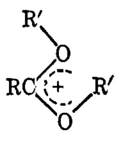
There emerges from this interpretation of the nmr data a pattern of consistency for the protonated acids VI,[4] the protonated esters VII, and the O-alkylated esters IV. For the formates (VI, VII, and IV where R = H; R′ = alkyl) the "*cis,trans*" form predominates to the extent of 70–90%, and for the acetates and higher homologs (VI, VII, and IV where R and R′ = alkyl) the "*cis,trans*" form is the exclusive isomer. This result is not unexpected in view of the known[5] conformational preference of aliphatic esters (VIII), where the alkyl group is coplanar and "*cis*" to the carbonyl oxygen.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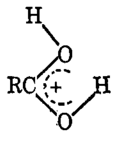
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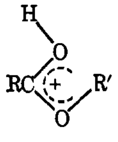
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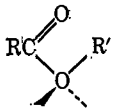
VIII

Acknowledgment. The author is indebted to the Petroleum Research Fund (No. 710-G), administered by the American Chemical Society, for financial support, and to R. M. Dodson for helpful discussions during the course of this work.

(5) J. E. Piercy and S. V. Subrahmanyan, *J. Chem. Phys.*, **42**, 1475 (1965), and references cited therein.

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Diastereoisomeric Four-Coordinate Complexes. VII.[1] Proton Resonance Detection of the Nonequivalence of Enantiomeric Nickel(II) Complexes in an Optically Active Solvent

Sir:

Recent reports have dealt with the pmr spectra of enantiomeric mixtures of organic compounds dissolved in optically active solvents and recorded in either liquid[2] or nematic phases.[3] Observations in the liquid phase are of considerable importance because in favorable instances of large chemical shift separations between signals of enantiomers, produced by diastereoisomeric solute–solvent interactions, assessment of optical purities[2a] and assignment of absolute configurations[2d] of solutes have been possible. We report here the first instance of diastereoisomeric interactions between a dissymmetric metal complex and an optically active solvent observable by proton resonance.

The quadridentate nickel(II) complexes Ni(3*s*Bu,5X′-sal)$_2$B (*cf.* Figure 1), derived from 2,2′-bis(3-*sec*-butyl-5-X′-salicylideneamino)biphenyl (B = bp) or -6,6′-dimethylbiphenyl (B = bmp, Y = CH$_3$), have been shown to undergo the dynamic planar (diamagnetic) $\rightleftharpoons$ tetrahedral (paramagnetic) equilibrium in chloroform solution with mole fraction tetrahedral $N_t^{298°} = 0.06–0.12$.[4] Unlike the situation with numerous bis-chelate complexes involved in this equilibrium,[1,4–6] the structural interconversion proceeds *without* racemization of the absolute configuration (Δ, Λ[6]) at the metal in the tetrahedral stereoisomers. These configurations are consequently stable on the pmr time scale (and for much longer periods[4]), and the three possible diastereoisomers, $\Delta(+,+) \equiv \Lambda(-,-)$, $\Delta(-,-) \equiv \Lambda(+,+)$, $\Delta(+,-) \equiv \Lambda(+,-)$, are detectable by virtue of three 5-CH$_3$ and three azomethine proton signals, whose large downfield shifts arise from the contact interaction present in the tetrahedral stereoisomers and whose separations result from unequal ΔF values for the structural change.[4,6] Ni(3*s*Bu,5Me-sal)$_2$bp when dissolved in nearly optically pure *l*-α-pinene[7] ([α]^{25}D −52.2° (neat)) gives a pmr spectrum in the azomethine region very similar to that in Figure 1a. The spectrum differs from that in CDCl$_3$ solution in that each of the three signals is split into a doublet with separations of 80, 50,

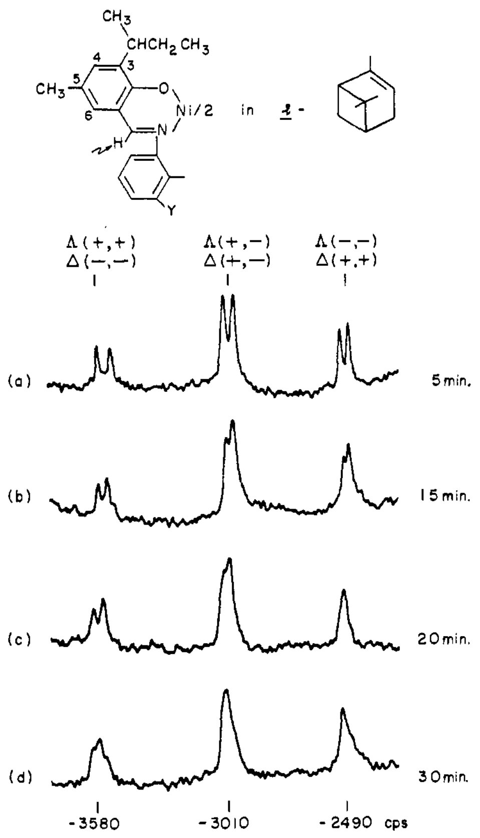

Figure 1. Pmr spectra (60 Mc, ~30°) of the complete isomeric mixture of Ni(3*s*Bu,5Me-sal)$_2$bp (Y = H) in −47.1° α-pinene illustrating the time dependence of the solvent-induced splittings of the azomethine proton signals. Intensities of components of each pair were shown to be equal by alternation of field-sweep direction. Frequencies (cps) are the chemical shifts relative to TMS.

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[1] Part VI: R. E. Ernst, M. J. O'Connor, and R. H. Holm, *J. Am. Chem. Soc.*, in press.

[2] (a) W. H. Pirkle and S. D. Beare, *ibid.*, **89**, 5485 (1967); (b) W. H. Pirkle and T. G. Burlingame, *Tetrahedron Letters*, 4039 (1967); (c) T. G. Burlingame and W. H. Pirkle, *J. Am. Chem. Soc.*, **88**, 4294 (1966); (d) W. H. Pirkle, *ibid.*, **88**, 1837 (1966).

[3] E. Sackmann, S. Meiboom, and L. C. Snyder, *ibid.*, **90**, 2183 (1968).

[4] M. J. O'Connor, R. E. Ernst, and R. H. Holm, *ibid.*, **90**, 4561 (1968).

[5] R. H. Holm, A. Chakravorty, and G. O. Dudek, *ibid.*, **86**, 397 (1964).

[6] R. E. Ernst, M. J. O'Connor, and R. H. Holm, *ibid.*, **89**, 6104 (1967).

[7] Commercial α-pinene ([α]^{25}D −48.7° (neat), J. T. Baker Chemical Co.) was fractionated on a spinning-band column and further resolved by means of its AgClO$_4$ complex.[8] Pmr spectra of the two samples were identical. The highest reported rotation of an α-pinene enantiomer is stated[9] to be [α]^{25}D +52.4° (neat).[8]

[8] A. E. Comyns and H. J. Lucas, *J. Am. Chem. Soc.*, **79**, 4339 (1957).

[9] D. V. Banthorpe and D. Whittaker, *Chem. Rev.*, **66**, 643 (1966).

and 25 cps (100 Mc) in order of increasing field. These splittings can only be due to diastereoisomeric solute–solvent interactions; for example, splitting of the −3580-cps signal arises from the species (*l*)-Λ(+,+) and (*l*)-Δ(−,−), in which (*l*) indicates the optical sense of the solvent molecules in the immediate solvation spheres.[10] This observation is entirely analogous to those made on organic enantiomers in optically active solvents. Doubling of the −3010-cps signal requires that the asymmetric structural feature responsible for the differentiating solute–solvent interactions be the chirality of the tetrahedral forms of the Λ(+,−), Δ(+,−) enantiomeric pair and suggests a similar origin of splitting for the other two enantiomeric pairs.

The pmr spectrum of Ni(3*s*Bu,5Me-sal)$_2$bp dissolved in incompletely resolved α-pinene ($[\alpha]^{25}\mathrm{D}$ −47.1° (neat)) revealed an unexpected and interesting time dependence shown in Figure 1. The first recorded spectrum after sample preparation (Figure 1a) displays the splitting of each signal into Δ, Λ components. Over ~30 min (Figure 1b–d) the separations of the components of each doublet decrease at rates unequal for each doublet. The components of each pair remain equally intense during the collapse and converge to a point slightly downfield of the lower field component of the initial pair in Figure 1a. In −52.2° α-pinene resolvable splittings were observed in the −2490-cps signal after 1 hr and in the −3580-cps signal after 1 week. This unusual behavior must be explained by a mechanism which converts diastereoisomeric entities, presumably solvates formed initially in solution, to enantiomers. In incompletely resolved α-pinene the solvation equilibria of the Δ and Λ isomers of each of the three pairs can be presented in an approximate manner as (1) and (2).

$$(d) + (l)\text{-}\Delta \rightleftharpoons (d)\text{-}\Delta + (l) \tag{1}$$

$$(d) + (l)\text{-}\Lambda \rightleftharpoons (d)\text{-}\Lambda + (l) \tag{2}$$

In the initially prepared solution, reactions 1 and 2 are both considered to lie heavily toward the left, as both Δ and Λ isomers are solvated by the *l*-pinene present in large excess, thereby rendering them magnetically inequivalent. Equilibrium is reached within 1 hr, under the conditions employed,[11] by rapid exchange of molecules between bulk solvent and the solvation sphere of the complex such that the signals of the Δ and Λ isomers represent a time average of the species in reactions 1 and 2, respectively. The time-dependent behavior of the spectra indicates that the equilibrium constants, K_{eq}, are unequal for reactions 1 and 2 such that, at equilibrium, the predominant species become (*l*)-Δ and (*d*)-Λ or (*d*)-Δ and (*l*)-Λ, depending on the relative magnitudes of K_{eq} for (1) and (2). The components of these pairs are strictly enantiomeric and thus are indistinguishable by pmr. The arguments presented above are easily generalized to the case in which more than one solvent molecule is involved in the solvation spheres. Reaction 1 then represents the end products in a series of reactions such as (*l*)(*l*)-Δ ⇄ (*l*)(*d*)-Δ ⇄ (*d*)(*d*)-Δ. The −52.2° α-pinene, in which this decay process is greatly retarded but not eliminated, is evidently not fully resolved. These results indicate that the Δ, Λ forms of these complexes manifest stereoselective solvation at equilibrium and that, compared to certain organic systems,[2] equilibrium solvation is not necessarily reached during the time required for an initial pmr measurement.

Finally, a similar but much smaller splitting of the azomethine signals of Ni(3*s*Bu,5Me-sal)$_2$bp into Δ and Λ components has been observed in solutions of *d*-limonene ($[\alpha]^{25}\mathrm{D}$ +120.8° (neat)).

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[10] Assignment of the Δ, Λ components of each doublet, which is in principle possible by deliberately controlling the absolute configuration at the metal in the B = bmp complexes,[4] could not be accomplished due to the low solubility of isomers such as Λ-Ni(3-(+)-*s*Bu-sal)$_2$bmp in *l*-pinene with the resultant poorly resolved pmr spectra. The spectrum of this complex did, however, permit assignment of the low-field signals to the Λ(+,+) and Δ(−,−) isomers. Assignment of the other two doublets to the Λ(+,−), Δ(+,−) and Λ(−,−), Δ(+,+) isomers (*cf.* Figure 1) follows directly from relative intensities. Signal assignments are thus identical with those proven in CDCl$_3$ solution which in order of increasing field are independent of 5-X′.[4]

[11] At the concentrations used, 0.11 *M* solute in 90% resolved *l*-α-pinene, the mole ratio of *d*-α-pinene to Δ or Λ isomers is ~6:1.

[12] NIH Predoctoral Fellow, 1966–1968.

Cyclopropanols. VIII. Low-Temperature Thermolysis of Cyclopropyl Nitrites

Sir:

Reactions in which a carbon free radical is formed are generally slightly accelerated by the presence of an adjacent cyclopropyl group, although the origin of the activating effect is still under discussion.[1,2] We wish to report that cyclopropyl groups enormously accelerate the rate of thermal homolysis of nitrite esters, so that substituted cyclopropyl nitrites undergo rearrangement at temperatures as low as −80°. In addition, we find that the rates of thermolysis are extremely sensitive to the nature of the 2 substituent on the cyclopropane ring, strongly suggesting that ring opening and O–NO bond breaking are concerted reactions. Thus, the results suggest that relief of strain in the transition state accounts for most, if not all, of the accelerating effect.

In a typical experiment, 1,2,2-trimethylcyclopropanol,[3] dissolved in CS$_2$ containing 2 equiv of pyridine-d_5, was cooled to −80° and treated with 1 equiv of NOCl. A portion of the cold solution was transferred to an nmr tube and the spectrum recorded at −60°. The spectrum was that expected for the nitrite ester,[4] and the cyclopropanol had been completely consumed. The probe temperature was gradually raised until changes in subsequent spectra indicated that decomposition was fairly rapid (*i.e.*, a half-life of ~1 hr). Further spectra were then recorded until complete decomposition had occurred. The product of the reaction, as shown in Scheme I, was the dimer of

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[3] C. H. DePuy, W. C. Arney, Jr., and D. H. Gibson, *J. Amer. Chem. Soc.*, **90**, 1830 (1968).

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