

## Conformations of $\alpha$ -chloroacetanilides: An IR spectroscopic study

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**Abstract.** The conformational analyses of  $\alpha$ -mono,  $\alpha$ -di and  $\alpha$ -trichloroacetanilides have been carried out using IR spectroscopy.  $\alpha$ -Monochloro, dichloro and trichloroacetanilides were found to exist in only one conformation in  $\text{CH}_2\text{Cl}_2$  and  $\text{CHCl}_3$ . The existence of all these anilides in single conformation is due to intramolecular H-bond formation between N-H and Cl.

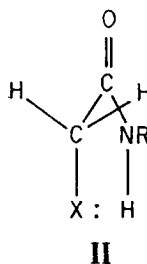
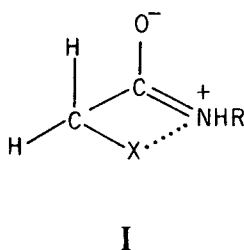
In  $\text{CH}_3\text{CN}$ , the broadening of C=O bands of monochloroacetanilides and their bifurcation in  $\alpha$ -dichloroacetanilides indicated the existence of two rotamers due to the breaking of chelation by the solvent.

**Keywords.**  $\alpha$ -Chloroacetanilides; intramolecular hydrogen bond; rotational isomerism; bisecting conformation; stabilities of conformations.

### 1. Introduction

While  $\alpha$ -halo ketones (Bellamy and Williams 1958) and esters (Brown 1958) were known to exist in two conformations viz. *cis* and *gauche*, characterised by two carbonyl bands, the  $\alpha$ -haloamides were shown to exist exclusively in the *gauche* conformation (Bellamy and Williams 1957; Nyquist 1963). The exclusive stability of this conformation was attributed to the electrostatic attraction between the halogen and N-atom rendered positive by the amide resonance (I). This view was also expressed by Mizushima *et al* (1956) from a study of the dipole moments of N-methyl chloroacetamide.

Nyquist (1963), on the other hand, attributed their existence in a single conformation to the formation of an intramolecular H-bond between the N-H and the halogen, which locks up the halogen atom in the *anti* conformation (II).



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It is of interest to note that  $\alpha$ -monohalo tertiary amides, which do not possess an intramolecular H-bond, also exist exclusively in the *gauche* conformation (Letaw and Gropp 1953).

It is, therefore, not quite clear whether the stability of the *anti* or *gauche* conformation is due to an intramolecular H-bond between N-H and halogen or due to electrostatic attraction between the nitrogen and halogen atoms.

If intramolecular H-bonding is responsible for the stability of the *anti* form in  $\alpha$ -halo amides, its cleavage should permit the molecule to have free rotation around the C-C bond leading to the existence of other conformers.

As basic solvents are known to cleave intramolecular H-bonds (Suryanarayana *et al* 1975), it appeared worthwhile to study the IR spectra of some  $\alpha$ -halo secondary amides in basic solvents to see if other conformers do make their appearance.

If the stability is due to electrostatic interactions between N and halogen atoms, it should vary with the change in the positive charge on the N-atom. In ring-substituted acetanilides the positive charge on the N-atom changes with the ring substituents (electron-donating or -attracting). To examine the influence of the two factors mentioned above, it is proposed to study the IR spectra of ring-substituted  $\alpha$ -chloroacetanilides. The  $\alpha$ -dichloro and  $\alpha$ -trichloroacetanilides were also included in the study for comparison of the spectra and identification of the conformers. Although the spectra of trichloroacetanilides were earlier reported by Nyquist (1963a) in connection with a study of the behaviour of N-H and C=O stretching frequencies and intensities as a function of substituents at the  $\alpha$ -carbon, they were rerecorded to obtain the spectra under identical conditions.

## 2. Experimental

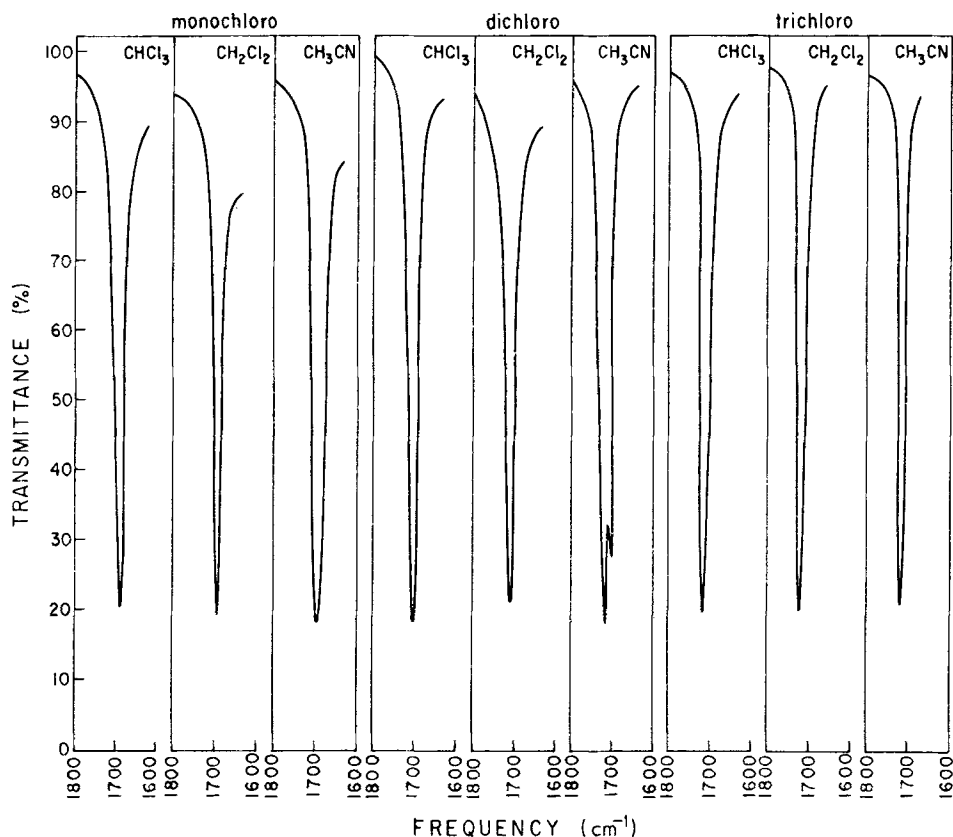
All the anilides were prepared by treating the substituted anilines with  $\alpha$ -chloro,  $\alpha$ -dichloro and  $\alpha$ -trichloroacetylchlorides (Vogel 1980). The solids separated were recrystallized twice from methanol and were TLC pure. The solvents used in the study were purified and freshly distilled before use. The spectra of equimolar (M/20) solutions of the samples in the solvents of varied dielectric constants were recorded at 28°C on a Perkin-Elmer 337 grating spectrophotometer at slow speed using NaCl matched cells of 1 mm path length.

## 3. Results and discussion

$\alpha$ -Mono and  $\alpha$ -trichloroacetanilides exhibited only one C=O band in all the three solvents, viz. CHCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub> and CH<sub>3</sub>CN. The  $\alpha$ -dichloro compounds also exhibited single C=O bands in CHCl<sub>3</sub> and CH<sub>2</sub>Cl<sub>2</sub>. They, however, exhibited doublets in CH<sub>3</sub>CN. The bands of the monochloro compounds became broader (figure 1). The frequencies of the C=O bands in different solvents, together with the ratios of the apparent optical densities of the higher/lower C=O bands of  $\alpha$ -dichloroanilides in CH<sub>3</sub>CN, are listed in table 1 and N-H frequencies in table 2.

### 3.1 Effect of $\alpha$ -substitution

Significant changes were observed in the C=O and N-H frequencies of acetanilides



**Figure 1.** The C=O bands of  $\alpha$ -monochloro,  $\alpha$ -dichloro and  $\alpha$ -trichloroacetanilides in different solvents.

on chlorination. The N–H and C=O frequencies of  $\alpha$ -monochloro compounds are lower than those of nonhalogen compounds. While the N–H frequencies are lowered by  $30\text{--}40\text{ cm}^{-1}$  the C=O frequencies were lowered by only  $5\text{--}10\text{ cm}^{-1}$ . The di- and trichlorination of acetanilides however produced progressive enhancement in the frequencies of both N–H and C=O bands. The frequencies of C=O are raised by  $18\text{--}20\text{ cm}^{-1}$  and the N–H by  $5\text{--}10\text{ cm}^{-1}$  for each additional chlorine atom. These observations are parallel to those of Nyquist (1963b) on  $\alpha$ -halo secondary amides.

### 3.2 Effect of ring substituents

Substituents in the *p*-position of  $\alpha$ -mono,  $\alpha$ -di and  $\alpha$ -trichloroacetanilides produced the same effect as in nonhalogen acetanilides. The C=O frequencies of these compounds bear linear relationships with Hammett  $\sigma$  constants (figure 2). The slopes of the lines are, however, lower than those of acetanilides. This shows that the sensitivity of the C=O frequency to the substituent is reduced by the halogen substitution in the  $\alpha$ -position. The N–H frequencies of the  $\alpha$ -mono,  $\alpha$ -di and  $\alpha$ -trichloroacetanilides also bear linear relationships with Hammett  $\sigma$  constants with negative slopes.

This indicates that the N–H frequency decreases with increasing electron-attracting

Table 1. The C=O stretching frequencies ( $\text{cm}^{-1}$ ) of acetanilides and  $\alpha$ -chloroacetanilides in different solvents.

Substituent	Acetanilides			Monochloroacetanilides			Dichloroacetanilides			Trichloroacetanilides									
	$\text{CHCl}_3$	$\text{CHCl}_3$	$\text{CHCl}_3$	$\Delta\nu_{1,2}$	$\text{CH}_2\text{Cl}_2$	$\Delta\nu_{1,2}$	$\text{CH}_3\text{CN}$	$\Delta\nu_{1,2}$	$\text{CH}_2\text{Cl}_2$	$\Delta\nu_{1,2}$	$\text{CH}_3\text{CN}$	$\Delta\nu_{1,2}$	$\text{CH}_2\text{Cl}_2$	$\Delta\nu_{1,2}$	$\text{CH}_3\text{CN}$	$\Delta\nu_{1,2}$			
$\text{CH}_3\text{O}$	1685	1679	30	1681	28	1690	44	1700	30	1702	28	1700*, 1719 (1:196) <sup>†</sup>	44	1720	23	1722	22	1718	22
$\text{CH}_3$	1685	1680	29	1682	28	1692	44	1702	32	1703	28	1702*, 1719 (1:694)	40	1721	24	1722	22	1718	22
H	1690	1683	28	1684	28	1695	42	1703	32	1705	27	1703*, 1720 (1:680)	40	1722	24	1724	22	1721	22
Cl	1695	1685	28	1686	25	1697	42	1705	30	1706	24	1704, 1722 (1:7)	40	1724	23	1725	22	1722	19
Br	1694	1685	30	1686	28	1697	44	1705	31	1706	28	1704, 1722 (1:7)	44	1724	24	1725	22	1722	19
$\text{NO}_2$	1711	1700	30	1702	25	1710	46	1717	30	1720	28	1718*, 1732 (1:76)	40	1734	24	1735	22	1732	19

\* Shoulder. † Values in parentheses correspond to the ratios of apparent optical densities of higher/lower frequency bands (i.e. bisecting/skew ratio).

Table 2. The N-H stretching frequencies ( $\text{cm}^{-1}$ ) of acetanilides and  $\alpha$ -chloroacetanilides in different solvents.

Substituent	Acetanilides			Monochloroacetanilides			Dichloroacetanilides			Trichloroacetanilides				
	$\text{CHCl}_3$	$\text{CHCl}_3$	$\text{CHCl}_3$	$\text{CH}_2\text{Cl}_2$	$\text{CH}_3\text{CN}$	$\text{CHCl}_3$	$\text{CH}_2\text{Cl}_2$	$\text{CH}_3\text{CN}$	$\text{CHCl}_3$	$\text{CH}_2\text{Cl}_2$	$\text{CH}_3\text{CN}$	$\text{CHCl}_3$	$\text{CH}_2\text{Cl}_2$	$\text{CH}_3\text{CN}$
$\text{OCH}_3$	3440	3400	3407	3300	3410	3410	3412	3310	3414	3416	3312	3414	3416	3312
$\text{CH}_3$	3437	3398	3401	3296	3409	3410	3410	3308	3414	3415	3310	3414	3415	3310
H	3435	3398	3402	3295	3408	3410	3410	3305	3414	3415	3310	3414	3415	3310
Cl	3435	3395	3400	3290	3408	3409	3409	3305	3413	3414	3308	3413	3414	3308
Br	3436	3395	3398	3290	3407	3408	3408	3304	3411	3412	3307	3411	3412	3307
$\text{NO}_2$	3430	3391	3388	3285	3402	3403	3403	3295	3406	3407	3305	3406	3407	3305

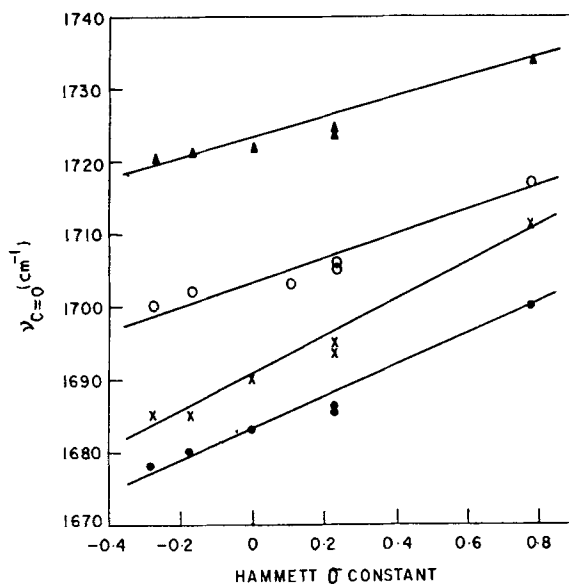


Figure 2. Plot of  $\nu_{C=O}$  of acetanilides ( $\times$ ),  $\alpha$ -monochloro ( $\bullet$ ),  $\alpha$ -dichloro ( $\circ$ ) and  $\alpha$ -trichloro acetanilides ( $\blacktriangle$ ) vs Hammett  $\sigma$  constants.

ability of the substituent. The electron-withdrawing substituent decreases the electron density on the N-atom resulting in a lowering of the N-H frequency. Similar trends were observed by Nyquist (1963a) in the case of  $\alpha$ -bromoacetanilides.

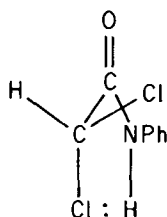
### 3.3 Conformations of the molecules and their stabilities

Appearance of single and sharp C=O bands in the spectra of  $\alpha$ -monochloroacetanilides in  $\text{CHCl}_3$  and  $\text{CH}_2\text{Cl}_2$  indicates that these compounds are exclusively stabilized in single conformations. The N-H and C=O frequencies of the compounds are lower than those of nonhalogenated anilides. The lowering of N-H frequencies in the  $\alpha$ -monochloro compounds may be due to the intramolecular H-bond formed between N-H and Cl. This also accounts for the decrease in the C=O frequency. Any tendency to pull the proton away from the N-atom will tend to increase the electron density on the latter, which enhances the C=O polarisation by the amide resonance resulting in a decrease of the C=O frequency (Nyquist 1963a). Thus, in  $\alpha$ -monochloroacetanilides the chlorine atom is locked up in the *anti* conformation.

Each of the  $\alpha$ -dichloroanilides also exhibited single C=O bands in  $\text{CHCl}_3$  and  $\text{CH}_2\text{Cl}_2$  showing the existence of these anilides also in single conformation.

Of the three conformations possible for  $\alpha$ -dichloroacetanilides depending upon the position of first chlorine atom, III, IV and V, the first one seems to be more likely, as one chlorine atom is locked up in the *anti* position due to the hydrogen bond between N-H and Cl, the second chlorine might enter one of the two skew positions with respect to the carbonyl group (III). Forms IV and V can be ruled out for the following reasons.

(i) The difference in the C=O frequencies of IV and  $\alpha$ -monochloroacetanilides is expected to be about  $25\text{ cm}^{-1}$ , due to the field inductive influence of the Cl atom eclipsing the C=O bond, and that between the V and  $\alpha$ -monochloroacetanilide should

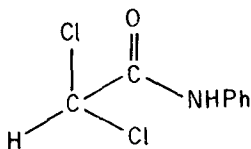


### III

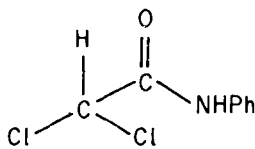
be small ( $2-4\text{ cm}^{-1}$ ). The change in  $\text{C}=\text{O}$  frequency due to normal inductive influence is small. The observed difference ( $18\text{ cm}^{-1}$ ) which is midway between the above two suggests that the second chlorine atom is in a skew position with respect to the  $\text{C}=\text{O}$  group where it would exert a reduced field inductive effect.

(ii) This is also supported by the frequency differences between  $\alpha$ -trichloro and  $\alpha$ -dichloroacetanilides. The observed differences are  $15-18\text{ cm}^{-1}$ . The difference between the  $\alpha$ -trichloroacetanilide and IV would be small ( $2-4\text{ cm}^{-1}$ ) and that between the  $\alpha$ -trichloroanilide and V would be large ( $23-25\text{ cm}^{-1}$ ) (Bellamy and Williams 1957). The observed difference which is midway between the two indicates that the replaceable H-atom in  $\alpha$ -dichloroacetanilides is in the skew position (form III).

The  $\alpha$ -trichloro compounds, however, exist in only one conformation which is evident from the single and sharp  $\text{C}=\text{O}$  bands exhibited by these compounds in all solvents. The  $\text{N}-\text{H}$  frequencies of the  $\alpha$ -trichloroacetanilides are, however, lower than those of the similarly substituted nonhalogenated acetanilides, due to involvement in intramolecular H-bonds between  $\text{N}-\text{H}$  and  $\text{Cl}$ , which suggest that  $\alpha$ -trichloroanilides exist in form VI.



### IV

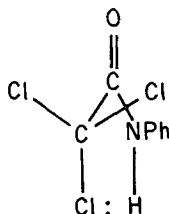


### V

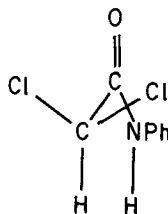
As mentioned earlier, the fact that the  $\text{C}=\text{O}$  frequencies of  $\alpha$ -trichloroacetanilides are  $15-18\text{ cm}^{-1}$  higher than those of  $\alpha$ -dichloroacetanilides (III) also supports the hypothesis that there are two  $\text{Cl}$  atoms skew to the  $\text{C}=\text{O}$  group (VI) and exert twice the field inductive effect.

In  $\text{CH}_3\text{CN}$ , the  $\alpha$ -dichloroanilides exist in two conformations as is evident from the split in the carbonyl band. The rupture of the intramolecular H-bond by  $\text{CH}_3\text{CN}$  accounts for the split in the  $\text{C}=\text{O}$  band. Considerable decrease in the  $\text{N}-\text{H}$  frequency ( $100-110\text{ cm}^{-1}$ ) and increase in the half-bandwidths provide ample evidence for the rupture of the intramolecular H-bond and formation of an intermolecular H-bond between  $\text{N}-\text{H}$  and  $\text{CH}_3\text{CN}$ . Breaking of chelation facilitates the rotation of the  $\text{CHCl}_2$  group around the  $\text{C}-\text{C}$  bond and results in the occurrence of  $\alpha$ -dichloroanilides in more than one form. The positions of the lower frequency components of the doublets are

closer to those of  $\alpha$ -dichloroanilides in  $\text{CH}_2\text{Cl}_2$ , while those of the higher frequency components are closer to those of  $\alpha$ -trichloroacetanilides. The lower frequency bands are, therefore, assigned to the skew conformation (III) and the higher frequency bands to the bisecting conformation (VII).



VI



VII

Analogously, the  $\alpha$ -monochloroacetanilides should have also exhibited two C=O bands in  $\text{CH}_3\text{CN}$ . Disappointingly, only one band is observed. But the bands were found to be broader than those observed in  $\text{CH}_2\text{Cl}_2$ . The half-bandwidths are nearly twice as large as those of  $\alpha$ -trichloroacetanilides, which exist in only one conformation, and are of comparable magnitude to the doublets of  $\alpha$ -dichloroacetanilides in  $\text{CH}_3\text{CN}$ . The general solvent effect, which could be one of the possible reasons for the broadening of the bands, is ruled out, as the half-bandwidth of  $\alpha$ -trichloro compounds remained nearly the same in both  $\text{CH}_2\text{Cl}_2$  and  $\text{CH}_3\text{CN}$ . The broadening of the C=O bands of  $\alpha$ -monochloroacetanilides, therefore, appears to be due to the overlap of two bands possibly due to those of two conformers. The failure to observe two separate bands may be due to a small frequency difference or to the possibility of one of the bands being less intense and getting buried under the intense band.

The relative ratios of the apparent optical densities of the bands due to the two conformers, bisecting (VII) and skew (III), in  $\text{CH}_3\text{CN}$ , show that the relative populations of the conformers of  $\alpha$ -dichloroanilides are dependent on the ring substituents. In *p*-nitroanilide the bisecting and skew ratio (1.76) is higher as compared to that of the unsubstituted compound (1.69). In the *p*-methoxy compound the ratio is still lower (1.19) (table 1). As mentioned earlier, if the relative stabilities of the conformers depend upon the electrostatic attraction between the N and Cl atoms, the electron-releasing groups viz. methoxy and methyl, which reduce the positive charge on the N atom, are expected to destabilize the skew form, while electron-withdrawing groups, viz. Cl, Br and  $\text{NO}_2$ , which increase the positive charge on the N atom, would stabilize it. When compared to unsubstituted anilides, the bisecting and skew ratio should be lower for the anilides with electron-releasing groups and higher for the anilides with electron-withdrawing groups. The values observed are, however, in the reverse order. This shows that the electrostatic repulsion between C=O and C-Cl dipoles across the space (Bellamy and Williams 1957) is more significant than the electrostatic attraction between the N and Cl atoms. Electron-releasing groups enhance the polarity of the C=O bond, which increases the electrostatic repulsion between C=O and C-Cl dipoles, destabilize the bisecting form and decrease the bisecting and skew ratio, whereas electron-withdrawing groups decrease the polarity of the C=O bond and stabilize the bisecting form, which leads to increase in the ratio of bisecting and skew forms.

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