Journal of Molecular Structure, 41 (1977) 177—182
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MICROWAVE SPECTRUM AND ROTATIONAL ISOMERS OF CYCLOPROPYLCARBINYL CHLORIDE AND EPICHLOROHYDRIN

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(Received 13 April 1977)

ABSTRACT

Microwave spectra of $\overline{\mathrm{CH_2CH_2C}}\mathrm{HCH_2Cl}$ and $\overline{\mathrm{CH_2OC}}\mathrm{HCH_2Cl}$ have been studied. $\overline{\mathrm{CH_2CH_2C}}\mathrm{HCH_2Cl}$ is found to exist in two rotameric forms. Their rotational constants, *A*, *B* and *C* are 7799.5, 2858 9 and 2550.0 MHz for the *cis* rotamer; and 11 745.9, 2049.8 and 1892.3 MHz for the *gauche* rotamer. Three rotameric forms are found for $\overline{\mathrm{CH_2OC}}\mathrm{HCH_2Cl}$, and their rotational constants, *A*, *B* and *C* are 13 297.2, 2007.1 and 1873.1 MHz for rotamer I (*gauche* I); 8487.6, 2899.0 and 2531.9 MHz for rotamer II (*cis*); and 13 508.8, 2055.1 and 1920.4 MHz for rotamer III (*gauche* II).

INTRODUCTION

From the IR analysis of cyclopropylcarbinyl chloride in gaseous, liquid and solid states and from Raman analysis of the liquid state spectra [1], it was concluded that the molecules take the *gauche* form in the gaseous state at room temperature and also predominantly *gauche* in the liquid and solid states. For epichlorohydrin, IR studies [2] in the liquid and solid phases identified two rotamers, one less polar than the other based on the intensity variation with respect to the solvents of differing dielectric strength, although the NMR spectrum [3] on the other hand was interpreted on the basis of three rotamers coexisting in the liquid state. However, for epifluorohydrin a recent microwave study [4] showed that it exists in three rotameric forms in the gaseous phase.

For both of these molecules, an asymmetric halomethyl top is bonded to the 3-membered ring frame. When the halomethyl top rotates clockwise as shown in Fig. 1, one would expect two staggered rotamers for cyclopropylcarbinyl chloride and three distinctive rotamers for epichlorohydrin. Cyclopropylcarboxaldehyde studied by both electron diffraction [5] and microwave spectroscopy [6], was found to have *trans* and *cis* rotamers, and it was suggested that the observed rotamers are in the direction of maximum conjugation with the ring bond. The cyclopropyl group has often been referred to the vinyl group in terms of π bond characteristics [7]. On the other hand, in 3-fluoropropene [8] and 3-chloropropene [9], where such conjugation is not expected to play an important role, *gauche* and *cis* rotamers were found to coexist in the gaseous phase.

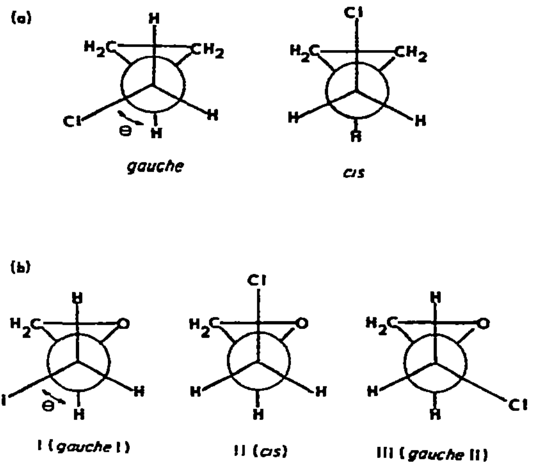

Fig. 1. Rotational isomers of cyclopropylcarbinyl chloride (a) and epichlorohydrin (b).

We have assigned rotational spectra of two rotamers, *cis* and *gauche*, for cyclopropylcarbinyl chloride and three rotamers, I, II and III for epichlorohydrin. A preliminary report of this work was presented at the Symposium on Molecular Structure and Spectroscopy at Ohio State University, Columbus, Ohio, U.S.A., June 14—18, 1971.

EXPERIMENTAL

The microwave spectrum was studied in a Stark-modulated Hughes-Wilson type spectrometer [10], and the 3 m long X-band cell was cooled to dry ice temperature for most of the measurements.

The sample of cyclopropylcarbinyl chloride was prepared by the reaction of cyclopropylcarbinol with thionylchloride [11] and its purity was confirmed through VPC. The spectrum was studied in the 8—40 GHz region. Trial rotational constants based on the structural parameters of methyl cyclopropane [12] and ethyl chloride [13], as shown in Fig. 2, were used to predict the spectrum. The bond moments calculation indicates that we could expect *b*-dipole transitions for both conformers. A series of *b*-dipole Q-branch transitions were observed for both *cis* and *gauche* rotamers and are assigned on the basis of $(A - C)/2$ vs. κ plots. For R-branches, *b*-dipole transitions were found for the *cis* rotamer and *a*-dipole transitions for the *gauche* rotamer. For the most part, intensities were weak, and we have not attempted to resolve the chlorine nuclear quadrupole splittings. Absorption peaks were used to fit the rigid rotor spectrum. The observed and calculated transitions and the corresponding rotational constants are given in Table 1. The deviations from the calculated frequencies arise mostly from the unresolved quadrupole splittings. A slight non-rigidity is observed in the Q-branch crossings.

The compound epichlorohydrin is commercially available and was distilled

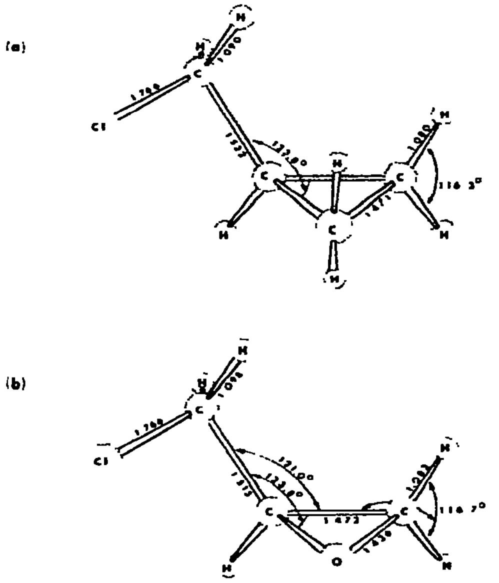

Fig. 2. Structural parameters adapted for cyclopropylcarbinyl chloride (a) and epichlorohydrin (b)

once and checked by VPC. Trial rational constants were calculated based on the structural parameters of propylene oxide [14] and ethyl chloride [13] as shown in Fig. 2. Bond moments calculation predicted *b*-dipole transitions. A series of Q-branch transitions for all 3 rotamers was found and assigned on the basis of $(A - C)/2$ vs. κ plots. *b*-Dipole R-branch transitions were predicted and found. The assigned transitions and their respective rotational constants are given in Table 2. Spectral intensities were found to be weak and the chlorine nuclear quadrupole splittings were not resolved.

ROTATIONAL ISOMERISM

The experimental constants obtained in our work are insufficient to determine complete structures of each rotamer. However, by assuming parameters of known structures for the frame and the top, the internal rotation angle, θ, can be assigned. We have calculated rotational constants for every 10° interval using the parameters shown in Fig. 2, and obtained smooth curves as plotted in Figs. 3 and 4. The observed rotational constants of $CH_2CH_2CHCH_2Cl$ are plotted in Fig. 3. A set of observed and calculated values crosses at $\theta = \pi/3$ for *gauche* rotamers and $\theta = \pi$ for *cis* rotamers. Based on our model structure, there is no indication of skewing from staggered configurations. We are not able to determine the relative stability of these rotamers in the gaseous phase, but judging from their intensities and our spectrometer sensitivity, both rotamers coexist in appreciable amounts at dry ice temperature. Similarly,

TABLE 1

Observed rotational transitions of cyclopropylcarbinyl chloride (MHz)

Transition	*Cis*		*Gauche*	
	Obs.	$\Delta\nu^a$	Obs.	$\Delta\nu^a$
$6_{24}-6_{15}$	13 106.1	−1.0		
$7_{25}-7_{16}$	12 828.9	−3.0		
$8_{26}-8_{17}$	12 747.8	−0.9		
$9_{27}-9_{18}$	12 912.9	1.0		
$10_{28}-10_{19}$	13 367.0	0.6		
$11_{29}-11_{110}$	14 151.6	2.4		
$2_{12}-2_{21}$	15 746.2	−1.5		
$3_{13}-3_{22}$	16 220.9	0.3		
$1_{01}-1_{10}$			9856.2	2.2
$3_{03}-3_{12}$			10 257.6	2.0
$4_{04}-4_{13}$			10 584.9	−0.8
$7_{07}-7_{16}$	10 629.7	1.4		
$8_{08}-8_{17}$	12 530.2	1.1	12 912.9	2.4
$9_{09}-9_{18}$	14 732.7	1.8	13 783.3	−0.8
$10_{010}-10_{19}$	17 211.7	0.0	14 792.4	−0.5
$11_{010}-11_{110}$	19 906.7	0.4	15 946.9	0.9
$12_{012}-12_{111}$			17 250.5	0.7
$0_{00}-1_{11}$	10 349.1	−0.5	13 637.2	−1.0
$1_{01}-2_{12}$	15 453.1	3.5		
$2_{02}-3_{13}$	20 413.1	3.0		
$3_{13}-4_{04}$	17 267.2	0.0		
$2_{02}-3_{03}$			11 819.3	0.4
$2_{21}-3_{22}$			11 827.3	0.8
$2_{20}-3_{21}$			11 835.2	1.1
$2_{11}-3_{12}$			12 066.4	−4.9
$3_{03}-4_{04}$			15 750.2	0.6
$3_{21}-4_{22}$			15 785.5	0.7
$3_{13}-4_{14}$			15 453.0	3.1
$3_{31}-4_{32}$			15 770.8	−1.7
$3_{30}-4_{31}$			15 774.7	+2.3
A	7799.5		11 745.9	
B	2858.9		2049.8	
C	2550.0		1892.3	

[a] $\Delta\nu = \nu_{\text{obs.}} - \nu_{\text{calc.}}$

the observed rotational constants of CH_2OCHCH_2Cl are plotted against the calculated values in Fig. 4. Good agreements are found at $\theta = 60°$, 170° and 310°. These internal rotation angles correspond very closely to those found in epifluorohydrin. Again, we are not able to determine their relative stability, but all three rotameric species show comparable weak intensities at dry ice temperature.

TABLE 2

Observed rotational transitions of epichlorohydrin

Transition	Rotamer I		Rotamer II		Rotamer III	
	Obs.	$\Delta\nu^a$	Obs.	$\Delta\nu^a$	Obs.	$\Delta\nu^a$
$1_{01} - 1_{10}$	11 425.8	1.6				
$2_{02} - 2_{11}$	11 558.1	−1.2				
$3_{03} - 3_{12}$	11 764.8	0.5			11 929.5	−0.9
$4_{04} - 4_{13}$	12 042.1	0.4			12 209.6	0.3
$5_{03} - 5_{14}$	12 394.0	−1.1	8806.2	0.9	12 564 7	0.2
$6_{06} - 6_{15}$	12 829.2	0.5	10 221.7	−2.0	13 003.2	2.9
$7_{07} - 7_{16}$	13 348.3	0.6	11 993.4	0.9	13 520.2	−1.5
$8_{08} - 8_{17}$	13 956.8	−1.1	14 119.9	1.8	14 137.8	3.1
$9_{09} - 9_{18}$			16 598.9	1.5	14 841.7	−3.6
$10_{010} - 10_{019}$	15 478.5	−1.1			15 661.1	0.6
$11_{011} - 11_{110}$	16 398.8	−1.4				
$12_{012} - 12_{111}$	17 441.7	0.7				
$1_{01} - 2_{12}$	18 914.0	−2.5	11 021.7	2.1	15 428.4	−0.9
$2_{02} - 3_{13}$	22 599.0	2.8	16 081.1	−2.3	19 267.7	−2.3
$3_{03} - 4_{14}$	26 210.0	−0.8	20 980.5	0.8	23 045.8	1.8
A	13 297.2		8487.6		13 508.8	
B	2007.1		2879.0		2055.1	
C	1873.1		2531.9		1920.4	

[a] $\Delta\nu = \nu_{\text{obs.}} - \nu_{\text{calc.}}$

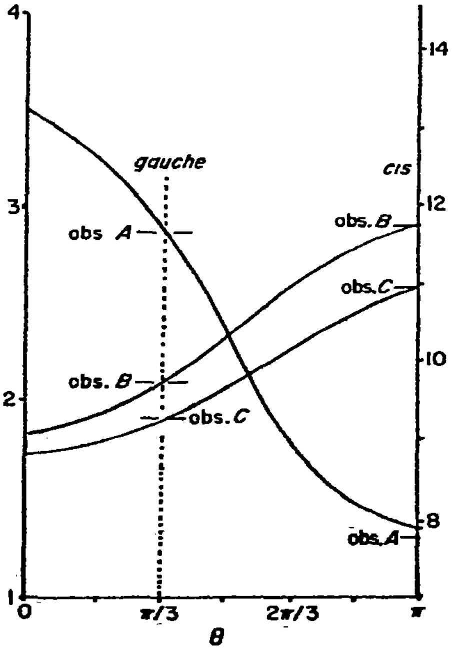

Fig. 3. Calculated and observed rotational constants vs. internal rotation angle θ for cyclopropylcarbinyl chloride.

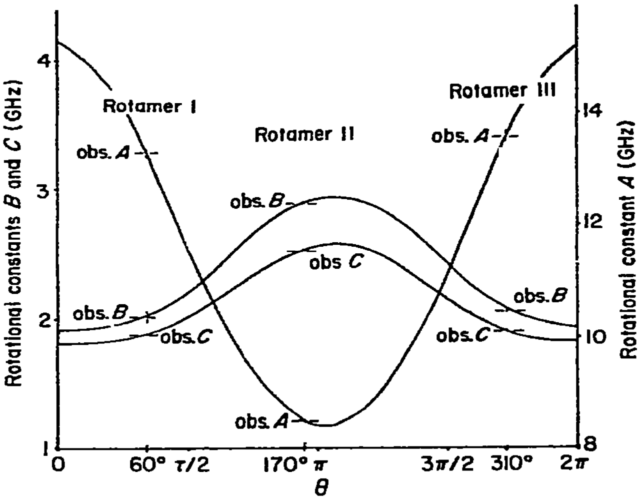

Fig. 4. Calculated and observed rotational constants vs. internal rotation angle θ for epichlorohydrin.

ACKNOWLEDGEMENTS

The financial support of the Research Corporation, ACS Petroleum Research Fund, and the University of Missouri is gratefully acknowledged.

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