

ELECTRON DIFFRACTION STUDY OF THE STRUCTURE AND INTERNAL ROTATION OF CYCLOBUTANECARBOXYLIC ACID CHLORIDE*

W. J. ADAMS AND L. S. BARTELL**

Department of Chemistry, University of Michigan, Ann Arbor, Mich. 48104 (U.S.A.)

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ABSTRACT

The conformational equilibrium of $(\text{CH}_2)_3\text{CH}-\text{COCl}$ in the vapor phase was studied as part of a broader investigation of molecules in the series $\text{R}-\text{COX}$. It was found that the cyclobutyl derivative exists almost entirely as *gauche* conformers, thereby closely resembling isopropyl and differing sharply from cyclopropyl homologues. The nonplanar ring can be bent toward the $-\text{COCl}$ substituent (axial conformation) or away from it (equatorial conformation). A coupling between the ring bending and torsional displacements is suggested by the electron diffraction intensities such that conformations on the *cis* side of *gauche* favor the equatorial ring pucker, and those on the *trans* side favor the axial pucker. Bond lengths, bond angles, and amplitudes of vibration were determined and found to be normal.

INTRODUCTION

Despite encouraging progress in ab initio calculations, restricted rotation about single bonds remains poorly understood. Several years ago, the conformation equilibria of isopropyl and cyclopropyl carbonyl derivatives of the form $(\text{CH}_3)_2\text{CH}-\text{CXO}$ and $(\text{CH}_2)_2\text{CH}-\text{CXO}$ were investigated¹⁻³. Isopropyl carboxaldehyde displayed normal *trans* and *gauche* conformers with all bonds staggered. In the cyclopropyl derivatives *trans* conformers were present, but *cis* forms were found instead of *gauche*. *Cis* conformers are remarkable in that they eclipse the bonds at the ends of the bond in question, thereby not conforming to Pauling's rationalization⁴ of restricted rotation. The effect must be attributed to the electronic interactions accompanying the closing down of the C-C-C angle

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** Author to whom correspondence concerning reprints should be addressed.

adjacent to the bond of interest from 112° (isopropyl) to 60° (cyclopropyl). It therefore seemed worthwhile to study the intermediate case (89°) of the cyclobutyl derivatives to establish whether *gauche* or *cis* conformers are the more stable in the case of moderate strain.

PROCEDURE

Cyclobutanecarboxylic acid chloride, obtained from the Aldrich Chemical Co., Milwaukee, Wisc., was vacuum distilled prior to use. Electron diffraction patterns were recorded at 40 kV on 4×5 in. Kodak process plates using an apparatus described previously⁵. The sample was introduced into the diffraction chamber through a heated nozzle assembly. A temperature of approximately 100°C was maintained at the nozzle while the temperature of the sample flask was regulated independently (22 – 52°) to provide the desired sample pressure. Data were recorded at camera distances of 21 cm using the r^2 rotating sector and at 21, 11 and 6.5 cm using the r^3 rotating sector under conditions described elsewhere⁶.

Photographic densities, measured with a recording microphotometer with digital output⁷, were converted to relative intensities. Six plates at each camera distance were averaged and included in the structural analysis.

ANALYSIS OF DATA

Experimental intensities were corrected for sector imperfections and extraneous scattering before division by the theoretical atomic intensity. The atomic scattering factors used to obtain leveled intensity curves were the analytical elastic factors of Strand and Bonham⁸ and the inelastic factors of Heisenberg^{9a} and Bewilogua^{9b}. Experimental leveled intensity, $I_0(s)$, and intensity background, $I_B(s)$, functions¹⁰ for each camera distance are available from ASIS*. Indices of resolution¹¹ were 1.00 for the 21 cm camera distance (r^2 -sector) and 1.02₅, 1.07 and 1.07 for the 21-, 11-, and 6.5-cm camera distances (r^3 -sector).

Experimental and calculated molecular intensities and radial distribution functions were computed as previously described^{10–12} with the usual corrections applied^{11,13–15}. Radial distribution functions, $f(r)$, were calculated using a damping factor of $\exp(-0.0015s^2)$ and calculated intensities were grafted onto the experimental intensities for s less than 3.5 \AA^{-1} . This makes the experimental distribution function moderately sensitive, in its broader peaks, to the assumed structure parameters. Therefore, in all comparisons between experimental and

* For a listing of experimental intensity data order document No. 01214 from ASIS National Auxiliary Publications Service, c/o CCM Information Sciences, Inc., 22 West 34th Street, New York, N.Y., 10001; remitting \$1.00 for microfiche or \$3.00 for photocopies.

calculated radial distribution functions the structure parameters incorporated in the small angle contributions to the experimental function were carefully made consistent with the structure parameters in the calculated function. Atomic scattering factors used in all phases of the analysis after leveling of experimental intensities were the partial wave elastic factors of Cox and Bonham¹⁶ and the inelastic factors of Tavard et al.¹⁷. Anharmonicity constants¹⁴ were estimated¹⁸ to be 2.0 \AA^{-1} , 2.0 \AA^{-1} , 1.5 \AA^{-1} and 1.6 \AA^{-1} for the C-H, C-C, C-O and C-Cl bonded distances respectively, and taken to be 1.0 \AA^{-1} for all nonbonded distances.

Preliminary values of the bonded parameters were obtained from a least squares analysis of the anharmonic radial distribution function¹⁹ in the interval $r = 0.0 \text{ \AA}$ to $r = 1.95 \text{ \AA}$ and were thereafter treated as constants until the final stages of the conformational analysis. The conformational analysis was carried out primarily through geometrically constrained¹⁹ least squares analyses of the composite molecular intensity. In order to facilitate the analyses and to limit variable parameters to a reasonable number, the following assumptions concerning the molecular model were made (see Fig. 1):

- (1) All C-H bonds have the same length;
- (2) All angles γ are equal, with the H-C-H or C₅-C₄-H plane perpendicular to the ring C-C-C plane;
- (3) All C-C-C valency angles in the ring are equal for a given dihedral angle, β ;
- (4) All bond lengths and the angles α , γ , \angle CCO and \angle CCl are independent of the angle of internal rotation, θ , and the dihedral angle of the cyclobutane ring, β ;
- (5) The C...C, C...O and C...Cl nonbonded distances are each assigned a single skeletal amplitude of vibration, independent of the nonbonded distance;
- (6) All C...H, O...H and Cl...H nonbonded distances are assigned the same skeletal amplitude of vibration;
- (7) The isomeric distribution in the angle of internal rotation and puckered ring conformations is represented by a small set of discrete conformers having maximum increments in internuclear distance of 0.1 \AA to 0.2 \AA between conformers. Although the valency angles α , γ , \angle CCO and \angle CCl were assumed to be independent of the angle of internal rotation and dihedral angle of the ring, these parameters were found to be somewhat dependent* on the assumed distribution among conformations.

Calculated standard errors took into account the effects of both random and known systematic errors^{20**}.

* The effects of these assumptions on the reported parameters are believed to be less than the reported uncertainties.

** The effects of systematic interactions implicit in eqn. (27) of this reference were not taken into account.

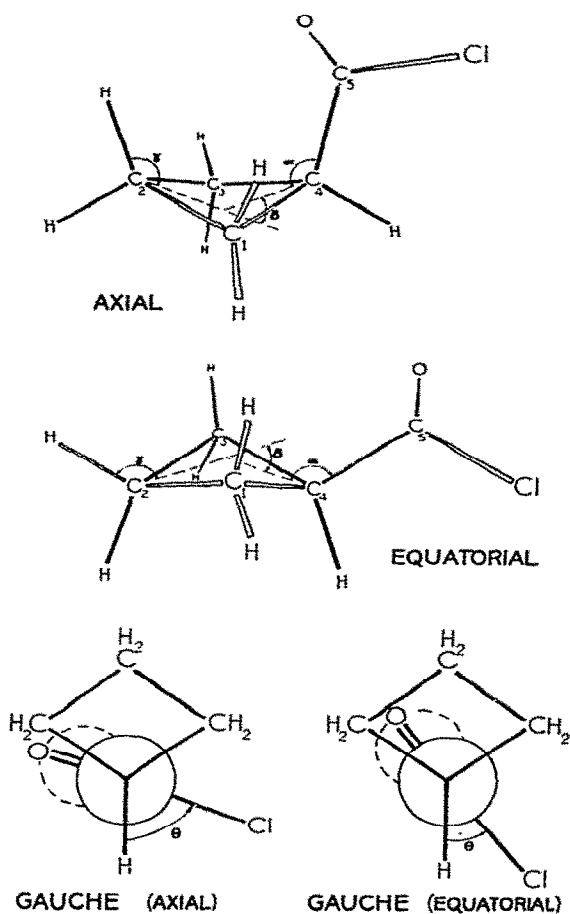


Fig. 1. Parameters characterizing the structure, ring conformation and torsional conformation of C_4H_7CClO . The correlation between the ring and torsional displacements suggested by the diffraction intensities is shown in the Newman projections at the bottom of the figure.

RESULTS

Internal rotation and ring puckering

The distribution among rotational isomers in cyclobutane-carboxylic acid chloride can be inferred from the relative areas and positions of the peaks in the radial distribution function beyond 2.8 Å. Experimental and calculated radial distribution functions for the *cis* ($\theta = 0^\circ$), *gauche* ($\theta = 60^\circ$), *antigauche* ($\theta = 120^\circ$) and *trans* ($\theta = 180^\circ$) rotational isomers are compared in Fig. 2. The calculated functions were based on parameters derived from least squares analyses of the composite intensity with the assumption that the cyclobutane ring is planar, since the major features of the distribution function are only moderately sensitive to ring puckering. The major scattering pairs contributing to the calculated distribution function are portrayed by vertical lines beneath their respective peaks.

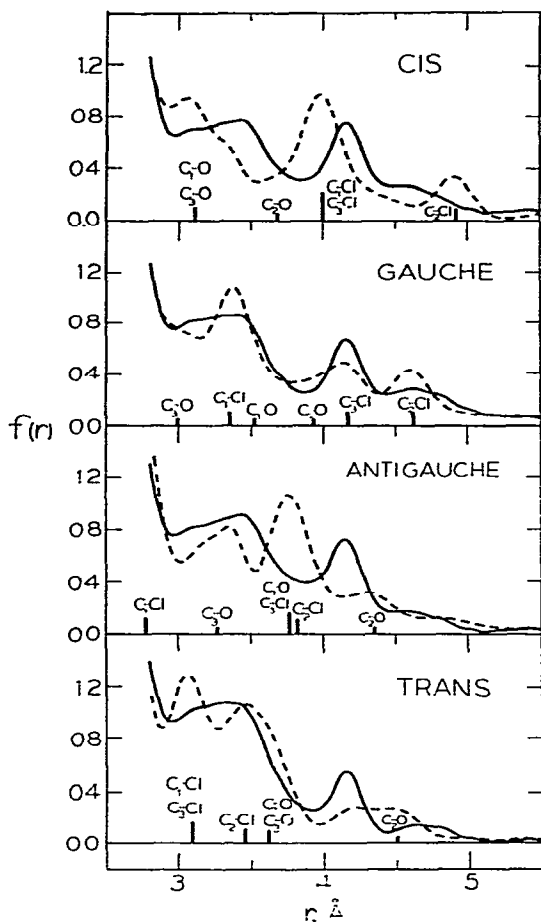


Fig. 2. Comparison between experimental radial distribution functions (solid lines) and functions calculated for various individual conformations (dashed lines).

Rotamers near the *gauche* conformation constitute the principal species. Significant concentrations of *cis* and *antigauche* rotamers may be immediately ruled out since they would give major peaks at positions where minima occur in the experimental distribution function. The *antigauche* conformation contributes adversely to the fit of the 2.6 Å peak (not shown in Fig. 2) and gives an unreasonably short $H \cdots Cl$ nonbonded distance of 2.25 Å. A major failing of the *trans* rotamer is that it shifts too much of the peak area inside 4 Å.

The predominance of the *gauche* or *gauche*-like conformers is indicated by radial distribution function (a), Fig. 3. In the model corresponding to this figure, the cyclobutane ring was constrained to be planar and a distribution among three *gauche*-like isomers was assumed. When the torsional angle of each was allowed to vary in the constrained least squares analysis, a minimum standard deviation occurred at isomeric concentrations and torsional angles of 27.5%, $\theta = 43^\circ$; 27.5%, $\theta = 51.6^\circ$; and 45%, $\theta = 73.9^\circ$.

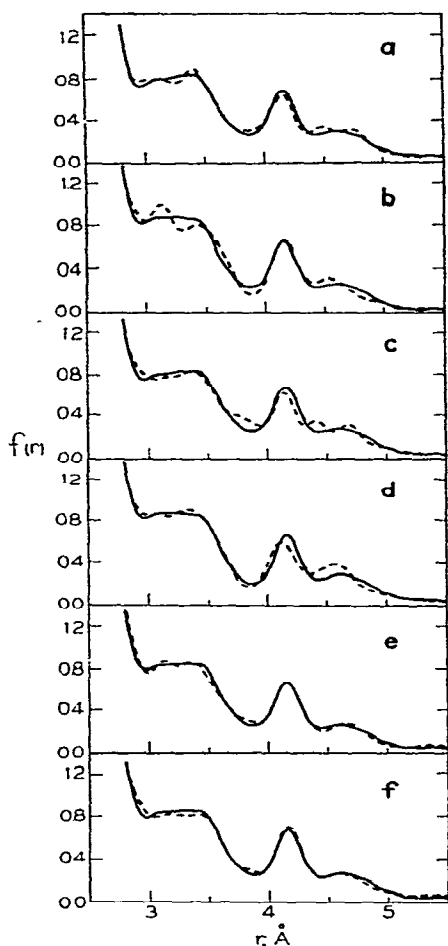


Fig. 3. Comparison between experimental radial distribution function of C_4H_7CClO (solid lines) and calculated functions (dashed lines) for various assumed populations among three *gauche*-like isomers and various assumed ring conformations. See Table 1 for details.

Discrepancies between this calculated distribution function and the experimental function can be reduced by allowing the ring to pucker. The effects of ring puckering are manifested in the radial distribution function primarily at distances greater than 3.6 Å, where the major scattering pairs, $C_2 \cdots O$ and $C_2 \cdots Cl$, dependent on ring puckering, appear. Results of various least squares analyses including small displacements from the *gauche* conformation and ring puckering are given in Table 1. The corresponding radial distribution functions constructed from the derived parameters are shown in Fig. 3. In these analyses, a distribution among three *gauche*-like isomers was assumed, and the torsional angle of each was allowed to vary in the least squares fitting of the molecular intensity function. The magnitude of the ring dihedral angle, β , was constrained to be the same for the axial and equatorial conformations in order to make the analysis tractable. In a number of analyses the latter constraint was relaxed and was shown to have no

TABLE I

LEAST SQUARES ANALYSES OF CONFORMATIONAL BEHAVIOR IN C_4H_7CClO , ASSUMING A DISTRIBUTION AMONG THREE *gauche*-LIKE ROTATIONAL ISOMERS^a
 In each analysis populations and ring conformations were preselected, and optimum skeletal parameters and torsional angles for the three isomers were derived.

Analysis	Assumed isomer concentration	Assumed ring conformation	θ	α	β^b	γ	$\angle CCO$	$\angle CCCI$	$\sigma(\theta)/I_0^c$	$\sigma[f(r)]^d$
(a)	27.5	planar	42.9		0.0					
	27.5	planar	51.6	126.4	0.0	128.0	127.0	111.8	1.628	0.047
	45.0	planar	73.9		0.0					
(b)	30.0	axial	30.8 ^e		18.6					
	30.0	axial	48.8 ^e	124.2	18.6	128.9	127.0	110.0	1.602	0.045
	40.0	axial	70.1		18.6					
(c)	27.5	equat.	38.7		12.6					
	27.5	equat.	50.0	129.1	12.6	134.2	128.9	111.3	1.495	0.039
	45.0	equat.	73.2		12.6					
(d)	27.5	axial	35.4		23.6 ^f					
	27.5	planar	43.6	124.6	0.0	130.1	126.4	110.7	1.674	0.043
	45.0	equat.	74.2		23.6 ^f					
(e)	30.0	equat.	42.1 ^g		17.7					
	30.0	equat.	59.1 ^g	122.0	17.7	130.2	126.5	111.3	1.451	0.030
	40.0	axial	72.0		17.7					
(f)	27.5	equat.	43.7		23.6					
	27.5	planar	56.2	124.6	0.0	129.8	127.3	110.6	1.435	0.026
	45.0	axial	68.7		23.6					

^a Concentrations in percent and angles in degrees.

^b The magnitude of β was constrained to be the same in axial and equatorial conformations.

^c Standard deviation in ppt. of the composite leveled molecular intensity using weight proportional to s .

^d Standard deviation between experimental and calculated radial distribution functions from 2.0 Å to 6.0 Å using a constant weighting function.

^e These internal rotation angles constrained to have an angular difference of $\Delta\theta = 18^\circ$.

^f Not varied in the least squares analysis.

^g These internal rotation angles constrained to have an angular difference of $\Delta\theta = 17^\circ$.

influence on the principal conclusions. The results suggest a correlation between internal rotation angle and ring conformation, with internal rotation angles less than or equal to the *gauche* angle predominating for the equatorial conformation and angles greater than the *gauche* angle predominating for the axial conformation, as illustrated in the Newman projections of Fig. 1. Slightly over half of the molecules appear to exist in the equatorial conformation.

Least squares analyses were also made in which various isomeric concentrations of a fourth isomer, the *trans* isomer, were assumed. No evidence for *trans* isomers was found (to within an estimated uncertainty in concentration of 15%).

The 12–15° breadth of the distribution in θ is consistent with a potential energy of internal rotation about the C₄–C₅ bond of the form

$$V(\theta) = V_3(1 - \cos 3\theta')$$

in the vicinity of the stable conformation (in which θ' is reckoned from the *gauche* reference angle) with V_3 from 2.5 to 4.0 kcal/mole.

Experimental and calculated molecular intensities, $sM(s)$ and radial distribution functions are compared in Figs. 4 and 5, respectively. In each of these comparisons the calculated functions were constructed using the bonded parameters reported in Table 2 and the bond angles and internal rotation angles reported in Table 1, analysis (e).

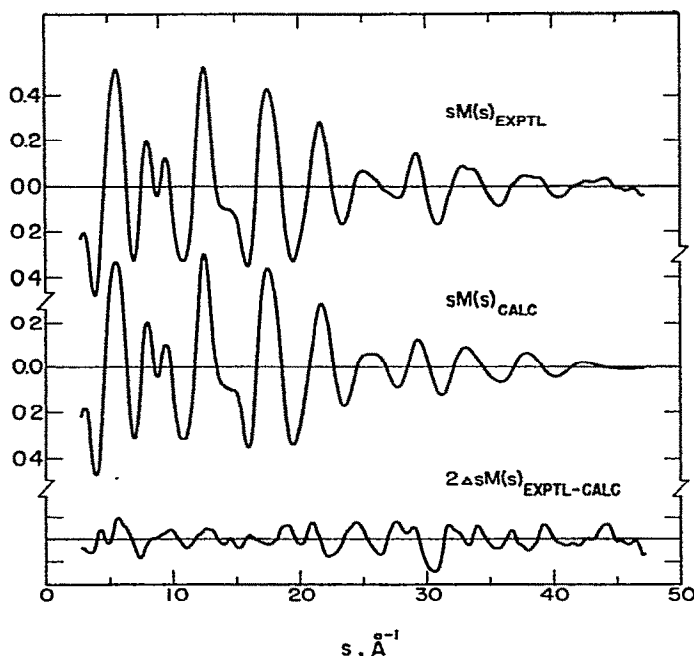


Fig. 4. Experimental and calculated molecular intensity functions for C₄H₇CClO. $\Delta sM(s) = sM(s)_{\text{exptl.}} - sM(s)_{\text{calc.}}$

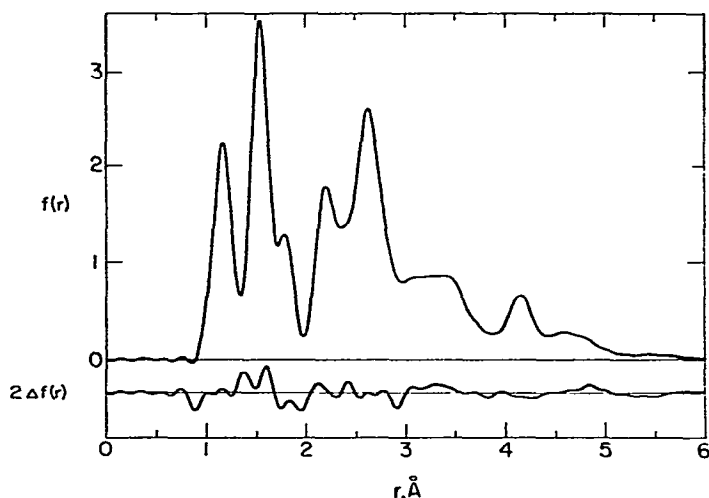


Fig. 5. Experimental radial distribution function for C_4H_7CClO . $\Delta f(r) = f(r)_{\text{exptl.}} - f(r)_{\text{calc.}}$

TABLE 2

STRUCTURAL PARAMETERS^a AND ESTIMATED STANDARD ERRORS^b FOR C_4H_7CClO

Parameter	$r_g(\text{\AA})$	I_g
C-H	1.128 ± 0.014	0.076 ± 0.020
C-O	1.195 ± 0.013	0.044 ± 0.008
C-C(mean)	1.540 ± 0.003	0.053 ± 0.005^c
C-Cl	1.793 ± 0.006	0.066 ± 0.006
C...C	—	{ 0.058 ± 0.01 (ring) 0.082 ± 0.03 (exo)}
$\angle CCO$ $127.0 \pm 1.5^\circ$, $\angle CCCI$ $111.0 \pm 2.0^\circ$		
$\alpha = 123.5 \pm 2.5^\circ$, $\beta = 21 \pm 5^\circ$		
$\gamma = 129 \pm 4^\circ$, $\theta_{\text{mean}}^d = 57 \pm 5^\circ$		

^a Angles were not corrected for shrinkage effects.

^b Including effects of both random and known systematic errors (see ref. 20). The effects of uncertainties in isomeric concentrations were also included.

^c Assuming C-C(ring) greater than C-C(exo) by 0.05 Å. Amplitude refines to 0.058 Å if all C-C bonds taken as equal.

^d Torsional angle distributed over an r.m.s. range of about 14°.

A matrix of correlation coefficients based on the least squares fit of the composite molecular intensity using a diagonal weight matrix proportional to the scattering variable s is available from ASIS.

Molecular parameters

The values of the bond lengths and selected bond angles are listed in Table 2. In initial analyses of the anharmonic radial distribution function when all C-C

bonds in the molecule were taken to be equal, the mean square amplitude of vibration of the C–C bond was found to be nearly as large as that of the ring C···C nonbonded distance. At this juncture the C–C bonds of the ring and the C–C bond adjacent the double bond were allowed to vary independently. A small but not very significant improvement in standard deviation resulted for a difference between these bonds of 0.05 Å. The derived C–C amplitude of vibration, however, decreased to 0.053 Å, a more normal value. The mean of the C–C bond lengths found in cyclobutane²¹ and in acetyl chloride²² is 1.538 ± 0.003 Å, in excellent agreement with our value for cyclobutanecarboxylic acid chloride.

DISCUSSION

Bond lengths, angles, and amplitudes of vibration in C_4H_7CClO are in reasonable agreement with those determined for related molecules. The ring dihedral angle, $\beta = 21 \pm 5^\circ$ is comparable to the values 35° (cyclobutane)²³, $20 \pm 1^\circ$ (chlorocyclobutane)²⁴, and $29.4 \pm 0.2^\circ$ (bromocyclobutane)²⁵ reported for other gas-phase cyclobutyl derivatives.

The principal question prompting this research was answered unequivocally. Rotational isomerization about the C–CClO bond in this moderately strained cyclobutyl compound is similar to that in *unstrained* alkyl carboxaldehydes^{1,26,27}. *Gauche*-like isomerization was found with no evidence for the *cis* isomerization observed in cyclopropyl derivatives^{1,3}.

The conformational behavior may be viewed in terms of a competition between forces tending to stagger bonds (Pauling's picture⁴, which treats double bonds as two bent single bonds – the dashed lines in Fig. 1) and a conjugative stabilization of *cis* and *trans* forms (Walsh's π electron model in the case of cyclopropyl derivatives)²⁸. The absence of *cis* isomerization in C_4H_7CClO is consistent with the much smaller tendency of cyclobutyl groups than cyclopropyl groups to conjugate with carbonyl groups. Rough extended Hückel molecular orbital calculations by Hoffmann²⁹ predicted in the case of cyclobutyl carboxaldehyde that *gauche* conformers would be more stable than *cis*.

The fact that only *gauche*-like isomers were detected in this molecule is in accord with a number of previous findings. In this and other examples, the carbonyl oxygen exhibits a propensity to eclipse a methyl or methylene group in preference to a hydrogen atom. Other examples include isopropyl carboxaldehyde¹, propionaldehyde³⁰, pivaldehyde³¹, and 2-methylcyclohexanone³².

One of the interesting aspects of the study is the apparent coupling between the ring bending and the –COCl internal rotation. Although the coupling is statistically significant, according to the standard deviations of Table 1, it is prudent to regard the evidence as marginal. Such a coupling would be consistent with an attraction between the carbonyl oxygen and the methylene hydrogen closest to the oxygen, and a repulsion between the oxygen and methylene group 2 (Fig. 1).

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REFERENCES

- 1 J. P. GUILLORY AND L. S. BARTELL, *J. Chem. Phys.*, 43 (1965) 654.
- 2 L. S. BARTELL AND J. P. GUILLORY, *J. Chem. Phys.*, 43 (1965) 647.
- 3 L. S. BARTELL, J. P. GUILLORY AND A. T. PARKS, *J. Phys. Chem.*, 69 (1965) 3043.
- 4 L. PAULING, *Nature of the Chemical Bond*, 3rd Ed., Cornell University Press, Ithaca, N.Y., 1960, p. 137.
- 5 L. S. BARTELL, K. KUCHITSU AND R. J. DE NEUI, *J. Chem. Phys.*, 35 (1961) 1211; L. S. BARTELL in A. WEISSBERGER AND B. W. ROSSITER (Editors), *Physical Methods in Chemistry*, 4th Ed., Interscience, New York, in press.
- 6 W. J. ADAMS, *Doctoral Dissertation*, The University of Michigan, 1969.
- 7 L. S. BARTELL AND H. W. HIGGINBOTHAM, *J. Chem. Phys.*, 42 (1965) 851.
- 8 T. S. STRAND AND R. A. BONHAM, *J. Chem. Phys.*, 40 (1964) 1686.
- 9a W. HEISENBERG, *Physik. Z.*, 32 (1931) 737.
- 9b L. BEWILOGUA, *Physik. Z.*, 32 (1931) 740.
- 10 R. A. BONHAM AND L. S. BARTELL, *J. Chem. Phys.*, 31 (1959) 703.
- 11 L. S. BARTELL, L. O. BROCKWAY AND R. H. SCHWENDEMAN, *J. Chem. Phys.*, 23 (1955) 1854.
- 12 R. M. GAVIN, JR. AND L. S. BARTELL, *J. Chem. Phys.*, 48 (1968) 2460.
- 13 V. SCHOMAKER AND R. G. GLAUBER, *Nature*, 170 (1952) 290; R. G. GLAUBER AND V. SCHOMAKER, *Phys. Rev.*, 89 (1953) 667; J. A. IBERS AND J. A. HOERNI, *Acta Cryst.*, 7 (1954) 405.
- 14 L. S. BARTELL, *J. Chem. Phys.*, 23 (1955) 1219; K. KUCHITSU AND L. S. BARTELL, *J. Chem. Phys.*, 35 (1961) 1945.
- 15 L. S. BARTELL AND L. O. BROCKWAY, *J. Chem. Phys.*, 32 (1960) 512.
- 16 H. L. COX, JR. AND R. A. BONHAM, *J. Chem. Phys.*, 47 (1967) 2599.
- 17 C. TAVARD, D. NICOLAS AND M. ROUAULT, *J. Chim. Phys.*, 64 (1967) 540.
- 18 D. R. HERSCHBACH AND V. W. LAURIE, *J. Chem. Phys.*, 35 (1961) 458; E. R. LIPPINCOTT AND R. SCHROEDER, *J. Chem. Phys.*, 23 (1955) 1131.
- 19 L. S. BARTELL, D. A. KOHL, B. L. CARROLL AND R. M. GAVIN, JR., *J. Chem. Phys.*, 42 (1965) 3079; T. L. BOATES AND L. S. BARTELL, to be published.
- 20 L. S. BARTELL in A. WEISSBERGER AND B. W. ROSSITER (Editors), *Physical Methods in Chemistry*, 4th Ed., Interscience, New York, in press.
- 21 A. ALMENNINGEN, O. BASTIANSEN AND P. N. SKANCKE, *Acta Chem. Scand.*, 15 (1961) 711.
- 22 K. M. SINNOT, *J. Chem. Phys.*, 34 (1961) 851.
- 23 O. BASTIANSEN AND P. N. SKANCKE, unpublished work (private communication from S. CYVIN quoted in R. C. LORD AND I. NAKAGAWA, *J. Chem. Phys.*, 39 (1963) 2951).
- 24 H. KIM AND W. D. GWINN, *J. Chem. Phys.*, 44 (1966) 865.
- 25 W. G. ROTHSCHILD AND B. P. DAILEY, *J. Chem. Phys.*, 36 (1962) 2931.
- 26 R. W. KILB, C. C. LIN AND E. B. WILSON, JR., *J. Chem. Phys.*, 26 (1957) 1695.
- 27 C. C. LIN AND J. D. SWALEN, *Rev. Mod. Phys.*, 31 (1959) 841.
- 28 A. D. WALSH, *Nature*, 159 (1947) 165, 712; A. D. WALSH, *Trans. Faraday Soc.*, 45 (1949) 179.
- 29 R. HOFFMAN, *Tetrahedron Letters*, 43 (1965) 3819.
- 30 R. J. ABRAHAM AND J. A. POPLI, *Mol. Phys.*, 3 (1960) 609; S. S. BUTCHER AND E. B. WILSON, JR., *J. Chem. Phys.*, 40 (1964) 1671.
- 31 A. M. RONN AND R. C. WOODS, III, *J. Chem. Phys.*, 45 (1966) 3831.
- 32 N. L. ALLINGER AND H. M. BLATTER, *J. Am. Chem. Soc.*, 83 (1961) 994.