transition state

a mechanism suggested for the aminolysis of carboxylic esters.[23]

Another possibility is that the proton removal step (eq. 12a) is rate limiting and that leaving group expulsion from II is fast. This interpretation, presented by Bunnett and Randall,[4] now seems unattractive because of the accumulation of evidence that proton transfers from rather strong acids to rather strong bases are exceedingly fast.[24] A third possibility is that proton removal and leaving group detachment are concerted, as in E2 olefin-forming eliminations.[25] A fourth is that a base which carries a proton on its basic site, such as piperidine or hydroxide ion, may assist intramolecular detachment of a proton from nitrogen and protonation of the leaving group as it departs, without BH ever separating from II.[12] This possibility is unlikely for reactions in good ionizing solvents like aqueous dioxane, but it is attractive for reactions in benzene.

Recently, Kirby and Jencks[26] have reported observations similar to those recorded in this paper. They studied reactions of amines with p-nitrophenyl phosphate in water, and in particular observed a curvilinear dependence of k_A on base concentration similar to that of our Figure 2. Their interpretation is substantially the same as ours.

In this laboratory, we have found the reaction of 2,4-dinitroanisole with piperidine, to form 2,4-dinitrophenylpiperidine, to be strongly catalyzed by sodium methoxide in methanol. Also, Mr. Claude Bernasconi has shown that in reactions of piperidine with the 2,4-dinitrophenyl ethers of a series of phenols in 10% dioxane–90% water, the incidence of base catalysis depends on the substituents present in the leaving phenoxy group. The reaction of bis(2,4-dinitrophenyl) ether is not catalyzed by bases, while that of 2,4-dinitrophenyl phenyl ether is base catalyzed, much as in 60% dioxane. These studies will be reported shortly.

Acknowledgment. We thank Dr. Kevork V. Nahabedian for discussions and counsel.

(24) M. Eigen, *Angew. Chem.*, 75, 489 (1963).

(25) J. F. Bunnett, *ibid.*, 74, 731 (1962); *Angew. Chem. Intern. Ed. Engl.*, 1, 225 (1962).

(26) A. J. Kirby and W. P. Jencks, *J. Am. Chem. Soc.*, 87, 3217 (1965). We thank Professor Jencks for sending us a copy of their manuscript in advance of publication.

Nuclear Magnetic Resonance Spectroscopy. Conformational Properties of Cyclobutanes. Variation of Geminal Fluorine–Fluorine Chemical-Shift Differences with Temperature[1]

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Contribution No. 3229 from the Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, California. Received May 12, 1965

The temperature dependence of the geminal fluorine–fluorine chemical-shift differences in a variety of unsymmetrically substituted cyclobutanes is interpreted in terms of a classical equilibrium between axial and equatorial conformations. With the assumption that the conformations have the same entropy, free-energy differences between the conformers are calculated and discussed. The axial conformer in monosubstituted cyclobutanes may be nearly planar. The absence of temperature effects in the spectra of a cyclobutene and a cyclobutanone indicates that these systems are statically planar. The angle of puckering of 1,1-difluoro-3-phenylcyclobutane is calculated by the dipole moment method to be about 27°.

Introduction

The nonplanar nature of cyclohexane and the resulting axial and equatorial orientation of substituents, although suggested as early as 1890, was not established until the 1920's.[3] Conformational properties have been usefully ascribed to the more flexible five- and seven-membered ring systems in terms of the pseudorotation process.[4–7] A planar representation, however, has generally been accepted for the four-membered ring systems in spite of a limited number of demon-

(3) L. F. Fieser and M. Fieser, "Advanced Organic Chemistry," Reinhold Publishing Corp., New York, N. Y., 1961, p. 553.

(4) J. E. Kilpatrick, K. S. Pitzer, and R. Spitzer, *J. Am. Chem. Soc.*, 69, 2483 (1947).

(5) J. B. Hendrickson, *ibid.*, 83, 4537 (1961).

(6) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 248 ff.

(7) The cycloheptane system is capable of ring inversion as well.

strations to the contrary. Conceivably, this misconception has arisen because of incorrect conclusions of early workers. The original decision of Wilson[8] that cyclobutane itself is planar was reversed by Dunitz and Schomaker,[9] who showed by electron diffraction studies that the molecule has a dihedral angle, θ, of about 20°. The later infrared–Raman studies of
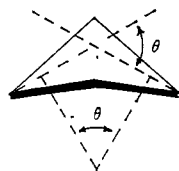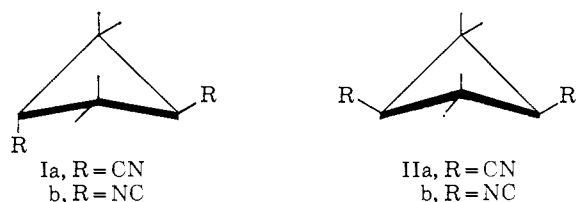

Rathjens, et al.,[10] resolved this controversy by establishing the presence of both D_{4h} and D_{2d} cyclobutane molecules. According to the calculations of these authors, a barrier of about 400 cm.$^{-1}$ hinders the out-of-plane bending process. Those molecules in vibrational states below this value will be of D_{2d} symmetry; the remaining molecules will possess D_{4h} symmetry. The average dihedral angle at any given time is therefore nonzero.

The extent of deviations from planarity should be a sensitive function of the nature of any ring substituent. Nevertheless, Edgell[11] and Claassen[12] concluded from infrared–Raman studies that octafluorocyclobutane is planar. Electron diffraction data, however, again required a molecule of lower symmetry.[13] Intensity patterns could best be accounted for by a D_{2d} model with $\theta = 20 \pm 4°$. The description of octachlorocyclobutane by Owen and Hoard[14] similarly included a dihedral angle of 22°, although the X-ray crystallographic data is of questionable significance for molecules in noncrystalline states. Detailed analysis of the microwave spectrum of bromocyclobutane[15] permitted assignment of a dihedral angle of 29° 22' ± 08' to this molecule.

Replacement of a methylene group by a heteroatom, as in trimethylene oxide, would remove two 1,3(crossring)-interactions and four 1,2(vicinal)-interactions. The barrier to inversion in this oxygen heterocycle was determined by Chan, et al.,[16,17] by microwave spectroscopy to be only 35 ± 5 cm.$^{-1}$. Since the lowest vibrational level is about 8 cm.$^{-1}$ above the top of the barrier, the inversion doubling associated with the nonplanarity of cyclobutane[10] does not occur. The microwave spectrum of cyclobutanone[18] was similarly consistent with a planar structure. Reduction of substituent interactions associated with the introduction of an sp^2 center thus has a substantial effect on the inversion barrier.

On the other extreme of substitution, Lautenschlaeger and Wright[19] have determined the extent of nonplanarity for systems I and II from a careful application of the dipole moment method. The dihedral angles of the

Ia, R = CN
b, R = NC

IIa, R = CN
b, R = NC

trans isomers were found to be about 24°, whereas the angles for IIa and IIb were approximately 42 and 51°, respectively (benzene solution, 20°). The lowering of the barrier associated with the removal of substituents in trimethylene oxide and cyclobutanone and the increase in the degree of nonplanarity in going from 1,3-trans isomers (I) to 1,3-cis isomers (II) substantiate the view that nonbonded substituent repulsions are the primary cause of ring puckering.

Nonplanarity may arise in highly substituted, four-membered rings even if one methylene group has been replaced by an unsubstituted fragment such as the carbonyl group, provided that substituent interactions elsewhere in the molecule are high. By an extension of the octant rule to four-membered cyclic ketones, Conia and Goré[20,21] have demonstrated that IIIa and IIIb


IIIa, R = H
b, R = Br
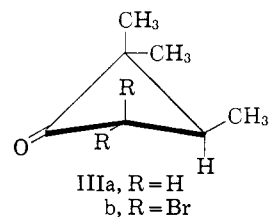
are nonplanar. Although the presence of a Cotton effect excludes the planar form, and the sign of the effect determines the orientation of substituents,[22] these experiments can give no indication of the degree of nonplanarity. It may actually be rather small.[23]

Results and Discussion

The evidence presented thus far indicates that a cyclobutane ring will accommodate a substituent by puckering in such a way as to minimize nonbonded interactions. A deformation of this sort will not increase the strain associated with bond angles and bond lengths, since the changes in these quantities are small.

(8) T. P. Wilson, J. Chem. Phys., 11, 369 (1943).

(9) J. D. Dunitz and V. Schomaker, ibid., 20, 1703 (1952).

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

(11) W. F. Edgell, ibid., 69, 660 (1947).

(12) H. H. Claassen, J. Chem. Phys., 18, 543 (1950).

(13) H. P. Lemaire and R. L. Livingston, J. Am. Chem. Soc., 74, 5732 (1952).

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

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

(16) S. I. Chan, J. Zinn, J. Fernandez, and W. D. Gwinn, ibid., 33, 1643 (1960).

(17) S. I. Chan, J. Zinn, and W. D. Gwinn, ibid., 34, 1319 (1961).

(18) A. Bauder, F. Tank, and Hs. H. Günthard, Helv. Chim. Acta, 46, 1453 (1963).

(19) F. Lautenschlaeger and G. F. Wright, Can. J. Chem., 41, 863 (1963).

(20) J.-M. Conia and J. Goré, Tetrahedron Letters, 1379 (1963).

(21) J.-M. Conia and J. Goré, Bull. soc. chim. France, 1968 (1964).

(22) W. Moffitt, R. B. Woodward, A. Moscowitz, W. Klyne, and C. Djerassi, J. Am. Chem. Soc., 83, 4013 (1961).

(23) Mention of the question of planarity in four-membered rings may also be found in the following references: (a) S. H. Bauer and J. Y. Beach, ibid., 64, 1142 (1942); (b) W. Shand, Jr., V. Schomaker, and J. R. Fischer, ibid., 66, 636 (1944); (c) J. D. Dunitz, Acta Cryst., 2, 1 (1949); (d) H. P. Lemaire and R. L. Livingston, J. Am. Chem. Soc., 74, 5732 (1952); (e) R. Zbinden and H. K. Hall, ibid., 82, 1215 (1960); (f) A. Almenningen, O. Bastiansen, and P. N. Skancke, Acta Chem. Scand., 15, 711 (1961); (g) W. D. Phillips in "Determination of Organic Structures by Physical Methods," Vol. II, F. C. Nachod and W. D. Phillips, Ed., Academic Press Inc., New York, N. Y., 1962, p. 451 ff.; (h) A. Wilson and D. Goldhamer, J. Chem. Educ., 40, 504 (1963); (i) N. L. Allinger, M. A. Miller, and L. A. Tushaus, J. Org. Chem., 28, 2555 (1963); (j) G. J. Fonken and S. Shiengthong, ibid., 28, 3435 (1963); (k) O. H. Wheeler annd E. G. de Rodriguez, ibid., 29, 718 (1964).

By analogy with the nomenclature of higher ring systems, the position assumed by a substituent in such a deformation may be termed equatorial (IVb), and the
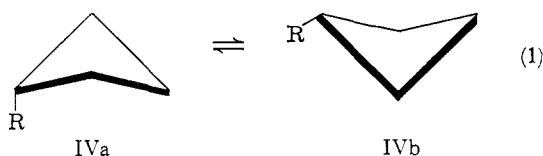
corresponding position which arises after the ring-inversion process occurs may be called axial (IVa). The double-well potential barrier for the monosubstituted model IV would be unsymmetrical, the equatorial conformer being of lower energy. The existence of a classical equilibrium of this sort could be established by the temperature dependence of a molecular property which varies with changes in conformational populations. To this end, the chemical-shift difference between nonequivalent geminal fluorine atoms in variously substituted cyclobutanes (V–VIII) was measured as a function of temperature (Table I).[24]
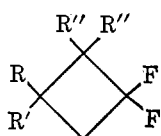
Table I

Compd.	R	R′	R″
V	C_6H_5	H	H
VI	C_6H_5	H	Cl
VII	Cl	H	Cl
VIII	C_6H_5	Br	H
IX	$p\text{-}NO_2C_6H_4$	H	H

At a given temperature, the observed chemical-shift difference, δ, is the weighted average of the values for the axial (IVa) and equatorial (IVb) conformers, δ_a and δ_b (eq. 2), where p is the temperature-dependent

$$\delta = p\delta_b + (1 - p)\delta_a \qquad (2)$$

population of the equatorial conformer. Lower temperatures will increase the population of IVb, whereas higher temperatures will bring about an approach to equal populations of both conformations.

The fluorine spectra of compounds V–VIII, X, and
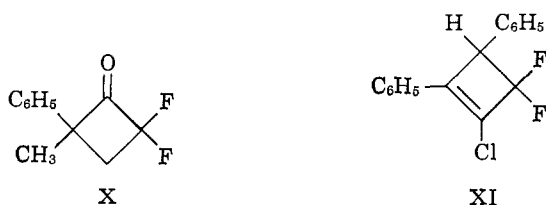
XI accordingly were analyzed at −85, −30, 30, 85, and 140°.[25] Compounds V–VIII and XI were examined in 20% carbon disulfide solutions, whereas X was a neat sample. Simultaneous irradiation of the samples at 60.0 Mc.p.s. simplified the spectra to the familiar AB pattern by removing hydrogen–fluorine

(24) J. B. Lambert and J. D. Roberts, *J. Am. Chem. Soc.*, **85**, 3710 (1963).
(25) The temperatures listed here are only approximate. See Table II for the precise figures.

couplings. The chemical shifts and coupling constants were calculated to ±1 c.p.s. from at least 15 measurements calibrated by the side-band technique. Examination of these data, which are displayed in Table II and Figure 1, reveals a large temperature dependence

Table II. Fluorine–Fluorine Chemical-Shift Differences and Coupling Constants

V	Temp., °C.	−87	−29	31	87	139
	δ, c.p.s.	1093	1039	979	933	908
	J, c.p.s.	192	192	195	194	195
VI	Temp., °C.	−84	−30	31	88	141
	δ, c.p.s.	635	609	569	543	522
	J, c.p.s.	183	182	182	183	184
VII	Temp., °C.	−84	−29	31	88	141
	δ, c.p.s.	425	393	358	336	323
	J, c.p.s.	187	188	187	187	189
VIII	Temp., °C.	−88	−33	32	83	134
	δ, c.p.s.	413	302	225	175	136
	J, c.p.s.	196	197	197	199	200
X	Temp., °C.	−79	−31	31	85	139
	δ, c.p.s.	116	123	133	135	141
	J, c.p.s.	248	250	249	249	250
XI	Temp., °C.	−79	−29	31	85	139
	δ, c.p.s.	470	468	472	473	470
	J, c.p.s.	192	192	192	194	193

of the chemical-shift difference between the fluorine atoms of the saturated cyclobutanes V–VIII, a small dependence for the cyclobutanone X, and none at all for the cyclobutene XI. This is the behavior which would be expected of the model depicted by eq. 1. The large variation of δ for V–VIII cannot be explained with planar structures. Conversely, the absence of any temperature effect in the spectrum of the cyclobutene XI points toward a completely planar structure. Furthermore, it is indicative that effects not arising from conformational considerations, such as medium effects, are negligible or nullified by cancellation. From the small changes in the spectrum of the cyclobutanone X, no clear-cut decision between models may be made, although deviations from planarity must be small.

It should be noted that a temperature dependence of the fluorine–fluorine chemical-shift difference does not require two distinct conformations with the associated inversion barrier. The data could also be accommodated by a highly asymmetric potential well which possesses only a single minimum. Increased population of higher vibrational states at higher temperatures would cause a change in δ as well, although it is doubtful that the magnitude could be as large as that observed here. Since two distinct minima have been demonstrated spectroscopically for cyclobutane[10] and trimethylene oxide,[16–17] this model will be accepted for the present study.

Since only a single AB spectrum was observed at low temperatures for compounds V–VIII, the equilibrium represented by eq. 1 must be fast on the n.m.r. time scale. The equilibrium constant for the process is given by eq. 3, where ΔF, the free-energy difference between

$$K = \frac{p}{1 - p} = e^{-\Delta F/RT} \qquad (3)$$

conformers, is negative since the equatorial form IVb is more stable. Solving for p, one obtains eq. 4.

$$p = \frac{1}{1 + e^{\Delta F/RT}} \qquad (4)$$

Table III. Conformational Properties of Substituted Cyclobutanes

	V	VI	VII	VIII
ΔF, cal./mole	-950 ± 100	-1100 ± 100	-750 ± 100	-400 ± 100
δ_a, c.p.s.	40 ± 50	-60 ± 40	-120 ± 20	-1210 ± 200
δ_b, c.p.s.	1175 ± 20	670 ± 10	500 ± 20	960 ± 200
p, 140°	0.761 ± 0.025	0.792	0.713	0.621
p, 85°	0.791	0.823	0.740	0.638
p, 31°	0.828	0.861	0.776	0.659
p, −30°	0.877	0.907	0.825	0.698
p, −85°	0.929	0.949	0.881	0.748

Equation 2 may be rearranged to the form (eq. 5)

$$\delta = \delta_a + p(\delta_b - \delta_a) \qquad (5)$$

in which δ is a linear function of p, since δ_a and δ_b are constant for a given molecule. The appropriate value of ΔF is taken as that value which gives the best linear plot of δ vs. p. In order to obtain this quantity, a Fortran program was written which calculates the slope and intercept of eq. 5 from a least-squares fit of a plot of δ vs. p for steps of 50 cal. in the free-energy difference. The values of ΔF (50 to 4000 cal.) were ordered according to the magnitude of the sum of the squares of the deviations. In all cases, the data converged from both directions to a "best" value of ΔF.
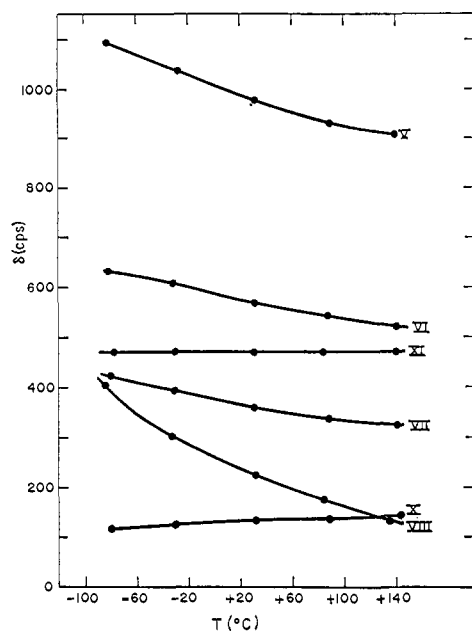

Figure 1. Temperature dependence of chemical-shift differences. Roman numerals refer to the formulas given in the text.

It was observed from visual plots that deviations from linearity develop in both directions sufficiently rapidly to warrant placing an error of ±100 cal. on the magnitude of ΔF. Furthermore, the "best" value of ΔF remains within a 100 cal. range when the input parameters (δ and T) are varied over the range of experimental error. Table III presents the values of the conformational properties obtained in this way.[26]

(26) This analysis assumes the constancy of ΔF over the temperature range, i.e., that the entropy of the two conformers is the same. A systematic error will be introduced if this is not the case (K. Mislow, private communication). Only the quantitative interpretation will be affected; the temperature dependence of δ is still an unambiguous demonstration of nonplanarity.

The bulky phenyl group gives rise to the largest free-energy difference between conformers. The values for V and VI are experimentally the same. Replacement of the phenyl group by the smaller chlorine atom (VI → VII) reduces the value of ΔF by about 0.35 kcal./mole, thereby decreasing the proportion of the equatorial conformer. If two substituents are placed in the 3-position, as in VIII, the free-energy difference becomes rather small. The large variation of δ with temperature for VIII (277 c.p.s.) indicates that the increase in nonbonded repulsions accentuates the ring-inversion process, rather than causing the molecule to become more nearly static and planar. This particular situation probably arises because bromine and phenyl are approximately equivalent in size.[27]

Examination of the theoretical plots of δ vs. p over the extrapolated range of populations (Figure 2) shows that the disubstituted cyclobutane VIII behaves in a totally
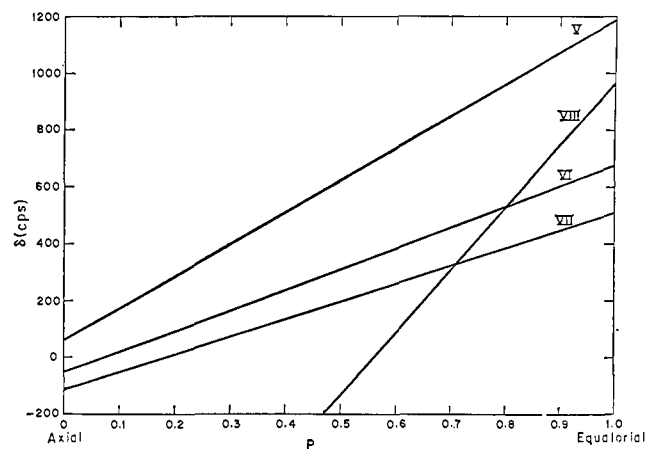

Figure 2. Chemical-shift difference as a function of population. Roman numerals refer to formulas given in the text.

different manner from the monosubstituted systems V–VII. For the latter group of compounds, the chemical-shift difference approaches a value near zero as the population of the axial conformer approaches unity ($\delta \to 0$ as $p \to 0$), whereas at the other extreme ($p \to 1$), δ_b varies greatly with the nature of the substituents. The values of δ_a and δ_b for VIII, on the other hand, are large and more or less symmetrical with respect to $\delta = 0$. The appearance of Figure 2 suggests that among the axial conformers of V–VII, there is a geometrical similarity which is not shared by the disubstituted molecule VIII. This is reasonable, since the equatorially oriented substituent in the conformer

(27) D. R. Davis, R. P. Lutz, and J. D. Roberts, J. Am. Chem. Soc., 83, 246 (1961).

resembling IVa is hydrogen for V–VII, but the axial substituent is a large group such as phenyl. Furthermore, it is significant that the common value of δ_a is close to zero, for this is the value expected if the chemical-shift difference between the fluorine atoms arises principally from the anisotropy of the ring carbon–carbon bonds. McConnell[28] has employed the point–dipole approximation to describe the shielding of a nucleus by an axially symmetric group such as the carbon–carbon single bond such as in eq. 6, where r

$$\sigma_{av} = \frac{(3 \cos^2 \theta - 1)(\chi_L - \chi_T)}{3r^3} \qquad (6)$$

is the distance from the nucleus to the electrical center of gravity of the group (the midpoint of the bond), θ is the angle which the vector r makes with the axis of symmetry (the bond), and $\chi_L - \chi_T$ is the difference between the longitudinal and transverse magnetic susceptibilities (a measure of the diamagnetic anisotropy of the group). As in the case of cyclohexane,[29] contributions to the shieldings from the 1,2- and 1,4-bonds in XII and XIII are the same for both nuclei, since r and θ are

XII   XIII
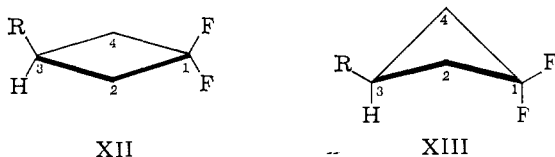
identical. Although this is also true of the 2,3- and 3,4-bonds in XII, these bonds in XIII will shield the two fluorine nuclei to different extents, thus giving rise to a chemical-shift difference. In this description, as in that for cyclohexane,[29] it is necessary that the contributions from distant bonds be negligible. Consequently, the freely rotating group R serves only to pucker the ring without contributing directly to δ.[30] This model therefore predicts that only nonplanar cyclobutanes will exhibit magnetically nonequivalent geminal fluorine atoms, provided the only unsymmetrical substitution pattern occurs at the 3-position. This model also suggests that the axial conformer is nearly planar for V–VII, since δ_a is consistently near zero, but that two distinct nonplanar conformers must exist for VIII, since δ_a is large and negative. A planar axial conformer is reasonable for monosubstituted cyclobutanes because 1,3 cross-ring interactions would increase with the deviations from planarity required of a conformer resembling IVa.

Although the model based on diamagnetic anisotropies as the principal source of the chemical-shift difference explains the general features of Figure 2, there are numerous assumptions inherent in the derivation of eq. 6 which militate against its application in a detailed manner to geometrical problems. The magnitude of the effect may be too small to explain the large observed chemical shifts. The magnetic properties of the 2,3- and 3,4-bonds need not be constant with substituent changes at the 3- and 4-positions. A more direct test of the contention that a value of δ close to

zero implies that θ is also near zero would be to observe the properties of a molecule known to be planar. Evidence cited thus far points to the planarity of cyclobutenes (XI and XIV), but in the two molecules studied, the source of asymmetry has shifted from the 3-posi-

XIV   XV   XVI
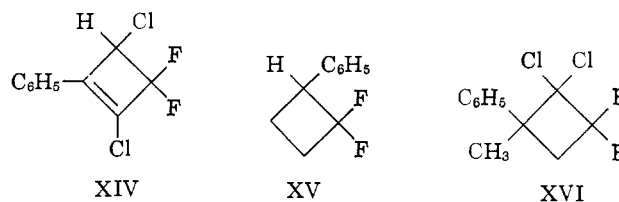
tion to the 2- or 4-position. Substituents in the 2-position would almost certainly contribute a neighbor-anisotropy effect, and, in fact, the chemical-shift differences (31°) are 472 and 438 c.p.s. for XI and XIV, respectively. Similar movement of the phenyl substituent from the 3-position in V to the 2-position in XV raises the chemical-shift difference at 31° from 979 to 1778 c.p.s. Thus, these cyclobutenes cannot offer a direct test of planarity because unsymmetrical substitution at the 2- or 4-positions introduces rather large chemical-shift effects without necessarily causing substantial nonplanarity.

The cyclobutanone X was judged to be nearly planar (*vide supra*), and in this molecule unsymmetrical substitution is restricted to the 3-position. In fact, replacement of the *gem*-dichloro group in XVI by an oxo group in X lowers δ (31°) from 430 to 133 c.p.s. The chemical-shift difference in X therefore supports the neglect of anisotropic properties of 3-substituents and indicates that a small value of δ corresponds to small average deviations from planarity.

The method of dipole moments was used to determine the geometry of 1,1-difluoro-3-phenylcyclobutane (V) and 1,1-difluoro-3-*p*-nitrophenylcyclobutane (IX). That both compounds have nearly identical angles of puckering derives not only from the small change in substituent size, but also from the observed identity of the chemical-shift differences between the fluorine atoms of the two compounds. From the previous discussion, this observation alone would suffice to prove the assertion that θ is nearly the same for both compounds.

The dipole moments of V and IX were measured to be 2.09 and 2.81 ± 0.02 D., respectively, in benzene solutions at 27.5° (see Experimental). The C–H bond moment was taken to be 0.4 D., with hydrogen negative with respect to carbon, in accordance with the evidence presented by Coulson, Wheland, and others.[31] This is not a critical decision, although the convention must be maintained throughout the analysis. The C–*p*-NO$_2$C$_6$H$_4$ group moment was derived from the dipole moment of *p*-nitrotoluene in benzene, 4.45 D. The angle of puckering, θ, and the CF$_2$ group moment were calculated from the four simultaneous equations which arise from consideration of the dipoles present in V and IX. The object of including system V was to obviate an independent designation of the value for the CF$_2$ group moment. The unique solution of these equations was $\theta = 26° 45' \pm 40'$, and CF$_2 = 2.54 \pm 0.01$ D. The validity of the solution was checked by construction.

(28) H. M. McConnell, *J. Chem. Phys.*, 27, 226 (1957).
(29) L. M. Jackman, "Applications of NMR Spectroscopy in Organic Chemistry," Pergamon Press, Oxford, 1959, p. 115 ff.
(30) Similar behavior has been observed in 3-substituted difluorocyclopentanes: J. B. Lambert, L. K. Oliver, and J. D. Roberts, unpublished results.
(31) G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, p. 200 ff.

The listed errors are those which arise from the experimental error in the dipole-moment measurements, and do not include extensive systematic errors inherent in the dipole moment method itself. The calculative procedure was designed to minimize such errors. The two polar groups in IX are on opposite sides of the molecule, so mutual polarization is minimized. The results are independent of the choice of convention for the C–H bond moment, a source of considerable controversy in the literature.[31]

Contributions to the observed moment from solvent effects prevent the results from being considered as absolute. If the study were repeated in several solvents, more nearly absolute numbers could be obtained. The geometrical representation is another source of systematic error. The measured dipole moment is the root mean square of the moments of all the species in solution. To interpret the chemical-shift data, we have assumed the presence of two distinct species, but to calculate θ from the dipole moment data, only one species, with an average geometry similar to IVb, was taken into account. Since at 27.5° there is about 83% equatorial conformer present, this approximation is not completely unsatisfactory. A correction, however, may be made for the 17% of axial conformer if its geometry is assumed to be planar. The dipole moment of the equatorial conformer may be computed from the measured molecular moment and the moment of the axial conformer calculated from an assumed planar model. Substitution of the moment of the equatorial conformer for the molecular moment in the dipole moment equations will yield θ_b, rather than θ, as the solution. The value of θ is then obtained by correction for the conformer population, since $\theta = p\theta_b + (1 - p)\theta_a$, and $\theta_a = 0$. The resulting value of θ, 29.1°, represents an average geometry. The small difference between this value and the solution obtained with the assumption of a single geometry probably represents a more realistic approximation to the error. The angle of puckering is therefore $27 \pm 3°$.

The dipole moment and n.m.r. data are thus complementary. If the analysis of the plot of δ vs. p over the extrapolated range of populations (Figure 2) is correct, the value of δ is a direct measure of the degree of nonplanarity, since, at 27.5°, $\theta \cong 27°$ and $\delta = 985$, but also, $\theta \cong 0$ when $\delta = 0$. Measurement of the chemical-shift difference at any temperature will give an approximate, but direct indication of the degree of nonplanarity for this system. The systematic error derived from the assumption of a constant value of ΔF and the approximations inherent in deductions from an extrapolation (Figure 2) vitiate only the quantitative aspect of this study. The temperature dependence of the geminal fluorine–fluorine chemical-shift difference nevertheless furnishes a qualitative indication of the presence and extent of nonplanarity in cyclobutanes.

Experimental

Melting points and boiling points are uncorrected. Melting points were measured on either the Büchi or the Hershberg apparatus. Infrared spectra were recorded on the Beckman infrared spectrometer, Model IR-7. Gas–liquid partition chromatography experiments were performed on the Perkin-Elmer vapor fractometers, Models 154-C and 800. Ele-

mental analyses were carried out by Spang Microanalytical Laboratory, Ann Arbor, Mich.

Proton magnetic resonance spectra were measured at room temperature on the Varian Associates Model A-60 and V-4300B spectrometers operated at 60.0 Mc.p.s. and 14,100 gauss. The latter instrument was used for variable-temperature experiments.[32] All heteronuclear double-resonance experiments were accomplished with the Nuclear Magnetic Resonance Specialities Model SD-60 spin decoupler. Fluorine magnetic resonance spectra were measured on the V-4300B spectrometer operated at 56.4 Mc.p.s. Calibration was effected by the sideband technique with the use of the Hewlett-Packard Model 200AB audio oscillator and Model 521-C frequency counter.[33]

1,1-Difluoro-2,2-dichloro-3-phenylcyclobutane was prepared from styrene and 1,1-dichloro-2,2-difluoroethylene in 72.9% yield according to the method of Manatt.[34]

1,1-Difluoro-3-phenylcyclobutane was prepared from 1,1-difluoro-2,2-dichloro-3-phenylcyclobutane in 82.0% yield according to the method of Manatt.[35]

1,1-Difluoro-3-p-nitrophenylcyclobutane. Into a 500-ml., three-necked, round-bottomed flask equipped with a dropping funnel were placed 140 ml. of concentrated nitric acid and 120 ml. of concentrated sulfuric acid. The temperature was lowered to 10°, and 60 g. (0.357 mole) of 1,1-difluoro-3-phenylcyclobutane was added with stirring at such a rate that the temperature did not exceed 15°. After 1 hr., the temperature was raised to 35° for 10 min. The solution was cooled and poured into 220 ml. of an ice-water mixture. The layers were separated and the aqueous portion was extracted six times with diethyl ether. The combined organic portions were extracted five times with 15% aqueous potassium hydroxide. The basic aqueous extract was neutralized and extracted four times with ether. All organic portions were combined and dried over magnesium sulfate. After the drying agent was removed by filtration and the ether by distillation at atmospheric pressure, the residue, upon flash distillation at 0.5 mm., gave 30 g. (0.141 mole, 39.5%) of a yellow oil. The product was fractionally recrystallized in several steps from methanol to remove small amounts of impurities. In this manner, 15.3 g. (0.072 mole) of white needles, m.p. 37.3–39.7°, was obtained free of all impurities according to thin layer chromatography. The n.m.r. spectrum contained an $(AB)_2$ pattern in the aromatic region, characteristic of *para* substitution, and the infrared spectrum exhibited bands at 1540 and 1349 cm.$^{-1}$, characteristic of antisymmetric and symmetric stretching modes of the nitro group.

Anal. Calcd. for $C_{10}H_9F_2NO_2$: C, 56.33; H, 4.26; F, 17.82; N, 6.57. Found: C, 56.10; H, 4.13; F, 17.81; N, 6.56.

(32) G. M. Whitesides, Ph.D. Thesis, California Institute of Technology, 1964, p. 155.
(33) The authors are indebted for the use of temperature-adaptable A-60 spectrometers to Dr. S. L. Manatt and Dr. D. D. Elleman, Jet Propulsion Laboratory, Pasadena, Calif.; Dr. H. Goldwhite, California State College at Los Angeles, Los Angeles, Calif.; and Dr. D. L. Dreyer, Fruit and Vegetable Chemical Laboratory, Agricultural Research Service, U. S. Department of Agriculture, Pasadena, Calif.
(34) S. L. Manatt, Ph.D. Thesis, California Institute of Technology, 1959, p. 68.
(35) Reference 34, p. 72.

1,1-Difluoro-3-bromo-3-phenylcyclobutane was prepared from 1,1-difluoro-3-phenylcyclobutane and N-bromosuccinimide in 75.6% yield according to the method of Manatt.[36]

1,1-Difluoro-2,2,3-trichlorocyclobutane. A sample of this material was obtained from the work of Dr. E. F. Kiefer.[37]

1,1-Difluoro-2,2-dichloro-3-methyl-3-phenylcyclobutane. A sample of this material was obtained from the work of Mr. M. Takahashi.[38]

1,1-Difluoro-2-chloro-3,4-diphenylcyclobutene-2. A sample of this material was obtained from the work of Dr. K. Nagarajan.[39]

1,1-Difluoro-2-phenylcyclobutane. A sample of this material was obtained from the work of Dr. S. L. Manatt.[40]

1,1-Difluoro-3-methyl-3-phenylcyclobutanone-2. A sample of this material was kindly supplied by Dr. D. C. England of the Central Research Department of the Du Pont Co.

Dipole Moment Measurements. For the purpose of measuring dielectric constants, an apparatus which operates according to the heterodyne-beat method was constructed after the model of Chien,[41] with the incorporation of several modifications. The detailed operation procedure has been described elsewhere.[42] The standard condenser was a General Radio Type 722-D precision capacitor (Cambridge, Mass.). The dielectric cell and pycnometer have been described previously.[43,44] Voltages to the apparatus were obtained from a Heathkit variable voltage regulated power supply Model PS-3. Molar polarizations were calculated from the slopes of plots of solute mole fraction as a function of the density and of the dielectric constant of dilute benzene solutions.[45] Molar refractions were calculated directly from the index of refraction if the solute was a liquid. For solids, this

quantity was obtained from the index of refraction of the solvent, together with refractive index increment measurements of dilute solutions.[46] The difference between the molar polarization and the molar refraction gave the orientation polarization at infinite dilution, from which the dipole moment was calculated. The accompanying tables present the data for the compounds studied. Since the value of the dipole moment of the nitro compound was extremely important, the measurements were duplicated on a different heterodyne apparatus.[47] These data gave a value of 2.84 D. As a further check, both sets of dielectric constant data were combined with refractive index increment measurements and analyzed according to the method of Guggenheim,[48] which avoids the direct measurement of the molar refraction. In this manner, values of 2.83 and 2.79 D. were obtained. Thus, all four methods are in excellent agreement (see Tables IV and V).

Table IV. Mole Fractions, Densities, and Dielectric Constants in Benzene at 27.5°

f_2	d_{12}	ϵ_{12}
1,1-Difluoro-3-*p*-nitrophenylcyclobutane (A)		
0.00000	0.87050	(2.274)
0.01089	0.87907	2.3952
0.02108	0.88706	2.5077
0.03091	0.89445	2.6164
0.03882	0.90054	2.6975
1,1-Difluoro-3-phenylcyclobutane (B)		
0.006699	0.87305	2.3150
0.01478	0.87626	2.3605
0.02063	0.87859	2.3990
0.02749	0.88129	2.4394

Table V. Molar Refractions, Polarizations, and Dipole Moments

Compd.	MR	$P_2{}^\circ$ (27.5°)	μ, D.
A[a]	51.29[b]	210.08	2.80[c]
B[d]	43.36[e]	132.34	2.09

[a] 1,1-Difluoro-3-*p*-nitrophenylcyclobutane. [b] Obtained from measurements on solutions of A. [c] This quantity was checked in the manner described in the text. [d] 1,1-Difluoro-3-phenylcyclobutane. [e] Obtained from direct measurements on the liquid.

(36) Reference 34, p. 73.
(37) E. F. Kiefer, Ph.D. Thesis, California Institute of Technology, 1961, p. 74.
(38) M. Takahashi, M.S. Thesis, California Institute of Technology, 1962, p. 20.
(39) Y. Kitahara, M. C. Caserio, F. Scardiglia, and J. D. Roberts, *J. Am. Chem. Soc.*, 82, 3106 (1960).
(40) Reference 34, p. 108.
(41) J.-Y. Chien, *J. Chem. Educ.*, 24, 494 (1947).
(42) J. B. Lambert, "Instruction Manual for the Use of the Heterodyne-Beat Apparatus," California Institute of Technology, 1962.
(43) J. D. Roberts, R. Armstrong, R. F. Trimble, Jr., and M. Burg, *J. Am. Chem. Soc.*, 71, 843 (1949).
(44) M. T. Rogers and J. D. Roberts, *ibid.*, 68, 843 (1946).
(45) C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill Book Co., Inc., New York, N. Y., 1953, p. 221 ff.

(48) E. A. Guggenheim, *Trans. Faraday Soc.*, 45, 714 (1949).