

Mean Amplitudes of Vibration and Perpendicular Amplitude Correction Coefficients for the *cis* and *trans* Isomers of 1,3,5-Hexatriene

S. J. CYVIN and G. HAGEN

Institutt for teoretisk kjemi, Norges tekniske høgskole, Trondheim, Norway

and

M. TRÆTTEBERG

Kjemisk institutt, Norges lærerhøgskole, Trondheim, Norway

The mean amplitudes of vibration have been calculated from spectroscopic data for *cis*-1,3,5-hexatriene and *trans*-1,3,5-hexatriene. The results are compared with recent electron diffraction data. Also given are the calculated results of perpendicular amplitude correction coefficients (*K* values).

The purpose of this work is to report the mean amplitudes of vibration for *cis* and *trans* 1,3,5-hexatriene as calculated from a normal-coordinate analysis of the molecules. The same principles were used in the similar work on 1,3-butadiene.¹

Structural data from recent electron diffraction investigations^{2,3} were adopted as equilibrium parameters. The experimental frequencies from Lippincott *et al.*^{4,5} were employed. The same references are cited in a recent spectroscopic work on butadiene and *trans*-hexatriene.⁶

An initial force field was constructed from assumed compliants transferred from related molecules. It was attempted to apply as far as possible the same compliant values for similar coordinates in the two isomer forms of hexatriene. Table 1 shows the calculated frequencies for *cis* and *trans* based on formally the same force field. Several steps of iterations were executed for both molecules before the final force fields were established. During this process it was found reasonable to abandon the reported value⁵ of 758 cm⁻¹ for $\nu_4(B_g)$ in the *trans* isomer on the basis of the frequency values calculated here. Otherwise all the observed fundamentals from Lippincott and Kenney⁵ were adopted.

Table 1. Calculated (I) and observed (II) frequencies (cm^{-1}) for the *cis* and *trans* 1,3,5-hexatriene isomers.

C_{2v}		<i>cis</i>		C_{2h}		<i>trans</i>	
		I	II			I	II
A_1	1	3091	3097	A_g	1	3091	3085
	2	3042	3030		2	3044	3054
	3	3035	3015		3	3036	3054
	4	2995	3015		4	3008	2989
	5	1603	1622		5	1644	1623
	6	1568	1570		6	1574	1573
	7	1396	1392		7	1390	1394
	8	1298	1314		8	1295	1280
	9	1214	1182		9	1211	1245
	10	1152	1136		10	1177	1187
	11	1085	1083		11	1126	1128
	12	386	393		12	473	444
	13	148	167		13	362	347
B_1	1	961	990	B_g	1	1088	990
	2	906	910		2	954	928
	3	743	818		3	901	897
	4	571	589		4	607	589 ^a
	5	294	358		5	448	395
A_2	1	1030	978	A_u	1	957	1011
	2	948	902		2	912	941
	3	909	883		3	842	899
	4	735	709		4	639	658
	5	341	331		5	274	(274) ^b
	6	261	264		6	157	(157)
B_2	1	3100	3110	B_u	1	3100	3091
	2	3061	3080		2	3059	3040
	3	3032	3050		3	3029	3012
	4	3001	3050		4	3001	2953
	5	1626	1612		5	1604	1623
	6	1468	1449		6	1409	1429
	7	1286	1280		7	1286	1294
	8	1202	1148		8	1207	1255
	9	1133	1148		9	1138	1130 ^c
	10	978	950		10	971	1000
	11	531	479		11	469	540
	12	248	243		12	98	(98)

^a Transferred from the *cis* isomer.

^b Frequencies in parenthesis are calculated in the present work.

Table 1 shows the final assignments used in the present calculations. For the *trans* isomer in particular it deviates in some respects from the assignment of Popov *et al.*⁶

The final force constants of the present calculations were adjusted to fit exactly the assigned frequencies (II) shown in Table 1. These refinements were performed individually for the two rotational isomers.

The final force fields were used to calculate the mean amplitudes of vibration.⁷ The results at absolute zero and 298°K for every type of bonded and nonbonded atom pairs are shown in Tables 2 (*cis*-hexatriene) and 3 (*trans*-

Table 2. Calculated and observed mean amplitudes of vibration (u) and calculated perpendicular amplitude correction coefficients (K) for *cis*-1,3,5-hexatriene; Å units.

Distance	(Equil.)	u		Obs. ³	K	
		$T=0$	298°K		$T=0$	298°K
C ₆ -H ₆	(1.104)	0.0770	0.0770	0.085 ₄	0.0192	0.0232
C ₆ '-H ₆ '	(1.104)	0.0770	0.0770		0.0213	0.0253
C ₅ -H ₅	(1.104)	0.0774	0.0774		0.0180	0.0213
C ₄ -H ₄	(1.104)	0.0774	0.0774		0.0173	0.0201
C ₅ =C ₆	(1.337)	0.0446	0.0447	0.043 ₀	0.0042	0.0067
C ₃ =C ₄	(1.368)	0.0456	0.0458	0.044 ₂	0.0035	0.0051
C ₄ -C ₅	(1.458)	0.0473	0.0476	0.052 ₅	0.0026	0.0039
C ₄ ···C ₆	(2.442)	0.0624	0.0704	0.057 ₃	0.0022	0.0040
C ₃ ···C ₅	(2.500)	0.0633	0.0747	0.059 ₃	0.0018	0.0029
C ₂ ···C ₅	(3.015)	0.0783	0.1125	0.066 ₆	0.0017	0.0028
C ₃ ···C ₆	(3.707)	0.0636	0.0706	0.087 ₇	0.0011	0.0020
C ₂ ···C ₆	(4.351)	0.0786	0.1121	0.090 ₂	0.0008	0.0012
C ₁ ···C ₆	(5.686)	0.0784	0.1106	0.095 ₀	0.0003	0.0005
C ₆ ···H ₅	(2.085)	0.1008	0.1020		0.0126	0.0181
C ₃ ···H ₄	(2.089)	0.0976	0.0995		0.0114	0.0150
C ₅ ···H ₆ '	(2.094)	0.1009	0.1012		0.0127	0.0169
C ₅ ···H ₆	(2.150)	0.0972	0.0975		0.0132	0.0191
C ₅ ···H ₄	(2.232)	0.0973	0.0987		0.0094	0.0124
C ₄ ···H ₅	(2.239)	0.0999	0.1009		0.0100	0.0137
C ₃ ···H ₆	(2.725)	0.1335	0.1447		0.0089	0.0124
C ₆ ···H ₄	(2.729)	0.1266	0.1419		0.0074	0.0101
C ₂ ···H ₅	(2.751)	0.1497	0.1898		0.0080	0.0115
C ₃ ···H ₅	(2.810)	0.1339	0.1528		0.0072	0.0100
C ₂ ···H ₄	(3.452)	0.1005	0.1058		0.0061	0.0080
C ₄ ···H ₆ '	(3.431)	0.0982	0.1010		0.0080	0.0117
C ₁ ···H ₅	(4.040)	0.1502	0.1943		0.0048	0.0063
C ₃ ···H ₆	(4.091)	0.1322	0.1427		0.0053	0.0075
C ₁ ···H ₄	(4.531)	0.1073	0.1122		0.0043	0.0057
C ₃ ···H ₆ '	(4.592)	0.1090	0.1158		0.0049	0.0069
C ₂ ···H ₆ '	(4.991)	0.1350	0.1681		0.0045	0.0061
C ₂ ···H ₆	(5.014)	0.1262	0.1463		0.0040	0.0050
C ₁ ···H ₆	(6.318)	0.1274	0.1432		0.0030	0.0040
C ₁ ···H ₆ '	(6.319)	0.1365	0.1722		0.0031	0.0039
H ₆ ···H ₆ '	(1.902)	0.1274	0.1276		0.0243	0.0315
H ₂ ···H ₅	(2.106)	0.1879	0.2367		0.0208	0.0300
H ₃ ···H ₄	(2.301)	0.1440	0.1482		0.0194	0.0268
H ₅ ···H ₆ '	(2.354)	0.1614	0.1637		0.0181	0.0239
H ₄ ···H ₆	(2.547)	0.1909	0.2150		0.0133	0.0170
H ₆ ···H ₅	(3.099)	0.1224	0.1230		0.0177	0.0265
H ₄ ···H ₅	(3.211)	0.1230	0.1235		0.0130	0.0177
H ₄ ···H ₆ '	(3.825)	0.1443	0.1565		0.0121	0.0172
H ₃ ···H ₅	(3.893)	0.1499	0.1650		0.0092	0.0116
H ₂ ···H ₆ '	(4.459)	0.1904	0.2380		0.0092	0.0125
H ₃ ···H ₆	(4.706)	0.1722	0.1883		0.0081	0.0110
H ₆ ···H ₂	(4.893)	0.1732	0.2080		0.0070	0.0084
H ₃ ···H ₆ '	(5.504)	0.1312	0.1339		0.0061	0.0073
H ₆ ···H ₁	(6.805)	0.1659	0.1750		0.0055	0.0076
H ₁ '···H ₆	(6.808)	0.1876	0.2319		0.0055	0.0071
H ₆ '···H ₁	(7.068)	0.1607	0.1837		0.0051	0.0062

Table 3. Calculated and observed mean amplitudes of vibration (u) and calculated perpendicular amplitude correction coefficients (K) for *trans*-1,3,5-hexatriene; Å units.

Distance	(Equil.)	u		Obs. ^a	K	
		$T=0$	Calc. 298°K		$T=0$	Calc. 298°K
C ₆ -H ₆	(1.104)	0.0773	0.0773	0.089 ₃	0.0188	0.0258
C ₆ -H ₅ '	(1.104)	0.0773	0.0773		0.0225	0.0313
C ₅ -H ₅	(1.104)	0.0775	0.0775		0.0172	0.0226
C ₄ -H ₄	(1.104)	0.0778	0.0778		0.0169	0.0197
C ₅ =C ₆	(1.337)	0.0441	0.0442	0.043 ₈	0.0048	0.0122
C ₃ =C ₄	(1.368)	0.0457	0.0458	0.044 ₃	0.0023	0.0027
C ₂ -C ₅	(1.458)	0.0467	0.0470	0.053 ₁	0.0033	0.0067
C ₄ ···C ₅	(2.442)	0.0595	0.0675	0.058 ₂	0.0040	0.0126
C ₃ ···C ₅	(2.500)	0.0598	0.0739	0.058 ₀	0.0020	0.0039
C ₃ ···C ₆	(3.707)	0.0610	0.0674	0.084 ₀	0.0024	0.0082
C ₂ ···C ₅	(3.857)	0.0618	0.0688	0.066 ₀	0.0007	0.0009
C ₂ ···C ₆	(4.941)	0.0723	0.1010	0.095 ₂	0.0009	0.0025
C ₁ ···C ₆	(6.126)	0.0699	0.0818	0.092 ₅	0.0002	0.0002
C ₃ ···H ₄	(2.089)	0.0970	0.0994		0.0093	0.0112
C ₅ ···H ₆	(2.094)	0.1000	0.1002		0.0149	0.0283
C ₆ ···H ₅	(2.085)	0.0993	0.1004		0.0124	0.0238
C ₅ ···H ₆	(2.150)	0.0974	0.0976		0.0130	0.0257
C ₅ ···H ₄	(2.232)	0.0966	0.0985		0.0096	0.0151
C ₄ ···H ₅	(2.239)	0.0987	0.0996		0.0101	0.0169
C ₂ ···H ₄	(2.665)	0.1274	0.1613		0.0080	0.0113
C ₄ ···H ₆	(2.725)	0.1304	0.1413		0.0098	0.0219
C ₆ ···H ₄	(2.729)	0.1221	0.1401		0.0095	0.0194
C ₃ ···H ₅	(2.810)	0.1277	0.1519		0.0076	0.0122
C ₄ ···H ₆ '	(3.431)	0.0967	0.0993		0.0111	0.0260
C ₁ ···H ₄	(3.996)	0.1259	0.1557		0.0059	0.0120
C ₃ ···H ₆	(4.091)	0.1291	0.1390		0.0062	0.0142
C ₂ ···H ₅	(4.265)	0.1273	0.1496		0.0037	0.0048
C ₃ ···H ₆ '	(4.592)	0.1067	0.1145		0.0078	0.0186
C ₂ ···H ₆	(5.103)	0.1528	0.2092		0.0042	0.0076
C ₁ ···H ₅	(5.137)	0.1501	0.2207		0.0038	0.0059
C ₂ ···H ₆ '	(5.913)	0.1042	0.1127		0.0046	0.0090
C ₁ ···H ₆	(6.385)	0.1461	0.1823		0.0023	0.0028
C ₁ ···H ₆ '	(7.033)	0.1125	0.1296		0.0032	0.0044
H ₆ ···H ₆ '	(1.902)	0.1274	0.1276		0.0249	0.0383
H ₅ ···H ₆ '	(2.354)	0.1582	0.1603		0.0196	0.0352
H ₃ ···H ₅	(2.513)	0.1836	0.2399		0.0157	0.0223
H ₄ ···H ₆	(2.547)	0.1840	0.2109		0.0157	0.0283
H ₅ ···H ₄	(3.049)	0.1207	0.1212		0.0114	0.0131
H ₆ ···H ₅	(3.099)	0.1221	0.1226		0.0170	0.0342
H ₄ ···H ₅	(3.211)	0.1223	0.1229		0.0125	0.0205
H ₄ ···H ₆ '	(3.825)	0.1408	0.1551		0.0155	0.0322
H ₃ ···H ₆	(4.625)	0.1538	0.1632		0.0080	0.0154
H ₂ ···H ₅	(4.894)	0.1538	0.1591		0.0053	0.0058
H ₃ ···H ₆ '	(4.683)	0.1682	0.2119		0.0111	0.0227
H ₆ ···H ₃	(5.060)	0.2157	0.3264		0.0079	0.0126
H ₂ ···H ₆ '	(6.193)	0.1616	0.2134		0.0061	0.0101
H ₆ ···H ₁ '	(6.816)	0.1709	0.1823		0.0037	0.0039
H ₆ '···H ₁	(7.178)	0.1849	0.2504		0.0050	0.0066
H ₁ '···H ₆	(7.989)	0.1346	0.1391		0.0053	0.0063

hexatriene). In order to facilitate the identification of atom pairs their equilibrium separations as calculated from the adopted parameters are included (in Å units) as parenthesized values in the tables.

Tables 2 and 3 include the recently observed^{2,3} mean amplitudes from electron diffraction. The agreement with those of the present calculations is seen to be generally good.

Finally the perpendicular amplitude correction coefficients, also referred to⁷ as values of \bar{K} , were calculated for the hexatriene isomers. The results are included in Tables 2 (*cis*-hexatriene) and 3 (*trans*-hexatriene). The \bar{K} values, as well as the mean amplitudes, are of great interest in the refined interpretations of modern gas electron diffraction measurements.

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