Refinement

Refinement on F
$R = 0.055$
$wR = 0.073$
$S = 1.710$
1170 reflections
128 parameters
H atoms riding
$w = 4F_o^2/[\sigma(F_o^2)+0.0036F_o^4]$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.23$ e Å^{-3}
$\Delta\rho_{min} = -0.29$ e Å^{-3}
Extinction correction: isotropic (Zachariasen, 1963)
Extinction coefficient: 0.46×10^{-6}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Data collection: CAD-4 (Enraf-Nonius, 1977). Backgrounds were obtained from analysis of the scan profile (Blessing, Coppens & Becker, 1974). Cell refinement: CAD-4. Data reduction: *MolEN PROCESS* (Fair, 1990). Program(s) used to solve structure: direct-methods *MULTAN* (Main *et al.*, 1980). Program(s) used to refine structure: *MolEN LSFM*. Molecular graphics: *ORTEP* (Johnson, 1976). Software used to prepare material for publication: *MolEN CIF*.

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

$U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
N1	−0.0083 (3)	−0.1644 (2)	0.60548 (9)	0.0376 (6)
C2	0.0293 (4)	−0.1646 (3)	0.5528 (1)	0.0514 (9)
C3	0.0104 (4)	−0.3028 (3)	0.5274 (1)	0.0553 (9)
O4	−0.0159 (4)	−0.3072 (2)	0.48279 (8)	0.0855 (9)
N5	0.0232 (4)	−0.4114 (3)	0.5562 (1)	0.0663 (9)
C6	0.0529 (4)	−0.0408 (3)	0.6303 (1)	0.0429 (8)
C7	0.2341 (3)	−0.0419 (2)	0.6429 (1)	0.0337 (6)
O8	0.3040 (3)	0.0688 (2)	0.65097 (8)	0.0454 (5)
N9	0.3109 (3)	−0.1594 (2)	0.6451 (1)	0.0481 (7)
C10	−0.1875 (4)	−0.1778 (3)	0.6141 (1)	0.0485 (8)
C11	−0.2315 (3)	−0.2360 (3)	0.6640 (1)	0.0460 (8)
O12	−0.3698 (3)	−0.2140 (3)	0.6814 (1)	0.0731 (8)
N13	−0.1217 (3)	−0.3136 (3)	0.68684 (9)	0.0517 (7)
C14	−0.1533 (4)	−0.3783 (4)	0.7344 (1)	0.071 (1)

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

N1—C2	1.448 (4)	C7—O8	1.239 (3)
N1—C6	1.466 (3)	C7—N9	1.307 (3)
N1—C10	1.477 (4)	C10—C11	1.499 (5)
C2—C3	1.520 (4)	C11—O12	1.234 (4)
C3—O4	1.219 (4)	C11—N13	1.321 (4)
C3—N5	1.318 (4)	N13—C14	1.450 (4)
C6—C7	1.507 (4)		
C2—N1—C6	112.0 (2)	C6—C7—O8	118.6 (2)
C2—N1—C10	111.1 (2)	C6—C7—N9	118.8 (2)
C6—N1—C10	109.6 (2)	O8—C7—N9	122.6 (3)
N1—C2—C3	114.8 (2)	N1—C10—C11	114.1 (2)
C2—C3—O4	119.5 (3)	C10—C11—O12	119.4 (3)
C2—C3—N5	116.1 (3)	C10—C11—N13	118.2 (3)
O4—C3—N5	124.4 (3)	O12—C11—N13	122.3 (3)
N1—C6—C7	115.3 (2)	C11—N13—C14	122.8 (3)

Table 3. *Hydrogen-bond geometry* (Å, °)

D	A	$D\cdots A$	D—H$\cdots A$
N5	O4^{i}	2.940 (4)	173.0 (2)
N5	O8^{ii}	2.914 (4)	149.4 (2)
N9	O8^{ii}	2.815 (3)	155.3 (2)
N13	O8^{ii}	2.980 (3)	157.0 (2)
N9	O12^{iii}	2.817 (4)	161.9 (2)

Symmetry codes: (i) $-x, -y-1, -z+1$; (ii) $-x+\frac{1}{2}, y-\frac{1}{2}, z$; (iii) $1+x, y, z$.

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Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and least-squares-planes data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71472 (32 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HH1070]

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2,2,6,6-Tetramethylpiperidinium Thiocyanate, $2C_9H_{20}N^+.2SCN^-$

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Abstract

The synthesis and crystal structure of bis(2,2,6,6-tetramethylpiperidinium) dithiocyanate are reported. Geometric parameters for the component species are typical.

There are two formula units in the asymmetric unit which differ in their hydrogen-bonding connectivity.

Comment

We have been interested in the synthesis and properties of hindered *N*-chloro compounds and their derivatives for some time. In the course of this work, *N*-chloro-2,2,6,6-tetramethylpiperidine was prepared and reacted in a straightforward manner with NaSCN in acetonitrile. After several months, during which time some contamination with water occurred, the solvent was stripped off and a white crystalline solid was sublimed from the solid residue under vacuum at 363 K. The volatile solid was recrystallized from hot acetone to yield the needle-like crystals used in this study. Elemental analysis (calculated for $C_{10}H_{20}N_2S$ in parentheses): C 59.92 (60), H 9.97 (10), N 13.78 (14), S 15.38% (16%); m.p. 498 K.

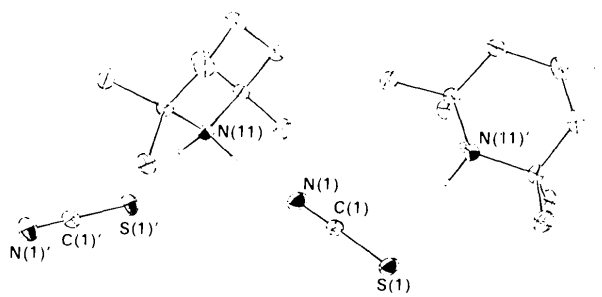

Fig. 1. *ORTEP* (Johnson, 1976) view showing the atomic configuration of the first asymmetric molecular unit in 2,2,6,6-tetramethylpiperidinium thiocyanate with C—H protons omitted for clarity. Thermal ellipsoids are illustrated at the 30% probability level and protons are drawn with arbitrary radii. Hydrogen bonds, which form an infinite chain, are indicated by dotted lines.

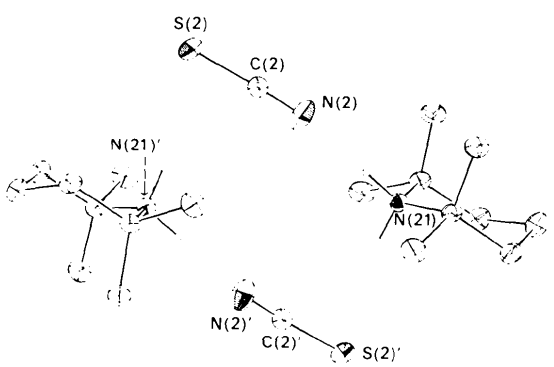

Fig. 2. *ORTEP* (Johnson, 1976) view showing the atomic configuration of the second asymmetric molecular unit in 2,2,6,6-tetramethylpiperidinium thiocyanate with C—H protons omitted for clarity. Thermal ellipsoids are illustrated at the 30% probability level and protons are drawn with arbitrary radii. Hydrogen bonds, which form a closed loop, are indicated by dotted lines.

Each of the two 2,2,6,6-tetramethylpiperidinium cations in the asymmetric unit adopts a typical chair configuration (Figs. 1 and 2) and each molecule makes two hydrogen bonds to neighboring NCS anions, one *via* an N—H···N—C—S bond and the other *via* an N—H···S—C—N bond (Table 3). The hydrogen-bonding scheme for one 2,2,6,6-tetramethylpiperidinium/thiocyanate pair (Fig. 1) leads to an infinite zigzag string of hydrogen bonds which propogate in the **c** direction. The other hydrogen-bonding network (Fig. 2) leads to a self-contained 'ring' configuration.

Experimental

Crystal data

$2C_9H_{20}N^+.2SCN^-$
M_r = 400.69
Tetragonal
$I4_1/a$
a = 21.381 (3) Å
c = 21.487 (3) Å
V = 9822 (3) Å^3
Z = 16
D_x = 1.084 Mg m^{-3}
Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 27 reflections
θ = 6.0–12.0°
μ = 0.22 mm^{-1}
T = 298 K
Block broken from needle
0.70 × 0.30 × 0.30 mm
Colorless

Data collection

Huber automated diffractometer
$\theta/2\theta$ scans
Absorption correction: none
4683 measured reflections
4683 independent reflections
1893 observed reflections [$I > 3\sigma(I)$]
θ_{max} = 25.0°
$h = -16 \rightarrow 17$
$k = 0 \rightarrow 24$
$l = 0 \rightarrow 24$
3 standard reflections monitored every 97 reflections
intensity variation: <±2%

Refinement

Refinement on F
R = 0.054
wR = 0.051
1893 reflections
236 parameters
H atoms riding on respective C/N atoms
w = 1.0
$(\Delta/\sigma)_{max}$ = 0.01
$\Delta\rho_{max}$ = 0.20 e Å^{-3}
$\Delta\rho_{min}$ = −0.22 e Å^{-3}
Extinction correction: Larson (1970)
Extinction coefficient: 373 (20)
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

Data collection: *UCLA* crystallographic software (Strouse, 1982, with local modifications). Cell refinement: *UCLA* crystallographic software. Data reduction: *UCLA* crystallographic software. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1986). Program(s) used to refine structure: *CRYSTALS* (Carruthers, Watkin & Betteridge, 1990). Molecular graphics: *ORTEP*II (Johnson, 1976, with local modifications). Software used to prepare material for publication: local routines.

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

$U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
S(1)	0.35062 (8)	0.64888 (6)	0.05172 (7)	0.0748
C(1)	0.3516 (2)	0.5789 (2)	0.0214 (2)	0.0604
N(1)	0.3530 (2)	0.5297 (2)	−0.0004 (2)	0.0823
S(2)	0.16997 (7)	0.69593 (9)	−0.25357 (8)	0.0901
C(2)	0.0965 (3)	0.6766 (3)	−0.2637 (3)	0.0730
N(2)	0.0470 (3)	0.6661 (3)	−0.2716 (3)	0.1172
N(11)	0.3539 (2)	0.4045 (2)	−0.0486 (2)	0.0525
C(11)	0.4063 (2)	0.3722 (2)	−0.0120 (2)	0.0602
C(12)	0.4625 (2)	0.4147 (3)	−0.0190 (3)	0.0857
C(13)	0.4216 (3)	0.3082 (2)	−0.0397 (3)	0.0863
C(14)	0.3850 (3)	0.3681 (3)	0.0554 (2)	0.0791
C(15)	0.3201 (3)	0.3405 (3)	0.0639 (3)	0.0892
C(16)	0.2719 (3)	0.3789 (3)	0.0282 (2)	0.0774
C(17)	0.2855 (2)	0.3828 (2)	−0.0416 (2)	0.0580
C(18)	0.2470 (2)	0.4339 (2)	−0.0730 (2)	0.0731
C(19)	0.2748 (3)	0.3209 (2)	−0.0756 (3)	0.0765
N(21)	0.0903 (2)	0.6635 (2)	0.0211 (2)	0.0578
C(21)	0.1122 (2)	0.6450 (2)	0.0864 (2)	0.0571
C(22)	0.0579 (3)	0.6607 (3)	0.1293 (2)	0.0815
C(23)	0.1695 (3)	0.6839 (3)	0.1053 (2)	0.0797
C(24)	0.1257 (3)	0.5754 (2)	0.0857 (3)	0.0756
C(25)	0.1690 (3)	0.5561 (3)	0.0329 (3)	0.0903
C(26)	0.1406 (3)	0.5739 (3)	−0.0303 (3)	0.0882
C(27)	0.1268 (2)	0.6431 (2)	−0.0367 (2)	0.0630
C(28)	0.1853 (3)	0.6829 (3)	−0.0452 (3)	0.0869
C(29)	0.0824 (3)	0.6558 (3)	−0.0908 (2)	0.0906

Table 2. *Geometric parameters* (Å, °)

S(1)—C(1)	1.632 (6)	C(17)—C(18)	1.525 (6)
C(1)—N(1)	1.153 (6)	C(17)—C(19)	1.528 (6)
S(2)—C(2)	1.638 (6)	N(21)—C(21)	1.532 (5)
C(2)—N(2)	1.096 (6)	N(21)—C(27)	1.530 (6)
N(11)—C(11)	1.533 (6)	C(21)—C(22)	1.520 (6)
N(11)—C(17)	1.541 (6)	C(21)—C(23)	1.535 (6)
C(11)—C(12)	1.514 (7)	C(21)—C(24)	1.515 (7)
C(11)—C(13)	1.527 (6)	C(24)—C(25)	1.522 (7)
C(11)—C(14)	1.521 (7)	C(25)—C(26)	1.534 (7)
C(14)—C(15)	1.518 (7)	C(26)—C(27)	1.513 (7)
C(15)—C(16)	1.525 (7)	C(27)—C(28)	1.523 (7)
C(16)—C(17)	1.531 (6)	C(27)—C(29)	1.527 (7)
N(1)—C(1)—S(1)	179.2 (5)	C(19)—C(17)—C(18)	109.1 (4)
N(2)—C(2)—S(2)	177.0 (7)	C(27)—N(21)—C(21)	120.9 (4)
C(17)—N(11)—C(11)	120.5 (4)	C(22)—C(21)—N(21)	105.4 (4)
C(12)—C(11)—N(11)	105.0 (4)	C(23)—C(21)—N(21)	110.3 (4)
C(13)—C(11)—N(11)	111.1 (4)	C(23)—C(21)—C(22)	109.2 (4)
C(13)—C(11)—C(12)	109.2 (5)	C(24)—C(21)—N(21)	107.5 (4)
C(14)—C(11)—N(11)	107.2 (4)	C(24)—C(21)—C(22)	111.6 (4)
C(14)—C(11)—C(12)	111.6 (4)	C(24)—C(21)—C(23)	112.5 (4)
C(14)—C(11)—C(13)	112.5 (5)	C(25)—C(24)—C(21)	112.9 (5)
C(15)—C(14)—C(11)	114.3 (5)	C(26)—C(25)—C(24)	110.6 (5)
C(16)—C(15)—C(14)	110.3 (5)	C(27)—C(26)—C(25)	113.6 (5)
C(17)—C(16)—C(15)	113.2 (5)	C(26)—C(27)—N(21)	107.7 (4)
C(16)—C(17)—N(11)	107.0 (4)	C(28)—C(27)—N(21)	110.9 (4)
C(18)—C(17)—N(11)	104.7 (4)	C(28)—C(27)—C(26)	113.4 (5)
C(18)—C(17)—C(16)	111.7 (4)	C(29)—C(27)—N(21)	104.5 (4)
C(19)—C(17)—N(11)	110.9 (4)	C(29)—C(27)—C(26)	111.4 (5)
C(19)—C(17)—C(16)	113.2 (4)	C(29)—C(27)—C(28)	108.6 (4)

Table 3. *Contact distances* (Å)

N(1)···H(111)	1.929	N(2)···H(211^{ii})	1.909
S(1)···H(112^{i})	2.413	S(2)···H(212^{iii})	2.647

Symmetry codes: (i) $\frac{3}{4}-y, x+\frac{1}{4}, z+\frac{1}{4}$; (ii) $y-\frac{3}{4}, \frac{3}{4}-x, -\frac{1}{4}-z$; (iii) $\frac{1}{4}-y, x+\frac{3}{4}, -\frac{1}{4}-z$.

We thank the National Science Foundation and Office of Naval Research for partial financial support.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71473 (19 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HH1074]

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Structure of 8-(4-Acetylphenyl)-1,4-dioxa-8-azaspiro[4.5]decane: a New Potential Nonlinear Optical Material

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Abstract

The crystals of the title compound (APDA), $C_{15}H_{19}NO_3$, which belong to a non-centrosymmetric space group $Pna2_1$, show significant second harmonic generation efficiency and no absorption for light with a wavelength longer than 400 nm.