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Structure of Choline Picrate

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Abstract. $C_5H_{14}NO^+.C_6H_2N_3O_7^-$, $M_r = 332.2$, monoclinic, $P2_1/n$, $a = 6.7895$ (9), $b = 22.054$ (2), $c = 9.713$ (1) Å, $\beta = 103.50$ (1)°, $V = 1414.2$ (5) Å^3, $Z = 4$, D_x (105 K) = 1.561 Mg m^{-3}, m.p. (hot-stage microscope) 516–518 K (corrected), λ(Cu $K\alpha$) = 1.5418 Å, $\mu = 1.116$ mm^{-1}, $F(000) = 696$, $T = 105$ K, $R = 0.039$ for 2581 observed reflections [$I \geq 3\sigma(I)$]. The choline ion adopts a folded conformation, τ(O—C—C—N) = ±90.1 (1)°. Strands of choline ions are formed *via* C···O contacts of length 3.305 (2) Å [C9···O4 ($x - 1$, y, z)] oriented along the *a* axis. Only weaker contacts are observed between parallel strands, which together form layers perpendicular to the *b* axis. The picrate ions are stacked in columns along the *a* axis with an average distance of 3.263 Å between the benzene rings. The parallel columns of picrate ions form layers perpendicular to the *b* axis. The picrate ions are not stacked exactly on top of each other; the shift releaves strain. One nitro group overlaps the neighbouring benzene ring. The other nitro group close to the phenolate O atom makes an angle of 40.35 (4)° to the plane of the benzene ring, and is found on the outside of the column. The choline hydroxy group donates a hydrogen bond [O4···O21 2.781 (1) Å] to the phenolate O atom of the picrate ion. Many weak contacts, shorter than the sum of the van der Waals radii, are found involving the quaternary ammonium group and O atoms of the picrate ion.

Experimental. Choline picrate was prepared following *Pharmacopoea Nordica, Editio Danica* (1963). Single crystals were obtained by slow cooling of a saturated hot ethanol–water solution. Crystal size 0.1 × 0.2 × 0.4 mm. Intensity data were sampled on an Enraf–Nonius CAD-4 diffractometer equipped with a low-temperature device, using graphite-

Table 1. *Atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
O4	0.4383 (2)	0.23339 (4)	−0.0540 (1)	2.05 (2)
C5	0.2444 (2)	0.25310 (6)	−0.1306 (1)	1.68 (2)
C6	0.2051 (2)	0.31654 (6)	−0.0839 (1)	1.47 (2)
N7	0.1020 (2)	0.32010 (5)	0.0388 (1)	1.24 (2)
C8	0.2104 (2)	0.28263 (6)	0.1613 (1)	1.76 (2)
C9	−0.1142 (2)	0.29968 (6)	−0.0063 (1)	1.68 (2)
C10	0.1048 (2)	0.38522 (6)	0.0848 (1)	1.62 (2)
C21	0.2846 (2)	0.06509 (6)	−0.1272 (1)	1.35 (2)
C22	0.2023 (2)	0.02199 (6)	−0.2398 (1)	1.25 (2)
C23	0.1551 (2)	−0.03724 (6)	−0.2209 (1)	1.40 (2)
C24	0.1748 (2)	−0.05805 (6)	−0.0827 (1)	1.43 (2)
C25	0.2370 (2)	−0.01983 (6)	0.0325 (1)	1.52 (2)
C26	0.2868 (2)	0.03943 (6)	0.0115 (1)	1.45 (2)
O21	0.3510 (2)	0.11557 (4)	−0.15114 (9)	1.91 (2)
N22	0.1750 (2)	0.04245 (5)	−0.3861 (1)	1.42 (2)
O221	0.1035 (2)	0.09327 (4)	−0.4167 (1)	1.88 (2)
O222	0.2219 (2)	0.00755 (4)	−0.47176 (9)	1.94 (2)
N24	0.1234 (2)	−0.12023 (5)	−0.0601 (1)	1.82 (2)
O241	0.0789 (2)	−0.15417 (4)	−0.1638 (1)	2.62 (2)
O242	0.1254 (2)	−0.13671 (5)	0.0619 (1)	2.50 (2)
N26	0.3477 (2)	0.07652 (6)	0.1379 (1)	1.82 (2)
O261	0.3618 (2)	0.05255 (6)	0.2539 (1)	3.43 (3)
O262	0.3811 (2)	0.13041 (5)	0.1258 (1)	3.58 (3)

monochromated Cu $K\alpha$ radiation. Temperature, recorded with a thermocouple, showed variation within 1 K. Cell parameters and orientation matrix were determined from 18 reflections ($38.96 \leq \theta \leq 45.10°$). No corrections for absorption were made. Three intensity control reflections were measured every 10^4 s and decay (-4.3% in 130 h) corrections were applied. $\omega/2\theta$ scan, $\theta_{max} = 75°$, range of hkl: $-8 \leq h \leq 8$, $-27 \leq k \leq 27$, $-12 \leq l \leq 11$. 7720 reflections were measured, of which 2950 were unique and 369 unobserved [$I < 3\sigma(I)$]; $R_{int} = 0.018$ (on F_{obs}).

All non-H atoms except O4 were localized by direct methods (*MULTAN80*; Main *et al.*, 1980). The atom O4 of the choline ion was only found in a $\Delta\rho$ map. This indicated that large displacements could

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

O4—C5	1.421 (2)	C25—C26	1.378 (2)
C5—C6	1.514 (2)	C21—O21	1.243 (2)
C6—N7	1.518 (2)	C22—N22	1.462 (2)
N7—C8	1.494 (2)	C24—N24	1.444 (2)
N7—C9	1.500 (2)	C26—N26	1.453 (2)
N7—C10	1.503 (2)	N22—O221	1.231 (1)
C21—C22	1.458 (2)	N22—O222	1.229 (2)
C21—C26	1.458 (2)	N24—O241	1.234 (1)
C22—C23	1.367 (2)	N24—O242	1.238 (1)
C23—C24	1.395 (2)	N26—O261	1.228 (2)
C24—C25	1.386 (2)	N26—O262	1.221 (2)

O4—C5—C6	109.4 (1)	C23—C24—N24	119.1 (1)
C5—C6—N7	115.4 (1)	C25—C24—N24	119.6 (1)
C6—N7—C8	111.4 (1)	C24—C25—C26	119.8 (1)
C6—N7—C9	110.77 (9)	C21—C26—C25	123.7 (1)
C6—N7—C10	107.8 (1)	C21—C26—N26	120.1 (1)
C8—N7—C9	109.5 (1)	C25—C26—N26	116.1 (1)
C8—N7—C10	108.79 (9)	C22—N22—O221	118.0 (1)
C9—N7—C10	108.6 (1)	C22—N22—O222	118.2 (1)
C22—C21—C26	111.1 (1)	O221—N22—O222	123.9 (1)
C22—C21—O21	122.5 (1)	C24—N24—O241	118.3 (1)
C26—C21—O21	126.5 (1)	C24—N24—O242	118.4 (1)
C21—C22—C23	125.6 (1)	O241—N24—O242	123.3 (1)
C21—C22—N22	117.9 (1)	C26—N26—O261	118.6 (1)
C23—C22—N22	116.4 (1)	C26—N26—O262	119.4 (1)
C22—C23—C24	118.1 (1)	O261—N26—O262	122.1 (1)
C23—C24—C25	121.3 (1)		

O4—C5—C6—N7	−90.2 (1)	C5—C6—N7—C9	−70.1 (1)
C5—C6—N7—C8	52.0 (1)	C5—C6—N7—C10	171.3 (1)

D—H···A	D—H	D···A	H···A	D—H···A
O4—H4···O21	0.89 (2)	2.781 (1)	1.96 (2)	151 (1)

be expected for this O atom, and this was in agreement with the final results. H atoms were observed in the $\Delta\rho$ map in calculated positions. Structure refinement (positional and anisotropic displacement parameters for non-H atoms, positional parameters for H atoms, except the H atoms of the three methyl groups on the quaternary ammonium group) on F with weights $w^{-1} = \sigma^2(F_o) + \frac{1}{4}(0.02F_o)^2$. Final $R = 0.039$, $wR = 0.052$ for 2581 observed reflections $[I \geq 3\sigma(I)]$ and 229 variables. $S = 2.72$, $(\Delta/\sigma)_{max} = 0.07$, $\Delta\rho_{max}/\Delta\rho_{min} = 0.24/-0.33$ e Å^{-3}. Atomic scattering factors for uncharged atoms are used as implemented in the *SDP Structure Determination Package* (B. A. Frenz & Associates, Inc., 1982), which was used for all calculations (including *MULTAN*). Final atomic coordinates for non-H atoms are listed in Table 1.* The bond lengths, bond angles, selected torsion angles and hydrogen-bond dimensions are given in Table 2. Fig. 1 shows the ions with displacement ellipsoids and atomic numbering. Fig. 2 presents a crystal packing diagram with hydrogen bonds shown.

Related literature. Several crystal structures of choline salts, mainly halogenides, have been published, as revealed by a search of the Cambridge Structural Database (1991, version 4.5) (Allen *et al.*, 1979): choline reineckate (Takéuchi & Saito, 1957), choline choride, α form (Senko & Templeton, 1960; Hjortås & Sørum, 1971), choline chloride, β form (Petrouleas, Lemmon & Christensen, 1978), choline iodide (Wemmer, Petrouleas, Panaglotopoulos, Fillippakis & Lemmon, 1983), bis(choline) di-μ-hydroxo-bis[dinitratodioxouranate(VI)] (Viossat, Dung & Soye, 1983) and choline meclofenamate
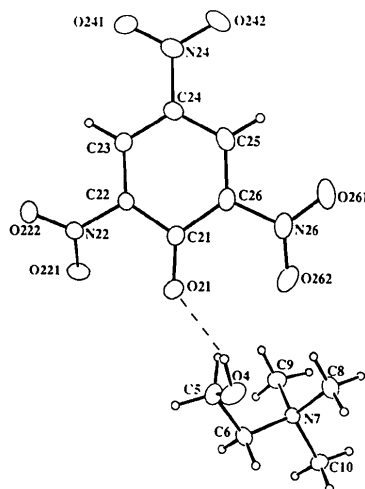

Fig. 1. *ORTEP*II drawing (Johnson, 1976) of the title compound with the atom-labelling scheme. The ions are shown with displacement ellipsoids at the 50% probability level. The hydrogen bond is shown.
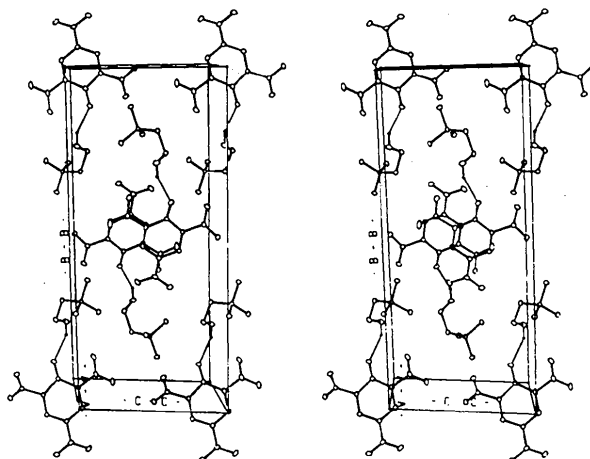

Fig. 2. Stereo diagram of the crystal packing of choline picrate. The axis directions are **c** horizontal, **b** vertical and **a** into the plane of the paper. Hydrogen bonds are indicated by thin lines between H and phenolate O atoms.

monohydrate (Dhanaraj & Vijayan, 1987). Owing to different complications with the structures, accurate results are available only for a few of these determinations (the α form of choline chloride and choline meclofenamate monohydrate). The uranium(VI) complex has $R = 0.041$ (due to U), but the choline ion has high displacement parameters. Bond lengths and angles in the present structure are within the expected ranges.

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Structure of [N,N,N',N'-Tetramethylguanidinium(1+) Pentachlorophenolate(1−) Pentachlorophenol]₂

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Abstract. $(C_5H_{14}N_3^+ \cdot C_6Cl_5O^- \cdot C_6Cl_5OH)_2$, $M_r = 1295.71$, monoclinic, $P2_1/n$, $Z = 4$, $a = 15.603\,(3)$, $b = 13.7397\,(6)$, $c = 23.717\,(5)$ Å, $\beta = 90.280\,(15)°$, $V = 5084.4\,(15)$ Å^3, $D_x = 1.693$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 11.12$ cm^{-1}, $F(000) = 2592$, $R = 0.048$ for 6593 unique reflections with $I > 2.5\sigma(I)$. In the crystal structure the two tetramethylguanidine (TMG) fragments act as a 'proton sponge' by accepting a proton from two of the four pentachlorophenols in the asymmetric unit. The TMG fragments are planar and approach C_{3h} symmetry. With the exception of one N—H donor, all N—H and O—H hydrogen-bond donors are involved in intermolecular hydrogen bonds.

Experimental. Crystals of the title compound were obtained from a solution in acetonitrile of pentachlorophenol and N,N,N',N'-tetramethylguanidine in

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a ratio of 2:1. A colourless crystal of dimensions 0.18 × 0.30 × 0.35 mm was used for data collection on an Enraf–Nonius CAD-4 diffractometer with Zr-filtered Mo $K\alpha$ radiation with the ω–2θ scan mode, $\omega = [0.60 + 0.35\tan\theta]°$. Lattice parameters were determined from the setting angles of 25 reflections in the range $14.1 < \theta < 19.0°$. Intensity data of 13 263 reflections were measured (h −20→20; k 0→18; l 0→31, $2\theta_{max} = 55°$), 11 253 unique ($R_{int} = 0.034$) and 6593 above the $2.5\sigma(I)$ level.

Three periodically measured standard reflections ($\overline{2}40$, 204, $0\overline{4}4$) showed an average deviation of less than 1% during 190 h of X-ray exposure. Intensities were corrected for Lp effects. The structure was solved by direct methods with *SHELXS*86 (Sheldrick, 1986). The methyl-group H atoms were placed at calculated positions (C—H 1.00 Å) and refined riding on their carrier atoms. The phenolic and amino-group H atoms were located in electron-density difference maps and kept fixed during