

Without monomer metallic cobalt was soon precipitated at room temperature.

Thus, the stereospecificity of the catalyst can be ascribed to the "naked" Co(O) ( $d^9$ ) which may loosely be coordinated by butadiene and/or  $AlEt_3$  molecules and not to the metallic cobalt (ground state,  $3d^7 4s^2$ ).

If the same catalyst system is applied in a solvent containing highly electronegative groups, e.g.,  $CH_2Cl_2$ , it produces solid polybutadiene of high 1,4-*cis* content. This may be explained by the strong ligand field effects of chlorine on the electronic structure of Co(O).

It is to be noted that Ni(O) has a filled 3d orbital of spherical symmetry and, in contrast to Co(O), it catalyzes the formation of the cyclic trimer of butadiene.<sup>1</sup> Again, this reaction should be carried out in a hydrocarbon medium of weak ligand field.

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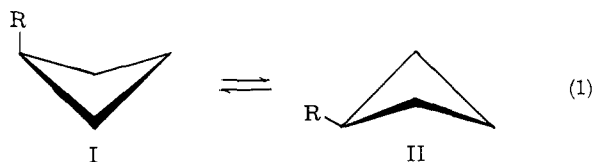
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### Conformational Studies of Cyclobutane Systems<sup>1</sup>

Sir:

Isolated attempts have been made to detect the presence of nonplanarity in cyclobutane rings. Significant deviations from planarity have been measured for cyclobutane,<sup>2,3</sup> octafluorocyclobutane,<sup>4</sup> octachlorocyclobutane,<sup>5</sup> and bromocyclobutane.<sup>6</sup> The results in the first two cases, however, have not been without controversy. It was the object of the present work to devise a fairly general, but still straightforward, method of detecting the presence and determining the magnitude of puckering in substituted cyclobutane rings, and to ascertain whether the results could be interpreted in terms of an equilibrium between axial (I) and equatorial (II) conformations.



Puckering of the ring reduces 1,2 substituent interactions by staggering adjacent groups, with relatively small changes in the bond angles. Monosubstituted cyclobutanes, like monosubstituted cyclohexanes, are expected to show a preference for the equatorial conformation II, which should reduce 1,3 interactions.

Dipole-moment measurements have particular value for the determination of the average degree of puckering of variously substituted 1,1-difluorocyclobutanes. The

	R	R'	R''
IIIa	<i>p</i> -NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub>	H	H
IIIb	C <sub>6</sub> H <sub>5</sub>	H	H
IIIc	C <sub>6</sub> H <sub>5</sub>	H	Cl
IIId	Cl	H	Cl
IIIe	C <sub>6</sub> H <sub>5</sub>	Br	H

geometries of 1,1-difluoro-3-(*p*-nitro)-phenylcyclobutane (IIIa) and of 1,1-difluoro-3-phenylcyclobutane (IIIb) were ascertained in this manner, with the aid of the

(1) Supported in part by the Office of Naval Research and the National Science Foundation.

(2) J. D. Dunitz and V. Schomaker, *J. Chem. Phys.*, **20**, 1703 (1952).

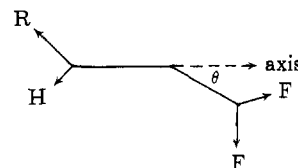
(3) G. W. Rathjens, Jr., N. K. Freeman, W. D. Gwinn, and K. S. Pitzer, *J. Am. Chem. Soc.*, **75**, 5634 (1953).

(4) H. P. Lemaire and R. L. Livingston, *ibid.*, **74**, 5732 (1952).

(5) T. B. Owen and J. L. Hoard, *Acta Cryst.*, **4**, 172 (1951).

(6) W. G. Rothschild and B. P. Dailey, *J. Chem. Phys.*, **36**, 2931 (1962).

assumption that the angle of puckering,  $\theta$ , is the same for both compounds.



The dipole moments of IIIa and of IIIb were found to be (benzene solution at 27.5°), respectively, 2.81 and 2.09 ± 0.02 D. The C-H bond moment was taken to be 0.4 D., with hydrogen negative with respect to carbon.<sup>7</sup> This choice is not vital, because the moments of the methine hydrogens and of the methylene hydrogens tend to cancel each other. With this convention, the group moment for C-(*p*-nitro)phenyl was calculated to be 4.85 D. from the dipole moment of *p*-nitrotoluene, 4.45 D. Consideration of the vector quantities which are involved yields four equations in four unknowns:  $\theta$ , the angle of puckering; the CF<sub>2</sub> bond moment; and  $\phi$ (IIIa) and  $\phi$ (IIIb), the angles which the molecular moments make with the indicated axis. The unique solutions were found to be  $\theta = 26^\circ 45' \pm 40'$ ;  $\phi$ (IIIa) =  $76^\circ 30' \pm 40'$  (above the minus direction of the axis);  $\phi$ (IIIb) =  $26^\circ 40' \pm 40'$  (below the plus direction of the axis); CF<sub>2</sub> = 2.54 ± 0.01 D. The puckering angle obtained in this manner compares favorably with the results in other systems: octafluorocyclobutane, 20°<sup>4</sup>; octachlorocyclobutane, 22°<sup>5</sup>; and bromocyclobutane, 29°.<sup>6</sup> Although the experimental error in the measured values of the dipole moments is small, the calculated value of  $\theta$  is subject to the usual limitations for determination of molecular geometry from dipole moments.<sup>7</sup> It is important to recognize also that  $\theta$  is an average angle of puckering, calculated assuming the geometry of the dominant species, II. The value of  $\theta$  might be refined by resolution of the molecular moment into components for each conformation. This will require more precise knowledge of the geometry of the axial conformation (*vide infra*). However, when the equilibrium is far on the side of one isomer, the correction has been shown to be small.

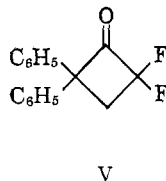
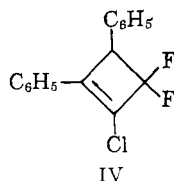
The possibility of extending this result to other systems was investigated by nuclear magnetic resonance spectroscopy (n.m.r.). For nonplanar compounds such as IIIb, the chemical-shift difference,  $\delta$ , between the nonequivalent fluorine atoms will vary with temperature as the equilibrium, I  $\rightleftharpoons$  II, shifts.<sup>8</sup> Lower temperatures should favor conformer II, whereas higher temperatures will bring about an approach to equal population of both conformations. Absence of a temperature effect, conversely, should indicate planarity. The fluorine magnetic resonance spectra of six compounds, IIIb-e, IV, and V,<sup>10</sup> accordingly were investigated at five temperatures ranging from -85 to +140°. The chemical shifts (Table I) were measured to ±1 c.p.s. by the side-band technique; coupling of the fluorine nuclei with the protons was removed by simultaneous irradiation of the sample at the proton frequency. The cyclobutene IV and the cyclobutanone

(7) G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, pp. 200 ff.

(8) Although the data are interpreted in terms of a classical equilibrium between I and II, they could also be accommodated by consideration of an asymmetric potential well which lacks the two distinct minima required by the two conformations. However, distinct minima have been demonstrated spectroscopically for cyclobutane<sup>2</sup> and trimethylene oxide.<sup>9</sup>

(9) S. I. Chan, J. Zinn, and W. D. Gwinn, *J. Chem. Phys.*, **34**, 1319 (1961).

(10) We are indebted to Dr. D. C. England for furnishing us with this sample.



V, which were included for control purposes since the systems most likely are planar, exhibited essentially constant values of  $\delta$  over the 225° range, whereas compounds IIIb–e showed variations from 102 (IIIId) to 277 c.p.s. (IIIe).

TABLE I

CONFORMATIONAL PROPERTIES OF SUBSTITUTED CYCLOBUTANES

	IIIb	IIIc	IIIId	IIIe	IV	V
$\Delta F$ , cal./mole	900 $\pm$ 100	1100	700	400	...	...
$p$ , 31°	0.816 $\pm$ 0.025	0.859	0.761	0.659	...	...
$J$ , c.p.s.	193 <sup>a</sup>	183	187	198	192	249
$\delta$ , -85°, c.p.s.	1093	635	425	413	470	37
$\delta$ , -30°, c.p.s.	1039	609	393	302	468	39
$\delta$ , 31°, c.p.s.	979 <sup>c</sup>	569	358	225	472	42
$\delta$ , 85°, c.p.s.	933	543	336	175	472	43
$\delta$ , 140°, c.p.s.	908	522	323	136	470	45
$\delta_{II}$ , c.p.s.	1185 $\pm$ 10	670	510	965	...	...
$\delta_I$ , c.p.s.	60 $\pm$ 50	-50	-110	-1220	...	...

<sup>a</sup> The coupling constants and chemical shifts are accurate to  $\pm 1$  c.p.s. except where noted. <sup>b</sup> Although the temperatures were measured accurately, these figures are only approximate. <sup>c</sup> Data for IIIa and IIIb are nearly identical. This corroborates the assumption regarding the similarity of the geometry of these compounds.

The free-energy difference between the two conformations and the populations of each are related to the equilibrium constant  $K$  for eq. 1

$$K = p/(1 - p) = e^{-\Delta F/RT} \quad (2)$$

where  $p$  is the mole fraction of II. At fast exchange, the measured chemical shift  $\delta$  is the weighted average of the chemical shifts of the individual conformers,  $\delta_{II}$  and  $\delta_I$ .

$$\delta = p\delta_{II} + (1 - p)\delta_I \quad (3)$$

Thus, one obtains the linear equation

$$\delta = \delta_I + p(\delta_{II} - \delta_I) \quad (4)$$

where  $p = e^{-\Delta F/RT}/(1 + e^{-\Delta F/RT})$ . The best linear plots of eq. 4 ( $\delta$  vs.  $p$  from assumed values of  $\Delta F$ ) readily give values of  $\Delta F$ ,  $p$ ,  $\delta_{II}$ , and  $\delta_I$  (Table I). The results qualitatively fulfill expectations. The bulky phenyl group (IIIb and IIIc) prefers to reside in the equatorial position. Replacement of the phenyl group by chlorine (IIIId) raises the population of the axial conformer and lowers the free energy difference between the conformers. When there are two substituents (IIIe) the populations are more nearly equal, and the free-energy difference is considerably smaller. The fact that  $\delta_I$  for all monosubstituted compounds is in the vicinity of 0 c.p.s., whereas  $\delta_{II}$  varies greatly with the substituent, indicates that conformation I may be nearly planar for IIIb–IIIId. Further evidence on this point will be forthcoming.

In summary, the n.m.r. method determines the presence or absence of planarity and the dipole-moment method determines the magnitude of puckering. Investigations are in progress to combine these methods in order to predict the angle of puckering in all cases studied.

(11) National Science Foundation Predoctoral Fellow, 1962–1964.

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## Microcatalytic Tracer Studies of the Isomerization of Cyclopropane over Silica–Alumina Catalysts

Sir:

According to a widely accepted notion stemming from Roberts,<sup>1</sup> the cyclopropane ring is opened when a catalyst proton attaches itself to a ring carbon forming an *n*-propyl carbonium ion. The isomerization is completed by loss of another proton to the catalyst surface. Indeed, if protons are involved, it is difficult to visualize an alternative reaction path if the tetrahedral valence requirement of carbon is not to be exceeded. The results presented herein do not support this notion; instead, they are indicative of a bimolecular process. These experiments incidentally demonstrate a new technique for the study of catalytic mechanisms.

If an exhaustively deuterated catalyst is contacted with cyclopropane, the Roberts mechanism<sup>1</sup> predicts that the initial product propylene should contain nearly one deuterium atom per molecule. The microcatalytic technique affords an advantageous way of testing this point. Successive small slugs of reactant may be passed quickly over the catalyst and onto a chromatographic column where propylene is separated from unisomerized cyclopropane. These fractions are collected separately and analyzed by mass spectrometry. A plot of the deuterium concentration in the product propylene vs. slug number should extrapolate to unity at zero slug number. Two situations can be visualized depending upon the ratio of cyclopropane molecules,  $n_g$  per slug, to the available D<sup>+</sup>,  $n_a$ . If  $n_a \gg n_g$ , the plot should have a gentle slope; if  $n_a \ll n_g$ , the slope should be high, the fraction of deuterated propylene falling nearly to zero with the first several slugs. No deuterium is expected in the unisomerized cyclopropane and any that appears lowers the amount of propylene that might have formed by reaction with a catalyst deuterium.

A typical set of results selected from one of over a dozen such experiments is shown in Fig. 1. In this

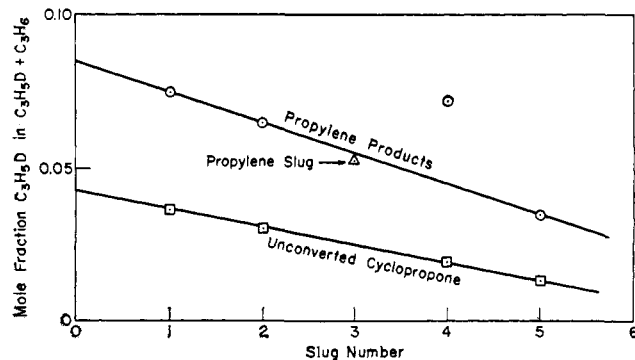


Fig. 1.—Analysis of products from a microcatalytic tracer experiment.

experiment, 8.3 cc. (NTP) slugs of cyclopropane was passed at 148° over 1.657 g. of Houdry M-46 catalyst (265 m.<sup>2</sup>/g.) which had been repeatedly exchanged with excess D<sub>2</sub>O before a final overnight evacuation at 550°. Multiply deuterated products were not obtained.

The behavior was not as predicted by the Roberts mechanism. Less than 10% of the initial propylene can be accounted for on this basis. Moreover, nearly as much deuterium appeared in the unconverted cyclopropane as in the propylene. When propylene was passed instead of cyclopropane (third slug) it became deuterated to the same extent as that produced in the ring-opening reaction. Evidently, most of the deuterium

(1) R. M. Roberts, *J. Phys. Chem.*, **63**, 1400 (1959).