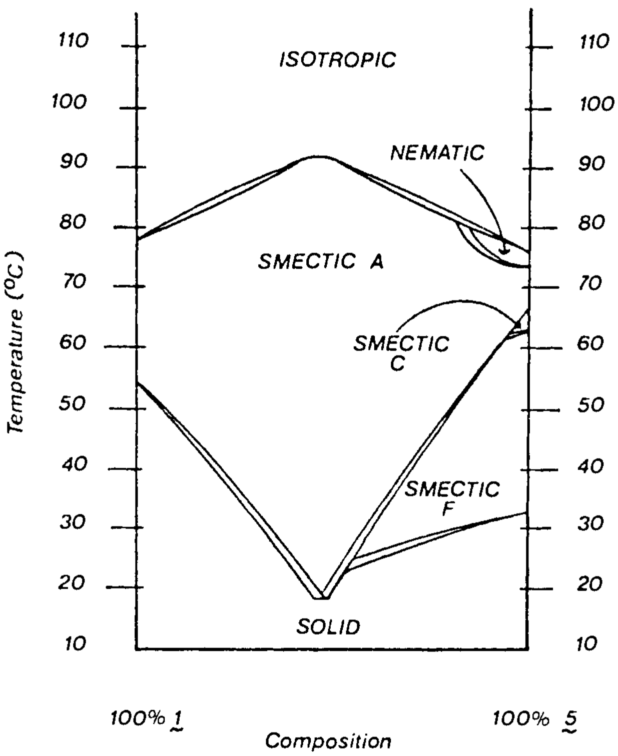
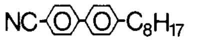
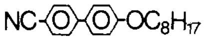


Figure 1. Condensed, isobaric binary phase diagram for compounds **1** and **5** obtained using Kofler contact preparation (mixed fusion).

exception is for the smectic A mesophases of 4-cyano-4′-octylbiphenyl (**2**) and 4-cyano-4′-octyloxybiphenyl (**3**) as

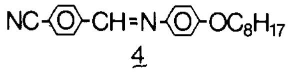


2



3

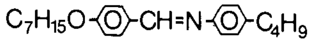
described by Gray and Lydon.[3] These authors proposed a bilayer arrangement of constituent molecules involving interdigitated alkyl (or alkoxyl) tails to explain the unusual *d* value (1.4 times the molecular length) for these molecules. McMillan[4] has obtained similar x-ray data for 4-cyanobenzylidine 4′-octyloxyaniline (**4**). According to Cladis,[5] mixtures



4

of **4** and a structurally similar nematogen exhibit a new liquid-crystal phase diagram, one in which a smectic phase appears at lower *and* higher temperatures than a nematic phase. A general similarity in molecular structural features is apparent between these compounds and **1**, the presence of a molecule with a flexible hydrocarbon chain on one end and a small, compact group on the other end.[6] The unusual *d* value for **1**, possibly also arising from a bilayered structure, appears related to nonlinear transition temperature behavior as described below. (No monochromator was used with our Rigaku x-ray generator and thus the middle ring seen in reference 3, if present in our photograph of **1**, may have been masked by "white" radiation.)

Labes et al.[7] and Oh[8] have reported nonlinear mesophase-isotropic transition temperatures for binary mixtures containing 4-cyano-4′-pentylbiphenyl which is considered[9] to have this bilayered molecular arrangement. It was found that **1** also promotes nonlinear mesophase-isotropic behavior in mixtures. A condensed, isobaric binary phase diagram, obtained microscopically using the Kofler contact method,[10] for **1** and 4-heptyloxybenzylidine 4′-butylaniline[11,12] (**5**) is shown in Figure 1 as an example of this phenomenon. The pure components show mesophase-isotropic transitions at 77.5 and 76



5

°C, respectively. The mesophase existence temperature is considerably raised by use of **1** in mixtures. This finding is reminiscent of work by Schroeder and Schroeder[13] in which they found increased S → I temperatures for 4,4′-dihexyloxyazoxybenzene when it was admixed with nonmesomorphic nitro-containing aromatic compounds. Compounds such as **1** may prove quite useful in applications where increased mesophase-isotropic temperatures are desired. Preliminary work[14] has revealed that several 4-nitrophenyl 4′-alkoxybenzoates and other nitro-terminated liquid crystals are likewise effective in producing pronounced nonlinear mesomorphic behavior in mixtures.

Acknowledgment. This research was supported in part by a Cottrell Grant to ACG from Research Corporation.

References and Notes

(1) Part 1: A. C. Griffin, *Mol. Cryst. Liquid Cryst., Lett.*, **34**, 111 (1976). Part 2: A. C. Griffin, S. F. Thames, and M. S. Bonner, *ibid.*, **34**, 135 (1977).
(2) A. de Vries, *Pramana*, Suppl. No. 1, 93 (1975).
(3) G. W. Gray and J. E. Lydon, *Nature*, **252**, 221 (1974).
(4) W. L. McMillan, *Phys. Rev.*, **A9**, 1720 (1974).
(5) P. E. Cladis, *Phys. Rev. Lett.*, **35**, 48 (1975).
(6) A discussion with Dr. Mary Neubert on this point was quite helpful.
(7) J. W. Park, C. S. Bak, and M. M. Labes, *J. Am. Chem. Soc.*, **97**, 4398 (1975).
(8) C. S. Oh, paper presented at Sixth International Liquid Crystal Conference, Kent, Ohio, Aug 1976.
(9) A. J. Leadbetter, R. M. Richardson, and C. N. Colling, *J. Phys. (Paris), Colloq. C1*, Suppl. No. 3, **36**, C1-37 (1975).
(10) L. Kofler and A. Kofler, "Thermomikromethoden", Verlag Chemie, Weinheim, 1954.
(11) J. Billard, *C. R. Hebd. Seauces Acad. Sci., Ser. B*, **280**, 573 (1975).
(12) G. W. Smith and Z. G. Garlund, *J. Chem. Phys.*, **59**, 3214 (1973).
(13) J. P. Schroeder and D. C. Schroeder, *J. Org. Chem.*, **33**, 591 (1968).
(14) A. C. Griffin, unpublished work.

Anselm C. Griffin*
Department of Chemistry, University of Southern Mississippi
Hattiesburg, Mississippi 39401

Julian F. Johnson
Institute of Materials Science and Department of Chemistry
University of Connecticut, Storrs, Connecticut 06268

Received April 4, 1977

Directional Preferences of Nonbonded Atomic Contacts with Divalent Sulfur. 1. Electrophiles and Nucleophiles

Sir:

Our studies of nonbonded atomic contacts with sulfur in crystal structures of three sulfur-containing α-amino acids[1] have prompted us to reexamine 69 additional published crystal structures of organic, inorganic, and organometallic compounds containing divalent sulfur (S bonded to two ligands, neither one being H). This examination reveals, among other things, that electrophiles tend to approach S roughly 20° from the perpendicular to the plane through atoms Y—S—Z, whereas nucleophiles tend to approach approximately along the extension of one of the covalent bonds to S.[2] We believe that these regularities portray features of the electron distribution and indicate preferred directions of electrophilic and nucleophilic attack on divalent sulfur.

For each crystal structure examined, all interatomic vectors up to 4.0 Å long (occasionally 4.2 Å) were recalculated from published coordinates. An atom X, not covalently bonded to a particular S, was considered to make a "nonbonded contact" if the S···X distance was not greater than the sum of the

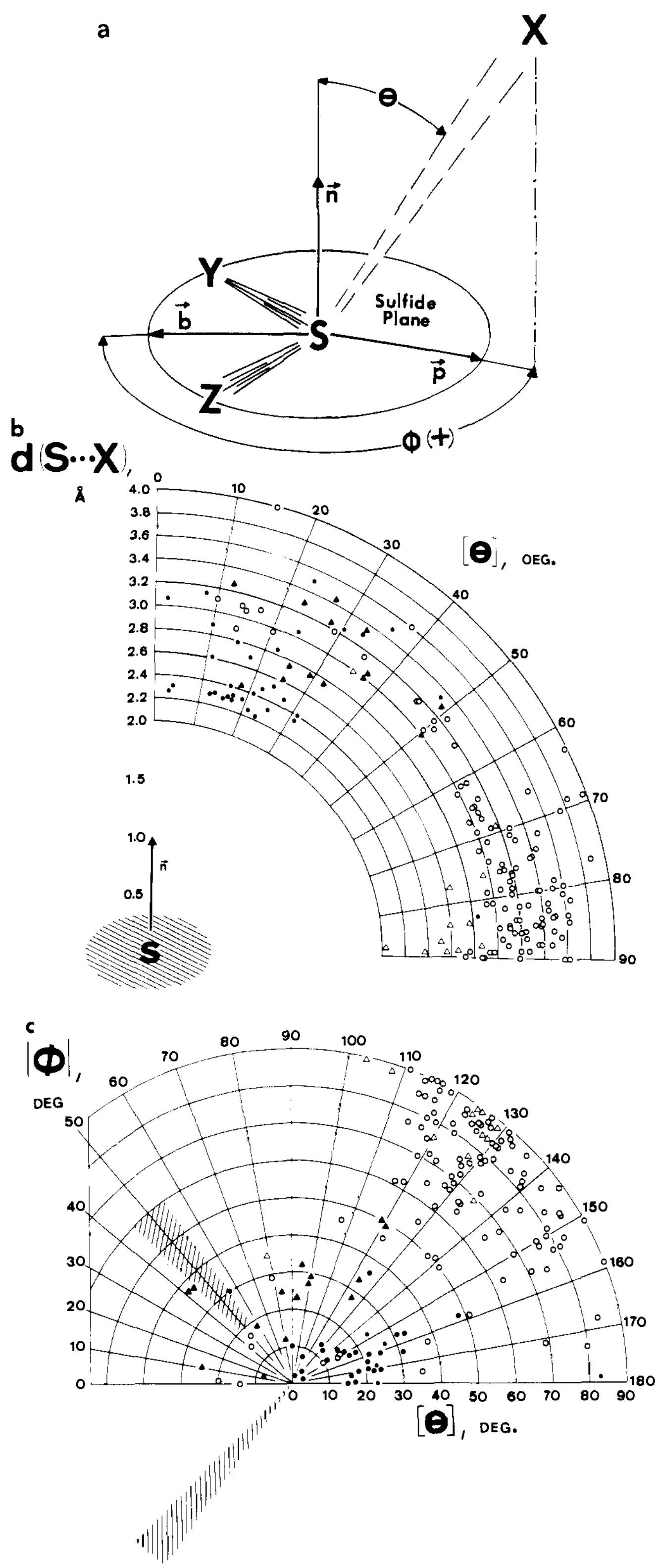


Figure 1. (a) The polar angle θ ($0 \le \theta \le 180°$) and azimuthal angle ϕ ($-180 < \phi \le 180°$) are spherical polar coordinates specifying the direction of S···X. Vector **n** is normal to the sulfide plane, **b** bisects angle α(Y—S—Z), and **p** shows the direction of S···X projected onto the sulfide plane. (b and c) Polar graphs of d(S···X) vs. $[\theta]$ and of $[\theta]$ vs. $|\phi|$ indicate the spatial distribution of S···X contacts. $[\theta]$ is the lesser of θ or $180° - \theta$, and $|\phi|$ is the absolute value of ϕ. Hence, no distinction is made here between contacts above or below the sulfide plane, or between S—Y and S—Z. Filled symbols represent nonbonded contacts with electrophiles; open symbols, nucleophiles; triangles distinguish intramolecular contacts. Overlapping symbols have been slightly displaced for clarity. Striped areas represent the sulfide plane in b and the S—Y and S—Z bonds in c. For nearly every S, the position of Y or Z in c falls in the arc $45 \le |\phi| \le 55°$, $[\theta] = 90°$.

corresponding van der Waals radii.[3] Contacts with metals, such as Cu(I), Cu(II), Ni(II), Pd(II), or Hg(II), were considered “nonbonded”. Contacts between atoms separated by two or three covalent bonds were usually excluded. Hydrogen bonds to sulfur, S···H—R, were considered either as S···H or as S···R nonbonded contacts, depending on whether hydrogen coordinates had been accurately determined. For each S, the relative positions of atoms Y—S—Z and N nonbonded neighbors X_i, $i = 1$, to N, were defined by $3N + 3$ independent parameters, d(S—Y), d(S—Z), α(Y—S—Z), d(S···X_i), and the polar and azimuthal angles θ_i and ϕ_i (Figure 1a).

Nonbonded S···X contacts were separated into various classes, based on the nature of X. We report here the results for one class (Table I, supplementary material, lists numerical data used in Figures 1b and 1c),[2] in which X was either a presumed electrophile (e.g., X = Na^+, $H^{\delta+}$, $C^{\delta+}$, $I^{\delta+}$, Cu(I), Cu(II), Ni(II), Pd(II), Hg(II), or Cl) or a presumed nucleophile (e.g., X = Cl^-, Br^-, I^-, $N^{\delta-}$, $O^{\delta-}$, $F^{\delta-}$, $Cl^{\delta-}$, or $Br^{\delta-}$). The 163 contacts fall mainly into two types, distinguished by the direction of S···X relative to Y—S—Z. Type I contacts (Figure 1b) have S···X directions <40° from the perpendicular to the Y—S—Z plane ($0 \le [\theta] < 40°$), and type II contacts have directions <30° from that plane ($60 < [\theta] \le 90°$). The mean values (and standard deviations) of $[\theta]$ for the 54 type I and the 99 type II contacts, respectively, are 21 (9) and 80 (8)°. Figure 1c shows that type II contacts tend to lie along the extension of one of sulfur's bonds.[4] Indeed, the larger of the contact angles, α(Y—S···X) or α(Z—S···X), averages 162 (10)°.

As Figure 1 (b and c) indicates, *nearly all type I contacts are with electrophiles, while nearly all type II contacts are with nucleophiles.* A few nucleophiles, atypically, are engaged in type I contacts. In all but two such cases, the S atom involved is part of a cation, or is covalently bonded to two electron-withdrawing atoms (two nitrogens or oxygens), or both.

The “frontier orbital” model[5] provides a convenient frame for discussing these results. According to this model, electrophiles should interact preferentially with the highest occupied (HOMO) and nucleophiles with the lowest unoccupied (LUMO) molecular orbital. The observed approach directions should then indicate the approximate nature and orientations of these orbitals, insofar as they are centered on sulfur. The type I pattern suggests that the HOMO is essentially a sulfur lone-pair orbital extending nearly perpendicular to the Y—S—Z plane,[6] while the type II pattern identifies the LUMO as a σ^*(S—Y) or σ^*(S—Z) orbital. The second lone-pair orbital on S is conspicuous by the absence of contacts with nucleophiles in the region $|\phi| \sim 180°$.

Attractive nonbonded interactions may be regarded as representing incipient stages of chemical reactions.[7] From this point of view, our results indicate the preferred directions of electrophilic and nucleophilic attack on divalent sulfur, the former being roughly perpendicular to the Y—S—Z plane (type I), the latter roughly along the extension of the S—Y or S—Z bond (type II).[8-11]

Acknowledgments. We thank Professor D. Harker and Dr. H. B. Bürgi for stimulating discussions. R.P. and R.E.R. thank the National Institutes of Health (Grant No. CA 16844) and the Swiss National Fund for Scientific Research, respectively, for partial financial support.

Supplementary Material Available: Table I listing numerical data and references used in Figure 1b and 1c (5 pages). Ordering information is given on any current masthead page.

References and Notes

(1) These crystal structures are *meso*-lanthionine dihydrochloride, D-penicillamine disulfide dihydrochloride, and L-cystine dihydrobromide dihydrate: R. E. Rosenfield, Jr., and R. Parthasarathy, *J. Am. Chem. Soc.*, **96**, 1925 (1974), *Acta Crystallogr.*, **B31**, 462 (1975), and **B31**, 816 (1975), respec-

tively.
(2) A preliminary report (by R.E.R. and R.P.) appeared in Abstracts, American Crystallographic Association, Twenty-fifth Anniversary Meeting, Charlottesville, Va., March 9–13, 1975, p 28. Complete results of the survey will be published elsewhere.
(3) L. Pauling, "The Nature of the Chemical Bond", 3rd ed, Cornell University Press, Ithaca, N.Y., 1960, p 260.
(4) Type II contacts have a mean $|\phi|$ value of 132 (15)°, roughly equal to $180° - \alpha(Y—S—Z)/2$.
(5) K. Fukui, T. Yonezawa, and H. Shingu, *J. Chem. Phys.*, **20,** 722 (1952); K. Fukui, T. Yonezawa, C. Nagata, and H. Shingu, *ibid.*, **22,** 1433 (1954); see also G. Klopman in "Chemical Reactivity and Reaction Paths," G. Klopman, Ed., Wiley, New York, N.Y., 1974, pp 83–90.
(6) The marked deviations of $[\theta]$ from 0°, for type I contacts, may be ascribed to the influence of the second lone-pair orbital on sulfur, or of Y• • •X or Z• • •X nonbonded interactions, or of both.
(7) H. B. Bürgi, J. D. Dunitz, and E. Shefter, *J. Am. Chem. Soc.*, **95,** 5065 (1973); *Acta Crystallogr.*, **B30,** 1517 (1974); H. B. Bürgi, *Angew. Chem., Int. Ed. Engl.* **14,** 460 (1975); J. D. Dunitz, *Phil. Trans. R. Soc. London*, **B.272,** 99 (1975).
(8) From results of EHMO calculations[9] and other chemical studies,[10] it has been proposed that nucleophiles and electrophiles attack an S—S bond roughly in the same directions as those found in the present study.
(9) H. Yamabe, H. Kato, and T. Yonezawa, *Bull. Chem. Soc. Jpn.*, **44,** 604 (1971).
(10) For a recent summary of chemical evidence regarding a "back-side" attack mechanism on sulfur by nucleophiles; see W. A. Pryor and K. Smith, *J. Am. Chem. Soc.*, **92,** 2731 (1970).
(11) Using crossed molecular beams of oriented molecules, it has recently been possible to study *directly* the geometrical requirements for chemical reactions. For a review, see P. R. Brooks, *Science*, **193,** 11 (1976).
(12) Center for Crystallographic Research.
(13) Laboratory of Organic Chemistry.

Richard E. Rosenfield, Jr.,[12,13] R. Parthasarathy*[12]
J. D. Dunitz[13]

Center for Crystallographic Research
Roswell Park Memorial Institute, Buffalo, New York 14263
and Laboratory of Organic Chemistry
Federal Institute of Technology, 8092 Zürich, Switzerland

Received December 20, 1976

Reactions of Tetrathionaphthalene with Transition Metal Carbonyls. Synthesis and Characterization of Two New Organometallic Semiconductors $(C_{10}H_4S_4Ni)_x$ and $[C_{10}H_4S_4Co_2(CO)_2]_x$ and a Tetrairon Cluster $C_{10}H_4S_4Fe_4(CO)_{12}$

Sir:

In an attempt to synthesize new planar organometallic complexes which will form multiparallel chains[1] bridged by a highly delocalized π system, tetrathionaphthalene (TTN)[2] was reacted with $Ni(CO)_4$, $Co_2(CO)_8$, and $Fe_2(CO)_9$ to give two new organometallic semiconductors $(TTN\ Ni)_x$ (TTN: metal ratio, 1:1) and $[TTN\ Co_2(CO)_2]_x$ (1:2) and a tetrairon cluster TTN $Fe_4(CO)_{12}$ (1:4), respectively. We report here the preparation, characterization, and the intriguing physical properties of these novel compounds.

The compound $(TTN\ Ni)_x$ (**1**) was prepared by reacting TTN with excess $Ni(CO)_4$ in freshly distilled benzene under a nitrogen atmosphere at room temperature. The dark brown-red amorphous precipitate (which shows no x-ray powder pattern but exhibits a copper-metallic luster upon grinding) which formed as the red TTN crystals gradually disappeared was then filtered, washed thoroughly with benzene, and vacuum dried. Insolubility of **1** in most organic solvents precludes further purification by recrystallization. However, elemental analysis[3] indicated the stoichiometry of $C_{10}H_4S_4Ni$. The infrared spectrum of **1** (CsI pellet) exhibits (1) no carbonyl stretching frequencies; (2) four strong bands at 1528 (s), 1338 (s), 1320 (sh), 1185 (m), and 800 (m) cm^{-1} which correspond to the four strongest bands in free TTN;[4] (3) a new band at 965 cm^{-1} which is absent in free TTN; and (4) a weak Ni-S band at 329 cm^{-1}. Based on these observations, and by analogy to the known linear polymers $[M(SR)_2]_x$ (M = Ni, Pd),[5] we propose the linear polymeric structure I for **1**.

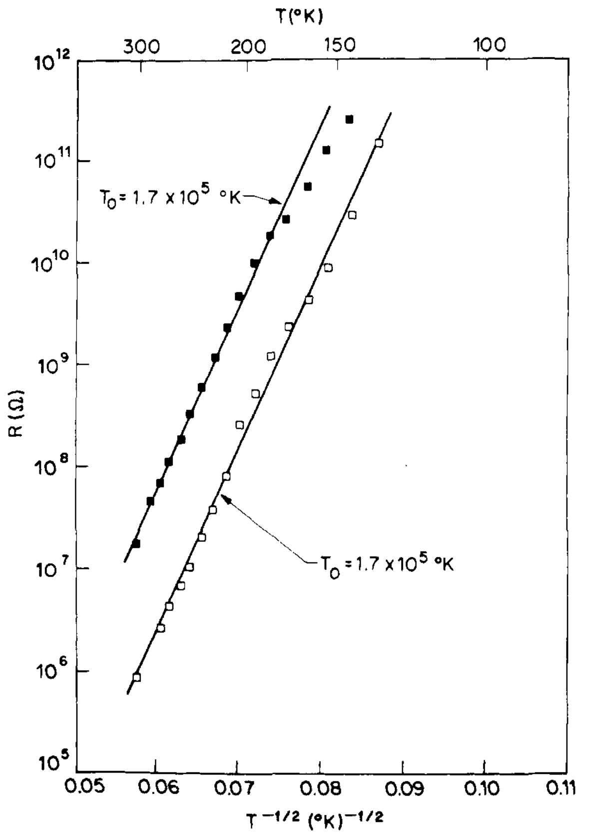


Figure 1. Temperature dependence of the resistance of compressed powder $(C_{10}H_4S_4Ni)_x$ (□) and $[C_{10}H_4S_4Co_2(CO)_2]_x$ (■). The resistance in ohms is approximately equal to three times the resistivity in ohm-centimeters. The bending of the latter curve at low temperature is due to the sample holder.

. . . Ni TTN Ni TTN . . .
I

Reaction of TTN with a stoichiometric amount of $Co_2(CO)_8$ in benzene under similar conditions initially gave rise to a dark green solution which, upon dissolution of the TTN crystals, yielded a dark red precipitate (quantitative reaction). The product, which shows no x-ray powder pattern, is insoluble in most organic solvents and analyzes as $C_{10}H_4S_4Co_2(CO)_2$ (**2**).[3] The infrared spectrum of **2** indicates the presence of (1) only terminal carbonyls (broad band at 2010 (s) with a tailing shoulder at ~1990 cm^{-1}); (2) the coordinated TTN ligand (1525 (m), 1339 (m), 1320 (sh), 1190 (m), and 810 (br, w) cm^{-1}); (3) a weak Co-S stretching frequency at 325 (w) cm^{-1}; and (4) a new band at 970 cm^{-1}. These observations for **2** are consistent with the linear polymeric structure II (where each of the dimeric $Co_2(CO)_2$ units are bridged by four sulfur atoms, two from each of the adjacent TTN ligands) though we cannot rule out other more complicated structures with similar stoichiometry.

. . . $Co_2(CO)_2$ TTN $Co_2(CO)_2$ TTN . . .
II

Reaction of 1 mol of TTN with 2 mol (slight excess) of $Fe_2(CO)_9$ in benzene at room temperature afforded a deep red solution from which a dark red crystalline product was isolated. Elemental analysis[3] suggested the stoichiometry $C_{10}H_4S_4Fe_4(CO)_{12}$ (**3**). The measured molecular weight was 850 (by vapor pressure osmometry with chloroform as solvent and triphenylphosphine as standard) compared with the calculated value of 810. Infrared spectroscopy of **3** indicates the presence of terminal carbonyls (2080 (s), 2041 (vs), and 2000 (vs) cm^{-1}), coordinated TTN ligand (1532 (m), 1341 (m),