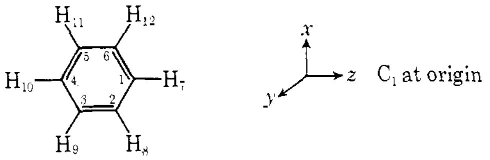
participate in the equivalent NH bond orbitals is 104.5, 105.3, and 105.0° from ER, INDO, and CNDO, respectively. The corresponding bond angle is 106.8°. All three calculations predict substantially less participation of the nitrogen 2s orbital in the lone pair of NH_3 than in N_2.

Table II lists the most important parts of the INDO CH and CR (R = C or O) bond orbitals for methane, ethane, ethylene, acetylene, benzene, and formaldehyde. It has been pointed out[4,10] that localization of the π orbitals of benzene leads to a continuous "infinity of sets of equally localized equivalent orbitals." [4] However, if the σ orbitals are included, this is no longer true and in fact INDO predicts three equivalent CC σ bonds and three pairs of equivalent banana bonds, *i.e.*, a Kekulé structure.



The similarity of the CH orbitals in methane and ethane is noteworthy. The slightly different s and p character in these two LMO's is in agreement with previous results[4] and is related to the fact that in ethane the CH orbitals no longer point along the bonds (Table II). The decrease in H participation from ethane to acetylene reflects the observed corresponding increase in $C-H^+$ character. The carbon s character increases in the same direction.

INDO predicts that all of the unsaturated molecules have equivalent banana-like CR bonds in agreement with the *ab initio* calculations.[5,6] It is interesting to note that CNDO predicts σ and π orbitals for these molecules. The calculated angle between the carbon (oxygen) hybrid of the banana bond and the CR axis is in good agreement with the *ab initio* calculations except for formaldehyde. In the latter case, INDO (experimental geometry) also predicts the oxygen lone pairs to span an angle of 119.5° while Newton, using a slightly different geometry,[6,11] finds 132.4°. It should be pointed out that INDO yields a considerably better dipole moment (1.88) for this molecule than the *ab initio* calculation[11] (0.98). The experimental value is 2.34 D. In fact, one would expect the C hybrid to make a slightly smaller angle with the CO axis than the oxygen hybrid.[5] Ninety-one per cent of the electron density of the benzene banana bond is shared by the bonded carbons with the remainder primarily on the remaining carbons and symmetrically decreasing with increasing distance from the bond.

These results indicate that INDO is superior to CNDO for the study of localized orbitals. In later work, a more quantitative comparison of these INDO results with *ab initio* LMO's will be given. Future papers will also deal with application of the method to internal rotation as well as the transferability of and effect of chemical substitution on particular localized orbitals.

Acknowledgment. The authors are grateful to Dr. M. D. Newton for making his results available prior to publication and for helpful discussions.

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Received July 29, 1969

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(10) D. D. Ebbing and R. C. Henderson, *J. Chem. Phys.*, **42**, 2225 (1965).

(11) M. D. Newton and W. N. Lipscomb, *J. Am. Chem. Soc.*, **89**, 4261 (1967).

Nuclear Magnetic Resonance Detection of Isomeric Structures of Bispyridoxylideneserinatoaluminum(III) and of Related Complexes in Deuterium Oxide

Sir:

Vitamin B_6 catalyzes many reactions of amino acids such as transamination, elimination of electronegative groups, and carbon–carbon bond fission. Many of these reactions also proceed at appreciable rates *in vitro* in the presence of pyridoxal and transition metal ions. Snell has proposed that amino acids form Schiff bases with pyridoxal which complex the metal ion as tridentate ligands, and he has suggested mechanisms by which these reactions may proceed.[1] The mechanisms in these metal-catalyzed model systems have been widely applied to pyridoxal enzyme catalyzed systems with considerable success, although many of the enzymes involved in pyridoxal catalysis do not require metal ions for activation.

Inasmuch as the aluminum(III) ion is one of the best metal ion catalysts for these model reactions, the structure of its complexes with pyridoxal–amino acid Schiff bases are of considerable significance. Recently Gansow and Holm[2] have published an nmr study from which they concluded that bispyridoxylidenealanatoaluminum(III) exists in two isomeric forms, the bis-tridentate octahedral complex (I) and the "dangling carboxyl" complex (II). In this paper are presented data indicating that the principle resonances of the nmr spectrum of bispyridoxylideneserinatoaluminum(III) are also consistent with the formation of three isomeric bis-tridentate octahedral complexes which are readily distinguishible because of a fortuitous juxtapositioning of the methyl group of one ligand and the magnetically anisotropic azomethine nitrogen of the other.

Pyridoxal and serine condense above pD[3] 7 to form pyridoxylideneserine (III) which can be detected by nmr.[6] As with the alanine–pyridoxal system,[2] Schiff base resonances can be detected at much lower pD's in the presence of aluminum(III) ion and these resonances are most logically assigned to the coordinated Schiff base. The resonances of the 4-CH, 5-CH_2, 6-H, and the amino acid portion of the Schiff base are within a few hertz of those for the coordinated Schiff base, but the 2-CH_3 resonances of the coordinated Schiff base are found as much as 100 Hz to higher field than those of the 2-CH_3 of the free Schiff base. This is shown in Fig-

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(1) D. E. Metzler, M. Ikawa, and E. E. Snell, *J. Amer. Chem. Soc.*, **76**, 648 (1954).

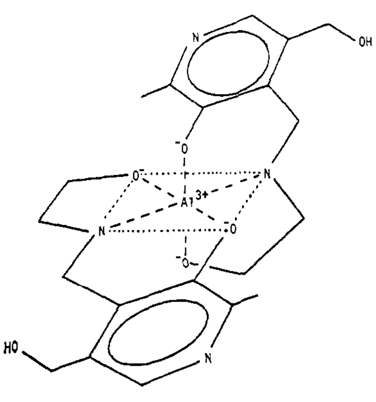
(2) O. A. Gansow and R. H. Holm, *ibid.*, **91**, 573 (1969).

(3) In this report pD is $-\log(D^+)$. Deuterium ion activity was calculated by the method of Covington, *et al.*,[4] and converted to concentration by means of tabulated activity coefficients.[5]

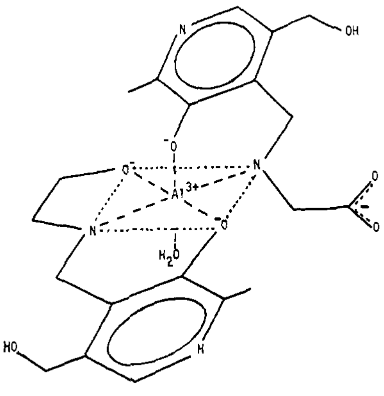
(4) A. K. Covington, M. Paabo, R. A. Robinson, and R. G. Bates, *Anal. Chem.* **40**, 700 (1968).

(5) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corporation, New York, N. Y., 1958.

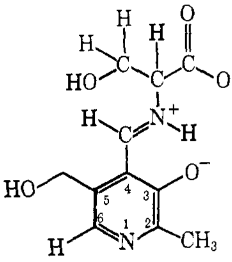
(6) E. H. Abbott and A. E. Martell, submitted for publication.



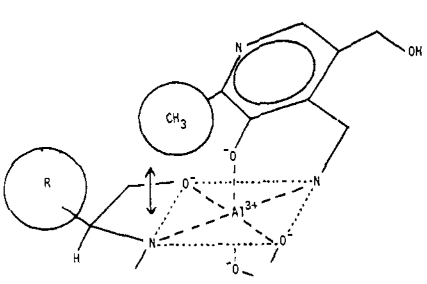
I NORMAL 2:1 COMPLEX



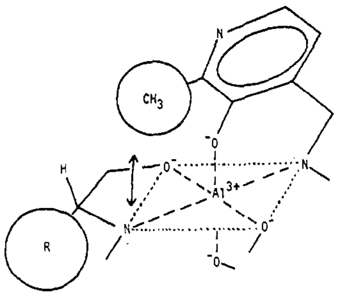
II 2:1 COMPLEX WITH PROPOSED "DANGLING" CARBOXYLATE GROUP



III PYRIDOXYLIDENESERINE



IV MAXIMUM STERIC REPULSION; MINIMUM SHIELDING



V MINIMUM STERIC REPULSION; MAXIMUM SHIELDING

ure 1a and 1b for pD's 6.1 and 9.3. By analogy to the alanine system, the resonances labeled A and B would be assigned to diasterioisomers of the dangling carboxyl forms of the complex, II.[2] Aluminum, however, has a powerful affinity for hydroxide ion, and it can be safely conjectured from the coordination chemistry of aluminum[7] that such dangling carboxyl species could only be formed through displacement from the coordination sphere of the metal ion by a deuterioxide ion. Even if it were replaced by a water molecule, the latter would readily hydrolyze in the pD range 6–10. The concentrations of such species would be strongly dependent on the concentration of the hydroxide ion. However, it is found that over the range of pD 6–10 peaks A, B, and C are each a fairly constant 20% of the area of peak D. These resonances cannot, therefore, be assigned to complexes having uncoordinated carboxylate species.

If it is hypothesized that the bis complex is formed from two approximately planar pyridoxylideneserinato ligands, the one bound to the two polar and one of the equatorial sites, the other bound to the remaining three equatorial sites, then the 2-CH$_3$ group of one ligand is directly above the π cloud of the azomethine nitrogen of the other ligand. The methyl resonance is then expected to be strongly shielded by the anisotropy of the azomethine nitrogen and this is probably the reason for the wide range over which the 2-CH$_3$ resonances of the bis complex are found. In addition if, as in the serine case, there is optical activity at the α carbon of the amino acid, the 2-CH$_3$ of the one ligand should be influenced by the steric requirements of the groups on the α-carbon atom of the amino acid moiety of the other ligand. This is shown in IV and V. In the case of the Schiff base formed from a single enantiomorph of an optically active amino acid, two configurations are possible: that in which the 2-CH$_3$'s of both ligands are crowded, as in IV, and where neither is crowded, as in V. If, however, a D and an L Schiff base are both coordinated to the same metal ion, one methyl group is crowded and the other is not. Thus, in the DL case, the two methyl groups are nonequivalent.

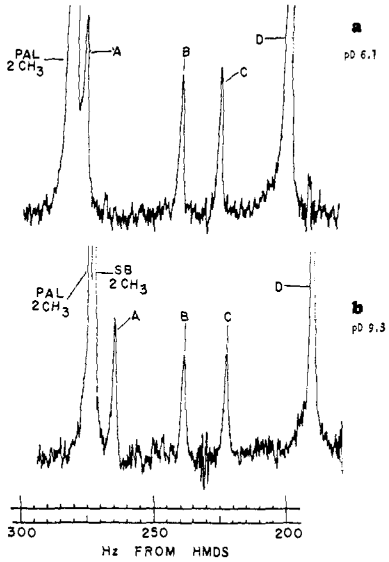


Figure 1. The 100-MHz spectra of: (a) 0.10 *M* DL-serine, 0.10 *M* pyridoxal, and 0.025 *M* Al(III) ion at pD 6.1; (b) 0.10 *M* DL-serine, 0.10 *M* pyridoxal, and 0.025 *M* Al(III) ion at pD 9.8. $T = 30°$, ionic strength adjusted to 1.0 with NaCl, HMDS = hexamethyldisiloxane in an internal capillary, PAL = pyridoxal, SB = Schiff base.

Figures 2a and 2b contrast the 2-CH$_3$ resonances of the bispyridoxylidenevalinatoaluminum(III) when the

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(7) L. G. Sillen and A. E. Martell, "Stability Constants," The Chemical Society, London, 1964.

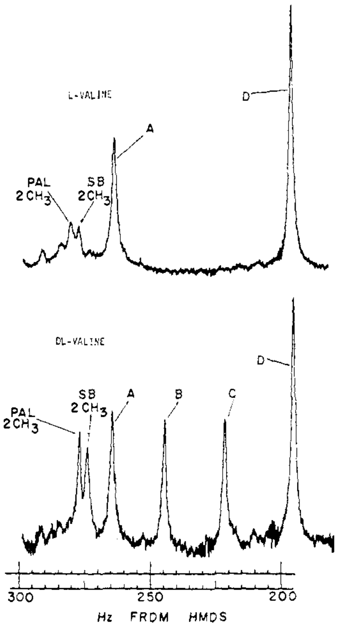

Figure 2. The 100-MHz nmr spectra of: (a) 0.102 *M* L-valine, 0.104 *M* pyridoxal, and 0.050 *M* Al(III) at pD 8.9; (b) 0.102 *M* DL-valine, 0.102 *M* pyridoxal, and 0.050 *M* Al(III) at pD 9.7. *T* = 30°, ionic strength adjusted to 1.0 with NaCl, HMDS = hexamethyldisiloxane in an internal capillary, PAL = pyridoxal, SB = Schiff base.

complex is prepared from the racemic amino acid and from the pure L isomer. The racemic complex has two resonances, B and C, which are absent from the pure L complex. These are assigned to the crowded and uncrowded 2-CH$_3$ resonances of the identical DL and LD complexes. Therefore, the doubly crowded DD and LL 2-CH$_3$'s give rise to the resonance at A in Figure 1b. As expected, the most abundant species are the doubly uncrowded DD and LL forms. Their identical methyl groups give rise to resonance D.[7a]

Interestingly, in the DL and LD cases, crowding, and subsequent relative deshielding, at one methyl results in deshielding at the other methyl group as well. The effect is as expected because the aromatic portions of these ligands are probably quite rigid and thus steric crowding which forces one 2-CH$_3$ group from its favored position above an azomethine nitrogen is transmitted as a shearing force to the other azomethine nitrogen, also forcing it away from its 2-methyl group, but probably by a smaller distance than occurs at the crowded position. Accordingly, in Figures 1 and 2 the resonance at B is assigned to the crowded methyl group and the one at C is assigned to the uncrowded methyl group of the DL and LD complexes.

The relative proportions of the various species suggest that the DL and LD states are about 0.5 kcal/mol above the uncrowded DD and LL, and that the doubly crowded DD and LL states are about 0.4 kcal/mol above the DL and LD states.

Preliminary investigations of alanine, α-aminobutyric acid, norvaline, valine, and threonine indicate that similar species are also the prevalent components of these systems, and that increasing the steric requirements of the amino acid accentuates the energy separation and relative deshielding of the 2-CH$_3$ resonances of the various isomers. In the case of glycine, only a single peak is observed, in the region of 200 Hz, since glycine lacks optical activity and therefore cannot form distinguishible isomers.

Apparently, the ability of the unsaturated bonds to shield the methyl groups is a very sensitive function of distance and it is this effect which makes it possible to resolve these nearly isoenergetic forms. The 6-H, 4-CH, and 5-CH$_2$ signals for these isomers cannot be resolved.

This research is part of a continuing investigation into the structure and catalytic properties of pyridoxal systems. Further details will be forthcoming shortly.

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[7a] NOTE ADDED IN PROOF. Resonances B and C appear slowly in the optically active amino acid systems, as the result of α-proton exchange, and resulting racemization, of the bis complex.

A Carbanion Rearrangement *via* Two Homoenolate Ions

Sir:

Several reports have appeared in recent years of carbanion rearrangements that are considered to proceed *via* homoenolate ions;[1] we now wish to report on a transformation that we consider involves the rearrangement of a carbanion *via* two homoenolate ions.

Reaction of diazoacetone with diphenylketene[2] gave the enol lactone **1** (11%):[3,4] mp 49–52°; $\lambda_{max}^{CCl_4}$ 5.54, 5.92 (m) μ; δ^{CCl_4} 2.10 (d, *J* = 1.5 Hz, 3 H), 5.63 (q, *J* = 1.5 Hz, 1 H), 7.26 (s, 10 H) (the major product from this reaction was 1-acetyl-3-phenylindan-2-one[5]). Treatment of **1** with phenyllithium in ether for 20 min followed by work-up with aqueous acid gave 1,2,2-triphenyl-1,4-pentanedione (**2**)[4] (42%), mp 154.5–155.5°, 1,3,3-triphenyl-1,4-pentanedione (**3**) (4.2%), mp 152.5–154°, and 3,3-diphenylpropiophenone (**4**) (5.5%);[6] examination of the spectra of the crude reaction product failed to reveal the presence of other reaction products. The structures of compounds **2** and **3** were established by their spectra [**2**: $\lambda_{max}^{CCl_4}$ 5.79, 5.96, 7.36 (m) μ; λ_{max}^{EtOH} 239 (ε 9800), 316 mμ (ε 310); δ^{CDCl_3} 1.91 (s, 3 H), 3.71 (s, 2 H), 7.0–7.6 (m, 15 H); **3**: $\lambda_{max}^{CCl_4}$ 5.85 (sh), 5.90, 7.40 (m) μ; λ_{max}^{EtOH} 242.5 (ε 13,800), 276.5 mμ (ε 1580); δ^{CDCl_3} 2.17 (s, 3 H), 4.14 (s, 2 H), 7.1–7.5 (m, 13 H), 7.7–7.9 (m, 2 H)] and by their conversion on treatment with ethanolic aqueous potassium hydroxide to 3,4,4-triphenyl-2-cyclopentenone[4] (**5**), mp 173–179°,[7] and 3,5,5-triphenyl-2-cyclopentenone (**6**), mp 155–156.5°, respectively [**5**: $\lambda_{max}^{CCl_4}$ 5.80 (sh), 5.87 μ; λ_{max}^{EtOH} 290 mμ (ε 17,000); δ^{CDCl_3} 3.30 (s, 2 H), 6.84 (s, 1 H), 7.0–7.5 (m, 15 H); **6**: $\lambda_{max}^{CCl_4}$ 5.87 μ; λ_{max}^{EtOH} 288.5 mμ (ε 22,900);

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(1) See, for example, A. Nickon and J. L. Lambert, *J. Amer. Chem. Soc.*, **84**, 4604 (1962); A. Nickon, J. Kwasnik, T. Swartz, R. O. Williams, and J. B. DiGiorgio, *ibid.*, **87**, 1615 (1965); R. Howe and S. Winstein, *ibid.*, **87**, 915 (1965); T. Fukunaga, *ibid.*, **87**, 916 (1965); J. P. Freeman and J. H. Plonka, *ibid.*, **88**, 3662 (1966).

(2) *Cf.* P. Yates and T. J. Clark, *Tetrahedron Lett.*, 435 (1961).

(3) Satisfactory elemental analyses have been obtained for all new compounds.

(4) First prepared by Dr. L. L. Williams, Ph.D. Thesis, Harvard University, 1961.

(5) *Cf.* A. S. Kende, *Chem. Ind.* (London), 1053 (1956).

(6) Identified by comparison with an authentic sample kindly provided by Professor R. E. Lutz, University of Virginia; *cf.* R. E. Lutz and J. O. Weiss, *J. Amer. Chem. Soc.*, 77, 1814 (1955).

(7) The wide melting range is attributable to the presence of two dimorphs.