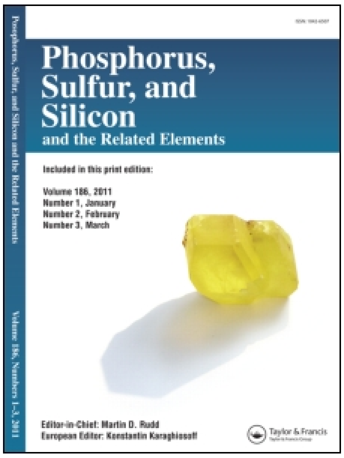

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Synthesis, Spectral Characterization, and Crystal Structure of Two Polymorphs of *o,o'*-Dichloro Dibenzyl Disulfide

S. K. Srivastava[a]; Rupali Rastogi[a]; P. Rajaram[b]; R. J. Butcher[c]; Jerry P. Jasinski[d]
[a] School of Studies in Chemistry, Jiwaji University, Gwalior, India [b] School of Studies in Physics, Jiwaji University, Gwalior, India [c] Department of Chemistry, Howard University, Washington, DC, USA [d] Department of Chemistry, Keene State College, Keene, New Hampshire, USA

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SYNTHESIS, SPECTRAL CHARACTERIZATION, AND CRYSTAL STRUCTURE OF TWO POLYMORPHS OF *o,o′*-DICHLORO DIBENZYL DISULFIDE

S. K. Srivastava,[1] Rupali Rastogi,[1] P. Rajaram,[2] R. J. Butcher,[3] and Jerry P. Jasinski[4]

[1]School of Studies in Chemistry, Jiwaji University, Gwalior, India
[2]School of Studies in Physics, Jiwaji University, Gwalior, India
[3]Department of Chemistry, Howard University, Washington, DC, USA
[4]Department of Chemistry, Keene State College, Keene, New Hampshire, USA

2-Chlorophenyl methanethiol undergoes air oxidation catalyzed by different selenides and yields the corresponding disulfide 1 in two polymorphic forms, 1a and 1b. In the molecular structures of the two new polymorphs of* o,o′*-dichloro dibenzyl disulfide, the dihedral angles between the dibenzyl groups are 82.0(1)°, (1a), and 73.7(4)°, (1b), respectively [(1a):* P-1, a *= 8.424(2) Å,* b *= 8.838(2) Å,* c *= 10.5823(19) Å, α = 90.122(18)°, β = 112.19(2)°, γ = 95.19(2)°, V = 725.9(3) Å^3; (1b):* $P2_1/n$, a *= 10.5888(10) Å,* b *= 9.1590(6) Å,* c *= 15.2489(14) Å, β = 103.072(9)°, V = 1440.6(2) Å^3]. MOPAC computational studies yield dihedral angles of 89.6(5)° and 71.9(9)°. Crystal packing is stabilized by weak π-ring (C—H···Cg) intermolecular interactions in both 1a and 1b and by additional weak Cg ··· Cg intermolecular interactions in 1b, which influence the bond distances, bond angles, and torsion angles of the dibenzyl groups in each polymorph. Additional characterization of each polymorph has been carried out by TEM, IR, ^{1}H and ^{13}C NMR spectroscopy, microanalysis, and by FAB mass spectrometry. TEM studies of a sample of 1a show that it contains cigar-shaped crystallites.

Supplemental materials are available for this article. Go to the publisher's online edition of* Phosphorus, Sulfur, and Silicon and the Related Elements *to view the free supplemental file.

Keywords 2-Chlorophenyl methanethiol; disulfides; polymorphs; selenides; TEM; X-ray structure

INTRODUCTION

Conversion of thiols to disulfides is an important chemical synthetic scheme in many biological systems.[1,2] Dehydroascorbic acid, flavins, and cytochromes oxidize thiols

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Address correspondence to S. K. Srivastava, School of Studies in Chemistry, Jiwaji University, Gwalior-474011 (M.P.), India. E-mail: sksrivas7@yahoo.com

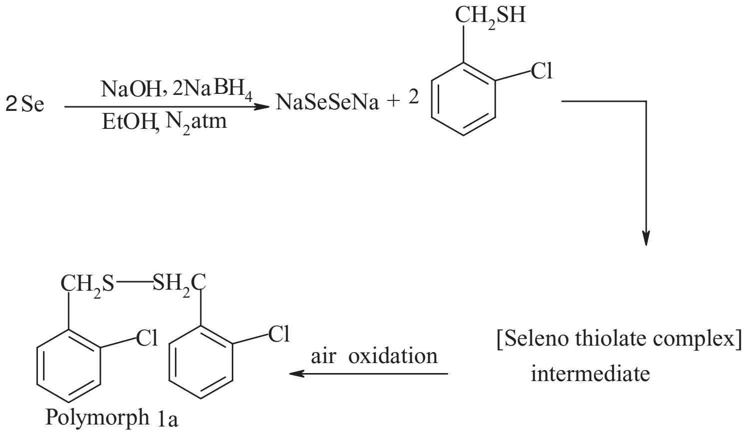
to control the cellular redox potential and prevent biological oxidative damage.[3–5] On the other hand, certain organic disulfides are used as additives for lubricating oils, since their presence increases the load-bearing properties of oil, especially at high pressures.[6] The formation of diphenyl disulfide[7,8] as well as dibenzyl disulfide[9] and their molecular structures are well characterized. Recently, three polymorphs[10] of bis(5-methylthio-1,2-dithiole-3-thione)-disulfide were obtained by the oxidation of the ammonium salt of 5-methylthio-1,2-dithiole-3-thione-4-thiole. Because of the importance of these compounds, we report the synthesis, spectral characterization, and crystal structure of two polymorphs (**1a** and **1b**) of *o,o'*-dichloro dibenzyl disulfide (**1**). The structural data are compared to those of dibenzyl disulfide, which crystallizes in the space group *Cc*.[9]

RESULTS AND DISCUSSION

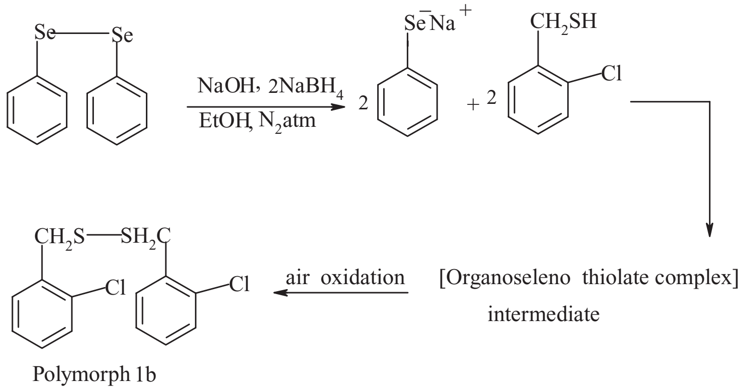
o,o'-Dichloro dibenzyl disulfide (**1**) was prepared by stirring an aqueous THF solution of 2-chlorophenyl methanethiol with an ethanolic solution of Na_2Se_2 or $C_6H_5Se^-Na^+$ (obtained by the reduction of elemental selenium or $(C_6H_5)_2Se_2$ in the presence of NaOH with $NaBH_4$ under N_2 atmosphere) overnight. The resulting solution, which might contain a selenium thiolate complex, was converted to *o,o'*-dichloro dibenzyl disulfide by air oxidation for three days. However, the yield was only about 2%, due to the absence of diselenides. Formation of a Fe-thiolate complex as an intermediate is also reported to account for the formation of $[Fe(nta)Cl_2]^{2-}$, which is generally observed in the catalyzed air oxidation of thiols and dithiols.[11]

Crystal Structures

Most disulfide molecules exist in a skewed non-planar configuration like that typically found in dibenzyl disulfide,[9] peroxides,[12] and disulfides.[13] The degree of skewing is generally governed by steric hindrance of substituents at the disulfide moiety. In *o,o'*-dichloro dibenzyl disulfide, the molecular structures of two polymorphs (**1a** and **1b**) are observed with chlorine atoms at the *ortho* position in each compound. A view of the molecular structure of **1a** and **1b** is shown in Schemes 1 and 2, respectively. Crystal and experimental data for **1a** and **1b** are listed in Table I. Bond lengths and bond angles are all within the expected ranges (Table II).[14] The dihedral angles between the dibenzyl groups are 82.0(1)° in **1a** and 73.7(4)° in **1b** (Figures 1 and 2). The benzyl groups are twisted relative to each other in **1a** with S1A-C1A-C2A-C7A and S1B-C1B-C2B-C3B torsion angles of –94.03(14)° and –77.24(16)° and in **1b** with S1B-C7B-C6B-C5B and S1A-C7A-C6A-C1A torsion angles of –101.47(14)° and –78.39(16)°, respectively. MOPAC calculations[15] yield dihedral angles between the benzyl groups of 89.6(5)° (**1a**) and 71.9(9)° (**1b**), respectively. In dibenzyl disulfide,[9] this angle is 89.0(9)°, and the benzyl groups are twisted with respect to each other with S2-C13-C14-C2 and S1-C1-C7-C8 torsion angles of –70.4(3)° and –72.1(2)°, respectively. It is apparent that these differences are influenced by the presence of the chlorine atoms in the *ortho* position in each of the polymorphs. In polymorphs **1a** and **1b**, the disulfide molecule itself is inherently chiral due to the twist orientation of the two halves with respect to the S—S vector. Since both polymorphs crystallize in a centrosymmetric space group, they contain both P- or M-helical enantiomers.[10] The S—S bond length



Scheme 1 Synthetic scheme and chemical structure of polymorph **1a**.



Scheme 2 Synthetic scheme and chemical structure of polymorph **1b**.

measures 2.025(1) Å (S1A-S1B) in **1a** and 2.020(1) Å (S1A-S1B) in **1b**, which closely resembles the 2.020 Å (S1-S2) value observed in dibenzyl disulfide.[9]

In polymorph **1a**, there are intermolecular π-ring C—H interactions with the center of gravity of both chloro benzyl rings [C(5B)···Cg1 = 3.792(3) Å, C(5B)—H(5A)···Cg1 = 165°, (*−1 + x, y, z*); C(1A)—H(1AB)···Cg2, C(1A)···Cg2 = 3.647(2) Å, C(1A)—H(1AB)···Cg2 = 155°, (*x, y, z*); C(1B)···Cg2 = 3.742(2) Å, C(1B)—H(1BB)···Cg2 = 135°, (*−x, 1−y, −z*), where Cg1 = C(2A)—C(7A) and Cg2 = C(2B)—C(7B)] that help to stabilize the crystal packing in the unit cell (see Figure 3S in the Supplemental Materials online). In polymorph **1b** there are both intermolecular π-ring C—H interactions [C(7A)···Cg2 = 3.7291(19) Å, C(7A)—H(7AA)···Cg2 = 155° (*x, y, z*) where Cg2 = C(1B)—C(6B)] and intermolecular π–π stacking interactions between adjacent chlorobenzyl rings [Cg2···Cg2 = 3.8813(10) Å (*−x, 2 − y, −z*)], which also influence the crystal packing in the unit cell (see Figure 4S in the Supplemental Materials online).

Table I Crystal and structure refinement data for polymorphs **1a** and **1b**

	Polymorph 1a		Polymorph 1b	
Empirical formula	$C_{14}\,H_{12}\,Cl_2\,S_2$		$C_{14}\,H_{12}\,Cl_2\,S_2$	
Formula weight	315.26		315.26	
Temperature, K	296(2)		296(2)	
Wavelength, Å	0.71073		0.71073	
Crystal system	Triclinic		Monoclinic	
Space group	*P-1*		*P21/n*	
Unit cell dimensions, Å, °	a = 8.424(2)	α = 90.122(18)	a = 10.5888(10)	
	b = 8.838(2)	β = 112.19(2)	b = 9.1590(6)	β = 103.072(9)
	c = 10.5823(19)	γ = 95.19(2)	c = 15.2489(14)	
Volume, Å^3	725.9(3)		1440.6(2)	
Z	2		4	
Density (calculated), g/cm^3	1.442		1.454	
Absorption coefficient, mm-1	0.713		0.719	
F(000)	324		648	
Crystal size, mm^3	0.51 × 0.43 × 0.23		0.51 × 0.45 × 0.18	
Theta range for data collection, °	4.64 to 32.54		4.66 to 32.59	
Index ranges	$-12 \le h \le 12$, $-13 \le k \le 13$, $-15 \le l \le 15$		$-15 \le h \le 15$, $-12 \le k \le 13$, $-22 \le l \le 12$	
Reflections collected	12565		13365	
Independent reflections	4823 [R(int) = 0.0205]		4720 [R(int) = 0.0406]	
Completeness to theta = 25.00°,%	99.1		97.4	
Absorption correction	Semi-empirical from equivalents		Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.80484		1.00000 and 0.66165	
Refinement method	Full-matrix least-squares on F^2		Full-matrix least-squares on F^2	
Data / restraints / parameters	4823 / 0 / 163		4720 / 0 / 164	
Goodness-of-fit on F^2	1.029		0.778	
Final R indices $[I>2\sigma(I)]$	R1 = 0.0330, wR2 = 0.0901		R1 = 0.0315, wR2 = 0.0669	
R indices (all data)	R1 = 0.0667, wR2 = 0.1027		R1 = 0.1136, wR2 = 0.0786	
Extinction coefficient	none		0.038(3)	
Largest diff. peak and hole, e·Å^{-3}	0.374 and –0.329		0.204 and –0.258	

Table II Selected geometric parameters for polymorphs **1a** and **1b**

Bond lengths [Å]		Bond angles [°]		Torsion angles [°]	
Polymorph 1a					
S1A−S1B	2.025(1)	C1A−S1A−S2A	103.83(6)	S1A−S1B−C1B−C2B	−59.56(12)
C1A−S1A	1.836(2)	S1A−C1A−C2A	114.20(9)	S1B−S1A−C1A−C2A	67.25(11)
C1A−C2A	1.492(2)	C1A−C2A−C3A	122.67(13)	S1A−C1A−C2A−C3A	86.14(15)
C3A−Cl1A	1.739(2)	C1B−S1B−S1A	103.66(6)	S1A−C1A−C2A−C7A	−94.03(14)
C1B−S1B	1.837(2)	S1B−C1B−C2B	114.11(10)	S1B−C1B−C2B−C3B	−77.24(16)
C1B−C2B	1.489(2)	C1B−C2B−C3B	123.02(14)	S1B−C1B−C2B−C7B	101.78(15)
C3B−Cl1B	1.740(2)			C1A−S1A−S1B−C1B	89.39(7)
Polymorph 1b					
S1A−S1B	2.020(1)	C7A−S1A−S2A	105.12(6)	S1A−S1B−C7B−C6B	60.38(12)
C7A−S1A	1.829(2)	S1A−C7A−C6A	114.15(9)	S1B−S1A−C7A−C6A	−59.63(13)
C7A−C6A	1.488(2)	C7A−C6A−C1A	123.25(15)	S1A−C7A−C6A−C1A	−78.39(16)
C1A−Cl1A	1.734(2)	C7B−S1B−S1A	104.94(6)	S1A−C7A−C6A−C5A	101.35(15)
C7B−S1B	1.827(2)	S1B−C7B−C6B	113.24(10)	S1B−C7B−C6B−C1B	75.62(17)
C7B−C6B	1.492(2)	C7B−C6B−C1B	122.78(13)	S1B−C7B−C6B−C5B	−101.47(14)
C1B−Cl1B	1.735(2)			C7A−S1A−S1B−C7B	−89.45(7)

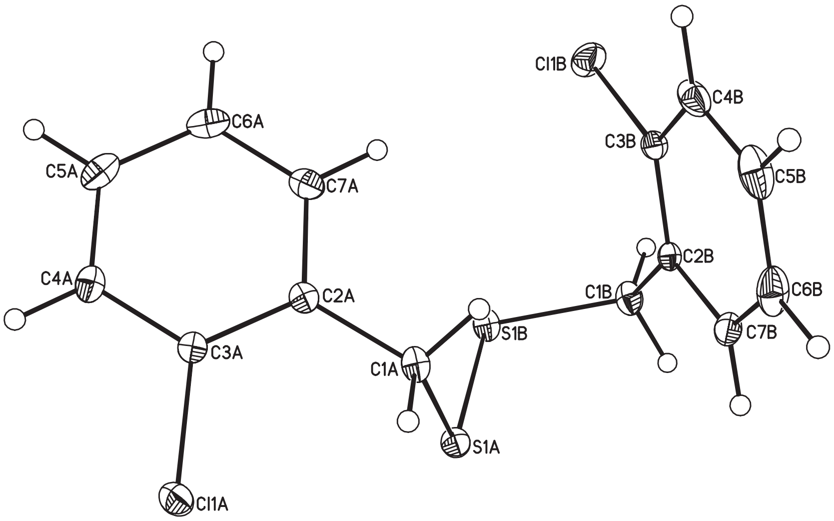


Figure 1 ORTEP drawing of the molecular structure of polymorph **1a** in the crystal showing the atom numbering scheme of the asymmetric unit. Displacement ellipsoids are drawn at 50% probability level.

In summary, the dihedral angles between the benzyl groups of two new polymorphs of *o,o'*-dichloro dibenzyl disulfide, are affected by weak π-ring (C—H· · ·Cg) intermolecular interactions in both **1a** and **1b** and by additional weak Cg· · ·Cg intermolecular interactions in **1b**. These intermolecular interactions also influence the bond distances, bond angles, and torsion angles of the benzyl groups in each polymorph, which can be seen when comparing with the geometric and crystal packing parameters of dibenzyl disulfide.[9]

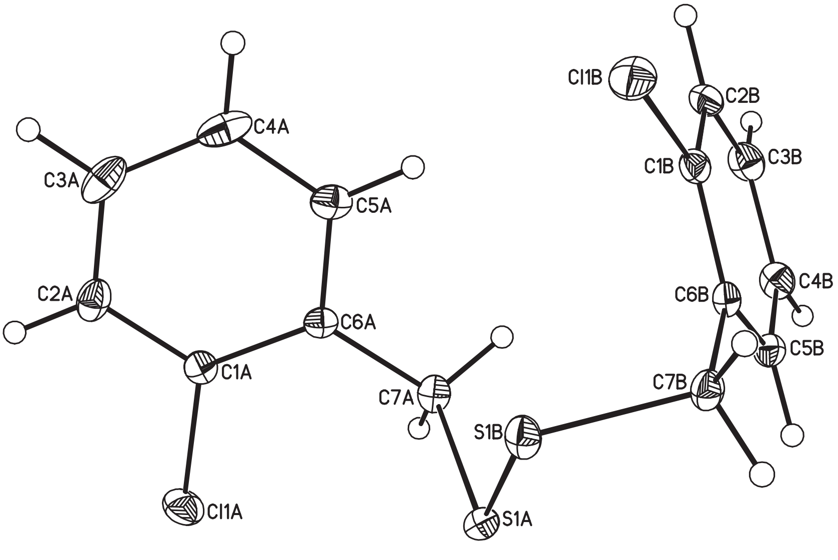


Figure 2 ORTEP drawing of the molecular structure of polymorph **1b** in the crystal showing the atom numbering scheme of the asymmetric unit. Displacement ellipsoids are drawn at 50% probability level.

Spectral Data

In the FAB$^+$ mass spectrum of polymorphs **1a** and **1b**, the molecular ion peak was observed at *m/z* 315, which is in agreement with the molecular weight of the proposed structure. The molecular ion further loses $[C_7H_6SCl]^+$, and a peak is observed at *m/z* 157, whereas the base peak at *m/z* 125 corresponds to a $[C_7H_6Cl]^+$ fragment. Figure 5S (in the Supplemental Materials online) shows the transmission electron micrograph (TEM) of a powder sample of polymorph **1a**. The explicit feature in the IR spectra of all the polymorphs shows the absence of the band in the region 2590–2550 cm^{-1}, which appears in the free thiol as the S—H vibration, indicating disulfide bond formation through this site. Because of the presence of a center of symmetry in the molecule, the band, ν(S—S), does not appear in the IR spectra. The ^{1}H NMR data show the absence of a signal due to an S—H proton, which again is in accord with the formation of an S—S bond.[16] Moreover, the ^{1}H NMR spectrum contains signals for the aromatic protons at 7.2–7.3 ppm. A singlet at 3.78 ppm is assigned to the $S—CH_2$ protons. In the $^{13}C\{^1H\}$ NMR spectrum, the significant deshielding of the $S—CH_2$ carbon atom in **1a** and **1b**, as compared to the free thiol, is in accord with the presence of a disulfide moiety.

CONCLUSION

Air oxidation of 2-chlorophenyl methanethiol to *o,o'*-dichloro dibenzyl disulfide is catalyzed by the addition of diselenides (Na_2Se_2 or $(C_6H_5)_2Se_2$); the disulfide is formed upon standing on air for three days. It appears that both diselenides control the stereochemistry of the formation of the disulfide of two different polymorphs of the disulfide with high yields. In the polymorphs **1a** and **1b**, the disulfide molecule itself is inherently chiral due to the twist orientation of the two halves with respect to the S—S vector. Since both polymorphs crystallize in a centrosymmetric space group, they contain both P- or M-helical enantiomers.

EXPERIMENTAL

Diphenyl diselenide,[17] sodium phenyl selenolate,[18] and disodium diselenide[19] were prepared according to published procedures. 2-Chlorophenyl methanethiol was obtained from Aldrich. Selenium powder and sodium borohydride were purchased from CDH (India).

The C and H analysis were carried out with an Elementary Varo EL III Carlo Erba1108 analyzer. The ^{1}H and ^{13}C NMR spectra were recorded with a JEOL AL300 FT NMR spectrometer at 300 and 75.45 MHz, respectively. TEM studies were performed on JEOL JEM 1230 microscope using an accelerating voltage of 115kV. FAB mass spectra were recorded with a JEOL SX-102/DA-6000 mass spectrometer using argon/xenon (6 kV, 10 mA) as the FAB gas. The accelerating voltage was 10 kV, and the spectrum was recorded at room temperature using *m*-nitrobenzyl alcohol as matrix. IR spectra in the range of 4000–400 cm^{-1} were recorded with a Shimadzu Prestige 21 FTIR spectrometer as KBr pellets. The melting points were determined in open capillary and are reported as such.

Structure Determination and Refinement

X-ray data for **1a** and **1b** were collected with an Oxford Diffraction Gemini R CCD area detector using CrysAlisPro software and graphite-monochromated Mo-Kα radiation

(λ = 0.71073 Å) at 200(2) K. The structure was solved by direct methods using SHELXS97,[20] and all of the non-hydrogen atoms were refined anisotropically by full-matrix least-squares on F^2 using SHELXL97.[20] The hydrogen atoms were placed in their calculated positions and included in the refinement using the riding model. An absorption correction was performed using CrysAlis RED, and all calculations were performed using SHELXTL.[21]

Supporting Information

Crystallographic data (CIF) for the structures reported in this article have been deposited with the Cambridge Crystallographic Data Centre and allocated the deposition numbers CCDC 667838 for **1a** and CCDC 667839 for **1b**, respectively. These data can be obtained, free of charge, *via* www.ccdc.cam.ac.uk/data_request/cif, by sending an e-mail to data_request@ccdc.cam.ac.uk, from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

Synthesis of Polymorph 1a

To a stirred suspension of elemental selenium (0.79 g, 10 mmol) and NaOH (0.88 g, 22 mmol) in aqueous THF (20 mL + 0.2 mL H_2O) under N_2 atmosphere, $NaBH_4$ (0.84 g, 22 mmol) was added. The reaction was exothermic, and the pink color of the diselenide developed soon, which gradually faded to a colorless solution of the monoselenide (usually taking only a few minutes). The colorless solution of sodium selenide was treated with one equivalent of elemental selenium (0.79 g, 10 mmol), and the reaction solution became purple in color. The reaction mixture was stirred for 2–3 h. During this period, a complete dissolution of the selenium was observed and a brownish red aqueous solution of Na_2Se_2 was obtained. This solution was then treated with a solution of 2-chlorophenyl methanethiol (5.46 g, 21 mmol) in THF (20 mL) under N_2 atmosphere. The mixture was stirred for 24 h at room temperature. It was hydrolyzed with 100 mL of water, extracted with 200 mL of chloroform, washed with 100 mL of water, and dried over anhydrous magnesium sulfate. The extract was concentrated to 15 mL under reduced pressure. After allowing the solution to stand for 3 days, transparent block-like crystals were formed. The crystals were washed with petroleum-ether (60–80°C) to remove the yellowish oil that formed during the air oxidation process. The yield of the compound obtained by this method was 80%; however in the absence of Na_2Se_2, the yield was only 2%. Yield: 80%. Mp: 74°C. Anal. Calcd. for $C_{14}H_{12}Cl_2S_2$: C, 53.49; H, 3.84%. Found: C, 52.90; H, 3.81%.

Synthesis of Polymorph 1b

To an aqueous THF solution (20 mL + 0.2 mL H_2O) of diphenyl diselenide (3.14 g, 10 mmol) and NaOH (0.80 g, 20 mmol) under N_2 atmosphere, $NaBH_4$ (0.75 g, 20 mmol) was added in pinches. The yellow color of the diselenide darkened and then gradually faded to colorless. To this colorless solution, 2-chlorophenyl methanethiol (5.46 g, 21 mmol) in THF (20 mL) was added dropwise, and the solution was stirred for 24 h at room temperature. The reaction mixture was hydrolyzed with 100 mL of water, extracted with 200 mL of chloroform, washed with 100 mL of water, and dried over anhydrous magnesium sulfate. The extract was concentrated to 15 mL under reduced pressure. After allowing the solution to stand for 3 days, yellow block-like crystals were formed. The crystals were washed with petroleum-ether (60–80°C) to remove the yellow crystals of diphenyl diselenide that were formed during the air oxidation process. The compound obtained by this method was in 84% yield; however in the absence of diphenyl diselenide, the yield was only 2%. Yield: 84%. Mp: 76°C. Anal Calcd. for $C_{14}H_{12}Cl_2S_2$: C, 53.49; H, 3.84%. Found: C, 53.36; H, 3.64%. FAB: (**1a, 1b**) m/z = 315 (50%) for $[M^+]$, 157 (10%) for $[C_7H_6SCl]^+$, 125 (100%) for $[C_7H_6Cl]^+$. ^1H NMR (**1a, 1b**; $CDCl_3$): $\delta = 3.78$ (s, 4H, CH_2S), 7.23–7.36 (m, 8H, C_6H_4). ^{13}C NMR (**1a, 1b**; $CDCl_3$): $\delta = 41.2$ ($CH_2{-}S$), 135.1 (C—Cl), 134.2 ($C{-}CH_2$), 131.7, 126.8, 129.8, 129.0.

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