[CONTRIBUTION NO. 1118 FROM STERLING CHEMISTRY LABORATORY, YALE UNIVERSITY]

The Carbon–Oxygen Absorption Band in the Infrared Spectra of Alcohols

BY HAROLD H. ZEISS AND MINORU TSUTSUI

RECEIVED JULY 21, 1952

A systematic study of the region of carbon–oxygen absorption bands lying between 1250–1000 cm.$^{-1}$ (8–10 µ) in the infrared spectra of alcohols permits some refinement in the method of structural characterization of alcohols by infrared analysis and renders invalid a previous classification of alcohols into primary, secondary and tertiary types on the basis of sharp differentiations in the C–O band position. Two large and opposing displacement effects are observed in the shifts of the C–O band with variation in the structure of alcohols. These effects are discussed with respect to an empirical correlation between alcohol structure and C–O band position.

Absorption of infrared radiation by alcohols in the region of 3500–3100 cm.$^{-1}$ is attributed to oxygen–hydrogen stretching vibrations, a useful observation for the confirmation of the presence of hydroxyl functions in organic molecules. In addition, an equally significant but less studied absorption band in the 1250–1000 cm.$^{-1}$ (8–10 µ) region appears, ranging in intensity from strong to medium, in the spectra of alcohols and is considered to arise from carbon–oxygen stretching vibration. Early in the history of the application of infrared absorption to structural problems Weniger[1] noted that the position of this C–O band in the spectra of alcohols depended upon the primary, secondary or tertiary character of the hydroxylated carbon atom, from which the inference may be drawn that these types can be distinguished from one another by the appearance of the C–O band at 9.6, 9.1 and 8.6 µ, respectively. The results of a more recent survey of a number of secondary and tertiary alcohols by Tuot and Lecompte[2] appear to be in agreement with these assignments of band position. The study of the infrared spectra of alcohols reported in this paper establishes the fact that this differentiation is not valid but permits some refinement in the method of structural characterization of alcohols by infrared analysis.

The location of the C–O band in the spectra of the majority of the alcohols measured here has been attended by little ambiguity, owing to strong band intensity and relative isolation. In those cases where ambiguity existed comparison of the spectra with the spectra of parent hydrocarbons[3] has sufficed usually to render a more certain assignment of wave frequency. Those spectra which did not yield to this expedient have been compared with the spectra of analogous alcohols and tentative assignments made.

Results

Saturated Aliphatic Secondary Alcohols.—The position of the C–O absorption band in homologous series of straight-chain aliphatic secondary alcohols are recorded in Table I. It is apparent that while lengthening of the R′ chain in the CH_3CHOHR' and C_2H_5CHOHR' series shifts the band position only slightly to higher frequencies, further lengthening of both R and R′ chains results in more marked, though still small, shifts in the same direction. It is concluded from this data that alcohols of this classification absorb consistently at about 1110 cm.$^{-1}$ (9.0 µ).

TABLE I

STRAIGHT-CHAIN SATURATED ALIPHATIC SECONDARY ALCOHOLS

R	R'	B.p., °C.	Mm.	$\eta^{25}D$	C–O absorption	
					Cm.$^{-1}$	µ
Methyl	Methyl	84–84.5		1.3750	1105	9.05
Methyl	Ethyl	99		1.3956	1105	9.05
Methyl	*n*-Propyl	118–119		1.4047	1106	9.04
Methyl	*n*-Butyl	138–139		1.4131	1106	9.04
Methyl	*n*-Pentyl	159–160		1.4197	1108	9.03
Methyl	*n*-Hexyl	178–179		1.4248	1109	9.02
Methyl	*n*-Octyl	125–126	29	1.4334	1111	9.00
Methyl	*n*-Nonyl	130–131	28	1.4358	1111	9.00
Ethyl	Ethyl	116–116.5		1.4058	1106	9.04
Ethyl	*n*-Propyl	65–65.5	32	1.4150	1108	9.03
Ethyl	*n*-Butyl	78–78.5	56	1.4200	1108	9.03
Ethyl	*n*-Pentyl	89.5–90	25	1.4250	1109	9.02
Ethyl	*n*-Hexyl	91–91.5	29	1.4286	1111	9.00
Ethyl	*n*-Heptyl	105–105.5	45	1.4325	1111	9.00
n-Propyl	*n*-Propyl	74–75	30	1.4186	1115	8.97
n-Propyl	*n*-Butyl	87	21	1.4232	1116	8.96
n-Propyl	*n*-Pentyl	101–101.5	30	1.4275	1117	8.95
n-Propyl	*n*-Hexyl	116.5–117	30	1.4340	1118	8.94
n-Butyl	*n*-Butyl	106–107	30	1.4295	1115	8.97
n-Butyl	*n*-Pentyl	117–118	31	1.4310	1118	8.94
n-Pentyl	*n*-Pentyl	130–132	28	1.4334	1119	8.93

The effect of chain branching in aliphatic secondary alcohols is reflected in Table II. In the methyl series, CH_3CHOHR', any branching at the carbon atom alpha to the hydroxylated carbon is marked by a shift to lower frequencies by about 15 cm.$^{-1}$ from the band positions of the isomeric straight-

TABLE II

BRANCHED SATURATED ALIPHATIC SECONDARY ALCOHOLS

R	R'	B.p., °C.	Mm.	$\eta^{25}D$	C–O absorption	
					Cm.$^{-1}$	µ
Methyl	*i*-Propyl	111–112		1.4069	1090	9.17
Methyl	*i*-Butyl	130–131		1.4095	1109	9.02
Methyl	*i*-Hexyl	90–91	27	1.4222	1110	9.01
Methyl	*t*-Butyl	120–121		1.4138	1093	9.15
Methyl	*t*-Heptyl[a]	91.5	20	1.4480	1093	9.15
Methyl	*t*-Tridecyl[a]	99–99.5	0.5	1.4546	1093 ?	9.15
i-Propyl	*i*-Propyl	137–138		1.4222	1098	9.11
i-Propyl	*t*-Butyl	74	45	1.4262	1114 or 1093	8.98 9.15
i-Butyl	*i*-Butyl	91–91.5	25	1.4220	1126	8.88
t-Butyl	*t*-Butyl	46–48[b]			1163	8.6

[a] Samples of 3,3-diethylpentan-2-ol and of 3,3-di-*n*-butylheptan-2-ol were kindly supplied by Dr. W. von E. Doering, Columbia University. [b] Melting point.

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[1] W. Weniger, *Phys. Rev.*, **31**, 388 (1910).

[2] M. Tuot and J. Lecompte, *Bull. soc. chim.*, [5] **10**, 542 (1943).

[3] American Petroleum Institute Research Project 44, Carnegie Institute of Technology, Catalog of Infrared Spectra Data.

chain alcohols. An increase in the length of the α-branched chain appears to have no further effect. It is to be especially noted that branching beyond the α-carbon causes no similar shift to longer wave length. However, branching at both α-carbons does not intensify this effect but rather seems to reverse it.

Alkenyl and Aryl Secondary Alcohols.—A pronounced displacement of the C–O band of secondary alcohols to lower frequencies by unsaturation is shown by the alcohols of Table III. The simplest representatives of this class are methylcyclopropylcarbinol and methylvinylcarbinol with C–O band displacements of 30 and 50 cm.$^{-1}$, respectively, from their parent straight-chain saturated alcohols. Also in the methyl series, when R′ is varied, a phenyl group causes a shift of 30 cm.$^{-1}$, an α-naphthyl group, 40 cm.$^{-1}$, a β-naphthyl group, 35 cm.$^{-1}$ and an α-furyl group, 35 cm.$^{-1}$ from the 1110 cm.$^{-1}$ (9.0 μ) position. Thus, double-bond interaction with the C–O bond has resulted in 30–50 cm.$^{-1}$ displacements of the C–O band to longer wave lengths in the methyl series. It is of interest to observe that the cyclopropyl ring exhibits double-bond character in this connection. Introduction of the point of unsaturation at the β-carbon atom, as in methylbenzylcarbinol, appears to cause no analogous shift. However, the band assignment in this case is not satisfactorily established.

TABLE III

ALKENYL AND ARYL SECONDARY ALCOHOLS

R	R'	B.p. °C.	Mm.	η^{25}D	C–O absorption Cm.$^{-1}$	C–O absorption μ
Methyl	Cyclopropyl[a]			1.4284	1076	9.29
Methyl	Phenyl	202–203		1.5252	1073	9.32
Methyl	α-Furyl	83–83.5	25	1.4782	1068	9.36
Methyl	β-Naphthyl	71–72.5[d]			1066[e]	9.38
					1074[d]	9.31
Methyl	α-Naphthyl	64–65[d]			1059[e]	9.44
					1066[d]	9.38
Methyl	Vinyl	96–98		1.4070	1060	9.45
Methyl	Benzyl	116	25	1.5195	1106	? 9.04
Phenyl	Methyl	202–203		1.5252	1073	9.32
Phenyl	Ethyl	110	20	1.5120	1039	? 9.63
Phenyl	*i*-Propyl[b]	115.5	20	1.5112	1020	9.81
Phenyl	Cyclohexyl[b]	41[d]			1014[e]	9.86
					1009[f]	9.92
Phenyl	*t*-Butyl[c]	50–51[d]			1004[e]	9.96
					1000[f]	10.00
Phenyl	Phenyl	65–66[d]			1014[e]	9.86
					1016[f]	9.84
Phenyl	*p*-Tolyl	53–54[d]			1012[g]	9.88

Samples were generously furnished by [a] Dr. J. D. Roberts, Massachusetts Institute of Technology. [b] Dr. W. von E. Doering, Columbia University. [c] Dr. S. Winstein, University of California at Los Angeles. [d] Melting point. [e] Measured as melt. [f] Measured as crystalline film. [g] Measured as supercooled melt at room temperature.

In the phenyl series, C_6H_5CHOHR', when R′ is varied from methyl to isopropyl, a profound shift from normal to lower frequency is found (85 cm.$^{-1}$). A similar shift is also observed when R′ is cyclohexyl (90 cm.$^{-1}$). A *t*-butyl group causes an even greater displacement (100 cm.$^{-1}$). However, no additional shifts are found when R′ is also unsaturated: phenyl (90 cm.$^{-1}$) and *p*-tolyl (90 cm.$^{-1}$).

It is concluded that introduction of unsaturation at the α-carbon atom of secondary alcohols causes large displacements of the C–O band to lower frequencies, thereby extending the region of absorption to that of primary alcohols (*vide infra*). Further, α-unsaturation coupled with α-branching promotes band shifts of 65–100 cm.$^{-1}$, thus overlapping and extending the range beyond the primary alcohol region of absorption.

Saturated Alicyclic Secondary Alcohols.—Similar overlapping of absorption regions is to be found in the C–O bands of saturated, cyclic secondary alcohols (Table IV). Band shifts of up to 85 cm.$^{-1}$ from normal to lower frequencies are observed. Cyclopropanol, by virtue of its apparent absorption band at relatively high frequency, 1205 cm.$^{-1}$ (8.3 μ), appears to be related to the unknown vinyl alcohol (see Discussion), whereas cyclobutanol absorbs at close to normal secondary alcohol frequency. Further increase in ring size causes a shift of 45 cm.$^{-1}$ from normal to lower frequencies as in cyclopentanol and cyclohexanol. Other examples of six-membered ring alcohols including a decalol support the conclusion that these types of alcohols absorb between 1065–1040 cm.$^{-1}$ (9.4–9.6 μ). Ring expansion shifts the band to lower frequency in the case of cycloheptanol but apparently returns it to the above range in cyclooöctanol.

TABLE IV

SATURATED ALICYCLIC SECONDARY ALCOHOLS

Carbinol	B.p., °C.	Mm.	η^{25}D	C–O absorption Cm.$^{-1}$	C–O absorption μ
Cyclopropanol[a]				1205	8.3
Cyclobutanol[a]				1090	9.18
				1117 or	8.95
Cyclopentanol	66–66.5	27	1.4500	1064	9.40
Cyclohexanol	159		1.4644	1064	9.40
Thujyl alcohol[b]	141–142	50	1.4264	1062	9.41
Fenchyl alcohol[b]	46[d]			1055	9.48[e]
cis-α-Decalol	92–93[d]			1051	9.51[f]
				1057	9.46[g]
l-Menthol	41–42[d]			1039	9.63[e]
Cycloheptanol[c]	95	24	1.4772	1025	9.75
Cyclooöctanol[b]	35	0.015	1.4848	1047 ?	9.55

For their generous assistance we wish to thank [a] Dr. J. D. Roberts, M. I. T., for the loan of these spectra. [b] Dr. W. von E. Doering Columbia University, for samples of *d*-thujone, *l*-fenchone and cyclooöctanone. [c] Cycloheptanol from the Hickrill Chemical Foundation. [d] Melting point. [e] Measured as supercooled melt at room temperature. [f] Measured as melt. [g] Measured as a crystalline film.

Primary Alcohols.—An examination of the infrared spectra of primary alcohols, recorded in most part elsewhere,[3] emphasizes the overlapping of absorption regions of alcohols. The C–O band of these alcohols (Table V) extend over the range of

TABLE V[3]

PRIMARY ALCOHOLS

Carbinol	C–O absorption Cm.$^{-1}$	C–O absorption μ	Carbinol	C–O absorption Cm.$^{-1}$	C–O absorption μ
Methanol	1030	9.7	2-Methylbutan-1-ol	1040	9.6
Ethanol	1050	9.5	3-Methylbutan-1-ol	1060	9.45
n-Propanol	1060	9.45	2-Methylpropan-1-ol	1050	9.55
n-Butanol	1075	9.30	2,2-Dimethylpropan-1-ol[a]	1030	9.7
n-Pentanol	1060	9.45	Allyl alcohol[b]	1030	9.7
n-Hexanol	1060	9.45	Benzyl alcohol[c]	1010	9.9
n-Octanol	1060	9.45			
n-Nonanol	1060	9.45			

[a] Recorded in this Laboratory; m.p. 52–53°. [b] Spectrum reproduced in "Allyl Alcohol," Shell Chemical Corp., 1946, p. 46. [c] Recorded in this Laboratory; b.p. 204°, n^{25}D 1.5388.

1075–1010 cm.$^{-1}$ (9.3–9.9 μ). As in the case of the secondary alcohols single branching of the carbon chain at the α-carbon atom produces a shift of about 15 cm.$^{-1}$ to lower frequencies from the C–O band position of the unbranched parent alcohol, whereas β-branching produces no similar effect. Also, α-unsaturation promotes greater shifts to longer wave lengths.

Tertiary Alcohols.—The measurement of a relatively small number of tertiary alcohols taken together with the bands reported by Tuot and Lecompte[2] for seventeen tertiary alcohols (Table VI) allows the conclusion to be drawn that straight-chain aliphatic tertiary alcohols have a C–O band at about 1140 cm.$^{-1}$ (8.75 μ). The simplest tertiary alcohol, *t*-butanol, however, absorbs at 1205 cm.$^{-1}$ (8.3 μ). In general, as in the case of primary and secondary alcohols, branching at the α-carbon in tertiary alcohols causes small shifts to longer wave length, while α-unsaturation is reflected in stronger displacements in the same direction. β-Branching appears to have no appreciable effect and β-unsaturation effect is small. Triphenyl- and tri-*p*-anisylcarbinols are of interest in that they absorb at the same frequencies as do phenyl- and diphenylcarbinols (1010 cm.$^{-1}$). The cyclic tertiary alcohol, 1-methylcyclohexan-1-ol, absorbs at 1117 cm.$^{-1}$ showing, by virtue of its ring structure, a similar displacement of its C–O band to lower frequency as in the examples of the cyclohexanols.

TABLE VI

TERTIARY ALCOHOLS[4]

Carbinol	B.p., °C.	Mm.	η^{25}D	C–O absorption Cm.$^{-1}$	μ
Trimethyl[3]				1205	8.3
Methylethyl-*i*-butyl	152–153		1.4234(28°)	1142	8.75
Methylethylphenyl	90–91	4	1.5160	1100	9.1
Dimethylbenzyl	112–113	26	1.5124	1125 ?	8.9
Triphenyl	161–162^a			1009	9.92
Tri-*p*-anisyl	85–86^a			1020	9.8^b
1-Methylcyclohexan-1-ol	154 24–25.5^a		1.4599	1117	8.95

^{a} Melting point. ^{b} Measured as melt and as crystalline film.

Experimental

Purification of Alcohols. (a) By Distillation or Recrystallization.—These alcohols were distilled through a 40-cm. Vigreux column with or without reduced pressure: dimethyl- (from aluminum isopropoxide, Eastman), methylethyl- (from calcium oxide, Eastman), diethyl- (Matheson synthetic), ethyl-*n*-propyl- (Sapon), *n*-propyl-*n*-butyl- (Sapon), diisobutyl- (Delta), methylphenyl- (Matheson), dimethylbenzyl- (Delta), carbinols, benzyl alcohol (Eastman), cyclopentanol (Sapon) and cyclohexanol (Eastman). Diphenyl-, triphenylcarbinols and *l*-menthol (Eastman) were recrystallized.

(b) **Through Hydrogen Phthalates.**—Any ketonic impurities in these alcohols were removed by converting the alcohol to its half ester with phthalic anhydride in pyridine, extraction and washing of the sodium carbonate solution of the acid ester, regeneration of the alcohol in hot aqueous potassium hydroxide solution, steam distillation and final distillation as described in (a)[5]: methyl-*n*-propyl- (Eastman), methyl-*n*-pentyl- (Matheson), methyl-*n*-butyl- (Eastman), methyl-*n*-hexyl- (Eastman), methylisopropyl- (Eastman), methylisobutyl- (Carbide & Carbon), methyl-*t*-heptyl-(3,3-diethylpentan-2-ol)-carbinols and cycloheptanol.

Preparation of Alcohols. (a) By Lithium Aluminum Hydride Reduction of Corresponding Ketones.—The following alcohols were prepared by reduction of the corresponding ketones (Sapon) according to the method of Nystrom and Brown[6] and distilled as described above: methyl-*n*-octyl-, methyl-*n*-nonyl-, ethyl-*n*-butyl-, ethyl-*n*-pentyl-, ethyl-*n*-hexyl-, ethyl-*n*-heptyl-, di-*n*-propyl-, *n*-propyl-*n*-pentyl-, *n*-propyl-*n*-hexyl-, di-*n*-butyl-, *n*-butyl-*n*-pentyl-, di-*n*-pentyl-, methylisohexyl - (6 - methylheptan - 2 - ol), methylvinyl- (Delta), methyl-β-naphthyl- (Eastman), ethylphenyl- (Matheson), phenyl-*p*-tolyl- (Eastman) carbinols and cyclooctanol.

(b) **By Synthesis.**—These alcohols were synthesized by known procedures: methyl-*t*-butyl- (by Dwight Pease, Jr.),[7] diisopropyl-,[8] isopropyl-*t*-butyl-,[8] di-*t*-butyl-,[9] methylbenzyl-,[10] methyl-α-furyl,[11] methyl-α-naphthyl-,[12] methylethylisobutyl-,[13] methylethylphenyl-,[14] tri-*p*-anisylcarbinols,[15] *cis*-α-decalol[16] (by William B. Martin, Jr.), neopentanol[6] and 1-methylcyclohexan-1-ol (by Dwight Pease, Jr., from cyclohexanone and methylmagnesium bromide).

Measurement of Infrared Spectra.—Spectra were recorded between 5000 and 665 cm.$^{-1}$ with a Perkin–Elmer model 21 recording spectrophotometer equipped with a rock salt prism. All liquids were measured in a 0.025-mm. sodium chloride cell, and in those cases in which the C–O absorption was too intense at this thickness the liquid was pressed out between two rock salt windows to a thinner layer and the region then rerun. When the alcohol was measured in solvent, one molal concentrations in chloroform were used. Solids were melted and resolidified into a thin, crystalline film between two 55-mm. salt windows. The windows were then fitted into a brass-jacketed, electrically heated cell holder having a thermocouple well for temperature readings. Measurements were taken of the solid at room temperature and as a melt slightly above the melting point of the alcohol. A slit schedule of 4 with this instrument was employed throughout all runs and the speed of recording was maintained at about three to four minutes per micron.

Discussion of Results

Infrared records of alcohols now available permit an empirical interpretation of the C–O band position in their spectra. It seems clear that an *electronic effect* is in operation and that this effect can be correlated with structure. An increase in the force constant associated with the C–O bond is reflected in displacements of the C–O band to lower frequencies. The range of C–O bond distances may be arbitrarily shown by the series, $—N{=}C{=}O$ (2200 cm.$^{-1}$), $R_2C{=}O$ (1725 cm.$^{-1}$), $R_2C{=}C—O$ (*ca.* 1250 cm.$^{-1}$), $R_2C—O$ (1110 cm.$^{-1}$), $R_2C{=}C—C—O$ (*ca.* 1070 cm.$^{-1}$), $(C{=}C)_3C—O$ (1000 cm.$^{-1}$), with limits of $—C{\equiv}\overset{+}{O}$ and $—\overset{+}{C}\ldots.\overset{-}{O}$. In the secondary alcohols this displacement is shown by methylethylcarbinol (1105 cm.$^{-1}$), methylisopropylcarbinol (1090 cm.$^{-1}$), methylphenylcarbinol (1073 cm.$^{-1}$), methylvinylcarbinol (*ca.* 1060 cm.$^{-1}$) and diphenylcarbinol (1014 cm.$^{-1}$). The combined effect of unsaturation and branching at the α-carbons enhance this effect even more markedly as shown in Table III. Similar displacements are observed in the primary alcohols: 1-propanol (1060 cm.$^{-1}$), 2-methylpropan-1-ol (1050 cm.$^{-1}$),

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(4) Wave numbers of absorption peaks in the spectra of seventeen tertiary aliphatic alcohols are listed in reference (2).

(5) This general procedure is described in "Organic Reactions," Vol. II, J. Wiley and Sons, Inc., New York, N. Y., 1944, pp. 393–398.

(6) R. F. Nystrom and W. G. Brown, This Journal, **69**, 1197 (1947).

(7) A. Richard, *Ann. chim.*, [8] **21**, 346 (1910).

(8) J. B. Conant and A. H. Blatt, This Journal, **51**, 1227 (1929).

(9) N. C. Cook and W. C. Percival, *ibid.*, **71**, 4141 (1949).

(10) G. Austerweil and G. Cochin, *Compt. rend.*, **150**, 1693 (1910).

(11) F. N. Peters and F. Fischer, This Journal, **52**, 2079 (1930).

(12) R. H. Pickard and J. Kenyon, *J. Chem. Soc.*, **105**, 1115 (1914).

(13) L. Clarke, This Journal, **30**, 1144 (1908).

(14) A. Klages, *Ber.*, **35**, 3506 (1902).

(15) A. Baeyer and V. Villiger, *ibid.*, 1189 (1902).

(16) W. Hückel, *Ann.*, **441**, 1 (1925).

neopentyl alcohol (1030 cm.$^{-1}$), allyl alcohol (1030 cm.$^{-1}$) and benzyl alcohol (1010 cm.$^{-1}$). Likewise in the tertiary series these shifts are found: methylethylisobutylcarbinol (1142 cm.$^{-1}$), methylethylphenylcarbinol (1100 cm.$^{-1}$) and triphenylcarbinol (1009 cm.$^{-1}$). Considerable caution, however, is necessary in dealing with C–O bands appearing at lower frequencies than about 1050 cm.$^{-1}$, for it is quite apparent that the sensitivity of this band with respect to variation in structure diminishes very rapidly as the frequency approaches 1000 cm.$^{-1}$ (compare benzyl alcohol, benzhydrol, trityl alcohol and tri-*p*-anisylcarbinol). It is also important to note that no C–O band absorptions have been identified beyond 1000 cm.$^{-1}$. This limit of sensitivity is ascribed to increasing vibrational interaction between the C–O and a C–C bond frequency as these frequencies approach one another in magnitude. The resultant coupling acts to prevent any further approach to each other and to cause a loss of identity in their absorption bands.[17] Another limiting factor may be the *mass-symmetry effect* discussed below.

It is evident that while consistency is observed within a given alcohol series, primary, secondary or tertiary, in relation to electronic effects, it does not exist among the three classes of alcohols on the same terms. This is well illustrated by the alcohols, *t*-butanol (1205 cm.$^{-1}$), isopropyl alcohol (1105 cm.$^{-1}$) and methanol (1030 cm.$^{-1}$). This second effect, independent of the C–O bond force constant and demonstrably of large magnitude and opposite in operation to that of the electronic effect, may be interpreted in terms of mass symmetry. This is to say that an increase in the masses and in the symmetry of the masses of the substituents attached to the hydroxylated carbon atom results in a C–O band shift to higher frequencies. This effect is most clearly observed in saturated alcohols, inasmuch as alkenyl and aryl groups strongly displace the C–O band frequency to lower values and mask the symmetry effect, as in the case of tri-*p*-anisylcarbinol.[18] In alicyclic alcohols, both secondary and tertiary, the restrictions in freedom of the substituents may be considered in terms of the decrease in symmetric properties to account for displacements to lower frequencies than those of the aliphatic type. Exceptions are, of course, cyclopropanol and cyclobutanol.

Tentative conclusions can be drawn from a correlative point of view. The appearance of the C–O band in the region of 1205–1125 cm.$^{-1}$ is indicative of a tertiary alcohol, saturated and aliphatic, or a highly symmetrical secondary alcohol. From 1125 to 1085 cm.$^{-1}$ it is highly probable that the alcohol is a saturated secondary aliphatic, an α-unsaturated or cyclic tertiary carbinol. If the band lies between 1100 and 1085 cm.$^{-1}$ the secondary alcohol is probably branched on one α-carbon atom. Between 1085 and 1050 cm.$^{-1}$ the alcohol is an α-unsaturated secondary, a straight-chain primary or an alicyclic secondary carbinol having a five- or six-membered carbon ring skeleton. Beyond 1050 cm.$^{-1}$ are grouped di-unsaturated secondary, both α-branched and unsaturated secondary, α-branched and/or unsaturated primary, highly unsaturated tertiary and seven- and eight-membered alicylic secondary alcohols.

Studies on the intensities of the C–O absorption bands and solvent and temperature effects on these bands are incomplete. In general, the band is shifted toward lower frequencies when the alcohol is measured in benzene, chloroform or carbon disulfide.

[17] We are indebted to Professor J. G. Kirkwood, Professor R. S. Halford of Columbia University and Professor R. C. Lord of the Massachusetts Institute of Technology for discussions of this and other theoretical points.

[18] Hydrogen atoms are not regarded here as contributory toward this effect for the reason that their interactions with C–O bonds are undoubtedly quite small in comparison to that of C–C–O.

NEW HAVEN, CONNECTICUT

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE POLYTECHNIC INSTITUTE OF BROOKLYN]

The Absorption Spectra of Tetracyclones

BY STEPHEN B. COAN,[1] DONALD E. TRUCKER[1,2] AND ERNEST I. BECKER[3]

RECEIVED JULY 3, 1952

The absorption spectra of a series of tetracyclones have been measured. Those with substituents in the *p*-position of the 2-phenyl ring affect mainly the absorption maximum at 512 $m\mu$, while those with substituents in the *p*-position of the 3-phenyl ring affect mainly the absorption maximum at 342 $m\mu$. On the basis of these data assignments of excited electronic paths in the tetracyclone molecule have been made to include the 2-phenyl (Y-path) and the 3-phenyl (X-path) rings.

I. Introduction

The specific assignment of particular excited electronic paths in a molecule to observed ultraviolet and visible absorption maxima has been carried out on only a few types of systems. Jones[4,5] has studied naphthalene and anthracene most thoroughly. Lewis and Calvin[6] have summarized data in the triphenylmethane dyes. In each class, it has been possible to associate a particular excited electronic structure with certain absorption maxima. However, only in anthracene has a broad

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[1] Taken from the Dissertations of S. B. Coan and D. E. Trucker presented to the Graduate Faculty of the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements for the Ph.D. degree.

[2] Research fellow, June, 1949, to May, 1951, supported by the U. S. Army Signal Corps.

[3] To whom correspondence concerning this paper should be directed.

[4] Y. Hirshberg and R. N. Jones, *Can. J. Research*, **27B**, 437 (1949).

[5] R. N. Jones, *Chem. Revs.*, **41**, 353 (1943).

[6] G. N. Lewis and M. Calvin, *ibid.*, **25**, 273 (1939).