

Vibrational frequencies and structural determination of dewar benzene

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Abstract

The vibrational frequencies and corresponding normal mode assignments of dewar benzene are examined theoretically using the GAUSSIAN 98 set of quantum chemistry codes. All normal modes were successfully assigned to one of six types of motion predicted by a group theoretical analysis (C–H stretch, C–C stretch, C=C stretch, CH wag, C–C–C bend, and C–C–C–C torsion) utilizing the C_{2v} symmetry of the molecule. The molecular orbitals and bonding of dewar benzene are examined. Predicted normal mode frequencies for *trans*-dewar benzene (C_{2h} symmetry) are presented.

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1. Introduction

When benzene was discovered in the early 19th century, a number of structures of the empirical formula C_6H_6 were proposed. A C_6H_6 isomer consisting of two four-membered rings was first proposed by James Dewar in “On the Classification of Chemical Substances, by means of Generic Radicals”, which was read to the Royal Society of Edinburgh on February 5, 1866 [1]. This structure later became known as dewar benzene [1–3].

Although the structure of dewar benzene was proposed in the late 1800s, the molecule was not synthesized and isolated until the 1960s [4]. However, it is possible that dewar benzene may have been formed in some earlier experiments on the photolysis of benzene [5]. A number of methods for preparing this interesting molecule [4,6–10] have appeared in the literature and it has been used as a reagent [11,12] in the synthesis of novel hydrocarbons.

Due to its high symmetry and unusual bonding, dewar benzene is an ideal candidate for a quantum chemical normal mode analysis. In this study, the infrared and Raman spectra of dewar benzene are examined using the GAUSSIAN 98 suite of quantum chemical codes [13]. Experimental data of the vibrational spectra of dewar benzene exists in the literature [14–20]. A detailed quantum chemical study will

aid in making definitive assignments to the fundamental normal modes of dewar benzene and in clarifying the experimental data available for this important molecule.

2. Computational methods

The vibrational frequencies of dewar benzene were calculated at the Hartree–Fock, DFT (B3LYP), and MP2 levels of theory using the standard 6-311G** basis set. The calculations utilized the C_{2v} symmetry of the dewar benzene molecule (see Fig. 1). The computations were performed using the GAUSSIAN 98 program package [13]. Each of the vibrational modes was assigned to one of six types of motion (C–H stretch, C–C stretch, C=C stretch, CH wag, C–C–C bend, and C–C–C–C torsion) by means of visual inspection using the Gaussview program [21].

The symmetry of the molecule was also helpful in making vibrational assignments. The symmetries of the vibrational modes were determined using the standard procedure [22] of decomposing the traces of the symmetry operations into the irreducible representations of the C_{2v} group. The symmetry analysis for the vibrational modes of dewar benzene is presented in some detail to serve as a basis for the assignments the normal modes. The symmetry elements of the C_{2v} group are ordered according to Cotton [22].

For the C–H stretching modes, the six C–H bonds were used as the basis of the analysis. The $\sigma'_v(yz)$ operator has

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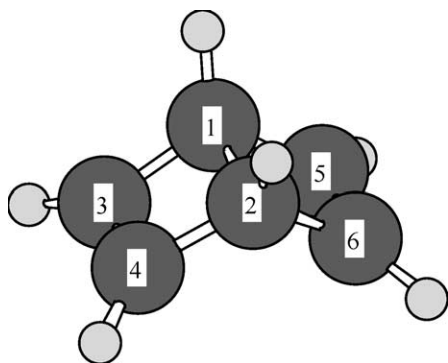


Fig. 1. Structure of dewar benzene.

a trace of two. All other operators except E have a trace of 0. Thus the six C–H stretching modes possess symmetries two A_1 , A_2 , B_1 , and two B_2 . For the C–C stretching modes the five C–C bonds were used as a basis. The $\sigma_v(xz)$, $\sigma'_v(yz)$, and C_2 operators have a trace of 1. Thus the five C–C stretching modes possess symmetries two A_1 , A_2 , B_1 , and B_2 .

For the two C=C stretching modes, the $\sigma_v(xz)$ operators has a trace of two. All other operators except E have a trace

of 0. Thus the two C=C stretching modes possess symmetries A_1 and B_1 . For the 12 C–H wagging modes, all operators except E have a trace of 0. Thus the 12 C–H wagging modes possess symmetries three A_1 , three A_2 , three B_1 , and three B_2 .

There are three C–C–C bending modes. These bending modes correspond to distortion of the two four-membered rings and to the butterfly motion of the two four-membered rings relative to each other. The $\sigma'_v(yz)$ and C_2 operators have a trace of 1. The $\sigma_v(xz)$ operator has a trace of -1 . Thus the three C–C–C bending modes possess symmetries A_1 , A_2 , and B_2 . There are two C–C–C–C torsion modes, one for each of the four-membered rings. For the C–C–C–C torsion modes, the $\sigma_v(xz)$ operator has a trace of -2 . All other operators except E have a trace of 0. Thus the two C–C–C–C torsion modes possess symmetries A_2 and B_2 .

Combining the results of the Gaussview program [21] with the symmetry considerations, vibrational frequency assignments were made with a high degree of confidence. There is always some choice in the definition of internal coordinates for a normal mode analysis. However,

Table 1

Normal modes of dewar benzene calculated at the Hartree–Fock level of theory using the standard 6-311G** basis set

Symmetry	Normal mode	Calculated frequency	IR activity (km/mol)	Raman intensity ($\text{\AA}^4/\text{amu}$)	Assignment	Experimental frequency ^a	Corrected frequency ^b
A_1	ν_1	3361	9	247	C–H stretch	3106	3103
	ν_2	3246	55	150	C–H stretch	2989	2997
	ν_3	1766	0	45	C=C stretch	1561	1567
	ν_4	1301	5	23	C–H wag	1148	1153
	ν_5	1140	1	13	C–H wag	1013	1010
	ν_6	1025	27	13	C–C stretch	927	932
	ν_7	942	0	5	C–C stretch	847	856
	ν_8	892	78	8	C–H wag	790	790
	ν_9	422	5	8	C–C–C bend	388	385
A_2	ν_{10}	3324	IR inactive	159	C–H stretch	3071	3069
	ν_{11}	1424		7	C–H wag	1264	1262
	ν_{12}	1317		9	C–H wag	1178	1167
	ν_{13}	1062		1	C–C stretch	927	941
	ν_{14}	1021		1	C–H wag	–	905
	ν_{15}	856		4	C–C–C bend	778	781
	ν_{16}	364		2	C–C–C–C torsion	347	339
B_1	ν_{17}	3358	43	64	C–H stretch	3094	3101
	ν_{18}	1738	10	1	C=C stretch	1549	1543
	ν_{19}	1343	8	0	C–H wag	1178	1190
	ν_{20}	1186	0	0	C–H wag	–	1051
	ν_{21}	1071	0	10	C–C stretch	994	973
	ν_{22}	801	47	3	C–H wag	705	710
B_2	ν_{23}	3326	32	43	C–H stretch	3094	3071
	ν_{24}	3236	27	127	C–H stretch	2976	2988
	ν_{25}	1416	43	0	C–H wag	1276	1255
	ν_{26}	1282	7	1	C–H wag	1146	1136
	ν_{27}	1082	3	3	C–H wag	942	959
	ν_{28}	1021	6	0	C–C–C bend	927	931
	ν_{29}	912	11	1	C–C stretch	824	808
	ν_{30}	542	8	5	C–C–C–C torsion	494	505

^a H.F. Shurvell, D.W.T. Griffith, J.E. Kent, J. Raman Spectrosc. 2 (1974) 147.

^b Raw calculated frequencies multiplied by the correction factors in Table 4.

the coordinates defined above form a complete set and match the motion observed using the Gaussview program.

3. Results

Tables 1–3 present the calculated vibrational frequencies for dewar benzene at the Hartree–Fock, DFT (B3LYP), and MP2 levels of theory, respectively. The allowed infrared transitions are the vibrational modes having A_1 , B_1 , and B_2 symmetries. All modes are Raman active. Correction factors for the different types of vibrational modes were calculated following a procedure that was previously proposed [23]. The correction factors are obtained by taking the average of the ratios between the computed and experimental frequencies for all modes within a particular motion type. In all cases, there is very little variation in the ratios within a given motion type. The consistency of the correction factors extends across all the levels of theory. This indicates that the procedure should lead to reliable predictions. The computed correction factors

at the Hartree–Fock, DFT (B3LYP), and MP2 levels of theory are presented in Table 4. These correction factors were used to generate the predicted frequencies in the last column of Tables 1–3, respectively.

Fig. 2 presents a view of the normal modes of dewar benzene using the NCAPLOT utility in SPIROVIB [24]. The normal modes of dewar benzene have been studied in some detail [14–20], and the normal mode assignments have been presented in earlier papers [16,19]. The assignments given in Tables 1–3 are very similar to the earlier assignments [16,19] and generally confirm the earlier results. However, the internal coordinates are defined somewhat differently in this effort and will hopefully provide scientists with a more complete picture of the normal modes of dewar benzene.

Table 5 presents the calculated geometric parameters for the C_{2v} geometry of dewar benzene. The calculated geometry is compared against available experimental data [25–27]. The molecular orbitals and orbital energies of dewar benzene are presented in Fig. 3. The molecular orbitals were generated using the Chem3D program [28].

Table 2

Normal modes of dewar benzene calculated at the DFT (B3LYP) level of theory using the standard 6-311G** basis set

Symmetry	Normal mode	Calculated frequency	IR activity (km/mol)	Raman intensity ($\text{\AA}^4/\text{amu}$)	Assignment	Experimental frequency ^a	Corrected frequency ^b
A_1	ν_1	3202	9	300	C–H stretch	3106	3102
	ν_2	3096	38	166	C–H stretch	2989	2999
	ν_3	1626	0	34	C=C stretch	1561	1568
	ν_4	1176	5	21	C–H wag	1148	1153
	ν_5	1034	3	12	C–H wag	1013	1013
	ν_6	941	8	10	C–C stretch	927	933
	ν_7	866	0	6	C–C stretch	847	859
	ν_8	813	76	5	C–H wag	790	797
	ν_9	390	5	10	C–C–C bend	388	386
A_2	ν_{10}	3168	IR inactive	188	C–H stretch	3071	3069
	ν_{11}	1283		5	C–H wag	1264	1258
	ν_{12}	1199		12	C–H wag	1178	1175
	ν_{13}	954		0	C–C stretch	927	935
	ν_{14}	934		1	C–H wag	–	915
	ν_{15}	792		3	C–C–C bend	778	783
	ν_{16}	340		2	C–C–C–C torsion	347	345
B_1	ν_{17}	3199	45	74	C–H stretch	3094	3099
	ν_{18}	1599	10	2	C=C stretch	1549	1542
	ν_{19}	1202	2	2	C–H wag	1178	1178
	ν_{20}	1095	0	0	C–H wag	–	1073
	ν_{21}	982	0	8	C–C stretch	994	974
	ν_{22}	720	46	4	C–H wag	705	706
B_2	ν_{23}	3170	31	50	C–H stretch	3094	3071
	ν_{24}	3088	18	133	C–H stretch	2976	2991
	ν_{25}	1294	38	0	C–H wag	1276	1268
	ν_{26}	1160	7	1	C–H wag	1146	1137
	ν_{27}	968	3	1	C–H wag	942	949
	ν_{28}	938	6	0	C–C–C bend	927	927
	ν_{29}	832	11	2	C–C stretch	824	815
	ν_{30}	490	6	5	C–C–C–C torsion	494	497

^a H.F. Shurvell, D.W.T. Griffith, J.E. Kent, J. Raman Spectrosc. 2 (1974) 147.

^b Raw calculated frequencies multiplied by the correction factors in Table 4.

Table 3

Normal modes of dewar benzene calculated at the MP2 level of theory using the standard 6-311G** basis set

Symmetry	Normal mode	Calculated frequency	IR activity (km/mol)	Raman intensity (Å ⁴ /amu)	Assignment	Experimental frequency ^a	Corrected frequency ^b
A ₁	ν_1	3245	8	284	C–H stretch	3106	3096
	ν_2	3153	28	151	C–H stretch	2989	3008
	ν_3	1582	0	16	C=C stretch	1561	1567
	ν_4	1178	4	21	C–H wag	1148	1155
	ν_5	1035	2	9	C–H wag	1013	1015
	ν_6	967	4	10	C–C stretch	927	939
	ν_7	879	1	5	C–C stretch	847	854
	ν_8	816	76	5	C–H wag	790	800
	ν_9	390	5	10	C–C–C bend	388	393
A ₂	ν_{10}	3211	IR inactive	166	C–H stretch	3071	3064
	ν_{11}	1295		5	C–H wag	1264	1270
	ν_{12}	1201		10	C–H wag	1178	1178
	ν_{13}	976		0	C–C stretch	927	957
	ν_{14}	896		0	C–H wag	–	879
	ν_{15}	772		2	C–C–C bend	778	778
	ν_{16}	314		2	C–C–C–C torsion	347	336
B ₁	ν_{17}	3243	39	70	C–H stretch	3094	3094
	ν_{18}	1558	7	2	C=C stretch	1549	1543
	ν_{19}	1220	2	2	C–H wag	1178	1196
	ν_{20}	1110	0	0	C–H wag	–	1089
	ν_{21}	1022	0	7	C–C stretch	994	992
	ν_{22}	719	48	4	C–H wag	705	705
B ₂	ν_{23}	3212	22	46	C–H stretch	3094	3065
	ν_{24}	3146	11	117	C–H stretch	2976	3002
	ν_{25}	1298	34	0	C–H wag	1276	1273
	ν_{26}	1157	6	1	C–H wag	1146	1135
	ν_{27}	934	7	0	C–H wag	942	916
	ν_{28}	907	7	1	C–C–C bend	927	914
	ν_{29}	833	7	1	C–C stretch	824	817
	ν_{30}	476	5	5	C–C–C–C torsion	494	510

^a H.F. Shurvell, D.W.T. Griffith, J.E. Kent, J. Raman Spectrosc. 2 (1974) 147.^b Raw calculated frequencies multiplied by the correction factors in Table 4.

The bonding is difficult to determine directly from Fig. 3. Orbitals 6–19 form the 13 σ -orbitals of dewar benzene. The two π -bonds are readily identified with orbitals 20 and 21. The Mulliken overlap terms for the carbon–carbon single bonds are close to what would be expected for a single bond ($Q_{12} = 0.299$ and $Q_{13} = 0.337$). Likewise the Mulliken overlap term for the C=C double bond is also close to what would be expected for a typical double bond ($Q_{34} = 0.637$).

Normal modes of the same symmetry are always mixed to some degree. For example, a C–C stretching mode may have some C–H wagging character. However, in the case of dewar benzene, it was possible to determine the dominant motion type for all modes. This dominant motion type corresponds to the ‘assignment’ of the normal mode frequency. The consistency between empirical assignments based on correlating structure and vibrational modes frequencies for a large number of molecules and theoretical observations such as quantum chemical normal mode analysis is remarkably good. The assignments given in Tables 1–3 were straightforward and relatively unambiguous.

4. Discussion

Table 6 presents the predicted normal mode frequencies for dewar benzene-d₆. On deuteration of a molecule, all vibrational frequencies are shifted to lower frequencies. However, the ordering of the dominant motion types can be altered, causing an apparent ‘blue-shift’ in a particular normal mode type. These shifts often occur during deuteration when an accidental degeneracy occurs that is not present in the undeuterated compound.

Table 4
Correction factors for dewar benzene

	Hartree–Fock	DFT (B3LYP)	MP2
C–H stretch	0.9234	0.9686	0.9541
C=C stretch	0.8876	0.9644	0.9905
C–C stretch	0.9088	0.9914	0.9710
C–H wag	0.8862	0.9802	0.9807
C–C–C bend	0.9121	0.9885	1.0082
C–C–C–C torsion	0.9324	1.0144	1.0715

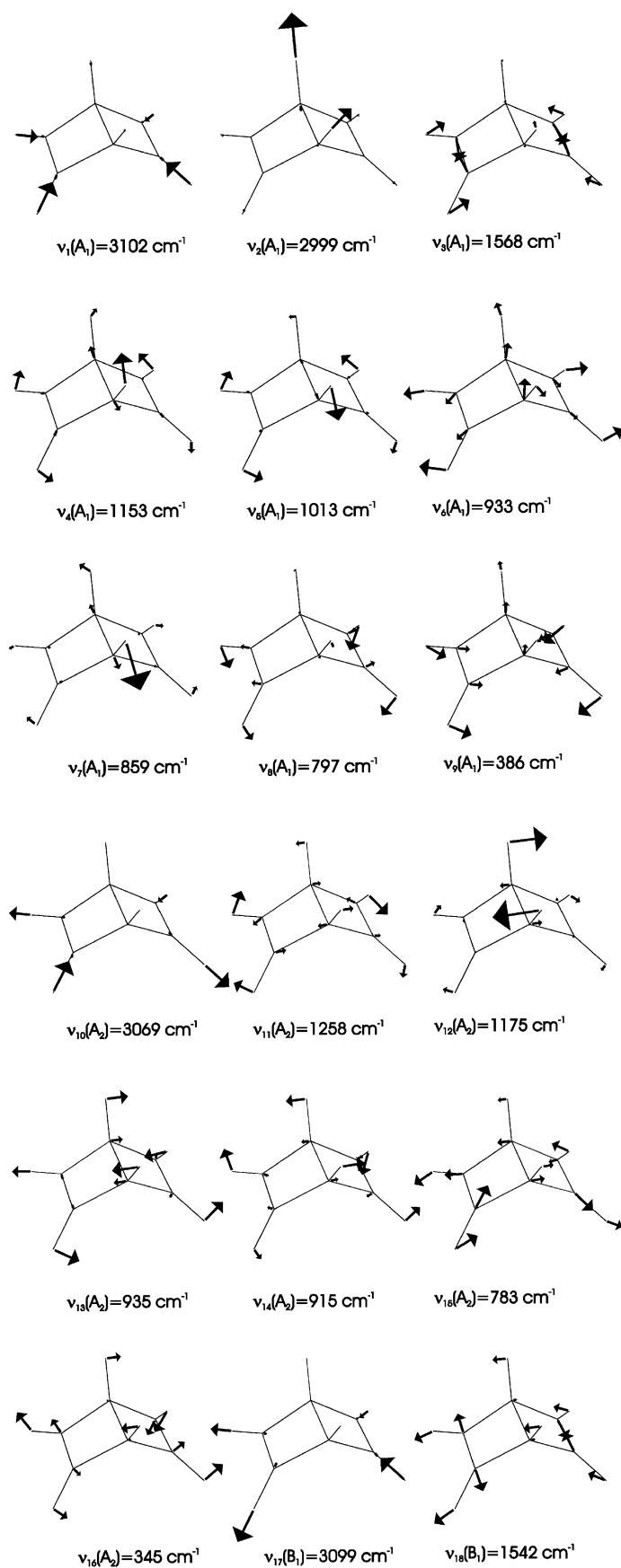


Fig. 2. Normal modes of Dewar benzene. Corrected DFT (B3LYP) normal mode frequencies are also displayed.

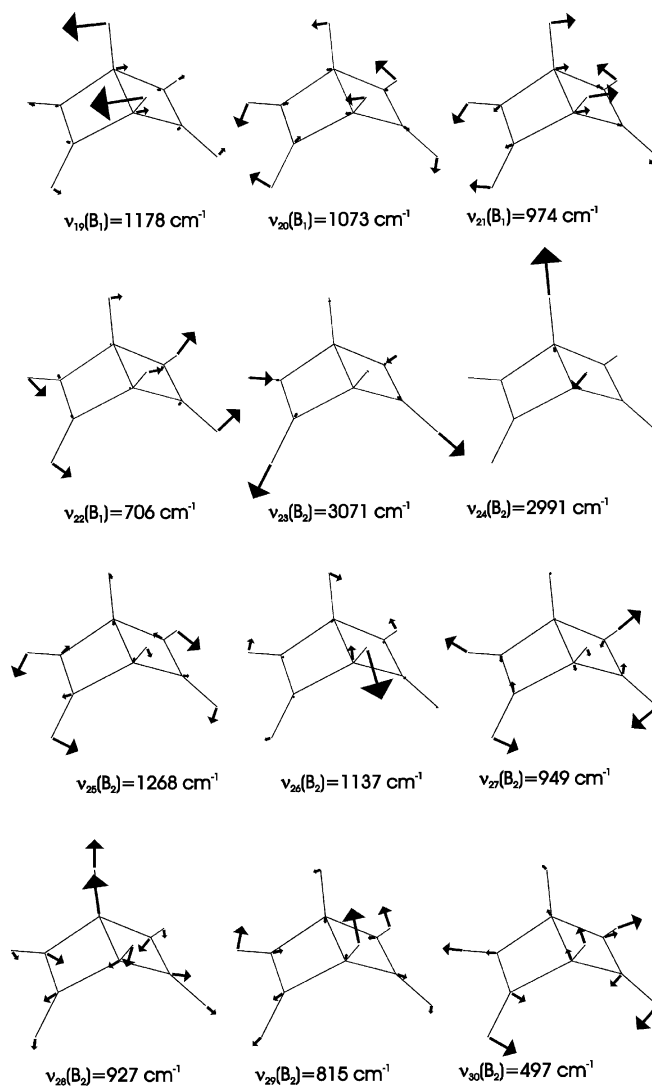


Fig 2. (continued)

In the case of dewar benzene, there are 12 C–H wagging modes. Eight of these C–H wagging modes are in the 1100–1200 cm^{-1} region. In these eight modes, (ν_4 , ν_5 , ν_{11} , ν_{12} , ν_{19} , ν_{20} , ν_{25} , and ν_{26}) the C_6 skeleton of the molecule remains relatively motionless. In the remaining four C–H wagging modes (ν_8 , ν_{14} , ν_{22} , and ν_{27}), the C_6 skeleton undergoes a significant translation or rotation, causing the normal mode frequencies to be lowered somewhat. The five C–C stretching modes (ν_6 , ν_7 , ν_{13} , ν_{21} , and ν_{29}) of dewar benzene occur in the 900–1000 cm^{-1} region.

During the substitution of hydrogen atoms by deuterium atoms, an accidental degeneracy occurs between the high frequency C–H wagging modes (C–D wagging modes) and the C–C stretching modes. This accidental degeneracy causes a remixing and reordering of the normal modes. In particular all five of the C–C stretching modes appear to be blue-shifted. By comparing Table 2 with Table 6, it is seen that normal modes (ν_6 , ν_7 , ν_{13} , ν_{21} , and ν_{29}) in Table 2 get mapped to normal modes (ν_4 , ν_5 , ν_{11} , ν_{19} , and ν_{25}) in

Table 5
Geometric parameters for dewar benzene

	Hartree–Fock	DFT (B3LYP)	MP2	Experiment ^a
C1–C2	155.7	157.6	157.8	157.4
C3–C4	132.3	133.7	135.1	134.5
C1–C3	152.6	153.0	152.6	152.4
C1–H	108.2	109.1	109.2	113.4
C3–H	107.5	108.4	108.6	112.4
C3–C1–C2	85.6	85.5	85.7	85.7
C1–C3–C4	94.4	94.5	94.3	94.3
C2–C1–H	121.6	121.2	120.7	108.0
C3–C1–H	118.7	118.7	119.0	–
C1–C3–H	132.1	131.8	131.9	126.7
C4–C3–H	133.4	133.7	133.7	–
C3–C1–C5	117.0	117.2	116.6	116.7
C3–C1–C2–C6	117.6	117.8	117.1	117.25
H–C1–C3–H	58.9	59.9	60.8	–
C2–C4–C3–H	177.2	176.7	176.1	180.0

Distance are presented in pm and angles in degrees. The numbering of the carbon atoms is given in Fig. 1.

^a E.A. McNeill, F.R. Scholer, J. Mol. Struct. 31 (1976) 65.

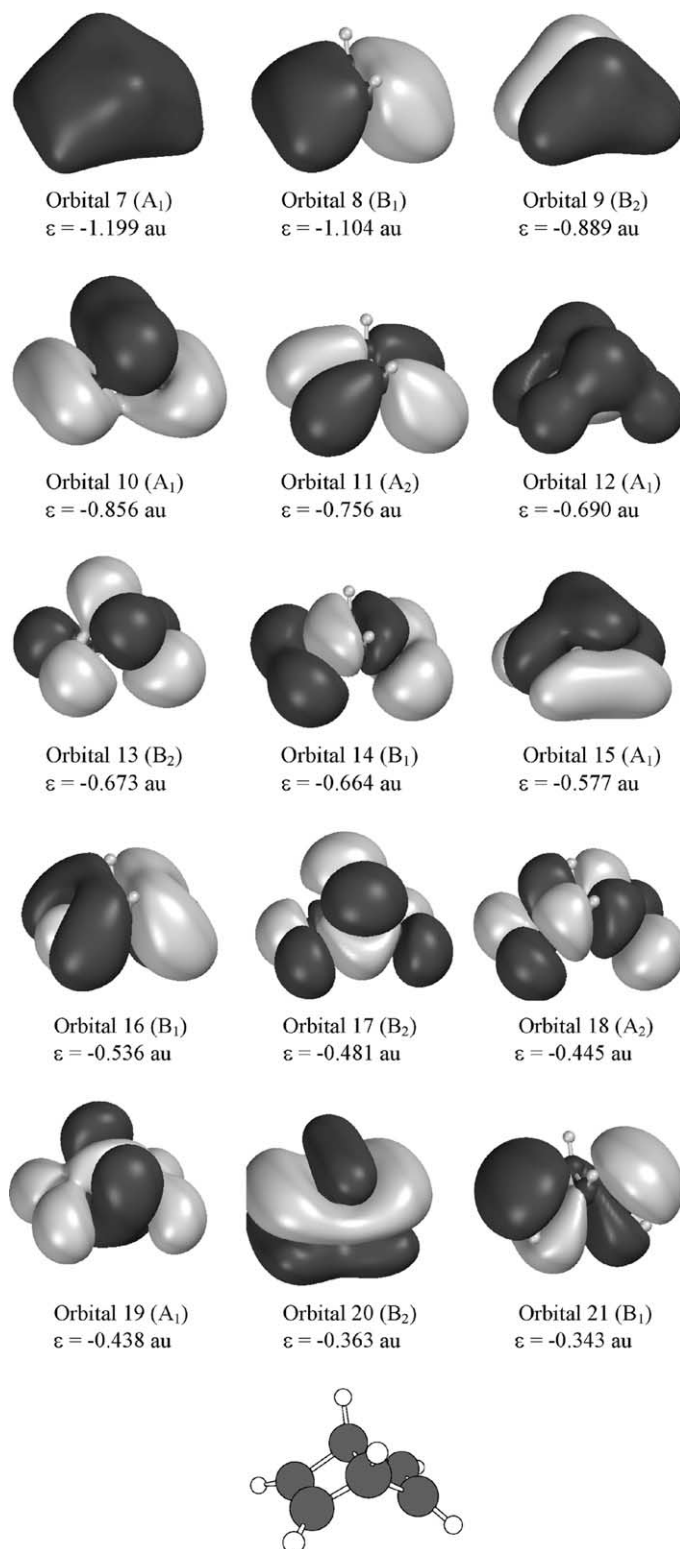


Fig. 3. Occupied molecular orbitals of dewar benzene. Atomic core orbitals have been omitted.

Table 6. It should be stressed that all normal modes were shifted to lower frequencies. However, a reordering of the normal modes can cause certain motion types (C–C stretch in this case) to be shifted to higher frequencies.

A high-energy conformer of dewar benzene with C_{2h} symmetry exists (see Fig. 4). This has sometimes been called *trans*-dewar benzene [29,30]. Tables 7 and 8 present the predicted normal mode frequencies for the C_{2h} form for

Table 6

Normal modes of dewar benzene-d₆ calculated at the DFT (B3LYP) level of theory using the standard 6-311G** basis set

Symmetry	Normal mode	Calculated frequency	IR activity (km/mol)	Raman intensity (Å ⁴ /amu)	Assignment	Corrected frequency ^a
A ₁	ν_1	2403	4	118	C–D stretch	2328
	ν_2	2280	24	77	C–D stretch	2208
	ν_3	1563	0	45	C=C stretch	1507
	ν_4	1066	2	19	C–C stretch	1057
	ν_5	920	0	10	C–C stretch	912
	ν_6	761	10	6	C–D wag	746
	ν_7	668	37	4	C–D wag	655
	ν_8	658	0	4	C–D wag	650
	ν_9	332	6	8	C–C–C bend	328
A ₂	ν_{10}	2330	IR inactive	91	C–D stretch	2257
	ν_{11}	1164		12	C–C stretch	1154
	ν_{12}	974		2	C–D wag	955
	ν_{13}	783		2	C–D wag	767
	ν_{14}	738		2	C–C–C bend	730
	ν_{15}	712		1	C–D wag	698
	ν_{16}	295		1	C–C–C–C torsion	299
B ₁	ν_{17}	2402	17	34	C–D stretch	2327
	ν_{18}	1528	13	3	C=C stretch	1474
	ν_{19}	1083	2	0	C–C stretch	1074
	ν_{20}	849	1	2	C–D wag	832
	ν_{21}	747	0	4	C–D wag	732
	ν_{22}	542	26	2	C–D wag	531
B ₂	ν_{23}	2332	22	23	C–D stretch	2259
	ν_{24}	2276	7	74	C–D stretch	2205
	ν_{25}	1128	18	0	C–C stretch	1118
	ν_{26}	956	2	0	C–D wag	937
	ν_{27}	905	4	0	C–C–C bend	895
	ν_{28}	812	1	4	C–D wag	796
	ν_{29}	655	16	0	C–D wag	642
	ν_{30}	412	3	4	C–C–C–C torsion	418

^a Raw calculated frequencies multiplied by the correction factors in Table 4.

dewar benzene (*trans*-dewar benzene). The predicted frequencies in Tables 7 and 8 may be of use to scientists in the search for this interesting molecule. Since the structures and bonding of the C_{2v} and C_{2h} forms of dewar

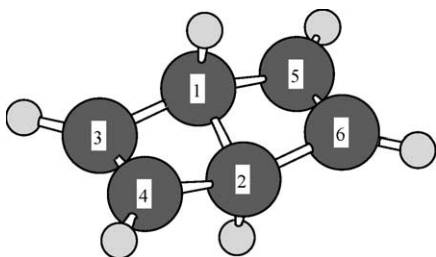


Fig. 4. Structure of *trans*-dewar benzene (C_{2h} symmetry).

Table 7

Normal modes of the *trans*-dewar benzene (C_{2h} form of dewar benzene) calculated at the DFT (B3LYP) level of theory using the standard 6-311G** basis set

Symmetry	Normal mode	Calculated frequency	IR intensity (km/mol)	Raman activity (Å ⁴ /amu)	Assignment	Corrected frequency ^a	
A _g	ν_1	3205	IR inactive	496	C–H stretch	3104	
	ν_2	3024		150	C–H stretch	2929	
	ν_3	1540		52	C=C stretch	1485	
	ν_4	1226		10	C–H wag	1200	
	ν_5	1106		27	C–H wag	1082	
	ν_6	978		18	C–C stretch	970	
	ν_7	909		5	C–H wag	890	
	ν_8	713		13	C–C–C–C torsion	723	
	ν_9	589		15	C–C stretch	584	
	B _g	ν_{10}	3174	IR inactive	303	C–H stretch	3074
ν_{11}		1436		7	C–H wag	1405	
ν_{12}		1209		0	C–H wag	1183	
ν_{13}		977		5	C–C stretch	969	
ν_{14}		803		9	C–C–C bend	794	
ν_{15}		689		9	C–H wag	674	
A _u		ν_{16}	3205	70	Raman inactive	C–H stretch	3104
		ν_{17}	1527	27		C=C stretch	1473
		ν_{18}	1401	8		C–H wag	1371
		ν_{19}	1091	1		C–C stretch	1082
	ν_{20}	1001	2		C–H wag	980	
	ν_{21}	887	1		C–H wag	868	
	ν_{22}	416	2		C–C–C–C torsion	422	
	B _u	ν_{23}	3175	13	Raman inactive	C–H stretch	3075
ν_{24}		3028	28		C–H stretch	2933	
ν_{25}		1223	26		C–H wag	1197	
ν_{26}		1112	27		C–H wag	1088	
ν_{27}		835	14		C–C–C bend	825	
ν_{28}		753	111		C–H wag	737	
ν_{29}		463	27		C–C stretch	459	
ν_{30}		324	7		C–C–C bend	320	

^a Raw calculated frequencies multiplied by the correction factors in Table 4.

benzene are very similar, it is likely that the use of the correction factors in Table 4 to predict the normal mode frequencies of the C_{2h} form of dewar benzene will lead to reliable predictions. The geometric parameters for the C_{2h} form of dewar benzene are presented in Table 9. The results are similar to earlier calculations [29]. Table 10 presents an energetic comparison of the C_{2v} and C_{2h} forms of dewar benzene. The free energy of the C_{2h} form of dewar benzene is approximately 300 kJ/mol more energetic than the C_{2v} form [29].

Table 8
Normal modes of *trans*-dewar benzene (the C_{2h} form of dewar benzene) calculated at the MP2 level of theory using the standard 6-311G** basis set

Symmetry	Normal mode	Calculated frequency	IR intensity (km/mol)	Raman activity ($\text{\AA}^4/\text{amu}$)	Assignment	Corrected frequency ^a
A_g	ν_1	3241	IR inactive	468	C–H stretch	3092
	ν_2	3096		130	C–H stretch	2954
	ν_3	1483		24	C=C stretch	1469
	ν_4	1219		8	C–H wag	1189
	ν_5	1110		24	C–H wag	1083
	ν_6	982		16	C–C stretch	954
	ν_7	889		4	C–H wag	867
	ν_8	729		14	C–C–C–C torsion	781
	ν_9	592		11	C–C stretch	575
B_g	ν_{10}	3211	IR inactive	269	C–H stretch	3064
	ν_{11}	1438		7	C–H wag	1403
	ν_{12}	1219		0	C–H wag	1189
	ν_{13}	1001		6	C–C stretch	972
	ν_{14}	810		6	C–C–C bend	817
	ν_{15}	680		9	C–H wag	663
A_u	ν_{16}	3241	61	Raman inactive	C–H stretch	3092
	ν_{17}	1469	21		C=C stretch	1455
	ν_{18}	1394	7		C–H wag	1360
	ν_{19}	1125	0		C–C stretch	1092
	ν_{20}	1013	2		C–H wag	988
	ν_{21}	861	0		C–H wag	840
	ν_{22}	410	2		C–C–C–C torsion	439
B_u	ν_{23}	3211	9	Raman inactive	C–H stretch	3064
	ν_{24}	3100	18		C–H stretch	2958
	ν_{25}	1228	25		C–H wag	1198
	ν_{26}	1114	27		C–H wag	1087
	ν_{27}	834	17		C–C–C bend	841
	ν_{28}	756	104		C–H wag	737
	ν_{29}	475	26		C–C stretch	461
	ν_{30}	333	6		C–C–C bend	336

^a Raw calculated frequencies multiplied by the correction factors in Table 4.

5. Summary and conclusions

The normal mode frequencies and corresponding vibrational assignments of dewar benzene in C_{2v} symmetry were examined theoretically using the GAUSSIAN 98 set of quantum chemistry codes. All normal modes were successfully assigned to one of six types of motion predicted by a group theoretical analysis (C–H stretch, C–C stretch, C=C stretch, CH wag, C–C–C bend, and C–C–C–C torsion) predicted by a group theoretical analysis. Comparing the vibrational frequencies with IR and Raman spectra available in the literature, a set of scaling factors is derived. Theoretical IR and Raman intensities are reported. The molecular orbitals of dewar benzene were examined. The predicted normal mode frequencies of *trans*-dewar benzene are presented.

Table 9
Geometric parameters for C_{2h} form of dewar benzene (*trans*-dewar benzene)

	Hartree–Fock	DFT (B3LYP)	MP2
C1–C2	149.7	151.5	152.2
C3–C4	133.4	134.9	136.6
C1–C3	157.0	157.9	157.3
C1–H	108.1	109.2	109.3
C3–H	107.4	108.3	108.6
C3–C1–C2	85.3	85.3	85.3
C1–C3–C4	91.0	91.2	90.8
C2–C1–H	109.3	108.7	107.9
C3–C1–H	100.1	99.9	100.4
C1–C3–H	135.0	137.7	135.1
C4–C3–H	132.8	133.0	132.8
C3–C1–C5	159.6	160.0	158.9
C3–C1–C2–C6	180.0	180.0	180.0
H–C1–C3–H	81.1	81.1	82.1
C2–C4–C3–H	170.8	171.2	176.1
C1–C3–C4–C2	–20.3	–19.8	–21.0
C4–C2–C1–C3	–18.1	–17.7	–19.9

Distance are presented in pm and angles in degrees. The numbering of the carbon atoms is given in Fig. 4.

Table 10

Comparison of the energetics of the C_{2v} and C_{2h} forms of dewar benzene

	E (hartree)	ΔE (kJ/mol)	S (J/mol K)	ΔS (J/mol K)	H (hartree)	ΔH (kJ/mol)	G (hartree)	ΔG (kJ/mol)
(a) At the DFT (B3LYP) level of theory								
C_{2v}	-232.0765860	0.00	284.47	0.00	-232.0710720	0.00	-232.1033760	0.00
C_{2h}	-231.9512358	329.11	287.65	3.19	-231.9455208	329.63	-231.9781868	328.68
(b) At the MP2 level of theory								
C_{2v}	-231.3553353	0.00	285.25	0.00	-231.3497723	0.00	-231.3821653	0.00
C_{2h}	-231.2292548	331.02	287.35	2.10	-231.2235618	331.37	-231.2561938	330.74

All calculation utilized the standard 6-311G** basis set. The C_{2h} form of dewar benzene is also called *trans*-dewar benzene.

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