

RAMAN EFFECT AND CHEMICAL CONSTITUTION

Influence of Constitutive and Other Factors on the Double Bonds in Organic Compounds

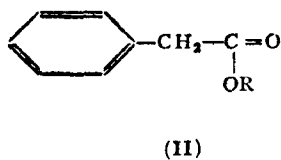
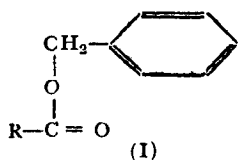
Part III. Effect of the Benzyl Group on the C = O Bond in Esters

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IN a previous communication (Part II)¹ it was shown that a phenyl group attached directly to the carbon of the C = O as in the esters of aromatic acids and in aromatic ketones markedly lowers the frequency of the C = O bond whereas the same group attached to the oxygen of the COO as in phenyl esters definitely increases it. These phenomena were explained as due to the existence of resonance in the first group of compounds and in the second group as due to the reinforcement by the phenyl nucleus of the normal electro-meric polarisation of esters towards the C = O resulting in greater electron access. That the explanation is correct and that the marked changes in the C = O frequencies are neither due to the bulk of the phenyl group nor due to the general inductive effect is confirmed by the study of the benzyl esters of various acids (I) and the esters of phenyl acetic acid (II) recorded in this paper. The new feature introduced in these compounds is the presence of a CH₂ group adjacent to the phenyl ring which prohibits the transmission of electromeric effects from it to the carbonyl group.



Benzyl esters as a class do not seem to have received much attention in connection with the Raman Effect. Benzyl acetate² appears to be the only compound so far investigated and here too the results are not satisfactory since very few lines have been recorded and the Raman line corresponding

to the C = O bond has been missed. This substance has therefore been reinvestigated and the spectra of the benzyl esters of propionic, benzoic and cinnamic acids have been studied in detail. The results have been compared with those relating to the corresponding phenyl and ethyl esters. Further, the spectra of the phenyl esters of propionic and phenyl acetic acid have been studied in detail and those of ethyl propionate and ethyl phenyl acetate reinvestigated. Particulars regarding experimental procedure are the same as recorded in Part II. Spectra of a few typical cases are reproduced at the end of the paper and the C = O frequencies are indicated by arrows.

Preparation of the Esters.—Ethyl propionate and the ethyl ester of phenyl acetic acid were prepared by heating mixtures of the appropriate acid and alcohol along with a few c.c. of concentrated sulphuric acid. Phenyl propionate was obtained by heating dry phenol with sodium propionate and propionic anhydride at 160° in an oil-bath for 4 hours. For producing the phenyl ester of phenyl acetic acid the acid chloride was first obtained by the action of thionyl chloride and was made to react with dry phenol in the presence of pyridine. All the esters were repeatedly washed with aqueous sodium carbonate, dried and finally purified by distillation *in vacuo*. As for the other esters pure samples from Kahlbaum were available. They were however subjected to redistillation *in vacuo* before being employed for taking the Raman spectra.

TABLE I

Esters of Acetic Acid.

Benzyl acetate.	Benzyl acetate. (Morris ²).	Phenyl acetate ¹ .	*Ethyl acetate.
187 (2)	..	185 (1)	..
223 (2)	..	239 (4)	..
263 (1)	..	272 (4)	..
300 (1)
329 (1)	364 (1)	341 (1)	376 (9)
426 (0)
499 (1)	479 (1)
..	..	529 (5)	..
580 (5)	..	597 (1)	..
619 (3)	..	618 (4)	633 (9)
642 (2)	633 (1)	664 (4)	..
..	..	694 (2)	..
751 (1)	..	744 (5)	..
..	..	815 (5)	784 (3)
820 (1)	..	829 (1)	..
839 (3)	846 (10)
..	..	892 (2)	..
919 (2)	..	926 (1)	916 (1)
..	938 (1)
1002 (10)	998 (4)	1004 (10)	999 (1)
1028 (4)	1022 (2)	1027 (3)	1045 (2)
1077 (3)	..	1079 (1)	1096 (1)
1119 (3)	1114 (3)
1157 (3)	..	1163 (6)	..
1181 (2)	..	1195 (6)	..
1213 (1)
1244 (1)
1263 (2)	..	1262 (1)	..
..	..	1311 (1)	..
..	..	1369 (1)	..
..	..	1429 (1)	..
1452 (2)	..	1448 (1)	1452 (6 b)
1585 (2)	..	1596 (8)	..
1606 (8)	1602 (1)
1745 (4)	..	1766 (3)	1739 (6 b)
..	..	2912 (3)	2880 (1)
2940 (2)	2933 (2)	..	2940 (9 b)
..	3046 (2)	..	2982 (7 b)
3070 (7)	..	3070 (7)	..

TABLE II

Esters of Propionic Acid.

TABLE III

Esters of Benzoic Acid.

Benzyl propionate.	Phenyl propionate.	Ethyl propionate*.	Benzyl benzoate.	Phenyl benzoate ¹ .	Ethyl benzoate.
184 (1)	186 (1)	..	202 (2)	..	193 (3)
220 (2)	230 (2)	..	239 (2)	..	214 (2)
263 (2)	268 (2)	..	274 (2)
300 (1)	332 (1)	340 (3)	326 (4)
329 (1)	338 (1)	376 (9)	381 (1)	..	395 (1)
425 (1)	446 (1)	..	488 (1)
495 (1)	545 (1)	..	558 (1)
..	529 (3)
580 (2)	618 (5)	610 (3)	619 (6)
620 (4)	618 (2)	635 (9)	676 (3)	674 (1)	677 (4)
640 (2)	660 (2)	..	754 (2)	..	783 (2)
753 (2)	740 (3)	784 (2)	805 (1)	..	809 (2)
824 (2)	820 (4)	..	883 (2)	850 (2)	852 (5)
840 (5)	..	846 (10)	1003 (10)	1000 (10)	1004 (10)
..	890 (0)	..	1030 (2)	1030 (2)	1029 (3)
921 (2)	926 (0)	938 (0)	1111 (2)	1115 (2)	1112 (3)
1000 (10)	1004 (10)	1000 (0)	1158 (2)	1158 (2)	1160 (2)
1030 (2)	1030 (2)	1045 (1)	1179 (1)	1176 (1)	1178 (2)
1078 (1)	1215 (1)
1120 (2)	..	1114 (2)	1269 (2)	1274 (3)	1277 (5)
1158 (2)	1163 (3)	..	1313 (1)	1310 (1)	1314 (2)
1180 (2)	1195 (3)	..	1378 (1)	1365 (1)	1371 (2)
1214 (4)	1391 (2)
1242 (2)	1451 (1)	1450 (2)	1453 (3)
1264 (1)	1493 (1)	..	1493 (1)
1453 (2)	..	1452 (6 b)	1602 (10)	1604 (10)	1602 (10)
1510 (1)	1719 (7)	1740 (7)	1720 (8)
1548 (2)	1598 (6)	..	2868 (1)
1604 (8)	2956 (1)	2930 (1)	2935 (2)
1745 (5)	1760 (3)	1740 (6 b)	2975 (1)	..	2972 (2)
2938 (1)	2912 (1)	2940 (9 b)	3067 (5)	3070 (5)	3076 (6)
2978 (1)	..	2982 (7 b)
3068 (8)	3072 (5)

* These esters were investigated by earlier workers but with a view to effect a more satisfactory comparison between the various results they were reinvestigated and the results given are those obtained by the authors.

TABLE IV
Esters of Cinnamic Acid.

TABLE V
Esters of Phenyl Acetic Acid.

Benzyl cinnamate.	Phenyl cinnamate.	Ethyl cinnamate ¹ .	Phenyl ester.	Ethyl ester.
270 (1)	274 (1)	270 (1)	240 (1)	242 (3)
355 (1)	357 (1)	357 (1)	480 (1)	475 (2)
584 (1)	580 (1)	582 (1)	528 (1)	527 (2)
620 (1)	618 (1)	619 (2)	620 (3)	619 (5)
715 (2)	715 (2)	713 (2)	761 (2)	764 (3 b)
834 (2)	840 (2)	830 (1)	840 (1)	842 (2)
941 (2)	945 (2)	943 (2)	878 (1)	875 (2)
970 (1)	974 (2)	972 (2)	1002 (10)	1004 (10)
1000 (7)	1000 (7)	999 (7)	1030 (4)	1033 (6)
1030 (2)	1030 (3)	1030 (2)	..	1108 (0)
1156 (2)	1153 (2)	1160 (3)	1160 (2)	1159 (3)
1182 (4)	1180 (4)	1186 (5)	1188 (2)	1193 (3 b)
1204 (6)	1202 (6)	1204 (6)	1216 (0)	1215 (2)
1250 (2)	1255 (2)	1250 (2)	..	1300 (1)
1300 (1)	1301 (1)	1305 (1)	1450 (1)	1454 (2 b)
1452 (2)	1450 (2)	1450 (2)	1582 (1)	1587 (2)
1514 (1)	..	1516 (1)	1602 (4)	1604 (6)
1540 (2)	1540 (2)	1540 (2)	1761 (2 b)	1736 (3 b)
1575 (2)	1570 (2)	1578 (2)	..	2875 (0)
1598 (7)	1596 (7)	1598 (7)	2930 (2)	2933 (3 b)
1634 (10)	1633 (10)	1634 (10)	2972 (2 b)	2972 (3 b)
1713 (5 b)	1742 (4 b)	1712 (5 b)	3066 (6 b)	3064 (6 b)
2940 (1)	2940 (1)	2940 (1)		
3065 (1)	3067 (1)	3066 (1)		

Discussion of Results.—1. A comparison of the spectra of the esters of acetic and propionic acids indicates that there is a large general agreement between the phenyl and benzyl esters because of the existence in their molecules of a phenyl ring which is absent in the ethyl esters. As regards the carbonyl frequency, however, the resemblance between the ethyl and benzyl esters is very close, being much lower than that exhibited by the phenyl esters.

2. The general resemblances between the spectra of the esters of phenyl acetic, benzoic and cinnamic acids are greater since there is at least one benzene ring in all of them besides other similar structural features. Here again the carbonyl frequencies of the ethyl and benzyl esters agree closely and differ from those of the phenyl esters.

3. The Raman spectrum of ethyl propionate was studied by Kohlrausch, Koppel and Pongratz³ who recorded the C = O frequency as $1731 \pm 9 \text{ cm.}^{-1}$

Working on the same substance subsequently Paranjpe and Savanur⁴ reported the C = O frequency as 1719 cm.⁻¹ which is much lower than the C = O frequency for benzyl propionate recorded by us and that of the ethyl esters of other aliphatic acids. Hence ethyl propionate was reinvestigated and the C = O frequency, 1740 cm.⁻¹, now obtained falls into line with expectations.

4. A comparison of the spectra of the esters of phenyl acetic acid with those of the corresponding esters of acetic, propionic and benzoic acids shows that the C = O frequencies in the esters of phenyl acetic acid agree closely with those given by the esters of acetic and propionic acids and are always higher than those of the esters of benzoic acid.

TABLE VI
C = O Frequencies.

	Benzyl ester.	Phenyl ester.	Ethyl ester.
Ester of acetic acid ..	1745	1766	1739
„ Propionic acid ..	1745	1760	1740
„ Phenyl acetic acid	1761	1736
„ Benzoic acid ..	1719	1740	1720
„ Cinnamic acid ..	1713	1742	1712

The above Table VI in which the results are summarised as far as the C = O frequencies are concerned shows clearly that the separation of the phenyl group from the carbonyl by a CH₂ completely prevents the transmission of the effect that was originally found to lower or enhance markedly the carbonyl frequency. The same feature can be noticed in the examples which are given in Table VII relating to other carbonyl compounds.

TABLE VII
C = O Frequencies.

Acetophenone	1679	Acetaldehyde ..	1716	Acetyl chloride ..	1798
Benzyl phenyl ketone ..	1675	Phenyl acetaldehyde ..	1718	Phenyl acetyl chloride ..	1797
Benzophenone ..	1652	Benzaldehyde ..	1700	Benzoyl chloride	1770

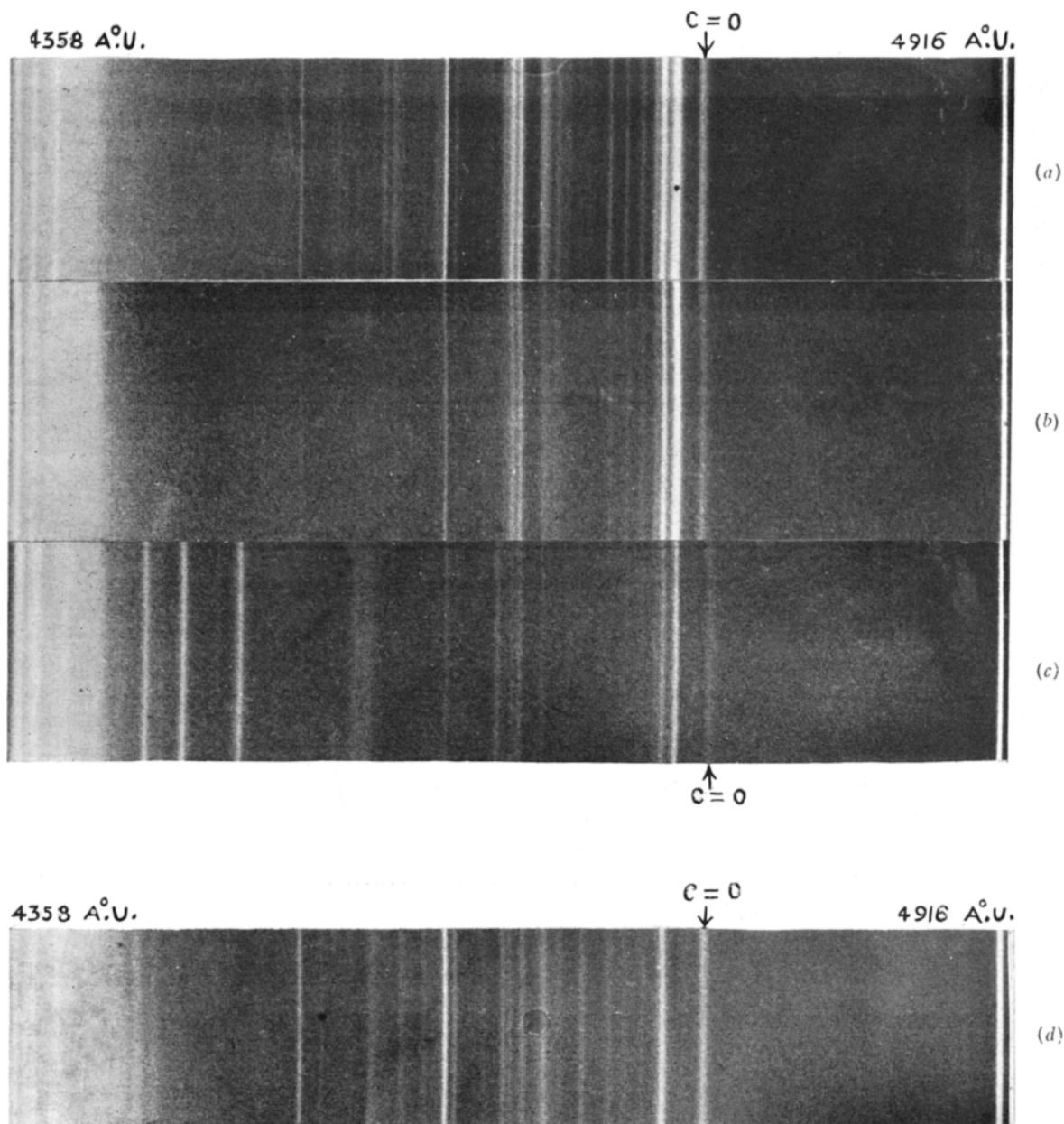
The results given in this series of papers indicate that the carbonyl group is readily susceptible to small changes in the structure of the molecule. It could further be concluded that the bulk and general inductive effect of adjacent groups do not have any appreciable influence as compared with the electromeric effect since a benzyl group plays the same part as an ethyl or methyl group and differs markedly from the phenyl group. The explanation obviously lies in the fact that the transmission of the electromeric effects from the benzene ring is prevented by the introduction of a CH_2 group.

Summary

Raman spectra of esters containing the benzyl group, (i) benzyl esters of various acids and (ii) esters of phenyl acetic acid derived from different alcohols, have been investigated. Data relating to other carbonyl compounds such as ketones, aldehydes and acid chlorides have been collected. In regard to its influence on the $\text{C} = \text{O}$ frequency the benzyl group is found to resemble closely alkyl groups and to differ markedly from the phenyl. This confirms the views already expressed in Part II and establishes that the $\text{C} = \text{O}$ group is influenced mainly by the electromeric effect. The introduction of an additional CH_2 prevents the transmission of this effect.

REFERENCES

1. Murty and Seshadri . . *Proc. Ind. Acad. Sci.*, 1939, **10**, 307.
2. Morris *Phy. Rev.*, 1931, **33**, 141.
3. Kohlrausch, Koppel and Pongratz . . *Z. Phys. Chem.*, Abt. B., 1933, **22**, 359.
4. Paranjpe and Savanur . . *Ind. J. Phys.*, 1934, **8**, 503.



(a) Ethyl cinnamate. (b) Benzyl cinnamate. (c) Phenyl cinnamate in carbon tetrachloride. (d) Benzyl benzoate.