

## Rotational isomerism in $\omega$ -bromoacetophenones

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MS received 27 August 1979; revised 30 January 1980

**Abstract.** The infrared spectra of substituted  $\omega$ -bromoacetophenones were recorded in solvents of varied dielectric constants. All the compounds exhibited two carbonyl bands. The splitting of the bands was attributed to existence of rotomers. The higher and lower frequency bands were assigned to cis and gauche conformations respectively. A linear plot was obtained between the frequencies of the bands and Hammett  $\sigma$  constants. The ratio of the cis and gauche conformers increased with increase in the dielectric constant of the solvent. The results suggest that the relative stabilities of the conformers are determined by the electrostatic repulsion between the C=O and C-Br dipoles in the cis form and electrostatic attraction between negative bromine atom and the carbon atom para to the ring substituent which is rendered positive by the electron withdrawing groups.

**Keywords.**  $\omega$ -bromoacetophenones; carbonyl band splitting; rotational isomerism; cis/gauche ratio; Hammett  $\sigma$  constants.

### 1. Introduction

$\omega$ -haloacetophenones have been shown (Bellamy *et al* 1956; Bellamy and Williams 1957) to exhibit rotational isomerism which gives rise to two carbonyl frequencies, the higher of which was assigned to the cis conformation in which the carbonyl oxygen is eclipsed by the halogen atom and the lower one to the gauche conformation in which it is eclipsed by the hydrogen atom.

The greater stability of the gauche form was ascribed to the preponderance of the electrostatic repulsion between the oxygen and chlorine atoms over the steric repulsion exerted by the phenyl group. In the series of ring substituted chloroacetophenones (Bellamy and Williams 1957) the gauche/cis ratios reported are in the order 2,4 dichloro > 2,5 dichloro > 3,4 dichloro > 4 chloro > unsubstituted > 2,4,6 trichloro. No explanation of the influence of the substituents on the above ratio has been offered but for a remark that doubling of the C=O absorption was found markedly in the ortho substituted compounds in which the influence of steric repulsions would be at maximum.

Jones and Spinner (1958) who studied the isomerism in acetophenone derivatives containing Br, I, CN, C<sub>6</sub>H<sub>5</sub> and OH substituents in the methyl group

showed that the stability of the cis form increase with increased electron withdrawing effect of the group and steric effects in the gauche conformation are less important. They also pointed out that the relative stabilities of the conformers depend upon a complex interplay of the factors which cannot be evaluated *a priori*.

When more than one factor is involved it is desirable to study the influence of any one factor keeping the others common. It is therefore proposed to study the influence of electrostatic repulsion between C=O and C-X dipoles keeping other factors, viz, the inductive influence of the halogen and the steric effects in the cis as well as gauche conformations common. To accomplish this, we have chosen a series of  $\omega$ -bromoacetophenones with electron donor and acceptor groups in the *p*-position, which alter the C=O bond polarity by resonance interaction and thereby the electrostatic repulsion between the C=O and C-Br dipoles.

## 2. Experimental

### 2.1 Preparation of compounds

All the substituted  $\omega$ -bromoacetophenones were prepared by bromination of the corresponding acetophenones (Rather and Reid 1919). The melting points of the compounds agreed well with those reported. The compounds were recrystallised before use.

### 2.2 Purification of the solvents

The solvents used in the study were purified by the methods available in the literature and they were freshly distilled before use and the middle fractions were collected.

### 2.3 Measurement of the spectra

The infrared spectra of equimolar solutions (M/20) of the samples in solvents of varied dielectric constants were recorded at slow speed on Perkin-Elmer 337 grating spectrophotometer at 28° C using NaCl matched cells of 0.5 mm path length.

Extensive overlap of the two carbonyl bands prevented measurement of the integrated intensities. The relative proportions of the cis and gauche conformers were, therefore, estimated by measuring the relative apparent optical densities (Rao 1963) of the high and low frequency bands. The positions of the bands together with the values of relative optical densities of cis/gauche bands in different solvents are presented in table 1. For comparison the positions of C=O bands of substituted acetophenones together with Hammett substituent constants are also presented.

## 3. Results and discussion

All the compounds under investigation exhibited two carbonyl bands. The intensities of the higher frequency bands ( $\nu_1$ ) increased with increase in the dielectric constant of the solvent (table 1). These are therefore assigned to the C=O groups

Table 1. Positions of C=O stretching bands of *p*-substituted acetophenones and  $\omega$ -bromoacetophenones.

X	Hammett $\sigma$ constant	$\omega$ -Bromoacetophenones							
		Aceto- phenones C=O cm <sup>-1</sup>	CCl <sub>4</sub> cm <sup>-1</sup>	CHCl <sub>3</sub> cm <sup>-1</sup>	CH <sub>2</sub> Cl <sub>2</sub> cm <sup>-1</sup>	C <sub>6</sub> H <sub>5</sub> CN cm <sup>-1</sup>	CH <sub>3</sub> CN cm <sup>-1</sup>	CH <sub>3</sub> NO <sub>2</sub> cm <sup>-1</sup>	
OMe	-0.27	1684	1674, 1691 (0.1644)*	1669, 1684 (0.3556)	1669, 1686 (0.4024)	1667, 1683 (0.4877)	1667, 1689 (0.4812)	1672, 1689 (0.4833)	
Me	-0.17	1690	1678, 1704 (0.1832)	1678, 1698 (0.3429)	1672, 1689 (0.4164)	1672, 1689 (0.5110)	1669, 1685 (0.5478)	1668, 1683 (0.5226)	
H	0	1692	1679, 1697 (0.1764)	1678, 1692 (0.3559)	1673, 1689 (0.4562)	1673, 1689 (0.5414)	1677, 1692 (0.5529)	1678, 1691 (0.6148)	
Cl	0.23	1692	1679, 1700 (0.1401)	1678, 1694 (0.2902)	1678, 1698 (0.3761)	1678, 1694 (0.4609)	1678, 1695 (0.5419)	1678, 1696 (0.4984)	
Br	0.23	1693	1678, 1694 (0.1542)	1683, 1700 (0.2828)	1678, 1697 (0.3876)	1674, 1694 (0.5005)	1678, 1692 (0.5672)	1678, 1697 (0.5729)	
NO <sub>2</sub>	0.778	1700	1695, 1716 (0.1455)	1685, 1705 (0.2621)	1689, 1706 (0.3670)	1689, 1706 (0.5543)	1689, 1706 (0.6483)	1689, 1706 (0.5781)	

\*The values in the parenthesis correspond to the ratios of the apparent optical densities of the  $\nu_1$  and  $\nu_2$  bands (i.e. *cis/gauche* ratio)

in the cis conformation and the lower frequency bands ( $\nu_2$ ) to those in the gauche conformation.

The frequencies of the gauche bands of all the compounds are lower than the C=O bands of the corresponding substituted acetophenones. The frequencies, in fact, should have been higher due to the inductive effect of the bromine atom. The mass and steric effects seem to outweigh the inductive influence. To relieve

steric strain the angle  $\angle \text{C}_6\text{H}_5\overset{\text{O}}{\parallel}\text{CCH}_2\text{Br}$  is widened which results in decrease in the C=O frequency (Jones and Spinner 1958). The frequencies of the cis bands are about 18 to 20  $\text{cm}^{-1}$  higher than those of the gauche bands. This is due to the interaction of C=O and C-Br dipoles across space.

Like the C=O bands of substituted acetophenones the gauche and cis bands of  $\omega$ -bromoacetophenones bear a roughly linear relationship with Hammett  $\sigma$  constants (figure 1).

This indicates that the C=O groups of cis and gauche conformers are affected by electrical effects which are quite analogous to those in the substituted acetophenones. The electron donor groups like methyl and the methoxy lower the C=O frequency by their positive mesomeric effects whereas the electron attracting groups, viz, Cl, Br and  $\text{NO}_2$  increase the C=O frequency by retarding the C=O polarisation by their negative inductive and mesomeric effects.

The low cis/gauche ratio in  $\omega$ -bromoacetophenones indicates predominance of electrostatic repulsion between C=O and C-Br dipoles in the cis conformation over the steric repulsion exerted by the phenyl group. If the above ratio is controlled by the electrostatic repulsion in the cis conformation, the value should be lower in the compounds with electron releasing groups compared to that of the unsubstituted due to the increase in the C=O bond polarity and the values should be higher in the compounds with electron attracting groups. The values in general are in the expected order in the case of the former. But in the case of the latter, the values instead of being greater than that of the unsubstituted one

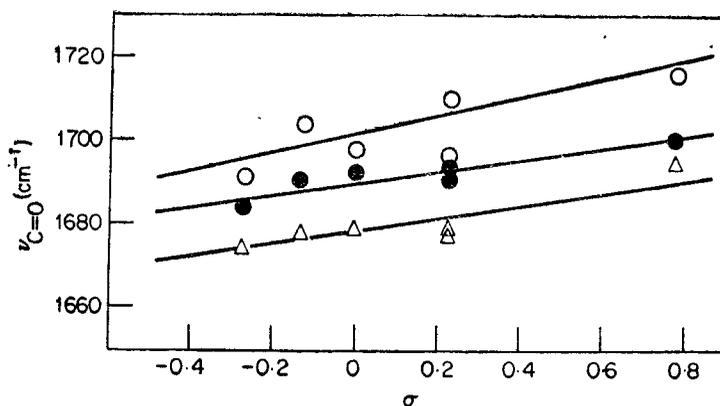
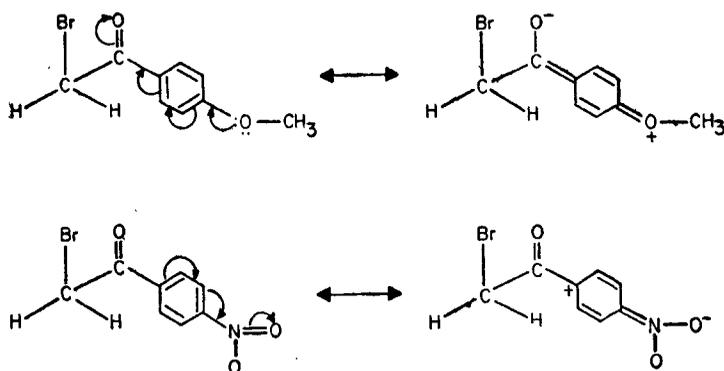


Figure 1. Plot of  $\nu_{\text{C=O}}$  (●) of acetophenones,  $\nu_1$  (○) and  $\nu_2$  (Δ) of *p*-substituted  $\omega$ -bromoacetophenones versus Hammett  $\sigma$ -constants.



are lower. They are even lower than the values of the compounds with electron-releasing substituents. This shows that in these cases the electrostatic repulsion between  $C=O$  and  $C-Br$  dipoles plays a less significant part, and is outweighed by some other factor which leads to greater stability of the gauche conformation. This may probably be the electrostatic attraction between the negative bromine atom and the carbon atom para to the ring substituent which is rendered positive by the electron attracting groups.

Similar explanation was earlier offered for explaining the predominance of the gauche form in *N*-methyl chloroacetamide (Mizushima *et al* 1956). The attraction between the chlorine atom and positive nitrogen renders the gauche form more stable.

Thus the values in general suggest that the relative stabilities of the conformers of  $\omega$ -bromoacetophenones are determined by the electrostatic repulsion between  $C=O$  and  $C-Br$  dipoles in the cis form and electrostatic attraction between the bromine atom and the positive carbon para to the ring substituent in the gauche form.

### Acknowledgements

The authors are grateful to Prof. V R Srinivasan, Principal, University College of Science, Osmania University, for helpful discussions and suggestions and Prof. T Navaneeth Rao for providing facilities.

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