

Structure of N,N,N',N' -Tetramethyldiazonia-18-crown-6 with PF_6^- and I^- as the Counterions

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Abstract. 1,1,4,4-Tetramethyl-1,4-diazonia-7,10,13,16-tetraoxacyclooctadecane bis(hexafluorophosphate), $\text{C}_{16}\text{H}_{36}\text{N}_2\text{O}_4^{2+} \cdot 2\text{PF}_6^-$, $M_r = 610.4$, monoclinic, $P2_1/c$, $a = 6.700$ (1), $b = 20.911$ (9), $c = 9.609$ (2) Å, $\beta = 104.24$ (2)°, $V = 1305$ (1) Å³, $Z = 2$, $D_x = 1.553$ g cm⁻³, $\lambda(\text{Cu } K\alpha) = 1.54178$ Å, $\mu = 25.843$ cm⁻¹, $F(000) = 632$, $T = 298$ K, final $R = 0.053$ for 2027 reflections. 1,1,4,4-Tetramethyl-1,4-diazonia-7,10,13,16-tetraoxacyclooctadecane diiodide, $\text{C}_{16}\text{H}_{36}\text{N}_2\text{O}_4^{2+} \cdot 2\text{I}^-$, $M_r = 574.34$, monoclinic, $P2_1/n$, $a = 6.482$ (1), $b = 16.932$ (2), $c = 10.871$ (1) Å, $\beta = 106.63$ (2)°, $V = 1143.3$ (5) Å³, $Z = 2$, $D_x = 1.668$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71078$ Å, $\mu = 27.393$ cm⁻¹, $F(000) = 568$, $T = 298$ K, final $R = 0.026$ for 2034 reflections. In both structures the macrocyclic rings are centrosymmetric but they exist in two different conformations. Some energy calculations were performed to establish the source of the differences. As it was found that the two conformations have similar energies the differences could be due to the different counterions.

Introduction. Synthesis of diazacoronands with very high yields is possible under high-pressure conditions via N,N' -dimethyldiazacorons as the intermediate crystalline product (Jurczak, Ostaszewski & Sałański, 1989). N,N' -Dimethyldiazacorons containing two quaternary N atoms in the ring are a new class of synthetic macrocyclic compound. The geometry of macrocyclic rings containing two positively charged N atoms must be very different from their known neutral analogues, *i.e.* diazacoronands. The aim of the present work was to study the conformation of N,N,N',N' -tetramethyldiazonia-18-crown-6 and its change when relatively small I^- anions are exchanged with much larger PF_6^- anions.

Experimental. The compounds studied were synthesized in the Institute of Organic Chemistry of the Polish Academy of Sciences. Numerical information concerning the collection and reduction of the intensity data and the structure refinement is given in Table 1.

The unit-cell dimensions were refined by a least-squares treatment of 25 reflections. An Enraf-

Nonius CAD-4 four-circle diffractometer was used for the collection of X-ray data. After every hour of data collection, the intensity of standard reflections was checked but no systematic change was observed. Intensity values were corrected for Lorentz and polarization effects. The structure of $\text{C}_{16}\text{H}_{36}\text{N}_2\text{O}_4^{2+} \cdot 2\text{PF}_6^-$ was solved by *MULTAN*11/82 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982) and the structure of $\text{C}_{16}\text{H}_{36}\text{N}_2\text{O}_4^{2+} \cdot 2\text{I}^-$ was solved by Patterson methods. Both structures were refined with the *SDP* system (B.A. Frenz & Associates, Inc., 1985). After convergence of the isotropic refinement an empirical absorption correction (maximum/minimum transmission factors 1.226/0.784) using the *DIFABS* procedure (Walker & Stuart, 1983) was applied. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). All the H atoms were included in the refinement with isotropic B values. All calculations were performed on a Micro-PDP11/73 computer. The final atomic coordinates are given in Tables 2 and 3.* *ORTEPII* plots (Johnson, 1976) of the cations with atom-numbering schemes are given in Fig. 1.

Discussion. Selected bond lengths and bond angles are given in Table 4. In both structures the macrocyclic cation lies on the crystallographic centre of symmetry. The bond distances and angles in the two quaternary macrocyclic cations reported are very similar to each other and follow the observed trends in 18-crown-6 and its derivatives, *i.e.* the shortening of the $\text{C}(sp^3)\text{—C}(sp^3)$ bond length to 1.493 (4) Å in the PF_6^- structure and 1.500 (5) Å in the I^- structure (the values given are the average). In the case of reported quaternary salts this shortening is slightly larger when compared with 18-crown-6 [1.51 Å

* Lists of structure factors, anisotropic thermal parameters for the non-H atoms, positional and isotropic thermal parameters for the H atoms, and shortest non-bonded contacts have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54863 (53 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: GE0275]

Table 1. Details of the collection and reduction of the intensity data, and the least-squares refinement

	$C_{16}H_{36}N_2O_4^{2+} \cdot 2PF_6^-$	$C_{16}H_{36}N_2O_4^{2+} \cdot 2I^-$
Crystal dimensions (mm)	$0.07 \times 0.18 \times 0.50$	$0.10 \times 0.21 \times 0.35$
Scan mode	$\omega-2\theta$	$\omega-2\theta$
Scan width ($^\circ$)	0.6	0.7
θ range for unit-cell determination ($^\circ$)	$8 < \theta < 29$	$7 < \theta < 16$
$(\sin \theta / \lambda)_{\max}$ (\AA^{-1})	0.609	0.660
h, k, l range	$-8 \leq h \leq 0$ $0 \leq k \leq 25$ $-11 \leq l \leq 11$	$-8 \leq h \leq 8$ $0 \leq k \leq 22$ $0 \leq l \leq 14$
No. of standard reflections, intensity change (%)	3, < 4	3, < 2
No. of reflections measured	2780	2994
No. of unique reflections	2470	2756
No. of observed reflections	2027	2034
Criteria for observed reflections	$I_o > 3\sigma(I_o)$	$I_o > 3\sigma(I_o)$
Structure refinement (on F)	Full matrix	Full matrix
No. of parameters	307	181
Weighting scheme	$1/\sigma^2(F)$	$1/\sigma^2(F)$
Average shift to e.s.d. ratio	0.01	0.01
Maximum, minimum $\Delta\rho$ ($e \text{\AA}^{-3}$)	0.27, -0.24	0.69, -0.52
S	4.21	2.02
R, wR	0.053, 0.053	0.026, 0.023

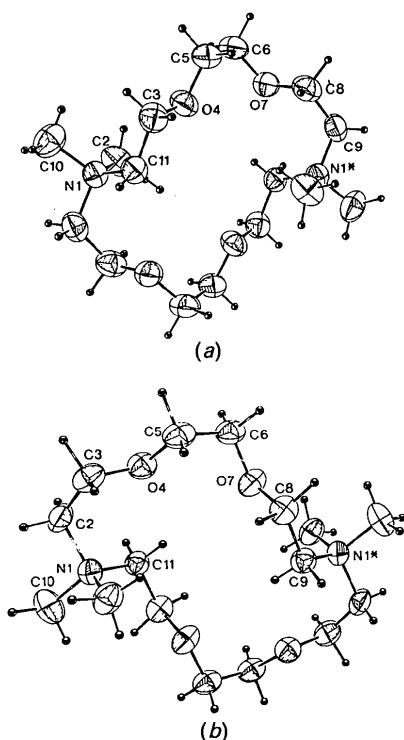


Fig. 1. ORTEPII (Johnson, 1976) view of the cations with the atom numbering: (a) $C_{16}H_{36}N_2O_4^{2+} \cdot 2PF_6^-$ and (b) $C_{16}H_{36}N_2O_4^{2+} \cdot 2I^-$. The thermal ellipsoids are drawn at 50% probability.

(Dunitz & Seiler, 1974)]. The bond angles on the C atoms C(2), C(6) and C(9) are larger than the expected values by $3-8^\circ$ (see Table 4). This suggests the presence of strains in the rings which are caused by two positively charged quaternary N atoms and the two methyl groups attached to each of them.

Table 2. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters (\AA^2) for non-H atoms of $C_{16}H_{36}N_2O_4^{2+} \cdot 2PF_6^-$, with e.s.d.'s in parentheses

$$B_{eq} = (4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)].$$

	x	y	z	B_{eq}	S.o.f.
N(1)	729 (3)	1417 (1)	1093 (2)	3.83 (5)	
C(2)	1690 (4)	794 (1)	1751 (3)	4.07 (6)	
C(3)	617 (4)	445 (1)	2716 (3)	4.68 (7)	
O(4)	-1183 (3)	151 (1)	1896 (2)	4.90 (5)	
C(5)	-2171 (5)	-240 (2)	2745 (3)	5.23 (7)	
C(6)	-4046 (4)	-524 (2)	1787 (3)	5.36 (7)	
O(7)	-3657 (3)	-875.6 (9)	606 (2)	4.64 (4)	
C(8)	-2562 (5)	-1448 (2)	962 (3)	5.24 (7)	
C(9)	-2199 (4)	-1758 (1)	-361 (3)	4.70 (7)	
C(10)	-1294 (4)	1298 (2)	52 (4)	5.58 (8)	
C(11)	395 (5)	1855 (2)	2255 (4)	6.05 (8)	
P	3490 (1)	-1617.6 (4)	4817.1 (8)	4.24 (2)	
F(1)	5776 (3)	-1438 (1)	4876 (2)	9.38 (7)	
F(2)	1201 (3)	-1812 (1)	4767 (2)	8.73 (6)	
F(3)	4050 (9)	-1544 (4)	6454 (6)	8.9 (2)	0.33
F(4)	4446 (10)	-2159 (3)	5891 (8)	10.0 (2)	0.33
F(5)	4361 (11)	-2269 (4)	5334 (10)	13.4 (2)	0.33
F(6)	3664 (13)	-2312 (3)	5239 (11)	13.3 (3)	0.33
F(7)	3680 (9)	-2137 (4)	3624 (8)	9.8 (2)	0.33
F(8)	3249 (8)	-1891 (3)	3318 (5)	6.3 (1)	0.33
F(9)	2883 (9)	-1641 (4)	3125 (6)	8.1 (2)	0.33
F(10)	2665 (8)	-1094 (3)	3712 (7)	8.1 (2)	0.33
F(11)	2457 (15)	-924 (4)	4548 (12)	16.3 (3)	0.33
F(12)	3189 (11)	-922 (3)	4333 (9)	12.1 (2)	0.33
F(13)	3414 (11)	-1132 (3)	6047 (9)	10.6 (2)	0.33
F(14)	3620 (7)	-1351 (3)	6414 (6)	5.6 (2)	0.33

Table 3. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters (\AA^2) for non-H atoms of $C_{16}H_{36}N_2O_4^{2+} \cdot 2I^-$, with e.s.d.'s in parentheses

$$B_{eq} = (4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)].$$

	x	y	z	B_{eq}
N(1)	726 (4)	-1310 (1)	2248 (2)	3.36 (5)
C(2)	3018 (5)	-1306 (2)	3140 (3)	3.90 (7)
C(3)	4099 (5)	-519 (2)	3385 (3)	4.33 (8)
O(4)	4334 (3)	-201 (1)	2229 (2)	3.81 (5)
C(5)	4940 (5)	614 (2)	2326 (3)	3.95 (7)
C(6)	4922 (5)	883 (2)	1014 (3)	3.92 (7)
O(7)	2861 (3)	789 (1)	95 (2)	4.04 (5)
C(8)	1327 (5)	1376 (2)	155 (3)	3.90 (7)
C(9)	-770 (5)	1223 (2)	-866 (3)	3.45 (6)
C(10)	-232 (6)	-2095 (2)	2427 (3)	5.30 (9)
C(11)	-559 (5)	-665 (2)	2630 (3)	4.24 (7)
I	-699.4 (3)	-1734.9 (1)	6003.1 (2)	4.310 (5)

The conformation of the macrocyclic rings is different in the two structures (Table 5). The sequence of torsion angles in the structure with the PF_6^- anion is $g^+ aag^+ g^+ ag^+ g^- a$ (for the asymmetric half of the ring), while in the structure with the I^- anion the sequence is $g^- aag^+ g^+ ag^- ag^-$. From the comparison above it is clear that the macrocycles have identical conformation in the parts of the rings starting with atom C(2) through O(7) (and symmetrically through the centre of symmetry), and different conformation for the parts O(7) through C(2*) in which the sequence of torsion angles has the opposite direction. The difference in conformation of the two rings is also clearly visible when looking at the r.m.s.

Table 4. Selected bond distances (Å) and bond angles (°) for non-H atoms with *e.s.d.*'s in parentheses

	$C_{16}H_{36}N_2O_4^{2+} \cdot 2PF_6^-$	$C_{16}H_{36}N_2O_4^{2+} \cdot 2I^-$
N(1)—C(2)	1.522 (3)	1.524 (3)
N(1)—C(10)	1.494 (3)	1.503 (3)
N(1)—C(11)	1.502 (4)	1.502 (4)
C(2)—C(3)	1.495 (4)	1.496 (5)
C(3)—O(4)	1.409 (3)	1.415 (4)
O(4)—C(5)	1.427 (4)	1.430 (4)
C(5)—C(6)	1.486 (4)	1.494 (5)
C(6)—O(7)	1.430 (4)	1.429 (3)
O(7)—C(8)	1.402 (4)	1.421 (5)
C(8)—C(9)	1.498 (5)	1.511 (4)
C(9)—N(1*)	1.521 (3)	1.518 (4)
C(2)—N(1)—C(10)	110.9 (3)	106.6 (2)
C(2)—N(1)—C(11)	109.8 (2)	109.8 (2)
C(10)—N(1)—C(11)	108.9 (2)	108.9 (3)
N(1)—C(2)—C(3)	117.2 (2)	116.0 (3)
C(2)—C(3)—O(4)	110.0 (2)	110.2 (3)
C(3)—O(4)—C(5)	112.5 (2)	113.5 (2)
O(4)—C(5)—C(6)	108.4 (2)	107.3 (2)
C(5)—C(6)—O(7)	113.9 (2)	112.5 (3)
C(6)—O(7)—C(8)	115.6 (2)	114.6 (2)
O(7)—C(8)—C(9)	110.3 (2)	109.9 (2)
C(8)—C(9)—N(1*)	116.7 (2)	116.2 (3)
C(9)—N(1*)—C(2*)	109.7 (2)	109.8 (2)

* Symmetry code: $-x, -y, -z$.

planes through the six heteroatoms of the ring. In the PF_6^- structure the deviations of the six heteroatoms from the r.m.s. plane are in the range 0.308 (2) to 0.451 (2) Å while in the I^- structure the six atoms are planar within 0.008 (2) Å.

In order to find the energy differences between the two conformations of the macrocyclic rings, *MM2* calculations were performed (Allinger, 1977). The optimized conformations expressed by torsion angles are shown in Table 5; the energies are 44.5 and 45.1 kcal mol⁻¹ (1 kcal mol⁻¹ = 4.184 kJ mol⁻¹), respectively, for the structures with PF_6^- and I^- anions. The difference could be a result of the different counterions, and, consequently, of different packing forces.

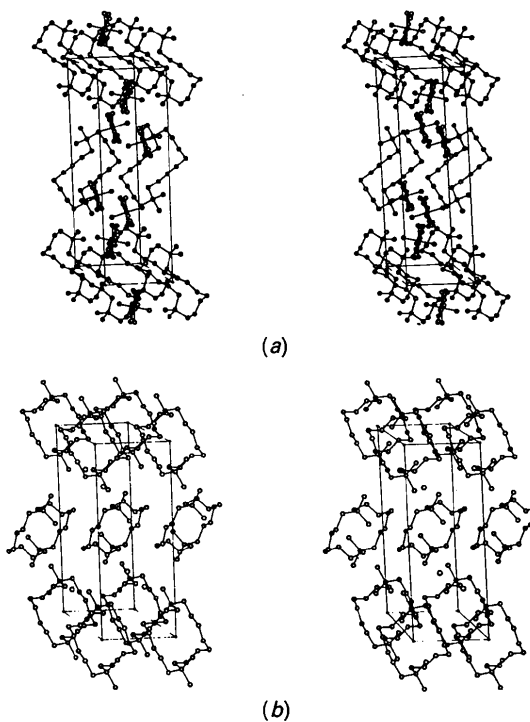
The PF_6^- anion is highly disordered in the crystal structure, four F atoms occupying three orientations in a PF_4 plane. These three orientations differ by *ca* 30°.

Packing of the *N,N,N',N'*-tetramethyldiazonia-18-crown-6 cations and PF_6^- anions in the unit cell is shown in Fig. 2(a). One PF_6^- anion is in van der Waals contact with the methyl groups C(10)H₃ or C(11)H₃ of four organic cations in symmetry positions (1) $-x, -y, -z$, (2) $-x, -y, 1-z$, (3) $1-x, -y, 1-z$ and (4) $-x, -\frac{1}{2}+y, \frac{1}{2}-z$. There are no contacts shorter than the sum of the van der Waals radii.

For the other structure [Fig. 2(b)], one I^- ion is in contact with two adjacent cations related by symmetry operations (1) x, y, z and (2) $-\frac{1}{2}+x, -\frac{1}{2}-y, \frac{1}{2}+z$. The distances between N and I^- are 4.494 (3) and 4.468 (3) Å for the molecule at x, y, z and the molecule transformed by symmetry operation (2), respectively. There are no contacts shorter than the sum of the van der Waals radii.

Table 5. Selected torsion angles (°) as found in the crystal structure and after *MM2* optimization, with *e.s.d.*'s in parentheses

	$C_{16}H_{36}N_2O_4^{2+} \cdot 2PF_6^-$		$C_{16}H_{36}N_2O_4^{2+} \cdot 2I^-$	
	Crystal	<i>MM2</i>	Crystal	<i>MM2</i>
C(10)—N(1)—C(2)—C(3)	-67.1 (3)	-62.6	-164.8 (3)	-179.0
C(11)—N(1)—C(2)—C(3)	53.2 (3)	57.1	-47.0 (3)	-61.4
N(1)—C(2)—C(3)—O(4)	73.9 (3)	72.4	-63.0 (3)	-72.3
C(2)—C(3)—O(4)—C(5)	174.4 (2)	-177.9	167.8 (3)	-179.1
C(3)—O(4)—C(5)—C(6)	179.8 (2)	-173.7	-174.8 (3)	-168.3
O(4)—C(5)—C(6)—O(7)	55.8 (3)	48.1	59.0 (3)	51.8
C(5)—C(6)—O(7)—C(8)	68.8 (3)	64.9	77.9 (3)	70.0
C(6)—O(7)—C(8)—C(9)	-178.1 (2)	176.3	179.3 (3)	176.8
O(7)—C(8)—C(9)—N(1*)	68.4 (3)	73.0	-66.3 (3)	-72.5
C(8)—C(9)—N(1*)—C(2*)	-68.4 (2)	-61.7	-168.3 (2)	-175.5
C(9)—N(1*)—C(2*)—C(3*)	-170.5 (2)	175.3	-76.3 (1)	-61.0
C(10)—N(1)—C(9*)—C(8*)	-54.2 (3)	-60.6	51.5 (3)	57.3
C(11)—N(1)—C(9*)—C(8*)	-172.6 (3)	-178.2	-69.6 (3)	-62.5

* Symmetry code: $-x, -y, -z$.Fig. 2. Packing diagrams: (a) $C_{16}H_{36}N_2O_4^{2+} \cdot 2PF_6^-$ and (b) $C_{16}H_{36}N_2O_4^{2+} \cdot 2I^-$. H atoms are omitted for clarity.

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Structure of Benzo-1,2,3,4-tetrazine 1,3-Dioxide

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Abstract. C₆H₄N₄O₂, $M_r = 164.12$, orthorhombic, *Pcab*, $a = 13.602(1)$, $b = 14.477(2)$, $c = 6.969(1)$ Å, $V = 1372.3(3)$ Å³, $Z = 8$, $D_x = 1.589$ Mg m⁻³, $\lambda(\text{Cu } K\alpha_1) = 1.54050$ Å, $\mu = 1.025$ mm⁻¹, $F(000) = 672$, $T = 295$ K, final $R = 0.049$ for 692 reflections. The benzotetrazine ring is planar indicating extensive π -electron delocalization. Shortened semipolar N—O bonds [N(2)—O(5) 1.255(4) and N(4)—O(6) 1.238(4) Å] were observed.

Introduction. 1,2,3,4-Tetrazines, containing an unstable six-membered aza-aromatic ring system, are of interest from the viewpoint of their physical and chemical properties (Wiley, 1978; Neunhoeffer, 1984; Kaihoh, Itoh Yamaguchi & Ohsawa, 1990). However, 2-phenyl-1,2,3-triazole[4,5-*e*][1,2,3,4]tetrazine (Kaihoh, Itoh, Yamaguchi & Ohsawa, 1991) was the sole example and its structure was established by X-ray crystallography (Yamaguchi, Kaihoh, Itoh & Ohsawa, 1991). The crystal structure of the title compound, the second example of a 1,2,3,4-tetrazine, has been determined as part of a continuing study of 1,2,3,4-tetrazines.

Experimental. The preparation and physical properties are given by Churakov, Ioffe, Strelenko & Tartakovskii (1990). Crystal dimensions 0.10 × 0.08 × 0.55 mm, by recrystallization from C₂H₅OH, having m.p. 440–441 K. Rigaku AFC-5 four-circle diffractometer used with ω -2 θ -scan method, ω -scan width (1.3 + 0.5tan θ)° and scan speed 16° min⁻¹. Lattice parameters obtained from least-squares analysis of 20 reflections with 2 θ values ranging from 42 to 46°. Of 1255 reflections scanned [within index range h 0–15, k 0–16, l 0–7 up to (sin θ)/ $\lambda < 0.56$ Å⁻¹], 1020 unique reflections [$F > \sigma(F)$] classified as observed [125 unobserved reflections with

$\sigma(F) > F > 0$]. Three standard reflections measured every 150 reflections, intensity variation < 3%. Intensities corrected for Lorentz and polarization factors, but absorption correction not applied. Structure solved using program package *SAPI85* (Yao, Zheng, Qian, Han, Gu & Fan, 1985). Refinement by full-matrix least-squares method with anisotropic temperature factors for non-H atoms. The function minimized was $\sum w(|F_o|^2 - |F_c|^2)^2$ with $w = 1/[\sigma^2(F_o) + 0.02(F_c)]$, $\sigma(F_o)$ from counting statistics. All H atoms located from the difference map and refined, initial thermal parameters set at equivalent isotropic thermal parameter of each bonded atom. Final discrepancy indices $R = 0.049$, $wR = 0.051$, $S = 1.276$ for 125 variables and 692 reflections with $F > 3\sigma(F)$. Maximum $\Delta/\sigma = 0.13$ in the final least-squares cycle. Final difference Fourier excursions 0.18 and -0.19 e Å⁻³. All computations performed on a PANAFACOM computer with *RCRYSTAN* (Rigaku Corporation, 1985) X-ray analysis program system. The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV).

Discussion. Final atomic parameters are listed in Table 1.* Bond lengths and angles are listed in Table 2. Fig. 1 shows an *ORTEP* drawing (Johnson, 1976) of the molecule with atomic labels.

The benzotetrazine ring system is almost planar, with maximum displacement out of the least-squares

* Tables of H-atom coordinates, anisotropic thermal parameters and structure-factor amplitudes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54875 (5 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AS0556]