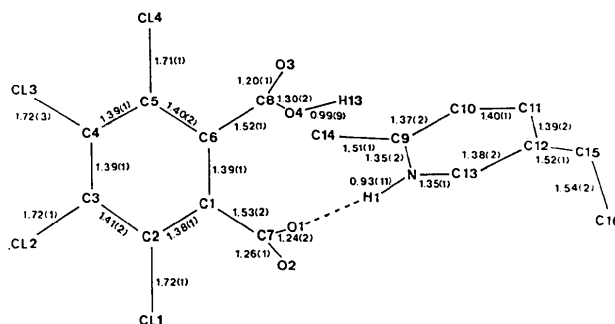

Fig. 1. Bond distances (Å) with standard deviations.

Table 1. *Final atomic parameters* ($\times 10^4$, *hydrogen atoms* $\times 10^3$)

Anisotropic temperature factor: $\exp[-2\pi^2(h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12} + \ldots)]$.

	$x(\sigma)$	$y(\sigma)$	$z(\sigma)$	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	3809 (7)	345 (6)	2367 (3)	39	25	8	23	3	−1
C(2)	2997 (7)	816 (6)	3039 (4)	36	31	14	24	5	1
C(3)	3945 (8)	1632 (6)	4059 (3)	32					
C(4)	5665 (8)	1917 (7)	4381 (4)	43	40	6	25	1	−3
C(5)	6455 (8)	1410 (7)	3709 (3)	40	38	6	26	−2	−3
C(6)	5507 (7)	611 (6)	2694 (3)	33	27	5	19	2	−4
C(7)	2820 (7)	−557 (6)	1259 (3)	29	29	10	21	0	−9
C(8)	6327 (7)	31 (6)	1940 (3)	37	34	10	26	2	−3
C(9)	2168 (8)	4497 (7)	10810 (4)	38	37	14	25	−1	−8
C(10)	2167 (9)	3226 (7)	10367 (4)	47	37	22	29	−1	−5
C(11)	2538 (8)	3208 (7)	9309 (4)	42	34	23	28	−1	−4
C(12)	2866 (8)	4447 (6)	8698 (4)	37	34	13	24	−1	−7
C(13)	2843 (8)	5695 (7)	9175 (4)	40	36	25	25	1	−3
C(14)	1798 (11)	4665 (9)	11944 (4)	71	59	16	44	7	−6
C(15)	3264 (10)	4459 (9)	7541 (4)	62	63	16	44	14	6
C(16)	1605 (11)	4142 (9)	6817 (5)	78	66	21	52	−3	2
N	2478 (7)	5674 (6)	10195 (3)	44	36	22	28	1	−5
O(1)	2126 (6)	−2081 (5)	1107 (3)	54	33	20	30	0	−9
O(2)	2864 (6)	327 (5)	585 (2)	52	43	7	36	−2	−2
O(3)	6333 (7)	−1127 (6)	2085 (3)	84	65	29	65	20	12
O(4)	6979 (6)	938 (5)	1137 (3)	52	43	13	34	13	4
Cl(1)	833 (2)	406 (2)	2661 (1)	45	55	24	40	4	−3
Cl(2)	2994 (3)	2296 (2)	4886 (1)	78	84	23	64	8	−15
Cl(3)	6860 (3)	2961 (2)	5611 (1)	69	69	10	44	−9	−18
Cl(4)	8591 (2)	1794 (2)	4093 (1)	46	73	21	42	−7	−7

Fig. 2. Angles (°) with standard deviations.

Table 1 (cont.)

	x (σ)	y (σ)	z (σ)	U
H(1)	249 (12)	651 (10)	1055 (6)	43
H(2)	192 (11)	227 (10)	1080 (6)	43
H(3)	256 (11)	222 (10)	895 (6)	43
H(4)	308 (11)	658 (9)	887 (6)	39
H(5)	155 (14)	378 (12)	1230 (7)	73
H(6)	87 (14)	486 (12)	1187 (8)	73
H(7)	325 (14)	575 (12)	1241 (8)	73
H(8)	347 (10)	354 (9)	733 (6)	31
H(9)	443 (11)	564 (9)	742 (6)	35
H(10)	154 (13)	512 (11)	703 (7)	61
H(11)	38 (13)	304 (11)	682 (7)	61
H(12)	220 (13)	446 (11)	605 (7)	61
H(13)	728 (10)	50 (9)	1053 (6)	32

The structure was solved with *MULTAN* (Declercq, Germain, Main & Woolfson, 1973). H atoms were located on a difference map. R was 0·081 after refinement by block-diagonal least squares with the X-RAY system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). C(3) tends to give a non-positive-definite matrix with anisotropic parameters (Table 1). The weighting scheme is of the form: $w = (a + |F_o| + b|F_o|^2 + c|F_o|^3)^{-1}$ with $a = 4·082$, $b = 0·015$ and $c = 0·003$. Scattering factors were taken from *International Tables for X-ray Crystallography* (1962).*

Discussion. The bond distances and angles are given in Figs. 1 and 2, and Table 2. The mean C–Cl of 1·716 Å is in agreement with the 1·709 Å estimated by Rudman (1971) for compounds containing *ortho* C–Cl bonds.

The crystal is formed from centrosymmetric dimeric units made up of two tetrachlorophthalate ions, linked together by hydrogen bonds, and two pyridinium ions, each hydrogen-bonded to a phthalate ion (Fig. 3). The hydrogen-bond distances are reported in Table 3. O(3) is not involved in hydrogen bonds.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31824 (11 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. Intramolecular bond distances (Å) and angles (°) involving hydrogen atoms

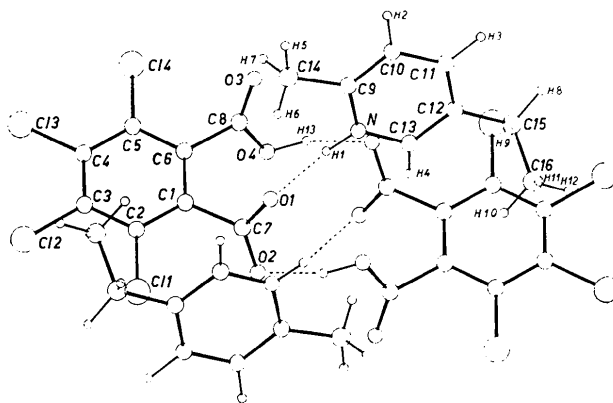|				
C(10)–H(2)	1·05 (10)	C(9)—C(10)–H(2)	122 (5)
C(11)–H(3)	1·09 (11)	C(11)–C(10)–H(2)	118 (5)
C(13)–H(4)	0·90 (10)	C(10)–C(11)–H(3)	121 (4)
C(14)–H(5)	0·93 (13)	C(12)–C(11)–H(3)	119 (4)
C(14)–H(6)	0·96 (16)	C(12)–C(13)–H(4)	126 (6)
C(14)–H(7)	1·13 (8)	N——C(13)–H(4)	114 (6)
C(15)–H(8)	1·08 (11)	C(9)—C(14)–H(5)	111 (7)
C(15)–H(9)	0·99 (7)	C(9)—C(14)–H(6)	103 (6)
C(16)–H(10)	1·05 (14)	C(9)—C(14)–H(7)	109 (5)
C(16)–H(11)	0·93 (7)	H(5)—C(14)–H(6)	123 (10)
C(16)–H(12)	1·09 (9)	H(5)—C(14)–H(7)	97 (8)
		H(6)—C(14)–H(7)	115 (10)
		C(12)–C(15)–H(8)	111 (4)
		C(12)–C(15)–H(9)	108 (4)
		C(16)–C(15)–H(8)	112 (4)
		C(16)–C(15)–H(9)	103 (6)
		H(8)—C(15)–H(9)	112 (8)
		C(15)–C(16)–H(10)	108 (5)
		C(15)–C(16)–H(11)	114 (8)
		C(15)–C(16)–H(12)	104 (6)
		H(10)–C(16)–H(11)	113 (10)
		H(10)–C(16)–H(12)	103 (9)
		H(11)–C(16)–H(12)	115 (7)

Fig. 3. Hydrogen-bond network within a centrosymmetric dimeric unit.

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Table 3. *Hydrogen-bond distances* (Å) *and angles* (°)

D—H$\cdots\cdots A$	H$\cdots A$	$D\cdots A$	D–H$\cdots A$
O(4)–H(13)$\cdots$O(2^i)	1·57 (8)	2·53 (2)	161 (8)
N$^+$—H(1)$\cdots\cdots$O(1^{ii})	1·76 (12)	2·69 (2)	171 (8)

Notation: (i) $1-x,\bar{y},\bar{z}$; (ii) $x,1+y,1+z$.

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Ditellurium(IV) Trioxosulphate

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Abstract. $Te_2O_3SO_4$, $P2_1nm$, orthorhombic, $a=4·654$ (1), $b=6·936$ (1), $c=8·879$ (2) Å, $Z=2$, $V=286·6$ (1) Å^3, $M=399·26$, $D_x=4·63$ g cm^{-3}. The S–O distances are 1·47 (1)–1·49 (1) Å. The Te^{IV} coordination is threefold pyramidal with Te–O distances of 1·89 (1), 1·91 (1) and 2·00 (1) Å. In addition there are three longer Te–O bonds of 2·26 (1), 2·63 (1) and 2·84 (1) Å. The TeO_3 and SO_4 units are connected to form sheets.

Introduction. The preparation of $Te_2O_3SO_4$ has been described by Hubková, Loub & Syneček (1966), who found that $Te_2O_3SO_4$ belonged to space group $P2_1nm$. Since there were, however, uncertainties about the proposed structure, a complete redetermination has been performed. Single crystals were prepared and provided by Dr Moret, Montpellier. The cell dimensions were refined (Lindqvist & Wengelin, 1967) from 48* lines measured on a Guinier powder photograph, taken with KCl as an internal standard ($a_{KCl}=6·2919$ Å at 20°C; Hambling, 1953).

Intensities were collected on a two-circle Pailred diffractometer with Mo $K\alpha$ radiation and a graphite monochromator. The ω-scan procedure was used with a scan speed of 2·5° min^{-1} and the background was measured for 24 s at each end of the scan interval ($\Delta\omega=3$–6°). The layers $0kl$–$8kl$ were registered out to $2\theta=100°$ and 1050 unique reflexions for which $\sigma(I)/I<0·3$ were used in the structure analysis. The intensities were corrected for absorption (program $DATAP2$; Coppens, Leiserowitz & Rabinovich, 1965).

* Lists of observed and calculated $\sin^2\theta_{hkl}$ and d_{hkl} values, and structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31788 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

A drawing of the crystal used for the data collection is shown in Fig. 1. μ(Mo $K\alpha$) = 177·6 cm^{-1} (*International Tables for X-ray Crystallography*, 1962).

The structure was solved from Patterson and electron density calculations (program DRF; A. Zalkin, Berkeley) and the space group confirmed to be $P2_1nm$ in accordance with the systematic absences $h+l=2n+1$ for the $h0l$ reflexions. The structural parameters were refined with the block-diagonal approximation (program $BLOCK$; O. Lindgren, Göteborg), initially with isotropic temperature factors and separate scale factors for each layer ($R=0·052$) and subsequently with anisotropic temperature factors and an overall scale factor ($R=0·047$). The positional parameters obtained from
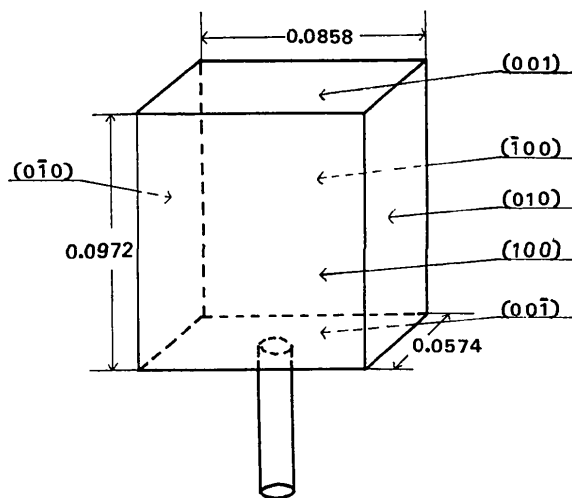

Fig. 1. The crystal used for data collection. The distances are given in mm.