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Molecular Mechanics Study of Cyclic and Unsymmetrical Diborane(4) Compounds

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Abstract — The results of a theoretical study on the structure of some diborane(4) compounds are presented in order to analyze the ralative stabilities of the 1,1- and 1,2-isomers. Using the molecular mechanics method, characteristic distances and angles have been calculated and compared with available experimental data. In order to rationalize the results, different energy components are discussed in a comparative fashion. A fairly satisfactory agreement between the theoretical and experimental data have been found. Some possible extensions are pointed out to complement this kind of analysis.

Derivatives of diborane(4) constitute an important class of compounds in boron chemistry. In particular, interest in these compounds originates from the presence of an unsupported two-center two-electron $B-B$ bond [1]. Knowledge of the chemistry of boron compounds has accelerated rapidly in recent years, and a variety of new boron compounds have been prepared and studied in detail. However, there are several aspects of the chemistry of such species that have been developed only recently.

Among the most relevant molecular features under present discussion, the existence of structural 1,1- and 1,2-isomers poses the natural question about their relative stabilities. Actually, the 1,1- vs. 1,2-isomer issue has been raised long ago and first discussed by Shore *et al.* [2, 3] and later on by Noth *et al.* [4, 5]. Recently, some experimental papers on this topic have been published and some preliminary electronic structure calculations have been reported to complement those studies [6, 7]. In most cases, 1,1-isomers are preferred over 1,2-isomers, although cyclic 1,2-species can be found. In addition, derivatives of diborane(4) are essentially planar, but there are structural data for some molecules, which show a slight twist about the $B-B$ bond.

The diversity of experimental information is worthy of a systematic theoretical analysis in order to understand basic reasons determining the molecular structure of different diborane(4) derivatives. This paper gives the results of a theoretical structural study of some diborane(4) compounds on the basis of an empirical procedure, and it may be considered as a first step in such a direction. The selected molecular set consists of the following six molecules: $B_2(cat)_2$ (**I**, cat = $1,2-O_2C_6H_4$), $B_2(1,2-S_2C_6H_4)_2$ (**II**), $1,2-B_2(NMe_2)_2(cat)$ (**III**), $1,2-B_2(NMe_2)_2(thiocat)$ (**IV**, thiocat = $1,2-S_2C_6H_4$), $B_2(thiocat)(pin)$ [**V**, pin = $(OCH_2)_2$], and $B_2(thiocat)(cat)$ (**VI**). The scheme below shows geometrical arrangements of the 1,1- and 1,2-isomers of compound **I**:

| 1,2-Isomer | 1,1-Isomer |
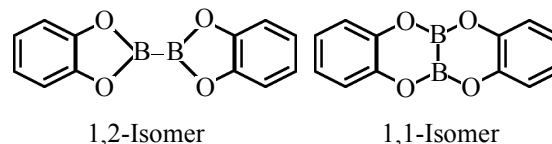
Unfortunately, many problems that one would like to tackle in molecular modeling are too large to be considered by quantum-mechanical methods based upon strict first principles. Molecular mechanics methods (also known as force field methods) ignore electronic motions and calculate the energy of a system as a function of the nuclear positions only. In some cases, force fields can provide answers that are as accurate as even the highest level quantum-mechanical calculations, in a fraction of the computer time. Molecular mechanics cannot of course provide properties that depend on electronic distributions in a molecule. That molecular mechanics works at all is due to the validity of several assumptions. The first of these is the Born–Oppenheimer approximation, without which it would be impossible to contemplate writing the energy as a function of the nuclear coordinates solely.

Molecular mechanics is based upon a rather simple model of interactions within a system with contribu-

Experimental[a] and calculated bond lengths in diborane(4) compounds **I–VI**

Comp. no	Isomer	Energy, kcal/mol	Bond length, Å								
			B–B	B–O	C–O	C–C	C–H	B–N	N–C	B–S	C–S
I	1,1	0.8640	1.69	1.48	1.36	1.39	1.10	–	–	–	–
	1,2	20.3200	1.67	1.46	1.37	1.40	1.10	–	–	–	–
II	1,1	–1.0077	1.69	–	–	1.40	1.10	–	–	1.94	1.83
	1,2	25.5554	1.68	–	–	1.40	1.10	–	–	1.92	1.82
III	1,1	14.3605	1.69	1.47	1.37	1.37	1.10	1.53	1.45	–	–
	1,2	5.1375	1.69	1.47	1.37	1.35	1.10	1.53	1.45	–	–
IV	1,1	3.3755	1.69	–	–	1.40	1.10	1.53	1.44	1.93	1.83
	1,2	19.6126	1.70	–	–	1.40	1.10	1.53	1.45	1.93	1.82
V	1,1	8.9914	1.68	1.46	1.37	1.40	1.11	–	–	1.93	1.83
	1,2	26.7193	1.68	1.46	1.37	1.40	1.11	–	–	1.92	1.82
VI	1,1	–1.0228	1.69	1.48	1.36	1.40	1.10	–	–	1.93	1.83
	1,2	23.0862	1.68	1.46	1.37	1.40	1.10	–	–	1.92	1.82

[a] Average experimental bond lengths, Å: B−O 1.40, B−S 1.0, C−C 1.40, B−B 1.70, C−S 1.76.

tions from processes such as stretching of bonds, opening and closing of angles, and rotations about single bonds. Even though simple functions (e.g., Hooke's law) are used to describe these contributions, the force field can perform quite acceptably. The idea that a molecule can be simulated as a collection of balls joined together with springs is as old as the hills. The molecular mechanics model capitalizes on this idea by seeking to express the intramolecular potential energy as a sum of terms that comprises differences between the actual and reference geometric parameters [8]. The large number of applications of this method, interesting results derived for a number of physico-chemical and structural properties, and its present use in several chemistry areas makes it unnecessary to present further justifications for its employment [9].

We have resorted to the MM+ force field included in the HYPERCHEM for Windows package [10]. This force field was developed for organic molecules, and it is an "all atom" force field. The provision of additional parameters (i.e., force constants) through two alternative schemes [11] extends the range of chemical compounds to which MM+ can be applied. We have chosen the Pollack–Ribiére (conjugated gradient) minimization algorithm, with an RMS gradient of 0.01 kcal/mol as termination condition. The minimization procedure was run without any restriction, and in all cases convergence condition was reached in quite sensible computing times.

Table 1 displays the most relevant theoretical and experimental data obtained for the six molecules. Since the total energies calculated in terms of the molecular mechanics method represent not an absolute

quantity but a sort of deviation with respect to reference equilibrium values, it is not possible to give a direct interpretation to such data. Energy differences between isomers can be interpreted as a measure of relative stabilities. Analysis of the results shows that preferred conformations differ from the nonpreferred ones by a large amount of energy. Molecule **III** is the only one predicted to be a 1,2-isomer, in close agreement with the experimental results [6]. The other molecules favor the unsymmetrical isomers, i.e., 1,1-isomers, and a satisfactory agreement between the theoretical and experimental results is also observed here. In fact, compounds **I**, **II**, and **V** and almost all related structurally characterized species exist as 1,1-isomers. Moreover, comparison of the experimental and theoretical distances and angles reveals that the theoretical method used predicts fairly well experimentally available data. The B−O, B−S, and C−S bond lengths are rather overestimated, while the B−B and C=C bond lengths are predicted in good agreement with average experimental values. Since there is some dispersion among available experimental structural data for diborane(4) compounds, we have performed the corresponding comparisons with average experimental bond distances.

Thus the theoretical results presented in this paper show that in general 1,1-isomers of diborane(4) compounds are more stable than 1,2-isomers, in agreement with the results of some previous studies. In addition, quite a satisfactory quantitative correspondence between the calculated bond lengths and available experimental data has been obtained. A more rigorous analysis based on the molecular orbital theory or/and

density functional theory will give a more complete and comprehensive notion of the nature of chemical bonding for the title compounds. Work along this line is actually under development in our laboratory and the results will be presented elsewhere.

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