Synthesis and crystal structure of cyclotris-(4,4′-thiodiphenylene ketone)

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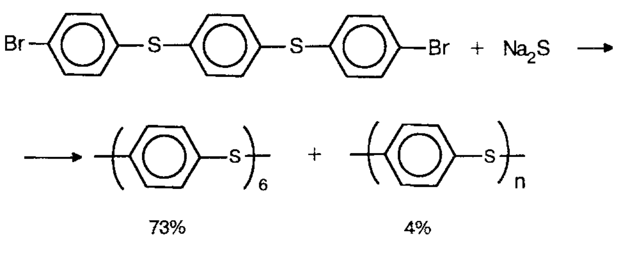
The side reaction of macrocyclization that occurs during the synthesis of poly-(1,4-phenylenesulfide ketone) by polycondensation of a 4,4′-dihalobenzophenone with sodium sulfide was studied. It was found that the major product of this reaction is a cyclic trimer, cyclotris-(4,4′-thiodiphenylene ketone) (**1**). Despite the fact that ketone bridges are more rigid than sulfide bridges, the yield of the macrocycle is rather high, as it is in the synthesis of poly-(1,4-phenylenesulfide), and reaches 20% under high dilution conditions. The structure of **1** was investigated by X-ray diffraction analysis (R = 0.069 on 3138 reflections). Macrocycle **1** is strongly flattened in the crystal; the conformation observed is determined by the packing, since stereochemical analysis indicates high flexibility of the macrocycle. The solvate acetone molecules incorporated in the crystal are disordered, nevertheless, they are strongly fixed in the cavities and channels of the crystal structure.

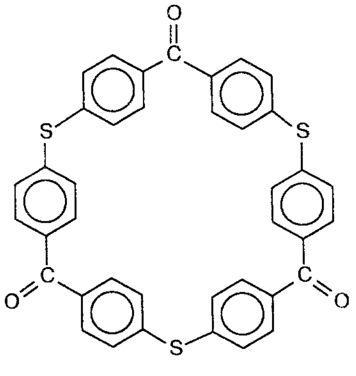
Key words: synthesis, macrocyclic thiophenylene ketone, crystal structure.

Macrocyclic phenylene sulfides (MPS) of the general formula $(C_6H_4{-}S)_n$ represent a novel class of crown thioethers. The diversity of observed conformations of these macrocycles when $n \geq 5$ indicates that there are no noticeable steric strains,[1–3] which is due to the high flexibility of the sulfide linkages and favors macrocyclization processes.[4,5] In particular, MPS are by-products of the synthesis of linear high-molecular weight polyphenylene sulfides by polycondensation of various dihalobenzenes with sodium sulfide or dithiophenoxides. The relative role of macrocyclization in these processes is so great that under certain conditions, macrocycles may be the major reaction products,[6] for example:



The nominal rigidity of a ketone bridge is 1/3 of that of a 1,4-phenylene fragment, and the rigidity of an ether bond is close to zero.[7] For this reason we expected that the use of binuclear 4,4′-dihalobenzophenone, rather than 1,4-dichlorobenzene, for polycondensation with sodium sulfide in the synthesis of heat-resistant aromatic poly(ketone sulfides) would considerably hamper macrocyclization.

The polycondensation of equimolar amounts of 4,4′-difluorobenzophenone and Na_2S (concentration of the starting monomers was 1 mol L^{-1}) carried out by us at 285°C yielded, apart from the linear high-molecular poly-4,4′-thiodiphenylene ketone soluble in conc. H_2SO_4, a low-molecular-weight product (~5 %) soluble in CH_2Cl_2. According to elemental and mass spectroscopic analyses, the latter contained, along with linear halogen-containing oligomers, a macrocyclic fraction, which we managed to isolate in 38 % yield (of the overall low-molecular-weight products) by recrystallization from acetone as light-yellow crystals of compound **1**, which did not melt up to 350°C. The composition of these crystals corresponds to that of an elementary unit of poly-4,4′-thiodiphenylene ketone. Found (%): C, 72.33; H, 3.74; S, 14.87. $C_{13}H_8OS$. Calculated (%): C, 73.55; H, 3.81; S, 15.10. Based on the data of mass



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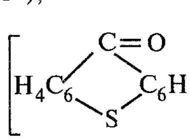
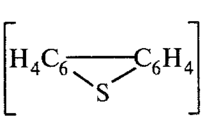
spectrometry, compound **1** was identified as the previously unknown cyclotris-(4,4′-thiodiphenylene ketone).

The mass spectrum of compound **1** [(EI, 70 eV), *m/z* (I_{rel}(%)] contains the molecular ion peak, 636 $[M]^+$ (100), and the peaks of its fragmentation products: 608 $[M^+-CO]$ (6), 348 $[M^+-C_6H_4S-C_6H_4-C(O)-C_6H_4-]$ (4), 316 $[M^+-C_6H_4-S-C_6H_4-C(O)-C_6H_4-S]$ (10),

212  (14), 184  (21),

136 $[-S-C_6H_4-C(O)-]$ (7), 108 $[-C_6H_4S-]$ (10). The IR spectrum of **1** (KBr, ν/cm^{-1}) is identical to that of the linear polymer and exhibits absorption bands at 1660 (C=O), 1085 (S—Ar), 1590, 1490, 1400, and 840 (deformation vibrations of the benzene rings).

Later we found that the proportion of the low-molecular-weight fraction can be increased to 20 % by conducting the polycondensation of 4,4′-dichlorobenzophenone in a highly dilute solution in N-methylpyrrolidone (with a concentration of monomers of 0.1 *M*). The macrocyclic compound **1** constitutes the major part of this fraction. Thus, contrary to expectations, the processes of macrocyclization are not substantially suppressed by the introduction of ketone groups into the monomers and thus to the growing polymer chain. To elucidate the possible relationship of this fact with the characteristic features of the molecular structure of macrocycle **1**, we carried out an X-ray structural study of this compound.

Experimental

Cyclotris-(4,4′-thiodoiphenylene ketone) (1). A mixture of $Na_2S \cdot 5.64\ H_2O$ (34.13 g, 0.19 mol) and 4,4′-dichlorobenzophenone (47.68 g, 0.19 mol) in 1.9 L of *N*-methylpyrrolidone was stirred in an argon flow at 200 °C for 16 h. The reaction mixture was poured into 2.0 L of water, the resulting mixture was acidified with HCl to pH ≈ 5, and the precipitate was filtered off, dried at 150 °C, and extracted with dichloromethane in a Sohxlet apparatus for 16 h. After evaporation of CH_2Cl_2, the solid residue (7.8 g) was additionally extracted with acetone for 16 h. Evaporation of acetone afforded 3.02 g of compound **1**.

The X-ray diffraction experiment initially carried out at room temperature gave a quite unsufficient number of observed ($I > 2\sigma$) reflections owing to a strong decrease in the reflectivity of the crystal at $2\theta > 40°$. Therefore, the experiment was repeated at 140 K. The main crystal structure data of compound **1** at 140 and 293 K and the parameters of the X-ray diffraction experiment are summarized in Table 1. The structure at 293 K (referred to below as structure **1a**) was refined with constrained equalization of the lengths of chemically equivalent bonds and fixation of the positional and thermal parameters of the atoms of the solvate molecules at the final stages. In view of the low accuracy of the results obtained, the coordinates of the atoms in structure **1a** are not presented, and only the general characteristics of this structure are used in the discussion. The structure at 140 K (structure **1**) was solved by the direct method and refined by the block-diagonal least-squares method in the anisotropic approximation for nonhydrogen atoms. The H atoms of the aryl groups localized by the difference synthesis were included in the refinement according to the rigid model (fixed C—H distances and thermal parameters $U = 0.08$ Å^2). The peaks of the electron density associated with atoms of the solvate acetone molecules were specified as C atoms with the populations corresponding to the accepted model of disorder for the first molecule (see below) and somewhat arbitrarily (0.25—0.5) for the second molecule, for which we could not obtain a model of disorder. Atoms of the solvate molecules were refined isotropically, and their H atoms were not located. The coordinates of the atoms in structure **1** are listed in Table 2; the calculations were carried out on an IBM PC/AT computer.

Results and Discussion

The bond lengths and angles in molecule **1** (Table 3) are close to the values obtained for molecules built of

Table 1. The main crystal structure data and characteristics of the X-ray diffraction experiment for compound **1**

T/K	140	293
Diffractometer	Siemens P3/PC	Siemens P3/PC
Radiation, scanning, $2\theta_{max}$	λMo, θ/2θ, 50°	λMo, θ/2θ, 40°
a/Å	9.469(3)	9.630(5)
b/Å	18.474(5)	18.661(9)
c/Å	20.663(7)	20.711(10)
β/deg	97.40(2)	97.48(4)
V/Å^3	3585(4)	3691(7)
$Z(C_{39}H_{24}O_3S_3 \cdot 1.5C_3H_6O)$	4	4
d_{calc}/g cm^{-3}	1.341	1.303
Space group	$P2_1/n$	$P2_1/n$
The number of reflections in the least-squares method	3138($I > 2\sigma$)	1743($I > 3\sigma$)
$R(R_w)$	0.069(0.069)	0.085(0.077)
The set of programs	SHELXTL PLUS[8]	SHELXTL PLUS

analogous fragments.[1–3, 9–12] However, the conformation of the molecule in the crystal (Fig. 1) possesses some peculiarities that distinguish it from the abovementioned series. Table 4 presents the values of the pseudotorsion angles determining the general shape of the molecule (S(1)...C(1)...S(2)...C(2) and analogous angles) as well as the CSCC torsion angles describing the orientation of the benzene rings in molecule **1** and related molecules (both macrocyclic and acyclic). The large spread in these values in the structures of individual compounds and between them suggests high flexibility of these molecules.

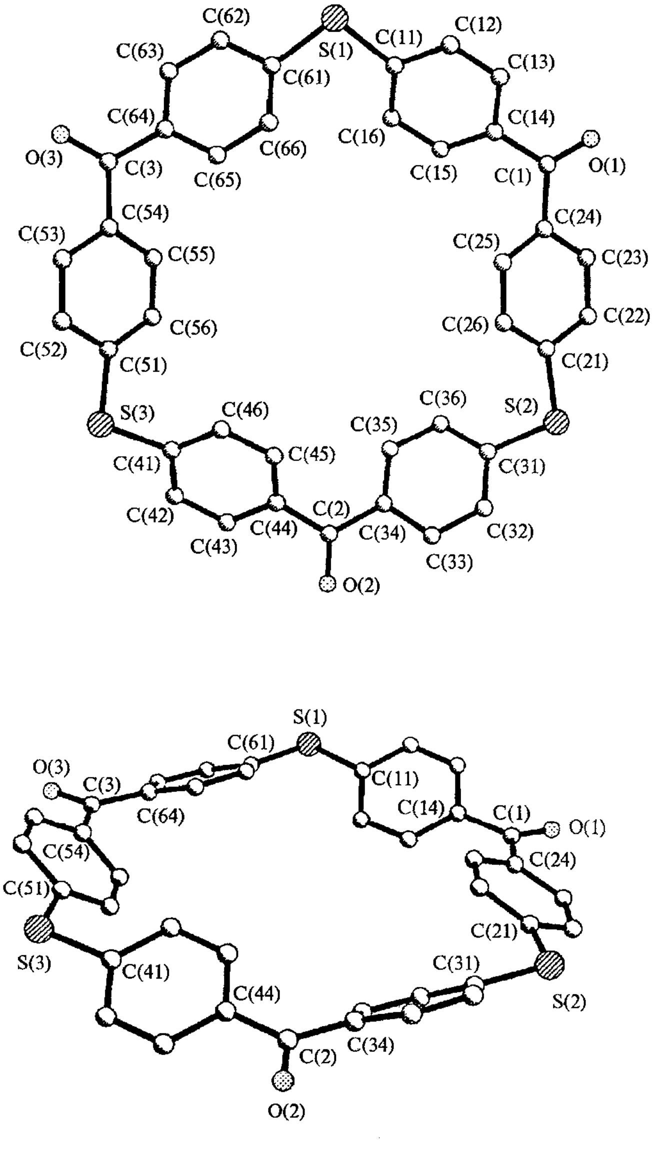


Fig. 1. The general view of molecule **1** in the crystal; projection onto the mean plane of the macrocycle and the perspective projection. The H atoms are not shown.

Table 2. The coordinates of the atoms ($\times 10^4$) and their thermal parameters ($\times 10^3$/Å^2) in structure **1**

Atom	x	y	z	U_{eq} (U_{iso})
S(1)	4122(3)	−1822(1)	7068(1)	36(1)
S(2)	2385(3)	469(1)	2241(1)	36(1)
S(3)	−2040(3)	3004(1)	6176(1)	47(1)
O(1)	5964(7)	−2101(4)	4052(3)	55(3)
O(2)	−1253(6)	3404(3)	3032(3)	38(2)
O(3)	756(6)	771(3)	8554(3)	41(2)
C(1)	5188(9)	−1646(5)	4240(4)	34(3)
C(2)	−758(9)	2911(5)	3389(4)	32(3)
C(3)	899(9)	739(4)	7972(4)	34(3)
C(11)	4349(8)	−1722(4)	6245(4)	23(2)
C(12)	4548(9)	−2357(4)	5899(4)	30(3)
C(13)	4819(9)	−2326(5)	5259(4)	36(3)
C(14)	4881(9)	−1662(4)	4937(4)	34(3)
C(15)	4737(8)	−1042(4)	5292(4)	25(3)
C(16)	4507(8)	−1050(4)	5941(4)	24(2)
C(21)	3165(8)	−94(4)	2884(4)	27(3)
C(22)	4367(9)	−476(4)	2750(4)	31(3)
C(23)	4980(9)	−968(4)	3199(4)	32(3)
C(24)	4456(9)	−1096(4)	3792(4)	30(3)
C(25)	3253(8)	−712(4)	3907(4)	27(3)
C(26)	2596(8)	−226(4)	3463(4)	26(3)
C(31)	1511(8)	1181(4)	2616(4)	23(2)
C(32)	361(8)	1501(4)	2241(4)	30(3)
C(33)	−362(8)	2071(4)	2493(3)	26(2)
C(34)	75(8)	2316(4)	3130(4)	22(2)
C(35)	1253(8)	2007(4)	3491(4)	28(3)
C(36)	2002(9)	1455(4)	3234(4)	31(3)
C(41)	−1526(9)	2930(5)	5389(4)	33(3)
C(42)	−1562(11)	3565(5)	5035(4)	48(4)
C(43)	−1278(11)	3554(4)	4387(4)	48(4)
C(44)	−958(9)	2909(4)	4094(4)	33(3)
C(45)	−919(8)	2279(5)	4461(4)	31(3)
C(46)	−1223(8)	2278(4)	5105(4)	29(3)
C(51)	−1125(9)	2312(4)	6655(4)	29(3)
C(52)	−1794(9)	2054(4)	7176(4)	30(3)
C(53)	−1107(8)	1557(4)	7600(4)	29(3)
C(54)	216(8)	1284(4)	7507(4)	30(3)
C(55)	887(8)	1553(4)	6989(4)	29(3)
C(56)	242(8)	2069(5)	6577(4)	33(3)
C(61)	3205(9)	−1036(4)	7279(4)	31(3)
C(62)	3462(9)	−827(4)	7937(4)	30(3)
C(63)	2703(9)	−252(4)	8147(4)	31(3)
C(64)	1726(9)	136(4)	7726(4)	28(3)
C(65)	1489(8)	−86(4)	7068(4)	27(3)
C(66)	2184(8)	−679(4)	6855(4)	28(3)
*C(71)^a	−330(34)	−268(15)	4951(16)	91(9)
C(72)^b	910(40)	−512(20)	5146(17)	122(11)
C(73)^a	−1635(33)	−621(17)	4766(14)	99(9)
C(74)^c	47(53)	−384(27)	5604(25)	97(15)
C(81)^a	−7449(41)	4080(21)	4267(19)	123(12)
C(82)^a	−7576(28)	3539(15)	5385(13)	82(8)
C(83)^a	−8141(49)	4608(26)	5021(21)	119(14)
C(84)^d	−4885(108)	4426(55)	5641(46)	131(30)
C(85)^d	−4301(87)	4857(50)	5521(40)	112(22)
C(86)^d	−8238(59)	4442(31)	4238(26)	80(15)
C(87)^d	−5067(149)	4476(63)	5220(63)	177(42)
C(88)^a	−8770(38)	4687(19)	5153(17)	96(11)
C(89)^d	−5905(86)	4136(39)	5477(38)	118(23)
C(90)^d	−6223(117)	4699(65)	4793(58)	182(38)
C(91)^a	−7644(51)	4152(28)	4934(24)	156(17)

* Solvate molecules. The populations of the positions: *a*, 0.5; *b*, 0.6; *c*, 0.4; *d*, 0.25.

Table 3. The main bond lengths (Å) and angles (deg.) in molecule **1**

Bond	*d*	Angle	φ	Angle	φ
S(1)—C(11)	1.753(8)	C(11)S(1)C(61)	106.1(4)	S(3)C(41)C(42)	115.6(7)
S(1)—C(61)	1.774(8)	C(21)S(2)C(31)	106.3(4)	S(3)C(41)C(46)	123.7(6)
S(2)—C(21)	1.771(8)	C(41)S(3)C(51)	106.7(4)	S(3)C(51)C(52)	116.0(6)
S(2)—C(31)	1.782(8)	O(1)C(1)C(14)	119.5(7)	S(3)C(51)C(56)	124.0(6)
S(3)—C(41)	1.761(8)	O(1)C(1)C(24)	122.0(8)	S(1)C(61)C(62)	115.7(6)
S(3)—C(51)	1.774(8)	C(14)C(1)C(24)	118.4(7)	S(1)C(61)C(66)	124.0(6)
O(1)—C(1)	1.21(1)	O(2)C(2)C(34)	120.7(7)	C(1)C(14)C(13)	119.8(7)
O(2)—C(2)	1.23(1)	O(2)C(2)C(44)	120.1(7)	C(1)C(14)C(15)	122.6(7)
O(3)—C(3)	1.23(1)	C(34)C(2)C(44)	119.2(7)	C(1)C(24)C(23)	118.1(7)
C(1)—C(14)	1.51(1)	O(3)C(3)C(54)	120.5(8)	C(1)C(24)C(25)	124.8(7)
C(1)—C(24)	1.49(1)	O(3)C(3)C(64)	119.9(7)	C(2)C(34)C(33)	117.9(6)
C(2)—C(34)	1.49(1)	C(54)C(3)C(64)	119.6(7)	C(2)C(34)C(35)	122.5(7)
C(2)—C(44)	1.49(1)	S(1)C(11)C(12)	116.7(6)	C(2)C(44)C(43)	119.1(7)
C(3)—C(54)	1.48(1)	S(1)C(11)C(16)	124.0(6)	C(2)C(44)C(45)	122.5(7)
C(3)—C(64)	1.49(1)	S(2)C(21)C(22)	114.8(6)	C(3)C(54)C(53)	119.0(7)
C—C(Ar)	1.37—1.41(1)	S(2)C(21)C(26)	125.2(6)	C(3)C(54)C(55)	122.2(7)
		S(2)C(31)C(32)	116.7(6)	C(3)C(64)C(63)	120.8(7)
		S(2)C(31)C(36)	123.1(6)	C(3)C(64)C(65)	121.4(7)
				CCC(Ar)	117.1—123.0(7)

Table 4. The values of pseudotorsion and torsion angles (deg.) determining the conformation of molecule **1** and related molecules

Molecule	Angle			
	S...S...S...S (S...C(O)...S...C(O))	CSCC	CC(O)CC	min($\tau_1+\tau_2$)
1	10—13	31—35	17—40	65(CSCC) 58(CC(O)CC)
$(SC_6H_4)_5$[3]	4—33	4—78	—	74
$(SC_6H_4)_6$[1]	64—66	20—95	—	74
$(SC_6H_4)_7$[2]	13—116	3—96	—	70
$(SC_6H_4)_8$[2]	48, 71	21—79	—	78
SPh_2[9]	—	56	—	112
$S(C_6H_4SH)_2$[10]	—	4, 62	—	66
$PhSC_6H_4SPh$[11]	—	15, 59	—	74
$(PhOC_6H_4C(O)C_6H_4)_2$[12]	—	—	29, 32	61

Macrocycles with even *n* values tend to be located on the crystallographic symmetry elements. Molecule **1** is substantially flattened in the crystal, not only compared with its structural analog, $(SC_6H_4)_6$, which may be due to the fact that the CC(O)C angles are much greater than the CSC angles, but also compared with the pentamer $(SC_6H_4)_5$ in which the average decrease in the CSC endocyclic bond angle with respect to the planar configuration is approximately the same as in molecule **1**. This implies that the general shapes of molecule **1** and related MPS molecules are strongly affected by intermolecular interactions. The orientation of the benzene rings depends on the effects of packing to an even greater extent.

In fact, the only steric restrictions on the rotation of the rings around the S...S (S—C) axes are contacts between C—H groups like C(16)...C(66) in **1**. As follows from Table 5, C...C and C...H repulsions are the main steric factor (the H...H distances are more than twice the van der Waals radius of hydrogen, 2.4 Å).[13] The authors of Refs 14 and 15 point to the fact that the lone electron pairs (LEP) of S atoms may be involved in the steric interactions. However, judging by the relatively uniform distribution of the CSCC torsion angles (some of them are close to zero) observed in the structures in question, this type of interaction is not of much importance, and neither are the effects of conjugation between LEP and the benzene π-systems. Replacement of the S atoms by C=O groups probably introduces an additional steric restriction, since a planar conformation of the O=C—C_6H_4 fragment is unfavorable (it involves an O...H contact of 2.52 Å, which is ~0.2 Å shorter than the sum of the van der Waals radii): structures incorporating these fragments contain no OCCC torsion angles less than 11°. However, the general conformational behavior of the $C_6H_4SC_6H_4$ and $C_6H_4C(O)C_6H_4$ fragments is similar:

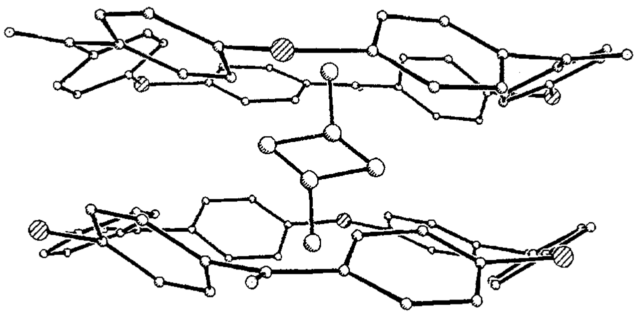


Fig. 2. A disordered acetone molecule in a cavity between macrocycles **1**; its two most populated orientations are shown.

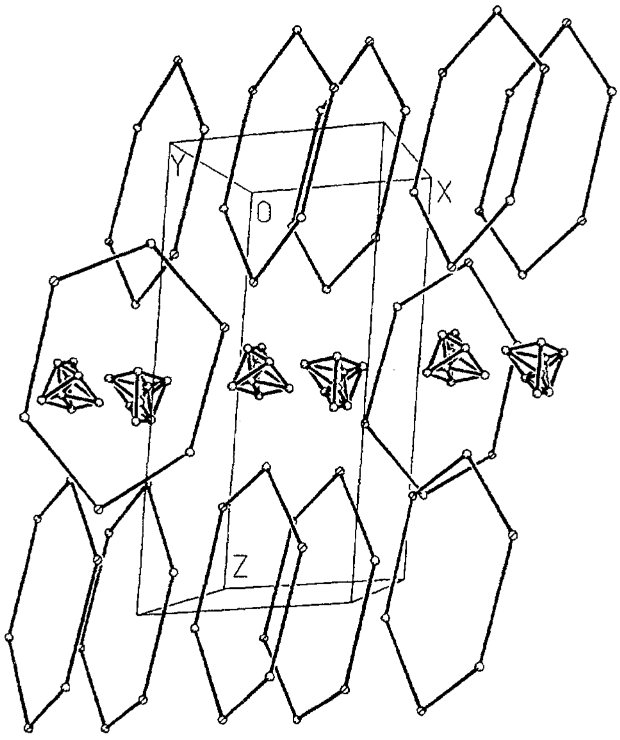


Fig. 3. Strongly disordered solvate molecules in the channels of the crystal structure of **1** stretched along the *x* axis. Molecules **1** are shown schematically (only the S atoms and the C atoms of the carbonyl groups).

the sums of the CSCC or CC(O)CC "endocyclic" torsion angles ($\tau_1 + \tau_2$) have minima corresponding to close contact of the neighboring benzene rings (Table 4). A conformational calculation of the $(SC_6H_4)_n$ polymeric chain directly confirms this conclusion:[14] the energy minima on the (τ_1, τ_2) conformational map are slit-shaped and stretch along the lines where $\tau_1 + \tau_2$ = const; the very steep slopes of these minima are stretched in the same direction.

Table 5. The interatomic non-bonded contacts (*d*/Å) determining the conformation and the ($\tau_1+\tau_2$/deg.) sums in the $C_6H_4SC_6H_4$ and $C_6H_4C(O)C_6H_4$ fragments in molecule **1**

Distance	*d*	$\|\tau_1+\tau_2\|$
C(15)...C(25)	3.08	
C(15)...H(25)	2.69	
C(25)...H(15)	2.81	58(CC(O)CC)
H(15)...H(25)	2.58	
C(26)...C(36)	3.18	
C(26)...H(36)	2.80	
C(36)...H(26)	2.81	65(CSCC)
H(26)...H(36)	2.66	
C(35)...C(45)	3.09	
C(35)...H(45)	2.57	
C(45)...H(35)	2.80	62(CC(O)CC)
H(35)...H(45)	2.46	
C(46)...C(56)	3.20	
C(46)...H(56)	2.78	
C(56)...H(46)	2.84	67(CSCC)
H(46)...H(56)	2.64	
C(55)...C(65)	3.08	
C(55)...H(65)	2.65	
C(65)...H(55)	2.73	62(CC(O)CC)
H(55)...H(65)	2.47	
C(16)...C(66)	3.15	
C(16)...H(66)	2.68	
C(66)...H(16)	2.81	66(CSCC)
H(16)...H(66)	2.58	

The minimum ($\tau_1 + \tau_2$) values are actually achieved or almost achieved in all of the fragments of molecule **1**, as indicated by the corresponding interatomic distances and by the closeness of the values of this sum (Table 5). In the molecules of MPS $(SC_6H_4)_n$ having a more "free" conformation, the minimum ($\tau_1 + \tau_2$) values exceed those observed in molecule **1** by 5—13°.[1–3] Molecule **1**, existing in the crystal in a chair-like conformation flattened as much as possible, possesses high noncrystallographic symmetry C_{3v}, fulfilled for almost all of the pertinent torsion angles with an accuracy of ±2°, and a less precise D_{3d} symmetry distorted due to the discrepancy between the stereochemical parameters of the S atom and the C=O group. It is of interest that the more uniform macrocycle, $(SC_6H_4)_6$, is much less symmetrical in the crystal, though it is located at the crystallographic inversion center.

The mutual stipulation of the conformation of molecules **1** and their packing is beyond question. The crystal of **1** is built of centrosymmetrical pairs of molecules, brought ultimately closely to each other, so that the distance between the mean planes of the macrocycles (actually equal to the distance between their centers) is 3.82 Å, which is only slightly greater than the doubled van der Waals radii of the C and S atoms. The vacant space thus formed near the (0 0 1/2) crystallographic inversion center is filled with disordered acetone molecules (Fig. 2). These molecules also fill the channels stretched along the *x* axis in the stack-type packing of molecules **1** (Fig. 3). The observed geometry of the arrangement of the atoms of the solvate molecule in the cavity makes it possible to propose a model of its disorder; we did not manage to obtain such a model for solvate molecules in the channels. Despite the fact that the solvate molecules of acetone are strongly disordered, the stability of crystals of **1** attests to strong interaction between these molecules and molecules **1**, and the packing as a whole suggests a substantial role of the solvate molecules in its formation.*

The data on the structure at 293 K (**1a**) complement the conclusions made above. As one could expect, at higher temperatures the symmetry of the macrocycle is somewhat higher: its general configuration is even more planar (the average S...C(O)...S...C(O) pseudotorsion angle is 10°, which is 2° smaller than that at 140 K), and the τ_1 and τ_2 values related to the same fragment of the CC(O)CC torsion angles differ, on average, by 13° (at 140 K, by 17°). The distance between the planes of the pairs of molecules brought together in structure **1a** is 0.12 Å greater than that obtained at 140 K. This increase ensures almost the whole thermal expansion of the crystal along this direction; the values of the "local" linear expansion of the "sandwich" composed of two closely spaced molecules (3.1 %) is greater than the average value for the crystal (1.1 %) by a factor of almost 3 and is twice as great as the expansion along the crystallographic axes (1.7 % along the *x* axis). Hence it follows that the "molecule **1**—acetone—molecule **1**" system has a very soft intermolecular potential with a strong anharmonicity. It is of interest that the similar expansion in the directions perpendicular to the channels with solvate molecules is small. This is probably due to the fact that the size of the cavities in the "sandwich" pairs is determined to a considerable extent by the geometry of molecules **1**, whereas the geometry of the channels depends essentially on the mode of the inclusion of the acetone molecules into them.

Thus, the data of the X-ray structural investigation of compound **1** and related compounds indicate high flexibility and, therefore, lack of strain in this macrocycle, which accounts for the ease of its formation on polycondensation.

In addition, the above analysis proves that the hypothesis[14] that assumes that the asymmetry of the CSCC torsion angles (τ_1 and τ_2) observed in acyclic oligomers $(SC_6H_4)_n$ is caused by intramolecular interactions and may be to some extent extrapolated to the polymeric chain in the crystalline poly(1,4-phenylene sulfide), is poorly justified. The results of an X-ray diffraction study of this polymer,[16] according to which the benzene rings are rotated 45° with respect to the S...S...S plane, are not in contradiction with the calculation,[14] since this conformation falls within the region of the $\tau_1+\tau_2 \approx 90°$ energy minimum. However, symmetrization of the τ_1 and τ_2 values in the polymer is most likely due to the fact that the more symmetric conformation has a lower entropy component of the free energy of the crystal. Of course, the foregoing is also valid for chain polymers with $C(O)C_6H_4$ units: in the general case, only oligomers with sufficiently long chains may serve as adequate models of their structure.

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* According to preliminary data, compound **1** can also crystallize without inclusions, of course, with a different packing of the molecules