tained 4.90% oxygen-18. The remainder, 16.15%, must have been at O-3. On this basis isopropyl alcohol (**9**) should have contained 8.07 + 2.45 or 10.52% oxygen-18. The observed value of 11.88% constitutes a discrepancy of $\sim$10%, probably attributable to a small steric effect. Methide displacement on O-4 would be favored, thus producing isopropyl alcohol rich in O-3. From this experiment we conclude that about 77% of ozonide **6** was formed according to a reaction scheme which places the isotopic label at O-3, probably the molozonide–aldehyde interchange mechanism. We find, therefore, that hydride reduction of **6** places the amount of ozonide formed by the molozonide–aldehyde mechanism at about 68%, while methyllithium reduction provides an estimate of 77%. Since the steric effects are most likely opposite in direction, we consider it probable that the 9% spread in the two values provides a rough evaluation of the sum of the steric effects.

The labeling experiments, therefore, provide strong support for the mechanism written to account for the dependency of ozonide *cis/trans* ratios on olefin geometry.[2] In this particular case, under conditions of added aldehyde, approximately 75% of ozonide **6** was apparently formed through the molozonide–aldehyde reaction. It must be noted, however, that in a normal ozonolysis, aldehyde is not present initially and that, before the molozonide–aldehyde mechanism can become important, a sufficient quantity of aldehyde must be produced, presumably by fission of the molozonide to zwitterion and aldehyde. Under these conditions it would not be surprising to find the new mechanism somewhat less important than in the present study. Once sufficient aldehyde is obtained in the normal ozonolysis, however, production of zwitterion may well nearly cease since the molozonide–alehyde reaction does not deplete aldehyde concentration, and at sufficiently high aldehyde concentrations it is apparent that this reaction competes well with molozonide fission. The effect of reaction temperature must also be considered since at higher temperatures molozonide lifetime will be shortened.

The results obtained in this study are compatible with the Criegee mechanism[5] and, in fact, serve to further confirm it. It should also be understood that the conclusions drawn in this work are not necessarily inconsistent with the mechanistic proposal recently championed by Bailey in which it is suggested that the dependence of cross-ozonide *cis/trans* ratios of olefin geometry is a result of the formation of configurationally stable *syn* and *anti* zwitterions.[9]

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## Circular Dichroism in Copper(II) Complexes of Some Bisglycylethylenediamine Analogs

*Sir:*

Some principles underlying the stereoselectivity of polydentate ligands have been delineated by Corey and Bailar,[1] imposition of a particular chiral hand depending in part upon nonplanarity of a five-membered chelate ring which in this respect is similar to a six-membered carbocyclic ring. Support for these principles has, for example, been obtained[2] where a nonplanar propane-1,2-diamine ring may be presumed present.[3] An apparent absence of stereoselectivity in some bis($\alpha$-amino acid)copper(II) complexes has been interpreted in favor of chelate ring planarity.[4] The data of Wellman, *et al.*, concerning helicity of bis($\alpha$-amino acid)copper(II) complexes and the nonplanarity of the bidentate amino acid ligands is of some interest, then, and we report here some observations concerning the three ligands (see Figure 1): I, N,N′-bisglycyl-(−)-propane-1,2-diamine; II, N,N′-bisglycyl-(−)-cyclohexane-1,2-*trans*-diamine; and III, N,N′-bis(+)-alanylethane-1,2-diamine, which support their empirical octant rule.[5] I and II have been prepared by modification of Asperger and Liu's method for III[6] using respectively (+)-propane-1,2-diamine (dihydrochloride, $[\alpha]_D$ −3.7°) and (−)-cyclohexane-1,2-*trans*-diamine, (dihydrochloride, $[\alpha]_D$ −16°), resolved *via* their *d*-tartrates. For III, L-alanine ($[\alpha]_D$ +14.25°), purchased from Nutritional Biochemicals Corp., was used. I, then, possesses absolute configuration *S*[7] and III configuration *S*,[8] and II may by inference[9] be assigned configuration *R*.

In basic solution (pH >10), formation of a biuret complex with Cu(II) is signalled by development of a red color, maximum absorbance at 520–550 m$\mu$. Under these circumstances, when 2 equiv of hydrogen ion is liberated per mole of complex,[10] the four ligand atoms are constrained approximately in a plane. The bisamide complexes may be viewed operationally as bisaminoacidates, the amino acid ligands making the same octant contribution[5] whether they be *cis* or *trans*. III, then, is virtually identical with bis-(+)-alaninatocopper(II) with $\alpha$-CH and CO in negative octants and a presumed minor contribution from the bridging $CH_2$'s in positive octants, that is, a negative Cotton effect over-all. In I the situation is reversed, any preference being wholly with the bridging ring which lying in positive octants produces a minor positive Cotton effect. In I there is little induced asymmetry required of the terminal rings, but in II, although the bridging $CH_2$'s are evidently in negative octants, the terminal CO's are very strongly directed into positive octants. In

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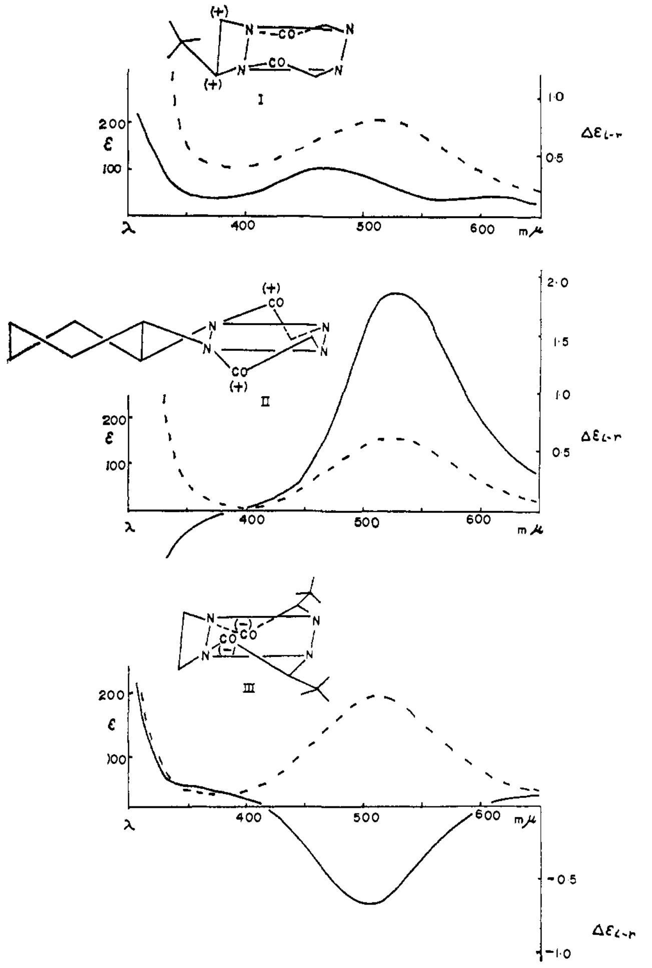
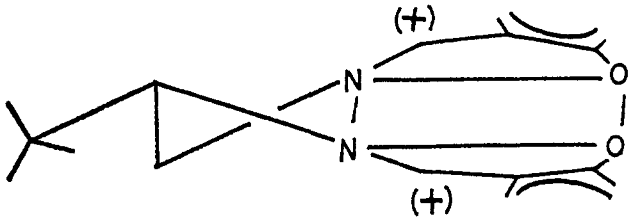
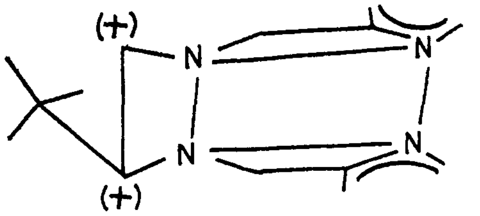




IV



V

Figure 1. Absorption (- - - -) and CD (———) spectra for I, N,N′-bisglycyl-(+)-propane-1,2-diiminecopper(II), II, N,N′-bisglycyl-(−)-cyclohexane-1,2-*trans*-diiminecopper(II), III, N,N′-bis-(+)-alanylethane-1,2-diiminecopper(II). Structures I–III and IV and V (text) show suggested significant octant contributions. CD spectra were measured using a Jasco Model ORD/UV/5 with a cell length of 10 mm at an ambient temperature of 28 ± 1°. The instrument was standardized by means of camphorsulfonic acid. Aqueous solutions were $10^{-1}$ *M* in NaOH, $10^{-2}$ *M* in ligand, and $10^{-3}$ *M* in $CuSO_4$.

increasing contribution to the octants around Cu(II), the CD amplitude of the complexes should be in the order I < III < II. We observe a pronounced positive Cotton effect at 525 mμ, the absorption maximum of II–Cu(II), and a smaller negative Cotton effect at 500 mμ, with an absorption maximum at 510 mμ, for III–Cu(II). Bis-(+)-alaninatocopper(II) has a predominantly negative Cotton effect in this region.[11] The spectrum of I–Cu(II) shows a much smaller positive Cotton effect at about 480 mμ, with an absorption maximum at 510 mμ. A strong positive Cotton effect in bissalicylaldehyde-(−)-propane-1,2-diiminecopper(II)[12] (IV) may be attributed to the larger terminal and planar chelate rings, these necessarily causing the C=N's to lie in positive octants. This is in contrast to the monohydrate's crystal structure[13] where the orientation is reversed, attributed to the exigencies of packing the methyl substituent and a neighboring water molecule. We would predict anomalous rotatory dispersion to be almost entirely absent in the copper chromophore of N,N′-bis(picolinoyl)propane-1,2-diiminecopper(II)[14] (V), since here the terminal chelate rings should be essentially planar, the residual asymmetry being wholly with the bridging ring, more restricted than in I, and a small positive Cotton effect resulting from the *S* ligand.

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## The Application of the Pfeiffer Effect to the Resolution of Dissymmetric Coordination Compounds

*Sir:*

The Pfeiffer effect[1,2] is the change in optical rotation of an optically active substance (hereinafter called the "environment" compound) in solution upon the addition of a racemic mixture of certain other optically active compounds (until now, complex inorganic compounds). In 1954 Gyarfas and Dwyer[3] postulated that the effect is due to a change in the displacement of an equilibrium between the *dextro* and *levo* enantiomers (in favor of one of them) of an optically labile, racemic complex (where the equilibrium constant is 1) in the presence of an optically active environment.

In support of this idea, Kirschner and coworkers[4–6] have described the increase in Pfeiffer rotation observed for the tris(*o*-phenanthroline) complexes of zinc(II), cadmium(II), and mercury(II), respectively—a series in which the equilibrium constants decrease, which may be indicative of the relative optical lability of these

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