Vibrational Analysis of the Radical Anion and Cation of Biphenyl Based on Density Functional Calculations

Kazuhiko Furuya,[†,††] Hajime Torii,[††] Yukio Furukawa,[††] and Mitsuo Tasumi*[††]
[†]*Ashigara Research Laboratories, Fuji Photo Film Co. Ltd., 210 Nakanuma, Minami Ashigara, Kanagawa 250-01*
[††]*Department of Chemistry, School of Science, The University of Tokyo, Bunkyo-ku, Tokyo 113*

(Received July 11, 1996)

The density functional theory has been used for calculating the structures and vibrational wavenumbers of the radical anion and cation of biphenyl. The radical anion has a planar structure, while the radical cation is twisted. Upon ionization, structural changes occur in the direction from benzenoid to quinoid. Unscaled wavenumbers calculated at the Becke-Lee-Yang-Parr/6-31G* level are mostly in agreement with observed vibrational wavenumbers in the literature.

Poly(p-phenylene) (PPP) is one of conducting polymers,[1] which has received much attention from viewpoints of pure and applied sciences. PPP shows high electrical conductivities when oxidized with acceptors or reduced with donors, while it is an insulator in the undoped state.[2] Its high conductivities have been interpreted in terms of polarons and bipolarons, which are elementary excitations in nondegenerate conjugated polymers such as PPP.[1] A positive (negative) polaron and a positive (negative) bipolaron correspond to a radical cation (radical anion) and a dication (dianion), respectively.

The Raman spectra of Na-doped PPP have been analyzed on the basis of the Raman spectra of the radical anions and dianions of p-oligophenyls, and it has been concluded that negative polarons and bipolarons are formed in Na-doped PPP.[3] Theoretical studies of the radical ions (polaron models) and divalent ions (bipolaron models) of p-oligophenyls are thus useful for characterizing polarons and bipolarons in PPP. The structures of the divalent ions of p-oligophenyls consisting of up to 11 rings have been calculated by using the *ab initio* Hartree-Fock (HF) method.[4-6] However, treatments incorporating electron correlation are required for a correct understanding of polarons and bipolarons in conjugated systems.[1,7] Rubio *et al.*[8] have studied the structures of the radical anion and cation of biphenyl using the complete active space self-consistent field (CASSCF) method. It is practically impossible to calculate the vibrational wavenumbers of the radical ions and divalent ions of long-chain p-oligophenyls at such a high theoretical level. As an alternative, the density functional theory (DFT) may be used, since it has the ability to incorporate electron correlation in treating quite large molecules and charged species. In this letter, we apply the DFT approach to studies on the structures and vibrational spectra of the radical anion and cation of biphenyl, which is the smallest of p-oligophenyls, in order to evaluate the usefulness of the DFT approach in studying charged species of longer p-oligophenyls.

The structures and harmonic vibrational wavenumbers were calculated for biphenyl and its radical anion and cation. Counter ions were not included in the calculations of the radical ions. Density functional calculations were performed by using the Gaussian 92/DFT program[9] on a Kubota Titan 3000 computer and a Silicon Graphics Power Onyx workstation. The 6-31G* and 6-311G* basis sets were used. Two sets of calculations were carried out with the following functionals, *i.e.*, (i) Becke's exchange functional[10] in combination with the Lee-Yang-Parr correlation functional[11] (BLYP) and (ii) Becke's three-parameter hybrid method[12] using the Lee-Yang-Parr correlation functional[11] (B3LYP) as implemented in the Gaussian 92/DFT program. The default grid was used for numerical evaluation of two-electron integrals. Geometry optimizations were performed under D_2 symmetry for biphenyl and its radical ions. Since an almost planar structure was obtained for the radical anion, the geometry optimization of this species was finally performed under D_{2h} symmetry. No imaginary-frequency mode was found at the optimized structures of all the species.

Table 1. Torsional angles and CC bond lengths calculated at the BLYP/6-31G* level for biphenyl and its radical ions

	Angles / ° and bond lengths / Å		
Parameter	Neutral	Radical anion	Radical cation
$\tau(C_2C_1C_1'C_2')$	38.4	0	18.7
$r(C_1C_1')$	1.494	1.451	1.458
$r(C_1C_2)$	1.416	1.451	1.443
$r(C_2C_3)$	1.404	1.394	1.390
$r(C_3C_4)$	1.406	1.421	1.418

The torsional angles and CC bond lengths calculated at the BLYP/6-31G* level for biphenyl and its radical ions are shown in Table 1. Biphenyl in the neutral state has a twisted structure (D_2 symmetry); the torsional angles around the inter-ring C_1C_1' bond calculated at the BLYP/6-31G*, BLYP/6-311G*, B3LYP/6-31G*, and B3LYP/6-311G* levels are 38.4, 41.9, 39.3, and 42.2°, respectively. The torsional angle in the vapor phase has been determined to be 44.4° by means of electron diffraction.[13] The calculated structure of the radical anion is planar (D_{2h} symmetry). On the other hand, the radical cation has a twisted structure (D_2 symmetry); the torsional angles calculated at the BLYP/6-31G*, BLYP/6-311G*, B3LYP/6-31G*, and B3LYP/6-311G* levels are 18.7, 20.1, 16.8, and 16.9°, respectively. In a study of the Raman spectra of the radical anion and cation in solutions, Sasaki and Hamaguchi[14] have proposed that the radical cation is slightly twisted, whereas the radical anion is planar. Rubio *et al.*[8] have reported a planar structure for the radical cation, because they have optimized its geometry with the constraint of D_{2h} symmetry. The CC bond lengths of biphenyl and its radical ions depend on the exchange and correlation functionals rather than the basis sets. Except for the C_1C_1' bond, the CC bond lengths calculated by the B3LYP method are in agreement with those calculated by the CASSCF method,[8] while those calculated by the BLYP method are longer by about 0.01 Å. The calculated length of the C_1C_1' bond varies with the theoretical level to a greater extent. As shown in Table 1, the C_1C_1' and C_2C_3 bonds are shortened and the C_1C_2 and

Table 2. Calculated and observed vibrational wavenumbers of biphenyl and its radical ions

Neutral			Radical anion			Radical cation		
Mode	Obs[b] cm^{-1}	Calc[a] cm^{-1}	Mode	Obs[c] cm^{-1}	Calc[a] cm^{-1}	Mode	Obs[d] cm^{-1}	Calc[a] cm^{-1}
a ν_4	1613	1595	a_g ν_4	1587	1604	a ν_4	1615	1607
ν_5	1505	1508	a_g ν_5	1493	1495	ν_5	1502	1490
ν_6	1282	1268	a_g ν_6	1326	1312	ν_6	1342	1307
ν_7	1192	1194	a_g ν_7	1201	1215	ν_7	1224	1225
ν_8	1029	1031	a_g ν_8	1017	1003	ν_8	1018	1012
ν_9	1003	990	a_g ν_9	979	966	ν_9	989	977
ν_{10}	964	929	a_u ν_{12}	—	840	ν_{10}	—	954
ν_{11}	841	831	a_u ν_{13}	—	709	ν_{11}	—	795
ν_{12}	740	735	a_g ν_{10}	721	703	ν_{12}	737	726
ν_{13}	410	410	a_u ν_{14}	—	409	ν_{13}	391	377
ν_{14}	307	307	a_g ν_{11}	327	326	ν_{14}	334	323

[a] Unscaled wavenumbers calculated at the BLYP/6-31G* level. [b] In the vapor or liquid phase (Ref. 15). [c] In THF (Ref. 16). [d] In CH_3CN (Refs. 14 and 17).

C_3C_4 bonds are lengthened on going from the neutral molecule to either the radical anion or cation. Similar structural changes have been obtained by the B3LYP and CASSCF methods. It may be concluded therefore that the removal or addition of one electron from or to biphenyl leads to changes from a benzenoid structure to a quinoid structure.

In Table 2, the unscaled vibrational wavenumbers calculated at the BLYP/6-31G* level for biphenyl and its radical ions are compared with wavenumbers observed in the Raman spectra.[14–17] The a_g and a_u modes of the radical anion (D_{2h} symmetry) are correlated to the a modes of the neutral species and the radical cation (D_2 symmetry). The differences between the observed and calculated wavenumbers are less than 18 cm^{-1}, except for ν_{10} of the neutral molecule and ν_6 of the radical cation. Such agreements between the observed and calculated wavenumbers lead to an expectation that the BLYP/6-31G* method will be useful in assigning the vibrational spectra of the radical ions of longer *p*-oligophenyls. Sasaki and Hamaguchi[14] have concluded that the presence of the weak 391-cm^{-1} band in the Raman spectrum of the radical cation results from its slightly twisted structure (D_2 symmetry). Their assignment has been confirmed by the present calculation. The calculation also shows that ν_6 of each species is mainly due to the inter-ring C_1C_1' stretch. The upshifts of the inter-ring C_1C_1' stretch on going from the neutral molecule to the radical ions are consistent with the structural changes in the direction from benzenoid to quinoid. The calculated wavenumber of 1307 cm^{-1} for the radical cation is 35 cm^{-1} lower than the observed, while the calculated wavenumbers for the neutral molecule and the radical anion are in better agreement with the observed. Since the calculated length of the inter-ring C_1C_1' bond in the twisted structure of the radical cation is longer than that in the planar radical anion, it seems to be natural that the calculated wavenumber for the inter-ring C_1C_1' stretch of the radical cation is lower than that of the radical anion. Actually, however, the wavenumber of the observed Raman band of the radical cation is significantly higher than that of the radical anion. The origin of this discrepancy between the calculated and observed wavenumbers is yet to be clarified.

We have demonstrated that the density functional theory is useful in evaluating the structures and vibrational wavenumbers of the radical anion and cation of biphenyl. We are now extending our studies to the radical anions and dianions of long-chain *p*-oligophenyls in order to gain a deeper understanding of polarons and bipolarons in nondegenerate conducting polymers.

One of the authors (KF) thanks Mr. J. Hayashi, director and general manager of the Ashigara Research Laboratories, for allowing KF to publish the results of calculation in this letter. Thanks are also due to Mrs. M. Kobayashi for her help in data processing.

References

1 H. Kiess, *Conjugated Conducting Polymers*, Springer-Verlag, Berlin (1992).
2 L. W. Shacklette, R. R. Chance, D. M. Ivory, G. G. Miller, and R. H. Baughman, *Synth. Met.*, **1**, 307 (1979).
3 Y. Furukawa, H. Ohtsuka, and M. Tasumi, *Synth. Met.*, **55**, 516 (1993).
4 J. L. Brédas, B. Thémans, J. G. Fripiat, J. M. André, and R. R. Chance, *Phys. Rev. B*, **29**, 6761 (1984).
5 L. Cuff, C. Cui, and M. Kertesz, *J. Am. Chem. Soc.*, **116**, 9269 (1994).
6 Ch. Ehrendorfer and A. Karpfen, *J. Phys. Chem.*, **99**, 10196 (1995).
7 Y. Shimoi and S. Abe, *Phys. Rev. B*, **50**, 14781 (1994).
8 M. Rubio, M. Merchán, E. Ortí, and B. O. Roos, *J. Phys. Chem.*, **99**, 14980 (1995).
9 M. J. Frisch, G. M. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. W. Wong, J. B. Foresman, M. A. Robb, M. Head-Gordon, E. S. Replogle, R. Gomperts, J. L. Andres, K. Raghavachari, J. S. Binkley, C. Gonzalez, R. L. Martin, D. J. Fox, D. J. Defrees, J. Baker, J. J. P. Stewart, and J. A. Pople, *Gaussian 92/DFT*, Gaussian Inc., Pittsburgh, PA, 1993.
10 A. D. Becke, *Phys. Rev. A*, **38**, 3098 (1988).
11 C. Lee, W. Yang, and R. G. Parr, *Phys. Rev. B*, **37**, 785 (1988).
12 A. D. Becke, *J. Chem. Phys.*, **98**, 5648 (1993).
13 A. Almenningen, O. Bastiansen, L. Fernholt, B. N. Cyvin, S. J. Cyvin, and S. Samdal, *J. Mol. Struct.*, **128**, 59 (1985).
14 Y. Sasaki and H. Hamaguchi, *Spectrochim. Acta*, **50A**, 1475 (1994).
15 R. M. Barrett and D. Steele, *J. Mol. Struct.*, **11**, 105 (1972).
16 C. Takahashi and S. Maeda, *Chem. Phys. Lett.*, **24**, 584 (1974).
17 G. Buntinx and O. Poizat, *J. Chem. Phys.*, **91**, 2153 (1989).