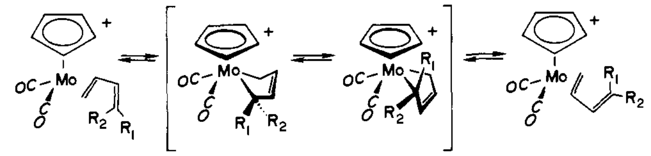
indicated by the presence of four methyl doublets at δ 1.765, 1.740, 1.830, and 1.810 and four cyclopentadienyl singlets at δ 6.050, 6.034, 6.129, and 6.113 in the ratio of 222:93:22:1. The four sets of coordinated piperylene resonances are consistent with those expected based on the possibilities arising from exo-endo and cis-trans isomerism.

As the temperature was raised the signals assigned to endo-cis and exo-cis, as well as those assigned the endo-trans and exo-trans, isomers averaged pairwise. Thus at −32 °C two sets of resonances have averaged and one observes two methyl doublets at δ1.77 and 1.84 and two cyclopentadienyl singlets at δ 6.045 and 6.125, respectively, in the ratio of 11:1. Increasing the temperature results in further line broadening in the methyl and cyclopentadienyl regions. These signals coalesce at 20 °C to two sharp resonances, a doublet (6.0 Hz) and a singlet at δ 1.82 and 6.04, respectively. At this temperature the resonances assigned to the syn and anti protons on the unsubstituted terminal diene carbon atoms show broadening. A process by which this exchange may be accomplished is one involving the formation of a solvated metallocyclopentene intermediate.[17]



Configurational interconversion of syn and anti substituents in **5** may be achieved by flip of the metallocycle envelope followed by collapse to the η^4-butadiene structure. Passage through a metallocyclopentene intermediate also serves to interconvert conformational isomers, but it is a path of higher energy than the rotational motion corresponding to that observed for **1.** The ^{1}H NMR spectrum of cation **5** at 70 °C in the presence of 1 equiv of piperylene shows sharp resonances for the piperylene,[18] whereas the syn and anti protons are extremely broad. Thus we conclude that the configurational averaging is intramolecular.

In addition to the unusual stereochemical nonrigidity displayed by the η^4-diene cations, the η^3-allyl complexes derived by stereospecific addition reactions can be used as intermediates in homologation sequences by activation with $NOPF_6$.[13]

We are continuing to explore the stereochemistry associated with these species and to enlarge the scope of their reactivity.

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(3) Calcd for $C_{11}H_{11}O_2MoBF_4$ (**1**): C, 36.91; H, 3.10. Found: C, 36.57; H, 3.07.

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(5) The recent x-ray structure of η^5-$C_5H_5Mo(Ph_2PCH_2CH_2PPh_2)C_6H_8$ cation supports this assignment. The endo isomer is found in spite of the bulky ethano bridge. See J. A. Segal, M. L. H. Green, J. C. Darin, and K. Prout, *J. Chem. Soc., Chem. Commun.*, 766 (1976).

(6) At −43 °C under slow exchange conditions resonances for both conformers are observed for **11.** The upfield shift of the terminal protons in the endo conformer and those of the 2 and 3 protons in the exo conformer mirror the ring current induced shifts observed in **9** and **10** and their indenyl analogues.[4] The chemical shifts, δ (the ring current shifts relative to **1**), for the indenyl complex in acetone follow: endo, anti −0.34 (1.94), syn 3.18 (0.11), central 6.39 (−0.06); exo, anti 1.84 (0.25), syn 4.71 (1.35), central 5.27 (0.90).

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(12) ^{1}H NMR assignments (δ) are given for selected η^4-diene cations as BF_4^- salts relative to internal acetone (δ 2.04).

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(15) This is supported by the ^{1}H NMR spectrum where **13** displays an ABX_3 multiplet with the diastereotopic methylenes resonating at δ 0.96 and 1.30. The syn proton adjacent to the ethyl group is observed as a doublet of triplets at δ 2.83 (J = 7.0, 2.0 Hz).

(16) The allyl complex containing the aldehyde function showed the following characteristics: IR (cyclohexane) ν_{CO}, 1957, 1884 cm^{-1}, ν_{CHO} 1733 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 9.40 (s, 1 H, CHO), 5.26 (s, 5 H, η^5-C_5H_5), 4.07 (dt, 1 H, H_c, J = 11.0, 7.5 Hz), 3.59 (complex t, 1 H, H_s), 2.87 (ddd, 1 H, H_s, J = 7.5, 2.5, 1.5 Hz), 2.06 (dd, 1 H, diastereotopic CH_2, J = 14.5, 3.0 Hz), 1.25 (dd, 1 H, H_a, J = 11.0, 1.5 Hz), 1.07, 104 (2 s, 6 H, diastereotopic CH_3), 0.26 (dd, 1 H, diastereotopic CH_2, J = 14.5, 12.5 Hz). ^{1}H NMR assignments were confirmed by spin decoupling at 270 MHz. We have not yet explored detailed methodology for decomplexation of the functionalized allkyl ligand from **14,** but note that protonation of **9** with CF_3COOH liberates propene.

(17) The geometric and electronic requirements necessary to accommodate the metallo cyclic intermediate in configurational and conformational rearrangements have not been fully delineated as piperylene iron tricarbonyl does not evidence line broadening to 100 °C. Intermediates of the type discussed herein may be important in the formation of 2-alkenes arising from pyrolysis of platinometallocycles: J. X. McDermott, J. F. White, and G. M. Whitesides, *J. Am. Chem. Soc.*, **98**, 6521 (1976). A stable 3,4-platinometallocyclopent-3-ene of this type has been reported: M. Green, Conference on the Place of Transition Metals in Organic Synthesis, New York Academy of Science, New York, N.Y., Nov 10, 1976.

(18) This research was supported in part by the National Science Foundation. The services of the 270-MHz NMR were made available by a grant from the Biotechnology Resources Program of the National Institutes of Health (RR-798).

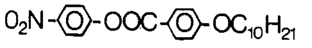
J. W. Faller,* A. M. Rosan
Department of Chemistry, Yale University
New Haven, Connecticut 06520

Received February 21, 1977

Effect of Molecular Structure on Mesomorphism. 3. 4-Nitrophenyl 4'-Decyloxybenzoate: A Liquid Crystal with Novel Mesomorphic Properties[1]

Sir:

As nonideal behavior of binary liquid crystal mixtures is of considerable current interest both from a theoretical viewpoint and in device technology, we wish to report the unusual x-ray diffraction of 4-nitrophenyl 4'-decyloxybenzoate (**1**) and its relation to nonlinear mixture properties of **1.** This compound



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was prepared by the reaction in pyridine of 4-nitrophenol and 4-decyloxybenzoyl chloride. Repeated recrystallization of crude product from ethanol-water afforded **1** as a white crystalline solid. It melts at 55 °C to a smectic A phase and at 77.5 °C transforms from the smectic A phase to an isotropic liquid. The smectic phase often appears, between microscope slide and coverslip, in a homeotropic texture, but can be obtained in a focal-conic fan texture. An x-ray photograph of **1** at 62 °C in its smectic phase showed two prominent diffraction rings. Using the relation λ = 2 d sin θ, the outer diffuse ring corresponds to a D value of 4.65 Å, related to the intermolecular distance in the smectic layers. This value is consistent with current theory.[2] The sharp, intense inner ring corresponds to a d value of 31.4 Å—considerably greater than the length, l, of 27.4 Å for the most extended molecular configuration of **1.** This is quite unusual. Almost without exception this d value, thought[2] to be related to smectic layer thickness, tends to be several angstroms less than the molecular length. A notable

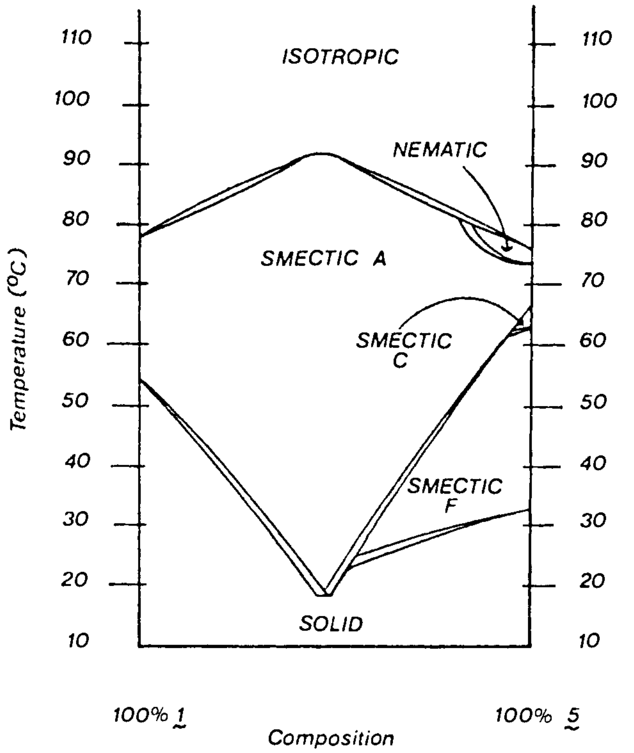
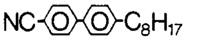


Figure 1. Condensed, isobaric binary phase diagram for compounds **1** and **5** obtained using Kofler contact preparation (mixed fusion).

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



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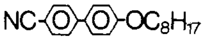
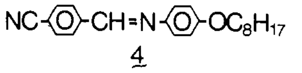


3

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



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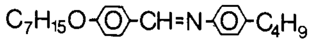
of **4** and a structurally similar nematogen exhibit a new liquid-crystal phase diagram, one in which a smectic phase appears at lower *and* higher temperatures than a nematic phase. A general similarity in molecular structural features is apparent between these compounds and **1**, the presence of 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 °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 $S \rightarrow I$ 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.



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

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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 $S\cdots X$ distance was not greater than the sum of the