Journal of Physical Organic Chemistry

Received: 27 January 2008, Revised: 25 April 2008, Accepted: 25 May 2008,

(www.interscience.wiley.com) DOI 10.1002/poc.1408

DFT study of the biphenylene–NO_2^+ complexes formed in nitration mechanism

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The most probable complexes formed in biphenylene (BP) nitration pathway have been investigated at B3LYP/6-31+G(d,p) level of theory in the gas phase. To obtain more accurate energies, single point calculations were carried out at B3LYP/6-31++G(2d,2p), B3PW91/6-31+G(d,p), and B3PW91/6-31++G(2d,2p) levels using B3LYP/6-31+G(d,p) optimized geometry. The six intermediates and one transition state were found before the subsequent formation of the arenium ion on the potential energy surface of the electrophilic nitration of BP. It was also shown that the position β in the BP is much more susceptible to electrophilic attack than the competing position α. The Natural Bond Orbital (NBO), Charges from Electrostatic Potentials using a Grid based method (CHelpG), and Merz–Singh–Kollman (MK) charges and s-characters of atoms involved in the reaction mechanism were calculated. Inspection of charges in the moieties indicates that the positive charge in all complexes is chiefly located on the BP, which means that the NO_2 moiety received the electron from the BP. To investigate the nature of BP–NO_2^+ interaction in the five π-complexes, atoms in molecules (AIM) analysis was performed. The AIM results suggested that the BP–NO_2^+ interactions have an electrostatic characteristic. In addition, high electrostatic interactions were predicted in π-complexes in which one of the oxygen atoms of NO_2^+ interacts with the BP. Nucleus-independent chemical shift (NICS) methodology has been applied to study the change of antiaromaticity in four-membered ring of BP upon complexation with NO_2^+. The results based on NICS calculations show that antiaromaticity of four-membered ring decreases upon complexation. Copyright © 2008 John Wiley & Sons, Ltd.

Keywords: nitration; biphenylene; DFT; NBO; AIM; NICS

INTRODUCTION

Biphenylene (BP) is an unusual molecule which promises to have special properties due to presence of a formal cyclobutadiene ring. It is the dibenzo derivative of the unstable cyclobutadiene system. The centrally located cyclobutadiene ring fused to two benzene rings is the source of the strain. Ring strain, the nature of the bonding, reactivity and other chemical, physical, and theoretical problems are the reasons for the continuing interest in this peculiar hydrocarbon skeleton.[1] BP was first prepared by Lothrop[2] in 1941 by an Ullman reaction of 2,2′ dibromo- or 2,2′ diiodobiphenyl and was for many years the only known derivative of cyclobutadiene fused to benzene. Many alternative procedures have been developed for its synthesis.[3] The planar tricyclic structure of BP was demonstrated by electron diffraction in the gas phase [4] and by X-ray crystal structure analysis.[5–7] Recently, density functional theory (DFT) calculations and the spectroscopic method of inelastic neutron scattering (INS) were used to investigate the structure of BP in its crystalline state.[8]

In view of the strained four-membered ring in the BP molecule, one might think that many reactions would cause ring-opening. Nevertheless, this is rarely observed; a case in point is catalytic hydrogenation,[9] which yields biphenyl. Jones *et al.*[10] have studied cleavage of the carbon—carbon bond in BP using transition metals. BP can be substituted by electrophiles under the usual conditions without change of the molecular skeleton. It is somewhat more reactive than benzene. The Friedel–Crafts acylation, halogenation, and nitration yield almost exclusively 2-substituted BPs.[1]

Electrophilic aromatic substitution and nitration in particular have been among the most intensively studied organic reactions. They have played a key role in the study of aromatic reactivity and selectivity.[11–13] Electrophilic aromatic substitution proceeds through the formation of cationic Wheland σ-complex or arenium ion. Olah *et al.*[14] suggested the existence of intermediates prior to the subsequent formation of the Wheland σ-complex or arenium ion in nitration of benzene.

Maksic *et al.*[15] have studied the electronic and geometric structures of benzocyclobutadiene, BP, and their protonated forms at HF/6-31G* level. They have shown that the β-protonated species are more stable than α-protonated ones indicating greater susceptibility of the β-positions toward electrophilic substitutions.

DFT methods have limitations for taking the dispersion energy into account. In medium strength interactions, the dispersion forces are a minor component of the interaction energy. Therefore, B3LYP hybrid functional with a suitable basis set is expected to predict reasonably accurate interaction energies. To our knowledge, theoretical investigation of the mechanism of nitration of BP has not been reported.

In the present study, complexes formed in the reaction between BP and NO_2^+ have been investigated at the several level of theory to get some useful information about the reaction mechanism in electrophilic substitution of BP. In addition to the

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interaction energies and geometrical changes upon complexation, discussions will focus on the results obtained by population analysis. The nature of interaction between BP rings and NO_2^+ in **A1–5** complexes has been also studied by means of atoms in molecules (AIM) analysis.

The presence of four-membered antiaromatic ring in BP induces significant π-bond localization within the aromatic rings, which is responsible for the enhanced chemical reactivity of BP. Schleyer *et al.* [16–18] have proposed a simple and efficient probe for aromaticity: Nucleus-independent chemical shift (NICS), which is computed as the negative magnetic shielding at some selected point in space, e.g., at a ring or cage center. Negative NICS values denote aromaticity and positive NICS values denote antiaromaticity while small NICS values indicate non-aromaticity. Studies have demonstrated that NICS is a useful indicator of aromaticity that usually correlates well with the other energetic, structural, and magnetic criteria for aromaticity.[19–21] To evaluate the antiaromaticity of the four-membered ring of BP upon complexation with NO_2^+, NICS criterion has been used.

COMPUTATIONAL METHODS

The structural and energetic properties corresponding to all species in the electrophilic substitution of BP by NO_2^+ ion were investigated at B3LYP/6-31+G(d,p) [22,23] level using Gaussian 98 program package.[24] The harmonic vibrational frequency calculations were performed for all optimized species at the B3LYP/6-31+G(d,p) level to characterize the optimized stationary points as minima or saddle points, and to evaluate the corresponding zero-point vibrational energies. The intrinsic reaction coordinate (IRC) analysis was carried out at the B3LYP/6-31+G(d,p) level to make sure that the desired ground states be connected to the transition structure obtained. To obtain more accurate energies, we also carried out a single point calculations with 6-31++G(2d,2p) basis set using B3LYP/6-31+G(d,p) optimized geometry. In addition, we have performed a single point calculation at the B3PW91 level with 6-6-31+G(d,p) and 31++G(2d,2p) basis sets. NICS values were obtained by calculating absolute NMR shielding at ring center (NICS(0)) and at 1.0 Å above the ring center (NICS(1)) of cyclobutadiene of BP at B3LYP/6-31++G(2d,2p)//B3LYP/6-31+G(d,p) level using GIAO method.[25] To compute the NICS(0), it is essential to perform Bader's AIM analysis [26] first in order to pinpoint the ring critical point (rcp). The three different types of charges, namely, NBO(Natural Bond Orbital),[27] MK (Merz–Singh–Kollman),[28] and CHelpG (Charges from Electrostatic Potentials using a Grid based method) [29] charges were computed at B3LYP/6-31++G(2d,2p)//B3LYP/6-31+G(d,p) level. To investigate the nature of BP–NO_2^+ interaction, AIM analysis [26,30] was performed using AIM2000 [31] package at B3LYP/6-31++G(2d,2p)//B3LYP/6-31+G(d,p) level.

RESULTS AND DISCUSSION

The possible isomeric structures on the potential energy surface of the reaction between NO_2^+ ion and BP are shown in Figs. 1, 2, and 4. The relative energies of the structures at different level of theory are listed in Table 1. Figure 3 is a representation of the potential energy surface of the nitration of BP in the gas phase at the B3LYP/6-31+G(d,p) level. The calculations show that all complexes are local minima on the potential energy surface of nitration of BP, with the exception of structure **A2**, **E**, and **K** with the imaginary frequencies of 743.8i, 1774.3i, and 1134.8i cm^{-1}, respectively. Imaginary frequency of **A4** and **G** is smaller than 80i cm^{-1}. It is evident that all species are much more stable than the separated reactants. Therefore, their formations are energetically favorable, in agreement with a well-known fact that the electrophilic agent NO_2^+ has a strong tendency to interact with BP as an electron-rich aromatic.

Our present data indicate that more than one intermediate may be involved prior to the formation of σ-complex **W1** (Wheland intermediate). Five π-complexes **A1**–**5** were found as stationary points in the BP/NO_2^+ system prior to the formation of arenium intermediate **W1**. Structures **A1**–**5** correspond to various ways by which NO_2^+ can interact the BP (Fig. 1). The most stable structure among these π-complexes is **A5**. Complex **A1** is the less stable structure (the first potential-energy minimum) among all the studied complexes. In complex **A1**, nitrogen atom of NO_2^+ interacts with cyclobutadiene ring of BP. The isolated NO_2^+ is initially linear with N—O bond length of 1.129 Å and to be bent in the π-complexes **A1**, **A3**, **A4**, and **A5**. The O—N—O angle and BP–NO_2^+ distance in the π-complex **A1** are 155.7° and 2.755 Å, respectively. In this complex, BP–NO_2^+ interaction causes about 76.0 kJ/mol stability at the B3LYP/6-31+G(d,p) level. In unoriented complex **A2**, as a transition state, interaction between NO_2^+ and cyclobutadiene ring of BP is made through the oxygen of NO_2^+. This interaction stabilizes the complex by 126.1 kJ/mol. The O—N—O angle and BP–NO_2^+ distance in the oriented π-complex **A2** are 155.7° and 2.622 Å, respectively. Among the π-complexes on the potential energy surface of the approach of NO_2^+ ion to BP, π-complexes **A3**, **A4**, and **A5** are more stable than others. They are at 205.1, 244.9, and 257.1 kJ/mol below the reactants (BP + NO_2^+) at B3LYP/6-31+G(d,p) level. The N—O_b bond length and O—N—O bond angle are 1.214 Å and 133.0°, respectively in **A3**. These structural parameters have the values of 1.194 Å and 135.2.0° in **A4** and 1.196 Å and 134.9° in **A5**, respectively. The O—N—O bond angle in **A3**, **A4**, and **A5** being close to the angle of an isolated $NO_2^{\bullet}$ molecule (134.1°) indicates that the NO_2^+ moiety undergoes effectively an almost complete reduction to $NO_2^{\bullet}$ upon complexation. In the over-rim structures of **A4** and **A5**, acceptor NO_2^+ binds to BP directly above the C2—C3 and C11—C12 centers (at their midpoint), respectively. Similar π-complexes have also been found in theoretical studies of the C_6H_6/NO_2^+ system.[12] At all levels of theory, relative stability of isomers decreases in the order **H** > **F** > **G** > **L** > **W1** > **C** > **B** > **A5** > **A4** > **A3** > **K**(TS) > **E**(TS) **A2** > **A1**. As shown in Table 1, zero-point energy (ZPE) correction has a significant effect on the energy of some structures. The stabilization energy of isomers decreases upon going from the 6-31+G(d,p) basis set to the 6-31++G(2d,2p) one. As shown in the table, stabilization energy of isomers computed by same basis set at the B3LYP level is greater than that at the B3PW91 level.

The NICS values calculated at B3LYP/6-31++G(2d,2P)//B3LYP/6-31+G(d,p) level for five π-complex **A1**–**5** are listed in Table 2. Two NICS values were calculated at two positions in the cyclobutadiene ring of BP: the rcp and points 1.0 Å above the one, which are denoted by NICS(0) and NICS(1), respectively. From Table 2 we find that NICS values for all π-complexes **A1**–**5** are positive, with the exception of NICS(1) for **A1** complex. The NICS(0) and NICS(1) values for cyclobutadiene ring of BP are 21.4 and 10.5 ppm, respectively. The positive NICS values at the center of ring are greater than those of 1.0 Å above the ring. Thus,

Table 1. Relative energy (kJ/mol) of structures for the interaction of BP with NO_2^+ at several levels

	E_{elec}	E_0^a	ΔE_{elec}	ΔE_0	E_{elec}	E_0^a	ΔE_{elec}	ΔE_0
		B3LYP/6-31+G(d,p)				B3LYP/6-31++G(2d,2p)		
BP + NO_2^+	−666.776059	−666.606088	0.0	0.0	−666.802073	−666.63210	0.0	0.0
A1	−666.805277	−666.635120	−76.6	−76.2	−666.828393	−666.65824	−69.0	−68.5
A2	−666.824116	−666.655796	−126.1	−130.4	−666.846437	−666.67812	−116.4	−120.7
A3	−666.85424	−666.685977	−205.1	−209.5	−666.873793	−666.70553	−188.1	−192.6
A4	−666.869423	−666.699750	−244.9	−245.7	−666.890531	−666.72086	−232.0	−232.8
A5	−666.872027	−666.702303	−251.7	−252.4	−666.892293	−666.72257	−236.6	−237.3
B	−666.872808	−666.70179	−253.8	−251.0	−666.893691	−666.72267	−240.3	−237.6
C	−666.876171	−666.704664	−262.6	−258.6	−666.897132	−666.72562	−249.3	−245.3
E	−666.838793	−666.672204	−164.6	−173.4	−666.860749	−666.69416	−153.9	−162.8
F	−666.898475	−666.726727	−321.1	−316.4	−666.920648	−666.74890	−311.0	−306.4
G	−666.898391	−666.727243	−320.9	−317.8	−666.920510	−666.74936	−310.7	−307.6
H	−666.914342	−666.741887	−362.7	−356.2	−666.935430	−666.76297	−349.8	−343.3
K	−666.840375	−666.672968	−168.7	−175.4	−666.862644	−666.69524	−158.9	−165.6
L	−666.8797532	−666.708885	−272.0	−269.6	−666.901026	−666.73016	−259.6	−257.2
W1	−666.8781161	−666.706614	−267.7	−263.7	−666.899131	−666.72763	−254.6	−250.6
W2	−666.862801	−666.691927	−227.5	−225.2	−666.883487	−666.71261	−213.5	−211.2
		B3PW91/6-31+G(d,p)				B3PW91/6-31++G(2d,2p)		
BP + NO_2^+	−666.521567	−666.351597	0.0	0.0	−666.55004	−666.38007	0.00	0.00
A1	−666.5486455	−666.378489	−71.0	−70.5	−666.573876	−666.40372	−62.5	−62.0
A2	−666.526626	−666.358306	−130.3	−17.6	−666.590615	−666.42229	−106.4	−110.8
A3	−666.5922107	−666.423948	−185.3	−189.8	−666.614037	−666.44577	−167.9	−172.3
A4	−666.6096316	−666.439959	−231.0	−231.8	−666.633107	−666.46343	−217.9	−218.7
A5	−666.6120078	−666.442284	−237.2	−237.9	−666.634576	−666.46485	−221.7	−222.4
B	−666.614333	−666.443315	−243.3	−240.6	−666.637835	−666.46682	−230.3	−227.5
C	−666.6177606	−666.446254	−252.3	−248.3	−666.641427	−666.46992	−239.7	−235.7
E	−666.585120	−666.418531	−166.7	−175.6	−666.610219	−666.44363	−157.9	−166.7
F	−666.6411008	−666.469353	−313.5	−308.9	−666.666115	−666.49437	−304.5	−299.8
G	−666.6407777	−666.46963	−312.7	−309.6	−666.665665	−666.49452	−303.3	−300.2
H	−666.6567886	−666.484334	−354.7	−348.2	−666.680659	−666.50820	−342.6	−336.1
K	−666.5860195	−666.418613	−169.1	−175.8	−666.611334	−666.44393	−160.8	−167.5
L	−666.6224753	−666.451607	−264.7	−262.3	−666.646591	−666.47572	−253.3	−250.9
W1	−666.6201153	−666.448613	−258.5	−254.5	−666.643782	−666.47228	−245.9	−241.9
W2	−666.604937	−666.434063	−218.7	−216.3	−666.628284	−666.45741	−205.2	−202.9

[a] $E_0 = E_{elec} + ZPE$.

NICS(1) values are recommended as a better measure of the aromaticity than NICS(0) for these structures. The NICS(1) value for **A1** is −1.0 ppm, which indicates the non-aromaticity of cyclobutadiene ring. For minimum structures (**A3**, **A4**, and **A5**), positive NICS(1) value decreases upon complexation. This indicates that the antiaromaticity decreases upon complexation. In addition, NICS values decrease in going from **A3** to **A5**, suggesting that the antiaromaticity decreases. It can be observed that there is a correlation between the decrease of antiaromaticity in cyclobutadiene ring of these π-complexes and increasing stability.

It is predicted that complexes **A4**, **B**, **C**, and **W1** contribute directly in the electrophilic attack of position 2 (β) of BP. As can be seen from Figs. 1 and 2, N—C2 distance in complexes **A4**, **B**, **C**, and **W1** are 2.372, 1.758, 1.608, and 1.587 Å, respectively, and the values O—N—O bond angles are 135.2, 130.2, 128.0, and 127.9°, respectively. As the NO_2^+ approaches the BP, N—C2 bond length decreases from 2.372 Å in **A4** to 1.587 Å in **W1** and O—N—O bond angle changes from 135.2 to 127.9°. The tetrahedral C—H bond length increases from 1.086 in **A4** to 1.087 in **B**, 1.094 in **C**, and 1.102 Å in **W1**. The change of these structural parameters indicates that the interaction between NO_2^+ and BP is strongly increasing as the NO_2^+ approaches the BP.

The s-character and three different types of charges, namely, NBO, MK, and CHelpG obtained at the B3LYP/6-31++G(2d,2p) level are given in Table 3. It seems that the changes in the charges computed by the CHelpG method are more reasonable than NBO and MK methods on going from **A4** to **W1**. As can be seen from this table, values of charges calculated according to the CHelpG scheme for the NO_2^+ ion and BP moiety in complexes **A4**–**W1** are as follows:

$$NO_2 : \mathbf{A4}(0.0161), \mathbf{B}(-0.0089), \mathbf{C}(-0.0666), \text{and } \mathbf{W1}(-0.0703)$$
$$\mathbf{BP} : \mathbf{A4}(0.9839), \mathbf{B}(1.0089), \mathbf{C}(1.0666), \text{and } \mathbf{W1}(1.0702)$$

A common feature of complexes **A4**, **B**, **C**, and **W1** is the marked decrease in the electronic charge on the BP and the increase in the electronic charge on the NO_2 moiety. Thus,

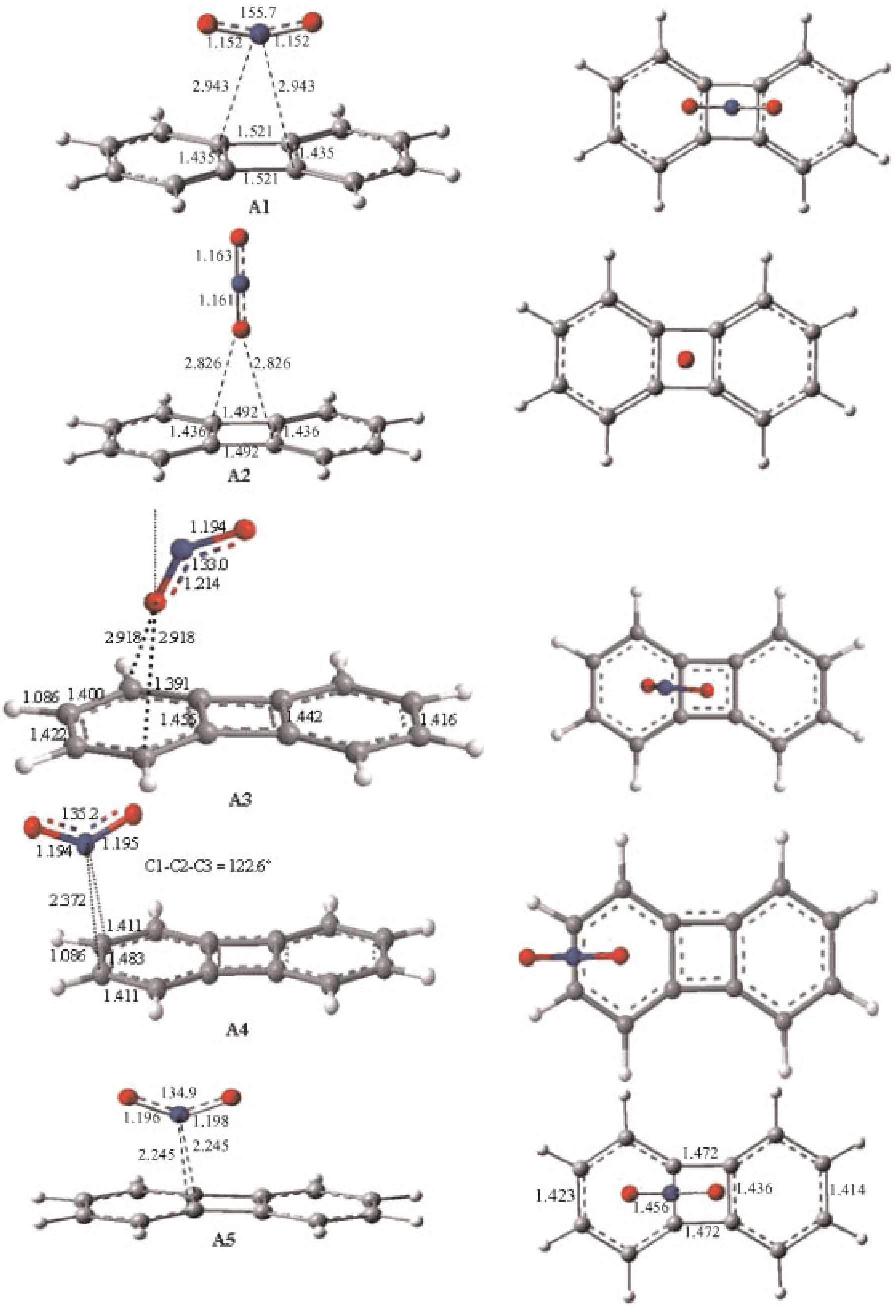

Figure 1. B3LYP/6-31+G(d,p) NO_2^+–BP complexes **A1–5**

inspection of these results shows that the charge transfer occurs from BP to NO_2 in the nitration process. Among the complexes found before the **W1**, complex **B** can better describe the BP as a cation-radical $BP^{+\cdot}$ interacting with $NO_2^{\bullet}$.

Table 3 shows that in σ-complexes **B**, **C**, and **W1**, percentage of s-character of carbon C2 (nitration site) is smaller than C1 and C3, which causes considerable decrease in the bond length of vicinal bonds (C3—C4 and C1—C11) with respect to C2—C1 and C2—C3 bonds. As a result, substantial π-localization occurs in the vicinal bonds with respect to the nitration site. The s-character of C2 atom in σ-complex **W1** is greater than σ-complexes **B** and **C**.

As noted above, position 2 (β) in the BP is much more susceptible to electrophilic attack than the competing position 1 (α) as a consequence of competition between the aromaticity of the benzene rings and antiaromaticity of the cyclobutadiene fragment. Direction of electrophile (NO_2^+) to position 2 can be explained by analyzing the energies and the possible structures of the σ-complexes. Two Wheland intermediates **W1** and **W2** were found to be minima on the potential energy surface of the reaction at B3LYP/6-31+G(d,p) level of theory. Geometry of these intermediates is shown in Fig. 2. As can be seen from Table 1, interaction energy of complex **W1** is greater than complex **W2**.

Table 2. NICS values (ppm) calculated at the ring critical point (rcp) and 1 Å above the one at B3LYP/6-31++G(2d,2p)//B3LYP/6-31+G(d,p) level

	NICS(0)	NICS(1)
BP	21.4	10.5
A1	14.0	−1.0
A2	25.8	29.6
A3	14.3	5.2
A4	15.0	2.7
A5	10.7	1.1
W1	15.0	2.2
W2	22.0	8.0
H	18.3	5.9

Consequently, intermediate **W1** is more stable than **W2** one on the potential energy surface of the reaction of BP with NO_2^+ in the gas phase. Thus, the structure of the transition state in the BP electrophilic substitution correlates more with the intermediate **W1** which facilitates the formation of TS.

In addition, sum of bond lengths of four-membered ring in complexes **W1** and **W2** can also be used as a criterion for the stability of the intermediates. The sum of bond lengths of four-membered ring in complex **W1** (5.838 Å) is greater than complex **W2** (5.822 Å). In other words, the double bond character of bonds in the four-membered ring of complex **W1** is smaller than that of complex **W2**. Thus, complex **W1** with smaller double bond character in the four-membered ring is energetically favorable. On the other hand, deviation of bond angle around the C1 position from the ideal 120° angle of a benzene sp^2 hybrid orbital in intermediate **W2** (7.1°) is greater than that of bond angle around the C2 position in intermediate **W1** (2.2°). Consequently, computational data confirm that the C2 position should be more disposed to electrophilic substitution than that of C1.

The selected structural parameters of **E–L** species are shown in Fig. 4. It can be seen that the N—C bond length decreases on going from **E** to **L**. Comparison of binding energies of **W1** and **L** reveals that σ-complex **L** is more stable than **W1** by 6.0 kJ/mol at the B3LYP/6-31+G(d,p) level. The hydrogen migration from carbon to oxygen restores the aromaticity character to BP. Therefore, most stable structure on the potential energy surface of nitration of **BF** must be complex O-protonated nitrobiphenylene $[PB\text{-}NO_2]^+$ (**H**) (Fig. 3 and Table 1). It lies in a deep energy minimum of −356.2 kJ/mol. According to IRC calculations, the isomerization of **W1** → **L** → **F** can take place via transition states **K** and **E,** respectively. From Table 1 we can calculate the energy barriers of 99.00 kJ/mol (B3LYP/6-31+G(d,p)) and 95.7 kJ/mol (B3LYP/6-31++G(2d,2p)) for the **W1** → **L** transformation and 107.4 ((B3LYP/6-31+G(d,p)) and 105.6 kJ/mol (B3LYP/6-31++G(2d,2p)) for **L** → **F** transformation. The energy barrier obtained by the B3PW91 method is smaller than the B3LYP method with

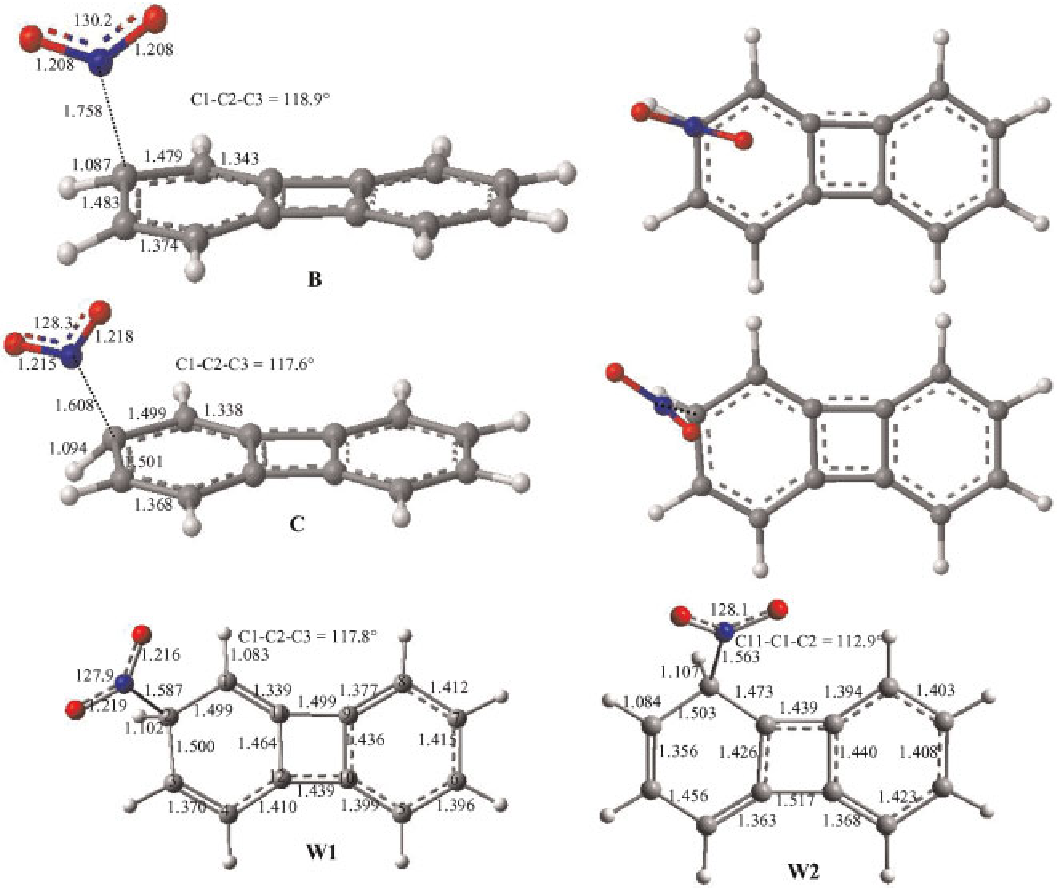

Figure 2. B3LYP/6-31+G(d,p) geometry of **B**, **C**, **W1**, and **W2**

Table 3. Atomic charges (a.u.) and percentage of s-character obtained at B3LYP/6-31++G(2d,2p) level

	A3	A4	B	C	W1
Natural charge					
NO_2	0.0356	0.0861	−0.0607	−0.1313	−0.1265
BP	0.9645	0.9139	1.0607	1.1313	1.1265
MK charge					
NO_2	0.0341	0.0989	0.0052	−0.0363	−0.0333
BP	0.9659	0.9011	0.9948	1.0363	1.0333
CHelpG charge					
NO_2	0.0161	0.0876	−0.0089	−0.0666	−0.0702
BP	0.9839	0.9124	1.0089	1.0666	1.0702
s-character					
C1	33.2	33.8	35.8	36.5	36.8
C2	35.1	33.6	29.8	29.9	30.9
C3	35.1	33.6	36.4	37.3	37.4
C4	33.2	33.8	32.3	32.1	32.5

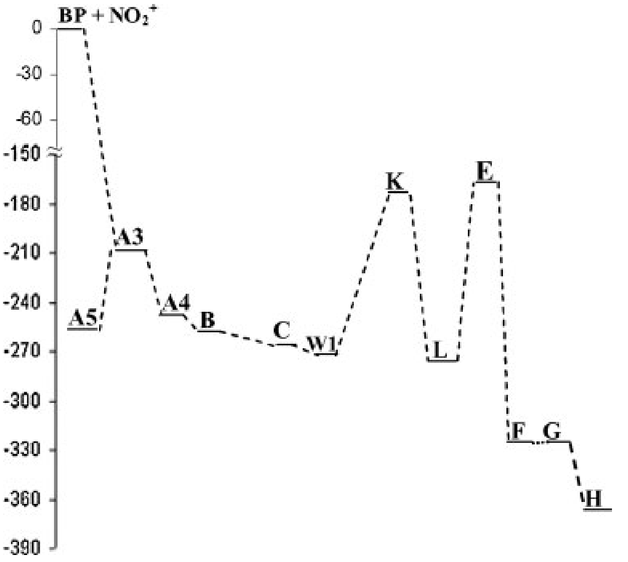

Figure 3. Schematic energy diagram for potential energy surface of nitration of BP predicted at B3LYP/6-31+G(d,p) level

the same basis set. Table 1 shows that the inclusion of ZPE reduces the energy barrier. It seems that **G** structure with a low imaginary frequency is a conformation of **F**.

In AIM analysis, topological properties of the electron density are analyzed to define bond path between bonding atoms. Chemical bonds can be characterized by the so-called bond critical point (BCP).[24] To investigate the nature of BP–NO_2^+ interaction in π-complex **A1–5**, AIM analysis was performed at the B3LYP/6-31++G(2d,2p) level. The molecular graph and values of electron density (ρ), Laplacian of electron density ($\nabla^2\rho$), and total energy density (H) at the BCP of the BP–NO_2^+ interaction are given in Fig. 5. As can be seen, order of increase electron density at BP–NO_2^+ of ground state structures **A1**, **A3**, **A4**, and **A5** is consistent with the order of stability of structures and with the contraction of the BP–NO_2^+ intermolecular distance. The sign of the H at BCP assigns whether the interaction is electrostatic dominant ($H > 0$) or covalent dominant ($H < 0$). According to the positive values of $\nabla^2\rho$ and H, it seems that the BP–NO_2^+ interaction in π-complexes **A1–5** has an electrostatic characteristic. $\nabla^2\rho$ and H values in **A2** and **A3** π-complexes are more positive than those of the other complexes. Here, comparison of $\nabla^2\rho$ and H in these π-complexes indicates that the electrostatic nature of BP–NO_2^+ interaction in **A2** and **A3** is greater than other π-complexes. As a result, π-complexes **A2** and **A3** are expected to be initial ones formed in the interaction between BP and NO_2^+.

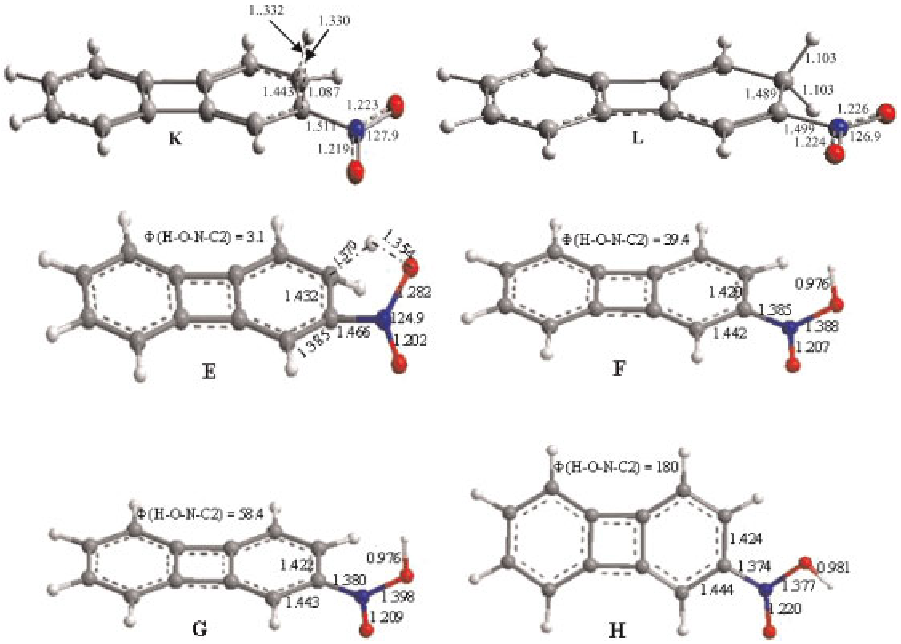

Figure 4. B3LYP/6-31+G(d,p) geometry of structures **K**, **L** and **E–H**

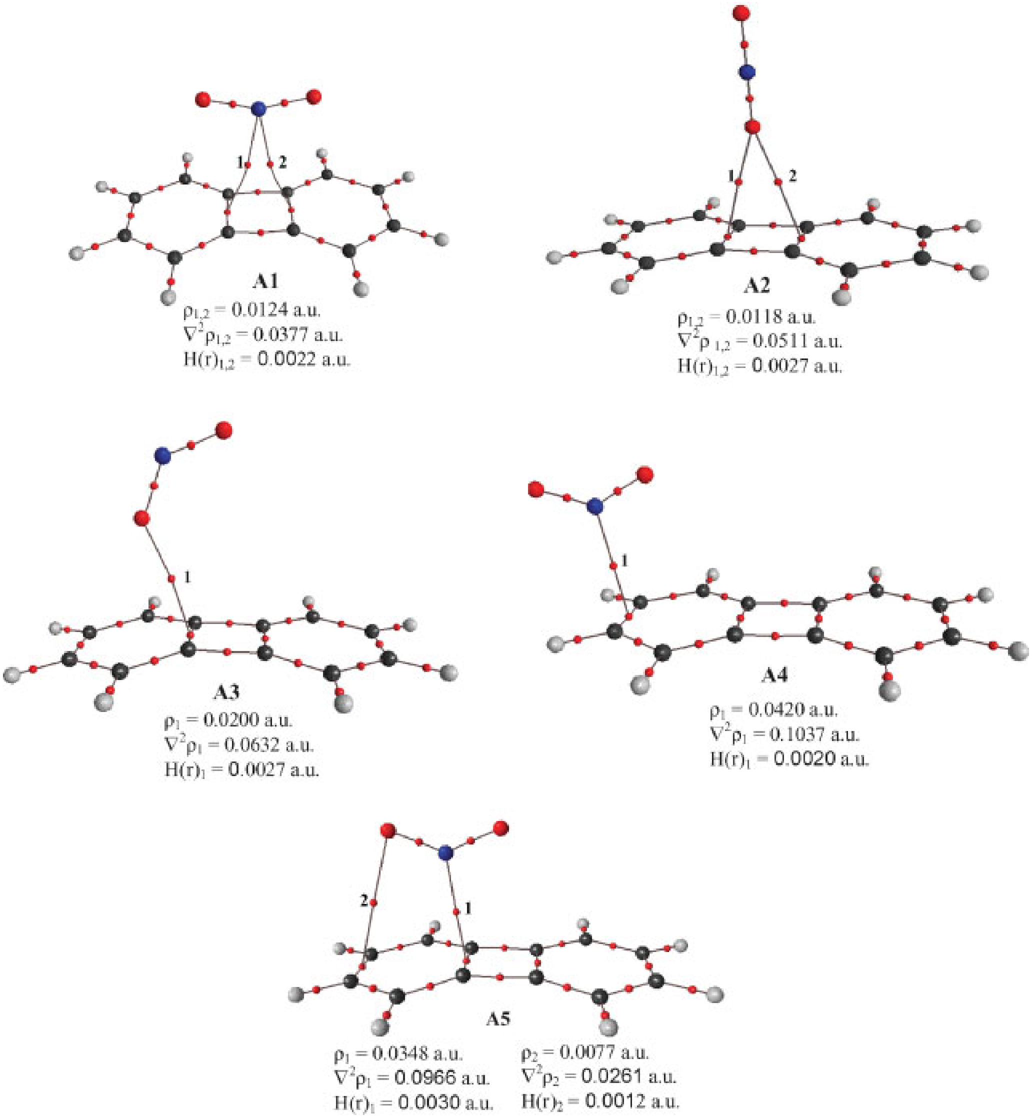

Figure 5. Molecular graphs of **A1**–**5** π-complexes together with properties calculated at the BCP of BP–NO_2^+. Nuclei and critical points are represented by big and small circles, respectively

CONCLUSIONS

The complexes formed in reaction between BP and NO_2^+ have been investigated at several levels. It is expected that the π-complexes **A2** and **A3** are the initial complexes formed prior to the formation of arenium intermediate **W1**. These complexes react to give the, respectively, π-complex **A4** and σ **-complexes B, C**, and then **W1**. Finally, the hydrogen migration from C2 to C3 through the transition state **K** and then from C3 to oxygen of NO_2 via transition state **E** results in the structure **F** on the potential energy surface. The computational data confirm that the C2 position in BP should be more disposed to electrophilic substitution than that of C1.

For minimum structures (**A3**, **A4**, and **A5**), positive NICS(1) value in the four-membered ring of BP decreases upon complexation. This reveals that the antiaromaticity decreases upon complexation.

Inspection of charges indicates that the positive charge in all complexes is chiefly located on the BP, which means that the NO_2 moiety received electron from the BP. AIM analysis suggested that the BP—NO_2^+ interaction in complex **A** has an electrostatic characteristic. The π-complexes **A2** and **A3** are expected to be initial ones formed in the interaction between BP and NO_2^+.

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