

486. *Periodate Oxidation. Part VI.*¹ *Infrared Spectra of Some Hemialdal Esters.*

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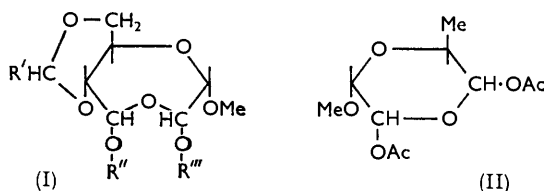
Hemialdal diesters (acetates, benzoates, and *p*-phenylazobenzoates) have carbonyl stretching absorptions at frequencies higher than those reported for normal esters. Reasons for this phenomenon are discussed. The high carbonyl stretching frequencies of *gem*-diol diacetates are also discussed.

DURING work on periodate-oxidised carbohydrate derivatives,^{1,2} it was observed that acetates of the hemialdal group [$\text{CH}(\text{OH})\cdot\text{O}\cdot\text{CH}(\text{OH})$] had ester carbonyl stretching absorptions in the infrared spectrum at frequencies much higher than those normally reported for acetates of carbohydrates or aliphatic alcohols; a similar effect was noted with benzoates and *p*-phenylazobenzoates. Most of the hemialdal compounds studied were esters of periodate-oxidised methyl 4,6-*O*-alkylidene- or -arylidene- α -D-glucosides (I), with the exception of the diacetate of periodate-oxidised methyl α -L-rhamnoside (II). The results obtained, together with those for other compounds studied for comparison, are

¹ Part V, Colbran, Guthrie, and Parsons, *J.*, 1960, 3532.

² Guthrie and Honeyman, *J.*, 1959, 2441.

shown in Table I. Each sample was examined as a mull in Nujol and also as a solution in chloroform; the hemialdal diester values were high in both media. When a spectrum had



two carbonyl bonds, both were higher than the normal frequency, showing that vibrational interaction had not occurred. The normal frequencies quoted³ for saturated esters are 1750—1735 cm.⁻¹; for aryl esters, 1730—1717 cm.⁻¹.

TABLE I. Hemialdal diester frequencies are in bold-face type.

Acetates	$\nu_{C=O}$ (Nujol) (cm. ⁻¹)	$\nu_{C=O}$ (CHCl ₃) (cm. ⁻¹)
1. Ethyl acetate	—	1734
2. 2,3-5,6-Di- <i>O</i> -isopropylidene- <i>D</i> -mannose 1-acetate	—	1748
3. 7,9-Diacetoxy-6 α -methoxy-2-phenyl- <i>trans-m</i> -dioxano-[5,4- <i>e</i>][1,4]dioxepan, ^a (I; R' = Ph, R'' = R''' = Ac) ²	1784, 1773 1770, 1760sh ^c	1775, 1764sh 1767sh, 1757
4. 3,5-Diacetoxy-2 α -methoxy-6 β -methyl-1,4-dioxan (II) ^b		
5. 7(or 9)-Acetoxy-9(or 7)-benzyloxy-6 α -methoxy-2-phenyl- <i>trans-m</i> -dioxano[5,4- <i>e</i>][1,4]dioxepan (I; R' = Ph, R'' or R''' = Ph·CH ₂ , R''' or R'' = Ac) ² ...	1757	—
6. Methyl 4,6- <i>O</i> -benzylidene- α - <i>D</i> -glucoside 2,3-diacetate ^d	—	1743
<i>p</i> -Phenylazobenzoates		
7. Ethyl <i>p</i> -phenylazobenzoate	1719 1713sh	1716
8. 2,3-5,6-Di- <i>O</i> -isopropylidene- <i>D</i> -mannose 1- <i>p</i> -phenylazobenzoate ^e	1725	1732
9. 2,3,4,6-Tetra- <i>O</i> -methyl- <i>D</i> -glucose 1- <i>p</i> -phenylazobenzoate ^f	1739	—
10. 6 α -Methoxy-2-phenyl-7,9-di- <i>p</i> -phenylazobenzoyloxy- <i>trans-m</i> -dioxano[5,4- <i>e</i>][1,4]dioxepan (I, R' = Ph, R'' = R''' = Az) ^g	1764, 1751	1746
11. 6 α -Methoxy-2-methyl-7,9-di- <i>p</i> -phenylazobenzoyloxy- <i>trans-m</i> -dioxano[5,4- <i>e</i>][1,4]dioxepan (I, R' = Me, R'' = R''' = Az)	1762, 1750	1747
<i>Benzoates</i>		
12. Ethyl benzoate	—	1716
13. Methyl 4,6- <i>O</i> -benzylidene- α - <i>D</i> -glucoside 2,3-dibenzoate	1726	1731
14. Methyl 4,6- <i>O</i> - <i>o</i> -bromobenzylidene- α - <i>D</i> -glucoside 2,3-dibenzoate ¹	1725	1729
15. 2,3-5,6-Di- <i>O</i> -isopropylidene- <i>D</i> -mannose 1-benzoate ^h	1727	1732
16. 7,9-Dibenzoyloxy-6 α -methoxy-2-phenyl- <i>trans-m</i> -dioxano[5,4- <i>e</i>][1,4]dioxepan (I; R' = Ph, R'' = R''' = Bz) ²	1734	1743
17. 7,9-Dibenzoyloxy-2- <i>o</i> -chlorophenyl-6 α -methoxy- <i>trans-m</i> -dioxano[5,4- <i>e</i>][1,4]dioxepan (I; R' = <i>o</i> -Cl·C ₆ H ₄ , R'' = R''' = Bz) ¹	1758, 1746	1747
18. 7(or 9)-Benzoyloxy-2- <i>o</i> -chlorophenyl-6 α ,9(or 7)dimethoxy- <i>trans-m</i> -dioxano[5,4- <i>e</i>][1,4]dioxepan (I; R' = <i>o</i> -Cl·C ₆ H ₄ , R'' or R''' = Bz, R''' or R'' = Me) ¹	1746	—

sh = shoulder; ^a see ref. 2 for an explanation of this nomenclature; ^b the methyl group is arbitrarily defined as β , so that the original anomeric carbon atom (now C₂) bears the same Greek suffix as in the unoxidised compound); ^c syrup; ^d Bourne, Stacey, Tatlow, and Tatlow, *J.*, 1951, 833; ^e Coleman and McCloskey, *J. Amer. Chem. Soc.*, 1943, **65**, 1588; ^f Freudenberg and Plankenhorn, *Ber.*, 1940, **73**, 621; ^g Az = *p*-C₆H₅·N·N·C₆H₄·CO; ^h Guthrie and Honeyman, *J.*, 1959, 853.

The most marked shift was with the hemialdal acetates (nos. 3 and 4). The *p*-phenylazobenzoates (nos. 10 and 11) showed a more marked change in the solid state than in

³ Bellamy, "Infrared Spectra of Complex Molecules," Methuen, 1958, p. 178.

solution. The benzoates (nos. 16 and 17) showed a marked shift in solution, but one compound (16) showed a much smaller shift in the solid. The frequency shifts for the spectra of solutions, measured relative to the corresponding ethyl ester, were 30—41 cm^{-1} . In the hemialdal monoesters (nos. 9 and 18; examined in the solid state only), the frequencies were higher than expected, but not as high as for the diesters.

The origin of the large shift is not clear. A field effect⁴ would not seem to be the explanation, even though the conformation of the seven-membered ring (in nos. 3, 10, 11, 16, and 17) is not known, since the effect in a six-membered ring was similar (cf. nos. 3 and 4). It is not unreasonable to suppose that in the last compound the acetate groups are equatorial (cf. ref. 5), and hence would not be close to each other. If a field effect were the cause then a similar effect would be expected with sugar $\alpha\gamma$ - and $\alpha\beta$ -diesters, particularly in the latter where the ester groups were axial-equatorial or diequatorial, so that they were close to each other. However, the spectra of methyl 4,6-*O*-benzylidene- α -D-glucoside 2,3-diacetate, methyl 4,6-*O*-benzylidene-, and 4,6-*O*-*o*-bromobenzylidene- α -D-glucoside 2,3-dibenzoates (nos. 6, 13, and 14) had ester carbonyl absorption at lower frequencies than the hemialdal diesters, in chloroform solution.

Another possible explanation is that the inductive effect of the oxygen atom adjacent to the carbon atom bearing the ester group causes the frequency shift (cf. the higher carbonyl frequency in esters than in ketones⁶). To examine this effect some glycosyl esters (nos. 2, 8, 9, and 15) were prepared. The values of the carbonyl stretching frequencies obtained showed a shift of 14—16 cm^{-1} from the corresponding value for ethyl esters; the shift suggests a slight inductive effect of the oxygen atom. The slightly higher-than-normal value for the hemialdal monoesters (nos. 5 and 18) is probably due to this effect. However, in the hemialdal diesters the inductive effect of the oxygen atom would be shared between the two ester groups and hence should be smaller per ester group; on this reasoning alone the frequency shift should be smaller for hemialdal diesters than for monoesters, and not the reverse as found in practice. Field and inductive effects are shown therefore to be inadequate explanations of this phenomenon.

In searching the literature for analogous phenomena, it was found that 1,1-diacetoxypropane showed⁷ an abnormally high ester carbonyl stretching frequency at 1761 cm^{-1} . The spectra of two further examples of *gem*-diol diacetates have now been studied; the carbonyl stretching frequencies, of the same order as that above, are shown in Table 2. This phenomenon was originally attributed to an inductive effect,⁷ but has more recently been ascribed to a field effect.⁸ The latter would seem more likely as the inductive effect of one acetate group on the other would mutually cancel. It was expected that the frequency of the *o*-phthalaldehyde derivative would be higher than that of benzylidene

TABLE 2. Carbonyl stretching frequencies of *gem*-diol diacetates.

	$\nu_{\text{C=O}}$ (Nujol) (cm^{-1})	$\nu_{\text{C=O}}$ (CHCl_3) (cm^{-1})
Benzylidene diacetate	1753	1763
Tetra-acetoxy- <i>o</i> -phthalaldehyde	1767, 1751	1766br
1,1-Diacetoxypropane ⁷	1761 ^a	—

br = broad. ^a Liquid.

diacetate, owing to a greater crowding of the ester groups. No difference was found, except for a broadening of the band.

EXPERIMENTAL

The spectra were examined on a Unicam S.P. 100 infrared spectrometer, fitted with a 1500 lines/in. grating. The compounds were examined as Nujol mulls or as chloroform solutions of 1.5—5.0% concentration. Preparation of new compounds will be described elsewhere.

⁴ Ref. 3, p. 400.

⁵ Goldstein, Lewis, and Smith, *J. Amer. Chem. Soc.*, 1958, **80**, 939.

⁶ Ref. 3, p. 222.

⁷ Rasmussen and Brattain, *J. Amer. Chem. Soc.*, 1949, **71**, 1073.

⁸ Bellamy and Williams, *J.*, 1957, 861.

The author is indebted to Dr. H. Spedding for helpful discussion and to Miss S. Burgess for experimental assistance. Part of this work was carried out at the University, Leicester; the rest was sponsored by the U.S. Department of Army, through its European Office.

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[Received, November 25th, 1960.]
