719. *Infrared Spectra and Polar Effects. Part IV.* Steric Restrictions of Polar Effects and their Application in Studies on Rotational Isomerism.*

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A halogen atom in the α-position to a carbonyl group does not influence the C=O frequency unless it is close in space to the oxygen atom. This effect is utilised in the differentiation of rotational isomers of a number of derivatives of ω-chloroacetophenone. In each case the more stable isomer is shown to be that in which the chlorine atom is *cis* with respect to the carbonyl group.

The frequency shifts of mass-insensitive vibrations in the infrared region are, in general, directly related to the inductive and mesomeric effects of the substituents attached to the group concerned.[1,2] However, there are a few anomalous cases which cannot be explained on this basis, one of the most interesting being the observation that the carbonyl frequencies of cyclic ketones show a rise of about 20 cm.$^{-1}$ when an α-halogen atom is introduced equatorially but remain substantially unaffected by an α-halogen atom in the polar position.[3-6] This cannot be reconciled with an inductive effect which should be independent of steric considerations, or with a mesomeric effect which would be expected to lead to a fall in frequency, and we have therefore studied it further. Consideration of the available data on α-halogenated carbonyl compounds suggests that this steric effect is not limited to cyclic compounds, and that in contrast to Gillette's findings [7] it is only the first α-halogen atom which has any major influence upon the carbonyl frequency. This results in an initial

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* Part III, *J.*, 1956, 2753.

[1] Bellamy, *J.*, 1955, 2818.

[2] *Idem, ibid.*, p. 4221.

[3] Jones, Ramsey, Herling, and Dobriner, *J. Amer. Chem. Soc.*, 1954, **74**, 2828.

[4] Dickson and Page, *J.*, 1955, 447.

[5] Corey, Topie, and Wezniak, *J. Amer. Chem. Soc.*, 1955, **77**, 5415.

[6] Corey and Burke, *ibid.*, p. 5418.

[7] Gillette, *ibid.*, 1936, **58**, 1143.

rise of some 20—30 cm.$^{-1}$, but thereafter further halogen substitution at the same carbon atom either has no effect or results in only small shifts which can be associated with residual inductive effects. Thus the ethyl esters of mono-, di-, and tri-chloro- and bromofluoro-, and chlorofluoro-acetic acid absorb [1, 4, 8, 9] within the range **1761**—**1753** cm.$^{-1}$ in the liquid state. Similarly, the introduction of an α-fluorine atom into ethyl acetate raises the carbonyl frequency by 27 cm.$^{-1}$ but the difluorinated material absorbs only 4 cm.$^{-1}$ higher, with a further rise of 9 cm.$^{-1}$ in the trifluorinated ester.[10] Recent work on trichloroacetic acid [11] has also shown that in monomeric form this compound has a carbonyl frequency only 18 cm.$^{-1}$ higher than the original acid and this corresponds to the shift which would be expected from the influence of a single chlorine atom. Many other parallel cases can be cited such as the observation that ωω'-dibromoacetophenone-*o*-carboxylic acid has the same carbonyl frequency as the monobromo-derivative,[12] and our own similar results on mono- and di-chloroacetophenones (see below). These findings contrast with the results obtained from compounds containing the group $\cdot CHBr\cdot CO\cdot CH_2Br$. In these cases it is possible for both the halogen atoms to be near in space or coplanar with the carbonyl group, and the frequency shift shown is then approximately double that of the monosubstituted product.[3]

These results indicate that inductive effects are playing only a relatively small part in the alterations of these carbonyl frequencies and that the major effect is due to some other cause which only becomes effective when the halogen atom is close in space to the carbonyl oxygen. Further, as the introduction of an α-halogen atom into any open-chain structure $\cdot CH_2\cdot CO\cdot$ invariably results in a rise in the carbonyl frequency, it follows that the structure in which the halogen atom is close to the carbonyl oxygen is the preferred stable form. Nevertheless, as rotation is possible about the C–C bond of this group one would expect to find a second carbonyl absorption when such compounds are examined in the liquid or vapour state. This second form would correspond to a rotational isomer in which the chlorine atom was twisted away from the oxygen and the carbonyl frequencies should therefore be unaffected by it; hence, it is satisfying to find that compounds such as bromoacetic and fluoroacetic ester, in which this effect should be most clearly marked, do in fact exhibit a second C=O absorption in the liquid and solution state which is very close to the carbonyl frequency of acetic ester itself.[8, 9] Josien and Calas [13] have noted similar effects in both mono- and di-chlorinated esters and have already suggested that they may be associated with restricted rotation effects.

This finding therefore provides further confirmation of the steric limitation of this effect and suggests a useful application in restricted rotation studies. Mizushima *et al.*[14, 15] have studied rotational isomerism in compounds such as bromo- and chloro-acetyl chloride and chloroacetone. They have used dipole-moment and similar studies to differentiate the two configurations but have used infrared data in their recognition. A study of the latter data shows that all these compounds have two carbonyl frequencies in the liquid or vapour state and only one in the crystalline solid. Further, the two frequencies in the liquid state differ by the expected amount of 20—30 cm.$^{-1}$, whilst dipole-moment data, etc., indicate that in every case the more stable isomer is that in which the halogen atom is *cis* with respect to the carbonyl group and therefore close to it in space.

Owing to the frequency shifts in carbonyl absorptions which accompany changes of state, and which themselves amount to as much as 20 cm.$^{-1}$ in the case of acetophenones,[16, 17] the frequencies given in various states cannot be compared directly to determine which is

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[8] Hampton and Newell, *Analyt. Chem.*, 1949, **12**, 914.
[9] McBee and Christman, *J. Amer. Chem. Soc.*, 1955, **77**, 755.
[10] Bender, *ibid.*, 1953, **75**, 5986.
[11] Fuson, Josien, Jones, and Lawson, *J. Chem. Phys.*, 1952, **20**, 1627.
[12] Grove and Willis, *J.*, 1951, 877.
[13] Josien and Calas, *Compt. rend.*, 1955, **240**, 1641.
[14] Nakagawa, Ichishima, Kuratani, Miyazawa, Shimanouchi, and Mizushima, *J. Chem. Phys.*, 1952, **20**, 1720.
[15] Mizushima, Shimanouchi, Miyazawa, Ichishima, Kuratani, Nakagawa, and Shido, *ibid.*, 1953, **21**, 815.
[16] Soloway and Freiss, *J. Amer. Chem. Soc.*, 1951, **73**, 5000.
[17] Fuson, Josien, and Shelton, *ibid.*, 1954, **76**, 2526.

the stable form in the solid. However, the knowledge that the isomer in which the halogen and the carbonyl group are *cis* can be expected to show a carbonyl frequency some 20 cm.$^{-1}$ higher than that in which they are not should enable the more stable rotational isomer to be identified readily by a study of relative intensities of the two carbonyl absorptions of the liquids at a variety of temperatures. This possibility has been explored in the case of a series of derivatives of ω-chloroacetophenone, and the results obtained are given below.

EXPERIMENTAL

Samples were examined in either a Perkin-Elmer 21 or a Grubb-Parsons S.3A double-beam spectrometer fitted with a rock-salt prism. Solids were examined as pressed discs in potassium bromide and as films pressed between rock-salt plates. Experiments on solutions were carried out in carbon tetrachloride. The liquids and molten films were examined in a conventional hot cell of the type described by Richards and Thompson.[18] The spectra of the liquids were run at a stepwise series of temperatures above the m. p. and changes in the relative intensities of the two carbonyl absorptions were recorded.

Results.—The compounds studied and the results obtained are listed in the Table. The relative intensity changes with temperature of the two carbonyl frequencies of one typical compound—ω : 3 : 4-trichloroacetophenone—are illustrated in the Figure.

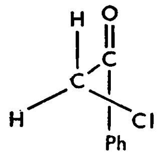
Carbonyl frequencies (cm.$^{-1}$) of ω-chloroacetophenone derivatives in various states.

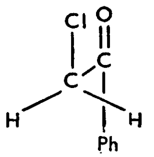
				Effect of rising temperature on liquid :	
Acetophenone	Solid	Liquid	Solution	C=O intensity grows	C=O intensity falls
ω-Chloro-	—	1697, 1685	1704, 1682	1685	1697
ω : 4-Dichloro-	1684	1695, 1683	1704, 1684	1683	1695
ω : 3 : 4-Trichloro-	1699	1695, 1681	1706, 1686	1681	1695
ω : 2 : 5-Trichloro-	1706	1718, 1703	1724, 1704	1703	1718
ω : 2 : 4-Trichloro-	1701	1706, 1694	1721, 1701	1694	1706
ω : 2 : 4 : 6-Tetrachloro-	1727	1730, 1711	1733, 1715	1711	1730
ωω-Dichloro-	—	1698, 1684	1701, 1681	1684	1698

These results raise a number of interesting points. The occurrence of a single C=O frequency in the solids and of two in the liquids is clear evidence for the existence of rotational isomerism in these compounds. In ω-chloroacetophenone, one of the two carbonyl bands shown in the liquid state occurs at precisely the same frequency as the carbonyl absorption of liquid acetophenone (1682 cm.$^{-1}$) whilst the other absorbs 12 cm.$^{-1}$ higher. In the light of the above discussion, the 1682 cm.$^{-1}$ band must be associated with the form (I) in which the chlorine atom is twisted away from the carbonyl group and does not therefore affect its frequency. Similarly, the 1697 cm.$^{-1}$ band must correspond to the form (II) in which the oxygen and the chlorine atom are close together.

Very similar results are given by the 4-chloro- and the 3 : 4-dichloro-derivative. However, when a further chlorine atom is introduced into the 2-position of the ring a further small frequency rise is shown by both the carbonyl frequencies of the liquid forms. This could be due to a small degree of twisting of the chloroacetyl group out of the plane of the ring, but it is perhaps more likely to be associated with a direct effect upon the carbonyl group of the ring-chlorine atom. This is also very close in space to the carbonyl oxygen atom and could therefore influence its frequency in the same way as an α-halogen substituent. In one configuration,

(I)





(II)

therefore, the carbonyl group would come under the influence of two halogen atoms whilst in the other only the ring-halogen would exert any effect. In the case of the 2 : 4 : 6-trichloro-derivative it is clear from molecular models that the introduction of halogen atoms on each side of

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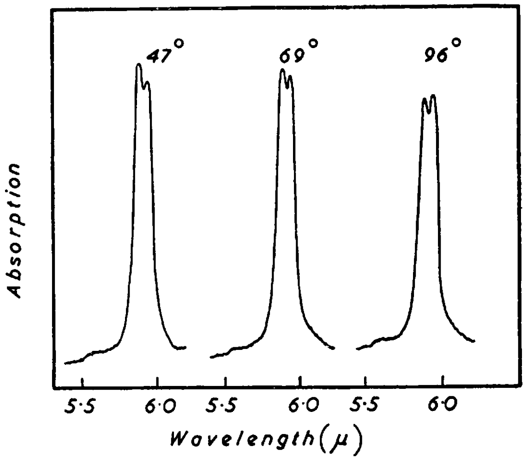
[18] Richards and Thompson, *Trans. Faraday Soc.*, 1945, **41**, 183.

the chloroacetyl group compels the latter to rotate out of the plane of the ring. Two configurations of this group are possible, as before, but in neither of these is the ring coplanar with the carbonyl group, and the frequencies of both rise sharply owing to the elimination of the mesomeric effect of the ring.



The detailed study of the relative intensities of the two carbonyl absorptions of each of the liquids fully confirms the expectation that the form in which the chlorine atom is *cis* with respect to the carbonyl group is the more stable one. The results shown in the Figure are typical of all the cases studied, and it will be seen that as the temperature is raised the proportion of the form giving rise to the lower carbonyl band is increased. From the data given earlier this is clearly the form in which the halogen atom and the carbonyl group are not *cis*, which is accordingly the less stable isomer.

It would also have been interesting to study the C–Cl absorptions of these isomers. Mizushima *et al.*[14, 15] have found that in all the cases in which the halogen atom is *cis* with respect to the carbonyl oxygen, the C–Cl frequency also rises. This is indirectly confirmed by McBee and Christman[7] who find a similar effect in chlorinated esters. However, in the present series the occurrence of a number of absorptions in the expected region, coupled with the low intensities of the C–Cl bands and the presence of other C–Cl frequencies in many cases, has rendered any reasonable identification of these bands impracticable.

DISCUSSION

These findings show that the existence of a steric factor in determining whether or not an α-halogen substituent will raise a carbonyl frequency is very real. Also, this effect must have some stabilising power, since, despite the steric repulsions which might be expected between the chlorine and oxygen atoms, the stable form of all the compounds studied is that in which these atoms approach as closely together as possible. This holds also for the compounds studied by Mizushima[14, 15] and it can be deduced from the high carbonyl frequencies of halogenated esters that they also take up this preferred orientation. Furthermore, as has been indicated above, there is evidence that in many cases the C–Cl frequency is also increased when the chloro-group is *cis* to the carbonyl group. The apparent strengthening of both the C=O and C–Cl bands in this orientation points to some form of resonance stabilisation, but this cannot be a normal mesomeric effect, which would lead to a fall in the carbonyl frequency owing to an increase in the proportion of the polar form $>\overset{+}{C}-\overset{-}{O}$. A very similar situation appears to arise in acid chlorides in which both the C=O and C–Cl links appear to be strengthened, and it is perhaps noteworthy that both these instances differ sharply from the behaviour of the corresponding vinyl compounds. Thus the substitution of a trifluoromethyl group in the α-position to a C=C bond has little or no effect upon the C=C frequency,[19] whilst in vinyl chloride the C=C frequency is actually lowered, through the operation of a normal mesomeric effect.

[19] Haszeldine, *Nature*, 1951, **168**, 1028.

The origins of this effect are still obscure and we intend to study other related anomalous cases in the hope that some common factor may emerge. It is, however, clear that an electrical effect which is neither an inductive nor a mesomeric effect is operating in the case of α-halogenated carbonyl compounds, and that this effect is subject to a steric limitation which can be turned to good account in the differentiation of rotational isomers.

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