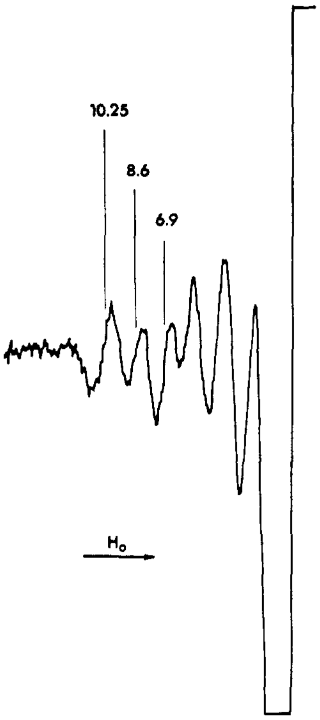


Figure 2. Low-field ^{13}C satellites of the anion of compound I; 1.25 mM solution in acetonitrile.

coupling to both groups does occur, giving rise to the relatively large line width (105 mG) of the undeuterated anion.[6]

The observation of apparent coupling with the bridgehead protons raises another interesting point. Since these protons are in the nodal plane of the π-orbital containing the unpaired electron, the hyperconjugative coupling mechanism can be ruled out. The consecutive polarization mechanism must be invoked,[7] which argues for a high spin density on the ethylenic carbons and also for relatively high spin densities on the bridgehead carbons as well. This is borne out by the observation of three different ^{13}C coupling constants as seen in Figure 2, which shows the low-field satellites. The three lines at lowest field are the ^{13}C satellites from the $|M_{IN}| = 2$ line and the next group of three lines arises from the $|M_{IN}| = 1$ nitrogen line. The intensities of the ^{13}C lines, with respect to the parent nitrogen lines, are the correct values for doubly degenerate carbon sites. The values of the ^{13}C coupling constants are 10.25, 8.6, and 6.9 G and are presumably due to the cyano, ethylenic, and bridgehead carbon atoms, respectively; molecular orbital calculations have not yet been initiated to confirm this assignment.

Returning momentarily to the question of bridgehead proton coupling, it may be that the dicyanoethylene spin label concentrates significantly more spin density at the bridgeheads than do the previously reported labels. Thus, the other bicyclo[2.2.2]octane anions[1e,2a,3] do not exhibit coupling with the bridgehead protons.

An example in which bridgehead proton coupling is unequivocal appears in the anion radical of compound II. A spectrum of this radical together with the computed reconstruction appear in Figure 3. The parameters used in the computed spectrum along with the provisional assignments are as follows: 2.34 (two nitrogens); 1.805 (two ethylenic hydrogens); 1.255 (two *anti* hydrogens); 0.45 (two *syn* hydrogens); 0.225 (two bridgehead hydrogens); and a Lorentzian line width of 0.14 (values in gauss).

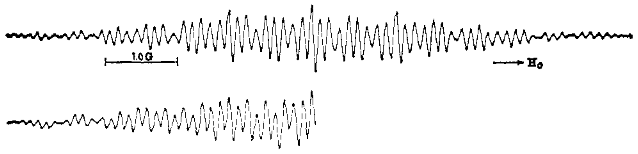
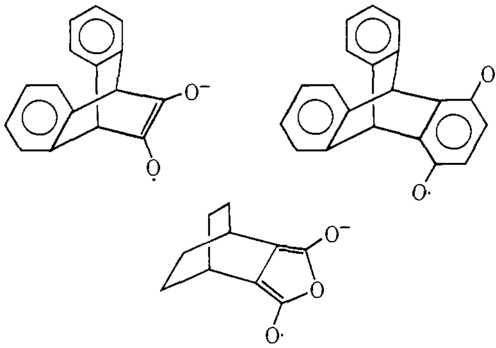


Figure 3. Anion radical from the reduction of compound II; 0.72 mM solution in acetonitrile. One-half of spectrum simulated using parameters in the text.



Further deuteration experiments will be undertaken to elucidate these preliminary observations. Other radicals containing the dicyanoethylene spin label will be discussed subsequently, as will the question of through-space *vs.* through-bond delocalization mechanisms.

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[6] In the analogous semidione anion radical,[1e] all eight ring protons were observed to couple equally and no bridgehead proton coupling was discernible.

[7] J. P. Colpa and E. de Boer, *Mol. Phys.*, 7, 333 (1964).

Magnetic Ordering of Poly-γ-benzyl-L-glutamate Solutions

Sir:

The liquid crystalline nature of concentrated solutions of poly-γ-benzyl-L-glutamate (PBLG) in solvents such as CH_2Cl_2, $CHCl_3$, dichloroacetic acid, and N,N-dimethylformamide (DMF) has been well established by optical, microscopic,[1] and X-ray[2] studies. In these anisotropic phases, rigid (α helix) polymer molecules are aligned in a parallel fashion.[2] Because of the optically active nature of the polymer, each molecule is tilted slightly relative to its neighbor, and a helical structure develops that is manifested optically as a series of equidistant, parallel lines with a spacing equal to half the helical pitch. This structure is similar in many respects to that of thermotropic cholesteric melts.[3]

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[1] C. Robinson, *Trans. Faraday Soc.*, **52**, 571 (1956).

[2] C. Robinson, J. C. Ward, and R. B. Beevers, *Discussions Faraday Soc.*, **25**, 29 (1958); D. A. D. Parry and A. Elliott, *J. Mol. Biol.*, **25**, 1 (1967).

[3] G. W. Gray, "Molecular Structure and the Properties of Liquid Crystals," Academic Press Inc., New York, N. Y., 1962.

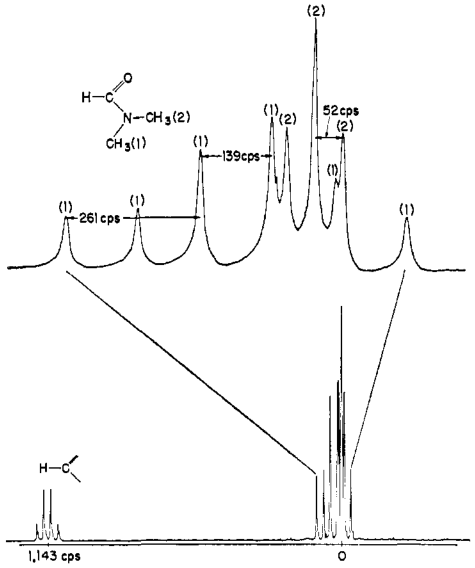

Figure 1. 220-Mcps pmr spectrum of N,N-dimethylformamide (DMF) in a PBLG-DMF (0.3 g/ml) solution (40°). The resonance absorption of the methyl region of DMF is shown in expanded scale in the upper spectrum. The spectrum is referenced with respect to peak 2 of the methyl region of DMF.

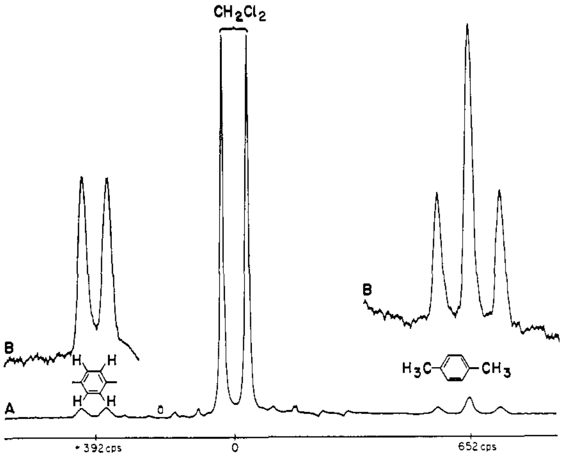

Figure 2. 220-Mcps pmr spectrum of *p*-xylene (0.05 ml) dissolved in a PBLG-CH_2Cl_2 (0.3 g/0.95 ml) solution (23°). In B the resonance absorption of *p*-xylene is shown under higher spectrometer gain conditions than in A. The spectrum is referenced with respect to the center of the dipole-dipole doublet of CH_2Cl_2.

We have observed that such cholesteric PBLG solutions when subjected to a magnetic field are converted to aligned, structured solutions which are indistinguishable optically from similarly ordered nematic solutions, *e.g.*, solutions containing equal proportions of the D and L isomers of poly-γ-benzylglutamate. The times required for these reorientations and structural conversions to occur depend on the square of the magnetic field strength. Such a field dependence is expected theoretically for rotational alignment of ellipsoids in a uniform field. Two rates are discernible: (a) that for orientation with the field, and (b) that for the "unwinding" of the cholesteric structure.

The nematic nature of these PBLG solutions in magnetic fields is further reflected in proton magnetic resonance (pmr) spectroscopy by the appearance of well-resolved nuclear dipole-dipole and quadrupole splittings similar to those observed in thermotropic nematic melts.[4] Similar dipolar splittings have recently been reported in PBLG solutions by Sobajima[5] and in cholesteric melts by Sackmann, *et al.*[6] The spectrum of the PBLG solute is not detected under conditions of high-resolution pmr spectroscopy because of the very large intramolecular nuclear dipolar interactions and consequent very broad resonance widths of this highly oriented component of the solution. The pmr spectrum of the solvent is time-averaged over environments in which solvent molecules are highly oriented by the solute and over environments remote from the PBLG in which solvent ordering is nonexistent. The resulting observed dipole-dipole and quadrupole splittings are small because the fraction of time the solvent molecules spend in disordered environments is relatively great compared to that with which they are associated with the ordered PBLG solute. An example of the effect is seen in the well-resolved dipolar splittings of DMF when it is employed as solvent for PBLG (Figure 1). The spectrum is amenable to a simple first-order analysis in which the average dipolar coupling between the C-H proton and the three protons of $CH_3(1)$ is 139 cps, and the internal couplings between each of the three protons of $CH_3(1)$ and $CH_3(2)$ are 261 and 52 cps, respectively.

Relaxation times for magnetically oriented PBLG solutions depend on such variables as molecular weight, solvent, concentration, and temperature and can be as long as 0.5 hr or more. The slow reorientation and relaxation rates of these solutions have enabled us to establish that the angular dependence of the average doublet dipolar splitting of the two protons of CH_2Cl_2 in a solution consisting of 0.3 g of PBLG and 1.0 ml of CH_2Cl_2 at 23° is given very accurately by $10.7(3\cos^2\theta - 1)$ cps, where θ is the angle between H_0 and the initial magnetic field polarization direction. The dipole splittings of aromatic and methyl protons of anisoles and xylenes dissolved in PBLG-CH_2Cl_2 solutions exhibit the same $(3\cos^2\theta - 1)$ dependence. The dipolar splitting for a spinning sample is one-fourth that for a stationary sample when the axis of sample spin and H_0 are perpendicular (the geometry of conventional nmr spectrometers). This reduction factor is precisely that expected if, prior to spinning, the time-averaged solvent dipole-dipole vector and H_0 are parallel. The above results would obtain if (1) solvent molecules can exchange rapidly between the nematic aggregates and (2) the nematic axes are parallel to H_0. Analyses of relative intramolecular splittings and angular dependences of such splittings in other PBLG-solvent systems confirm this interpretation. The exchange mechanism postulated here also accounts for the angular dependence of dipolar splittings of small molecules in biological structures such as water in nerve fibers.[7]

These systems based on PBLG solutions are useful in determining molecular structure from angular de-

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(4) A. Saupe and G. Englert, *Phys. Rev. Letters*, **11**, 462 (1963); J. C. Rowell, W. D. Phillips, L. R. Melby, and M. Panar, *J. Chem. Phys.*, **43**, 3442 (1965).

(5) S. Sobajima, *J. Phys. Soc. Japan*, **23**, 1070 (1967).

(6) E. Sackmann, S. Meiboom, and L. C. Synder, *J. Am. Chem. Soc.*, **89**, 5981 (1967).

(7) G. Chapman and K. A. McLauchlan, *Nature*, **215**, 391 (1967).

pendences of dipolar splittings as well as in providing information about the ultrastructure and solvent–solute interactions of the solution.[8] A spectrum of a PBLG–CH_2Cl_2 solution containing 5% of *p*-xylene is shown in Figure 2. The triplet arising from the dipolar interactions between the three protons of each rotating methyl group of *p*-xylene is cleanly resolved as is the doublet arising from interactions of the 2,3 and 5,6 protons of the phenyl ring. Quadrupolar splittings in the deuterium resonances of solutions consisting of PBLG–CD_2Cl_2 have also been observed, an additional manifestation of solute and solvent ordering in these nematic systems.

These and other aspects of the structures of concentrated PBLG solutions will be detailed in a subsequent paper. The results of such studies appear to provide new insights of some generality into the structure of anisotropic solution phases.

[8] For related system see K. D. Lawson and T. J. Flautt, *J. Am. Chem. Soc.*, **89**, 5489 (1967).

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Stable Carbonium Ions. LXXII.[1] Raman and Nuclear Magnetic Resonance Spectroscopic Study of the Nortricyclonium Ion (Protonated Tricyclo[2.2.1.$0^{2,6}$]heptane) and Its Relationship to the 2-Norbornyl (Bicyclo[2.2.1.]heptyl) Cation. Clarification of the Nature of the Stable, Long-Lived Norbornyl Cation in Strong Acid Solutions

Sir:

Recently the direct observation of the stable, long-lived norbornyl cation was achieved in SbF_5–SO_2, HF–SbF_5–SO_2,[2] FSO_3H–SbF_5–SO_2,[3] and $GaBr_3$–SO_2[4] solutions and its nmr spectrum was reported. Owing to the slowness of the nmr method, no clear differentiation on the nmr time scale between a rapidly equilibrating pair of ions or a bridged symmetrical ion was possible. In order to be able to study the structure of the norbornyl cation without regard to possible rapid equilibration, instead of the slow nmr method, a fast physical method was needed. We selected Raman spectroscopy for our continued studies, assuming that vibrational transition rates are faster than hydride shifts or Wagner–Meerwein rearrangement.

In our studies a Cary Model 81 Raman spectrometer equipped with a helium–neon laser source was used. In order to avoid the observation of fluorescent spectra and to keep the solution of the ion colorless and stable, a low-temperature cell was constructed which allowed studies at temperatures as low as −100°.

Ionization of 2-*exo*-norbornyl chloride was carried out in FSO_3H–SbF_5–SO_2 solution. The 100-MHz pmr resonance spectrum of ion I at −80° was similar to that observed previously for stable, long-lived 2-norbornyl cation, showing resonances at δ 5.2, 3.1, and 2.1 with relative peak areas of 4:1:6. We also observed fine structure of the spectrum, similar to that reported by Jensen[4] at 60 MHz. The high-field resonance is split into what appears to be a broad sextet ($J \sim 1.5$ Hz) coupled to both the four low-field protons and the lone methine bridgehead proton. The δ 3.1 resonance is very broad due to coupling to both the low- and high-field protons. The low-field resonance seems to be a broad septuplet, coupled to the six high-field methylene protons ($J \sim 1.5$ Hz). The broadness of the peak likely arises from a further small coupling with the bridgehead methine proton. The couplings were experimentally verified by decoupling experiments.

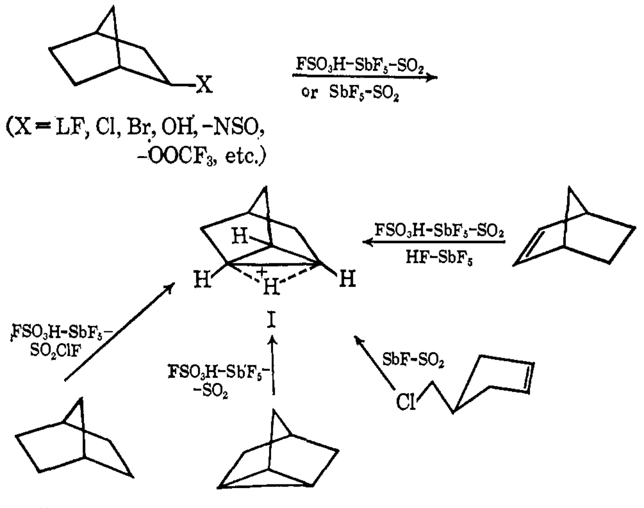
In order to be able to carry out the Raman spectroscopic studies, the acid solvent system was studied first and will be reported in detail separately.[5] This study allowed us to assign all Raman lines due to the solvent and gegenion. The Raman spectrum of ion I, obtained at −80°, is shown in Figure 1 with the absorption lines due to the solvent and gegenion deleted. In the C–C stretching frequency region there is only one strong line observed at 972 cm^{-1} with a depolarization factor, ρ, of 0.35. The C–H stretching frequency region shows five lines, one of which is at 3110 cm^{-1}.

Comparison of the Raman spectrum of ion I with the Raman spectra of nortricyclene (Figure 2) and 3-bromonortricyclene on the one hand and norbornane (Figure 3) and 2-*exo*-norbornyl halides on the other hand gives a clear indication of its structure.

The C–C stretching frequency region in nortricyclene and its derivatives shows only *one* strong absorption line, at around 950 cm^{-1}, with a depolarization factor of 0.31. In contrast, norbornane and 2-norbornyl halides show *two* intense lines around 871 and 920 cm^{-1} ($\rho = 0.25$).

In the C–H stretching frequency region, norbornane and 2-*exo*-halonorbornanes show only three lines at frequencies below 3000 cm^{-1}. In contrast, nortricyclene and 3-bromonortricyclene show five lines in this region, one of them at 3080 cm^{-1}, characteristic of the cyclopropane ring.

When nortricyclene was protonated in FSO_3H–SbF_5–SO_2 solution at −80°, the pmr and Raman spectra obtained were identical with those obtained for



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[1] Part LXXI: G. A. Olah and R. H. Schlosberg, *J. Am. Chem. Soc.*, in press.

[2] P. von R. Schleyer, W E Watts, R. C. Fort, Jr., M. B. Comisarow, and G. A. Olah, *ibid.*, **86**, 5679 (1964); M. Saunders, P. von R. Schleyer, and G. A. Olah, *ibid.*, **86**, 5680 (1964).

[3] G. A. Olah and J. Lukas, *ibid.*, **90**, 933 (1968).

[4] F. R. Jensen and B. H. Beck, *Tetrahedron Letters*, 4287 (1966).

[5] A. Commeyras and G. A. Olah, to be submitted for publication.