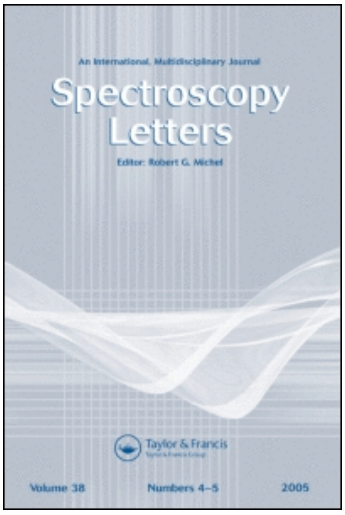


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# Conformational Analysis of 4,4-Dimethylheptane

G. A. Crowder[a]
[a] Department of Chemistry, West Texas State University, Canyon, Texas, USA

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# CONFORMATIONAL ANALYSIS OF 4,4-DIMETHYLHEPTANE

Keywords: 4,4-Dimethylheptane, Vibrational spectra, Normal coordinate calculations, Conformational analysis

G. A. Crowder

Department of Chemistry
West Texas State University
Canyon, Texas 79016 USA



## ABSTRACT

Infrared and Raman spectra were obtained for 4,4-dimethylheptane and were interpreted with the aid of normal coordinate calculations. It was shown that this compound exists in three conformations. Force constant values transferred from dimethylpentanes resulted in an overall average difference between observed and calculated wavenumbers of 4.5 $cm^{-1}$ for the three conformers.



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## INTRODUCTION

Vibrational spectra have been obtained recently for several dimethylalkanes, including four dimethylpentanes,[1] four dimethylhexanes[2] and five dimethylheptanes.[3] Eleven of those thirteen compounds were found to exhibit rotational isomerism. The spectra were interpreted and most of the conformations were identified with the aid of normal coordinate calculations. Those calculations all utilized a thirty-two parameter modified valence force field whose values were determined from 2,2-dimethylpentane, 2,4-dimethylpentane and the $C_2$ conformer of 3,3-dimethylpentane. The force constant values obtained for those three molecules were used without modification for the other molecules and were also used in the present work for interpretation of the vibrational spectra of 4,4-dimethylheptane. This compound is unique in the following way: All the conformers considered for the previous dimethylalkanes[1,2,3] other than the one with all the chain carbons coplanar had one or both terminal methyl groups out of the plane of remaining chain carbons. All stable conformations of 4,4-dimethylheptane other than the one with all seven chain carbons coplanar must have one or both ethyl groups rotated out of the plane of the remaining chain carbons. The conformations with only methyls rotated out of the plane would be high-energy forms.

## EXPERIMENTAL

Infrared spectra were obtained with a Nicolet MX-1 Fourier Transform Spectrometer. Raman spectra were obtained with a SPEX Ramalog system equipped with a Spectra-Physics model 2020 argon ion laser. The 488.0 nm line was used at about 100 mw power with the sample contained in a 1 ml cell. The sample was obtained from Wiley Organics and was 99% pure. In order to conserve space, the spectra are not given here, 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[4,5] were used for calculations 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.[6] The molecular parameters used were: C-C = 0.154 nm, C-H = 0.109 nm and all angles were $109.47^{o}$.

## RESULTS AND DISCUSSION

A molecule of 4,4-dimethylheptane can exist in a large number of conformations that result from internal rotation about the $C_2$-$C_3$, $C_3$-$C_4$, $C_4$-$C_5$ and $C_5$-$C_6$ bonds. However, the conformations formed from rotation about

only $C_2$-$C_3$ and $C_5$-$C_6$ would be high energy forms because of overlapping methyl groups, and they would not be present in appreciable amounts. The most likely stable conformer has all seven chain carbons coplanar and belongs to the $C_{2v}$ point group (called conformer I). The only other stable conformers would have one or both ethyl groups rotated out of the plane of remaining chain carbons. Therefore, normal coordinate calculations were made initially only for the $C_{2v}$ conformer to see if all the observed vibrational bands could be explained by the presence of only this conformer.

The calculations showed that only one band should be observed in the 450-700 $cm^{-1}$ region for the $C_{2v}$ conformer (calc. 567 $cm^{-1}$), whereas there were four bands observed in this region. The intensities show these bands to be fundamentals and must therefore be due to at least one other conformer. Calculations were then made for the two conformers whose structures, along with conformer I, can be represented by the following skeletal formulas, where a + indicates a carbon on one side of the plane of remaining chain carbons and a - indicates a carbon on the other side of the plane:

Conformer I: $C_1$-$C_2$-$C_3$-$C_4(C_8)^+(C_9)^-$-$C_5$-$C_6$-$C_7$

Conformer II: $C_1$-$C_2$-$C_3$-$C_4(C_8)^+(C_9)^-$-$C_5$-$C_6^+$-$C_7^+$

Conformer III: $C_1^-$-$C_2^-$-$C_3$-$C_4(C_8)^+(C_9)^-$-$C_5$-$C_6^+$-$C_7^+$

Conformer II belongs to the $C_1$ point group and conformer III belongs to the $C_2$ point group.

The observed and calculated wavenumbers for the three conformers are given in Tables 1 through 3, and all the conformation-dependent bands and the calculated values for all three conformers are given in Table 4. It can be seen that the 545 and 493 $cm^{-1}$ bands can only be assigned to conformers II and III, respectively, and there is little doubt that all three conformers are present. There are five bands assigned solely to conformer I, one band assigned solely to conformer II and three bands assigned solely to conformer III.

The transferred force constant values resulted in average errors of 4.1 $cm^{-1}$ for forty-seven wavenumbers of conformer I, 4.7 $cm^{-1}$ for forty-five wavenumbers of conformer II and 4.7 $cm^{-1}$ for forty-nine wavenumbers of conformer III. The overall average error for 141 wavenumbers of the three conformers was 4.5 $cm^{-1}$.



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TABLE 1

Observed and Calculated Wavenumbers for 4,4-Dimethylheptane

Conformer I

| Obs. $cm^{-1}$ | Calc. $cm^{-1}$ | Obs. $cm^{-1}$ | Calc. $cm^{-1}$ | Obs. $cm^{-1}$ | Calc. $cm^{-1}$ |
|---|---|---|---|---|---|
| 1470 | 1475 | 1295 | 1295 | 740 | 728 |
| 1470 | 1470 | 1271 | 1286 | 701 | 708 |
| 1470 | 1469 | 1257 | 1252 | 570 | 567 |
| 1470 | 1467 | 1221 | 1216 | 436 | 436 |
| 1460 | 1464 | 1207 | 1210 | - | 402 |
| 1460 | 1464 | 1207 | 1206 | 352 | 360 |
| 1460 | 1463 | 1105 | 1108 | 352 | 352 |
| 1460 | 1462 | - | 1092 | - | 332 |
| 1460 | 1461 | 1076 | 1071 | - | 294 |
| 1450 | 1456 | 1039 | 1038 | - | 236 |
| 1450 | 1454 | 1028 | 1032 | - | 232 |
| 1450 | 1452 | 1028 | 1032 | - | 231 |
| 1384 | 1391 | 997 | 1010 | - | 220 |
| 1379 | 1381 | 960 | 962 | - | 206 |
| 1379 | 1379 | 944 | 945 | - | 112 |
| 1379 | 1378 | 934 | 935 | - | 94 |
| 1363 | 1368 | 910 | 907 | - | 87 |
| 1363 | 1365 | 879 | 877 | - | 56 |
| 1314 | 1324 | 856 | 865 | - | 40 |
| 1295 | 1298 | 856 | 864 | | |
| 1295 | 1298 | 750 | 753 | | |

TABLE 2

Observed and Calculated Wavenumbers for 4,4-Dimethylheptane

Conformer II

| Obs. $cm^{-1}$ | Calc. $cm^{-1}$ | Obs. $cm^{-1}$ | Calc. $cm^{-1}$ | Obs. $cm^{-1}$ | Calc. $cm^{-1}$ |
|---|---|---|---|---|---|
| 1470 | 1472 | 1295 | 1291 | 740 | 728 |
| 1470 | 1469 | 1295 | 1287 | 740 | 728 |
| 1470 | 1467 | 1257 | 1259 | 545 | 531 |
| 1470 | 1466 | 1221 | 1230 | 463 | 455 |
| 1460 | 1464 | 1207 | 1208 | - | 417 |
| 1460 | 1463 | 1186 | 1196 | 352 | 360 |
| 1460 | 1463 | 1105 | 1098 | 352 | 357 |
| 1460 | 1461 | - | 1090 | 318 | 319 |
| 1450 | 1456 | 1076 | 1074 | - | 310 |
| 1450 | 1456 | - | 1051 | - | 235 |
| 1450 | 1452 | 1028 | 1032 | - | 232 |
| 1450 | 1452 | 1028 | 1031 | - | 227 |
| 1384 | 1390 | 997 | 1009 | - | 221 |
| 1379 | 1382 | 960 | 957 | - | 198 |
| 1379 | 1379 | 944 | 948 | - | 148 |
| 1379 | 1376 | 944 | 941 | - | 91 |
| 1363 | 1366 | 902 | 904 | - | 83 |
| 1363 | 1365 | 879 | 877 | - | 67 |
| 1314 | 1319 | 879 | 872 | - | 59 |
| - | 1306 | 856 | 860 | | |
| 1295 | 1297 | 750 | 756 | | |

TABLE 3

Observed and Calculated Wavenumbers for 4,4-Dimethylheptane

Conformer III

| Obs. $cm^{-1}$ | Calc. $cm^{-1}$ | Obs. $cm^{-1}$ | Calc. $cm^{-1}$ | Obs. $cm^{-1}$ | Calc. $cm^{-1}$ |
|---|---|---|---|---|---|
| 1470 | 1474 | 1295 | 1290 | 740 | 730 |
| 1470 | 1468 | 1271 | 1286 | 740 | 727 |
| 1470 | 1467 | 1257 | 1264 | 493 | 487 |
| 1470 | 1466 | 1221 | 1234 | 463 | 478 |
| 1470 | 1465 | 1221 | 1217 | 436 | 432 |
| 1460 | 1463 | 1186 | 1177 | 352 | 363 |
| 1460 | 1463 | - | 1092 | 352 | 356 |
| 1460 | 1461 | - | 1090 | 318 | 315 |
| 1460 | 1457 | 1076 | 1078 | 318 | 312 |
| 1450 | 1454 | - | 1062 | - | 236 |
| 1450 | 1452 | 1028 | 1033 | - | 230 |
| 1450 | 1452 | 1028 | 1030 | - | 223 |
| 1384 | 1390 | 997 | 1008 | - | 222 |
| 1384 | 1386 | 960 | 954 | 185 | 183 |
| 1379 | 1377 | 960 | 953 | - | 168 |
| 1379 | 1376 | 944 | 940 | - | 96 |
| 1363 | 1365 | 902 | 898 | - | 83 |
| 1363 | 1365 | 879 | 876 | - | 82 |
| 1314 | 1314 | 879 | 869 | - | 42 |
| 1314 | 1314 | 856 | 862 | | |
| 1295 | 1295 | 765 | 765 | | |

TABLE 4

Conformation-Dependent Bands of 4,4-Dimethylheptane

| Obs. $cm^{-1}$ | Calc. $cm^{-1}$ | | |
|---|---|---|---|
| | Conf. I | Conf. II | Conf. III |
| 1271 | 1286 | | 1286 |
| 1207 | 1210 | 1208 | |
| | 1206 | | |
| 1186 | | 1196 | 1177 |
| 1105 | 1108 | 1098 | |
| 1039 | 1038 | | |
| 934 | 935 | | |
| 910 | 907 | | |
| 902 | | 904 | 898 |
| 765 | | | 765 |
| 750 | 753 | 756 | |
| 701 | 708 | | |
| 570 | 567 | | |
| 545 | | 531 | |
| 493 | | | 487 |
| 463 | | 455 | 478 |
| 436 | 436 | | 432 |
| 318 | | 319 | 315 |
| 185 | | | 183 |

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