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Theoretical prediction on the structures of the $HMgN^-$ and $HNMg^-$ using multiconfigurational methods

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Abstract: The nine-valence-electron $HMgN^-$ and $HNMg^-$ have been investigated for the first time theoretically using complete active space self-consistent field (CASSCF) and multiconfiguration second-order perturbation theory (CASPT2) methods in conjunction with the contracted atomic natural orbital (ANO) basis sets. The structures of the low-lying electronic states of $HMgN^-$ and $HNMg^-$ were predicted. The possible unimolecular conversions between $HMgN^-$ and $HNMg^-$ were discussed. The calculated results indicated that the ground-state of $HMgN^-$ is linear, while the ground-state $HNMg^-$ is bent, which is in contradiction to the Walsh rules, which predict linear structures for HXY systems containing 10 or fewer valence electrons.

Keywords: $HMgN^-$; $HNMg^-$; complete active space self-consistent field; multiconfiguration second-order perturbation theory.

INTRODUCTION

One of the predictions of the Walsh rules is that molecules of the class HXY containing 10 or fewer valence electrons should be linear in their ground electronic states.[1] However, some ten-valence-electron HXY systems,[2] such as HSB, HSAl, HOAl, and HOB, and some nine-valence-electron systems, such as HSB^+,[3] $HSAl^+$,[4] HPB,[5] and HNAl[6] have been predicted to be bent in their ground states using theoretical calculations.

$HMgN^–$ and its tautomer $HNMg^–$ are iso-electronic species with HMgO, HOMg, HAlN and HNAl, which all have nine valence electrons. The high-level *ab initio* theoretical calculations indicated that the ground states of HMgO,[7] HOMg[7] and HAlN[6] are linear, which obey the Walsh rules. However, the ground state of HNAl[6] is bent, which is in contradiction to the Walsh rules. $HMgN^–$ and $HNMg^–$have not hitherto been studied by any experimental and theoretical works. What are the structures of the $HMgN^–$ and $HNMg^–$? Are their ground

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states linear or bent? Do the two anions obey the Walsh rules or not? What are the unimolecular conversions between the low-lying states of two anions? All of the above questions inspired the present large-scale theoretical studies on $HMgN^–$ and $HNMg^–$. In the present paper, calculated results are reported, which include the geometries, energies and the frequencies of the low-lying states of $HMgN^–$ and $HNMg^–$, and the potential energy curves (PECs) for the isomerization reactions between the two anions.

COMPUTATIONAL DETAILS

The low-lying states of $HMgN^-$ and $HNMg^-$ were calculated using the complete active space self-consistent field (CASSCF)[8] and the multiconfiguration second-order perturbation theory (CASPT2)[9,10] methods. The CASSCF and CASPT2 calculations were performed using MOLCAS 7.4 quantum chemistry software.[11] In the CASSCF and CASPT2 calculations, the atomic natural orbital basis setswere used:[12-14] [3s2p1d] for H, [5s3p2d1f] for N and [6s4p3d1f] for Mg, denoted as ANO. All stationary points along the potential energy surfaces (PESs) of the $HMgN^-$ and $HNMg^-$ isomerization reactions were optimized at the CASSCF//ANO level. To confirm the stationary points as minima or transition states, the vibrational frequencies of all stationary points were calculated at the same level. The CASPT2/ANO energies were calculated at the respective CASSCF/ANO optimized geometries. Nevertheless, for the method of CASSCF does not contain dynamic electron correlation, the CASSCF optimized geometries might not be sufficiently accurate. Therefore, CASPT2/ANO geometry optimization calculations on all stationary points were also performed. The potential energy curves (PECs) for the isomerization reaction between $HMgN^-$ and $HNMg^-$ were computed as functions of the HMgN bond angle at the CASPT2/ANO level. In the point-wise calculations of the surfaces, the HMgN bond angle (denoted as θ, ranging from 0 to 180°) was fixed and other geometric parameters were optimized at the CASSCF/ANO level. In the CASSCF calculation, full-valence space was selected as the active space: nine electrons were active and the active space included nine orbitals [CASSCF (9,9)]. For the linear isomers, the calculations were performed in the C_{2v} subgroup of $C_{\infty v}$, where Σ^+ corresponds to the A_1 irreducible representation, Σ^- to A_2, and Π to $B_1 + B_2$. Labeling the orbital within the C_{2v} point group in the order of a_1, a_2, b_2 and b_1, the active space was identified as (5022). Labeling the orbitals within the C_s point group (in the calculation for the PECs) in the order a' and a'', the active space was identified as (72).

Throughout this article, CASSCF/ANO is referred to as CAS and CASPT2/ANO////CASSCF/ANO as CASPT2.

RESULTS AND DISCUSSIONS

The CAS optimized geometries and the CASPT2 energies of all stationary points along the $HMgN^– \leftrightarrow HNMg^–$ PECs are listed in Table I. The CASSCF//ANO calculated frequencies are listed in Table II. The CASPT2 PECs calculated as functions of the HMgN bond angle for the $HMgN^– \leftrightarrow HNMg^–$ system are shown in Fig. 1.

TABLE I. CAS optimized geometries and CASPT2 relative energies for all stationary points of the $1^2A'$, $1^2A''$ and $2^2A'$ surfaces of the $HMgN^- \leftrightarrow HNMg^-$ system; data in brackets were calculated using the CASPT2 ^{c} method (CASPT2/ANO optimized geometries and CASPT2/ /ANO//CASPT2/ANO energies

Stationary point	$R_{Mg\text{-}N}$ / Å	$R_{H\text{-}Mg}$ / Å	$R_{H\text{-}N}$ / Å	∠HMgN / °	ΔE^a / kcal* mol^{-1}
$HNMg^-$ ($X^2\Sigma^+$)	1.821 [1.816]	–	1.016 [1.013]	0.0	0.00 [0.00]
M1 ($1^2A'$)	1.892 [1.903]	–	1.032 [1.029]	19.2 [19.7]	–1.25 [–1.26]
TS1 ($1^2A'$)	1.944 [1.912]	1.807 [1.797]	–	69.9 [67.1]	65.59 [67.43]
$HMgN^-$ ($X^2\Pi$)	1.957 [1.955]	1.785 [1.779]	–	180.0	41.40 [41.41]
$HNMg^-$ ($A^2\Pi$)	2.000 [1. 990]	–	1.024 [1.022]	0.0	2.81 [2.81]
M2 ($1^2A''$)	2.048 [2.038]	–	1.031 [1.030]	15.7 [16.5]	2.46 [2.45]
TS2 ($1^2A''$)	2.052 [2.024]	1.859 [1.824]	1.982 [1.992]	60.7 [62.1]	64.26 [64.16]
TS3($2^2A'$)	1.962 [1.892]	1.750 [1.755]	–	89.4 [92.5]	88.19 [89.56]
$HMgN^-$ ($A^2\Sigma^+$)	1.845 [1.838]	1.751 [1.740]	–	180.0	52.12 [52.11]

^{a}Relative energy to the $X^2\Sigma^+$ state of $HNMg^-$

TABLE II. The CASSCF/ANO calculated frequencies (in cm^{-1}) of the stationary points

Stationary point	ν(H–Mg)^a	ν(H–N)^a	ν (Mg–N)^a	ν(HMgN/HNMg)^b
$HNMg^-$ ($X^2\Sigma^+$)	–	3546	798	93i
M1 ($1^2A'$)	–	3515	646	97
TS1 ($1^2A'$)	1335	–	613	1693i
$HMgN^-$ ($X^2\Pi$)	1409	–	638	300
$HNMg^-$ ($A^2\Pi$)	–	3441	522	176i
M2 ($1^2A''$)	–	3358	503	294
TS2 ($1^2A''$)	1156	–	518	1254i
TS3($2^2A'$)	1237	–	580	1469i
$HMgN^-$ ($A^2\Sigma^+$)	1504	–	742	452

^{a}Stretching vibration; ^{b}bending vibration

Geometries for stationary points

Based on the CASPT2 calculations, it is predicted that the ground and first excited states of the linear structure of $HMgN^–$ are the $X^2\Pi$ and $A^2\Sigma^+$ states, respectively. At the CASPT2 level, the $A^2\Sigma^+$ state is about 10.72 kcal mol$^{–1}$ higher in energy than the $X^2\Pi$ state. The CAS frequency calculations indicated that the $X^2\Pi$ and $A^2\Sigma^+$ states of $HMgN^–$ have no imaginary frequency and there should be minima on the PESs.

The CASPT2 calculations indicated that the energy of the $A^2\Pi$ state for the linear $HNMg^–$ is about 2.81 kcal mol$^{–1}$ higher than the $X^2\Sigma^+$ state. Therefore, the ground and first excited states of the linear $HNMg^–$ were predicted to be the $X^2\Sigma^+$ and $A^2\Pi$ states. However, the CAS frequency calculations showed the $X^2\Sigma^+$ and $A^2\Pi$ states both have a unique imaginary frequency. Therefore, the $X^2\Sigma^+$ and $A^2\Pi$ states of the linear $HNMg^–$ should be first-order saddle points. In other words, the ground-state $HNMg^–$ should not be linear.

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* 1 kcal = 4.184 kJ

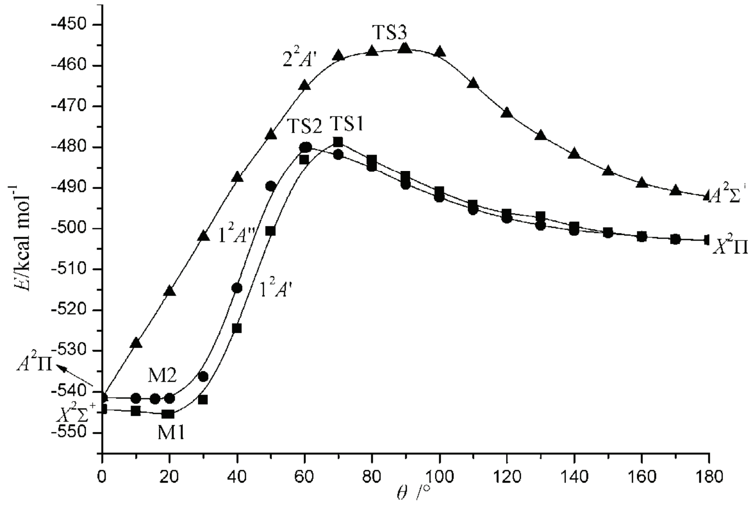

Fig. 1. The CASPT2/ANO potential energy curves as functions of HMgN angle (θ) for the HMgN$^-$ ↔ HNMg$^-$ system calculated at the CASSCF/ANO partly optimized geometries.

There is a bent equilibrium conformation M1 on the $1^2A'$ potential energy surface (see Fig. 1). The energy of M1 is about 1.25 kcal mol^{-1} lower than the $X^2\Sigma^+$ state of HNMg$^-$ and about 42.65 kcal mol^{-1} lower than the $X^2\Pi$ state of HMgN$^-$ at the CASPT2 level (see Table I). The CAS frequency calculation indicated that M1 has no imaginary frequency (see Table II). Therefore, M1 is a global minimum and the $X^2\Sigma^+$ state of HNMg$^-$ should be the transition state of the isomerization reactions of M1 ↔ M1. At the CAS level, the Mg–N and H–N bond lengths of M1 are 1.892 and 1.032 Å, respectively, and the HMgN bond angle is 19.2° (the HNMg bond angle is about 123.7°).

There is a bent equilibrium conformation M2 on the $1^2A''$ potential energy surface (see Fig. 1). The energy of M2 is about 0.35 kcal mol^{-1} lower than the $A^2\Pi$ state of HNMg$^-$ and about 38.94 kcal mol^{-1} lower than the $X^2\Pi$ state of HMgN$^-$ at the CASPT2 level (see Table I). The CAS frequency calculation indicated that M2 has no imaginary frequency (see Table II). Therefore, the M2 is also a global minimum and the $A^2\Pi$ state of HNMg$^-$ should be the transition state of the isomerization reactions of M2↔M2. At the CAS level, the Mg–N and H–N bond lengths of M2 are 2.048 and 1.031 Å, respectively, and the HMgN bond angle is 15.7° (the HNMg bond angle is about 131.8°).

There are three bent transition states TS1, TS2, and TS3 along the PECs at the CAS geometry optimization level (see Fig. 1). They are all in C_s symmetry and in A', A'' and A' states, respectively. The CAS calculations indicated that they have a unique imaginary frequency. The CAS calculated HMgN bond angles of TS1, TS2 and TS3 are 69.9, 60.7 and 89.4°, respectively. In the next section, "Potential energy curves", it will be shown that the three transition states should be the transition states for the three different PECs of the isomerization reactions of HMgN$^–$ ↔ HNMg$^–$.

CASPT2/ANO geometry optimization calculations were also performed on all the stationary points (see Table I). The results showed that the CASPT2 optimized geometries of the stationary points are different from the CASSCF optimized geometries though the CASPT2//CASPT2 and CASPT2//CASSCF calculated relative energies are almost equal. The difference in the optimized bond lengths between the two methods is not larger than 0.07 Å and the difference in the bond angles is not larger than 3.1°. This is due to the absence of a dynamic electron correlation with the CASSCF method. The CASSCF calculated frequency results, which give the theoretical evidence for future analysis of the infrared spectrum of HMgN$^–$ and HNMg$^–$, are listed in Table II.

Potential energy curves

It was found that there are three surfaces ($1^2A'$, $1^2A''$ and $2^2A'$) on the isomerization reaction of the HMgN$^–$ ↔ HNMg$^–$ system. From Fig. 1, it can be seen that the shape of the $1^2A'$ curve is the same as that of the $1^2A''$ curve, *i.e.*, there is one minimum and one saddle point connecting the two linear structures. Along the $1^2A'$ curve, M1 connects with the $X^2\Pi$ state of HMgN$^–$ *via* the transition state TS1. The $X^2\Sigma^+$ state of HNMg$^–$ should be the transition state between the two same M1 structures. Along the $1^2A''$ curve, M2 connects with the $X^2\Pi$ state of HMgN$^–$ *via* the transition state TS2. The $A^2\Pi$ state of HNMg$^–$ should be the transition state between the two same M2 structures. On the $2^2A'$ curve, the $A^2\Pi$ state of HNMg$^–$ connects with the $A^2\Sigma^+$ state of HMgN$^–$ *via* the transition state TS3.

Based on the CASPT2 calculations, M1 is the mot stable conformation among all the stationary points; therefore, it is the global minimum. According to the CASPT2 calculated relative energies listed in Table I, the energy barrier for isomerization from M1 to the $X^2\Pi$ state of HMgN$^–$ on the $1^2A'$ curve is 66.84 kcal mol$^{–1}$, whereas the energy barrier in the reverse order is 24.19 kcal mol$^{–1}$. The CASPT2 energy barrier for isomerization from M1 to M1 is 1.25 kcal mol$^{–1}$.

Along the $1^2A''$ curve, the CASPT2 calculated energy barrier for isomerization from M2 to the $X^2\Pi$ state of HMgN$^–$ is 61.80 kcal mol$^{–1}$, whereas the energy barrier in the reverse order is 22.86 kcal mol$^{–1}$. The CASPT2 energy barrier for isomerization from M2 to M2 is 0.35 kcal mol$^{–1}$.

Along the $2^2A'$ curve, the CASPT2 calculated energy barrier for isomerization from the $A^2\Pi$ state of HNMg$^–$ to the $A^2\Sigma^+$ state of HMgN$^–$ is 85.38 kcal mol$^{–1}$, whereas the energy barrier in the reverse order is 36.07 kcal mol$^{–1}$. Therefore, the isomerization of the $A^2\Sigma^+$ state of HMgN$^–$ to the $A^2\Pi$ state of HNMg$^–$ is easier than in the reverse order.

As shown in Fig. 1 for the HMgN$^–$ ↔ HNMg$^–$ system, $1^2A'$ and $1^2A''$ are the two components of the Renner-splitting of the $X^2\Pi$ state of HMgN$^–$, and $1^2A''$

and $2^2A'$ are the two components of the Renner-splitting of the $A^2\Pi$ state of HNMg$^-$. The Renner-splitting pattern for the $X^2\Pi$ state of HMgN$^-$ is pattern (a) of the Pople and Longuet–Higgins Scheme,[15] and the Renner-splitting pattern for the $A^2\Pi$ state of HNMg$^-$ is pattern (b) of the Pople and Longuet–Higgins Scheme.[15]

CONCLUSIONS

HMgN$^-$ and HNMg$^-$ were studied for the first time by large-scale theoretical calculations using the CASSCF and CASPT2 methods in conjunction with the contracted atomic natural orbital (ANO) basis sets. The possible unimolecular conversions between HMgN$^-$ and HNMg$^-$ were discussed.

The geometries of all stationary points along the potential energy surfaces were optimized at the CASSCF/ANO level. The CASPT2/ANO potential energy curves of the isomerization reactions were calculated as functions of the HMgN bond angle. The CASPT2 calculations indicated that the ground and the first excited states of the linear HMgN$^-$ are the $X^2\Pi$ and $A^2\Sigma^+$ states, respectively; the ground and the first excited states of the linear HNMg$^-$ are the $X^2\Sigma^+$ and $A^2\Pi$ states, respectively. The $X^2\Sigma^+$ and $A^2\Pi$ states of HNMg$^-$ are first-order saddle points because they have a unique imaginary frequency. Two bent structures M1 and M2 were found along the $1^2A'$ and $1^2A''$ curves respectively. In addition, M1 and M2 are two global minima. The $X^2\Sigma^+$ state of HNMg$^-$ should be the transition state of the isomerazation reactions for M1 ↔ M1 and the $A^2\Pi$ state of HNMg$^-$ should be the transition state of the isomerazation reactions for M2 ↔ M2. Based on the calculated results, it was concluded that the ground-state of HMgN$^-$ is linear, while HNMg$^-$ is strongly bent in the ground state, which is in contradiction to the Walsh rules that predict linear structures for HXY systems containing 10 or less valency electrons.

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ИЗВОД

ТЕОРЕТСКО ПРЕДВИЂАЊЕ СТРУКТУРЕ HMgN$^-$ И HNMg$^-$ МУЛТИКОНФИГУРАЦИЈСКИМ МЕТОДАМА

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HMgN$^-$ и HNMg$^-$ са девет валентних електрона испитивани су по први пут теоретски, применом метода CASSCF i CASPT2 повезаним са ANO базичним сетом. Одређене су структуре најнижих електронских стања за HMgN$^-$ и HNMg$^-$. Разматрана је могућност унимолекулске конверзије HMgN$^-$ и HNMg$^-$. Резултати израчунавања указују на то да је основно стање HMgN$^-$ линеарно док је HNMg$^-$ савијен, што је супротно Walsh правилима која предвиђају да су сви HXY системи са 10 или мање валентних електрона линеарни.

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REFERENCES

1. A. D. Walsh, *J. Chem. Soc.* (1953) 2288
2. E. R. Talaty, Y. Huang, M. E. Zler, *J. Am. Chem. Soc.* **113** (1991) 779
3. W.-Z. Li, Y.-W. Pei, H.-J. Zhu, J.-B. Cheng, Q.-Z. Li, *Mol. Phys.* **109** (2011) 2671
4. W.-Z. Li, Y.-W. Pei, F.-F. Geng, J.-B. Cheng, Q.-Z. Li, B.-A. Gong, *Int. J. Quantum Chem.* **112** (2012) 2499
5. W.-Z. Li, Y.-W. Pei, C.-X. Sun, Q.-Z. Li, J.-B. Cheng, *Chem. Phys. Lett.* **532** (2012) 36
6. Y.-W. Pei, W.-Z. Li, Q.-Z. Li, J.-B. Cheng, *Comput. Theor. Chem.* **999** (2012) 126
7. W.-Z. Li, F.-F. Geng, Y.-W. Pei, J.-B. Cheng, Q.-Z. Li, B.-A. Gong, *Int. J. Quantum Chem.* **112** (2012) 1209
8. B. O. Roos, in *Advances in Chemical Physics: Ab Initio Methods in Quantum Chemistry*, Part 2, Vol. 69, K. P. Lawley, Ed., Wiley, Hoboken, NJ, 2007, p. 399
9. K. Andersson, P.-A. Malmqvist, B. O. Roos, A. J. Sadley, K. Wolinski, *J. Phys. Chem.* **94** (1990) 5483
10. K. Andersson, P.-A. Malmqvist, B. O. Roos, *J. Chem. Phys.* **96** (1992) 1218
11. F. Aquilante, L. De. Vico, N. Ferré, G. Ghigo, P-Å. Malmqvist, P. Neogrády, T. B. Pedersen, M. Pitoňák, M. Reiher, B. O. Roos, L. Serrano-Andrés, M. Urban, V. Veryazov, R. Lindh, *J. Comput. Chem.* **31** (2010) 224
12. J. Almlof, P. R. Taylor, *J. Chem. Phys.* **86** (1987) 4070
13. P. O. Widmark, P. A. Malmqvist, B. O. Roos, *Theor. Chim. Acta* **77** (1990) 291
14. P. O. Widmark, B. J. Persson, B. O. Roos, *Theor. Chim. Acta* **79** (1991) 419
15. J. A. Pople, H. C. Longuet-Higgins, *Mol. Phys.* **1** (1958) 372.