

chemical measurements and Prof. Taek Hyeon Kim and Prof. Jae Nyoung Kim at Chonnam National University for NMR measurements and Korea Basic Science Institute for fluorescence lifetime and FAB-mass spectral measurements.

References

- Juris, A.; Balzani, V.; Barigelletti, F.; Campagna, S.; Belser, P.; Von Zelewsky, A. *Coord. Chem. Rev.* **1988**, *84*, 85.
- Kalyanasundaram, K. *Coord. Chem. Rev.* **1982**, *46*, 159.
- Balzani, V.; Juris, A.; Venturi, M.; Campagna, S.; Seroni, S. *Chem. Rev.* **1996**, *96*, 759.
- Treadway, J. A.; Barbara, L.; Lopez, R.; Anderson, P. A.; Keene, F. R.; Meyer, T. J. *Inorg. Chem.* **1996**, *35*, 2242.
- Strouse, G. F.; Schoonover, J. R.; Duesing, R.; Boyde, S.; Jones, Jr., W. E.; Meyer, T. J. *Inorg. Chem.* **1995**, *34*, 473.
- Anderson, P. A.; Deacon, G. B.; Haarmann, K. H.; Keene, F. R.; Meyer, T. J.; Reitsma, D. A.; Skelton, B. W.; Strouse, G. F.; Thomas, N. C.; Treadway, J. A.; White, A. H. *Inorg. Chem.* **1995**, *34*, 6145.
- Meyer, T. J. *Pure and Appl. Chem.* **1986**, *58*, 1576.
- Kober, E. M.; Caspar, J. V.; Lumpkin, R. S.; Meyer, T. J. *J. Phys. Chem.* **1986**, *90*, 3722.
- Sauvage, J.-P.; Collin, J. P.; Chambron, J. C.; Guillerez, S.; Coudret, C.; Balzani, V.; Barigelletti, F.; De Colar, L.; Flamigni, L. *Chem. Rev.* **1994**, *94*, 993.
- Kelly, L. A.; Rodgers, M. A. *J. Phys. Chem.* **1995**, *99*, 13132.
- Xu, X.; Shreder, K.; Iverson, B.; Bard, A. J. *J. Am. Chem. Soc.* **1996**, *118*, 3656.
- Ciana, L. D.; Hamachi, I.; Meyer, T. J. *J. Org. Chem.* **1989**, *54*, 1731.
- Weinheimer, C.; Choi, Y.; Caldwell, T.; Gressham, P.; Olmsted III, J. J. *Photochem. Photobiol. A: Chem.* **1994**, *78*, 119.
- Sprintschnik, G.; Sprintschnik, H. W.; Kirsch, P. P.; Whitten, D. G. *J. Am. Chem. Soc.* **1977**, *99*, 4947.
- Bartocci, G.; Masetti, F.; Mazzucato, U.; Spalletti, A.; Orlandi, G.; Poggi, G. *J. Chem. Soc., Faraday Trans. 2* **1988**, *84*, 385.
- Aloisi, G. G.; Elisei, F.; Latterini, L.; Passerini, M.; Galiazzo, G. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 3315.
- Shin, E. J.; Bae, E. Y.; Kim, S. H.; Kang, H. K.; Shim, S. C. *J. Photochem. Photobiol. A: Chem.* **1997**, *107*, 137.
- Sun, L.; Gorner, H. *J. Phys. Chem.* **1993**, *97*, 11186.
- Gorner, H. *J. Photochem. Photobiol. A: Chem.* **1988**, *43*, 263.
- Takagi, K.; Ogata, Y. *J. Org. Chem.* **1982**, *47*, 1409.

Molecular Structure and Vibrational Spectra of Biphenyl in the Ground and the Lowest Triplet States. Density Functional Theory Study

Sang Yeon Lee

Department of Industrial Chemistry, Kyungpook National University, Taegu 702-701, Korea
Received September 24, 1997

The molecular geometries and harmonic vibrational frequencies of biphenyl in the ground and the first excited triplet states have been calculated using the Hartree-Fock and Becke-3-Lee-Yang-Parr (B3LYP) density functional methods with 6-31G* basis set. Structural change occurs from a twisted benzene-like to a planar quinone-like form upon the excitation to the first excited state. Scaled harmonic vibrational frequencies for the ground state obtained from the B3LYP calculation show good agreement with the available experimental data. A few vibrational fundamentals for both states are newly assigned based on the B3LYP results.

Introduction

Biphenyl (BP) and its derivatives have been extensively studied experimentally¹⁻¹⁴ and theoretically¹⁵⁻¹⁸ to investigate the molecular structure and the spectroscopic properties. Recently, Sasaki and Hamaguchi recorded the transient resonance Raman spectra of BP and its perdeuterated one (BP-d₁₀) in the first excited triplet state and suggested that BP in the first excited triplet state takes a planar structure.³ To assign peaks in the Raman spectra and confirm their suggestion, it is necessary to perform the complete vibrational analysis for BP in the ground and the first triplet states. The complete vi-

brational analysis for BP in the ground state will be very useful for the interpretation of the vibronic structures in the absorption and fluorescence spectra. Although the symmetry assignments of observed vibrational frequencies of BP in the ground state by Zerbi and Sandroni (ZS)¹⁰ and by Bree, Pang and Rabeneck (BPR)¹¹ on the basis of the polarized infrared and Raman spectra are very excellent, their selection of fundamental frequencies from the complicated infrared and Raman spectra is not complete, and has some ambiguities because the selection was done based on the force field calculation and the assumption that the fundamental modes show the most intense bands in the spectra.

Density functional theory calculations¹⁹⁻²⁹ are reported to provide excellent vibrational frequencies of organic compounds if the calculated frequencies are scaled to compensate for the approximate treatment of electron correlation, for basis set deficiencies, and for the anharmonicity. There are some results that the vibrational frequencies and intensities from the density functional calculations are better than those from the second order Möller-Plesset perturbation theory calculation.^{19,27}

Rauhut and Pulay²⁵ calculated the vibrational spectra of thirty one molecules by using the Becke-Lee-Yang-Parr (BLYP)³⁰ and Becke-3-Lee-Yang-Parr (B3LYP)³¹ functionals with 6-31G* basis set. They could reproduce the experimental vibrational frequencies and infrared intensities very well. In their work, they calculated vibrational frequencies of twenty smaller molecules (the training set) whose experimental vibrational frequencies are well assigned, and derived transferable scaling factors by using the least square procedure. The scaling factors are successfully applied to other eleven larger molecules (the test set). Even when a single scaling factor of 0.995 (0.963) for the BLYP (B3LYP) method is employed, rms deviations for the training and test sets are 26.2 (18.5) and 26.9 (19.7) cm⁻¹, respectively. Thus, vibrational frequencies calculated by using the B3LYP functional with 6-31G* basis can be utilized to eliminate the uncertainties in the fundamental assignments in infrared and Raman vibrational spectra.

By using the HF/6-31G* and B3LYP/6-31G* methods, we calculated the vibrational frequencies of BP in the ground state to distinguish the fundamentals from the many experimental vibrational frequencies and to predict the spectral positions of the missing lines. Furthermore, the same theoretical vibrational analysis is performed for the BP in the first excited triplet state to make certain of Sasaki and Hamaguchi's suggestion based on the analysis of the transient Raman spectra that the BP in the first excited state takes a planar structure.

Calculations

The molecular structures of BP in the ground and the first excited triplet states are optimized at the levels of Hartree-Fock and B3LYP with the 6-31G* basis set. Two sets of vibrational frequencies for these species and the corresponding perdeuterated species are calculated with the HF and B3LYP methods and then scaled by 0.8929³² and 0.963, respectively. The scaling factor for the B3LYP frequencies is recommended by RP.²⁵ All the calculations are performed by using the Gaussian 94 program³³ on the CRAY-C90 supercomputer at SERI in Korea.

Results and Discussion

Molecular geometry. BP in the ground state has D₂ symmetry. The optimized geometries at the levels of HF and B3LYP with 6-31G* are listed in Table 1 with an experimental geometry obtained from an electron diffraction experiment.⁸ The atomic numbering in BP is shown in Figure 1.

The CC bond lengths obtained from the B3LYP calculation are longer than those from the HF one by about 0.01 Å except the C₁-C_{1'} bond length. The B3LYP C₁-C_{1'}

Table 1. Optimized and experimental geometries of biphenyl in the ground state and the lowest triplet states

Parameter ^a	Ground state			Lowest triplet state	
	HF	B3LYP	Exp. ^b	HF	B3LYP
r(C ₂ -C ₁)	1.394	1.405	1.404	1.396	1.469
r(C ₃ -C ₂)	1.386	1.394	1.395	1.384	1.368
r(C ₄ -C ₃)	1.385	1.396	1.396	1.384	1.420
r(C ₁ -C _{1'})	1.491	1.486	1.507	1.501	1.393
r(C ₂ -H)	1.075	1.087	1.102	1.072	1.083
r(C ₃ -H)	1.077	1.087	1.102	1.076	1.087
r(C ₄ -H)	1.075	1.087	1.102	1.075	1.085
∠C ₁ -C ₂ -C ₃	120.9	121.0	119.9	121.7	121.8
∠C ₂ -C ₃ -C ₄	120.2	120.3	120.9	120.5	121.3
∠C ₃ -C ₄ -C ₅	119.5	119.4		118.8	118.8
∠C ₂ -C ₁ -C ₆	118.3	118.1	119.4	116.8	115.0
∠C ₂ -C ₁ -C _{1'}	120.8	121.0		121.6	122.5
∠C ₁ -C ₂ -H	119.6	119.4		120.7	119.5
∠C ₂ -C ₃ -H	119.7	119.6		119.3	119.4
∠C ₃ -C ₄ -H	120.3	120.3		120.6	120.6
∠C ₁ -C ₁ -C ₂ -H	1.2	1.6		0.0	0.0
∠H-C ₂ -C ₃ -H	-0.8	-1.1		0.0	0.0
∠H-C ₃ -C ₄ -H	-0.4	-0.5		0.0	0.0
∠C ₂ -C ₁ -C ₁ -C ₂	45.5	38.4	44.3	0.0	0.0

^aBond lengths in Angstrom and ∠s in degree. ^bValues from ED in gas phase. Reference 8.

bond is shorter than the corresponding one by marginally small 0.005 Å. This pattern is also observed in the optimized geometries of carbazole, fluorene and 9-fluorenone at the HF and B3LYP levels.^{26,27,29} The dihedral angle between both ring planes through the interring bond becomes smaller at the B3LYP than the HF level.

It is well known that the HF calculation with the 6-31G* basis set underestimates bond lengths and the inclusion of the electron correlation makes them longer. This elongation usually makes the agreement better between the optimized and the experimental geometric parameters. This pattern is also observed here. One exception to this pattern is C₁-C_{1'}, the interring bond distance. Inclusion of the electron correlation makes this bond shorter because of the increased resonance in the correlated wavefunction. The optimized bond lengths at both levels are in good agreement with the corresponding bond lengths obtained from the electron diffraction. The bond angles from either of calculations and the experiment are in good accord with each other.

The molecular structure optimized at the HF and B3LYP levels for the first excited triplet state is also included in Table 1. Upon the excitation to the first excited triplet state, structural change occurs so that both phenyl rings are in the

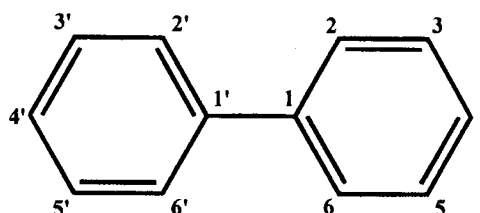


Figure 1. The atomic numbering in Biphenyl.

same plane. That is, the first excited state is predicted to have D_{2h} symmetry at both levels. This geometry is consistent with Sasaki and Hamaguchi's suggestion based on the analysis of the transient Raman spectra. The optimized parameters at the HF level are very similar to the corresponding ones in the ground state except the dihedral angle between the ring planes but the B3LYP optimized parameters change significantly. The C_2-C_1 and C_4-C_3 bond lengths in the first excited state are longer than the corresponding ones in the ground state by 0.064 and 0.024 Å, respectively and the C_3-C_2 and C_1-C_1' are shorter than the corresponding ones in the ground state by 0.026 and 0.093 Å, respectively. Upon the excitation from the ground state to the first excited triplet state, the structure changes from a benzene-like to a quinone-like form. The large deviations of the B3LYP optimized geometric parameters from the corresponding HF ones reflect the relaxation upon the inclusion of the electron correlation.

Vibrational frequencies of biphenyl in the ground state. BP in the ground state has 60 fundamentals with the

various symmetries of $15a_1+16b_1+16b_2+13b_3$. According to the group theoretical analysis of selection rule for BP in infrared and Raman spectra, all the symmetric modes are Raman active but only the b_1 , b_2 , and b_3 symmetric modes are infrared active. Calculated and scaled vibrational frequencies, infrared intensities, Raman activities, and depolarization ratio obtained from the HF calculation are listed in Table 2. Also the calculated frequencies with the infrared intensities from the B3LYP calculation for BP (BP- h_{10}) and perdeuterated BP (BP- d_{10}) are represented in Table 2. The experimental vibrational frequencies reported by ZS are also included for comparison. The frequencies noted in **boldface** under the experiment column are newly assigned to fundamental vibrational frequencies. The frequencies in *italics* are tentatively assigned to fundamental modes based on the present calculations.

Since almost all the vibrational modes are delocalized over whole molecule, they cannot be ascribed to several local vibrational motions. This is a characteristic feature of cyclic compounds, particularly aromatic compounds. Thus the modes for BP- h_{10} are described approximately in Table 2.

Table 2. Comparison of calculated and experimental vibrational frequencies of biphenyl (BP- h_{10}) and perdeuterated biphenyl (BP- d_{10})

Symmetry mode	Biphenyl- h_{10}						Biphenyl- d_{10}				Approx. mode description ^b
	HF		B3LYP		Exp. ^a	B3LYP		Exp. ^a			
	Freq ^c	I _{IR} ^d	I _{Raman} ^e	DP ^f		Freq ^c	I _{IR} ^d		Freq ^c	Freq ^c	
a_1 Symmetry											
ν_1	60	0.00	11.05	0.72	68	0.00	70	62	0.00	70	IR tors
ν_2	295	0.00	4.44	0.28	303	0.00	315	291	0.00	300	IR str+R ip def
ν_3	412	0.00	2.03	0.57	407	0.00	400	357	0.00	359 ^j	R oop def
ν_4	721	0.00	11.28	0.11	729	0.00	742	646	0.00	659	R ip def+IR str+CC str
ν_5	857	0.00	8.24	0.33	830	0.00	838	683	0.00	688	CH oop bend
ν_6	973	0.00	73.71	0.12	935	0.00	965	758	0.00	790 ^j	CH oop bend
ν_7	986	0.00	1.26	0.07	982	0.00	1003	837	0.00	835	R ip def
ν_8	1012	0.00	20.90	0.08	1023	0.00	1030	864	0.00	869	CC str
ν_9	1167	0.00	5.91	0.20	1177	0.00	1190	942	0.00	960	CH ip bend
ν_{10}	1255	0.00	101.57	0.19	1264	0.00	1285	1175	0.00	1188	IR str+R ip def
ν_{11}	1503	0.00	8.52	0.21	1499	0.00	1507	1405	0.00	1412	IR str+CH ip bend
ν_{12}	1621	0.00	269.36	0.46	1600	0.00	1612	1566	0.00	1571	CC str+R ip def
ν_{13}	2995	0.00	48.79	0.70	3062	0.00	3031	2262	0.00	2275 ⁱ	CH str
ν_{14}	3013	0.00	116.19	0.74	3080	0.00	3052	2282	0.00	2285 ⁱ	CH str
ν_{15}	3026	0.00	551.38	0.06	3092	0.00	3083	2298	0.00	2290 ⁱ	CH str
b_1 Symmetry											
ν_1	94	0.77	2.64	0.75	92	0.57	104	86	0.52	90	IR oop bend+R oop def
ν_2	349	0.10	0.03	0.75	359	0.10	360	327	0.46	355	R oop def+IR bend
ν_3	494	6.85	0.03	0.75	483	4.41	484	433	9.85	435 ⁱ	R oop def+IR ip bend+IR oop bend
ν_4	602	0.00	8.23	0.75	605	0.00	608	537	42.53	540	R ip def
ν_5	696	35.25	0.22	0.75	689	30.42	698	581	0.01	589	R oop def+CH oop bend
ν_6	746	96.25	0.54	0.75	728	70.71	736	619	3.20	627	R oop def+CH oop bend
ν_7	924	3.78	0.23	0.75	887	2.84	903	728	2.56	744	CH oop bend
ν_8	1004	0.25	0.23	0.75	959	0.24	970	792	0.62	816 ⁱ	CH ip bend
ν_9	1057	0.21	1.03	0.75	1075	0.37	1090	815	0.24	817 ⁱ	CC str+CH ip bend
ν_{10}	1093	0.07	14.75	0.75	1149	0.00	1156	833	0.09	840	CH ip bend
ν_{11}	1193	0.02	0.23	0.75	1298	0.00	1282^g	1034	0.00	1070	CC str
ν_{12}	1322	0.03	1.31	0.75	1314	0.07	1316	1293	0.00	1272	CC str
ν_{13}	1451	2.51	3.59	0.75	1451	1.14	1452	1337	0.29	1345	CH ip bend
ν_{14}	1595	0.26	6.39	0.75	1583	0.11	1595	1549	0.02	1566	CC str
ν_{15}	3000	0.06	188.89	0.75	3066	0.03	3068	2269	0.00	2285 ⁱ	CH str
ν_{16}	3017	16.70	20.22	0.75	3082	10.42	3069	2287	5.99	2290 ⁱ	CH str

Table 2. Continued

Symmetry mode	Biphenyl-h ₁₀					Biphenyl-d ₁₀				Approx. mode description ^b	
	HF		B3LYP			Exp. ^a	B3LYP		Exp. ^a		
	Freq ^c	I _{IR} ^d	I _{Raman} ^e	DP ^f	Freq ^c		I _{IR} ^d	Freq ^c			Freq ^c
b₂ Symmetry											
v ₁	117	0.13	4.40	0.75	125	0.06	116	115	0.05	110	IR ip bend+R oop def
v ₂	266	0.06	5.31	0.75	261	0.02	260	240	0.01	249 ⁱ	R oop def+IR ip bend
v ₃	544	3.00	1.75	0.75	539	1.59	545	463	3.52	-	R oop def+IR oop bend+CH oop bend
v ₄	612	0.05	1.58	0.75	617	0.03	626	547	2.94	555 ^j	R ip def
v ₅	698	10.49	2.33	0.75	688	6.06	708	590	0.00	590	R ip def
v ₆	785	10.06	0.00	0.75	767	5.32	780	645	0.41	659 ^j	R oop def+CH oop bend
v ₇	940	1.24	2.75	0.75	904	0.91	897 ^h	761	0.47	-	CH oop bend
v ₈	1004	0.07	0.96	0.75	959	0.06	955 ⁱ	808	1.20	790	CH oop bend
v ₉	1059	4.25	0.04	0.75	1071	5.87	1074	823	2.92	826	CC str+CH ip bend
v ₁₀	1077	0.01	3.46	0.75	1150	0.07	1156	837	3.32	845 ^j	CH ip bend
v ₁₁	1183	0.09	0.24	0.75	1267	2.55	1272	1012	0.32	1010	CC str
v ₁₂	1308	2.56	1.22	0.75	1324	0.88	1340	1263	1.08	1266	CH ip bend+CC str
v ₁₃	1424	11.70	0.74	0.75	1423	7.32	1432	1318	1.00	1328	CH ip bend
v ₁₄	1580	5.80	0.95	0.75	1568	4.17	1570	1526	0.82	1531	CC str+CH ip bend
v ₁₅	3003	8.25	40.74	0.75	3069	9.10	3068	2270	2.35	2276 ⁱ	CH str
v ₁₆	3019	67.34	0.49	0.75	3085	57.28	3069	2289	35.77	2307 ⁱ	CH str
b₃ Symmetry											
v ₁	406	0.29	0.11	0.75	401	0.33	400	351	0.19	-	R oop def
v ₂	597	7.90	0.73	0.75	601	8.00	609	579	6.95	590	R ip def
v ₃	856	0.11	2.69	0.75	829	0.52	838	647	0.42	-	CH oop bend
v ₄	968	0.15	6.65	0.75	933	0.76	965	756	0.77	-	CH oop bend
v ₅	982	4.69	1.25	0.75	977	0.47	990 ^h	810	5.29	816	R ip def
v ₆	984	1.26	0.45	0.75	989	4.90	1008	855	1.61	846	R ip def+CC str
v ₇	1029	0.90	0.01	0.75	1035	2.09	1040	937	0.00	952	CC str
v ₈	1163	0.40	1.65	0.75	1169	0.58	1176	962	4.43	983	CH ip bend
v ₉	1480	44.12	0.00	0.75	1478	28.66	1482	1340	13.68	1346	CC str
v ₁₀	1612	15.57	2.72	0.75	1602	11.85	1597	1567	11.11	1568	CC str
v ₁₁	2994	7.85	5.88	0.75	3061	8.67	3054	2262	4.84	2255 ⁱ	CH str
v ₁₂	3010	49.14	30.39	0.75	3076	33.46	3062	2279	14.80	2287 ⁱ	CH str
v ₁₃	3025	45.01	55.06	0.75	3090	41.13	3068	2297	24.24	2307 ⁱ	CH str

^aReference 10. ^bR, ring; IR, inter-ring; def, deformation; str, stretching; bend, bending; tors, torsion; oop, out-of-plane; ip, in-plane. ^cVibrational Frequencies in cm⁻¹. ^dInfrared Intensities in KM/mole. ^eRaman Scattering Activities in A³/AMU. ^fRaman Depolarization Ratios. ^gReference 12. ^hReference 13. ⁱReference 14. ^jReference 11.

When the HF and B3LYP calculated frequencies are compared, almost all the frequencies are in good accord with each other. However, the HF frequencies of 5a, 6a, 7b₁, 8b₁, 7b₂, 8b₂, 3b₃, and 4b₃ modes are larger than the corresponding B3LYP ones while the HF frequencies of 10b₁, 11b₁, 10b₂ and 11b₂ modes are smaller. All these modes are thought to have nonnegligible correlation contributions.

The calculated B3LYP frequencies are in good agreement with experimental values. The root-mean-square(rms) deviations of vibrational frequencies of BP calculated at the HF and B3LYP levels from experiment are 33.88 and 12.93 cm⁻¹, respectively. That for BP-d₁₀ at the B3LYP level is 12.65 cm⁻¹.

a Symmetry. On the basis of the computational results and the symmetry assigned peaks in infrared and Raman spectra reported by ZS, we have made a reliable one-to-one correspondence between our fundamentals and the experimental data. The a symmetric fundamental modes for BP-h₁₀ are observed at 70, 315, 400, 742, 838, 965, 1003, 1030, 1190, 1285, 1507, 1612, 3031, 3051, and 3070 cm⁻¹.

These symmetry modes are totally symmetric vibrations. The fundamental modes below 1650 cm⁻¹ consist of interring torsion, ring bendings, CC stretchings, and CH bendings. The higher frequencies are from CH stretchings.

b₁ Symmetry. Although these modes are Raman active, their Raman scattering activities are calculated to be relatively low. Fundamentals attributable to b₁ for BP-h₁₀ are observed at 360, 484, 608, 698, 903, 970, 1090, 1156, 1282, 1316, 1452, 1595, 3068 and 3069 cm⁻¹. The unobserved fundamental 1b₁ is predicted to be the second lowest fundamental and to be located at 92 cm⁻¹. Since the third lowest fundamental, 1b₂ is predicted to be located at 125 cm⁻¹ and observed at 116 cm⁻¹, and the fourth lowest fundamental is observed at 260 cm⁻¹, the peak observed at 170 (160) cm⁻¹ for BP (BP-d₁₀) can be assigned to the combination band of 1a+1b₁ (or the overtone band of 1b₁). Then the 1b₁ mode is tentatively assigned to around 104 (85) and 90 (80) cm⁻¹ for undeuterated and perdeuterated biphenyl, respectively. The observed frequencies at 970 and

1282 cm^{-1} are newly assigned to the 8th and 11th modes, respectively. The peak at 1373 cm^{-1} that was ascribed to a fundamental turns out to be not the real fundamental. These symmetry modes below 1600 cm^{-1} consist of interring out-of-plane bending, ring deformations, CH bendings and CC stretching. The other modes are CH stretchings

b₂ Symmetry. Thirteen fundamentals assigned to b₂ mode are at 116, 260, 545, 626, 780, 1074, 1156, 1272, 1340, 1432, 1570, 3068 and 3069 cm^{-1} . The observed frequency at 1340 cm^{-1} is newly assigned to the 12th modes. The peaks observed at 441 and 1383 cm^{-1} were tentatively assigned to a fundamental but it is not the case. Based on the B3LYP results, the remaining three fundamentals are tentatively assigned to the peaks observed at 708, 897 and 955 cm^{-1} , respectively. These symmetry modes below 1600 cm^{-1} consist of interring in-plane bending, ring deformations, CH bendings and CC stretching. The other modes are CH stretchings

b₃ Symmetry. Thirteen fundamentals attributable to b₃ mode are observed at 400, 609, 838, 965, 990, 1008, 1040, 1176, 1482, 1597, 3054, 3062, and 3068 cm^{-1} . The observed peaks at 990 cm^{-1} is newly assigned to the 5th mode that was assigned to the peak at 965 cm^{-1} . The modes whose frequencies are smaller than 1600 cm^{-1} consist of ring bendings, CC stretchings, and CH bendings. The other modes are CH stretchings

Vibrational frequencies of biphenyl in the first triplet state. Sasaki and Hamaguchi observed seven bands (1568, 1475, 1364, 1204, 983, 963 and 335 cm^{-1}) for BP and four bands (1537, 1420, 863 and 825 cm^{-1}) for BP-d₁₀ in the transient Raman spectra. There is a peak at 400 (359) cm^{-1} in the Raman spectra for BP (BP-d₁₀) in the ground state and that peak has some contribution from the interring torsional motion. But the corresponding peak of BP in the first triplet state could not be observed around 400 cm^{-1} . Thus, they suggested that BP in the first triplet state has a planar structure. As discussed in the molecular structure section, geometry optimization confirmed that their suggestion is correct. BP in the first triplet state has D_{2h} symmetry and has 60 fundamentals with the various symmetries of 11a_g+4a_u+3b_{1g}+10b_{1u}+6b_{2g}+10b_{2u}+10b_{3g}+6b_{3u}.

Since this species has the center of inversion, only the

gerade modes are Raman active and the ungerade modes are infrared active. Since the assignment of the observed frequencies in the transient Raman spectra is tried here, observed vibrational frequencies and the corresponding frequencies calculated at the B3LYP level for BP and BP-d₁₀ are listed in Table 3 to save space.³⁴ The calculated and observed vibrational frequencies for BP in the ground state that correspond to the vibrational modes observed in the transient Raman spectra are also included in the Table 3 for the comparison. The vibrational modes for the BP in the ground state are classified according to D_{2h} symmetry.

Since the rms deviation of the calculated frequencies from the observed ones is only about 13 cm^{-1} for BP in the ground state and nearly the same deviation is expected for BP in the first triplet state, the assignment of the observed Raman frequencies could be made with confidence by comparing the calculated frequencies with observed ones, by comparing the ratio of a calculated frequency of BP to the corresponding one of BP-d₁₀, v_H/v_D , with the corresponding ratio from the observed frequencies for BP and BP-d₁₀, and by considering the calculated scattering activities. All the observed peaks turn out to be a_g symmetric mode. The peaks at 1475, 1364, 1204, 983, 963 and 335 cm^{-1} for BP are assigned to 7a_g, 6a_g, 5a_g, 4a_g, 3a_g, and 1a_g, respectively while those at 1420, 863, 825, and 319 cm^{-1} for BP-d₁₀ are attributed to 7a_g, 4a_g, 3a_g, and 1a_g, respectively. The peak at 1568 cm^{-1} for BP (the peak at 1537 cm^{-1} for BP-d₁₀) could be ascribed to 8a_g mode but the difference between the calculated and observed frequencies is quite larger than those for other observed and assigned modes. Maybe it is a combination band of 8a_g+lower frequencies mode.

Summary

The molecular structure of biphenyl in the ground and the first excited triplet states and the vibrational spectra of biphenyl are calculated by using the HF and B3LYP with 6-31G* basis set. Upon the excitation to the first triplet state, the structural change occurs from a twisted benzene-like to a planar quinone-like form. Based on the calculated and the experimental vibrational frequencies, a few fundamental frequencies are newly assigned.

Acknowledgment. The present research was supported by Kyungpook National University Research Fund, 1996.

References

1. Furuya, K.; Tori, H.; Furukawa, Y.; Tasumi, M. *Chem. Lett.* **1997**, 913.
2. Liu, X.-H.; Satoh, N.; Abe, K.; Shigenari, T. *J. Phys. Soc. Jap.* **1996**, *65*, 2259.
3. Sasaki, Y.; Hamaguchi, H.-O. *Spectrochim. Acta A* **1994**, *50*, 1475.
4. Ishii, K.; Nakayama, H.; Tanabe, K.; Kawahara, M. *Chem. Phys. Lett.* **1992**, *198*, 236.
5. Swiderek, P.; Michaud, M.; Hohlneicher, G.; Sanche, L. *Chem. Phys. Lett.* **1991**, *187*, 583.
6. Buntinx, G.; Poizat, O. *J. Chem. Phys.* **1989**, *91*, 2153.
7. Matsunuma, S.; Yamaguchi, S.; Hirose, C.; Maeda, S. *J. Phys. Chem.* **1988**, *92*, 1777.

Table 3. Calculated and observed vibrational frequencies of biphenyl and Biphenyl-d₁₀ in the lowest triplet state

Symmetry ^a	BP S ₀		BP T ₁		BP-d ₁₀ T ₁	
	Cal. ^b	Exp. ^c	Cal. ^b	Exp. ^d	Cal. ^b	Exp. ^d
a _g Symmetry						
v ₁	303	315	325	335	313	319 ^e
v ₃	982	1003	946	963	817	825
v ₄	1023	1030	973	983	858	863
v ₅	1177	1190	1215	1204	943	
v ₆	1264	1285	1378	1364	1194	
v ₇	1499	1507	1486	1475	1442	1420
v ₈	1600	1612	1627	1568	1597	1537

^aAlthough the point group of the biphenyl in the ground state is D₂, the symmetry modes are classified according to D_{2h} to be correlated with those of the biphenyl in the T₁ state. ^bAll the calculated frequencies are obtained from the B3LYP with 6-31G* basis set. ^cSee Table 2. ^dReference 3. ^eReference 6.

8. Almeningen, A.; Bastiansen, O.; Fernholt, L.; Cyvin, B. N.; Cyvin, S. J.; Samdal, S. *J. Mol. Struct.* **1986**, 128, 59.
9. Bastiansen, O.; Samdal, S. *J. Mol. Struct.* **1985**, 128, 115.
10. Zerbi, G.; Samdrone, S. *Spectrochim. Acta A*, **1968**, 24, 483.
11. Bree, A.; Pang, C. Y.; Rabeneck, L. *Spectrochim. Acta A*, **1971**, 27, 1293.
12. Pasquier, B.; Lebas, J. M. *J. Chim. Phys.* **1966**, 64, 765.
13. Peregodov, G. V. *Opt. Spectry* **1960**, 9, 155.
14. Katon, J. E.; Lippincott, E. R. *Spectrochim. Acta* **1959**, 15, 627.
15. Rubio, M.; Merchán, M.; Ortí, E.; Roos, B. O. *Chem. Phys. Lett.* **1995**, 234, 373.
16. Lenstra, A. T. H.; Alsenoy, C. V.; Verhulst, K.; Geise, H. J. *Acta Cryst. B* **1994**, 50, 96.
17. Rubio, M.; Merchà, M.; Ortí, E. *Theoret. Chim. Acta* **1995**, 91, 17.
18. Häfelinger, G.; Regelmann, C. J. *Comp. Chem.* **1985**, 6, 368.
19. Handy, N. C.; Maslen, P. E.; Amos, R. D.; Andrews, J. S.; Murray, C. W.; Laming, G. *Chem. Phys. Lett.* **1992**, 197, 506.
20. Handy, N. C.; Murray, C. W.; Amos, R. D. *J. Phys. Chem.* **1993**, 97, 4392.
21. Johnson, B. G.; Gill, P. M. W.; Pople, J. A. *J. Chem. Phys.* **1993**, 98, 5612.
22. Stephens, P. J.; Devlin, F. J.; Chavalowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, 98, 11623.
23. Devlin, F. J.; Finley, J. W.; Stephens, P. J.; Frisch, M. J. *J. Phys. Chem.* **1995**, 99, 16883.
24. Wheelless, C. J. M.; Zou, X.; Liu, R. *J. Phys. Chem.* **1995**, 99, 12488.
25. Rauhut, G.; Pulay, P. *J. Phys. Chem.* **1995**, 99, 3093.
26. Lee, S. Y.; Boo, B. H. *J. Phys. Chem.* **1996**, 100, 8782.
27. Lee, S. Y.; Boo, B. H. *J. Phys. Chem.* **1996**, 100, 15073.
28. Lee, S. Y.; Boo, B. H. *Bull. Korean Chem. Soc.* **1996**, 17, 754.
29. Lee, S. Y.; Boo, B. H. *Bull. Korean Chem. Soc.* **1996**, 17, 760.
30. Miehllich, B.; Savin, A.; Stoll, H.; Preuss, H. *Chem. Phys. Lett.* **1989**, 157, 200.
31. Becke, A. D. *J. Chem. Phys.* **1993**, 98, 5648.
32. Foresman, J. B.; Frisch, A. *Exploring Chemistry with Electronic Structure Methods*, Second Ed.; Gaussian, Inc.: 1996.
33. 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 B.2*; Gaussian, Inc.: Pittsburgh PA, 1995.
34. A table including all calculated vibrational frequencies of BP in the triplet state can be available upon the request to the author.

Crystal Structure of Dehydrated Rb⁺-Exchanged Zeolite X, Rb₇₁Na₂₁Si₁₀₀Al₉₂O₃₈₄

Seok Hee Lee, Yang Kim, Duk-Soo Kim[†], and Karl Seff[‡]

Department of Chemistry, Pusan National University, Pusan 609-735, Korea

[†]*Department of Chemistry, Cheju National University, Cheju 690-756, Korea*

[‡]*Department of Chemistry, University of Hawaii, Honolulu, Hawaii 96822, U.S.A.*

Received September 28, 1997

The crystal structure of dehydrated Rb⁺-exchanged zeolite X, stoichiometry Rb₇₁Na₂₁-X (Rb₇₁Na₂₁Si₁₀₀Al₉₂O₃₈₄) per unit cell, has been determined from single-crystal X-ray diffraction data gathered by counter methods. The structure was solved and refined in the cubic space group *Fd3*, *a*=25.007(3) Å at 21(1) °C. The crystal was prepared by ion exchange in a flowing stream using a 0.05 M aqueous RbOH solution (pH=12.7). The crystal was then dehydrated at 360 °C and 2 × 10⁻⁶ torr for two days. The structure was refined to the final error indices, R₁=0.047 and R₂=0.040 with 239 reflections for which *I*>3σ(*I*). In this structure, 71 Rb⁺ ions per unit cell are found at six different crystallographic sites and 21 Na⁺ ions per unit cell are found at two different crystallographic sites. Four and a half Rb⁺ ions are located at site I, the center of the hexagonal prism. Nine Rb⁺ ions are found at site I' in the sodalite cavity (Rb-O=2.910(15) Å and O-Rb-O=78.1(4)°). Eighteen Rb⁺ ions are found at site II in the supercage (Rb-O=2.789(9) Å and O-Rb-O=92.1(4)°). Two and a half Rb⁺ ions, which lie at site II', are recessed ca. 2.07 Å into the sodalite cavity from their three O(2) oxygen planes (Rb-O=3.105(37) Å and O-Rb-O=80.6(5)°). Thirty-two Rb⁺ ions are found at site III deep in the supercage (Rb-O=2.918(12) Å and O-Rb-O=71.9(4)°), and five Rb⁺ ions are found at site III'. Seven Na⁺ ions also lie at site I. Fourteen Na⁺ ions are found at site II in the supercage (Na-O=2.350(19) Å and O-Na-O=117.5(6)°).