TABLE I

ACTIVATION ENERGIES AND SULFUR–SULFUR BOND DISTANCES

Cyanide + XSSY → NCSX + $^-$SY

XSSY	X	Y	r_{ss}, Å.	Ref.	E_a, kcal./mole	Ref.
$^-SSO_3{}^-$	—	$O_3{}^-$	1.97	a	13.0	b
S_8	S	S	2.048	c	11.7	d
$S_4O_6{}^{-2}$	$SO_3{}^-$	$SO_3{}^-$	2.02	e	11.3	f
$S_3O_6{}^{-2}$	$SO_3{}^-$	$O_3{}^-$	2.15	g	9.5	h

Sulfite + XSSY^k → $^-O_3$SSX + $^-$SY

$^-SSO_3{}^-$	—	$O_3{}^-$	1.97	a	14.5	i
$S_3O_6{}^{-2}$	$SO_3{}^-$	$O_3{}^-$	2.15	g	10 to 11	j

^{a} O. Foss and A. Hordnik, *Acta Chem. Scand.*, **11**, 1443 (1957); P. G. Taylor and C. A. Beevers, *Acta Cryst.*, **5**, 341 (1952). ^{b} R. E. Davis, *J. Phys. Chem.*, **66**, 956 (1962); P. D. Bartlett and R. E. Davis, *J. Am. Chem. Soc.*, **80**, 2513 (1958). ^{c} S. C. Abrahams, *Acta Cryst.*, **8**, 611 (1955); A. Caron and J. Donohue, *ibid.*, **14**, 548 (1961). ^{d} P. D. Bartlett and R. E. Davis, *J. Am. Chem. Soc.*, **80**, 2513 (1958), and ref. 6. E_a estimated in pure water from the data in aqueous methanol. ^{e} O. Foss and A. Hordnik, *Acta Chem. Scand.*, **12**, 1700 (1958). ^{f} R. E. Davis, *J. Phys. Chem.*, **62**, 1599 (1958). ^{g} W. H. Zachariasen, *J. Chem. Phys.*, **2**, 109 (1934). ^{h} This study. ^{i} D. P. Ames and J. E. Willard, *J. Am. Chem. Soc.*, **73**, 164 (1951). ^{j} A. Fava and G. Pajaro, *Ann. chim.* (Rome), **44**, 551 (1954). ^{k} Data are available for the reaction of sulfite ion with cystine and N,N-diacetylcystine with E_a of 12.8 and 13.3 kcal./mole for a bond distance of 2.04 Å. (R. Cecil and J. R. McPhee, *Biochem. J.*, **60**, 496 (1955); L. K. Steinrauf, J. Peterson, and L. H. Jensen, *J. Am. Chem. Soc.*, **80**, 3835 (1958). While these fit the r^{-3} relationship quite well, we are not sure how general the rule is for these materials. Work is in progress.

the shorter the bond the higher the activation energy and (2) the difference between the data for cyanide ion and for sulfite ion is quite regular, with the activation energy difference about 1 kcal. for a given bond distance. Statistical treatment of the data in Table I by the "t test" indicates the best correlation between E_a and r as being

$$E_a = \frac{99.9}{r^3} \quad \frac{\text{kcal.}}{\text{mole}} \text{ (cyanide)} \quad (3)$$

$$E_a = \frac{110}{r^3} \quad \frac{\text{kcal.}}{\text{mole}} \text{ (sulfite)} \quad (4)$$
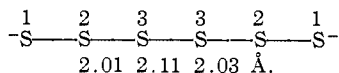
with a standard deviation of 1.5% for the cyanide data.

The equation has been tested in the present study with the reaction of cyanide ion with trithionate. Extensive kinetic investigations place E_a as 9.5 kcal./mole, in good agreement with the inverse cubic relationship.

The relationship is expected on the basis of current theory. The use of Gordy's rule[7] predicts $E_a = f(1/r)^n$, $n > 2$. More revealing have been molecular orbital calculations. As a result of our calculations we conclude that the greater stability and shorter length of an S–S bond implies a greater instability of the sulfur antibonding acceptor orbital. As the nucleophile such as cyanide approaches, the antibonding orbital of the sulfur–sulfur bond *accepts* the electron pair while the sulfur–sulfur bond breaks. The energy differences between bonding and antibonding orbitals are related by an exponential term in the bond distance which has been expanded in a power series.

These ideas really explain the relative rate data of the elemental sulfurs (Table II) even though dihedral angle effects are present.

The new correlation will allow an *a priori* estimate of which bond of a polythio compound will cleave the fastest.

$$\overset{1}{\underset{}{-S}}\overset{2}{\underset{2.01}{-S}}\overset{3}{\underset{2.11}{-S}}\overset{3}{\underset{2.03 \text{ Å.}}{-S}}\overset{2}{\underset{}{-S}}\overset{1}{\underset{}{-S^-}}$$

The displacement should occur most readily on atom three, breaking bond 2–3. A quantitative estimate has

(7) W. Gordy, *J. Chem. Phys.*, **14**, 305 (1946).

TABLE II

RATES OF REACTION OF TRIPHENYLPHOSPHINE WITH VARIOUS ELEMENTAL SULFURS IN BENZENE AT $7.35^{o\,a}$

Allotrope	S–S, Å.	k_2, M^{-1} sec.$^{-1}$
S_8	2.048^b	7.54×10^{-4}
S_6	2.06^c	19.1
S_x (polymeric)	2.08^d	Too fast to measure

^{a} P. D. Bartlett, E. F. Cox, and R. E. Davies, *J. Am. Chem. Soc.*, **83**, 103 (1961). ^{b} Table I. ^{c} J. Donohue, A. Caron, and E. Goldish, *J. Am. Chem. Soc.*, **83**, 3748 (1961). ^{d} N. S. Gingrich, *J. Chem. Phys.*, **8**, 29 (1940).

been presented for hexasulfide and cyanide ions.[8] Work is in progress on the reaction of cyanide ion with the polysulfide ions to test the predictions.

We expect the correlation to fit the data for other thiophiles such as $^-$SH. Experimental work is in progress to test the usefulness and generality.

Acknowledgment.—The present study was supported by the Walter Reed Army Institute and the National Science Foundation, NSF-G15750.

(8) R. E. Davis, "Nucleophilic Displacement Reactions at the Sulfur–Sulfur Bond," in Vol. II, "Survey of the Progress of Chemistry," A. Scott, Ed., in press.

(9) Alfred P. Sloan Fellow, 1962–1964.

(10) In part from M.Sc. thesis of A. Cohen.

(11) Undergraduate NSF Research Student, 1962 and 1963.

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The Configuration of (+)-Methyl-α-naphthylphenylmethane, -silane, and -germane[1]

Sir:

Methyl-α-naphthylphenylsilane (II, Si*H) was synthesized and resolved by Sommer and Frye[2] in 1959 and recently Brook and Peddle[3] synthesized and resolved methyl-α-naphthylphenylgermane (III, Ge*H). The absolute configurations of the enantiomers of these compounds have been established[3,4] and the absolute configuration of the silicon compound, established by X-ray methods by Pepinsky and co-workers,[5] is in agreement with our proposal. We have now completed the synthesis and resolution of methyl-α-naphthyl-phenylmethane (1-(α-naphthyl)-1-phenylethane) (I, C*H) and have shown through the similarities of their optical rotatory dispersion curves that enantiomers of I, II, and III with the same sign of rotation have the same configuration.

The enantiomers of these compounds, being optically active with the same sign of rotation, being identical in structure and configuration, and differing only in the nature of the central asymmetric atom, define a unique series of a type which, to the best of our knowledge, has not been described previously.[6]

The absolute configurations of the (+)-enantiomers of the series of compounds, together with their melting points and specific rotations (all in cyclohexane, c 10.3) are shown in Chart I. It is evident that the size of the central atom, and hence steric crowding, has

(1) Presented in part at the XIX Congress of the International Union of Pure and Applied Chemistry, London, England, July 10–17, 1963.

(2) L. H. Sommer and C. L. Frye, *J. Am. Chem. Soc.*, **81**, 1013 (1959).

(3) A. G. Brook and G. J. D. Peddle, *ibid.*, **85**, 1869 (1963).

(4) A. G. Brook and W. W. Limberg, *ibid.*, **85**, 832 (1963).

(5) R. Pepinsky, Y. Okaya, *et al.*, to be published.

(6) Should future study of the properties of series of compounds such as those described here indicate that some general descriptive nomenclature is warranted, we would suggest the term "isoconfigurational series" be employed. An isoconfigurational series may be defined as a series of enantiomers $R_1R_2R_3R_4M$ of identical structure and configuration differing only in the nature of the asymmetric atom M.
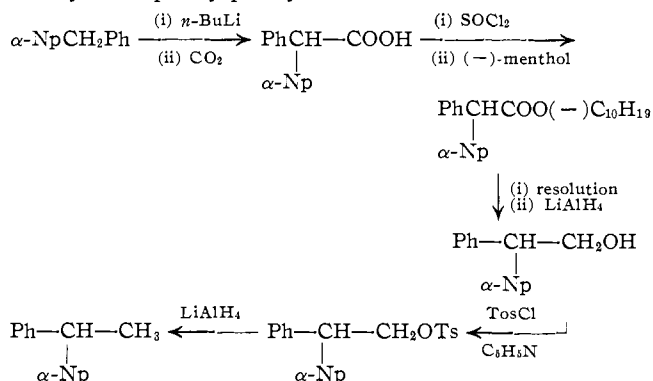
CHART I

ABSOLUTE CONFIGURATIONS AND PHYSICAL CONSTANTS OF (+)-
ENANTIOMERS

	Ph	Ph	Ph
	α-Np—C—Me	α-Np—Si—Me	α-Np—Ge—Me
	H	H	H
Compound	I	II	III
M.p., °C.	54–55°	63–64°	74–75°
$[\alpha]^{23}$D	7.5°	34.9°	26.7°

far less to do with the specific rotation than has the electronegativity of the asymmetric atom. Indeed, a linear plot of electronegativity of the central atom (C = 2.60, Si = 1.90)[7] vs. specific rotation predicts a value of 2.06 for the electronegativity of germanium, in excellent agreement with the value of 2.00 determined by Allred and Rochow from n.m.r. data.

We have initiated studies comparing the physical properties of the members of this and related series, and hope to report shortly the synthesis and resolution of the related tin compound.

The synthetic sequence leading to (+)- and (−)-methyl-α-naphthylphenylmethane is shown.

$$\alpha\text{-NpCH}_2\text{Ph} \xrightarrow[\text{(ii) CO}_2]{\text{(i) }n\text{-BuLi}} \underset{\alpha\text{-Np}}{\text{PhCH—COOH}} \xrightarrow[\text{(ii) (−)-menthol}]{\text{(i) SOCl}_2}$$

$$\underset{\alpha\text{-Np}}{\text{PhCHCOO(−)C}_{10}\text{H}_{19}}$$

$$\downarrow \begin{array}{l}\text{(i) resolution}\\\text{(ii) LiAlH}_4\end{array}$$

$$\underset{\alpha\text{-Np}}{\text{Ph—CH—CH}_2\text{OH}}$$

$$\underset{\alpha\text{-Np}}{\text{Ph—CH—CH}_3} \xleftarrow{\text{LiAlH}_4} \underset{\alpha\text{-Np}}{\text{Ph—CH—CH}_2\text{OTs}} \xleftarrow[\text{C}_5\text{H}_5\text{N}]{\text{TosCl}}$$

α-Benzylnaphthalene[8] was metalated with n-butyllithium in ether–hexane and the resulting purple-red solution was carbonated to give α-naphthylphenylacetic acid, m.p. 139–141°, lit.[9] 140–141°, in 65% yield. After conversion to the acid chloride with thionyl chloride the crude acid chloride was treated directly with one equivalent of (−)-menthol in pyridine–benzene. The crude ester was crystallized from ethanol to give 79% of a diastereomeric mixture of menthyl esters, m.p. 59–68°, $[\alpha]^{23}$D −61.5° (cyclohexane, c 5).[10] The ester was crystallized from methanol (about 20 ml./g.) several times, finally yielding large needles. During this process the rotation increased to $[\alpha]^{23}$D −68.7° and the m.p. rose to 95–96°. The filtrates from these crystallizations were concentrated and the residue was recrystallized from methanol, two fractions of solid being removed. The filtrate was concentrated, yielding material melting at 74–80° with $[\alpha]^{23}$D −55.4°. After two recrystallizations from hexane (5 ml./g.) and one from heptane (2 ml./g.) the solid, m.p. 77–83°, $[\alpha]^{23}$D −52.0°, was crystallized from methanol (3 ml./g.) containing a trace of hexane to give the second diastereomeric ester, m.p. 84.5–85.5°, $[\alpha]^{23}$D −51.1°, as fine needle clusters.

Reduction of the more soluble (−)-menthoxy-α-naphthylphenylacetate, m.p. 84.5–85.5°, $[\alpha]^{23}$D − 51.1°, with lithium aluminum hydride in ether gave

(7) A. L. Allred and E. G. Rochow, J. Inorg. Nucl. Chem., 5, 269 (1958).

(8) E. Koike and M. Okawa, J. Chem. Soc. Japan, Pure Chem. Sect., 74, 971 (1953).

(9) C. J. Collins, L. S. Ciereszko, and J. G. Burr, J. Am. Chem. Soc., 75, 405 (1953).

(10) All rotations unless otherwise indicated were determined in CHCl₃, c 10.0–10.3.

as a gum after removal of the menthol by steam distillation 2-(α-naphthyl)-2-phenylethanol, $[\alpha]^{23}$D 1.95° (cyclohexane, c 5), not further purified but converted directly to the crystalline tosylate in pyridine at 0° in 86% yield, m.p. 132–134°, from ethyl acetate–hexane, $[\alpha]^{23}$D 35.2°. Finally, reduction with lithium aluminum hydride in tetrahydrofuran gave, after alkaline extraction, 95% of (−)-methyl-α-naphthylphenylmethane, m.p. 54–55°, from ethanol, $[\alpha]^{23}$D − 7.3° (cyclohexane, c 10.3).

A similar procedure employing the less soluble ester, m.p. 95–96°, $[\alpha]^{23}$D −68.7°, gave tosylate in 82% yield, m.p. 132–134°, $[\alpha]^{23}$D −35.8°, which gave (+)-methyl-α-naphthylphenylmethane in 85% yield, m.p. 54–55°, $[\alpha]^{23}$D 7.5° (cyclohexane, c 10.3).

The hydrocarbon was identified by comparison of the infrared spectra and mixture melting point behavior of a synthetic racemate, m.p. 64.5–66.5°, with an authentic racemic sample, m.p. 64–66°, lit.[11] 65–66°, prepared by hydroboration, followed by protonolysis, of a sample of 1-(α-naphthyl)-1-phenylethene,[12] m.p. 57–59°, lit.[11] 58–59°.

Analyses and infrared spectra of all compounds were in accord with the structures assigned.

The configuration of (+)-C*H could not be related to (+)-Si*H by mixture melting point techniques, as had been done for (+)-Si*H with (+)-Ge*H,[3] since mixtures of (+)-C*H with both (+) and (−)-Si*H formed eutectics. All three compounds gave essentially similar optical rotatory dispersion curves with positive Cotton effects, that for (+)-Si*H being in accord with the results of Sommer, et al.[13] From the results it is apparent that all three (+)-enantiomers have the same configuration, namely R.

Rotatory dispersion curves were determined in cyclohexane at about 25° at the concentrations (g./100 ml.) shown.

(+)-C*H (c 0.7) $[\alpha]_{589}$ 4.7, $[\alpha]_{500}$ 13, $[\alpha]_{400}$ 40, $[\alpha]_{350}$ 72, $[\alpha]_{325}$ 83 (peak), $[\alpha]_{310}$ 50°.

(+)-Si*H (c 0.25) $[\alpha]_{589}$ 32, $[\alpha]_{500}$ 53, $[\alpha]_{400}$ 102, $[\alpha]_{350}$ 168, $[\alpha]_{324}$ 251 (peak), $[\alpha]_{310}$ 232°.

(+)-Ge*H (c 0.32) $[\alpha]_{589}$ 21, $[\alpha]_{500}$ 41, $[\alpha]_{400}$ 75, $[\alpha]_{350}$ 122, $[\alpha]_{321}$ 171 (peak), $[\alpha]_{310}$ 160°.

(11) B. R. Brown and O. Ll. Hammick, J. Chem. Soc., 1395 (1948).

(12) This experiment was performed by Mr. J. B. Pierece following the general procedures described by H. C. Brown, et al.

(13) L. H. Sommer, C. L. Frye, et al., J. Am. Chem. Soc., 83, 2210 (1961).

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The Synthesis and Stability of N,N′-Bisuccinimidyl

Sir:

The nature of the chain-carrying species in free radical brominations by N-bromosuccinimide (NBS) has been the focus of continuing controversy.[1] It has recently been shown that the relative reactivities of NBS and bromine toward alkylbenzenes are experimentally indistinguishable over a wide range of substrate structure and reaction conditions,[1] indicating

(1) (a) R. E. Pearson and J. C. Martin, J. Am. Chem. Soc., 85, 354 (1963);
(b) G. A. Russell, C. DeBoer, and K. M. Desmond, ibid., 85, 365 (1963);
(c) C. Walling, A. L. Rieger, and D. Tanner, ibid., in press.