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Can periodane accommodate neon?

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ABSTRACT

Periodane is a molecule in which each of the atoms from the second period other than neon occur exactly once. The isomers of a neon analogue of periodane are studied computationally using density functional theory and Møller–Plesset perturbation theory. We were unable to find stable structures in which neon was tightly bound; all the minima are found to be weakly bound NCB(F)OLi $\cdots$ Ne complexes. However, the novel NCB(F)OLi and NCBF molecules were found during the search.

1. Introduction

The search for molecules with novel and unusual structures is at the heart of chemistry. A computational search led Krüger [1] to periodane, an extraordinary molecule in which each of the atoms from the second period except neon appear exactly once. Later work by Bera et al. [2] showed that Krüger's search of the potential energy surface had not been sufficiently thorough. They found a planar global minimum, shown in Fig. 1, that contains a six-membered CNLiOBBe ring bound to a fluorine atom by a Be—F bond. Moreover, they also found 26 other isomers of periodane that were lower in energy than Krüger's structure. McDowell [3] reported further calculations on the lowest-energy isomer of periodane and three analogues. Forte et al. [4] showed that the lowest-energy structure of periodane can be found by bringing together FBeCN and LiOB molecules.

Many novel molecules with bonded rare-gas atoms (Ar, Kr, and Xe) have been found to date [5] but chemically bonded Ne atoms remain elusive. We thought that periodane might provide chances for a bound neon atom to be introduced into it as a replacement for beryllium. In this work, we report a systematic computational search for LiBCNOFNe isomers.

2. Calculations

Standard computational methods [6] were used: second-order Møller–Plesset (MP2) perturbation theory and Kohn–Sham density functional theory with the hybrid B3LYP functional. Initial geometry optimizations were carried out at the B3LYP/6-31+G(d) level using 67 starting structures. The latter included 28 structures obtained by substituting Ne for Be in the periodane isomers found by Bera et al. [2] and by Krüger [1]. Vibrational frequencies were calculated for the stationary points found and the number of imaginary frequencies was used to distinguish between true minima and saddle points. In this way, 40 unique minima and 16 saddle points were obtained. The 12 minima with a relative energy less than 5 kcal/mol were further optimized at the MP2/6-31+G(d) level. Note that the 6-31+G(d) basis set is equivalent to 6-31++G(d,p) for our systems because they have no hydrogen atoms. Five additional structures that we thought of later were optimized directly at the MP2 level without bothering with the B3LYP stage. Since the lowest energy structures all turned out to be weakly bound complexes, it was imperative to perform more reliable energy calculations including counterpoise corrections and using a larger basis set that also contained diffuse functions. Hence, we calculated MP2/aug-cc-pVTZ single-point energies including counterpoise corrections for each of the 17 MP2 minima we found. All calculations were performed using Gaussian 03 [7].

3. Results

No minima in which neon was bonded to another atom were found. All 17 MP2 minima consist of a neon atom weakly bound to the novel NCB(F)OLi molecule in one of three planar forms: fork (f), Y-shape (y), or key (k). Hence, MP2/6-31+G(d) geometry optimizations followed by frequency calculations were also carried out for the three NCB(F)OLi isomers shown in Fig. 2. The optimized geometrical parameters are listed in Table 1.

The 14 lowest-energy minima for NCB(F)OLi $\cdots$ Ne are shown in Fig. 3. The structures are labeled by a letter for the NCB(F)OLi isomer, followed by symbols for the atoms within 3.5 Å of Ne, and

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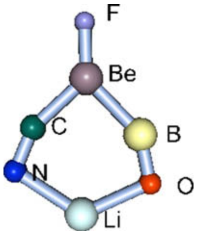


Fig. 1. The most stable isomer of periodane.

ended by a distinguishing numeral if required. The relative counterpoise-corrected MP2/aug-cc-pVTZ energies are given in parentheses in Fig. 3. The three MP2 minima not shown are analogues of fLi, yLi, and kLi with interchanged C and N atoms. They all lie at least 3.5 kcal/mol higher in energy than kN.

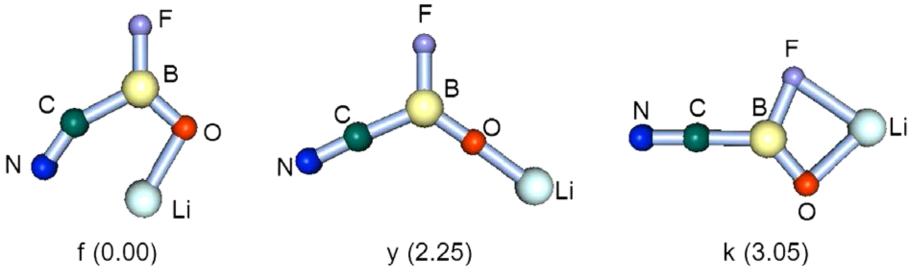
Now consider the NCB(F)OLi $\cdots$ Ne minima shown in Fig. 3. All structures except fBF and yBF are planar. The geometries of the NCB(F)OLi moieties are almost the same as those of the free monomers. Bond angles differ by no more than 0.3° from their monomer counterparts except for $\angle$LiOB in the yF1 and yF2 structures where the differences are 1.4 and 0.5°, respectively. Bond lengths differ by no more than 0.002 Å except in fLi, yLi, and kLi where the LiO bond length is about 0.005 Å shorter in the dimer.

Table 2 shows that the counterpoise-corrected MP2/aug-cc-pVTZ binding energies E_b for these 14 dimers range between 0.1 and 0.8 kcal/mol. The energy required to distort the NCB(F)OLi monomers to the geometries they adopt in the dimers is no more than 0.02 kcal/mol. The weak complexes are held together by long-range induction and dispersion. For a fixed NCB(F)OLi isomer, the induction interactions with Ne differ only through orientational effects relative to the dipole moment of NCB(F)OLi that points more or less from B to Li. The dispersion interaction is roughly proportional to the product of the polarizabilities of Ne and the interacting atom. The polarizability decreases sharply from 164 atomic units for lithium [8] to 37.3 for beryllium [9], and to 20.4, 11.7, 7.3, 5.2, and 3.7 atomic units for the B, C, N, O, and F atoms, respectively [10]. Hence, compared with the other complexes, fLi, yLi, and kLi have binding energies that are at least 0.5 kcal/mol larger, and NeLi distances shorter by about an angstrom than the distances between Ne and the interacting atoms in any of the other complexes.

The MP2/aug-cc-pVTZ energies listed in Fig. 2 show that the Y-shape and key isomers of NCB(F)OLi, respectively, lie 2.25 and 3.05 kcal/mol higher in energy than the fork isomer. These energy gaps are very similar to those among the most stable complexes of these monomers with Ne; yLi and kLi, respectively, are 2.14 and 2.97 kcal/mol higher in energy than fLi as shown in Fig. 3. This is because the Ne $\cdots$ Li interaction is very similar in these complexes: the binding energies are 0.77, 0.73, and 0.68 kcal/mol for yLi, kLi, and fLi, respectively, as seen in Table 2. Since the binding energies are less than 0.8 kcal/mol, all the complexes with a NCB(F)OLi fork are lower in energy than those with a Y-shape NCB(F)OLi which in turn are lower in energy than the complexes involving the key isomer.

Since NCB(F)OLi is a novel molecule, we probed its stability by computing dissociation energies along eight possible pathways for each of the three isomers. The MP2/aug-cc-pVTZ dissociation energies listed in Table 3 show that all three isomers are stable with respect to each dissociation pathway considered. Of the fragments considered in Table 3, NCBF and CNBF have not, to our knowledge, been reported previously. However, these two doublet-state molecules are likely to be experimentally elusive. Harmonic vibrational frequencies for NCBF, CNBF, and the three isomers of NCB(F)OLi are listed in Table 4.

Finally, we consider a complete periodane which consists of one atom of each of the eight elements in the second period. We did not perform a thorough search. Instead, we examined periodane $\cdots$ Ne complexes with geometries optimized at the MP2/6-31+G(d) level followed by counterpoise corrected MP2/aug-cc-pVTZ single-point energy calculations. Seven unique minima were found; they were complexes where the neon atom was interacting with one or two of the atoms in periodane. The planar complex where neon was interacting with the lithium atom in periodane (see Fig. 4) turned out to be the strongest in harmony with the data



f (0.00) y (2.25) k (3.05)

Fig. 2. MP2/6-31+G(d) minimum-energy fork, Y-shape, and key structures of NCB(F)OLi. The MP2/aug-cc-pVTZ energy in kcal/mol relative to $E(\mathrm{f}) = -299.9936088\ E_h$ is shown in parentheses.

Table 1
MP2/6-31+G(d) geometries of three isomers of NCB(F)OLi.

Bond length (Å)				Bond angle (°)			
Length	Fork	Y-shape	Key	Angle	Fork	Y-shape	Key
NC	1.189	1.184	1.184	NCB	152.6	177.1	179.1
CB	1.625	1.579	1.555	CBF	116.8	113.4	112.3
BF	1.352	1.369	1.459	FBO	131.9	124.8	116.0
BO	1.302	1.309	1.293	BOLi	101.4	179.3	89.0
OLi	1.818	1.683	1.833	BFLi	–	–	79.3
FLi	–	–	1.972				