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Crystal structure of 1-nonylpyridazin-1-ium iodide, $C_{13}H_{23}N_2I$

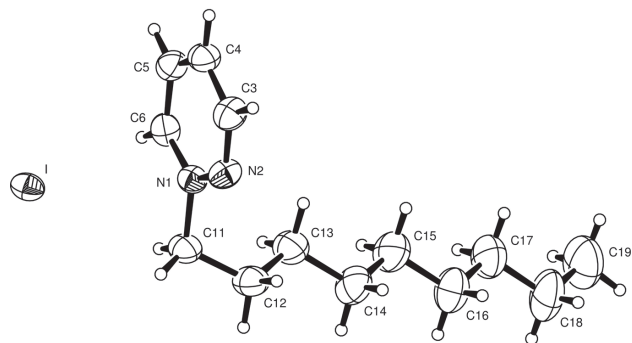


Table 1: Data collection and handling.

Crystal:	Yellow prism
Size:	0.22 × 0.06 × 0.04 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	1.95 mm ⁻¹
Diffractometer, scan mode:	Oxford Diffraction Xcalibur-3 Sapphire-3, ϕ and ω
θ_{\max} , completeness:	25.0°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	10743, 2866, 0.059
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 2345
$N(\text{param})_{\text{refined}}$:	145
Programs:	CrysAlis ^{PRO} [1], SHELX [2, 3], WinGX/ORTEP [4]

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Abstract

$C_{13}H_{23}N_2I$, triclinic, $P\bar{1}$ (no. 2), $a = 5.6693(3)$ Å, $b = 8.9457(4)$ Å, $c = 16.2919(7)$ Å, $\alpha = 83.341(4)^\circ$, $\beta = 89.534(4)^\circ$, $\gamma = 82.491(4)^\circ$, $V = 813.63(7)$ Å³, $Z = 2$, $R_{\text{gt}}(F) = 0.0446$, $wR_{\text{ref}}(F^2) = 0.0873$, $T = 295(2)$ K.

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The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

All chemicals were used without further purification. The title ionic liquid was prepared by a method reported earlier [5, 6]. To a solution of pyridazine (1.00 g, 12.5 mmol in

10 mL of toluene) was added dropwise 1-iodononane (3.18 g, 12.5 mmol) and the mixture was placed in a closed container and exposed to irradiation for 5 h at room temperature using a sonication bath. Completion of the reaction was marked by the precipitation of a solid from the initially clear and homogenous mixture in toluene. The pyridazinium-based ionic liquid was isolated by filtration and washed three times with ethyl acetate to remove any unreacted starting materials and solvent. Finally the 1-nonylpyridazin-1-ium iodide was dried at a reduced pressure to remove all volatile organic compounds. (Yield 75%, yellow powder, m.p. 94–95 °C). Crystals were obtained from a mixture of dichloromethane and *n*-hexane (1:2). Elemental analysis: Anal. Calc. For $C_{13}H_{23}IN_2$: C, 46.72%; H, 6.94%; N, 8.38%; Found: C, 46.80%; H, 6.99%; N, 8.32%. ¹H-NMR (DMSO, 400 MHz): δ [p.p.m.] = 0.85 (t, 3H), 1.29 (m, 12H), 1.99 (quin, 2H), 4.82 (t, 2H), 8.63 (t, 1H), 8.76 (t, 1H), 9.65 (d, 1H), 9.99 (d, 1H); ¹³C-NMR (DMSO, 100 MHz): δ [p.p.m.] = 14.1 (CH₃), 22.6 (CH₂), 26.1 (CH₂), 28.9 (CH₂), 29.1 (CH₂), 29.2 (CH₂), 30.3 (CH₂), 31.7 (CH₂), 66.1 (CH₂), 136.8 (CH), 136.9 (CH), 149.9 (CH), 154.3 (CH).

Experimental details

The non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included in idealised positions and their U_{iso} values were set to ride on the parent carbon atoms. In the final difference map, the highest peaks (to ca 0.6 e Å⁻³) were close to the iodide ion.

Scattering factors for neutral atoms were taken from ‘International Tables’ [7]. Computer programs used in this

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
I	0.11316(6)	0.74147(3)	0.42796(2)	0.06645(16)
N1	0.3798(7)	0.6652(4)	0.6368(2)	0.0559(10)
N2	0.2229(7)	0.7671(4)	0.6679(3)	0.0639(11)
C3	0.2714(10)	0.9060(6)	0.6580(3)	0.0751(15)
H3	0.1651	0.9803	0.6789	0.090*
C4	0.4726(10)	0.9501(6)	0.6180(3)	0.0725(15)
H4	0.5005	1.0509	0.6124	0.087*
C5	0.6252(9)	0.8435(7)	0.5878(3)	0.0702(14)
H5	0.7635	0.8676	0.5613	0.084*
C6	0.5710(9)	0.6964(6)	0.5972(3)	0.0651(13)
H6	0.6706	0.6200	0.5754	0.078*
C11	0.3125(10)	0.5107(5)	0.6461(3)	0.0749(15)
H11A	0.4314	0.4441	0.6199	0.090*
H11B	0.1618	0.5119	0.6180	0.090*
C12	0.2904(11)	0.4490(7)	0.7349(4)	0.0850(17)
H12A	0.2360	0.3502	0.7376	0.102*
H12B	0.1708	0.5156	0.7608	0.102*
C13	0.5189(11)	0.4337(7)	0.7827(4)	0.0915(18)
H13A	0.5616	0.5342	0.7864	0.110*
H13B	0.6436	0.3791	0.7525	0.110*
C14	0.5080(12)	0.3514(8)	0.8698(4)	0.101(2)
H14A	0.3866	0.4074	0.9007	0.121*
H14B	0.4616	0.2516	0.8664	0.121*
C15	0.7394(13)	0.3337(8)	0.9156(4)	0.111(2)
H15A	0.7811	0.4338	0.9214	0.133*
H15B	0.8623	0.2830	0.8829	0.133*
C16	0.7371(13)	0.2453(9)	1.0001(4)	0.115(2)
H16A	0.6902	0.1465	0.9945	0.138*
H16B	0.6183	0.2979	1.0335	0.138*
C17	0.9766(14)	0.2234(9)	1.0449(4)	0.120(2)
H17A	1.0963	0.1747	1.0103	0.144*
H17B	1.0201	0.3224	1.0522	0.144*
C18	0.9802(14)	0.1309(11)	1.1273(4)	0.140(3)
H18A	0.9368	0.0319	1.1200	0.168*
H18B	0.8604	0.1795	1.1619	0.168*
C19	1.2147(15)	0.1097(11)	1.1712(5)	0.159(4)
H19A	1.2032	0.0494	1.2234	0.238*
H19B	1.3340	0.0591	1.1382	0.238*
H19C	1.2575	0.2069	1.1801	0.238*

analysis have been noted above, and were run through *WinGX* [4] on a Dell Optiplex 780 PC at the University of East Anglia.

Comment

In recent decades, ionic liquids (ILs) appeared as an emerging class of ecofriendly compounds alternative to volatile organic compounds (VOCs) due to their outstanding physical and chemical properties such as negligible vapor pressure, excellent thermal and chemical stability, outstanding dissolving capacity, excellent ionic conductivity, non-flammability, and recyclability [8].

These characteristics make ILs strongly attractive for applications in a myriad different fields and these compounds have, therefore, been investigated for a broad range of applications including as potential corrosion inhibitors [9], as liquid crystals [10], in separation technology [11], in electrochemistry [12, 13], in pharmacology [14], and bio-catalysis [15].

The synthesis of the title IL took place through the nucleophilic attack of the *sp*²-nitrogen pyridazine atom, which acts as a nucleophile in the nucleophilic displacement of halogen on the nonyl iodide to afford the corresponding 1-nonylpyridazin-1-ium iodide in 75% yield as solid material.

The structure of this newly synthesized IL was confirmed by ¹H-NMR, ¹³C-NMR, single-crystal X-ray diffraction methods and elemental analysis. The ¹H-NMR spectrum showed a triplet around δ H 0.85 p.p.m. corresponding to three protons of the methyl group (CH₃). The protons of the various methylene groups (CH₂) were observed at their usual chemical shifts. The signals of the pyridazinium protons appeared as two doublets and two triplets, respectively, around δ H 8 and 9 p.p.m.. The ¹³C-NMR spectrum showed CH₂ and CH₃ at their usual chemical shifts, and all the aromatic carbons and C=N gave the signals between δ C 136–154 p.p.m.

There are many similarities between this nonyl derivative and the smaller heptyl compound recently reported [16]. The two structure are essentially isostructural even though a different choice of the unit cell is reported. The nonyl group, too, has an all-*trans* arrangement and is aligned about C(11) with a *cis* N(2)–N(1)–C(11)–C(12) torsion angle of –61.4(6)°; the N(2)–N(1)–C(11)–H(11a) angle is *trans* at 177.5°. The iodide ion lies over the pyridazinium ring, 3.688 Å from N(1). There are five short H...I contacts in the range 3.03–3.14 Å, to neighboring cations, forming weak C–H...I hydrogen bonds. All the short inter-ion distances involve the iodide ion. As observed for the heptyl structure, the long alkyl chains are arranged in parallel/antiparallel stacks.

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