ORGANIC LETTERS

2001
Vol. 3, No. 23
3639−3641

Solid State Optical Activity of Dichalcogenides: Isolation by Chiral Crystallization and Determination of Absolute Configuration

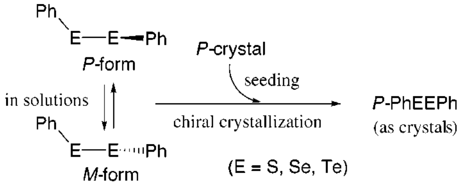
Toshio Shimizu, Hiromi Isono, Masanori Yasui,[†] Fujiko Iwasaki,[‡] and Nobumasa Kamigata*,[§]

Department of Chemistry, Graduate School of Science, Tokyo Metropolitan University,
Minami-ohsawa, Hachioji, Tokyo 192-0397, Japan, Centre for Instrumental Analysis,
The University of Electro-Communications, Chofu, Tokyo 182-8585, Japan, and
Department of Applied Physics and Chemistry, The University of
Electro-Communications, Chofu, Tokyo 182-8585, Japan

kamigata-nobumasa@c.metro-u.ac.jp

Received August 8, 2001

ABSTRACT



Optically active diphenyl dichalcogenides were isolated in bulk for the first time by chiral crystallization. The absolute configuration of the *P*-helical enantiomer of diphenyl disulfide was determined by X-ray crystallography. On the basis of this determination and considering the similarities of the Cotton effects of diphenyl diselenide and ditelluride, the absolute configuration of optically active diphenyl dichalcogenides could be assigned. Furthermore, stereochemistry of chiral crystallization could be controlled by using an optically active crystal as a seed crystal.

Acyclic disulfides are well-known to show skewed structures[1] in their crystalline states[2−5] or in the gas phase,[6,7] except for disulfides with congested substituents,[8] and many theoretical studies have indicated that such skewed geometries are global minima.[7,9−11] Dynamic NMR studies of disulfides also support these results.[5,11−13] Similar findings have been reported for diselenides[10,12,14−17] and ditellurides.[10,16,18,19] The skewed geometries of dichalcogenides have been explained on the basis of a gauche effect proposed by Wolfe.[5,11,20,21]

[†] Centre for Instrumental Analysis, The University of Electro-Communications.

[‡] Department of Applied Physics and Chemistry, The University of Electro-Communications.

[§] Tel: +81 (426) 77-2556. Fax: +81 (426) 77-2525.

(1) Review: Steudel, R. *Angew. Chem.* **1975**, *87*, 683; *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 655.

(2) Lee, J. D.; Bryant, M. W. R. *Acta Crystallogr.* **1969**, *B25*, 2094.

(3) Sacerdoti, M.; Gilli, G.; Domino, P. *Acta Crystallogr.* **1975**, *B31*, 327.

(4) For examples: (a) Kansikas, J.; Sipilä, K. *Acta Crystallogr.* **2000**, *C56*, 72. (b) Koritsanszky, T.; Buschmann, J.; Luger, P.; Schmidt, H.; Steudel, R. *J. Phys. Chem.* **1994**, *98*, 5416. (c) Rindorf, G.; Jørgensen, F. S.; Snyder, J. P. *J. Org. Chem.* **1980**, *45*, 5343. (d) Ladd, M. F. C.; Povey, D. C.; Yu, P.-Y.; Chan, T.-L.; Mak, T. C. W. *Acta Crystallogr.* **1978**, *B34*, 2935. (e) Lee, J. D.; Bryant, M. W. R. *Acta Crystallogr.* **1969**, *B25*, 2497. (f) Hordvik, A. *Acta Chem. Scand.* **1966**, *20*, 1885, and references therein.

(5) Borghi, R.; Lunazzi, L.; Placucci, G.; Cerioni, G.; Foresti, E.; Plumitallo, A. *J. Org. Chem.* **1997**, *62*, 4924.

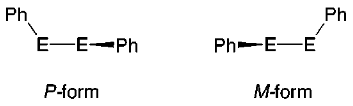
(6) (a) Yokozeki, A.; Bauer, S. H. *J. Phys. Chem.* **1976**, *80*, 618. (b) Winnewisser, G.; Winnewisser, M.; Gordy, W. *J. Chem. Phys.* **1968**, *49*, 3465.

(7) Steudel, R.; Schmidt, H.; Baumeister, E.; Oberhammer, H.; Koritsanszky, T. *J. Phys. Chem.* **1995**, *99*, 8987.

(8) Ostrowski, M.; Jeske, J.; Jones, P. G.; du Mont, W.-W. *Chem. Ber.* **1993**, *126*, 1355.

10.1021/ol010172g CCC: $20.00

Therefore, dichalcogenides can be considered to exist in chiral *P*- and *M*-helical forms.[22] However, the barriers of rotation of chalcogen−chalcogen bonds for racemization are not high enough, as estimated by theoretical[9−11] and dynamic NMR studies,[5,11,13] to isolate the optical isomers. Thus, racemization readily occurs in solution. On the other hand, some optical properties of cyclic[23] and acyclic[24] disulfides with chiral ligands have been examined, and similar chiroptical properties have been obtained for diselenides and ditellurides with chiral ligands.[25,26] Disulfide linked to the 2- and 2′-positions of a chiral 1,1′-binaphthyl group is considered a chiral disulfide.[27] However, this compound is configurationally restricted by atropisomerism of the binaphthyl group. The crystal structures of diphenyl disulfide,[2,3,28] diselenide,[14,28] and ditelluride[18] have already been determined by X-ray crystallographic analysis; all are orthorhombic and belong to the chiral space group $P2_12_12_1$. The composition of one unit cell for diphenyl disulfide shows that the chirality of the crystal is due to the skewed structure of the disulfide moiety, although the report does not mention the chirality.[2] We report here the first isolation of simple optically active dichalcogenides (diphenyl disulfide, diselenide, ditelluride) in bulk without any configurational restriction by means of chiral crystallization. We also show a relationship between the absolute configuration and the circular dichroism spectra in the crystalline state.



(E = S, Se, Te)

First, recrystallization of diphenyl disulfide from hot ethanol gave colorless needles in 74% recovery yield.[29] The circular dichroism (CD) spectrum in the solid state (KBr disk made from a single crystal)[30] showed a negative first Cotton effect at around 330 nm, as shown in Figure 1, although a Cotton effect was not observed for the disulfide in solution due to rapid racemization. Facile racemization of diphenyl dichalcogenides in solution has also been supported by

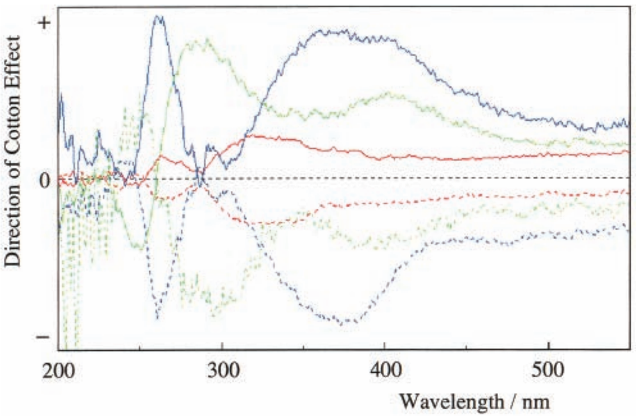


Figure 1. Circular dichroism spectra of optically active diphenyl dichalcogenides in their solid states (KBr disk): red, PhSSPh; blue, PhSeSePh; green, PhTeTePh.

---

(9) For examples: (a) Steudel, R.; Drozdova, Y.; Miaskiewicz, K.; Hertwig, R. H.; Koch, W. *J. Am. Chem. Soc.* **1997**, *119*, 1990. (b) Shimizu, T.; Iwata, K.; Kamigata, N.; Ikuta, S. *J. Chem. Res., Synop.* **1997**, 38; *Miniprint* **1997**, 344. (c) Bainbrigge, N.; Butler, A. R.; Görbitz, C. H. *J. Chem. Soc., Perkin Trans. 2* **1997**, 351. (d) Miaskiewicz, K.; Steudel, R. *J. Chem. Soc., Dalton Trans.* **1991**, 2395. (e) Dixon, D. A.; Zeroka, D.; Wendoloski, J. J.; Wasserman, Z. R. *J. Phys. Chem.* **1985**, *89*, 5334. (f) Rauk, A. *J. Am. Chem. Soc.* **1984**, *106*, 6517. (g) Jørgensen, F. S.; Snyder, J. P. *Tetrahedron* **1979**, *35*, 1399. (h) Hinchcliffe, A. *J. Mol. Struct.* **1979**, *55*, 127. (i) Snyder, J. P.; Carlsen, L. *J. Am. Chem. Soc.* **1977**, *99*, 2931. (j) Allinger, N. L.; Hickey, M. J.; Kao, J. *J. Am. Chem. Soc.* **1976**, *98*, 2741. (k) Allinger, N. L.; Kao, J.; Chang, H.-M.; Boyd, D. B. *Tetrahedron* **1976**, *32*, 2867. (l) Dixon, R. N.; Hugo, J. M. V. *Mol. Phys.* **1975**, *29*, 953. (m) Van Wart, M. E.; Shipman, L. L.; Scheraga, H. A. *J. Phys. Chem.* **1974**, *79*, 1848. (n) Boyd, D. B. *J. Phys. Chem.* **1974**, *78*, 1554. (o) Webb, J.; Strickland, R. W.; Richardson, F. S. *J. Am. Chem. Soc.* **1973**, *95*, 4775. (p) Boyd, D. B. *J. Am. Chem. Soc.* **1972**, *94*, 8799. (q) Linderberg, J.; Michl, J. *J. Am. Chem. Soc.* **1970**, *92*, 2619. (r) Veillard, A.; Demuynck, J. *Chem. Phys. Lett.* **1970**, *4*, 476. (s) Hillier, I. H.; Saunders, V. R.; Wyatt, J. F. *Trans. Faraday Soc.* **1970**, *66*, 2665. (t) Schwartz, M. E. *J. Chem. Phys.* **1969**, *51*, 4182. (u) Bergson, G. *Arkiv. Kemi.* **1962**, *18*, 409. (v) Bergson, G. *Arkiv. Kemi.* **1958**, *12*, 233.

(10) (a) Block, R.; Jansen, L. *J. Chem. Phys.* **1985**, *82*, 3322. (b) Ewig, C. S.; Mei, E. H.; Van Wazer, J. R. *Mol. Phys.* **1980**, *40*, 241.

(11) Cerioni, G.; Cremonini, M. A.; Lunazzi, L.; Placucci, G.; Plumitallo, A. *J. Org. Chem.* **1998**, *63*, 3933.

(12) Kessler, H.; Rundel, W. *Chem. Ber.* **1968**, *101*, 3350.

(13) (a) Pinto, R. M.; Leung, R. Y. N.; Sharma, R. D. *Magn. Reson. Chem.* **1988**, *26*, 729. (b) Anderson, J. E.; Henriksen, L. *J. Chem. Soc., Chem. Commun.* **1985**, 1397. (c) Bushweller, C. H. Int. *J. Sulfur Chem.* **1973**, *8*, 103. (d) Fraser, R. R.; Boussard, G.; Saunders, J. K.; Lambert, J. B.; Mixan, C. E. *J. Am. Chem. Soc.* **1971**, *93*, 3822. (e) Seel, F.; Gombler, W.; Budenz, R. *Liebigs Ann. Chem.* **1970**, *725*, 1. (f) Thompson, Q. E.; Crutchfield, M. M.; Dietrich, M. W.; Pierron, E. *J. Org. Chem.* **1965**, *30*, 2692. (g) Claeson, G.; Androes, G.; Calvin, M. *J. Am. Chem. Soc.* **1961**, *83*, 4357.

(14) Marsh, R. E. *Acta Crystallogr.* **1952**, *5*, 458.

(15) For examples: (a) Jeske, J.; Salzen, A. M.; de Mont, W. W.; Jones, P. G. *Acta Crystallogr.* **1998**, *C54*, 1873. (b) Ellison, J. J.; Ruhlandt-Senge, K.; Hope, H. H.; Power, P. P. *Inorg. Chem.* **1995**, *34*, 49. (c) du Mont, W.-W.; Martens, A.; Pohl, S.; Saak, W. *Inorg. Chem.* **1990**, *29*, 4847. (d) Morris, G. D.; Einstein, F. W. B. *Acta Crystallogr.* **1986**, *C42*, 1433. (e) Van den Bossche, G.; Spirlet, M. R.; Dideberg, O.; Dupont, L. *Acta Crystallogr.* **1984**, *C40*, 1979. (f) Back, T. G.; Codding, P. W. *Can. J. Chem.* **1983**, *61*, 2749. (g) Woodard, C. M.; Brown, D. S.; Lee, J. D.; Massey, A. G. *J. Organomet. Chem.* **1976**, *121*, 333.

(16) Kruse, F. M.; Marsh, R. E.; McCullough, J. D. *Acta Crystallogr.* **1957**, *10*, 201.

(17) D'Antonio, P.; George, C.; Lowrey, A. H.; Karle, J. *J. Chem. Phys.* **1971**, *55*, 1071.

(18) Llabres, P. G.; Dideberg, O.; Dupont, L. *Acta Crystallogr.* **1972**, *B28*, 2438.

(19) For examples: (a) Dukat, W.; Gall, F.; Meyer, C.; Mootz, D.; Naumann, D.; Nowicki, G.; Schulz, K. *Z. Anorg. Allg. Chem.* **1996**, *622*, 617. (b) Lang, E. S.; Maichle-Mössmer, C.; Strähle, J. *Z. Anorg. Allg. Chem.* **1994**, *620*, 1678. (c) Ludlow, S.; McCarthy, A. E. *J. Organomet. Chem.* **1981**, *219*, 169. (d) Spirlet, M. R.; Van den Bossche, G.; Dideberg, O.; Dupont, L. *Acta Crystallogr.* **1979**, *B35*, 1727.

(20) Wolfe, S. *Acc. Chem. Res.* **1972**, *5*, 102.

(21) (a) Burdon, J.; Hotchkiss, J. C.; Jennings, W. B. *J. Chem. Soc., Perkin Trans. 2* **1976**, 1052. (b) Raban, M.; Noyd, D. A.; Bermann, L. *J. Org. Chem.* **1975**, *40*, 752.

(22) While the term "chiral dichalcogenide" has sometimes been used, the chiralities of most of those compounds have been due to the substituents on the chalcogen atoms, see: (a) Wirth, T. *Tetrahedron* **1999**, *55*, 1. (b) Nishibayashi, Y.; Uemura, S. *Rev. Heteroatom Chem.* **1996**, *14*, 83.

(23) (a) Neubert, L. A.; Carmack, M. *J. Am. Chem. Soc.* **1974**, *96*, 943. (b) Nagarajan, R.; Woody, R. W. *J. Am. Chem. Soc.* **1973**, *95*, 7212. (c) Carmack, M.; Neubert, L. A. *J. Am. Chem. Soc.* **1967**, *89*, 7134. (d) Fridrichsons, J.; Mathieson, A. M. *Acta Crystallogr.* **1967**, *23*, 439. (e) Beecham, A. F.; Mathieson, A. M. *Tetrahedron Lett.* **1966**, 3139. (f) Beecham, A. F.; Fridrichsons, J.; Mathieson, A. M. *Tetrahedron Lett.* **1966**, 3131. (g) Djerassi, C.; Wolf, H.; Bunnenberg, E. *J. Am. Chem. Soc.* **1962**, *84*, 4552. (h) Djerassi, C.; Fredga, A.; Sjöberg, B. *Acta Chem. Scand.* **1961**, *15*, 417.

theoretical studies; barriers of rotation for racemization of diphenyl disulfide, diselenide, and ditelluride were calculated to be 8.6, 8.2, and 5.3 kcal mol^{-1} through the *cisoid* geometry and 5.4, 5.2, and 3.7 kcal mol^{-1} through the *transoid* geometry, respectively.[31] When nine other pieces of crystal obtained from the same pot were subjected to measurement of the CD spectra in a similar manner, all of the crystals showed a negative first Cotton effect. This result indicates that all of the crystals obtained in the pot are composed of the same stereoisomer of the disulfide. When recrystallization was repeated (nine additional times), crystals that showed a positive Cotton effect in the corresponding region were obtained in two cases, and the crystals in the same pot were composed of one stereoisomer on the basis of measurements of the CD spectra of 10 crystals selected at random. In these recrystallizations, this phenomenon does not depend on the recovery yield (even over 50% yield), which means that chiral crystallization occurs in the pot.

In the case of diphenyl diselenide, crystals obtained from hot ethanol showed a positive (one time) or negative (seven times) first Cotton effect at around 375 nm in their CD spectra, and crystals in the same pot were composed of a single stereoisomer in all cases (eight recrystallizations). The bathochromic shift upon changing from sulfur to selenium corresponds to that with 1,2-dithiane-3,6-dicarboxylic acid and the corresponding diselenide.[32] However, in the case of diphenyl ditelluride, some of the crystals that precipitated from hot petroleum ether in a pot showed a positive first Cotton effect at around 400 nm while others showed a negative effect in the corresponding region, although sometimes crystals of only one stereoisomer were obtained.

When a single crystal of diphenyl ditelluride which showed a positive first Cotton effect was seeded in a petroleum ether solution of the ditelluride in recrystallization, 10 pieces of crystal in the resulting precipitate all showed a positive Cotton effect. Similarly, seeding of a crystal with a negative first Cotton effect gave crystals with a negative Cotton effect. These results mean that seeding a crystal with a known absolute configuration in recrystallization can control the stereochemistry of chiral recrystallization. This phenomenon was also observed with diphenyl disulfide and diselenide; seeding a crystal with a positive first Cotton effect gave crystals with a positive first Cotton effect, while seeding a crystal with a negative first Cotton effect yielded negative crystals.

The absolute configuration of chiral diphenyl disulfide with a negative first Cotton effect was determined by X-ray crystallographic analysis at 120 K.[33] As a result, diphenyl disulfide with a negative first Cotton effect in its CD spectrum was found to have a *P*-helical form; the absolute structure parameter was −0.02(5) [1.02(6) as *M*-form]. On the basis of the similarities of the first Cotton effects of diphenyl diselenide and ditelluride with that of the disulfide, the diselenide and ditelluride with a negative first Cotton effect can be assigned the *P*-form and those with a positive effect are the *M*-form. The relationship between the absolute configuration and the CD spectra is summarized in Table 1.

Table 1. Relationship between Absolute Configuration and Circular Dichroism Spectra (KBr Disk) of Diphenyl Dichalcogenides

	sign of Cotton effect	
PhEEPh	*P*-form	*M*-form
PhSSPh	−(ca. 330 nm)	+(ca. 330 nm)
	−(ca. 270 nm)	+(ca. 270 nm)
PhSeSePh	−(ca. 375 nm)	+(ca. 375 nm)
	−(ca. 265 nm)	+(ca. 265 nm)
PhTeTePh	−(ca. 400 nm)	+(ca. 400 nm)
	−(ca. 290 nm)	+(ca. 290 nm)

Supporting Information Available: The X-ray crystallographic CIF data for *P*-diphenyl disulfide. This material is available free of charge via the Internet at http://pubs.acs.org.

OL010172G

---

(24) (a) Casey, J. P.; Martin, R. B. *J. Am. Chem. Soc.* **1972**, *94*, 6141. (b) Coleman, D. L.; Blout, E. R. *J. Am. Chem. Soc.* **1968**, *90*, 2405. (c) Beychok, S.; Breslow, E. *J. Biol. Chem.* **1968**, *243*, 151. (d) Beychok, S. *Science* **1966**, *154*, 1288.

(25) Review: Snatzke, G. In *The Chemistry of Organic Selenium and Tellurium Compounds*, Vol. 1; Patai, S., Rappoport, Z., Ed.; John Wiley & Sons: New York, 1986; Chapter 17.

(26) (a) Ringdahl, B.; Craig, J. C.; Zdansky, G.; Fredga, A. *Acta Chem. Scand*. **1980**, *B34*, 735. (b) Foss, O.; Johnsen, K.; Reistad, T. *Acta Chem. Scand*. **1964**, *18*, 2234.

(27) (a) Armarego, W. L. F.; Turner, E. E. *J. Chem. Soc.* **1957**, 13. (b) Kuroda, R.; Mason, S. F. *Tetrahedron* **1981**, *37*, 1995.

(28) Egartner, L.; Halla, F.; Schacherl, R. *Z. Phys. Chem. B* **1932**, *18*, 189.

(29) **Typical procedure for chiral crystallization of diphenyl dichalcogenides:** ca. 1.0 g of diphenyl disulfide or diphenyl diselenide, which was preliminary purified by silica gel column chromatography and then recrystallization, was dissolved in refluxing ethanol (ca. 15 or 40 mL, respectively), and the solution was cooled slowly to room temperature. Precipitated crystals were collected by suction filtration to give chiral crystals of the disulfide (32−74%) or diselenide (16−73%). Similarly, 0.6 g of diphenyl ditelluride was recrystallized from hot petroleum ether (ca. 45 mL) to yield chiral crystals of the ditelluride (57−84%).

(30) A mixture of a single crystal (ca. 2 mg) of the dichalcogenide and 100 mg of KBr was ground and formed into disk with a radius of 6.5 mm.

(31) Theoretical study: Geometries, vibrational frequencies, and energies were calculated by using Density Functional Theory (B3LYP). The double-ζ plus polarization basis set of hydrogen, carbon, and sulfur atoms was used. The (5s 4p 2d/12s 8p 5d) and (10s 8p 4d/16s 11p 6d) basis sets were also used for the selenium and tellurium atoms, respectively.

(32) (a) Djerassi, C.; Wolf, H.; Bunnenberg, E. *J. Am. Chem. Soc.* **1962**, *84*, 4552. (b) Djerassi, C.; Fredga, A.; Sjöberg, B. *Acta Chem. Scand*. **1961**, *15*, 417.

(33) Crystal data of diphenyl disulfide with negative first Cotton effect (KBr disk): $C_{12}H_{10}S_2$, $M_r = 218.32$; orthorhombic, space group $P2_12_12_1$, $a = 23.455(3)$, $b = 8.073(3)$, and $c = 5.524(2)$ Å, $V = 1045.9(6)$ Å^3, $Z = 4$, $T = 120$ K, $D_c = 1.386$ g cm^{-3}, $\mu = 0.462$ mm^{-1} (Mo Kα 0.71073 Å). A total of 5295 reflections were measured of which 2417 reflections ($R_{\text{int}} = 0.014$) including Bijvoet pairs were independent and 2387 reflections with $I > 2\sigma(I)$. Lorentz and polarization corrections were made. Absorption correction was applied using a Ψ scan method with $T_{\min} = 0.854$, $T_{\max} = 0.891$. All H-atoms were located on the *D*-map and refined with isotropic thermal parameters. Final refinement with 168 parameters against 2417 reflections gave $R = 0.0193$, $wR = 0.0554$, and $\Delta\rho_{\min} = -0.19$, $\Delta\rho_{\max} = 0.21$ e Å^{-3}. Absolute structure parameter was −0.02(5) for the *P*-form and 1.02(6) for the *M*-form.