INTERPRETATION OF THE VIBRATIONAL SPECTRA OF *TRANS,TRANS-, CIS,CIS-* AND *TRANS,CIS-*HEXA-2,4-DIENES, 2,5-DIMETHYL-HEXA-2,4-DIENE, 4-METHYL-PENTA-1,3-DIENE AND *TRANS-*2-METHYL-PENTA-1,3-DIENE BASED ON CNDO/2 QUANTUM MECHANICAL FORCE FIELD CALCULATIONS

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Complete assignments of the recently remeasured vibrational spectra of *trans, trans-*(**I**), *cis,cis-*(**II**), *trans,cis-*hexa-2,4-dienes (**III**) and 2,5-dimethyl-hexa-2,4-diene (**IV**) are presented on the basis of scaled quantum mechanical (SQM) force fields calculated previously at the semiempirical CNDO/2 level. Using the same method, SQM force fields and vibrational frequencies are calculated for 4-methyl-penta-1,3-diene (**V**) and *trans-*2-methyl-penta-1,3-diene (**VI**). Choice of the structural parameters of similar molecules (isoprene and 2,3-dimethyl-buta-1,3-diene) as reference geometry for force field calculations of compounds **I—VI** proved to be successful for *trans* methyl substitutions and less satisfactory for *cis* methyl substitutions. Similar correlations are found between the structure and the vibrational spectra of these compounds as were found previously for eight other methyl derivatives of buta-1,3-diene.

Introduction

In recent years details of the vibrational spectra of buta-1,3-diene and its methyl derivatives drew a lot of attention. It was shown, by interpretation of the solid phase vibrational spectra of buta-1,3-diene [1, 2] and by ab initio quantum chemical calculations for a non-rigid molecular model [3, 4], that the second stable form of buta-1,3-diene, at least in the solid phase, is the *gauche* conformer rather than the *cis* one. Similar results were obtained for 2-methyl-buta-1,3-diene (isoprene) [5]. In order to gain further insight into this possible "gauche-effect" it is of interest to study and assign the vibrational spectra of some selected methyl derivatives of buta-1,3-diene.

Vibrational assignments, based on *empirically corrected* semiempirical quantum chemical force field calculations at the CNDO/2 level, are available

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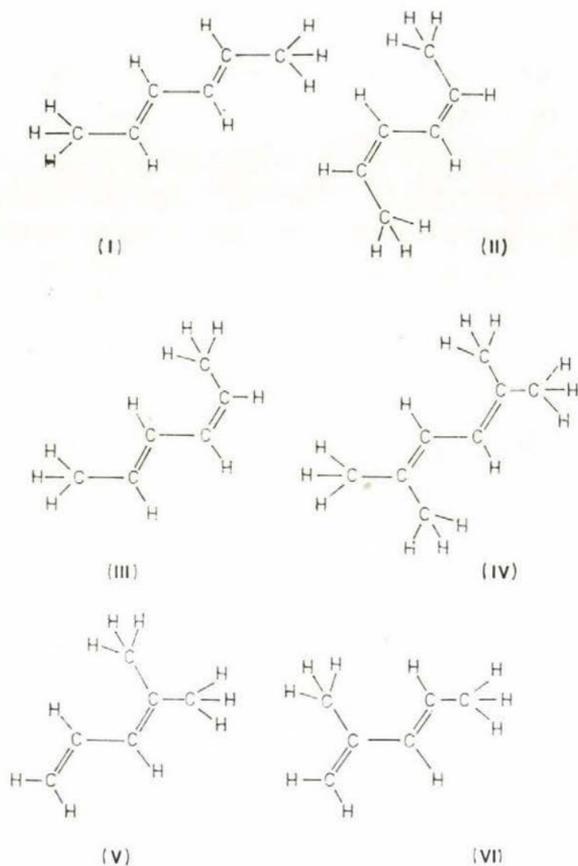
Fig. 1. Simplified chemical structures of the molecules considered in the present study:
I = *trans,trans*-hexa-2,4-diene; **II** = *cis,cis*-hexa-2,4-diene; **III** = *trans,cis*-hexa-2,4-diene;
IV = 2,5-dimethyl-hexa-2,4-diene; **V** = 4-methyl-penta-1,3-diene; **VI** = *trans*-2-methyl-penta-
1,3-diene

for the lowest energy planar structures of several buta-1,3-diene derivatives
(Roman numbers denote compounds considered in this paper, see also Fig. 1):
cis- and *trans*-penta-1,3-dienes [6], isoprene [7], *trans,trans*(**I**), *cis,cis*-(**II**)
and *trans,cis*-hexa-2,4-dienes (**III**) [8], 2,3-dimethyl-buta-1,3-diene [6] and
2,5-dimethyl-hexa-2,4-diene (**IV**) [9]. These results suggests that for the over-
whelming majority of the fundamental frequencies the calculated values,
even on this rather low level of theory, do not deviate more than 20—40 cm^{-1}
from the experimental ones. Occurrence of considerably larger deviations
might either be explained as simple consequence of assumptions in the model
applied, or assignments of the spectrum should be reconsidered. It should also
be mentioned that vibrational frequencies calculated from the force fields

reported in Refs. [8 and [9] were compared with incompletely assigned vibrational spectra. Since then IR and Raman spectra of these molecules have been measured again [10—12], thus it seemed worth-while repeating inter-pretation of the new experimental data on the basis of the above-mentioned calculations. In Ref. [12] the vibrational spectra of 4-methyl-penta-1,3-diene (V) and *trans*-2-methyl-penta-1,3-diene (VI) were measured for the first time. Analysis of these spectra, based on semiempirical calculation of the vibra-tional frequencies, was carried out, and is also reported in the present paper.

Computational details

In this paper the scaled quantum mechanical (SQM; a term introduced for empirically adjusted ab initio calculated harmonic force fields in Ref. [13]) approach will be used to obtain the harmonic force fields. Force constants of 4-methyl-penta-1,3-diene (V) and *trans*-2-methyl-penta-1,3-diene (VI) were computed by the force (gradient) method of Pulay [14] using the semiempirical CNDO/2 method [15].

Use of the geometry of buta-1,3-diene as reference parameters for the semiempirical force field calculation of its next homologue, hexa-1,3,5-triene, proved to be successful [16]. Therefore the reference geometry parameters of compounds I—VI were taken from molecules of similar structure, iso-prene [17] and 2,3-dimethyl-buta-1,3-diene [18], without optimization of any of the transferred bond lengths or bond angles, as follows: $r(C-C) = = 1.491$ Å, $r(C=C) = 1.349$ Å, $r(C-C_{sp3}) = 1.511$ Å, $r(C-H) = 1.093$ Å, $r(C_{sp3}-H) = 1.123$ Å, $\angle C=C-C = 122°$, $\angle H-C=C = 120.4°$, $\angle C=C-CH_3 = = 120.4°$ and $\angle H-C-H = 109°47'$. In the case of the methyl derivatives, however, use of these standard geometry parameters turned out to be suc-cessful only for *trans* substitution; for *cis* substitution, in some molecules (e.g. in 2,5-dimethyl-hexa-2,4-diene) significant proton-proton interactions in the planar form cause important geometry changes, e.g. distortion of the planar carbon skeleton (see Ref. [19]), the neglect of which makes, of course, some calculated frequencies less reliable.

The directly calculated force constants, suffering from a fairly system-atic error, were corrected by scale factors (for details of the procedure, see Ref. [13]; shortly, a few scale factors are assigned to the various types of internal coordinates). The above discussed choice of the reference geometries allowed us to utilize the earlier determined empirical scale factors of Ref. [6], which are as follows: 0.377 for $C-C$ and $C=C$ stretchings, 0.393 for $C-H$ stretchings, 1.136 for the in-plane deformation of the $C=C-C$ angles, 0.812 for the deformation of the $H-C=C$ and $H-C-H$ angles and for the wagging motion of $C-CH_3$, 0.692 for wagging and torsion of the methyl groups and

Table I

Experimental and calculated fundamental vibrational frequencies of trans, trans-C_6H_{10}(I), cis, cis-C_6H_{10}(II) and trans, cis-C_6H_{10}(III) (cm^{-1})

Assignment	Sym.	trans, trans-C_6H_{10} Exptl. (10, 11) Raman	IR	Calcd.	cis, cis-C_6H_{10} Exptl. (10, 11) Raman	IR	Calcd.	Sym.	trans, cis-C_6H_{10} Exptl. (10, 11) Raman	IR	Calcd.
1. $\nu(\mathrm{CCH_3{-}H})$ str.	A_g	3022		3038	3026		3041	A'	3039		3045
2. $\nu(\mathrm{{\gtrsim}C{-}H})$ str.		2997		3035	3005		3026		3020		3029
3. $\nu(\mathrm{CH_3})$ as.str.		2957		2983	2970		2983		2963	2963	2983
4. $\nu(\mathrm{CH_3})$ s.str.		2915		2932	2915		2932		2916		2931
5. $\nu(\mathrm{C{=}C})$ str.		1658		1642	1648		1631		1655	1656	1636
6. $\delta(\mathrm{CH_3})$ as.def.		1451		1473	1448		1519		1450		1511
7. $\delta(\mathrm{CH_3})$ s.def.		1380		1413	1371		1460		1375		1424
8. $\delta(\mathrm{{\gtrsim}C{-}H})$ def.				1356	1435		1416				1438
9. $\delta(\mathrm{CCH_3{-}H})$ def.		1302		1296	1262		1265		1307	1307	1340
10. $\nu(\mathrm{C{-}C})$ str.		1168		1158	1145		1135		1152		1146
11. $\nu(\mathrm{C{-}CH_3})$ str.		1092		1095	905		962			932	946
12. $\varrho(\mathrm{CH_3})$ rock.		927		940	1028		993		1082		1100
13. $\delta(\mathrm{C{=}C{-}C})$ bend.		435		429	620		623		465	466	490
14. $\delta(\mathrm{C{=}C{-}CH_3})$ bend.		334		354	470		400		445ª	435	417
15. $\nu(\mathrm{CH_3})$ as.str.	A_u		2961	2981		2974	2981	A''	2963	2963	2981
16. $\delta(\mathrm{CH_3})$ as.def.				1460		1448	1437			1444	1437
17. $\chi(\mathrm{{\gtrsim}C{-}H})$ wag.			990	1018		982	1027		992	981	1003
18. $\varrho(\mathrm{CH_3})$ rock.				979			970			943	949
19. $\chi(\mathrm{CCH_3{-}H})$ wag.			742	723		680	731		717	705	697
20. $\tau(\mathrm{C{=}C})$ tw.			228	219			270			150	126
21. $\tau(\mathrm{CH_3})$ tors.			185ª	208			150			194	198
22. $\tau(\mathrm{C{-}C})$ tors.			110	90		80	13			100	73
23. $\nu(\mathrm{CH_3})$ as.str.	B_g	2957		2981	2970		2981		2963	2963	2982
24. $\delta(\mathrm{CH_3})$ as.def.		1435		1460	1435		1436		1438	1438	1460
25. $\chi(\mathrm{{\gtrsim}C{-}H})$ wag.				985	950		952				979
26. $\varrho(\mathrm{CH_3})$ rock.				975			967		956ª		966
27. $\chi(\mathrm{CCH_3{-}H})$ wag.		834		809	775		757		823ª	818	789
28. $\tau(\mathrm{C{=}C})$ tw.		355		323	270		336		333	319	342
29. $\tau(\mathrm{CH_3})$ tors.		142		176	162		159		181		188
30. $\nu(\mathrm{{\gtrsim}C{-}H})$ str.	B_u		3018	3041		3001	3030	A'		3020	3038
31. $\nu(\mathrm{CCH_3{-}H})$ str.			3008	3036		3028	3044		2998	2998	3032
32. $\nu(\mathrm{CH_3})$ as.str.			2961	2983		2974	2983		2963	2963	2980
33. $\nu(\mathrm{CH_3})$ s.str.			2916	2931		2931	2931			2919	2932
34. $\nu(\mathrm{C{=}C})$ str.			1627	1599		1609	1578		1612	1614	1590
35. $\delta(\mathrm{CH_3})$ as.def.			1443	1471		1456	1518			1444	1472
36. $\delta(\mathrm{CH_3})$ s.def.			1378	1406		1394	1439			1373	1409
37. $\delta(\mathrm{{\gtrsim}C{-}H})$ def.			1302	1322		1348	1342		1280	1280	1273
38. $\delta(\mathrm{CCH_3{-}H})$ def.			1237	1247		1233	1211		1238	1238	1219
39. $\nu(\mathrm{C{-}CH_3})$ str.			1070	1091		927	920			1033	1042
40. $\varrho(\mathrm{CH_3})$ rock.			935	936		1060	1117		920		926
41. $\delta(\mathrm{C{=}C{-}CH_3})$ bend.			554	560		540	544		595	594	594
42. $\delta(\mathrm{C{=}C{-}C})$ bend.				159		310	318				194

ª Crystalline phase.

Table II

Experimental and calculated fundamental vibrational frequencies of 2,5-dimethylhexa-2,4-diene (**IV**) (cm⁻¹)

Assignment	Sym.	Exptl. (12)		Calcd.	Assignment	Sym.	Exptl. (12)		Calcd.
		Raman	IR				Raman	IR	
1. $\nu(\geq C-H)$ str.	A_g	3032		3028	31. $\tau(C-C)$ tors.				13
2. $\nu(CH_3)$ as.str.		2996		2954	32. $\nu(CH_3)$ as.str.	B_g			2984
3. $\nu(CH_3)$as.str.		2980		2950	33. $\nu(CH_3)$ as.str.		2925		2952
4. $\nu(CH_3)$ s.str.		2965		2936	34. $\delta(CH_3)$ as.def.		1445		1464
5. $\nu(CH_3)$ s.str.		2912		2907	35. $\delta(CH_3)$ as.def.		1435		1441
6 $\nu(C=C)$ str.		1654		1646	36. $\varrho(CH_3)$ as.rock.		1068		1021
7. $\delta(CH_3)$ as.def.		1460		1527	37. $\varrho(CH_3)$ s.rock.		982		950
8. $\delta(CH_3)$ as.def.		1435		1472	38. $\chi(\geq C-H)$wag.		860		817
9. $\delta(CH_3)$ s.def.		1380		1468	39. $\chi(=C(CH_3)_2)$wag.		340		380
10. $\delta(CH_3)$ s.def.		1365		1433	40. $\tau(C=C)$ tw.		305		331
11. $\delta(\geq C-H)$ def.				1415	41. $\tau(CH_3)$ tors.		172		166
12. $\nu(=C(CH_3)_2)$ s.str.		1227		1247	42. $\tau(CH_3)$ tors.		127		129
13. $\nu(C-C)$ str.		1153		1153					
14. $\varrho(CH_3)$ as.rock.		1032		1077	43. $\nu(\geq C-H)$ str.	B_u		3024	3034
15. $\varrho(CH_3)$ s.rock.		953		975	44. $\nu(CH_3)$ as.str.			2979	2955
16. $\nu(=C(CH_3)_2$ s.str.		838		863	45. $\nu(CH_3)$ as.str.			2970	2953
17. $\delta(C=C-C)$ nend.		502		502	46. $\nu(CH_3)$ s.str.			2970	2953
18. $\varrho(=C(CH_3)_2)$ rock		467		402	47. $\nu(CH_3)$ s.str.			2928	2905
19. $\delta(=C(CH_3)_2)$ sci.		292		316	48. $\nu(C=C)$ str.			1626	1612
					49. $\delta(CH_3)$ as.def.			1460	1534
20. $\nu(CH_3)$ as.str.	A_u		2942	2983	50. $\delta(CH_3)$ as.def.			1449	1470
21. $\nu(CH_3)$ s.str.			2925	2905	51. $\delta(CH_3)$ s.def.			1386	1452
22. $\delta(CH_3)$ as.def.			1437	1466	52. $\delta(CH_3)$ s.def.			1377	1417
23. $\delta(CH_3)$ as.def.			1435	1442	53. $\delta(\geq C-H)$ def.			1320	1347
24. $\varrho(CH_3)$ as.rock.			1070	1025	54. $\nu(=C(CH_3)_2)$ as.str.			1171	1243
25. $\chi(\geq C-H)$ wag.			988	986	55. $\varrho(CH_3)$ as.rock.			1052	1052
26. $\varrho(CH_3)$ s.rock.			840	868	56. $\varrho(CH_3)$ s.rock.			960	970
27. $\chi(=C(CH_3)_2)$ wag.			446	425	57. $\nu(=(CH_3)_2)$ s.str.			814	842
28. $\tau(CH_3)$ tors.			205	229	58. $\varrho(=C(CH_3)_2)$ rock.			546	526
29. $\tau(CH_3)$ tors.			185	197	59. $\delta(=(CH_3)_2)$ sci.				453
30. $\tau(C=C)$ tw.			100	115	60. $\delta(C=C-C)$ bend.			205	199

torsion around C=C, 0.598 for wagging of the C—H bonds and 1.302 for torsion around the central C—C bond.

The calculated and the experimental frequencies together with the characterization of the normal modes based on the M-matrix method [20] are given in Tables I—IV.

Results and Discussion

Instead of listing the force constants of compounds **I—VI**, we focus our attention on the vibrational frequencies calculated from the respective SQM force fields by use of Wilson's GF-method [21]. The set of internal coordinates and the SQM force fields can be obtained from the authors upon request.

Table III

Experimental and calculated fundamental vibrational frequencies of 4-methylpenta-1,3-diene (V) (cm⁻¹)

Assignment	Sym.	Raman	IR	Calcd.	Assignment	Sym.	Raman	IR	Calcd.
1. $\nu(=CH_2)$ as.str	A'	3088	3094	3080	22. $\varrho(=CH_2)$ rock.		942		956
2. $\nu(C-H)$ str.[a]			3054	3039	23. $\nu(=C(CH_3)_2)$ s.str.		812	812	832
3. $\nu(C-H$ str.[b]		3010	3010	3031	24. $\delta(C=C-C)$ bend.		525	521	513
4. $\nu(=CH_2)$ s.str.			2984	3012	25. $\varrho(C=(CH_3)_2)$ rock.		435	428	434
5. $\nu(CH_3)$ as.str.		2973	2974	2983	26. $\delta(C=(CH_3)_2)$ sci.		360	360	414
6. $\nu(CH_3)$ as.str.		2963		2980	27. $\delta(C=C-C)$bend.				257
7. $\nu(CH_3)$ s.str.		2912	2930	2932					
8. $\nu(CH_3)$ s.str.		2912	2930	2931	28. $\nu(CH_3)$ as.str.	A''	2973	2974	2982
9. $\nu(C=C)$ s.str.		1657	1662	1643	29. $\nu(CH_3)$ as.str.		2963		2981
10. $\nu(C=C)$ as.str.		1601	1605	1586	30. $\delta(CH_3)$ as.def.		1382	1389	1399
11. $\delta(CH_3)$ as.def.		1452	1454	1516	31. $\delta(CH_3)$ as.def.			1379	1384
12. $\delta(CH_3)$ as.def.			1444	1443	32. $\varrho(CH_3)$ as.rock.		1068	1070	1056
13. $\delta(=CH_2)$ sci.		1415	1420	1470	33. $\chi(C-H)$ wag.[a]		995	996	1020
14. $\delta(CH_3)$ s.def.		1382	1389	1407	34. $\chi(C-H)$ wag.[b]		975	976	977
15. $\delta(CH_3)$ s.def.			1379	1397	35. $\chi(=CH_2)$ wag.		895	900	923
16. $\delta(C-H)$ def.[a]		1332	1334	1377	36. $\varrho(CH_3)$ as.rock.		862	864	887
17. $\delta(C-H)$ def.[b]		1290	1295	1343	37. $\tau(=CH_2)$ tw.		657	660	647
18. $\nu(=C(CH_3)_2)$ as.str.		1215	1218	1225	38. $\chi(=C(CH_3)_2)$ wag.		440	440	388
19. $\nu(C-C)$ str.		1147	1152	1167	39. $\tau(CH_3)$ tors.		235	226	233
20. $\varrho(CH_3)$ s.rock.		1060	1060	1077	40. $\tau(=C(CH_3)_2)$ tw.		133		122
21. $\varrho(CH_3)$ s.rock.		1015		1000	41. $\tau(CH_3)$ tors.		200	208	182
					42. $\tau(C-C)$ tors.			112	115

[a] The H atom is attached to the third carbon atom.
[b] The H atom is attached to the second carbon atom.

Table IV

Experimental and calculated fundamental vibrational frequencies of trans-2-methylpenta-1,3-diene (VI) (cm⁻¹)

Assignment	Sym.	Raman	IR	Calcd.	Assignment	Sym.	Raman	IR	Calcd.
1. $\nu(=CH_2)$ as.str.	A'	3083	3090	3079	22. $\nu(C-CH_3)$ t.str.		935	940	955
2. $\nu(C-H)$ c.str.		3025	3034	3039	23. $\nu(C-CH_3)$ c.str.		825		847
3. $\nu(CCH_3-H)$ str.		3025	3034	3035	24. $\delta(C=C-C)$ s.bend.		536		530
4. $\nu(=CH_2)$ s.str.		3010	3010	3011	25. $\delta(C=C-CH_3)$ t.bend.		448	444	424
5. $\nu(CH_3)$ t.as.str.			2990	2983	26. $\delta(C=C-CH_3)$ c.bend.		360	350	351
6. $\nu(CH_3)$ c.as.str.			2990	2983	27. $\delta(C=C-C)$ as.bend.				195
7. $\nu(CH_3)$ c.s.str.			2945	2932					
8. $\nu(CH_3)$ t.s.str.		2919	2930	2932	28. $\nu(CH_3)$ c.as.str.	A''	2972	2978	2982
9. $\nu(C=C)$ s.str.		1660	1665	1648	29. $\nu(CH_3)$ t.as.str.		2972	2978	2980
10. $\nu(C=C)$ as.str.		1610	1615	1600	30. $\delta(CH_3)$ c.as.def.		1437	1435	1481
11. $\delta(CH_3)$ c.as.def.			1458	1524	31. $\delta(CH_3)$ t.as.def.			1430[a]	1471
12. $\delta(CH_3)$ t.as.def.		1448	1447	1501	32. $\varrho(CH_3)$ c.as.rock.		1035		1044
13. $\delta(=CH_2)$ sci.		1413		1446	33. $\varrho(CH_3)$ t.as.rock.		1035		1021
14. $\delta(CH_3)$ c.s.def.		1378	1380	1469	34. $\chi(C-H)$ c.wag.			964	1002
15. $\delta(CH_3)$ t.s.def.		1365	1360	1464	35. $\chi(=CH_2)$ wag.		882	888	904
16. $\delta(C-H)$ c.def.			1317	1328	36 $\chi(CCH_3-H)$ wag.		815	815	829
17. $\nu(C-C)$ c.str.		1305	1305	1360	37. $\tau(=CH_2)$ tw.		685	682	690
18. $\delta(CCH_3-H)$ def.		1277		1273	38. $\chi(CH_3)$ c.wag.		494	492	524
19. $\varrho(CH_3)$ t.s.rock.		1102	1099	1114	39. $\tau(CH_3)$ t.tors.			220[a]	209
20. $\varrho(CH_3)$ c.s.rock.		1016	1020	1041	40. $\tau(C=C)$ t.tw.				189
21. $\varrho(=CH_2)$ rock.			993	1013	41. $\tau(CH_3)$ c.tors.		200	184	178
					42. $\tau(C-C)$ tors.			120	109

[a] Crystalline phase. The abbreviations t. and c. stand for terminal and central, respectively.

It can be said, in general, that the calculated vibrational frequencies corroborated the assignments of the experimental spectra of Refs. [10—12]. In some cases, where the experimental assignments were ambiguous or different frequencies were assigned to the same type of vibration, the present calculations allowed to choose among the proposed bands. In other cases it was possible to refine the interpretation of certain experimental bands. In the following we discuss only those normal modes for which the assignment has been modified or whose interpretation requires extra attention. Note that relatively large deviations of the calculated frequencies from the experimental ones may result from two sources: (a) deficiences of the present calculation; (b) some experimental data were obtained in the solid rather than in the gas phase.

In the following discussion, assignments of the vibrational spectra of each molecule will be presented separately.

Trans, trans-hexa-2,4-diene (I)

Assignments of the vibrational spectrum of I presented here differ from the experimental interpretation [10, 11] mainly for the stretching vibrations of the $=C-CH_3$ bonds and for the rocking vibrations $\varrho(CH_3)$ (see Table I).

The band at 1092 cm^{-1} in the Raman spectrum is rather intensive and strongly depolarized, which is characteristic of the symmetric stretching of the $=C-CH_3$ bonds (ν_{11}). The 1070 cm^{-1} frequency (ν_{39}) is also reassigned; it is the antisymmetric stretching vibration of the $=CH-CH_3$ bonds.

As to the symmetric rocking vibration of the CH_3 groups (ν_{12}), such bands are usually weak and depolarized, which is indeed observed [10, 11] in the experimental spectrum. The band at 935 cm^{-1} was assigned as the antisymmetric rocking vibration of the CH_3 groups (ν_{40}) because it shows the expected hybrid contour of A/B type.

The band at 142 cm^{-1} is chosen for the symmetric torsional vibration of the CH_3 groups (B_g, ν_{29}). This band was assigned as a crystalline lattice vibration in Ref. [11]. However, since the corresponding vibration of A_u type (ν_{21}) is predicted by our calculation quite correctly, it should be expected that the calculated value of ν_{29} does not deviate significantly from the measured one either. It should also be noted that lattice vibrations of this molecular series are situated usually in a lower spectral region.

As a final remark, we note that the 1302 cm^{-1} band in the Raman spectrum (A_g, ν_9) should be attributed to the deformation vibration of the terminal $C-H$ bonds, since it is strongly polarized.

Cis, cis-hexa-2,4-diene (II)

It is rather obvious from the geometry model of this compound that relatively large differences should be presumed among some of the measured and calculated vibrational frequencies of **II**. Large deviations of the calculated frequencies from the experimental ones belonging to vibrations of the methyl groups in *cis* positions are indeed observed (see Table I): (a) the calculated ν_6 frequency in **II** (and also in *trans,cis*-hexa-2,4-diene, **III**) is strongly overestimated; (b) the deformational vibration $\delta(C=C-CH_3)$ is significantly underestimated, by some 70 cm^{-1} (ν_{14}). It should also be pointed out that an imaginary value was obtained for the force constant of the torsional coordinate around the central C—C bond. To avoid obtaining a negative frequency, in the course of the solution of the vibrational problem this value was substituted by the corresponding diagonal element of the force constant matrix of **I**. Thus the vibrational frequency obtained is meaningless (ν_{22} in Table I). (Note that the same procedure was applied for **IV**, see ν_{31} in Table II).

Methyl substitution of buta-1,3-diene in *cis* positions results in an increase of the frequencies of the in-plane deformation vibrations of the central C—H bonds (ν_8 and ν_{37}). This feature is excellently predicted by theory.

Appearance of two Raman bands in the crystal spectrum of **II** at 1268 and 1278 cm^{-1} is due to Davydov splitting. This makes impossible to assign the band at 1278 cm^{-1} to $\delta(>C-H)$, ν_8, as it was done in Ref. [11]. This is further supported by the fact that the corresponding B_u vibration is at 1348 cm^{-1}, i.e. it is increased in comparison with the analogous vibration of buta-1,3-diene.

In the present work the band at 905 cm^{-1} is assigned as the symmetric stretching vibration of the C—CH$_3$ bonds (ν_{11}). Although the calculated value deviates from the experimental one by 57 cm^{-1}, the assignment is supported by the intensity and the depolarization nature of the experimental band.

As to the band at 1028 cm^{-1} (ν_{12}), it is assigned as an in-plane rocking vibration. Unfortunately, the intensity and the degree of depolarization of this band does not allow us to decide if this band belongs to an A_g or a B_g type vibration.

There are some difficulties in explaining the Raman bands at 470 and 270 cm^{-1}, as the degree of depolarization of these bands are 0.9 and 0.2, respectively.

In Ref. [11] the frequency at 162 cm^{-1} was assigned to the A_u symmetry species. This frequency is active in the Raman spectrum, so we assign it to the torsional vibration of the CH$_3$ group (ν_{29}); thus it belongs to species B_g.

Trans, cis-hexa-2,4-diene (III)

The above-mentioned deviations of the calculated frequencies from the experimental ones, whenever they are applicable, can also be observed for **III**. As expected for the methyl group in *trans* position, the assumed molecular model provides a good description of the experimental spectrum (see Table I).

2,5-Dimethyl-hexa-2,4-diene (IV)

The non-adequacy of the assumed molecular model of **IV** and the known weaknesses of the theoretical model used have their consequences on the calculated spectrum (Table II): (a) an imaginary value is obtained for the diagonal force constant of the torsional coordinate around the central C—C bond, in analogy with **II**; (b) an artificial increase is observed for some deformational frequencies of the CH_3 group (v_7 and v_{49}). However, the other calculated frequencies, as will be shown, can successfully be used for the interpretation of the vibrational spectra of **IV**.

Calculation of the frequencies of the stretching vibrations of the C—CH_3 bonds (v_{12} and v_{54}) shows that splitting between the symmetric and the antisymmetric stretchings is not too large. Accordingly, the band at 1227 cm^{-1} in the Raman spectrum was chosen as v_{12}, and the band at 1171 cm^{-1} in the IR spectrum was selected as v_{54}. The relatively large deviation between the calculated and the selected experimental fundamental for v_{54} shows the limitations of frequency calculations at the CNDO/2 level.

The present calculations resulted in reassignments of the symmetric rocking and scissoring vibrations, v_{18} and v_{19}, respectively; e.g. the band at 292 cm^{-1} in the Raman spectrum is assigned to the symmetric scissoring vibration.

It follows from our previous experience that difficulties may arise in the assignment of the wagging vibrations of the central C—H bonds and of the rocking vibrations of the —CH_3 groups. Thus it is appropriate to note that the present assignments of vibrations v_{25} and v_{26} are based on results of the present calculations.

Based also on the present calculations, assignments of the bands at 340 and 305 cm^{-1} have been revised (v_{39} and v_{40}, respectively).

The 127 cm^{-1} band in the Raman spectrum of **IV** (v_{42}) is attributed to the B_g type torsional vibration of the CH_3 group. It lies quite close to the analogous vibration of **I**. The frequency at 100 cm^{-1}, measured in the IR spectrum, has been reassigned as the antisymmetric twisting vibration around the C=C bond (v_{30}).

4-Methyl-penta-1,3-diene (V)

A theoretical vibrational analysis has been performed for the first time for V. It can be seen from Table III that all vibrational frequencies of V appear in spectral regions similar to those of buta-1,3-diene and its eight methyl derivatives [6—9]. It should also be noted that regions of the vibrational frequencies characteristic of the methyl derivatives of buta-1,3-diene are narrower than regions determined for other derivatives, including chloro- and mixed chloro- and methyl derivatives [10]. This helps, of course, to make a more detailed analysis of the spectra of new methyl derivatives of buta-1,3-diene.

As it was observed during the comparison of the experimental and theoretical vibrational spectra of the previously discussed molecules, the stretching vibration of the $C-CH_3$ bond and the positions of the rocking vibrations, $\varrho(CH_3)$, of V must be reassigned, while the calculated symmetrical deformational vibration of the CH_3 group (ν_{11}) is considerably overestimated.

The calculations performed made possible to choose between the experimental frequencies, suggested as two alternative assignments in Ref. [12], in the case of ν_{25}, ν_{26} and ν_{37}.

Based on the calculations, the 1215 cm^{-1} line in the Raman spectrum is assigned as the asymmetric stretching vibration of the $=C(CH_3)_2$ group.

The vibrational spectra of V must obviously show the difference between the chemical nature of the two central $C-H$ bonds. Although there is only a small difference between the appropriate stretching vibrations, the in-plane bending and the out-of-plane wagging vibrations of these bonds, it still can be seen that the vibrational frequencies referring to C_3-H are higher than the fequencies of C_2-H.

Trans-2-methyl-penta-1,3-diene (VI)

There are at least two facts which suggest that the real geometry of VI might differ appreciably from the geometry model applied in the present study: (a) methyl substitution took place in *cis* position; (b) calculation considerably overestimates the vibrational frequencies of $\delta(CH_3)^{as}_{centr.}$ (ν_{11}) and $\delta(CH_3)^{as}_{term.}$ (ν_{12}). In spite of these difficulties, the present assignments of the vibrational spectrum of VI mostly confirm the analysis presented in Ref. [12], so only those few exceptions where they differ require further discussion. The experimental and the theoretical fundamental vibrational frequencies of V are presented in Table IV.

The strongly polarized band at 1305 cm^{-1} in the Raman spectrum can be described as the stretching vibration of the central $C-C$ bond (ν_{17}), while

the 1317 cm^{-1} IR band possessing hybrid A/B type contour is assigned to δ(C—H)$_{centr.}$ (ν_{16}).

According to the present calculations, the rocking vibration of the terminal CH$_3$ group and the stretching of the C—CH$_3$ bond mix considerably. Nevertheless, the strongly polarized band at 935 cm^{-1} can be best described as ν(C—CH$_3$) (ν_{22}), in agreement with data obtained earlier for cis-penta-1,3-diene [6].

Assignment of the twisting vibration (ν_{40}) and the torsional motions of the CH$_3$ groups (ν_{39} and ν_{41}) is rather problematic: the three calculated frequencies are in the interval of 178—209 cm^{-1}, while there are only two experimental bands reported in this IR region, at 184 and 220 cm^{-1}. Furthermore, the band at 220 cm^{-1} in the liquid phase is a shoulder on the contour of a stronger band. In the absence of the third band, only a later high-resolution experiment might result in the correct positioning of these normal modes.

The bands at 685, 448 and 360 cm^{-1} in the Raman spectrum were also reassigned as the twisting vibration of the =CH$_2$ group (ν_{37}), and the deformation vibrations of the terminal and central C=C—CH$_3$ moieties (ν_{25} and ν_{26}), respectively.

Conclusion

The repeated analysis, based on semiempirical quantum chemical force field calculations at the CNDO/2 level, of the newly measured vibrational spectra of 2,5-dimethyl-hexa-2,4-diene and of the structural isomers of hexa-2,4-diene resulted in reassignments of some experimental frequencies and corroborated the correlations between the structures and vibrational spectra of these molecules. For 4-methyl-penta-1,3-diene and $trans$-2-methyl-penta-1,3-diene a theoretical vibrational analysis, based again on similar semiempirical quantum chemical force field calculations at the CNDO/2 level, was performed for the first time. Assignments of the experimental vibrational spectra of these compounds connect these spectra with the earlier found structural and spectral regularities in this series of molecules.

Note added in proof:

After submitting this paper, we learned about the paper of X. Jing, J. Wang and Zh. Feng, Spectrochim. Acta, **44A**, 1391 (1988), in which the vibrational spectra of $trans,trans$-C$_6$H$_{10}$ and $trans,cis$-C$_6$H$_{10}$ were measured and the vibrational problems were solved using modified valence-type force fields. The majority of the experimental vibrational fundamentals of this paper coincide with the data of Refs. [10] and [11]. Their assignments of the fundamentals agree, in most cases, with ours. The exceptions are: ν_4, ν_8, ν_{12}, ν_{21}, ν_{25}, ν_{40} and ν_{41} for $trans,trans$-C$_6$H$_{10}$; the theoretical frequencies at 2869, 2868, 1251, 804, 760 and 321 cm^{-1} for $trans,cis$-C$_6$H$_{10}$.

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