INFRARED SPECTRA OF CYCLIC ETHERS AND THEIR DERIVATIVES

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

A. P. Kilimov, M. A. Svechnikova, V. I. Shevchenko, V. V. Smirnov,
S. B. Zotov, and F. V. Kvasnyuk-Mudryi

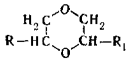
Khimiya Geterotsiklicheskikh Soedinenii, Vol. 5, No. 2, pp. 208–211, 1969

UDC 547.841:543.422.4

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 800–950, 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.



R=H (I—VII), CH_3 (VIII), ICH_2 (IV), $HOCH_2$ (X, XI)
R_1=H (I), CH_2Cl (II), CH_2SCH_3 (III), $CH_2S(CH_2)_2CN$ (IV)
CH_2SCOCH_3 (V), $CON(CH_3)_2$ (VI), $CH_2N(CH_3)_2$ (VII),
CH_2I (VIII—X), $CH_2SC_2H_5$ (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_{2h} 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 850 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}.

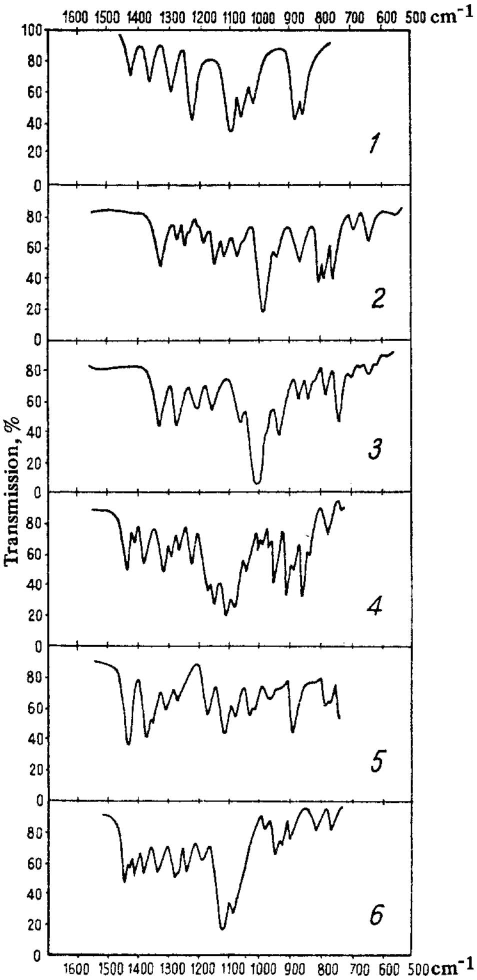
All the bands mentioned owe their appearance to the removal of the prohibition from a series of vibrations, with a change in the symmetry of the molecule, and appear clearly in the spectra of monosubstituted and asymmetrically disubstituted dioxanes, although, of course, the intensity in the narrow limits 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.

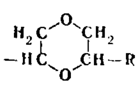
---

*For part I, see [3].



IR spectra of: 1) 1, 4-dioxane (I); 2) methylthiomethyl-1, 4-dioxane (III); 3) dimethylaminomethyl-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).

Table 1



Compound	R	R_1	Bp, °C (pressure, mm)	d_4^{20}	n_D^{20}	MR_D		Empirical formula	Found, %					Calculated, %					Yield, %
						found	calculated		C	H	N	S	halogen	C	H	N	S	halogen	
I	H	H	101,4	1.0354	1.4224	—	—	—	—	—	—	—	—	—	—	—	—	—	—
II	H	CH_2Cl	115 (93)	1.2315	1.4646	31.1	30.8	$C_5H_9ClO_2$	43.8	6.70	—	—	25.9	43.9	6.60	—	—	26.0	30
III	H	CH_2SCH_3	80—82 (8)	1.1337	1.4918	38.9	39.0	$C_6H_{12}SO_2$	48.5	8.20	—	21.7	—	48.6	8.12	—	21.6	—	60
IV	H	$CH_2S(CH_2)_2CN$	166—168 (2)	1.1835	1.5090	48.0	47.9	$C_7H_{13}NSO_2$	48.1	7.60	7.9	18.1	—	48.0	7.44	8.0	18.3	—	65
V	H	CH_2SCOCH_3	85—86 (25)*	—	—	—	—	$C_7H_{12}SO_3$	47.7	6.85	—	18.12	—	47.7	6.82	—	18.17	—	81
VI	H	$CON(CH_3)_2$	110 (2)	1.1292	1.4770	39.8	39.8	$C_7H_{13}NO_3$	52.3	8.3	8.5	—	—	52.8	8.17	8.8	—	—	64.3
VII**	H	$CH_2N(CH_3)_2$	94 (47)	1.0549	1.4520	39.5	37.1	$C_7H_{15}NO_2 \cdot HCl$	—	—	6.42	—	32.6	—	—	6.42	—	32.5	55
VIII	CH_3	CH_2I	92 (5)	1.7009	1.5264	43.8	43.8	$C_6H_{11}IO_2$	29.6	4.50	—	—	52.8	29.8	4.55	—	—	52.5	70
X	$HOCH_2$	CH_2I	123—125 (1)	1.7995	1.5452	45.3	45.3	$C_6H_{11}IO_3$	27.8	4.30	—	—	50.1	27.9	4.27	—	—	49.2	55
XI	$HOCH_2$	$CH_2SC_2H_5$	132 (1)	1.1442	1.5032	49.7	49.6	$C_8H_{16}SO_3$	50.3	8.60	—	16.2	—	50.0	8.32	—	16.9	—	57

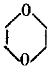
---

*Mp 35° C (from ethanol).

**Analyzed in the form of hydrochloride.

Table 2

Frequencies of the Vibrations in the IR Spectra of the Dioxane Derivatives (I–X), cm^{-1}

Compound	Stretching vibration of the ring, ν 	Wagging vibrations, δ_{C-H}	Fanlike vibrations	Twisting vibrations	Scissors vibrations
I	IK 865 w. 1126 w. 1075 m. KR 830 1020 m. 1110 w.	850 w.' 1050 m. 890 w. 1220 m.	1290 w. 1260 m. 1300 m.	1320 w. —	1370 w. 1450 w. 1430 m. 1460 w.
II	850 m. 900 m. 1005 m. 1075 w. 1260 w.	880 m. 1050 s. 925 w. 1190 w.	1250 m. 1260 w. 1280 s. 1300 s.	1320 w.	1370 w.
III	882 s. 905 s. 917 s. 975 m.	1060 m. 1120 v.s.	1133 v.s.	1195 s. 1220 m.	1280 s. 1300 w.
IV	860 w. 890 s. 930 m. 960 s. 980 s.	1040 m. 1075 w.	1125 v.s.	1185 w. 1285 s. 1290 s.	1310 — Inflection 1250 s.
V	860 s. 890 s. 930 m. 960 s. 980 s.	1035 w. 1070 m.	1120 v.s.	1225 m. 1240 m. 1310 m.	1280 m.
VI	840 w. 850 w. 880 s. 920 s. 980 m.	1060 m. 1085 s.	1126 v.s.	1170 m. 1230 s. 1300 s.*	1320 m. 1260 s.
VII	840 s. 865 s. 900 s. 980 m.	1040 m. 1070 m.	1120—1130 v.s.	1230 m. 1270 m.	1300 m.
VIII	860 m. 880 s. 915 s. 960 m. 1000 w.	1050 m. 1100 v.s.	1130 v.s.	1240 m. 1285 m.	1310 s.
IX	870 s. 908 s. 1000 — Inflection	1040 m. 1070 s.	1120 s.**		
X	860 m. 885 m. 920 s. 940 s.	1030 s. 1070 s.	1120 v.s.	1190 m. 1230 m.	1290—1310 m.
XI	840 m. 860 m. 905 s. 920 s.	1050 s. 1100 v.s.	1220—1240 v.s.	1300 s.	1310 Inflection

---

*Unassigned bands are present in this region.

**Spectrum poorly resolved because it was recorded in paraffin oil.

Note: w = weak, m = medium, s = strong, and v.s. = very strong.

The correctness of our explanation of the causes of the appearance of the new bands in the IR spectra of the 1, 4-dioxane derivatives can be demonstrated in a striking manner with bis(2, 6-iodomethyl)-1, 4-dioxane (IX) as an example. In view of the increase in the symmetry of this molecule to the C_s group as compared with the monosubstituted derivatives, the A_{1g}, E_g skeletal vibrations are not accompanied by changes in the dipole moment, and the bands corresponding to them do not appear in the IR spectrum. Consequently, in the 800–1000-cm^{-1} region this substance exhibits only two (and not four) bands—at 870 and 908 cm^{-1}.

Thus, in the spectrum of 1, 4-dioxane and its derivatives, in addition to the characteristic band ν = 1126 cm^{-1} which is frequently mentioned in the literature, $\delta_{CH_2 \text{wag}} = 1020–1050$ cm^{-1} and $\gamma_{C—C \text{ ring}} = = 1050–1090$ cm^{-1} are very typical. The skeletal and wagging vibrations of the dioxane ring form a group of intense bands in the region from 800 to 900 cm^{-1} consisting of two bands in the case of 1, 4-dioxane itself and of three or four bands in the case of its derivative. In a study of the molecular structure of compounds which are expected to include 1, 4-dioxane rings, one must take into account not only the characteristic band at 1126 cm^{-1}, but the whole group of absorption bands due to the skeletal vibrations of the ring and the deformation vibrations of the methylene groups in the range of frequencies from 800 to 1150 cm^{-1}.

EXPERIMENTAL

The physicochemical constants of compounds I–XI are given in Tables 1 and 2. All the compounds were carefully dried and redistilled or recrystallized before study. The IR absorption spectra of all the compounds were measured in the 650–1800-cm^{-1} region on an IKS-14 spectrophotometer. For recording a spectrum, a thin film of the substance was obtained by pressing out 1–2 drops of the substance between plates of potassium bromide. In the case of the solid substances, the spectra were recorded in paraffin oil.

2-Chloromethyl-1, 4-dioxane (II) was prepared from ethylene glycol and ethylene chlorohydrin in the presence of sulfuric acid in a similar manner to the process described by Summerbell et al. [5].

2-Iodomethyl-6-methyl-1, 4-dioxane (VIII), 2-hydroxymethyl-6-iodomethyl-1, 4-dioxane (X), 2, 6-bis(iodomethyl)-1, 4-dioxane (IX), and 1, 4-dioxanecarboxylic acid were synthesized by published methods [6, 7].

Methylthiomethyl-1, 4-dioxane (III), cyanoethylthiomethyl-1, 4-dioxane (IV), and 2-ethylthiomethyl-6-hydroxymethyl-1, 4-dioxane (XI) were prepared from the corresponding halogen derivatives of 1, 4-dioxane and thiourea with subsequent alkylation of the mercaptans in an alkaline medium as described previously for tetrahydrofuran derivatives [3].

Acetylthiomethyl-1, 4-dioxane (V) was synthesized by the acetylation of the corresponding mercaptomethyl derivative [8].

1, 4-Dioxanecarboxylic anhydride was prepared in a similar manner to 1, 4-benzodioxane-2-carboxylic anhydride [9].

1, 4-Dioxanecarboxydimethylamide (VI). With stirring, a solution of 3.1 g of 1, 4-dioxanecarboxylic acid chloride in 30 ml of ether was added at 25° C over 20 min to a solution of 5 ml of dimethylamine in 50 ml of dry ether. The mixture was boiled for 30 min. Then the dimethylamine hydrochloride was filtered off, the ether was driven off from the filtrate, and the residue was distilled in vacuum.

Dimethylaminomethyl-1, 4-dioxane (VII). A mixture of 17.5 g (0.13 mole) of II and 17.7 g (0.4 mole) of dimethylamine was poured into a tube and kept at 100° C for 12 hr. After cooling, the crystals of dimethylamine hydrochloride were filtered off and the filtrate was distilled in vacuum.

REFERENCES

1. L. Bellamy, Infrared Spectra of Complex Molecules [Russian translation], IL, Moscow, 1963.

2. W. West, ed., Chemical Application of Spectroscopy [Russian translation], IL, Moscow, 1959.

3. A. P. Kilimov, M. A. Svechnikova, V. I. Shevchenko, V. V. Smirnov, F. V. Kvasnyuk-Mudryi, and S. B. Zotov, KhGS [Chemistry of Heterocyclic Compounds], 3, 579, 1967.

4. M. I. Astle and B. E. Jacobson, J. Org. Chem., 24, 1766, 1959.

5. R. K. Summerbell, G. Lestina, and H. Waite, J. Am. Chem. Soc., 79, 234, 1957.

6. S. C. Barket and R. M. Badger, J. Am. Chem. Soc., 72, 4397, 1950.

7. R. K. Summerbell and I. R. Stephens, J. Am. Chem. Soc., 76, 731, 1954.

8. Collection: Organic Syntheses, Vol. II [Russian translation], Moscow, p. 171, 1962.

9. A. L. Mndzhoyan, V. G. Afrikyan, and L. Z. Kazaryan, Izv. AN ArmSSR, XVIII, 3, 297, 1965.

7 December 1966

Serafimovich Volgograd State
Pedagogic Institute