The Interpretation of the Vibrational Spectra of the C6 Hydrocarbons 22Dimethyl Butane, 22Dimethyl−3Butene, and 22Dimethyl−3Butyne

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The Interpretation of the Vibrational Spectra of the C₆ Hydrocarbons 22-Dimethyl Butane, 22-Dimethyl-3-Butene, and 22-Dimethyl-3-Butyne*

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Assignments have been made for the observed infra-red and Raman frequencies of the molecules 22-dimethyl butane, 22-dimethyl-3-butene, and 22-dimethyl-3-butyne. By using the previously assigned characteristic frequency regions associated with the ethyl, vinyl, and C≡CH groups, it has been shown that the tertiary butyl group in all these molecules has frequencies near 1250, 1210(2), 1025(2), 880, and 700 cm⁻¹, in the range 1350–600 cm⁻¹. The assignment of these frequencies to skeletal $C-C$ stretching and to methyl wagging modes is discussed.

INTRODUCTION

IN a recent communication[1] an analysis was made of the infra-red and Raman spectra of some hydrocarbons containing the ethyl, vinyl, and C≡CH groups. It was shown that the various hydrogenic deformation modes of these three groupings all have fairly characteristic frequencies, i.e., occur in well defined and reasonably narrow regions of the spectra. It is clear that an extension of our knowledge of such frequencies will considerably simplify the interpretation of the spectra of polyatomic hydrocarbons. In the present paper the three molecules are considered in which a tertiary butyl group is attached in turn to each of the above structural units. In this manner it is hoped to obtain, by difference, similar characteristic frequency regions for the tertiary butyl group. Partial analyses of characteristic frequencies of the tertiary butyl group have already been published,[2–4] and these will be used as a guide in obtaining the complete assignments.

This series of molecules has the additional advantage that because of the trigonal symmetry of the tertiary butyl group, only one spectroscopically distinguishable rotational isomer will be obtained by skeletal rotation about the central $C-C$ linkage. Hence, no preliminary low temperature study of these spectra is necessary before a vibrational analysis can be made, in contrast to the case of the normal paraffins.[5–7]

I. THE EXPERIMENTAL DATA

The infra-red spectrum of 22-dimethyl butane has been published by Avery and Ellis,[8] and as part of the *Catalog of Infra-Red Spectrograms* of the American Petroleum Institute Research Project 44.[9] The spectrum of 22-dimethyl-3-butene (33-dimethyl-1-butene) is also available from the latter compilation,[10] but no infra-red spectrum of 22-dimethyl-3-butyne (33-dimethyl-1-butyne) seems to be available.

The Raman spectra of 22-dimethyl butane and 22-dimethyl-3-butene have been obtained by Fenske *et al.*[11] (spectra Nos. 6 and 83) in their compilation of the Raman spectra of hydrocarbons, and that of 22-dimethyl-3-butyne has been published by Cleveland and Murray,[12] Rosenbaum, Grosse, and Jacobson.[13] Bazhulin,[14] has also obtained the Raman spectrum of 22-dimethyl butane. A schematic assignment for 22-dimethyl butane has been given by Kilpatrick and Pitzer,[15] and a partial analysis of the spectrum of 22-dimethyl-3-butyne has been made by the authors of the Raman spectrum.[12]

The observed frequencies, taken from the above sources, are given in Table I, and are followed by bracketed values for the relative intensities and, in the case of the Raman data, by the qualitative polarizations rounded off to a single significant figure. The table is set out so that corresponding regions of the spectra are opposite each other. No frequencies greater than 3350 cm⁻¹ are included,

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[8] W. H. Avery and C. F. Ellis, J. Chem. Phys. 10, 10 (1942).
[9] Spectrograms Nos. 655 and 670, contributed by the U. S. Naval Research Laboratory, Washington, D. C.
[10] Spectrogram No. 199 contributed by the Shell Development Company, Emeryville, California, and Nos. 586 and 587 contributed by the U. S. Naval Research Laboratory, Washington, D. C.
[11] Fenske, Braun, Wiegand, Quiggle, McCormick, and Rank, Ind. Eng. Chem. Anal. Ed. 19, 1700 (1947).
[12] F. F. Cleveland and M. J. Murray, J. Chem. Phys. 11, 450 (1943).
[13] E. J. Rosenbaum, A. V. Grosse, and H. F. Jacobson, J. Am. Chem. Soc. 61, 689 (1939).
[14] P. A. Bazhulin, Bull. Acad. Sci. U.R.S.S., Classe Sci. Chim. 198 (1943).
[15] J. E. Kilpatrick and K. S. Pitzer, J. Am. Chem. Soc. 68, 1066 (1946).

TABLE I. The observed Raman and infra-red frequencies of 22-dimethyl butane, 22-dimethyl-3-butene, and 22-dimethyl-3-butyne.

| 22-dimethyl butane | | 22-dimethyl-3-butene | | 22-dimethyl-3-butyne |
Raman[a,b]	Infra-red[c,d]	Raman[a]	Infra-red[e]	Raman[f]
				3307 (1)
			3090 (w)	
2967 (6)	2960 (v.s.)		2960 (s)	2968 (50) 0.8
2942 (6)				2923 (35) 0.2
2906 (10)				2905 (20) p
2890 (3)			2880 (m)	2887 (10) p
2871 (5)				2865 (9) p
2856 (2)				
				2105 (32) 0.4
		1648 (9) 0.1	1645 (s)	
1467 (5) 0.8	1468 (s)		1481 (s)	
1448 (5) 0.8		1456 (5) 0.7	1466 (s)	1453 (9) dp.
		1424 (4) 0.4	1420 (m)	
	1395 (w)	1390 (2) 0.4	1387 (m)	1390 (v.w.)
	1381 (m)			
	1366 (s)		1364 (s)	
1313 (0.5) 0.9	1307 (w)	1311 (6) 0.3		
1258 (1) 0.8	1252 (m)	1272 (2) 0.6	1271 (m)	1247 (1)
1221 (2) 0.8	1217 (s)	1209 (5) 0.7	1209 (s)	1205 (8) dp.
1080 (0.5)	1074 (s)	1067 (0.9)	1068 (m)	
1021 (1) 0.7	1018 (s)	1026 (1)	1027 (m)	1029 (1)
995 (0.5)	996 (m)	999 (2)	1000 (s)	
	986 (m)			
929 (2) 0.8	929 (m)	922 (6) 0.7		931 (6) dp.
			912 (v.s.)	
873 (1) 0.9	870 (w)	879 (3) 0.3	881 (m)	885 (4) p.
			821 (w)	
	782 (s)			
				722 (3)
714 (7) 0.1	711 (w)	715 (13) 0.1	715 (w)	690 (16) 0.1
	663 (v.w.)		683 (s)	633 (5)
			620 (w)	
484 (0.5)	486 (w)			
411 (0.5)		519 (2) 0.3	523 (w)	544 (2)
361 (1) 0.5				389 (2)
344 (1) 0.8		353 (4) 0.6		359 (3)
260 (0.5)		304 (4) 0.9		
194 (0.5)				183 (100) 0.90

(v.s.) very strong; (s) strong; (m) medium; (w) weak; (v.w.) very weak; (p) polarized; dp. (depolarized).

a See reference 11.
b See reference 13.
c See reference 8.
d See reference 9.
e See reference 10.
f See reference 12.

nor are any in the region $2800-1500$ cm^{-1} except for the obvious $C\equiv C$ and $C=C$ stretching frequencies. It is well known that these regions are otherwise free of fundamentals. The weak frequencies at 659 and 612 cm^{-1} in the 22-dimethyl butane Raman spectrum, and at 657 and 615 cm^{-1} in the 22-dimethyl-3-butene spectrum, as given by Fenske et al.,[11] have not been included in the table as they are probably caused by double and triple excitation of the very strong 714- and 715-cm^{-1} lines by the five structure satellites of the 4358A Hg exciting line.[16] In the case of 22-dimethyl butane, these frequencies were not observed in the Raman spectrum of Rosenbaum, Grosse, and Jacobson.[13]

II. THE ASSIGNMENT OF FUNDAMENTALS

The most interesting region of the spectrum for our present purpose is that between 1350 and 600 cm^{-1}, as this will contain most of the CH deformation modes and all of the $C-C$ skeletal stretching modes. Our assignments for these three molecules in this region are summarized in Table II, which is subdivided into the modes of vibration of different

molecular groups so that closely related frequencies in the different molecules can be compared. The third and fourth columns of this table give the characteristic regions already known to be associated with certain of the modes, and the fifth column gives the appropriate references.[1, 3, 4, 7, 17] The frequencies above 1350 cm^{-1} can all be assigned with the help of well established rules, and those below 600 cm^{-1} are almost certainly all skeletal deformation or methyl torsional modes.

The probable symmetry of the 22-dimethyl-3-butyne molecule is C_{3v}, and hence the fundamentals can be divided into the three symmetry classes A_1, A_2, E. The first and last of these classes correspond to fundamentals with infra-red and Raman activity, whereas the A_2 modes are forbidden in both absorption and scattering. The degeneracies indicated in brackets after the description of the vibrations of the tertiary butyl group in Table II are strictly applicable to the 22-dimethyl-3-butyne molecule, and are apparently in practice also obeyed for the corresponding vibrations of the other less symmetrical molecules. The maximum symmetry that either of the other molecules could possess would be a single plane of symmetry, and hence all the fundamentals are allowed in the infra-red and Raman spectra. The detailed interpretation of the spectra will now be discussed according to the three regions distinguished above.

(a). The Region 3350–1350 cm^{-1}

The assignment of frequencies in this region to the normal modes of vibration of hydrocarbon groups is now a well established procedure. The types of fundamental that occur in this frequency range are the CH stretching fundamentals between 3350 and 2800 cm^{-1},[18] $C\equiv C$ stretching modes near 2100 cm^{-1},[19] $C=C$ stretching modes between 1700 and 1600 cm^{-1},[19] CH$_3$ asymmetrical and symmetrical deformation modes near 1450 and 1375 cm^{-1},[19] and the CH$_2$ bending modes of saturated and unsaturated groups near 1450[19] and 1420[17] cm^{-1}, respectively. Because of overlapping in the regions 3000–2800 cm^{-1} and 1470–1440 cm^{-1}, semi-schematic assignments only are possible within these frequency ranges. Our assignments for these three molecules in this region of the spectrum are given below without further comment.

22-Dimethyl-3-Butyne

CH$_3$ symmetrical stretching, 2887(2), 2865; CH$_3$ asymmetrical stretching, 2968(4), 2923(2); $\equiv$CH

[16] D. H. Rank and J. S. McCartney, J. Opt. Soc. Am. **38**, 279 (1948).

[17] N. Sheppard and G. B. B. M. Sutherland, Proc. Roy. Soc. (London), in press.

[18] J. J. Fox and A. E. Martin, Proc. Roy. Soc. (London) **A175**, 208 (1940).

[19] G. Herzberg, *Infra-Red and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Company, Inc. New York, 1945), p. 195 and discussions of individual molecules.

TABLE II. The assignment of the fundamental frequencies in the spectral region 1350–600 cm⁻¹ for the molecules 22-dimethyl butane, 22-dimethyl-3-butene, and 22-dimethyl-3-butyne.

Group	Description of vibration	Frequency range in cm⁻¹	Strong in:	Reference	22-dimethyl butane	22-dimethyl-3-butene	22-di-methyl-3-butyne
Tertiary	C—C stretching (1)				1258	1271	1247
	C—C stretching (2)	1250–1200*	i.r. and R	3*	1217	1209	1205
	C—C stretching (1)	750–690	R	3	714	715	690
Butyl	CH₃ wagging (2)	?			1018	1026	1029
	CH₃ wagging (2)	930–910*	R	3*	929	922	931
	CH₃ wagging (1)	?			870	879	885
	CH₃ wagging (1)	?			(950)	(950)	(950)
CCH	CH wagging (2)	650–600	i.r. and R		—	—	633
Vinyl	CH₂ rocking (in-plane)	1170–1090		1		1067	
	CH CH-bending (in-plane)	1320–1280	R	17, 1		1311	
	CH₂ wagging (out-of-plane)	920–900	i.r.	17, 1	—	912	—
	CH₂ twisting (out-of-plane)	680–600		1		683	
	CH CH-wagging (out-of-plane)	1010–980	i.r.	17, 1		1000	
Ethyl	C—C stretching	1100–880		7	996		
	CH₂ wagging	1340–1290	R	3, 4	1313		
	CH₂ twisting	1300–1240		3, 4	(1250)		
	CH₂ rocking	760–720	i.r.	3, 4	782	—	—
	CH₃ wagging (in-plane)	1150–1000		1	1074		
	CH₃ wagging (out-of-plane)	960–900		1	986		

* But see later discussion of results.
(R-Raman, i.r.-infra-red).

stretching, 3307; C≡C stretching, 2105; CH₃ symmetrical deformation, *1365*(2), 1390; CH₃ asymmetrical deformation, 1453(6).

22-Dimethyl-3-Butene

CH₃ symmetrical stretching, 2880(3); CH₃ asymmetrical stretching, 2960(6); =CH₂ symmetrical stretching, *3000*; =CH₂ asymmetrical stretching, 3090; =CH stretching, *3000*; C=C stretching, 1645; CH₃ symmetrical deformation 1364(2), 1387; CH₃ asymmetrical deformation, 1481(2), 1466(2), 1456(2); =CH₂ bending, 1424 cm⁻¹.

22-Dimethyl Butane

CH₃ symmetrical stretching, 2871(3), 2890 cm⁻¹; CH₃ asymmetrical stretching, 2967(4), 2942(4); CH₂ symmetrical stretching, 2856; CH₂ asymmetrical stretching, 2942; CH₃ symmetrical deformation, 1366(2), 1381, 1395; CH₃ asymmetrical deformation, 1468(4), 1448(4); CH₂ bending, 1448 cm⁻¹.

The frequencies are followed in brackets by the assigned degeneracies, and those not experimentally observed are printed in italics. In the case of the symmetrical 22-dimethyl-3-butyne molecule, some of the degeneracies are due to symmetry considerations, and two of the frequencies (one asymmetrical CH₃ stretching, and one CH₃ asymmetrical deformation mode) are forbidden in the Raman and infra-red spectra. These have not been distinguished separately above.

(b). The Region 1350–1600 cm⁻¹

Our assignments in this region are given in Table II and will be discussed below, molecule by molecule, starting with the symmetrical 22-dimethyl-3-butyne.

22-Dimethyl-3-Butyne

Although there does not appear to be an infra-red spectrum available for this compound, there are enough lines in the Raman spectrum for assignment to all the expected fundamentals in this region. The line at 633 cm⁻¹ is clearly the expected deformation mode of the CH linkage attached to the triple bond, and the frequencies at 1247, 1205, 931, and 690 cm⁻¹ correspond to characteristic frequencies previously found in the spectra of molecules containing the tertiary butyl group.[3] Of the remaining three frequencies, those at 1029 cm⁻¹ and 885 cm⁻¹ are chosen as the two remaining fundamentals because of their persistence in the spectra of the other two hydrocarbons. The remaining line at 722 cm⁻¹ is probably the summation frequency 544+183 = 727 cm⁻¹. Of these six frequencies which are associated with the tertiary butyl group, viz., 1247, 1205, 1029, 931, 885, and 690 cm⁻¹, the lowest one can be assigned with little doubt to the breathing frequency of the C₅ skeletal unit.[3] Of the others, those at 1247, 1205, and 931 cm⁻¹ have previously been assigned to the remaining two C—C stretching modes and a methyl wagging mode, respectively, on the bases of studies of characteristic frequencies.[2, 3]

Sutherland and Simpson[2] in particular showed that the 1247 and 1205-cm^{-1} modes could be explained as C—C stretching modes with the assumption of a reasonable value of the C—C stretching force constant. If this is correct the remaining two frequencies at 1029 and 885 cm^{-1} are the remaining methyl wagging modes, the latter being the symmetrical one on the basis of the polarization data. This assignment scheme is shown in Table II, and will be discussed in more detail below. The remaining A_2 type methyl wagging mode is forbidden in both the infra-red and Raman spectra, and has been given a schematic value of 950 cm^{-1} as being the center of the range of observed methyl wagging modes. It is possible, however, that it may have a value near 1200 cm^{-1} (see later discussion of results).

22-Dimethyl-3-Butene

If the assumption is made that the set of frequencies found for the vibrations of the tertiary butyl group in the case of 22-dimethyl-3-butyne will be reproduced fairly accurately in the spectrum of this compound, the frequencies at 1272, 1209, 1026, 922, 879, and 714 cm^{-1} can tentatively be assigned to these modes. This leaves frequencies at 1311, 1067, 999, 912, 821, 683 and 620 cm^{-1} to be assigned to the five CH deformation modes of the vinyl group that should occur in this region. As can be seen in Table II, such an assignment can easily be made with the previously established correlation rules. The 1067 cm^{-1} = CH$_2$ rocking frequency is slightly outside the expected region, but the correlation rule in this case is less well established than most of the others.[1] The weak 821 and 620-cm^{-1} frequencies are left unaccounted for. It is possible that the 821-cm^{-1} frequency is the remaining methyl wagging mode that was forbidden in the spectrum of 22-dimethyl-3-butyne, but as no corresponding frequency is found in the spectrum of 22-dimethyl butane, it seems more likely that it is to be assigned to the combination band $519+304=823$ cm^{-1}. The weak 620-cm^{-1} infra-red frequency is presumed to be a skeletal bending mode and will be discussed in the next section.

22-Dimethyl Butane

Having elucidated the spectra of the previous two compounds, the assignment of the 22-dimethyl butane spectrum in this region is a fairly straightforward matter, as shown in Table II. The weak infra-red absorption at 664 cm^{-1} is tentatively assigned to the combination level $411+260=671$ cm^{-1}.

(c). The Region below 600 cm^{-1}

The assignments in this region will necessarily be less complete because of the lack of infra-red data,

but, even so, fairly complete assignments can be made for the skeletal bending modes. In general, the methyl torsion modes do not seem to be spectroscopically observable, undoubtedly because of the fact that to a first approximation the rotation of a single symmetrical —CH$_3$ group about its trigonal axis gives rise to no change in either dipole moment (infra-red) or polarizability (Raman spectrum).
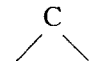
22-Dimethyl-3-Butyne

This molecule would be expected to have four different skeletal bending modes in this region, three of them being of symmetry class E and one of class A_1. We make the assignment 544(2), 389(2), 359(1), 183(2). The Raman line at 183 cm^{-1} can probably be associated with the bending of the C≡C—C group as a low frequency at about this position seems to occur in the spectra of several acetylene derivatives.[20] If this is correct, the remaining five frequencies are mainly associated with bending modes of the C$_5$ skeletal unit, and the distribution of frequencies is in fair agreement with that of the analogous frequencies of neopentane, viz., 414(3), 335(2).[3]

22-Dimethyl-3-Butene

Because of the lack of symmetry in this molecule, there should be six different skeletal bending modes in this region, and one skeletal torsional mode. Although only four frequencies have been noted in this region, viz., 620, 519, 353, and 304 cm^{-1}, examination of the original Raman spectrum suggests that the frequency at 304 cm^{-1} may be double, and that there may also be a weak line at 400 cm^{-1}. We therefore assign the spectrum as follows: 620, 519, 400, 353, 304(2) cm^{-1}. The skeletal torsional mode does not appear to be observable in the spectrum.

22-Dimethyl Butane

In this case, we assign the following value to the skeletal bending modes: 484, 411, *400*, 361, 344, 260 cm^{-1}. We have replaced the 276-cm^{-1} line in the assignment of Kilpatrick and Pitzer[15] by the schematic frequency of 400 cm^{-1}, because the 276-cm^{-1} line does not appear to be observable in the recent Raman spectrum of Fenske et al.[11] Also, on the assumption that the mode associated mainly

$$\overset{\displaystyle C}{\diagup \diagdown}$$

with the bending of the lone C   C unit corresponds to one of the frequencies between 300 and 400 cm^{-1}, the schematic value of 400 cm^{-1} makes

[20] F. F. Cleveland, M. J. Murray, and H. J. Taufen, J. Chem. Phys. 10, 172 (1942).

the average value of the remaining bending modes of the C_5 unit nearer to that found with neopentane.[3] The frequency at 194 cm⁻¹ may be the skeletal torsion or one of the methyl torsional modes.

Although skeletal bending modes would be expected to have much less characteristic frequencies than the stretching modes, there is a frequency between 350 and 365 cm⁻¹ in all these three compounds which is probably the symmetrical bending mode of the tertiary butyl group. A frequency near this value has previously been assigned as a characteristic frequency of this group.[3]

III. DISCUSSION OF RESULTS

Although the assignments for the fundamentals of the tertiary butyl group in the region 1350–600 cm⁻¹ seem fairly straightforward, an interesting point has arisen with respect to their division between $C-C$ stretching and methyl wagging modes. Our assignments were based on the results of calculations of Sutherland and Simpson,[2] who concluded that the frequencies near 1250 and 1200 cm⁻¹ in branched hydrocarbons were probably $C-C$ stretching modes. However, Rasmussen,[4] on the basis of similar calculations with a rather lower $C-C$ stretching constant, has concluded that in neopentane the triply degenerate frequency at 1252 cm⁻¹ is a methyl wagging mode and that the corresponding $C-C$ skeletal mode is the 925-cm⁻¹ Raman line in this compound. This carries corresponding implications for the spectra of doubly branched paraffins, and if this latter view were correct, the assignment given for 22-dimethyl-3-butyne would probably have to be changed to $C-C$ stretching (1), 885; $C-C$ stretching (2), 931; CH_3 wagging (2), 1205; CH_3 wagging (1), 1247 cm⁻¹, with corresponding changes for the other compounds. Also, the non-observed methyl wagging mode should probably then be assigned a value of ca. 1200 cm⁻¹ rather than 950 cm⁻¹. On the other hand, evidence against this formulation comes from the observation that the frequency near 1200 cm⁻¹ in all doubly branched paraffins seems to be relatively independent of the pattern of methyl substitution around the quaternary carbon atom, whereas the 925-cm⁻¹ frequency is more sensitive to such changes.[3] This would seem to be surprising if the 1200-cm⁻¹ frequency is a methyl wagging mode. Secondly, independent calculations by Ahonen, which have recently been shown to be in good general agreement with the observed $C-C$ stretching modes of straight chain paraffins,[7] also predict frequencies at 1270 cm⁻¹ and 847 cm⁻¹ for infra-red active skeletal modes of the branched paraffin di-tertiary butyl (i.e., 2233 tetramethyl butane). There are, in fact, strong lines in the infra-red spectrum

of this substance,[21] at 1180 cm⁻¹ and 800 cm⁻¹. Clearly fair agreement between theory and experiment would be achieved in this case if Ahonen's original $C-C$ force constant were lowered somewhat, as was found to be necessary for the normal paraffins.[7]

However, it must be concluded that none of these points of evidence are completely satisfactory, and it is true that normal coordinate calculations in the past have not been very successful in predicting the frequencies of new structural groups, particularly when the force constants are in some doubt. Probably the best way to settle this problem would be to obtain the spectrum of a completely deuterated branched hydrocarbon such as neopentane. It should be a fairly straightforward matter to decide from such a spectrum which of the two neopentane frequencies had shifted most, and hence which was essentially the methyl wagging mode. Similar considerations apply also to the 1172 and 965-cm⁻¹ frequencies of isobutane, and to the spectra of the corresponding singly branched paraffins.[2-4]

The assignment of 22-dimethyl butane spectrum differs in several respects from the schematic one of Kilpatrick and Pitzer.[15] The new values of the fundamentals were used to compute the gaseous specific heat of this compound at 342 and 449°K for comparison with the experimental data of Waddington and Douslin.[22] Using the Kilpatrick and Pitzer value of 4375 cal. mole⁻¹ for the barrier restricting rotation of the methyl groups, the calculated specific heats (assuming values of either ca. 1200 or ca. 950 cm⁻¹ for the non-observed methyl wagging mode) were both too high by several tenths of a calorie, although the slope of the calculated curve was in fair agreement with experiment. However, in view of the satisfactory nature of the numerical spectroscopic assignments above 600 cm⁻¹, and because the magnitude of the specific heat values depends to some extent on the low frequencies (one at least of which is doubtful in magnitude) and on the simplified treatment of the restricted rotation of the four methyl groups, a more exact treatment was not attempted.

It can be seen that the assignments given above afford a very satisfactory explanation of all the strong features in both the Raman and infra-red spectra of these large molecules and at the same time give a very consistent set of fundamentals for the tertiary butyl group. It is important that this method of analysis by group frequencies can give reasonable interpretations to what has often been

[21] American Petroleum Institute, Research Project 44. Infra-Red Spectrogram No. 444, contributed by the Shell Development Company, Emeryville, California.
[22] G. Waddington and D. R. Douslin, J. Am. Chem. Soc. 69, 2275 (1947).

considered the impossibly complex spectra region between 1350 and 600 cm^{-1} in polyatomic molecules. It is certain that a similar method of attack on the spectra of other series of structurally related molecules can yield valuable results, although it should be borne in mind that the very symmetrical tertiary butyl group may be exceptional in this respect. We would like to emphasize at this point that very

considerable aid in making the assignments came from the results of previous empirical determinations of characteristic group frequencies[2-4] and that these two methods of approach (empirical correlations on series of large molecules, and detailed analyses of a few structurally related molecules) probably together constitute the best approach to the understanding of polyatomic spectra.

Substituted Borazole Spectra: Gain and Loss of Aromatic Character

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The far ultraviolet spectra of N-trimethyl, B-trimethyl, and B-trichloroborazole in *n*-heptane solution are compared with previous spectra of borazole and of the organic analogs, benzene and mesitylene. By N-substitution the negative charge on the boron atoms of the borazole ring is increased, increasing the double-bond character and the spectral resemblance to a benzene derivative. By B-substitution, the opposite effect is produced, increasing the spectral resemblance to a saturated compound. The physical and chemical properties of these borazoles show corresponding behavior.

INTRODUCTION

THE absorption spectra of *n*-heptane solutions of three trisubstituted borazoles have been obtained and examined in the region 2300–1790A. The compounds were: N-trimethylborazole, B-trimethylborazole and B-trichloroborazole. This study is a continuation of previous work on the borazole spectrum from this laboratory.[1,2]

Borazole and the boron-nitrogen compounds studied here have a striking resemblance to the corresponding isosteric and isoelectronic aromatic carbon compounds, benzene, mesitylene and 1,3,5-trichlorobenzene. This similarity is apparent in the comparison of the physical properties of the analo-

gous boron-nitrogen and organic compounds given in Table I. This comparison suggests that the borazole ring possesses the Kekulé structure (II). However, the two analogous series of compounds do not exhibit the same close similarity in their chemical properties. For example, the borazoles add Lewis acids to the ring nitrogens and Lewis bases to the ring borons; they are easily hydrolyzed by dilute acids; and hydrogen halides, alcohols and similar reagents add to the ring, the negative addendum going to the boron atom of the ring, to give derivatives structurally similar to cyclohexane. These properties can be most conveniently interpreted by assuming a triborine-triamine structure (I).

The importance of the Kekulé structures may be seen from the following considerations. The single tricovalent B−N bond distance is, correcting for trigonal conjugation,[3] 1.48A, as compared with a B,N distance of 1.45A in boron nitride, 1.44A in borazole, and a B=N distance of 1.30A, as calculated from the single bond distance assuming Pauling's factor of 0.86.[4] (The notation X, Y is used here to denote a general bond between X and Y.) These data are compared with the corresponding data for the analogous carbon compounds in Table II. The analogy is of course not perfect because the B−N single bond distance is for tri-

Structure I   Structure II
                     (two forms)
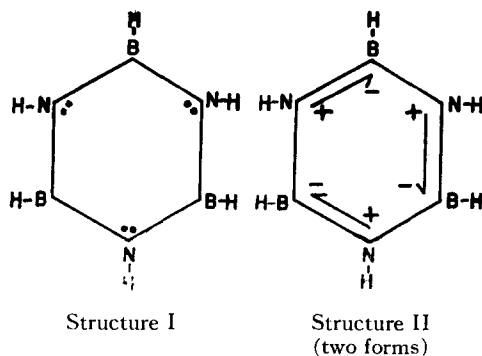
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