UDC 547.722 + 543.422

ALKYLATION OF FURAN BY OLEFINS

VII. Vibration Spectra of Alkyl Furans*

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IR and Raman spectra of 17 mono- and polyalkyl furans, with alkyl groups in various positions in the furan ring, are investigated. A change in Raman spectrum is found for C—H bond valence vibrations when alkyl groups substitute the furan ring at the β position. Characteristic frequencies are found for 2-substituted and 2, 5-disubstituted furans.

Our convenient preparative method of synthesizing alkyl furans by alkylating furan with olefins in the presence of boron trifluoride etherate catalyst plus tetrahydrofuran as promoter, made it possible to obtain various alkyl-substituted furans. The latter, on account of their high purity, are suitable for optical investigations [1-6].

We investigated their vibration spectra, as the results are of great interest not only for investigating the detailed electron structure of furan and its derivatives, but also for developing analytical methods for determining alkyl furans when they are simultaneously present in complex organic mixtures.

The literature records only quite incomplete and incidental data for the vibration spectra (mainly IR spectra) of furan and its alkyl derivatives [7-12].

Recently the Raman spectra [13] of some 2-monoalkyl-substituted furans, prepared by reducing the corresponding carbinols over Pd/C, have been investigated, and also the effects of type and number of substitutents on furan ring valence vibration line frequencies and intensities.

The present paper is concerned with IR and Raman spectra of furan, and its 2-mono-, 3-mono-, 2, 5-di, 2, 3, 5-tri-, and 2, 3, 4, 5- tetraalkyl-substituted derivatives.

Unless otherwise mentioned, the alkyl furans studied were obtained by direct alkylation of furan by olefins in the presence of boron trifluoride etherate, followed by fractional distillation of the reaction products through a column containing 58 theoretical plates.

The IR spectra of the alkylfurans were determined with an IKS-14 spectrophotometer (Table 1), and the Raman spectra with an ISP-51 spectrograph (Table 2). In all cases, the spectra were obtained without use of a solvent.

Furan was obtained by vapor phase catalytic decarbonylation of furfural, followed by distillation through a 58 theoretical plate column, bp 31–32° C (760 mm); n_D^{20} 1.4210; d_4^{20} 0.9378.

2, 5-Dimethylfuran was prepared from 5-methylfurfural, bp 91° C (750 mm); n_D^{20} 1.4470; d_4^{20} 0.9002.

2-Ethylfuran: bp 92–93° C (765 mm); n_D^{20} 1.4400; d_4^{20} 0.8990.

2, 5-Diethylfuran: bp 103° C (100 mm); n_D^{20} 1.4550; d_4^{20} 0.8810.

2, 3, 5-Triethylfuran: bp 111° C (50 mm); n_D^{20} 1.4830; d_4^{20} 0.8647.

2, 3, 4, 5-Tetraethylfuran: bp 60° C (11 mm); n_D^{20} 1.4970; d_4^{20} 1.0324.

2-n-Propylfuran: bp 115–117° C (760 mm); n_D^{20} 1.4429 d_4^{20} 0.8900.

Synthetic 2-n-propylfuran was prepared by the Kishner reaction from furylethyl ketone, bp 115°C (755 mm); n_D^{20} 1.4430; d_4^{20} 0.8910.

2-Isopropylfuran: bp 106–107° C (755 mm); n_D^{20} 1.4450; d_4^{20} 0.8770.

3-Isopropylfuran: bp 110–112° C (750 mm); n_D^{20} 1.4350; d_4^{20} 0.8900.

Synthetic 3-isopropylfuran: prepared by the Friedel-Crafts alkylation of ethyl-5-bromofuran-2-carboxylate, followed by hydrolysis, elimination of bromine, and decarboxylation, bp 110–112° C (750mm); n_D^{20} 1.4336; d_4^{20} 0.8929.

2, 5-Diisopropylfuran: bp 50° C (5 mm); n_D^{20} 1.4550; d_4^{20} 0.8860.

2-tert-Butylfuran: bp 118–119° C (765 mm); n_D^{20} 1.4380; d_4^{20} 0.8688.

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*For Part VI see [6].

Table 1
IR Absorption Spectra of Alkylfurans

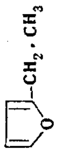
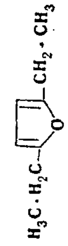
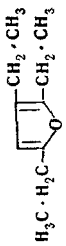
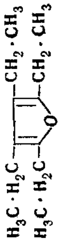
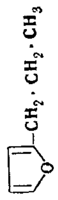
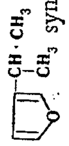
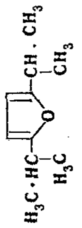
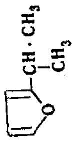
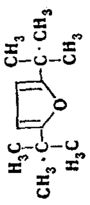
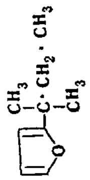
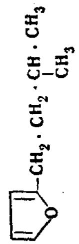
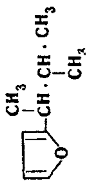
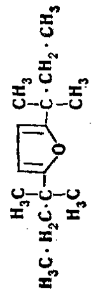
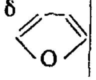
Frequencies for									 synthetic							
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
Out-of-plane δ_{C-H}			700 (20)	700 (25)			700 (45)	700 (40)	700 (40)							
Plane δ 				732 (37)		736 (92)		729 (99)	730 (99)	733 (98)	729 (50)	732 (100)	730 (99)	731 (80)	735 (80)	733 (78)
Out-of-plane δ_{C-H}	749 (10) 857 (25)	781 (15)	858 (25)	781 (72)	798 (56) 802 (8)	784 (65) 802 (70)	817 (38) 857 (40)	794 (38) 815 (32)	790 (38) 814 (32)	780 (95) 802 (95)	817 (40) 856 (42)	781 (98) 800 (95)	836 (85)		800 (70)	781 (90) 800 (18)

Table 1 continued

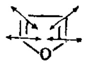
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
Out of plane δ_{C-H}	874 (10)	918 (45)	876 (60)	882 (50)	802 (40)	886 (60) 912 (40) 927 (60) 946 (50)	874 (99)	872 (65) 895 (38) 919 (40)	870 (65)	878 (77) 927 (80) 939 (42)	873 (80) 921 (50)	886 (98) 916 (40) 926 (99) 940 (95)	874 (20) 886 (55) 909 (50) 928 (80)	874 (38) 887 (42) 910 (25) 927 (38)	886 (58) 927 (60)	886 (25) 910 (22) 929 (30)
Breathing 		961 (10) 1005 (15)	1012 (38)			963 (37) 1012 (97)	1005 (62)	1008 (48)	1010 (49)	961 (75) 1010 (98)	1013 (68)	935 (38) 1013 (65)	1017 (85)	960 (45) 1015 (80)	960 (45) 1015 (75)	960 (70) 1015 (83)
$\nu_{C-C-C}\langle^{C}_{C}$	1075 (99)	1075 (30)	1090 (80)	1075 (55) 1090 (68)		1076 (58) 1090 (37)	1090 (99)	1031 (65) 1048 (65) 1086 (75)	1030 (65) 1050 (70) 1090 (80)	1076 (80)	1033 (63) 1051 (79) 1091 (85)	1076 (79)	1058 (45) 1083 (70) 1114 (60)	1058 (45) 1084 (62) 1129 (70)	1125 (58)	1065 (50) 1077 (32) 1129 (80)
Plane δ_{C-H}	1171 (5)	1171 (20)	1160 (65) 1198 (18)	1198 (60)		1160 (83)	1158 (50) 1198 (98)	1160 (38) 1192 (40)	1166 (38) 1198 (60)	1158 (82)	1161 (62) 1198 (82)	1162 (98)	1162 (90)	1158 (70) 1198 (62)	1168 (80)	1172 (75) 1198 (70)

Table 1 continued

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
Plane δ_{C-H}	1205 (5) 1222 (99)	1222 (15)				1223 (68)				1222 (100)		1221 (95)	1200 (60)		1225 (82)	
Outward δ_{-CH_3}		1250 (15)	1259 (22)				1260 (38)				1260 (40)		1251 (55)			
δ^a			1274 (24)	1274 (30)	1274 (18)	1274 (38)	1274 (40)	1274 (20)	1275 (22)	1270 (60)	1278 (58)	1275 (60)				
$\delta_{-CH,\,-CH_3}$			1300 (25) 1350 (18)	1350 (32)	1350 (32)	1306 (30)	1301 (43)	1300 (12)	1298 (25)		1301 (43)		1312 (78)	1290 (60)	1308 (50)	1317 (50)
	1365 (99) 1382 (98)	1365 (20) 1386 (99)	1365 (20) 1384 (25)	1384 (40) 1420 (42)	1384 (35) 1420 (33)	1362 (37) 1384 (45)	1365 (48) 1384 (57)	1362 (22) 1382 (25)	1365 (30) 1384 (40)	1365 (62) 1384 (78)	1365 (48) 1384 (47)	1366 (75) 1381 (76)	1365 (65) 1386 (80)	1365 (62) 1386 (70)	1364 (70) 1386 (80)	1366 (60) 1386 (78)
$\delta_{-CH_2,\,-CH_3}$	1457 (85)	1457 (5)	1442 (40) 1456 (50)	1456 (43)	1442 (34)	1456 (60)	1456 (65)	1452 (50)	1457 (50)	1452 (90)	1445 (58) 1457 (59)	1453 (95)				

Table 1 concluded

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
$\nu_{C=C}^{s'}$	1490 (20)		1469 (38) 1496 (22)			1504 (70)	1490 (40)	1498 (50)	1500 (52)	1504 (85)			1464 (85)	1464 (80)	1464 (85)	1464 (82)
	1541 (35) 1575 (30)	1574 (5)				1543 (38) 1564 (46)				1560 (88)	1510 (37)	1515 (95) 1552 (76)	1509 (82)	1506 (38)	1506 (90)	1508 (40) 1561 (62)
$\nu_{C=C}^{as}$	1590 (25) 1712 (50)	1712 (10)	1604	1650 (18)	1650 (10)	1666 (55) 1679 (28) 1707 (30) 1712 (30)	1593			1590 (78) 1661 (37)	1586 (25) 1729 (28)	1594 (80) 1655 (60) 1686 (62) 1713 (63)	1580 (60) 1651 (20) 1707 (25)	1590 (42) 1651 (18) 1715 (38)	1590 (70) 1655 (38) 1715 (38)	1590 (30) 1656 (20)

The measurements were made by A. K. Grinvalda. Absorption % in parentheses.

Table 2

Raman Spectra of Alkylfurans

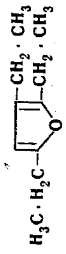
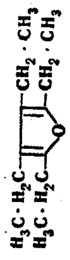
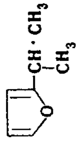
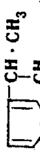
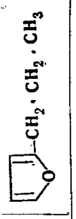
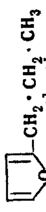
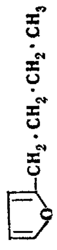
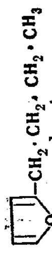
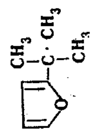
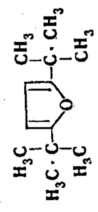
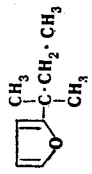
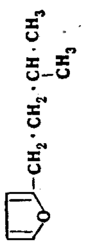
Frequencies for								 synthetic		 synthetic		 synthetic				
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
δ_{C-H}		285 (15)							288 (5) 312 (8)	288 (50) 312 (52)					288 (50) 311 (38)	282 (10) 312 (12)
$\delta_{C=C}$						346 (5)							333 (5)	332 (5)	340 (50) 370 (55)	334 (50) 366 (55)
δ_{-CH_2-}			460 (55) 519 (58)			522 (50) 589 (45)	522 (38) 590 (37)	520 (40) 591 (45)	450 (10) 522 (12) 594 (13)	456 (2) 522 (3)	460 (25) 596 (35)	461 (25)	586 (15)		468 (35) 578 (98)	466 (45) 572 (60)
Plane δ 	598 (5)	610 (99)			601 (2)	624 (60)	624 (30)	626 (50)	620 (3)	620 (15)					628 (55)	626 (65)

Table 2 continued

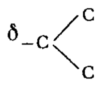
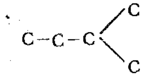
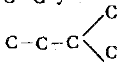
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
		691 (10)				729 (65)	730 (35)	729 (65)							699 (65)	694 (40) 724 (10)
Out of plane δ_{C-H}	884 (10)	923 (10)	816 (80)	814 (75) 882 (8) 935 (5)	886 (10)	818 (45)	818 (38) 846 (50)	816 (58) 845 (50)	836 (7) 870 (12) 935 (15)	840 (2) 864 (37) 938 (10)	854 (10) 940 (10)	854 (10) 940 (10)	816 (80) 932 (10)	813 (98) 886 (20) 932 (5)	817 (35) 856 (25) 887 (28) 945 (38)	813 (50) 850 (12) 893 (45) 926 (10) 941 (8)
ν_{C-C} y In the group 		989 (15)					976 (20)	974 (8)								978 (13) 991 (15)
	1037 (30)	1024 (99)	1002 (20) 1028 (10)	1003 (28) 1030 (24)	1012 (30)	1003 (48) 1030 (52)	1004 (55) 1032 (40)	1006 (55) 1027 (62)	1008 (14) 1040 (21)	1007 (23) 1040 (8)	1032 (8)	1032 (8)	1004 (10) 1030 (10)	1015 (30)	1004 (36) 1032 (12)	1010 (55)
ν_{C-C} y Outward 						1050 (63)		1051 (10)							1058 (10)	
External δ_{C-H}					1076 (20)	1080 (8)	1082 (22)						1082 (1)	1077 (40)	1082 (95)	1078 (98)
δ_{-CH_2-}															1113 (12)	1114 (20)

Table 2 continued

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
δ^{s}_{C-H}			1057 (9)								1150 (35)	1146 (30)	1158 (5)		1140 (18)	1158 (98)
Plane δ_{C-H}		1214 (20)		1211 (8)		1211 (45)	1210 (22)	1210 (25)	1211 (5)	1220 (30)	1210 (30)	1210 (30)		1220 (15)		1212 (18)
External δ_{-CH_3}			1254 (5)			1239 (5) 1260 (2)	1238 (28)	1236 (28)	1265 (8)	1265 (2)					1231 (52) 1248 (58)	1227 (53) 1244 (62)
$\delta_{-CH_2, -CH_3}$	1370 (89)	1343 (15) 1381 (15) 1452 (20)	1300 (10) 1382 (2) 1454 (5)	1385 (28) 1450 (15)	1375 (30)	1300 (15) 1380 (55) 1450 (60)	1303 (12) 1343 (15) 1381 (35) 1450 (60)	1300 (15) 1349 (18) 1381 (55) 1450 (60)	1299 (10) 1343 (12) 1381 (11) 1453 (15)	1305 (1) 1355 (53) 1385 (50) 1454 (67)	1302 (17) 1340 (35) 1396 (26) 1450 (12)	1302 (17) 1340 (35) 1392 (26) 1450 (12)	1303 (5) 1379 (5) 1450 (60)	1321 (15) 1379 (20) 1450 (80)	1311 (61) 1334 (8) 1380 (38) 1450 (97)	1306 (42) 1332 (12) 1376 (35) 1450 (90)
$\nu_{C=C}^{s}$	1486 (100)			1483 (16)	1507 (10)	1508 (7)			1505 (95)	1505 (40)	1504 (96)	1505 (96)	1507 (98)	1507 (99)	1510 (99)	1504 (95)
2, 5-dialkylfuran		1573 (100)			1562 (15)									1562 (40)		
ν_{C-H} $\nu_{C=C}^{as}$ 	1590 (98)		1604 (2)	1607 (15)	1584 (15)	1606 (2)	1606 (62)	1606 (65)	1593 (12)	1592 (90)	1586 (61)	1586 (61)	1587 (10)	1587 (15)	1586 (58)	1584 (62)
ν_{-CH_2-}		2744 (5)			1673 (10)	2738 (12)	2738 (61)	2738 (8)	1670 (52)	1670 (100)				1669 (30)		1664 (58) 2730 (13)

Table 2 concluded

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
			2753 (3)						2778 (55)	2785 (95)	2784 (96)	2784 (96)	2753 (5)			2753 (5)
$\nu_{C-H}^{s'}$									2828 (45)	2814 (77)						2818 (18)
$\nu_{-CH_2, -CH_3}$	2921 (72)	2884 (5) 2923 (100) 2952 (10)	2909 (52) 2932 (92) 2962 (80)	2929 (72)		2856 (68) 2920 (65) 2961 (63)	2862 (58) 2919 (85)	2864 (12) 2917 (89)	2886 (68) 2909 (95) 2935 (45) 2962 (91)	2875 (95) 2903 (95) 2934 (98) 2965 (100)	2860 (75) 2910 (57) 2950 (70)	2860 (75) 2910 (57) 2950 (70)	2905 (40) 2962 (50)	2871 (10)	2862 (48) 2882 (45) 2915 (89) 2936 (92) 2976 (95)	2860 (58) 2876 (32) 2908 (35) 2933 (25) 2970 (98)
ν_{C-H}^{as}	3042 (35) 3090 (20)	2988 (10)	3054 (5)	3056 (5)	2990 (30) 3046 (2)	2980 (52) 3054 (56)	2983 (68) 3058 (38)	3003 (68) 3052 (95)	3052 (11)	3052 (2)	3045 (8)	3045 (8)	3042 (20)	3040 (5)		
ν  -C-H	3120 (30) 3156 (50)	3110 (20) 3143 (50)	3124 (2) 3150 (50)	3128 (5)	3120 (8) 3146 (50)	3122 (59) 3150 (11)	3122 (51)	3121 (52)	3119 (60) 3142 (5)	3110 (98) 3145 (80)	3115 (87) 3150 (52)	3115 (87) 3150 (52)	3118 (30) 3150 (55)	3119 (50) 3150 (40)	3122 (98) 3150 (50)	3116 (50) 3152 (58)

Absorption % in parentheses.

2-n-Butylfuran: bp 142°C (765 mm); n_D^{20} 1.4440; d_4^{20} 0.8870.

Synthetic 2-n-butylfuran was prepared by the Kishner reaction from furylpropyl ketone, bp 140° (760 mm); n_D^{20} 1.4440; d_4^{20} 0.8890.

2, 5-di-tert-Butylfuran: bp 101°C (24 mm); n_D^{20} 1.4360; d_4^{20} 0.8386.

2-(2'-Furyl)-3-methylbutane: bp 147°C (750 mm); n_D^{20} 1.4420; d_4^{20} 0.8700.

2-Isoamylfuran: bp 170°C (750 mm); n_D^{20} 1.4420; d_4^{20} 0.8968.

2-tert-Amylfuran: bp 65° C (5 mm); n_D^{20} 1.4440; d_4^{20} 0.8780.

2, 5-Di-tert-amylfuran: bp 85° C (5 mm); n_D^{20} 1.4555; d_4^{20} 0.8726.

Tables 1 and 2 show that, to some extent, alkyl groups in the furan ring shift the frequencies observed for the latter. More particularly, the regions of furan ring C—C bond symmetric and assymmetric vibrations and C—H bond valence vibrations are displaced, e.g., in the IR spectra of alkylfurans, the double bond $\nu_{C-C}{}^{as}$ asymmetric vibrations band is displaced towards the high frequency side, to 1592 cm^{-1}, and the same holds for the $\nu_{C-C}{}^{s}$ and $\nu_{C-H}{}^{as}$ which appear in their Raman spectra.

These results can be explained by donor-donor interaction between furan ring and alkyl group, this being known to result in increased C—H bond frequency [14].

There are three interesting lines, at 3156, 3120, and 3090 cm^{-1} in the C—H bond valence vibrations frequency region of the furan Raman spectrum. According to published data [13], the presence of an alkyl group in the furan ring leads to disappearance of the 3090 cm^{-1} line, and diminution of the intensities of the other two. This checked with the Raman spectra of almost all the present alkylfurans.

An hypothesis has been put forward [13] regarding change of Raman spectrum in the 3100–3150 cm^{-1} region when the furan ring is β-substituted. Actually, the Raman spectrum of 3-isopropylfuran, whether prepared by direct alkylation of furan, or by retrosynthesis, lacked the 3150 cm^{-1} line characteristic of 2-substituted furans.

Further, the IR spectra of 3-monosubstituted furans have characteristic bands in the 790–794 cm^{-1} region.

This all shows that frequencies due to C—H bonds at the α and β positions differ quite considerably, and this further checks the known inequality between substituents in those positions [15–16].

The literature mentions a number of bands characteristic of 2-mono- and 2, 5-disubstituted furans. Bands at the frequency intervals 875–890 cm^{-1} [11], 727–766 cm^{-1}, and 793–858 cm^{-1} [7], and 945–915 cm^{-1} [9] are ascribed to 2-substituted furans. Frequencies 776–806 cm^{-1} [7] and 945–970 cm^{-1} [9] are ascribed to 2, 5-disubstituted furans.

The IR spectra of all the 2-substituted monoalkylfurans of the present work show an intense absorption band in the 873 cm^{-1} region. Generally, it is absent from the spectra of 2, 5-disubstituted furans, but on the other hand the IR spectra of the latter always show rather intense maxima at 781 cm^{-1} and 961 cm^{-1}. It is significant that the 873 cm^{-1} band characteristic of all the monosubstituted furans, as well as of furan itself, but not shown by the disubstituted furans, should obviously be ascribed to deformation vibrations of the C—H bond at the second free α position of the furan ring. The 1562–1573 cm^{-1} line in the Raman spectrum of 2, 5-di-tert-butylfuran is also shown by disubstituted furans.

The 1075 cm^{-1} band is, as we showed, only found in the IR spectra of dialkylfurans. Finally, published data [7] show that an intense absorption band at 792–799 cm^{-1} is characteristic of 2, 3, 5-trimethylfuran, and it also shows clearly in the spectrum of 2, 3, 5-triethylfuran which we prepared.

The Raman spectra of 2-isoamylfuran, 2- and 3-isopropylfuran show a line at 724–729 cm^{-1}, checking the presence of an isopropyl group in a side chain [17]. The Raman spectra of the other alkylfurans do not show that line.

The characteristic frequencies of furan and its alkyl derivatives obtained in the present work can be used to determine the compositions of complex mixtures of alkylfurans.

REFERENCES

1. S. A. Hiller, A. E. Berzin, and L. Ya. Lauberte, Izv. AN LatvSSR, 4, 71, 1958.
2. S. A. Hiller and A. E. Berzin, Izv. AN LatvSSR, 5, 142, 109, 1959.
3. S. A. Hiller and A. E. Berzin, Izv. AN LatvSSR, ser. khim., 103, 1962.
4. S. A. Hiller and A. E. Berzin, Izv. AN LatvSSR, ser. khim., 113, 1962.
5. S. A. Hiller and A. E. Berzin, Izv. AN LatvSSR, ser. khim., 445, 1962.
6. S. A. Hiller, A. N. Anderson, A. E. Berzin, and M. V. Shimanskaya, Izv. AN LatvSSR, ser. khim., 575, 1965.

7. M. Fetison and J. Guy, C. R., 247, 1182, 1956.
8. A. R. Katritzky and J. M. Lagowsky, J. Chem. Soc., 657, 1959.
9. A. H. Cross, S. G. E. Stevens, and T. H. E. Watts, J. Appl. Chem., 7, 562, 1957.
10. A. H. Cross and T. H. E. Watts, Chem. Ind., 1161, 1958.
11. L. W. Daasch, Chem. Ind., 1113, 1958.
12. A. P. Dunlop and F. N. Peters, The Furans, Reinhold Corp., NY, 8, 11, 1953.
13. E. V. Sobolev, V. T. Aleksanyan, R. A. Karakhanov, I. F. Bel'skii, and V. A. Ovodova, ZhSKh, 4, 358, 1963.
14. L. J. Bellamy, The Infra-Red Spectra of Complex Molecules [Russian translation], IL, Moscow, 34, 389, 1961.
15. F. L. Pilar and J. R. Morris, J. Chem. Phys., 34, 389, 1961.
16. D. S. Sappenfield and M. Kreevoy, Tetrah., 19, 157, 1963.
17. G. S. Landsberg, P. A. Bazhulin, and M. M. Sushinskii, Fundamental Parameters of the Raman Spectra of Hydrocarbons [in Russian], Izd-vo AN SSR, Moscow, 277, 1956.

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