mechanism of this reaction is the virtually complete absence of a kinetic solvent effect (entries 9, 11–13 in Table II).

The absence of a solvent effect on the rate of reaction but the presence of a solvent effect on the product distribution require a mechanism in which the kinetic step and product step are clearly separated in two distinct events.[4] For this reason we propose a mechanism (Scheme I) in which the phosphorus nucleophile is initially inserted into the peroxide bond *via* a slow step leading to the pentacovalent phosphorus intermediate **5**.[9] In a subsequent fast step the unstable pentacovalent intermediate **5** then opens up to produce the two possible dipolar ions **6** and **7**.[10] The dipolar ion **6** fragments into α-alkylstyrene (**2**) and carbon dioxide, while the dipolar ion **7** disproportionates into alkyl phenyl ketone **3** and ketene.[11] The small amount (about 6–9%) of β-alkyl-β-phenyl-β-propiolactone (**4**) is presumably formed by internal nucleophilic displacement of phosphine oxide or phosphate from either dipolar ion. All attempts to trap the pentacovalent phosphorus intermediate **5** have failed so far.[12] In fact, a kinetic experiment has shown that the rate of peroxylactone consumption is identical within experimental error with the rates of formation of styrene, ketone, and β-lactone. Therefore, no appreciable amount of the pentacovalent intermediate **5** accumulates during the course of the reaction.

The experimental details and the elaborate discussion of the mechanism of this novel ketene elimination and decarboxylation reaction will be presented shortly.

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(9) F. Ramirez, *Accounts Chem. Res.*, **1**, 168 (1968).

(10) D. B. Denney and S. T. D. Gough, *J. Am. Chem. Soc.*, **87**, 138 (1965).

(11) A. Eschenmoser, D. Felix, and G. Ohloff, *Helv. Chim. Acta*, **50**, 708 (1967).

(12) J. S. Cohen, *J. Am. Chem. Soc.*, **89**, 2543 (1967).

(13) M.S. Thesis, University of Puerto Rico, Sept 1966.

(14) M.S. Thesis, University of Puerto Rico, Aug 1968.

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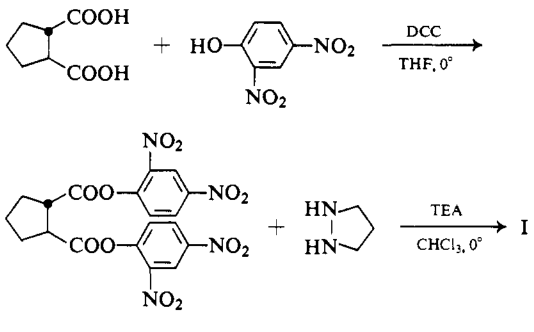
Optical Rotatory Properties of Cyclic Compounds Related to Diketopiperazines

Sir:

We have been interested in the optical rotatory properties of rigid molecules containing at least two identical neighboring chromophores as a way of further exploring the predictions of the exciton theory[1,2] and of providing useful models for macromolecular systems.

We wish to report some preliminary results on the optical properties of four cyclic compounds (Table I) that are related isomerically to diketopiperazine systems. These cyclic compounds were obtained from the appropriate optically active dicarboxylic acids and cyclic hydrazines by a method, chosen to avoid racemization,[3] which is illustrated in Scheme I. Compound I is isomeric with prolylprolyldiketopiperazine.

Scheme I



The optical rotatory properties of amino acid diketopiperazines, which have been investigated recently,[4–6] show a relatively strong n–π* Cotton effect together with a rather weak π–π* Cotton effect. Although diketopiperazines show an unusually high rotation, our cyclic compounds display rotation four times higher, a remarkable result obtained by rearranging the disposition of the amide chromophores in the molecule.[7]

Optical rotatory dispersion (ORD), circular dichroism (CD), and ultraviolet (uv) data obtained in trifluoroethanol (TFE) for these cyclic compounds are reported in Table I. Generally, measurements were carried out at concentrations of about 10^{-2} *M*, but dilutions up to 10^{-6} *M* did not appreciably affect the results.

The uv spectrum of compound IV shows a band at 210 mμ and another strong band at about 250 mμ (Figure 1). The presence of the latter band in the spectrum is also evident in the related open-chain compound V, diisobutyrylpyrazolidine (Figure 2). The assignment of the shorter wavelength band in the uv spectrum to a π–π* transition of the amide group and of the longer wavelength band to an n–π* transition of the same chromophore seems reasonable enough in compound V. These results would have provided a basis for a similar assignment in the remaining compounds, except for the high intensity of the longer wavelength band which must be taken into account (Figure 1, Table I). Approximately the same situation occurs in the other compounds that were investigated (Table I).

Although there is little doubt that an n–π* transition is present in that region, it seems unlikely that it can be responsible for the high absorption observed. Probably, the bulk of the effect comes from the longer wavelength

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(1) For a review of exciton theory and its applications to organic molecules, see: M. Kasha, *Radiat. Res.*, **20**, 55 (1963).

(2) J. A. Schellman, *Accounts Chem. Res.*, **1**, 144 (1968).

(3) D. F. DeTar, M. Gouge, W. Honsberg, and U. Honsberg, *J. Amer. Chem. Soc.*, **89**, 988 (1967).

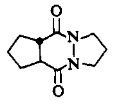
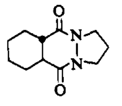
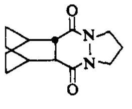
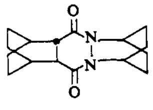
(4) (a) D. Balasubramanian and D. B. Wetlaufer, *ibid.*, **88**, 3449 (1966); (b) D. Balasubramanian and D. B. Wetlaufer in "Conformation of Biopolymers," G. N. Ramachandran, Ed., Academic Press, New York, N. Y., 1967, p 147.

(5) J. A. Schellman and E. B. Nielsen, in ref 4b, p 109.

(6) F. A. Bovey, private communication.

(7) Molecular models indicate that the geometry of the central ring differs from a planar diketopiperazine and this may cause the chromophore to be inherently dissymmetric.

Table I. Optical Data in 2,2,2-Trifluoroethanol[a]

	ORD		CD		Uv	
	λ, mμ	[m]	λ, mμ	Δε/residue	λ, mμ	ε/residue
 I	250	−23,800	232	−16.6	202	4500
	236	0				
	210	+78,000	212	0	230–40	485
	195	0	200	+18.2		
	(190)	(−15,500)				
 II	266	−13,400	246	−11.2	248	3200
	251	0				
	228	+59,000	228	0	202	2600
	211	0	215	+17.0		
	202	−15,000				
 III	260	−20,000	245	−15.0	245	2500
	247	0				
	224	+68,000	230	0	205	2500
	208	0	213	+15.5		
	(190)	(−25,000)				
 IV	270	−21,000	247	−13.5	250	2500
	254	0	227	0	208	2900
	224	+78,500	212	+20.2		
	208	0				
	(190)	(−32,000)				

[a] Measured with a JASCO ORD/CD/UV spectropolarimeter. Values in parentheses do not represent maxima.

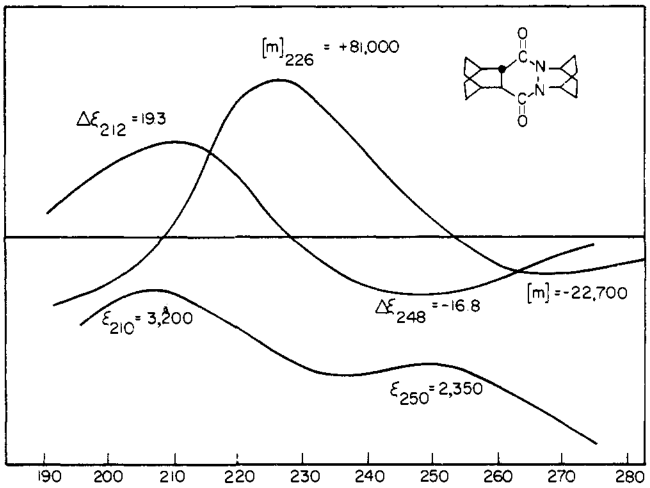


Figure 1. ORD–CD–uv curves of compound IV in methanol, at 25°.

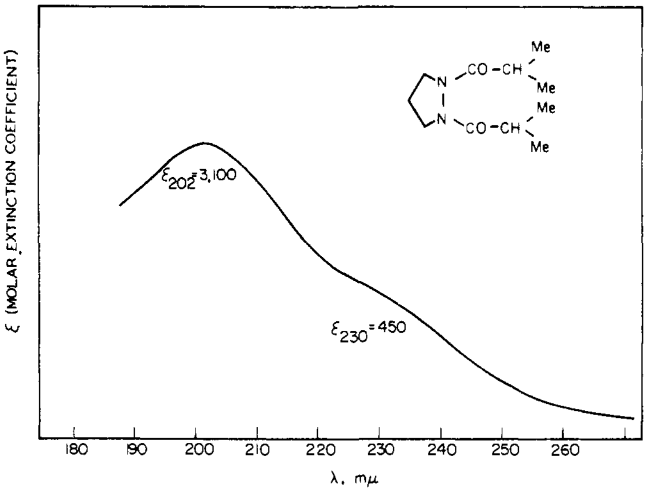


Figure 2. Uv spectra of diisobutyrylpyrazolidine (V) in 2,2,2-trifluoroethanol.

component of a split π–π* transition.[1-6,8] This statement would be rather difficult to make on the basis of the uv spectra alone; however, ORD and CD data support this suggestion strongly. The ORD and CD curves in Figure 1 are an almost ideal example of a rotatory strength "couplet" described by Schellman,[2] which is a characteristic form of dispersion that arises when two Cotton effects of equal but opposite rotatory strength lie less than a band width from one another. This "couplet" arises from interactions of large electric dipoles, *via* a dipole–dipole coupling mechanism.[1,2]

This rules out a significant contribution of the n–π* transition to the rotatory strength of these compounds and supports strongly our assignments of the uv absorption. Thus, it appears that the particular geometry of the amide bonds, in these cyclic molecules, gives rise to a very pronounced interaction which results in a large splitting of the π–π* transition.[9,10]

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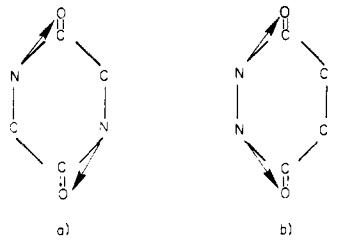
(8) For a review article see: W. B. Gratzer in "Poly-α-Amino Acids," G. D. Fasman, Ed., Marcel Dekker Inc., New York, N. Y., 1967, p 177.

(9) A referee has suggested that we may underestimate the contribution of the n–π* transition in the higher wavelength lobe of the split π–π* transition. We agree that there are known n–π* transitions in ketone moieties [R. C. Cookson and N. S. Wariyar, *J. Chem. Soc.*, 2302 (1956)] of highly dissymmetric rigid structures and that our interpretation is subject to more scrutiny in related systems.

(10) For related rigid amide systems with strong n–π* bands, see S. Feinleib, F. A. Bovey, and J. W. Longworth, *Chem. Commun.*, 238 (1968) (CD of spirobihydantoin), and F. A. Bovey, *Pure Appl. Chem.*, **16**, 417 (1968) (D-oxolupanine).



a) b)

Figure 3. The arrangements of transition dipoles of peptide groups in diketopiperazines (a) and in diketopiperidazines (b).

The exciton splitting dominates both the uv spectra and the rotatory behavior, in contrast with the features exhibited by diketopiperazines.[4-6] Exciton theory[1] predicts no actual splitting of the π–π^* transition for dimers with parallel arrangements of transition dipoles, as is the case in diketopiperazines (Figure 3a). Rotatory strength in diketopiperazines consists, mainly, of contributions from a one-electron mechanism and a dipole–quadrupole coupling mechanism, both of which stress the importance of the n–π^* transition. Instead, a large splitting is predicted by the exciton theory for an oblique arrangement of transition dipoles[1] (Figure 3b). This situation is probably responsible for part of the high rotations which we observed for our cyclic compound.

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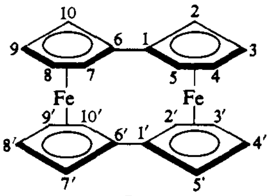
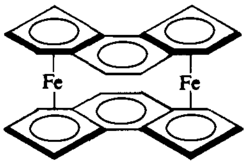
The Synthesis of 1,1′-Biferrocenylene

Sir:

Although the parent member of the novel 1,1′-biferrocenylene (I)[1] family has not been described, the synthesis of a homologous ferrocenophane, bis(*as*-indacenyliron) (II), has been reported.[2] In addition, mass spectral evidence has been reported for the formation of I during the reaction of cobalt(II) chloride with a mixture of lithiated ferrocenes, but the compound itself was not isolated.[3]



I



II

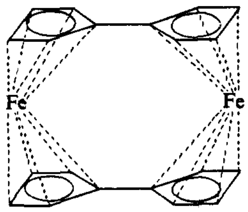
Because of internal strain resulting from the high degree of rigidity present in I, and the intramolecular repulsion of the nonbonding electrons of the iron atoms, it was thought that I might possess unusual physical and chemical properties.

We wish to report the preparation of I by a modification of the Ullman coupling reaction which has been shown to be very effective in the ferrocene system.[4] 1,1′-Diiodoferrocene (99% purity by vpc) was heated at 140–160° for 3 hr in the presence of copper bronze using a large excess of either *n*-butylferrocene or diethylbenzene as solvent. The reaction mixture was filtered hot, and the product precipitated by the addition of the filtrate to a large volume of hexane. The crude product was recrystallized from benzene (solubility of I in cold benzene is approximately 0.2 mg/ml), yielding dark orange needles which exhibited both sublimation and decomposition >300°, with rapid decomposition occurring at 380°. *Anal.* Calcd for $C_{20}H_{16}Fe_2$: C, 65.54; H, 4.39; Fe, 30.16; mol wt, 367.9950. Found: C, 65.44, 65.46; H, 4.50, 4.44; Fe, 30.26, 30.33; mol wt (high-resolution mass spectroscopy), 367.9978. The fragmentation pattern observed in the mass spectrum of II at 70 V contained only three predominant peaks (amplitudes for each peak are given relative to 100 for the parent peak): m/e 56 (11.7), 128 (11.9), and 184 (13.4). The first two masses correspond to iron and fulvalene, respectively, from cleavage of the "sandwich" structure. The peak at m/e 184 may be assigned to a doubly charged parent species. An interesting feature of the mass spectral pattern is a small but significant peak at m/e 102 (3.8) which can be attributed to triafulvene, probably formed by a loss of acetylene from the fulvalene fragment as indicated below.

The infrared spectrum of I showed C–H stretch only in the ferrocene region (3090 cm^{-1}). Medium-weak absorption at 1100 cm^{-1} and medium-strong absorption at 997 cm^{-1} were also observed, analogous to absorptions in these regions reported in the infrared spectra of substituted biferrocenyls.[5] The electronic spectrum of a chloroform solution of I showed a maximum at 4660 Å (ε 255) and an inflection at 3600 Å (ε 562), while that of a cyclohexane solution revealed a shorter wavelength band at 2175 Å.

The low solubility of I in common solvents precluded any nmr studies at room temperature. Spectra were obtainable at elevated temperatures in benzene-d_6, however, and showed two triplets centered at 3.77 and 5.27 ppm from TMS. The signals appeared to be temperature independent in the range from 70 to 100°. By comparison, biferrocenyl, at 60° in benzene-d_6, shows a singlet at 3.97 ppm and two triplets centered at 4.08 and 4.30 ppm from TMS.

The unusually high- and low-field signals shown by I can be explained by structure III in which the iron atoms



III

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(1) The numbering system used for I is based upon that suggested for biferrocenyls by S. I. Goldberg and R. L. Matteson, *J. Org. Chem.*, **29**, 323 (1964).

(2) T. J. Katz and J. Schulman, *J. Am. Chem. Soc.*, **86**, 3169 (1964).

(3) I. J. Spilners and J. P. Pellegrini, Jr., *J. Org. Chem.*, **30**, 3800 (1965).

(4) M. D. Rausch, *ibid.*, **26**, 1802 (1961).

(5) A. N. Nesmeyanov, V. N. Drozd, V. A. Sazonova, V. I. Romanenko, A. K. Prokof'ev, and L. A. Nikonova, *Izv. Akad. Nauk SSSR*, 667 (1693).