Structure and Bonding of the Polytopic Molecule Li[BO]. A Theoretical Investigation

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The potential energy surface of the reaction Li(2S/2P) + BO(X2Σ+) was investigated theoretically using multireference variational methods in conjunction with flexible correlation consistent basis sets. On the ground-state singlet surface (X 1A′), three practically degenerate minima were detected, two linear Li–BO and Li–OB (X2Σ+) and one bent Li–OB (X1A′), the latter formally being the global one. An energy barrier of about 10 kcal/mol was found to separate the two linear configurations. Potential energy curves of excited singlet and triplet linear states were also examined. The involvement of the ionic interacting fragments Li+(1S) + BO−(X1Σ+) seems to affect all states via avoided crossings, giving rise to highly ionic equilibrium states, particularly in the Li–OB isomer. As a result, the Li atom rotates freely around the O-site of BO moiety within a LiOB angle from 100° to 180°.

1. Introduction

The BO molecule (X2Σ+) is known to interact with a variety of radicals,1 forming molecular systems which have been characterized as polytopic, meaning that they feature multiple, energetically close, isomers.2 In our recent study of the cation ScBO+, three minima have been detected on the ground-state potential energy surface (PES), two linear Sc–BO+ and Sc–OB+ (X2Δ) and one bent Sc–OB+ (X2A′), the last being the global one. An analogous situation seems to hold for the Li[BO] system which exhibits also three minima on its ground PES, two linear and one bent.2,3

The literature on the Li[BO] system is very limited. First, Nemukhin et al.2 and later Nemukhin and Stepanov,4 using SCF, CASSCF/DZ+P, and CASSCF + limited CISD/DZ+P methods, respectively, concluded that the Li[BO] molecule shows polytopic behavior and that the linear Li–BO isomer is more stable than the (linear) Li–OB by about 4 kcal/mol.4 Recently, Fuentealba,5 using G2MP2 and B3LYP/6-311G** methods, came to the conclusion that all three isomers, the two linear (Li–BO and Li–OB) and one bent Li–OB, are essentially isoenergetic within the accuracy of his calculations. Finally, the experimental investigation of the reaction Li(g) + BO(g) → Li[BO](g) by Knudsen effusion mass spectrometry5 seems to favor the linear Li–OB more than the linear Li–BO by 4 ± 1 kcal/mol.

In an effort to clarify the Li + BO interaction and, perhaps, to give a definitive answer on the details of the Li[BO] PES and bonding mechanisms, we have performed large-scale variational multireference calculations, coupled with quantitative correlation-consistent basis sets. In particular, we have examined the singlet and triplet potential energy surfaces of the reaction Li(2S/2P) + BO(X2Σ+) and the role of the ionic interaction Li+(1S) + BO−(X1Σ+).

2. Methods

For the Li, B, and O atoms, the correlation-consistent quadruple-ζ quality basis sets of Dunning6a were employed but with the functions of g angular momentum removed, cc-pVQZ-g. To obtain a reasonable description of the BO− anion (vide infra), we augmented the B and O atomic sets by a complete set of diffuse functions, resulting to the aug-cc-pVQZ-g basis set.6b Our final, generally contracted one-electron space, [(6s5p4d3f) B,O /(5s4p3d2f) Li ], numbers 170 spherical Gaussian functions.

In a complete (valence) active space SCF (CASSCF) description, the 10 active electrons (1(Li) + 3(B) + 6(O)) should be allowed to occupy a 12-orbital space, CASSCF(10/12). Such an allotment produces under C1 symmetry restrictions about 85 000 (singlets) or 142 000 (triplets) configuration functions (CF), rendering subsequent configuration interaction (CI) calculations out of this space impractical. Instead, a CASSCF wave function was constructed by distributing two electrons only, the 2s on Li and 5σ on BO (X2Σ+, 1σ2σ2σ3σ22σ5σ1π2,π2), among five orbitals, the four (valence) Li orbitals + the singly occupied 5σ MO of BO. This CASSCF scheme gives rise to a 11A′, 4A″ singlet or 6A′, and 4A″ triplet configurational space, ensuring correct asymptotic description (size consistency), i.e., Li(2S/2P) + BO(X2Σ+) or Li+(1S) + BO−(X1Σ+) fragments. All our CASSCF calculations were state averaged7 over the 4A′+1A″ states, corresponding to one Π and three Σ+ states of the linear geometries. Valence “dynamical” correlation was obtained by single and double excitations of the 10 valence electrons of this space (CASSCF+1+2 = MRCI), keeping the core ~1s2(Li/B/O) electrons always doubly occupied and applying at the same time the internal contraction approach,8 referred to as MRCI(2/5).

All equilibrium structures thus obtained were recalculated employing MRCI calculations out of the “large” 10/12 (CASSCF-(10/12)) multireference space, but truncated according to the criterion \( \sum C_i^2 = 0.999 \), where \( \{C_i\} \) are variational CASSCF coefficients. This reduces the number of CASSCF(10/12) CFs to about 1000, accompanied by CASSCF energy losses of less than 2 mhartrees as compared to the complete CASSCF(10/12) calculations. The corresponding MRCI “2/5” and “10/12” (truncated CASSCF(10/12)) expansions contain about 1.25 \( \times 10^5 \) and 105 \( \times 10^6 \) CFs for the singlets and 2.9 \( \times 10^5 \) and 432 \( \times 10^6 \) CFs for the corresponding triplets, respectively. These

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spaces are further reduced to 0.25 Å.

Figure 1. Minimum MRCI(2/5) energy profile of the rearrangement Li–BO(X^2Σ^+) → bent Li–OB(X^1A’) → Li–OB(X^2Σ^+); bond lengths are in Å.

Table 1: Total Energies E (hartree), Bond Distances r_e (Å), Dissociation Energies D_e (kcal/mol), Mulliken Charges q_0, Dipole Moments µ (Debye), and Adiabatic Electron Affinities EA (eV) of the X^2Σ^+ State of BO in Different Methods

<table>
<thead>
<tr>
<th>Method</th>
<th>E</th>
<th>r_e</th>
<th>D_e</th>
<th>q_0</th>
<th>µ</th>
<th>EA^a</th>
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<tr>
<td>CISD</td>
<td>99.85903</td>
<td>1.196</td>
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<td>2.47</td>
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<td>-</td>
<td>-</td>
<td>-2.42</td>
<td></td>
</tr>
<tr>
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<td>1.211</td>
<td>191.0</td>
<td>-0.37</td>
<td>2.29</td>
<td>2.16^d</td>
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<tr>
<td>MRCI(9/8)+Q^e</td>
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<td>190.0</td>
<td>-</td>
<td>-</td>
<td>-2.35</td>
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<tr>
<td>t-MRCI(9/8)^f</td>
<td>99.88211</td>
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<td>2.31</td>
<td>2.17</td>
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<tr>
<td>CCSD(T)^g</td>
<td>99.91213</td>
<td>1.2079</td>
<td>193.4</td>
<td>-</td>
<td>2.50</td>
<td></td>
</tr>
<tr>
<td>expt</td>
<td>-</td>
<td>1.2049^h</td>
<td>193.6^h</td>
<td>-</td>
<td>-2.508 ± 0.008^h</td>
<td></td>
</tr>
</tbody>
</table>

^a EA(X) = E(X) – E(X^-). ^b CISD+Davidson correction. ^c Internally contracted MRCI out of 9e-7/8 orbital CASSCF reference. ^d Obtained from a MRCI(10/8) BO^- calculation; at this level, r_e(B^-:X^2Σ^-) = 1.244 Å. ^e MRCI+multireference Davidson correction, ref 14. ^f Truncated MRCI, see text. ^g Ref 13; doubly aug-cc-pV6Z basis; r_e(B^-:X^2Σ^-) = 1.240 Å. ^h Ref 15. ^i Ref 16; D_e = D_0^e+ω^e/2. ^j Ref 12.

The Polytopic Molecule Li[BO]

3. The Li and BO Fragments

The SCF energy of the ground 3S of Li, E = -7.43270Eh, is in practical agreement with the Hartree-Fock value of -7.432727Eh.10 Also, the calculated 3P → 3S excitation and ionization (Li → Li^+ + e^-) energies, 1.841 and 5.342 eV, are in harmony with the experimental values,11 1.848 and 5.390 eV, respectively.

Concerning now the BO(X^2Σ^+) radical, related structural properties at the CI and MRCI levels are listed in Table 1. The agreement with experimental values can be considered as fair; the discrepancy in the D_e at the CISD level is expected and is due, primarily, to the size nonextensivity of the CISD method. Note that results obtained with the (truncated) t-MRCI(7/6) technique compare well with the (complete) MRCI(9/8) values. Our computed (adiabatic) electron affinities (EA) of BO(X^2Σ^+) are in acceptable agreement with the most recent experimental value of 2.508 ± 0.008 eV.12 The best theoretical EA(BO) value so far is that of Papakondylis and Mavridis,13 who obtained EA(BO) = 2.50 eV at the CCSD(T)/doubly aug-cc-pV6Z level of theory. We believe that the overall description of the BO and BO^- entities is adequate, since the purpose of the present study is not the accurate characterization of these species but their interaction with the Li atom.

4. Results and Discussion

We can envisage the Li atom approaching the BO(X^2Σ^+) moiety from either end in a linear fashion, or laterally resulting to singlets or triplets.

4.1 Singlets. Figure 1 presents a minimum-energy profile of the isomerization process

Li–BO(X^1Σ^+) → bent Li–OB(X^1A’) → Li–OB(X^2Σ^+)

at the MRCI(2/5) level of theory. The curve was constructed by optimizing all bond distances involved for every selected angle value θ (= LiOB). Linear geometries Li–BO and Li–OB correspond to θ = 0° and 180°, respectively. As can be seen, three minima were found, two linear and one bent, the latter formally being the global one. As Table 2 shows, the energy difference ∆E[MRCI(2/5)] = E[Li–OB] – E[Li–OB] is -0.6 kcal/mol, or ∆E[t-MRCI(10/12)/MRCI(2/5)] = +0.5 kcal/mol, so the two linear isomers are degenerate within the accuracy of our methods. On the other hand, the bent X^1A’ state is 0.5–1.0 kcal/mol lower in energy than the linear isomers (Table 2). Therefore, we are dealing with a genuine polytopic system and a very floppy (bent) Li–OB(X^1A’) isomer with respect to the linear Li–OB X^1Σ^+ state with an insignificant barrier between them. For the rearrangement Li–OB → Li–BO an energy barrier of 10.5 kcal/mol is obtained (Figure 1), as compared to an experimental thermochemical value of about 19 kcal/mol.13

Figures 2 and 3 present potential energy curves (PEC) of singlets (and triplets) of the interaction BO + Li in a linear fashion at the MRCI(2/5) level of theory. All curves were constructed by keeping the geometrical parameters fixed at their equilibrium values but the relative Li–BO or Li–OB distance.

Li–BO. Figure 2 depicts the approach of the Li atom to the B-site of the BO moiety. Using valence bond-Lewis (vBL)
TABLE 2: Total Energies $E$ (hartree), Bond Distances $r_e$ (Å) and Angles $\theta$ (LiOB) (deg), Dissociation Energies $D_e$ (kcal/mol), Dipole Moments $\mu$ (Debye), and Mulliken Charges $q$ of the Linear Li$^+$BO, Li$-$BO, and Bent Li$-$BO Isomers at the MRCI (2/5) and t-MRCI(10/12)$^a$ Level of Theory

<table>
<thead>
<tr>
<th>state</th>
<th>method</th>
<th>$-E$</th>
<th>$r_e$(B–O)</th>
<th>$r_e$(B–Li)</th>
<th>$r_e$(O–Li)</th>
<th>$\theta$</th>
<th>$D_e$</th>
<th>$D_e$+Q$^{ex}$</th>
<th>$\mu$</th>
<th>$q_a$</th>
<th>$q_b$</th>
<th>$q_o$</th>
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<tbody>
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<td>linear Li$-$BO</td>
<td>$\Sigma^+$</td>
<td>(2/5)</td>
<td>107.40171</td>
<td>1.209</td>
<td>2.124</td>
<td>–</td>
<td>0.0</td>
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<tr>
<td>1$^\Sigma^+$</td>
<td>(2/5)</td>
<td>107.27178</td>
<td>1.205</td>
<td>4.133</td>
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<tr>
<td>bent Li$-$OB</td>
<td>$\Lambda^+$</td>
<td>(2/5)</td>
<td>107.40330</td>
<td>1.247</td>
<td>–</td>
<td>1.717</td>
<td>108.4</td>
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<td>77.6</td>
<td>7.54</td>
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<td>1.247</td>
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<td>0.41</td>
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<td>1.806</td>
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<td>5.73</td>
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<td>1.69</td>
<td>0.24</td>
<td>0.57</td>
<td>0.81</td>
</tr>
</tbody>
</table>

"MRCI out of CASSCF(2/5) or truncated CASSCF(10/12), see text. "Dissociation energies with respect to the asymptotic products. "D$_e$+Davidson correction.

The three $^2\Sigma^+$ states, $^2\Sigma^+$, $^1\Sigma^+$, and $^2\Pi^+$ (Figure 2), stem from the mixing of schemes (I), (II) and (IV), i.e., $|\Sigma^+\rangle \approx C_1|\Sigma^+\rangle + C_2|\Pi^+\rangle + C_4|\Pi^0\rangle$, where $C_1$, $C_2$, and $C_4$ are variational coefficients. For instance, for the $^2\Sigma^+$ state the CASSCF(2/5) vector $\langle C_1$, $C_2$, $C_4 \rangle$ at distances 10.0, 4.5, and 2.12 (≈equilibrium A), are (0.91, 0.42, 0.00), (0.61, 0.68, –0.40), and (0.07, 0.31, –0.95), respectively. These numbers imply that the $^2\Sigma^+$ PEC suffers an avoided crossing around 5 Å with the $^1\Sigma^+$ state correlating to Li$^+$BO (0) + BO($^2\Sigma^+$), which has already experienced an avoided crossing at about 9 Å with the $^2\Sigma^+$ state correlating to Li$^+$+ BO$^+$ fragments. From Table 2, we read that the Li$^+$BO($^2\Sigma^+$) $D_e$(Li$^+$BO) = 73.5 kcal/mol at the t-MRCI(10/12)/MRCI(2/5) level, with an estimated Davidson corrected value of 80 kcal/mol with respect to the ground-state fragments. These values are in agreement with the results of Fuentealba.$^5$

Around equilibrium (4 Å) the (C$_1$, C$_2$, C$_4$) coefficients for the $^1\Sigma^+$ state are (–0.11, 0.79, 0.61), corroborating our previous analysis. Its binding energy with respect to Li$^+$BO is $D_e$ (Li$^+$BO) = 30 kcal/mol at the t-MRCI(10/12)/MRCI(2/5) level (Table 2).

The $^2\Sigma^+$ state correlates adiabatically to the ionic fragments Li$^+$(S) + BO($^2\Sigma^+$), with a very flat minimum of “Coulombic” character around 8 Å due to the avoided crossing with the $^1\Sigma^+$ state, as previously discussed. An approximate $D_e$(Li$^+$BO) value of 30 kcal/mol is obtained at the MRCI(2/5) level.

The $^1\Pi$ (...$4\sigma^2$5$p^5$6$s^3$1$\pi^2$, 1$\pi^2$, 2$\pi^1$) Li$^+$BO state correlating to Li$^+$BO (±1) + BO($^2\Sigma^+$) (scheme III), is practically repulsive.

Li$^+$BO. We discuss now the singlets due to the linear Li approach from the O-site of the BO molecule; Figure 3 shows corresponding PECs. One would expect that such an approach
would lead to a repulsive Pauli interaction. On the contrary, an interactive attraction is observed leading to the strongly bound \( X' ^{2} \Sigma^+ \) state of the Li–OB “isomer”, Table 2. The reason is, obviously, the avoided crossing around 3.5 Å with the \( 1^{1} \Sigma^+ \) state correlating to Li(\( ^2S;M = 0 \)) + BO(\( ^3X' \Sigma^+) \). However, the \( 1^{1} \Sigma^+ \) state has already suffered an avoided crossing at 8 Å, with the \( 2^{1} \Sigma^+ \) state correlating to the ionic fragments Li(\( ^2P;M = 1 \)) + BO(\( ^1X' \Sigma^+) \). As a result, the \( X' ^{2} \Sigma^+ \) Li–OB linear state shows an intenseionic character as is also revealed by the population analysis at the t-MRCI(10/12)/MRCI(2/5) level, Table 2. This ionic character is responsible for the extreme floppiness of the Li–OB system mentioned previously (Figure 1).

The Li–OB binding energy is \( D_e = 73 \) (82) kcal/mol at the t-MRCI(10/12)/MRCI(2/5) (+Q) level of theory, accidentally isoenergetic with the Li–BO(\( ^3X' \Sigma^+) \) isomer.

It is of interest at this point to mention the important difference between the Li[BO] and H[BO] isovalent systems. The latter has two nonisoenergetic isomers, one linear H–BO (\( X' ^{2} \Sigma^+ \)) and one strongly bent H–OB (\( \tilde{A} ^{1} \Pi \); \( \theta = 121^\circ \)), the linear being more stable by 45 kcal/mol. In the H[BO] case, the linear \( \sigma \)-type bonding is fully explained by scheme I. However, in the bent H–OB molecule, the bending entails the first excited \( \tilde{A} ^{1} \Pi \) state of BO, as indicated succintly by the following valence bond Lewis diagrams (see also ref 1):

In the Li–OB case, there is competition between the Li(\( ^2S;M = \pm 1 \)) + BO(\( ^3X' \Sigma^+) \) reactants, almost isoenergetically located on the energy surface: BO(\( ^3X' \Sigma^+) \rightarrow \tilde{A} ^{1} \Pi \) = 2.96 eV.16 IP(Li)11 = EA(BO)11 = 5.39 – 2.50 = 2.89 eV. The ionic interaction takes over resulting finally to the \( X' ^{2} \Sigma^+ \) Li–OB state already discussed.

The \( 1^{1} \Sigma^+ \) state presents a minimum at \( r_e(\text{Li–OB}) = 1.926 \) Å, with \( D_e(\text{Li–OB}) = 49.4 \) kcal/mol with respect to Li(\( ^2P;M = 0 \)) + BO(\( ^3X' \Sigma^+) \), or 6.9 kcal/mol with respect to the ground state products (Table 2). It is interesting that the in situ Li atom is slightly negatively charged (0.11 \( e^- \)) due to electron promotion to the \( 2p_\pi \) Li orbital.

The \( ^1 \Pi \) state correlates to Li(\( ^2P;M = \pm 1 \)) + BO(\( ^3X' \Sigma^+) \), with \( r_e(\text{Li–OB}) = 1.643 \) Å and \( D_e(\text{Li–OB}) = 17.1 \) kcal/mol at the t-MRCI(10/12)/MRCI(2/5) level. The bonding and the in situ negatively charged Li atom (0.18 \( e^- \)) can be rationalized by the vbL scheme V:

\[
\text{Li}(^2P; M = \pm 1) + \text{BO}(^3X' \Sigma^+) \rightarrow \text{Li}[\text{BO}] (\text{V})
\]

The \( 2^{1} \Sigma^+ \) state correlates adiabatically to Li(\( ^2S;M = \pm 1 \)) + BO(\( ^3X' \Sigma^+) \), but due to an avoided crossing with the \( 1^{1} \Sigma^+ \) state around 8 Å, it correlates diabatically to Li(\( ^2P;M = 0 \)) + BO(\( ^3X' \Sigma^+) \). The observed minimum at \( r_e(\text{Li–OB}) = 1.834 \) Å with \( D_e(\text{Li–OB}) = 28 \) kcal/mol is caused instead by an avoided crossing due to an incoming (not calculated) higher \( 1^{1} \Sigma^+ \) state.

4.2. Tripletts. We now examine the Li–BO and Li–OB linear triplets of \( ^3 \Sigma^+ \) and \( ^3 \Pi \) symmetries (Figures 2 and 3, respectively).

Li–OB. The \( 1^{3} \Sigma^+ / 2^{3} \Sigma^+ \) states correlate to Li(\( ^2S/^2P;M = 0 \)) + BO(\( ^3X' \Sigma^+) \) and are purely repulsive as expected referring to schemes I and II but with the two open electrons coupled into a triplet. The \( ^3 \Pi \) state corresponds to scheme III and is characterized by a slight \( \sigma \)-interaction and a strong electron transfer from the Li \( p_\pi \) orbital to the \( \pi \)-system of BO, giving rise to \( D_e(\text{Li–OB}) = 17 \) kcal/mol at \( r_e(\text{Li–OB}) = 2.215 \) Å (Table 2).

Li–OB. The \( 1^{3} \Sigma^+ / 2^{3} \Sigma^+ \) states trace their lineage to Li(\( ^2S/^2P;M = 0 \)) + BO(\( ^3X' \Sigma^+) \). Both show shallow minima with \( D_e(\text{Li–OB}) = 8.7 \) and 6.0 kcal/mol at \( r_e(\text{Li–OB}) = 1.923 \) and 1.807 Å, respectively. In the \( 1^{3} \Sigma^+ \) state, the bonding is caused by a charge transfer to a 2p orbital of Li, thus rendering the Li atom slightly negative (0.15 \( e^- \)). For the \( 2^{3} \Sigma^+ \) state, the minimum is, perhaps, due to an avoided crossing with a higher \( ^3 \Sigma^+ \) state, the situation being analogous to the \( 2^{1} \Sigma^+ \) Li–OB state (vide supra).

The potential energy curve of the \( ^3 \Pi \) state at infinity is described by the wave function [Li, \( ^2P; M = \pm 1 \) \( \otimes \) BO, \( ^3X' \Sigma^+) \) (scheme V). The \( ^3 \Pi \) curve follows closely the \( ^3 \Pi \) PEC up to 2 Å; at this point, it seems to experience an avoided crossing with a higher \( ^3 \Pi \) state of strong ionic character, as the Mulliken charges indicate (Li(\( ^{+0.65} \) at equilibrium). This higher \( ^3 \Pi \) state could stem from a \( ^3 \Pi \) BO \(^+\) state stabilized in the Coulomb field of Li(\( ^1S \)).19

Finally, the \( ^3 \tilde{A}' \) Li–OB bent state (Table 2) with \( \angle \text{Li–OB} = 101.2^\circ \) and \( r_e(\text{Li–OB}) = 1.806 \) Å results through a partial electron transfer from Li(\( ^2S \)) to the \( \pi \)-system of BO.

5. Summary and Remarks

In the present report, we have examined the interaction Li + BO using multireference methods and basis sets of quadruple quality. Our main conclusions are the following:

a. The Li[BO] is a genuine polytopic system with three minima, two linear (Li–BO, Li–OB) and one bent, practically degenerate within the accuracy of our methods. Formally, the bent isomer is the global minimum (\( X' A' \)) at the t-MRCI(10/12)/MRCI(2/5) level, its total energy being lower by 0.5 or 1 kcal/mol from the linear Li–BO or Li–OB \( ^3 \Sigma^+ \) state, respectively. However, at the t-MRCI(10/12)/MRCI(2/5) + Davidson correction level, the linear Li–OB and bent Li–OB isomers are isoenergetic. According to our calculations, the Li atom can move practically freely around the O-site of BO and within a \( \angle \text{Li–OB} \) angle range of 100–180°.

b. The two linear isomers, Li–BO and Li–OB, are separated by an energy barrier of 10.5 kcal/mol. It is of interest to note at this point that the isoelectronic Li[CN] molecule behaves similarly to Li[BO], presenting an energy isomerization barrier
Li−CN to Li−NC of about 10 kcal/mol, with the Li−NC being the stablest isomer by 6.5 kcal/mol at the SCF level. In addition, the study of the Li[CN] dynamics has revealed interesting phenomena related to chaos, leading us to surmise that similar behavior should be expected for the Li[BO] system.

c. The presence of a low-lying ionic state Li+BO− (1"+), affects strongly all states of the same symmetry, imparting finally its character to all three minima, thus explaining the ionic character of the Li[BO] system.

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References and Notes

(19) For the BO− anion, we have calculated an energy gap a"Ii ← X"Σg+ of 2.70 eV at the CCSD(T)/d-aug-cc-pV5Z level, very close to the IP = 2.50 eV of BO−.