Crystal Structure of the Complex of 1,2-Bis[2-(*o*-hydroxyphenoxy)ethoxy]ethane with Ammonium Thiocyanate

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Abstract—The complex of the podand 1,2-bis[2-(*o*-hydroxyphenoxy)ethoxy]ethane (L) with ammonium thiocyanate, $[NH_4(SCN)L]$, was prepared and studied by single crystal X-ray diffraction. This is a host–guest complex; in its molecule the podand L is "wrapped" around the NH_4^+ cation, which forms hydrogen bonds with all the six oxygen atoms of the podand and one hydrogen bond with the sulfur atom of the SCN⁻ anion. The geometric parameters (bond lengths, bond angles, torsion angles, etc.) of the molecule of $[NH_4(SCN)L]$ and packing of the molecules in the crystal were determined. The molecules are linked into infinite polymeric chains by intermolecular hydrogen bonds O–H…NCS.

It is well known [1] that ammonium ion NH_4^+ resembles alkali metal ions in its properties. Its effective ionic radius, 1.43 Å [1], is intermediate between the ionic radii of K⁺ and Rb⁺. Therefore, the NH_4^+ ion, like alkali metal ions, forms host–guest complexes with crown ethers and cryptands [2]. However, the related complexes with podands have not been reported. In this work we prepared and studied by single crystal X-ray diffraction the first such complex of a podand, 1,2-bis[2-(*o*-hydroxyphenoxy)ethoxy]ethane (L), with ammonium thiocyanate. By analogy with the related metal complexes, it can be named {1,2-bis[2-(*o*-hydroxyphenoxy)ethoxy]ethane how more than a studied by analogy with the related metal complexes.

The structure of **I** is shown in the figure; the bond lengths and the selected bond and torsion angles are listed in Tables 1–3. Complex **I** is a host–guest complex [2]; in its molecule, podand L is "wrapped" around the NH_4^+ cation, forming hydrogen bonds with six oxygen atoms of the podand and one hydrogen bond with the sulfur atom of the SCN⁻ anion. The geometric paameters of these and other hydrogen bonds are listed in Table 4.

In the molecule of **I**, three atoms H^1 , H^2 , and H^3 of the NH_4^+ ion form bifurcate hydrogen bonds, i.e., each of them participates in two H bonds simultaneously (with two different oxygen atoms of podand L). One of the H bonds involving H^2 is disordered over two positions O^{10} and $O^{10'}$ of the same disordered oxygen atom. The H^4 atom of the NH_4^+ cation forms one H bond, which is also disordered over two close

psitions S^A and S^B of the disordered S atom of the SCN⁻ anion.

In complex I, the NH_4^+ cation is an analog of a metal cation, and the hydrogen bonds that it forms can be considered as analogs of coordination bonds of a metal ion. In terms of coodination chemistry, the "coordination number" of the ammonium ion in I is 7, and its "coordination polyhedron" is a distorted hexagonal pyramid with all the six oxygen atoms of L in the base and the disordered sulfur atom of the SCNanion in the apex. Deviations of six oxygen atoms of podand L from their least-squares plane are within ± 0.34 Å, and the N¹ atom of the NH₄⁺ ion deviates from this plane by 0.969(2) Å toward the SCN⁻ anion with which it forms an H bond. Two close positions S^A and S^B of the disordered sulfur atom of the SCN⁻ anion are at distances of 4.266(6) and 4.242(9) Å, respectively, from this plane.

In the structure of **I**, atoms of one of the $-CH_2-O-CH_2-CH_2-$ chains of podand L are disordered each over two relatively close positions, forming two alternative chains C⁹-O¹⁰-C¹¹-C¹² and C⁹-O¹⁰-C¹¹-C¹² with different conformations and with occupancies of 0.885(5) and 0.115(5), respectively. The conformation of podand L is characterized in detail by the torsion angles (Table 3). In the long chain of podand L (16 nonhydrogen atoms with numbers from 1 to 16 and the H^{O1} and H¹⁶ atoms), two torsion angles O¹C²C³O⁴ and O¹³C¹⁴C¹⁵O¹⁶ are synperiplanar (of *cis* type), three torsion angles O⁴C⁵C⁶O⁷, O⁷C⁸C⁹O¹⁰ (or O⁷C⁸C⁹O¹⁰), and O¹⁰C¹¹C¹²O¹³ (or O¹⁰C¹¹.



Molecular-ionic structure of **I** in the crystal. The hydrogen atoms at the C atoms are omitted for clarity. The S and C atoms of the SCN⁻ anion and atoms of the C⁹–O¹⁰–C¹¹–C¹² chain of podand L are disordered each over two relatively close positions (for comments, see text). Atoms of the SCN⁻ anion related by the (x, y - 1, z) translation are marked with an asterisk. Thin dashed lines denote hydrogen bonds.

 $C^{12}O^{13}$) are synclinal (of the *gauche* type), and one torsion angle $C^8C^9O^{10}C^{11}$ is anticlinal (partially eclipsed); the other torsion angles are antiperiplanar (of *trans* type).

In the structure of **I**, the lengths of four C–O bonds in podand L (O¹–C², C³–O⁴, O¹³–C¹⁴, and C¹⁵–O¹⁶) virtually coincide with the statistical average values for C_{ar}–OH and C_{ar}–O–C_{sp³} fragments: 1.362(15) and 1.370(11) Å, respectively [3]. Two bonds, O⁴–C⁵ and C¹²–O¹³, are slightly shorter compared to the statistical average value (for C_{ar}–O–CH₂–C fragments) of 1.431(13) Å [3]. Four bonds, C⁶–O⁷, O⁷–C⁸, C⁹–O¹⁰, and O¹⁰–C¹¹, are somewhat shorter compared to the statistical average value (for C_{sp³}–O–CH₂–C fragments) of 1.426(11) Å [3]. Three bonds, C⁵–C⁶, C⁸– C⁹, and C¹¹–C¹², are noticeably shorter compared to the statistical average value (for C[#]–CH₂–CH₂–C[#] fragments) of 1.524(14) Å [3]. Appreciable shortening of these C–C bonds is typical of O–CH₂–CH₂–O fragments and is well known for crown ethers [4].

In the structure of **I**, two benzene rings in L are virtually planar [within $\pm 0.008(1)$ and $\pm 0.006(1)$ Å for the six carbon atoms of the first and second rings, respectively, in the order of numbering of their atoms]. The least-squares planes of these two benzene rings form an angle of $137.87(7)^{\circ}$ wth each other and angles of $139.71(5)^{\circ}$ and $169.83(6)^{\circ}$, respectively, with the least-squares plane of the six oxygen atoms of podand L, from which both these two rings are bent to the same side, opposite to the NH⁴₄ cation and SCN⁻

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Bond	d	Bond	d
$\begin{array}{c} S^{A}=C^{A}\\ S^{B}=C^{B}\\ C^{A}=N\\ C^{B}=N\\ N^{1}-H^{1}\\ N^{1}-H^{2}\\ N^{1}-H^{3}\\ N^{1}-H^{4}\\ H^{O1}-O^{1}\\ O^{1}-C^{2}\\ C^{2}-C^{3}\\ C^{2}-C^{20}\\ C^{3}-O^{4}\\ C^{3}-C^{17}\\ O^{4}-C^{5}\\ C^{5}-C^{6}\\ C^{6}-O^{7}\\ O^{7}-C^{8} \end{array}$	$\begin{array}{c} 1.630(3)\\ 1.630(4)\\ 1.141(4)\\ 1.143(5)\\ 0.91(1)\\ 0.92(1)\\ 0.91(1)\\ 0.91(1)\\ 0.91(1)\\ 0.86(1)\\ 1.362(2)\\ 1.362(2)\\ 1.382(2)\\ 1.382(2)\\ 1.369(2)\\ 1.379(3)\\ 1.428(2)\\ 1.488(3)\\ 1.411(2)\\ 1.422(2)\\ \end{array}$	$\begin{array}{c} C^8 - C^9 \\ C^9 - O^{10} \\ O^{10} - C^{11} \\ C^{11} - C^{12} \\ C^{12} - O^{13} \\ O^{13} - C^{14} \\ C^{14} - C^{15} \\ C^{14} - C^{24} \\ C^{15} - O^{16} \\ C^{15} - C^{21} \\ O^{16} - H^{16} \\ C^{17} - C^{18} \\ C^{18} - C^{19} \\ C^{19} - C^{20} \\ C^{21} - C^{22} \\ C^{22} - C^{23} \\ C^{23} - C^{24} \end{array}$	$\begin{array}{c} 1.485(4)\\ 1.407(3)\\ 1.407(3)\\ 1.506(5)\\ 1.426(3)\\ 1.374(2)\\ 1.383(3)\\ 1.384(3)\\ 1.366(2)\\ 1.373(2)\\ 0.85(1)\\ 1.385(3)\\ 1.370(3)\\ 1.378(3)\\ 1.374(3)\\ 1.367(3)\\ 1.381(3)\\ \end{array}$

Table 1. Valence bond lengths (d, A) in the structure of I^{a}

^a See note ^a to Table 5. The same for Tables 2-4.

Table 3. Selected torsion angles $(\tau, \text{ deg})$ in podand L in the structure of I

Angle	τ	Angle	τ
$H^{O1}O^1C^2C^3$	-170(1)	C ⁸ C ⁹ O ¹⁰ C ¹¹	-106(2)
$O^1 C^2 C^3 O^4$	1.3(2)	$C^9O^{10}C^{11}C^{12}$	-176.5(3)
$C^2C^3O^4C^5$	176.6(1)	$C^{9'}O^{10'}C^{11'}C^{12'}$	-154(1)
$C^{3}O^{4}C^{5}C^{6}$	179.7(1)	$O^{10}C^{11}C^{12}O^{13}$	60.0(5)
$O^4 C^5 C^6 O^7$	67.3(2)	$O^{10}C^{11}C^{12}O^{13}$	-55(2)
$C^{5}C^{6}O^{7}C^{8}$	168.9(2)	$C^{11}C^{12}O^{13}C^{14}$	151.3(2)
$C^{6}O^{7}C^{8}C^{9}$	179.3(2)	$C^{11}C^{12}O^{13}C^{14}$	-169.4(9)
$C^{6}O^{7}C^{8}C^{9}$	-176.0(7)	$C^{12}O^{13}C^{14}C^{15}$	163.7(3)
$O^7 C^8 C^9 O^{10}$	-66.3(3)	$C^{12}O^{13}C^{14}C^{15}$	176.4(8)
$O^7 C^8 C^{9'} O^{10'}$	-44(1)	O ¹³ C ¹⁴ C ¹⁵ O ¹⁶	-2.7(2)
C ⁸ C ⁹ O ¹⁰ C ¹¹	-178.1(3)	C ¹⁴ C ¹⁵ O ¹⁶ H ¹⁶	-160(1)

anion. The mean $C \\ \cdots C$ bond length in the two benzene rings is 1.379(5) Å, which is somewhat less than the statistical average value for C,H-substituted benzene rings, 1.384(13) Å [3].

In the crystal structure of I, the SCN⁻ anion is orientationally disordered as shown in the figure. Its N atom is ordered, i.e., it occupies one crystallographic

Table 2. Selected bond angles (0, deg) in the structure of I

Angle	d	Angle	d
$\begin{array}{c} S^{A}C^{A}N \\ S^{B}C^{B}N \\ H^{1}N^{1}H^{2} \\ H^{1}N^{1}H^{3} \\ H^{1}N^{1}H^{4} \\ H^{2}N^{1}H^{3} \\ H^{2}N^{1}H^{4} \\ H^{3}N^{1}H^{4} \\ H^{0}^{1}0^{1}C^{2} \\ O^{1}C^{2}C^{3} \\ O^{1}C^{2}C^{20} \\ C^{3}C^{2}C^{20} \\ C^{2}C^{3}O^{4} \\ C^{2}C^{3}C^{17} \\ O^{4}C^{3}C^{17} \\ C^{3}O^{4}C^{5} \\ O^{4}C^{5}C^{6} \\ C^{5}C^{6}O^{7} \\ C^{6}O^{7}C^{8} \\ O^{7}C^{8}C^{9} \end{array}$	$\begin{array}{c} 179.0(7) \\ 179.0(9) \\ 109(1) \\ 110(1) \\ 110(1) \\ 108(1) \\ 109(1) \\ 110(1) \\ 109(1) \\ 116.8(2) \\ 123.3(2) \\ 119.9(2) \\ 115.2(2) \\ 119.6(2) \\ 125.2(2) \\ 117.2(1) \\ 108.2(1) \\ 110.2(2) \\ 112.2(1) \\ 109.3(2) \end{array}$	$\begin{array}{c} C^8 C^9 O^{10} \\ C^9 O^{10} C^{11} \\ O^{10} C^{11} C^{12} \\ C^{11} C^{12} O^{13} \\ C^{12} O^{13} C^{14} \\ O^{13} C^{14} C^{15} \\ O^{13} C^{14} C^{24} \\ C^{15} C^{14} C^{24} \\ C^{14} C^{15} C^{11} \\ O^{16} C^{15} C^{21} \\ O^{16} C^{15} C^{21} \\ C^{15} O^{16} H^{16} \\ C^3 C^{17} C^{18} \\ C^{17} C^{18} C^{19} \\ C^{18} C^{19} C^{20} \\ C^2 C^{20} C^{19} \\ C^{15} C^{21} C^{22} \\ C^{21} C^{22} C^{23} \\ C^{22} C^{23} C^{24} \\ C^{14} C^{24} C^{23} \end{array}$	108.5(2) 110.7(2) 110.7(3) 108.4(3) 119.2(2) 115.1(2) 125.6(2) 119.3(2) 117.1(2) 120.0(2) 122.9(2) 109(1) 119.8(2) 120.7(2) 119.8(2) 120.2(2) 120.4(2) 120.1(2) 120.0(2) 120.2(2)
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Table 4. Geometric parameters of hydrogen bonds in the crystal structure of I^a

H bond X–H…Y	<i>d</i> (H…Y), Å	<i>d</i> (X⋯Y), Å	X−H…Y angle, deg
$N^1 - H^1 \cdots O^1$	2.07(1)	2.891(2)	151(2)
N^1 – H^1 ···· O^4	2.29(1)	3.001(2)	136(2)
$N^1 - H^2 \cdots O^7$	2.12(1)	2.926(2)	147(2)
N^1 – H^2 ···· O^{10}	2.24(1)	2.920(3)	131(2)
N^1 – H^2 ···O ¹⁰	2.28(3)	3.03(2)	138(3)
N^1 – H^3 ···· O^{13}	2.32(1)	3.075(2)	140(2)
N^1 – H^3 ···· O^{16}	2.10(1)	2.898(2)	145(2)
$N^1 - H^4 \cdots S^A$	2.52(1)	3.417(6)	170(1)
$N^1 - H^4 \cdots S^B$	2.51(1)	3.396(9)	166(2)
$O^1 - H^{O1} \cdots N$	1.96(1)	2.791(2)	164(2)
$O^{16}-H^{16}-N^*$	2.00(1)	2.837(2)	170(1)

^a The N atom related by the symmetry transformation (x, y - 1, z) is marked with an asterisk.

position, whereas the S and C atoms are disordered each over two close positions; S^A and S^B , and C^A and C^B , separated by the following distances: $S^A \dots S^B$ 0.30(2) and $C^A \dots C^B$ 0.12(2) Å. The disordered SCN⁻ anion in each of the two close orientations is almost linear, and the lengths of its covalent bonds are close to the average values for this anion.

In the crystal structure of **I**, the molecules of the complex $[NH_4(SCN)L]$ formed, as already noted, by hydrogen bonding exist not as isolated species but as infinite (along *y* axis) polymeric chains, which are also formed by hydrogen bonds but of a different type: between the hydrogen atoms of both OH groups of L and N atom of the SCN⁻ anion (see H bonds $O^1-H^{O1}...N^*$ and $O^{16}-H^{16}...N^*$ in the figure and in Table 4).

All the other short interatomic contacts between molecules of I in the crystal are close to, or slightly shorter than the sums of the corresponding van der Waals atomic radii.

EXPERIMENTAL

Complex I was prepared as follows. Podand L and ammonium thiocyanate NH_4SCN (molar ratio 1 : 1) were dissolved in an acetone–water mixture (5 : 1), and the solvent was allowed to evaporate until a crystalline precipitate formed. Colorless transparent crystals of I of X-ray quality were obtained by recrystallization of this precipitate from ethanol at room temperature.

The unit cell parameters and three-dimensional set of reflection intensities were obtained with an Enraf– Nonius CAD-4 autodiffractometer (Mo K_{α} radiation, graphite monochromator). Crystals of **I** are monoclinic: C₁₈H₂₂O₆·NH₄SCN, *M* 410.48; *a* 13.222(3), *b* 8.865(2), *c* 17.772(5) Å; β 93.98(2)°, *V* 2078.1(9) Å³, *Z* 4, d_{calc} 1.312 g cm⁻³, μ (Mo K_{α}) 1.93 cm⁻¹, space group *P*2₁/*n*.

The intensities of 3660 reflections were measured in the reciprocal space quadrant $(2\theta \le 48^{\circ})$ in the $\omega/2\theta$ scanning mode using a $0.15 \times 0.34 \times 1.00$ -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 exclusion of 256 systematically absent reflections and averaging of the intensities of 157 pairs of equivalent reflections 0kl and $0k\bar{l}$ (R_{int} 0.029), the working set of the measured $F^2(hkl)$ and $\sigma(F^2)$ consisted of 3247 unique reflections.

The structure of **I** was solved by the direct method using the SHELXS 97 program [5] and refined by the full-matrix least-squares method (with respect to F^2) using the SHELXL 97 program [5] in the approximation of anisotropic thermal vibrations of all nonhydrogen atoms. For the structure refinement, we used almost all the 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.

From the E synthesis (direct method), we revealed the disordered SCN⁻ anion and the ordered molecule of podand L. However, after anisotropic refinement of the ordered structure of I (taking into account all the hydrogen atoms), the detailed analysis of the peaks of the check differential electron density synthesis showed that the S and hence C atoms of the SCNanion are disordered each over two close positions A and B, and in podand L the atoms of its chain -CH₂-O¹⁰-CH₂-CH₂- are also disordered each over two relatively close positions considerably differing, however, in the occupancy (see above discussion). Then, when refining the parameters of all the atoms of **I**, we imposed soft equality conditions of the SADI and DFIX types [5] on the structurally equivalent 1,2 and 1,3 interatomic distances involving the disordered atoms. The total occupancies of the positions of the disordered atoms were also refined by the leastsquares method.

The four disordered hydrogen atoms of the NH_4^+ cation and almost all the hydrogen atoms of podand L were objectively localized in the intermediate differential electron density synthesis. Then, in the course of the least-squares refinement of the structure of I, the coordinates of almost all the hydrogen atoms of podand L (except the H^{O1} and H¹⁶ atoms of two OH groups), including those at the disordered carbon atoms, were calculated geometrically using the rider model [5], with the individual isotropic thermal parameters U_{iso} being refined. For the hydrogen atoms of the NH₄⁺ cation and for the H^{O1} and H¹⁶ atoms of podand L, the coordinates (and individual parameters U_{iso}) were refined by the least-squares method as for free atoms.

For the exposed crystal of **I**, we also refined by the least-squares method the isotropic extinction coefficient: $g \ 0.0019(5)$ [5]. In the last cycle of the full-matrix refinement of the structure of **I**, the absolute shifts of all the 354 varied parameters were less than 0.001σ . The final coordinates and thermal parameters of the atoms are listed in Tables 5 and 6.

The final *R* factors are as follows: *R*1 0.036 and wR_2 0.092 for 2500 observed reflections with $I \ge$

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Table 5. Coordinates $(\times 10^4)$ and equivalent isotropic thermal parameters $(\mathring{A}^2\times 10^3)$ of nonhydrogen atoms in the crystal structure of I^a

x	у	Z.	U _{eq} ^b
2348(4)	5176(4)	5638(3)	63(1)
2058(7)	6741(8)	5192(7)	52(4)
2122(8)	5117(7)	5636(4)	89(2)
1973(10)	6709(10)	5184(8)	59(6)
1869(2)	7837(2)	4877(1)	75.9(5)
2245(2)	2710(2)	4158(1)	54.6(5)
773(1)	349(1)	4337.8(7)	58.5(3)
-62(1)	49(2)	3869.1(9)	48.0(4)
-434(1)	1224(2)	3410(1)	49.5(4)
105.9(9)	2541(1)	3477.7(7)	55.6(3)
-214(1)	3752(2)	2988(1)	60.0(5)
468(2)	5061(2)	3161(1)	64.6(5)
1457(1)	4734(1)	2955.4(7)	58.5(3)
2085(2)	6036(2)	2975(1)	72.7(6)
3113(2)	5608(4)	2763(2)	68.6(6)
3558(2)	4656(2)	3327(1)	55.9(6)
4549(2)	4256(3)	3164(2)	62.0(8)
5001(3)	3161(3)	3741(3)	69(1)
3078(8)	5602(17)	2699(10)	69(6)
3468(10)	4230(15)	2995(10)	76(5)
4275(12)	4470(15)	3533(10)	86(6)
4979(10)	3130(14)	3585(12)	54(8)
4380.9(9)	1844(1)	3726.8(8)	62.8(4)
4814(1)	478(2)	3924(1)	50.9(4)
4139(1)	-647(2)	4087.1(9)	47.9(4)
3136.2(9)	-265(1)	4065.7(8)	58.1(4)
-1277(1)	991(2)	2922(1)	65.8(5)
-1730(2)	-419(3)	2880(1)	76.8(6)
-1366(2)	-1575(3)	3333(1)	71.1(6)
-538(1)	-1340(2)	3833(1)	58.8(5)
4486(1)	-2072(2)	4263(1)	57.2(5)
5506(2)	-2387(2)	4287(1)	65.6(5)
6182(2)	-1279(2)	4138(1)	68.2(6)
5841(1)	156(2)	3954(1)	63.0(5)
	x 2348(4) 2058(7) 2122(8) 1973(10) 1869(2) 2245(2) 773(1) -62(1) -434(1) 105.9(9) -214(1) 468(2) 1457(1) 2085(2) 3113(2) 3558(2) 4549(2) 5001(3) 3078(8) 3468(10) 4275(12) 4979(10) 4380.9(9) 4814(1) 4139(1) 3136.2(9) -1277(1) -1730(2) -1366(2) -538(1) 4486(1) 5506(2) 6182(2) 5841(1)	x y 2348(4)5176(4)2058(7)6741(8)2122(8)5117(7)1973(10)6709(10)1869(2)7837(2)2245(2)2710(2)773(1)349(1)-62(1)49(2)-434(1)1224(2)105.9(9)2541(1)-214(1)3752(2)468(2)5061(2)1457(1)4734(1)2085(2)6036(2)3113(2)5608(4)3558(2)4656(2)4549(2)4256(3)5001(3)3161(3)3078(8)5602(17)3468(10)4230(15)4275(12)4470(15)4979(10)3130(14)4380.9(9)1844(1)4139(1)-647(2)3136.2(9)-265(1)-1277(1)991(2)-1730(2)-419(3)-1366(2)-1575(3)-538(1)-1340(2)4486(1)-2072(2)5506(2)-2387(2)6182(2)-1279(2)5841(1)156(2)	x y z 2348(4)5176(4)5638(3)2058(7)6741(8)5192(7)2122(8)5117(7)5636(4)1973(10)6709(10)5184(8)1869(2)7837(2)4877(1)2245(2)2710(2)4158(1)773(1)349(1)4337.8(7)-62(1)49(2)3869.1(9)-434(1)1224(2)3410(1)105.9(9)2541(1)3477.7(7)-214(1)3752(2)2988(1)468(2)5061(2)3161(1)1457(1)4734(1)2955.4(7)2085(2)6036(2)2975(1)3113(2)5608(4)2763(2)3558(2)4656(2)3327(1)4549(2)4256(3)3164(2)5001(3)3161(3)3741(3)3078(8)5602(17)2699(10)3468(10)4230(15)2995(10)4275(12)4470(15)3533(10)4979(10)3130(14)3585(12)4380.9(9)1844(1)3726.8(8)4814(1)478(2)3924(1)4139(1)-647(2)4087.1(9)3136.2(9)-265(1)4065.7(8)-1277(1)991(2)2922(1)-1730(2)-419(3)2880(1)-1366(2)-1575(3)3333(1)-538(1)-1340(2)3833(1)4486(1)-2072(2)4263(1)5506(2)-2387(2)4287(1)6182(2)-1279(2)4138(1)5841(1)156(2)3954(1)

The occupancies of the positions of the disordered atoms are as follows: 0.57(4) for S^A and C^A and 0.43(4) for S^B and C^B;

0.885(5) for C⁹, O¹⁰, C¹¹, C¹², and hydrogen atoms bonded

to them and 0.115(5) for $C^9,\,O^{10},\,C^{11},\,C^{12},$ and hydrogen

atoms bonded to them. ^b The U_{eq} values were calculated as

 $2\sigma(I)$; R1 0.050 and wR2 0.139 for all the 3247

unique measured reflections; goodness of fit S 1.05

(for the definitions of wR2 and S, see [5]). In the final

differential electron density synthesis, $-0.14 < \Delta \rho < 0.17$ e Å⁻³. The *f* curves and anomalous-dispersion

corrections to them ($\Delta f'$ and $\Delta f''$) were taken from the

International Tables [6].

1/3 of the trace of the orthogonalized U_{ij} tensor.

Table 6. Coordinates (×10³) and isotropic thermal parameters (Å² × 10³) of hydrogen atoms in the crystal structure of I^a

Atom	x	у	z	U _{iso}
H^{1}	164(1)	222(2)	413(1)	117(11)
H^2	227(2)	333(2)	375(1)	132(12)
H ³	276(1)	203(2)	415(1)	124(11)
H^4	232(1)	328(2)	458(1)	88(8)
H^{O1}	100(1)	-47(2)	454(1)	61(6)
H^{16}	282(1)	-91(2)	432(1)	65(6)
$H^{5.1}$	-91	402	307	76(7)
H ^{5.2}	-18	345	247	66(6)
$H^{6.1}$	21	594	289	83(7)
H ^{6.2}	49	529	370	79(7)
$H^{8.1}$	213	647	348	85(7)
$H^{8.2}$	180	679	263	90(7)
$H^{9.1}$	307	509	228	76(8)
$H^{9.2}$	353	650	272	76(7)
$H^{11.1}$	497	516	316	64(6)
$H^{11.2}$	454	380	267	65(7)
$H^{12.1}$	569	290	363	79(8)
$H^{12.2}$	503	362	424	80(9)
${ m H}^{17}$	-155	179	262	74(6)
H^{18}	-230	-58	253	99(8)
H^{19}	-168	-254	330	82(7)
H^{20}	-29	-214	415	62(5)
H^{21}	402	-285	437	64(6)
H^{22}	574	-338	441	75(6)
H ²³	689	-150	416	69(6)
H ²⁴	631	92	385	76(6)

^a The numbering of the hydrogen atoms (except H^1-H^4) corresponds to the numbering of the nonhydrogen atoms to which they are bonded. See also note ^a to Table 5.

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