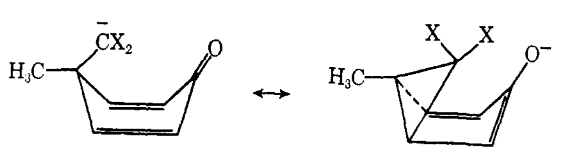

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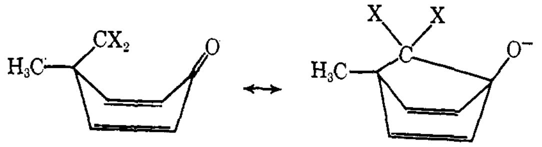

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a resonance structure resembling a *t*-alkoxide anion should be less stable than one resembling an enolate anion. A clear choice cannot yet be made, however, between these two types of "nonclassical" resonance interaction.

Acknowledgment. This work was begun at The Chemical and Development Laboratories, Agricultural Division, American Cyanamid Co., Princeton, N. J., and was partially supported by Grant GP8998 from the National Science Foundation.

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(12) See R. Turner, W. R. Meador, and R. E. Wenkler, *J. Am. Chem. Soc.*, **79**, 4116 (1957); A. F. Bedford, A. E. Beezer, C. T. Mortimer, and H. D. Springall, *J. Chem. Soc.*, 3823 (1963).

(13) R. A. Nelson and R. S. Jessup, *J. Res. Natl. Bur. Std.*, **48**, 206 (1952); S. Kaarsemaker and J. Coops, *Rec. Trav. Chim.*, **71**, 261 (1952).

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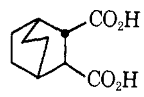
Optical Rotatory Properties and Conformational Rigidity of Cyclic Dicarboxylic Acids

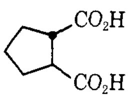
Sir:

We wish to report a case in which the analysis of optical rotatory properties of some cyclic dicarboxylic acids has allowed us to suggest whether these molecules are fixed in a rigid conformation or if they are flexible systems. Some nmr data supporting the optical data are also reported.

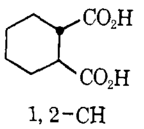
We have investigated the optical properties (uv, ORD, and CD spectra) of four optically active *trans*-dicarboxylic acids. The 2,2,2-bicyclooctane-2,3-dicarboxylic acid (2,3-BCO) is structurally rigid, and 1,3-cyclohexanedicarboxylic acid (1,3-CH) is, presumably, a flexible molecule undergoing chair interconversion.[1] Cyclopentanedicarboxylic acid (1,2-CP) and 1,2-cyclohexanedicarboxylic acid (1,2-CH) are less defined cases.



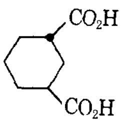
2, 3-BCO



1, 2-CP



1, 2-CH



1, 3-CH

In Figure 1 are reported the ORD curves for the four acids in trifluoroethanol (TFE). The curves of 2,3-BCO and 1,2-CH are quite similar and show a trough at 225–227 mμ, a crossover point at about 215 mμ, and a positive lobe which continues to increase beyond the limit of measurement. The curves of 1,2-CP and 1,3-CH, on the contrary, are much weaker and do not show any definite features, being almost plain curves. This is taken as an indication that 1,2-CH exists in a somewhat rigid, fixed conformation and that 1,2-CP is a flexible molecule.

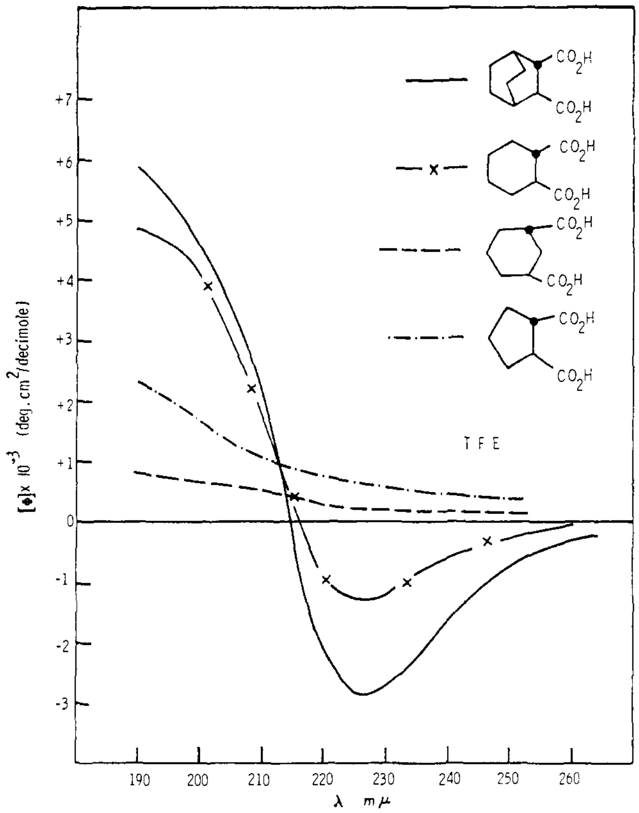


Figure 1. ORD spectra in 2,2,2-trifluoroethanol (TFE) of some cyclic dicarboxylic acids.

Looking at the marked asymmetry of the curves of 1,2-CH and 2,3-BCO, it becomes apparent that this is due to the interaction of the two neighboring carboxyl groups (exciton splitting). This interaction, or coupling, is lost when the molecule becomes flexible.[2]

CD spectra confirm this interpretation and allow assignment of the transitions responsible for the Cotton effects. Data and relative assignments are collected in Table I. It is interesting to note that although the uv spectra show only the n–π^* transition at 280–210 mμ, ORD and CD spectra are dominated by the π–π^* transition. The latter appears at 200–203 mμ in the flexible systems 1,2-CP and 1,3-CH, but is shifted to 209–210 mμ in 1,2-CH and 2,3-BCO. This red shift supports strongly the hypothesis that the carboxyl groups are coupled in the latter molecules since this behavior is predicted by theory and has been observed in other, similar cases.[2]

Reported data on the question of which conformation (diaxial or diequatorial) is preferred in the 1,2-CH acid are conflicting. Measurements of ΔpK_a were at first interpreted as indicating that the diaxial confor-

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(1) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 211.

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

Table I. Optical Data for Cyclic Dicarboxylic Acids in TFE[a]

	Uv		ORD		CD		
Compd	λ, mμ	ϵ/res	λ, mμ	[ϕ], deg	λ, mμ	[θ]/res, deg	Assignment
			227	−2900			
2,3-BCO	208	74	215	0	210	−4620	$\pi \rightarrow \pi^*$
			(190)	(+6000)			
1,2-CP	207	55	(190)	(+2300)	203	−561	$\pi \rightarrow \pi^*$
			226	−1400			
1,2-CH	208	83	216	0	210	−3366	$\pi \rightarrow \pi^*$
			(190)	(+4800)			
					219	−362	$n \rightarrow \pi^*$
1,3-CH	210	59	(190)	(+780)	204	0	
					200	+132	$\pi \rightarrow \pi^*$

[a] Measured with a Jasco ORD/CD/UV-5 spectropolarimeter, 0.1–10-mm cells, concentration range 10^{-2}–10^{-4} residue/l., in TFE. Values in parentheses do not represent maxima.

mation was preponderant in solution,[3] but these conclusions were questioned later and the diequatorial conformation was proposed.[4] Crystal structure studies[5] have recently shown that, in the solid state, 1,2-CH exists in the diequatorial conformation. Since repulsion of polar groups and solvent interaction could, in principle, convert the conformation from diequatorial to diaxial in going from the solid state to solution, we have investigated the nmr spectra of 1,2-CH and some related compounds seeking independent evidence. The results are collected in Table II.

Table II. Chemical Shifts of Axial and Equatorial Tertiary Hydrogen Nuclei of Cyclohexanecarboxylic Acids

	δ[a]	Conformation
trans-1,2-CH	140	e,e
cis-1,2-CH	161	a,e
trans-1,3-CH	150	a,e
cis-1,3-CH	140[b]	e,e
trans-1,4-CH	130[b]	e,e
CHCA	137[b]	e

[a] Measured in cycles per second from TMS as internal reference, in DMSO-d_6, with a Varian A-60 spectrometer. [b] Approximate center of broad band.

The tertiary hydrogen peak in *trans*-1,2-CH is shifted upfield (21 cps) with respect to the corresponding peak for the *cis*-1,2-CH. This is what would be expected if *trans*-1,2-CH exists in the diequatorial conformation.[6,7]

In fact, *cis*-1,2-CH is undergoing inversion (a,e $\leftrightarrows$ e,a) and its tertiary protons experience an averaged shielding. If *trans*-1,2-CH existed preferentially in the a,a conformation, its tertiary protons should experience a deshielding effect and would, therefore, appear downfield with respect to the *cis*-1,2-CH.

Furthermore, as shown in Table II, this peak in *trans*-1,2-CH is very close to that of cyclohexanecarboxylic acid (CHCA), *trans*-1,4-CH, and *cis*-1,3-CH, all of which should exist, preferentially, with the carboxyl groups in the equatorial position.

From the difference between the tertiary hydrogen peak of *trans*- and *cis*-1,2-CH (about 20 cps), it can be calculated[7] that the chemical shift value for the *trans*-1,2-CH in the diaxial conformation would be approximately 180 cps. Unfortunately, no compound of this kind is available, at the moment, to us, but it is interesting to note here that for *trans*-2,3-BCO (which structurally approximates a diaxial *trans*-1,2-CH arrangement) the tertiary hydrogen peak is found at 172 cps.

In the 1,2-CP case, our evidence that the molecule is flexible agrees with what is known from the conformational behavior of *trans*-1,2-dihalogencyclopentanes. These molecules were, in fact, found to be in dynamic equilibrium between two conformers (diaxial and diequatorial).[8]

It can be concluded that if an optically active molecule possesses two identical neighboring chromophores, optical rotatory techniques provide a way to test for conformational rigidity through application of the exciton theory.[2]

The four acids investigated have been prepared and resolved according to previously reported procedures.[9]

Acknowledgment. The authors wish to thank Mr. R Veneski for his help in the preparation of the acids.

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(3) J. C. Speakman, *J. Chem. Soc.*, 490 (1941); D. H. R. Barton and G. A. Scheidler, *ibid.*, 1197 (1948); G. S. Hammond in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley & Sons, New York, N. Y., 1956, p 434; ref 1.

(4) J. Sicher, F. Sipos, and J. Jonas, *Collection Czech. Chem. Commun.*, 26, 262 (1961).

(5) P. Corradini, private communication.

(6) L. M. Jackman and R. H. Wiley, *Proc. Chem. Soc.*, 196 (1958).

(7) E. L. Eliel and M. H. Gianni, *Tetrahedron Lett.*, 97 (1962).

(8) C. Altona, H. R. Buys, and E. Havinga, *Rec. Trav. Chem.*, **85**, 973 (1966).

(9) Y. Nishimura, Ph.D. Dissertation, Polytechnic Institute of Brooklyn, 1966; J. Boeseken and E. J. Peck, *Rec. Trav. Chim.*, **44**, 841 (1925); A. Werner and H. E. Conrad, *Ber.*, 32, 3046 (1899); D. E. Applequist and N. D. Werner, *J. Org. Chem.*, 28, 48 (1963); F. W. Kay and W. H. Perkin, *J. Chem. Soc.*, 87, 1073 (1905).

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Stereochemistry of the Rapid Equilibration of Protonated Bicyclo[3.1.0]hexenones

Sir:

We recently demonstrated[1] that protonation of hexamethylbicyclo[3.1.0]hexenone (**1**) by 97% sulfuric acid results in rapid successive migrations of C_6, leading to the enantiomer **1′**. The equilibrium **1** $\rightleftharpoons$ **1′** is rapid compared with ring opening to dienone **2**, which occurs

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(1) D. W. Swatton and H. Hart, *J. Am. Chem. Soc.*, **89**, 5075 (1967).