

Three salts of I have been prepared; their compositions are established by the data below.⁸ The good agreement among the magnetic moments (*cf.* Table I) of the pure crystalline solids and among the results for the $(n\text{-Bu}_4\text{N})^+$ salt in the pure solid, in solution, and in mixed crystals of the isomorphous diamagnetic $[(n\text{-Bu}_4\text{N})_2[\text{CoS}_4\text{C}_4(\text{CN})_4]]$ leaves no doubt as to the authenticity of the doublet ground state and the lack of strong magnetic interactions in the pure solid. The lower Curie magnetic moments at 77°K. are often found for low-spin planar Co(II).^{4,9}

TABLE I
MAGNETIC MEASUREMENTS ON $[\text{CoS}_4\text{C}_4(\text{CN})_4]^{-2}$

Compound	State	μ_{eff} , B.M. ^a
$[(\text{C}_6\text{H}_5)_4\text{As}]_2[\text{CoS}_4\text{C}_4(\text{CN})_4]$	Solid	2.16
$(\text{Et}_4\text{N})_2[\text{CoS}_4\text{C}_4(\text{CN})_4]$	Solid	2.08
	Solid (77°K.)	1.87
$(n\text{-Bu}_4\text{N})_2[\text{CoS}_4\text{C}_4(\text{CN})_4]$	Solid	2.16
	Solid (77°K.)	1.93
	50.9% in Ni diluent	2.19
	32.9% in Ni diluent	2.18
	18.0% in Ni diluent	2.20
	11.5% in Ni diluent	2.22
	5.3% in Ni diluent	2.11
	Acetone soln.	2.17
	DMSO soln.	2.14
	DMF soln.	2.09

^a All measurements at 300°K. unless otherwise stated; all moments are calculated from the Curie law.

We have made extensive magnetic resonance measurements on I, the results of which appear in Table II. The single crystal measurements were made by rotating the magnetic field in three mutually perpendicular crystal planes, and the data were treated by least squares and analyzed according to the procedure outlined by Schonland.¹⁰

TABLE II
PARAMAGNETIC RESONANCE MEASUREMENTS ON
 $(n\text{-Bu}_4\text{N})_2[\text{CoS}_4\text{C}_4(\text{CN})_4]^{-2}$

State	g -Values	Co ⁵⁹ hyperfine interaction (cm. ⁻¹)
Solution, acetone	2.255 ^b	...
20% solid solution in Ni diluent, powdered sample	$g_1 \sim g_2 \sim 2.0$ $g_3 = 2.80 \pm .01$	$ a_3 = 4.8 \times 10^{-3}$
5% solid solution in Ni diluent, single crystal	$g_1 = 1.977^c$ $g_2 = 2.025^c$ $g_3 = 2.798^c$	$ a_1 = 2.3 \times 10^{-3d}$ $ a_2 = 2.8 \times 10^{-3d}$ $ a_3 = 5.0 \times 10^{-3d}$

^a Measurements made at room temperature, ~298°K. ^b Single broad line, ~220 gauss peak-peak. g -Value reported is $(g)_{\text{av}}$, estimated accuracy ± 0.010 . ^c Estimated accuracy ± 0.003 . ^d Estimated accuracy $\pm 0.1 \times 10^{-3}$ cm.⁻¹.

The r.m.s. g -value of 2.297 obtained from the single crystal measurement requires for $S = 3/2$ a moment of 4.45 B.M. and for $S = 1/2$, 1.99 B.M. The reported high-spin moment is in poor agreement with the e.s.r. result, contrary to a previous conclusion based on the average of g_1 and g_2 only.⁵ Deviations of 0.1–0.2 B.M. between the Curie law moments (Table I) and the crystal g -values (Table II) may be due to thermal accessibility of excited electronic states.

(8) For $\text{R}_2\text{CoS}_4\text{C}_4(\text{CN})_4$ melting points, analyses, and conductivities (nitromethane) are as follows. *Anal.* R = $(n\text{-Bu}_4\text{N})$ (141–143°); Calcd: C, 58.29; H, 8.81; N, 10.25; S, 15.56. Found: C, 58.20; H, 8.78; N, 10.34; S, 15.80; $\Lambda = 161$. R = (Et_4N) (197.5–200°); Calcd: C, 48.06; H, 6.72. Found: C, 47.87; H, 6.51; $\Lambda = 181$. R = $(\text{C}_6\text{H}_5)_4\text{As}$ (227–230°); Calcd: C, 60.82; H, 3.65; N, 5.07. Found: C, 60.75; H, 3.70; N, 4.98; $\Lambda = 197$ cm.² equiv.⁻¹ ohm.⁻¹.

(9) We thank Professor F. A. Cotton for the use of low temperature magnetic susceptibility equipment.

(10) D. S. Schonland, *Proc. Phys. Soc. (London)*, **73**, 788 (1959).

It would be premature, without structural information, to identify the magnetic axis system in terms of the principal symmetry axes of the presumably planar ion 1. Especially dangerous would be the identification of g_3 with g_{\parallel} for the planar complex, in light of the paramagnetic resonance results on cobalt(II) phthalocyanine,¹¹ for which $g_{\parallel} = 1.92$, $g_{\perp} = 2.90$. It would perhaps be more reasonable to associate g_1 and g_2 in which case the large in-plane anisotropy must be explained by a significant splitting of the energies of the d_{xz} and d_{yz} orbitals by the ligand field. Such a splitting could arise if there is delocalization of these orbitals over the π -system of the ligands and would indeed be a consequence of the D_{2h} symmetry of the complex as contrasted with the D_{4h} symmetry of the phthalocyanine. However, the ground state configuration may not be the same in this complex as that deduced by Griffith¹² for cobalt(II) phthalocyanine.

Following are the d -spacings of all lines in the X-ray powder pattern of $(n\text{-Bu}_4\text{N})_2[\text{CoS}_4\text{C}_4(\text{CN})_4]$ occurring in the range $4 < d < 5$ Å.: 4.00(s), 4.12(w), 4.18(m), 4.50(m), 4.63(vw), 4.76(w), 4.88(s), 4.96(w), and 5.08(s).

Acknowledgment.—Financial support by the National Institutes of Health, National Science Foundation, and the Advanced Research Projects Agency (Contract SD-88) is gratefully acknowledged.

(11) J. F. Gibson, D. J. E. Ingram, and D. Schonland, *Discussions Faraday Soc.*, **26**, 72 (1958).

(12) J. S. Griffith, *ibid.*, **26**, 81 (1958).

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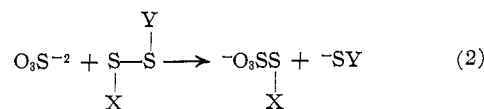
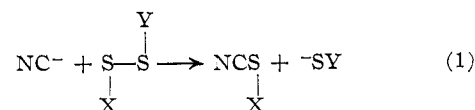
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A Novel Correlation of Activation Energy with Sulfur–Sulfur Bond Distance¹

Sir:

The sulfur–sulfur bond is unique in that the bond distance varies from 1.89 Å. in diatomic sulfur² to 2.39 Å. in sodium dithionite.³ While both of these extreme values are for atypical sulfur–sulfur bonds, numerous compounds contain sulfur–sulfur bonds from 1.97 to 2.2 Å. in length.^{4,5} In continuing an exploration of the SN2 reaction we expected to find some correlation between the length of the sulfur–sulfur bond and the activation energy of cleavage of that bond with various thiophilic reagents.⁶

Both cyanide ion and sulfite ion are good thiophilic reagents. In Table I the results of numerous investi-



gators on sulfur–sulfur bond lengths and activation energies of displacement reactions in aqueous media near 25° are presented. It is of interest to note (1)

(1) Displacement Reactions. IV. Paper III: R. E. Davis, *J. Phys. Chem.*, **66**, 956 (1962). Presented at the 145th National Meeting of the American Chemical Society, New York, N. Y., September, 1963.

(2) K. Ikenoue, *J. Phys. Soc. Japan*, **8**, 646 (1953).

(3) J. D. Dunitz, *Acta Cryst.*, **9**, 579 (1956).

(4) S. C. Abrahams, *Quart. Rev. (London)*, **10**, 407 (1956).

(5) W. A. Pryor, "Mechanisms of Sulfur Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp. 16–24.

(6) R. E. Davis, Thesis, Harvard University, under P. D. Bartlett, 1958.

TABLE I

ACTIVATION ENERGIES AND SULFUR-SULFUR BOND DISTANCES

Cyanide + XSSY \rightarrow 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* \rightarrow $^{-}O_3SSX$ + ^{-}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. Steirner, 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

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

$$E_a = \frac{110}{r^3} \frac{\text{kcal.}}{\text{mole}} \text{ (sulfite)} \quad (4)$$

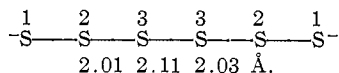
with a standard deviation of 1.5% for the cyanide data.

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 rule⁷ 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.



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°C^a

Allotrope	S-S, Å.	$k_2, M^{-1} \text{ sec.}^{-1}$
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.

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The Configuration of

(+)-Methyl- α -naphthylphenylmethane, -silane, and -germane¹

Sir:

Methyl- α -naphthylphenylsilane (II, Si*H) was synthesized and resolved by Sommer and Frye² in 1959 and recently Brook and Peddle³ 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 -naphthylphenylmethane (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.