Computational and Theoretical Chemistry 1019 (2013) 78–84

Contents lists available at SciVerse ScienceDirect

Computational and Theoretical Chemistry

journal homepage: www.elsevier.com/locate/comptc

Computational studies of dative bond containing heterocyclic ring structures

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ARTICLE INFO

Article history:
Received 3 June 2013
Received in revised form 18 June 2013
Accepted 18 June 2013
Available online 28 June 2013

Keywords:
Molecular structure
Dative bonding
Dimerization
Ab initio
Ring strain

ABSTRACT

Ab initio calculations are reported for several related heterocyclic compounds, each of which contains two dative bonds when they self-dimerize. Thus, these molecules are nominally dimers that contain either a boron–carbon–nitrogen (BCN) or boron–carbon–phosphorous (BCP) segment. Molecules with this motiff have been found experimentally to have several unusual properties that may be related to a "multi-polar framework" that results from charge separation associated with the two dative bonds. Structures obtained from full geometry optimizations without symmetry constraints, dative bond energies and charge distributions for four multipolar molecules are reported, the BCN–BCN dimer and the BCN–BCP dimer with and without carboxylation of one boron atom. Comparisons to single dative bond, self-cyclized monomers and the role of ring strain in molecular stabilities are also discussed.

1. Introduction

Experimental work with heterocyclic ring compounds containing two boron nitrogen dative bonds was reported over 30 years ago [1–4]. Since initial work by Miller and Muetterties, a number of these compounds have been synthesized, with a variety of permutations of the heteroatoms and substituents on the ring system [3,4]. The general class of molecules shows an interesting feature with dimers formed by two Lewis acid-base adducts, or dative bonds. These compounds, form heterocycles of the form BCNBCN, and have been labeled Multipolar Framework Heterocycles [4].

Experimental studies of compounds that contain B–N dative bonds have been fairly limited. The prototype molecule for this class of compound BH_3NH_3 has received substantial attention [5–8], and the B–N analog of benzene, borazine, likewise has attracted attention [9]. Bartlett and coworkers have studied the BCN fragment with an eye towards comparing it to its all carbon analog [10]. Despite their rich synthetic history and the intriguing nature of the multi-polar framework hypothesis, the specific class of dimer compounds for which we are reporting calculations has been the subject of only one calculation study, by Hseu using semi-empirical procedures [11].

From the perspective of a model system for computational investigation, this category of molecules presents several positive attributes. First, the previously noted concept of a multipolar heterocyclic system provides an interesting theoretical challenge. Because the dative bond forms due to electron donation from the nitrogen (or phosphorous) to the boron, the charge separation is commonly designated with a positive nitrogen and negative boron, $^{\delta+}N–B^{\delta-}$. A canonical perspective of this bond using electronegativity arguments, however, would predict the negative charge on the nitrogen atoms. Because charge separation plays a role in the way molecules are solvated or act in biochemical environments, such a model system may provide an important template for study of these effects.

Second, as a theoretical target, this set of molecules provides interesting questions. The determination of atomic charges poses a difficult challenge for electronic structure calculations, and this system admits particular difficulties for consideration. Because the system is rather large in its experimentally stabilized forms [2–4] there is little ability to utilize large basis sets simultaneously with computationally expensive models for inclusion of electron correlation. Thus, the calculations presented here provide insight at levels of theory that may be possible in relatively large molecular systems. Finally, in principle this class of molecules allows the exploration of Lewis acid–base reaction chemistry in a unimolecular system.

In this study two related heterocyclic compounds are considered. The first category are those molecules composed of like monomers, such as 1,1,4,4-Tetramethyl-1,4-diazonia-2,5-diboratacyclohexane, (Fig. 1a). This system will generally be designated as BCNBCN. The second category includes heterocycles composed of different monomers, such as 1,1,4,4-Tetramethyl-1-azonia-4-phosphonia-2,5-diboratacyclohexane, (Fig. 1b). The basic designation of this system will be BCNBCP throughout. The carboxylic acid derivatives of both types of rings have also been synthesized and are

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http://dx.doi.org/10.1016/j.comptc.2013.06.022

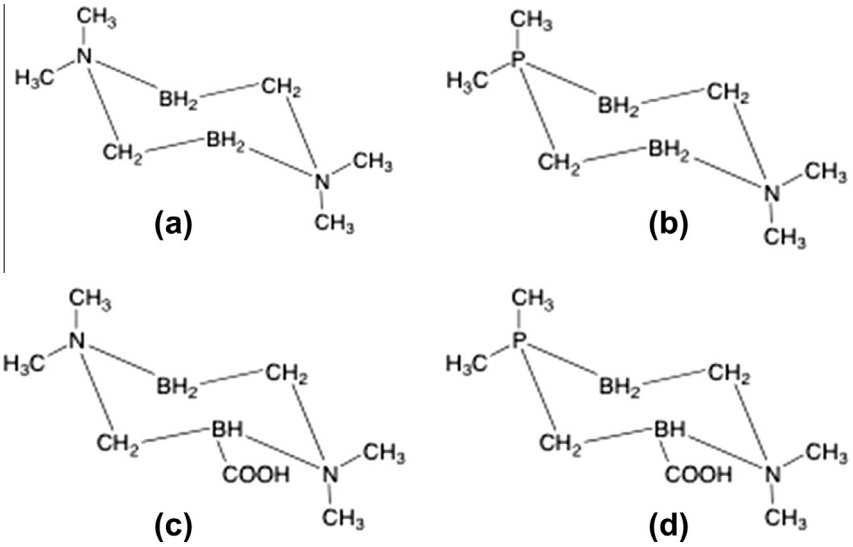

Fig. 1. Basic structures for all the cyclic dimer systems.

therefore calculated. Thus, Fig. 1c shows 1,1,4,4-Tetramethyl-1,4-diazonia-2,5-diboratacyclohexane-2-carboxylic acid, designated (COOH) BCNBCN and Fig. 1d shows 1,1,4,4-Tetramethyl-1-azonia-4-phosphonia-2,5-diboratacyclohexane-2-carboxylic acid, designated (COOH) BCPBCN. In addition to these ring structures with two dative bonds, dimerization may also occur via the formation of a single dative bond (referred to as a linear dimer, hereafter). This category of dimer is also investigated for both BCNBCN and BCNBCP in order to help elucidate the role of ring formation relative to that of dative bond formation.

In order to estimate energetics of dative bond formation, the monomers from which these dimers form have also been calculated, in both a cyclic and open (referred to as linear, hereafter) form. For these smaller systems the relative role of ring strain may compete energetically with dative bond formation. To estimate the role of ring strain an additional set of cyclic monomers with increasing number of carbon atoms in the cycle were also calculated. Thus additional monomers such as $BH_2CH_2CH_2N(CH_3)_2$ (designated BCCN) and $BH_2CH_2CH_2CH_2N(CH_3)_2$ (designated BCCCN) were calculated in both linear and cyclic form. These systems may form 8 member and 10 member rings by dimerization and comparisons of energies of species in this set provide insight into the relative roles of ring-strain and dative bond strength in the overall stability of this category of molecule. Calculations reveal that the cyclic monomers of all three cases are lower in energy than the linear monomer, indicating that the stabilization of the dative bond formation (for self-cyclization) exceeds ring strain concerns even in the case of a three-member ring. Not surprisingly the relative added stability from self-cyclization of the monomers increases with the increasing number of atoms in the linear monomers.

2. Computational details/methodology

All calculations were performed using the GAMESS [12,13] electronic structure code, and the molecules were visualized with MacMolPlt [14]. All molecules were fully optimized in gas phase with C1 symmetry, using 2nd order Moller–Plesset perturbation theory (MP2) [15] and the 6-311G(d,p) [16] basis set. All MP2 calculations utilize a frozen-core approximation. Zero point energy was calculated for all the molecules. Conformational searches for all heterocyclic rings were carried out using the Complete Rotation from the Evaluation of Potential Energy Surface (CREPES) program [17] at MP2/6-311G(d,p) level and the lowest energy conformers were optimized. Positive definite Hessian calculations confirm the reported structures are true minima.

Dative bond energies were estimated by comparing the energy of the entire molecule with that of the fragments derived from breaking both dative bonds simultaneously. Linear structures were obtained for each heterocyclic molecule by breaking each dative bond. Atomic charges were estimated using the Generalized Atomic Polar Tensors method (GAPT) [18] which is derived from the trace of the dipole derivative tensor, calculated numerically. Ring Strain Energy for monomers and some dimers were calculated using a method given by Dudev and Lim [19]. In this method Ring Strain Energy (E_{RS}) of a cyclic molecule is calculated relative to its acyclic counterpart containing the same number of heavy atoms.

3. Results and discussion

The primary system of interest arises from the dimerzation of boron-carbon-nitrogen/phosphorous systems into six-member rings. Four such cyclic dimer structures are depicted in Fig. 1. Each has a chair conformation that is the lowest energy conformer. For the BCNBCN cyclic dimer the lowest energy conformer is a regular chair and other structures show a slightly twisted chair conformation with a twisted angle varying from 1° to 4°. In the experimentally synthesized structure (COOH)BCPBCN, carboxylic acid is attached to boron that forms a dative bond with nitrogen rather than phosphorous, because the carboxyl group originates on the BCP monomer. Calculations have also been carried out for (COOH)BCNBCP where the carboxylic acid is attached to boron bonded to phosphorous. The energy of this structure is 0.41 kcal/mol less than that of the experimentally reported structure. Nonetheless, because this energy difference is very small, indeed smaller than the likely accuracy of the calculation methods applied here, for subsequent discussions, the experimental (COOH)BCPBCN structure will be used for this system.

As noted earlier, self-cyclization of the monomers provides an important set of heterocycles to consider as well. In order to understand effects of ring strain in these systems, additional monomers were considered in this study, beyond those that have been experimentally reported. Fig. 2 shows the basic structures of the cyclized monomers whose geometries and energies have been calculated.