Infrared Spectra of p-Bromophenacyl Esters

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In previous papers[1,2] it has been demonstrated that aureothinic acid and *N*-benzoyl aminotetrahydroaureothinic acid have structures (I) and (II), respectively. The location of an etheric oxygen at an α-position of the carboxyl group in these acids was suggested by the comparison of infrared spectra of several model compounds[1] and was established rigorously by oxidative studies[2].

During the course of the structural elucidation of these acids, however, attention was called to the fact that the infrared spectra of their *p*-bromophenacyl esters in chloroform solution show ester carbonyl absorption at

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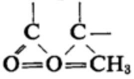
[1] H. Nakata, Y. Hirata, K. Okuhara, K. Yamada, T. Naito and K. Iwadare, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **79**, 379 (1958).

[2] Y. Hirata, H. Nakata and K. Yamada, ibid., **79**, 390 (1958).

TABLE I. INFRARED SPECTRA OF *p*-BROMOPHENACYL ESTERS ($RCOOCH_2COC_6H_4Br$-*p*) IN CHLOROFORM SOLUTION

No.	Compound R-	m. p.[a] °C	Ester C=O cm^{-1}	Keto C=O cm^{-1}	$\sum(\sigma^*)$[b]
1	n-C_7H_{15}-	65∼ 66	1743	1707	-0.130[c]
2	n-C_5H_{11}-	71∼ 72	1742	1707	-0.130[c]
3	n-C_3H_7-	62∼ 63	1743	1707	-0.115
4	C_2H_5-	55∼ 58	1743	1705	-0.100
5	CH_3-	75∼ 78	1744	1703	0.000
6	$C_6H_5CH_2$-	84∼ 86	1748	1708	$+0.215$
7	$CH_3OCOCH_2CH_2$-[d]	105∼106	1746	1708	$+0.254$[e]
8	$CH_3CHClCH_2$-	75∼ 76	1749	1708	$+0.270$[f]
9	$CH_3CH(OH)$-	111∼112	1750	1708	$+0.455$[f]
10	H-	100∼101[g]	1737	1706	$+0.490$
11	$C_2H_5OCH_2$-	106∼107	1763	1706	$+0.520$
12	n-$C_4H_9OCH_2$-	90∼ 91	1764	1706	$+0.520$
13	$HOCH_2$-	136∼138	1751	1707	$+0.555$
14	$C_6H_5CONHCH_2$-[h]	148∼149	1753	1706	$+0.727$[i]
15	$C_6H_5CH(OH)$-	113∼114	1750	1707	$+0.765$
16	$C_6H_5OCH_2$-	149∼150	1774	1707	$+0.850$
17	ICH_2-	99∼100	1751	1710	$+0.850$
18	CH_3CH_2CHBr-	(oil)	1753	1712	$+0.885$[f]
19	$(C_6H_5)_2C(OH)$-	154∼155	1743	1710	$+0.960$[f]
20	$ClCH_2$-	105∼106	1756	1705	$+1.050$
21	Aureothinic acid (Ia)	174∼175	1758	1706	$+0.390$[f]
22	*N*-Benzoyl aminotetrahydroaureothinic acid (IIa)[j]	145∼146	1758	1707	$+0.390$[f]
23	$CH_3COCH(CH_3)CH_2$-[k]	91	1745	1698	$+0.099$[f]
24	CH_2-CH-CH_3[k,l]  $\begin{array}{lll} CH_2- & CH- & CH_3 \\ \mid & \mid & \\ C & C- & \\ O=O=CH_3 & & \end{array}$	105∼106	1751	1702	$+0.720$[m]

a) All melting points are uncorrected.

b) The value is taken from Taft (Refs. 3 and 4), unless otherwise indicated.

c) Approximated with the value for n-C_4H_9- substituent.

d) The ester carbonyl group appeared at 1738 cm^{-1}.

e) Calculated from the value for CH_3OCO- substituent using the inductive parameter of 2.8 (Refs. 3 and 4).

f) Calculated using the additive nature of σ^* values (Refs. 3 and 4).

g) T. Kubota and T. Matsuura, *J. Chem. Soc. Japan, Pure Chem. Sec. (Nippon Kagaku Zasshi)*, **72**, 482 (1951).

h) The amide carbonyl group appeared at 1663 cm^{-1}.

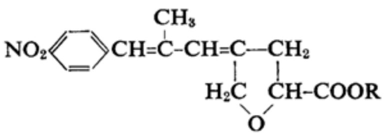
i) Estimated from the relations $\sigma^*=\sigma_I/0.45$ and $\sigma_I=(\alpha\cdot\sigma_p-\sigma_m)/(\alpha-1)$ (Refs. 3 and 4, and R. W. Taft, Jr. and I. C. Lewis, *J. Am. Chem. Soc.*, **80**, 2436 (1958).), using σ_p of $+0.078$ and σ_m of $+0.217$ (H. H. Jaffe, *Chem. Revs.*, **53**, 191 (1953).) and $\alpha=+0.443$ (J. L. Roberts and H. H. Jaffe, *J. Am. Chem. Soc.*, **81**, 1635 (1959).).

j) The amide carbonyl group appeared at 1660 cm^{-1}.

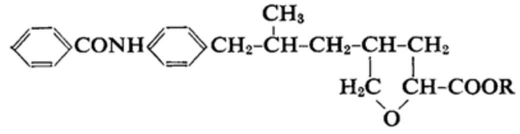
k) R. B. Bradbury and S. Masamune, *J. Am. Chem. Soc.*, **81**, 5201 (1959).

l) The lactone carbonyl group appeared at 1779 cm^{-1}.

m) The σ^* value for CH_3COOCH_2- group was estimated as $+1.010$ from the same relations cited in foot-note i) of this Table using σ_p of $+0.31$ and σ_m of $+0.39$ (D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, **23**, 420 (1958).), and $\alpha=+0.448$ (J. L. Roberts and H. H. Jaffe, *J. Am. Chem. Soc.*, **81**, 1635 (1959).). The additive nature of σ^* values then leads to the value of $+0.720$ for this γ-lactone grouping.



(I) R=H, aureothinic acid
(Ia) $R=CH_2COC_6H_4Br$-*p*



(II) R=H, *N*-benzoyl aminotetrahydro-aureothinic acid
(IIa) $R=CH_2COC_6H_4Br$-*p*

1758 cm^{-1}, which is considered to be an abnormally high frequency, and it became desirable to examine the infrared spectra of several *p*-bromophenacyl esters. Consequently, twenty *p*-bromophenacyl esters were prepared and their spectra were measured in chloroform solution. The results are summarized in Table I.

The absorption bands of keto carbonyl groups appear in the same frequency range of 1705~1710 cm^{-1}. On the other hand, in the spectra of the ester carbonyl groups an etheric function located at an α-position of the carboxyl group causes a considerable shift of frequency, as is evident from Table I (compounds No. 11, 12, 16, 21 and 22). While the inductive effect of electronegative α-oxygen substituents has usually been cited as the probable cause for the frequency shifts, it has not been possible to differentiate this from direct field effects. A more quantitative understanding of these may be discussed in terms of inductive parameters of the substituents. When the polar substituent constant σ^* reported by Taft[3,4] is taken as a measure of inductive effects, the ester carbonyl frequencies presented in Table I define a straight line when plotted against the appropriate σ^*-values (Fig. 1). The linear correlation obtained is reasonably good and it was found possible to write the following approximate relation:

$$\nu_{C=O}\,\mathrm{cm}^{-1}=1745\,\mathrm{cm}^{-1}+9.1(\sum\sigma^*)\mathrm{cm}^{-1} \qquad (1)$$

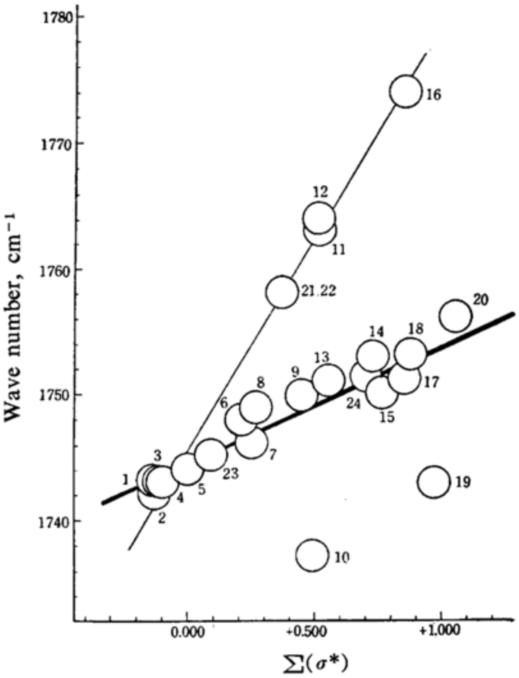


Fig. 1. The linear correlation between polar substituent constants and ester carbonyl frequencies of *p*-bromophenacyl esters. (The numbers refer to the compounds listed in Table II.)

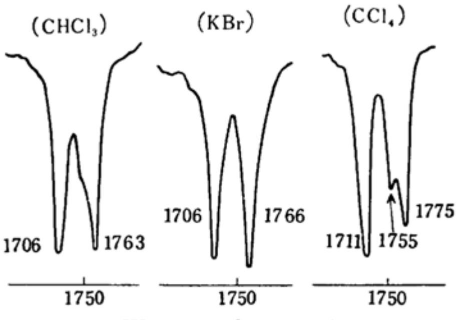


Fig. 2. Infrared spectra of *p*-bromophenacyl ethoxy acetate.

It is apparent from Fig. 1 that the absorption bands of both aureothinic (No. 21) and *N*-benzoyl aminotetrahydroaureothinic (No. 22) esters deviate from the correlation line by an amount of 10 cm^{-1}. The deviations are more serious with the ethoxy- (No. 11) and *n*-butoxy-acetic (No. 12) esters and even more so with phenoxy-acetic (No. 16). Therefore, it may be concluded that these deviations are characteristic with esters having an etheric oxygen at their α-positions.

As is shown in Fig. 2, the band of these esters in chloroform solution had a shoulder at a low frequency region, while only a sharp band appeared when the spectrum was measured in the solid state (potassium bromide disks). Recently, House and Blaker[5] have reported that in the carbonyl region glycidic esters such as III and ethyl tetrahydrofuroate (IV) both

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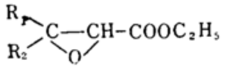
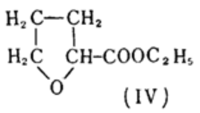
[3] R. W. Taft, Jr., *J. Am. Chem. Soc.*, **75**, 4231 (1953).

[4] R. W. Taft, Jr., in M. S. Newman ed., "Steric Effects in Organic Chemistry", Chapter 13, John Wiley & Sons, Inc., New York (1956).

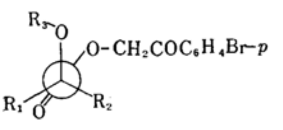
[5] H. O. House and J. W. Blaker, *J. Am. Chem. Soc.*, **80**, 6389 (1958).

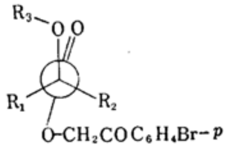
exhibited two bands attributable to the presence of two conformations of esters in the solution[6]. The same explanation can be applied to *p*-bromophenacyl esters having an α-oxygen substituent.


(III)


(IV)

These esters would exist in two conformations V and VI in solution. Since the C=O and C-O dipoles are oriented in opposite directions in the conformation V, the spectrum of this structure would be expected to have a normal carbonyl absorption band of *p*-bromophenacyl esters in the range of 1740~1755 cm^{-1}, while in the conformation VI, where these dipoles are oriented in the same direction, the direct field effects between these dipoles would be expected, which would result in the carbonyl vibration shifting towards higher frequencies.


(V)


(VI)

These considerations are exactly parallel with those employed in interpret the infrared spectra of α-haloketones and α-haloesters[7].

The molecular extinctions of the two conformations are not known and the actual concentrations of the two conformations could not be calculated. However, it may be concluded that these esters exist largely as the conformation VI in chloroform solution, since the lower frequency band of the conformation V is a shoulder and since a study of α-bromoketo steroids suggests that the molecular extinction of the conformation VI should have a lower value than that of V[8]. Recently, Brown[9] has reported the value 3.36 : 2.77 for the ratio of apparent intensities of the corresponding conformations for ethyl α-ethoxy acetate.

To explore the validity of the above presumption, infrared spectra of these esters were examined in carbon tetrachloride solution. As was evident from studies[10] of α-bromocyclohexanone in various solvents, the less polar conformation V is stabilized by the less polar solvent so that the spectra of conformations V and VI would be separated from each other. This is actually the case; thus, as is shown in Fig. 2, the spectrum of *p*-bromophenacyl ethoxyacetate in carbon tetrachloride solution exhibits two bands at 1755 and 1775 cm^{-1} in ester carbonyl region corresponding to the conformations V and VI, respectively. The same is true for *n*-butoxyacetic and monochloroacetic esters. The band frequencies of some esters in carbon tetrachloride solution are shown in Table II. Monoiodoacetic ester and α-bromobutyric ester did not exhibit two bands even in this non-polar solvent. This observation agrees with the conclusion of Brown[9] that the distribution of two conformations of these esters is controlled largely by the size of the group rather than by the dipole-dipole repulsion.

TABLE II. INFRARED SPECTRA OF *p*-BROMOPHENACYL ESTERS ($RCOOCH_2COC_6H_4Br$-*p*) IN CARBON TETRACHLORIDE SOLUTION

Compound[a]		Ester C=O	Keto C=O
No.[b]	R-	cm^{-1}	cm^{-1}
3	*n*-C_3H_7-	1753	1712
4	C_2H_5-	1755	1712
5	CH_3-	1759	1712
6	$C_6H_5CH_2$-	1751	1711
8	$CH_3CHClCH_2$-	1753	1711
9	$CH_3CH(OH)$-	1753	1710
10	H-	1745	1713
11	$C_2H_5OCH_2$-	{1775 1755	1711
12	*n*-$C_4H_9OCH_2$-	{1773 1753	1712
17	ICH_2-	1754	1712
18	CH_3CH_2CHBr-	1755	1711
20	$ClCH_2$-	{1781 1758	1711

a) Most of the compounds not listed in this table were sparingly soluble in carbon tetrachloride and their spectra could not be examined.

b) The number refer to the compounds listed in Table I.

Another peculiarity observed in the spectra of most *p*-bromophenacyl esters was the appearance of a set of three strong to medium intensity bands around 1000 cm^{-1}, which probably originate from the *p*-bromophenacyl

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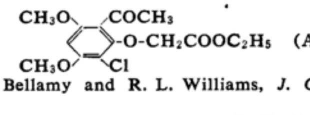
[6] Dawkins and Mulholland noticed that the ester carbonyl band of the ester (A) splitted (1763 and 1753 cm^{-1}) even in the solid state (Nujol). See, A. W, Dawkins and T. P. C. Mulholland, *J. Chem. Soc.*, **1959**, 2211.


(A)

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

[8] R. N. Jones, D. A. Ramsay, F. Herling and K. Dobriner, *J. Am. Chem. Soc.*, **74**, 2828 (1952).

[9] T. L. Brown, *J. Am. Chem. Soc.*, **80**, 3513 (1958).

[10] J. Allinger and N. L. Allinger, *Tetrahedron*, **2**, 64 (1958).

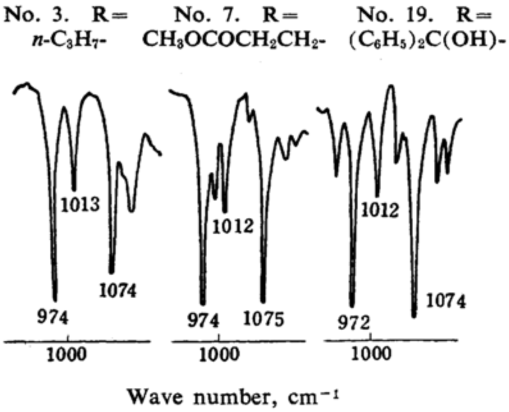


Fig. 3. Characteristic bands of p-bromophenacyl ester ($RCOOCH_2COC_6H_4Br$-p) around 1000 cm^{-1} ($CHCl_3$).

group. Thus, these bands appear at 1076±2 cm^{-1} (strong), 1014±2 cm^{-1} (medium), and 972±4 cm^{-1} (strong), and are almost independent of the structure of respective acids. These bands are therefore useful for the recognition of p-bromophenacyl esters. The characteristic shapes of these bands are shown in Fig. 3.

Provided that direct comparisons of spectra of p-bromophenacyl esters with the linear correlation of Eq. 1 are possible, the ester carbonyl absorption band would enable one to evaluate the appropriate $\sum\sigma^*$ value, which, in turn, would predict the nature of substituents around the carboxyl group of the respective acid, since only a few anomalies have been observed in the correlation except for those described above. While the abnormal frequency lowering in formic ester (No. 10) is not unexpected, the cause for the considerable deviation from the correlation in benzilic ester (No. 19) is not known.

Finally it is of interest to note that the frequencies of esters having an etheric function at their α-position define another straight line in Fig. 1. Since the abnormally high frequency of these esters is ascribable to the direct field effect of alkoxyl groups, this linear correlation would probably suggest the linearity between the field effect and the inductive effect, at least, for these alkoxyl groups. However, more accurate and sufficient data may be required in order to test such a quantitative correlation.

Experimental

General Procedure for Preparation of p-Bromophenacyl Esters. — About 500 mg. of the acid are added to a mixture of 1 ml. of water and 2 ml. of alcohol in a small flask and are neutralized carefully with crystalline sodium bicarbonate. The mixture is warmed very gently on a water bath until evolution of carbon dioxide ceases. The remaining sodium bicarbonate is filtered and the filtrate is added with one or two drops of the acid. Five ml. of alcohol and 500 mg. of p-bromophenacyl bromide are added and the mixture is then heated under reflux for 1 hr. Occasionally the addition of a few more milliliters of alcohol may be necessary if a solid separates during the refluxing. The solution is allowed to cool, and the precipitated ester is purified by recrystallization from alcohol or from aqueous alcohol. The melting point of the ester is listed in Table I.

Infrared Absorption Measurements.—The spectra were recorded on a Hilger H 800 double beam instrument equipped with sodium chloride optics. Spectra of the solution were measured using 0.16 mm. sodium chloride cells.

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