Revisiting symmetry breaking in BNB: The key role of electronic correlation

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ABSTRACT

Spontaneous symmetry breaking in the ground state of the BNB molecule is revisited by employing a series of high-level multireference methods based on updated SA-CASSCF wavefunctions with larger active space. It supports our previous determination of two equivalent linear-noncentrosymmetric equilibrium configurations. The calculated magnitude of the barrier between them increases with the level of electronic correlation taken into account. The inadequate centrosymmetric structure obtained by MRCI calculations is caused by insufficient account of electronic correlation. The origin of the off-center distortion in BNB, as in many other systems, is due to the Pseudo Jahn–Teller effect.

1. Introduction

Off-center displacements of central atoms in polyatomic systems are known as a well-studied and experimentally confirmed phenomenon (see, e.g. in [1,2]). The problem of the noncentrosymmetric equilibrium configuration of the linear BNB molecule, as a representative of a whole class of molecular systems and solids with possible off-center position of central atom, is of general importance because it relates to the fundamental understanding of the origin of chemical bonding and its influence on the shapes of polyatomic systems. Theoretical exploration of spontaneous symmetry breaking in the $X^2\Sigma_u^+$ ground state of the BNB molecule has a long history beginning with the first Hartree–Fock study by Martin et al. in 1989 [3], to the latest Kalemos’ arguments in 2013 [4] and following comment by Stanton [5]. Various theoretical investigations produced conflicting results: in some of them, the BNB configuration emerges as linear noncentrosymmetric [6–10]; whereas other papers concluded that its structure is linear centrosymmetric [4,11–13].

In our previous study [8], we performed high-level multireference calculations and found that the linear configuration of the BNB molecule is noncentrosymmetric, and explained the origin of its polar instability by the well-known Pseudo Jahn–Teller effect (PJTE) [1,2]. This result was challenged recently by AK [4] stating that the noncentrosymmetric equilibrium configuration obtained by us and other authors is an artifact that occurs due to the lack of correct permutational symmetry in the wavefunctions. The AK paper characterized the previous conclusions of noncentrosymmetric configuration of BNB as ‘a pseudo problem in molecular physics’, indirectly equated the PJTE to configuration interaction (CI), and concluded that the correct ground state configuration of BNB is centrosymmetric with $D_{\infty h}$ symmetry. This conclusion of AK paper casts a shadow on the phenomenon of off-center equilibrium configuration in polyatomic systems; by stating that the conclusion of noncentrosymmetric configuration of BNB is an artifact, it indirectly suggests that the other conclusions of off-center distortions may be artifacts. In order to further clarify this issue, we extend the calculations to higher level and show that the BNB molecule is noncentrosymmetric in the minima of the APES. We show also that the opposite conclusion is most probably based on the calculations with insufficient electronic correlation. We give also some additional description of PJTE origin of the off-center distortions and its relation to configuration interaction.

2. Computational details

Compared with our previous calculations for BNB [8], the updated state averaged complete active space self-consistent field (SA-CASSCF) [14] wavefunctions were constructed by averaging all symmetry related symmetry-breaking structures and including a larger active space of all 11 valence electrons in 13 orbitals of $(2s+2p)b \times 2 + (2s+2p+s')N$. The SA-CASSCF/(11e⁻/13orb)

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http://dx.doi.org/10.1016/j.cplett.2014.04.027
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method of averaging two $^2A_1$ and two high-lying $^{12}A_1$ electronic states in $C_{2v}$ symmetry (which are $X^3\Sigma_u^+,$ $2\Sigma_g^+,$ $12\Sigma_g^+,$ and $2\Sigma_u^+$ in $D_{sh}$ symmetry) is denoted as 4R-SACASSCF. Following AK paper, the way of including two $^{12}A_1$ states is used to ensure that the $2S^0$ electrons will be in different orbitals along the $\sigma$ frame of the molecule, and this reference orbitals effectively takes into account their permutational symmetry. Using 4R-SACASSCF as the reference orbitals, the one and two states is used to ensure that the $2S^0$ symmetry) is denoted as 4R-SACASSCF. Following AK paper, the minima increases geometry vary from 2.6595 to 2.6602 Å which $= 1.3310 \text{ Å}$ is exactly the same and asymmetric $2$ $^1A_1$ symmetry (which are $C_{u}$ structures of BNB are also calculated at the MRCI+Q and MR-AQCC levels. The cc-pVTZ [18] basis set and the MOLPRO 2010.1 [19] program are used for all the electronic structure calculations.

3. Results and discussion

3.1. Computational refinement

Based on the updated SA-CASSCF/(11e−/13orb) reference orbitals, the 2R-MRCI total energy of the ground state ($\Delta E = R_{\text{BN}-\text{B1}} - R_{\text{BN}-\text{B2}}$) and constraining the B1–B2 bond distance at 2.6620 Å taken from the MRCI optimized $D_{sh}$ geometry with two equal B–N bond lengths at 1.3310 Å. The fully optimized symmetric $D_{sh}$ and asymmetric $C_{uv}$ structures of BNB are also calculated at the MRCI+Q and MR-AQCC levels.

The results above indicate that the electronic correlation plays a very important role in predicting the geometrical structure of BNB. Additionally, we note that the estimated barrier of 29 cm$^{-1}$ in with the 2R-MRCI+Q method is very close to our previously obtained value of about 20 cm$^{-1}$ [8]. Thus the present results support the previous determination of two equivalent linear-noncentrosymmetric equilibrium configurations of BNB in the ground state obtained by us and other authors [6–10].

3.2. Physical reason behind: PJTE vs. CI

With computationally predicted noncentrosymmetric equilibrium configuration of BNB, it is important to reveal the physical (chemical) origin of the symmetry breaking phenomenon in this case involving the PJTE. At first sight, without detailed analysis, it looks somewhat strange that in the optimized geometry of BNB the nitrogen atom may prefer a shorter distance to one (anyone) of the B atoms than to the other one. But if we take into account the PJTE, the explanation is straightforward: the two optimized B–N distances are controlled by the stronger $\sigma$ bonding that may

Figure 1. Calculated APES cross sections along the asymmetric stretching (linear polar) distortion of B1–N–B2 in the ground state with 4R-SACASSCF, 1R-MRCI, 2R-MRCI, 1R-MRAQCC, 1R-MRCI+Q, 2R-MRAQCC, and 2R-MRCI+Q methods as a function of the difference in the B–N bond lengths ($\Delta r = R_{\text{BN}-\text{B1}} - R_{\text{BN}-\text{B2}}$) in cm$^{-1}$. The total energies ($\Delta E$) at $\Delta r = 0.00$ Å are shifted to the zero point ($\Delta r = 0.00$ Å, and $R_{\text{BN}-\text{B1}} = R_{\text{BN}-\text{B2}} = 1.3310$ Å, the total energies are: -103.873002 (4R-SACASSCF), -104.087428 (1R-MRCI), -104.087950 (2R-MRCI), -104.104774 (1R-MRCI+Q), -104.105568 a.u. (2R-MRAQCC), and -104.105568 a.u. (2R-MRCI+Q)).

Table 1. The bond distances in Å at fully optimized linear centrosymmetric ($D_{sh}$) and noncentrosymmetric ($C_{uv}$) configurations and the energy barriers $\Delta E$ ($E(C_{uv}) - E(D_{sh})$) in cm$^{-1}$.

<table>
<thead>
<tr>
<th>Method</th>
<th>$R(D_{sh})$</th>
<th>$R_{\text{BN}-\text{B1}}$</th>
<th>$R_{\text{BN}-\text{B2}}$</th>
<th>$\Delta E$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1R-MRAQCC</td>
<td>1.3295</td>
<td>1.3169</td>
<td>1.3426</td>
<td>0.54</td>
</tr>
<tr>
<td>1R-MRCI+Q</td>
<td>1.3289</td>
<td>1.3067</td>
<td>1.3532</td>
<td>6.93</td>
</tr>
<tr>
<td>2R-MRAQCC</td>
<td>1.3292</td>
<td>1.3051</td>
<td>1.3551</td>
<td>12.78</td>
</tr>
<tr>
<td>2R-MRCI+Q</td>
<td>1.3286</td>
<td>1.2991</td>
<td>1.3606</td>
<td>29.19</td>
</tr>
</tbody>
</table>
leave the weaker π overlap not fully optimized (in the sense that at shorter distances they would get a better overlap). Under this condition, a better π overlap with one of the B atoms, adding to the covalence bonding, may compete with the deteriorating σ bonding producing an APES with two minima and a barrier between them, or just a flat (or low-frequency) minimum. If the barrier between the minima is small, it may be difficult to reveal it and estimate its exact value in numerical calculations with existing computer programs.

As shown in our previous study [8], in the case of BNB, the PJTE can be presented in a two-level problem of the (\(2\Sigma_u^+ + 2\Sigma_g^-\)) \(\otimes\) \(\sigma_u^+\) type, in which the two electronic states of opposite parity \(2\Sigma_u^+\) and \(2\Sigma_g^-\) are mixed by the asymmetric B–N stretching distortion Q of \(\sigma_u^+\) symmetry. Figure 2 shows the adiabatic potential energy profiles of the two coupled electronic states along the nuclear displacements Q in the case of respective weak and strong PJTE (the dashed lines show the terms without vibronic coupling). In the case of weak PJTE, the ground state is softened and remains stable, whereas for the strong PJTE, as in BNB, the ground state is unstable, thereby producing the double minimum well on the ground APES. It is seen that the interaction of the two states (of opposite parity in the high-symmetry configuration) under odd nuclear displacements makes the curvature of ground state decrease and the one of excited state increase, thereby producing the double minimum well on the ground APES when the effect is strong enough and the condition of instability is obeyed. The two states \(2\Sigma_u^+\) and \(2\Sigma_g^-\) which are orthogonal in the high-symmetry configuration (at Q = 0), under the Q displacements become, respectively, \(2\Sigma\) and \(2\Sigma\) states, in which the atomic function’s overlap (that produces the additional covalency) is implemented.

In the AK paper, as in some other publications in the literature, it is tacitly assumed (and vaguely noted) that CI takes into account the influence of the excited states and hence equates to the PJTE. The essential difference between the PJTE and CI is seen directly from their definitions. Both effects are based on admixing excited states to the ground one; the misunderstanding comes from the confusion of the kind of operator that produces the admixing and the kind of excited states that are admixed by that operator. In CI it is the Coulomb interactions (at fixed nuclei) that mix electronic states of the same symmetry, whereas in the PJTE it is the vibronic coupling operator which is a function of the nuclear displacements (in the expansion of the Hamiltonian) which mixes electronic states of different symmetry, thus partially involving non-adiabatic couplings.

4. Conclusions

In accordance with our and other author’s previous results, the present higher-level multireference electronic structure calculations based on updated SA-CASSCF(11e–13orbs) reference wavefunctions show that, contrary to a recent conclusion, the BNB molecule is linear noncentrosymmetric in its equilibrium configuration. The tendency of forming noncentrosymmetric \(C_m\) minima of the APES and the energy barrier between them increase with increasing levels of electronic correlation taken into account in the methods of calculations from SA-CASSCF, MRCI, to MRAQCC or MRCl+Q. The physical reason of the symmetry breaking in this system, as in many others, is the PJTE.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (Grant No. 21203041), the open project of State Key Laboratory of Urban Water Resource and Environment, Harbin Institute of Technology (No. H201213), and Fundamental Research Funds for Central Universities of China.

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