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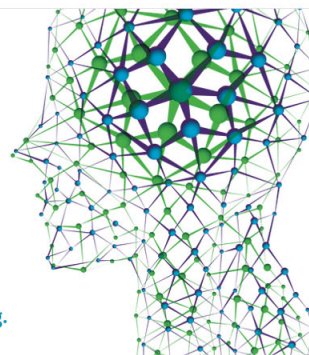
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p-benzoquinone-benzene clusters as potential nanomechanical devices: A theoretical study

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The equilibrium structures and binding energies of the benzene complexes of *p*-benzoquinones (PBQ) and its negatively charged anionic species (PBQ⁻ and PBQ²⁻) have been investigated theoretically using second-order Møller-Plesset calculations. While neutral *p*-benzoquinone-benzene clusters (PBQ-Bz) prefer to have a parallel displaced geometry (**P-c**), CH $\cdots\pi$ interactions (*T*-shaped geometries) prevail in the di-anionic PBQ-benzene (PBQ²⁻-Bz) complexes (**T-e²⁻**). Studies on dianionic *p*-benzoquinone-benzene clusters showed that two nonbonded intermolecular interactions compete in the most stable conformation. One is H-bonding interaction (C-H \cdots O type) between carbonyl oxygen of *p*-benzoquinone and one of the hydrogen atoms of benzene, and the other is a π -H interaction between π -electron cloud of PBQ²⁻ and another hydrogen atom of benzene. Blueshifted H-bonds were observed in *T*-shaped clusters. The changes in the geometrical preference of PBQ-Bz complex upon addition of electrons would be useful in designing optimized molecular mechanical devices based on the edge-to-face and face-to-face aromatic interactions. © 2004 American Institute of Physics.
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I. INTRODUCTION

The intermolecular interactions involving nonbonded interactions are highly important in supramolecular structures and biological systems.^{1,2} The structure and properties of van der Waals clusters have recently been studied extensively not only for understanding the effect of weak interactions on the physical and chemical properties of the system, but also for the design of new inophores and receptors.³ Among the nonbonded interactions, aromatic-aromatic interactions play crucial roles in base-base interaction of DNA,⁴ tertiary structure formation of proteins,⁵ and protein stability.⁶ Interactions of π electronic systems of aromatic/nonaromatic molecules are important forces in governing molecular recognition,⁷ host-guest complexation,⁸ and stereochemistry of organic reactions.⁹ Although among various types of nonbonded interactions such as H-bonded^{10,11} or interactions involving π electron systems (π - π , cation/anion- π ,¹² etc.) aromatic π - π interactions are the weakest, these interactions have received much attention because of their important role in molecular assembly and biomolecular recognition.¹³

The benzene dimer is a prototypical case of π - π interactions, and a large number of experimental and theoretical studies have been carried out on this molecular system.¹⁴ Different minima were proposed for the benzene dimer, since the interaction energy often depends on the method employed. Nevertheless it is known that the edge to face (*T* shaped) and the parallel displaced arrangements are nearly isoenergetic,¹⁵ while energy barriers for the interconversion

of the two structures along with the sandwich model is very small.¹⁶

Investigations of supramolecular systems are not only of fundamental importance for understanding of their complex behavior, but also a starting point for construction of molecular machines.¹⁷ The changes in the intermolecular interaction of the supermolecular structures upon oxidation/reduction or photoirradiation can be applied in designing molecular mechanical devices. Recently our research group has shown that the structural change of the quinone-benzene system upon electrochemical reduction has been useful in designing a nanomechanical device.¹⁸ In 1997, Stowell and co-workers showed that the orientation of quinone in photosynthetic reaction center (PSRC) depends upon the charged state of that molecule.¹⁹ A systematic investigation on the geometrical changes upon PBQ-Bz clusters on addition of electrons is necessary to explain these observations. A number of earlier studies have investigated the properties of quinones and their H-bonded analogues.²⁰ In the present work, we have done calculations to investigate the interactions between benzene (Bz) and *p*-benzoquinone (PBQ) in different charged states. We further studied the changes in geometrical preference of this molecular system as a function of the number of extra electrons. Neutral PBQ is known to be nonaromatic, while addition of electrons induces aromaticity. Therefore this study shows how the interaction changes as the PBQ changes from a nonaromatic to an aromatic molecule.

II. COMPUTATIONAL METHODS

Geometries of PBQ-Bz complexes were fully optimized at the second-order Møller-Plesset (MP2) level of theory

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TABLE I. Binding energies and geometries of PBQ-Bz clusters. ΔE is the median values of BSSE corrected and uncorrected binding energies which are the lower and upper limits, respectively. The values after \pm are the half of the BSSE. Δx is the lateral displacement of center of mass of the two rings. Δz is the vertical displacement of the center of mass of the two rings. $R_{CM}-R_{CM}$ is the distance between the center of mass of the two rings. $\Delta x; \Delta z$ shown in italic letters and $R_{CM}-R_{CM}$ given in bold letters. Partial optimizations are performed on P-b²⁻ and P-c²⁻, keeping the benzene and quinone in parallel planes. MP2 energies at B3LYP geometries are reported for L-a⁻, L-b⁻, and L-c⁻.

| System | $\Delta E(\text{MP2}/6-31+G^*)$ (kcal/mol) | $\Delta E(\text{MP2}/6-311++G^{**})$ (kcal/mol) | $\Delta x; \Delta z$ or $R_{CM}-R_{CM}$ (Å) (MP2/6-311++G ^{**}) |
|---|---|--|--|
| S-a S-a ⁻ S-a ²⁻ | 5.92±2.33 4.12±2.45 6.73±3.00 | 6.82±2.52 5.31±2.45 9.11±2.52 | 3.45 3.50 3.35 |
| S-b S-b ⁻ S-b ²⁻ | 6.15±2.56 4.39±2.70 7.10±3.33 | 7.72±2.07 5.34±2.95 8.66±3.54 | 3.40 3.40 3.35 |
| P-a P-a ⁻ P-a ²⁻ | 5.57±2.79 4.41±2.84 13.73±2.59 | 6.64±2.96 5.80±2.97 14.34±1.51 | <i>2.50;3.40 1.00;3.35 0.60;3.45</i> |
| P-b P-b ⁻ P-b ²⁻ | 7.18±2.93 6.20±3.05 8.24±3.73 | 8.59±3.42 7.75±3.28 11.42±4.20 | <i>1.40;3.10 1.30;3.30 1.60;3.00</i> |
| P-c P-c ⁻ P-c ²⁻ | 7.21±2.95 6.27±3.13 9.35±3.70 | 8.58±3.41 9.00±2.14 11.67±4.30 | <i>1.30;3.10 1.30;3.30 1.60;2.95</i> |
| T-a T-a ⁻ T-a ²⁻ | 2.37±1.62 6.70±1.82 15.71±3.08 | 2.99±1.95 7.18±2.40 17.16±3.18 | 4.85 4.70 4.50 |
| T-b T-b ⁻ T-b ²⁻ | 1.95±1.65 4.91±2.01 13.01±2.69 | 2.67±1.95 5.95±2.26 14.62±2.80 | 4.80 4.70 4.50 |
| T-c T-c ⁻ T-c ²⁻ | 2.86±1.64 6.74±1.85 15.34±2.48 | 3.42±1.55 7.21±1.88 15.92±2.45 | 4.80 4.70 4.65 |
| T-d T-d ⁻ T-d ²⁻ | 2.11±1.64 4.90±1.90 12.38±2.47 | 2.62±1.64 5.60±1.87 13.66±2.47 | 4.90 4.80 4.75 |
| T-e T-e ⁻ T-e ²⁻ | 2.87±1.67 7.09±2.08 17.87±2.96 | 3.40±1.79 7.76±2.23 19.04±3.11 | <i>0.90;4.80 0.95;4.65 1.30;4.35</i> |
| T'-a T'-a ⁻ T'-a ²⁻ | 4.15±1.55 1.79±1.51 1.78±1.65 | 4.45±1.61 4.38±1.56 2.42±1.67 | 4.55 4.75 4.60 |
| T'-b T'-b ⁻ T'-b ²⁻ | 0.75±1.49 -0.91±1.41 0.35±1.68 | -1.37±1.53 -0.41±1.47 1.01±1.76 | 4.90 4.95 4.90 |
| T''-a T''-a ⁻ T''-a ²⁻ | 4.36±1.76 4.78±1.03 14.06±1.40 | 5.19±2.13 5.15±1.01 14.44±1.63 | <i>0.10;4.75 6.10;2.15 6.35;1.50</i> |
| T''-b T''-b ⁻ T''-b ²⁻ | 3.57±1.50 5.02±1.14 14.11±1.23 | 5.14±2.23 5.43±1.01 14.25±1.75 | <i>0.00;4.75 5.25;2.90 6.80;0.00</i> |
| L-a L-a ⁻ L-a ²⁻ | 1.69±0.52 2.52±0.68 14.05±1.03 | 1.75±0.58 3.05±0.70 14.42±1.04 | 7.60 7.40 7.10 |
| L-b L-b ⁻ L-b ²⁻ | 1.93±0.59 3.11±0.69 14.03±1.08 | 1.97±0.65 3.59±0.72 14.34±1.07 | 7.20 7.10 6.90 |
| L-c L-c ⁻ L-c ²⁻ | 2.03±0.74 2.99±0.85 14.11±1.23 | 2.08±0.80 3.45±0.91 14.25±1.75 | 7.10 7.00 6.80 |

with 6-31+G* and 6-311++G** basis sets. The important geometries were further optimized at the MP2/aug-cc-pVDZ level. The binding energies of important geometries optimized at MP2/aug-cc-pVDZ are computed using the coupled-cluster singles and doubles level augmented by a perturbative correction for triple excitations [CCSD(T)] level of theory employing 6-31+G* basis set. The basis set superposition error (BSSE) corrections for the complexes were carried out using the counterpoise method.²¹ The minimum energy clusters were confirmed from the harmonic vibrational frequencies at the MP2/6-31+G* level. Natural bond orbital (NBO) calculations were done at the MP2/6-311++G** level on the geometries optimized at the same level. The calculations were carried out using the GAUSSIAN 98 suite of programs.²²

III. RESULTS AND DISCUSSION

The MP2/6-31+G* and MP2/6-311++G** predicted interaction energies (ΔE) and important geometrical parameters of PBQ-Bz system are listed in Table I and the geometries with MP2/6-311++G** energies are shown in Fig. 1. We have investigated stacked configurations (**S-a** and **S-b**), parallel displaced configurations (**P-a**, **P-b**, and **P-c**), T-shaped edge to face conformations with facial quinones (**T-a**, **T-b**, **T-c**, **T-d**, and **T-e**), T-shaped edge to face conformations with facial benzene (**T'-a** and **T'-b**), T-shaped and slanted configurations with facial benzene (**T''-a** and **T''-b**), and linearly aligned or lateral configurations (**L-a**, **L-b**, and **L-c**).

Here we begin with the discussions of neutral systems; the fully stacked geometries **S-a** and **S-b** (face to face interactions) are slightly less stable (~2 kcal/mol) than the parallel displaced geometries (**P-b** and **P-c**). At MP2/6-31+G* **P-b** has one imaginary frequency, which corresponds

to the rotation of **P-b** to **P-c**. The parallel displaced geometry **P-a** is energetically less stabilized than **P-b** and **P-c**.

The staggered and stacked benzene ring over PBQ (**S-b**) is slightly more stable by ~0.5 kcal/mol than the fully stacked one (**S-a**). In Hexafluorobenzene (HFBz), the components of quadrupole moments have opposite signs (compared with that of benzene) because of the presence of electron-withdrawing fluorine atoms. Thus, a parallel-stacked geometry (alternative benzene-HFBz rings) was already observed for HFBz-Bz complexes.²³ In the case of PBQ-Bz complex, the quadrupole moments of benzene and PBQ are similar in sign, as in the case of benzene dimer; therefore no attractive interactions exist between quadrupole moments of PBQ and Bz. The PBQ-Bz dimer structures with CH- π interactions (both facial benzene and facial quinone) are calculated to have higher energy than the parallel displaced geometries. The most stable edge to face conformers **T-e** is less stable by about 6.7 kcal/mol than the geometry **P-c**. **T''-a** and **T''-b** are ~4.5 kcal/mol less stable than **P-c**. The clusters which allow the direct interaction between the carbonyl oxygen of PBQ with the H-atom of benzene (**L-a**, **L-b**, and **L-c**) are calculated to have much higher energy (>9 kcal/mol) than **P-c**. Thus parallel displaced configurations are more stable than the T-shaped configurations and lateral conformers (**L-a**, **L-b**, and **L-c**). The global minimum energy conformers for the neutral PBQ-benzene complex are calculated to be the parallel displaced structures **P-b** and **P-c** which are almost isoenergetic. For the two lowest energy structures of neutral clusters (**P-b** and **P-c**), CCSD(T)/6-31+G* calculations were performed at MP2/aug-cc-pVDZ optimized geometries to obtain more reliable energy. At the CCSD(T)/6-31+G**//MP2/aug-cc-pVDZ level of theory, **P-c** is energetically stabilized only by 0.04 kcal/mol over **P-b**.

The Hartree-Fock theory-predicted binding energies (at

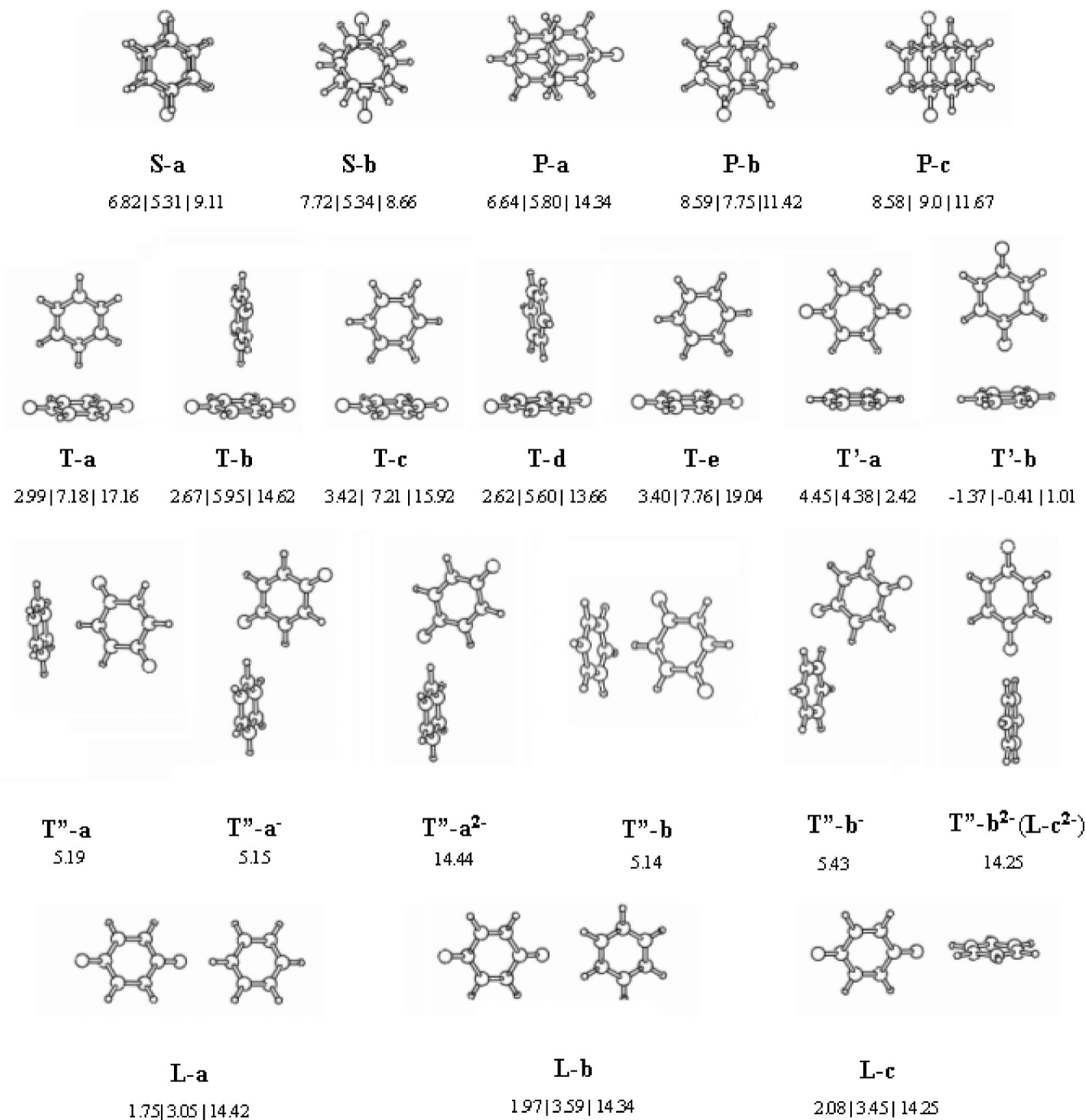


FIG. 1. Geometries and binding energies (MP2/6-311+ + G**, 50% BSSE corrected) of *p*-benzoquinone-benzene clusters. The first, second, and third values are the binding energies of neutral, anionic, and dianionic states, respectively.

the MP2 optimized geometries) for most of the geometries shown in Fig. 1 lead to repulsive interactions (Fig. 2). A similar situation is also observed for Bz-Bz and HFBz-Bz cases.²³ These results lead to a conclusion that dispersive forces are very important in obtaining an accurate estimate of the interaction energy. Nevertheless it should be noted that significant electrostatic interaction energy is compensated by the equally significant large exchange repulsion energy.

Addition of a single electron to the PBQ-Bz complex makes a competition between the parallel displaced and *T*-shaped geometries. The BSSE and zero point vibrational energy (ZPE) corrected binding energies at MP2/6-31 + G*

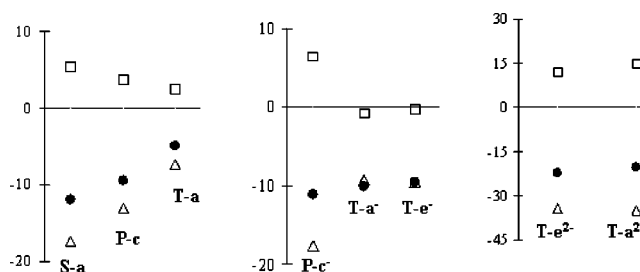


FIG. 2. Relative energies of some of the important conformations of PBQ-Bz clusters (\square — $-\Delta E_{scf}$, \bullet — $-\Delta E_{MP2}$, \triangle — $-\Delta E_{Corr}$).

TABLE II. Binding energies and geometries of the two lowest energy conformers for neutral, anionic and di-anionic structures. ΔE is the median values of BSSE corrected and uncorrected binding energies which are the lower and upper limits, respectively. The values after \pm are the half of the BSSE. Δx is the lateral displacement of center of mass of the two rings. Δz is the vertical displacement of the center of mass of the two rings. $R_{CM}-R_{CM}$ is the distance between the center of mass of the two rings. ΔE_b is the binding energy. ΔE_0 is the zero point vibrational energy corrected ΔE . $\Delta x; \Delta z$ shown in italic letters and $R_{CM}-R_{CM}$ given in bold letters.

| System | ΔE_0 (MP2/6-31+G*) (kcal/mol) | ΔE (MP2/aug-cc-pVDZ) (kcal/mol) | $\Delta x; \Delta z$ or $R_{CM}-R_{CM}$ (Å) (MP2/aug-cc-pVDZ) | ΔE_b (CCSD(T)/6-31+G*) (kcal/mol) |
|--------------------------------------|--|--|--|--|
| P-b P-c | 5.98±2.93 5.97±2.95 | 10.03±2.98 10.21±3.04 | <i>1.40;3.10</i> 1.25;3.15 | 6.70 6.74 |
| P-c ⁻ T-e ⁻ | 3.77±3.13 5.59±2.08 | 9.45±2.81 8.97±2.22 | <i>1.10;3.20</i> 1.00;4.55 | 6.22 7.85 |
| T-a ²⁻ T-e ²⁻ | 14.45±3.08 16.90±2.96 | 18.57±2.91 20.98±2.86 | 4.45 <i>1.25;4.35</i> | 16.45 18.50 |

shows a preference of **T-e⁻** (*T*-shaped geometry) over **P-c⁻** (parallel displaced geometry), while BSSE corrected binding energies at MP2/6-311++G** shows the preference of **P-c⁻** over **T-e⁻**, but the energy difference between the two conformers in both cases are in the order of ~ 1 kcal/mol only. As seen from Table II, at MP2/aug-cc-pVDZ, the preference of P-c⁻ or T-e⁻ depends on the extent of basis set correction, but the energy difference are in the range of 0.5 kcal/mol. Calculations at CCSD(T)/6-31+G**//MP2/aug-cc-pVDZ shows that the *T*-shaped geometry is almost 1.6 kcal/mol more stable than the parallel displaced geometry. These results indicate the importance of electron correlation in the calculation of weak molecular complexes where dispersive forces are very important in determining the geometry. The energy difference between anionic **P-b⁻** and **P-c⁻** is less than 0.1 kcal/mol. In **P-c⁻**, the rings of benzene and quinone are not fully parallel, but the benzene ring makes an angle ($\sim 7^\circ$) with respect to the PBQ ring. NBO calculations show that there is no significant charge transfer between PBQ and Bz moieties in the anionic **P-c⁻** (Table III).

In all PBQ-Bz²⁻ complexes, the calculations reveal that the parallel geometries tend towards CH $\cdots\pi$ conformers. Upon full optimization of the di-anionic geometries such as **P-b²⁻** or **P-c²⁻**, geometries converged automatically to **T-a²⁻** and **T-c²⁻**, respectively. The global minimum energy geometry obtained for the di-anionic complex is **T-e²⁻** and the frequency calculations at MP2/6-31+G* level confirmed that the geometry is a minimum. In **T-e²⁻** a strong C-H \cdots O type H-bonded interaction (C \cdots O=3.18 Å) exists in addition to the CH $\cdots\pi$ interaction between the electron cloud of PBQ and the H atom of Bz. **T-e²⁻** is lower in energy than **T-a²⁻** by 1.8 kcal/mol. Our calculations at different levels of theory and basis set suggest that for neutral PBQ-Bz complex, the parallel displaced geometries are highly favored over all other alternatives, and for dianionic PBQ-Bz complex *T*-shaped arrangements are strongly stabilized over all

other types of conformers. Therefore we expect the similar behavior at the complete basis set limit. Calculations on monoanionic PBQ-Bz indicate that improvement of basis set and extent of electron correlation in the calculations stabilize *T*-shaped form compared to parallel displaced form, therefore we are expecting that *T*-shaped form would be more stable than other alternatives by employing complete basis set limit for monoanionic PBQ-Bz clusters.

It would be interesting to note some of the geometrical properties of the PBQ-Bz clusters. The calculations show that the addition of an extra electron to the PBQ-Bz cluster decreases the distance between the rings. For **T-a**, **T-b**, etc., the reduction decreases the distance between the center of mass of the two rings. For **T-a**, the $R_{CM}-R_{CM}$ of the neutral state is 4.85 Å, while that in the di-anionic state is 4.50 Å. It can also be seen in Table II that the $R_{CM}-R_{CM}$ distance in C-H \cdots O type H-bonded clusters (H-A, etc.) got decreased by addition of an extra electron, which implies that the CH \cdots O type interaction between PBQ and Bz is strong in anionic complexes compared to neutral systems. In *T*-shaped clusters (for neutral, anionic, and dianionic **T-a** and **T-b**) the C-H bond length of benzene interacting with the π electron cloud of PBQ is calculated to be smaller (~ 1.082 Å) than the C-H bond lengths in free benzene molecule (1.089 at MP2/6-311++G**). The C-H stretching frequencies of these CH bonds are blueshifted with respect to that of the free molecule (e.g., C-H bond stretching frequencies of **T-a²⁻** are blueshifted by 60 cm⁻¹ at MP2/6-31+G*). Similar reports on blueshifted H-bonds were reported for some H-bonded complexes and also for benzene dimer.^{24,25}

Anionic C-H \cdots O type H-bonded complexes **L-a⁻**, **L-b⁻**, and **L-c⁻** show spin contamination at the MP2 level upon optimization, similar to which we have reported for the PBQ radical-water complex.²⁶ The C=O bond length of the carbonyl carbon atom of PBQ interacting with the benzene molecule is shortened by about ~ 0.2 Å in these complexes. Therefore, we have optimized these structures at the B3LYP

TABLE III. Relative energies of P-c and T-e. E is the binding energy, E_b is 100% BSSE corrected binding energy and $E_{b/2}$ is 50% BSSE corrected binding energy. The energies are reported in kcal/mol. On full optimization, P-c²⁻ automatically converged to T-c²⁻.

| Charge | MP2/aug-cc-pVDZ | | | MP2/6-311++G** | | |
|--------|------------------------|------------------------|------------------------------|------------------------|------------------------|------------------------------|
| | P-c($E E_b E_{b/2}$) | T-e($E E_b E_{b/2}$) | Δ ($E E_b E_{b/2}$) | P-c($E E_b E_{b/2}$) | T-e($E E_b E_{b/2}$) | Δ ($E E_b E_{b/2}$) |
| 0 | 13.25 7.17 10.21 | 6.09 2.19 4.14 | 7.16 4.98 6.07 | 11.98 5.16 8.57 | 5.19 1.5 3.4 | 6.79 3.66 5.08 |
| -1 | 12.26 6.64 9.45 | 11.20 6.75 8.97 | 1.10 -0.11 0.48 | 11.13 6.85 8.99 | 9.99 5.53 7.76 | 1.41 1.32 1.23 |
| -2 | 20.96 15.48 18.22 | 23.84 18.12 20.98 | -2.88 -2.64 -2.76 | 18.70 13.8 16.25 | 22.15 15.93 19.04 | -3.45 -2.13 -2.79 |

TABLE IV. NBO charge populations on benzene in PBQ-Bz dimer complexes (in a.u.). NBO charges computed at MP2/6-311++G**.

| P-b0.024 | P-c0.027 | T-a-0.004 | T-e-0.003 |
|-------------------------|-------------------------|--------------------------|--------------------------|
| P-b ⁻ -0.006 | P-c ⁻ -0.007 | T-a ⁻ -0.013 | T-e ⁻ -0.014 |
| | | T-a ²⁻ -0.036 | T-e ²⁻ -0.053 |

level, and single point MP2 calculations were performed using the same basis set on these optimized geometries. The spin contamination problem arises only in the case of **L-a⁻**, **L-b⁻**, and **L-c⁻**. This issue has been well discussed in our earlier paper about *p*-benzoquinone-water clusters.²⁶

Now it is interesting to investigate the application of these molecular interactions as nanomechanical devices. In the molecular flipper, 2,11-dithio(4,4) metameta quinocyclophane, the benzene and quinone moieties are almost in a staggered conformation in the neutral system (similar to **S-b**), while the double anionic system exists in *T*-shaped conformation, similar to **T-b**. The binding energies of PBQ and Bz in **S-b** and **T-b²⁻** are 7.7 and 14.6 kcal/mol (MP2/6-311++G**), respectively. The energy difference between the neutral and dianionic states of **S-b** and **T-b** are about 5.1 kcal/mol (in favor of **S-b**) and 5.2 kcal/mol (in favor of **T-b**), respectively. The present results are not far from the previous system. Present results indicate that the most favorable conformation for PBQ-Bz clusters are **P-c** and **T-e²⁻** in the neutral and dianionic systems, respectively. The binding energies of **P-c** and **T-e²⁻** at MP2/6-311++G** level are 8.6 and 19.0 kcal/mol, respectively. As seen in Tables I and II, for the **P-c** and **T-e**, the neutral state favor **P-c** by 6.8 kcal/mol, but the doubly charged anion state **T-e²⁻** is favored over **P-c²⁻** by 6.2 kcal/mol. This clearly shows that upon addition of electrons, the conformer changes from **P-c** to **T-e²⁻** and vice versa. Thus electrochemical conformation control is possible which is very useful for designing nanomechanical devices which is used as a precursor of molecular flipper. Therefore it is possible to synthesize a more efficient nanomechanical device, if the bridging molecules are properly designed.

The geometrical changes of PBQ-Bz clusters on reduction can be explained from the changes in the aromatic nature of the PBQ ring. For benzene, the electrostatic map shows that the outer plane of the benzene ring has a positive charge density, while the upper/lower part of the ring has negative charge density.²⁷ Neutral PBQ is nonaromatic and does not have a significant π electron density as in the case of benzene. Therefore, the *T*-shaped geometry with facial PBQ is not preferred. The possible interaction between PBQ and Bz is either the interaction between π electron cloud of Bz and the π electrons of PBQ (in a parallel displaced manner) or interaction through CH \cdots O weak hydrogen bonding between the benzene hydrogen with that of PBQ oxygen atom. Calculations reveal that benzene prefers to interact with PBQ in a parallel displaced conformer. The increase in the negative charge density centered on the PBQ plane by reduction is reflected in the energy difference between parallel displaced and CH \cdots π type conformers (**P-c⁻** and **T-e⁻**) of the complex. PBQ²⁻-Bz prefers to have a CH \cdots π con-

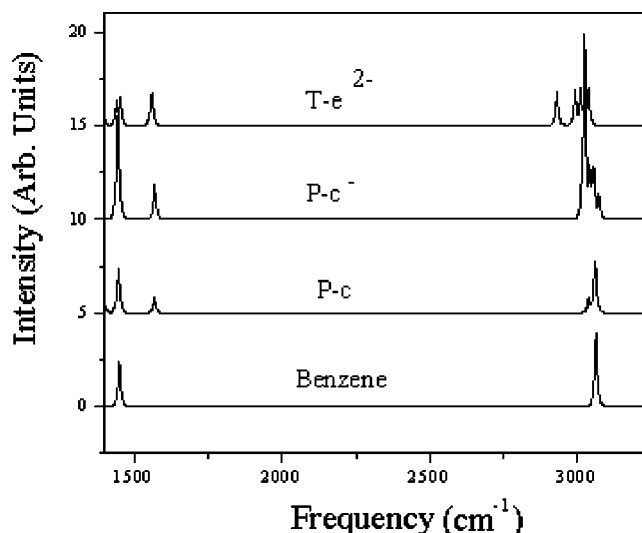


FIG. 3. Vibrational spectra of benzene moiety in stable PBQ-Bz clusters.

former, which resulted from the interaction of the positive charge density of the C-H bond of benzene with the π electron density of quinone (PBQ²⁻) ring. As in the case of PBQ-Bz system, in PSRC, there can be a change in geometrical preference between the DQ_AQ_B (dark structure) and the charge separated D⁺Q_AQ_B⁻, which may finally result in the 180° twist. Recent calculations showed that neutral quinones and indole molecule prefer a π -stacked arrangement, while semiquinone radical anions prefer a *T*-shaped conformation with significant N-H π hydrogen bonding interaction.²⁸

On examining calculated IR frequency shifts of benzene moiety in the cluster, fingerprints of complexation can be identified (Fig. 3, frequencies are scaled by 0.95). The splitting of C-H in-plane bending modes of benzene in the clusters correspond to the symmetry breaking of the benzene molecule due to complexation. Similarly CH stretching modes of benzene also become nonequivalent in the cluster. NBO calculations show that even in **T-e²⁻** the charge transfer between PBQ and Bz ring (Table IV) in the cluster is very small (~ 0.05 a.u.).

IV. CONCLUDING REMARKS

We have performed *ab initio* molecular orbital calculations at MP2 and CCSD(T) level of theory to study the geometries and binding energies of different charged states of *p*-benzoquinone-benzene clusters which could be realized as molecular machines. From our results, it can be concluded that the most efficient PBQ-Bz cluster based molecular machine is the one in which the benzene and *p*-benzoquinone moieties interact in a parallel displaced fashion (similar to **P-c**) in neutral state and edge-to-face manner (**T-e²⁻**) in dianionic state. In the neutral PBQ-Bz cluster, the parallel displaced geometry (**P-c**), which is preferred over all other alternative arrangements, is about 6.8 kcal/mol more stable than **T-e** at MP2/6-311++G** level. The edge-to-face conformer **T-e²⁻** is calculated to be the most stable dianionic conformer and is about 6.2 kcal/mol lower in energy than **P-c²⁻**. For monoanionic systems, the conformers **P-c⁻** and

$T-e^-$ are competitive, while $T-e^-$ is slightly better favored by ~ 2 kcal/mol at the MP2 (ZPE corrected) and CCSD(T) levels. Nonbonded interactions involving aromatic rings are also pivotal to protein-ligand recognition and helpful in drug design, and *p*-benzoquinone and benzene play a central role in many biochemical reactions. Therefore, the present results would be of great use in probing the mechanisms of many biologically important processes.

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