differences all have the same sign as expected although the actual numerical agreement is indifferent. A view of the molecular structure as found in the crystal is shown in Figure 1.

Chromatography of fraction A on SilicAR CC-7 followed by preparative tlc on silica gel and SilicAR CC-7 gave triptonide (3) (0.001%): $C_{20}H_{22}O_6$; mp 251–252°; $[\alpha]^{25}D$ −175° (c 0.148, CH_2Cl_2); uv max (EtOH) 218 nm (ϵ 12,000); ir (KBr) 5.63, 5.81, 5.92 μ; mass spectrum (CI) m/e 359.1474 (M + 1)$^+$ (calcd, 359.1495); nmr (CDCl₃) τ 9.01 (3 H, d, $J_{15,16}$ = 7 Hz, 16-CH₃), 8.92 (3 H, d, $J_{15,17}$ = 7 Hz, 17-CH₃), 8.82 (3 H, s, 20-CH₃), 6.50 (1 H, d, $J_{6\alpha,7}$ = 5 Hz, 7-H), 6.08, 5.86 (d, $J_{11,12}$ = 3 Hz, 11,12-H), 5.19 (2 H, m, 19-CH₂). The characteristics of triptonide, including the molecular weight and carbonyl ir absorption at 5.81 μ, supported the 14-dehydrotriptolide structure 3. The structural assignment was confirmed by oxidation of triptolide (1) with CrO₃–pyridine complex in dichloromethane, whereupon triptonide was obtained in excellent yield.

Chromatography of fraction C on SilicAR CC-7 followed by preparative tlc on alumina gave tripdiolide (2) (0.001%): $C_{20}H_{24}O_7$; mp 210–211°; $[\alpha]^{25}D$ −138° (c 0.139, CH_2Cl_2); uv max 217 nm (ϵ 11,000); ir (KBr) 2.78, 2.88, 5.63, 5.93 μ; mass spectrum (CI) m/e 377.1621 (M + 1)$^+$ (calcd, 377.1600); nmr (CDCl₃) τ 8.59 (3 H, s, 20-CH₃), 8.24 (1 H, bs, 2-OH), 5.29 (1 H, m, 2-H), 5.14 (1 H, t, J = 1.5 Hz, 19-CH₂). Characterization of tripdiolide as a 2-hydroxytriptolide was based on its empirical formula and nmr spectrum. Furthermore, the marked downfield shift of the C-20 methyl group signal of 2, relative to 1 and 3, indicated a 1,3-diaxial interaction of the hydroxyl group and the angular methyl group,[12,13] and supported the 2β-hydroxytriptolide structure 2.

The postulated structure 2 was confirmed by direct X-ray analysis. Crystals of tripdiolide are isostructural with those of triptolide. The space group is $P2_1$ with a = 13.680 (2), b = 6.253 (1), and c = 11.864 (1) Å, and β = 119.05 (1)°. Monochromatic Mo Kα radiation was used to measure the intensities of 1472 reflections significantly above background. The structure was solved by the direct attribution of the phases for the reflections in triptolide to the corresponding reflections in tripdiolide, and the additional oxygen atom was clearly revealed from a difference electron-density function calculated in this way. The structure was refined in the same way as for triptolide to R = 0.082, with the contributions from 15 identifiable hydrogen atoms included.

The diepoxide functionality has been shown to confer tumor-inhibitory activity upon certain classes of acyclic synthetic compounds[14,15] as well as the naturally occurring cyclohexane diepoxide, crotepoxide.[16] The α,β-unsaturated lactone function has been shown to be important for the tumor-inhibitory activity of several classes of terpenoids.[17] Investigations are in progress
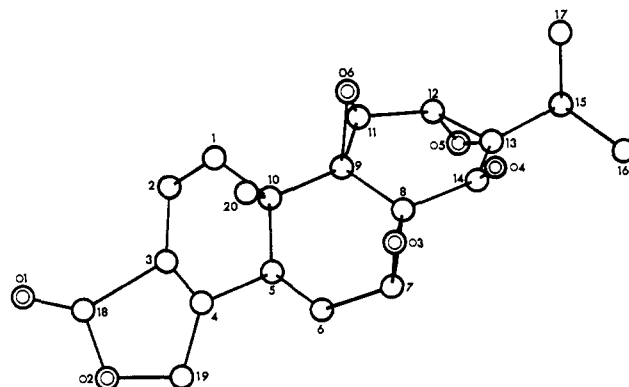

Figure 1. View of the molecule of triptolide as seen in projection down the b axis of the unit cell and showing the numbering scheme adopted. Atoms are carbon unless otherwise indicated. The molecule is shown in the presumed absolute configuration with respect to a right-handed axial system.

to determine the potential significance of the epoxide and unsaturated lactone functions, and of intramolecular catalysis by the hydroxyl groups of the selective alkylation of biological macromolecules by these functions, in relation to the tumor-inhibitory activity of the triptolides.

S. Morris Kupchan,* William A. Court, Richard G. Dailey, Jr.
Christopher J. Gilmore, Robert F. Bryan
Department of Chemistry, University of Virginia
Charlottesville, Virginia 22901

Cholesteric Solids

Sir:

We report iridescent substances that combine the optical properties of cholesteric liquid crystals with the mechanical properties of solids at room temperature. These compositions are glasses that provide the full visible spectrum of cholesteric colors and remain unchanged for years.[1]

Cholesteryl hydrogen phthalate is the key ingredient for these compositions. This compound melts at 165° to an isotropic liquid that supercools easily and becomes birefringent (cholesteric focal conic) at 100°. There is no indication of devitrification in 1 year at ambient laboratory temperatures. Crystal growth is slow between 80 and 100° and negligible at higher and lower temperatures. A maximum in the nucleation rate of a supercooled cholesteric has been described,[5] but since the maximum in this instance coincides with a phase change we ascribe slow crystal growth above 100° to the absence of ordered material. Slow rates at low temperature are due to high viscosity. The temperature dependence of the limiting high-shear

(12) K. Tori and E. Kondo, Tetrahedron Lett., 645 (1963).
(13) Y. Kawazoe, Y. Sato, M. Natsume, H. Hasegawa, T. Okamoto, and K. Tsuda, Chem. Pharm. Bull., 10, 338 (1962).
(14) W. C. J. Ross, J. Chem. Soc., 2257 (1950).
(15) K. Gerzon, J. E. Cochran, Jr., L. A. White, R. Monahan, E. V. Krumkalns, R. E. Scroggs, and J. Mills, J. Med. Pharm. Chem., 1, 223 (1959).
(16) S. M. Kupchan, R. J. Hemingway, P. Coggon, A. T. McPhail, and G. A. Sim, J. Amer. Chem. Soc., 90, 2982 (1968).
(17) S. M. Kupchan, Pure Appl. Chem., 21, 227 (1970).

(1) Mixtures of cholesteryl cinnamate and rosin have been quenched to a glassy state under limited special conditions.[2] The rosin does not appear to be essential.[3] Some scarabaeid beetles display cholesteric-like iridescence in their cuticles.[4]
(2) I. G. Chistyakov and E. A. Kosterin, Rost. Kristallov, 4, 68 (1964).
(3) S. E. B. Petrie, Abstracts, 162nd National Meeting of the American Chemical Society, Washington, D. C., 1971, No. PHYS 210.
(4) A. C. Neville and S. Caveney, Biol. Rev., 44, 531 (1969).
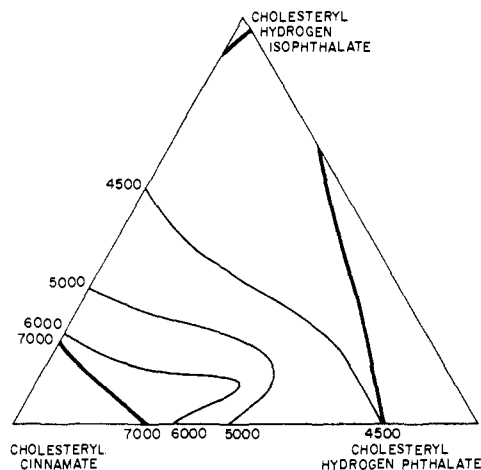(5) J. M. Pochan and H. W. Gibson, J. Amer. Chem. Soc., 94, 5573 (1972).

Figure 1. Isochromes (λ_0 in Å) of a three-component system (weight per cent) prepared by spontaneous cooling from the melt after cover slip displacement.

Figure 2. Isochromes (λ_0 in Å) of a three-component system prepared by spontaneous evaporation of 20% solutions of the mixtures in toluene.

viscosity[6] measured between 68 and 165° is given by the equation

$$\log \eta = 480/(T - 273) - 3.00$$

where η is in poise and T is °K. This type of equation has been used to describe the temperature–viscosity relationships of silicate melts[7] and supercooled alcohols.[8] The glass transition temperature, T_g, of a wide range of glasses occurs at a temperature where the viscosity is about 10^{13} poise.[8,9] According to the equation, supercooled cholesteryl hydrogen phthalate should have a viscosity of 10^{13} poise at 30°. The glass transition temperature was observed at 30° by differential scanning calorimetry[10] and at 32° by thermal expansion.

A "cover slip displacement"[11] on supercooled cholesteryl hydrogen phthalate below 100° produces the Grandjean plane texture[11] having blue iridescence which persists only if quenched rapidly under shear to 25° or below.

In contrast to pure cholesteryl hydrogen phthalate, certain of its mixtures are stable in the iridescent Grandjean plane texture relative to the uncolored textures. Some compositions give the iridescent state spontaneously on slow or fast cooling from the melt or after evaporation of a solvent. Iridescent compositions having a Knoop hardness (KHN$_{25}$) of 4–7 kg mm^{-2} at 25° are obtained[12] on cooling binary melts of cholesteryl hydrogen phthalate (4400 Å) with cholesteryl hydrocinnamate (25,000 Å), cholesteryl cinnamate (5000 Å), cholesteryl benzoate (5500 Å), or cholesteryl hydrogen isophthalate (4170 Å). The effective wavelengths given in parentheses are obtained by extrap-

(6) R. S. Porter and J. F. Johnson, *J. Appl. Phys.*, **34**, 55 (1963).
(7) G. S. Fulcher, *J. Amer. Ceram. Soc.*, **8**, 339 (1925).
(8) G. Tammann and W. Hesse, *Z. Anorg. Allg. Chem.*, **156**, 245 (1926).
(9) A. A. Miller, *J. Polym. Sci., Part A-2*, **6**, 249 (1968).
(10) K. Tsuji, M. Sorai, and S. Seki, *Bull. Chem. Soc. Jap.*, **44**, 1452 (1971), report $T_g = 27°$ and the cholesteric–isotropic transition at 90° on a supercooled sample of cholesteryl hydrogen phthalate initially melting at 160°.
(11) G. W. Gray, "Molecular Structure and the Properties of Liquid Crystals," Academic Press, New York, N. Y., 1962, p 42.
(12) The values tend to be closer to 7 kg mm^{-2} for higher (>60%) concentrations of cholesteryl hydrogen phthalate. For comparison, polyethylene has KHN$_{25}$ of 0.3, lead 5, and poly(methyl methacrylate) 19 kg mm^{-2}.
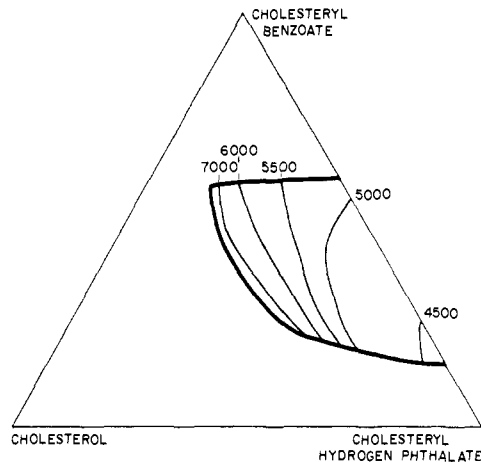
olating reciprocal wavelengths of binary compositions to the value for pure compound.[13,14] All have a left-handed sense and they mix by a weighted averaging.[13,14] Combinations with a large amount of cholesteryl cinnamate can be red because in high concentration it goes to an infinite wavelength state. A similar observation has been made for cholesteryl nonanoate in fluid mixtures.[14] The binary system cholesteryl hydrogen phthalate–cholesteryl benzoate is limited to blue and green, but further addition of right-handed cholesterol[13] affords the complete visible spectrum from the ternary mixtures. Diagrams mapping these colors are shown in Figures 1 and 2. The heavy lines represent the limits of the compositions having stable colors at 25°.

The iridescence of these glassy compositions is similar to those of the fluid cholesterics[15] in intensity, angular dependence, and reflective circular dichroism but not in pressure or temperature sensitivity. Both the glassy and the fluid cholesterics appear nearly white in the bulk material because of the summation of the scattered wavelengths due to the multidirectional optical axes. The process of spreading, by pressing while warm between glass or plastics, or coating with a hot spatula, or evaporation of solvent, lines up the optical axes and develops the iridescent color. The inherent Grandjean plane texture of the glassy cholesterics in the bulk is revealed by electron microscopy[16] of a fractured sample which looks like a fingerprint[17,18] with a spacing between striae equal to the pitch of the helix where $\lambda_0 = 2np$ (λ_0 is the wavelength observed with normal incidence and reflection, n is the refractive index, and p is the pitch).[19]

At high temperature these compositions respond to temperature and pressure in the same way as the known liquid cholesterics[15] and the color variation so produced can be quenched in by rapid cooling; subsequently, the glass may be annealed somewhat above the glass transition temperature to the equilibrium color. This

(13) J. Adams and L. Leder, *Chem. Phys. Lett.*, **6**, 90 (1970).
(14) L. B. Leder, *J. Chem. Phys.*, **54**, 4671 (1971).
(15) J. L. Fergason, *Mol. Cryst.*, **1**, 293 (1966).
(16) We are indebted to R. R. Hebert for electron microscopy studies.
(17) C. Robinson, *Trans. Faraday Soc.*, **52**, 571 (1956).
(18) S. Caveney, *Proc. Roy. Soc., Ser. B*, **178**, 205 (1971).
(19) M. Panar and R. R. Hebert, unpublished results.

Journal of the American Chemical Society / *94:20* / *October 4, 1972*

complex dependence of color on thermal history enhances the artistic possibilities of these cholesteric glasses.

Walter Mahler,* M. Panar
Contribution No. 1921, Central Research Department E. I. du Pont de Nemours and Company, Experimental Station Wilmington, Delaware 19898

Photochemically Induced Dynamic Electron Spin Polarization. The 1,4-Naphthosemiquinone Radical in 2-Propanol

Sir:

Anomalous electron spin resonance emission spectra have been observed for a few free radicals in liquid systems produced by radiolysis,[1,2] by photolysis,[3,4] and by thermal reactions.[5] These relatively few observations, however, have generated a great deal of theoretical interests in recent years,[6-9] but the mechanisms of the dynamic electron polarization in various systems remain controversial. In the course of a systematic esr study of semiquinone radicals by flash photolysis and by the popular rotating sector techniques, we have unexpectedly observed esr emission from the photochemically produced 1,4-naphthosemiquinone radicals in liquid 2-propanol. We wish to report here these interesting experimental observations and to suggest a preliminary account for the dynamic electron polarization in this particular system.

Samples of degassed 2-propanol solution of 1,4-naphthoquinone were intermittently photolyzed within the cavity of a Varian 4502 esr 100-kc modulation spectrometer. The light source was an unfiltered 200-W super pressure Hg lamp which was coupled to a rotating disk capable of varying the dark-to-light ratio between 20 and 200 and the light period being as short as 200 μsec. Steady irradiation of the solution led to a well-resolved spectrum which is readily interpreted as due to the 1,4-naphthosemiquinone radicals. Under intermittent irradiation, the buildup and the decay curves of the esr signal at a constant magnetic field were obtained by thousands of sweeps using a Fabri-tek 1074 computer. A typical curve observed is shown in Figure 1.

Immediately after the light pulse the esr signal was in the form of emission which reverted to the normal absorption mode as the light pulse decayed with a time constant of about 300 μsec. The esr absorption further decayed according to a second-order kinetics due to self-reaction of the radicals. It was established that all hyperfine components of the radical exhibited the same behavior. Atkins and coworkers[3] have also observed
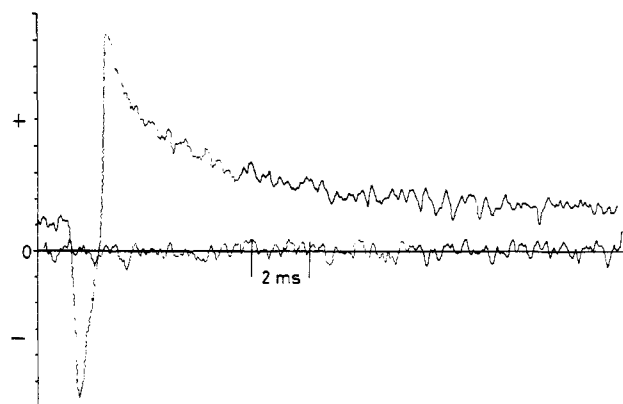

Figure 1. Time dependence of the esr signal intensity at constant magnetic field of the 1,4-naphthosemiquinone radicals in 2-propanol: absorption mode (+), emission mode (−).

similar phenomenon in the laser flash photolysis of some carbonyl compounds. However, in the present experiment using relatively much slower pulses from a rotating sector, it is rather surprising that emission could be observed.

We suggest that the chemically induced dynamic electron polarization (CIDEP) of the semiquinone radical in the present system is due to initially optically spin-polarized triplet states of the parent quinone, which subsequently abstract a hydrogen atom from the solvent 2-propanol with retention of the electron polarization. The phenomenon of optical spin polarization in organic triplet states is now fairly well established.[10-13] The following sequence of events is proposed to account for the experimental observation. The quinone is firstly excited by light to some higher singlet states which cross over to a triplet state. One might expect that the rates of the intersystem crossing from the excited singlet to the three sublevels of the lowest triplet state are not equal;[10,11] hence, it is possible that the upper sublevel, $|\alpha,\alpha\rangle$ is more populated than the lower sublevel $|\beta,\beta\rangle$. Further theoretical calculation will be performed to justify this polarization of the triplet 1,4-naphthoquinone molecules. If the hydrogen abstraction occurs before the triplet spin depolarization takes place by spin–lattice relaxation, the resultant semiquinone radical will be initially populated in a manner that is mainly determined by the triplet polarization; i.e., $|\alpha,\alpha\rangle \rightarrow |\alpha,\alpha,\beta\rangle$ and $|\beta,\beta\rangle \rightarrow |\beta,\beta,\alpha\rangle$. This means that the spin polarization is retained in the semiquinone radical and esr emission is expected from all hyperfine components. This mechanism also predicts that the counter 2-propanol radical would give a totally emissive esr spectrum.

Selective population of triplet sublevels as a route to electron polarization has been considered by other authors but has been discarded on the grounds of a too long lifetime of the triplet state as compared to the spin–lattice relaxation times.[8,14] It should be pointed out here that spin–lattice relaxation times have not

(1) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963); P. Neta, R. W. Fessenden, and R. H. Schuler, *J. Phys. Chem.*, **75**, 1654 (1971).
(2) B. Smaller, J. R. Remko, and E. C. Avery, *J. Chem. Phys.*, **48**, 5174 (1968); **55**, 2414 (1971).
(3) P. W. Atkins, I. C. Buchanan, R. C. Gurd, K. A. McLauchlan, and A. F. Simpson, *Chem. Commun.*, 513 (1970).
(4) R. Livingston and H. Zeldes, *J. Chem. Phys.*, **53**, 1406 (1970).
(5) H. Paul and H. Fischer, *Z. Naturforsch., A*, **25**, 443 (1970).
(6) R. Kaptein and J. L. Oosterhoff, *Chem. Phys. Lett.*, **4**, 195 (1969).
(7) H. Fischer, *ibid.*, **4**, 611 (1970).
(8) P. W. Atkins, R. C. Gurd, K. A. McLauchlan, and A. F. Simpson, *ibid.*, **8**, 55 (1971).
(9) F. J. Adrian, *J. Chem. Phys.*, **54**, 3918 (1971).

(10) M. Schwoerer and H. Sixl, *Chem. Phys. Lett.*, **2**, 14 (1968).
(11) M. S. deGroot, I. A. M. Hesselmann, J. Schmidt, and J. H. van der Waals, *Mol. Phys.*, **15**, 17 (1968).
(12) M. A. El-Sayed, D. S. Tinti, and D. V. Owens, *Chem. Phys. Lett.*, **3**, 339 (1969).
(13) H. Levanon and S. I. Weissman, *J. Amer. Chem. Soc.*, **93**, 4309 (1971).
(14) G. L. Closs and L. E. Closs, *ibid.*, **91**, 4549, 4550 (1969).