INFRARED SPECTRA OF CYCLIC ETHERS AND THEIR DERIVATIVES

I. Pecularities in the Skeletal Vibrations of the Tetrahydrofuran Ring

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Data for the characteristic bands of cyclic ethers are reviewed. The infrared spectra of a number of 2-mono- and 2, 5-di-substituted derivatives of tetrahydrofuran are investigated. Absorption bands at about 900 cm^{-1} are related to pulsation vibrations, and those at about 1200 cm^{-1} to antisymmetric skeletal vibrations, of the tetrahydrofuran ring. It is shown that to confirm the presence of a tetrahydrofuran ring in a molecule, it is necessary to take into account not only the band of valence antisymmetric vibrations of the group C—O—C (ν^{as}_{C-O-C} 1075 cm^{-1}), but also bands due to ring pulsation vibrations (ring symmetric valence vibrations $\nu^{S}_{sk} \sim 900$ cm^{-1}).

Spectroscopic studies of cyclic ethers made with 5- and 6-membered rings by Shrive and Tschamler and coworkers [1–3], and by Barrow and Searles [4], made it possible to come to a conclusion regarding the characteristic nature of the asymmetric valence vibrations of the ether group C—O—C in compounds of that kind.

From literature data [4–7] the frequency of the asymmetric valence vibrations of the ether group in the interval 1075–1000 cm^{-1} can be considered characteristic of the tetrahydrofuran ring.

Despite the high intensity of this band, however, it alone can hardly serve for unequivocal detection of the tetrahydrofuran ring, as it is close to the absorption bands of asymmetric valence vibrations of the group C—O—C in open-chain aliphatic and aliphatic-aromatic ethers, and the bands of the same group in cyclic 6-membered ring ethers.

Table 1

C—O Bond Valence Vibration Frequencies of Various Classes of Organic Compounds*

Class of compound	Frequency, cm^{-1}	Notes
Aliphatic alcohols		
primary	1015—1075	
secondary	1105—1120	
tertiary	1150—1140	
Open-chain ethers	1030—1150	
Cyclic ethers		Frequency of the asymmetric valence vibration of the C—O—C group in the ring
ethylene oxide	840—860	
trimethyleneoxide	970—980	
tetrahydrofuran	1075—1098 1090	
dioxane	1125	
acetals and ketals	1038—1200	Usually 4 bands
Phenols	1125—1200	
Esters	1150—1250	
Carboxylic acids	1370 1420—1450	
Vinyl ethers	1200—1260	
Acid anhydrides	1045—1175	

Table 1 gives the characteristic absorption bands of the C—O—C group for some types of organic compounds. It can be seen that strong absorption bands in the 1000–1100 cm^{-1} region are found for quite a wide range of compounds. If there is an unsaturated substitutent or part of a molecule of increased electron density immediately adjacent to the C—O—C group, the frequency of the asymmetric valence vibrations then lies in the interval 1200–1400 cm^{-1}.

Table 2

Characteristic Frequencies of the IR Spectra of the Compounds Investigated

Compound	ν^{as}_{C-O-C}, cm^{-1}	ν^{s}_{sk}, cm^{-1}
I	1076	918
II	1040, 1078, 1100	925
III	1017, 1070, 1114	876, 930, 971
IV	1000, 1045, 1085	855, 915, 938
V	1015, 1080, 1110	890, 915, 940
VI	980, 1010, 1080, 1130	860, 905
VII	1005, 1060, 1100	892, 910
VIII	970, 1000, 1050, 1095	885, 905
IX	990, 1020, 1040, 1078, 1125	885, 912
X	980, 1010, 1050, 1075, 1125	885, 916
XI	1040, 1070, 1092	888, 885, 918, 955
XII	1000, 1062, 1095	878, 910
XIII	1000, 1055, 1075	890, 915, 940
XIV	1012, 1065, 1110	875, 919

Because of the difficulty of assigning this absorption band precisely to the tetrahydrofuran ring, in the present work an attempt was made to elucidate the characteristic nature of the skeletal vibrations of the C—C bond in the ring.

Figures 1 and 2 (see also Table 2) show the general nature of the IR spectra of the compounds now investigated.

The spectrum of tetrahydrofuran itself is dominated by a very intense absorption band, frequency 1075 cm^{-1}, due to the asymmetric valence vibration of the ether group. The second intense band is at 918 cm^{-1}. This band is obviously due to symmetric (pulsating) vibrations of the tetrahydrofuran ring skeleton. Similar bands were studied in detail by Batuev and coworkers [13] for cycloparaffins. It was found that in the case of cyclopentane the frequency of the pulsating vibrations of the ring (a frequency in evidence in a Raman spectra) is 890 cm^{-1}. Replacement of one of the ring methylene groups by an oxygen atom, while affecting dimensions and valence angles of the ring comparatively little, substantially alters the symmetry of the system, dropping from the group D_{5h} to group C_{2v}. The symmetry lowering must be ascribed to activation of the pulsation vibrations in the IR spectrum, and so, to appearance of an absorption band having a maximum at

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*From the data of [5, 6].

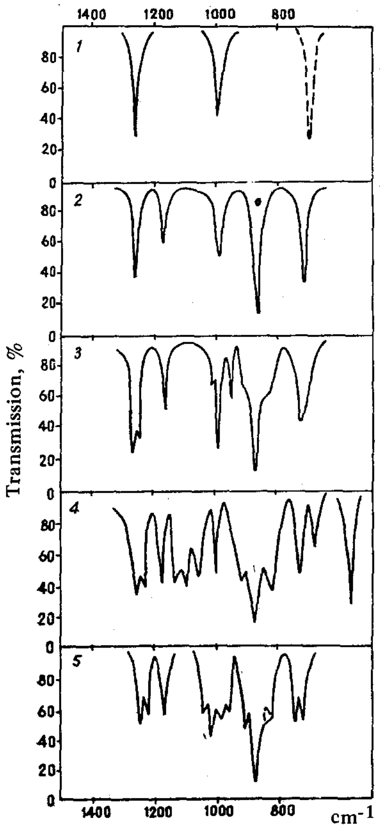

Fig. 1. IR spectra: 1) Cyclopentane, 2) tetrahydrofuran (I), 3) 2-methyltetrahydrofuran (II), 4) 2-chloromethyltetrahydrofuran (III), 5) 2-bromomethyltetrahydrofuran (IV).

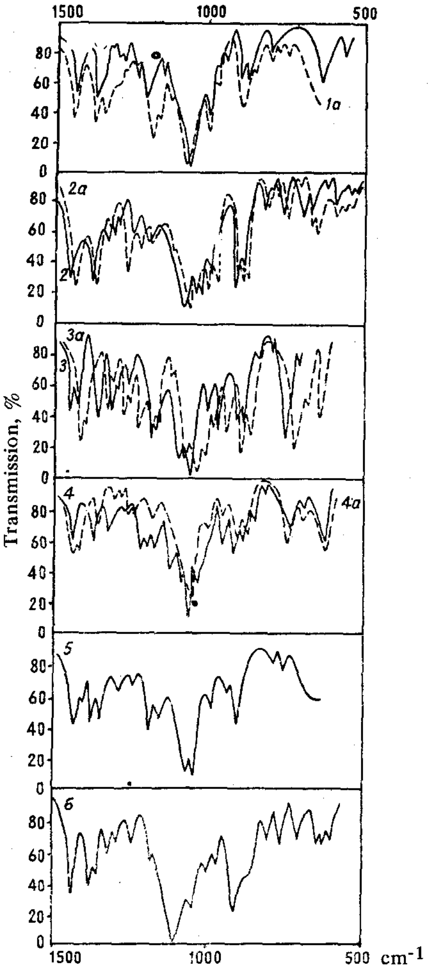

Fig. 2. IR spectra: 1) 2-Methyl-5-bromoethyltetrahydrofuran (VI), 2) methyl(2-methyltetrahydrofuryl-5)-methylsulfide (IX), 2a) ethyl(2-methyltetrahydrofuryl-5)methylsulfide (X); 3) 2-chloromethyl-5-iodomethyltetrahydrofuran (VIII), 3a) 2-chloromethyl-5-bromomethyltetrahydrofuran (VII); 4) (2-chloromethyltetrahydrofuryl-5)methylmercaptan (XI), 4a) methyl (2-chloromethyltetrahydrofuryl-5)methylmercaptan (XII); 5) 2-ethoxymethyl-5-iodomethyltetrahydrofuran (XIII), 6) methyl(2-ethoxymethyl-5-iodomethyltetrahydrofuryl-5)-methysulfide (XIV).

Table 3

Tetrahydrofuran Derivatives Investigated

Compound	R_1	R_2	Bp, °C (pressure, mm)	d_4^{20}	n_D^{20}	MR_D		Empirical formula	Found, %				Calculated, %				Yield, %
						Found	Calculated		C	H	S	Halogen	C	H	S	Halogen	
I	H	H	64—65	0.888	1.4076	—	—		—	—	—	—	—	—	—	—	—
II	H	CH_3	80 (761)	0.8534	1.4059	—	—		—	—	—	—	—	—	—	—	60
III	H	$ClCH_2$	55—56 (20)	—	1.4552	—	—		—	—	—	—	—	—	—	—	85
IV*	H	$BrCH_2$	80 (14)		1.4810	—	—		—	—	—	—	—	—	—	—	54
V**	CH_3	$BrCH_2$	45—57 (7)	1.3628	1.4760	37.04	37.30		—	—	—	—	—	—	—	—	40
VI	CH_3	ICH_2	55—56 (3)	1.6386	1.5230	42.17	42.15	$C_6H_{11}OI$	31.10	4.40		57.10	31.87	4.86	—	56.62	80
VII	$ClCH_2$	$BrCH_2$	82—83 (3)	1.4779	1.5063	42.80	41.98	$C_6H_{10}OClBr$	32.90	5.04	—	—	33.80	4.68	—	—	30
VIII	$ClCH_2$	ICH_2	94—96 (3)	1.7148	1.5445	47.70	47.02	$C_6H_{11}OClI$	28.79	3.85	***	48.36 13.00	27.65	3.84	***	47.70 13.60	80
IX	CH_3	CH_3SCH_2	64—66 (5)	1.0036	1.4790	41.96	41.25	$C_7H_{14}SO$	57.4	9.45	21.9	—	57.6	9.58	21.9	—	72
X	CH_3	$C_2H_5SCH_2$	82—84 (11)	0.9715	1.4743	46.10	46.20	$C_8H_{16}SO$	60.07	10.0	19.8	—	60.01	10.0	20.0	—	81
XI	$ClCH_2$	$HSCH_2$	79—80 (7)	1.0833	1.4610	42.02	42.00	$C_6H_{11}SOCl$	43.35	6.65	19.25	21.2	43.25	6.61	19.18	21.3	52
XII	$ClCH_2$	CH_3SCH_2	107—109 (7)	1.1295	1.4975	46.83	46.80	$C_7H_{13}SOCl$	46.4	7.74	17.55	19.3	46.55	7.22	17.7	19.2	68
XIII	C_2H_5—OCH_2	ICH_2	118—121 (5)	1.5398	1.5160	52.82	53.03	$C_8H_{15}O_2I$	35.73	5.54	—	47.04	35.78	5.55	—	47.00	60
XIV	C_2H_5—OCH_2	CH_3SCH_2	106—108 (6)	1.0297	1.4820	52.86	52.70	$C_9H_{18}SO_2$	57.1	9.64	16.44	—	56.8	9.48	16.85	—	75

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*The literature [15] gives: 61–63° (13 mm) n_D^{20} 1.4850; d_4^{20} 1.3653.

**The literature [16] gives: 67° (20 mm) n_D^{24} 1.4748; d^{24} 1.357.

***Analyzed for iodine

about 900 cm^{-1}*. The absence of a strong absorption band in this region for open-chain ethers indicates the impossibility of assigning the absorption of tetrahydrofuran in the 890 cm^{-1} region to symmetric vibrations of the ether group. It is natural to expect preservation of the absorption band in this region with various tetrahydrofuran derivatives. In point of fact, as Fig. 1 shows, without a single exception, the tetrahydrofuran derivatives which we investigated show a group of absorption bands comprising 2–4 bands at about 900 cm^{-1}.

Actually, for substituted tetrahydrofurans there is splitting of the band of ring symmetric pulsation vibrations, due to the decrease in symmetry of the molecule from C_{2v} to the group C_1 when a substitutent is introduced.

Also very characteristic is another group of bands, near 1200 cm^{-1}. Obviously it is due to ring asymmetric valence vibrations. In the cases of unsubstituted derivatives the maximum of this band has frequency 1190 cm^{-1}; its intensity is substantially less than that of the band of pulsation vibrations.

Introducing a substituent leads to splitting of this band, and this is well marked in the spectra shown in Figs. 1 and 2.

For the substituted tetrahydrofurans investigated by us, no anomalies were detected in the display of characteristic vibrations connected with the presence of substituents (e. g., $\nu_{C—S}$; $\nu_{C—Hal}$; $\nu_{O—H}$ and others).

Of the bands found in the spectrum of tetrahydrofuran derivatives, the most suitable for confirming the presence in the molecule of a 5-membered oxygen ring are those bands due to antisymmetric valence vibrations of the C—O—C group (1000–1100 cm^{-1}), and the bands of symmetric (pulsation) vibrations of the ring (900–950 cm^{-1}).

Ring antisymmetric vibrations bands (about 1200 cm^{-1}) are less convenient for this because of the abundance of absorption bands in that region, and the difficulty of assigning the individual bands to particular vibrations of the structural elements of the molecule.

To a certain extent the nature of the splitting of the bands ν^{s}_{CK} and $\nu^{as}_{C—O—C}$ is connected with the number and nature of the substituents. Thus, for 2-monosubstituted derivatives the $\nu^{as}_{C—O—C}$ band appears as a triple peak with maxima 1020–1040; 1075 ± ± 15 and 1090–1100 cm^{-1}. There is particularly sharp splitting when there is halogen in the side chain.

For 2, 5-disubstituted derivatives, the first two of the three bands mentioned above show up well, but the band with a maximum at about 1100 cm^{-1} appears as an inflection at the short wave limb of the main absorption peak.

EXPERIMENTAL

Table 3 gives properties and analytical data of the compounds. Pure tetrahydrofuran (I) was isolated from technical material by distilling over sodium. 2-methyltetrahydrofuran (II) was prepared by cyclizing pent-4-en-1-ol with sulfuric acid [8]. 2-chloromethyltetrahydrofuran (III) was synthesized from tetrahydrofurfuryl alcohol [9].

2-methyl-5-iodomethyltetrahydrofuran (VI), 2-chloromethyl-5-iodomethyltetrahydrofuran (VIII), 2-ethoxymethyl-5-iodomethyltetrahydrofuran (XIII) were prepared by cyclizing, respectively, hex-1-en-5-ol, 6-chlorohex-1-en-5-ol, and 6-ethoxyhex-1-en-5-ol with iodine, as described in [10].

2-bromomethyltetrahydrofuran (IV), 2-methyl-5-bromomethyltetrahydrofuran (V), and 2-chloromethyl-5-bromomethyltetrahydrofuran were respectively prepared by the action of bromine on pent-1-en-5-ol, hex-1-en-5-ol, and 6-chlorohex-1-en-5-ol.

5-substituted tetrahydrofurfurylalkylsulfides were synthesized as described in [11].

Bromocyclization of unsaturated alcohols. 0.1 mole unsaturated alcohol in 30 ml CCl_4 was put in a 3-necked flask fitted with mechanical stirrer, reflux condenser, and dropping funnel. The solution of alcohol was stirred and cooled to −10°, and 0.1 mole bromine in 30 ml CCl_4 was added. Then the products were allowed to warm up slowly to room temperature. To remove HBr formed, the reaction products were treated with KOH, with cooling. After separating off the precipitated KBr and distilling off the solvent, the residue was vacuum distilled.

Synthesis of S-(2-chloromethyltetrahydrofurfuryl-5)methylthiourea hydriodide. A mixture of 0.1 mole 2-chloromethyl-5-iodomethyltetrahydrofuran, 0.1 mole powdered thiourea, and 50 ml absolute ethanol was heated on a water bath for 2 hr. Then 25–30 ml ethanol was distilled off and, after cooling, 100–150 ml dry ether was added to the residue. The crystals obtained were filtered off with suction and washed with ether.

The other hydriodides were prepared similarly.*

Methyl-(2-chloromethyltetrahydrofuryl-5)methylsulfide (XII). 0.02 mole S-(2-chloromethyltetrahydrofuryl-5)methylthiourea hydriodide was dissolved with stirring and heating in 15 ml ethanol. The water bath was removed, 0.03 mole MeI was added, then dropwise 0.1 mole NaOH in 50 ml ethanol-water (1:1). Then the whole was stirred and heated for 2–3 hr, after which almost all the ethanol was distilled off. After cooling the solid was extracted twice with ether. The ether was distilled off, and the residue vacuum distilled.

The other sulfides were synthesized similarly.

(2-chloromethyltetrahydrofuryl-5)methylmercaptan (XI) was prepared by saponifying the corresponding thiourea hydroiodide [12].

All compounds were purified by vacuum distillation.

An IKS-14 spectrometer was used to measure the IR spectra in the 650–1800 cm^{-1} region, and Table 2 gives the characteristic frequencies. For the determination 1–2 drops of material were pressed between KBr plates.

REFERENCES

1. O. D. Shrive, M. R. Heether, H. B. Knight, and D. Swern, Anal. Chem., 23, 277, 1951.

2. H. Tschamler and H. Voetter, Mon., 83, 302, 1952.

3. H. Tschamler and J. Leutner, Mon., 83, 1502, 1953.

4. I. M. Barrow and S. Searles, J. Am. Chem. Soc., 75, 1175, 1953.

5. A. B. F. Duncan, W. Gordy, R. N. Jones, F. Matsen, C. Sandorfy, and W. West, Chemical Applications of Spectroscopy [Russian translation], IL, Moscow, 1959.

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*A similar case of activation of a series of vibrations of the skeleton in the IR spectra, is considered by Lecomte for benzene, pyridine, and α-picoline [14].

*The hydriodides separated as oils which crystallized on cooling.

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

7. Yu. K. Yur'ev, Yu. A. Pentin, and O. M. Revenko, Neftekhimiya, 1, 742, 1961.

8. B. N. Dashkevich and V. N. Cheren, Nauchn. zap. Uzhgorodsk. univ., 12, 18, 1955.

9. M. F. Ansell and S. S. Brown, J. Chem. Soc., 1788, 1957.

10. B. I. Staninets and E. A. Shilov, DAN USSR, 11, 1474, 1962.

11. A. L. Mndzhoyan and A. A. Aroyan, Izv. AN ArmSSR, ser. khim., 14, 590, 1961.

12. Sint. org. prep., 3, 246, 1952.

13. M. I. Batuev, Izv. AN SSSR, OKhN, 1, 3, 1947.

14. J. Lecomte, Le spectre infrarouge [Russian translation], 485, 1958.

15. R. Ya. Levina and F. A. Viktorova, Vestn. MGU, ser. fiz.-mat. i estestv. nauk, 6, 1, 89, 1951.

16. J. Colonge and A. Lagier, C. r., 224, 572, 1947.

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