J. Phys. Chem. A **1998,** *102,* 2679−2684 **2679**

Infrared and Raman Spectroscopy of Bis(4,4-dimethyl-2,5-cyclohexadien-1-ylidene). Vibrational Assignment by Hartree−Fock and Density Functional Theory Calculations and Depolarization Method

Bong Hyun Boo,*,† Sang Yeon Lee,‡ and Hoon-Kyun Na§

Department of Chemistry, Chungnam National University, Taejon 305-764, Korea, Center for Molecular Science, 373-1 Kusung-dong, Yusung-gu, Taejon 305-701, Korea, Department of Industrial Chemistry, Kyungpook National University, Taegu 702-701, Korea, and Korea Basic Science Institute, 52 Yeoeun-dong, Yusung-gu, Taejon 305-333, Korea

Received: October 7, 1997; In Final Form: January 5, 1998

IR and Raman spectra are measured to elucidate both the conformation and vibrational modes of bis(4,4-dimethyl-2,5-cyclohexadien-1-ylidene) in the fundamental state. It is found that the rule of mutual exclusion holds for the IR and Raman spectra. Ab initio Hartree−Fock and density functional theory (DFT) calculations with scaling were carried out to study the molecular structure and vibrational spectra. The HF and DFT calculations predict that the molecule has a planar D_{2h} structure, showing a little discrepancy between theory and experiment. In the Raman spectra, the most intense line is observed at 1640 cm^{-1}, which is consistent with the DFT value of 1647 cm^{-1} and is found to be a totally symmetric ring stretching along the long axis and in-plane C−H bending. In the IR spectra, however, the most outstanding line is 780 cm^{-1}, in excellent agreement with the theoretical value of 775 cm^{-1} and also found to be a z-polarized out-of-plane C−H and C−C−C bending (b_{1u}). The results of analysis have been confirmed by measuring the depolarization ratios from the solution Raman scattering. Comparison of the calculated and experimental vibrational spectra reveals that the DFT calculations are quite accurate in predicting the fundamental frequencies and intensities in the region below 1700 cm^{-1}.

Introduction

The electronic structure of the cross-conjugated polyenes has drawn a great deal of attention owing to their interesting features in the electronically excited[1] and ionized doublet states.[2−4] Previous spectroscopic studies showed that the conformation of bis(4,4-dimethyl-2,5-cyclohexadien-1-ylidene) (BDCY) in the fundamental state corresponds to that of biphenyl in the first electronically excited state.[1] Evidence of this structural behavior is supported by the spectroscopic observation that the spectral shape of BDCY in the fundamental state corresponds to that of biphenyl in the first electronically excited state and vice versa.[1] This spectroscopic behavior is explained by the specific difference of their π-electron distribution.[1]

The molecular structure of BDCY has been studied in the gas phase[5] and crystal[6] by the gas electron and X-ray diffraction methods, respectively. In the gas phase, the molecule BDCY was found to have a dihedral angle of 9.7° in nonplanar carbocyclic rings[5] that is described by $C_6{-}C_1{-}C_2{=}C_3$. The molecular model and the numbering of the atoms are presented in Figure 1. In the crystal, however, the molecule was found to deviate from planarity to different extents such that the torsional angles about the single and double bonds vary by only 5.1° and 1.2°, respectively.[6] It is noted for comparison that the torsional angle of the bond between the two phenyl rings in biphenyl is about 42° in the gas phase.[7,8] In the solid state, however, the biphenyl molecule is planar.[9−13] This can be taken as an indication that crystal-packing forces are sufficiently large to favorably compensate the steric strain. All six-membered rings are slightly in boat conformations owing to the interactions between the ortho hydrogen atoms across the central double bond.[6]

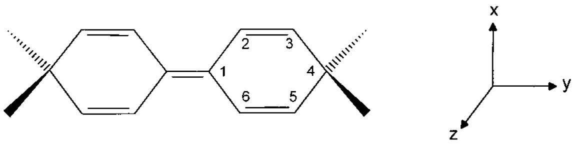

Figure 1. Molecular model of bis(4,4-dimethyl-2,5-cyclohexadien-1-ylidene) and the numbering of the atoms.

Of particular importance is the determination of fundamental vibrational frequencies and modes in the ground state in order to provide insight into the vibronic spectra in the electronically excited state. As revealed in the literature, the vibrational progression appended to the 0−0 band origin in fluorene includes fundamentals, overtones, second overtones, and combination bands as well as fundamentals.[14−19] Exact assignment of fundamentals in the ground state is quite necessary for the determination of overtone and combination bands in the excited state.

Thus a reliable theoretical study is required to predict the weak bands as well as the bands of both IR and Raman inactive modes and to distinguish fundamentals and modes among the peaks appearing in the vibrational−electronic spectra. Recent density functional theory (DFT) calculations on vibrational spectra predict fundamentals of molecules with high accuracy and with moderate computational efforts.[20−30] DFT calculations have been applied as a cost-effective procedure to estimate physical properties of molecules.[31−33] It is reported that the

---

[†] Chungnam National University and Center for Molecular Science.

[‡] Kyungpook National University.

[§] Korea Basic Science Institute.

S1089-5639(97)03260-X CCC: $15.00

DFT method reproduces observed vibrational frequencies with higher accuracy than obtained by the HF and MP2 calculations. Even when an uniform scaling is performed for the computed vibrational frequencies, the DFT study shows better consistency with the experimental frequencies than do the HF and MP2 ones.[20,22−25] As an example, we wish to consider a recent theoretical work for the vibrational assignment of benzene.[22,23,26] MP2 calculations obtained by using the 6-311G(d,p) basis set still underestimate the fundamentals of benzene such as 707, 967, and 990 cm^{-1}, the frequencies corresponding to the CCC out-of-plane bending, and overestimate that of 1309 cm^{-1}, the frequency corresponding to a b_{2u} mode that tends to dissociate into three acetylene molecules. These fundamentals are, however, accurately predicted by the DFT calculation using the Becke-Lee−Yang−Parr (BLYP) functional.[22,23,26]

Rauhut and Pulay (RP) applied the BLYP functional and Becke 3-Lee−Yang−Parr (B3LYP) functional methods to 20 small molecules such as benzene, ether, and methanol, etc. of which fundamentals are exactly assigned, and then derived uniform scaling factors, 0.995 and 0.963, having the root-mean-square (rms) deviations of 26.2 and 18.5 cm^{-1}, respectively.[27] It is reported in the literature that the scaling factors are derived by the least-squares procedure.[27] When these scaling factors are applied to another 11 molecules such as aniline, ethanol, and oxetane, etc., the rms deviations turned out to be 26.9 and 19.7 cm^{-1} for the BLYP and B3LYP methods, respectively.

We have measured the infrared and Raman spectra of BDCY and performed the normal vibrational mode analyses at the HF and DFT levels of theory using the 6-31G* basis set. By using the HF and DFT methods with the scaling factors, we could reproduce the vibrational spectra of BDCY and could identify some fundamentals of the molecule by comparing the observed peak position and peak intensities with the theoretically derived ones. However, it should be noticed that the overconfidence should be avoided in the comparison of the theory and the experiment since the IR and Raman spectra were measured in the crystal, and the calculations were carried out for the isolated molecule.

It is found in this study that this DFT approach is sufficiently powerful to predict fundamentals of BDCY in view of accuracy and computational effort.

Experimental and Calculations

The compound BDCY was prepared by a reductive coupling of 4,4-dimethyl-2,5-cyclohexadienone (DCY) with $TiCl_3$/$LiAlH_4$.[34] Compound DCY was prepared from 4,4-dimethylcyclohexenone by an oxidation reaction using 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ).[35]

A Spectra-Physics 2060-7S Beam Lok Ar ion laser at the wavelength of 514.5 nm was used for the sample excitation. The scattered light was collected through a collecting lens and focused on the slit of a Jobin-Yvon U-1000 double monochromatized of which the focal length is 1 m. The monochromatized photon was detected by a Hamamatsu R943-02 photomultiplier tube, which can be cooled to −20 °C. A saturated CCl_4 solution was used to obtain Raman bands as strong as possible. The depolarization ratio in the solution was obtained by dividing the count rate of the scattered light of which the electric vector is perpendicular to the electric vector of the incident light by the count rate of the parallel vector signals. The spectral resolution was 0.15 cm^{-1} at the slit width of 10 μm. The IR spectra of the KBr pellet were measured by a Digilab-FTS-80 FTIR spectrometer. The infrared resolution was 2 cm^{-1}.

The molecular geometries are optimized at the HF and B3LYP levels of theory with the standard 6-31G* basis set by using the Gaussian 94 program[36] at SERI in Korea. Fundamentals are computed with the HF and DFT methods and then scaled by 0.8929 and 0.963, respectively. The frequencies and normal modes for BDCY were determined by diagonalizing the mass-weighted force-constant matrix.

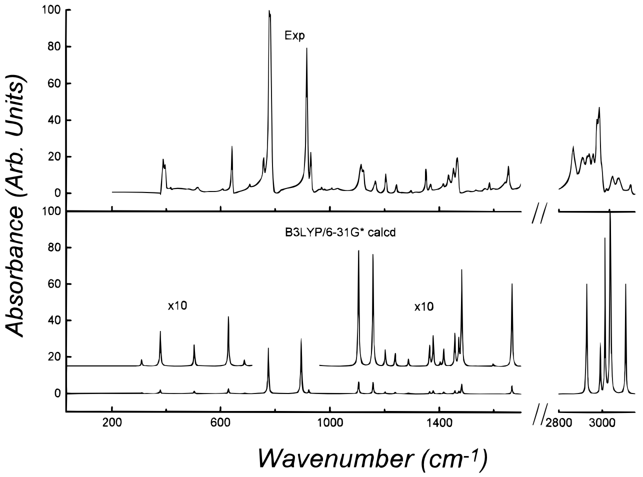

Figure 2. Comparison of the experimental (upper) and calculated (lower) infrared spectra of bis(4,4-dimethyl-2,5-cyclohexadien-1-ylidene).

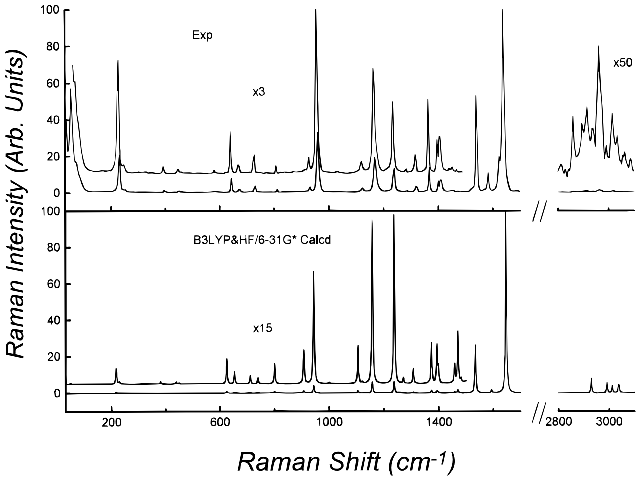

Figure 3. Comparison of the experimental (upper) and calculated (lower) Raman spectra of bis(4,4-dimethyl-2,5-cyclohexadien-1-ylidene).

Results and Discussion

IR and Raman spectra are measured to elucidate both the conformation and vibrational modes of BDCY in the fundamental state. In Figures 2 and 3, we present the observed infrared and Raman spectra, respectively. We have avoided the analysis of the lattice modes appearing at the wavenumbers under 100 cm^{-1}. As seen in Table 1, it is found that the rule of mutual exclusion holds for the IR and Raman spectra. This indicates that the BDCY molecule is centrosymmetric.

To predict the experimental frequencies, the uniform scaling factors of 0.8929 and 0.963 are used for HF and DFT, respectively, the factor of 0.8929 has been used in our previous HF calculations on fluorene,[29] pyrrole,[25] and carbazole,[25] and the factor of 0.963 has been used by RP and been verified as one of the good scaling factors.[27] The simulated spectra presented in Figures 2 and 3 are scaled by 0.963. It is noticed that the simulated spectra have a Lorentzian distribution having a fwhm of 4 cm^{-1}.

The rms deviations of the scaled frequencies listed in Table 1 from experiment turned out to be 22.9 cm^{-1} for HF and 20.4 cm^{-1} for DFT. It is noticed that the comparison between theory and experiment is made for 53 fundamentals listed in Table 1, and the fundamentals are assigned on the basis of this DFT calculation. It is shown in this study that for the 53 experimental frequency data, scaling factors of 0.889 for the HF calculation and 0.960 for the DFT calculation slightly better reproduce the experimental fundamentals with the rms deviations of 22.3 and 19.9 cm^{-1}, respectively. Compared to the published results, the rms deviations in both of the method's values are close to each other. The large deviation of the DFT calculation from experiment occurs in the C−H stretching mode as shown in Table 1. The DFT calculation too much overestimates the C−H stretching frequencies. This large deviation from experiment in the C−H stretching region is also observed by RP.[27] If we do not include the fundamentals at 2857 and 2958 cm^{-1} in the optimization of the scaling factors, the scaling factors are optimized as 0.889 and 0.966 for the HF and DFT calculations, respectively. Notice that the scaling factor for the HF calculation is invariant with respect to the exclusion of the C−H stretching fundamentals and also that the rms value is not significantly reduced. However, the scaling factor for the DFT calculation varies and also the rms value is significantly reduced to 14.0 cm^{-1}. Since these scaling factors are quite close to the previously used scaling factors by RP,[27] we confirmed that our assignment of the vibrational frequencies and their modes are correctly made and that the DFT method can correctly estimate the fundamentals of cross-conjugated polyene molecules below 1700 cm^{-1}.

The observed peak positions and intensities in the IR and Raman spectra are quite consistent with those in the simulated IR and Raman spectra shown in Figures 2 and 3. But the DFT method slightly overestimates the vibrational frequencies above 2950 cm^{-1} corresponding to the C−H stretching vibration and too much overestimates the infrared and Raman intensities in the C−H stretching region. In the Raman spectrum, the most intense line is observed at 1640 cm^{-1}, being consistent with the DFT value 1647 cm^{-1}, and is found to correspond to a totally symmetric ring stretch (a_g) along the long axis (y-axis). In the IR spectra, however, most outstanding line is 780 cm^{-1} being in excellent agreement with the DFT value 775 cm^{-1}, and is also found to being due to a z-polarized out-of-plane C−H and CCC bending (b_{1u}). Taking this most intense band as a reference IR peak, we established the percent relative intensities of the fundamentals predicted by the HF and DFT methods and those of the observed bands as shown in Table 1 and could direcltly compare the qualities of the two calculation methods in the estimation of the intensities.

Assignment of Fundamentals

The BDCY molecule involves 102 fundamentals having the various symmetries of $17a_{1g} + 9a_u + 14b_{1g} + 12b_{1u} + 8b_{2g} + 16b_{2u} + 12b_{3g} + 14b_{3u}$. We seek to determine fundamentals making a one-to-one correspondence between the observed frequencies and calculated ones. Fundamentals in the region $\nu < 1700$ cm^{-1} are well-separated and thus almost straightforward identification is achieved. The scaled vibrational frequencies and modes calculated with the DFT and HF methods are presented in Table 1. However, the assignments of some of fundamentals are not straightforward due to the slight band separations and/or probably to the band overlapping and due to the low intensities.

Almost all the modes are delocalized over the whole molecule and thus cannot be assigned to several local vibrations. This is a characteristic feature of cyclic compounds, particularly aromatic compounds.[37] Therefore we represent in Table 1 only the approximate mode descriptions.

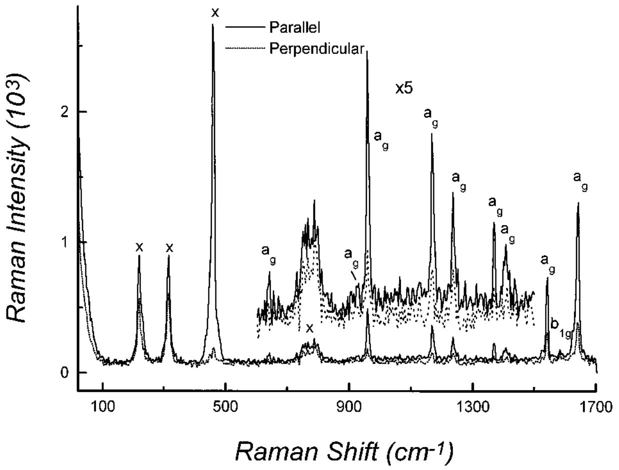

Figure 4. Polarized Raman spectra of the saturated solution of bis-(4,4-dimethyl-2,5-cyclohexadien-1-ylidene) in CCl_4. The "x" refers to the solvent peaks. The spectra denoted by the solid and dotted lines were obtained with the electric vector of the scattered light parallel and perpendicular to the electric vector of the incident light, respectively.

a_g Symmetry. On the basis of our calculations and the Raman spectra reported here, we made a reliable one-to-one correspondence between the observed frequencies and any of our fundamentals calculated with the DFT and HF methods in the region below 1700 cm^{-1}.

Among the 17 a_g fundamentals, 13 fundamentals except the C−H stretching modes are identified. These are 232, 396, 644, 704, 932, 960, 1168, 1240, 1368, 1408, 1472, 1540, and 1640 cm^{-1}. The fundamentals at 644, 932, 960, 1168, 1240, 1368, 1408, 1540, and 1640 cm^{-1} are actually observed in the polarized solution Raman spectrum presented in Figure 4, and their depolarization ratios are found to be smaller than 0.75 and are close to the theoretical values listed in Table 1, indicating that the modes belong to a_g.

The DFT calculation indicates that the intense Raman lines at 1540 and 1640 cm^{-1} almost involve the ring stretching vibration along the long axis (here the y-axis). Literature shows that the Raman scattering intensity is proportional to the square of the magnitude of the oscillating dipole moment.[38] As shown in Table 2, the equilibrium polarizability α_{yy} is much greater than α_{xx} and α_{zz}. Therefore, we presume that the major contribution of the intensities of the Raman bands are from the tensor component yy and that the derivative with respect to the normal coordinate q_i for a given vibration i, $d\alpha_{yy}/dq_i$, is also the greatest. These effects give rise to high effectiveness of the Raman scattering of the vibrations of 1540 and 1640 cm^{-1}. It is also shown in the DFT calculation that the fundamental at 704 cm^{-1} corresponds to the ring contraction along the short axis (x). This is the reason the Raman intensity of the fundamental is too low.

It is shown in the DFT calculation that most of the fundamentals involve more or less in-plane CH and CCC bending, CH_3 bending, CCC scissoring, and CH and CH_3 stretching modes.

a_u Symmetry. Under D_{2h} symmetry, a_u modes are infrared and Raman inactive, and thus their fundamentals are not assigned. Our DFT calculations predict nine fundamentals identifiable as a_u, 47, 219, 239, 476, 739, 926, 1001, 1459, and 2986 cm^{-1}. Most of the fundamentals include more or less ring

TABLE 1: Comparison of the Experimental and Calculated Vibrational Frequencies of Bis(4,4-dimethyl-2,5-cyclohexadien-1-ylidene)[a]

		HF/6-31G*				B3LYP/6-31G*		exptl				
sym	no.[b]	freq	$I_{\rm IR}$ (%)	$I_{\rm Ram}$ (%)	DP[c]	freq	$I_{\rm IR}$ (%)	freq	$I_{\rm IR}$ (%)	$I_{\rm Ram}$ (%)	DP[c]	approximate type of mode[d]
a$_g$	7	216	0	0.6	0.32	218	0	232	0	21		ip (CCC), b (CH$_3$), sci (CCC)
	18	378	0	0.1	0.13	382	0	396	0	2		ip (CCC), sci (CCC), b (CH$_3$)
	26	615	0	0.9	0.29	625	0	644	0	8	~0	ip (CCC), b (CH$_3$), sci (CCC)
	30	691	0	0.3	0.72	712	0	704	0	0.4		ip (CH and CCC), sci and str (CCC), b (CH$_3$)
	38	902	0	0.9	0.43	907	0	932	0	3	~0	ip (CH and CCC), b (CH$_3$), roc (CCC)
	43	945	0	3.8	0.27	944	0	960	0	33	0.21	ip (CH and CCC), sci (CCC), b (CH$_3$)
	54	1171	0	6.1	0.38	1158	0	1168	0	19	0.27	ip (CH), str (CCC), b (CH$_3$)
	57	1242	0	6.2	0.40	1238	0	1240	0	13	0.46	ip (CH)
	64	1390	0	1.5	0.33	1374	0	1368	0	14	0.28	b (CH$_3$), ip (CH), str and sci (CCC)
	67	1409	0	0.5	0.36	1399	0	1408	0	7	0.38	ip (CH and CCC), b (CH$_3$)
	74	1469	0	1.9	0.64	1471	0	1472	0	1		b (CH$_3$)
	78	1582	0	26	0.32	1535	0	1540	0	53	0.31	ip (CH and CCC)
	81	1697	0	100	0.30	1647	0	1640	0	100	0.25	ring str, ip (CH)
	86	2858	0	8.1	0.04	2929	0					str (CH$_3$)
	94	2929	0	3.6	0.71	3012	0					str (CH$_3$)
	98	2976	0	3.4	0.13	3039	0					str (CH)
	102	3060	0	2.9	0.18	3108	0					totally symmetric CH stretching
a$_u$	2	55	0	0	0.42	47	0					ring tor, two (CCC), b (CH$_3$)
	8	229	0	0	0.45	219	0					b (CH$_3$)
	11	245	0	0	0.32	239	0					b (CH$_3$), twi (CCC)
	22	486	0	0	0.35	476	0					ring tor, b (CH$_3$)
	31	757	0	0	0.43	739	0					oop (CH and CCC)
	42	984	0	0	0.63	926	0					oop (CH and CCC)
	49	1012	0	0	0.73	1001	0					b (CH$_3$), str (CCC)
	72	1457	0	0	0.40	1459	0					b (CH$_3$)
	87	2905	0	0	0.72	2986	0					str (CH$_3$)
b$_{1g}$	12	260	0	0.01	0.75	254	0					b (CH$_3$)
	15	313	0	0.02	0.75	316	0	336	0	0.5		ip C$=$C$_{1'}$ bend, wag (CCC), b (CH$_3$)
	19	432	0	0.07	0.75	439	0	452	0	1		ring defm, wag (CCC)
	24	565	0	0.01	0.75	576	0	584	0	0.8		b (CH$_3$), ip (CH and CCC)
	36	895	0	0.03	0.75	897	0	920	0	0.9		b (CH$_3$), ip (CH and CCC), wag (CCC)
	53	1124	0	0.06	0.75	1122	0					ip (CH)
	59	1272	0	0.2	0.75	1271	0	1288	0	1		ip (CH and CCC), b (CH$_3$)
	61	1312	0	0.6	0.75	1307	0	1320	0	4		ip (CH and CCC), wag (CCC), b (CH$_3$)
	66	1397	0	1.4	0.75	1394	0	1400	0	6		ip (CH and CCC), b (CH$_3$)
	76	1478	0	0.1	0.75	1482	0					b (CH$_3$)
	79	1633	0	1.6	0.75	1594	0	1584	0	11	~1	ring str, ip (CH)
	89	2911	0	5.8	0.75	2991	0					str (CH$_3$)
	95	2972	0	3.8	0.75	3036	0					str (CH)
	99	3027	0	0.01	0.75	3086	0					str (CH)
b$_{1u}$	1	24	0.1	0	0.00	27	0.2					ring tor, roc (CCC)
	5	148	0.08	0	0.69	145	0.02					ring tor, roc (CCC), b (CH$_3$)
	17	372	7.6	0	0.50	379	7.6	389	19	0		ring tor, roc (CCC), b (CH$_3$)
	27	625	8.0	0	0.75	629	11	642	26	0		ring tor, wag and str (CCC), b (CH$_3$)
	33	791	100	0	0.37	775	100	780	100	0		oop (CH and CCC)
	39	914	0.4	0	0.41	909	0.02					b (CH$_3$), str and roc (CCC)
	46	1007	0.03	0	0.33	961	0.01					oop (CH and CCC)
	51	1135	28	0	0.37	1105	25	1115	16	0		oop (CH and CCC), roc (CCC), b (CH$_3$)
	63	1352	4.1	0	0.42	1365	4.5	1352	13	0		b (CH$_3$), str and wag (CCC)
	70	1458	3.5	0	0.34	1457	7.0	1434	10	0		b (CH$_3$)
	83	2852	43	0	0.35	2925	47					str (CH$_3$)
	92	2927	52	0	0.35	3011	53					str (CH$_3$)
b$_{2g}$	6	220	0	0.04	0.75	215	0					b (CH$_3$), twi (CCC)
	10	240	0	0.01	0.75	234	0					b (CH$_3$), twi (CCC), ring tor
	21	459	0	0.03	0.75	450	0	464	0	0.5		ring tor, b (CH$_3$), twi (CCC)
	32	755	0	0.2	0.75	740	0	732		4		oop (CH and CCC)
	45	994	0	0.02	0.75	946	0					oop (CH and CCC)
	48	1014	0	0.05	0.75	1001	0	1036	0	0.6		b (CH$_3$), twi (CCC)
	73	1457	0	0.6	0.75	1459	0					b (CH$_3$)
	88	2905	0	0.2	0.75	2986	0					str (CH$_3$)
b$_{2u}$	14	308	1.4	0	0.41	310	1.5	336	0.2	0		sci (CCC), b (CH$_3$), ip (CCC)
	23	497	1.4	0	0.49	504	4.7	516	3	0		ip (CH and CCC), sci (CCC), b (CH$_3$)
	29	673	0.1	0	0.33	688	1.3	707	5	0		ip (CH and CCC), str and sci (CCC), b (CH$_3$)
	35	889	0.7	0	0.39	895	121	917	79	0		ip (CH and CCC), b (CH$_3$), sci (CCC)
	41	895	86	0	0.35	923	7.7	931	22	0		ip (CH and CCC)
	47	964	5.0	0	0.37	963	0.1					ip (CH and CCC), sci (CCC), b (CH$_3$)
	55	1169	25	0	0.39	1158	25	1166	7	0		ip (CH), str (CCC), b CH$_3$)
	56	1208	13	0	0.53	1203	3.5	1205	11	0		ip (CH)
	65	1393	1.3	0	0.42	1378	6.7	1368	5	0		sci and str (CCC), b (CH$_3$), ip (CH)

TABLE 1 (Continued)

		HF/6-31G*				B3LYP/6-31G*		exptl				
sym	no.[b]	freq	I_{IR} (%)	I_{Ram} (%)	DP[c]	freq	I_{IR} (%)	freq	I_{IR} (%)	I_{Ram} (%)	DP[c]	approximate type of mode[d]
	69	1417	4.4	0	0.36	1417	3.8	1415	5	0		ip (CH and CCC), b (CH_3)
	75	1470	3.4	0	0.37	1472	5.6	1452	14	0		b (CH_3)
	82	1696	7.6	0	0.34	1667	18	1655	15	0		ring str, i p (CH)
	85	2858	181	0	0.35	2928	232	2857	26	0		str (CH_3)
	93	2929	92	0	0.38	3012	82					str (CH_3)
	97	2974	44	0	0.52	3038	44	2958	47	0		str (CH)
	100	3028	4.4	0	0.34	3087	3.1					str (CH)
b_{3g}	3	42	0	0.03	0.75	48	0					oop ($C_1-C_{1'}$), roc (CCC), b (CH_3)
	9	221	0	0.07	0.75	230	0					roc (CCC), ring tor, b (CH_3)
	20	441	0	0.01	0.75	445	0					oop (CH and CCC), b (CH_3), wag (CCC)
	28	658	0	0.4	0.75	654	0	672	0	2		oop (CH and CCC), roc and str (CCC), b (CH_3)
	34	807	0	0.7	0.75	801	0	812	0	2		oop (CH and CCC)
	40	914	0	0.6	0.75	909	0					b (CH_3), roc and str (CCC)
	44	995	0	0.6	0.75	945	0					ip (CH and CCC)
	52	1135	0	1.4	0.75	1105	0	1124	0	2		roc (CCC), ip (CH and CCC), b (CH_3)
	62	1379	0	0.02	0.75	1365	0					b (CH_3), str and wag (CCC)
	71	1458	0	0.05	0.75	1457	0	1456	0	1		b (CH_3)
	84	2852	0	0.08	0.75	2925	0					str (CH_3)
	91	2927	0	0.6	0.75	3011	0					str (CH_3)
b_{3u}	4	130	0.03	0	0.53	133	0.07					ip (CH and CCC), wag (CCC), b (CH_3)
	13	268	0	0	0.60	261	0					b (CH_3)
	16	369	0.03	0	0.38	373	0.3	396	sh	0		ip $C_1{=}C_{1'}$ bend, wag (CCC), b (CH_3)
	25	591	0.1	0	0.41	602	0.01	608	2	0		ring defm
	37	897	0	0	0.52	900	0.2					b (CH_3), ip (CH and CCC)
	50	1088	1.7	0	0.35	1103	2.7					ip (CH and CCC), b (CH_3)
	58	1232	1.1	0	0.47	1239	2.8	1244	5	0		ip (CH and CCC), wag (CCC)
	60	1292	0.08	0	0.37	1288	1.6	1297	2	0		ip (CH and CCC), wag (CCC), b (CH_3)
	68	1409	0.1	0	0.51	1404	0.9					ip (CH and CCC)
	77	1479	13	0	0.37	1483	21	1467	20	0		b (CH_3)
	80	1637	0.5	0	0.75	1598	0.5	1585	6	0		ring str, ip (CH)
	90	2911	120	0	0.34	2991	110					str (CH_3)
	96	2973	57	0	0.39	3037	63					str (CH)
	101	3058	55	0	0.62	3106	77					str (CH)

[a] Vibrational frequencies in cm^{-1}. [b] Mode numbers are extracted from the output of the DFT calculation. [c] Depolarization ratio. [d] Approximate mode descriptions are extracted from output of the DFT calculation. ip refers to in-plane; oop to out-of-plane, "b" to bending, sci to scissoring, roc to rocking, tor to torsion, twi to twisting, and wag to wagging, and the modes assigned are sorted in the order of their contributions to the vibrational motions.

TABLE 2: Polarizabilities of Bis(4,4′-dimethyl-2,5-cyclohexadien-1-ylidene) Calculated with the HF/6-31G* and B3LYP/6-31G* Methods

component	α_{xx}	α_{xy}	α_{yy}	α_{xz}	α_{yz}	α_{zz}
HF	131.774	0.000	352.092	0.000	0.000	93.407
B3LYP	144.342	0.000	383.776	0.000	0.000	98.177

torsion, CCC twisting, CH_3 stretching or bending, and out-of-plane CH and CCC bending modes.

b_{1g} Symmetry. Among the 14 fundamentals attributable to the b_{1g} mode, only eight fundamentals are identified owing to the weak intensities in the Raman spectrum. These are 336, 452, 584, 920, 1288, 1320, 1400, and 1584 cm^{-1}. The assignment of the fundamental at 1584 is confirmed by the depolarization measurement in which the depolarization ratio turned out to be almost unity (Figure 4), indicating that the vibrational mode is antisymmetric.

Almost all the vibrations include CH_3 bending, CCC wagging, in-plane CH and CCC bending, and CH and CH_3 stretching modes.

b_{1u} Symmetry. Among the 12 b_{1u} fundamentals, the only six fundamentals that we could identify are 389, 642, 780, 1115, 1352, and 1434 cm^{-1}. These fundamentals are found to have high intensity in the IR spectrum (Figure 2). The fundamental at 780 cm^{-1}, having out-of-plane CH and CCC bending modes, is most intense in the observed IR spectrum.

Most of the vibrations include ring torsion, CCC rocking and wagging, CH_3 bending, out-of-plane CH and CCC bending, and CH_3 stretching modes.

b_{2g} Symmetry. Among the eight b_{2g} fundamentals, only three fundamentals are identified owing to the weak Raman intensities. These are 464, 732, and 1036 cm^{-1}.

Most of the vibrations include ring torsion, CCC twisting, CH_3 bending, out-of-plane CH and CCC bending, and CH_3 stretching modes.

b_{2u} Symmetry. This mode involves the in-plane *y* (long axis)-polarized vibration of which intensities are quite high compared to the in-plane vibration (b_{3u} mode) along the short axis (*x*). Among the 16 b_{2u} fundamentals, as many as 13 fundamentals are identified owing to their relatively higher intensities in the IR spectrum. These are 336, 516, 707, 917, 931, 1166, 1205, 1368, 1415, 1452, 1655, 2857, and 2958 cm^{-1}. The DFT calculation correctly estimates the observed IR intensities of the fundamentals at 917 and 931 cm^{-1}, but the HF calculation too much underestimates the intensity of 917 cm^{-1} and overestimates that of 931 cm^{-1} as shown in Table 1.

Most of the vibrations include CCC scissoring, CH_3 bending, in-plane CH and CCC bending, and CH and CH_3 stretching modes.

b_{3g} Symmetry. Among the 12 b_{3g} fundamentals, only four fundamentals are identified because of the weak Raman intensities. These are 672, 812, 1124, and 1456 cm^{-1}.

Most of the vibrations include ring torsion, CCC rocking and wagging, CH_3 bending, in-plane and out-of-plane CH and CCC bending, and CH_3 stretching modes.

b_{3u} Symmetry. Among the 14 b_{3u} fundamentals, only six fundamentals are identified owing to their low intensities in the IR spectrum. These are 396, 608, 1244, 1297, 1467, and 1585 cm^{-1}.

Most of the vibrations include CCC wagging, CH_3 bending, in-plane CH and CCC bending, and CH and CH_3 stretching modes.

Acknowledgment. The present studies were supported by Ministry of Education, Korea through the Basic Science Research Institute Program, 1997−1998, Project No. BSRI-97-3432. B.H.B. is grateful to Center for Molecular Science (CMS) for partial financial support.

References and Notes

(1) Janssen, J.; Lüttke, W. *J. Mol. Struct.* **1982**, *81*, 207.

(2) Bally, T.; Neuhaus, L.; Nitsche, S.; Haselbach, E.; Janssen, J.; Lüttke, W. *Helv. Chim. Acta* **1983**, *66*, 1288.

(3) Bally, T.; Haselbach, E.; Lanyiova, Z.; Bärtschi, P. *Helv. Chim. Acta* **1978**, *61*, 2488.

(4) Haselbach, E.; Klemm, U.; Gschwind, R.; Bally, T.; Chassot, L.; Nitsche, S. *Helv. Chim. Acta* **1982**, *65*, 2464.

(5) Traetteberg, M.; Bakken, P.; Almenningen, A.; Lüttke, W.; Janssen, J. *J. Mol. Struct.* **1982**, *81*, 87.

(6) Noltemeyer, M.; Janssen, J.; Lüttke, W. *J. Mol. Struct.* **1982**, *81*, 105.

(7) Almenningen, A.; Bastiansen, O. *Det. Kgl. Norske Videnskabers Selskab Skrifter* **1958**, *4*, 1.

(8) Bastiansen, O.; Traetteberg, M. *Tetrahedron* **1962**, *17*, 147.

(9) Robertson, G. B. *Nature (London)* **1961**, *191*, 593.

(10) Trotter, J. *Acta Crystallogr.* **1961**, *14*, 1135.

(11) Hargreaves, A.; Rizvi, S. H. *Acta Crytallogr.* **1962**, *15*, 365.

(12) Charbonneau, G. P.; Delugeard, Y. *Acta Crystallogr., Sect. B* **1976**, *32*, 1420.

(13) Charbonneau, G. P.; Delugeard, Y. *Acta Crystallogr., Sect. B* **1976**, *33*, 1586.

(14) Kauffman, J. F.; Côté, M. J.; Smith, P. G.; McDonald, J. D. *J. Chem. Phys.* **1989**, *90*, 2874.

(15) Saigusa, H.; Itoh, M. *J. Phys. Chem.* **1985**, *89*, 5486.

(16) Amirav, A.; Even, U.; Jortner, J. *Chem. Phys.* **1982**, *67*, 1.

(17) Boo, B. H.; Choi, Y. S.; Kim, T.-S.; Kang, S. K.; Kang, Y. H.; Lee, S. Y. *J. Mol. Struct.* **1996**, *377*, 129.

(18) Amirav, A.; Even, U.; Jortner, J. *J. Chem. Phys.* **1981**, *75*, 3151.

(19) Leutwyler, S.; Even, U.; Jortner, J. *J. Chem. Phys.* **1983**, *79*, 5769.

(20) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, *98*, 11623.

(21) Devlin, F. J.; Finley, J. W.; Stephens, P. J.; Frisch, M. J. *J. Phys. Chem.* **1995**, *99*, 16883.

(22) Handy, N. C.; Maslen, P. E.; Amos, R. D.; Andrews, J. S.; Murray, C. W.; Laming, G. J. *Chem. Phys. Lett.* **1992**, *197*, 506.

(23) Handy, N. C.; Murray, C. W.; Amos, R. D. *J. Phys. Chem.* **1993**, *97*, 4392.

(24) El-Azhary, A. A.; Suter, H. U. *J. Phys. Chem.* **1995**, *99*, 12751.

(25) Lee, S. Y.; Boo, B. H. *J. Phys. Chem.* **1996**, *100*, 15073.

(26) Wheeless, C. J. M.; Zhou, X.; Liu, R. *J. Phys. Chem.* **1995**, *99*, 12488.

(27) Rauhut, G.; Pulay, P. *J. Phys. Chem.* **1995**, *99*, 3093.

(28) Johnson, B. G.; Gill, P. M. W.; Pople, J. A. *J. Chem. Phys.* **1993**, *98*, 5612.

(29) Lee, S. Y.; Boo, B. H. *J. Phys. Chem.* **1996**, *100*, 8782.

(30) Langhoff, S. R. *J. Phys. Chem.* **1996**, *100*, 2819.

(31) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 1372.

(32) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(33) Johnson, B. G.; Gill, P. M. W.; Pople, J. A. *J. Chem. Phys.* **1993**, *98*, 5612.

(34) Janssen, J.; Lüttke, W. *Chem. Ber.* **1982**, *115*, 1234.

(35) Zimmermann, H. E.; Hackett, P.; Juers, D. F.; McCall, J. M.; Schröder, B. *J. Am. Chem. Soc.* **1971**, *93*, 3653.

(36) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*, Revision C.2; Gaussian, Inc.: Pittsburgh, PA, 1995.

(37) Szczepanski, J.; Vala, M.; Talbi, D.; Parisel, O.; Ellinger, Y. *J. Chem. Phys.* **1993**, *98*, 4494.

(38) Long, D. A. *Raman Spectroscopy*; McGraw-Hill: New York, 1977; p 63.