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Crystal Structure of 1-(2-Pyridiniomethyl)-2,4-bis(phenylsulfonyl)benzene Chloride Ethanol Solvate

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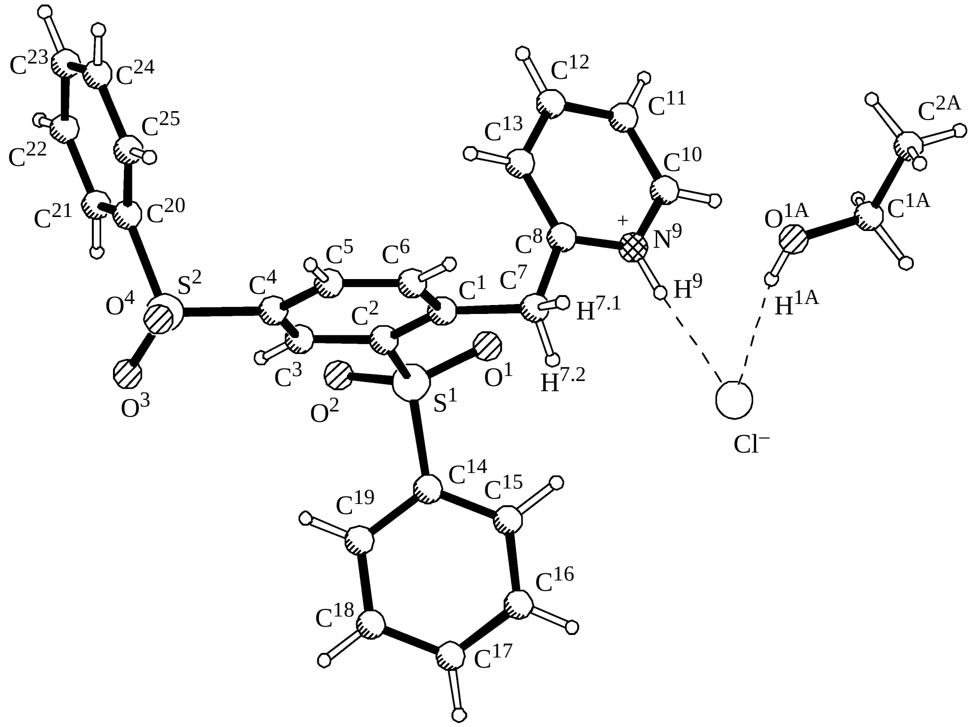
Abstract — 1-(2-Pyridiniomethyl)-2,4-bis(phenylsulfonyl)benzene chloride ethanol solvate was studied by single crystal X-ray diffraction. The conformation and geometric parameters (bond lengths, bond and torsion angles) of the molecular cation $(C_{24}H_{20}NO_4S_2)^+$ and an EtOH solvation molecule (which is disordered over three orientations) were determined. In the crystal structure, the hydrogen bonds are formed with the Cl^- anion only; it is involved in two H bonds. The stronger H bond is formed with the PyH hydrogen atom, and the weaker H bond, with the hydroxyl hydrogen atom of the disordered EtOH molecule in any of the three possible positions.

Salts with the molecular cation containing a benzene core with a 2-pyridiniomethyl substituent and phenylsulfonyl substituents may exhibit useful properties; however, such salts have not been reported. In this work we prepared 1-(2-pyridiniomethyl)-2,4-bis(phenylsulfonyl)benzene chloride ethanol solvate (**I**) and studied it by single crystal X-ray diffraction.

The molecular-ionic structure of **I** in the crystal is shown in the figure; the bond lengths, bond angles, and selected torsion angles are given in Tables 1–3. The asymmetric part of the unit cell of **I** contains the 1-(2-pyridiniomethyl)-2,4-bis(phenylsulfonyl)benzene molecular cation (X^+), Cl^- anion, and EtOH molecule which appeared to be disordered over three different orientations (see below).



Molecular-ionic structure of **I** in the crystal. The less occupied positions (B, C) of the atoms of the disordered EtOH solvation molecule are not shown for simplicity. The hydrogen bonds are shown by dashed lines.

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Table 1. Bond lengths (*d*, Å) in the structure of **I**[a]

Bond	*d*	Bond	*d*
S^1=O^1	1.434(2)	C^{12}–C^{13}	1.384(3)
S^1=O^2	1.432(2)	C^{14}–C^{15}	1.384(3)
S^1–C^2	1.795(2)	C^{14}–C^{19}	1.387(3)
S^1–C^{14}	1.763(2)	C^{15}–C^{16}	1.385(3)
S^2=O^3	1.431(2)	C^{16}–C^{17}	1.381(4)
S^2=O^4	1.425(2)	C^{17}–C^{18}	1.381(4)
S^2–C^4	1.790(3)	C^{18}–C^{19}	1.377(3)
S^2–C^{20}	1.757(2)	C^{20}–C^{21}	1.376(3)
C^1–C^2	1.397(3)	C^{20}–C^{25}	1.384(3)
C^1–C^6	1.387(3)	C^{21}–C^{22}	1.378(3)
C^1–C^7	1.512(2)	C^{22}–C^{23}	1.384(4)
C^2–C^3	1.382(3)	C^{23}–C^{24}	1.366(4)
C^3–C^4	1.372(3)	C^{24}–C^{25}	1.370(3)
C^4–C^5	1.377(3)	O^{1A}–C^{1A}	1.417(9)
C^5–C^6	1.374(3)	C^{1A}–C^{2A}	1.501(9)
C^7–C^8	1.502(2)	O^{1B}–C^{1B}	1.418(9)
C^8–C^{13}	1.382(3)	C^{1B}–C^{2B}	1.493(9)
N^9–C^8	1.335(2)	O^{1C}–C^{1C}	1.42(1)
N^9–C^{10}	1.341(2)	C^{1C}–C^{2C}	1.50(1)
N^9–H^9	0.86	H^{1A}–O^{1A}	0.86
C^{10}–C^{11}	1.365(3)	H^{1B}–O^{1B}	0.88
C^{11}–C^{12}	1.373(3)	H^{1C}–O^{1C}	0.86

[a] Subscripts A, B, and C correspond to different positions of the same atoms in the disordered EtOH molecule; the same for Tables 2–4. See also note [a] to Table 5.

Table 2. Bond angles (ω, deg) in the structure of **I**

Angle	ω	Angle	ω
$O^1S^1O^2$	118.95(9)	$C^8N^9C^{10}$	123.8(2)
$O^1S^1C^2$	109.39(8)	$N^9C^{10}C^{11}$	119.8(2)
$O^1S^1C^{14}$	108.67(9)	$C^{10}C^{11}C^{12}$	118.7(2)
$O^2S^1C^2$	106.31(9)	$C^{11}C^{12}C^{13}$	120.3(2)
$O^2S^1C^{14}$	107.61(9)	$C^8C^{13}C^{12}$	119.7(2)
$C^2S^1C^{14}$	105.03(8)	$S^1C^{14}C^{15}$	120.0(2)
$O^3S^2O^4$	119.70(9)	$S^1C^{14}C^{19}$	118.4(2)
$O^3S^2C^4$	107.10(9)	$C^{15}C^{14}C^{19}$	121.6(2)
$O^3S^2C^{20}$	108.27(9)	$C^{14}C^{15}C^{16}$	118.2(2)
$O^4S^2C^4$	106.83(9)	$C^{15}C^{16}C^{17}$	120.5(2)
$O^4S^2C^{20}$	108.88(9)	$C^{16}C^{17}C^{18}$	120.7(2)
$C^4S^2C^{20}$	105.11(9)	$C^{17}C^{18}C^{19}$	119.5(3)
$C^2C^1C^6$	116.9(2)	$C^{14}C^{19}C^{18}$	119.5(2)
$C^2C^1C^7$	125.0(2)	$S^2C^{20}C^{21}$	119.2(2)
$C^6C^1C^7$	118.1(2)	$S^2C^{20}C^{25}$	119.3(2)
$S^1C^2C^1$	123.4(2)	$C^{21}C^{20}C^{25}$	121.6(2)
$S^1C^2C^3$	114.7(2)	$C^{20}C^{21}C^{22}$	118.8(2)
$C^1C^2C^3$	121.9(2)	$C^{21}C^{22}C^{23}$	119.7(3)
$C^2C^3C^4$	118.7(2)	$C^{22}C^{23}C^{24}$	120.7(2)
$S^2C^4C^3$	119.4(2)	$C^{23}C^{24}C^{25}$	120.3(2)
$S^2C^4C^5$	119.2(2)	$C^{20}C^{25}C^{24}$	118.9(2)
$C^3C^4C^5$	121.4(2)	$O^{1A}C^{1A}C^{2A}$	109.9(8)
$C^4C^5C^6$	118.9(2)	$O^{1B}C^{1B}C^{2B}$	109.9(8)
$C^1C^6C^5$	122.2(2)	$O^{1C}C^{1C}C^{2C}$	110(1)
$C^1C^7C^8$	113.8(1)	$H^{1A}O^{1A}C^{1A}$	109
$C^7C^8N^9$	116.9(2)	$H^{1B}O^{1B}C^{1B}$	108
$C^7C^8C^{13}$	125.3(2)	$H^{1C}O^{1C}C^{1C}$	108
$N^9C^8C^{13}$	117.7(2)		

In the cation X^+, both hexavalent S^1 and S^2 atoms have almost the same distorted tetrahedral coordination; the O=S=O angle is the largest among the six bond angles, the C–S–C angle is the smallest, and the other four bond angles O=S–C are somewhat smaller than the ideal tetrahedral angle of 109.5°. All the S=O bond lengths are close; their mean value, 1.431(3) Å, is slightly smaller than the average statistical value of 1.436(10) Å [1].

The mean S–C bond length is 1.776(16) Å, which slightly exceeds the average statistical (for $C–SO_2–C_{ar}$ fragments) value of 1.763(9) Å [1]; the lengths of particular S–C bonds noticeably differ. The S^1–C^2 and S^2–C^4 bond lengths are close to each other but larger [by 0.033(2) Å on the average] than the lengths of the seemingly equivalent S^1–C^{14} and S^2–C^{20} bonds, which are also close to each other. This difference may be due to stronger conjugation of the d_π orbitals of the S^1 and S^2 atoms with the π orbitals of the terminal benzene rings and weaker conjugation of these orbitals with the π orbitals of the central benzene ring, due to the presence of two $PhSO_2$ substituents.

The pyridinium ring in the X^+ cation is planar to within ±0.010(1) Å (for the six ring atoms), and the least-squares plane of this ring is almost perpendicular to the least-squares plane of the central benzene ring [dihedral angle 86.89(6)°]. The lengths of the covalent bonds in this pyridinium ring are typical of such structures [1].

All the three benzene rings in the X^+ cation are planar to within ±0.005(2) Å (for the six C atoms). The least-squares planes of the two terminal phenyl rings form dihedral angles of 104.26(7)° and 107.71(7)° with the least-squares plane of the central benzene ring. The mean $C\underline{\cdots}C$ bond length in these three benzene rings is 1.380(6) Å, being slightly shorter than the statistical average bond length in C,H-substituted benzene rings, 1.384(13) Å [1].

In the three benzene rings of the X^+ cations, the endocyclic bond angles $C^1C^2C^3$, $C^3C^4C^5$, $C^{15}C^{14}C^{19}$, and $C^{21}C^{20}C^{25}$ (at the atoms with exocyclic SO_2 groups) slightly but systematically exceed the ideal value of 120°. A similar effect of other electronegative

Table 3. Selected torsion angles (τ, deg) in the structure of **I**

Angle	τ	Angle	τ
$S^1C^2C^1C^7$	3.4(2)	$O^3S^2C^4C^5$	–155.0(2)
$O^1S^1C^2C^1$	–29.3(2)	$O^4S^2C^4C^5$	–25.6(2)
$O^2S^1C^2C^1$	–158.9(1)	$C^{20}S^2C^4C^5$	90.0(2)
$C^{14}S^1C^2C^1$	87.2(2)	$O^3S^2C^{20}C^{21}$	–22.5(2)
$O^1S^1C^2C^3$	152.5(1)	$O^4S^2C^{20}C^{21}$	–154.2(2)
$O^2S^1C^2C^3$	22.9(2)	$C^4S^2C^{20}C^{21}$	91.7(2)
$C^{14}S^1C^2C^3$	–91.0(1)	$O^3S^2C^{20}C^{25}$	156.2(2)
$O^1S^1C^{14}C^{15}$	12.0(2)	$O^4S^2C^{20}C^{25}$	24.5(2)
$O^2S^1C^{14}C^{15}$	142.1(2)	$C^4S^2C^{20}C^{25}$	–89.7(2)
$C^2S^1C^{14}C^{15}$	–104.9(2)	$C^2C^1C^7C^8$	76.3(2)
$O^1S^1C^{14}C^{19}$	–164.9(2)	$C^6C^1C^7C^8$	–103.4(2)
$O^2S^1C^{14}C^{19}$	–34.8(2)	$C^1C^7C^8N^9$	–154.9(2)
$C^2S^1C^{14}C^{19}$	78.2(2)	$C^1C^7C^8C^{13}$	26.6(2)
$O^3S^2C^4C^3$	23.1(2)	$H^{1A}O^{1A}C^{1A}C^{2A}$	179
$O^4S^2C^4C^3$	152.5(2)	$H^{1B}O^{1B}C^{1B}C^{2B}$	58
$C^{20}S^2C^4C^3$	–91.9(2)	$H^{1C}O^{1C}C^{1C}C^{2C}$	–132

Table 4. Geometric parameters of hydrogen bonds in the crystal structure of **I**[a]

H bond $Z–H\cdots Cl^-$	$d(H\cdots Cl)$, Å	$d(Z\cdots Cl)$, Å	$Z–H\cdots Cl$ angle, deg
$N^9–H^9\cdots Cl$	2.13(2)	2.985(2)	176(2)
$O^{1A}–H^{1A}\cdots Cl$	2.32(3)	3.172(6)	169(3)
$O^{1B}–H^{1B}\cdots Cl$	2.35(3)	3.180(7)	155(3)
$O^{1C}–H^{1C}\cdots Cl$	2.32(4)	3.163(8)	166(4)

[a] $\angle N^9\cdots Cl\cdots H^{1A}$ 63°.

substituents on the endocyclic bond angles in substituted benzene rings was considered in [2].

As seen, the overall conformation of the X^+ cation in the crystal of **I** is as follows: The pyridinium ring and Ph ring of the phenylsulfonyl substituent at the C^4 atom are oriented toward one side of the least-squares plane of the central benzene ring, and the Ph ring of the phenyl substituent at the C^2 atom is oriented toward the opposite side. The deviations of the adjacent atoms from the least-squares plane of the central benzene ring are as follows: C^7 0.026(3), C^8 1.370(3), S^1 −0.085(2), O^1 0.532(3), O^2 0.416(3), C^{14} −1.805(3), S^2 −0.034(2), O^3 −0.596(3), O^4 −0.657(3), and C^{20} 1.652(3) Å.

The EtOH solvation molecule in the crystal structure of **I** is disordered; in the same place of the unit cell, it has three different orientations (A, B, C) relative to the cell axes, with the occupancies of 0.40(1), 0.38(1), and 0.22(1), respectively. Hereinafter, in the text and in tables, the indices A, B, and C at the atom number denote different (though fairly close) positions of the same atoms of the EtOH molecule, corresponding to one of its three orientations. The disordered EtOH molecule in each of its three orientations has normal bond lengths and bond angles [3].

The geometric parameters of hydrogen bonds formed in the crystal structure of **I** are given in Table 4. All these H bonds (see figure) are formed with the Cl^- anion only; it participates in two H bonds. The stronger H bond is formed with the H^9 atom at the pyridinium nitrogen atom, and the weaker bond, with the hydroxyl hydrogen atom of the OH group of the disordered EtOH molecule in each of the three possible positions H^{1A}, H^{1B}, and H^{1C}.

All the other short intermolecular (interionic) contacts in the crystal structure of **I** are close to, or slightly shorter than the sums of the corresponding van der Waals radii of the atoms.

EXPERIMENTAL

The crystals of **I** were prepared as follows. A slight molar excess of dilute HCl was added to a solution of 1-(2-pyridylmethyl)-2,4-bis(phenylsulfonyl)benzene (**II**) in ethanol, and the mixture was allowed to evaporate at room temperature. In 2 days, ethanol solvate of salt **I** precipitated in the form of colorless transparent crystals. The synthesis, characteristics, and properties of **II** and some other related compounds will be described in a separate paper.

The unit cell parameters and the three-dimensional set of reflection intensities were obtained with an Enraf-Nonius CAD-4 automatic diffractometer (MoK_α radiation, graphite monochromator). Crystals of **I** are triclinic; $(C_{24}H_{20}NO_4S_2)^+ \cdot Cl^- \cdot C_2H_5OH$, M 532.05; a 8.491(2), b 9.033(2), c 18.237(4) Å; α 81.29(2)°, β 87.19(2)°, γ 70.47(2)°; V 1303.1(5) $Å^3$, Z 2, d_{calc} 1.356 g cm^{-3}, $\mu(MoK_\alpha)$ 3.44 cm^{-1}, space group $P\bar{1}$ (no. 2).

The intesities of 4900 reflections were measured in the reciprocal sphere hemisphere ($2\theta \le 50°$) by the $\omega/2\theta$ scanning method using a 0.20 × 0.50 × 0.80-mm single crystal of **I**. When measuring the intensities, we used a special mode in which the final scanning was performed for all (including very weak) reflections. After averaging the intensities of 342 pairs of equivalent reflections $0kl$ and $0\bar{k}\bar{l}$ (R_{int} 0.030), the working set of measured $F^2(hkl)$ and $\sigma(F^2)$ consisted of 4558 unique reflections.

The structure of **I** was solved by the direct method

Table 5. Coordinates ($\times 10^4$) and equivalent isotropic thermal parameters (Å^2 $\times$ 10^3) of non-hydrogen atoms in the crystal structure of **I**[a]

Atom	*x*	*y*	*z*	U_{eq}[b]
Cl^-	894.8(6)	1846.9(7)	5388.9(3)	64.4(2)
S^1	3316.8(5)	2265.7(5)	2630.0(3)	43.6(1)
S^2	2743.9(5)	7706.5(6)	799.7(2)	44.6(1)
O^1	3928(2)	1536(2)	3361.3(8)	61.5(4)
O^2	4328(2)	1757(2)	2004.3(8)	55.7(3)
O^3	2558(2)	6697(2)	300.1(7)	58.2(4)
O^4	1594(2)	9281(2)	767.7(8)	61.0(4)
C^1	2412(2)	5220(2)	3149.6(9)	40.9(4)
C^2	2888(2)	4369(3)	2550(1)	39.2(4)
C^3	3018(2)	5106(2)	1839(1)	41.2(4)
C^4	2644(2)	6723(3)	1721(1)	41.8(5)
C^5	2143(2)	7613(2)	2293(1)	48.1(4)
C^6	2045(2)	6852(2)	2997(1)	48.8(4)
C^7	2279(2)	4497(2)	3944(1)	44.9(4)
C^8	3938(2)	3688(2)	4326.0(9)	41.5(4)
N^9	4009(2)	2542(2)	4891.7(8)	45.4(3)
C^{10}	5401(2)	1707(2)	5283(1)	53.9(5)
C^{11}	6852(2)	2016(3)	5107(1)	56.4(5)
C^{12}	6833(2)	3213(3)	4541(1)	56.3(5)
C^{13}	5376(2)	4058(3)	4149(1)	50.0(4)
C^{14}	1363(2)	2041(2)	2516(1)	45.6(4)
C^{15}	543(3)	1529(2)	3124(1)	59.1(5)
C^{16}	–946(3)	1285(3)	3006(2)	76.7(7)
C^{17}	–1598(3)	1574(3)	2300(2)	82.1(8)
C^{18}	–770(3)	2091(3)	1697(2)	73.5(7)
C^{19}	725(3)	2313(2)	1804(1)	55.5(5)
C^{20}	4784(2)	7789(2)	710(1)	45.7(4)
C^{21}	6015(3)	6582(3)	432(1)	66.5(6)
C^{22}	7600(3)	6680(4)	341(2)	86.9(8)
C^{23}	7928(3)	7967(4)	541(2)	89.4(9)
C^{24}	6693(4)	9149(4)	821(1)	77.8(7)
C^{25}	5106(3)	9080(3)	906(1)	59.4(5)
O^{1A}	1989(12)	3997(10)	6345(5)	86(3)
C^{1A}	2528(15)	3018(14)	7031(5)	88(4)
C^{2A}	2900(20)	3963(19)	7568(6)	106(6)
O^{1B}	1465(13)	4146(10)	6430(5)	88(4)
C^{1B}	2021(15)	3672(15)	7177(5)	90(6)
C^{2B}	3551(22)	2234(20)	7227(8)	139(8)
O^{1C}	2836(23)	3211(21)	6403(8)	87(8)
C^{1C}	2829(30)	2750(24)	7184(8)	95(9)
C^{2C}	2330(37)	4202(25)	7567(9)	110(10)

[a] The occupancies of the atomic positions of the disordered EtOH molecule are 0.40(1), 0.38(1), and 0.22(1) for positions denoted by indices A, B, and C, respectively. [b] The U_{eq} values were calculated as 1/3 of the trace of the orthogonalized U_{ij} tensor.

Table 6. Coordinates ($\times 10^3$) and isotropic thermal parameters (Å^2 $\times$ 10^3) of hydrogen atoms in the crystal structure of **I**[a]

Atom	*x*	*y*	*z*	U_{iso}
H^3	336	451	144	46(5)
H^5	188	871	220	60(6)
H^6	172	745	338	64(7)
H$^{7.1}$	161	533	422	54(5)
H$^{7.2}$	170	373	395	57(6)
H^9	311	233	501	51(5)
H^{10}	538	92	567	65(7)
H^{11}	783	143	536	72(7)
H^{12}	780	346	442	64(6)
H^{13}	537	488	377	63(6)
H^{15}	101	134	363	60(6)
H^{16}	–151	92	341	82(8)
H^{17}	–265	141	223	109(10)
H^{18}	–123	229	121	95(9)
H^{19}	131	265	140	74(7)
H^{21}	577	566	30	85(8)
H^{22}	850	583	13	105(10)
H^{23}	900	803	48	110(10)
H^{24}	693	1000	96	95(9)
H^{25}	426	988	109	75(7)
H^{1A}	180	343	604	103
H^{11A}	352	214	696	106
H^{12A}	166	259	723	106
H^{21A}	326	329	803	135
H^{22A}	191	483	765	135
H^{23A}	377	437	737	135
H^{1B}	128	334	628	106
H^{1C}	230	272	620	104

[a] The numbering of hydrogen atoms corresponds to the numbering of the non-hydrogen atoms to which they are bonded. See also note [a] to Table 5.

using the SHELXS 97 program [4] and refined by the full-matrix least-squares method (with respect to F^2) using the SHELXL 97 program [4] in the approximation of anisotropic thermal vibrations for all non-hydrogen atoms. In the structure refinement, we used almost all reflections from the working set [including very weak reflections with $I < 2\sigma(I)$], except several reflections for which the measured and calculated F^2 values were poorly consistent.

First we revealed in the *E* synthesis an ordered EtOH solvation molecule for which the coordinates of nonhydrogen atoms approximately corresponded to the major orientation, A. However, after anisotropic refinement of the structure of **I** (with ordered EtOH molecules and with all the hydrogen atoms set geometrically), the detailed analysis of the peaks of the check difference electron density synthesis showed that all the non-hydrogen atoms of the EtOH molecule (and hence all its hydrogen atoms) are disordered each over three positions A, B, and C corresponding to three different orientations of the EtOH molecule (see above). Then, in the course of refinement of the structure of **I**, soft equality conditions of the SADI and DFIX type [4] were imposed on the structurally equivalent (for orientations A, B, and C) 1,2 and 1,3 interatomic distances of the EtOH molecule. Also, the total occupancies of positions A, B, and C were refined by the least-squares method.

All the hydrogen atoms of the X^+ molecular cation were localized objectively in the difference electron density synthesis in the intermediate step of the refinement. Then, in the course of the least-squares refinement of the structure of **I**, the coordinates of all the hydrogen atoms of the X^+ cation and of the EtOH molecule disordered over three orientations were calculated geometrically using the rider model [4] with the varied C–H bond lengths in the X^+ cation and varied individual isotropic thermal parameters U_{iso}.

In the last cycle of the full-matrix refinement of the structure of **I**, the absolute shifts of all the varied 412 parameters were less than 0.001σ. The final coordinates and thermal parameters of atoms in the structure of **I** are listed in Tables 5 and 6.

The final R factors are as follows: $R1$ 0.035 and $wR2$ 0.089 for 3850 observed reflections with $I \geq 2\sigma(I)$; $R1$ 0.048 and $wR2$ 0.136 for all the 4558 measured unique reflections; goodness of fit S 1.03 (for the definitions of $wR2$ and S, see [4]). In the final difference electron density synthesis, $-0.23 < \Delta\rho < 0.25$ ” Å^{-3}. The f curves used and the anomalous-dispersion corrections to them ($\Delta f'$ and $\Delta f''$) were taken from [5].

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