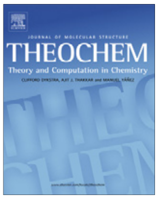
Journal of Molecular Structure: THEOCHEM 962 (2010) 85–89

Contents lists available at ScienceDirect

Journal of Molecular Structure: THEOCHEM

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



A comparative computational study of novel X–Be–N_2–Li and X–Mg–N_2–Li species (X = F, Cl, Br)

Sean A.C. McDowell *, Katrina P. Price

Department of Biological and Chemical Sciences, The University of the West Indies, Cave Hill Campus, Barbados

A R T I C L E   I N F O

Article history:
Received 8 May 2010
Received in revised form 14 September 2010
Accepted 16 September 2010
Available online 25 September 2010

Keywords:
Beryllium compound
Magnesium compound
Novel species
Energetic stability

A B S T R A C T

A computational study predicts a number of unusual Be- and Mg-containing compounds with general formula X–M–N_2–Li (X = F, Cl, Br; M = Be, Mg). Generally, the X–Be–N_2–Li species were found to be energetically stable with respect to the LiX + Be + N_2 fragments and with respect to the LiBeX + N_2 fragments, whereas the Mg-containing species by comparison were found to be unstable. Harmonic vibrational frequencies and various bonding parameters were also computed and found useful in rationalizing the relative stabilities and trends (for varying X) of these unusual compounds. The high stability of X–Be–N_2–Li is thought to be due mainly to strong electrostatic interactions between the constituent atoms and especially the Be atom in its +2 valence state.

1. Introduction

An important aspect of chemical research is the identification and prediction of new and potentially useful compounds. The pursuit of unusual new compounds is a satisfying goal in itself and requires little self-justification. A recent article by Hoffmann and Hopf even explores the psychological motivation for studying and preparing unusual molecules, especially highly strained or "stressed" molecules [1]. The advances in computer technology and the development of accurate and efficient theoretical methods has made this a realistic and feasible pursuit and can facilitate the exploration of novel combinations of atoms, molecules and clusters without a heavy investment in experimental resources. In fact, theory can provide the inspiration for experimental effort if unusual compounds can be reliably predicted from computations.

An example of a theoretically predicted compound that has generated some interest is an extraordinary molecule called periodane, which consists of one atom each of the elements of the second period of the periodic table, except neon, and which was predicted by Kruger [2]. A more systematic and exhaustive search of the potential energy surface by Bera et al. [3] found an additional 27 isomers lower in energy than Kruger's structure, including a planar global minimum consisting of a six-membered BeBOLiCN ring bound to a fluorine atom via a Be–F bond, which can be represented as FBeBOLiCN. An attempt at incorporating a chemically bound neon atom into the periodane structure by replacing the beryllium atom by neon was unsuccessful but several weakly bound NCB(F)OLi···Ne isomers were predicted by Blair et al. [4].

An interesting feature of the lowest energy periodane structure, which probably confers great stability to the molecule, is a three-coordinate Be atom, with Be at the centre and F, B and C atoms forming a triangular geometry around the Be atom [3]. Several analogues of periodane, with the F, B and C atoms replaced by other atoms were also predicted to form stable molecules [5]. The theoretically predicted stability of periodane and its analogues was the motivation for the present study.

In this work, we explore the stability of a series of molecules consisting of five atoms with general formula X–Be–N_2–Li (where X represents either F, Cl or Br) – the three molecules were all predicted to be more stable than the fragments Li–X + Be + N_2, Li–Be–X + N_2 and X–Be + N_2 + Li (except Li–Be–F + N_2, which is slightly more stable than F–Be–N_2–Li). We also compared these species with the analogous X–Mg–N_2–Li species, where the Be atom is replaced by an Mg atom. Magnesium and beryllium are Group II metals and so having the same valence shell configuration would be expected to have similar chemical behaviour. Interestingly, although all three X–Mg–N_2–Li species are minima on their respective potential energy surfaces, they are energetically unstable relative to the LiX + Mg + N_2 and Li–Mg–X + N_2 fragments.

Standard *ab initio* electronic structure methods were used to predict the optimized geometries, energies and other properties of interest. The relative stabilities of the X–Be–N_2–Li and X–Mg–N_2–Li species were rationalized from the harmonic vibrational frequencies and bonding parameters computed by these high-level theoretical methods. Recent computational studies on complexes

---

* Corresponding author. Fax: +1 (246) 417 4325.
E-mail addresses: sacm@mail.com, sacm1@cam.ac.uk (S.A.C. McDowell).

0166-1280/$ - see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.theochem.2010.09.019

that contain beryllium indicate that it forms strong bonds with a dominant electrostatic character and which, though stronger than normal hydrogen bonds, bears some similarities [6]. In fact, the ability of beryllium to displace a proton from a number of hydrogen-bonded complexes of varying strengths has been previously reported [7,8]. The computational methods used in this study are outlined below.

2. Computational methods

All calculations were performed using the Gaussian 03 suite of programs [9]. Preliminary calculations of optimized geometries were performed at the SCF, B3LYP, MP2 and QCISD levels of theory to assess the sensitivity of the predicted structures to the theoretical method used. The QCISD method is the method of choice, being the most accurate, and was used to produce the definitive set of results.

In addition to the optimized geometries, harmonic vibrational frequencies were computed for the stationary points found and used to verify that they were minima and not transition state structures (by the absence of any imaginary frequencies). All species reported here were found to be minima at all levels of theory. We also computed the atomic charge distribution and bond order for these unusual molecules using the natural bond orbital (NBO) method [10] and the electron density (ρ) and the Laplacian of the electron density (Lρ) obtained by the atoms in molecule (AIM) approach [11].

Table 1 shows the optimized geometry and dipole moment for the F–Be–N_2–Li and F–Mg–N_2–Li species, respectively, computed at the SCF, B3LYP, MP2 and QCISD levels of theory. The geometries and dipole moments computed at QCISD for the three X–Be–N_2–Li species, and for the three X–Mg–N_2–Li species, are compared in Table 2. Table 3 shows the dissociation energies for the X–M–N_2–Li molecules with respect to the LiX + M + N_2, Li–M–X + N_2 and X–M + N_2 + Li fragmentation routes (X = F, Cl, Br; M = Be, Mg). These dissociation energies were computed at the QCISD/6-311G(d) level of theory.

Table 4 compares the NBO atomic charge and the Wiberg bond index (WBI), which is a measure of the bond order for a pair of atoms, as well as the AIM electron density and Laplacian of the electron density for these novel compounds. Tables 5 and 6 show the QCISD computed harmonic vibrational frequencies for the F–Be–N_2–Li and F–Mg–N_2–Li species, respectively.

Table 1
Optimized geometry and dipole moment (μ) for the F–Be–N_2–Li and F–Mg–N_2–Li molecules computed at different levels of theory with a 6-311G(d) basis set. Refer to Fig. 1 for the structure of the molecules.

Property	SCF	B3LYP	MP2	QCISD
R(F–Be) (Å)	1.408	1.409	1.412	1.409
R(Be–N) (Å)	1.586	1.603	1.614	1.606
R(N–Li) (Å)	1.819	1.825	1.845	1.841
R(N–N) (Å)	1.260	1.290	1.318	1.302
∠N–Be–N (°)	46.8	47.4	48.2	47.8
∠F–Be–N (°)	156.6	156.5	156.0	156.1
∠N–Li–N (°)	40.5	41.4	41.9	41.4
∠Be–N–Li (°)	136.3	135.6	135.0	135.4
μ/debye	7.7041	7.1512	7.3654	7.4157
R(F–Mg) (Å)	1.761	1.777	1.781	1.778
R(Mg–N) (Å)	1.994	2.013	2.025	2.018
R(N–Li) (Å)	1.809	1.822	1.837	1.833
R(N–N) (Å)	1.258	1.284	1.311	1.297
∠N–Mg–N (°)	36.8	37.2	37.8	37.5
∠F–Mg–N (°)	161.7	161.4	161.2	161.3
∠N–Li–N (°)	40.7	41.3	41.8	41.4
∠Mg–N–Li (°)	141.3	140.8	140.2	140.5
μ/debye	6.7902	6.3441	6.5071	6.5421

Table 2
Comparison of the optimized geometry and dipole moment (μ) for the X–M–N_2–Li (X = F, Cl, Br; M = Be, Mg) species computed at QCISD using a 6-311G(d) basis set (6-311G for Br–Mg–N_2–Li).

Property	F–Be–N_2–Li	Cl–Be–N_2–Li	Br–Be–N_2–Li
R(X–Be) (Å)	1.409	1.843	2.007
R(Be–N) (Å)	1.606	1.597	1.596
R(N–Li) (Å)	1.841	1.848	1.849
R(N–N) (Å)	1.302	1.299	1.298
∠X–Be–N (°)	156.1	156.0	155.9
∠N–Be–N (°)	47.8	48.0	48.0
∠N–Li–N (°)	41.4	41.1	41.1
∠Be–N–Li (°)	135.4	135.4	135.4
μ/debye	7.4157	8.2599	8.4226
	F–Mg–N_2–Li	Cl–Mg–N_2–Li	Br–Mg–N_2–Li
R(X–Mg) (Å)	1.778	2.202	2.423
R(Mg–N) (Å)	2.018	2.014	2.038
R(N–Li) (Å)	1.833	1.836	1.866
R(N–N) (Å)	1.297	1.296	1.348
∠X–Mg–N (°)	161.3	161.3	160.7
∠N–Mg–N (°)	37.5	37.5	38.6
∠N–Li–N (°)	41.4	41.3	42.3
∠Mg–N–Li (°)	140.5	140.6	139.5
μ/debye	6.5421	7.2089	7.8848

Table 3
QCISD/6-311G(d) dissociation energies (D_e in kJ mol^{-1}) for the X–M–N_2–Li species (X = F, Cl, Br; M = Be, Mg) with respect to various fragmentation routes.

Molecular species	D_e(Li–X + N_2 + M)	D_e(Li–M–X + N_2)	D_e(X–M + N_2 + Li)
F–Be–N_2–Li	186.7	−3.2	195.6
Cl–Be–N_2–Li	130.1	19.9	214.9
Br–Be–N_2–Li	111.0	24.0	217.8
F–Mg–N_2–Li	−89.6	−114.6	46.1
Cl–Mg–N_2–Li	−102.9	−109.2	53.7
Br–Mg–N_2–Li[a]	−131.7	−513.8	44.9

[a] QCISD/6-311G calculations.

Table 4
QCISD NBO atomic charges (q), Wiberg bond index (WBI), the atoms in molecule (AIM) computed electron density (ρ) and Laplacian of the electron density (Lρ), for X–M–N_2–Li using a 6-311G(d) basis set. The values for the Mg species are in brackets.

	q	WBI	ρ	Lρ
F–M–N_2–Li				
F	−0.814 (−0.862)			
M	1.599 (1.700)			
N	−0.843 (−0.854)			
Li	0.901 (0.869)			
F–M		0.28 (0.21)	0.122 (0.069)	1.154 (0.703)
M–N		0.16 (0.12)	0.090 (0.047)	0.621 (0.365)
N–N		1.81 (1.81)	0.412 (0.416)	−0.771 (−0.829)
N–Li		0.08 (0.10)	0.041 (0.042)	0.339 (0.343)
Cl–M–N_2–Li				
Cl	−0.721 (−0.833)			
M	1.472 (1.646)			
N	−0.830 (−0.844)			
Li	0.910 (0.875)			
Cl–M		0.41 (0.25)	0.082 (0.050)	0.333 (0.291)
M–N		0.18 (0.14)	0.092 (0.048)	0.639 (0.370)
N–N		1.81 (1.82)	0.415 (0.418)	−0.786 (−0.837)
N–Li		0.07 (0.09)	0.040 (0.042)	0.333 (0.340)
Br–M–N_2–Li				
Br	−0.691 (−0.784)			
M	1.433 (1.574)			
N	−0.828 (−0.833)			
Li	0.913 (0.875)			
Br–M		0.45 (0.32)	0.071 (0.036)	0.211 (0.161)
M–N		0.19 (0.15)	0.092	0.642
N–N		1.81 (1.77)	0.416 (0.333)	−0.788 (0.322)
N–Li		0.07 (0.09)	0.040 (0.038)	0.332 (0.299)