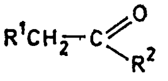
Nuclear Magnetic Resonance Study of α-Halogenobutyraldehydes and a Re-appraisal of Rotational Isomerism in Dihalogenoaldehydes and Related sp^2–sp^3 Hybridised Systems

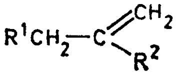
By D. F. Ewing, Department of Chemistry, The University, Hull HU6 7RX

From the temperature and solvent dependence of the vicinal coupling between the aldehydic and α-protons the rotational isomerism about the C(1)–C(2) bond in α-chloro-, α-bromo-, and α-iodo-butyraldehydes has been interpreted in terms of a three-fold barrier to rotation. The rotamer with the halogen atom eclipsing the carbonyl group contributes to a negligible extent in non-polar solvents. Published data for dichloro- and dibromo-acetaldehyde have been shown to be more consistent, for non-polar solvents, with an equilibrium involving skew rotamers. For these compounds the positions of the minima in the potential energy curve appear to be sensitive to solvent. Trends in the effect of halogen substitution on the rotational isomerism about the sp^2–sp^3 hybridised bond in carbonyl-containing compounds are discussed, and the anomalous effect of fluorine is rationalised.

SEVERAL techniques [1,2] have been applied to the study of rotational isomerism about the bond between sp^2–sp^3 hybridised atoms and the weight of evidence [1,2] suggests that in most cases the stable form has the α-substituent eclipsing the carbonyl group in compound (1) or a hydrogen atom eclipsing the double bond in the olefin (2). However, much uncertainty still exists [1–8] concerning the number and nature of the other stable forms. Some compounds [7,9] appear to exhibit a two-fold barrier to rotation but a three-fold barrier is more general.[1,3–6,9–11] In some cases only one rotamer is stable.[3,9,12–14] I.r. spectral studies [9,12,13,15,16] are often handicapped by overlapping bands and cannot readily provide quantitative data relating to the rotamer equilibria. Rotational energy barriers can be estimated from microwave spectra [7,10,14,17,18] and in favourable cases this method can yield a complete potential energy curve. However the analyses are complex and not always conclusive. In recent years the application of n.m.r. spectroscopy [1,3–6,8,11,19,20] to the problem of rotational isomerism has had some success but again the nature of the second stable form of the systems (1) and (2) cannot always be determined with certainty.[1,5,11,19]



(1)



(2)

Substituted aldehydes can readily be studied by n.m.r. spectroscopy since the vicinal coupling between the α-proton and the aldehyde proton is a sensitive probe of the rotational equilibrium.[1,3–6] Only monosubstituted or symmetrically disubstituted aldehydes have been extensively investigated [3–6] because in these cases there are just two distinct rotamers irrespective of whether a two or a three-fold barrier is assumed. We have extended the n.m.r. method to the α-halogenobutyraldehydes, a system involving three distinct rotamers, and present here an analysis of the isomerism about the C(1)–C(2) bond in terms of the vicinal coupling constant. We have also reassessed the published data for several dihalogenoacetyl derivatives.

EXPERIMENTAL

The three α-halogenoaldehydes were prepared by standard procedures.

α-Chlorobutyraldehyde.—Butyraldehyde was treated with chlorine according to the method of Schukina.[21] The monomeric product tended to polymerise, particularly at 0°. No significant impurities were indicated by the n.m.r. spectrum of a freshly prepared sample.

α-Bromobutyraldehyde.—Bromination of butyraldehyde with bromine–dioxan complex [4,22] gave 40% of the α-bromoaldehyde, which was stable for at least a month when stored under nitrogen in the dark.

α-Iodobutyraldehyde.—Reaction of α-chlorobutyraldehyde with an excess of potassium iodide in refluxing acetone afforded the α-iodoaldehyde in high yield. This compound very readily lost iodine [23] when exposed to light and even in the dark decomposed completely in a month. A fresh

---

[1] G. J. Karabatsos and D. J. Fenoglio, *Topics Stereochem.*, 1970, **5**, 167.

[2] J. P. Lowe, *Progr. Phys. Org. Chem.*, 1968, **6**, 1.

[3] G. J. Karabatsos and N. Hsi, *J. Amer. Chem. Soc.*, 1965, **87**, 2864.

[4] G. J. Karabatsos and D. J. Fenoglio, *J. Amer. Chem. Soc.*, 1969, **91**, 1124.

[5] G. J. Karabatsos, D. J. Fenoglio, and S. S. Lande, *J. Amer. Chem. Soc.*, 1969, **91**, 3572.

[6] G. J. Karabatsos and D. J. Fenoglio, *J. Amer. Chem. Soc.*, 1969, **91**, 3577.

[7] E. Saegebarth and E. B. Wilson, *J. Chem. Phys.*, 1967, **46**, 3088.

[8] A. A. Bothner-By and H. Günther, *Discuss. Faraday Soc.*, 1962, **34**, 127.

[9] T. L. Brown, *Spectrochim. Acta*, 1962, **18**, 1615.

[10] E. Hirota, *J. Chem. Phys.*, 1965, **42**, 2071.

[11] V. I. P. Jones and J. A. Ladd, *J. Chem. Soc.* (*B*), 1970, 1719.

[12] L. J. Bellamy and R. L. Williams, *J. Chem. Soc.*, 1958, 3465.

[13] K. Radcliffe and J. L. Wood, *Trans. Faraday Soc.*, 1966, **62**, 2043.

[14] O. L. Stiefvater and E. B. Wilson, *J. Chem. Phys.*, 1969, **50**, 5385.

[15] L. J. Bellamy and R. L. Williams, *J. Chem. Soc.*, 1957, 4294.

[16] A. Y. Khan and N. Jonathan, *J. Chem. Phys.*, (*a*) 1969, **50**, 1801; (*b*) 1970, **52**, 147.

[17] R. W. Kilb, C. C. Lin, and E. B. Wilson, *J. Chem. Phys.*, 1957, **26**, 1695.

[18] S. S. Butcher and E. B. Wilson, *J. Chem. Phys.*, 1964, **40**, 1671.

[19] A. A. Bothner-By, S. Castellano, and H. Günther, *J. Amer. Chem. Soc.*, 1965, **87**, 2439.

[20] A. A. Bothner-By, S. Castellano, S. J. Ebersole, and H. Günther, *J. Amer. Chem. Soc.*, 1966, **88**, 2466.

[21] M. N. Schukina, *J. Gen. Chem.* (*U.S.S.R.*), 1948, **18**, 1653.

[22] L. A. Yanovskaya, A. P. Terentiev, and L. I. Belenskiy, *J. Gen. Chem.* (*U.S.S.R.*), 1952, **22**, 1594.

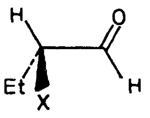
[23] C. Djerassi and C. T. Lenk, *J. Amer. Chem. Soc.*, 1953, **75**, 3493.

sample was shaken with sodium thiosulphate solution before use but prolonged n.m.r. measurements could not be made on this compound.

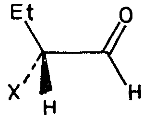
Spectra were obtained on a JEOL JNM-4H-100 instrument operating at 100 MHz. Temperatures accurate to ±2° were measured with a directly inserted thermocouple and a solute concentration of *ca.* 25 mg in 0·5 ml was used for all experiments. In selected cases measurements were made at various temperatures. Coupling constants were taken directly from the aldehyde doublet and are accurate to ±0·08 Hz. Although fully deuteriated solvents were used for this work this is not specifically mentioned in the text since isotope effects are negligible.

RESULTS AND DISCUSSION

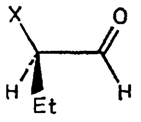
If we assume a three-fold barrier [1,3,4] to rotation about the C(1)–C(2) bond in the α-halogenobutyraldehydes the three stable forms are (3)—(5). Rotational isomerism about the C(2)–C(3) bond is unlikely to interfere to any significant extent. If y_1, y_2, and y_3 are the fractional populations of these three rotamers then the observed coupling constant J, the weighted mean of the *trans*-coupling (J_t) and the two *gauche*-couplings (J_g and $J_{g'}$), is given by equation (1).



(3)



(4)



(5)

$$J = y_1J_t + y_2J_g + y_3J_{g'} \qquad (1)$$

In a three-rotamer problem of the present type it is not possible to deduce directly from J the equilibrium constants between each of the rotamers. Previous studies [1,3,6] of aldehydes have been restricted to cases where two of the rotamers have equal energy. Such cases are effectively two-component systems and only one equilibrium need be considered. In the present case we begin by assuming that rotamers (4) and (5) are energetically equivalent (but of course still distinguishable as are mirror image forms). This is an essential initial assumption but one which will be relaxed subsequently. It is convenient to further assume that the two *gauche*-couplings are equal. This assumption is not likely to lead to appreciable error since both *gauche*-couplings are small (*ca.* 1 Hz). With these assumptions this three-component system can now be treated as a two-component system.

Equation (1) simplifies to equation (2) where y is the

$$J = yJ_t + (1 - y)J_g \qquad (2)$$

fractional population of rotamer (3). Since rotamers (4) and (5) are taken to be a degenerate pair the free-energy difference for the equilibrium (3) $\rightleftharpoons$ (4) or (5) is given by equation (3) where $K\,[= (1 - y)/2y]$ is the corresponding equilibrium constant. The three unknown quantities

$$\Delta G^0 = -RT\ln K = -RT\ln[(J_t - J)/2(J - J_g)] \qquad (3)$$

in equation (3) could be evaluated [1,11] by fitting to the values of J determined at various temperatures but in view of the very small range of J and of the inaccuracies in T a more approximate method of determining y and ΔG^0 has been adopted.[1,3,4]

In the case where J is temperature invariant or tends to a limiting value then, since rotamers (4) and (5) are assumed to be energetically equivalent,* the populations of rotamers (3)—(5) are approximately equal and J is given by equation (4). Taking the limiting value of J

$$J = (J_t + 2J_g)/3 \qquad (4)$$

for α-chlorobutyraldehyde as 2·4 (Table 1) and J_g as 0·3 Hz (the value for chloroacetaldehyde [4]) we obtain from equation (4) J_t 6·6 Hz. Since the limiting value of J for α-bromobutyraldehyde is 2·8 Hz (Table 1) equal to that for bromoacetaldehyde,[4] we use the values, J_t 7·4 and J_g 0·5 Hz, estimated for the latter compound.[4] For α-iodobutyraldehyde the estimated values are J_t 7·6 and J_g 0·5 Hz. All the above values of J_t and J_g are necessarily approximate and errors may be as high as 15%. Since J_g may increase or decrease [24] with substituent electronegativity (E_X) little significance can be attached to the variations in this parameter. In contrast J_t will decrease as E_X increases and the above values compare reasonably well with those estimated for acetaldehyde [25] (8·3), butyraldehyde [3] (7·2), chloro-

TABLE 1

Coupling constants (J/Hz) for α-halogenobutyraldehydes

		α-Chloro		α-Bromo		α-Iodo	
Solvent	T/°C	J	(3) % [a]	J	(3) % [a]	J	(3) % [a]
C_6D_{12}	25	2·20	30	2·60	30	2·60	30
	72	2·23		2·65			
	86	2·26					
CCl_4	25	2·20	30	2·55	29	2·60	30
$CDCl_3$	−52			2·95		2·95	
	−23	2·28		2·95			
	−10					2·90	
	0	2·30		2·93			
	25	2·34	32	2·88	34	2·93	34
	58	2·35		2·84		2·90	
	85	2·36		2·80		2·83	
Neat	−21	1·83		2·50			
	−10					2·30	
	5			2·58			
	25	1·95	26	2·55	29	2·55	29
	60	1·98				2·63	
	75	2·03		2·65			
	87	2·05					
$(CD_3)_2CO$	25	1·83	24	2·33	26		
CD_3CN	−7	1·60		2·29			
	25	1·70	22	2·40	27		
	47	1·79		2·50			
	75	1·88		2·52			
$(CD_3)_2SO$	25	1·43	18	1·98	21	2·18	24

[a] Percentage of rotamer (3).

---

* This assumption is not strictly essential at this point. Provided that the energy of rotamer (3) is approximately equal to the mean energy of rotamers (4) and (5) then the relative populations of (4) and (5) can vary without disturbing the validity of equation (4).

[24] R. J. Abraham and G. Gatti, *J. Chem. Soc.* (*B*), 1969, 961.

[25] R. J. Abraham and J. A. Pople, *Mol. Phys.*, 1960, **3**, 609.

acetaldehyde[4] (6·9), and bromoacetaldehyde[4] (7·5 Hz). Reported[5] J_t values for dichloroacetaldehyde (9·1) and dibromoacetaldehyde (10·3 Hz) do not compare well and are probably wrong (see later Discussion).

From the values of J in Table 1 the percentage population (y) of rotamer (3) was calculated and is included in Table 1. Using equation (3) ΔG^0 values were determined for the α-halogenobutyraldehydes in various solvents and in some cases ΔH^0 values were estimated in the usual way from the variable-temperature data. These values of ΔG^0 and ΔH^0 are not included in Table 1 since they relate to the unreal situation in which rotamers (4) and (5) have equal energy. Since the trends in ΔG^0 follow parallel trends in y it is less confusing * to discuss the significance of these trends in terms of population rather than free energy.

The values of y in Table 1 show that the equilibrium in all cases slightly favours the rotamers in which a substituent eclipses the carbonyl group, *i.e.* that the population of rotamer (3) is always $<33\%$. Two distinct trends can be seen in this data. First, for each compound the population of (3) decreases as the dielectric constant of the solvent increases. Similar variations of rotamer distribution with solvent polarity have been widely reported,[1,2] and can be related to the relative stabilisation of the more polar forms. Electrostatic repulsions between intramolecular bond dipoles are more effectively relaxed the more polar the medium and hence solvent stabilisation of a rotamer is related to the overall dipole moment. Abraham and his co-workers[24,26,27] have developed a quantitative theory of such solvent effects and have successfully rationalised the effect of solvent on the ^3J coupling in some simple halogenoalkanes[24] and chloropropenes.[28] Chloro- and bromoacetaldehydes[4] show a similar solvent-induced enhancement in the population of that rotamer with the halogen atom eclipsing the carbonyl group [(7), $R^1 = Cl$ or Br, $R^2 = H$] and analogous solvent effects are observed for a series of steroid derivatives with halogenoacetyl side chain[29] [(7), $R^1 = Cl$, Br, or I, $R^2 =$ pregn-4-en-3-on-17-yl]. The trends in the geminal coupling constants for the side chain of this steroid again indicate solvent stabilisation of the rotamer with the halogen atom eclipsing the carbonyl group. Although our treatment of the coupling constant data does not distinguish between rotamers (4) and (5) in the halogenobutyraldehydes it seems likely that the energy of rotamer (4) relative to (3) is little affected by solvent and the observed changes in J reflect the increasing relative stability of rotamer (5).

The second trend apparent in the population of rotamer (3) is the increase, for polar solvents, as the substituent is changed from chlorine to iodine. The evaluation of the significance of this trend in y (and of the absence of a trend in the data for inert solvents) required an examination of the intramolecular interactions[1,2] which determine rotamer stability. In principle the energies of all three rotamers (3)—(5) are affected by changing the halogen atom (from Cl through Br to I). However we assume these changes are significant only for rotamer (5). This is clearly a gross simplication but is a reasonable one for these closely related compounds. For the series X = Cl, Br, or I, increasing substituent size must increase the repulsive steric interactions with the eclipsed oxygen atom and hence *decrease* the population of rotamer (5). Conversely, the decreasing dipole moment of the C–X bond reduces the electrostatic repulsion between the C–X and C=O dipoles with a concomitant *increase* in the population of rotamer (5). Dipole induced-dipole effects can operate in this case but these are likely to be small.[1,4,5] Since we must estimate the net effect of opposing steric and electrostatic effects we have collected for comparison values of the energy differences (Table 2) between the stable rotamers of

TABLE 2

Energy differences (J mol^{-1}) between rotamers in several sp^2–sp^3 hybridised systems[a]

R^1 [b]	R^2 [b]	ΔG^0	Method	Ref.
Me	H	$-3700, -3750$	n.m.r., m.w.	3, 18
Et	H	-2900	n.m.r.	3
Pr^i	H	-1600	n.m.r.	3
Bu^t	H	$+1400$	n.m.r.	3
Cl	H	-1300	n.m.r.	4
Br	H	$+170$	n.m.r.	4
Me	F	-5400	m.w.	14
F	F	-3800 [c]	m.w.	7
Cl	F	$-3200, -4500$	i.r., n.m.r.	11, 16*a*
Br	F	-2700	n.m.r.	11
F	Cl	-4100	i.r.	35
Cl	Cl	$-4050, -5000$	i.r.	4, 16*a*
Br	Cl	-4200	i.r.	36
F	Br	-4200 [c]	i.r.	16*b*
Cl	Br	-7750	i.r.	16*a*
Br	Br	-7900	i.r.	36
F	OEt	$-2300, -2600$ [d]	i.r.	9
Cl	OEt	$-2100, -2100$ [d]	i.r.	9
Br	OEt	$0, -400$ [d]	i.r.	9
Et, Me	H	-750	n.m.r.	3
Et, Cl	H	-2050	n.m.r.	*e*
Et, Br	H	-2050	n.m.r.	*e*
Cl, Cl	H	$+2500$	n.m.r.	*f*
Br, Br	H	$+2700$	n.m.r.	*f*
Cl, Cl	F	-1620	n.m.r.	11
Cl, Cl	Cl	$+830$ [g]	i.r.	33, 34*a*
Cl, Cl	Br	$<+400$ [g]	i.r.	34*a*
F, F	OEt	-790 [g]	i.r.	9
Cl, Cl	OEt	-500 [g]	i.r.	9

[a] These are experimental ΔG^0 or ΔH^0 values, the two quantities being assumed equal for equilibria between individual isomers [*i.e.*, (6) $\rightleftharpoons$ (7) for monosubstituted and (9) $\rightleftharpoons$ (10) for disubstituted systems]. In the n.m.r. studies where both quantities have been measured, ΔG^0 values are used since these are more reliable (refs. 3 and 4). In all cases data refer to the gas phase or to solution in inert solvents. [b] In rotamers (6)—(11). [c] For an equilibrium (6) $\rightleftharpoons$ (8). [d] Calculated [using $\Delta G^0 = \Delta G^0_{\text{meas.}} + RT\ln 2$] from data relating to an equilibrium in which the degenerate rotamers were not distinguished. [e] Calculated on the basis of an equilibrium (3) $\rightleftharpoons$ (4) with no contribution from (5). [f] Data of ref. 3 re-analysed as discussed in the text. [g] Equilibrium probably (9) $\rightleftharpoons$ (11).

---

* I thank a Referee for comment on this point.

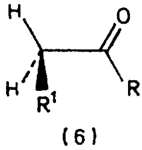
[26] R. J. Abraham, L. Cavalli, and K. G. R. Pachler, *Mol. Phys.*, 1966, **11**, 471.

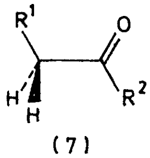
[27] R. J. Abraham, *J. Phys. Chem.*, 1969, **73**, 1192.

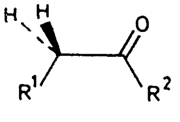
[28] R. J. Abraham and K. Parry, *J. Chem. Soc.* (*B*), 1971, 724.

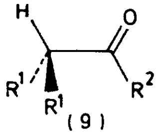
[29] W. G. Cole and D. H. Williams, *J. Chem. Soc.* (*B*), 1970, 748.

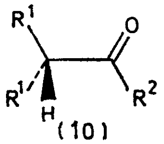
various alkyl- and halogen-substituted compounds, all of which contain an sp^2–sp^3 hybridised linkage incorporating a carbonyl group. These ΔG^0 values relate to equilibria between individual isomers, [*e.g.* (6) $\rightleftharpoons$ (7) for monosubstituted compounds and (9) $\rightleftharpoons$ (10) for disubstituted compounds] and are equal to the corresponding enthalpy values assuming zero entropy difference between rotamers.[1] Experimentally, at least for n.m.r. studies, ΔG^0 values are more reliable than ΔH^0 values although the reverse may apply to other spectroscopic techniques. For this reason the ΔG^0 values (in some cases ΔH^0 values) in Table 2 must be viewed with some caution. It should be noted that the energy terms in Table 2 are expressed in J mol^{-1} and are not directly comparable with literature data in cal mol^{-1}.

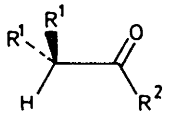

(6)

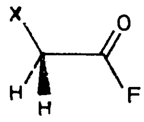

(7)

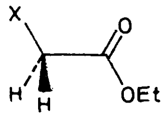

(8)

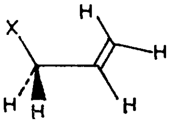

(9)


(10)


(11)


(12)


(13)


(14)

A steric effect alone is very evident in the ΔG^0 values of the alkyl substituted aldehydes but the extent to which steric and electrostatic effects cancel is best seen in the ΔG^0 values for chloro- and bromo-acetaldehydes.[4] The difference in ΔG^0 values for these two compounds in cyclohexane (CXE) is, from Table 2, 1500 J mol^{-1} indicating a predominant steric effect. This predominance is further enhanced in polar solvents which stabilise rotamer (6); the difference in ΔG^0 values for dimethyl sulphoxide (DMSO) solution[4] is 3200 J mol^{-1}.

Further evidence of a predominant steric effect can be found in a wide range of compounds in which the aldehyde hydrogen atom is replaced by other atoms or groups. Halogenoacetyl fluorides[11] (12) and the corresponding ethyl acetates[9] (13) (Table 2) show a similar change in ΔG^0 with variation of the halogen substituent. The difference for the chloro- and bromo-compounds is *ca.* 1800 J mol^{-1} in both cases, comparable with the 1500 J mol^{-1} noted above for the halogenoacetaldehydes. Although ΔG^0 values are available for the corresponding halogen-substituted acid chlorides and bromides these data are less accurate and no clear trends are apparent. Allyl halides (14) exist largely in the form with a hydrogen atom eclipsing the double bond,[8,13,20] but a similar substituent effect is still observed and the difference in ΔG^0 for the chloro- and bromo-compounds is, in this case,[8] >5000 J mol^{-1}. Here only steric effects are important and these are not partly offset by electrostatic effects.

Returning to the α-halogenobutyraldehydes, it is clear that the trend in the population of rotamer (3) in DMSO reflects the now well established predominance of a steric effect. Furthermore the relatively small difference in *y* for the chloro- and bromo-compounds suggests that the population of rotamer (5) is small and the constant value of *y* for all three compounds in cyclohexane indicates that rotamer (5) does not contribute to any significant extent in non-polar solvents. This means that for these compounds the rotamer equilibrium in non-polar solvents is effectively between rotamers (3) and (4) and we might expect an appreciable temperature dependence of J, as the population of rotamer (5) increases from 0 to 33%. In fact, because the population of (3) (the only rotamer involving J_t) is already very close to the 33% required in the high temperature limit, the increase in rotamer (5) is largely at the expense of (4) and little change is observed in J with increasing temperature. Since only one *gauche*-isomer (4) contributes to the equilibrium, the value of ΔG^0 for (3) $\rightleftharpoons$ (4) in inert solvent at 25° can now be recalculated from equation (3) with the degeneracy factor of 2 removed. These values of ΔG^0 refer to a genuine equilibrium for the chloro- and bromo-butyraldehydes and are included in Table 2. It is noteworthy that butyraldehyde has a slightly larger ΔG^0 value indicating that the presence of the halogen atom in rotamers (3) and (4) shifts the equilibrium towards (3). This is reasonable since there is a *gauche* 1 : 2 methyl–chlorine interaction in rotamer (4) which can become a *trans* 1 : 2 interaction in rotamer (3).

The coupling constant between the aldehydic proton and fluorine in α-fluorobutyraldehyde is reported[30] as *ca.* 5 Hz. The dependence of $^3J_{\mathrm{HF}}$ on the dihedral angle is similar to the well known Karplus relationship for $^3J_{\mathrm{HH}}$ and a typical curve has been reported.[31] Even allowing for a reduction in J_{HF} at all angles owing to the effect of an sp^2-hybridised carbon atom, the above value of J_{HF} indicates a high percentage of *gauche*-coupling, *i.e.* rotamers (3) and (4) (X = F), in agreement with our conclusions regarding the chloro- and bromo-compounds.

Anomalies were found for all three α-halogenobutyraldehydes in chloroform. There is a slight enhancement of the population of rotamer (3) (*ca.* 4%) and this may represent a specific solvent interaction. The apparent absence of a similar anomaly for the halogenoacetaldehydes[4] may be due to the greater population of rotamer (6) [corresponding to (3)]; the relatively minor effect observed here is effectively swamped.

The coupling constant data for dichloro- and dibromoacetaldehyde have been interpreted in terms of the model involving a three-fold barrier to rotation.[1,5] For an equilibrium between rotamers of type (9) and (10)

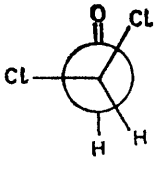
---

[30] J. Cantacuzène and D. Ricard, *Bull. Soc. chim. France*, 1967, 1587.

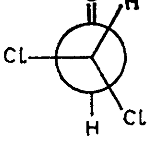
[31] K. L. Williamson, Y.-F. Li Hsu, F. H. Hall, S. Swager, and M. S. Coulter, *J. Amer. Chem. Soc.*, 1968, **90**, 6717.

Karabatsos *et al.*[5] obtained for dichloroacetaldehyde $\Delta G^0_{\text{CXE}} = +1450$, $\Delta G^0_{\text{MeCN}} = -4200$ J mol^{-1}, and for dibromoacetaldehyde $\Delta G^0_{\text{CXE}} = +1350$, $\Delta G^0_{\text{MeCN}} = -2700$ J mol^{-1}; values for acetonitrile (MeCN) solution are included since the dimethyl sulphoxide values seem anomalous.[5] The steric effect evident in the data for the polar solvent is negligible in cyclohexane. Although the enthalpy differences (ΔH^0) for these two compounds in non-polar solvents do show a substituent effect of *ca.* 800 J mol^{-1}, this is much smaller than the 1500 J mol^{-1} shown by the monohalogenoaldehydes (see above). Taken together the ΔG^0 and ΔH^0 values indicate only a small contribution from rotamer (10), the conformation which should produce a substantial steric effect. However a small population for rotamer (10) is not in agreement with the 50% estimated by Karabatsos *et al.*[5] Their analysis, based on an equilibrium between rotamers of type (9) and (10), required very high values of J_t (9·1 and 10·3 Hz for dichloro- and dibromo-acetaldehydes respectively). These values are much higher than would be expected on electronegativity grounds and, in view of the inconsistencies discussed above, they can probably be rejected. This raises some doubt about the conclusion of Karabatsos *et al.* but, as these workers pointed out, the alternative description of these systems in terms of an equilibrium between rotamers (9) and (11), *i.e.* a two-fold barrier, is also unacceptable if we assume that the lowest observed couplings (*ca.* 1 Hz) indicate the upper limit for J_{cis} in the rotamer of type (11). J_{cis} would certainly be greater than 1 Hz but it is significant that these low J values are only observed in highly polar solvents.

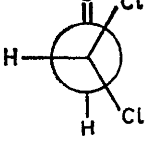
If we disregard the low values of J and consider only the data for non-polar solvents then, with reasonable values for J_t (6·0 and 7·0 Hz for dichloro- and dibromo-acetaldehyde respectively) and the limiting values reported by Karabatsos *et al.*[5] (3·4 and 4·5 Hz respectively) we obtain from equation (4) the coupling constant for the other rotamer, J_{skew} 2·0 and 3·25 Hz respectively. If the relationship of J to dihedral angle for these systems can be represented by the usual type[32] of Karplus curve, then these values of J_{skew} indicate, for non-polar solvents, a rotamer of type (15) or (16). The H–C–C–O dihedral angle is *ca.* 150 in (15) and *ca.* 30° in (16) and both forms could contribute although it seems unlikely that rotamers (9) and (16) can represent distinct minima in the potential energy curve. An equilibrium between rotamers (9) and (15) still involves a three-fold barrier to rotation since rotamer (15) has a mirror image but this allows quite satisfactory values to be assigned to the couplings in the individual rotamers. It is interesting to note that changes in the dihedral angle of rotamers of *ca.* 30° are normally assumed to be beyond the sensitivity of the n.m.r. method.[1]



(15)



(16)



(17)

To explain the low values of J in very polar solvents we suggest that not only does the population of rotamer (15) increase but also (15) tends to become rotamer (10), *i.e.* the halogen substituent can progressively approach the eclipsed position as the solvent polarity increases. If this is the case then it means that the positions of the minima in the potential energy curve for these compounds are sensitive to solvent. This is of course quite distinct from changes in the energies of the minima which are widely recognised and are responsible for the normal solvent-induced changes in rotamer population.[2] Little attention appears to have been paid to the above aspect of the effect of the medium on the potential energy curve for simple rotational isomerism, and although large changes are unlikely, small changes in the position of a minimum (of the order of 30°) may be quite common. In fact these changes are not really remarkable as can be seen from the Figure which shows a schematic plot of potential energy against the H–C–C–O dihedral angle in dichloroacetaldehyde. Curve A shows the 'normal' case, with minima at 0, 120, and 240° [rotamers (9) and (10) in polar solvents] and curve B shows the situation in non-polar solvents [rotamers (9) and (15)] with minima at 0, 150, and 210°. A change such as this in the potential energy curve seems quite reasonable especially if the minima are broad and the barrier at 180° is low. It is difficult to predict the effect of torsional vibrations in these systems, particularly when solvent stabilisation of high energy forms is possible. A significant contribution to the observed changes in J may come from this source but without knowledge of the exact nature of the potential energy curve no estimate is possible.

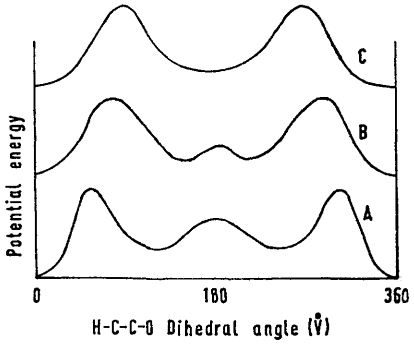


FIGURE Potential energy curves for rotation in α-disubstituted aldehydes corresponding to a three-fold barrier with rotamers (9) and (10) (curve A) or with rotamers (9) and (15) (curve B) or to a two-fold barrier with rotamers (9) and (11) (curve C)

Using the above values of J_t and J_{skew} the calculated ΔG^0_{CXE} values for the equilibrium (9) $\rightleftharpoons$ (15) at 25° are +2500 and +2700 J mol^{-1} for dichloro- and dibromo-acetaldehyde respectively, indicating a high percentage of rotamer (9) and only a small substituent effect.

[32] S. Sternhell, *Quart. Rev.*, 1969, **23**, 235.

With this new picture of the rotamer equilibrium in the dihalogenoaldehydes it is interesting to consider the situation in analogous compounds. Miyake *et al.*[33] found for dichloroacetyl chloride that rotamer (9) ($R^1 = R^2 = Cl$) was the more stable. The structure of the other rotamer was less certain but probably either (17) or (11) ($R^1 = R^2 = Cl$). These workers preferred rotamer (17) to (11) since the latter form had not been observed for any other system. Recently Woodward and Jonathan[34] reported a more detailed study of dichloroacetyl chloride and a number of other dihalogenoacetyl halides and in most cases found the stable rotamer to be of type (9). The other rotamer had a H–C–C–O dihedral angle in the range 90—135° but could not be more precisely defined. A structure for the less stable rotamer in these compounds analogous to that proposed above for the dihalogenoaldehydes [*i.e.*, rotamer (15)] is possible especially in view of the results of Brown[9] for the corresponding esters. Brown[9] found from i.r. measurements that both ethyl dichloroacetate and ethyl difluoroacetate exhibited a two-fold barrier to rotation about the carbon–carbon bond with rotamer (9) being less stable than rotamer (11) ($R^1 = Cl$ or F, $R^2 = OEt$). In the latter case the H–C–C–O dihedral angle is 180°.

The existence of a two-fold (curve C in the Figure) rather than a three-fold barrier in these compounds can now be seen as part of a trend. As the size of the group attached to the carbonyl group increases, the stability of rotamer (9) decreases and the nature of the other rotamer changes from (10) through (15) to (11), *i.e.* the potential energy curve changes from A to C (Figure). This trend is apparent in the ΔG^0 values for the dichloroacetyl derivatives (Table 2). As the group attached to the carbonyl carbon atom changes from H through Cl to Br and OEt, ΔG^0 decreases from +2500 to −500 J mol^{-1}. An exception to this trend is found for dichloroacetyl fluoride.[11]

Rotational isomerism in this compound has been studied[11] by means of the vicinal coupling constant $^3J_{HF}$ and the stable rotamer was found to be of type (10).* An i.r. study[34] of this compound also indicated some anomaly in the rotational isomerism. A calculated potential energy curve was not consistent with experimental data, which suggested an equilibrium between rotamers of types (11) and (17). These inconsistencies and the large negative ΔG^0 value for this compound (compared with the positive values for the corresponding aldehyde and acid chloride) (Table 2) indicate some anomaly in this case. An important factor is likely to be an attraction between hydrogen and fluorine in rotamer (10) ($R^1 = Cl$, $R^2 = F$) with a preference for a form analogous to (15) or even to rotamer (11) ($R^1 = Cl$, $R^2 = F$). There is some evidence from i.r. studies[34] for the existence of rotamer (11) and this would be in line with the other dihalogenoacetyl compounds discussed above. It would also allow a maximum attractive potential to develop between hydrogen and fluorine.

I thank Dr. K. A. W. Parry for the synthesis of some of the compounds used in this work.

[1/1273 *Received*, 26*th July*, 1971]

---

* These workers wrongly claim agreement between their conclusions and those of ref. 33.

[33] A. Miyake, I. Nakagawa, T. Miyazawa, I. Ichishima, T. Shimanouchi, and S. Mizushima, *Spectrochim. Acta*, 1958, **13**, 161.

[34] A. J. Woodward and N. Jonathan, (*a*) *J. Phys. Chem.*, 1970, **74**, 798; (*b*) *J. Mol. Spectroscopy*, 1970, **35**, 127.

[35] J. E. F. Jenkins and J. A. Ladd, *J. Chem. Soc.* (*B*), 1968, 1237.

[36] I. Nakogawa, I. Ichishima, K. Kuratani, T. Miyazawa, T. Shimanouchi, and S. Mizushima, *J. Chem. Phys.*, 1952, **20**, 1720.