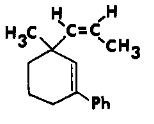
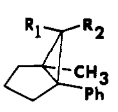


1



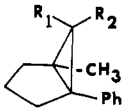
2, R_1=H; R_2 = cis, -CH=CHCH$_3$

3, R_1=H; R_2 = trans,-CH=CHCH$_3$

4, R_1=cis,-CH=CHCH$_3$; R_2=H

5, R_1=trans,-CH=CHCH$_3$; R_2=H

product II was carried out by a sequence involving ozonolysis, followed by sodium borohydride reduction. This afforded one of the two alcohols, **6** and **7**, prepared from the copper-catalyzed addition of ethyl diazoacetate to 1-methyl-2-phenylcyclopentene followed by saponification and lithium aluminum hydride reduction.[6a] The actual alcohol produced was found to be 1-methyl-5-phenyl-6-*endo*-hydroxymethylbicyclo[3.1.0]hexane (**6**) on the basis of the differences between the europium-induced shifts of the methyl *vs.* methylene proton resonances in **6** and its exo isomer **7**.[8] In addition, the infrared spectrum of II displayed an intense band at 10.3 μ, allowing assignment of the structure of 1-methyl-5-phenyl-6-*endo*-(*trans*-1-propenyl)bicyclo[3.1.0]hexane (**5**) to this photoproduct. When I was subjected to this same degradation sequence it also afforded the endo alcohol **6**. Thus, its structure must be that of 1-methyl-5-phenyl-6-*endo*-(*cis*-propenyl)bicyclo[3.1.0]hexane (**4**), differing from II only in configuration about the double bond.[9]

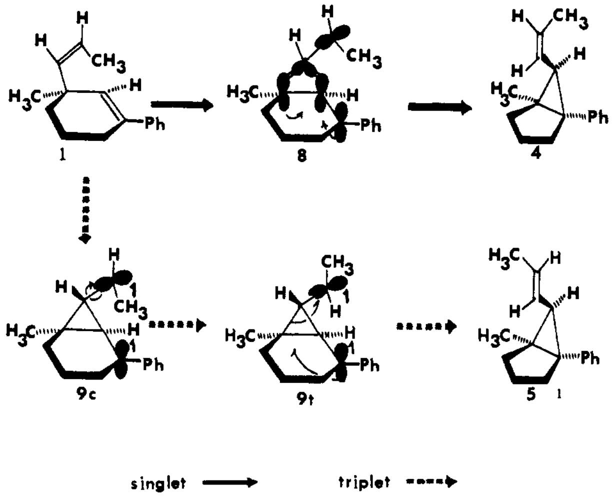


6, R_1=CH$_2$OH; R_2=H

7, R_1=H; R_2=CH$_2$OH

The photosensitized irradiation of **1** with benzophenone[10] proceeded with remarkable efficiency and gave, as the only detectable product,[11] the *endo-trans*-propenyl product **5** in near quantitative yield.[7]

In the di-π-methane reorganization pathway of **1**, a preference for disrotatory ring closure between C-3 and C-5 anti to the migrating propenyl group exists, independent of excited state multiplicity, as demonstrated by the exclusive formation of the *endo*-propenyl products, **5** and **4**, from the triplet and singlet excited states of diene **1**, respectively.[12] These results can best be explained in terms of two mechanisms, differing only in the simultaneity of bond formation and cleavage during rearrangement. A totally concerted singlet mechanism, *via* the electronically and structurally allowed[13] anti-disrotatory transition-state **8**, would lead to a singlet product with correct stereochemistry, *i.e.*, **4**. The alternate concerted pathway, through the syn-disrotatory closure, of apparent equal energy,[13] is not followed.



The triplet pathway requires a mechanism in which inversion of configuration about the double bond and stereospecific anti-disrotatory ring closure occur. A mechanism that accommodates both observations involves the intermediacy of diradical **9c** in which rotation about the C-1–C-2 bond results in the transoid conformation **9t**, capable of proceeding to **5** by "backside" attack of the anti lobe at C-5 on C-3. Further studies, directed at determining the role of structure and multiplicity on the preferred stereochemical pathways in the di-π-methane rearrangement, are in progress.

Acknowledgment. Support of this research by the Petroleum Research Fund of the American Chemical Society, the Research Corporation, and the Texas A&M Research Council is gratefully acknowledged.

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(8) A change in the molar ratio of Eu(fod)$_3$ to endo alcohol **6** from 0 to 0.6 resulted in a $\Delta\nu$ for the methyl resonance of 139 Hz and for the low-field methylene of 247 Hz. This is compared to the striking reversal for the exo alcohol **7** which displayed a $\Delta\nu$ for the methyl resonance of 241 Hz and for the low-field methylene of 109 Hz on changing from 0 to 0.75 molar ratio of the lanthanide. In addition, dramatic differences in the patterns displayed by the hydroxymethylene protons in **6** and **7** were observed (**6**, A_2X, d, J_{AX} = 7.5 Hz; **7**, ABX, dd, J_{AX} = 7.0 Hz, J_{BX} = 7.5 Hz, J_{AB} = 11.0 Hz). This is in accord with the expected differences between the magnetic environments of the diastereotopic protons in the endo and exo isomers.

(9) The absence of bands in the 9.8–12.5-μ region in the ir and the similarity of the nmr spectra of I and II (except in the olefinic region) support our structural assignments.

(10) The conditions used allowed for greater than 99% light absorption by benzophenone and efficient energy transfer to **1** from benzophenone triplet, only.

(11) That no detectable quantities of the trans isomer of **1** were observed, even in low conversion sensitized runs, is interesting and leads to the conclusion that isomerization about the propenyl double bond is slower than reaction by the di-π-methane pathway of the triplet monocyclic diene. A contrastingly different result was obtained by Zimmerman and Pratt[2a] for an acyclic 1,4-diene system.

(12) (a) For the direct irradiation reaction, the assumption is made that the trans product **5** results from the triplet of **1**, itself formed by intersystem crossing from its sluggishly reacting singlet excited state. Quenching studies are now in progress to determine if this is the case. (b) Another explanation for the exclusive formation of trans product **5** in the sensitized irradiation, which involves preliminary isomerization of **1**, *via* its triplet, to either (1) *trans*-**1** exclusively, followed by reaction in which the configuration about the double bond is retained, or (2) a mixture of *cis*- and *trans*-**1** in which trans reacts much more rapidly, can be ruled out on the basis of our varying conversion runs.[11]

(13) Both the syn and anti disrotatory transition states are isoconjugate with Möbius benzene and, therefore, are predicted to be of lowest energy (allowed) in the excited state process of **1**.[14] The two higher energy orbital arrangements, involving conrotatory closure, are also forbidden on structural grounds, since both would lead to the excessively strained trans-fused bicyclo[3.1.0]hexane ring system.

(14) H. E. Zimmerman, *J. Amer. Chem. Soc.*, **88**, 1564, 1566 (1966).

Patrick S. Mariano,* Jan-kwei Ko
Department of Chemistry, Texas A&M University
College Station, Texas 77843

Received November 15, 1971

Solvent Effects on the Visible Circular Dichroism of Copper(II) Complexes with N,N-Dialkylated Amino Acids

Sir:

With the exception of L-proline, the visible circular dichroism spectra thus far reported for 2:1 complexes of amino acid anions with copper(II) in aqueous solution all

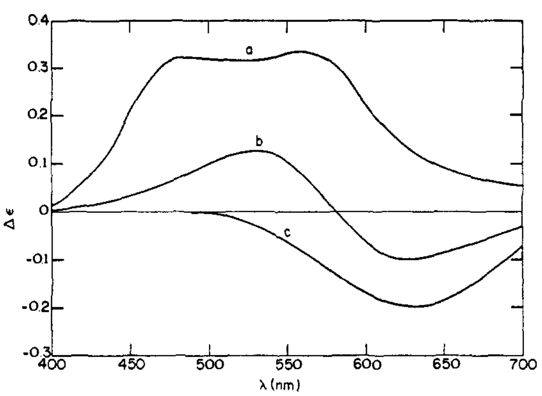

Figure 1. CD spectra of bis(L-*N*,*N*-diethyl-α-alaninato)copper-(II): (a) 10^{-3} *M* in benzene; (b) 10^{-3} *M* in water; (c) 1:1 complex with pyridine in benzene.

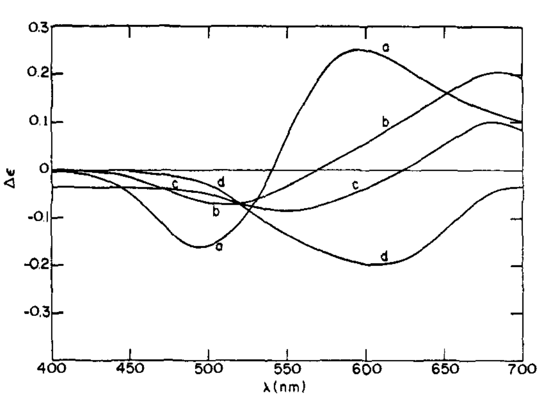

Figure 2. CD spectra of bis(L-*N*,*N*-dimethyl-α-alaninato)copper-(II): (a) 10^{-3} *M* in ethylene chloride; (b) 10^{-2} *M* in ethylene chloride; (c) 10^{-3} *M* in water; (d) 1:2 complex with pyridine in nitromethane.

exhibit a net negative sign.[1] Although the copper complex of *N*-methyl-L-alanine shows two weak positive bands at 510 and 560 nm, a more intense, negative band occurs at 656 nm.[2] We wish to report the visible CD spectra of copper complexes with the anions of L-*N*,*N*-dimethyl- and L-*N*,*N*-diethyl-α-alanine. For both of these complexes in noncoordinating solvents, a net positive CD sign results. Complexes with the diethyl-substituted ligand yield particularly useful information, since in some instances the coordination number of copper and the structure of the complex in solution may be established with considerable certainty.

The crystal structure of bis(DL-*N*,*N*-diethyl-α-alaninato)copper(II) shows that the chelate rings are trans to each other, and each is in a conformation in which the *C**-methyl substituent is equatorial.[3] The solid nickel(II) and copper(II) compounds with this racemic ligand are isostructural. The 100-MHz proton magnetic resonance spectra of the monomeric, diamagnetic nickel(II) bis complexes with the anions of either D- or L-diethylalanine in benzene or methylene chloride solution show only a 3-Hz downfield shift of the *C**-methyl proton doublet *vs.* the DL complex. Since Warner, *et al.*,[4] have shown that in several rigid, diamagnetic nickel(II) chelates the resonances of the protons of geminal axial and equatorial methyl groups are separated by 0.5–0.8 ppm, we conclude that in solution the ring conformations in our monomeric *all*-L and DL amino acid chelates are similar. Moreover, since the closest nonbonded interaction distance in the crystal is 3.2 Å,[3] it is unlikely that the conformations of the rings in the crystal and in solution would differ.

The visible spectra of four-coordinate, monomeric complexes of copper(II) with N,N-dialkylated amino acids in benzene, methylene chloride, or ethylene chloride solution all show a principal absorption maximum at *ca.* 490 nm and a shoulder near 600 nm.[3] In Figure 1 the CD spectrum of bis(L-*N*,*N*-diethyl-α-alaninato)copper(II) (compound I) in benzene solution is seen to exhibit two positive bands. Both the visible spectrum and the CD spectrum of I in benzene may be reconstructed satisfactorily by superimposing two Gaussian functions centered on 470 and 570 nm. According to Richardson,[5] the magnetic-dipole-allowed d–d transition of lowest energy for *trans*-amino acid complexes of copper is $d_{xy} \leftarrow d_{x^2-y^2}$ and that of highest energy is $d_{xz} \leftarrow d_{x^2-y^2}$. Vincent[6] has obtained *g* values of 2.043 and 2.220 from a single crystal of the DL isomer of compound I which are fully consistent with $d_{xz} \leftarrow d_{x^2-y^2}$ and $d_{xy} \leftarrow d_{x^2-y^2}$ transitions occurring at 470 and 570 nm, respectively.

When I in benzene is treated with pyridine a weak 1:1 complex forms (formation constant 0.4 M^{-1}) whose visible spectrum maximizes at 610 nm, and whose visible CD spectrum is shown in Figure 1 to be a single negative band. We presume that pyridine coordinates in one of the axial positions of copper without greatly perturbing the chelate rings, since the exceptionally high carbonyl vibration frequency found for this class of compounds[3] was essentially unchanged in the pyridine adduct. Moreover, the bathochromic shift in the visible absorption maximum is of the same magnitude as that observed by Musker and Hussain[7] upon the axial coordination of one halide ion to bis(1,4-diazacycloheptane)copper(II) perchlorate in nonaqueous media. When I was dissolved in water the structureless visible spectrum maximized at 610 nm while the CD spectrum exhibited a negative band at 620 nm and a positive band at 540 nm. The nature of the species in aqueous solution is unknown.

When bis(L-*N*,*N*-dimethyl-α-alaninato)copper(II) (compound II) was studied, a more complicated situation was obtained. In ~10^{-3} *M* solution in ethylene chloride the visible spectrum strongly resembled those found for the diethyl homolog in either ethylene chloride or benzene, *i.e.*, a maximum at 480 nm and a shoulder at ~600 nm. At the same concentration in nitromethane, only a single maximum at 510 nm was observed. Essentially the same CD spectrum was found, however, for both solutions. In Figure 2 this spectrum shows a long wavelength band which is positive together with a short wavelength band which is less intense and negative. A 10^{-2} *M* solution of II in ethylene chloride, in which extensive self-association has evidently occurred, is blue, λ_{max} = 620 nm. The

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[1] J. M. Tsangaris and R. B. Martin, *J. Amer. Chem. Soc.*, **92**, 4255 (1970), and references cited therein.

[2] E. W. Wilson, Jr., and R. B. Martin, *Inorg. Chem.*, **10**, 1197 (1971).

[3] C. P. Nash and W. P. Schaefer, *J. Amer. Chem. Soc.*, **91**, 1319 (1969).

[4] L. G. Warner, N. J. Rose, and D. H. Busch, *ibid.*, **90**, 6938 (1968).

[5] F. S. Richardson, *J. Chem. Phys.*, **54**, 2453 (1971).

[6] J. S. Vincent, private communication.

[7] W. K. Musker and M. S. Hussain, *Inorg. Chem.*, **8**, 528 (1969).

CD bands have shifted to longer wavelengths, and the net circular dichroism is now less positive. In dilute aqueous solution the CD spectrum of II is net negative, although a small positive component exists at 680 nm. Finally, a 2:1 pyridine adduct of II in nitromethane has a visible CD spectrum which is totally negative to 700 nm, the longest wavelength we can attain with the Jasco ORD/UV-5 instrument used in our investigations.

From models we find that for both I and II the sterically favored conformation of the chelate rings has the *C**-methyl groups equatorial. In this conformation of I the terminal methyl groups of the ethyl substituents which are on the same side of the coordination plane as the *C**-methyl groups lie directly above the metal ion.[3] With II, however, the *z* axis of the molecule is completely unobstructed.

The CD spectrum of monomeric II shown in Figure 2a has the form predicted by Richardson[5] for the first-order charge-transfer contribution to the total rotatory strength of four-coordinate trans copper–L-alanine complexes; *i.e.*, bands from $d_{xz} \leftarrow d_{x^2-y^2}$ and $d_{xy} \leftarrow d_{x^2-y^2}$ transitions having opposite signs, the long wavelength band being the more intense by a factor of 2. The nonbonded methyl groups near the *z* axis of I evidently perturb the copper d_{xz} orbital in such a way as to alter radically the CD band associated with it, even though the visible spectra of I and II are not appreciably different. In this connection it is also noteworthy that with II, changing the solvent from ethylene chloride to nitromethane alters the energy levels and/or the transition probabilities but not the CD spectrum.

With both I and II, as the coordination number of the metal increases from 4 the visible spectrum shifts to longer wavelengths, and with strong complexing agents the net CD sign becomes negative. The signs of the CD bands of II in aqueous solution are opposite to those of the corresponding bands of the copper complex with *N*-methyl-L-alanine in this medium.[2] If the same number of water molecules is bound to each complex, this result may be rationalized since the chelate ring conformation suggested by Wilson and Martin[2] for the monomethylated ligand is opposite to the one we propose for II.

Charles P. Nash,* Charles A. Jacks
Department of Chemistry, University of California
Davis, California 95616
Received August 14, 1971

A New π-Interaction Process.[1] A Di-π-propane Reaction

Sir:

During the last few years one of the most extensively studied photochemical processes has been the di-π-methane rearrangement.[2] Recently we have discovered that the photolysis of 1,1,2,2-tetraphenylethane leads to a di-π-ethane reaction,[3] a discovery which suggested that the di-π-methane rearrangement might be only the first in a homologous series of π-interaction processes.[1] We have now investigated the photochemical reactions of 1,1,3,3-tetraphenylpropane (**1**), 1,1,4,4-tetraphenylbutane (**2**), and 1,1,5,5-tetraphenylpentane (**3**),[4] compounds capable of experiencing the di-π-propane (compound **1**), di-π-butane (**2**), and di-π-pentane (**3**) reactions, and wish to report that the first of these processes is observed while the latter two do not take place in this series of compounds. These and earlier observations[3,5] establish that π-interaction processes in the tetraphenylalkanes can occur when the π systems are separated by one or more atoms but that there is a limit to the number of separating atoms which will allow reaction to proceed.

Vycor-filtered irradiation of 1.00 mmol of 1,1,3,3-tetraphenylpropane (**1**) in 350 ml of methanol for 1 hr with a 450-W Hanovia mercury vapor lamp under nitrogen caused the reaction of 43% of the starting material to produce biphenyl (**4**, 93%), *cis*- and *trans*-1,2-diphenylcyclopropane (**5**, 24%, and **6**, 23%), and 1,3-diphenyl-1-methoxypropane (**7**, 44%).[6] The identity of these photoproducts, as with all photoproducts described in this communication, was established by comparison with independently synthesized samples.[7]

Critical to the understanding of this reaction is a determination not only of the original position in the starting material of the various benzene rings present in the products but also of any change in point of attachment within a given benzene ring to the rest of the molecule. These determinations were achieved by studying the photochemical reactions of 1,1,3,3-tetra-*p*-tolylpropane (**8**) and 1,1-diphenyl-3,3-di-*p*-tolylpropane (**9**). The general features of these reactions were the same as those of 1,1,3,3-tetraphenylpropane (**1**). From the photolysis of **7** the only biphenyl formed was 4,4′-dimethylbiphenyl while the only cyclopropanes were the cis and trans isomers of 1,2-di-*p*-tolylcyclopropane. This experiment demonstrated that the number one carbon atoms in the benzene rings of the starting material retained their numbering in product molecules. During the irradiation of 1,1-diphenyl-2,2-di-*p*-tolylpropane, aside from methyl ethers, only 4-methylbiphenyl and *cis*- and *trans*-1-phenyl-2-*p*-tolylcyclopropane were formed, thus showing that the interacting phenyl groups were 1–3 related in the starting material.

Combining the information resulting from these three photochemical reactions, we suggest the mech-

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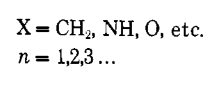
[1] A π-interaction process is a photochemical reaction between nonconjugated π systems which passes through one or more of the following stages.



$X = CH_2$, NH, O, etc.
$n = 1,2,3 \ldots$

[2] See H. E. Zimmerman, P. Hackett, D. F. Juers, J. M. McCall, and B. Schröder, *J. Amer. Chem. Soc.*, **93**, 3653 (1971), and references therein.

[3] J. A. Ross, W. C. Schumann, D. B. Vashi, and R. W. Binkley, *Tetrahedron Lett.*, 3283 (1971).

[4] C. R. Hauser, C. F. Hauser, and P. J. Hamrick, *J. Org. Chem.*, **24**, 397 (1959).

[5] T. D. Walsh and D. R. Powers, *Tetrahedron Lett.*, 3855 (1970).

[6] It is possible in this reaction to have a 100% yield of biphenyl (**4**) along with a combined 100% yield of the methyl ether 7 and cyclopropanes **5** and **6**.

[7] The biphenyls were purchased from the Aldrich Chemical Co., Milwaukee, Wis. The cyclopropanes were synthesized by a modification of the Simmons–Smith reaction as reported by S. Savada, J. Oda, and Y. Inouye, *J. Org. Chem.*, 33, 2141 (1968). The methyl ethers were prepared by photolysis of the corresponding cyclopropanes in methanol (ref 8).