163. *Infrared Spectra and Polar Effects. Part V.*[1] *Carbonyl–Carbonyl Interactions.*

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Compounds containing the group ·CO·O·C·CO· are known to exhibit a curious interaction effect whereby both carbonyl groups show an increase in their infrared absorption frequencies. Evidence obtained from the study of 17-acetoxy-16-oxo-steroids suggests that steric factors play an important part in this effect.

In Part IV [1] we pointed out that group frequency shifts in the infrared region show a number of anomalies which cannot be readily explained in terms of inductive or mesomeric effects. One such instance—the stereospecificity of the interaction between carbonyl groups and α-halogen substituents—has already been discussed, but another and in some ways related anomaly occurs in compounds containing the group ·CO·O·C·CO·. This structure occurs in 21-acetoxy-20-oxo-steroids, and many compounds of this type have

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[1] Part IV, Bellamy, Thomas, and Williams, *J.*, 1956, 3704.

been studied by Jones and his co-workers.[2-4] In all cases they have observed an interaction effect between the two carbonyl frequencies resulting in rises of *ca.* 20 cm.$^{-1}$ and of *ca.* 10 cm.$^{-1}$ in the keto- and ester absorptions as compared with the normal values for the individual groups in these positions. Within the steroid series a very high degree of consistency is shown by the frequency of any particular type of carbonyl group in a particular position, so that these shifts are highly significant. Comparable cases involving slightly larger shifts have been noted in 12-acetoxy-11-oxo-steroids [5] in which the same structure occurs, and the effect persists when the acetoxy-group is in either the equatorial or the polar position. A related interaction has also been observed outside the steroid series, in benzil-*o*-carboxylic acid *pseudo*acetate [6] which contains a similar structure.

This effect is difficult to reconcile with any changes in inductive or mesomeric effect, but it is equally difficult to envisage any coupling effects along the chain which would account for it. Thus, there is little or no interaction between the carbonyl frequencies of ordinary α-, β-, or γ-diketones, and the unenolised forms of acetylacetone and of ethyl acetoacetate also have essentially normal frequencies. However, interactions occur in certain cyclic α-diketones in which the C=O groups are forced to adopt a *cis*-configuration with respect to each other.[7] It therefore occurred to us that some steric factors might be operating, similar to this and to those found in α-halogeno-ketones. We have therefore examined the spectra of some 17-acetoxy-16-oxo-steroids in which the inclusion of the keto-group within a five-membered ring might be expected to lead to a markedly different steric arrangement of the interacting groups.

DISCUSSION

Jones and his co-workers [2-4] have already demonstrated that the keto-carbonyl absorptions of five-membered ring systems occur near 1750 cm.$^{-1}$, and the value of 1751 cm.$^{-1}$ found for the 16 : 17-dione is in agreement with this, and implies that no major frequency shift is introduced by the change of solvent from chloroform in our case to carbon disulphide in theirs. All the 17-acetoxy-compounds studied show this absorption in the range 1754—1757 cm.$^{-1}$, which suggests that no marked interaction is taking place. This is confirmed by a study of the corresponding ester frequencies, which fall in the range 1736—1742 cm.$^{-1}$ and are also essentially normal. Comparison of the individual pairs of 17-hydroxy- and 17-acetoxy-compounds studied does show a fall of 6—15 cm.$^{-1}$ in the frequency of the 16-oxo-group in the hydroxyl compounds, but the lowered OH frequencies indicate clearly that this is due to intramolecular hydrogen-bonding rather than to any interaction between the two carbonyl vibrations. It therefore appears that the carbonyl–carbonyl interactions which occur in 21-acetoxy-20-oxo- and in 12-acetoxy-11-oxo-steroids do not occur in the corresponding 17-acetoxy-16-oxo-compounds. This is reported at this stage as it may have some diagnostic value. However, this observation is perhaps more important for its implication that the elevated carbonyl frequencies of 21-acetoxy-20-oxo-steroids and similar materials do not arise from mechanical coupling effects but are due to some other interaction which is itself dependent upon the steric arrangements of the two groups. The origin of these frequency shifts, and of the similar effect in α-halogenoketones, is not clear but they may very well arise from intramolecular dipolar effects, in which one strong dipole exerts a direct field effect upon another which is close to it in space. Such interactions would then be very similar to the well-known frequency shifts which accompany changes of state, with the exception that with less freedom for the dipoles to orient themselves in the most favourable directions, the resulting frequency shifts could be either positive or negative in character. Jones and

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[2] Jones, Humphries, and Dobriner, *J. Amer. Chem. Soc.*, 1950, **72**, 956.
[3] Jones, Humphries, Herling, and Dobriner, *ibifd.*, 1952, **74**, 2820.
[4] Jones and Herling, *J. Org. Chem.*, 1954, **19**, 1252.
[5] Dickson and Page, *J.*, 1955, 447.
[6] Grove and Willis, *J.*, 1951, 877.
[7] Alder, Schaefer, Esser, and Krieger, *Annalen*, 1955, **593**, 23.

Sandorfy[8] have recently put forward a very similar tentative explanation of effects of this kind and it is one that might explain a number of other anomalous frequencies such as, *e.g.*, the unexpectedly high carbonyl frequencies of ethyl ββ-diethoxyacrylate[9] and of 1 : 1-diacetoxypropane. It is hoped to develop this suggestion later.

EXPERIMENTAL

The spectra were measured of very dilute solutions in chloroform, in a Perkin-Elmer 21 double-beam spectrometer fitted with a rock-salt prism. A compensating solvent cell of the same thickness was used in the reference beam.

Results.—The compounds examined, and the results obtained insofar as the carbonyl and hydroxyl frequencies are concerned, are listed in the Table.

	CO and OH absorptions (cm.$^{-1}$)		
Compound	6-CO	Other CO bands	OH
3β : 17β-Dihydroxyandrost-5-en-16-one	1751	—	3679, 3509
3β : 17β-Diacetoxyandrost-5-en-16-one	1757	1739	—
17β-Hydroxyandrost-4-ene-3 : 16-dione	1748	1661	3497
17β-Acetoxyandrost-4-ene-3 : 16 dione	1757	1742, 1661	—
17β-Hydroxy-3β-methoxyandrost-5-en-16-one	1742	—	3497
17β-Acetoxy-3β-methoxyandrost-5-en-16-one	1754	1739	—
17β-Hydroxyandrost-5-ene-3 : 16-dione 3-ethylene ketal	1742	—	3500
17β-Acetoxyandrost-5-ene-3 : 16-dione 3-ethylene ketal	1757	1736	—
3β-Methoxyandrost-5-ene-16 : 17-dione	1751	—	—

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[8] Jones and Sandorfy "Chemical Applications of Spectroscopy," Interscience, New York, 1956.
[9] Rasmussen and Brattain, *J. Amer. Chem. Soc.*, 1949, **71**, 1073.