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The low-temperature phase of diisopropylammonium bromide

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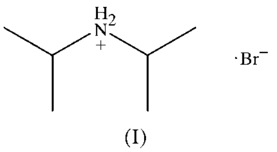
The title compound, $C_6H_{16}N^+\cdot Br^-$, was refined against room-temperature data in space group $P2_1$ as a racemic twin by Kociok-Köhn, Lungwitz & Filippou [*Acta Cryst.* (1996). C**52**, 2309–2311]. At low temperature, we found a different phase, which is characterized by a different cell (twice as big as the cell at room temperature) and a different space group ($P2_1/n$). Surprisingly, the cell parameters obtained at low temperature can be transformed into those measured at ambient temperature. Even the coordinates can be transformed and the structure can be refined in the small cell. However, some warning signs (*e.g.* a low $|E^2 - 1|$ value, apparent twinning and peaks in the electron-density map) point to the correct cell and space group.

Comment

Phase transition is a phenomenon which does not occur very often when data are collected at low temperature, but which is noticed from time to time. Since data collection is nowadays performed almost routinely at low temperature, a new phase of an already known crystal structure might be encountered. The title compound, diisopropylammonium bromide, (I), has already been described by Kociok-Köhn *et al.* (1996) in space group $P2_1$ as a racemic twin, based on data collected at room temperature. At low temperature (173 K), however, we found a different phase, which is characterized by a different cell (twice as big as the cell at room temperature) and a different space group ($P2_1/n$).



(I)

We noticed from the first frames that the cell determination was not straightforward, because there were many weak, but nevertheless observable, reflections. Including these weak reflections in the cell determination yielded a monoclinic cell with the cell parameters given in the *Crystal data* (see *Experimental*). The weak reflections belonged to the class $h+l = 2n+1$ (for all *hkl*). Whereas the mean intensity and the mean intensity-to-sigma ratio for all reflections were 130.8 and 22.7, respectively, these values were 19.4 and 4.8 for the $h+l = 2n+1$ reflections. Thus, a *B*-centred lattice is mimicked. Since these reflections are rather weak, they can be easily overlooked on a diffractometer equipped with a point counter, the result of which would be a halved cell.

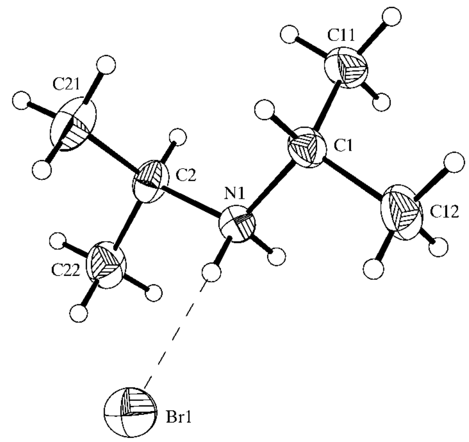


Figure 1
A perspective view of the title compound with the atom-numbering scheme. Displacement ellipsoids are shown at the 50% probability level.

The reason for the weakness of these reflections is that the structure contains one fairly heavy atom, *i.e.* Br, on a pseudo-special position. The coordinates of the four Br atoms in the cell (Table 3) show that Br1 and Br1^{i}, as well as Br1^{ii} and Br1^{iii}, are related by an approximate translation of $(x + \frac{1}{2}, y, z + \frac{1}{2})$. However, the *y* coordinates are not exactly equal, but are related by a mirror plane. Nevertheless, the differences between the *y* coordinates of related atoms are rather small, *viz.* 0.0213, which corresponds to 0.1697 Å.

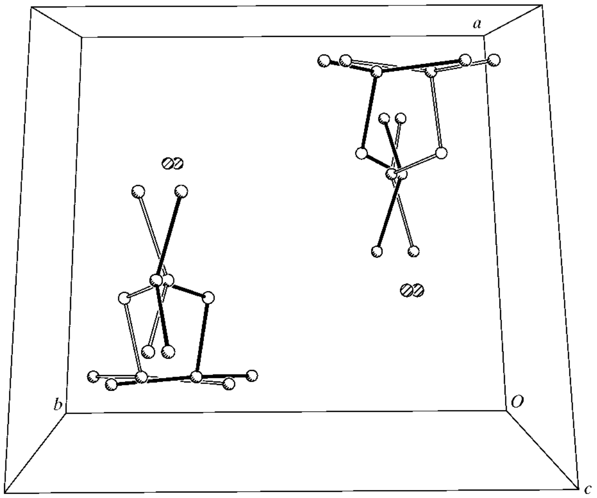


Figure 2
View of the unit cell when the correct cell is halved by applying the matrix $(-\frac{1}{2}\ 0\ -\frac{1}{2}/0\ -1\ 0/-\frac{1}{2}\ 0\ \frac{1}{2})$ to the cell parameters and the matrix (–1 0 –1/0 –1 0/ –1 0 1) to the coordinates.

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If the weak reflections are overlooked, the resulting cell parameters would be $a = 7.822$, $b = 7.973$, $c = 7.916$ Å, $\alpha = 90$, $\beta = 116.59$, $\gamma = 90°$ and $V = 441.46$ Å^3. The same cell parameters can be obtained by applying the matrix ($-\frac{1}{2}\ 0\ -\frac{1}{2}/0\ -1\ 0/-\frac{1}{2}\ 0\ \frac{1}{2}$) to the correct cell parameters. The resulting space group is $P2_1$. However, the structure appears as the average of two mirror-related images. It might be surprising that the structure could be solved at all and refined in a halved cell. The reason for this is that the two images nearly overlap when the cell is halved (Fig. 2). Whereas the atoms overlap exactly in x and z, the differences between the y coordinates are very small (Table 4). The Br atoms fall so close to each other that they cannot be resolved as a result of the resolution of the data. On the other hand, an electron-density difference map reveals that the highest peaks show up exactly where the atoms of the second molecule would be (Fig. 3). The heights of the peaks, however, are rather small. Thus, they can be easily overlooked. Refinement against the data collected at room temperature by Kociok-Köhn *et al.* (1996) does not show this pattern in the electron-density difference map.

Refinement in the small cell (including the *TWIN* −1 0 0 0 −1 0 0 0 −1 and *BASF* instructions), using unit weights, yields the results listed in Table 5. The explanation for the slightly better R values could be that the omitted reflections were all very weak and, as a result, less accurately determined. Nevertheless, the s.u.'s of the coordinates are significantly better in the correct space group. Furthermore, refinement in $P2_1$ resulted in many correlations between the refined parameters. These correlations vanished when the correct space group was used. Further warning signs are the low $|E^2 - 1|$ value and the mimicked twinned crystal structure. The geometric parameters of the structure in the false cell look normal, but the two N—C bonds are significantly different, although they should be more or less equal (Table 6).

After having realised that the title compound had been found in a different phase at room temperature, we checked our crystals at room temperature and ended up with the same results as Kociok-Köhn *et al.* (1996). Upon cooling, the crystals underwent a phase transition with doubling of the cell. When we determined the cell again after warming the (previously cooled) crystal to room temperature, we still found the cell of the low-temperature phase. Thus, the phase transition is irreversible.

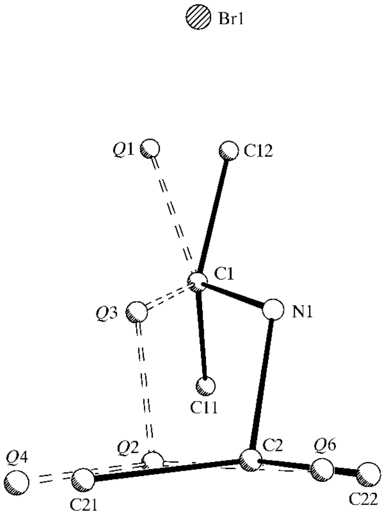

Figure 3
The difference electron-density map obtained when the structure is refined in the small cell. The peaks heights are (e Å^{-3}): $Q1 = 0.76$, $Q2 = 0.60$, $Q3 = 0.57$, $Q4 = 0.55$ and $Q6 = 0.49$.

The importance of weak reflections during structure refinement has already been stressed by Watkin (1994). The present case is an instructive example of the importance of weak reflections for cell determination. Furthermore, we presume that errors of this type can be more easily avoided when the data are collected on an area detector.

Experimental

The title compound was obtained by stirring a solution of 5-bromopent-1-ene (5 mmol) in MeOH (10 ml) in the presence of i-Pr$_2$NH (5 mmol) at ambient temperature. Colourless crystals of [i-Pr$_2$NH$_2$]-Br were grown by storing this solution at room temperature for 2 d.

Crystal data

$C_6H_{16}N^+ \cdot Br^-$
$M_r = 182.11$
Monoclinic, $P2_1/n$
$a = 8.2712\ (13)$ Å
$b = 7.9726\ (12)$ Å
$c = 13.390\ (2)$ Å
$\beta = 90.762\ (12)°$
$V = 882.9\ (2)$ Å^3
$Z = 4$

$D_x = 1.370$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 9603 reflections
$\theta = 3.6$–25.°
$\mu = 4.58$ mm^{-1}
$T = 173\ (2)$ K
Needle, colourless
$0.46 \times 0.14 \times 0.12$ mm

Table 1
Selected geometric parameters (Å, °).

N1—C2	1.517 (5)	C1—C12	1.529 (6)
N1—C1	1.519 (5)	C2—C22	1.514 (7)
C1—C11	1.523 (6)	C2—C21	1.516 (7)
C2—N1—C1	118.0 (3)	C22—C2—C21	112.3 (4)
N1—C1—C11	110.6 (3)	C22—C2—N1	107.2 (4)
N1—C1—C12	107.7 (3)	C21—C2—N1	110.2 (4)
C11—C1—C12	112.3 (4)		

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1B···Br1	0.92	2.38	3.301 (3)	178
N1—H1A···Br1^{i}	0.92	2.40	3.314 (4)	176

Symmetry code: (i) $\frac{3}{2} - x, y - \frac{1}{2}, \frac{3}{2} - z$.

Table 3
The coordinates (Å) of the four Br atoms in the unit cell.

	x	y	z
Br1	0.75616	0.76064	0.88941
Br1^{i}	0.25616	0.73936	0.38941
Br1^{ii}	0.24384	0.23936	0.11059
Br1^{iii}	0.74384	0.26064	0.61059

Symmetry codes: (i) $-\frac{1}{2} + x, \frac{3}{2} - y, -\frac{1}{2} + z$; (ii) $1 - x, 1 - y, 1 - z$; (iii) $\frac{3}{2} - x, -\frac{1}{2} + y, \frac{3}{2} - z$.

o556 Monika Haberecht et al. • $C_6H_{16}N^+ \cdot Br^-$ Acta Cryst. (2002). C58, o555–o557

Data collection

Stoe IPDS-II two-circle diffractometer
ω scans
Absorption correction: empirical (*MULABS*; Spek, 1990; Blessing, 1995)
$T_{\min} = 0.227$, $T_{\max} = 0.610$
5310 measured reflections
1538 independent reflections
1299 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.044$
$\theta_{\max} = 25.0°$
$h = -9 \rightarrow 9$
$k = -9 \rightarrow 9$
$l = -15 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.114$
$S = 1.12$
1538 reflections
73 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0563P)^2 + 1.4082P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.57$ e Å^{-3}
$\Delta\rho_{\min} = -0.56$ e Å^{-3}

Table 4
The differences between the coordinates when the correct cell is halved by applying the matrix ($-\frac{1}{2}$ 0 $-\frac{1}{2}$/0 −1 0/$-\frac{1}{2}$ 0 $\frac{1}{2}$) to the cell parameters and the matrix (−1 0 −1/0 −1 0/−1 0 1) to the coordinates.

	y (atom 1)	y (atom 2)	$\lvert\Delta y\rvert$	Distance between the atoms in Å
Br1—Br1	0.76063	0.73937	0.02126	0.170
N1—N1	0.66364	0.83636	0.17272	1.377
C1—C1	0.76131	0.73869	0.02262	0.180
C11—C11	0.73088	0.76912	0.03824	0.305
C12—C12	0.70813	0.79187	0.08374	0.668
C2—C2	0.69229	0.80771	0.11542	0.920
C21—C22	0.87524	0.92331	0.04807	0.903
C22—C21	0.57669	0.62476	0.04807	0.903

Table 5
A comparison of the refinement results in the correct and the halved cell.

	Correct cell	False cell
Unique reflections	1538	1529
$R_{\rm int}$	0.0439	0.0349
R_σ	0.0337	0.0307
$\lvert E^2 - 1\rvert$	1.016	0.663
Mean $\sigma(x)$	0.00048 (19)	0.0008 (3)
Mean $\sigma(y)$	0.0006 (2)	0.0011 (7)
Mean $\sigma(z)$	0.00032 (13)	0.0008 (4)
$wR2$	0.1389	0.1326
Goodness-of-fit	1.059	1.161
$R1$	0.0536	0.0449
$\Delta\rho_{\min}$	0.58	0.81
$\Delta\rho_{\max}$	−0.59	−0.51

Table 6
A comparison of the bond lengths (Å) in (I) with those in the falsely halved cell, (II), and those published by Kociok-Köhn *et al.* (1996), (III).

	(I)	(II)	(III)
N1—C1	1.517 (5)	1.475 (8)	1.510 (5)
N1—C2	1.519 (5)	1.537 (8)	1.516 (7)
C1—C11	1.523 (6)	1.496 (7)	1.508 (7)
C1—C12	1.529 (6)	1.499 (9)	1.518 (6)
C2—C21	1.516 (7)	1.520 (14)	1.516 (5)
C2—C22	1.514 (7)	1.512 (11)	1.508 (5)

All H atoms were located by difference Fourier synthesis. They were refined as riding, with fixed individual displacement parameters [$U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(C) or 1.2$U_{\rm eq}$(N)], and with N—H distances of 0.92 Å, methyl C—H distances of 0.98 Å and tertiary C—H distances of 1.0 Å.

Data collection: *X-AREA* (Stoe & Cie, 2001); cell refinement: *X-AREA*; data reduction: *X-AREA*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL-Plus* (Sheldrick, 1991).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1562). Services for accessing these data are described at the back of the journal.

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