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Infrared Spectra of Isotopically Labeled Compounds. II.[1] Compounds Possessing the 2,4-Dimethyl-3-pentyl Skeleton

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The infrared spectra of some C^{13} and deuterium labeled diisopropylcarbinols, diisopropylmethanes, 1,1-diisopropylethylenes, diisopropyl ketoximes, and diisopropylcarbinylamines were investigated. The 1236 cm.$^{-1}$ frequency of diisopropylcarbinol is shown to be an O—H deformation and the 1096 cm.$^{-1}$ frequency a skeletal vibration. The 1115 cm.$^{-1}$ frequency of hydrocarbons is a skeletal vibration and the 920 cm.$^{-1}$ a methyl rocking mode. The shifts observed upon O-deuteration of alcohols and oximes are in better agreement with calculations based on the reduced masses of (O—H) and (O—D) than on (H) and (D). The C=N stretch of oximes is less pure than either the C=O stretch of ketones and acids or the C=C stretch of ethylenes. The C—N stretch of aliphatic amines is much less coupled with other vibrations than the C—O stretch of alcohols, and quite different from the C—N stretch of anilines. Examples of displacements to higher wave numbers upon substitution with heavier isotopes are reported.

The infrared spectra of isotopically labeled diisopropyl ketones were reported in the first paper of this series.[1] Evidence was presented there indicating that the 1024 cm.$^{-1}$ frequency of diisopropyl ketone is an uncoupled vibration. Furthermore, it was shown that useful information could be obtained by examining the spectra of compounds isotopically labeled at various atoms. These facts prompted the examination of the infrared spectra of compounds derived from diisopropyl ketone.

This paper reports the spectra of isotopically labeled diisopropylcarbinols, diisopropylmethanes, 1,1-diisopropylethylenes, diisopropyl ketoximes, and diisopropylcarbinylamines. As in the case of diisopropyl ketones the purity of the samples used for infrared analysis was ascertained by vapor phase chromatography. The procedure followed in obtaining the spectra and analyzing them was the same as the one used for the ketones.

The pertinent spectral frequencies, the experimental frequency differences (Δ_ν), and some calculated Δ_ν values of the investigated compounds are presented in Tables I–V. The frequencies of diisopropylcarbinols (Table I) and diisopropyl ketoximes (Table IV) were determined in carbon disulfide. All other frequencies were determined in solutions of carbon tetrachloride, with the exception of the frequencies of the amines in the region of 800 cm.$^{-1}$ which were determined in carbon disulfide.[3] Each spectrum was taken in various concentrations, the range being from 3% to 12%.

DISCUSSION

Diisopropylcarbinols. The infrared spectra of alcohols have been the subject of frequent discussion in the literature,[4–11] due to the uncertainty of band assignment in the 1500–1000 cm.$^{-1}$ region. The most controversial frequencies are the ones in the 1250 cm.$^{-1}$ and 1100 cm.$^{-1}$ regions, assigned either to O—H deformations or to the coupled C—O and C—C stretchings. It appeared reasonable that the spectra of isotopically labeled diisopropylcarbinols might shed some light on the controversy.

The data of Table I show that five frequencies are strongly affected by O-deuteration and unaffected by either C^{13} substitution or C-deuteration. Two of these frequencies, 3610 cm.$^{-1}$ and 3470 cm.$^{-1}$, are the well known O—H stretches of the monomer and its hydrogen bonded complex, respectively.[12] The other three frequencies, 1380 cm.$^{-1}$, 1236 cm.$^{-1}$, and 1117 cm.$^{-1}$, are O—H deformations with one of them perhaps due to the hydrogen bonded complex.

The 1096 cm.$^{-1}$ frequency (1100 cm.$^{-1}$ region frequency of alcohols) is not an O—H deformation as some investigators have suggested. Neither is it a simple C—O stretch or the result of only C—O and C—C coupled stretches. The magnitude and nature of its shifts upon isotopic substitution, 2 cm.$^{-1}$ upon C^{13} substitution, 31 cm.$^{-1}$ upon 2,4-

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[1] Part I. G. J. Karabatsos, *J. Org. Chem.*, **25**, 315 (1960).

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[3] Due to the reactivity of diisopropylcarbinylamine with carbon disulfide the frequencies in the 800 cm.$^{-1}$ region were determined immediately after solution of the amine in carbon disulfide.

[4] H. H. Zeiss and M. Tsutsui, *J. Am. Chem. Soc.*, **75**, 897 (1953).

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[11] E. L. Eliel, C. C. Price, R. J. Convery, T. J. Prosser, *Spectrochim. Acta*, **10**, 423 (1958).

[12] It is interesting to note that the experimental shifts of both 3610 cm.$^{-1}$ and 3740 cm.$^{-1}$ frequencies, 950 cm.$^{-1}$ and 886 cm.$^{-1}$, respectively, are in better agreement with the shifts calculated from the reduced masses of (O—H) and (O—D), than they are with the shifts calculated from the reduced masses of (H) and (D). It appears that the hydrogen is vibrating against the effective mass of the oxygen, and not against the effectively infinite mass of the whole molecule.

TABLE I

INFRARED SPECTRAL FREQUENCIES OF DIISOPROPYLCARBINOLS[a]

Compound	Wave Number (Cm.$^{-1}$)										$(\mu_2/\mu_1)^{1/2}$[b]
2,4-Dimethyl-3-pentanol	3610	3470	1380	1236	1152	1117	1096	993	977	848	
2,4-Dimethyl-3-pentanol-3-C^{13}	3610	3470	1380	1236	1147	1117	1094	982	966	844	
Δ_ν Experimental[c]					5		2	11	11	4	
Δ_ν Calcd. from (μ_{C-O}) and $(\mu_{C^{13}-O})$					25		24	22	22	19	1.023
Δ_ν Calcd. from (μ_{C-C}) and $(\mu_{C^{13}-C})$					23		21	19	19	17	1.020
2,4-Dimethyl-3-pentanol-O-*d*	2660	2584	1000	915	1143	807	1105	993	982	843	
Δ_ν Experimental[c]	950	886	380	321	9	310	−9		−5	5	
Δ_ν Calcd. from (μ_H) and (μ_D)	1055	1016									1.414
Δ_ν Calcd. from (μ_{O-H}) and (μ_{O-D})	983	944									1.374
2,4-Dimethyl-3-pentanol					1152		1096		977	848	
2,4-Dimethyl-3-pentanol-3-*d*					1145		1097		926	844	
Δ_ν Experimental[c]					7		−1		51	4	
2,4-Dimethyl-3-pentanol-2,4-d_2							1065		941		
Δ_ν Experimental[c]							31		36		

[a] Determined in carbon disulfide solutions. [b] μ_1 is the reduced mass calculated from the unlabeled alcohol and μ_2 the reduced mass calculated from the labeled alcohol. [c] Difference between the frequencies of the labeled compound and the corresponding frequencies of 2,4-dimethyl-3-pentanol. The Δ_ν's between the frequencies of 2,4-dimethyl-3-pentanol-3-C^{13} and 2,4-dimethyl-3-pentanol-O-*d*-3-C^{13} were identical with the Δ_ν's between the frequencies of 2,4-dimethyl-3-pentanol and 2,4-dimethyl-3-pentanol-O-*d*.

dideuteration, and displacement to higher frequencies (1105 cm.$^{-1}$) upon O-deuteration, suggest that it is a complex skeletal vibration characteristic of alcohols. The 1152 cm.$^{-1}$ and 848 cm.$^{-1}$ frequencies are also skeletal vibrations, the latter being equivalent to the 858 cm.$^{-1}$ frequency of diisopropyl ketone.

The spectrum of diisopropylcarbinol shows two strong bands at 993 cm.$^{-1}$ and 977 cm.$^{-1}$ The data of Table I suggest that the 993 cm.$^{-1}$ frequency is a skeletal vibration with no contribution from a C—H mode of either the tertiary or the secondary hydrogens. The 977 cm.$^{-1}$ frequency, having strong C—H contributions, behaves upon O-deuteration like the 1096 cm.$^{-1}$ frequency. Since either one or two strong bands appear in the spectra of many aliphatic alcohols in this region, the possibility of the usefulness of these bands as diagnostic tools, in conjunction with the 1100 cm.$^{-1}$ frequency, is under examination.

Diisopropylmethanes. In the infrared spectra of saturated hydrocarbons the assignment of the 1115 cm.$^{-1}$ and 920 cm.$^{-1}$ frequencies to specific vibrations has been rather difficult, and a great deal of controversy exist in the literature as to which frequency is the skeletal C—C stretch and which is the C—CH_3 rocking vibration.[13–17] The data presented in Table II suggest that the 1164 cm.$^{-1}$ frequency of diisopropylmethane (1115 cm.$^{-1}$ region), shifted to 1156 cm.$^{-1}$ upon C^{13} substitution, is a skeletal vibration rather than a methyl rocking mode. On the other hand, the 916 cm.$^{-1}$ frequency (920 cm.$^{-1}$ region) is unaffected by C^{13}, which is compatible with the methyl rocking mode.

TABLE II

INFRARED SPECTRAL FREQUENCIES OF DIISOPROPYLMETHANES[a]

Compound	Wave Number (Cm.$^{-1}$)				$(\mu_2/\mu_1)^{1/2}$
2,4-Dimethylpentane	1164	982	916	867	
2,4-Dimethylpentane-3-C^{13}	1156	972	916	862	
Δ_ν Experimental	8	8		5	
Δ_ν Calcd. from (μ_{C-C}) and $(\mu_{C^{13}-C})$	23	19	18	17	1.020

[a] Determined in carbon tetrachloride solutions.

TABLE III

INFRARED SPECTRAL FREQUENCIES OF DIISOPROPYLETHYLENES[a]

Compound	Wave Number (Cm.$^{-1}$)				$(\mu_2/\mu_1)^{1/2}$
1,1-Diisopropylethylene	1639	1101	1036	891	
1,1-Diisopropylethylene-1-C^{13}	1608	1097	1035	891	
Δ_ν Experimental	31	4	1	0	
Δ_ν Calcd. from (μ_{C-C}) and $(\mu_{C^{13}-C})$	32	22	20	18	1.020

[a] Determined in carbon tetrachloride solutions.

The 982 cm.$^{-1}$ and 867 cm.$^{-1}$ frequencies are assigned to skeletal vibrations, the latter being equivalent to the 858 cm.$^{-1}$ and 848 cm.$^{-1}$ frequencies of diisopropyl ketone and diisopropylcarbinol, respectively.

1,1-Diisopropylethylenes. The infrared spectrum of 1,1-diisopropylethylene-1-C^{13} exhibits few differences from that of 1,1-diisopropylethylene. The 1639 cm.$^{-1}$ frequency, the C═C stretch, is lowered upon C^{13} substitution to 1608 cm.$^{-1}$, a

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(14) K. W. F. Kohlrausch and F. Köppl, *Z. Phys. Chem.*, **B26**, 209 (1934).

(15) F. T. Wall and C. R. Eddy, *J. Chem. Phys.*, **6**, 107 (1938).

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(17) N. Sheppard and D. M. Simpson, *J. Chem. Phys.*, **23**, 582 (1955).

TABLE IV

INFRARED SPECTRAL FREQUENCIES OF DIISOPROPYL KETOXIMES[a]

Compound	Wave Number (Cm.$^{-1}$)												$(\mu_2/\mu_1)^{1/2}$
2,4-Dimethyl-3-pentanone oxime	3571	3257	1656	1314	1233	1221	1163	1153	1062	1023	941	865	
2,4-Dimethyl-3-pentanone-3-C^{13} oxime	3571	3257	1629	1309	1232	1214	1151	1152	1050	1015	941	863	
Δ_ν Experimental			27	5	1	7	12	1	12	8		2	
Δ_ν Calcd. from $(\mu_{C=N})$ and $(\mu_{C^{13}=N})$			36				25		23				1.022
Δ_ν Calcd. from (μ_{C-C}) and $(\mu_{C^{13}-C})$			32					20					1.020
2,4-Dimethyl-3-pentanone oxime-O-*d*	2602	2387	1642	1074	990								
Δ_ν Experimental	969	870	14	240	243								
Δ_ν Calcd. from (μ_H) and (μ_D)	1046	954											1.414
Δ_ν Calcd. from (μ_{O-H}) and (μ_{O-D})	972	887											1.374

[a] Determined in carbon disulfide solutions.

shift of 31 cm^{-1}. Calculations based on the reduced masses of (C=C) and (C^{13}=C) predict a shift of 32 cm^{-1}. However, as in the case of diisopropyl ketone, one cannot ascertain the degree of coupling between C=C and C—C without the aid of the spectrum of 1,1-diisopropylethylene-2-C^{13}.

The 891 cm.$^{-1}$ frequency, the =CH_2 bending, behaves upon C^{13} substitution as expected.

Diisopropyl ketoximes. Examination of the data of Table IV reveals that the C=N stretch (1656 cm.$^{-1}$) of diisopropylketone oxime has stronger contributions from other vibrations than either the C=O or C=C stretches of diisopropyl ketone and 1,1-diisopropylethylene; upon C^{13} substitution it is lowered to 1629 cm.$^{-1}$, or shift of 27 cm.$^{-1}$, as compared to 36 cm.$^{-1}$ calculated from the reduced masses of (C=N) and (C^{13}=N). Furthermore, upon O-deuteration it is shifted to 1642 cm^{-1}.

O-deuteration strongly affects five frequencies. The 3571 cm.$^{-1}$ and 3257 cm.$^{-1}$ frequencies are the O—H stretchings of the monomer and its hydrogen bonded complex, respectively.[18] It is interesting to note that two of the O—H deformations,[19] 1314 cm.$^{-1}$ and 1233 cm.$^{-1}$, seem to be coupled with other vibrations, as shown by their shifts, 5 cm.$^{-1}$ and 1 cm.$^{-1}$ respectively, upon C^{13} substitution. It should be further noticed that the magnitude of their shifts upon O-deuteration is much smaller than expected.

The N—O stretch of the oximes is supposed to occur in the 950 cm.$^{-1}$ region.[19] The 941 cm.$^{-1}$ frequency of diisopropyl ketoxime, a very strong band, is most likely the N—O stretch. It should be noticed that it is unaffected by either C^{13} substitution or O-deuteration.

Although certain other frequency changes are observed upon isotopic substitution, assigning of the affected frequencies is not possible from the available data.[20]

Diisopropylcarbinylamines. The C—N stretch of aliphatic amines has not been definitely identified. Colthup[21] suggests that absorptions of aliphatic amines in the 1220–1020 cm.$^{-1}$ region correspond to C—N stretches. In the spectrum of diisopropylcarbinylamine (Table V) the only frequency strongly affected by C^{13} substitution, and the only strong band in the 1220–1020 cm.$^{-1}$ region, is the 1117 cm.$^{-1}$ The experimental shift, 22 cm.$^{-1}$, is in fair agreement with the 24 cm.$^{-1}$ shift calculated from the reduced masses of (C—N) and (C^{13}—N).[22] The extent to which the C—N stretch may be coupled with C—C vibrations cannot be ascertained from the present data. The fact that it is unaffected by either *N,N*-dideuteration or C-deuteration at carbon three, indicates that it is not coupled with either N—H vibrations or C—H vibrations of carbon three.

In an attempt to compare the C—N stretch of aliphatic amines with the corresponding stretch of anilines, the spectrum of aniline-N^{15} (a sample of the labeled aniline was kindly provided by Profes-

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(18) As in the case of diisopropylcarbinol the experimental shifts are in much better agreement with calculations based on the reduced masses of (O—H) and (O—D) than (H) and (D).

(19) A. Palm and H. Werbin, *Can. J. Chem.*, **32**, 858 (1954) have assigned the 1265 cm.$^{-1}$ frequency of α-benzaloximes to the O—H bending.

(20) The 1163 cm.$^{-1}$ frequency has the same shape as, but it is weaker than, the 1203 cm.$^{-1}$ frequency of diisopropyl ketone. Since both frequencies show the same shift, 12 cm.$^{-1}$ and 13 cm.$^{-1}$ respectively, upon C^{13} substitution, it is possible that the 1163 cm.$^{-1}$ is the asymmetric C=N stretch. The 865 cm.$^{-1}$ frequency is the same band found in the spectra of diisopropyl ketone (858 cm.$^{-1}$), diisopropylcarbinol (848 cm.$^{-1}$) and diisopropylmethane (867 cm.$^{-1}$). Evidently, it is characteristic of the 2,4-dimethyl 3-pentyl group.

(21) N. B. Colthup, *J. Opt. Soc. Am.*, **40**, 397 (1950).

(22) It is interesting to note that the C—O stretch of diisopropylcarbinol (1096 cm.$^{-1}$) is coupled with other vibrations to a much larger extent than the C—N stretch of diisopropylcarbinylamine.

TABLE V

INFRARED SPECTRAL FREQUENCIES OF DIISOPROPYLCARBINYLAMINES[a]

Compound	Wave Number (Cm.$^{-1}$)						$(\mu_2/\mu_1)^{1/2}$
2,4-Dimethyl-3-pentylamine	1613	1348	1258	1117	919	807[b]	
2,4-Dimethyl-3-pentylamine-3-C^{13}	1613		1258	1095	919	804[b]	
Δ_ν Experimental				22		3	
Δ_ν Calcd. from (μ_{C-N}) and $(\mu_{C^{13}-N})$				24			1.022
2,4-Dimethyl-3-pentylamine-*N*,*N*-d_2	1118	1348	1258	1117		803[b]	
Δ_ν Experimental	495					4	
2,4-Dimethyl-3-pentylamine-3-*d*	1613	1254	1258	1117	919		
Δ_ν Experimental		94					

[a] Determined in carbon tetrachloride solutions. [b] Determined in carbon disulfide.

sor E. L. Eliel) was examined. The only frequency of aniline affected by N^{15} substitution is a strong band at 1271 cm.$^{-1}$ (carbon tetrachloride solution) which is shifted to 1267 cm.$^{-1}$ The magnitude of the shift, only 4 cm.$^{-1}$, suggested that the C—N stretch of aniline is strongly coupled with other vibrations. Examination of the spectra of aniline-N, N-d_2 and aniline-N, N-d_2-N^{15} showed a displacement of the C—N stretch to 1302 cm.$^{-1}$ and 1298 cm.$^{-1}$, respectively. Such displacements to higher wave numbers upon heavier isotope substitution were observed in the spectrum of diisopropylcarbinol upon O-deuteration (frequencies 1096 cm.$^{-1}$ and 977 cm.$^{-1}$, Table I). That this displacement is common in the spectra of *N*,*N*-dideuterated anilines is shown by Table VI.

TABLE VI

CARBON-NITROGEN STRETCH OF ANILINES AND ANILINES-N,N-d_2

Compound	Undeut. Compound (Cm.$^{-1}$)	Deut. Compound (Cm.$^{-1}$)	Δ_ν(Cm.$^{-1}$)
Aniline	1271	1302	31
Aniline-N^{15}	1267	1298	31
2-Bromoaniline	1307	1326	19
4-Bromoaniline	1274	1304	30
2,4,6-Tribromoaniline	1271	1284	13
2-Methylaniline	1269	1307	38
3-Methylaniline	1292	1314	22
4-Methylaniline	1271	1302	31
2-Methoxyaniline	1271	1307	36

One could explain these results by invoking the noncrossing over rule of two vibrations possessing the same symmetry properties. (In the case of anilines the vibrations would be the N—H deformation around 1600 cm.$^{-1}$ and the C—N stretch.) Calculations which would either confirm or refute the above suggestion are under consideration.

EXPERIMENTAL

2,4-Dimethyl-3-pentanol-3-C^{13}. A solution of 2,4-dimethyl-3-pentanone-3-C^{13} (2 g.) in anhydrous ether (20 ml.) was slowly added, at room temperature, to a dispersion of lithium aluminum hydride (0.5 g.) in anhydrous ether (55 ml.) with constant stirring. The product was heated at reflux for 1 additional hr. Cold water (1 ml.), followed by 10% aqueous sodium hydroxide (0.5 ml.), was added and the mixture was allowed to stand overnight. The ether solution was filtered through anhydrous sodium sulfate, the ether evaporated, and the residue (about 2 g.) was vapor phase chromatographed.

2,4-Dimethyl-3-pentanol-O-d. A solution of 2,4-dimethyl-3-pentanol (0.2 g.) in anhydrous ether (5 ml.) was shaken for 15 hr. with heavy water (5 g.). The ether layer was separated, dried over anhydrous sodium sulfate, the ether was evaporated, and the residue was vapor phase chromatographed. 2,4-Dimethyl-3-pentanol-O-*d*-3-C^{13} was prepared from 2,4-dimethyl-3-pentanol-3-C^{13}.

2,4-Dimethyl-3-pentanol-3-d was prepared by reduction of the ketone with lithium aluminum hydride.

2,4-Dimethyl-3-pentanol-2,4-d_2 was prepared by reduction of the dideuterated ketone with lithium aluminum hydride.

2,4-Dimethylpentane-3-C^{13}. Preparation of this hydrocarbon will be described elsewhere.

1,1-Diisopropylethylene. Preparation of 1,1-diisopropylethylene was achieved by application of the Wittig reaction.[23] Triphenylmethylphosphonium iodide (5 g.)[24] was added to a solution of phenyllithium (1.1 g.) in ether (100 ml.). Stirring was continued for 3 hr. the color of the reaction mixture turning orange-brown. Slow addition of a solution of 2,4-dimethyl-3-pentanone (1.4 g.) in ether (10 ml.) resulted in the discharge of the orange color and the formation of a fine gray-white precipitate. Stirring was continued for 1 additional hr. at room temperature, followed by 3 hr. of steam reflux. The ether layer was separated, washed with 5% aqueous hydrochloric acid, 10% aqueous sodium bicarbonate, and water, and dried over anhydrous magnesium sulfate. The ether was driven off and the residue was vapor phase chromatographed. The yields of 1,1-diisopropylethylene did not exceed 35%. 1,1-Diisopropylethylene-1-C^{13} was prepared by using 2,4-dimethyl-3-pentanone-3-C^{13}.

Preparation of the oximes was accomplished by use of standard methods. Preparation of the amines was achieved by reduction of the corresponding oximes with lithium aluminum hydride (deuteride).[25]

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