Isolation and Structural Characterization of the Macrocyclic Dimer Present in Bisphenol-A Polysulfone

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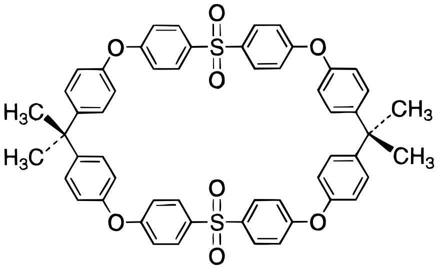
Introduction

The aromatic polysulfone [-OArCMe$_2$ArOArSO$_2$Ar-]$_n$ (Ar = 1,4-C$_6$H$_4$) is well established as an amorphous engineering thermoplastic, synthesized industrially by nucleophilic polycondensation of 4,4′-dichlorodiphenyl sulfone with bisphenol-A.[1] The commercial polymer, hereafter referred to simply as “polysulfone”, has long been known to contain a significant proportion (up to about 0.5 wt %) of cyclic [2 + 2] dimer (**1**).[2,3]



1

This macrocyclic oligomer crystallizes slowly from solutions of polysulfone in dipolar aprotic solvents such as dimethylformamide (DMF) or dimethylacetamide (DMAc), posing a significant problem in solvent-based polymer fabrication processes, such as the casting of ultrafiltration membranes.[4] The initial solubility, crystallization, and subsequent insolubility of the cyclic dimer **1** suggest that the compound must be present in granulated polysulfone, not as a discrete crystalline phase, but rather as a solid solution produced during melt-extrusion of the commercial polymer. The cyclic dimer deposits as a hard crystalline scale on the walls of solution storage vessels, and this scale, once formed, is highly intractable, being insoluble in conventional organic solvents and showing no melting point up to at least 430 °C.[4]

In a recent paper reporting a targeted synthesis of the cyclic dimer,[5] Ganguly and Gibson speculate that the variations in solubility they observe for this oligomer may stem from its potential ability to thread (reversibly) onto linear polysulfone to give more soluble rotaxane-type structures. We have recently succeeded in isolating the cyclic dimer in single crystal form as a DMAc solvate, and here we report the crystal and molecular structure of the macrocycle. Our results not only provide a definitive geometric description of the cyclic oligomer (and demonstrate an obvious potential for rotaxane formation) but also clear up a number of inconsistencies in the somewhat confused literature regarding this material.[2−5]

Results and Discussion

Crude cyclic dimer scale was obtained by scraping the internal surfaces of an industrial vessel previously used to store DMF-based casting solutions of Udel-3500 polysulfone, Alpharetta, GA.[1] Although insoluble in conventional organic solvents at room temperature, the recovered scale was found to have significant solubility in a 1:1 (v/v) mixture of trifluoroacetic acid and dichloromethane-d_2. Analysis by ^{13}C NMR indicated that the material contained cyclic dimer and linear polysulfone in a ratio of some 4:1 by weight. Recrystallization of the crude macrocycle from a mixture of 1,2,4-trichlorobenzene and DMAc led, on cooling, to slow growth of well-formed single crystals, which proved to consist of polymer-free cyclic dimer containing DMAc of crystallization. Washing the crystals with acetone, or simply allowing them to stand in air for several days, resulted in partial loss of DMAc. The differential scanning calorimetry (DSC) thermogram of a recrystallized sample showed three principal features, a solvent loss endotherm (confirmed by thermogravimetric analysis, TGA) centered at 208 °C (ΔH = 53 J/g), a very strong, sharp crystal melting endotherm (confirmed by visual observation) at 505 °C (ΔH = 123 J/g), and, at 530 °C, the onset of an endotherm which coincides with the decomposition point determined by TGA.[5] Earlier DSC studies of this oligomer were limited to temperatures below 430 °C, so that the melting point was not previously detected. Indeed, the apparent lack of a melting point led one recent study to conclude that the macrocycle “appears to be amorphous”.[5]

The structure of the macrocycle−DMAc solvate was determined by low-temperature (173 K) single-crystal X-ray diffraction. The molecular structure is shown in Figure 1, and a stereoscopic view of the crystal packing is given in Figure 2. Atomic coordinates for non-hydrogen atoms are given in Table 1, and listings of bond lengths, bond angles, and selected torsion angles are given in Tables 2 and 3.

X-ray analysis shows the macrocycle to adopt a rather open conformation, in which the transannular centroid-to-centroid distance between rings C(9)−C(14) and C(9)A−C(14)A is 14.98 Å. The corresponding distance between the centroids of rings C(23)−C(28) and C(23)A−C(28)A is 12.30 Å. The free pathway through the macrocycle (defined by van der Waals radii) is roughly rectangular and of minimum dimensions ca. 6.5 Å × 7.0 Å. Such dimensions could certainly accommodate the threading of an aromatic polymer chain, and so the recently-mooted possibility of polyrotaxane formation between polysulfone and its cyclic dimer [5] can by no means be ruled out.

The diaryl sulfone unit adopts a very characteristic “open-book” type of conformation,[6] with C−S−C−C and C−C−S−C torsion angles all in the range 88−98°. The conformation of the diarylisopropylidene unit also differs only slightly from that found in previous studies.[7,8] One methyl carbon atom, C(30), lies virtually in the plane of the adjacent aromatic ring, C(9)−C(14), with an average torsion angle between the ring and the C(15)−C(30) bond of 3°. The other torsion angle of this type, relating ring C(16)−C(21) to bond C(15)−C(29), is somewhat greater, at 23°. The bridging carbon atom, C(15), shows essentially tetrahedral bond angles, and the dihedral angle between the aromatic rings attached to this carbon atom is 94°. There are two independent

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Table 1. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for 1

	x	*y*	*z*	*U*(eq)^a
S(1)	3411(1)	2338(1)	1994(1)	55(1)
O(1)	4229(3)	1955(1)	2715(2)	71(1)
O(2)	2887(3)	1980(1)	1125(2)	66(1)
C(2)	4423(3)	3062(2)	1613(2)	46(1)
C(3)	4170(3)	3345(2)	691(2)	50(1)
C(4)	4978(3)	3898(2)	378(2)	48(1)
C(5)	6028(3)	4183(2)	999(2)	45(1)
C(6)	6263(3)	3912(2)	1922(2)	46(1)
C(7)	5455(3)	3352(2)	2238(2)	46(1)
O(8)	6730(2)	4753(1)	634(2)	56(1)
C(9)	8021(3)	4958(2)	1063(2)	48(1)
C(10)	8117(4)	5629(2)	1467(3)	59(1)
C(11)	9409(3)	5863(2)	1810(3)	60(1)
C(12)	10619(3)	5446(2)	1775(2)	46(1)
C(13)	10472(3)	4776(3)	1374(2)	50(1)
C(14)	9188(3)	4531(2)	1015(2)	50(1)
C(15)	12033(3)	5759(2)	2136(2)	50(1)
C(16)	11907(3)	6003(2)	3192(2)	48(1)
C(17)	11183(6)	5605(3)	3852(3)	93(2)
C(18)	11076(6)	5806(3)	4813(3)	102(2)
C(19)	11700(4)	6418(2)	5137(3)	57(1)
C(20)	12442(4)	6826(2)	4522(3)	57(1)
C(21)	12550(4)	6609(2)	3558(2)	55(1)
O(22)	11658(2)	6613(2)	6119(2)	65(1)
C(23)	10408(3)	6820(2)	6505(2)	51(1)
C(24)	10488(3)	6995(2)	7487(2)	50(1)
C(25)	9316(3)	7237(2)	7952(2)	51(1)
C(26)	8053(3)	7301(2)	7421(2)	49(1)
C(27)	7968(4)	7127(2)	6449(3)	64(1)
C(28)	9147(4)	6887(2)	5981(3)	68(1)
C(29)	12389(4)	6384(2)	1466(3)	58(1)
C(30)	13236(4)	5218(2)	2097(3)	66(1)
O(31)	4863(19)	4168(7)	4163(10)	148(6)
C(32)	4849(18)	4613(6)	4810(12)	103(5)
C(33)	3933(28)	4748(21)	5633(25)	277(20)
N(34)	5653(13)	5198(8)	4739(9)	136(9)
C(35)	6608(15)	5236(6)	3937(8)	99(4)
C(36)	5761(30)	5785(11)	5421(14)	129(8)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

diaryl ether fragments, both of which adopt conformations such that one aromatic ring lies close to the plane of the C−O−C bridge (average torsion angles are 2° and 18°), with its neighboring ring at a high angle to this plane (average torsion angles are 67 and 64°). This arrangement leads to a significant enlargement of the nominally trigonal bond angles C(6)−C(5)−O(8) (124.0°) and C(28)−C(23)−O(22) (124.9°), as a consequence of nonbonded repulsions between the hydrogens at C(6) and C(28) and the π-systems of their neighboring aromatic rings.[6] Overall, the macrocycle displays a relatively planar conformation, with only the sulfone oxygen atoms projecting significantly above and below the aromatic envelope. As shown in Figure 1, the molecule of DMAc is trapped close to the center of the macrocycle, adopting one of two partially overlapping positions, each of 50% occupancy in the crystal.

The X-ray powder pattern calculated from the present crystal structure provides an extremely good match to an already-published powder pattern, obtained some years ago from a crystalline oligomeric material precipitating spontaneously from DMF solutions of polysulfone.[4] Curiously, the authors of that study identified the precipitate as a mixture of *linear* oligomers. Even though mass spectrometry indicated the presence of **1**, this was apparently regarded as an artifact of the isolation procedure. It now seems clear, however, from comparison of calculated and experimental X-ray patterns and from spectroscopic data quoted in ref 4, that the precipitate was, in fact, a DMF solvate of the cyclic dimer **1**. The X-ray powder pattern was reported to be unchanged after removal of the solvating DMF.

Table 2. Bond Lengths (Å) and Bond Angles (Deg) for 1

S(1)−O(1)	1.434(3)	S(1)−O(2)	1.445(3)
S(1)−C(2)	1.755(3)	S(1)−C(26)A	1.762(3)
C(2)−C(3)	1.387(5)	C(2)−C(7)	1.394(4)
C(3)−C(4)	1.370(5)	C(4)−C(5)	1.399(4)
C(5)−O(8)	1.366(4)	C(5)−C(6)	1.376(4)
C(6)−C(7)	1.382(4)	O(8)−C(9)	1.398(4)
C(9)−C(14)	1.372(5)	C(9)−C(10)	1.381(5)
C(10)−C(11)	1.375(5)	C(11)−C(12)	1.394(4)
C(12)−C(13)	1.381(4)	C(12)−C(15)	1.535(4)
C(13)−C(14)	1.381(5)	C(15)−C(16)	1.528(5)
C(15)−C(30)	1.532(5)	C(15)−C(29)	1.537(5)
C(16)−C(17)	1.374(5)	C(16)−C(21)	1.382(5)
C(17)−C(18)	1.377(6)	C(18)−C(19)	1.363(5)
C(19)−C(20)	1.354(5)	C(19)−O(22)	1.397(4)
C(20)−C(21)	1.389(5)	O(22)−C(23)	1.369(4)
C(23)−C(28)	1.384(5)	C(23)−C(24)	1.387(4)
C(24)−C(25)	1.376(5)	C(25)−C(26)	1.390(4)
C(26)−C(27)	1.373(5)	C(27)−C(28)	1.382(5)
O(1)−S(1)−O(2)	120.2(2)	O(1)−S(1)−C(2)	107.8(2)
O(2)−S(1)−C(2)	107.2(2)	O(1)−S(1)−C(26)A	107.3(2)
O(2)−S(1)−C(26)A	107.3(2)	C(2)−S(1)−C(26)A	106.3(2)
C(3)−C(2)−C(7)	120.7(3)	C(3)−C(2)−S(1)	119.2(2)
C(7)−C(2)−S(1)	120.1(3)	C(4)−C(3)−C(2)	119.6(3)
C(3)−C(4)−C(5)	119.7(3)	O(8)−C(5)−C(6)	124.0(3)
O(8)−C(5)−C(4)	115.1(3)	C(6)−C(5)−C(4)	120.8(3)
C(5)−C(6)−C(7)	119.6(3)	C(6)−C(7)−C(2)	119.5(3)
C(5)−O(8)−C(9)	119.6(2)	C(14)−C(9)−C(10)	120.7(3)
C(14)−C(9)−O(8)	121.1(3)	C(10)−C(9)−O(8)	117.9(3)
C(11)−C(10)−C(9)	118.6(3)	C(10)−C(11)−C(12)	122.4(3)
C(13)−C(12)−C(11)	117.0(3)	C(13)−C(12)−C(15)	123.8(3)
C(11)−C(12)−C(15)	119.1(3)	C(12)−C(13)−C(14)	121.7(3)
C(9)−C(14)−C(13)	119.5(3)	C(16)−C(15)−C(30)	108.1(3)
C(16)−C(15)−C(12)	109.2(3)	C(30)−C(15)−C(12)	112.3(3)
C(16)−C(15)−C(29)	111.1(3)	C(30)−C(15)−C(29)	108.2(3)
C(12)−C(15)−C(29)	107.9(3)	C(17)−C(16)−C(21)	115.8(3)
C(17)−C(16)−C(15)	120.9(3)	C(21)−C(16)−C(15)	123.2(3)
C(16)−C(17)−C(18)	122.1(4)	C(19)−C(18)−C(17)	120.1(4)
C(20)−C(19)−C(18)	120.3(3)	C(20)−C(19)−O(22)	118.8(3)
C(18)−C(19)−O(22)	120.8(3)	C(19)−C(20)−C(21)	118.7(3)
C(16)−C(21)−C(20)	122.9(3)	C(23)−O(22)−C(19)	119.7(3)
O(22)−C(23)−C(28)	124.9(3)	O(22)−C(23)−C(24)	114.8(3)
C(28)−C(23)−C(24)	120.3(3)	C(25)−C(24)−C(23)	120.4(3)
C(24)−C(25)−C(26)	118.9(3)	C(27)−C(26)−C(25)	120.9(3)
C(27)−C(26)−S(1)A	120.6(3)	C(25)−C(26)−S(1)A	118.4(3)
C(26)−C(27)−C(28)	120.2(3)	C(27)−C(28)−C(23)	119.3(3)

Perhaps suprisingly, considering the intractability of **1** in the crystalline state, examination of the present structure reveals no significant intermolecular interactions over and above normal van der Waals contacts. The relatively high conformational rigidity of the macrocycle has, however, already been pointed out,[5] and we conclude that it is this absence of flexibility, affording only a slight increase in conformational entropy on dissolution or melting, which is responsible for the remarkable insolubility and very high melting point of macrocycle **1**.

Experimental Section

Instrumentation. ^{1}H and ^{13}C NMR spectra were recorded at 500 MHz on a Varian Unity-500 spectrometer, and DSC was performed under nitrogen using a Mettler DSC20 instrument at a heating rate of 20 °C/min. Single-crystal X-ray studies were carried out on a Siemens P4 rotating anode diffractometer using graphite-monochromated Cu Kα radiation. Elemental analyses were provided by the analytical service of Manchester University.

Isolation and Characterization of Macrocycle 1. Crude cyclic dimer containing some 20% of linear polysulfone was obtained from a 100-L vessel at the premises of a commercial membrane manufacturer. Repeated storage of DMF-based solutions of Udel-3500 polysulfone had led to the buildup of a significant quantity (ca. 50 g) of macrocycle **1** as a thin crystalline film on the walls of the vessel. Recrystallization of this material (0.7% w/v) from a refluxing mixture of 1,2,4-trichlorobenzene and DMAc (2:1 v/v), with hot filtration, led

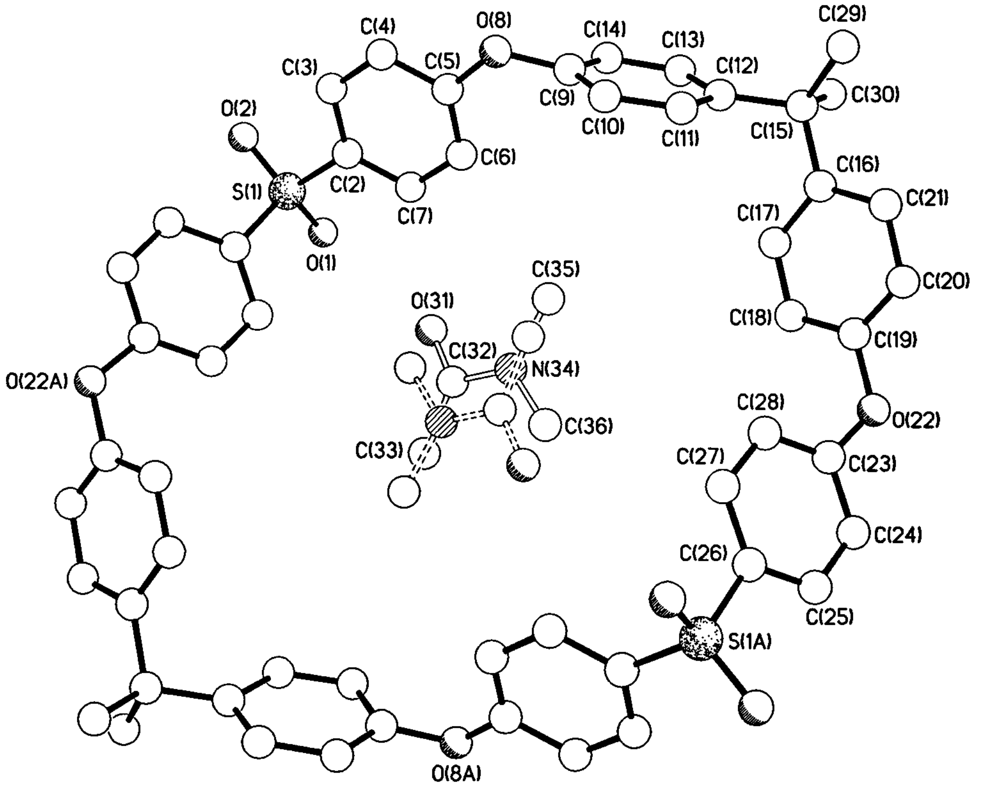

Figure 1. Molecular structure of **1,** showing also the disordered dimethylacetamide solvent molecule.

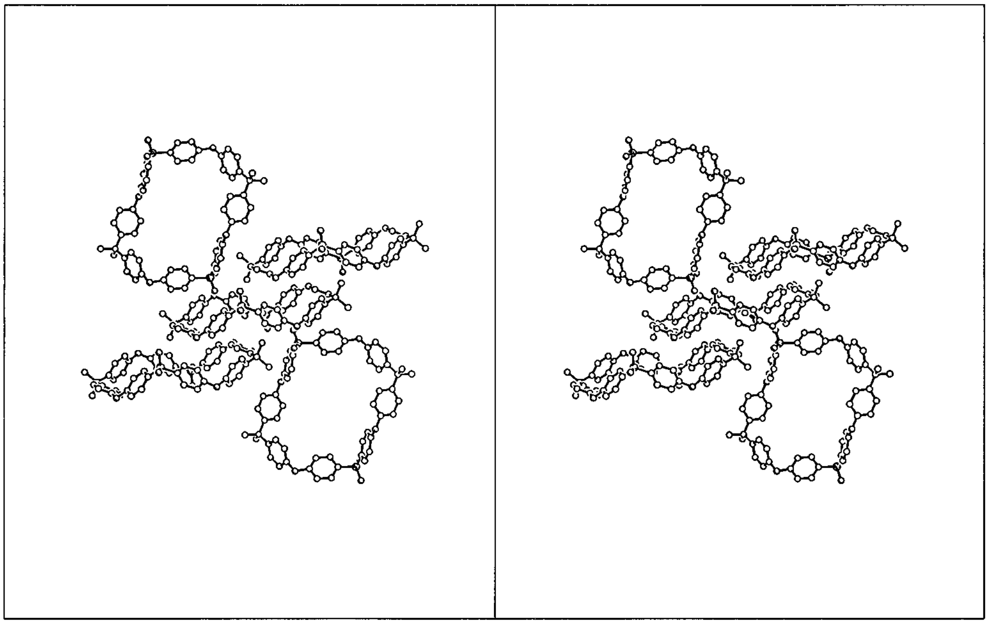

Figure 2. Stereoscopic view of the molecular packing in **1**. The solvent molecule is omitted for clarity.

Table 3. Selected Torsion Angles (Deg) for 1

C(26)A−S(1)−C(2)−C(3)	88.5(3)	C(13)−C(12)−C(15)−C(29)	113.2(4)
C(26)A−S(1)−C(2)−C(7)	−90.8(3)	C(11)−C(12)−C(15)−C(29)	−63.9(4)
C(2)−S(1)−C(26)A−C(25)A	97.8(3)	C(30)−C(15)−C(16)−C(17)	−82.1(5)
C(2)−S(1)−C(26)A−C(27)A	−86.0(3)	C(12)−C(15)−C(16)−C(17)	40.4(5)
C(6)−C(5)−O(8)−C(9)	19.8(4)	C(29)−C(15)−C(15)−C(17)	159.3(4)
C(4)−C(5)−O(8)−C(9)	−163.0(3)	C(30)−C(15)−C(16)−C(21)	95.0(4)
C(5)−O(8)−C(9)−C(14)	66.7(4)	C(12)−C(15)−C(16)−C(21)	−142.5(3)
C(5)−O(8)−C(9)−C(10)	−118.5(3)	C(29)−C(15)−C(16)−C(21)	−23.6(4)
C(13)−C(12)−C(15)−C(16)	−125.9(3)	C(20)−C(19)−C(22)−C(23)	114.3(4)
C(11)−C(12)−C(15)−C(16)	57.0(4)	C(18)−C(19)−C(22)−C(23)	−69.5(5)
C(13)−C(12)−C(15)−C(30)	−5.9(5)	C(19)−C(22)−C(23)−C(28)	−3.3(5)
C(11)−C(12)−C(15)−C(30)	176.9(3)	C(19)−C(22)−C(23)−C(24)	179.5(3)

to recovery of a DMAc−macrocycle solvate in ca. 50% yield. Crystallization at ambient temperature was unusually slow (being complete only after some 36 h) and yielded high-quality single crystals suitable for X-ray analysis. Elemental analysis and ^{1}H NMR spectra (CD_2Cl_2/CF_3COOH) were consistent with a [macrocycle:DMAc] mole ratio close to 1:1, though both analyses also suggested the presence of small quantities (1−2 wt %) of trichlorobenzene. It was not possible to remove the last traces of this low-volatility solvent without damaging the crystals, as they could not be extensively washed or dried before losing DMAc of crystallization. Mp (DSC) = 505 °C. ^{13}C NMR (CD_2Cl_2/CF_3COOH): δ 168.1 (Me*C*ON), 163.4, 151.8, 148.2, 132.4, 129.4, 128.6, 120.3, 117.1, 64.0 ($\mathit{C}H_3CON$), 42.4 ($Ar_2\mathit{C}Me_2$), 39.7 ($CON\mathit{C}H_3$), 37.8 ($CON\mathit{C}H_3$), 30.2, ($Ar_2C(\mathit{C}H_3)_2$) ppm. Anal. Calcd for $C_{54}H_{44}O_8S_2{\cdot}C_4H_9NO$: C, 71.6; H, 5.5; N, 1.4; S, 6.6%. Found: C, 69.3; H, 5.6; N, 1.6; S, 6.2.

X-ray Analysis. Data for a clear crystalline rhomb of dimensions 0.12 mm × 0.33 mm × 0.33 mm were measured at −100 °C using ω-scans. From a total of 3938 independent relections measured ($2\theta \leq 126°$), 2966 were found to have $|F_o| > 4\sigma(|F_o|)$, and these were considered to be observed. The data were corrected for Lorentz and polarization factors but not for absorption. The structure was solved by direct methods, and the non-hydrogen atoms were refined anisotropically. The included molecule of DMAc proved to be disordered, occupying two centrosymmetrically-related and partially-overlapping sites, each with 50% occupancy. The positions of the hydrogen atoms were idealized (C−H = 0.96 Å), assigned isotropic thermal parameters, and allowed to ride on their parent carbon atoms. Refinement was by full-matrix least-squares, based on F^2, and converged to give $R = 0.059$. Computations were carried out using the SHELXTL-PC program system.[9] Atomic coordinates, bond lengths and bond angles, and selected torsional angles are given in Tables 1−3.

Crystal Data: $C_{54}H_{44}O_8S_2{\cdot}C_4H_9NO$, MW 972.1, monoclinic, $P2_1/c$, $a = 9.494(1)$, $b = 18.825(2)$, and $c = 13.712(1)$ Å, $\beta = 91.63(1)°$, $V = 2449.6(4)$ Å^3, $Z = 2$ (the molecule is disposed about a center of symmetry), $D_c = 1.32$ g cm^{-3}, μ(Cu Kα) = 14.8 cm^{-1}, $F(000) = 1024$, $T = 173$ K.

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Supporting Information Available: Full crystallographic data, including thermal parameters and hydrogen atom coordinates; space-filling diagram; calculated X-ray powder pattern with listings of *d*-spacings and relative intensities; and a DSC thermogram (14 pages). Ordering information is given on any current masthead page.

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