## Vibrational spectra of 1,3,5-hexatriene and methylated derivatives II. The coupling pattern for lateral methylation

Langkilde, F.W.; Amstrup, B.; Wilbrandt, R.; Brouwer, A.M.

# Vibrational spectra of 1,3,5-hexatriene and methylated derivatives—II. The coupling pattern for lateral methylation

Frans W. Langkilde,*† Bjarne Amstrup,* Robert Wilbrandt* and Albert M. Brouwer‡§

*Chemistry Department, Risø National Laboratory, DK-4000 Roskilde, Denmark; and ‡Gorlaeus Laboratories, State University at Leiden, NL-2300 RA Leiden, The Netherlands

**Abstract**—The vibrational spectra of *E*-2-methyl-hexatriene (E2MH), 4-*d*-*E*-2-methyl-hexatriene (dE2MH), and *E*-3-methyl-hexatriene (E3MH) were measured and interpreted using semi-empirical QCFF/π calculations and empirical valence force field (VFF) calculations. The vibrational patterns of E2MH and E3MH are discussed on the basis of the VFF calculations. It is found that the vibrational pattern of E3MH resembles that of *E*-1,3,5-hexatriene whose normal modes to a high degree can be described by global symmetry coordinates, whereas the pattern of E2MH resembles that of isoprene whose normal modes are more influenced by local symmetry coordinates. The effect of steric hindrance on methyl group conformation and the coupling of the methyl group vibrations with those of the polyene chain are discussed.

## INTRODUCTION

Vibrational analysis of 1,3,5-hexatrienes has been reported by many authors [1–21]. We have been interested in the vibrations of hexatrienes in both the ground state [1] and the lowest excited triplet state, detected by time-resolved resonance Raman spectroscopy [22–27].

Since our first study of hexatriene ground state vibrations, four papers have appeared that analyze these vibrations by semi-empirical [13] and scaled *ab initio* [9, 20, 21] methods. These calculations support our vibrational analysis of hexatriene. One reason for the authors of these papers to study hexatriene vibrations is that hexatriene is a model for polyacetylene, the infinite length conducting polyene. With the growth in polyacetylene studies [28], it is important to understand the hexatriene vibrations, and to determine the properties that influence them.

In [1] we studied the Raman and i.r. spectra of the ground state of *E*-1,3,5-hexatriene and derivatives that were methylated in the terminal position: *E,E*-1,3,5-heptatriene and *E,E*-2,4,6-octatriene, or in lateral positions: *E*-2,5-dimethyl-1,3,5-hexatriene. The strongest effect observed in this study was seen upon lateral methylation. For *E*-2,5-dimethyl-1,3,5-hexatriene, the stretching vibrations of the C–C single bonds of the polyene chain and of the C–C single bonds between the chain and the methyl groups were strongly coupled. As a consequence, the C–C single bond stretching vibrations were split into high-wavenumber out-of-phase combinations and low-wavenumber in-phase combinations.

To investigate this effect further, we here study the two hexatrienes that are substituted laterally with only one methyl group: *E*-2-methyl-1,3,5-hexatriene (E2MH) and *E*-3-methyl-1,3,5-hexatriene (E3MH), because in this case it is possible to distinguish between the isolated C–C single bond and the methylated C–C single bond of the polyene chain. Moreover, as it turns out below, the influence of the lateral methyl group on the vibrational pattern is dependent upon whether the methyl group is in the 2- or the 3-position. Here, hexatriene is more interesting to study than butadiene, since it has two *different* lateral positions.

Scheme 1



E2MH    dE2MH    E3MH
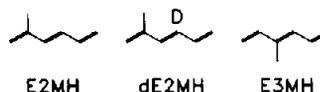
Consequently, from a vibrational analysis of E2MH and E3MH, we expect to gain information on the coupling between vibrations. As vibrations, through the force constants or force field, express the potential energy in chemical bonds, this study should further lead to increased insight into the interaction between chemical bonds.

In the present paper we report the Raman and Fourier transform (FT) i.r. spectra of *E*-2-methyl-hexatriene and *E*-3-methyl-hexatriene. To support the vibrational analysis, we also obtained the Raman spectrum of one deuterated derivative: 4-*d*-*E*-2-methyl-hexatriene (dE2MH).

The experimental spectra are interpreted by calculation, using two kinds of force fields: (1) An empirical valence force field, based on literature values for

---

† To whom correspondence should be addressed.
§ Present address: Laboratory of Organic Chemistry, University of Amsterdam, NL-1018, WS Amsterdam, The Netherlands.

butadiene, isoprene, and $E$-1,3,5-hexatriene and re-
fined in the present study, and (2) a valence force field
computed by the semi-empirical QCFF/$\pi$ program.
The coupling patterns are discussed on the basis of the
calculated internal coordinate contributions to the
normal modes.

## EXPERIMENTAL

The synthesis of E2MH, dE2MH, and E3MH has been
described in detail previously [29]. Analytical GC (BP10
capillary column, 62°C) of E2MH showed no detectable
impurities, whereas the E3MH sample was found to contain
97% $E$-3-methyl-hexatriene, 1% $Z$-3-methyl-hexatriene and
2% 2-methyl-1,3-cyclohexadiene.

The samples were captured in capillary glass tubes in a
cold trap under reduced pressure ($\sim 0.1$ mmHg). The capi-
llaries were sealed and kept in a freezer. The Raman spectra
were obtained from samples in capillary glass tubes (outer
diameter 3 mm), thermostatted at 15°C (22°C for dE2MH).
The FT-i.r. spectrum of matrix-isolated E2MH was obtained
from a 1:300 sample in argon at 15 K. E3MH was trans-
ferred under argon to a vacuum line, dried over $P_2O_5$, and
transferred to a spectroscopic cell for the gas phase FT-i.r.
spectrum. This spectrum was recorded at room temperature
at pressures from 6 to 13 mmHg.

The Raman spectra in the region 2000–10 cm$^{-1}$ were
recorded with a DILOR Z24 triple monochromator equip-
ped with a cooled Centronix P4283 PM-tube. The exciting
source was the green 514.5 nm line from a Spectra-Physics
model 165 argon-ion laser with an output of 400 mW. The
vertically polarized laser light was passed through a mono-
chromator to remove laser lines other than the 514.5 nm one,
reducing the laser power to 170 mW. Perpendicular illumin-
ation was used in a horizontal scattering plane. Spectra were
obtained in $I_{VV}$ and $I_{VH}$ configurations. A quarter-wave plate
was placed in front of the monochromator entrance slit to
ensure circularly polarized light. The spectral slit width was

2.9 cm$^{-1}$ or less, the registration speed was 60 cm$^{-1}$ per min,
and the step in frequency was 1 cm$^{-1}$.

The FT-i.r. spectrum of gas phase E3MH was recorded on
a Bruker IFS 113v spectrometer equipped with an Aspect
3000 computer. Mid i.r. spectra were obtained in the region
4000–550 cm$^{-1}$ with a resolution of 0.5 cm$^{-1}$. A Ge/KBr
beam splitter and a liquid nitrogen cooled MCT detector
with KBr windows were used. Far i.r. spectra were obtained
in the region 700–300 cm$^{-1}$ with 1 cm$^{-1}$ resolution using a
room temperature DTGS detector with polyethylene win-
dows. The spectroscopic cell was a 10 cm gas cell with KBr
windows.

The FT-i.r. spectrum of matrix-isolated E2MH was re-
corded on a Digilab FTS 15 spectrometer in the region
4000–400 cm$^{-1}$ with 2 cm$^{-1}$ resolution [30]. In these exper-
iments a mixture of E2MH and Ar (1:300) was deposited on
an aluminum mirror [31]. KBr windows and a TGS detector
were used.

We used two different approaches for the force field
calculations, one with an empirical valence force field from
the literature which was subsequently refined, the other with
a semi-empirical quantum chemical force field.

In the first approach, one program, VIBROT [32], calcu-
lates the wavenumbers and internal coordinate composition
of the normal modes from the molecular geometry, the
internal coordinates, the nuclear masses, and the valence
force field. The valence force field is refined using another
program, FLINDA [32]. Here, the input consists of the
molecular geometry, the internal coordinates, the nuclear
masses, the experimentally observed frequencies, and starting
values for the valence force field. For each force constant it is
specified whether it should be kept fixed or varied in the
refinement. Both the fixed and variable force constants are
divided into sets, where all the force constants in a set must
have the same value. By least-squares analysis, FLINDA
iterates a new force field.

In the second approach, the QCFF/$\pi$ program [33] was
obtained from QCPE in an IBM version [34].

The VIBROT and FLINDA calculations were implemen-
ted on an RC8000 computer at the H.C. Ørsted Institute,
Copenhagen University, and the QCFF/$\pi$ calculations were
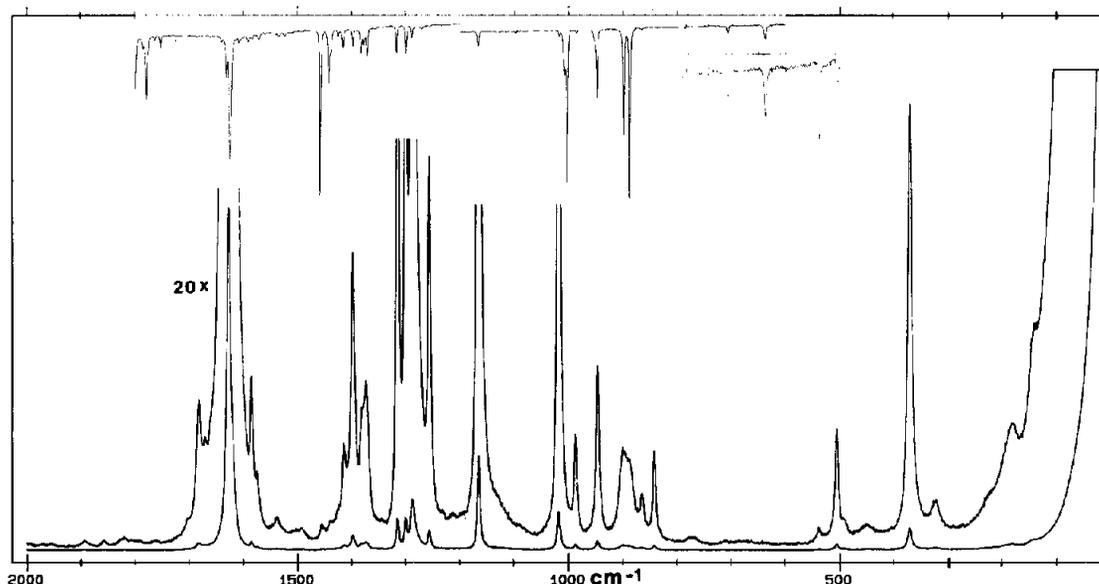


Fig. 1. Top: FT-i.r. spectrum of 1:300 $E$-2-methyl-hexatriene in argon matrix at 15 K. Linear in per cent
transmission, the relative scales are 1.5:3.5:1 in the regions 1800–1200, 1200–600 and 800–500 cm$^{-1}$
respectively. Resolution 2 cm$^{-1}$, windows KBr, detector TGS. Bottom: Raman spectrum of neat $E$-2-
methyl-hexatriene at 15°C, $I_{VV}$ configuration.

carried out at the computer centre at Leiden. In the following, the VIBROT and FLINDA programs shall be referred to as VFF, and the QCFF/$\pi$ as QCFF.

## RESULTS

The FT-i.r. spectrum of matrix-isolated $E$-2-methyl-hexatriene and the Raman spectrum of the neat compound are shown in Fig. 1. The wavenumbers and intensities of the observed bands are listed in Table 1, together with the Raman depolarization ratios. Also listed are calculated wavenumbers and i.r. intensities. The Raman spectrum of neat 4-$d$-$E$-2-methyl-hexatriene is shown in Fig. 2. Wavenumbers, intensities and Raman depolarization ratios are listed in Table 2, together with calculated wavenumbers. The FT-i.r. spectrum of gas phase $E$-3-methyl-hexatriene and the Raman spectrum of the neat compound are shown in Fig. 3. Wavenumbers, intensities, Raman depolarization ratios and i.r. band contours are listed in Table 3, together with calculated wavenumbers and i.r. intensities.

The Raman bands in the low frequency region are obscured by the strong Rayleigh line. An established method [35] to remove the Rayleigh line is to replace the Raman spectrum with the $R(\bar{v})$ spectrum. $R(\bar{v})$ is defined as

$$\bar{v}[1 - \exp(-h\bar{v}c/kT)]I(\bar{v}),$$

where $\bar{v}$ is the Raman shift in cm$^{-1}$, h is Planck's constant, k is Boltzmann's constant, $T$ is the absolute temperature, and c is the velocity of light.

The $R(\bar{v})$ spectra in the region below 400 cm$^{-1}$ are shown in Figs 4A–4C for E2MH, dE2MH and E3MH, respectively. The Raman wavenumbers, intensities and depolarization ratios listed in Tables 1–3 for bands below 400 cm$^{-1}$ were obtained from the $R(\bar{v})$ spectra.

The atom numbering, internal coordinates and bond lengths and angles used for E2MH, dE2MH and E3MH are shown in Fig. 5. To compensate for anharmonicity, we used spectroscopic masses [36, 37]. The results of the VFF calculations are shown in Tables 4–6 for E2MH, dE2MH and E3MH, respectively. The calculated wavenumber and potential energy distribution of each normal mode are listed. The potential energy distributions are normalized. They

Table 1. Observed wavenumbers (cm$^{-1}$) and depolarization ratios of Raman bands and wavenumbers of i.r. bands of $E$-2-methyl-hexatriene in the region 2000–10 cm$^{-1}$, together with approximate assignments and calculated wavenumbers and i.r. intensities

| Raman (liquid) | $I_{VH}/I_{VV}$ | Infrared (matrix) | Assignment | VFF wavenumber | QCFF wavenumber | QCFF intensity |
|---|---|---|---|---|---|---|
| 1893 w | 0.23 | | | | | |
| 1859 w | 0.23 | | | | | |
| 1820 w | 0.22 | | | | | |
| | | 1798 m | | | | |
| | | 1785 w | | | | |
| | | 1778 m | | | | |
| | | 1776 sh | | | | |
| 1762 w | 0.39 | 1763 w | | | | |
| | | 1752 w | | | | |
| 1702 sh | 0.43 | | | | | |
| 1682 m | 0.25 | | | | | |
| 1670 w | 0.34 | | | | | |
| | | 1640 w | | | | |
| | | 1631 m | $vC=C$ | 1644 | 1678 | 0.13 |
| 1627 s | 0.21 | 1623 s | $vC=C$ | 1626 | 1653 | 0.20 |
| | | 1608 w | | | | |
| | | 1591 w | | | | |
| 1585 m | p | | $vC=C$ | 1574 | 1600 | 0.02 |
| 1575 w | p | 1571 w | | | | |
| 1538 w | 0.25 | 1534 w | | | | |
| | | 1523 w | | | | |
| 1494 w | 0.23 | | | | | |
| 1455 w | 0.50 | 1457 s | $d$CH$_3$ | 1453 | 1469 | 1.49 |
| 1440 w | 0.75 | 1442 m | $d$CH$_3$ | 1449 | 1475 | 0.78 |
| | | 1437 sh | | | | |
| 1426 sh | | 1424 w | | | | |
| 1415 m | 0.34 | 1415 w | $s$CH$_2$ | 1428 | 1457 | 1.43 |
| 1398 m | 0.23 | 1397 w | $s$CH$_2$ | 1403 | 1435 | 0.75 |
| 1381 sh | 0.37 | 1383 m | | | | |
| | | 1378 w | | | | |
| 1374 m | 0.32 | 1371 m | $d$CH$_3$ | 1381 | 1444 | 2.22 |
| 1316 s | 0.30 | 1317 m | $v$C–C | 1320 | 1408 | 0.10 |
| 1301 s | 0.22 | 1299 m | $r$CH | 1287 | 1350 | 0.05 |
| 1288 s | 0.21 | 1288 w | $r$CH | 1284 | 1318 | 2.29 |
| | | 1270 w | | | | |

Table 1. (*continued*)

| Raman (liquid) | $I_{VH}/I_{VV}$ | Infrared (matrix) | Assignment | VFF wavenumber | QCFF wavenumber | QCFF intensity |
|---|---|---|---|---|---|---|
| 1257 m | 0.26 | | rCH | 1251 | 1293 | 0.57 |
| 1213 w | p | | | | | |
| | | 1167 sh | | | | |
| 1166 s | 0.30 | 1166 m | vC–C | 1162 | 1196 | 1.10 |
| | | 1040 w | wCH₃ | 1038 | 1060 | 2.44 |
| 1019 s | 0.23 | 1016 w | rCH₃ | 1008 | 1026 | 0.81 |
| | | 1007 m | | | | |
| | | 1002 s | wCH | 1002 | 1072 | 1.24 |
| 988 m | 0.25 | 986 w | rCH₂ | 985 | 982 | 0.29 |
| | | 953 sh | | | | |
| | | 950 sh | | | | |
| 947 m | 0.37 | 947 s | rCH₂ | 949 | 948 | 0.83 |
| 900 m | 0.70 | 898 s | wCH | 910 | 1001 | 1.28 |
| 894 sh | 0.70 | | wCH₂ | 908 | 952 | 0.43 |
| 888 m | 0.69 | 887 s | wCH₂ | 897 | 950 | 2.82 |
| | | 880 w | | | | |
| 865 m | 0.68 | 865 w | wCH | 870 | 864 | 0.02 |
| 843 m | 0.42 | | vC–C | 829 | 921 | 0.07 |
| 773 w | 0.56 | | | | | |
| 705 w | 0.70 | 707 w | tC=C | 707 | 732 | 0 |
| 684 w | 0.36 | | | | | |
| 634 w | 0.74 | 638 w | tC=C | 633 | 629 | 0.62 |
| 540 w | 0.59 | 538 m | dCCC | 549 | 606 | 0.15 |
| 507 m | 0.13 | 505 w | dCCC | 513 | 562 | 0.43 |
| 493 w | 0.75 | | wCH₃ | 484 | 476 | 0.59 |
| 452 w | 0.40 | | | | | |
| 372 s | 0.32 | | dCCC | 358 | 395 | 0 |
| 325 m | 0.63 | | dCCC | 330 | 374 | 0.11 |
| | | | tC–C | 309 | 227 | 0.13 |
| 229 w | | | rotCH₃ | 202 | 202 | 0.01 |
| 186 m | 0.74 | | tC=C | 174 | 162 | 0.19 |
| | | | dCCC | 134 | 166 | 0.14 |
| 146 w | 0.73 | | tC–C | 114 | 91 | 0.04 |
| 55 m | 0.76 | | inter-molecular | | | |

s = strong, m = medium, w = weak, sh = shoulder; p = polarized, dp = depolarized; v = stretch, d = deformation, s = scissoring, r = in-plane rock, w = out-of-plane wag, t = twist, rot = rotation.
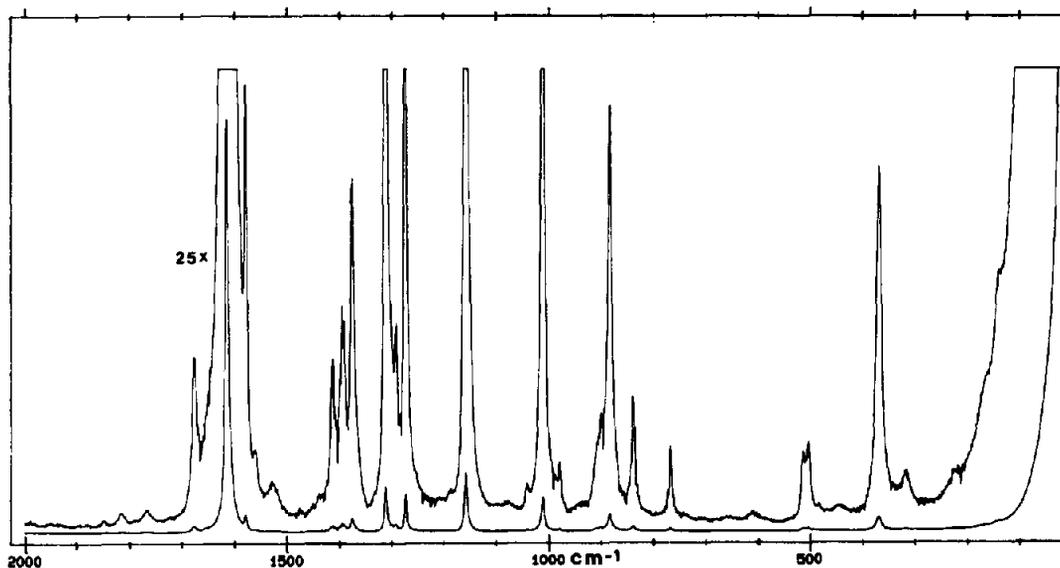


Fig. 2. Raman spectrum of neat 4-*d*-*E*-2-methyl-hexatriene at 22°C, $I_{vv}$ configuration.

Table 2. Observed wavenumbers (cm$^{-1}$) and depolarization ratios of Raman bands of 4-$d$-$E$-2-methyl-hexatriene in the region 2000–10 cm$^{-1}$, together with approximate assignments and calculated wavenumbers

| Raman (liquid) | $I_{VH}/I_{VH}$ | Assignment | VFF wavenumber | QCFF wavenumber |
|---|---|---|---|---|
| 1848 w | p | | | |
| 1816 w | 0.28 | | | |
| 1766 w | 0.30 | | | |
| 1677 m | 0.25 | | | |
| 1628 sh | | $v$C=C | 1644 | 1674 |
| 1615 s | 0.20 | $v$C=C | 1620 | 1646 |
| 1578 m | 0.42 | $v$C=C | 1563 | 1592 |
| 1561 w | 0.50 | | | |
| 1528 w | 0.24 | | | |
| 1475 w | p | | | |
| 1450 w | 0.47 | $d$CH$_3$ | 1453 | 1468 |
| 1439 w | 0.72 | $d$CH$_3$ | 1449 | 1475 |
| 1424 sh | p | | | |
| 1413 m | 0.35 | $s$CH$_2$ | 1426 | 1454 |
| 1393 m | 0.31 | $s$CH$_2$ | 1403 | 1434 |
| 1376 m | 0.36 | $d$CH$_3$ | 1381 | 1444 |
| 1311 s | 0.28 | $v$C–C | 1314 | 1406 |
| 1292 m | 0.19 | $r$CH | 1286 | 1330 |
| 1274 s | 0.19 | $r$CH | 1268 | 1298 |
| 1188 w | p | | | |
| 1159 s | 0.38 | $v$C–C | 1159 | 1197 |
| | | $w$CH$_3$ | 1036 | 1061 |
| 1039 w | 0.33 | $r$CD/$r$CH$_2$ | 1029 | 1049 |
| 1011 s | 0.26 | $r$CH$_3$ | 996 | 1021 |
| 992 w | dp | $w$CH | 1000 | 1052 |
| 980 w | 0.44 | $r$CH$_2$ | 985 | 981 |
| 907 sh | dp | $w$CH$_2$ | 909 | 953 |
| 900 m | dp | $w$CH | 899 | 937 |
| 897 sh | dp | $w$CH$_2$ | 897 | 950 |
| 884 m | 0.33 | $r$CD/$r$CH$_2$ | 890 | 895 |
| 839 m | 0.71 | $v$C–C | 829 | 922 |
| 768 m | 0.77 | $w$CD | 740 | 771 |
| 743 w | | | | |
| 707 w | 0.75 | $t$C=C | 707 | 727 |
| 657 w | 0.33 | | | |
| 612 w | 0.77 | $t$C=C | 611 | 615 |
| 515 m | 0.26 | $d$CCC | 530 | 588 |
| 506 m | 0.13 | $d$CCC | 512 | 558 |
| 485 w | 0.79 | $w$CH$_3$ | 478 | 473 |
| 446 w | 0.45 | | | |
| 370 m | 0.39 | $d$CCC | 358 | 394 |
| 320 w | 0.63 | $d$CCC | 326 | 370 |
| | | $t$C–C | 296 | 226 |
| 278 w | | | | |
| 225 w | dp | $rot$CH$_3$ | 201 | 199 |
| 169 w | dp | $t$C=C | 166 | 151 |
| | | $d$CCC | 134 | 165 |
| 143 w | dp | $t$C–C | 114 | 90 |
| 49 m | dp | inter-molecular | | |

are calculated as the square of the coefficient of an internal coordinate in a normal mode, multiplied by the pertinent diagonal force constant. However, the sign of the coefficients is retained in the potential energy distribution. Only the dominant contributions are shown; in most cases these are the internal coordinates that contribute more than 10% to the normal mode. The valence force field applied to E2MH and dE2MH is listed in Table 7, the one applied to E3MH in Table 8.

## DISCUSSION

### Empirical valence force fields

The valence force field in Table 7 for $E$-2-methyl-hexatriene and 4-$d$-$E$-2-methyl-hexatriene was constructed on the basis of force fields for butadiene, isoprene and $E$-hexatriene. These three latter force fields were again based on values from Ref. [15] (CT). In CT, force constants derived from smaller molecules are used to construct the force fields of retinals. This

Table 3. Observed wavenumbers (cm$^{-1}$) and depolarization ratios of Raman bands and wavenumbers and band contours of infrared bands of E-3-methyl-hexatriene in the region 2000–10 cm$^{-1}$, together with approximate assignments and calculated wavenumbers and infrared intensities

| Raman (liquid) | $I_{VH}/I_{VV}$ | Infrared (gas) | | | Contour | Assignment | VFF wavenumber | QCFF wavenumber | QCFF infrared intensity |
|---|---|---|---|---|---|---|---|---|---|
| | | R | Q | P | | | | | |
| 1966 w | 0.33 | | 1964 | | w | | | | |
| 1891 w | 0.35 | | 1878 | | w | | | | |
| | | | | | | | | | |
| 1869 w | 0.30 | | 1807 | 1798 | m | | | | |
| 1808 w | 0.49 | 1819 | 1766 | | w | | | | |
| | | | | | | | | | |
| 1744 w | p | | | | | | | | |
| 1679 m | 0.34 | | | | | | | | |
| 1624 s | 0.24 | 1628 | | 1620 | s B | $\nu$C=C | 1637 | 1672 | 0.05 |
| 1620 sh | 0.25 | 1624 | | 1617 | sh B | $\nu$C=C | 1623 | 1646 | 0.19 |
| 1602 sh | 0.25 | | | | w | | | | |
| 1577 m | p | | 1585 | | w | $\nu$C=C | 1583 | 1600 | 0.05 |
| 1550 w | p | | 1544 | | w | | | | |
| 1532 w | 0.30 | | 1515 | | w | | | | |
| | | | | | | | | | |
| 1459 w | 0.47 | | | | | dCH$_3$ | 1453 | 1496 | 1.72 |
| 1443 w | 0.56 | | 1448 | | sh C | dCH$_3$ | 1449 | 1471 | 0.74 |
| 1424 m | 0.41 | 1432 | 1428 | 1423 | m A | sCH$_2$ | 1429 | 1446 | 2.10 |
| 1413 s | 0.29 | | | | | | | | |
| 1402 s | 0.28 | | | | m B | sCH$_2$ | 1400 | 1424 | 0.74 |
| 1387 sh | 0.59 | 1395 | 1350 | 1387 | w A | dCH$_3$ | 1382 | 1440 | 2.96 |
| 1348 m | 0.29 | 1355 | 1319 | 1345 | w | $\nu$C–C | 1340 | 1479 | 0.51 |
| 1323 m | 0.21 | | 1295 | | w. A | | | | |
| 1298 s | 0.19 | 1300 | | 1291 | w | rCH | 1286 | 1330 | 0.24 |
| 1257 m | 0.31 | 1261 | | 1253 | w | rCH | 1272 | 1312 | 0.08 |
| 1226 s | 0.27 | 1230 | | 1219 | sh | rCH | 1223 | 1268 | 0.48 |
| 1155 sh | 0.43 | | 1154 | | m | | | | |
| 1145 m | 0.43 | | 1144 | | | $\nu$C–C | 1142 | 1203 | 0.63 |
| 1106 w | 0.43 | | | | | | | | |
| 1067 s | 0.32 | 1073 | 1069 | 1064 | m A | rCH$_3$ | 1037 | 1067 | 1.37 |
| 1034 w | 0.67 | | 1034 | | w | wCH$_3$ | 1022 | 1055 | 0.34 |
| | | | 990 | | s C | wCH | 996 | 1047 | 1.69 |

| Obs | ρ | | | | int | Assignment | | | |
|---|---|---|---|---|---|---|---|---|---|
| 985 m | 0.26 | | 984 | | s C | $rCH_2$ | 980 | 1019 | 0.36 |
| 946 w | 0.18 | 952 | 947 | 942 | w A | $wCH$ | 993 | 1036 | 0.64 |
| 906 m | 0.69 | | 906 | | s C | $rCH_2$ | 936 | 939 | 0.31 |
| 901 m | 0.73 | | 899 | | s C | $wCH_2$ | 908 | 956 | 0.85 |
| 843 w | 0.70 | | | | | $wCH_2$ | 906 | 954 | 4.18 |
| 803 m | 0.67 | | 806 | | w | $wCH$ | 812 | 904 | 0.15 |
| 738 w | p | 748 | 788 | 743 | w | $vC-C$ | 792 | 873 | 0.42 |
| 648 w | 0.73 | | 685 | | w | $tC=C$ | 687 | 657 | 0.01 |
| | | | | | | $CO_2$  Q-branch | | | |
| 584 w | 0.63 | | 668 | | m C | $tC=C$ | 655 | 642 | 1.01 |
| 567 w | dp | 588 | 641 | 579 | m C | $dCCC$ | 576 | 663 | 0.72 |
| 492 w | 0.30 | | 583 | | m C | $dCCC$ | 439 | 490 | 0.06 |
| 456 w | 0.06 | 458 | 550 | 448 | w A | $wCH_3$ | 421 | 441 | 0.64 |
| 420 w | 0.73 | | 454 | | w A | $dCCC$ | 360 | 425 | 0 |
| 392 s | 0.24 | 394 | 415 | 387 | m C | $dCCC$ | 291 | 372 | 0.09 |
| 337 w | | | 399 | | m C | $tC=C$ | 275 | 236 | 0.21 |
| 301 w | | | 391 | | w | $tC-C$ | 204 | 168 | 0 |
| 256 w | | | | | | $rotCH_3$ | 194 | 126 | 0.01 |
| 181 w | 0.72 | | | | | $dCCC$ | 158 | 208 | 0.20 |
| 156 w | 0.75 | | | | | $tC-C$ | 126 | 97 | 0.12 |
| 46 m | 0.77 | | | | | inter-molecular | | | |
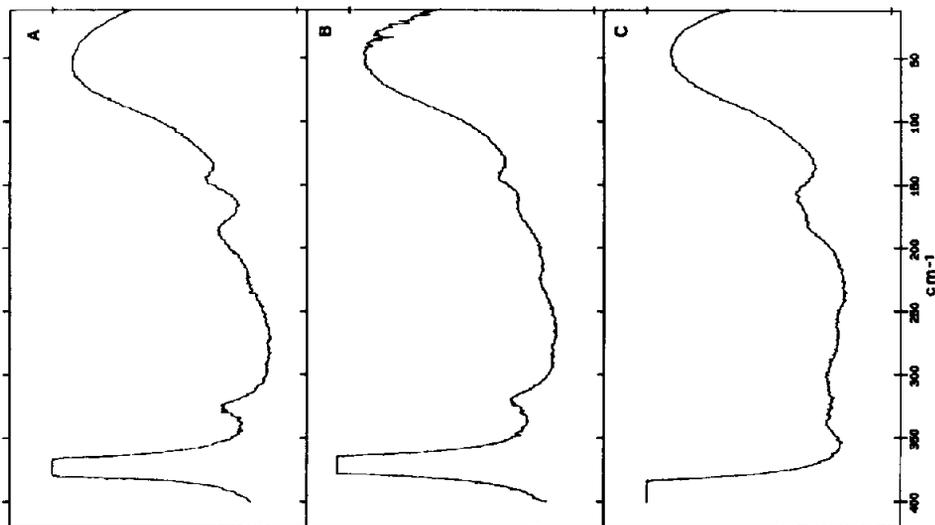
Fig. 4. Raman $R(\tilde{v})$ spectra of neat E-2-methyl-hexatriene at 15°C (A), 4-d-E-2-methyl-hexatriene at 22°C (B), and E-3-methyl-hexatriene at 15°C (C), $I_{vv}$ configuration.
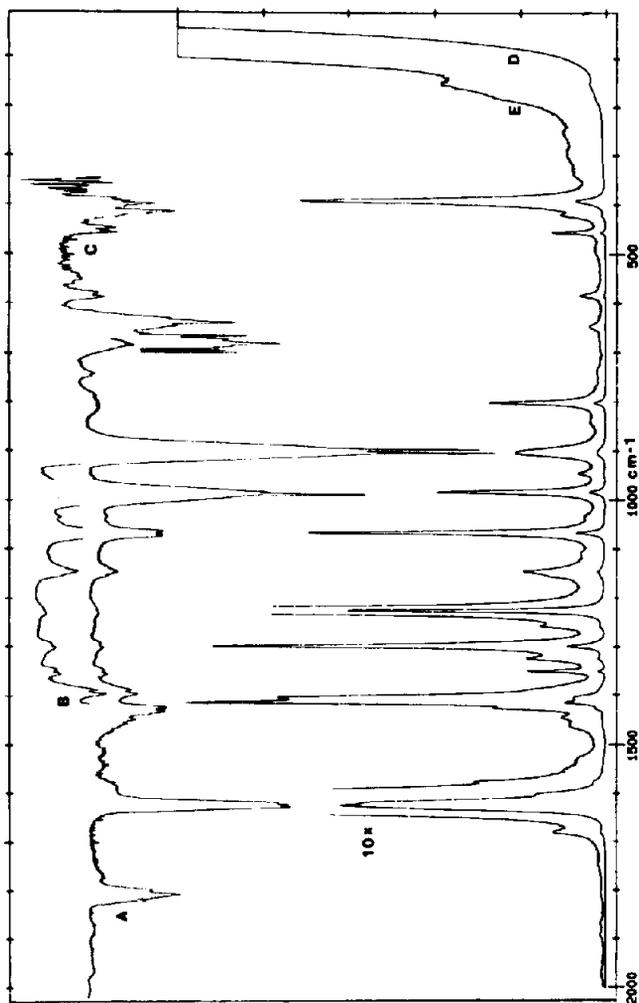


Fig. 3. (A–C): FT-i.r. spectrum of gas phase E-3-methyl-hexatriene at room temperature, pressure is ~6 mmHg (A) and ~13 mmHg (B, C). Linear in per cent transmission, the relative scales are 2.8 : 4.0 : 1 for (A), (B) and (C), respectively. Cell length 10 cm, windows KBr. Resolution 0.5 cm$^{-1}$ (A, B) and 1.0 cm$^{-1}$ (C) Detectors MCT with KBr windows (A, B) and DTGS with PE windows (C), beam splitter Ge/KBr. Cut-off in (C) at 700 cm$^{-1}$ due to detector PE windows, at 350 cm$^{-1}$ to cell KBr windows. (D) (E): Raman spectrum of neat E-3-methyl-hexatriene at 15°C, $I_{vv}$ configuration.

Fig. 5. Atom numbering and internal coordinates of $E$-2-methyl-hexatriene (E2MH) and $E$-3-methyl-hexatriene (E3MH). CH stretches, $q_i$ and $q'_j$, are numbered according to the hydrogen atoms involved. $Q$ CC stretch, $\alpha$ HCH scissoring, $\beta$ CCH rock, $\gamma$ CCC bend. $\omega$ CH or C–CH$_3$ out-of-plane wag, towards the reader. $\tau_1$ H$_2$C$_1$C$_2$C$_3$ torsion, H$_2$ and C$_3$ towards the reader. $\tau_2$ C$_1$C$_2$C$_3$C$_4$ torsion, C$_1$ and C$_4$ away from the reader. $\tau_3$C$_2$C$_3$C$_4$C$_5$ torsion, $\tau_4$C$_3$C$_4$C$_5$C$_6$ torsion, $\tau_5$C$_4$C$_5$C$_6$H$_7$ torsion. For E2MH: $\chi$ C$_4$C$_5$C$_7$H'$_1$ +C$_4$C$_5$C$_7$H'$_2$+C$_4$C$_5$C$_7$H'$_3$ torsions, with C$_4$ and H'$_3$ away from the reader. For E3MH: $\chi$ C$_5$C$_4$C$_7$H'$_1$ +C$_5$C$_4$C$_7$H'$_2$+C$_5$C$_4$C$_7$H'$_3$ torsions, with C$_5$ and H'$_3$ away from the reader. Geometrical parameters are $q_1$–$q_7 = 1.084$ Å, $Q_1 = Q_5 = 1.337$ Å, $Q_2 = Q_4 = 1.458$ Å, $Q_3 = 1.368$ Å, $Q' = 1.52$ Å, $\beta_1 = \beta_2 = \beta_9 = \beta_{10} = 120.5°$, $\beta_3 = \beta_4 = 119.15°$, $\beta_5 = \beta_6 = \beta_7 = \beta_8 = 117.8°$, $\alpha_1 = \alpha_2 = 119°$, $q' = 1.105$ Å, $\alpha' = \beta' = 109.47°$. For E2MH, $\gamma_1 = 121.7°$, $\gamma_2 = \gamma_3 = 124.4°$, $\gamma_4 = 123.2°$, $\gamma_5 = \gamma_6 = 118.4°$. For E3MH, $\gamma_1 = 121.7°$, $\gamma_2 = \gamma_6 = 124.4°$,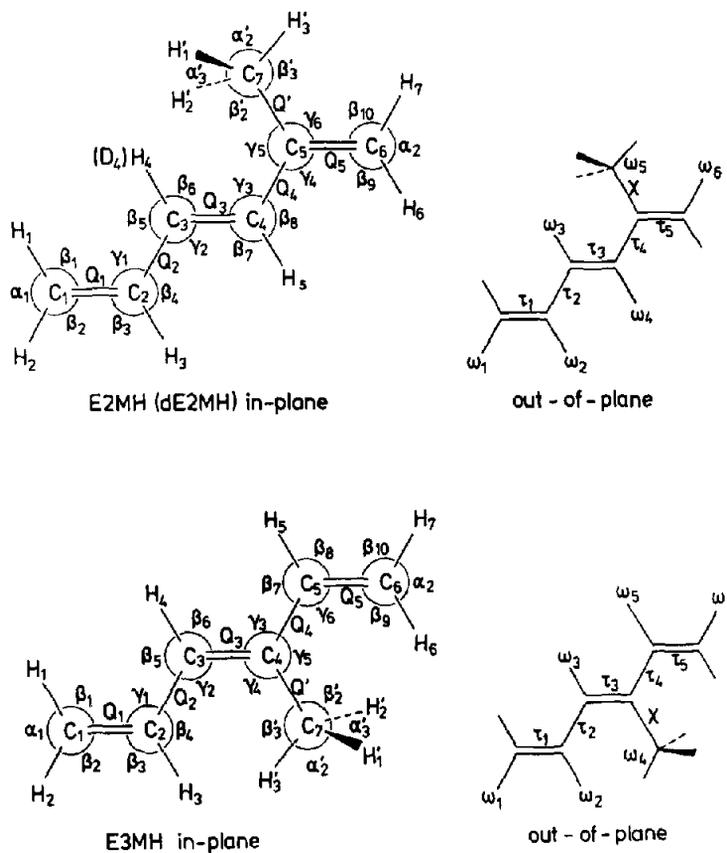 $\gamma_3 = 123.2°$, $\gamma_4 = \gamma_5 = 118.4°$. Atom numbering, internal coordinates, and geometrical parameters are identical for E2MH and dE2MH. Spectroscopic masses were used: $m_H = 1.088$, $m_D = 2.126$, $m_C = 12.0$.

work is probably the most thorough study of polyene vibrations; it is described at length in Ref. [38].

Since the butadiene force field in CT is iterated on the basis of observed vibrational spectra of as many as eleven different isotopic derivatives of butadiene, we used the CT butadiene force constants as the starting point in our iteration. Also the molecular geometry, i.e. bond lengths and angles, used in the present study, was transferred from CT, apart from the conformation of the methyl groups (see below). The molecular geometry in CT is closely related to the experimentally found one [39].

To model the effect of methylation, we constructed an isoprene valence force field after values from CT for propene and isoprene. For these compounds a good agreement is found in CT between calculated and observed vibrational wavenumbers. A more recent

study of isoprene [40] supports the CT isoprene values. CT mainly uses a modified Urey–Bradley force field [36, 41], whereas we use a valence type of force field. As seen from Table 7, we refined some of the isoprene force constants, using the VFF programs and experimental frequencies cited in CT (mostly from Ref. [42]).

The effect of elongation of the polyene chain going from butadiene to $E$-hexatriene, was only partly modelled after values from CT, since we disagree in the assignment of the $E$-hexatriene vibrations at 1288, 1283 and 1132 cm$^{-1}$ (our values) [1, 15]. Compared to CT, we modified the in-plane force field for $E$-hexatriene. In our choice of starting values for the refinement we took into account the values used in two of the most recent calculations [9, 20].

The valence force fields obtained as described above for butadiene, isoprene and $E$-hexatriene, were used to

Table 4. Calculated wavenumbers (cm$^{-1}$) and potential energy distributions of the normal modes of $E$-2-methyl-hexatriene in the region below 2000 cm$^{-1}$. Only the dominant contributions are shown. For notation, see Fig. 5

| Wavenumber | Potential energy distribution |
|---|---|
| 1644 | $0.54\ Q_5\ -0.10\ Q_4$ |
| 1626 | $0.47\ Q_1\ -0.10\ Q_2\ +0.09\ Q_3$ |
| 1574 | $0.45\ Q_3\ -0.10\ Q_1$ |
| 1453 | $0.64\ \alpha'_3\ -0.14\ \alpha'_1\ -0.14\ \alpha'_2$ |
| 1449 | $0.47\ \alpha'_1\ -0.47\ \alpha'_2$ |
| 1428 | $0.21\ \alpha_1\ -0.10\ \beta_2\ -0.20\ \alpha_2\ +0.10,\ \beta_{10}$ |
| 1403 | $0.19\ \alpha_1\ -0.09\ \beta_2\ +0.19\ \alpha_2\ -0.09\ \beta_{10}$ |
| 1381 | $0.15\ \alpha'_1\ +0.15\ \alpha'_2\ +0.08\ \alpha'_3$ $-0.14\ \beta'_1\ -0.14\ \beta'_2\ -0.14\ \beta'_3$ |
| 1320 | $0.20\ Q'\ -0.14\ Q_4\ -0.06\ \beta_6\ -0.07\ \beta_9\ +0.06\ \gamma_3\ +0.08\ \gamma_4$ |
| 1287 | $0.26\ \beta_3\ -0.18\ \beta_4\ +0.09\ \beta_1\ -0.09\ \beta_7\ +0.19\ Q_1$ |
| 1284 | $0.19\ \beta_7\ -0.14\ \beta_8\ +0.06\ \beta_3\ +0.11\ Q_3\ +0.08\ Q'$ |
| 1251 | $0.32\ \beta_5\ -0.28\ \beta_6\ +0.11\ \beta_7\ -0.11\ \beta_8$ |
| 1162 | $0.40\ Q_2\ +0.13\ \beta_4$ |
| 1038 | $0.31\ \beta'_1\ -0.31\ \beta'_2\ +0.12\ \omega_5\ -0.15\ \omega_6$ |
| 1008 | $0.40\ \beta'_3\ -0.09\ \beta'_1\ -0.09\ \beta'_2\ +0.11\ Q_4$ |
| 1002 | $0.79\ \omega_2\ -0.12\ \tau_1$ |
| 985 | $0.27\ \beta_9\ -0.31\ \beta_{10}\ +0.14\ \beta'_3\ -0.08\ Q_4$ |
| 949 | $0.29\ \beta_1\ -0.32\ \beta_2\ -0.19\ Q_2$ |
| 910 | $0.31\ \omega_3\ -0.31\ \omega_4\ +0.16\ \tau_5$ |
| 908 | $0.71\ \omega_1\ +0.25\ \tau_1$ |
| 897 | $0.63\ \omega_6\ +0.10\ \omega_4\ +0.17\ \tau_5$ |
| 870 | $0.43\ \omega_3\ +0.25\ \omega_4\ -0.11\ \omega_6$ |
| 829 | $0.61\ Q'\ +0.16,\ Q_4$ |
| 707 | $0.63\ \tau_5\ +0.11\ \tau_1$ |
| 633 | $0.46\ \tau_1\ +0.32\ \omega_2$ |
| 549 | $0.24\ \gamma_5\ -0.19\ \gamma_3\ +0.17\ \gamma_1\ -0.11\ \gamma_4$ |
| 513 | $0.35\ \gamma_6\ +0.10\ \gamma_2\ -0.09\ \gamma_4$ |
| 484 | $0.57\ \omega_5\ -0.10\ \tau_3\ +0.07\ \tau_5$ |
| 358 | $0.21\ \gamma_1\ +0.19\ \gamma_4\ -0.12\ \gamma_6\ +0.09\ Q_2\ +0.08\ Q_3\ +0.10\ Q_4$ |
| 330 | $0.21\ \gamma_5\ +0.18\ \gamma_2\ -0.14\ \gamma_1\ +0.11\ Q_4$ |
| 309 | $0.40\ \tau_2\ -0.36\ \tau_4$ |
| 202 | $0.76\ \chi$ |
| 174 | $0.57\ \tau_3\ +0.09\ \omega_3\ +0.10\ \omega_4\ +0.12\ \omega_5$ |
| 134 | $0.33\ \gamma_3\ -0.26\ \gamma_2\ +0.10\ \gamma_1$ |
| 114 | $0.33\ \tau_3\ -0.18\ \tau_2\ -0.15\ \tau_4\ +0.15\ \omega_3\ +0.13\ \omega_4$ |

construct an initial force field in the iteration of the $E$-2-methyl-hexatriene force field, using the VFF programs; this refinement caused only a few changes as seen from Table 7. The $E$-2-methyl-hexatriene force field was transferred to $E$-3-methyl-hexatriene with only minor changes, see Table 8.

A proper discussion of the valence force fields in Tables 7 and 8 would be quite extensive. Here, we shall only give a brief comparison of our values with the scaled *ab initio* values from Refs [9, 20, 21].

Our diagonal force constants for the CC stretches of the chain, $Q_1$–$Q_5$, tend to be lower than those of the references mentioned. So are our values for the interaction between neighbouring chain CC stretches, whereas our values for the interaction between next-neighbour chain CC stretches, i.e. $Q_1 Q_3$, $Q_3 Q_5$ and $Q_2 Q_4$, are (numerically) larger than in the references. Our diagonal force constants for the CH rocks are larger, those of the terminal CCC bends are smaller, and our value for the interaction between the two central CCC bends is larger than in the references mentioned.

## Molecular geometry and vibrational band types

$E$-2-methyl-hexatriene has been found by the gas electron diffraction method to be planar with $tEt$ geometry [39]. This result was confirmed for the liquid phase using u.v. absorption and NMR spectroscopy [29]. The latter study found $E$-3-methyl-hexatriene as well to be planar with $tEt$ geometry. Consequently, both molecules transform according to $C_s$ symmetry, and all 45 normal modes of vibration are in principle both Raman and i.r. active. Thirty in-plane modes of $a'$ symmetry have polarized Raman bands and $A$, $B$, or $A/B$ hybrid type gas phase i.r. bands, whereas 15 $a''$ out-of-plane modes have depolarized Raman bands and $C$ type gas phase i.r. bands. Among the 45 modes of vibration, 10 are CH stretch fundamentals around 3000 cm$^{-1}$. These shall not be dealt with in the present study; out of these, nine are in-plane ($a'$) and one is out-of-plane ($a''$).

The question of the conformation of the methyl group must be addressed separately. If one methyl hydrogen is assumed to be in the plane of the molecu-

Table 5. Calculated wavenumbers (cm$^{-1}$) and potential energy distributions of the normal modes of 4-$d$-$E$-2-methyl hexatriene in the region below 2000 cm$^{-1}$. Only the dominant contributions are shown. For notation, see Fig. 5

| Wavenumber | Potential energy distribution |
|---|---|
| 1664 | $0.56\ Q_5\ -0.09\ Q_4$ |
| 1620 | $0.52\ Q_1\ -0.09\ Q_2\ +0.10\ \alpha_1$ |
| 1563 | $0.53\ Q_3$ |
| 1453 | $0.64\ \alpha'_3\ -0.14\ \alpha'_1\ -0.14\ \alpha'_2$ |
| 1449 | $0.47\ \alpha'_1\ -0.47\ \alpha'_2$ |
| 1426 | $0.22\ \alpha_1\ -0.10\ \beta_2\ -0.19\ \alpha_2\ +0.09\ \beta_{10}$ |
| 1403 | $0.18\ \alpha_1\ -0.09\ \beta_2\ +0.19\ \alpha_2\ -0.09\ \beta_{10}$ |
| 1381 | $0.15\ \alpha'_1\ +0.15\ \alpha'_2\ +0.08\ \alpha'_3$ $-0.14\ \beta'_1\ -0.14\ \beta'_2\ -0.14\ \beta'_3$ |
| 1314 | $0.25\ Q'\ -0.17\ Q_4\ -0.09\ \beta_9\ +0.09\ \gamma_4$ |
| 1286 | $0.31\ \beta_3\ -0.18\ \beta_4\ +0.12\ \beta_1\ +0.23\ Q_1$ |
| 1268 | $0.42\ \beta_7\ -0.29\ \beta_8\ +0.12\ Q_3$ |
| 1159 | $0.38\ Q_2\ +0.13\ \beta_4$ |
| 1036 | $0.31\ \beta'_1\ -0.31\ \beta'_2\ +0.11\ \omega_5\ -0.15\ \omega_6$ |
| 1029 | $0.14\ \beta_1\ -0.16\ \beta_2\ +0.11\ \beta_5\ -0.17\ \beta_6\ -0.12\ \beta'_3$ |
| 1000 | $0.78\ \omega_2\ -0.11\ \tau_1$ |
| 996 | $0.28\ \beta'_3\ +0.12\ Q_4$ |
| 985 | $0.27\ \beta_9\ -0.31\ \beta_{10}\ +0.14\ \beta'_3$ |
| 909 | $0.56\ \omega_1\ +0.10\ \omega_4\ +0.29\ \tau_1$ |
| 899 | $0.58\ \omega_4\ -0.23\ \omega_1$ |
| 897 | $0.66\ \omega_6\ +0.27\ \tau_5$ |
| 890 | $0.26\ \beta_5\ -0.17\ \beta_6\ -0.16\ \beta_1\ +0.17\ \beta_2\ +0.15\ Q_2$ |
| 829 | $0.61\ Q'\ +0.16\ Q_4$ |
| 740 | $0.59\ \omega_3\ -0.12\ \omega_2\ -0.11\ \tau_1$ |
| 707 | $0.53\ \tau_5\ +0.15\ \tau_1\ +0.11\ \omega_2$ |
| 611 | $0.40\ \tau_1\ +0.27\ \omega_2$ |
| 530 | $0.26\ \gamma_5\ -0.18\ \gamma_3\ +0.13\ \gamma_1\ -0.10\ \gamma_4$ |
| 512 | $0.34\ \gamma_6\ -0.11\ \gamma_4\ +0.10\ \gamma_2$ |
| 478 | $0.51\ \omega_5\ -0.10\ \omega_3\ -0.10\ \tau_3$ |
| 358 | $0.20\ \gamma_1\ +0.18\ \gamma_4\ -0.13\ \gamma_6\ +0.09\ Q_2\ +0.08\ Q_3\ +0.11\ Q_4$ |
| 326 | $0.21\ \gamma_5\ +0.18\ \gamma_2\ -0.15\ \gamma_1\ +0.10\ Q_4$ |
| 296 | $0.39\ \tau_2\ -0.32\ \tau_4$ |
| 201 | $0.81\ \chi$ |
| 166 | $0.57\ \tau_3\ +0.10\ \omega_4\ +0.12\ \omega_5$ |
| 134 | $0.33\ \gamma_3\ -0.26\ \gamma_2\ +0.10\ \gamma_1$ |
| 114 | $0.33\ \tau_3\ -0.18\ \tau_2\ -0.15\ \tau_4\ +0.14\ \omega_3\ +0.13\ \omega_4$ |

le, the methyl group may be either staggered or eclipsed with respect to the neighbouring terminal hydrogen atom ($H_7$ for E2MH, $H_6$ for E3MH). For E2MH, the QCFF calculation led to an optimized geometry, where the in-plane methyl hydrogen is eclipsed with respect to the terminal hydrogen atom. This result agrees with expectations, since the interatomic distance is shorter between $H'_3$ and $H_4$ than between $H'_3$ and $H_7$ (after rotation by 180° of the methyl group), and this methyl conformation was used in our VFF calculations.

For E3MH, the interatomic distances $H'_3$–$H_3$ and $H'_3$–$H_6$ are nearly equal. Here, QCFF yielded an optimum geometry where the methyl hydrogens are staggered with respect to the terminal hydrogen atom, as shown in Fig. 5. However, QCFF geometry optimization starting with a terminal hydrogen-eclipsed geometry, led to non-planar structures with higher energies than for the planar, terminal hydrogen-staggered geometry. NMR experiments showed a conformation with the methyl hydrogens eclipsed with the terminal hydrogen atom to be predominant [29]. In the VFF calculations presented here, we used a methyl conformation with the methyl hydrogens staggered with the terminal hydrogen atom. We also carried out VFF calculations with the methyl hydrogens eclipsed with the terminal hydrogen atom, and these yielded vibrational frequencies that differed little from those presented in Tables 3 and 9.

*Spectral assignments*

It is clear from Tables 1–3 that the agreement between calculated and observed vibrational frequencies is far better for the VFF calculations than for the QCFF one. The QCFF frequencies are generally too high. QCFF is a semi-empirical method. *Ab initio* methods tend to over-estimate the force constants as well. Consequently, many *ab initio* calculations use "scaling factors" on the force constants [9, 20, 21, 43]. The experimental and calculated wavenumbers and assignments of the normal modes of E2MH, dE2MH and E3MH listed in Tables 1–6 are summarized together in Table 9, where only wavenumbers calculated by the VFF programs, not by the QCFF program, are listed.

Table 6. Calculated wavenumbers (cm$^{-1}$) and potential energy distributions of the normal modes of $E$-3-methyl-hexatriene in the region below 2000 cm$^{-1}$. Only the dominant contributions are shown. For notation, see Fig. 5

| Wavenumber | Potential energy distribution |
|---|---|
| 1637 | $0.16\ Q_1\ -0.07\ Q_2\ +0.28\ Q_3\ -0.07\ Q_4\ +0.11\ Q_5$ |
| 1623 | $0.26\ Q_1\ -0.32\ Q_5$ |
| 1583 | $0.16\ Q_1\ -0.33\ Q_3\ +0.16\ Q_5$ |
| 1453 | $0.66\ \alpha'_3\ -0.14\ \alpha'_1\ -0.14\ \alpha'_2$ |
| 1449 | $0.47\ \alpha'_1\ -0.47\ \alpha'_2$ |
| 1429 | $0.21\ \alpha_1\ -0.10\ \beta_2\ -0.19\ \alpha_2\ +0.09\ \beta_{10}$ |
| 1400 | $0.17\ \alpha_1\ -0.08\ \beta_2\ +0.21\ \alpha_2\ -0.10\ \beta_{10}$ |
| 1382 | $0.15\ \alpha'_1\ +0.15\ \alpha'_2\ +0.10\ \alpha'_3$ $-0.14\ \beta'_1\ -0.14\ \beta'_2\ -0.17\ \beta'_3$ |
| 1340 | $0.23\ Q'\ -0.08\ Q_4\ +0.08\ \beta_5\ -0.19\ \beta_6$ |
| 1286 | $0.35\ \beta_3\ -0.20\ \beta_4\ +0.12\ \beta_1\ +0.20\ Q_1$ |
| 1272 | $0.19\ \beta_7\ -0.34\ \beta_8\ -0.12\ \beta_9\ -0.20\ Q_5$ |
| 1223 | $0.26\ \beta_5\ -0.14\ \beta_6\ +0.05\ \beta_7$ $+0.13\ Q_4\ +0.05\ Q_2\ -0.05\ Q'\ +0.06\ \gamma_4$ |
| 1142 | $0.34\ Q_2\ -0.10\ Q_4\ +0.11\ \beta_4\ +0.09\ \beta_1\ -0.07\ \beta_2$ |
| 1037 | $0.19\ \beta_9\ -0.21\ \beta_{10}\ +0.24\ \beta'_3$ |
| 1022 | $0.35\ \beta'_1\ -0.35\ \beta'_2\ +0.12\ \omega_2$ |
| 996 | $0.66\ \omega_5\ -0.15\ \omega_2\ -0.09\ \tau_5$ |
| 993 | $0.45\ \omega_2\ +0.16\ \omega_5\ -0.11\ \tau_1$ |
| 980 | $0.13\ \beta_9\ -0.13\ \beta_{10}\ +0.08\ \beta_1\ -0.09\ \beta_2\ -0.16\ \beta'_3\ +0.12\ Q'$ |
| 936 | $0.21\ \beta_1\ -0.24\ \beta_2\ -0.19\ Q_2$ |
| 908 | $0.38\ \omega_1\ -0.35\ \omega_6\ +0.14\ \tau_1\ -0.12\ \tau_5$ |
| 906 | $0.35\ \omega_1\ +0.37\ \omega_6\ +0.12\ \tau_1\ +0.14\ \tau_5$ |
| 812 | $0.76\ \omega_3$ |
| 792 | $0.53\ Q'\ +0.18\ Q_4$ |
| 687 | $0.40\ \tau_5\ +0.25\ \omega_5$ |
| 655 | $0.51\ \tau_1\ +0.31\ \omega_2$ |
| 576 | $0.24\ \gamma_5\ -0.20\ \gamma_6\ +0.08\ \gamma_2\ -0.08\ \gamma_4$ |
| 439 | $0.26\ \gamma_4\ -0.20\ \gamma_3\ +0.11\ \gamma_1\ -0.12\ Q_4$ |
| 421 | $0.41\ \omega_4\ +0.11\ \tau_2\ -0.13\ \tau_4$ |
| 360 | $0.24\ \gamma_1\ -0.12\ \gamma_5\ +0.10\ Q_2\ +0.11\ Q_3$ |
| 291 | $0.20\ \gamma_5\ +0.34\ \gamma_6$ |
| 275 | $0.48\ \tau_3\ +0.17\ \tau_4\ +0.10\ \omega_4$ |
| 204 | $0.43\ \tau_2\ +0.19\ \tau_3\ -0.11\ \omega_4\ +0.10\ \chi$ |
| 194 | $0.81\ \chi\ +0.11\ \tau_4$ |
| 158 | $0.14\ \gamma_1\ -0.34\ \gamma_2\ +0.16\ \gamma_3$ |
| 126 | $0.33\ \tau_3\ -0.21\ \tau_2\ -0.15\ \tau_4\ +0.17\ \omega_3$ |

For most of the vibrations in Table 9, the agreement between observed and calculated frequencies is good, even for the normal modes that are dominated by the strongly coupled CH rocks and C=C and C–C stretches. In particular, the VFF calculations are able to correctly predict the splitting of the C–C stretches for both E2MH and E3MH. The agreement again indicates the description of the normal modes found in Tables 4–6 to be reliable. However, there is some disagreement between observed and calculated frequencies for the in-plane rock of the methyl group (E3MH), for the in-plane skeletal deformations (E3MH), and for the low wavenumber torsions around the C–C bonds.

The force constants in Tables 7 and 8 that are related to the methyl group, were refined by us for isoprene, and for this compound the agreement between calculation and experiment was good. For isoprene, our calculated wavenumbers were 1036 cm$^{-1}$ for the out-of-plane, and 992 cm$^{-1}$ for the in-plane rock of the methyl group, whereas the ob-

served values are 1034 [15] and 990 cm$^{-1}$ [42], respectively.

In our VFF calculations for E2MH and dE2MH, the agreement between experiment and calculation is good for the methyl deformations around 1400 cm$^{-1}$, and for the in-plane methyl rock around 1010 cm$^{-1}$. The E2MH out-of-plane methyl rock may be assigned to the i.r. band at 1007 cm$^{-1}$ or to the weak band at 1040 cm$^{-1}$. Only for the latter assignment does experiment and calculation (1038 cm$^{-1}$) agree.

For E3MH, our VFF calculations are in agreement with experiment for the methyl deformations and for the out-of-plane methyl rock, whereas the agreement is poor for the in-plane rock. The latter disagreement may be due to the interaction between the vibrations of the methyl group and those of the polyene chain being different for methylation in the 2- and 3-positions.

The in-plane skeletal C=C–C deformation at lowest wavenumber is unobserved for both E2MH, dE2MH and E3MH. For $E$-1,3,5-hexatriene, we have found a

$b_u$ symmetry C=C–C deformation with medium i.r. intensity at 152 cm$^{-1}$ [1]. In the present spectra of E2MH, dE2MH and E3MH, we observe the Raman $R(\bar{\nu})$ spectrum in the region below 400 cm$^{-1}$, not the far-i.r. spectrum. Consequently, a low wavenumber, mainly i.r. active vibration may very well be unobserved in the present study.

The agreement between calculation and experiment for the E3MH 456 and 392 cm$^{-1}$ modes is not as good as for the corresponding modes in E2MH and dE2MH. However, the lowering of the E2MH 507 cm$^{-1}$ mode, and the increase in the E2MH 372 cm$^{-1}$ mode upon 3-methylation are predicted correctly.

After the above discussion of the imperfections in the description by the VFF calculations of the vibrational frequencies, attention should again be called to the fact that for most of the vibrations the agreement between calculation and experiment is fine. Moreover, although the vibrational patterns of E2MH, dE2MH and E3MH are quite different, the same force field is able to describe all three molecules, after changes in only three force constants, related to the central out-of-plane wags (see Table 8).

## The vibrational patterns of E2MH, dE2MH and E3MH

Comparing Figs 1 and 3, the most notable difference between the Raman spectra of *E*-2-methyl-hexatriene and *E*-3-methyl-hexatriene is the high intensity of the E3MH 1226 cm$^{-1}$ band. The ratio of the integrated intensities of the E3MH 1624 and 1226 cm$^{-1}$ bands is *ca* 3. For the strongest bands of E2MH, at 1627 and 1166 cm$^{-1}$, the ratio is *ca* 5. The E2MH 1166 cm$^{-1}$ band is described in Table 4 as C–C stretch, whereas the nature of the E3MH 1226 cm$^{-1}$ band is described in Table 6 as CH rock, strongly coupled to C–C stretches. The E3MH 1145 cm$^{-1}$ band, which is described in Table 6 as C–C stretch, is quite weak.

We have seen above that the observed spectra are reproduced satisfactorily by our VFF calculations. Consequently, it seems justified to build the following discussion of the vibrational patterns of E2MH, dE2MH and E3MH, not on the observed spectra in Tables 1–3, but on the spectra from the VFF calculations, as listed in Tables 4–6 and 9. The vibrational bands shall be referred to according to their frequencies as calculated by the VFF programs.

### $\nu$C=C and sCH$_2$

For E2MH, the C=C stretching normal modes at 1644, 1626 and 1574 cm$^{-1}$, are centered on $Q_5$, $Q_1$ and $Q_3$, respectively. The same pattern is found for dE2MH, whereas for E3MH the C=C stretches resemble the $+++$, $+0-$, and $+-+$ combinations predicted by symmetry for unsubstituted *E*-1,3,5-hexatriene. For the 1637 cm$^{-1}$ E3MH mode we note a $+-+-+$ combination of the $Q_1$–$Q_5$ stretches. The CH$_2$ scissoring vibrations are symmetrical and similar for all three compounds, despite deuteriation and changes in methyl substitution.

### dCH$_3$, wCH$_3$ and rCH$_3$

The methyl deformations around 1450 and 1380 cm$^{-1}$ are highly localized in the methyl group, and they are similar for all three compounds investigated. For E2MH and dE2MH, the out-of-plane wag of the methyl group is coupled to the wag of H$_7$, for E3MH it is coupled to the wag of H$_3$. This difference may be related to the fact that the methyl group of E2MH is described as H$_7$-eclipsed, whereas that of E3MH is described as H$_3$-eclipsed. The in-plane methyl rock of E3MH is strongly coupled to the neighbouring CH$_2$ rock, more than for E2MH, and it is predicted at significantly higher wavenumbers than for E2MH and dE2MH. However, the observed frequency is even higher.

### rCH$_2$

For E2MH, the CH$_2$ rock at 985 cm$^{-1}$ is localized on C$_6$, and is barely changed upon deuteriation, whereas the one at 949 cm$^{-1}$ is localized on C$_1$. Deuteriation at H$_4$ lowers the H$_4$ rock, which then couples to the neighbouring 949 cm$^{-1}$ (E2MH value) CH$_2$ rock, splitting it into 1029 and 890 cm$^{-1}$ vibrations. Moving the methyl group from C$_5$ in E2MH to C$_4$ in E3MH, leaves the C$_1$-centered 949 cm$^{-1}$ CH$_2$ rock nearly unaltered (E2MH 949, E3MH 936 cm$^{-1}$), whereas the CH$_2$ rock localized next to the methyl group is coupled to the in-plane rock of the methyl group through the C$_4$C$_7$H$_3'$ bend, and is split into 1037 and 980 cm$^{-1}$ vibrations.

### wCH$_2$

The pattern found above for the in-plane CH$_2$ rocks, localized in one end of the molecule, is also encountered for the out-of-plane CH$_2$ wags of E2MH and dE2MH. For E3MH, the 908 and 906 cm$^{-1}$ modes are essentially $C_{2h}$ symmetrical out-of-phase and in-phase combinations of the CH$_2$ wags centered on C$_1$ and C$_6$. As for the C=C stretches, the methyl substitution in E3MH gives rise to a smaller perturbation of the vibrations of $C_{2h}$ symmetrical *E*-1,3,5-hexatriene.

### wCH

For E2MH, the 1002 cm$^{-1}$ vibration is described as a rather pure wag of H$_3$, whereas the wags of the two central hydrogen atoms are strongly coupled, giving rise to vibrations at 910 and 870 cm$^{-1}$. Deuteriation of H$_4$ decouples the two central CH wags of dE2MH. For E3MH, we again encounter the symmetrical pattern, since the wags of H$_3$ and H$_5$ are coupled. A nearly pure wag of H$_4$ is found at 812 cm$^{-1}$, an unusually low wavenumber.

### Skeletal modes

The C=C torsions are centered in order of decreasing frequency on $\tau_5$, $\tau_1$ and $\tau_3$, for all three com-

Table 7. Non-zero force constants for E-2-methyl-hexatriene and 4-d-E-2-methyl-hexatriene. Units are mdyn/Å for diagonal stretch constants and stretch–stretch interactions, mdynÅ/rad² for diagonal bend or torsion constants and bend–bend interactions, and mdyn/rad for stretch–bend interactions

| Constant | Value | Constant | Value | Constant | Value | Constant | Value | Constant | Value |
|---|---|---|---|---|---|---|---|---|---|
| $q_1q_1$ | 5.479 | $q_1q_2$ | 0.008 | $q_1Q_1$ | 0.405 | $q_1\alpha_1$ | 0.004 | $q_1\beta_1$ | 0.224 |
| $q_2q_2$ | 5.479 | $q_2q_3$ | 0.068 | $q_2Q_1$ | 0.405 | $q_2\alpha_1$ | 0.004 | $q_2\beta_2$ | 0.224 |
| $q_3q_3$ | 5.470 | $q_3q_4$ | −0.024 | $q_3Q_1$ | 0.395 | $q_3Q_2$ | 0.370 | $q_3\beta_3$ | 0.228 |
| $q_3\beta_4$ | 0.215 | | | | | | | | |
| $q_4q_4$ | 5.470 | $q_4Q_2$ | 0.370 | $q_4Q_3$ | 0.395 | $q_4\beta_5$ | 0.215 | $q_4\beta_6$ | 0.228 |
| $q_4q_5$ | −0.024 | | | | | | | | |
| $Q_1Q_1$ | 8.320* | $Q_1Q_2$ | 0.230* | $Q_1Q_3$ | −0.243* | $Q_1\beta_1$ | 0.254 | $Q_1\beta_2$ | 0.254 |
| $Q_1\gamma_1$ | 0.179 | $Q_1\beta_3$ | 0.262 | $Q_1\beta_5$ | −0.036 | | | | |
| $Q_2Q_2$ | 4.640* | $Q_2Q_3$ | 0.230* | $Q_2\beta_1$ | −0.036 | $Q_2\gamma_1$ | 0.189 | $Q_2\beta_4$ | 0.262 |
| $Q_2\gamma_2$ | 0.189 | $Q_2\beta_5$ | 0.262 | $Q_2Q_4$ | −0.126* | $Q_2\beta_7$ | −0.036 | | |
| $Q_3Q_3$ | 7.650* | $Q_3\beta_4$ | −0.036 | $Q_3\gamma_2$ | 0.179 | $Q_3\beta_6$ | 0.262 | $Q_3q_5$ | 0.395 |
| $Q_3Q_5$ | −0.243* | $Q_3Q_4$ | 0.230* | $Q_3\gamma_4$ | 0.059† | $Q_3\gamma_5$ | −0.059† | $Q_3\gamma_3$ | 0.179 |
| $Q_3\beta_7$ | 0.262 | | | | | | | | |
| $\alpha_1\alpha_1$ | 0.436 | | | | | | | | |
| $\beta_1\beta_1$ | 0.581 | $\beta_1\gamma_1$ | 0.026 | $\beta_1\beta_3$ | 0.067 | | | | |
| $\beta_2\beta_2$ | 0.581 | $\beta_2\gamma_1$ | −0.028 | | | | | | |
| $\gamma_1\gamma_1$ | 0.778 | $\gamma_1\gamma_2$ | 0.145 | $\gamma_1\beta_5$ | 0.026 | | | | |
| $\beta_3\beta_3$ | 0.571* | | | | | | | | |
| $\beta_4\beta_4$ | 0.571* | $\beta_4\gamma_2$ | 0.026 | $\beta_4\beta_5$ | 0.067 | | | | |
| $\gamma_2\gamma_2$ | 0.980* | $\gamma_2\gamma_3$ | 0.145 | $\gamma_2\beta_7$ | 0.026 | | | | |
| $\beta_5\beta_5$ | 0.557* | | | | | | | | |
| $\beta_6\beta_6$ | 0.557* | $\beta_6Q_4$ | −0.036 | $\beta_6\gamma_3$ | 0.026 | $\beta_6\beta_7$ | 0.067 | | |
| $q_6q_6$ | 5.479 | $q_6q_7$ | 0.008 | $q_6Q_5$ | 0.405 | $q_6\alpha_2$ | 0.004 | $q_6\beta_9$ | 0.224 |
| $q_7q_7$ | 5.479 | $q_7Q_5$ | 0.405 | $q_7\alpha_2$ | 0.004 | $q_7\beta_{10}$ | 0.224 | | |
| $q_5q_5$ | 5.470 | $q_5Q_4$ | 0.370 | $q_5\beta_8$ | 0.215 | $q_5\beta_7$ | 0.228 | $q_5\beta_{10}$ | 0.254 |
| $Q_5Q_5$ | 8.320* | $Q_5Q_4$ | 0.230* | $Q_5Q'$ | 0.340‡ | $Q_5\beta_9$ | 0.254 | $Q_5\beta_1'$ | 0.059† |
| $Q_5\gamma_4$ | 0.179 | $Q_5\gamma_6$ | 0.179 | $Q_5\gamma_3$ | 0.059† | $Q_5\beta_8$ | −0.059† | | |
| $Q_5\beta_2'$ | 0.059† | $Q_5\beta_3'$ | −0.059† | | | | | | |
| $Q_4Q_4$ | 4.640* | $Q_4Q'$ | 0.340‡ | $Q_4\beta_9$ | −0.059† | $Q_4\beta_{10}$ | 0.059† | $Q_4\gamma_4$ | 0.189 |
| $Q_4\gamma_5$ | 0.189 | $Q_4\gamma_3$ | 0.189 | $Q_4\beta_8$ | 0.262 | $Q_4\beta_1'$ | −0.059† | $Q_4\beta_2'$ | −0.059† |
| $Q_4\beta_3'$ | 0.059† | | | | | | | | |
| $Q'Q'$ | 4.160‡ | $Q'\beta_9$ | 0.059† | $Q'\beta_{10}$ | −0.059† | $Q'\gamma_6$ | 0.320§ | $Q'\gamma_5$ | 0.320§ |
| $Q'\gamma_3$ | −0.059† | $Q'\beta_8$ | 0.059† | $Q'\beta_1'$ | 0.287§ | $Q'\beta_2'$ | 0.287§ | $Q'\beta_3'$ | 0.287§ |
| $\alpha_2\alpha_2$ | 0.436 | | | | | | | | |
| $\beta_9\beta_9$ | 0.581 | $\beta_9\gamma_4$ | 0.026 | $\beta_9\gamma_6$ | 0.067† | | | | |
| $\beta_{10}\beta_{10}$ | 0.581 | $\beta_{10}\gamma_4$ | 0.067† | $\beta_{10}\gamma_6$ | 0.026 | | | | |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| $\gamma_4\gamma_4$ | 0.980* | $\gamma_4\gamma_3$ | 0.145 | $\gamma_4\beta_8$ | 0.026 | $\gamma_5\beta_3$ | 0.067† | $\beta'_1\omega_6$ | 0.018† |
| $\gamma_6\gamma_6$ | 1.250‖ | $\gamma_6\beta_3$ | −0.067† | $\gamma_5\beta_8$ | 0.067† | | | $\beta_2\tau_4$ | −0.056† |
| $\gamma_5\gamma_5$ | 1.250‖ | $\gamma_5\gamma_3$ | 0.338† | | | | | | |
| $\gamma_3\gamma_3$ | 0.980* | | | | | | | | |
| $\beta_8\beta_8$ | 0.557* | | | | | | | | |
| $\beta_7\beta_7$ | 0.557* | | | | | | | | |
| $q'_1q'_1$ | 5.064‡ | $q'_1q'_2$ | 0.101‡ | $q'_1q'_3$ | 0.101‡ | | | | |
| $q'_2q'_2$ | 5.064‡ | $q'_2q'_3$ | 0.101‡ | | | | | | |
| $q'_3q'_3$ | 5.064‡ | | | | | | | | |
| $\alpha'_1\alpha'_1$ | 0.581‡ | $\alpha'_1\alpha'_2$ | −0.009† | $\alpha'_1\alpha'_3$ | −0.009† | | | | |
| $\alpha'_2\alpha'_2$ | 0.581‡ | $\alpha'_2\alpha'_3$ | −0.009† | | | | | | |
| $\alpha'_3\alpha'_3$ | 0.581‡ | | | | | | | | |
| $\beta'_1\beta'_1$ | 0.673‡ | $\beta'_1\beta'_2$ | 0.034† | $\beta'_1\omega_4$ | 0.018† | $\beta'_1\omega_5$ | 0.080† | | |
| $\beta'_1\tau_4$ | 0.056† | $\beta'_1\tau_5$ | −0.056‡ | $\beta_2\omega_5$ | −0.080† | $\beta_2\omega_6$ | −0.018† | | |
| $\beta'_2\beta'_2$ | 0.673‡ | $\beta_2\omega_4$ | −0.018† | | | | | | |
| $\beta'_2\tau_5$ | 0.056† | | | | | | | | |
| $\beta'_3\beta'_3$ | 0.673‡ | | | | | | | | |
| $\omega_1\omega_1$ | 0.383 | $\omega_1\omega_2$ | 0.198 | $\omega_1\tau_1$ | −0.292 | $\omega_2\tau_2$ | 0.116 | $\omega_5\chi$ | 0.030‡ |
| $\omega_2\omega_2$ | 0.497 | $\omega_2\omega_3$ | 0.055¶ | $\omega_2\tau_1$ | −0.292 | $\omega_3\tau_3$ | −0.301¶ | | |
| $\omega_3\omega_3$ | 0.435‖ | $\omega_3\omega_4$ | 0.120‖ | $\omega_3\tau_2$ | 0.116 | $\omega_4\tau_4$ | 0.116 | | |
| $\omega_4\omega_4$ | 0.435‖ | $\omega_4\omega_5$ | 0.055¶ | $\omega_4\tau_3$ | −0.301¶ | $\omega_5\tau_5$ | −0.292 | | |
| $\omega_5\omega_5$ | 0.589¶ | $\omega_5\omega_6$ | 0.198 | $\omega_5\tau_4$ | 0.116 | | | | |
| $\omega_6\omega_6$ | 0.383 | $\omega_6\tau_5$ | −0.292 | | | | | | |
| $\tau_1\tau_1$ | 0.545 | $\tau_1\tau_2$ | 0.011 | $\tau_1\tau_3$ | −0.017 | | | | |
| $\tau_2\tau_2$ | 0.261‖ | $\tau_2\tau_3$ | 0.011 | $\tau_3\tau_5$ | −0.017 | | | | |
| $\tau_3\tau_3$ | 0.545¶ | $\tau_3\tau_4$ | 0.011 | | | | | | |
| $\tau_4\tau_4$ | 0.297‖ | $\tau_4\tau_5$ | 0.011 | | | | | | |
| $\tau_5\tau_5$ | 0.545 | | | | | | | | |
| $\chi\chi$ | 0.027‡ | | | | | | | | |

Values not superscripted are from Ref [15], butadiene.
*Iterated by us for $E$-1,3,5-hexatriene.
†From Ref. [15], isoprene.
‡Iterated by us for isoprene.
§From Ref. [15], propene.
‖Iterated by us for $E$-2-methyl-hexatriene.
¶From Ref. [15], $E$-1,3,5-hexatriene.

Table 8. Non-zero force constants for *E*-3-methyl-hexatriene. Units are mdyn/Å for diagonal stretch constants and stretch–stretch interactions, mdyn Å/rad$^2$ for diagonal bend or torsion constants and bend–bend interactions, and mdyn/rad for stretch–bend interactions

| Constant | Value | Constant | Value | Constant | Value | Constant | Value | Constant | Value |
|---|---|---|---|---|---|---|---|---|---|
| $q_1q_1$ | 5.479 | $q_1q_2$ | 0.008 | $q_1Q_1$ | 0.405 | $q_1\alpha_1$ | 0.004 | $q_1\beta_1$ | 0.224 |
| $q_2q_2$ | 5.479 | $q_2q_3$ | 0.068 | $q_2Q_1$ | 0.405 | $q_2\alpha_1$ | 0.004 | $q_2\beta_2$ | 0.224 |
| $q_3q_3$ | 5.470 | $q_3q_4$ | −0.024 | $q_3Q_1$ | 0.395 | $q_3Q_2$ | 0.370 | $q_3\beta_3$ | 0.228 |
| $q_3\beta_4$ | 0.215 | | | | | | | | |
| $q_4q_4$ | 5.470 | $q_4Q_2$ | 0.370 | $q_4Q_3$ | 0.395 | $q_4\beta_5$ | 0.215 | $q_4\beta_6$ | 0.228 |
| $Q_1Q_1$ | 8.320 | $Q_1Q_2$ | 0.230 | $Q_1Q_3$ | −0.243 | $Q_1\beta_1$ | 0.254 | $Q_1\beta_2$ | 0.254 |
| $Q_1\gamma_1$ | 0.179 | $Q_1\beta_3$ | 0.262 | $Q_1\beta_5$ | −0.036 | | | | |
| $Q_2Q_2$ | 4.640 | $Q_2Q_3$ | 0.230 | $Q_2\beta_1$ | −0.036 | $Q_2\gamma_1$ | 0.189 | $Q_2\beta_4$ | 0.262 |
| $Q_2\gamma_2$ | 0.189 | $Q_2\beta_5$ | 0.262 | $Q_2Q_4$ | −0.126 | $Q_2\gamma_4$ | −0.059 | | |
| $Q_3Q_3$ | 7.650 | $Q_3\beta_4$ | −0.036 | $Q_3\gamma_2$ | 0.179 | $Q_3\beta_6$ | 0.262 | $Q_3Q_5$ | −0.243 |
| $Q_3Q_4$ | 0.230 | $Q_3Q'$ | 0.340 | $Q_3\gamma_6$ | 0.059 | $Q_3\beta_7$ | −0.036 | $Q_3\gamma_3$ | 0.179 |
| $Q_3\gamma_4$ | 0.179 | $Q_3\beta_1$ | 0.059 | $Q_3\beta_2$ | 0.059 | $Q_3\beta_3$ | −0.059 | | |
| $\alpha_1\alpha_1$ | 0.436 | | | | | | | | |
| $\beta_1\beta_1$ | 0.581 | $\beta_1\gamma_1$ | 0.026 | $\beta_1\beta_3$ | 0.067 | | | | |
| $\beta_2\beta_2$ | 0.581 | $\beta_2\gamma_1$ | −0.028 | | | | | | |
| $\gamma_1\gamma_1$ | 0.778 | $\gamma_1\gamma_2$ | 0.145 | $\gamma_1\beta_5$ | 0.026 | | | | |
| $\beta_3\beta_3$ | 0.571 | | | | | | | | |
| $\beta_4\beta_4$ | 0.571 | $\beta_4\gamma_2$ | 0.026 | $\beta_4\beta_5$ | 0.067 | | | | |
| $\gamma_2\gamma_2$ | 0.980 | $\gamma_2\gamma_3$ | 0.145 | $\gamma_2\gamma_4$ | 0.338 | | | | |
| $\beta_5\beta_5$ | 0.557 | | | | | | | | |
| $\beta_6\beta_6$ | 0.557 | $\beta_6Q_4$ | −0.036 | $\beta_6\gamma_3$ | 0.026 | $\beta_6\gamma_4$ | 0.067 | | |
| $q_6q_6$ | 5.479 | $q_6q_7$ | 0.008 | $q_6Q_5$ | 0.405 | $q_6\alpha_2$ | 0.004 | $q_6\beta_9$ | 0.224 |
| $q_7q_7$ | 5.479 | $q_7q_5$ | 0.068 | $q_7Q_5$ | 0.405 | $q_7\alpha_2$ | 0.004 | $q_7\beta_{10}$ | 0.224 |
| $q_5q_5$ | 5.470 | $q_5Q_5$ | 0.395 | $q_5Q_4$ | 0.370 | $q_5\beta_8$ | 0.228 | $q_5\beta_7$ | 0.215 |
| $Q_5Q_5$ | 8.320 | $Q_5Q_4$ | 0.230 | $Q_5\beta_9$ | 0.254 | $Q_5\beta_{10}$ | 0.254 | | |
| $Q_5\beta_8$ | 0.262 | $Q_5\gamma_5$ | 0.059 | $Q_5\gamma_5$ | −0.059 | | | $Q_5\gamma_6$ | 0.179 |
| $Q_4Q_4$ | 4.640 | $Q_4Q'$ | 0.340 | $Q_4\beta_9$ | −0.036 | $Q_4\gamma_6$ | 0.189 | $Q_4\beta_7$ | 0.262 |
| $Q'Q'$ | 4.160 | $Q_4\gamma_5$ | 0.189 | $Q_4\beta_1$ | −0.059 | $Q_4\beta_2$ | −0.059 | $Q_4\beta_3$ | 0.059 |
| $Q'\beta_1$ | 0.287 | $Q'\gamma_6$ | −0.059 | $Q'\beta_7$ | 0.059 | | | | |
| $\alpha_2\alpha_2$ | 0.436 | $Q'\beta_2$ | 0.287 | $Q'\beta_3$ | 0.287 | $Q'\gamma_5$ | 0.320 | $Q'\gamma_4$ | 0.320 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| $\beta_9\beta_9$ | 0.581 | $\beta_9\gamma_6$ | 0.026 | $\beta_9\beta_8$ | 0.067 | | | | |
| $\beta_{10}\beta_{10}$ | 0.581 | $\beta_{10}\gamma_6$ | -0.028 | $\gamma_6\gamma_5$ | 0.338 | | | | |
| $\gamma_6\gamma_6$ | 0.778 | $\gamma_6\gamma_3$ | 0.145 | $\beta_7\gamma_5$ | 0.067 | | | | |
| $\beta_8\beta_8$ | 0.557 | | | | | | | | |
| $\beta_7\beta_7$ | 0.557 | $\beta_7\beta_3$ | 0.026 | | | | | | |
| $\gamma_3\gamma_3$ | 0.980 | | | | | | | | |
| $\gamma_5\gamma_5$ | 1.250 | $\gamma_5\beta'_3$ | 0.067 | | | | | | |
| $\gamma_4\gamma_4$ | 1.250 | $\gamma_4\beta'_3$ | -0.067 | | | | | | |
| $q_1q_1$ | 5.064 | $q_1q'_2$ | 0.101 | $q'_1q'_3$ | 0.101 | | | | |
| $q_2q_2$ | 5.064 | $q_2q_3$ | 0.101 | | | | | | |
| $q_3q_3$ | 5.064 | | | | | | | | |
| $\alpha_1\alpha_1$ | 0.581 | $\alpha_1\alpha'_2$ | -0.009 | $\alpha'_1\alpha'_3$ | -0.009 | | | | |
| $\alpha_2\alpha_2$ | 0.581 | $\alpha_2\alpha'_3$ | -0.009 | | | | | | |
| $\alpha_3\alpha_3$ | 0.581 | | | | | | | | |
| $\beta'_1\beta'_1$ | 0.673 | $\beta'_1\beta'_2$ | 0.034 | $\beta'_1\omega_3$ | 0.018 | $\beta'_1\omega_4$ | 0.080 | $\beta'_1\omega_5$ | 0.018 |
| $\beta'_1\tau_3$ | -0.056 | $\beta'_1\tau_4$ | 0.056 | $\beta'_2\omega_4$ | -0.080 | $\beta'_2\omega_5$ | -0.018 | $\beta'_2\tau_3$ | 0.056 |
| $\beta'_2\beta'_2$ | 0.673 | $\beta'_2\omega_3$ | -0.018 | | | | | | |
| $\beta'_2\tau_4$ | -0.056 | | | | | | | | |
| $\beta'_3\beta'_3$ | 0.673 | | | | | | | | |
| $\omega_1\omega_1$ | 0.383 | $\omega_1\omega_2$ | 0.198 | $\omega_1\tau_1$ | -0.292 | | | | |
| $\omega_2\omega_2$ | 0.497 | $\omega_2\omega_3$ | 0.055 | $\omega_2\tau_1$ | -0.292 | $\omega_2\tau_2$ | 0.116 | | |
| $\omega_3\omega_3$ | 0.405* | $\omega_3\omega_4$ | 0.196* | $\omega_3\tau_2$ | 0.116 | $\omega_3\tau_3$ | -0.301 | | |
| $\omega_4\omega_4$ | 0.557* | $\omega_4\omega_5$ | 0.055 | $\omega_4\tau_3$ | -0.301 | $\omega_4\tau_4$ | 0.116 | $\omega_4\chi$ | 0.030 |
| $\omega_5\omega_5$ | 0.497 | $\omega_5\omega_6$ | 0.198 | $\omega_5\tau_4$ | 0.116 | $\omega_5\tau_5$ | -0.292 | | |
| $\omega_6\omega_6$ | 0.383 | $\omega_6\tau_5$ | -0.292 | | | | | | |
| $\tau_1\tau_1$ | 0.545 | $\tau_1\tau_2$ | 0.011 | $\tau_1\tau_3$ | -0.017 | | | | |
| $\tau_2\tau_2$ | 0.261 | $\tau_2\tau_3$ | 0.011 | | | | | | |
| $\tau_3\tau_3$ | 0.545 | $\tau_3\tau_4$ | 0.011 | $\tau_3\tau_5$ | -0.017 | | | | |
| $\tau_4\tau_4$ | 0.297 | $\tau_4\tau_5$ | 0.011 | | | | | | |
| $\tau_5\tau_5$ | 0.545 | | | | | | | | |
| $XX$ | 0.027 | | | | | | | | |

Values not superscripted are transferred from Table 7.
*Iterated by us for E-3-methyl-hexatriene.

Table 9. Symmetry, observed (mostly Raman values) and calculated (VFF) wavenumbers (cm$^{-1}$), and approximate description of normal modes of vibration of E-2-methyl-hexatriene (E2MH), 4-d-E-2-methyl-hexatriene (dE2MH), and E-3-methyl-hexatriene (E3MH)

| | a' | | | | | | a'' | | | | | |
| | E2MH | | dE2MH | | E3MH | | E2MH | | dE2MH | | E3MH | |
| | obs | calc | obs | calc | obs | calc | obs | calc | obs | calc | obs | calc |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| dCH | 1455 | 1453 | 1450 | 1453 | 1459 | 1453 | 1440 | 1449 | 1439 | 1449 | 1443 | 1449 |
| rCH3 | 1374 | 1381 | 1376 | 1381 | 1387 | 1382 | | | | | | |
| wCH3 | 1019 | 1008 | 1011 | 996 | 1067 | 1037 | | | | | | |
| sCH2 | 1415 | 1428 | 1413 | 1426 | 1424 | 1429 | 1040 | 1038 | — | 1036 | 1034 | 1022 |
| | 1398 | 1403 | 1393 | 1403 | 1402 | 1400 | | | | | | |
| rCH2 | 988 | 985 | 980 | 985 | 985 | 980 | | | | | | |
| | 947 | 949 | 1039 | 1029 | 946 | 936 | | | | | | |
| wCH2 | | | | | | | 894 | 908 | 907 | 909 | 906 | 908 |
| | | | | | | | 888 | 897 | 897 | 897 | 901 | 906 |
| rCH | 1301 | 1287 | 1292 | 1286 | 1298 | 1286 | | | | | | |
| | 1288 | 1284 | 1274 | 1268 | 1257 | 1272 | | | | | | |
| | 1257 | 1251 | 884 | 890 | 1226 | 1223 | | | | | | |
| wCH | | | | | | | 1002 | 1002 | 992 | 1000 | 990 | 996 |
| | | | | | | | 900 | 910 | 900 | 899 | 984 | 993 |
| | | | | | | | 865 | 870 | 768 | 740 | 803 | 812 |
| *Skeleton* | | | | | | | | | | | | |
| vC=C | 1631 | 1644 | 1628 | 1644 | 1624 | 1637 | | | | | | |
| | 1627 | 1626 | 1615 | 1620 | 1620 | 1623 | | | | | | |
| | 1585 | 1574 | 1578 | 1563 | 1577 | 1583 | | | | | | |
| vC–C | 1316 | 1320 | 1311 | 1314 | 1348 | 1340 | | | | | | |
| | 1166 | 1162 | 1159 | 1159 | 1145 | 1142 | | | | | | |
| | 843 | 829 | 839 | 829 | 788 | 792 | | | | | | |
| dCCC | 540 | 549 | 515 | 530 | 584 | 576 | | | | | | |
| | 507 | 513 | 506 | 512 | 456 | 439 | | | | | | |
| | 372 | 358 | 370 | 358 | 392 | 360 | | | | | | |
| | 325 | 330 | 320 | 326 | 301 | 291 | | | | | | |
| | — | 134 | — | 134 | — | 158 | | | | | | |
| tC=C | | | | | | | 705 | 707 | 707 | 707 | 685 | 687 |
| | | | | | | | 634 | 633 | 612 | 611 | 648 | 655 |
| | | | | | | | 186 | 174 | 169 | 166 | 256 | 275 |
| wCH3 | | | | | | | 493 | 484 | 485 | 478 | 420 | 421 |
| rotCH3 | | | | | | | 229 | 202 | 225 | 201 | 181 | 194 |
| tC–C | | | | | | | — | 309 | — | 296 | — | 204 |
| | | | | | | | 146 | 114 | 143 | 114 | 156 | 126 |

pounds. The CC torsion at lowest frequency is a $- +$ $-$ combination of the $\tau_2$, $\tau_3$ and $\tau_4$ torsions for all three compounds. The 309 cm$^{-1}$ vibration of E2MH and the 296 cm$^{-1}$ vibration of dE2MH are combinations of the $\tau_2$ and $\tau_4$ torsions, whereas the 204 cm$^{-1}$ vibration of E3MH is centered on $\tau_2$. This is in contrast to the above, where E3MH has shown the most symmetrical vibrations, and indicates that the methyl substituent on $C_4$ decouples the C–C torsions.

The skeletal methyl wag and, especially, the torsion of the methyl group couple little to other vibrations for all three compounds. Because of the crowded environment of the methyl hydrogens in E3MH, the barrier to methyl rotation should be lower than for E2MH. This indeed seems to be the case, since the methyl rotation is observed experimentally at 229 cm$^{-1}$ for E2MH, at 225 cm$^{-1}$ for dE2MH, and at 181 cm$^{-1}$ for E3MH.

*vC–C and rCH*

For *E*-1,3,5-hexatriene, the two in-chain C–C stretches couple, and lead to an in-phase combination at 1188 cm$^{-1}$ and an out-of-phase combination at 1132 cm$^{-1}$ [1]. For isoprene, the two C–C stretches (one in-chain and one lateral) couple strongly, and give rise to an out-of-phase combination at 1303 cm$^{-1}$ and an in-phase combination at 778 cm$^{-1}$ [15]. The same pattern as for isoprene is encountered for lateral methylation in *E*-2,5-dimethyl-1,3,5-hexatriene [1].

For isoprene, *E*-2,5-dimethyl-hexatriene and E2MH, the methyl groups are substituted on terminal C=C bonds, whereas for E3MH the methyl group is substituted on the central C=C bond. Hence, we expect isoprene, *E*-2,5-dimethyl-hexatriene and E2MH to resemble each other with respect to coupling between CC stretches, whereas E3MH may be different.

For E2MH, one might envisage two situations. If the two ends of the molecule interact little, one would expect to find bands corresponding to the *E*-hexatriene case and bands that correspond to the *E*-2,5-dimethyl-hexatriene situation. If the two ends interact strongly, one would expect an intermediate situation. Actually, we find for E2MH, one normal mode that is close to those of *E*-hexatriene and two that correspond to *E*-2,5-dimethyl-hexatriene normal modes. Thus it seems that the chain C–C stretch, which has no atom in common with the C-methyl stretch, is coupled little to the other C–C stretches, so the two ends of the molecule interact little with respect to coupling between C–C stretching vibrations. Comparing E2MH and E3MH, we can also follow how the coupling of the C–C stretches with the CH rocks is altered with the position of the methyl group. We shall now discuss these effects more precisely.

For E2MH, the three CH rocks are centered on $H_3$, $H_5$ and $H_4$, in order of decreasing wavenumber, and are coupled to each other and to C=C and C–C stretches. The $Q_2$ stretch couples to the neighbouring $CH_2$ and $H_3$ rocks, whereas the $Q_4$ and $Q'$ stretches

couple and split into out-of-phase 1320 and in-phase 829 cm$^{-1}$ combinations. Deuteration at $H_4$ does not change this pattern for E2MH much, except for the $H_4$ rock, which is decoupled from the $H_5$ rock and lowered to a frequency where it can couple to the $C_1H_1H_2$ rock, leading to vibrational modes at 1029 and 890 cm$^{-1}$. Although 890 cm$^{-1}$ corresponds to a decrease by a factor of $\sqrt{2}$ of 1251 cm$^{-1}$ (the frequency of the $H_4$ rock in E2MH), there is a substantial $H_4$ rock contribution to both the 1029 and 890 cm$^{-1}$ modes.

For E2MH, we thus find that the $Q_4$ and $Q'$ stretches couple in the same way as for isoprene, whereas the $Q_2$ stretch couples little to the other C–C stretches, and is found at a frequency (1166 cm$^{-1}$ experimentally) close to the average of the 1188 and 1132 cm$^{-1}$ C–C stretches of *E*-1,3,5-hexatriene.

We now go on to E3MH. The vibrational pattern of E3MH is more complicated, with stronger coupling between C–C stretches and CH rocks, as reflected in the presence of two bands in the observed spectra, at 1413 and 1323 cm$^{-1}$, that cannot be assigned to fundamentals. We shall now assign these two bands.

With its high intensity, the experimental 1413 cm$^{-1}$ band is likely to be a Fermi resonance. The experimental 420 cm$^{-1}$ band, combined with the experimental 990 cm$^{-1}$ band (or with the 984 cm$^{-1}$ band), gives rise to a 1410 (or 1404) cm$^{-1}$ combination of $a'$ symmetry. This 1410 (or 1404) cm$^{-1}$ combination may be in Fermi resonance with the 1402 cm$^{-1}$ band of $a'$ symmetry. The 1323 cm$^{-1}$ band is likely to represent a combination, probably between the 420 cm$^{-1}$ methyl wag and one or both of the 906 and 901 cm$^{-1}$ $CH_2$ wags.

Turning now to the C–C stretches of E3MH, these may be viewed in two different ways. In the first view, the C–C stretches of E3MH may be described as for E2MH and dE2MH, with the out-of-phase combination of the $Q_4$ and $Q'$ stretches at 1340 cm$^{-1}$, the in-phase combination at 792 cm$^{-1}$, and the $Q_2$ stretch at 1142 cm$^{-1}$.

Alternatively, in the second view one may speak of hexatriene-like and isoprene-like combinations of the C–C stretches, that again couple to each other. The $Q_2$ and $Q_4$ stretches couple hexatriene-like, leading to a $Q_2 + Q_4$ combination around 1188 cm$^{-1}$ and a $Q_2 - Q_4$ combination around 1132 cm$^{-1}$. The $Q_4$ and $Q'$ stretches couple isoprene-like, leading to a $Q_4 - Q'$ combination around 1303 cm$^{-1}$ and a $Q_4 + Q'$ combination around 778 cm$^{-1}$. The two lowest of these vibrations ($Q_4 + Q'$ and $Q_2 - Q_4$) are sufficiently isolated in frequency and so do not couple further. Their calculated frequencies (792 and 1142 cm$^{-1}$) support this picture.

$Q_4 - Q'$ and $Q_2 + Q_4$ couple with each other and with the $H_4$ rock. The calculated 1223 cm$^{-1}$ mode thus contains both $Q_2 + Q_4$ and $Q_4 - Q'$ character, though it is dominated by the $H_4$ rock. The calculated 1340 cm$^{-1}$ mode contains $H_4$ rock, but is dominated by $Q_4 - Q'$. With the appearance of modes with $Q_2$

$+Q_4$ and $Q_2 - Q_4$ character, we again see a resemblance between E3MH and $E$-1,3,5-hexatriene.

The fact that the coupling between $Q'$ stretch and $H_4$ rock in E3MH is stronger than the coupling in E2MH between $Q'$ stretch and $H_5$ rock (and the coupling in E3MH between $Q'$ stretch and $H_5$ rock) is in agreement with expectations, since vibrational coupling is usually stronger through a C=C double bond than through a C–C single bond.

The character found in the present study for the C–C stretching modes of E2MH is in agreement with our interpretation of the C–C stretching modes of $E$-2,5-dimethyl-hexatriene in Ref. [1]. The coupling between chain and lateral C–C stretches has been observed previously for methylated derivatives of butadiene [15, 44], and has been termed a $\nu CC_2$ stretch.

We have here found that in E2MH the $Q_4 + Q'$ and $Q_4 - Q'$ combinations couple little with the $Q_2$ stretch. Moreover, we have found that for E3MH the $Q_2$ stretch is not isolated, since the $Q_4$ stretch couples with both the $Q'$ stretch and the $Q_2$ stretch. This result is important, since E3MH is an appropriate model for the longer polyenes like retinal and $\beta$-carotene, where the methyl groups are substituted on internal C=C bonds, as in E3MH.

## CONCLUSIONS

In the present paper we have obtained the vibrational spectra of $E$-2-methyl-hexatriene, 4-$d$-$E$-2-methyl-hexatriene, and $E$-3-methyl-hexatriene. The spectra are interpreted using semi-empirical QCFF/$\pi$ calculations and empirical valence force field calculations. For QCFF/$\pi$ the agreement with experiment was unsatisfactory. The empirical valence force fields of the three compounds were iterated on the basis of valence force fields of butadiene, isoprene and $E$-hexatriene, and the agreement of final calculated frequencies with experimental ones was fine. Consequently, our discussion of the molecular vibrations is based on the calculations using empirical valence force fields.

We have found that many normal modes of $E$-hexatriene are changed less by 3-methylation than by 2-methylation. Methylation in the 2-position seems to perturb the $C_{2h}$ symmetry of $E$-hexatriene more than does 3-methylation.

A distinction is made in Ref. [38] between unsubstituted polyenes with global symmetry coordinates, and retinal with local symmetry coordinates. The fact that the vibrations of $E$-3-methyl-hexatriene are more similar to the vibrations of $E$-hexatriene than are the vibrations of $E$-2-methyl-hexatriene indicates a modification of this distinction, since the position of the substitution also determines the degree to which the symmetry coordinates can be characterized as global or local. In this respect, the local symmetry of the methyl groups of the all-*trans* isomers of retinal and $\beta$-carotene rather corresponds to $E$-3-methyl-hexatriene than to $E$-2-methyl-hexatriene.

The coupling between chain C–C and C–methyl stretches takes place in both $E$-2-methyl-hexatriene and $E$-3-methyl-hexatriene. However, coupling between these C–C stretch combinations and the isolated C–C stretch is found only for $E$-3-methyl-hexatriene, where combinations of the chain C–C stretches similar to those of $E$-hexatriene are present and couple to the C–methyl stretch.

We also find that coupling between the chain C–C and C–methyl stretch combination and neighbouring CH rock is stronger through a C=C bond ($E$-3-methyl-hexatriene) than through a C–C bond ($E$-2-methyl-hexatriene). This result agrees with expectation.

On the basis of the QCFF/$\pi$ calculation we assume the methyl group of $E$-2-methyl-hexatriene to be eclipsed, and the $E$-3-methyl-hexatriene methyl group to be staggered with respect to the neighbouring $CH_2$ group. Greater steric hindrance in the most stable rotamer implies that the barrier to rotation of the methyl group must be lower for $E$-3-methyl-hexatriene than for $E$-2-methyl-hexatriene. This is qualitatively confirmed by a study of relaxation rates in $^1H$ NMR.

The methyl deformations are highly localized in the methyl group. The in-plane rocks and out-of-plane wags of the methyl group are strongly coupled to neighbouring CH and $CH_2$ in-plane rocks and out-of-plane wags, respectively. The differences between $E$-2-methyl-hexatriene and $E$-3-methyl-hexatriene in these couplings can be explained by the differences in methyl conformation mentioned above, and the differences in the barrier to methyl rotation is reflected in the frequencies of the methyl rotation.

## REFERENCES

[1] F. W. LANGKILDE, R. WILBRANDT, O. F. NIELSEN, D. H. CHRISTENSEN and F. M. NICOLAISEN, *Spectrochim. Acta* **43A**, 1209 (1987).
[2] E. R. LIPPINCOTT, C. E. WHITE and J. P. SIBILIA, *J. Am. chem. Soc.* **80**, 2926 (1958).
[3] E. R. LIPPINCOTT and T. E. KENNEY, *J. Am. chem. Soc.* **84**, 3641 (1962).
[4] R. M. GAVIN JR and S. A. RICE, *J. chem. Phys.* **55**, 2675 (1971).
[5] Y. N. PANCHENKO, Y. A. PENTIN and E. B. RUSACH, *Russ. J. phys. Chem.* **49**, 1536 (1975).
[6] Y. N. PANCHENKO and E. B. RUSACH, *Chem. Bull., Moscow State Univ.* **20**, 221 (1979).
[7] D. RAKOVIC, S. A. STEPANYAN, L. A. GRIBOV and Y. N. PANCHENKO, *J. molec. Struct.* **90**, 363 (1982).

[8] Y. N. PANCHENKO, P. CSÁSZÁR and F. TÖRÖK, *Acta chim. hung.* **113**, 149 (1983).

[9] C. W. BOCK, Y. N. PANCHENKO, S. V. KRASNOSHCHIOKOV and V. I. PUPYSHEV, *J. molec. Struct.* **148**, 131 (1986).

[10] A. C. LASAGA, R. J. AERNI and M. KARPLUS, *J. chem. Phys.* **73**, 5230 (1980).

[11] B. S. HUDSON, B. E. KOHLER and K. SCHULTEN, in *Excited States*, Vol. 6, pp. 1–95 (edited by E. C. LIM). Academic Press, New York (1982).

[12] D. G. LEOPOLD, R. D. PENDLEY, J. L. ROEBBER, R. J. HEMLEY and V. VAIDA, *J. chem. Phys.* **81**, 4218 (1984).

[13] R. J. HEMLEY, B. R. BROOKS and M. KARPLUS, *J. chem. Phys.* **85**, 6550 (1986).

[14] A. B. MYERS, R. A. MATHIES, D. J. TANNOR and E. J. HELLER, *J. chem. Phys.* **77**, 3857 (1982).

[15] B. CURRY, Ph.D. Thesis, University of California, Berkeley (1983).

[16] J. A. HERBIG, Dissertation, Universität zu Köln (1964).

[17] S. J. CYVIN, G. HAGEN and M. TRÆTTEBERG, *Acta chem. scand.* **23**, 3285 (1969).

[18] Y. FURUKAWA, H. TAKEUCHI, I. HARADA and M. TASUMI, *J. molec. Struct.* **100**, 341 (1983).

[19] R. MCDIARMID and A. SABLJIC, *J. phys. Chem.* **91**, 276 (1987).

[20] P. G. SZALAY, A. KARPFEN and H. LISCHKA, *J. chem. Phys.* **87**, 3530 (1987).

[21] G. FOGARASI, P. G. SZALAY, P. P. LIESCHESKI, J. E. BOGGS and P. PULAY, *J. molec. Struct.* **151** 341 (1987).

[22] F. W. LANGKILDE, Doctoral Dissertation, Risø-M-2644, Risø (1987).

[23] F. W. LANGKILDE, R. WILBRANDT and N.-H. JENSEN, *Chem. phys. Lett.* **111**, 372 (1984).

[24] F. W. LANGKILDE, N.-H. JENSEN and R. WILBRANDT, *Chem. phys. Lett.* **118**, (1985) 486.

[25] F. W. LANGKILDE, N.-H. JENSEN and R. WILBRANDT, *Springer Proc. Phys.* **4**, 175 (1985).

[26] F. W. LANGKILDE, N.-H. JENSEN, R. WILBRANDT, A. M. BROUWER and H. J. C. JACOBS, *J. phys. Chem.* **91**, 1029 (1987).

[27] F. W. LANGKILDE, N.-H. JENSEN and R. WILBRANDT, *J. phys. Chem.* **91**, 1040 (1987).

[28] J. C. W. CHIEN, *Polyacetylene, Chemistry, Physics and Material Science.* Academic Press, Orlando, FL (1984).

[29] A. M. BROUWER, Ph.D. Thesis, Leiden, Netherlands (1987).

[30] A. M. BROUWER and H. J. C. JACOBS, to be published.

[31] W. HAGEN, L. J. ALLAMANDOLA and J. M. GREENBERG, *Astrophys. Space Sci.* **65**, 215 (1979).

[32] S. BJØRKLUND, E. AUGDAHL, D. H. CHRISTENSEN and G. O. SØRENSEN, *Spectrochim. Acta* **32A**, 1021 (1976).

[33] A. WARSHEL and M. KARPLUS, *J. Am. chem. Soc.* **94**, 5612 (1972).

[34] A. WARSHEL and M. LEVITT, *Quantum Chem. Progm Exch.* **11**, 247 (1974).

[35] O. F. NIELSEN, P.-A. LUND and E. PRÆSTGAARD, *J. chem. Phys.* **77**, 3878 (1982).

[36] L. M. SVERDLOV, M. A. KOVNER and E. P. KRAINOV, *Vibrational Spectra of Polyatomic Molecules.* Wiley, New York (1974).

[37] M. RYTEL, *Opt. Spectrosc.* **16**, 402 (1964).

[38] B. CURRY, I. PALINGS, A. D. BROEK, J. A. PARDOEN, J. LUGTENBURG and R. MATHIES, in *Advances in Infrared and Raman Spectroscopy*, Vol. 12, pp. 115–178 (edited by R. J. H. CLARK and R. E. HESTER). Wiley Heyden (1985).

[39] M. TRÆTTEBERG and G. PAULEN, *Acta chem. scand.* **A28**, 1150 (1974).

[40] C. W. BOCK, Y. N. PANCHENKO, S. V. KRASNOSHCHIOKOV and R. AROCA, *J. molec. Struct.* **160**, 337 (1987).

[41] F. INAGAKI, M. TASUMI and T. MIYAZAWA, *J. Raman Spectrosc.* **3**, 335 (1975).

[42] D. A. C. COMPTON, W. O. GEORGE and W. F. MADDAMS, *J. chem. Soc. Perkin II* 1666 (1976).

[43] P. PULAY, G. FOGARASI, G. PONGOR, J. E. BOGGS and A. VARGHA, *J. Am. chem. Soc.* **105**, 7037 (1983).

[44] M. M. ABO ALY, M. H. BARON, M. J. COULANGE and J. FAVROT, *Spectrochim. Acta* **42A**, 411 (1986).