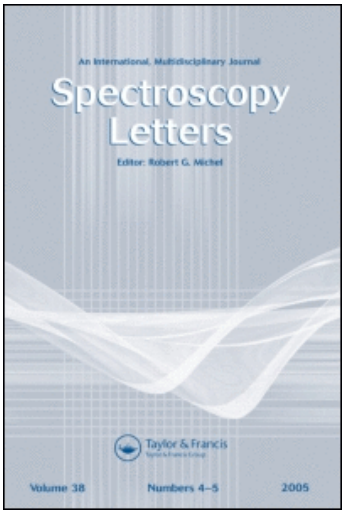

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Conformational Analysis of 2-Methylhexane and 3-Methylhexane

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CONFORMATIONAL ANALYSIS OF 2-METHYLHEXANE AND 3-METHYLHEXANE

Keywords: 2-Methylhexane, 3-Methylhexane, Infrared spectra, Normal coordinate calculations, Conformational analysis

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ABSTRACT

Infrared spectra were obtained for 2-methylhexane and 3-methylhexane, and were interpreted with the aid of normal coordinate calculations. It was shown that 2-methylhexane exists in three conformations. Evidence for the presence of three conformations of 3-methylhexane is presented, but a fourth conformer probably exists. Transferred force constant values resulted in an overall average difference between observed and calculated wavenumbers of 4.3 cm^{-1}, or 0.5%, for seven conformers of these two compounds.

INTRODUCTION

Vibrational spectra for n-paraffins were interpreted more than twenty years ago with the aid of normal coordinate calculations.[1] That work was then extended

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to some branched alkanes, cycloalkanes and substituted cycloalkanes.[2] Although several papers have appeared recently[3-8] on dimethyl-, trimethyl-, and tetramethyl-alkanes, no additional work had been done on monomethyl alkanes since the work on 2-methylbutane[2] until recently, when spectra of 2-methylpentane and 3-methylpentane were interpreted with the aid of normal coordinate calculations.[9] It was shown that 2-methylpentane exists in two molecular conformations and 3-methylhexane exists in four conformations. That work has now been extended to 2-methylhexane and 3-methylhexane, the results of which are reported here.

EXPERIMENTAL

Infrared spectra were obtained with a Nicolet MX-1 Fourier Transform spectrometer. Solid-state spectra were determined for a solid formed by cooling a liquid film to liquid nitrogen temperature. The samples were obtained from Wiley Organics and had purities of 97% or better. In order to conserve space, the spectra are not included in this report, but copies are available from the author.

CALCULATIONS

Normal coordinate calculations were made with a Digital Equipment Corporation PDP-10 computer. The computer programs written by Schachtschneider[1,10] were used for calculation of the G matrix (GMAT) and for solution of the vibrational secular equation (VSEC). The force constant matrix was set up for each molecule with the use of a program described by Crowder and Potter.[11] The molecular parameters used were C-C = 1.54A, C-H = 1.09A, and all angles were assumed to be 109.47^{o}.

RESULTS AND DISCUSSION

Infrared spectra were obtained for 2-methylhexane, and it seems certain from examination of the spectra that the solid of this compound did not crystallize, even with prolonged annealing. Therefore, it is not possible to tell if more than one conformer is present by examination of the spectra. In an effort to determine this, calculations were made for the three most likely conformers, which differ only in the position of the number 6 carbon. They can be described by referring to the formula C1-C2(C7)-C3-C4-C5-C6. Conformer I has all six chain carbons coplanar. Conformer II has carbons 1 through 5 coplanar, with carbon 6 on the same side of the plane as carbon 7. Conformer III has carbons 1 through 5 coplanar, with carbon 6 on the opposite side of the plane to carbon 7. All three conformers belong to the C_1 point group.

The observed and calculated wavenumbers for 2-methylhexane are listed in Tables 1, 2, and 3. Potential energy distributions in terms of symmetry coordinates are not given, but they are available from the author. The tables show six bands assigned solely to conformer I (1317, 1309, 1049, 1029, 894, and 304 cm^{-1}), two bands assigned solely to conformer II (956 and 918 cm^{-1}), and one band assigned solely to conformer III (433 cm^{-1}). In addition, several bands are assigned to conformers II and III (1284, 1250, 995, and 874 cm^{-1}). These bands cannot all be explained by one conformer, so there is little doubt that more than one exists. It is possible that the 433 cm^{-1} band might be due to conformer I or II, but the fit would not be nearly as good as for III. There is, therefore, evidence for the presence of all three conformers.

3-Methylhexane has one asymmetric carbon atom and can therefore exist as enantiomers. Each conformer of

TABLE 1

Observed and Calculated Wavenumbers for 2-Methylhexane Conformer I

obs. cm^{-1}	calc. cm^{-1}	obs. cm^{-1}	calc. cm^{-1}
1469	1472	1049	1050
1469	1469	1036	1036
1469	1468	1029	1022
1469	1465	968	963
1469	1465	942	937
1469	1463	928	929
1455	1456	905	905
1455	1455	894	897
1455	1455	823	823
1418	1413	-	808
1383	1380	781	793
1376	1376	-	488
1376	1374	446	447
1364	1365	412	415
1347	1356	-	355
1317	1320	-	345
1309	1312	-	341
1299	1295	304	310
1224	1235	304	300
1224	1230	-	192
1172	1179	-	142
1172	1172	-	122
1145	1141	-	83
1074	1074	-	

TABLE 2

Observed and Calculated Wavenumbers for 2-Methylhexane Conformer II

obs. cm^{-1}	calc. cm^{-1}	obs. cm^{-1}	calc. cm^{-1}
1469	1472	1062	1068
1469	1469	1036	1035
1469	1467	995	993
1469	1465	956	961
1469	1465	942	936
1469	1463	928	927
1455	1461	918	919
1455	1456	874	877
1455	1451	-	845
1393	1404	823	817
1376	1379	781	772
1376	1376	-	503
1376	1374	446	443
1347	1358	412	415
1347	1351	-	389
1336	1340	-	346
1299	1298	-	342
1284	1287	-	341
1250	1243	-	273
1224	1223	-	211
1172	1176	-	147
1172	1167	-	96
1145	1139	-	81
-	1086		

TABLE 3

Observed and Calculated Wavenumbers for 2-Methylhexane Conformer III

obs. cm^{-1}	calc. cm^{-1}	obs. cm^{-1}	calc. cm^{-1}
1469	1472	1062	1060
1469	1469	1036	1037
1469	1467	995	991
1469	1465	968	963
1469	1465	942	945
1469	1463	928	929
1455	1461	905	909
1455	1456	874	879
1455	1451	-	838
1393	1403	823	826
1383	1380	781	770
1376	1376	-	491
1376	1374	446	444
1347	1358	433	437
1347	1355	-	383
1336	1337	-	348
1299	1300	-	341
1284	1282	-	341
1250	1243	-	278
1224	1223	-	188
1172	1181	-	158
1172	1169	-	97
1145	1138	-	82
-	1088		

one enantiomer has a mirror image that is one conformer of the other enantiomer. The vibrational frequencies of each mirror image pair will be the same, so calculations need to be made for only one enantiomer.

Liquid and solid-state infrared spectra were obtained for 3-methylhexane. The solid for which the spectrum was obtained was obviously amorphous, with no simplification relative to the liquid-state spectrum taking place. Prolonged annealing did not result in crystallization. The liquid was melted and refrozen, with the same result. A large number of conformers of 3-methylhexane can exist, so internal rotation about only the C2-C3 and C4-C5 bonds was considered. Of the nine resulting conformers, three involve methyl-methyl overlap and would not be stable. Two of the remaining six would have a methyl group bisecting a C-C-C angle, whereas the other four would have all methyl groups bisecting only C-C-H angles, and these should be the four most stable. Calculations were therefore made for these four. They can be described by writing the formula in the following four ways, in which a + superscript indicates a methyl group on one side of the plane of chain carbons and a - superscript indicates a methyl on the other side of the plane:

conformer I $C1\text{-}C2\text{-}C3(C7)^{+}\text{-}C4\text{-}C5\text{-}C6$

conformer II $C1^{-}\text{-}C2\text{-}C3(C7)^{+}\text{-}C4\text{-}C5\text{-}C6$

conformer III $C1\text{-}C2\text{-}C3(C7)^{+}\text{-}C4\text{-}C5\text{-}C6^{-}$

conformer IV $C1^{-}\text{-}C2\text{-}C3(C7)^{+}\text{-}C4\text{-}C5\text{-}C6^{-}$

The observed and calculated wavenumbers for 3-methylhexane are listed in Tables 4, 5, 6, and 7. The calculated potential energy distributions are available from the author. The tables show only four bands assigned solely to one conformer. Two of these (809 and 739 cm^{-1}) are assigned to conformer IV and the other two (771 and 445 cm^{-1}) are assigned to conformer II.

TABLE 4

Observed and Calculated Wavenumbers for 3-Methylhexane Conformer I

obs. cm^{-1}	calc. cm^{-1}	obs. cm^{-1}	calc. cm^{-1}
1466	1471	1049	1051
1466	1469	1032	1029
1466	1467	1018	1025
1466	1465	983	979
1466	1465	963	968
1466	1465	929	934
1453	1457	878	883
1453	1455	878	873
1453	1454	825	825
-	1402	795	796
1376	1384	795	793
1376	1376	-	531
1376	1375	-	456
1376	1370	-	392
-	1361	-	366
1307	1310	-	341
1307	1307	326	323
1275	1273	-	312
1264	1252	-	267
1230	1237	-	263
1173	1176	-	146
-	1165	-	134
1153	1150	-	89
1075	1082		

TABLE 5

Observed and Calculated Wavenumbers for 3-Methylhexane Conformer II

obs. cm^{-1}	calc. cm^{-1}	obs. cm^{-1}	calc. cm^{-1}
1466	1470	1062	1061
1466	1468	1032	1032
1466	1467	1018	1023
1466	1466	963	971
1466	1465	963	969
1466	1465	929	923
1453	1460	-	897
1453	1456	866	867
1453	1453	845	844
-	1392	795	799
1376	1380	771	760
1376	1378	-	536
1376	1376	-	457
1376	1369	445	440
1351	1352	-	375
1338	1329	-	339
1294	1299	326	332
1275	1271	-	312
1264	1249	-	253
1230	1223	-	194
1173	1174	-	154
-	1165	-	101
1153	1155	-	84
1075	1077		

TABLE 6

Observed and Calculated Wavenumbers for 3-Methylhexane Conformer III

obs. cm^{-1}	calc. cm^{-1}	obs. cm^{-1}	calc. cm^{-1}
1466	1470	1049	1048
1466	1469	1032	1030
1466	1467	1011	1014
1466	1466	1011	1009
1466	1465	963	972
1466	1465	929	929
1453	1457	878	883
1453	1456	866	870
1453	1455	825	821
-	1403	795	799
1376	1386	795	793
1376	1376	-	481
1376	1375	-	466
1376	1370	427	423
1351	1353	-	367
1307	1314	-	347
1294	1295	326	332
1275	1284	-	316
1264	1255	-	247
1230	1235	-	183
1173	1181	-	146
1173	1169	-	122
1144	1143	-	97
1075	1072		

TABLE 7

Observed and Calculated Wavenumbers for 3-Methylhexane Conformer IV

obs. cm^{-1}	calc. cm^{-1}	obs. cm^{-1}	calc. cm^{-1}
1466	1470	1062	1060
1466	1468	1032	1035
1466	1467	1011	1012
1466	1466	1011	1003
1466	1465	963	973
1466	1465	-	916
1453	1460	-	896
1453	1457	866	868
1453	1453	845	837
-	1393	809	804
1376	1380	739	753
1376	1379	-	520
1376	1376	-	461
1376	1370	427	433
1338	1348	-	396
1307	1318	-	341
1294	1298	326	335
1274	1283	-	311
1264	1252	-	245
1230	1219	-	208
1173	1182	-	137
1153	1160	-	122
1153	1155	-	75
1062	1066		

In addition, three other bands (1368, 1062, and 845 cm^{-1}) are assigned to both conformers II and IV. However, there are three bands (1144, 1049, and 825 cm^{-1}) that are assigned to both conformers I and III, suggesting the presence of at least one of these two. It is possible, therefore, to explain all the observed bands by the presence of three conformers (I, II, and IV or II, III, and IV). However, it seems more likely that all four are present since their relative stabilities should be about the same. Indeed, it is also possible that the two conformers for which calculations were not done are present because one or two conformers with similar steric effects (methyl bisecting C-C-C) apparently exist for 3-methylpentane.[9]

The individual average differences between observed and calculated wavenumbers for the two compounds are as follows: 2-methylhexane, 3.4 (conf. I), 4.3 (conf. II), and 4.2 cm^{-1} (conf. III); 3-methylhexane, 3.6 (conf. I), 4.5 (conf. II), 4.1 (conf. III), and 5.6 cm^{-1} (conf. IV). The overall average difference for the seven conformers was 4.3 cm^{-1}, or 0.5%.

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