Table 1. Fractional 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}
S	0.2170(1)	0.2592(1)	0.47641(5)	2.64(2)
O1	0.3103(4)	0.2810(4)	0.7043(2)	4.35(7)
O2	0.3783(3)	0.3343(3)	0.4467(2)	3.02(5)
N	0.3482(4)	−0.1015(4)	0.5317(2)	2.49(6)
C1	0.1798(5)	0.0591(5)	0.4278(2)	2.55(7)
C2	0.0876(5)	0.0632(6)	0.3526(2)	3.31(8)
C3	0.0810(6)	−0.0814(6)	0.3067(2)	3.92(9)
C4	0.1639(5)	−0.2306(6)	0.3341(2)	3.85(9)
C5	0.2525(5)	−0.2376(5)	0.4083(2)	3.08(8)
C6	0.2601(5)	−0.0917(5)	0.4557(2)	2.43(7)
C7	0.3461(4)	0.0211(5)	0.5871(2)	2.37(7)
C8	0.2740(5)	0.1827(5)	0.5731(2)	2.47(7)
C9	0.4304(5)	−0.0371(5)	0.6662(2)	3.09(8)
C10	0.2677(5)	0.3131(5)	0.6352(2)	2.88(8)
C11	0.2082(7)	0.4916(6)	0.6126(3)	4.6(1)

Table 2. Selected geometric parameters ($Å$, °)

S—O2	1.517(3)	C2—C3	1.365(6)
S—C1	1.768(4)	C3—C4	1.380(6)
S—C8	1.765(3)	C4—C5	1.375(5)
O1—C10	1.216(4)	C5—C6	1.388(5)
N—C6	1.402(4)	C7—C8	1.382(5)
N—C7	1.342(4)	C7—C9	1.504(4)
C1—C2	1.400(5)	C8—C10	1.469(5)
C1—C6	1.385(5)	C10—C11	1.496(5)
O2—S—C1	106.1(2)	N—C6—C5	118.8(3)
O2—S—C8	108.0(2)	C1—C6—C5	119.9(3)
C1—S—C8	99.0(2)	N—C7—C8	123.7(3)
C6—N—C7	124.9(3)	N—C7—C9	112.5(3)
S—C1—C2	116.9(3)	C8—C7—C9	123.8(3)
S—C1—C6	122.3(3)	S—C8—C7	121.5(3)
C2—C1—C6	120.0(3)	S—C8—C10	114.8(3)
C1—C2—C3	119.4(4)	C7—C8—C10	122.9(3)
C2—C3—C4	120.4(4)	O1—C10—C8	122.1(4)
C3—C4—C5	120.9(4)	O1—C10—C11	118.9(4)
C4—C5—C6	119.3(4)	C8—C10—C11	118.9(3)
N—C6—C1	121.3(3)		

The structure was solved by the Patterson synthesis method and all H atoms were generated geometrically with C—H 0.95 Å; they were allowed to ride with B equal to 1.3 times that of the parent atom. All computer programs used for structure solution and refinement were from the *MolEN* package (Fair, 1990).

References

Brown, C. & Davidson, R. M. (1985). *Adv. Heterocycl. Chem.* **38**, 135–176.

Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis.* Enraf–Nonius, Delft, The Netherlands.

Ferguson, G. & Ruhl, B. (1982). *Cryst. Struct. Commun.* **11**, 1033–1038.

Walker, N. & Stuart, D. (1983). *Acta Cryst.* A39, 158–166.

Low-Temperature Phase of Tetrapropylammonium Iodide

TETSUO YOSHIDA, KIYOFUMI NAGATA, MUNEHISA YASUNIWA AND MITSURU YOSHIMATSU

Department of Applied Physics, Faculty of Science, Fukuoka University, 8-19-1 Nanakuma, Jonan-ku, Fukuoka 814-80, Japan

BERNHARD WUNDERLICH

Department of Chemistry, University of Tennessee, Knoxville, TN37996-1600, USA

Abstract

The I^- ion of the title compound, $C_{12}H_{28}N^+.I^-$, is surrounded by four $[(C_3H_7)_4N]^+$ cationic units and *vice versa*. The distance from the I^- ion to the nearest N atom is 4.65 Å.

Comment

Tetraalkylammonium halides (R_4NX: R = alkyl group; X = halogen) are ionic crystals composed of R_4N^+ and X^- ions. In the R_4N^+ ion, four alkyl chains with the same number of C atoms are joined to the N atom.

Tetraalkylammonium halides can be classified into three groups, each showing a different type of disordering behaviour (Xenopoulos, Cheng, Yasuniwa & Wunderlich, 1992). That is, methyl, ethyl and propyl salts only have orientational disordering transitions, giving plastic crystals with dynamic orientational disorder and long-range positional order. Butyl to heptyl salts may show a combination of orientational and conformational disorder, giving the possibility of both plastic crystals and 'condis' (conformationally disordered) crystals (Wunderlich, Möller, Grebowicz & Baur, 1988), which have dynamic conformational disorder and long-range positional and orientational order. Salts with longer alkyl chains display conformational disordering only.

Structural data give basic information on the phase-transition process. As reliable structure deter-

minations have not been carried out for R_4NX compounds with long alkyl chains, it was decided to perform such analyses.

As an initial step, the structure of tetrapropylammonium iodide was investigated since growth of single crystals for X-ray analysis was comparatively easy. According to the thermal analysis of tetrapropylammonium iodide (Xenopoulos, Cheng, Yasuniwa & Wunderlich, 1992), transitions are observed at 225.4 and 418.9 K. In the present paper, the three solid phases are named the low-, normal- and high-temperature phases, respectively.

The structure analyses were performed on the normal- and low-temperature phases. The result of the analysis of the normal-temperature phase will be reported in a future paper. The X-ray experiment on the high-temperature phase could not be carried out since it was difficult to heat a single-crystal sample of the normal-temperature phase to a temperature above 418.9 K without it cracking. The molecular configuration of the low-temperature phase with atom-numbering is shown in Fig. 1.
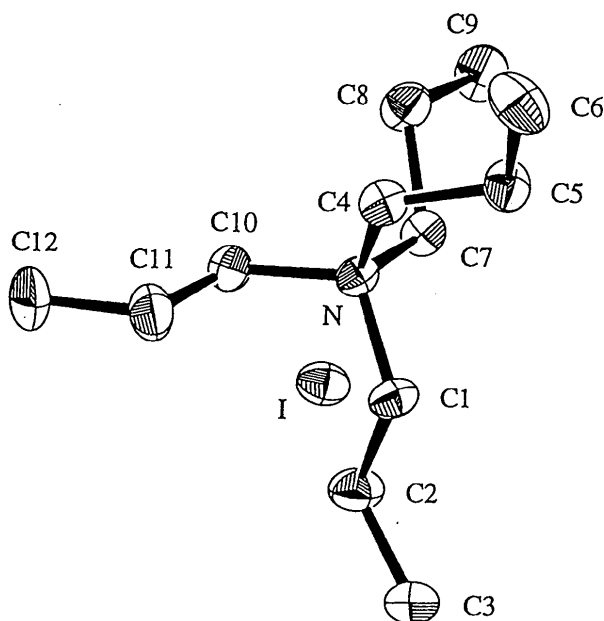

Fig. 1. Molecular structure of $(C_3H_7)_4N^+.I^-$ with atom numbering. Displacement ellipsoids are drawn at the 50% probability level. H atoms are omitted for clarity.

Experimental

The title compound was synthesized by a layering method (Matsuura, 1985; Salemme, 1972) from *n*-propyl iodide and tri-*n*-propylamine at room temperature.

Crystal data

$C_{12}H_{28}N^+.I^-$
$M_r = 313.3$
Orthorhombic
$P2_12_12_1$
$a = 14.037 (3)$ Å
$b = 11.716 (1)$ Å
$c = 9.302 (1)$ Å
$V = 1529.8 (5)$ Å^3
$Z = 4$
$D_x = 1.36$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 24 reflections
$\theta = 13–17°$
$\mu = 2.04$ mm^{-1}
$T = 173$ K
Needle
$0.3 \times 0.3 \times 0.3$ mm
Colorless

Data collection

Rigaku four-circle diffractometer
$2\theta–\omega$ scans
Absorption correction: none
4932 measured reflections
2559 independent reflections
2324 observed reflections
$[F_o > 3\sigma(F_o)]$

$R_{int} = 0.0166$
$\theta_{max} = 30.02°$
$h = -20 \rightarrow 20$
$k = 0 \rightarrow 16$
$l = 0 \rightarrow 13$
3 standard reflections monitored every 100 reflections
intensity variation: ±2.2%

Refinement

Refinement on F
$R = 0.0292$
$wR = 0.0315$
$S = 0.8657$
2324 reflections
239 parameters
H atoms refined isotropically
$w = a/[\sigma^2(F) + bF^2]$
where final $a = 0.9208$
and final $b = 0.001$

$(\Delta/\sigma)_{max} = 0.006$
$\Delta\rho_{max} = 0.913$ e Å^{-3}
$\Delta\rho_{min} = -0.989$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
I	0.06964 (1)	0.40763 (2)	-0.50775 (2)	0.0319 (1)
N	0.0559 (1)	0.5409 (2)	-0.0010 (3)	0.024 (1)
C1	0.0721 (2)	0.4178 (2)	0.0463 (3)	0.029 (1)
C2	0.0444 (3)	0.3258 (3)	-0.0610 (4)	0.037 (2)
C3	0.0766 (3)	0.2096 (3)	-0.0046 (5)	0.042 (2)
C4	0.0701 (3)	0.6185 (3)	0.1288 (3)	0.029 (1)
C5	0.1706 (2)	0.6249 (3)	0.1850 (4)	0.034 (2)
C6	0.1747 (4)	0.7119 (6)	0.3047 (5)	0.048 (3)
C7	0.1266 (2)	0.5697 (3)	-0.1207 (3)	0.026 (1)
C8	0.1263 (3)	0.6937 (3)	-0.1667 (4)	0.035 (2)
C9	0.2041 (3)	0.7118 (5)	-0.2794 (4)	0.041 (2)
C10	-0.0443 (2)	0.5588 (3)	-0.0582 (4)	0.031 (2)
C11	-0.1248 (3)	0.5293 (4)	0.0434 (5)	0.045 (2)
C12	-0.2191 (3)	0.5518 (4)	-0.0336 (7)	0.057 (3)

Table 2. *Selected geometric parameters* (Å, °)

N—C1	1.525 (3)	C4—C5	1.506 (5)
N—C4	1.525 (4)	C5—C6	1.511 (7)
N—C7	1.529 (4)	C7—C8	1.514 (5)
N—C10	1.518 (3)	C8—C9	1.529 (6)
C1—C2	1.520 (4)	C10—C11	1.513 (5)
C2—C3	1.527 (5)	C11—C12	1.528 (6)
C1—N—C4	108.4 (2)	N—C4—C5	115.3 (3)
C1—N—C7	108.8 (2)	N—C7—C8	114.6 (3)
C1—N—C10	111.7 (2)	N—C10—C11	116.2 (3)
C4—N—C7	111.1 (2)	C1—C2—C3	109.3 (3)
C4—N—C10	108.4 (2)	C4—C5—C6	109.0 (3)
C7—N—C10	108.4 (2)	C7—C8—C9	109.0 (3)
N—C1—C2	116.3 (3)	C10—C11—C12	108.4 (4)

The I atom was located from a Patterson map and the N and C atoms were found in a subsequent Fourier synthesis. All non-H atoms were refined anisotropically by full-matrix least-squares methods. H atoms were located from the difference Fourier map and were refined isotropically.

Computer programs for structure analysis: *SHELX*76 (Sheldrick, 1976) and *SHELXS*86 (Sheldrick, 1985). Molecular graphics: *ORTEP*II (Johnson, 1976).

References

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Matsuura, Y. (1985). *J. Jpn. Assoc. Cryst. Growth*, **12**, 108–116.
Salemme, F. R. (1972). *Arch. Biochem. Biophys.* **151**, 533–539.
Sheldrick, G. M. (1976). *SHELX*76. *Program for Crystal Structure Determination*. Univ. of Cambridge, England.
Sheldrick, G. M. (1985). *SHELXS*86. *Program for the Solution of Crystal Structures*. Univ. of Göttingen, Germany.
Wunderlich, B., Möller, M., Grebowicz, J. & Baur, H. (1988). *Advances in Polymer Science* 87. Berlin: Spring-Verlag.
Xenopoulos, A., Cheng, J., Yasuniwa, M. & Wunderlich, B. (1992). *Mol. Cryst. Liq. Cryst.* **214**, 63–79.

N^2-(4,6-Diméthylpyrid-2-yl)-N^1-méthyl-pyrazine-2-carboxamidine

N. Rodier

Laboratoire de Chimie minérale, Faculté des Sciences pharmaceutiques et biologiques, 5 Rue J.-B. Clément, 92296 Châtenay-Malabry CEDEX, France

O. Rideau, J.-M. Robert et G. Le Baut

Laboratoire de Chimie thérapeutique, Faculté de Pharmacie, 1 Rue Gaston-Veil, 44035 Nantes CEDEX, France
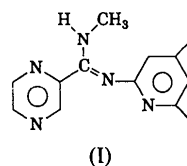
Abstract

The title molecule, $C_{13}H_{15}N_5$, shows a *cis* configuration. It comprises three approximately planar moieties: an N^2-(4,6-dimethylpyridine), an N^1-methyl-carboxamidine group and a pyrazinyl ring. To avoid steric hindrance, the two rings are twisted

out of the plane of the imine double bond. There is a delocalized orbital over the amidine group. The structure comprises two chains of molecules which spread out along the two 2_1 axes situated in the ($\bar{1}01$) plane. In each chain, the molecules are linked to one another by an N—H···N hydrogen bond [2.976 (2) Å, 160 (2)°].

Commentaires

Les dérivés de la 2-amino-4,6-diméthylpyridine sont des antiinflammatoires potentiels (Bouhayat, Piessard, Le Baut, Sparfel, Petit, Piriou, Welin, 1985; Robert-Piessard, Le Baut, Courant, Brion, Sparfel, Bouhayat, Petit, Sanchez, Juge, Grimaud & Welin, 1990). Le N^2-(4,6-diméthylpyrid-2-yl)-N^1-méthyl-pyrazine-2-carboxamidine, (I), est le chef de file d'une nouvelle série de dérivés. Son étude cristallographique a été entreprise dans le cadre des relations entre la structure et l'activité pharmacologique.

(I)

Les cycles pyridinyle et pyrazinyle sont appelés respectivement cycle *A* et cycle *B* et leurs plans moyens $P(A)$ et $P(B)$. Les cycles sont approximativement plans. Les valeurs absolues des angles de torsion endocycliques vont de 0,1 (3) à 2,6 (3)° dans le premier et de 0,3 (4) à 2,1 (4)° dans le second. Les distances de N(7), C(15) et C(16) à $P(A)$ ne dépassent pas 0.108 (2) Å tandis que celle de C(8) à $P(B)$ est de 0,016 (2) Å. C(2), N(7), C(8), C(9) et N(17) définissent le plan moyen $P(C)$ dont ils sont éloignés au plus de 0,077 (2) Å. La distance de C(18) à $P(C)$ est de 0,064 (3) Å. Les angles dièdres $P(A)P(B)$, $P(A)P(C)$ et $P(B)P(C)$ valent respectivement 62,85 (8), 63,68 (8) et 36,05 (6)°. Les angles de torsion N(1)—C(2)—N(7)—C(8) [58,7 (3)°], N(7)—C(8)—C(9)—N(10) [32,3 (3)°] et N(7)—C(8)—N(17)—C(18) [2,8 (3)°] indiquent les positions relatives des différentes parties de la molécule.

Dans les deux cycles, les distances N—C entre atomes contigus appartiennent à l'intervalle 1,335 (3)–1,347 (3) Å et sont pratiquement égales à leurs homologues dans la pyridine (Bak, Hansen-Nygaard & Rastrup-Andersen, 1958). N(7)—C(8) [1,286 (2) Å] est une double liaison. La longueur de C(8)—N(17) [1,346 (3) Å] exprime la conjugaison des électrons π de N(7)—C(8) avec le doublet de N(17) tandis que celle de C(2)—N(7) [1,392 (3) Å] indique une conjugaison très partielle entre les électrons π du cycle *A* et le doublet de N(7).