

Fig. 2. Stereodrawing of the structure. The origin is at the lower right. Hydrogen bonds are dotted.

scheme. Final parameters are given in Table 1. Bond lengths and angles are given in Table 2. The anion H atom and four of the H atoms on the cation are involved in hydrogen bonds. A stereodrawing of the structure is shown in Fig. 2.

**Related literature.** The anion geometry is virtually identical to that found in the ethylenediammonium salt of NTO (Cromer, Hall, Lee & Ryan, 1988). The cation geometry is close to that found in the 1,2,3-triaminoguanidinium ion (Bracuti, Troup & Extine, 1986) and in the guanidinium ion (Baldwin, Denner, Egan & Markwell, 1986). The H atoms on the central amino group are directed to the lone-pair regions of the terminal amino groups.

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## Structures of Three *N*-Methylated 4-Hydroxyproline Derivatives

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**Abstract.** (I)  $[C_6H_{12}NO_3][Cl]$ ,  $M_r = 181.6$ , orthorhombic,  $P2_12_12_1$ ,  $a = 6.099$  (1),  $b = 10.651$  (2),  $c = 13.692$  (1) Å,  $V = 889$  (2) Å<sup>3</sup>,  $Z = 4$ ,  $D_m = 1.37$  (1),  $D_x = 1.357$  Mg m<sup>-3</sup>,  $\lambda = 0.7107$  Å,  $\mu = 0.341$  mm<sup>-1</sup>,  $F(000) = 384$ ,  $T = 295$  (2) K,  $R = 0.053$  for 2027 reflections with  $I \geq 2.5(I)$ ; (II) *trans*- $[C_7H_{14}NO_3][Cl]$ ,  $M_r = 195.6$ , orthorhombic,  $P2_12_12_1$ ,  $a = 6.607$  (2),  $b = 11.079$  (2),  $c = 12.362$  (2) Å,  $V = 905$  (2) Å<sup>3</sup>,  $Z = 4$ ,  $D_m = 1.42$  (1),  $D_x = 1.436$  Mg m<sup>-3</sup>,  $\mu =$

$0.338$  mm<sup>-1</sup>,  $F(000) = 416$ ,  $R = 0.035$  for 1835 reflections; (III) *cis*- $[C_7H_{14}NO_3][Cl]$ ,  $M_r = 195.6$ , orthorhombic,  $P2_12_12_1$ ,  $a = 7.031$  (2),  $b = 10.797$  (2),  $c = 12.708$  (1) Å,  $V = 965$  (2) Å<sup>3</sup>,  $Z = 4$ ,  $D_m = 1.34$ ,  $D_x = 1.346$  Mg m<sup>-3</sup>,  $\mu = 0.317$  mm<sup>-1</sup>,  $F(000) = 416$ ,  $R = 0.051$  for 949 reflections. The crystal structures of (I) *N*-methyl- and (II) *N,N'*-dimethyl-4-hydroxy-L-proline and (III) *N,N'*-dimethyl-4-hydroxy-D-proline have been determined as their hydrochlorides. A *trans*

NTO is a good, insensitive explosive (Lee & Coburn, 1985) and DAGNTO has about the same impact sensitivity. See Federov & Sheffield (1975) for a description of the impact sensitivity test. It is thought that extensive hydrogen bonding can contribute to impact insensitivity.

See Cromer *et al.* (1988) for further triazole and small explosive molecule references.

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Table 1. *Crystal data for (I), (II) and (III)*

	(I)	(II)	(III)
Crystal size (mm)	0.16 × 0.18 × 0.48	0.20 × 0.40 × 0.85	0.15 × 0.20 × 1.00
$\theta$ range for cell dimensions ( $^\circ$ )	9–13	4–14	3–17
Reflections measured	3199	2742	1861
$\theta$ range ( $^\circ$ )	1–27.5	1–27.5	1–25
<i>hkl</i> range	–7→7, –13→1, –17→4	–8→9, –14→1, –16→1	–1→9, –1→14, –16→11
Intensity standards	135; 315; 224	140; 025; 034	212; 111; 221
Unique reflections	2027	2085	1638
$R_{\text{int}}$	0.077	0.029	0.039
Reflections used	1675	1835	949
Number of parameters refined	139	147	142
$R$	0.053	0.035	0.051
$wR$	0.058	0.037	0.052
$k$	1.0	1.0	2.5
$g$	0.0053	0.0041	0.0010
$S$	0.93	0.73	2.60
$(\Delta/\sigma)_{\text{max}}$	0.001	0.001	0.001
$\Delta\rho_{\text{max}}$ (e $\text{\AA}^{-3}$ )	1.10	0.41	0.59
$\Delta\rho_{\text{min}}$ (e $\text{\AA}^{-3}$ )	–0.45	–0.61	–0.49

Table 2. *Fractional atomic coordinates ( $\times 10^4$ ) and  $B_{\text{eq}}$  values ( $\text{\AA}^2$ ) for (I)*

$$B_{\text{eq}} = 8\pi^2(U_{11} + U_{22} + U_{33})/3.$$

	$x$	$y$	$z$	$B_{\text{eq}}$
Cl(1)	205 (1)	–38 (1)	–4089 (1)	4.32
O(1)	–961 (3)	2819 (3)	–3734 (2)	5.13
O(2)	6330 (3)	5823 (2)	–3185 (2)	4.87
O(3)	5576 (4)	4525 (3)	–1935 (2)	5.87
N(1)	2322 (3)	5383 (2)	–4048 (2)	3.55
C(2)	2945 (4)	4681 (3)	–3148 (2)	3.58
C(3)	2926 (5)	3325 (3)	–3496 (3)	4.32
C(4)	978 (5)	3252 (3)	–4192 (2)	3.90
C(5)	560 (4)	4604 (3)	–4509 (2)	4.16
C(6)	5145 (4)	5098 (3)	–2764 (2)	3.95
C(7)	1669 (7)	6723 (4)	–3910 (4)	6.50

Table 3. *Fractional atomic coordinates ( $\times 10^4$ ) and  $B_{\text{eq}}$  values ( $\text{\AA}^2$ ) for (II)*

$$B_{\text{eq}} = 8\pi^2(U_{11} + U_{22} + U_{33})/3.$$

	$x$	$y$	$z$	$B_{\text{eq}}$
Cl(1)	1622 (1)	876 (1)	4471 (1)	2.82
O(1)	–3788 (3)	1685 (2)	6788 (2)	3.74
O(2)	–5467 (3)	–2731 (2)	5681 (1)	3.61
O(3)	–2662 (3)	–3446 (1)	6462 (2)	3.05
N(1)	–1673 (2)	–1186 (1)	7401 (1)	2.00
C(2)	–3605 (3)	–1379 (2)	6751 (2)	2.05
C(3)	–3574 (4)	–333 (2)	5936 (2)	2.84
C(4)	–2507 (3)	710 (2)	6530 (2)	2.58
C(5)	–1801 (3)	156 (2)	7604 (2)	2.58
C(6)	–3982 (3)	–2606 (2)	6234 (2)	2.40
C(7)	244 (3)	–1451 (2)	6782 (2)	2.74
C(8)	–1688 (3)	–1871 (2)	8450 (2)	2.63

disposition of the carboxyl and hydroxyl groups is found in (I) whereas both *trans* and *cis* isomers are found in (II) and (III) respectively. The structures adopt an envelope conformation where C(2), C(3), C(4) and C(5) are essentially coplanar with N(1) out of this plane by 0.518 (2), 0.677 (2) and 0.650 (4)  $\text{\AA}$  for (I), (II) and (III) respectively. In (I) the interionic hydrogen bonding is dominated by three close contacts to the chloride anion; O(1)–H(8)···Cl 2.12 (4), O(3)–H(9)···Cl (symmetry operation:  $1-x, \frac{1}{2}+y, -\frac{1}{2}-z$ ) 2.17 (4) and N(1)–H(1)···Cl ( $\frac{1}{2}+x, \frac{1}{2}-y, -1-z$ ) 2.19 (4)  $\text{\AA}$ . In (II) and (III) only two significant contacts are found in each crystal lattice; (II): O(1)–H(7)···Cl ( $-\frac{1}{2}+x, \frac{1}{2}-y, 1-z$ ) 2.36 (3) and O(3)–H(8)···Cl ( $-\frac{1}{2}+x, -\frac{1}{2}-y, 1-z$ ) 2.39  $\text{\AA}$ , and (III): O(3)–H(8)···Cl ( $-1-x, \frac{1}{2}+y, -\frac{1}{2}-z$ ) 2.02 (4) and O(1)–H(7)···Cl 2.17 (4)  $\text{\AA}$ .

**Experimental.** The isolation of (I) and (II) from *Melaleuca* genus has been reported (Jones, Naidu, Paleb, Tiekink & Snow, 1987). (III) was prepared by base epimerization of (II) (Goodson & Clewer, 1919). Crystals as their hydrochlorides were grown by diffusion of diethyl ether in methanol solutions of the compounds at room temperature. Densities were measured by flotation. Enraf–Nonius CAD-4F diffrac-

Table 4. *Fractional atomic coordinates ( $\times 10^4$ ) and  $B_{\text{eq}}$  values ( $\text{\AA}^2$ ) for (III)*

$$B_{\text{eq}} = 8\pi^2(U_{11} + U_{22} + U_{33})/3.$$

	$x$	$y$	$z$	$B_{\text{eq}}$
Cl(1)	–2030 (2)	–5555 (2)	515 (1)	4.29
O(1)	–986 (7)	–3427 (5)	–1026 (4)	4.84
O(2)	–3714 (7)	–335 (6)	–3915 (4)	6.66
O(3)	–6163 (6)	–1554 (5)	–3546 (3)	4.19
N(1)	–2049 (6)	–728 (4)	–1900 (3)	3.03
C(2)	–3968 (8)	–1251 (6)	–2203 (5)	2.95
C(3)	–3882 (11)	–2568 (7)	–1831 (6)	3.71
C(4)	–2519 (8)	–2579 (6)	–886 (5)	3.16
C(5)	–1832 (9)	–1273 (6)	–811 (5)	3.47
C(6)	–4538 (8)	–992 (6)	–3327 (5)	3.37
C(7)	–2026 (10)	–669 (6)	–1844 (5)	4.40
C(8)	–437 (9)	–1158 (7)	–2590 (6)	4.69

tometer controlled by a PDP8/A computer, graphite-monochromated Mo  $K\alpha$  radiation;  $\omega$ – $2\theta$  scan technique. Data collection parameters are listed in Table 1. Cell parameters obtained from least-squares procedure (de Boer & Duisenberg, 1984) on 25 reflections. Some Friedel pairs were included in each data set. No decomposition of any crystal occurred during its respective data collection as monitored by three

standards every 3600 s. No corrections were applied for absorption or for extinction. Structures solved by direct methods (Gilmore, 1984) and refinement by full-matrix least squares based on  $F$  (Sheldrick, 1976) for reflections with  $I \geq 2.5\sigma(I)$ . Anisotropic thermal parameters for non-H atoms, and H atoms were located from a difference map and refined except for methyl H atoms which were included in the models at their calculated positions; H atoms were refined with individual isotropic thermal parameters except for the methyl bound H atoms in (III) which had a common thermal parameter. A weighting scheme of the form  $w =$

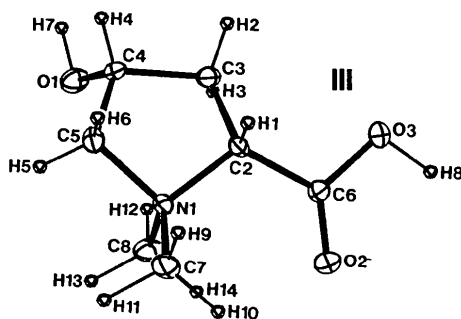
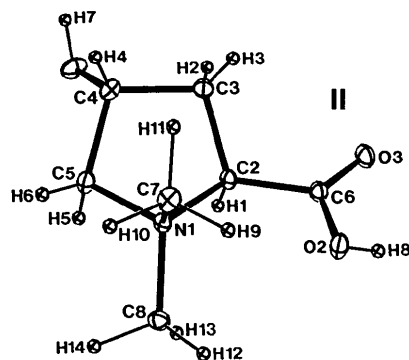
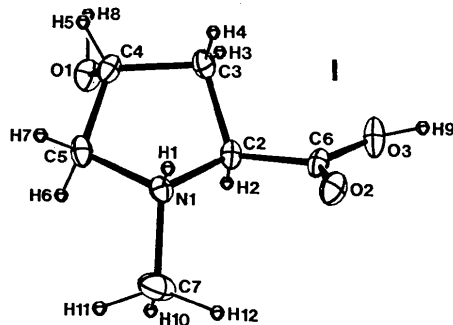


Fig. 1. Molecular structure and numbering scheme used for (I) *trans*- $[C_6H_{12}NO_3][Cl]$ , (II) *trans*- $[C_7H_{14}NO_3][Cl]$ , and (III) *cis*- $[C_7H_{14}NO_3][Cl]$  showing 15% probability ellipsoids (Johnson, 1971).

Table 5. Selected bond distances (Å) and bond angles ( $^\circ$ )

	(I)	(II)	(III)
N(1)—C(2)	1.491 (4)	1.524 (2)	1.512 (7)
N(1)—C(5)	1.497 (4)	1.510 (2)	1.511 (7)
N(1)—C(7)	1.493 (4)	1.507 (2)	1.510 (8)
N(1)—C(8)	—	1.502 (2)	1.505 (8)
C(2)—C(3)	1.522 (5)	1.535 (3)	1.500 (9)
C(2)—C(6)	1.508 (3)	1.523 (2)	1.509 (9)
C(3)—C(4)	1.525 (4)	1.540 (3)	1.537 (8)
C(4)—O(1)	1.416 (3)	1.409 (2)	1.426 (7)
C(4)—C(5)	1.525 (5)	1.535 (3)	1.493 (9)
C(6)—O(2)	1.204 (4)	1.204 (2)	1.182 (7)
C(6)—O(3)	1.315 (4)	1.306 (3)	1.323 (7)
C(2)—N(1)—C(5)	104.7 (2)	100.3 (1)	100.3 (4)
C(2)—N(1)—C(7)	116.3 (3)	114.1 (1)	113.2 (5)
C(2)—N(1)—C(8)	—	112.3 (1)	114.1 (4)
C(5)—N(1)—C(7)	113.1 (3)	108.8 (2)	110.2 (5)
C(5)—N(1)—C(8)	—	110.7 (1)	109.7 (5)
C(7)—N(1)—C(8)	—	110.2 (1)	109.1 (5)
N(1)—C(2)—C(3)	102.4 (2)	103.2 (1)	103.7 (5)
N(1)—C(2)—C(6)	111.6 (2)	118.9 (1)	114.1 (5)
C(3)—C(2)—C(6)	113.3 (2)	113.6 (2)	119.0 (5)
C(2)—C(3)—C(4)	104.5 (3)	105.1 (2)	106.2 (5)
C(3)—C(4)—O(1)	112.9 (3)	114.1 (2)	112.2 (6)
C(3)—C(4)—C(5)	105.1 (2)	104.5 (2)	104.1 (5)
O(1)—C(4)—C(5)	107.1 (2)	107.1 (2)	111.7 (5)
C(4)—C(5)—N(1)	106.5 (2)	105.5 (2)	106.1 (5)
C(2)—C(6)—O(2)	123.8 (3)	118.3 (2)	125.4 (6)
C(2)—C(6)—O(3)	110.0 (2)	115.9 (2)	110.1 (5)
O(2)—C(6)—O(3)	126.2 (3)	125.8 (2)	124.5 (6)

$k/[\sigma^2(F) + g|F|^2]$  was introduced for each refinement. Scattering factors for all atoms given in *SHELX76* (Sheldrick, 1976). All calculations on laboratory MicroVAX I computer system. Atomic parameters given in Tables 2–4, selected bond distances and angles in Table 5,\* and the numbering schemes used are shown in Fig. 1.

**Related literature.** The title compounds have been characterized as part of a wider study of the occurrence and physiological roles of proline analogues which accumulate in plants as a result of environmental stress (Naidu, Jones, Paleg & Poljakoff-Mayber, 1987; Jones, Naidu, Paleg, Tiekink & Snow, 1987; Jones, Naidu, Paleg & Tiekink, 1988).

\* Lists of structure factors, thermal parameters, H-atom parameters and mean-plane data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51217 (26 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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## Crystal Studies of Heterocyclic Compounds Containing One Oxygen and Two Nitrogen Atoms. IX. 2,7,8,9,10,15-Hexahydro-*N,N'*-ditosyldibenzo[*c,i*][1,5,8]oxadiazacycloundecene

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**Abstract.** C<sub>30</sub>H<sub>30</sub>N<sub>2</sub>O<sub>5</sub>S<sub>2</sub>, *M<sub>r</sub>* = 562.7, monoclinic, *A*2/a, *a* = 9.607(1), *b* = 13.368(2), *c* = 21.293(3) Å, β = 91.21(1)°, *V* = 2734.0(6) Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* = 1.3669(3) g cm<sup>-3</sup>, λ(Cu *Kα*) = 1.54178 Å, μ = 20.06 cm<sup>-1</sup>, *F*(000) = 1184, room temperature, *R* = 0.050 for 2010 reflections with *I* > 3σ(*I*). The molecule lies in a special position: the twofold axis runs through the O atom. The eleven-membered ring is in a quasi-chair conformation. The fused aromatic rings form a dihedral angle of 13.9(3)° and the benzene rings of the tosyl groups form a dihedral angle of 15.2(4)°. The sum of the angles at N is 351.8(2)°.

**Experimental.** Light yellow prismatic crystals from ethanol, room temperature: crystal size 0.2 × 0.2 ×

0.3 mm. CAD-4 diffractometer using θ–2θ scan technique; unit-cell parameters from 25 reflections in the θ range 8.5–40.7°; graphite-monochromatized Cu *Kα* radiation, range of *h*, *k* and *l* 0 to 11, 0 to 15, –26 to 26 respectively; total of 2412 independent reflections measured to (sinθ)/λ = 0.63 Å<sup>-1</sup>, data not corrected for absorption, *R<sub>int</sub>* = 0.0521; standard reflection 355, maximum change 2.1%; 2010 reflections with *I* > 3σ(*I*) used in calculations; solution by direct methods using *SHELX76* (Sheldrick, 1976), all H atoms located from a difference map, refinement by full-matrix least-squares procedure on *F* magnitudes (237 parameters)

Table 1. Final fractional coordinates (× 10<sup>4</sup>) and equivalent isotropic temperature factors (× 10<sup>4</sup>) with *e.s.d.*'s in parentheses

For non-H atoms  $U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33} - U_{12}\cos\beta)$ .

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U<sub>eq</sub></i> (Å <sup>2</sup> )
O3	2500	9316(2)	0	590(22)
C1	2560(4)	8703(3)	550(2)	539(22)
C11	4164(4)	7191(2)	707(1)	445(18)
C12	3965(4)	8223(2)	636(2)	482(20)
C13	5156(5)	8820(3)	618(2)	606(24)
C14	6467(5)	8435(3)	682(2)	672(27)
C15	6651(5)	7416(3)	769(2)	651(27)
C16	5498(4)	6800(3)	788(2)	538(22)
N1	2988(3)	6521(2)	678(1)	445(15)
C2	3080(4)	5649(2)	248(2)	450(20)
S1	2090(1)	6352(1)	1322(0)	479(04)
O1	930(2)	5733(2)	1136(1)	597(15)
O2	1842(3)	7324(2)	1578(1)	634(17)
C21	3141(4)	5690(2)	1867(1)	467(19)
C22	3000(4)	4664(3)	1925(2)	531(22)
C23	3824(4)	4159(3)	2362(2)	588(24)
C24	4793(4)	4656(3)	2733(2)	564(22)
C25	4904(5)	5692(3)	2668(2)	631(25)
C26	4089(4)	6203(3)	2239(2)	583(24)
C241	5711(6)	4099(5)	3193(2)	759(32)

Table 2. Bond lengths (Å) and angles (°)

O3–C1	1.430(4)	N1–C11	1.443(4)
C1–C12	1.502(5)	N1–C2	1.485(4)
C11–C12	1.400(4)	C21–C22	1.384(5)
C12–C13	1.396(5)	C22–C23	1.384(5)
C13–C14	1.365(6)	C23–C24	1.379(5)
C14–C15	1.385(6)	C24–C25	1.396(5)
C15–C16	1.381(5)	C25–C26	1.372(5)
C11–C16	1.391(5)	C21–C26	1.377(5)
C2–C2 <sup>1</sup>	1.520(7)	C24–C241	1.502(6)
S1–N1	1.649(3)	S1–C21	1.761(3)
S1–O1	1.437(2)	S1–O2	1.432(2)
C1–O3–C1 <sup>1</sup>	110.0(4)	O3–C1–C12	111.4(3)
C1–C12–C11	123.6(3)	C1–C12–C13	119.2(3)
C11–C12–C13	117.1(3)	C12–C13–C14	122.5(4)
C13–C14–C15	119.9(4)	C14–C15–C16	119.3(4)
C11–C16–C15	120.6(4)	C12–C11–C16	120.4(3)
N1–C11–C12	120.2(3)	N1–C11–C16	119.4(3)
C2–N1–C11	117.1(3)	N1–C2–C2 <sup>1</sup>	112.1(3)
C2–N1–S1	116.4(2)	C11–N1–S1	118.2(2)
N1–S1–C21	108.3(1)	C21–S1–O1	108.8(2)
N1–S1–O1	105.5(1)	C21–S1–O2	107.6(2)
N1–S1–O2	106.7(1)	O1–S1–O2	119.6(2)
S1–C21–C22	120.1(3)	S1–C21–C26	119.5(3)
C26–C21–C22	120.5(4)	C21–C22–C23	119.2(4)
C22–C23–C24	121.3(4)	C23–C24–C25	118.2(4)
C24–C25–C26	121.1(4)	C21–C26–C25	119.7(4)
C241–C24–C23	121.0(4)	C241–C24–C25	120.7(4)

Symmetry code: (i)  $\frac{1}{2}-x, y, -z$ .