INFRARED SPECTRA OF CYCLIC ETHERS AND THEIR DERIVATIVES

II. Characteristic Absorption of Mono- and Disubstituted 1,4-Dioxanes*

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The IR spectra of six monosubstituted and of four 2,6-disubstituted 1,4-dioxanes have been studied in the 650–1800-cm\(^{-1}\) region. The assignment of the bands due to the vibrations of the 1,4-dioxane ring and to the deformation vibrations of the methylene groups of the ring is given. The appearance of a whole series of new absorption bands on passing from unsubstituted 1,4-dioxane to its derivatives is explained by the change in the symmetry of the molecule and the removal of the prohibition from the vibrations previously inactive in the IR spectra connected with this reduction in symmetry. It is proposed to use, in order to confirm the presence of a 1,4-dioxane ring in a molecule from the results of IR spectroscopy, not only the 1126-cm\(^{-1}\) band but the whole group of bands lying in the frequency ranges 800–900, 1000–1150, and 1200–1300 cm\(^{-1}\).

It is considered that the 1,4-dioxane ring causes characteristic absorption at about 1126 cm\(^{-1}\). However, this band is very similar in intensity and position to the corresponding absorption bands of tertiary aliphatic alcohols, phenols, esters, and acid anhydrides [1, 2]. The coincidence of the band of the asymmetric stretching vibrations of the ester group of dioxane with the analogous bands of the classes of compounds mentioned frequently complicates its use for structural analysis or even makes it completely impossible.

In a similar manner to the case of tetrahydrofuran and its derivatives considered in the preceding paper [3], we have attempted to use for identifying compounds containing the 1,4-dioxane ring the whole group of absorption bands associated with the skeletal vibrations of the ring and with the deformation vibrations of its methylene groups. As the subjects of the investigation we used 1,4-dioxane and some of its derivatives (I–XI). The spectra of some of the compounds studied are given in the figure.

\[
\text{H}_2\text{C} = \text{O} - \text{CH}_2 - \text{R} \quad \text{R} = \text{H} \quad (\text{I}–\text{VII}), \text{CH}_3 \quad (\text{VIII}), \text{IC}_6\text{H}_4 \quad (\text{IX}, \text{XI})
\]

The IR spectrum of 1,4-dioxane itself has nine significant absorption bands in this region. On the basis of a comparison of the IR and Raman spectra with the results of the calculation of the vibrational spectra of cyclohexane and tetrahydrofuran, Barket and Badger [6] ascribe the bands observed to various stretching vibrations of the ring and to the deformation vibrations of the methylene groups of the ring.

When a substituent is introduced into the molecule of 1,4-dioxane, a series of new bands appears in the IR spectrum. As can be seen from the figure, in the 800–1000-cm\(^{-1}\) region, where the vibrations of the ring and the wagging vibrations of the methylene groups appear, monosubstituted dioxane derivatives show four bands instead of two doublet bands. The appearance of the two new bands in this region is probably connected with a reduction in the symmetry of the molecule of 1,4-dioxane from the C\(_2\)h group to the C\(_1\) group with the introduction of a substituent. This decrease in symmetry must lead to a change in the orientation of the dipole moment, in consequence of which vibrations, become active in the IR spectrum which were previously observed only in the Raman spectra—in particular, the A\(_{1g}\) stretching vibrations of the ring (about 830 cm\(^{-1}\)) and a component of the asymmetric E\(_g\) wagging vibrations (b), which are doubly degenerate in cyclohexane (at about 550 cm\(^{-1}\)). On the same basis, the appearance of two bands of the skeletal vibrations of the ring corresponding to the E\(_g\) vibrations of cyclohexane must be expected in the higher-frequency region of the spectrum of the monosubstituted 1,4-dioxanes. These bands actually appear at 1000–1020 and 1110 cm\(^{-1}\).

In the region of the fanlike vibrations of the CH\(_2\) groups (1250–1300 cm\(^{-1}\)), the introduction of substituents is accompanied by the appearance of two bands, one of which is connected genetically with the wagging vibrations (A\(_{1g}\)) and the second with the fanlike vibrations (E\(_g\)) of the methylene groups of cyclohexane.

The scissors vibrations appear in the form of two bands with frequencies of 1430 and 1460 cm\(^{-1}\). All the bands mentioned owe their appearance to the removal of the prohibition from a series of vibrations, with a change in the symmetry of the molecule, and appear clearly in the spectra of monosubstituted and asymmetrically disubstituted dioxanes, although, of course, the intensity in the narrow limits of the absorption bands varies from case to case.

The characteristic bands of the individual groupings such as C=O, C–Hal, C–OH, and others are observed in each case with no complications of any kind.

The spectra of the asymmetrically disubstituted 1,4-dioxanes do not differ in principle from the spectra of the monosubstituted derivatives. In these spectra, as a rule, all the bands of the vibrations of the dioxane ring and the methylene groups mentioned above are found.

*For part I, see [3].
IR spectra of: 1) 1, 4-dioxane (I); 2) methylthiomethyl-1, 4-dioxane (III); 3) dimethylamino-methyl-1, 4-dioxane (VIII); 4) 2-hydroxymethyl-6-iodomethyl-1, 4-dioxane (X); 5) 2, 6-bis(iodomethyl)-1, 4-dioxane (IX); 6) 2-ethylthiomethyl-6-hydroxymethyl-1, 4-dioxane (XI).