Molecules in clusters: the case of planar LiBeBCNOF built from a triangular form LiOB and a linear four-center species FBeCN

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Abstract

Krüger some years ago proposed a cluster LiBeBCNOF, now called periodane. His ground-state isomer proposal has recently been refined by Bera \textit{et al.} using DFT. Here, we take the approach of molecules in such a cluster as starting point. We first study therefore the triangular molecule LiOB by coupled cluster theory (CCSD) and thereby specify accurately its equilibrium geometry in free space. The second fragment we consider is FBeCN, but treated now by restricted Hartree-Fock (RHF) theory. This four-center species is found to be linear, and the bond lengths are obtained from both RHF and CCSD calculations. Finally, we bring these two entities together and find that while LiOB remains largely intact, FBeCN becomes bent by the interaction with LiOB. Hartree-Fock and CCSD theories then predict precisely the same lowest isomer found by Bera \textit{et al.} solely on the basis of DFT.

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1 Introduction

Though traditional chemical thinking in which ‘atoms in molecules’ was a prime focus goes back many decades (see e.g. the early work of Moffitt [1]), more recently the idea has been championed most notably by Bader and coworkers [2]. Here, we have been motivated by the proposal of Krüger [3] on LiBeBCNOF, termed periodane, to study a ‘molecules in clusters’ approach to this species. This cluster, treated subsequently, in a more refined quantum chemical manner than in [3], by Bera et al. [4], is found to be essentially planar. One molecular grouping which then seemed apparent was LiOB, with the strong bond being B–O. This left Be, C, and N, which would form a radical and would be spin-compensated in the ground state by adding F.

Below, calculations are reported on the ground-state isomer of periodane, by (a) both restricted Hartree-Fock (RHF) and coupled cluster (CCSD) theory, and (b) for LiOB by the coupled cluster singles and doubles (CCSD) methods. Thereby we can make a quantitative comparison with Bera et al. [4] of both bond lengths and angles in the final geometry of the predicted lowest isomer from DFT.

2 Quantum chemical methodology

Several isomers of periodane were considered and, for each of them, a geometry optimization has been performed by using a 6-311(d) standard basis set [5] for all the atoms at Hartree-Fock level. The geometry of the most stable isomer, thermodynamically speaking, was further optimized at coupled cluster with single and double excitations (CCSD) level [6,7,8]. All the calculations have been performed by using the G03 package [9].

3 Molecules in clusters

The triatomic molecule LiOB has then been studied specifically and accurately by CCSD (see e.g. Ref. [10] for a review). With the B–O strong bond, the geometry predicted by CCSD is shown in Fig. 1, the ground-state energy being $-107.422807$ Hartree. With the DFT functional of [4], a similar geometry was found with a lower energy of about 0.25 Hartree: It is not clear to us that the DFT variational value lies above the exact ground-state energy because of approximations in the energy functional that are needed to date.

For the spin-compensated four-center molecule FBeCN, a linear structure was
obtained as shown in Fig. 2, where the structural parameters are recorded in Tab. 1.

Figure 3 shows schematically the way the two isolated molecules, with the individual geometries cited above, are somewhat modified as they are brought together into what we predict, as do Bera et al. [4] by purely DFT, as the lowest isomer of periodane. The four-center molecule is clearly distorted from linearity, the bond lengths and angles being recorded in Table 1. The change in the triatomic LiOB is seen to be much smaller than in the four-center case. Table 2 reports the sum of the RHF eigenvalues for the occupied orbitals for (i) FBeCN as in Fig. 2 and for (ii) isolated FBeCN, but with all constituent atoms held rigid at the HF geometry in Fig. 3 for periodane. The HF eigenvalue sums are seen to be quite close for linear and bent geometries and hence somewhat subtle corrections to Walsh’s rules [11] discussed in [12] are required to determine the relative stability between linear and bent forms of FBeCN.

4 Summary

The structure of the lowest isomer as predicted by Hartree-Fock and CCSD theory is shown in Fig. 3. As stated above, our ‘molecules in clusters’ approach has led to an identical structure reached by Bera et al. [4] on the basis of DFT alone. We have argued that it is useful to be viewed as having building blocks of (a) the bent triatomic molecule LiOB, and (b) the linear four-center molecule formed from BeCN plus F. Both these molecules are stable against dissociation into their isolated neutral atoms (cf. Tab. 3 reporting the difference between the energies of the clusters LiOB and FBeCN and their isolated constituent atoms).
Fig. 2. (Color online) Depicts linear geometry found for FBeCN four-center molecule. Structural parameters are listed in Tab. [1]

atoms, respectively).

Of course, as pointed out very specifically in [4], it is never possible to exclude the possibility of a (slightly) lower energy isomer than that shown in Fig. 3. Nevertheless, we believe that the present picture of bringing together two molecules LiOB and the linear four-center system BeCN plus F is a favourable way of approaching the final structure of the lowest isomer.

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Fig. 3. (Color online) Shows predicted lowest isomer for periodane from RHF and CCSD theories (with 6-311(d) basis set). Bond lengths and angles (Tab. 1) agree excellently with DFT predictions [4]. The two strongest bonds are seen to be B–O and N–C, with Be–F also short.

generous hospitality.

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Table 1
Bond lengths (in Å), angles (in degrees), and energies (in Hartree) of the lowest isomers of LiOB (Fig. 1), FBeCN (Fig. 2), and periodane (LiBeBCNOF, Fig. 3), within RHF and CCSD methods.

|                  | LiOB   | FBeCN  | LiBeBCNOF |
|------------------|--------|--------|------------|
|                  | CCSD   | RHF    | CCSD       |
| Distances (Å)    |        |        |            |
| O–B              | 1.26   | 1.21   | 1.23       |
| Li–O             | 1.75   | 1.86   | 1.88       |
| C–N              |        | 1.13   | 1.17       |
| Be–C             | 1.67   | 1.66   | 1.83       |
| F–Be             | 1.36   | 1.37   | 1.39       |
| N–Li             |        | 2.00   | 1.98       |
| B–Be             |        | 1.96   | 1.94       |
| Angles (°)       |        |        |            |
| B–O–Li           | 101    |        | 105.3      |
| Be–C–N           |        | 155.3  | 154.9      |
| C–N–Li           |        | 101.6  | 100.1      |
| N–Li–O           |        | 120.2  | 123.0      |
| O–B–Be           |        | 146.9  | 147.3      |
| B–Be–C           |        | 90.6   | 91.8       |
| Energy (Hartree) | −107.423 | −206.545 | −207.176 |
|                  | −313.705 | −315.362 |            |

Table 2
Reports the sum of the RHF eigenvalues (in Hartree) for the occupied orbitals for (i) FBeCN as in Fig. 2 and for (ii) isolated FBeCN, but with all constituent atoms held rigid at the HF geometry in Fig. 3 for periodane.

|                  | (i) FBeCN | (ii) FBeCN |
|------------------|------------|------------|
|                  | HF         | CCSD       | HF          | CCSD       |
|                  | −129.992   | −129.972   | −129.640    | −129.642   |

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Table 3
Reports energy differences (in Hartree) between the given clusters and their constituent isolated atoms.

|          | HF  | CCSD |
|----------|-----|------|
| LiOB     | −0.306 | −0.414 |
| FBeCN   | −0.489 | −0.643 |

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