method for the study of proteins with a low α-helix content, such as ribonuclease.

If the same considerations are applied to pepsin, curve 2 indicates that the conformations of ribonuclease and pepsin are similar, and that pepsin probably has even less of the α helix than ribonuclease. It will be intriguing to see whether future X-ray diffraction work on pepsin crystals will support this prediction.

B. Jirgensons
The University of Texas
M. D. Anderson Hospital and Tumor Institute
Department of Biochemistry, Houston, Texas 77025
Received April 27, 1967

On the Relation of Nematic to Cholesteric Mesophases

Sir:

Friedel[1] suggested in 1922 that the nematic and cholesteric mesophases are closely related. He showed that two cholesteric compounds of opposite optical rotational power could produce a nematic liquid when mixed in the correct proportions. Friedel concluded,[2] "The cholesteric compounds are but a special form of the nematic compounds. When the rotatory power and the structural properties connected with it disappear..., a nematic material is obtained...." The purpose of this note is to report a number of our recent observations which are related to Friedel's suggestion.

It is believed that in the nematic liquid crystalline phase, intermolecular forces align the molecules with their long axes parallel in large regions, called swarms or domains. A modest magnetic field couples to the magnetic anisotropy of the domains and aligns them to give a macroscopically oriented sample. Molecules dissolved in such solvents give proton nmr spectra of many sharp lines.[3] The spectra are theoretically well understood.[3,4] It is thought that in the cholesteric phase the molecular axes are parallel within planes, while the direction of alignment changes smoothly in a direction perpendicular to the planes. The helical structure thus created is right-handed for some compounds and left-handed for others. No sharp nmr lines can be observed for molecules dissolved in the cholesteric phase. We have employed the proton nmr spectrum of dissolved benzene to differentiate a nematic phase from a cholesteric one.

Our first observations developed from an attempt to find a nematic phase consisting of optically active molecules. We hoped that the built-in screw sense of such a solvent would cause *d*- and *l*-active solute molecules to show different nmr spectra.[5] For this purpose we obtained *p,p'*-diactive amyloxyazoxybenzene. The pure compound did not form a mesophase, but a 1:1 mixture with *p,p'*-di-*n*-hexyloxyazoxybenzene did. Benzene dissolved in the mesophase of this mixture did not give the sharp spectrum characteristic of solution in a nematic medium. The same solvent mixture made from the racemic amyl derivative did produce the expected spectrum. We concluded that the liquid crystal containing the optically active component was in the cholesteric phase. We understand these observations in terms of a simple analogy, which assumes that optically active molecules behave like screws. When right-handed screws are stacked in an orderly manner, layer upon layer, the threads tend to interlock so that the screw axes gradually change direction from one layer to the next and a "cholesteric" structure results. On other hand, an equal mixture of right- and left-handed screws stacks so that their axes remain on the average parallel over long distances, and forms a "nematic" phase.

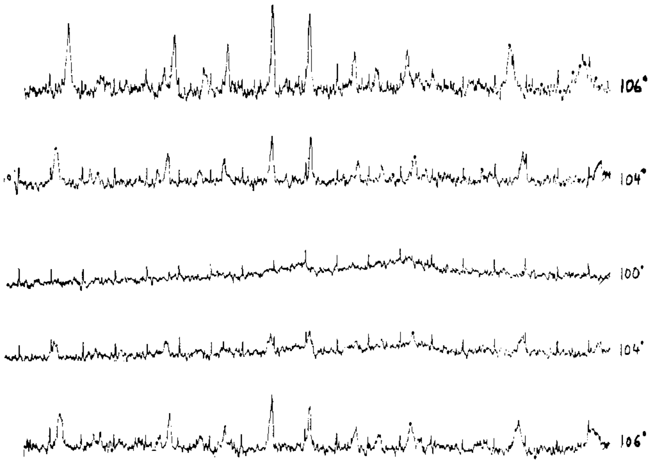

Figure 1. Nmr spectra at 60 MHz of a mixture of 0.013 g of optically active amyloxyazoxybenzene, 0.574 g of hexyloxyazoxybenzene, and 0.03 g of benzene. The spectra were obtained in succession from top to bottom, at the temperatures indicated at right. The small sharp peaks, most distinct in the center spectrum, are frequency markers, spaced 106 Hz apart. Total width of the spectra is about 2000 Hz.

We have observed a phase transition from cholesteric to nematic caused by an applied magnetic field. A solvent mesophase of 2.4 mole % of the active amyloxyazoxybenzene in the hexyloxyazoxybenzene is weakly cholesteric. Above 104° the typical nematic phase nmr spectrum is observed for dissolved benzene. With decreasing temperature the sharp lines suddenly disappear, and at 100° only some broad lines, typical for the cholesteric phase, are observed. These reversible changes are shown in Figure 1. The transition can also be observed as a large increase in turbidity as the liquid becomes cholesteric. Preliminary observations of this effect in fields up to 100 kgauss show that the transition field is roughly proportional to the concentration of the active amyloxyazoxybenzene. These experiments were done at constant temperature, the variation in the magnetic field strength inducing the phase transition in a reversible manner. We conclude that a magnetic field can produce a change of phase from cholesteric to nematic. The interaction of the field with the diamagnetic anisotropy of the nematic phase overcomes the weak intermolecular forces which favor the helical cholesteric structure.

We have extended our nmr studies to solvents which are mixtures of derivatives of cholesterol. Benzene in a 1.9:1 by weight mixture of cholesteryl chloride (*l* rotatory at long wavelengths) and cholesteryl myristate (*d* rotatory at long wavelengths) at 40° give a nematic

---

(1) (a) M. G. Friedel, *Ann. Phys.* [9], **18**, 273 (1922); (b) see also M. R. Cano, *Compt. Rend.*, **251**, 1139 (1960).
(2) Reference 1a, p 431.
(3) A. Saupe, *Z. Naturforsch.*, **20a**, 572 (1965).
(4) L. C. Snyder, *J. Chem. Phys.*, **43**, 4041 (1965).
(5) T. G. Burlingame and W. H. Pirkle, *J. Am. Chem. Soc.*, **88**, 4294 (1966).

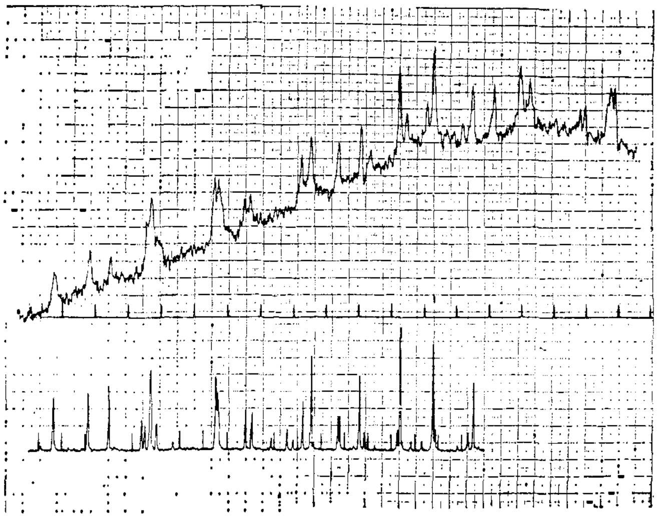

Figure 2. The top trace is the nmr spectrum at 40° of a mixture of 0.655 g of cholesteryl chloride, 0.344 g of cholesteryl myristate, and 0.01 g of benzene. The sharp lines are typical of the benzene spectrum in a nematic solvent. The very broad background resonance is due to the solvent. For comparison, the bottom trace gives a benzene spectrum in nematic hexyloxyazoxybenzene at 90°. Both traces cover a spectrum width of about 2 kHz. The center of the symmetrical benzene spectrum is midway between the two strongest lines; a number of lines at the high-field end of the spectrum are not reproduced. Frequency markers are 106 Hz apart; for the top spectrum they are given on the separate center trace, while for the bottom spectrum they are the sharp peaks superposed on the spectrum.

phase spectrum as shown in Figure 2.[5a] The alignment of the benzene is similar to that obtained in nematic *p,p′*-di-*n*-hexyloxyazoxybenzene. By proper choice of cholesteryl esters it is possible to obtain nematic phases from 23 to 130°. It is clearly possible to produce a nematic phase from a mixture of cholesterol derivatives, each of which alone would give a cholesteric mesophase. The cholesterol derivatives are colorless and lack the polarizable aromatic and conjugated systems which occur in most compounds which form a nematic phase. The mixtures are a possibly useful new solvent for studies of the polarization of optical transitions in oriented solute molecules.

In conclusion, it seems most appropriate to paraphrase Friedel's remarks: The nematic phase is but a special case of the cholesteric; it is one in which the pitch of the helical structure is infinite.

(5a) NOTE ADDED IN PROOF. The relative line positions and intensities in the top spectrum of Figure 2 differ to some degree from those in the bottom spectrum. Note for instance that the two lines nearest the center of the spectrum are stronger and farther apart in the top spectrum than in the bottom spectrum. We have recently found that this is due to the fact that in the first case the preferential alignment of the benzene is with its plane perpendicular to the magnetic field, while it is parallel to the magnetic field in the second case.

(6) On leave of absence from the Max-Planck Institut für Spektroskopie, Göttingen, Germany.

Erich Sackmann,[6] Saul Meiboom, Lawrence C. Snyder
Bell Telephone Laboratories, Inc.
Murray Hill, New Jersey

Received September 14, 1967

Thermal Instability of 1- and 2-Norbornyl and of 1-Bicyclo[2.2.2]octyl Radicals in a Mass Spectrometer

Sir:

In view of continuing interest in the energies of bridgehead species[1] (cations,[2] anions, and free radicals[3]), an attempt has been made to measure the ionization potentials of 1- and 2-norbornyl and 1-bicyclo[2.2.2]octyl free radicals in a mass spectrometer. For this purpose samples of 1-norbornylcarbinol,[4] 2-norbornylcarbinol,[5] and 1-bicyclo[2.2.2]octylcarbinol[6] were prepared and converted[7] to the corresponding nitrite esters (RCH_2ONO). These were subjected to thermal decomposition at pressures of $\sim 10^{-3}$ torr and temperatures of 400–450° in a fused-silica capillary furnace coupled to the ionization chamber of a mass spectrometer.[8] The decomposition of nitrites is known to proceed by the reactions[8]

$$RCH_2ONO \xrightarrow{E\,\sim\,36\text{ kcal}} RCH_2O\cdot + NO$$

$$RCH_2O\cdot \xrightarrow{E\,\sim\,12\text{ kcal}} R\cdot + CH_2O$$

In spite of the relatively low temperature and short contact time (~1 msec) employed, the radicals investigated were found to decompose further or to rearrange to more stable monocyclic radicals. This isomerization prevented the determination of the ionization potential of the parent species.

The thermal decomposition of 2-norbornylmethyl nitrite gave a small yield of C_7H_{11} radicals, as detected by an increase in the mass 95 peak when using a low-energy ionizing electron beam. The observed ionization potential was 8.1 v. Titration of this radical with phenyl radicals, produced simultaneously by thermal decomposition of *t*-butyl perbenzoate, yielded a coupling product whose mass spectrum was similar to, but not identical with, that of 2-*exo*-phenylnorbornane.[9] The main mode of dissociation of the C_7H_{11} radical was the loss of a hydrogen atom to give C_7H_{10}, which species might well have been norbornene. However, the ionization potential of the C_7H_{10} species was 8.6 v, compared to 9.05 v for an authentic sample of norbornene. It seems almost certain, therefore, that the C_7H_{11} radical observed was not the 2-norbornyl radical, but rather a rearrangement product of ring rupture.

The yield of C_7H_{11} radical from pyrolysis of 1-norbornylmethyl nitrite also was small, and the ionization potential, the behavior of the phenyl addition product, and the C_7H_{10} hydrocarbon resulting from hydrogen loss were not detectably different from those observed with 2-norbornylmethyl nitrite. The identity of both C_7H_{11} radicals could not be established.

The pyrolysis of 1-bicyclo[2.2.2]octylmethyl nitrite gave a good yield of C_8H_{13} radicals having an ionization

(1) Review: R. C. Fort, Jr., and P. von R. Schleyer in "Advances in Alicyclic Chemistry," Vol. 1, H. Hart and G. J. Karabatsos, Ed., Academic Press Inc., New York, N. Y., 1966, pp 283–370.

(2) G. J. Gleicher and P. von R. Schleyer, *J. Am. Chem. Soc.*, **89**, 582 (1967); W. G. Dauben and C. D. Poulter, *J. Org. Chem.*, in press; P. von R. Schleyer, P. R. Isele, and R. C. Bingham, *ibid.*, in press.

(3) I. Tabushi, J. Hamuro, and R. Oda, private communication; R. C. Fort, Jr., 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967, Abstract S-165.

(4) R. Bixler and C. Niemann, *J. Org. Chem.*, **23**, 742 (1958).

(5) Commercially available (Eastman) 5-norbornene-2-methanol was reduced to give a mixture of *endo* and *exo* isomers, both of which should give the same radical.

(6) C. A. Grob, M. Ohta, E. Renk, and A. Weiss, *Helv. Chim. Acta*, **41**, 1191 (1958). The precursor of this compound, 1-bicyclo[2.2.2]-octanecarboxylic acid, was prepared in 92% yield by a new way, the Koch–Haaf reaction (H. Koch and W. Haaf, *Ann.*, **618**, 251 (1958)), on 1-norbornylcarbinol.

(7) N. Kornblum and E. P. Oliveto, *J. Am. Chem. Soc.*, **69**, 465 (1947).

(8) R. F. Pottie, A. G. Harrison, and F. P. Lossing, *ibid.*, **83**, 3204 (1961).

(9) See D. C. Kleinfelter and P. von R. Schleyer, *J. Org. Chem.*, **26**, 3740 (1961).