

# Vibrational Spectra and Conformations of (Iodomethyl)cyclopropane and Epiiodohydrin

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The infrared (4000–400  $\text{cm}^{-1}$ ) spectra of (iodomethyl)cyclopropane and epiiodohydrin in all three physical states have been recorded. The Raman (3500–50  $\text{cm}^{-1}$ ) spectra of these two molecules in condensed phases have also been obtained. For (iodomethyl)cyclopropane no multiple Q branches were observed in the gas-phase infrared spectrum nor were any liquid-phase peaks observed to vanish upon crystallization. On the basis of these data and on the liquid-phase Raman depolarization ratios (which suggest that all observed Raman lines are polarized) it has been concluded that (iodomethyl)cyclopropane exists solely in the (nonsymmetric) gauche conformation in all states of matter. On the other hand, epiiodohydrin exhibits several gas-phase infrared band contours with "extra" Q branches and ten liquid-phase Raman conformer doublets, wherein one member of each doublet disappears when the annealed solid phase is obtained. These data have been interpreted in terms of a gauche-1 (70%)/gauche-2 (30%) conformational equilibrium for liquid epiiodohydrin at room temperature, with only the gauche-1 conformer remaining in the crystalline sample. From a variable-temperature (–74 to 25 °C) study of the base-line-resolved liquid-phase Raman doublet at 940/914  $\text{cm}^{-1}$ , an enthalpy difference between conformers of  $0.50 \pm 0.05$  kcal/mol has been determined, with the gauche-1 conformer the more stable. No evidence for a cis conformation of either molecule was found, apparently as a result of strong steric interactions between the iodine atom and  $\beta$ -ring hydrogen atoms. For these molecules, vibrational assignments, which are in excellent agreement with the vibrational assignments of other (halomethyl)cyclopropanes and epihalohydrins, have also been proposed.

## Introduction

In a recent series of articles we have used vibrational spectroscopic techniques to study the conformational equilibria in a series of three-membered ring compounds containing an asymmetrical halomethyl substituent.<sup>1–4</sup> In particular, these epihalohydrins and (halomethyl)cyclopropanes include epifluorohydrin (EFH),<sup>1</sup> epichlorohydrin (ECH),<sup>2</sup> epibromohydrin (EBH),<sup>3</sup> (chloromethyl)cyclopropane (CMCP),<sup>2</sup> and (bromomethyl)cyclopropane (BMCP).<sup>3</sup> The structural conclusions and enthalpy differences between conformers for these molecules are summarized in Table I. (See also Figure 1 for a description of the various conformers.)

A number of trends can be observed in Table I. (1) A decided gauche preference is exhibited by these molecules. This appears to be a consequence of both stabilizing electronic factors (the "gauche effect")<sup>5</sup> and destabilizing steric effects. (2) As the size of the halogen is increased in the epihalohydrin series, the amount of the gauche-2 conformer increases at the expense of the cis form. (3) As the size of the halogen atom is increased, smaller amounts of cis conformers and larger  $\Delta H$  values between gauche and cis structures are observed. This is apparently due to the increased steric problems associated with locating a larger halogen atom over the three-membered ring where its van der Waals radius overlaps that of the  $\beta$ -ring hydrogen atom (or atoms). An anomalously large percentage of cis conformer of EFH is found

as a result of the compactness of the fluorine atom or possibly as a result of some small amount of intramolecular hydrogen bonding which may be obtained only in the cis orientation. (4) Gauche-cis enthalpy differences are larger for the (halomethyl)cyclopropanes than they are for the corresponding epihalohydrins, presumably as a result of the steric interaction of the halogen atom with two  $\beta$ -ring hydrogen atoms instead of one. (5) Finally, there appears to be a trend in the epihalohydrin series wherein the gauche-2 conformer becomes progressively less stable or the gauche-1 conformer becomes progressively more stable, with increasing size of the halogen atom. In order to further explore these trends in conformer populations and stabilities, we have extended our studies to include the corresponding iodides, epiiodohydrin (EIH) and (iodomethyl)cyclopropane (IMCP).

While no previous structural results for IMCP have appeared in the chemical literature, a number of previous studies, including three vibrational spectroscopic investigations, have addressed the question of the conformational behavior of EIH. From their Raman spectra, Ballaus and Wagner<sup>6</sup> were the first to suggest the existence of multiple conformers of the epihalohydrins. In 1972, Hayashi et al.<sup>7</sup> concluded from their liquid and solution

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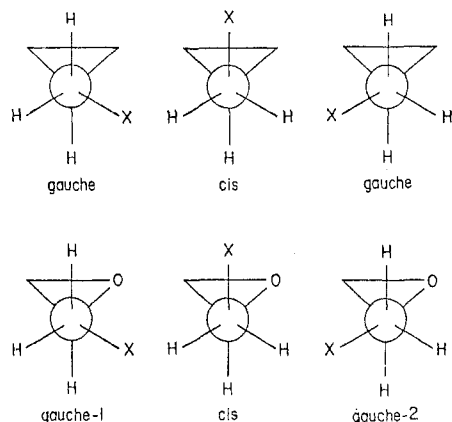
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**TABLE I: Conformer Abundances (Room Temperature) and Enthalpy Differences between Conformers of Halomethyl-Substituted Three-Membered Ring Compounds**

epihalohydrins	conformer percentage			$\Delta H$ , kcal/mol		ref
	gauche-1	gauche-2	cis	gauche-1/gauche-2	gauche-1/cis	
epifluorohydrin (EFH)	53	21	26	0.6	0.4	1
epichlorohydrin (ECH)	70	21	9	0.7	1.2	2
epibromohydrin (EBH)	$\geq 72$	$\geq 18$	$< 10$	0.8	$> 1.1$	3

(halomethyl)cyclopropanes	conformer percentage		$\Delta H$ , kcal/mol	ref
	gauche	cis	gauche/cis	
(chloromethyl)cyclopropane (CMCP)	95	5	1.4	2
(bromomethyl)cyclopropane (BMCP)	98	2	2.0	3

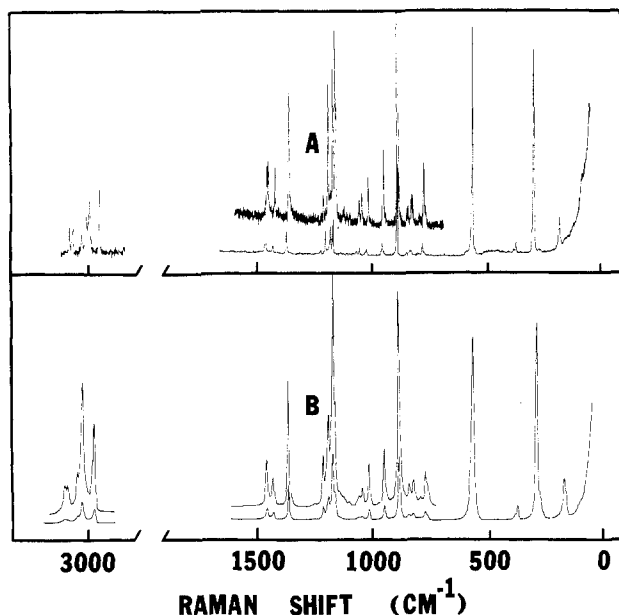
**Figure 1.** Possible conformations of (halomethyl)cyclopropanes and epihalohydrins ( $X = F, Cl, Br, I$ ).

infrared spectra that EIH existed in "more polar" and "less polar" forms, without specifically identifying these conformers. More recently, Charles and co-workers<sup>8</sup> concluded from their fluid-phase data that gauche-2 EIH predominates in the vapor, while their variable-temperature study of the 937/913  $\text{cm}^{-1}$  infrared doublet demonstrated that gauche-1 EIH is 0.56 kcal/mol more stable than the gauche-2 rotamer in the liquid. Interestingly, both of these latter two studies<sup>7,8</sup> found that the identity of the (single) conformer remaining in the solid phase depended upon the conditions used for annealing the sample. In addition, nuclear magnetic resonance investigations ( $^1\text{H}$  and  $^{13}\text{C}$ ) of EIH<sup>9,10</sup> have also stated that gauche-1 EIH is the most abundant liquid-phase form of this compound. However, a dipole moment/Kerr constant study<sup>11</sup> concluded that 40% of EIH molecules are in the gauche-2 arrangement with the remaining 60% due to gauche-1 and cis conformers in unspecified amounts.

Thus, in order to resolve the controversies surrounding the EIH conformational problem, to investigate for the first time the structural preferences of its isoelectronic counterpart, IMCP, and to extend our studies of the conformational behavior of halomethyl-substituted three-membered ring compounds, we have recorded the vibrational spectra of these two compounds in all phases and we have conducted variable-temperature studies on both molecules in the liquid-phase Raman spectra. The results and conclusions of these studies are reported herein.

### Experimental Section

EIH was synthesized by the direct exchange of the chlorine atom of ECH (Aldrich Chemical Co.) by  $\text{I}^-$  in the presence of 18-crown-6 ether (Aldrich), according to the method of Kawakami and Yamashita.<sup>12</sup> The crude EIH product was vacuum distilled (63  $^\circ\text{C}$ , 16 torr) through a glass-helices-packed column, and the distillate was found to be at least 99% pure by gas-phase chro-

**Figure 2.** Raman spectra of (iodomethyl)cyclopropane in condensed phases: (A) polycrystalline solid phase, (B) liquid phase.

matography. IMCP was prepared in a similar fashion, starting with CMCP (Aldrich) and sodium iodide. After a preliminary fractional distillation, the IMCP sample was purified by preparative gas-phase chromatography (6-ft FFAP column, 145  $^\circ\text{C}$ ). Both EIH and IMCP samples were stored under vacuum, in the dark, and over copper wire at 5  $^\circ\text{C}$  in order to prevent sample decomposition. Since IMCP slowly isomerizes into small percentages of cyclobutyl iodide and 4-iodo-1-butene, its spectra were always recorded with freshly purified samples. Except for transferring the liquid-phase samples into the infrared cell, all sample handling procedures were carried out under vacuum.

A Spex Ramalog DUV spectrometer equipped with a Spectra-Physics Model 171  $\text{Ar}^+$  laser was used to record the Raman spectra. A power of approximately 100 mW was used in either the green (514.5 nm) or blue (488.0 nm) laser lines. Liquid-phase Raman spectra were obtained with the samples sealed in glass capillaries. Solid-phase and variable-temperature Raman spectra were recorded with the glass capillaries enclosed in a Harney-Miller cell<sup>13</sup> fitted with an iron-constantan thermocouple and an Omega 199 digital thermometer. Raman spectra of strong sharp lines should be accurate to  $\pm 2 \text{ cm}^{-1}$ .

Infrared spectra of the vapor phase were collected at 0.5  $\text{cm}^{-1}$  resolution on a Nicolet 7199 Fourier transform interferometer equipped with a KBr/Ge beam splitter and a liquid-nitrogen-cooled MCT detector. The gaseous samples were loaded into a 15-cm O-ring cell fitted with KBr windows. IR spectra of the liquid and solid phases were recorded with a Perkin-Elmer Model 621 spectrophotometer. KBr cells of 0.025-mm spacing were employed for the liquid-phase spectra, while the solid-phase spectra were obtained by condensing EIH or IMCP vapors onto a liquid-ni-

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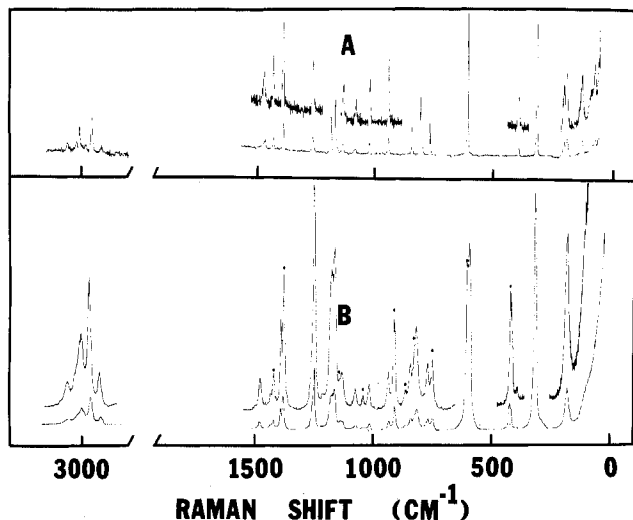


Figure 3. Raman spectra of epiiodohydrin in condensed phases: (A) polycrystalline solid phase, (B) liquid phase. The dotted liquid-phase peaks are for the gauche-2 conformer.

TABLE II: Comparison of Vibrational Frequencies ( $\text{cm}^{-1}$ ) of the (Halomethyl)cyclopropanes<sup>a</sup>

mode	CMCP <sup>b</sup>	BMCP <sup>c</sup>	IMCP <sup>d</sup>
CH <sub>2</sub> antisym str, in phase	3081	3083	3080
CH <sub>2</sub> antisym str, out of phase	3070	3073	3065
CH str	3037	3037	3028
CH <sub>2</sub> sym str, in phase	3033 <sup>e</sup>	3015	3010
CH <sub>2</sub> sym str, out of phase	3004	3007	3010
CH <sub>2</sub> (X) antisym str	2995 <sup>e</sup>	2990	2997
CH <sub>2</sub> (X) sym str	2964	2958	2951
CH <sub>2</sub> (X) def	1462 <sup>f</sup>	1461	1463
CH <sub>2</sub> def, in phase	{1451 1448}	1443	1456
CH <sub>2</sub> def, out of phase	1424	1422	1427
CH bend, in plane	{1377 1369}	1371	1370
CH <sub>2</sub> (X) wag	{1276 1268}	1256	1244 <sup>g</sup>
CH <sub>2</sub> (X) twist	1236	{1232 1226}	1217
ring breath	1195	1195	1197
CH <sub>2</sub> twist, out of phase	1171	1173	1178
CH <sub>2</sub> twist, in phase	1118	1112	1113 <sup>g</sup>
CH bend, out of plane	{1104 1097}	1083	1063
CH <sub>2</sub> wag, out of phase	1050 <sup>f</sup>	1056	1053
CH <sub>2</sub> wag, in phase	1028	{1030 1017}	1024
CC str	971	963	956
antisym ring def	916	902	896
sym ring def	883 <sup>h</sup>	872	846
CH <sub>2</sub> (X) rock	{838 <sup>h</sup> 832 <sup>h</sup> }	{843 824}	828
CH <sub>2</sub> rock, out of phase	797	794	800
CH <sub>2</sub> rock, in phase	{778 767}	805	782
CX str	687	609	578
CH <sub>2</sub> (X) bend, out of plane	402	388 <sup>h</sup>	374
CH <sub>2</sub> (X) bend, in plane	350	316 <sup>h</sup>	296
CCX bend, in plane	216	196	184
CC torsion	97 <sup>e</sup>	100	84

<sup>a</sup>Frequencies listed are for the major, gauche, conformer. All frequencies are from the solid-phase Raman spectrum except those denoted. <sup>b</sup>Reference 2. <sup>c</sup>Reference 3. <sup>d</sup>This work. <sup>e</sup>Gas-phase Raman frequency. <sup>f</sup>Liquid-phase Raman frequency. <sup>g</sup>Solid-phase infrared frequency. <sup>h</sup>Reassigned from ref 2 and 3 as suggested by these data.

trogen-cooled ( $\sim -190^\circ\text{C}$ ) CsI substrate held in a typical infrared cold cell having CsI windows. Condensed-phase IR frequencies should be accurate to  $\pm 2\text{ cm}^{-1}$ , while the FT-IR gas-phase frequencies should be accurate to better than  $1\text{ cm}^{-1}$ .

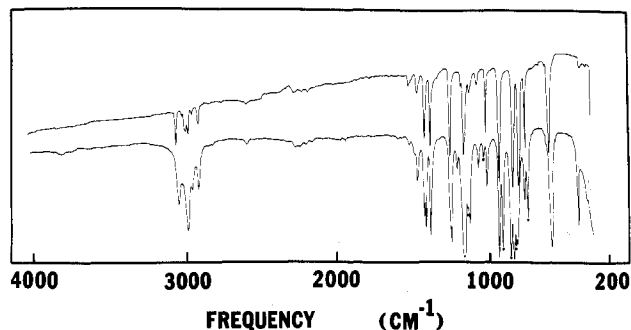


Figure 4. Infrared spectra of epiiodohydrin in condensed phases. The upper trace is the polycrystalline solid phase spectrum, while the lower trace is the liquid phase spectrum. The dotted liquid phase peaks are for the gauche-2 conformer.

TABLE III: Comparison of Vibrational Frequencies ( $\text{cm}^{-1}$ ) of the Epihalohydrins<sup>a</sup>

mode	EFH <sup>b</sup>	ECH <sup>c</sup>	EBH <sup>d</sup>	EIH <sup>e</sup>
ring CH <sub>2</sub> freq				
CH <sub>2</sub> antisym str	3079	3068	3063	3060
CH <sub>2</sub> sym str	3006	3016	3018	3006
CH <sub>2</sub> def	1426	1442	1437	1432
CH <sub>2</sub> twist	1147 <sup>g</sup>	1160	1154	1167
CH <sub>2</sub> wag	1138	1139	1137	1135
CH <sub>2</sub> rock	757	760	754	768
CH freq				
CH str	3036	3032	3032	3020
CH bend, in plane	1344	1405	1394	1389
CH bend, out of plane	1078	1091	1063	1080
CH <sub>2</sub> (X) freq				
CH <sub>2</sub> antisym str	2970	2972	2973	2954
CH <sub>2</sub> sym str	2940	2926	2916	2915
CH <sub>2</sub> def	1467	1475	1469	1468
CH <sub>2</sub> wag	1253	1266	1217	1264
CH <sub>2</sub> twist	1170	1213	1202	1185
CH <sub>2</sub> rock	900	910	892	1023
ring freq				
ring breath	1263	1254	1253	1255 <sup>f</sup>
ring antisym def	860	859	852	844
ring sym def	856	848	842	809
other freq				
CC str	980	921	913	942
CX str	991	717	643	612
CH <sub>2</sub> (X) bend, out of plane	504	446	427	395
CH <sub>2</sub> (X) bend, in plane	394	380	347	320
CCX bend, in plane	373 <sup>f</sup>	221 <sup>f</sup>	198	190
CH <sub>2</sub> (X) torsion	138	86 <sup>h</sup>	105 <sup>f</sup>	126

<sup>a</sup>Frequencies listed are for the major, gauche-1, conformer. All frequencies are from the solid-phase Raman spectrum except those denoted. <sup>b</sup>Reference 1. <sup>c</sup>Reference 2. <sup>d</sup>Reference 3. <sup>e</sup>This work. <sup>f</sup>Liquid-phase Raman peak. <sup>g</sup>Solid-phase IR peak. <sup>h</sup>Gas-phase Raman peak.

## Results and Vibrational Assignments

Typical condensed-phase Raman spectra of IMCP are shown in Figure 2 while condensed-phase Raman and infrared spectra of EIH are shown in Figures 3 and 4, respectively. Infrared spectra of liquid IMCP and FT-IR gas-phase spectra of both molecules are included in the supplementary material for this article. Also incorporated into the supplementary material are tables listing all the observed vibrational frequencies and their assignments for these two compounds.

Details of the vibrational assignments of IMCP and EIH are documented elsewhere<sup>14,15</sup> and will not be described here. However, the results of these assignments for the major conformers (gauche and gauche-1, respectively) of IMCP and EIH are listed in Tables II and III, and are compared to the vibrational assignments proposed for the other (halomethyl)cyclopropanes and

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epihalohydrins. As expected, excellent agreement is found among the (halomethyl)cyclopropanes, among the epihalohydrins, and even between IMCP and EIH. The seemingly high frequency for the CH<sub>2</sub>(I) rock of EIH could perhaps be attributed to mass or kinetic effects associated with the exceptionally large and heavy iodine atom, especially since the CH<sub>2</sub>(I) wag and C-C(H<sub>2</sub>I) stretch of EIH are also higher in frequency than their bromo and chloro counterparts.

Additionally, the torsional frequency of EIH (126 cm<sup>-1</sup>) is higher than those for ECH (86 cm<sup>-1</sup>) and EBH (105 cm<sup>-1</sup>). Since the reduced moment of inertia for internal rotation in EIH (its *F* number) is less than those for ECH and EIH, this implies that the barrier to gauche-1/gauche-2 interconversion is higher in EIH than in EBH, which in turn is higher than in ECH. No such conclusions can be made for the (halomethyl)cyclopropanes since their torsional frequencies do not follow the same trend.

### Conformational Results

*(Iodomethyl)cyclopropane.* An inspection of the spectra of IMCP reveals that every observed gas-phase peak has a liquid- and/or solid-phase counterpart. Furthermore, all but one of the liquid-phase peaks (the combination band at 1355 cm<sup>-1</sup>) have solid-phase counterparts as well. In fact, the solid-phase spectrum shows several additional fundamental modes not observed or not resolved in the liquid state. That no fluid-phase bands disappear upon solidification argues strongly for the presence of a single conformation of IMCP.

The identity of this sole rotamer of IMCP can be deduced from the Raman depolarization data. All observed liquid-phase Raman lines appear to be polarized—especially the conformationally sensitive, low-frequency skeletal bending vibrations. Since *cis*-IMCP has a plane of symmetry, it should exhibit 13 depolarized Raman bands, with two of these being low-frequency skeletal bending vibrations. Clearly, the Raman depolarization evidence identifies the sole conformation of IMCP as the gauche form.

Owing to the presence of the massive iodine atom, both gauche and *cis*-IMCP give rise to infrared gas-phase band contours with similar P-R spacings.<sup>14</sup> In addition, most of the observed infrared gas-phase band contours are A/C hybrid types, so P-R separations varying from 8 to 12 cm<sup>-1</sup> are observed. These spacings are, however, consistent with our conclusion that IMCP exists solely in the gauche conformation.

Since we were easily able to observe the presence of 2% *cis* conformers in BMCP,<sup>3</sup> we suspect that with the sensitivity of our vibrational spectroscopic techniques, the presence of 1/2–1% of a minor conformer could be detected. Thus, our results for IMCP would imply that, if a *cis* conformation of this molecule is indeed stable, it lies at least 2.3 kcal/mol (1% sensitivity) or 2.7 kcal/mol (1/2% sensitivity) higher in energy than the observed gauche rotamer.

*Epiiodohydrin.* Contrary to the spectral results for IMCP, the spectra of EIH show numerous instances of conformer multiplets. For example, the gas-phase infrared spectrum contains nine "extra" Q branches which are not attributable to fundamental vibrations or simple combination bands. Two of the extra Q branches of EIH are seen in the gas-phase (IR) C–H stretching region (Figure 5), which we have previously demonstrated to be conformationally sensitive in the other epihalohydrins and (halomethyl)cyclopropanes.<sup>1–4</sup> Whereas IMCP, which has only one (gauche) conformer, exhibits only single Q branches in this region, EIH displays a prominent Q-branch doublet at 3060 and 3056 cm<sup>-1</sup> and a weaker pair at 3032 and 3026 cm<sup>-1</sup>. This type of behavior suggests a gas-phase equilibrium of at least two conformers for EIH.

Additionally, the liquid-phase Raman spectrum of EIH exhibits ten conformer doublets wherein one member of each doublet vanishes when the liquid-phase sample is solidified and annealed. Six of these doublets also appear in the liquid-phase infrared spectrum. The ten Raman doublets occur at 1433/1424, 1394/1385, 1133/1141\*, 1021/1043\*, 940/914\*, 843/862\*, 817/827\*, 595/605, and 395/423 cm<sup>-1</sup>, where the peak listed first is the one remaining in the solid phase and the starred doublets

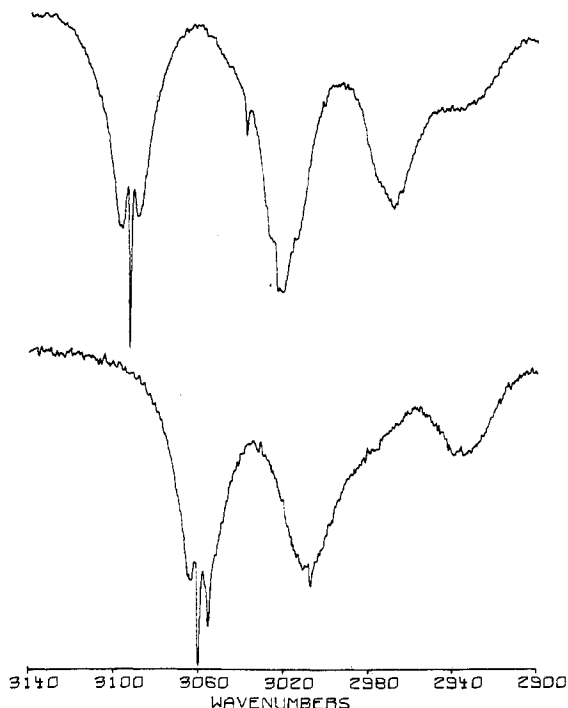


Figure 5. Fourier transform infrared gas-phase spectra in the C–H stretching region of (iodomethyl)cyclopropane (upper trace) and epiiodohydrin (lower trace).

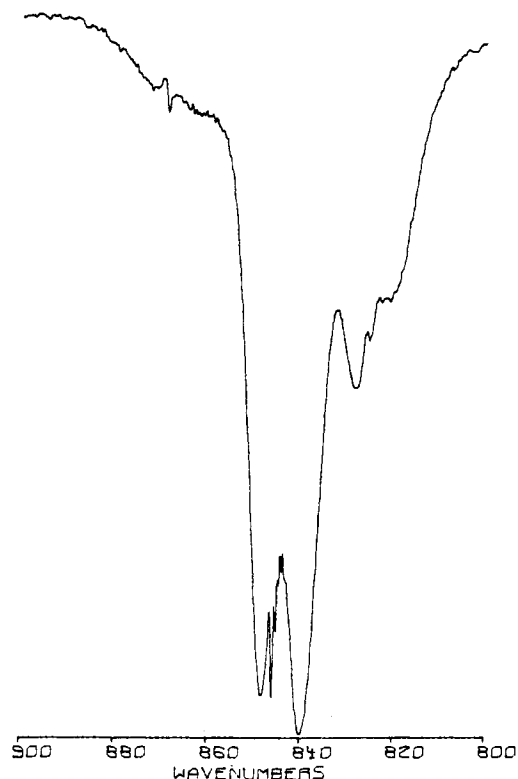


Figure 6. Fourier transform infrared gas-phase spectrum of epiiodohydrin between 800 and 900 cm<sup>-1</sup>.

are those which are coincident with infrared doublets.

By analogy with our previous results for EFH,<sup>1</sup> ECH<sup>2</sup>, and EBH<sup>3</sup> and by comparison with previous studies on EIH,<sup>7,8</sup> it is possible to account for the observed spectral features of EIH on the basis of a two-conformer equilibrium where gauche-1 (more polar) and gauche-2 (less polar) rotamers coexist in fluid phases. In the solid phase, we observe peaks attributable to the gauche-1 conformer only. Under none of our experimental conditions were

we ever able to obtain a solid-phase spectrum of gauche-2 EIH. Similarly, there were no peaks in any spectrum which could be confidently identified with a third, cis, conformer of EIH. Nevertheless, we should mention that the three bands observed in the 800–900-cm<sup>-1</sup> region of the gas-phase FT-IR spectrum of EIH (see Figure 6) could possibly be interpreted in terms of a three-conformer equilibrium. The three observed A-type band contours could possibly be assigned as  $\nu_{17}$  (the antisymmetric ring deformation) for *cis*-EIH (at 868 cm<sup>-1</sup>), gauche-1 EIH (at 846 cm<sup>-1</sup>), and gauche-2 EIH (at 825 cm<sup>-1</sup>). However, we prefer the present assignment, which attributes the 868- and 846-cm<sup>-1</sup> bands to  $\nu_{17}$  of the gauche-2 and gauche-1 conformers of EIH, respectively, and the 825-cm<sup>-1</sup> band to  $\nu_{18}$  (the symmetric ring deformation) of gauche-1 EIH (with  $\nu_{18}$  for gauche-2 EIH either masked by another of these bands or too weak to be observed). This latter assignment is much more consistent with the observed liquid-phase data for EIH than is the former. Thus, our results point to a gauche-1/gauche-2 equilibrium mixture for fluid phases of EIH, with only the gauche-1 conformer remaining in the solid phase.

In order to establish which of these two conformers is the more stable, we have carried out measurements of the relative intensity ratios of the ten liquid-phase Raman conformer doublets at four different temperatures (between 25 and -74 °C). Of these ten doublets, the only one which was suitably intense and sufficiently resolved from interference from adjacent peaks was the doublet at 940/914 cm<sup>-1</sup>. A linear regression/least-squares slope of a van't Hoff plot of the natural logarithm of the relative intensity ratio of these two peaks vs. reciprocal temperature yields an enthalpy difference between the gauche-1 and gauche-2 conformers of 0.50 ± 0.05 kcal/mol, with the gauche-1 form being the more stable, in spite of the fact that the 940-cm<sup>-1</sup> peak (gauche-1) is *less* intense than the 914-cm<sup>-1</sup> peak (gauche-2). This latter fact points out the potential error in deducing conformer stabilities from the intensities of a single conformer doublet at a single temperature. Variable-temperature experiments must be performed to extract this information. The temperature behavior of the 1021/1043-, 843/862-, and 817/827-cm<sup>-1</sup> doublets yields  $\Delta H$  values between 0.2 and 0.3 kcal/mol but with rather large dispersions. These data serve to emphasize the low value of the enthalpy difference between conformers in EIH, but we believe the 0.50 kcal/mol value for  $\Delta H$  to be the most reliable. It is also in excellent agreement with the  $\Delta H$  value reported by Charles et al.<sup>8</sup> (0.56 ± 0.04 kcal/mol) from their *infrared* study of the same conformer doublet.

In contrast to the conclusions reached by Charles and co-workers,<sup>8</sup> however, we believe that in the gas phase the gauche-1 conformer of EIH is also the more stable form. There are three gas-phase infrared conformer doublets (at 1130/1145, 941/927, and 846/868 cm<sup>-1</sup>) which correspond to liquid-phase infrared conformer doublets. In each case, the *weaker* gas-phase peak of the doublet corresponds to the liquid-phase peak<sup>8</sup> identified with the gauche-2 conformer (since it vanishes in the solid phase). Thus, by "tracking" peaks associated with the gauche-1 conformer from the solid through the liquid to the gas and by "tracking" the gauche-2 peaks from the liquid to the gas, we conclude that since *all three* gauche-2 peaks of these gas-phase doublets are weaker than their gauche-1 counterparts, the gauche-2 conformer is less populous (i.e., less stable) in the vapor phase as well as in the liquid phase. As mentioned above, there is a danger inherent in drawing such a conclusion based on a single-temperature measurement. However, we believe that for all three doublets to have the more populous conformer giving rise to the weaker peak in each doublet would be a very unfortunate and unlikely possibility. Thus, we feel justified in our conclusion that the gauche-1 conformer of EIH is the more stable form in all three states of matter.

From the  $\Delta H$  value of 0.50 kcal/mol, a Boltzmann population calculation yields the result that approximately 70% of EIH molecules at room temperature are in the gauche-1 arrangement and 30% are in the gauche-2 form. Assuming the same sensitivity for our techniques as we did for IMCP, it is possible to estimate the lower limit of the enthalpy difference between the gauche-1

and *cis* (if indeed stable) conformers of EIH to be 2.5 kcal/mol (1% sensitivity) or 2.9 kcal/mol (1/2% sensitivity).

## Discussion

The structural results for EIH and IMCP are quite similar—neither compound exhibits a *cis* conformation. This is certainly a consequence of the large steric hindrance associated with situating the iodine atom "over" the three-membered ring, where it can interact unfavorably with either one (EIH) or two (IMCP)  $\beta$ -ring hydrogen atoms. Apparently, this steric crowding problem in these two iodides is severe enough to destabilize the *cis* conformer of EIH and IMCP substantially when compared to the *cis* conformers of the other epihalohydrins and (halomethyl)cyclopropanes.<sup>1-4</sup>

In EIH, like the other three epihalohydrins, the gauche-1 conformation is more stable than the gauche-2 conformer. This results from the gauche effect,<sup>5</sup> which states that there is a polarizability/induced polarizability attraction which can overcome the dipole-dipole repulsion associated with gauche arrangements of polar bonds (and lone-electron pairs) and which can lead to a net stabilization of gauche conformations.

It is perhaps interesting to note that the room-temperature population of the gauche-1 conformer of ECH, EBH, and EIH remains virtually constant at approximately 70%, even though the physical and chemical properties of the halogen atom are changing considerably. This near constancy of the gauche-1 rotamer abundance is perhaps fortuitous, however. In the ECH/EBH/EIH series, the amounts of *cis* conformers steadily decrease with the increasing steric effects of larger and larger halogen atoms, while the amounts of gauche-2 conformers increase at the expense of the *cis* conformers. A more realistic comparison of the stabilities of the gauche-1 conformers of ECH, EBH, and EIH is probably the enthalpy difference between the gauche-1 and gauche-2 conformations of these molecules. This  $\Delta H$  value increases from 0.7 to 0.8 kcal/mol from ECH to EBH. No doubt this increase results from a net stabilization of the gauche-1 conformer of EBH due to smaller dipole-dipole repulsions and, possibly, increased polarizability/induced polarizability attractions. For EIH, however, the gauche-1/gauche-2  $\Delta H$  value *decreases* to 0.5 kcal/mol. Since the gauche-2 conformer of EIH is unlikely to acquire any further stabilization by any obvious electronic factors, this implies that the gauche-1 conformer of this molecule suffers from a net destabilization probably associated with bringing the large iodine atom close enough to the ring oxygen atom to cause a repulsive interaction.

Finally, we can note that since the proportion of *cis* conformer in the (halomethyl)cyclopropane series (CMCP, BMCP, and IMCP) decreases almost linearly with increasing van der Waals radius of the halogen atoms, we can predict that (fluoromethyl)cyclopropane (FMCP) should contain approximately 11% *cis* conformer at room temperature, if this trend extends to the fluorine analogue. Therefore, a study of the vibrational spectra of FMCP should help to determine if the anomalously large *cis* conformer population of EFH (26%) results from some additional stabilization of this structure—like hydrogen bonding, which should be minimal for FMCP. We are currently planning such a project and hope to report on it in the future.

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**Registry No.** (Iodomethyl)cyclopropane, 33574-02-6; epiiodohydrin, 624-57-7.

**Supplementary Material Available:** Figures 7 and 8, showing the infrared spectrum of liquid IMCP and gas-phase FT-IR spectra of IMCP and EIH, and Tables IV and V, listing the observed vibrational frequencies and assignments for IMCP and EIH, respectively (10 pages). Ordering information is given on any current masthead page.