Structural Studies by Nuclear Magnetic Resonance. XXI. Conformational Analysis of Dichloroacetaldehyde and Dibromoacetaldehyde

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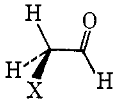
Abstract: The following conclusions were reached from the solvent and temperature dependence of the vicinal spin–spin coupling constants of dichloroacetaldehyde and dibromoacetaldehyde. (1) The data are consistent with a threefold barrier to rotation about the carbon–carbon bond. (2) In nonaromatic solvents whose dielectric constant is less than six, ΔG° for XIII $\rightleftharpoons$ XIV_a is positive, *i.e.*, the rotamer with the C–H bond eclipsing the carbonyl group is of lower energy than the others. (3) In nonaromatic solvents whose dielectric constant is higher than 7, ΔG° is negative. (4) Both free energies and enthalpies for XIII $\rightleftharpoons$ XIV_a vary over a range of about 2.5 kcal/mol, as the dielectric constant of the solvent varies from about 2 to 45.

In a recent publication,[1] we concluded that rotational isomerism about the carbon–carbon bond of chloroacetaldehyde and bromoacetaldehyde was best described in terms of a threefold barrier to rotation, with ΔH° for I $\rightleftharpoons$ II ranging from −300 cal/mol (chloroacetaldehyde) and 0 cal/mol (bromoacetaldehyde) in the least polar solvent *trans*-decalin, to −1500 cal/mol (chloroacetaldehyde) and −700 cal/mol (bromoacetaldehyde) in the most polar solvents formamide and dimethyl sulfoxide. Several other compounds containing a single halogen atom at the α-carbon have also been found to exhibit a threefold barrier to rotation about the sp^2–sp^3 carbon–carbon bond. For example, ΔH° for III $\rightleftharpoons$ IV is −560 cal/mol, −500 cal/mol and 0 cal/mol for ethyl fluoroacetate, chloroacetate, and bromoacetate, respectively;[2] it is −1000 cal/mol and −1900 cal/mol for bromoacetyl chloride and bromoacetyl bromide;[3] and it is −100 cal/mol, +100 cal/mol, and over +100 cal/mol, respectively, for 3-fluoropropene,[4,5] 3-chloropropene,[6] and 3-bromopropene.[7] Although in most cases the data have been interpreted in terms of perfectly eclipsing conformations, *i.e.*, dihedral angles of zero between planes HCC and CCZ in III and between planes XCC and CCZ in IV, for chloroacetyl chloride[8] and bromoacetyl chloride[3] a dihedral angle of 30° (V) for III best agrees with the experimentally determined vibrational frequencies. It was pointed out[1] that in cases where the assignments were made from nmr studies such distinctions in dihedral angles could not be made.



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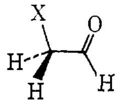

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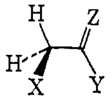

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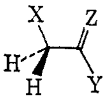

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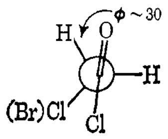
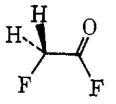


V

The only related α-substituted halo compound, where a twofold barrier to rotation about the sp^2–sp^3 carbon–carbon bond has been found,[9] is fluoroacetyl fluoride, whose ΔH° for VI $\rightleftharpoons$ VII is −910 cal/mol.



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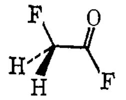
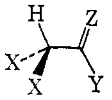


VII

The analogous dihalo compounds differ from the monohalo compounds in two respects. (a) The ΔH° values for VIII $\rightleftharpoons$ IX are much more positive than the corresponding ones for III $\rightleftharpoons$ IV. In all cases the more stable rotamer is the one with the carbon–hydrogen bond eclipsing the double bond. For example, ΔH° (VIII $\rightleftharpoons$ IX) for dichloroacetyl chloride[10] is +200 cal/mol, it is +500 to +1400 cal/mol for 3,3-difluoropropene[5] and +800 cal/mol for 3,3-dichloropropene.[6] (b) The ethyl dihaloacetates, in contrast to the ethyl monohaloacetates, exhibit twofold barriers to rotation, with ΔH° for X $\rightleftharpoons$ XI being +25 cal/mol and 0 cal/mol for ethyl difluoroacetate and ethyl dichloracetate, respectively.[2]



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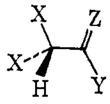

IX

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[2] T. L. Brown, *Spectrochim. Acta*, **18**, 1615 (1962).

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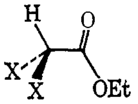

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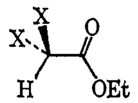
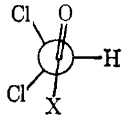


XI

From a comparison of the infrared carbonyl stretching frequencies of acetaldehyde, chloroacetaldehyde, dichloroacetaldehyde, and trichloroacetaldehyde, Bellamy and Williams[11] concluded that dichloroacetaldehyde exists, in both gas and liquid phase, essentially in one conformation, whose probable structure is XII.



XII

We wish to discuss in this paper the conformational analysis of dichloroacetaldehyde and dibromoacetaldehyde.

Results

Spin-Spin Coupling Constants. In Table I are summarized the vicinal spin-spin coupling constants between the aldehydic and methine protons of dichloroacetaldehyde and dibromoacetaldehyde in 2.5-4% solutions in several solvents. All values are averages of seven to ten measurements with a precision of ±0.03 cps. To ensure internal consistency and accuracy, values were always checked against those of acetaldehyde; 2.85, 2.88, and 2.90 cps at 36, 0, and −30°, respectively.[12]

Table I. Vicinal Spin-Spin Coupling Constants[a] of Dichloroacetaldehyde and Dibromoacetaldehyde

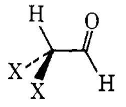
	J_{HH}, cps	
Solvent[b]	Dichloro-acetaldehyde	Dibromo-acetaldehyde
$CH_3(CH_2)_3CH_3$	4.65	5.65
Cyclohexane	4.50	5.56
trans-Decalin	4.40	5.47
CCl_4	4.35	5.36
$CHCl_3$	3.80	4.82
CH_2Br_2	3.30	4.27
CH_2Cl_2	3.35	4.25
CH_3COCH_3	1.90	3.08
$(CH_3)_2NCHO$	1.35	3.47
CH_3CN	1.30	2.89
$(CH_3)_2SO$	1.10	2.17
C_6H_6	3.00	4.16
$C_6H_5CH_3$	3.10	4.24
C_6H_5CN	2.10	3.22
$C_6H_5NO_2$	2.30	3.35
Neat	2.90	3.90

[a] Values at 36 ± 2°. [b] 2.5-4% solutions.

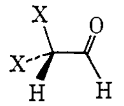
The coupling constants of the dihaloacetaldehydes are strongly dependent on the dielectric constant of the medium, decreasing sharply with increase of the dielectric constant of the solvent. For example, for dichloroacetaldehyde and dibromoacetaldehyde, respectively, they are 4.65 and 5.65 cps in the low dielectric constant solvent pentane ($\epsilon \sim 1.8$), and 1.10 and 2.17 cps in the high dielectric constant dimethyl sulfoxide ($\epsilon \sim 45$). Furthermore, in the low dielectric constant solvents, they are large when compared to coupling constants of other simple aldehydes.[1,13] The only other saturated aldehydes, whose coupling constants are large,[13] are di-*t*-butylacetaldehyde (J_{HH} = 6.0 cps) and cyclopropanecarboxaldehyde (J_{HH} = 5.75 cps). The former was found[13] to exist essentially in conformation VIII, and the latter in over 85% in this conformation. When compared in the same solvent, the coupling constants of dibromoacetaldehyde are larger than those of dichloroacetaldehyde. The same was true with the corresponding monohaloacetaldehydes.[1]

Tables II and III demonstrate the effect of temperature on the vicinal coupling constants, J_{HH}, of dichloroacetaldehyde and dibromoacetaldehyde, respectively. In both cases, increase of temperature causes the couplings observed in the low dielectric constant solvents to decrease, and those observed in the high dielectric constant solvents to increase. When the couplings of dibromoacetaldehyde in the various solvents are plotted against temperature, the lines converge toward a temperature independent J_{HH} value of about 4.5 cps. Similar treatment of the data of dichloroacetaldehyde yields a value of about 3.4 cps.

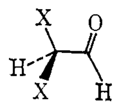
Treatment of Data. The data summarized in Tables I-III can be interpreted in terms of a threefold barrier to rotation about the carbon-carbon single bond, with XIII and XIV being the equilibrium configurations of the two dihaloacetaldehydes. Assuming $J_t > J_g$, where J_t and J_g are the *trans* and *gauche* vicinal coupling constants, respectively, we deduce that XIII is more stable than XIV_a (or XIV_b) in solvents in which the coupling decreases with increasing temperature, and less stable in solvents in which it increases with increasing temperature.



XIII



XIVa



XIVb

Rotamer populations and free energy differences, $\Delta G°$, between individual rotamers can be calculated, respectively, from eq 1 and 2, where p is the fractional

$$J_{\text{obsd}} = pJ_t + (1 - p)J_g \tag{1}$$

$$\Delta G°_{\text{XIII} \rightleftharpoons \text{XIV}_a} = RT \ln {}^1/_2(J_t - J_{\text{obsd}})/(J_{\text{obsd}} - J_g) \tag{2}$$

population of XIII and $(1 - p)$ that of XIV (a + b). The corresponding ethalpy differences, $\Delta H°$, can be calculated from plots of log K_{eq} *vs.* $1/T$, where K_{eq} is given by eq 3. Evaluation of these quantities requires

$$K_{eq} = (1 - p)/2p \tag{3}$$

knowledge of the parameters J_t and J_g. These parameters can be estimated as follows.

Equation 4 relates the experimental coupling constant

$$J_{av} = {}^1/_3(J_t + 2J_g) \tag{4}$$

of the two dihaloacetaldehydes to J_t and J_g, either when the three rotamers XIII, XIV_a, and XIV_b are equally

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Table II. Temperature Dependence of the Vicinal Spin–Spin Coupling Constant of Dichloroacetaldehyde

Solvent[a]	J_{HH}, cps								
	−30°	−15°	0°	15°	36°	50°	70°	90°	110°
Cyclohexane			4.52	4.46	4.34	4.33	4.28		
trans-Decalin	4.41	4.38	4.37	4.34	4.25	4.18	2.06	4.03	3.99
C_6H_5Cl	3.16	3.25	3.29	3.32	3.28	3.37	3.38	3.39	3.38
$C_6H_5CH_3$	2.74	2.90	2.98	3.08	3.09	3.25	3.26	3.28	3.29
C_6H_6			2.89	2.93	3.04	3.19	3.21		
C_6H_5CN		1.69	1.81	1.98	2.04	2.19	2.29	2.35	2,38
$(CH_3)_2NCHO$	0.90	1.04	1.13	1.19	1.28	1.41	1.50	1.60	1.70

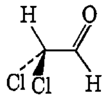
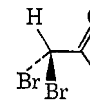
[a] 5% solutions.

Table III. Temperature Dependence of the Vicinal Spin–Spin Coupling Constant of Dibromoacetaldehyde

Solvent[a]	J_{HH}, cps						
	−30°	0°	15°	36°	60°	70°	100°
trans-Decalin	5.94	5.73		5.43		5.32	5.15
$CHCl_3$	5.26	4.98	4.95	4.77			
C_6H_5Cl	4.78	4.55		4.46		4.77	4.49 (4.48)[b]
$C_6H_5CH_3$	4.26	4.38		4.41	4.48	4.48	
CH_2Br_2	4.02			4.11		4.14	
$(CH_3)_2NCHO$	3.15	3.35		3.51		3.59	
CH_3CN	2.56	2.69		2.94		3.09	

[a] 5% solutions. [b] Value at 130°.

Table IV. Solvent Dependence of the Relative Rotamer Populations[a] of Dichloroacetaldehyde and Dibromoacetaldehyde

Solvent	, %	, %
$CH_3(CH_2)_3CH_3$	48	47
Cyclohexane	47	46
trans-Decalin	45	45
CCl_4	45	43
$CHCl_3$	38	37
CH_2Br_2	33	31
CH_2Cl_2	33	30
CH_3COCH_3	16	17
$(CH_3)_2NCHO$	10	21
CH_3CN	9	15
$(CH_3)_2SO$	7	7
C_6H_6	29	29
$C_6H_5CH_3$	30	30
C_6H_5CN	19	19
$C_6H_5NO_2$	21	20
Neat	27	26

[a] All values calculated for 36°.

Table V. Solvent Dependence of the Free Energy Difference, $\Delta G°$, between Rotamers of the Dihaloacetaldehydes

Solvent[a]	$\Delta G°$, cal/mol, for XIII $\rightleftharpoons$ XIV_a Dichloro-acetaldehyde	Dibromo-acetaldehyde
$CH_3(CH_2)_3CH_3$	+380	+340
Cyclohexane	+350	+320
trans-Decalin	+300	+290
CCl_4	+300	+260
$CHCl_3$	+120	+100
CH_2Br_2	−15	−75
CH_2Cl_2	−14	−80
CH_3COCH_3	−590	−550
$(CH_3)_2NCHO$	−930	−370
CH_3CN	−1000	−650
$(CH_3)_2SO$	−1200	−1200
C_6H_6	−120	−120
$C_6H_5CH_3$	−100	−90
C_6H_5CN	−340	−480
$C_6H_5NO_2$	−390	−420
Neat	−190	−210

[a] 5% solutions.

populated, or at the state of free rotation—usually at high temperatures—about the carbon–carbon bond. The experimental coupling constants satisfying eq 4 are 3.4 cps (dichloroacetaldehyde) and 4.5 cps (dibromoacetaldehyde). Since the lowest experimentally measured coupling constant of dichloroacetaldehyde is 0.9 cps (Table II), J_g of dichloroacetaldehyde must be equal to or smaller (in absolute value) than 0.9 cps. If J_t and J_g have the same sign, then from eq 4 we calculate: $J_g < 0.9$ cps and $J_t > 8.4$ cps, if they have opposite signs, $J_g < 0.9$ cps and $J_g > 12.0$ cps. We feel that a reasonable set (estimated $J_g \sim 0.5$) of J_t and J_g would be 9.1 cps and 0.5 cps, respectively (assume same sign).

Similar treatment of the data of dibromoacetaldehyde yields: $J_g < 2.17$ cps and $J_t > 9.16$ cps, if the signs are the same; and $J_g < 2.17$ cps and $J_t > 17.84$ cps, if the signs are opposite. Again a reasonable set (estimated $J_g \sim 1.6$) of J_t and J_g would be 10.3 and 1.6 cps (assume same sign).

Table IV shows the effect that solvent polarity has on the relative population of the rotamers that were calculated from eq 1. The values given were calculated by using our own best estimates of the coupling constants. Use of the other sets of coupling constants affects most of these values by less than ±10%.

In Table V are summarized the free energy differences, calculated from eq 2, between rotamers XIII and XIV_a (or XIV_b). In low dielectric constant solvents, $\epsilon < 5$, these values are positive, *i.e.*, XIII (less polar rotamer) is more stable than XIV_a (more polar rotamer). In solvents of dielectric constant higher than 9 (ϵ of methylene chloride is about 9), $\Delta G°$'s are negative, *i.e.*, XIV_a is more stable than XIII. The cross-over appears to occur in a dielectric constant of about six. For example, the dielectric constants of chloroform and methylene bromide are 4.8 and 7.4, respectively. The values in the aromatic solvents, especially benzene ($\epsilon \sim 2.3$) and toluene ($\epsilon \sim 2.4$), are anomalous, *i.e.*, they are negative instead of positive.

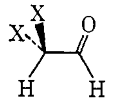
In Table VI are summarized the enthalpy differences calculated from reasonably linear plots of log K *vs.* $1/T$ between rotamers XIII and XIV. In the low dielectric constant saturated hydrocarbon solvents, the ethalpies and free energies are about equal. In the high dielectric constant solvents, the enthalpies are appreciably more negative than the free energies, the divergence being greater for dichloroacetaldehyde than dibromoacetaldehyde. This same trend was also found in the thermodynamic parameters of the monohaloacetaldehydes.[1]

Table VI. Enthalpy Differences, $\Delta H°$, between Rotamers of Dihaloacetaldehydes

	$\Delta H°$, cal/mol, for XIII $\rightleftharpoons$ XIV	
Solvent[a]	Dichloro-acetaldehyde	Dibromo-acetaldehyde
Cyclohexane	+300	
trans-Decalin	+300	+500
$CHCl_3$		+500
C_6H_5Cl	0	0
CH_2Br_2		−100
C_6H_6	−450	
$C_6H_5CH_3$	−500	−200
C_6H_5CN	−1000	
$(CH_3)_2NCHO$	−1400	−500
CH_3CN		−800

[a] 5% solutions.

Consideration of Twofold Barrier to Rotation. In view of the finding that the rotational isomerism about the sp^2–sp^3 carbon–carbon bond of ethyl dihaloacetates is best described in terms of a twofold barrier to rotation,[2] we will considerer the interpretation of our results in terms of such a barrier, *i.e.*, in terms of XIII and XV as the minimum energy configurations of the two dihaloacetaldehydes. The relevant vicinal spin–spin coupling constants would now be J_t and J_c, where



XV

J_c is the *cis* coupling constant (XV). Equation 4 now assumes the form of eq 5.

$$J_{av} = {}^1/_2(J_t + J_c) \qquad (5)$$

As pointed out, the values of J_{av} of dichloroacetaldehyde and dibromoacetaldehyde are 3.4 and 4.5 cps, respectively. When these values are compared to those of acetaldehyde (2.85 cps), chloroacetaldehyde (2.5 cps), and bromoacetaldehyde (2.75 cps), which apply to eq 4, they are found to be disturbingly larger than substituent electronegativity effects on vicinal proton–proton coupling would have predicted.[14,15] On the basis of a threefold barrier to rotation, the J_{av} values of dichloroacetaldehyde and dibromoacetaldehyde should have been smaller than 2.5 and 2.75 cps, respectively. They best fit, therefore, eq 5, *i.e.*, a twofold barrier to rotation about the carbon–carbon bond.

Let us now assume that a twofold barrier to rotation pertains to dichloroacetaldehyde and dibromoacetaldehyde. Since the smallest experimentally observed coupling constant of dichloroacetaldehyde is 0.9 cps, J_c must be equal to or smaller than this value. From this and eq 5, J_t must be equal to or greater than 5.9 cps, if the J_c and J_t have the same sign; and equal to or greater than 7.7 cps, if they have opposite signs. Analogous treatment of the data of dibromoacetaldehyde yields: $J_c < 2.17$ cps and $J_t > 6.83$ cps, if they have the same sign; and $J_c < 2.17$ cps and $J_t > 11.17$ cps, if they have opposite signs. We are now faced with the question of whether such relative values of J_t and J_c, especially those of dichloroacetaldehyde, are reasonable. From valence-bond theory, the contact interaction term describing the dihedral-angle dependence of vicinal proton–proton coupling is approximated[16] by eq 6. The relative magnitude of J_t and J_c depends on the values of A, B, and C. For

$$J_{HH} = A + B\cos\phi + C\cos 2\phi \qquad (6)$$

ethane (both carbons sp^3 and C–C distance 1.54 Å), $A = 4.22$, $B = -0.5$, and $C = 4.5$ cps, the treatment predicts $J_t = 9.22$ cps and $J_c = 8.22$ cps. For ethylene (both carbons sp^2 and C–C distance 1.35 Å), it predicts $J_t = 11.9$ cps and $J_c = 6.1$ cps. Experimentally determined J_t and J_c values of ethylenic compounds agree fairly well, if not always in absolute value at least in the relative magnitude of the two coupling constants, with the predicted values. There are no experimental J_t and J_c values for systems with one carbon atom sp^2 hybridized and the other sp^3 with which to compare our values. Some values are available for systems with both carbon atoms sp^2 hybridized, where the carbon–carbon length is between those of ethane and ethylene. The J_t of 1,3-butadiene[17] and J_c (single bond) of 1,3-cyclohexadiene[18] are 10.41 and 5.14 cps, respectively. For α,β-unsaturated aldehydes (malondialdehyde and acetylacetaldehyde) the analogous coupling constants have been estimated[19] by nmr to be about 7.7 and 2.8 cps, respectively. If one were to consider that the 0.9 cps value of J_c of dichloroacetaldehyde is an upper limit, as it is based on the assumption (incorrect) that at −30°, in N,N-dimethylformamide, dichloroacetaldehyde exists exclusively in conformation XV, then one would conclude that a threefold rather than a twofold barrier to rotation best fits the experimental results.

The discussion just concluded, having left unanswered the question of whether a twofold or a threefold barrier to rotation best fits the experimental results, cogently illustrates the major weakness of nmr in rendering an unambiguous verdict in such cases of rotational isomerism. Irrespective, however, of whether one chooses to interpret the results in terms of a two- or a threefold barrier to rotation, the conclusion that XIII is the most stable rotamer in the low dielectric constant solvents,

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Karabatsos, et al. / Conformational Analysis of Dichloro- and Dibromoacetaldehyde

Table VII. Comparison of Enthalpies[a] between Monohalosubstituted and Dihalosubstituted Systems

No.	System	$\Delta H_1° - \Delta H_2°$, cal/mol[b]	Ref
1	CH_2ClCHO *vs.* $CHCl_2CHO$	−600	1, this work
2	CH_2BrCHO *vs.* $CHBr_2CHO$	−500	1, this work
3	CH_2FCO_2Et *vs.* CHF_2CO_2Et	−500	2
4	CH_2ClCO_2Et *vs.* $CHCl_2CO_2Et$	−500	2
5	$CH_2ClCOCl$ *vs.* $CHCl_2COCl$	*Ca.* −1200[c]	10, 8
6	$CH_2FCH{=}CH_2$ *vs.* $CHF_2CH{=}CH_2$	−600 to −1500	4, 5
7	$CH_2ClCH{=}CH_2$ *vs.* $CHCl_2CH{=}CH_2$	−700	6

[a] The enthalpies are either in the gas phase or in low dielectric constant solvents. [b] For $\Delta H_1°$ and $\Delta H_2°$ see text. [c] The enthalpy for the monohalo compound was estimated from the data of ref 8.

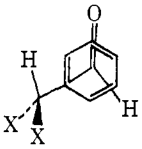
and the least stable rotamer in the high dielectric constant solvents, would remain valid.

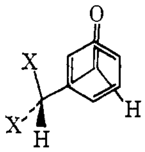
In order to further deter any overinterpretation of our results or any misconstruction of our conclusions, we wish to reemphasize[1,13] that, although we draw rotamers XIII and XIV as perfectly eclipsing, the nmr technique gives no accurate estimate of the dihedral angles. It is quite possible that XIV (assuming a threefold barrier to rotation) may be better represented as XII, with a dihedral angle of 30° instead of 0°. Such an angle was found to best fit the observed vibrational frequencies of the various haloacetyl halides.[3,8,10]

Discussion

Effect of Solvent on Rotamer Stabilities. The increase of the relative stability of rotamer XIV, reflected in the data of Tables IV–VI, with increase of the dielectric constant of the solvent, is reasonable, in view of the higher dipole moment of XIV over XIII. As pointed out,[1] this large difference between the dipole moments of the two rotamers is also responsible for $\Delta H°$ values being more negative than the corresponding $\Delta G°$ values in solvents of high dielectric constant, as such highly associated solvents suffer a large decrease of dielectric constant with increasing temperature. For this reason, in solvents of high dielectric constant, $\Delta G°$ values reflect better the enthalpy differences between highly polar rotamers whose dipole moments are quite different, than do the calculated $\Delta H°$ values. Indeed, the only meaningful $\Delta H°$ values calculated for such rotamers by the temperature dependence of vicinal spin–spin coupling constants are those in solvents of low dielectric constant with very weak solute–solvent interactions. Since in cyclohexane and *trans*-decalin $\Delta H° \simeq \Delta G°$, then $\Delta S°$ between the rotamers of the dihaloacetaldehydes must be about zero. The same was true for monohaloacetaldehydes.

The inadequacy of the solvent dielectric constant effect to explain all the changes observed in the $\Delta G°$ values has been already mentioned with references to aromatic solvents, particularly benzene and toluene. On the basis of the low dielectric constants of these two solvents, 2.3 and 2.4 for benzene and toluene, respectively, XIII should have been more stable than XIV_a, rather than the reverse that was experimentally found. This reversal is best interpreted in terms of solute–solvent interactions that destabilize XIII with respect to XIV. Some sort of stereospecific association,[20] such as pictured in XIII′ and XIV′, would rationalize the


XIII′


XIV′

results in terms of stronger nonbonded repulsions between benzene and halogen in XIII′ than in XIV′.

Comparison of Results with Those of Other Systems. The conclusion drawn from infrared studies[11] that dichloroacetaldehyde exists essentially in one minimum energy conformation, probably XII, is incompatible with the nmr results. In solvents of low dielectric constant both XIII and XIV (or XII) are present in about equal concentrations.

In comparing monochloroacetaldehyde[1] with dichloroacetaldehyde, we find that the rotamer with the hydrogen eclipsing the carbonyl group is the one of lowest energy (in saturated hydrocarbon solvents) in the case of dichloroacetaldehyde, but not in the case of monochloroacetaldehyde, *i.e.*, $\Delta H_1° - \Delta H_2°$ is negative, where $\Delta H_1°$ and $\Delta H_2°$ are defined as shown.

$$\mathrm{III} \xrightleftharpoons{\Delta H_1°} \mathrm{IV}$$

$$\mathrm{VIII} \xrightleftharpoons{\Delta H_2°} \mathrm{IX}$$

For comparison purposes, we have summarized in Table VII several $\Delta H_1° - \Delta H_2°$ values that refer either to the gas phase or to equilibria in solvents of low dielectric constant. In all cases the $\Delta H_1° - \Delta H_2°$ values are negative and of comparable magnitude.

In the case of halopropenes, entries 6 and 7, these differences were attributed[5,6] to less favorable van der Waals attractions between halogen and hydrogen of the olefinic methylene group in IX than in IV, on account of the C–X bond being less polar in IX than in IV. This kind of explanation cannot be applied very well to entries 1–5, as it would lead to opposite results, unless the arguments were applied only to III and VIII. A more attractive explanation for entries 1–5 would be to invoke electrostatic dipole–dipole interactions that favor III over IV and VIII over IX. The difference between the dipole moments of VIII and IX being much larger than that between III and IV, the dipole–dipole interactions would lead to greater energy differences between VIII and IX than between III and IV.

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(20) For a general discussion of stereospecific association between aromatic solvents and solutes related to carbonyl compounds see G. J. Karabatsos and R. A. Taller, *Tetrahedron*, **24**, 3923 (1968), and references cited therein.

Experimental Section

Dibromoacetaldehyde was prepared according to the procedure of Shchukina.[21] The following is a typical preparation. To 44 g of freshly distilled acetaldehyde maintained at 0° and stirred with a magnetic stirrer was added dropwise 80 g of bromine. At the end of the addition, the reaction mixture was allowed to warm up to room temperature. After dropwise addition of another 80 g of bromine, the reaction mixture was stirred for 20–25 hr. The resultant two layers were separated and the upper layer was discarded. Prepurified nitrogen was bubbled through the lower layer for about 1 hr in order to purge it of any hydrogen bromide present. After three vacuum distillations (3 mm of Hg, 26°) pure dibromoacetaldehyde was obtained.

Commercially available dichloroacetaldehyde was purified by preparative gas chromatography prior to use.

Nmr spectra were determined at 60 Mc on a Model A-60 spectrometer (Varian Associates, Palo Alto, Calif.), equipped with a variable-temperature probe and a V-6040 variable-temperature controller. Temperatures were controlled to ±2°.

Acknowledgment. We thank the National Science Foundation for generous financial support. We also thank Dr. N. Hsi for his assistance in the studies of dichloroacetaldehyde.

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Structural Studies by Nuclear Magnetic Resonance. XXII. Conformational Analysis of Glycidaldehyde, Phenoxyacetaldehyde, Methoxyacetaldehyde, and Methylmercaptoacetaldehyde

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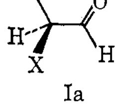
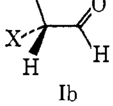
Received September 11, 1968

Abstract: The vicinal spin–spin coupling constants between aldehydic and α-protons of methoxyacetaldehyde, phenoxyacetaldehyde, methylmercaptoacetaldehyde, glycidaldehyde, and cyclopropanecarboxaldehyde were studied at 60 Mc as a function of temperature and solvent. The following conclusions were drawn. (1) A threefold barrier to rotation about the carbon–carbon bond best fits the data from the first three compounds. No unambiguous decision could be made regarding the analogous barrier to rotation of the last two compounds. (2) The most stable rotamer of methoxyacetaldehyde and phenoxyacetaldehyde is the one where the C–X bond eclipses the carbonyl group, and the most stable rotamer of the other three compounds is the one where the C–H bind eclipses the carbonyl. (3) The free energy and enthalpy values for $I \rightleftharpoons II$ ($X = OCH_3$, OC_6H_5) are strongly solvent dependent, being much more negative in solvents of high dielectric constant. Those of methylmercaptoacetaldehyde and glycidaldehyde are solvent insensitive. (4) Whereas the cyclopropyl group acts as an electron donor, the oxirane group acts as an electron withdrawer. This difference notwithstanding, the oxirane resembles more the cyclopropyl than it does the methoxy.

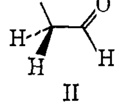
We have recently discussed the conformational analysis of chloro- and bromoacetaldehyde,[1] and of dichloro- and dibromoacetaldehyde.[2] As part of our program designed to probe into the nature of the factors controlling the relative stabilities of I and II, when X is a heteroatom, we have studied phenoxyacetaldehyde ($X = OC_6H_5$), methoxyacetaldehyde ($X = OCH_3$), and methylmercaptoacetaldehyde ($X = SCH_3$). Since there was some question from the nmr results[3] as to whether in the liquid phase cyclopropanecarboxaldehyde was best described in terms of a twofold barrier to rotation (III and IV as the minimum energy configuration), as found in the gas phase,[4] or in terms of a threefold barrier to rotation (III and V as the minimum energy configurations), we have studied this problem further. The obvious relation of glycidaldehyde to both systems under consideration, prompted us to study it, to see if a twofold (VI and VII) or a threefold (VI, VIII, and IX) barrier to rotation best describes this system.



Ia



Ib



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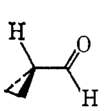

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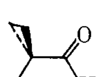
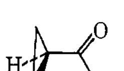
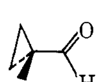


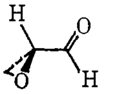
IV



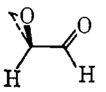
Va



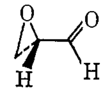
Vb



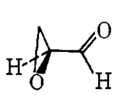
VI



VII



VIII



IX

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