Structural Studies by Nuclear Magnetic Resonance. XX. Conformational Analysis of Chloroacetaldehyde and Bromoacetaldehyde

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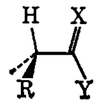
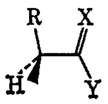
Abstract: From the temperature and solvent dependence of the vicinal spin-spin coupling constants of chloroacetaldehyde and bromoacetaldehyde the following conclusions were reached. (1) The data are best interpreted in terms of a threefold barrier to rotation about the carbon-carbon bond. (2) The most stable rotamer of these compounds is the one where the carbon-halogen bond eclipses the carbonyl group. (3) The free energy and enthalpy values for I $\rightleftharpoons$ II are strongly solvent dependent, being much more negative in solvents of high dielectric constant. For example, for chloroacetaldehyde and bromoacetaldehyde, respectively, they are -300 cal/mol and 0 cal/mol in saturated hydrocarbon solvents, and -1500 cal/mol and -700 cal/mol in such solvents as dimethyl sulfoxide and amides. The adequacies and inadequacies of the various explanations that have been invoked to rationalize the relative stabilities of rotamers I and II in several related systems are discussed.

In recent years we have addressed ourselves to the general problem of rotational isomerism about single bonds joining sp^2 to sp^3 hybridized carbon atoms,[1] with particular emphasis on the relative stabilities of I and II as a function of X, Y, and R. Our investigations established that in most cases nonbonded repulsions between vicinal groups played a minor role in determining the relative stabilities of the two rotamers. For example, in the case of aldehydes (X = O and Y = H), $\Delta H°$ for I $\rightleftharpoons$ II was -800 cal/mol and -500 cal/mole when R was methyl or isopropyl, respectively.[2] Out of the 800 cal/mol observed when R was methyl, nonbonded repulsions accounted for less than 200 cal/mol. Such repulsions became significant only when R was *t*-butyl, in which case I was favored over II by 250 cal/mol.



I



II

To probe further into the nature of the factors responsible for the relative stabilities of I and II, we undertook to investigate various aldehydes with one or two of their α-hydrogens having been replaced by a heteroatom function. Of special interest were chloroacetaldehyde and bromoacetaldehyde, as these compounds were good models on which to test the relative importance of nonbonded, dipole-dipole, and dipole-induced dipole interactions in determining the stabilities of I and II. Such interactions have been invariably invoked to explain the stabilities of I and II in compounds where at least R is a halogen atom. For example, in addition to electrostatic dipole-dipole interactions, nonbonded repulsions between R and Y in rotamer I of chloroacetone, chloroacetyl chloride, and N-methylchloroacetamide have been invoked to explain the different I/II ratios of these compounds.[3,4] The report[5] that chloroacetaldehyde exists essentially in conformation I, when taken in conjunction with the finding[3] that chloroacetone exists in both I and II, is certainly consistent with the view that nonbonded interactions between R and Y affect significantly the relative stabilities of I and II of chloroacetone.

Furthermore, these same factors have been invoked to correlate and interpret a large number of data[6] on the relative stabilities of the axial and the equatorial conformers of 2-halocyclohexanones. We felt that a comparison of the results obtained from acyclic systems with those obtained from cyclic systems might shed some light on this general problem.

We wish to discuss in this paper the conformational analysis of chloroacetaldehyde and bromoacetaldehyde.

Results

Spin-Spin Coupling Constants. In Table I are summarized the vicinal spin-spin coupling constants between the aldehydic and methylene protons of chloroacetaldehyde and of bromoacetaldehyde in 3-5% solutions in various 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.[7]

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(1) G. J. Karabatsos and R. A. Taller, *Tetrahedron*, **24**, 3923, (1968), and previous references cited therein.

(2) G. J. Karabatsos and N. Hsi, *J. Am. Chem. Soc.*, **87**, 2864 (1965).

(3) S. Mizushima, T. Shimanouchi, T. Miyazawa, I. Ichishima, K. Kuratani, I. Nakagawa, and N. Shido, *J. Chem. Phys.*, **21**, 815 (1953).

(4) S. Mizushima, T. Shimanouchi, I. Ichishima, T. Miyazawa, I. Nakagawa, and T. Araki, *J. Am. Chem. Soc.*, **78**, 2038 (1956).

(5) L. J. Bellamy and R. L. Williams, *J. Chem. Soc.*, 3465 (1958).

(6) (a) N. L. Allinger, J. Allinger, and N. A. LeBel, *J. Am. Chem. Soc.*, **82**, 2926 (1960); (b) N. L. Allinger, J. Allinger, L. A. Frieberg, R. F. Czaja, and N. L. Lebel, *ibid.*, **82**, 5876 (1960); (c) J. Allinger and N. L. Allinger, *Tetrahedron*, **2**, 64 (1958); (d) A. S. Kende, *Tetrahedron Letters*, No. 14, 13 (1959); (e) C. Y. Chen and R. J. W. LeFevre, *J. Chem. Soc.*, 3700 (1965); (f) Y. H. Pan and J. B. Stothers, *Can. J. Chem.*, **45**, 2943 (1967).

(7) R. J. Abraham and J. A. Pople, *Mol. Phys.*, **3**, 609 (1960); J. G. Powels and J. H. Strange, *ibid.*, **5**, 329 (1962).

Table I. Vicinal Spin-Spin Coupling Constants[a] of Chloroacetaldehyde and Bromoacetaldehyde

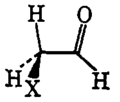
	J_{HH}, cps	
Solvent[b]	Chloro-acetaldehyde	Bromo-acetaldehyde
$CH_3(CH_2)_3CH_3$	2.17	
trans-Decalin	2.13	2.81
Cyclohexane	2.11	2.82
CCl_4	2.06	2.78
$CHCl_3$	1.78	2.62
CH_2Br_2	1.59	2.48
CH_2Cl_2	1.58	2.47
CH_3COCH_3	1.23	2.19
CH_3CN	1.09	2.06
$(CH_3)_2NCHO$	0.98	1.97
$(CH_3)_2SO$	0.83	1.81
H_2NCHO	0.81	1.80
C_6H_6	1.67	2.55
$C_6H_5CH_3$	1.68	2.54
C_6H_5Cl	1.65	2.54
C_6H_5CN	1.28	2.25

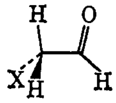
[a] Values at 36 ± 2°. [b] 3–5% solutions.

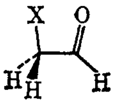
As the coupling constants of monosubstituted alkylacetaldehydes are smaller than that of acetaldehyde,[2] so are those of chloroacetaldehyde and bromoacetaldehyde. In contrast, however, to the coupling constants of the former compounds, which were essentially insensitive to solvent dielectric constant, those of the haloacetaldehydes decrease sharply with increase of the dielectric constant of the solvent. When compared in the same solvent, the coupling constants of bromoacetaldehyde are larger than those of chloroacetaldehyde.

Table II demonstrates the effect of temperature on the vicinal spin-spin coupling constants, J_{HH}, of chloroacetaldehyde and bromoacetaldehyde. The coupling constant of chloroacetaldehyde increases with increase in temperature in all solvents, the increase being more rapid in the solvents of high dielectric constant than in those of low dielectric constant. The coupling constant of bromoacetaldehyde increases in the high dielectric constant N,N-dimethylformamide, but is constant, about 2.75 cps, in the low dielectric constant *trans*-decalin.

Treatment of the Data. The data summarized in Tables I and II can be interpreted in terms of I and II as the equilibrium configurations of the monohaloacetaldehydes. Assuming $J_t > J_g$, where J_t is the *trans* coupling and J_g is the *gauche*, we deduce that the observed average vicinal coupling constants would be temperature independent if III_a, III_b, and IV were isoenergetic; they would decrease with increase in temperature, if III_a (or III_b) were more stable than IV; and they would increase with increase in temperature, if III_a were less stable than IV. From the temperature dependence of the spin-spin coupling constants we conclude: (a) In both low and high dielectric constant solvents, the most stable rotamer of chloroacetaldehyde is IV, *i.e.*, the one where the chlorine is *cis* to the carbonyl. (b) In the high dielectric constant solvents, the most stable rotamer of bromoacetaldehyde is also IV; and in the low dielectric constant solvents, such as *trans*-decalin, all three rotamers of bromoacetaldehyde are isoenergetic.


III_a


III_b


IV

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

$$J_{obsd} = p(J_t + J_g)/2 + (1 - p)J_g \qquad (1)$$

$$\Delta G° = -RT \ln [(J_t + J_g - 2J_{obsd})/(J_{obsd} - J_g)] \qquad (2)$$

population III ($III_a + III_b$) and $(1 - p)$ that of IV. Enthalpy differences, $\Delta H°$, between III and IV can be calculated either by solution of eq 2 to obtain $\Delta H°$, J_t, and J_g, or by assuming a $\Delta S°$ of zero for the equilibrium between rotamers and, therefore, equating $\Delta G°$ to $\Delta H°$, or from plots of log K_{eq} *vs.* $1/T$, where K_{eq} is given by eq 3.

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

If one were to choose not to solve eq 2 to obtain $\Delta H°$, J_t, and J_g, then calculation of rotamer populations, K_{eq}, and $\Delta H°$ requires knowledge of the parameters J_t and J_g. We have chosen to estimate J_t and J_g from the data.[8]

Equation 4 relates the experimental coupling constant

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

of the two haloacetaldehydes to J_t and J_g, either when the three rotamers III_a, III_b, and IV are equally populated, or, at least in terms of the absolute value of J_{obsd} at the state of free rotation—usually at very high temperatures—about the carbon-carbon bond. For bromoacetaldehyde, J_{obsd} of eq 4 is 2.75 cps, *i.e.*, the temperature-independent value in *trans*-decalin (Table II). The analogous value for chloroacetaldehyde is greater than 2.23 cps (highest value within increasing trend, Table II) and may be estimated to be about 2.5 cps from an extrapolation of the convergence of the curves obtained by plotting J_{obsd} *vs.* temperature. These values, when compared to the 2.85-cps value of the coupling constant of acetaldehyde, are certainly reasonable.

Having established the J_{obsd} value relating J_t and J_g according to eq 4, we can now set limits from the experimental results for J_t and J_g. For example, the lowest value observed for the coupling constant of chloroacetaldehyde is 0.60 cps (value in acetonitrile, at −30°). In absolute magnitude, J_g of chloroacetaldehyde must therefore be equal to or smaller than 0.6 cps. If J_t and J_g have the same sign, then from eq 4 and the 0.6 cps value we calculate: $J_g \leq 0.6$ cps and $J_t \geq 6.3$ cps; if they have opposite signs, $J_g \leq 0.6$ cps and $J_t > 8.7$ cps. Judging from the analogous coupling constants of acetaldehyde,[2] $J_g \simeq 0.5$ cps and $J_t \simeq$

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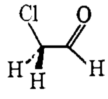
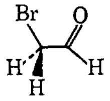
[8] Solution of eq 2 to give accurate values of $\Delta H°$, J_t, and J_g requires accurate spin-spin coupling constants and good temperature control. We feel that our coupling constants are sufficiently small to preclude their accurate measurement at high and low temperatures. Furthermore, the trust in the accuracy of the results from eq 2 is based on the implicit assumption that the potential minima are sharp enough to make contributions to the coupling constants by torsional oscillations insignificant. Such an assumption, however, is unwarranted and most probably incorrect.

Table II. Temperature Dependence of the Vicinal Spin–Spin Coupling Constants of Chloro- and Bromoacetaldehyde

Solvent[a]	−30°	−15°	0°	15°	36°	50°	60°	70°	80°	90°	100°	110°
	J_{HH}, cps, of chloracetaldehyde											
trans-Decalin	2.01		2.09		2.13			2.19			2.20	2.23[b]
Cyclohexane		2.06			2.10	2.13		2.17	2.18			
Chlorobenzene	1.34		1.61		1.74			1.88			1.95	1.98[c]
N,N-Dimethylformamide			0.71		1.02			1.18			1.30	
Acetonitrile	0.60		0.84		1.16		1.26		1.39			
	J_{HH}, cps, of Bromoacetaldehyde											
trans-Decalin		2.83	2.78		2.75	2.76		2.77		2.76		2.75
N,N-Dimethylformamide	1.48	1.65	1.75	1.81	1.93	2.06		2.08		2.09		

[a] 3–5% solutions. [b] Value at 130°. [c] Value at 120°.

Table III. Solvent Dependence of the Relative Rotamer Populations[a] of Chloroacetaldehyde and Bromoacetaldehyde

	, %			, %		
Solvent	A[b]	B[c]	C[d]	D[e]	E[f]	F[g]
trans-Decalin	44	46	41	32	30	31
Cyclohexane	45	47	42	32	29	31
CCl_4	47	49	43	33	32	31
$CHCl_3$	55	59	49	37	40	35
CH_2Br_2	61	65	53	41	47	38
CH_2Cl_2	61	66	53	42	48	38
CH_3COCH_3	72	78	61	50	63	42
CH_3CN	76	83	64	53	69	44
$(CH_3)_2NCHO$	79	87	66	56	74	46
$(CH_3)_2SO$	84	92	69	60	83	48
H_2NCHO	85	93	70	61	83	48
C_6H_6	58	63	51	39	44	36
C_6H_5Cl	59	63	52	40	44	37
C_6H_5CN	70	76	60	48	59	41

[a] All values calculated for 36°. [b] Coupling constants used: $J_t = 6.9$ and $J_g = 0.3$ cps (same sign). [c] Coupling constants used: $J_t = 6.3$ and $J_g = 0.6$ cps (same sign). [d] Coupling constants used: $J_t = 8.7$ and $J_g = 0.6$ cps (opposite sign). [e] Coupling constants used: $J_t = 7.5$ and $J_g = 0.4$ cps (same sign). [f] Coupling constants used: $J_t = 5.28$ and $J_g = 1.48$ cps (same sign). [g] Coupling constants used: $J_t = 11.21$ and $J_g = 1.48$ cps (opposite sign).

Table IV. Solvent Dependence of the Free Energy Difference,[a] $\Delta G°$, between Rotamers of Haloacetaldehydes

Solvent	Chloro-acetaldehyde $\Delta G°$, cal/mol, for $IIIa \rightleftharpoons IV$	Bromo-acetaldehyde $\Delta G°$, cal/mol, for $IIIa \rightleftharpoons IV$
$CH_3(CH_2)_3CH_3$	−70	
trans-Decalin	−300	+40
Cyclohexane	−310	+40
CCl_4	−350	∼0
$CHCl_3$	−560	−100
CH_2Br_2	−700	−200
CH_2Cl_2	−710	−230
CH_3COCH_3	−1000	−430
CH_3CN	−1100	−500
$(CH_3)_2NCHO$	−1250	−570
$(CH_3)_2SO$	−1450	−680
H_2NCHO	−1500	−700
C_6H_6	−640	−150
C_6H_5Cl	−650	−180
C_6H_5CN	−950	−380

[a] These values were calculated by using the rotamer populations under columns A and D of Table III.

Table V. Enthalpy Differences,[a] $\Delta H°$, between Rotamers of Haloacetaldehydes

Solvent	Chloro-acetaldehyde $\Delta H°$, cal/mol, for $III \rightleftharpoons IV$	Bromo-acetaldehyde $\Delta H°$, cal/mol, for $III \rightleftharpoons IV$
trans-Decalin	−300	0
Cyclohexane	−400	
C_6H_5Cl	−900	
$(CH_3)_2NCHO$	−2100	−1500
CH_3CN	−2500	

[a] These values were obtained by using the equilibrium constants calculated from the rotamer populations under columns A and D of Table III.

7.6 cps, we feel that a reasonable estimate of the coupling constants of chloroacetaldehyde would be: $J_g \simeq 0.3$ cps and $J_t \simeq 6.9$ cps, provided they have the same sign.

Similar treatment of the data of bromoacetaldehyde yields: $J_g \leqslant 1.48$ cps and $J_t \geqslant 5.28$ cps, if the signs are the same; and $J_g \leqslant 1.48$ cps and $J_t \geqslant 11.2$ cps, if the signs are opposite. Since the coupling constants of acetaldehyde and bromoacetaldehyde satisfying eq 4 are 2.80 cps and 2.75 cps, respectively, we estimate 0.4 cps and 7.5 cps as reasonable values for J_g and J_t of bromoacetaldehyde.

In Table III is shown the effect that solvent polarity has on the relative populations of the rotamers, calculated from eq 1, of chloroacetaldehyde and bromoacetaldehyde. The values in columns A and D were calculated by using our own best estimates of the coupling constants. The values in columns B and E were calculated from the coupling constants with the same sign; and those in columns C and F from the coupling constants with opposite signs. Inspection of the results reveals the substantial increase of the concentration of rotamer IV, the more polar rotamer, as the dielectric constant of the solvent increases. The same effect is seen in Table IV in terms of the free energy differences,[3] $\Delta G°$, that were calculated from eq 2, between rotamers III_a and IV. Whereas IV of chloroacetaldehyde is favored by only 70 cal/mol in the least polar solvent pentane ($\epsilon \sim 2$), it is favored by about 1500 cal/mol in the most polar solvent formamide ($\epsilon > 80$). The same is true, but to a smaller extent, in the case of bromoacetaldehyde. For example, whereas in the least polar solvents III_a is slightly favored over IV, in the most polar solvent formamide IV is favored by about 700 cal/mol.

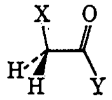
In Table V are summarized the enthalpy differences, $\Delta H°$, between the various rotamers. They were calculated from reasonably linear plots of log K_{eq} *vs.* $1/T$.

It is worth noticing that, whereas $\Delta G°$ and $\Delta H°$ are about equal in solvents of low dielectric constants, $\Delta H°$ is appreciably more negative than $\Delta G°$ in solvents of high dielectric constants. For example, $\Delta G°$ and $\Delta H°$ for $III_a \rightleftharpoons IV$ of chloroacetaldehyde are both -300 cal/mol in *trans*-decalin. In acetonitrile, whereas $\Delta G°$ is -1100 cal/mol, $\Delta H°$ is -2500 cal/mol. Similarly, whereas in *trans*-decalin $\Delta G°$ and $\Delta H°$ for $III_a \rightleftharpoons IV$ of bromoacetaldehyde are about zero, in the more polar solvent N,N-dimethylformamide $\Delta H°$ is more negative than $\Delta G°$ by about 900 cal/mol.

From arguments already discussed,[2] these values should not be taken as better than ±20%.

Discussion

In interpreting our results, we have assumed a dominant threefold barrier to rotation about the carbon–carbon bond. Before embarking on an interpretation of these results, we wish to consider the question of whether they are compatible with a dominant twofold barrier to rotation. Among all structurally relevant monohalo compounds studied and reported today, only fluoroacetyl fluoride[9] has been found to have a twofold barrier to rotation about the sp^2–sp^3 carbon–carbon bond. Let us assume that IV and V are the equilibrium configurations of the two monohaloacetaldehydes. The relevant vicinal spin–spin coupling constants would then be $J_g(J_{60°})$ for IV and $J_{120°}$ for V. For chloroacetaldehyde eq 4 now becomes eq 5. Since



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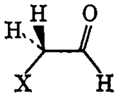
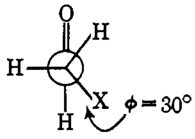


V

$$2.5 = {}^1/_2(J_g + J_{120°}) \qquad (5)$$

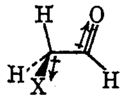
J_g must be equal to or smaller than 0.6 cps, $J_{120°}$ must be equal to or larger than 4.4 cps. This condition is certainly unprecedented and unreasonable as J_g and $J_{120°}$ are expected to be of similar magnitude.[10] Analogous treatment of the bromoacetaldehyde results leads to $J_g < 1.5$ cps and $J_{120°} > 4.0$ cps.

In order to prevent any overinterpretation and misunderstanding of our results, we wish to reemphasize[2] that, although we draw rotamers I and II as perfectly eclipsing, the nmr technique gives no accurate assessment of the various dihedral angles. It is quite possible that the equilibrium configuration of rotamer II might be VI, as this configuration—instead of II—best fits the observed vibrational frequencies of haloacetyl halides.[3,11]

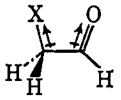


VI

Effect of Solvent Polarity on Rotamer Stabilities. The increase in the rotamer ratio IV/II, reflected in the data of Tables III and IV, as the dielectric constant of the medium increases, is reasonable in view of the higher dipole moment of IV over III. It is also understandable that this increase would be, as is, more pronounced among the rotamers of chloroacetaldehydes than among those of bromoacetaldehyde, on account of the carbon–chlorine bond being more polar than the carbon–bromine bond. This large difference in the dipole moments of the two rotamers is, furthermore, responsible for $\Delta H°$ values being much more negative than the corresponding $\Delta G°$ values in solvents of high dielectric constant. Increase in temperature decreases the dielectric constant of the solvent. This decrease, in turn, decreases the ratio IV/III far more rapidly than expected, and causes the coupling constants to increase rapidly with increasing temperature. The net result is the calculation of more negative and, hence, inaccurate $\Delta H°$ values. For this reason, in solvents of high dielectric constant, $\Delta G°$ values reflect better the enthalpy differences between rotamers whose dipole moments differ greatly, than do the calculated $\Delta H°$ values. The only meaningful $\Delta H°$ values calculated for such rotamers by the temperature dependence of the spin–spin coupling constants are those in solvents of low dielectric constant. Since in *trans*-decalin $\Delta H° \simeq \Delta G°$, the argument that $\Delta S°$ between the rotamers of the monohaloacetaldehydes is zero is indeed valid.



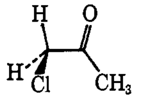
III



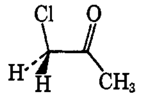
IV

Comparison of Results with Those from Other Systems. The conclusion drawn from infrared studies[5] that chloroacetaldehyde exists essentially in conformation III is certainly in conflict with the interpretation of our nmr results. In fact, III is the major rotamer, about 55%, only in the low dielectric constant hydrocarbon solvents and in carbon tetrachloride. If the degeneracy factor of two that favors it over IV were to be removed, then it is less stable than IV by 300 cal/mol in these solvents. The suggested,[5] therefore, nonbonded, repulsions between chlorine and carbonyl oxygen cannot be the factor controlling the relative stabilities of III and IV.

Let us now compare chloroacetaldehyde and chloroacetone. It was found[3] that in the liquid state ($\epsilon \sim 30$) VII and VIII are of comparable stability. It was suggested[4] that VII might have been even more stable, had it not been for nonbonded repulsions between the *gauche* groups chlorine and methyl. If this interpretation were correct, then chloroacetaldehyde would have been expected to exist predominantly in III, rather than IV, as the *gauche* chlorine–methyl interaction present in chloroacetone has been removed in



VII



VIII

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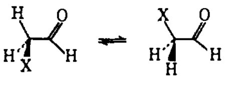
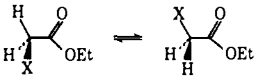
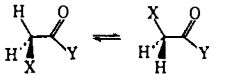
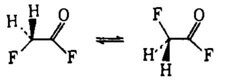
[9] E. Saegebarth and E. B. Wilson, Jr., *J. Chem. Phys.*, **46**, 3088 (1967).

[10] For the expected dependence of vicinal J_{HH} coupling on dihedral angle see M. Karplus, *ibid.*, **30**, 11 (1959); *J. Am. Chem. Soc.*, **85**, 2870 (1963).

[11] I. Nakagawa, I. Ichishima, K. Kuratani, T. Miyazawa, T. Shimanouchi, and S. Mizushima, *J. Chem. Phys.*, 20 1720 (1952).

Table VI. Energy Differences between Rotamers of Some Related Systems

System I	System II	X	ΔH°, cal/mol[a]	Method	Ref
		Cl	−350	Nmr	This work
		Br	0	Nmr	This work
		F	−560	Ir	13
		Cl	−500	Ir	13
		Br	0	Ir	13
		Cl (Y = Cl)[b]	*Ca.* −1200[c]	Raman & ir	19
		Br (Y = Cl)[b]	−1000	Raman & ir	3
		Br (Y = Br)[b]	−1900	Raman & ir	
			−910	Microwave	9

[a] These values are either in low dielectric constant solvents, such as pentane and CCl_4, or in the gaseous state. [b] For the structure of these *gauche* rotamers see text. [c] Estimated from ref 19.

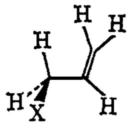
chloroacetaldehyde. Instead, in such high dielectric constant solvents the rotamer ratio III/IV of chloroacetaldehyde is smaller, rather than larger, than the ratio VII/VIII. If nonbonded interactions between the *gauche* chlorine and methyl groups of chloroacetone were affecting the rotamer ratio, then, to account for the results, these interactions would have to be attractive rather than repulsive.

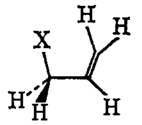
The finding that in the low dielectric constant solvents ΔH° for III $\rightleftharpoons$ IV of bromoacetaldehyde is less negative by 300 cal/mol than the corresponding ΔH° of chloroacetaldehyde argues against the polarizability of group X (dipole-induced dipole interaction) being especially important in controlling the ratio III/IV. If one were to consider that in these solvents ($\epsilon \sim 2$) the electrostatic dipole-dipole interactions would destabilize IV of chloroacetaldehyde more than they would IV of bromoacetaldehyde with respect to their other rotamers, then the contribution from the polarizability factor becomes even less significant.

In Table VI, we have summarized, for comparison purposes, the energy differences (either in low dielectric constant solvents or in the gaseous state) between XCH_2COY compounds, where X is halogen. In all cases, except fluoroacetyl fluoride,[9] the results have been interpreted in terms of the V_3 term of the potential function dominating the V_2 term, *i.e.*, in terms of a threefold rather than a twofold barrier to rotation about the sp^2-sp^3 carbon-carbon bond.

In all cases ΔH° for I $\rightleftharpoons$ II is negative or zero, *i.e.*, the rotamer with the lowest energy is the one where the C-X bond eclipses the carbonyl. The only exception appears to be N-methylchloroacetamide,[4] where ΔH° is quite positive. It is impossible to decide from the published results[3,11,12] whether ΔH° for I $\rightleftharpoons$ II of monohaloacetones is positive or negative in the gaseous state; it appears, however, that it is negative in the liquid state.

Several minor differences among the results may be explained in terms of nonbonded and electrostatic interactions. For example, substitution of bromine for chlorine in the monohaloacetaldehydes and in the ethyl acetates[13] increases ΔH° for I $\rightleftharpoons$ II. The same trend has been observed in 3-halopropenes, where

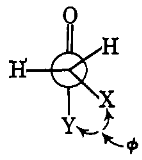

IX


X

ΔH° for IX $\rightleftharpoons$ X is −100 cal/mol in 3-fluoropropene,[14,15] +100 cal/mol in 3-chloropropene,[16] and progressively more positive in 3-bromopropene and 3-iodopropene.[17,18] The best rationalization of these results is increase in the nonbonded repulsions between halogen and oxygen (or methylene) in rotamers II (or X) as the size of the halogen increases.

The observation that the ΔH° values of the haloacetaldehydes are less negative than those of the ethyl acetates[13] and haloacetyl halides[3,9,11,19] may be attributed to differences in the energies of I and II arising from dipole-dipole interactions. For example, the difference between the dipole moments of I and II being larger in the case of haloacetaldehydes than in the case of haloesters and haloacetyl halides, the ratio I/II would be smaller for haloacetaldehydes than haloesters and haloacetyl halides. This argument has been used[4] to partly explain the differences in the relative stabilities of the rotamers of chloroacetyl chloride, chloroacetone, and N-methylchloroacetamide.

Nonbonded interactions between the *gauche* groups X and Y in rotamer I have been suggested[9] to explain why fluoroacetyl fluoride exhibits a twofold barrier to


XI

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(12) G. A. Crowder and B. R. Cook, *J. Chem. Phys.*, 47, 367 (1967); B. R. Cook and G. A. Crowder, *ibid.*, 47, 1700 (1967).

(13) T. L. Brown, *Spectrochim. Acta*, **18**, 1615 (1962).

(14) H. Hirota, *J. Chem. Phys.*, **42** 2071 (1961).

(15) A. A. Bothner-By, S. Castellano, and H. Günther, *J. Am. Chem. Soc.*, **87**, 2439 (1965).

(16) A. A. Bothner-By, S. Castellano, S. J. Ebersole, and H. Günther, *ibid.*, **88**, 2466 (1966).

(17) A. A. Bothner-By and H. Günther, *Discussions Faraday Soc.*, 34, 127 (1962).

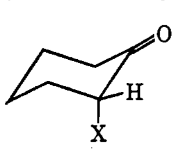
(18) K. Radcliffe and J. L. Wood, *Trans. Faraday Soc.*, **62**, 2038 (1966).

(19) Y. Morino, K. Kuchitsu, and M. Sugiura, *J. Chem. Soc. Japan*, **75**, 721 (1954).

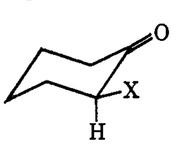
rotation, when all the other haloacetyl halides studies exhibit a threefold barrier to rotation. When both X and Y (XI) groups are the small fluorine atoms, the repulsion between them is very small, and hence $\phi = 0°$. When they are, however, the larger atoms chlorine and bromine, the nonbonded repulsions change the equilibrium configuration to $\phi = 30°$. As mentioned, this angle has been found to best fit the observed vibrational frequencies.[3,11]

Despite the relative success of these explanations in rationalizing some of the trends observed in the relative stabilities of rotamers I and II, the basic fact still remains that they are inadequate to explain why, in most cases, II is so much more stable than I. For example, had these arguments been applied to predict the relative stabilities of the rotamers of chloroacetaldehyde, the prediction would have been that I should be more stable than II. Yet the opposite is true. This point can be further illustrated by comparing the monohaloacetaldehydes with the 2-halocyclohexanones.

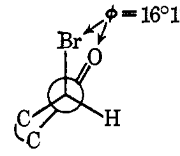
Monohaloacetaldehydes *vs.* 2-Halocyclohexanones. Several investigations[6] have established that the ratio XII_a/XII_e increases by changing X from fluorine to chlorine to bromine. When X is fluorine, the equatorial conformer is more stable than the axial,[6d,f] and when it is chlorine or bromine, the axial conformer is more stable[6a-c,f] in solvents of low dielectric constant.[20] In hydrocarbon solvents, the free energy difference, $\Delta G°$, for $XII_a \rightleftharpoons XII_e$ was found[6f] to be −170, +740, and +1280 cal/mol for 2-fluoro-, 2-chloro-, and 2-bromocyclohexanone, respectively. The corresponding values calculated[6f] by taking into account nonbonded, dipole–dipole, and dipole–induced dipole interactions were +1130, +1130, and +1100 cal/mole. If the results from 2-fluorocyclohexanone were to be disregarded, then the correspondence be tween calculated and experimental values might be termed as good. Irrespective of how one chooses to interpret the results, if the same criteria were to be applied to chloroacetaldehyde and bromoacetaldehyde, the $\Delta H°$ values for I $\rightleftharpoons$ II would turn out to be similar to those of 2-chloro- and 2-bromocyclohexanones. Yet, the experimental values are −300 cal/mol and about +40 cal/mol, *i.e.*, considerably different than the +740 and +1280 cal/mol found for the 2-halocyclohexanones. It seems to us that the basic factor, in addition to all those that have been already discussed, controlling rotamer stabilities might be the same one restricting the barrier to rotation about carbon–carbon single bonds, and which has been associated with the nature of the axial bonds.[21] The differences between monohaloacetaldehydes and 2-halocyclohexanones may very well arise from torsional strain, as the dihedral angles calculated[6c] for the equatorial ($XIII_e$), $\phi = 16° 17'$, and axial ($XIII_a$), $\phi = 102° 13'$, bromocyclohexanones are different than the corresponding ones of rotamers I and II. From all indications,[3,9,11,19] the corresponding dihedral angles ϕ of II and I are zero and 150°.



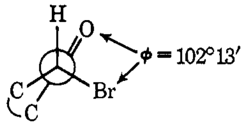
XII_a



XII_e



$XIII_e$



$XIII_a$

Experimental Section

Chloroacetaldehyde was prepared according to the procedure of Schukina.[22] The following is a typical preparation. Into a flame-dried, three-necked, round-bottomed flask equipped with a thermometer, condenser, and an adapter allowing the flow of nitrogen and of chlorine was placed 44 g of acetaldehyde. The flask was cooled to 15–17°. Chlorine was passed through the solution at such a rate as to allow the temperature to rise to 39° (refluxing) after about 30 min. The addition was maintained for about 1 extra hr. After the colorless, fuming liquid had been fractionally distilled, the fraction boiling at 80–90° was redistilled under vacuum (24–26° (3 mm)). The fresh distillate was then placed in the freezer section of a refrigerator and was allowed to stand for 2–4 days, until a white solid had formed. The solid, presumably the trimer of chloroacetaldehyde, was dried under vacuum at room temperature to yield about 2 g of material. Cautious heating of the solid, either at atmospheric pressure or under vacuum, yielded chloroacetaldehyde, which was used immediately, as it resolidified when it was let stand.

Bromoacetaldehyde was prepared according to the procedure of Yanovskava, Terentiev, and Belenskiy.[23] The following is a typical preparation. To 200 g of freshly distilled dioxane in a 1-l. flask, maintained at 0° with an ice bath, was added with stirring 360 g of bromine. The resulting hot, dark brown solution was poured, with stirring, into 500 ml of ice and water. A crystalline, orange precipitate (dioxane–bromine complex) was collected and dried on a Büchner funnel. After 300 g of the solid were dissolved in enough ether, two layers formed. Both layers were slowly added through a dropping funnel to a solution, maintained at 5–10°, of 54 g of acetaldehyde in 50 ml of ether. Approximately 1 hr after addition, the dark red solution turned light yellow. The ether layer was washed with water, a 5% sodium carbonate solution, and again with water and dried over anhydrous magnesium sulfate. After careful removal of the ether by distillation, the residue was gas chromatographed (preparative chromatography) through a 20% silicone column at 45°. The collected pure bromoacetaldehyde was used immediately, as it rapidly decomposed on standing.

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.

Acknowledgment. We thank the National Science Foundation for generous financial support.

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[20] In contrast to all other studies, it has been reported by K. Kozima and E. Hirato, *J. Am. Chem. Soc.*, **83**, 4300 (1961), and by K. Kozima and Y. Yamanouchi, *ibid.*, **81**, 4159 (1959), that, even in heptane, ΔE for $X_a \rightleftharpoons X_e$ is −0.75 kcal/mol, *i.e.*, the equatorial conformer is more suitable than the axial.

[21] E. B. Wilson, Jr., *Proc. Natl. Acad. Sci. U. S.*, **43**, 816 (1957); *Advan. Chem. Phys.*, **2**, 367 (1959).

[22] M. N. Schukina, *J. Gen. Chem. USSR*, **18**, 1653 (1948).

[23] L. A. Yanovskaya, A. P. Terentiev, and L. I. Belenskiy, *ibid.*, **22**, 1594 (1952).