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The Phenomenon of Conglomerate Crystallization of Organic Compounds. Part 4[1]. The Structures of 2,2′-Biphenyldisulfide (*I*) and 2,2′-Biphenyldisulfide Monoxide (*II*)

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ABSTRACT

A racemic solution of 2,2′-biphenyldisulfide (**I**), $C_{12}H_8S_2$, *produces conglomerate crystals of* (**I**) *belonging in space group* $P3_221$ *(no. 154) with lattice constants:* $a = 7.38$ *(3) Å,* $b = 7.38$ *(3),* $c = 16.20$ *(2) Å;* $V = 766.6$ Å^3 *and d(calc; M.W. = 216.32, z = 3) = 1.406 g-cm*$^{-3}$*, d(meas) = 1.47 g-cm*$^{-3}$*. A total of 1150 data were collected over the range of* $4° \leq 2\theta \leq 60°$ *using film data (Weissenberg); of these, 448 [independent and with* $I \geq 3\sigma(I)$*] were used in the structural analysis. Refinement converged to final residuals of 0.080 and 0.082 for R(F) and* $R_W(F)$*, respectively. The molecule is located at the twofold axis of the space group.*

A solution of 2,2′-biphenyldisulfide mono-oxide (**II**), $C_{12}H_8S_2O$, *produces centrosymmetric crystals of* **II** *belonging in space group* $P2_1/c$ *with lattice constants:* $a = 9.947$ *(1) Å,* $b = 7.162$ *(2),* $c = 15.420$ *(3) Å, and* $\beta = 107.56$ *(1)°;* $V = 107.56$ *(1)* Å^3 *and d(calc; M.W. = 232.31, Z = 4) = 1.473 g-cm*$^{-3}$*. A total of 2114 data were collected over the range of* $4° \leq 2\theta \leq 50°$*; of these, 1089 [independent and with* $I \geq 2.5\sigma(I)$*] were used in the structural analysis. Data were corrected for absorption (*$\mu = 4.539$ *cm*$^{-1}$*), and the relative transmission coefficients ranged from 0.9198 to 0.9998. Refinement converged to final residuals of 0.0313 and 0.0300 for R(F) and* $R_w(F)$*, respectively.*

For **I**, *the central six-membered ring* C_4S_2 *contains a helical* C_2S_2 *fragment whose conformational chirality is defined by a torsional angle of 59.98°. The benzene rings are the expected, planar hexagons characteristic of aryl rings. By comparison with* **I**, *the torsional angle of the* C_2S_2 *fragment of the mono-oxide is diminished (52.9°) by the introduction of the* $S=O$ *fragment. We believe alteration of molecules (such as functionalization) causing large changes in torsional angles of helical fragments of molecules may play a role in the selection of their crystallization mode; however, it is not the only factor dictating that choice, which is also affected by steric hindrance to the formation of short intermolecular contacts leading, in the solid state, to the formation of homochiral, infinite helical strings, as we shall demonstrate in the text. This study clearly shows the influence of those contacts on the formation of the strings.* © 1998 John Wiley & Sons, Inc. Heteroatom Chem **9:**65–74, 1998

Dedicated to Prof. William E. McEwen on the occasion of his seventy-fifth birthday.

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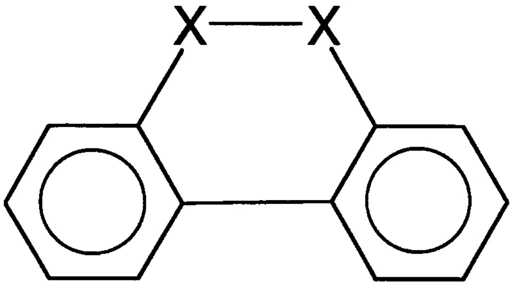
INTRODUCTION

Note: Conglomerate crystallization is the phenomenon whereby a racemic solution deposits, upon crystallization, a mechanical mixture of crystals, each of which is enantiomorphically pure. The phenomenon was previously known as "spontaneous resolution of a racemic solution."

In 1966, we reported the structure of compound **I** at a meeting of the International Union of Crystallography [1]. This compound was, at the time, one of a very small number of molecules that were observed to crystallize as a conglomerate. To put the reader in perspective, as late as 1981, only 248 cases of such phenomena had been identified [2], but the number was very much smaller in the mid-1960s. Thus, it was not easy to attempt to assign origin to the phenomenon either at the molecular level or at the level of crystallographic packing—especially since molecular graphics were painfully slow and clumsy then.

Using individual crystals, large enough to produce a useful solution for polarimetric measurements, we demonstrated that solutions of compound **I** gave zero optical rotation even in tubes 10 cm long, suggesting racemization as well as a low barrier to inversion [1b], and making it more difficult to justify an assignment of molecular origin to the mode of crystallization observed.

Sometime later, after acquiring a little more experience on the subject, we came to realize that similar phenomena had been observed in the realm of coordination chemistry [3], organometallics [4], and in organics [5], compounds that are only pure optically active in the solid state. Thus, we decided to revisit this problem hoping to provide some insight into the mechanism of conglomerate crystallization of compound **I.**



X= S, Se

Recently, we came to realize that some of our observations on the crystallization behavior, and chiral stability, on organometallics [4] was directly related to our observations on compound **I.** In that study, we noted [4] that the presence of a helical fragment that was stereochemically nonrigid was apparently able to cause conglomerate crystallization and that altering that fragment so as to reduce its torsional angle to nearly zero resulted in racemic crystals of the new compound [4]. Thus, we decided to prepare crystals of compound **II,** hoping the presence of an S=O fragment would induce a large enough reduction in the C-S-S-C torsional angle and result in racemic crystals, as we observed earlier [4].

Finally, a search of the Cambridge Structural Database (CSD) [6] revealed to us that no one had redone the structure of **I** nor studied that of **II** but that there was still some interest in this class of molecules and that very little was known about them structurally or about their crystallization modes. In fact, some interesting discoveries were made from the data in that file; namely, that the seleno analog of **I** had been structurally characterized, and it also crystallizes as a conglomerate, but in the enantiomorphic, tetragonal space group $P4_12_12$ [11]. There are a total of five structures containing the fragment

They are listed in the following (the six-letter acronym is the CSD reference code for faster access to their data base records)

(III) DAKKOP 4,4′,5,5′-Tetramethoxy-2,2′-dithiobiphenyl iodide, $C_{16}H_{16}IO_4S_2$ [7].
(IV) HAVROL, Dinaphtho(1,2-c:2′,1′-e)(1,2)dithiine, $C_{20}H_{12}S_2$ [8].
(V) JOVFEF, 6,7-Dithio-dibenzo(c,e)(1,2)dithiine, $C_{12}H_6S_4$ [9].
(VI) LIDFEJ, Phenanthro(4,5-cde)(1,2)dithiin, at −95°C, $C_{14}H_8S_2$ [10].
(VII) NAPTHS, (S)-(+)-1,1′-Binaphthyl-2,2′-disulfide, Dinaphtho(2,1-c,1′,2′-e) dithiine, $C_{20}H_{12}S_2$. Crystals prepared from pure optically active material [11].
(VIII) TAKFAM, Dibenzo(c,e)(1,2)diselenin, $C_{12}H_8Se_2$ [12].

In addition, the CSD contains four other compounds closely related to **I** in having a six-membered dichalcogeno ring whose crystallization behavior is pertinent to the discussion at hand. They are

(IX) DSELAC DL-1,2-Diselenane-3,6-dicarboxylic acid, $C_6H_8O_4Se_2$ [13].
(X) DTHIAC DL-1,2-Dithiane-3,6-dicarboxylic acid, $C_6H_8O_4S_2$ [13].
(XI) DTHDOM (4R,5R)-1,2-Dithiane-4,5-diol, $C_4H_8O_2S_2$ [14a] that crystallizes as a conglomerate in space group $P3_121$, the same as our biphenyldisulfide (**I**). However, a second polymorph of DTHOM, obtained under unspecified conditions, is **XII.**

(**XII**) DTHDOL, also (4R,5R)-1,2-dithiane-4,5-diol, $C_4H_8O_2S_2$ [14b], that crystallizes as a racemate in space group $P2_1/c$. This is a polymorph of **XII** whose source was never given.
(**XIII**) PICPOG, bis[Thieno(3,2-c;2′,3′-e)]-1,2-dithiine, $C_8H_4S_4$ [15].
(**XIV**) PICPIA, bis(4,4′,5,5′-Tetramethylthieno)(3,2-c;2′,3′-e)-1,2-dithiine,$C_{12}H_{12}S_4$ [16].
(**XV**) WEMHIF, bis[Benzo(4,5)thieno](3,2-c:2′,3′-e)(1,2)dithiine, $C_{16}H_{18}S_{14}$ [17].

Note the four oldest references date back to 1964 (a racemic diselenane) 1975 (one) and 1981 (two). Therefore, compound **I** was certainly an anomaly in 1966, being the only six-membered ring disulfide, of any kind, which crystallized as a conglomerate. Thus, our bafflement at the time is understandable.

EXPERIMENTAL

Syntheses

Compound **I** was prepared by a procedure closely related to that of Zweig and Hoffman [18] and described in Ricci's thesis (see Ref. [1b]). The compound melts sharply at 113°C. The crystals used in the X-ray study were obtained by sublimation, under partial vacuum, at 90°C. They are golden-yellow, hexagonal plates. One suitable for X-ray work was mounted on a precession camera, and the space group was determined to be one of two trigonal space groups $P3_121$ or $P3_221$.

Powdered material of compound **II** was a gift from Prof. John L. Kice (then at Texas Tech, Chemistry Department), whom we thank. Crystals suitable for X-ray work were also grown by vacuum sublimation.

Crystallography

Data for compound **I** was collected with a Weissenberg camera equipped with copper radiation, using equi-inclination techniques, and extended to 60°. Interscaling data were obtained from precession photographs of the same crystal, which was mounted with the *c* axis along the spindle direction. Details of data collection and refinement are given in Table 1. Lorentz and polarization effects were accounted for, but no absorption correction was applied to the data since the absorption coefficient is very small (μ = 4.314 cm^{-1}). See the results (Table 2) of the correction applied to compound **II** to illustrate how small the correction is for these compounds, specially when using Mo$K\alpha$ radiation.

TABLE 1 Summary of Data Collection and Processing Parameters for Compound (**I**)

Space group	$P3_221$ (No. 154)
Cell constants	a = 7.38(3) Å
	b = 7.38(3)
	c = 16.20 (2)
Cell volume	V = 764.1 $Å^3$
Molecular formula	$C_{12}H_8S_2$
Molecular weight	216.32 g-mole^1
Density (calc; z = 3 mol/cell)	1.406
Radiation employed	Mo$K\alpha$ (λ = 0.71073 Å)
Absorption coefficient	μ = 4.314 cm^{-1}
Data collection range	$4° \leq 2\Theta \leq 60°$
Total data collected	1150
Data used in refinement[a]	448
$R = \Sigma\Vert F_o\vert - \vert F_c\Vert/\Sigma\vert F_o\vert$	0.080
$Rw = [\Sigma w(\vert F_o\vert - \vert F_c\vert)^2/\Sigma\vert F_o\vert^2]^{1/2}$	0.082
Weights used	$w = [\sigma(F_o)]^{-2}$

[a] The difference between this number and the total is due to subtraction of 702 data that were systematically absent reflections, symmetry related, standards, or did not meet the criterion that $I \geq 3\sigma(I)$.

TABLE 2 Summary of Data Collection and Processing Parameters for Compound (**II**)

Space group	P21/c (No. 14)
Cell constants	a = 9.947 (1) Å
	b = 7.162 (2)
	c = 15.420 (3)
	β = 107.56 (1)°
Cell volume	V = 1047.34 $Å^3$
Molecular formula	$C_{12}H_8S_2O$
Molecular weight	232.32 g-mole^1
Density (calc; z = 4 mol/cell)	1.473 g-cm^{-3}
Radiation employed	Mo$K\alpha$ (λ = 0.71073 Å)
Absorption coefficient	μ = 4.539 cm^{-1}
Relative transmission coefficients	0.9198–0.9998
Data collection range	$4° \leq 2\Theta \leq 50°$
Scan width	$\Delta\Theta = 1.0 + 0.35 \tan\Theta$
Total data collected	2114
Data used in refinement[a]	1089
$R = \Sigma\Vert F_o\vert - \vert F_c\Vert/\Sigma\vert F_o\vert$	0.0313
$Rw = [\Sigma w(\vert F_o\vert - \vert F_c\vert)^2/\Sigma\vert F_o\vert^2]^{1/2}$	0.0300
Weights used	$w = [\sigma(F_o)]^{-2}$

[a] The difference between this number and the total is due to subtraction of 1025 data that were systematically absent reflections, redundant data collected to obtain reflections suitable for the absorption correction, symmetry related, standards, or did not meet the criterion that $I \geq 2.5\sigma(I)$.

Data for compound **II** were collected with an Enraf-Nonius CAD-4 diffractometer operating with a Molecular Structure Corporation TEXRAY-230 modification [19] of the SDP-Plus software package [20]. The procedure used for crystal alignment, cell constant determination, space group determination, and data collection were uniform for both crystals. They were centered with data in the $20° \leq 2\Theta \leq 30°$ range and examination of the cell constants, absences, and Niggli matrix [21] clearly showed **I** crystallizes in a primitive, monoclinic lattice. Systematic absences clearly show the presence of a twofold screw axis and a *c*-glide; thus, the space group was determined unambiguously to be $P2_1/c$. Data processing for **I** was carried out with the Brookhaven National Laboratory programs and that for **II** using the Nonius package [19,20].

The details of data collection are summarized in Tables 1 and 2, respectively, for compounds **I** and **II.** The intensity data for **II** were corrected for absorption using empirical curves derived from Psi scans [17,18] of suitable reflections.

The structures were solved from their Patterson maps using the S atoms as the heavy atom. After refinement of the scale factor and the positional parameters of the S atoms, a difference Fourier map produced, in both cases, all of the nonhydrogen atoms. The remaining atoms were found in subsequent difference maps. Heavy atoms were refined isotropically until convergence. Conversion of the heavy atoms to anisotropic resulted in refinement of the overall structure to final $R(F)$ and $R_w(F)$ factors listed in Tables 1 and 2.

Figures 1 and 2 give labeled views of the molecules. Figures 3 and 4 depict the packing of the ions in their respective unit cells. Figure 5 depicts the packing of compound **I** using van der Waals radii so as to emphasize the close contacts between sulfur atoms on adjacent molecules. This point is elaborated on below. Final positional and equivalent-isotropic thermal parameters are given in Tables 3 and 4. Bond lengths, angles and other significant data are listed in Tables 5 and 6.

Electric Dipole Moment Measurements on I

This quantity was determined at 25°C by refractive index measurements using a thermostated Bausch and Lomb ABBE-3L refractometer and with capacitance measurements carried out in thermostated WTW Dipolmeter Model DMO1. The value obtained is 2.05 D.

RESULTS AND DISCUSSION

Background and Assumptions

Let us provide perspective for the reader concerning the phenomenon of conglomerate crystallization: In a series of some 50 articles, we have demonstrated that conglomerate crystallization is always accompanied by crystal packing that consists of adjacent, homochiral, infinite spiral strings. This is true irrespective of the nature of the compound, as we have demonstrated with coordination compounds, organometallic compounds, and with organic compounds. Such infinite spiral strings are always similar to those displayed in Figures 3 and 5 of this document. The only difference is that some are left-handed and others right-handed helices, depending on the molecular chirality. Since in the case of conglomerate crystallization, crystals of both handedness are formed, one can obtain samples of both from a given crystallization batch and prove this to be so.

Compound **I** crystallizes as a conglomerate in the trigonal space group $P3_221$, and the molecule (Figure 1) sits at a twofold axis of the space group, as shown in Figure 1, where only half the atoms are labeled. The molecule itself is twisted in a helical

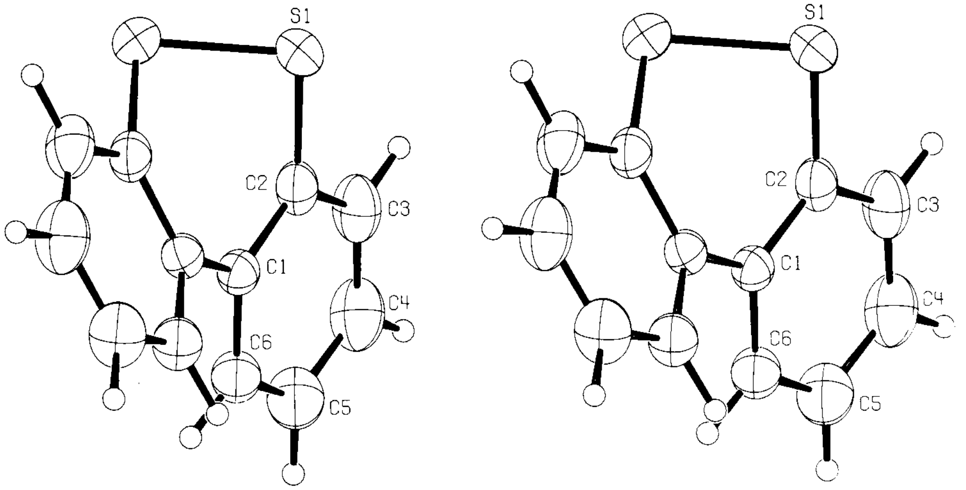


FIGURE 1 A view of the asymmetric unit of (**I**). Note that only half the atoms present in the molecule are labeled since it lies at a twofold axis of the space group; thus the asymmetric unit is only the labeled side.

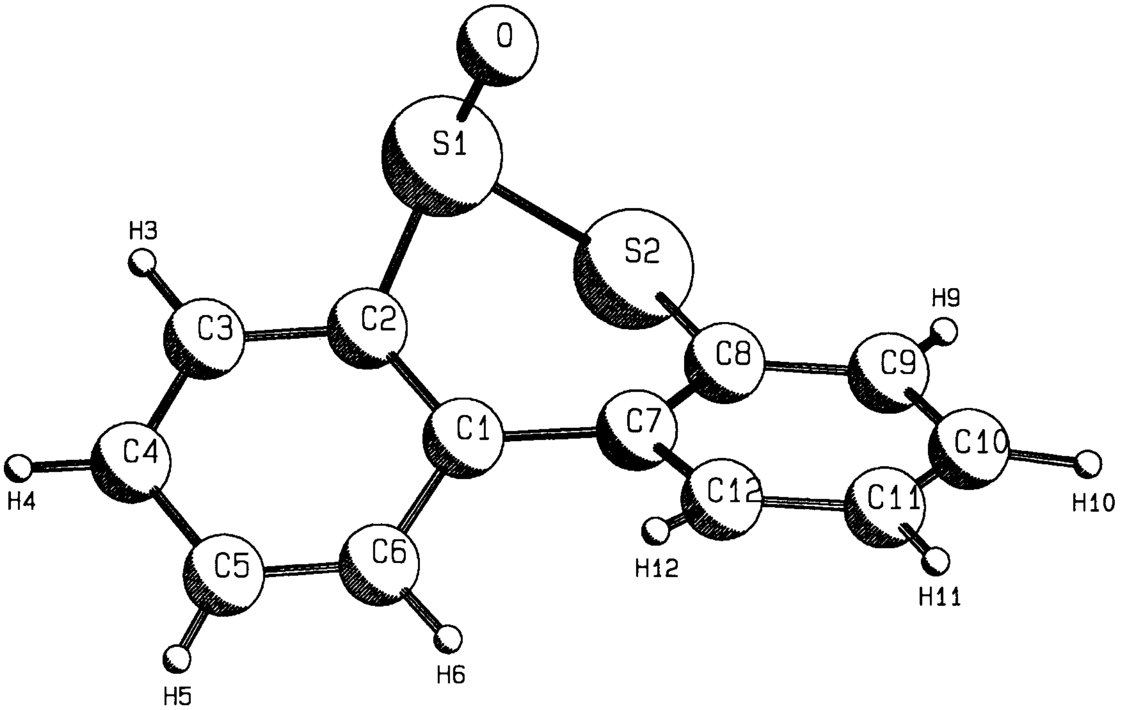


FIGURE 2 A view of the asymmetric unit of (**II**). Note the pyramidal nature of the S = O sulfur (S2).

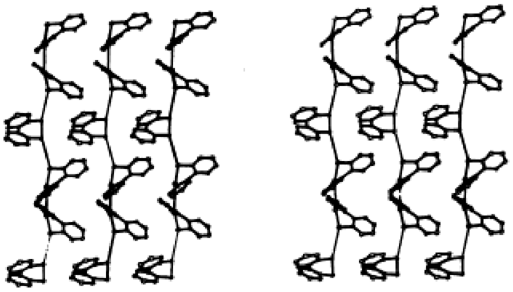


FIGURE 3 A view displaying the packing of the molecules in the unit cell of (**I**). Here, we show several of the helical strings discussed in the text for the reader to appreciate the intercalation of adjacent strings. All molecules in the figure are homochiral.

shape as shown by the C-S-S-C torsional angle of 59.98°.

In the past, we demonstrated that an organometallic compound of iron, bearing a similarly twisted fragment, crystallized as a conglomerate and that, if this fragment is flattened by the addition of double bonds, the molecule crystallizes as a racemate. We, therefore, proposed that flattening the C-S-S-C angle by the oxidation of one sulfur would result in a racemate. This is, of course, the case as shown by the space group symbols and the structural analyses. The important question is this: is this the one and only criterion needed for conglomerate crystallization to occur.

In order to test this theory, we scanned the data in the Cambridge Structural Database with the following results, shown in Table 7.

The tabular results (Table 7) clearly show that all those compounds share very similar bonding parameters; e.g., the C–S bonds are approximately 1.75–1.80 Å, the S–S distances are ca. 2.05 Å, and the C-S-S-C torsional angles are about 60°. Consequently, since oxidizing **I** into **II**, changed the C-S-S-C torsional angle very little, our previous remarks on the effect of torsional angles on crystallization pathway remain mute in this case. However, what is amply clear is that the intermolecular S. . .S distances do play a role on the crystallization pathway as follows:

A. All those molecules crystallizing as conglomerates have short S. . .S contacts, and they are packed in infinite helical strings resembling a polypeptide. This phenomenon is most clearly seen in the packing of **I**, shown in Figures 3 and 5. The latter gives a particularly clear demonstration of the helical nature of the intermolecular contacts and of how close these molecules are. Note that the same is true of **VII, VIII, XI,** and **XIII,** all four of which are also conglomerates. (Compound **VII** crystallizes in the

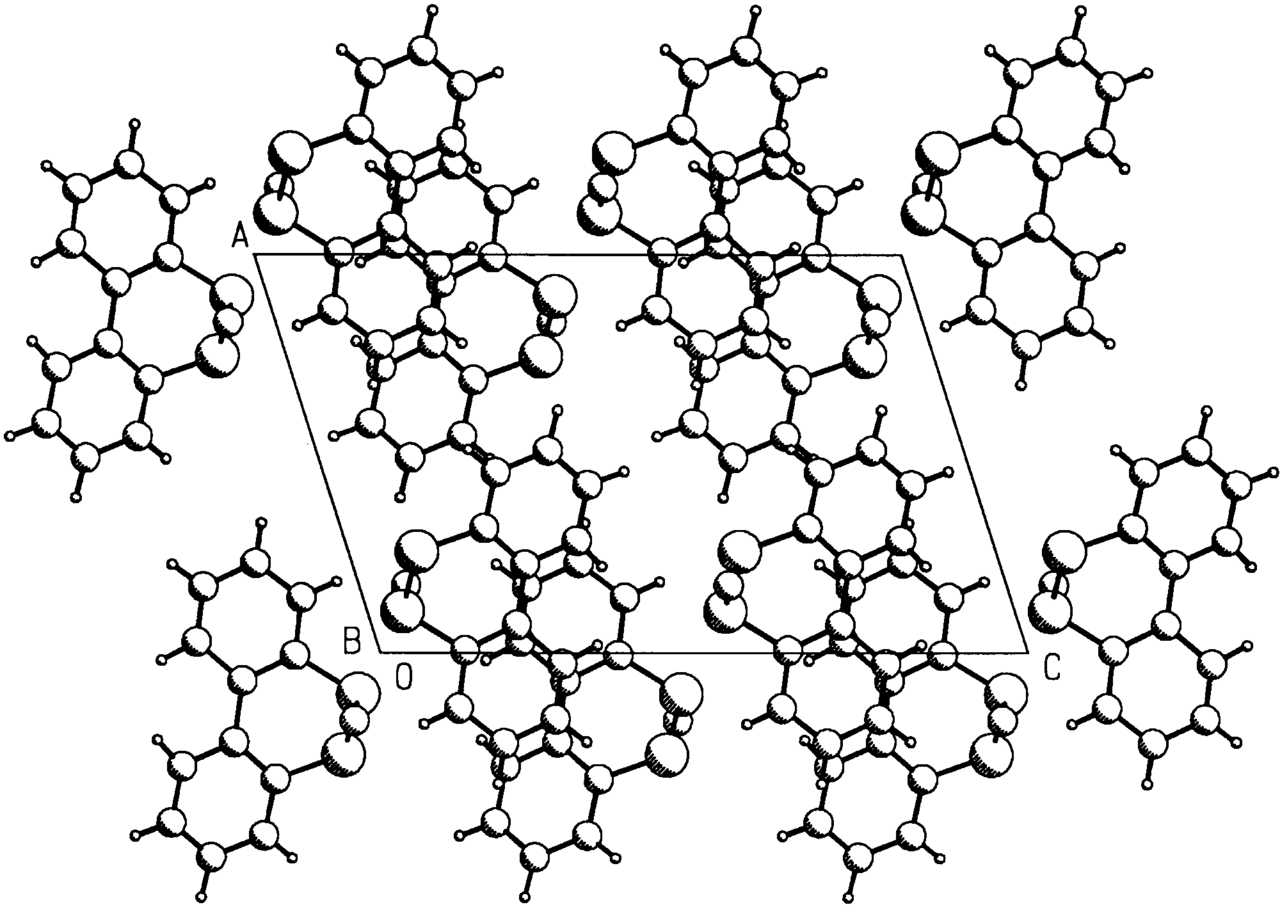


FIGURE 4 A packing diagram of the molecules in the unit cell of (**II**). This is a view down the *y* direction. Note the obvious presence of inversion centers, such as the ones located at the center of the cell and at each of the four corners.

enantiomorphic space group $P2_1$, but it was crystallized from pure optically active stock; nonetheless, it also displays short S. . .S contacts. Finally, the X–X and X. . .X bonds of **XIII** may appear a little long; however, note that that is a Se derivative.) All five compounds pack their molecules in infinite helical strings with short X. . .X contacts.

B. On the other hand, there are several racemates also exhibiting short contacts, such as in the cases of the remaining compound of Table 7 not mentioned in A. The difference is that in those compounds, there are no infinite helical strings associated with S. . .S intermolecular packing contacts. Their S. . .S contacts give rise to finite groupings such as dimers, etc. Here, we emphasize that there are no known examples of conglomerate crystallization failing to display infinite helical strings, and these may be the result of effects such as described in C and D.

C. The fact that the molecules pack in an infinite helical string does not insure that the result is a conglomerate. This is vividly illustrated by three examples from Table 7: (1) Molecule **V** has short contacts S. . .S, as befits such a molecular packing, and crystallizes in a helical string arrangement; but adjacent molecules are mirror images of each other. Thus, the string is internally compensated since the helical C-S-S-C fragments of the string are (R,R)-(S,S)--(R,R)-(S,S). . . which is an infinitely mesomeric arrangement. (2) The exact same phenomenon occurs in the cases of molecules **IX** and *X* that are arrayed in hydrogen-bonded, helical strings, with adjacent molecules of the strings being enantiomeric to one another. Thus, these are three examples of internally compensated, optically active systems.

D. A good example of the fact that steric hindrance can interfere with the process of infinite, spiral string formation is illustrated by molecules **II, III, IV, V, VI, VII, IX, X, XI, XIV,** and **XV,** all of which contain fragments that render the possibility of infinite S. . .helices difficult or impossible. A particularly fine pair of examples of such steric hindrance are (1) **III** is a racemic tetramethoxy derivative of **I**

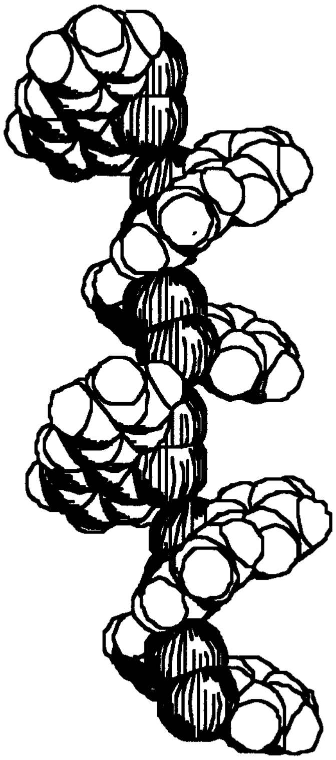


FIGURE 5 A packing diagram of (**I**) using van der Waals radii.

TABLE 3 Atomic Coordinates and Estimated Standard Deviations for Compound (**I**)

Atom	*x*	*y*	*z*	*B* (*Å*^{2})
S	0.0411(3)	0.0775(3)	0.06165(0)	4.3[a]
C1	0.3674(9)	0.4667(10)	0.0226(2)	2.7
C2	0.1745(10)	0.3521(10)	0.0644(3)	3.4
C3	0.0927(12)	0.4508(14)	0.1120(4)	4.4
C4	0.1992(16)	0.6683(16)	0.1157(4)	5.2
C5	0.3874(15)	0.7875(13)	0.0704(4)	4.5
C6	0.4635(11)	0.6849(11)	0.0242(4)	3.5
H3	−0.052(16)	0.373(15)	0.147(6)	5.0[b]
H4	0.113(17)	0.730(18)	0.154(6)	5.0
H5	0.435(18)	0.950(17)	0.071(6)	5.0
H6	0.600(16)	0.764(15)	−0.009(6)	5.0

[a] The form of the isotropic equivalent thermal parameter defined as (4/3) * [$a^{2*}\,\beta\,(1, 1) + b^{2*}\,\beta\,(2, 2) + c^{2*}\,\beta\,(3, 3) + ab\,(\cos\gamma) * \beta\,(1, 2) + ac\,(\cos\beta) * \beta\,(1, 3) + bc\,(\cos\alpha) * \beta\,(2, 3)$].

[b] The positions of the hydrogens were varied, but the isotropic thermal parameters were fixed at 5.0 Å^2.

and (2) **XIV** and **XV** are, respectively, racemic tetramethyl and benzyl racemic derivatives of **XIII.** In all those substances, there are groups attached to the carbon next to both of the sulfurs of the disulfide bond; thus, it is impossible for these molecules to form infinite helical strings. Note the large difference in packing distances among those two. If we remove those compounds with serious steric problems for helical string formation from the list in Table 7, that leaves us with only **XII** and **V** to try to account for their crystallizing as racemates: in the case of the former, no information was presented as to the origin of the crystals; thus, the issue is mute. The case of the latter is dealt with in E.

TABLE 4 Atomic Coordinates and Estimated Standard Deviations for Compound (**II**)

Atom	*x*	*y*	*z*	*B* (*Å*^{2})
S1	−0.1040(1)	0.2659(2)	−0.05420(5)	4.54(2)
S2	−0.2544(1)	0.0568(2)	−0.10574(6)	5.33(2)
O	−0.1691(2)	0.4530(4)	−0.0722(1)	5.25(6)
C1	−0.0698(3)	0.2009(4)	−0.2255(2)	2.97(7)
C2	−0.0062(3)	0.2295(5)	−0.1324(2)	3.31(7)
C3	0.1381(4)	0.2446(5)	−0.0947(2)	4.10(9)
C4	0.2256(4)	0.2269(5)	−0.1484(2)	4.65(9)
C5	0.1655(3)	0.1941(5)	−0.2402(2)	4.40(9)
C6	0.0227(3)	0.1825(5)	−0.2772(2)	3.54(8)
C7	−0.2226(3)	0.1861(4)	−0.2680(2)	3.22(8)
C8	−0.3140(3)	0.1175(5)	−0.2222(2)	3.79(8)
C9	−0.4547(4)	0.0868(5)	−0.2674(2)	5.1(1)
C10	−0.5092(4)	0.1231(6)	−0.3588(3)	6.0(1)
C11	−0.4226(4)	0.2002(6)	−0.4034(2)	5.7(1)
C12	−0.2824(4)	0.2312(5)	−0.3597(2)	4.20(9)

Heavy atoms were refined anisotropically and are given in the form of the isotropic equivalent thermal parameter defined as (4/3) * [$a^{2*}\,\beta(1, 1) + b^{2*}\,\beta(2, 2) + c^{2*}\,\beta(3, 3) + ab\,(\cos\gamma) * \beta(1, 2) + ac\,(\cos\beta) * \beta(1, 3) + bc\,(\cos\alpha) * \beta(2, 3)$].

TABLE 5 Distances (Å), Angles (°), and Selected Torsional Angles (°) for Compound (**I**)

A. Bond Distances			
S–S′	2.050(3)	C4–C5	1.433(13)
S–C2	1.757(8)	C5–C6	1.383(14)
C2–C3	1.386(12)	C6–C1	1.398(10)
C3–C4	1.409(14)	C1–C1′	1.476(13)
B. Angles			
S–S′–C2	98.15(24)	C4–C5–C6	118.2(8)
S–C2–C3	118.6(6)	C5–C6–C1	122.6(7)
S–C2–C1	119.4(6)	C6–C1–C2	117.7(6)
C1–C2–C3	121.8(8)	C1′–C1–C6	119.0(4)
C2–C3–C4	118.9(8)	C1′–C1–C2	123.2(5)
C3–C4–C5	120.3(8)		
C. Selected Torsional Angles			
C1′–S′–S–C1	59.98	S′–S–C2–C1	−44.16

E. Comparison of **XI** and **XII** bring forth, in dramatic fashion, the point that the energetics of conglomerate vs. racemic crystallization must differ by very small amounts since they are one and the same compound and with identical conformation and configuration. They both pack with short S. . .S con-

TABLE 6 Distances (Å), Angles (°), and Torsional Angles (°) for Compound (**II**)

A. Bond Distances

S1	S2	2.097(1)	S1	O	1.478(2)
S1	C2	1.782(2)	S2	C8	1.767(2)
C1	C7	1.466(3)	C7	C12	1.397(2)
C2	C3	1.380(3)	C8	C9	1.380(3)
C3	C4	1.377(3)	C9	C10	1.375(3)
C4	C5	1.380(3)	C10	C11	1.369(3)
C1	C2	1.399(2)	C5	C6	1.364(3)
C11	C12	1.371(3)	C1	C6	1.394(2)
C7	C8	1.398(3)			

B. Angles

S2	S1	O	110.74(7)	S2	S1	C2	96.44(7)
S1	S2	C8	101.05(8)	S1	C2	C3	114.5(1)
S2	C8	C7	122.0(2)	S1	C2	C1	123.1(2)
S2	C8	C9	116.9(2)	O	S1	C2	107.67(9)
C8	C7	C12	116.7(2)	C1	C2	C3	122.3(2)
C2	C3	C4	120.4(2)	C3	C4	C5	118.4(2)
C7	C8	C9	121.1(2)	C7	C12	C11	121.3(2)
C2	C1	C6	115.4(2)	C4	C5	C6	120.9(2)
C8	C9	C10	120.9(2)	C2	C1	C7	123.8(2)
C1	C6	C5	122.6(2)	C9	C10	C11	118.5(2)
C6	C1	C7	120.8(2)	C1	C7	C8	123.0(2)
C10	C11	C12	121.3(2)	C1	C7	C12	120.2(2)

C. Torsional Angles

O	S1	S2	C8	58.8
C2	S1	S2	C8	−52.9
S2	S1	C2	C1	43.4
C4	C5	C6	C1	−0.6
S2	S1	C2	C3	−140.9
O	S1	C2	C1	−70.8
O	S1	C2	C3	104.9
S1	S2	C8	C7	37.6
C1	C7	C8	S2	4.4
S1	S2	C8	C9	−145.1
C1	C7	C8	C9	−172.9
C6	C1	C2	S1	177.5
C12	C7	C8	S2	−179.3
C6	C1	C2	C3	2.0
C12	C7	C8	C9	3.5
C7	C1	C2	S1	−4.0
C1	C7	C12	C11	173.2
C7	C1	C2	C3	−179.4
C2	C1	C6	C5	−0.9
C8	C7	C12	C11	−3.3
C7	C1	C6	C5	−179.5
S2	C8	C9	C10	−177.5
C2	C1	C7	C8	−29.2
C7	C8	C9	C10	−0.2
C2	C1	C7	C12	154.6
C6	C1	C7	C8	149.3
C8	C9	C10	C11	−3.5
C6	C1	C7	C12	−27.0
S1	C2	C3	C4	−177.5
C1	C2	C3	C4	−1.7
C9	C10	C11	C12	3.7
C2	C3	C4	C5	0.0
C10	C11	C12	C7	−0.3
C3	C4	C5	C6	1.1

TABLE 7 Structural Parameters for Disulfides and Their Crystallization Mode

Compound	*C–X (Å)*	*X–X (Å)*	*C–X–X–C (°)*	*X–X contact Å*	*Crystal Type*[a]	*Ref.*
(I)	1.757	2.051	59.98	3.54	conglom	Here
(II)	1.775	2.096	52.90	4.03	racem	Here
(III)	1.756	2.055	55.6	5.83	racem	7
(IV)	1.773	2.054	60.85	7.37	racem	8
(V)	1.768	2.047	62.30	5.75	racem	9
(VI)	1.767	2.054	55.37	4.01	racem	10
(VII)	1.778	2.056	60.08	3.70	resolved	11
(VIII)[b]	1.922	2.349	59.29	4.39	conglom	12
(IX)	1.85	2.07	60	3.88	racem	13
(X)[c]	1.97	2.32	56	$>$6.50	racem	13
(XI)	1.805	2.032	58.8	3.36	conglom	14a
(XII)[d]	1.826	2.062	56.96	3.61	racem	14b
(XIII)	1.769	2.059	51.23	3.49	conglom	15
(XIV)[e]	1.764	2.061	52.66	3.43	racem	16
(XV)	1.743	2.062	53.1	3.59	racem	17

[a] Closest X–X intermolecular contact distance. Other quantities are the averaged values of those appearing more than once in a given study.
[b] The selenium analogue of compound (**I**); note that both are conglomerates.
[c] This is the seleno analog of compound (**IX**).
[d] This is a polymorph of compound (**VIII**), of unknown source since the authors did not give the method of crystal growth, as was done in (**VIII**).
[e] This is the tetramethyl derivative of compound (**X**) whose methyl groups hinder any approach to the sulfur atoms by adjacent molecules.

tacts, however, very differently. The former has an identical packing to that of **I,** shown in Figures 3 and 5, since they crystallize in the same space group.

F. If we eliminate **VI** from the list, since it was a pre-resolved molecule, 27% of the examples in Table 7 are conglomerates. This is more than six times the incidence of conglomerate crystallization for the entire CSD collection. Thus, one must conclude that there is particularly high incidence of such crystallization mode among the compounds of this class.

G. A final comment on the packing of molecule **II:** Note in Figure 4 that the molecules form, effectively, dimers linked by a bond from S1 of one to S2 of the other. This feature is most evident at each of the four corners. The apparent strings at $c = 1/4$ and 3/4 are enantiomorphic to one another and related by the c-glide.

*The Electric Dipole Moment of **I** and Its Effect on Packing*

The electric dipole measurements were carried out in order to determine how polar molecule **I** is, in the hope that this information is useful in understanding the packing exhibited by this and related substances. Also, we were interested in comparing the experimental result obtained with predictions previously made concerning the relationship between the magnitude of the electric dipole and the C-S-S-C torsional angle.

The intrinsic dipole moment of a C_6H_5S fragment was estimated some time ago to be 1.31 D [18]. If we use our measured value with their estimate of the dipole moment of two such fragments, one calculates the value of the angle between the two C–S vectors as 77°, whereas our observed value is approximately 60°. Again, if we use the estimate of Lumbroso and Marschalk together with the experimental value for di-p-tolydisulfide (2.50 D) measured by Vorontsova et al. [19], one obtains an angle of 125° for the torsional angle of this molecule. The experimentally observed value is about 107°. Thus, we suggest that there is no such thing as the intrinsic electric dipole moment of a C_6H_5S fragment; rather, that there are a series of values for this quantity as a function of torsional angle. Moreover, since the electric dipole moment of di-p-tolyldisulfide is nearly double that of biphenyldisulfide, and its torsional angle is much bigger, it is clear that the former quantity increases with an increase in the value of the latter, though surely not linearly.

The important point is that these molecules have sizable dipole moments and that these are responsible for the intermolecular interactions described in the packing of compound **I** and related species that also crystallize as conglomerates, as described earlier. Moreover, steric hindrance, such as observed in **V** vs. **VI** and in **X** and **XI,** are capable of obstructing the necessary intermolecular contacts while disrupting the possibility of formation of the infinite helical strings associated with the onset of conglomerate crystallization.

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