

Had the skeletal rearrangement during the cyclization occurred in the opposite sense to give the isomer of IV in which the groups at C-1 and C-2 are interchanged, the substance resulting from the aforementioned transformations would be an isomer of the ester VI in which the carbomethoxy group and the ethyl (at C-6) are interchanged. This isomer would have no hydrogens α to the carbomethoxy group. The presence of two such α hydrogens in the substance at hand (see nmr above) was confirmed by a deuterium exchange experiment (treatment for 10 hr at 25° with sodium dissolved in methanol- d_1). Partial exchange was observed by significant diminution of the intensity of the nmr signal at 2.23–2.53.

The configuration of the ring fusion of the chlorodiene IV was proved to be trans as follows. Selective ozonization, using a Rubin ozonizer, with 0.95 mol equiv of ozone in methylene chloride at –78°, followed by treatment with dimethyl sulfide and then preparative tlc (10% ethyl acetate in hexane), gave a 72% yield of the ketone VII which crystallized on standing. Bulb-to-bulb distillation at 75° (0.02 mm) afforded colorless, low-melting crystals (*Anal.* Found: C, 70.1; H, 8.8; Cl, 14.7): nmr⁵ 1.05 (3 H, s), and 1.11 (6 H, s), methyls at C-9 and C-5, 1.75 (3 H, t, $J = 1$ Hz), methyl at C-1. Wolff–Kishner reduction of the ketone VII by the Huang–Minlon modification⁶ gave, after preparative tlc (10% ethyl acetate in hexane), a 57% yield of the chloro olefin VIII. Bulb-to-bulb distillation at 78° (0.04 mm) gave an oil (*Anal.* Found: C, 74.2; H, 10.1; Cl, 15.4): mass spectrum m/e 226, M^+ ; nmr⁵ 0.83 (3 H, s), 1.03 (3 H, s), and 1.16 (3 H, s), methyls at C-5 and C-9, 1.70 (3 H, t, $J = 1$ Hz), methyl at C-1. A solution of the chloro olefin VIII in 2:1 ethyl acetate–methanol was treated with excess ozone at –78° and then with dimethyl sulfide. Preparative tlc (20% ethyl acetate in hexane) gave (78% yield) the keto ester IX. Bulb-to-bulb distillation at 105° (0.01 mm) afforded an oil (*Anal.* Found: C, 70.95; H, 10.1): mass spectrum m/e 254, M^+ ; nmr⁵ 0.93 (6 H, s), methyls at C-2, 1.20 (3 H, s), methyl at C-6, 2.14 (3 H, s), ketone methyl, 3.64 (3 H, s), ester methyl. The ester IX was saponified with aqueous methanolic sodium hydroxide and the resulting crude keto acid (0.54 mmol) was oxidized with sodium hypobromite (7.7 mmol) in aqueous alkaline solution (6.5 hr, 0°). Treatment of the product with diazomethane, followed by preparative tlc (10% ethyl acetate in hexane), gave the diester X in 43% yield. Bulb-to-bulb distillation at 125° (0.01 mm) afforded an oil (*Anal.* Found: C, 66.4; H, 9.5): mass spectrum m/e 270, M^+ . Saponification of the diester X with aqueous methanolic sodium hydroxide gave the crystalline diacid XI which on three recrystallizations from ether–hexane melted at 106–109°, undepressed on admixture with authentic material: mp 107–110°⁷ (*Anal.* Found: C, 64.3; H, 9.0); mass spectrum m/e 242, M^+ . The nmr⁵ spectrum of the diester X was identical with that of an authentic specimen prepared from the aforementioned authentic diacid. The vpc behavior (coinjection) of these two diester specimens was also identical.

Since the cyclization of the carbinol I evidently pro-

(6) The hydrazone formation was conducted at 0° for 12 hr in order to minimize the total heating period and concomitant loss of halogen.

(7) Prepared by Wolff–Kishner reduction of the keto diester 9 of ref 2.

ceeds so as to give, as the primary product, the 6/5 fused ring vinyl cation II which is readily trapped by ordinary nucleophiles (see above), the formation of the chlorodiene IV may be rationalized as follows. The vinyl cation II is first formed but, in the absence of a good nucleophile, it undergoes an equilibration, *via* a Wagner–Meerwein shift,⁸ with the 6/6 fused ring cation III which, in a relatively slow process, abstracts chloride ion from the solvent (CH_2Cl_2).⁹ Evidence from solvolysis experiments supports the view that vinyl cations like II and III, but lacking the fused A ring, “do not differ much in stability.”⁸ In the present case, the relief of torsional strain in the conversion of a 6/5 to a 6/6 trans-fused ring system could be a factor in determining the course of the reaction.

Acknowledgment. We are indebted to the National Institutes of Health and the National Science Foundation for support of this research.

(8) Products of similar rearrangements have been observed with vinyl cations generated by solvolysis of vinyl triflates. See, for example, W. D. Pfeifer, C. A. Bahn, P. v. R. Schleyer, S. Bocher, C. E. Harding, K. Hummel, M. Hanack, and P. J. Stang, *J. Amer. Chem. Soc.*, **93**, 1513 (1971).

(9) Cf. E. H. White, H. P. Tiwari, and M. J. Todd, *ibid.*, **90**, 4734 (1968), for the abstraction of chloride ion from methylene chloride by the 1-norbornyl cation.

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(11) Rockefeller Foundation Fellow.

William S. Johnson,* Michael B. Gravestock
Ronald J. Parry,¹⁰ Dominic A. Okorie¹¹

Department of Chemistry, Stanford University
Stanford, California 94305

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Raman Depolarization Ratio and Short-Range Order in Liquid Crystals

Sir:

Laser Raman scattering was recently used to investigate the phase transitions in liquid crystals.^{1–3} It was found that significant Raman spectral changes occur only in the solid nematic phase transition and not in the nematic liquid transition. The result, consistently with the observation of a very small change of latent heat associated with the nematic liquid phase transition,⁴ suggests that Raman spectra of the nematic and isotropic liquid phases are primarily affected by short-range order.

Despite the small change in the intermolecular potential, molecular motions in the nematic and isotropic liquid phases are different. In the nematic phase, only the reorientation around the molecular long axis is possible, whereas in the isotropic phase, reorientation around the short axis is also permitted. As a result, we expect that the depolarization ratio rather than the total scattering intensity should reflect the change of short-range order as the phase transition occurs, but no previous Raman study of the liquid crystals has considered the measurement of the depolarization ratio. Because of this neglect, the reorientational information that Raman scattering can be used to disclose has been overlooked. We report new results on

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(4) See, e.g., A. Saupe, *Angew. Chem., Int. Ed. Engl.*, **7**, 97 (1968).

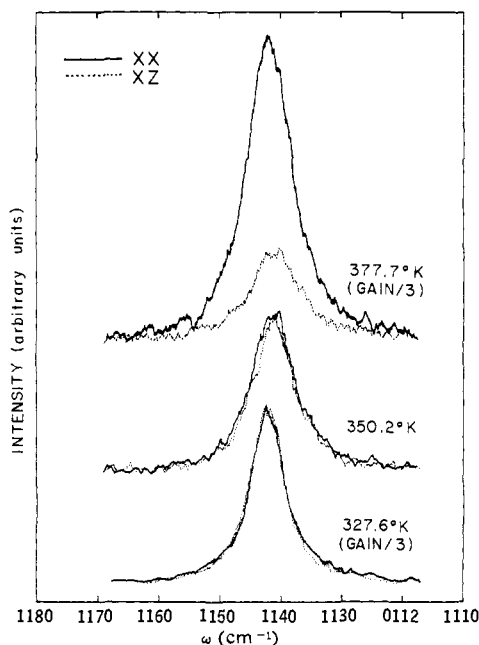


Figure 1. Polarized and depolarized Raman spectra of PPU at 377.7, 350.2, and 327.6°K in the 1145-cm⁻¹ region. Spectral resolution is 2 cm⁻¹.

the Raman polarization of PPU, *p*-(*p*-ethoxyphenylazo)-phenyl undecylenate. The result serves to illustrate the significance of such type of study in providing information on the change of short-range order at the vicinity of the nematic liquid phase transition.

Figure 1 shows representative polarized (XX) and depolarized (XZ) Raman spectra of the 1145-cm⁻¹ mode (the CH₂ twisting mode) of PPU at 327.6 (solid), 350.2 (nematic), and 377.7°K (liquid).⁵ The PPU sample was purified by zone refining before use. Except for using a Spectra-Physics 125 He-Ne laser as the excitation source, the spectra were obtained by a method similar to that reported previously.⁶ It is significant to note that, despite the large decrease in the scattering intensity, as the solid- to nematic-phase transition occurs, the XX and XZ spectra are rather similar in the nematic phase. This result is found not only in the 1145-cm⁻¹ band but in other internal bands as well, reflecting the fact that the Raman tensor of PPU in the nematic phase is very anisotropic.

The quantitative integrated intensities of the 1145-cm⁻¹ band are shown as a function of temperature in Figure 2. As the nematic liquid transition temperature (T_{λ}') is approached from below, the intensities of the XX and XZ scattering increase rapidly.

In the vicinity of T_{λ}' the integrated intensity increase for the XX scattering differs greatly from that for the XZ scattering. Immediately below T_{λ}' (still in the nematic phase) in about 0.1° the XZ scattering intensity increases by a factor of 1.3, but the XX scattering intensity increases only by a factor of 1.8. The

(5) The temperatures at which large Raman intensity variations were observed are respectively 8 and 10°K lower than the transition temperature provided by the report of Eastman Kodak Company. Although it has been observed that the phase transition temperatures, which are thermodynamic variables, need not coincide with the temperature at which large Raman spectral variations are observed (C. H. Wang, *Phys. Rev. Lett.*, **26**, 1226 (1971)), the reason for the temperature discrepancies for the present case is not yet known.

(6) C. H. Wang and R. B. Wright, *J. Chem. Phys.*, **55**, 3300 (1971).

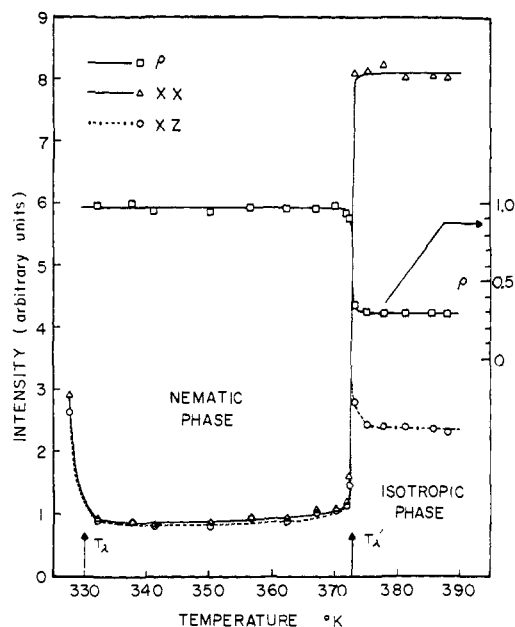


Figure 2. The integrated intensities and the depolarization ratio of the 1145-cm⁻¹ band as a function of temperature.

sum of the scattering intensity from the two polarizations in the isotropic phase is greater than the corresponding intensity sum in the nematic phase. This result, in contrast to the intensity behavior observed for PAA,³ indicates that the change of short-range order can in some situations affect the total scattering intensity. As T_{λ}' is traversed and the system is in the isotropic phase, the XX intensity first decreases slightly before approaching a constant value at higher temperature. Both intensity curves exhibit a quasidiscontinuity at T_{λ}' .

The depolarization ratio (ρ) displays the overall reorientation behavior of the molecule. For a normal mode possessing a cylindrically symmetric Raman tensor (a good approximation for the 1145-cm⁻¹ mode), ρ is given by $3\beta^2/(45\alpha^2 + 4\beta^2)$, where α and β are respectively the average part and the anisotropy of the Raman polarizability tensor.⁷ This expression is valid only if the molecular reorientation is isotropic. The fact that $\rho = 0.3$ (Figure 2) is observed in the isotropic liquid-phased PPU suggests that in the molecule-fixed coordinate frame the Raman tensor associated with the 1145-cm⁻¹ mode has only diagonal elements. In the laboratory frame, off-diagonal elements are also present. However, those elements are averaged out because of the isotropic reorientation in the liquid phase. At temperatures below T_{λ}' , because of short-range order, reorientation is not permitted around the molecular short axis. As a result, off-diagonal elements of the Raman tensor become important in the laboratory coordinate frame, and ρ is expected to increase in the nematic phase.

In Figure 2, one notes that, in the nematic phase, ρ decreases gradually before T_{λ}' is reached. This decrease reflects a more rapid intensity increase for the XX scattering than that for the XZ scattering, thereby indicating the reorientation of PPU around the short axis has already taken place before the onset of the

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phase transition. In the nematic phase, although the XZ scattering intensity is generally less than the XX intensity, the difference is within the experimental uncertainty. Therefore the depolarization ratio is nearly equal to 1 in most of the nematic phase. Except at the vicinity of T_{λ}' , the unit depolarization ratio observed in the solid and nematic phases is probably associated with the scattering of the domain structure and indicates that the size of the single domain PPU in the nematic phase is less than the wavelength of light. Because of this limitation arising from the domain fluctuation, in order to obtain accurate information on the reorientational process associated with the phase transition by the depolarization study, it is necessary to increase the domain size by orienting the nematic liquid by an external electric field. The electric field dependent-Raman scattering is presently in progress and will be the subject of a future publication.

Finally, it should be pointed out under the identical experimental conditions, in contrast to the Raman experimental result, that the depolarization measurement of the Rayleigh scattered light in PPU does not reflect a quasi-discontinuous intensity at the nematic isotropic liquid-phase transition. The difference is mainly due to the presence of the interference of the scattering light from different molecules in the Rayleigh scattering, but the interference is absent in the Raman scattering. Consequently, for the purpose of obtaining the effect of short-range reorientation order, the Raman scattering technique is presumably more useful than the Rayleigh scattering.

Despite the fact that Raman scattering has been proclaimed to be insensitive to the study of the nematic liquid-phase transition in liquid crystals, we have demonstrated that Raman depolarization ratio studies do provide information about this type of phase transitions.

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C. H. Wang,* A. L. Leu

Department of Chemistry, University of Utah
Salt Lake City, Utah 84112

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Dynamics of Axial Ligation in Metalloporphyrins.

I. Imidazole Exchange in Low-Spin Ferric Porphyrins

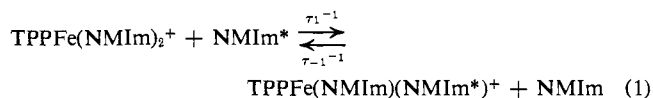
Sir:

The properties, structures, and reaction mechanisms, and their interrelation, of porphyrin complexes have been the subject of considerable interest recently¹⁻¹¹ in light

of their possible relevance as models for the structure-function relationships of the important class of iron hemoproteins^{12,13} and cobalt corrinoids.¹⁴ The frequent presence of an imidazole-coordinated residue in an axial position, coupled with the suggestions that metal-imidazole bond rupture may play a critical role in biological processes of coenzyme B₁₂¹⁴ and the cytochrome *c* system,¹³ indicates that a detailed characterization of the structure and dynamics of the imidazole-metal bond in such porphyrin complexes could have significant biological implications.

To date, relatively few studies have concerned themselves with the lability of the coordinated imidazole moiety.^{1,3,14b} A number of studies have characterized the lability of the nitrogenous bases in ruthenium(II) carbonyl porphyrin complexes with imidazole^{1,3} and pyrazoles,² as well as some six-membered ring ligands.² However, comparable data for the biologically functional iron systems are lacking, though some investigations of the substitution reactions of axially coordinated hemin have been reported.⁶⁻⁸ Axial ligand substitution reactions for a number of other metal porphyrins have also appeared,^{15,16} but the paucity of experimental data precludes any generalizations of the factors which govern the mechanism and rate of such reactions.

We report here one of the initial aspects of a systematic investigation of the kinetics and mechanism of axial ligation and ligand lability in iron porphyrin complexes. The complexes of interest here are the bisimidazole adducts of ferric porphyrins^{5,11,17} (*meso*-tetraphenylporphyrin = TPP, octaethylporphyrin = OEP, protoporphyrin IX dimethyl ester = PPDME), which in the case of TPP has been characterized by Mossbauer¹⁷ and esr and nmr,¹¹ as well as X-ray⁵ spectroscopy. Analyses¹⁷ as well as X-ray data⁵ substantiate a 2:1 adduct which magnetic data¹⁷ reveal to be in the low-spin ($S = 1/2$) state. The bis adduct of *N*-methylimidazole,¹⁸ NMIm, with TPPFeCl in CDCl₃ exhibits the proton nmr spectrum shown in Figure 1. The peaks labeled LS (low spin) arise¹¹ from TPPFe(NMIm)₂⁺; the 6:8 ratio peak intensities for the coordinated N-CH₃ and the pyrrole-H clearly establish the 2:1 stoichiometry of this species in solution. Of particular interest is that the N-CH₃ peaks exhibit dynamic line broadening due to exchange between free and coordinated NMIm according to (1). The rates



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(18) *N*-Methylimidazole was selected as the axial ligand since the NCH₃ yielded a well-resolved resonance for the complex which does not overlap with other peaks in the TPP and OEP complexes. Similar kinetic behavior was observed using unsubstituted imidazole, though seriously overlapping lines prevented detailed analysis of the line widths.