oil was vacuum distilled collecting 92.5 g. of III, b.p. 132–135° at 0.6–0.8 mm.

Anal. Calcd. for $C_{12}H_{20}S_2O$: C, 58.98; H, 8.24; S, 26.23. Found: C, 59.13; H, 8.03; S, 26.06.

Alcoholic hydrolysis of I. In a 4-l. flask there was placed 260 g. of I, 1200 ml. of 20% potassium hydroxide and 1200 ml. of 95% ethanol. This mixture was refluxed for 40 hr. and then carefully acidified with concd. sulfuric acid keeping the temperature below 50°. Copious amounts of hydrogen sulfide were liberated on acidification and a small amount of sulfur was isolated by filtration. The acidified solution was separated and extracted with 1 l. of ether and the ether solution evaporated on a water bath at 60°. The residue, 140 g., was fractionated and gave two major acidic fractions: A, b.p. 149–152°, 36.2 g.; B, b.p. 179–185°, 30.5 g.

A was identified as trimethyl acetic acid by conversion first to the acid chloride, b.p. 135–140°, using thionyl chloride, and then to the anilide by refluxing with aniline, m.p. 131°, reported m.p. 129° for trimethylacetanilide.

Anal. Calcd. for $C_{11}H_{15}ON$: N, 7.91. Found: N, 7.86.

The *p*-bromophenacyl ester of A (from 95% ethanol) melted at 75–76°, reported m.p. 76°.

Anal. Calcd. for $C_{12}H_{15}O_3Br$: Br, 27.83. Found: Br, 27.78.

B was identified as 4,4-dimethylvaleric acid by conversion to the amide and the anilide. B was refluxed with thionyl chloride and the acid chloride distilled. A solution of 5 g. of aniline in 50 ml. of benzene was added to 5 g. of the acid chloride, the solution refluxed 30 min., washed with water, 10% hydrochloric acid and 10% sodium hydroxide, and finally concentrated to 20 ml. total volume. White crystals separated from solution and were recrystallized from ethanol, m.p. 141–142°. The reported melting point for 4,4-dimethylvaleranilide is 141°.

Anal. Calcd. for $C_{13}H_{19}ON$: N, 6.82. Found: N, 6.83.

Conversion of the acid chloride of B to the amide with cold concd. ammonia gave white platelets, recrystallized from water, m.p. 139–141°; reported m.p. 140–141° for 4,4-dimethylvaleramide.

Anal. Calcd. for $C_7H_{15}ON$: N, 10.85. Found: N, 10.30.

PAULSBORO, N. J.

[CONTRIBUTION FROM THE DEPARTMENT OF APPLIED CHEMISTRY, COLLEGE OF ENGINEERING, UNIVERSITY OF OSAKA PREFECTURE]

Organic Polysulfides. II.[1] Polymorphism in Dibenzhydryl Tetrasulfide

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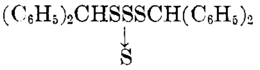
Two polymorphs of dibenzhydryl tetrasulfide were found. Observations of mutual convertibility and of their melting behaviors and determinations of ultraviolet and infrared absorption spectra support the conclusion that the two forms are rotational isomers in the solid state.

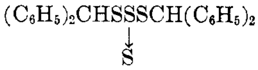
Synthesis of a series of dibenzhydryl polysulfides from mono- to hexasulfide was reported in the previous paper,[1] in which the sulfur-sulfur linkages in these polysulfides were linear. Dibenzhydryl tetrasulfide had been prepared[2] by condensation of two moles of the thiol with sulfur monochloride in carbon disulfide solution. The condensation reaction was exothermic. When all the procedures were carried out at temperatures below 30° by cooling, white pillars (I) were obtained. On the other hand, when the reaction temperature exceeded 30°, a mixture of white pillars and pale yellow needles (II) was obtained. The higher the temperatures, the greater was the proportion of yellow needles. Recrystallization of a mixture of pillars and needles from a solvent mixture of ether-petroleum ether led to an increase in the proportion of II. After two recrystallizations the white pillars disappeared completely and all the crystals were composed of the yellow needles (II). Such polymorphism was not found in other polysulfides previously reported,[1] *e.g.*, dibenzhydryl tri- and tetrasulfides and dibenzyl tri-, tetra-, and pentasulfides.

The ultraviolet absorption spectrum and molar refraction of benzhydryl tetrasulfide II were reported in the previous paper.[1] The spectrum of I overlapped with that of II within the experimental error. As II had[1] linear sulfur–sulfur linkages, by analogy, I would be expected to have the same sulfur linkages as II. Isomers such as III, IV and V are unlikely for the structure of I, as such a structure should have a different ultraviolet absorption spectrum from that of the linear one. Moreover, if the polymorphism resulted from such branched type isomers, the other polysulfides should have similar polymorphs. As stated above, such polymorphism could not be found in the other polysulfides.



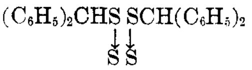
$(C_6H_5)_2CHS\underset{\overset{\downarrow}{S}}{S}SCH(C_6H_5)_2$

III



$(C_6H_5)_2CHS\underset{\overset{\downarrow}{S}}{S}SCH(C_6H_5)_2$

IV



$(C_6H_5)_2CH\underset{\overset{\downarrow}{S}}{S}\ \underset{\overset{\downarrow}{S}}{S}CH(C_6H_5)_2$

V

The remaining possibilities are either that these polymorphs are rotational isomers of each other (possibility A) or that molecules having the same configuration aggregate to different crystal structures I and II (possibility B). In order to decide whether the polymorphism of dibenzhydryl tetrasulfide can be ascribed to possibility A or B, mutual

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(1) Part I. J. Tsurugi and T. Nakabayashi, *J. Org. Chem.*, **24**, 807 (1959).

(2) J. Tsurugi and T. Nakabayashi, *Nippon Kagaku Zasshi*, **77**, 583 (1956).

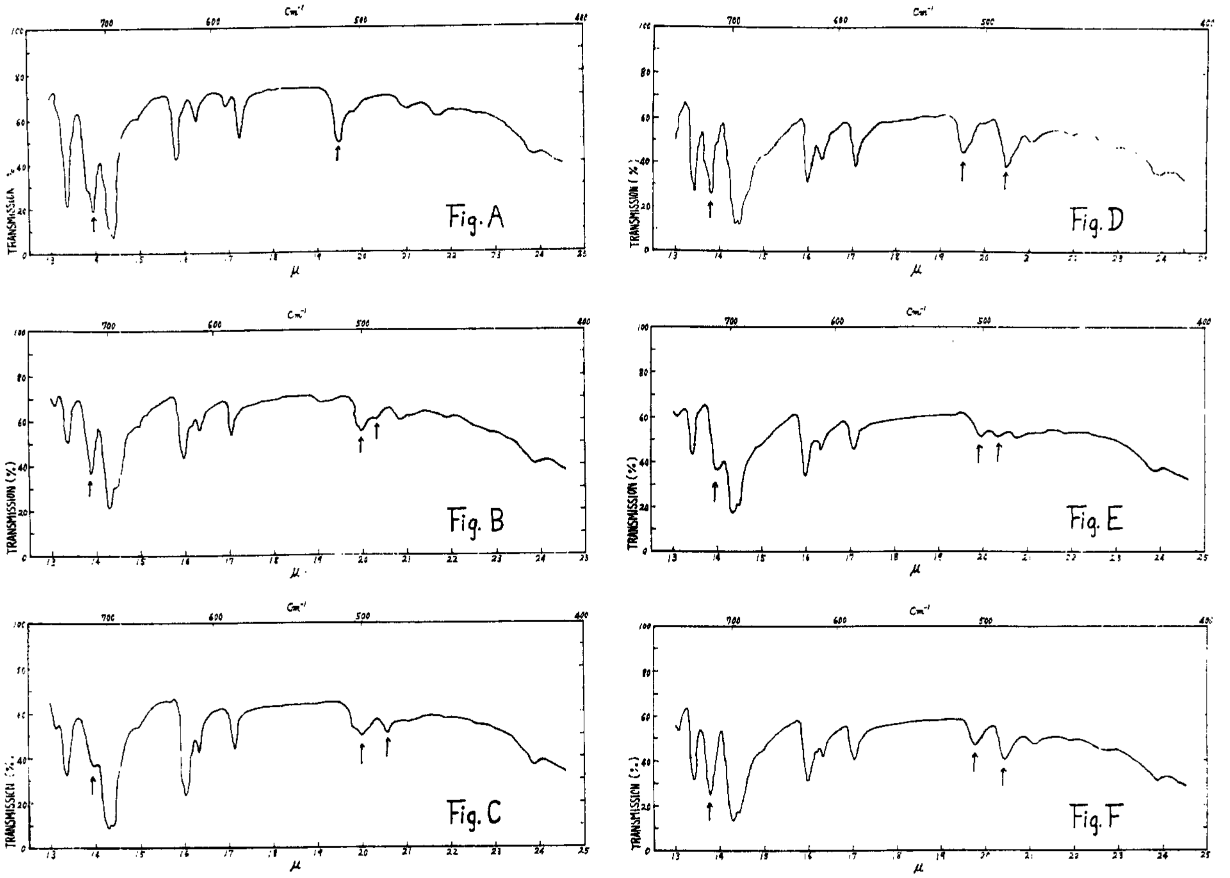

Fig. 1. A. Dibenzhydryl monosulfide. B. Dibenzhydryl disulfide. C. Dibenzhydryl trisulfide D. Dibenzhydryl tetrasulfide (I). E. Dibenzhydryl tetrasulfide (II). F. Dibenzhydryl pentasulfide

convertibility was attempted, and infrared absorption spectra of I and II and of the related compounds were determined. X-ray diffraction patterns of I and II were also determined.

The melting point of II was in the range of 82–83°,[1] while I began to melt at 73°, and in the range of 73–83°, solid remained mixed with melted substance. It melted completely at the same temperature as the melting point of II, *i.e.*, at 83°. However, when I was heated extremely slowly on the microscope hot stage, white pillars changed to pale yellow needles as soon as the former melted at 73°. The latter melted at 83°. This indicates that I was converted to II at 73°. Transformation of I to II was observed on recrystallization as stated above. The melt formed by heating I or II over 83° did not crystallize and remained as yellow viscous oil even after being kept at room temperatures. However, when one pillar of I or one needle of II was added to the oil at the temperatures near 70°, the oil crystallized to yellow needles (II). Transformation from II to I was also successful by adding one pillar of I to a saturated solution of the melted compound in petroleum ether below 30°. Observations mentioned above indicate that two polymorphs are easily interconvertible, and II is more stable than I. Easy convertibility with each other again precludes the possibility of isomers having branched sulfur chains. However, these observations do not decide whether possibility A or B is applicable.

Infrared absorption spectra of dibenzhydryl polysulfides, including I and II, were determined with a potassium bromide prism (12–25 μ) and indicated in Fig. 1a-f. In general, assignment of C—S and S—S vibrations are considered to be difficult because of their very weak intensities and wide range of the absorptions and because of the tendency to be shifted easily by neighboring groups. Moreover, only a few examples in this range can be found in the literature. Therefore, it is necessary here to determine the spectra of the homologous compounds and to compare them with each other, in order to correlate an absorption band to a given structural bond. Of the three spectral bands which appeared in the range of 700–770 cm.$^{-1}$ in Fig. 1, the central band near 716–727 cm.$^{-1}$ can be correlated with C—S vibration, and the other two to C—H out-of-plane deformations of monosubstituted aromatic ring in benzhydryl group. The latter two are well defined as such[3] and the former is observed in each spectrum of the polysulfides including the monosulfide. Moreover, no vibration

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(3) J. L. Bellamy, *The Infrared Spectra of Complex Molecules*, 2nd Ed., London, 1958, p. 350.

except those of C—H out-of-plane deformations of phenyl groups can be expected with respect to dibenzhydryl polysulfides. Absorption bands in the region of 590–625 cm.$^{-1}$ can be correlated with the dibenzhydryl group, because all these bands for each compound are observed in the same frequency except for those of the monosulfide. Moreover, infrared spectrum of dibenzhydryl ether was determined in potassium bromide region, and three bands (578, 601, and 617 cm.$^{-1}$) were observed. Absorption bands near 500 cm.$^{-1}$, which do not appear in the spectrum of dibenzhydryl ether, are correlated with C—S and S—S vibrations respectively, and that which does not appear in the spectrum for the monosulfide must be correlated to S—S vibration. The above considerations are summarized in Table I, in which some absorption bands are correlated to C—S and S—S bonds.

The identity period along the *c* axis of I and II were also determined by the x-ray rotating crystal method; these were 8.0 and 5.7 A for I and II respectively.

Whether possibility A or B is applicable to explain the polymorphism may be decided by considering the results obtained above and by referring to some literature references on sulfur chemistry. Table I indicates that I and II have C—S and S—S vibrations different from each other, and Fig. 1 indicates that absorption bands of I have stronger intensities than those of II, in general. This difference may be explained by an assumption that two polymorphs are rotational isomers of each other, and that II has better symmetry than I. Cymerman and Willis[4] reported that weak S—S vibration was found in a spectrum of diphenyl disulfide, while the corresponding vibration could not be found in that of diphenyl disulphone because of its symmetrical center. Woodrow, Carmack, and Miller[5] concluded from determination of dipole moments that *n*-hexadecyl tetrasulfide in benzene has three pairs of conformers, which result from rotation of S—S bonds. Thus, if one assumes that I is composed of one specific configuration among these conformers and II another, the slight shift of the infrared absorption bands from I to II could be explained. The weaker intensities of bands of II than those of I could be attributed to a better symmetry of the former, while possibility B predicts nothing about the infrared spectra. The observations that the melted tetrasulfide does not crystallize even after long standing at room temperatures and that I, II, or their mixture is obtained depending on the temperatures during preparation are explained by assuming that polysulfides in liquid state or solution are in equilibrium of several configurations, and that the tetrasulfide can take two specific configurations depending on conditions under which it solidifies or crystallizes. The reason why benzhydryl tetrasulfide has such rotational isomers in the solid state may be found in a similar example in the study of a series of polymethylene dihalides [$X(CH_2)_nX$]. Brown and Sheppard[6] found that trimethylene diiodide alone has two solid rotational isomers, one stable (TT) and one metastable (TG) isomer, while no other polymethylene dihalides have such metastable solid isomers. In this case, the bulky iodine atoms located at both ends of the molecule and the specific chain length of methylenes may lead to a metastable solid rotational isomer. The same situation may hold for the series of benzhydryl polysulfides. The bulky benzhydryl end groups and specific sulfur chain length of the tetrasulfide may lead to such a metastable rotational isomer as well.

TABLE I

ASSIGNMENT OF C—S AND S—S VIBRATIONS IN DIBENZHYDRYL POLYSULFIDES

	C—S, Cm.$^{-1}$		S—S, Cm.$^{-1}$
$[(C_6H_5)_2CH]_2S$	716.8	512.3	—
$[(C_6H_5)_2CH]_2S$	719.4	501.3	492.6
$[(C_6H_5)_2CH]_2S$	716.3	500.5	486.1
$[(C_6H_5)_2CH]_2S$, I	726.2	511.8	487.8
$[(C_6H_5)_2CH]_2S$, II	714.3	501.3	491.4
$[(C_6H_5)_2CH]_2S$	725.7	506.3	489.5

Palmer[7] reported the configuration of sulfur monochloride, in which the dihedral angle between Cl—SS—Cl is near 100°. When the synthesis of benzhydryl tetrasulfide is carried out at lower temperatures, the product may be assumed to maintain the same or similar dihedral angles between $<S_1S_2S_3$ and $<S_2S_3S_4$ as that of sulfur monochloride. This configuration corresponds to I. On the other hand, at higher temperatures S—S bond rotation may occur owing to steric repulsion of each bulky dibenzhydryl group. This leads to a more coiled and more stable configuration, which corresponds to II. The x-ray diffraction pattern and infrared spectra which indicate better symmetry of II are in accord with the above assumption.

In summary, polymorphism of dibenzhydryl tetrasulfide may be interpreted as due to rotational isomerism, and all the experimental results and literature references cited support this assumption.

EXPERIMENTAL

Preparation of I. White pillars of I were prepared by condensation of a slight excess of benzhydryl mercaptan (b.p. 98–99°/0.03 mm.) and freshly distilled sulfur monochloride.[2] In a stream of nitrogen gas and protected against moisture, sulfur monochloride in carbon disulfide was

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(4) J. Cymerman and J. B. Willis, *J. Chem. Soc.*, 1332 (1951).

(5) C. C. Woodrow, M. Carmack, and J. G. Miller, *J. Chem. Phys.*, **19**, 951 (1951).

(6) J. K. Brown and N. Sheppard, *Proc. Roy. Soc.*, **231**, 555 (1951).

(7) K. J. Palmer, *J. Am. Chem. Soc.*, **60**, 2360 (1938).

stirred into the mercaptan in carbon disulfide maintained in a cooling bath below 30°. After standing for 4 hr., the solvent was evaporated under vacuum and the remaining oil was taken up in ether. The ether solution was stored in a refrigerator and white pillars were obtained from the yellow solution a few days later.

Anal. Calcd. for $C_{26}H_{22}S_4$: C, 67.49; H, 4.79; S, 27.72. Found: C, 68.00; H, 4.86; S, 27.30.

Preparation of II. Yellow needles of II were obtained by recrystallization of the white pillars from ether-petroleum ether (b.p. 33–46°). The analysis and physical properties of II, including ultraviolet spectrum, have been reported.[1,2] The ultraviolet spectrum of I was identical with that of II within experimental error.

Infrared spectra of a series of dibenzhydryl polysulfides and dibenzhydryl ether in the range of potassium bromide were determined by using a Perkin-Elmer 21. Specimens were measured in a potassium bromide disk.

X-ray diffraction patterns of single crystals of I and II were determined by the rotating crystal method. An iron target was used (λ = 1.93728 A), and the radius of the casset was 50 cm. Distances between equatorial line and first layer line and between the former and second layer line were 12 and 27.5 mm. respectively in the case of I, and those of II 18 and 46 mm. respectively.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF TEXAS]

S-Alkylmercaptosuccinic Acids as Solid Derivatives of Olefins, Alkyl Bromides, and Mercaptans

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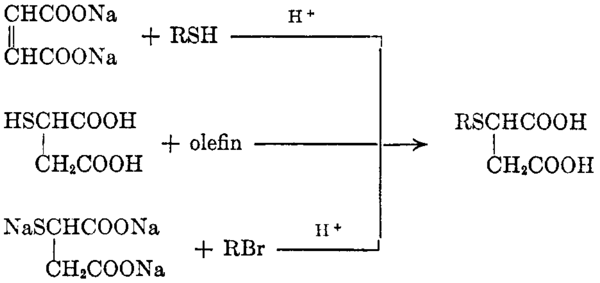
Solid *S*-alkylmercaptosuccinic acids have been prepared from olefins, mercaptans, and alkyl bromides and their melting points and solubilities have been studied as a function of the structure of the alkyl group. These properties vary with structure in a predictable manner. The acids are satisfactory solid derivatives for primary olefins and mercaptans and both primary and secondary alkyl bromides because of the ease with which the reaction can be effected, the good yields obtained, and the ease of purification. They have the added advantage of being acids; thus their neutralization equivalents may be obtained for confirmatory characterization.

In the present era of instrumental analyses by which compounds are characterized with scarcely a trace of chemistry, it may seem archaic to propose a new reagent for the preparation of a solid derivative to be used as an aid in compound characterization. There are times, however, when a good crystalline derivative is highly desirable, but hard to find. This is especially true with the olefins, mercaptans, and alkyl bromides.

2,4-Dinitrobenzenesulfenyl chloride[2,3] is the most generally useful reagent for olefins[4] and mercaptans.[5] Other reagents which have been proposed include nitrosyl chloride, 4-mercaptobiphenyl,[6] other sulfhydral compounds,[7] and silver 3,5-dinitrobenzoate plus iodine.[8]

The initial purpose of this investigation was to develop a satisfactory solid derivative for liquid olefins. The free radical addition of mercaptosuccinic acid to an olefin appeared to offer several desirable features. The reaction goes readily to give solid derivatives which are acids and can be titrated to confirm their identity. These derivatives also have the added advantage of ready synthesis by two independent methods. They can be formed by the free radical addition of the ap-



$$\left.\begin{array}{l}\begin{array}{l}\text{CHCOONa}\\ \|\\ \text{CHCOONa}\end{array} + \text{RSH} \xrightarrow{H^+} \\[1ex] \begin{array}{l}\text{HSCHCOOH}\\ \quad|\\ \text{CH}_2\text{COOH}\end{array} + \text{olefin} \longrightarrow \\[1ex] \begin{array}{l}\text{NaSCHCOONa}\\ \quad|\\ \text{CH}_2\text{COONa}\end{array} + \text{RBr} \xrightarrow{H^+}\end{array}\right] \longrightarrow \begin{array}{l}\text{RSCHCOOH}\\ \quad|\\ \text{CH}_2\text{COOH}\end{array}$$

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[1] Dow Chemical Co. Fellow, 1951–52; American Oil Co. Fellow, 1953–54. Present address: Dow Chemical Co., Freeport, Tex.

[2] N. Kharasch, *J. Chem. Ed.*, **33**, 585 (1956).

[3] R. B. Langford and D. D. Lawson, *J. Chem. Ed.*, **34**, 510 (1957).

[4] N. Kharasch and C. M. Buess, *J. Am. Chem. Soc.*, **71**, 2724 (1949); (b) N. Kharasch and A. J. Havlik, *J. Am. Chem. Soc.*, **75**, 3734 (1953).

[5] H. Bohme and H. O. Stachel, *Z. Analyt. Chem.*, **154**, 27 (1957).

[6] C. T. Lester, F. G. Rodgers, and E. E. Reed, *J. Am. Chem. Soc.*, **66**, 1674 (1944).

[7] (a) G. Axberg and B. Homberg, *Ber.*, **66**, 1193 (1933); (b) S. O. Jones and E. E. Reed, *J. Am. Chem. Soc.*, **60**, 2452 (1937); (c) E. P. Kohler and H. Potter, *J. Am. Chem. Soc.*, **57**, 1316 (1935); (d) W. H. Carothers, *J. Am. Chem. Soc.*, **56**, 2008 (1935).

[8] B. I. Halperin, H. B. Donahoe, J. Kleinberg, and C. A. VanderWerf, *J. Org. Chem.*, **17**, 623 (1952).