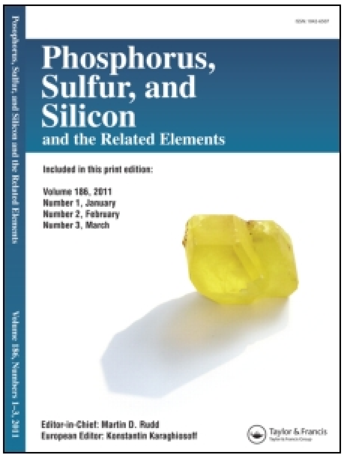


**Phosphorus, Sulfur, and Silicon and the Related Elements**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

# Maximizing the Solar Energy Storage of the Norbornadiene-Quadricyclane System: Mono-Heteroatom Effect by DFT Calculations

E. Vessally[a]
[a] Payame Noor University (PNU), Zanjan, Iran

**To cite this Article** Vessally, E.(2009) 'Maximizing the Solar Energy Storage of the Norbornadiene-Quadricyclane System: Mono-Heteroatom Effect by DFT Calculations', Phosphorus, Sulfur, and Silicon and the Related Elements, 184: 9, 2307 — 2313

**To link to this Article: DOI:** 10.1080/10426500802454037

**URL:** http://dx.doi.org/10.1080/10426500802454037

*Phosphorus, Sulfur, and Silicon*, 184:2307–2313, 2009
Copyright © Taylor & Francis Group, LLC
ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500802454037

Taylor & Francis
Taylor & Francis Group

# Maximizing the Solar Energy Storage of the Norbornadiene-Quadricyclane System: Mono-Heteroatom Effect by DFT Calculations

**E. Vessally**
Payame Noor University (PNU), Zanjan, Iran

*An attempt was made to maximize the solar energy storage in a norbornadiene (**1**)/quadricyclane (**2**) system, through the angling of mono-heteroatoms at $C_1$, $C_2$, or $C_7$ atoms of **1** and **2** and calculating the corresponding energies at the B3LYP/6-311++G(3df,2p) level of theory. Free energy gaps between $\mathbf{1}_{nX}$ and $\mathbf{2}_{nX}$, $\Delta G_{(1nx)\text{ - }(2nx)}$, as well as solar energy storage was the most for $\mathbf{1}_{1As}$ (–24.20), $\mathbf{1}_{2N}$ (–32.48), and $\mathbf{1}_{7As}$ (–29.77) in kcalmol$^{-1}$ from group V of the Periodic Table.*

**Keywords** Energy storage; mono-heteroatom effect; norbornadiene; quadricyclane; solar energy

## INTRODUCTION

Solving today's energy problems through the employment of environmentally safe "solar energy" has received much attention.[1] Intramolecular photochemical $[2\pi - 2\pi]$-cycloaddition of norbornadiene, **1**, to quadricyclane, **2**, has been studied from a mechanistic point of view.[2–4] The **1/2** system has been used for solar energy storage,[5–7] in molecular switching,[8–10] in optoelectronic devices,[11–14] as a data storage compound,[15,16] as photodynamic chemosensor for metal cations,[17,18] as a potential photoresponsive organic magnet,[19–21] and as an energetic binder for solid rocket propellants.[22] This system has an inherent disadvantage that **1** cannot absorb a visible wavelength of sunlight. Using sensitizers and chromophores are two improvements to solve this problem. An iridium complex has been proposed as the sensitizer for $\pi - \pi*$ excitation.[4] The donor-acceptor chromophores have been placed at the double bond of the norbornadiene molecule. The water soluble carbamoyl and carboxyl derivatives of **1** and **2** have also been used to absorb light of wavelengths longer than 300 nm.[23] Ab initio calculations

Received 8 July 2008; accepted 5 September 2008.

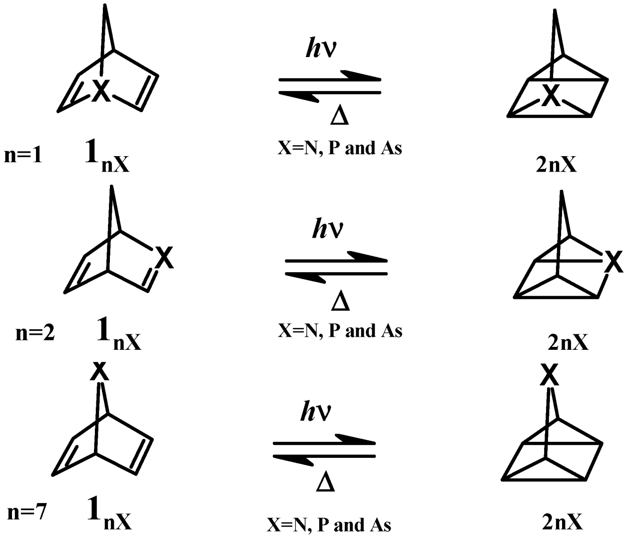
Address correspondence to E. Vessally, Payame Noor University (PNU), Postal Code 4513869987, Zanjan, Iran. E-mail: e_vesali@yahoo.com

have been used to study the energetics of **1** and **2** conversions.[4,24,25] Density functional calculations with the hybrid B3LYP function have been used to study the ground state of **1** bound to the photosensitizer [Cu(8-oxoquinolinato)].[26]

As a continuation of our research,[27,28] we studied the photochemical energy storage in the ground states of **1/2** system with exchanging of mono-heteroatoms at $C_1$, $C_2$, or $C_7$ atoms of **1** and **2**.

## COMPUTATIONAL METHODS

The molecular structures of norbornadienes ($\mathbf{1}_{nX}$) and quadricyclanes ($\mathbf{2}_{nX}$), shown in Scheme 1, were studied using ab initio methods. Geometry optimizations were carried out by HF and B3LYP[29,30] methods using 6-31G* basis set of the Gaussian 98 system of programs.[31] In order to find thermochemistry parameters including thermal energy (E), thermal enthalpy (H), and Gibbs free energy (G), keyword "Freq" was used. The Berny algorithm was employed for all minimizations using redundant internal coordinates.[32] For minimum state structures, only real frequency values were accepted. The calculations exhibit systematic errors and thus benefit from scaling. Thermodynamic functions, obtained through frequency calculations, were multiplied by a Hehre et al.[33] scaling factor of 0.89 for HF; and by 0.99 scaling factor of Rauhut



**SCHEME 1** Storage of solar energy in norbornadiene ($\mathbf{1}_{nX}$)/quadricyclane ($\mathbf{2}_{nX}$) system; where n = 1, 2 or 7 and X = N, P, and As.

and Pulay[34] for B3LYP. This is to account for the difference between the harmonic vibrational calculations and the anharmonic oscillations of the actual bonds.

## RESULTS AND DISCUSSION

Recently we have reported theoretical investigations on the electronic effects involved in the solar energy storage, for substituents "indirectly" attached to the $C_2$ of **1** and/or **2**, and "direct" attachment of the substituents at $C_1$, $C_2$, or $C_7$ atoms of **1** and **2**.[27,28] However, the effects of exchanging the "heteroatom" at $C_1$, $C_2$, or $C_7$ of **1** and **2**, which appear of "practical interest" to those whose primary goal is to replace fossil fuel and/or nuclear energy with the most economical and very available solar energy, have been not investigated. In this manuscript we studied the photochemical energy storage in the ground states of the **1/2** system with exchanging of the heteroatom at $C_1$, $C_2$, or $C_7$ of **1** and **2**.

The zero-point energies (ZPE), thermal and electronic energies (E), enthalpies (H), and Gibbs free energies (G) for optimized structures of $\mathbf{1}_{nX}$ and $\mathbf{2}_{nX}$ (X = N, P, As; X is a heteroatom that replaced carbons $C_1$, $C_2$, or $C_7$: **n** = 1, 2 or 7, respectively) were calculated at B3LYP/6-31+G* and B3LYP/6-311++G(3df,2p) levels of theory. Considering the size of molecules probed and the consistency of the results obtained, these ab initio levels are considered to be appropriate. For the sake of brevity, only the data acquired through the highest level of theory (B3LYP/6-311++G(3df,2p)) is reported (Table I). All calculations were presented for the phase. However, the aggregative state of the compounds in which form they might be employed for solar energy storage is liquid. The pressure and temperature of calculations are 1 atmosphere and 298 K, respectively. B3LYP/6-311++G(3df, 2p) calculations indicated that the stability of all norbornadienes, $\mathbf{1}_{nX}$, seem to be more than their corresponding quadricyclanes, $\mathbf{2}_{nX}$. Also, the stablity of $\mathbf{1}_{nX}$ is the most when the N atom is attached at $C_2$ carbon (X = N, n = 2), and the least when N atom is attached at $C_1$ carbon atom (X = N, n = 7) (Table I). However, the stablity of $\mathbf{1}_{nX}$ is the most when the P and As atoms are attached at $C_1$ carbon (X = P and As; n = 1), and the least when N atom is attached at $C_2$ carbon atom (X = N, n = 2) (Table I). Morever, the stablity of $\mathbf{2}_{nX}$ is the most when the X atoms (X = N, P, and As) are attached at $C_2$ carbon (n = 2), and the least when X atoms are attached at $C_7$ carbon atom (n = 7) (Table I). The stability of $\mathbf{2}_{nX}$ by replacing of heteroatoms X (X = N, P, and As) at cyclopropyl rings is mostly explained by the Walsh orbital model, where cyclopropyl rings may act both as good $\pi$ donors and good $\pi$ acceptors.[27,35]

**TABLE I The B3LYP/6-311++G(3df,2p) Zero-Point Energies (ZPE), Thermal and Electronic Energies (E), Enthalpies (H), and Gibbs Free Energies (G), in kcalmol$^{-1}$, for Optimized Norbornadienes ($1_{nX}$) and Quadricyclanes ($2_{nX}$); Where n = 1, 2, or 7, while X = N, P, and As**

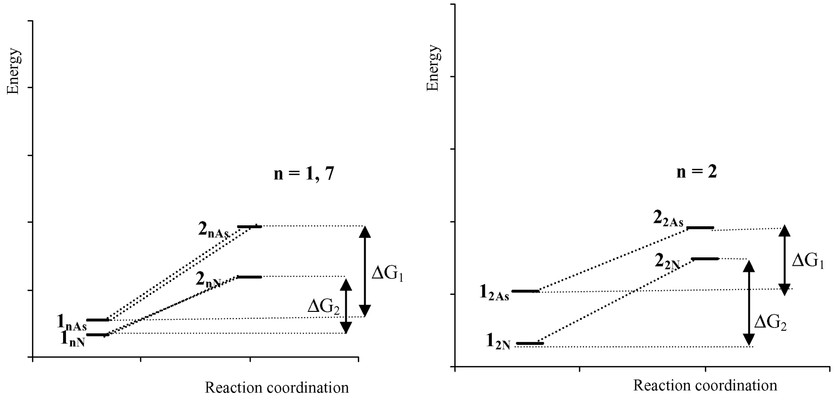
| nX (n = 1, 2, 7) | ZPE/kcalmol$^{-1}$ | E/kcalmol$^{-1}$ | H/kcalmol$^{-1}$ | G/kcalmol$^{-1}$ |
|---|---|---|---|---|
| | | $1_{n-X}$ | | |
| **1-N** | −178511.68 | −178508.72 | −178508.14 | −178529.10 |
| **1-P** | −356597.40 | −356593.99 | −356593.40 | −356615.44 |
| **1-As** | −1533509.51 | −1533505.85 | −1533505.26 | −1533528.21 |
| **2-N** | −178532.39 | −178529.46 | −178528.87 | −178549.81 |
| **2-P** | −356589.42 | −356586.13 | −356585.54 | −356607.45 |
| **2-As** | −1533500.30 | −1533496.83 | −1533496.25 | −1533519.01 |
| **7-N** | −178517.42 | −178514.44 | −178513.85 | −178534.86 |
| **7-P** | −356588.10 | −356584.73 | −356584.15 | −356606.12 |
| **7-As** | −1533501.47 | −1533497.88 | −1533497.29 | −1533520.18 |
| | | $2_{n-X}$ | | |
| | ZPE/kcalmol$^{-1}$ | E/kcalmol$^{-1}$ | H/kcalmol$^{-1}$ | G/kcalmol$^{-1}$ |
| **1-N** | −178498.96 | −178496.17 | −178495.59 | −178516.24 |
| **1-P** | −356574.00 | −356570.81 | −356570.23 | −356591.88 |
| **1-As** | −1533485.43 | −1533482.02 | −1533481.43 | −1533504.00 |
| **2-N** | −178500.04 | −178497.25 | −178496.66 | −178517.33 |
| **2-P** | −356580.76 | −356577.63 | −356577.04 | −356598.61 |
| **2-As** | −1533493.89 | −1533490.55 | −1533489.96 | −1533512.41 |
| **7-N** | −178497.92 | −178495.15 | −178494.56 | −178515.17 |
| **7-P** | −356562.34 | −356559.17 | −356558.59 | −356580.24 |
| **7-As** | −1533471.84 | −1533468.46 | −1533467.88 | −1533490.41 |

The extent of the solar energy stored in this system is measured simply by calculating the energy difference between the ground states of $\mathbf{1}_{nX}$ and $\mathbf{2}_{nX}$. Evidently, there was no practical need to consider the excited states and/or the type(s) of the mechanism involved. Thermal energy separations, $\Delta\ E_{(1nx)-(2nx)}$, enthalpy gaps, $\Delta\ H_{(1nx)-(2nx)}$, and free energy splittings, $\Delta\ G_{(1nx)-(2nx)}$, in kcal mol$^{-1}$, between norbornadienes ($\mathbf{1}_{nX}$) and their corresponding quadricyclanes ($\mathbf{2}_{nX}$) was presented using B3LYP/6-311++G(3df,2p) level of theory (Table II). Free energy gaps between $\mathbf{1}_{1X}$ and $\mathbf{2}_{1X}$, $\Delta\ G_{(11x)-(21x)}$, were increased from X = N to X = As (Table II), while free energy gaps between $\mathbf{1}_{2X}$ and $\mathbf{2}_{2X}$, $\Delta\ G_{(12x)-(22x)}$, were decreased from X = N to X = As (Table II). Furthermore, free energy gaps between $\mathbf{1}_{7X}$ and $\mathbf{2}_{7X}$, $\Delta\ G_{(17x)-(27x)}$, increased from X = N to X = As (Table II). Calculated free energy gaps between $\mathbf{1}_{nX}$ and $\mathbf{2}_{nX}$, $\Delta\ G_{(1nx)-(2nx)}$, indicate the extent of the solar energy storage in norbornadienes ($\mathbf{1}_{nX}$), and their corresponding quadricyclanes ($\mathbf{2}_{nX}$)

**TABLE II The B3LYP/6-311++G(3df,2p) Calculated Zero-Point Energy Gaps, Δ $ZPE_{(1nx)-(2nx)}$, Thermal Energy Gaps, Δ $E_{(1nx)-(2nx)}$, Enthalpy Gaps, Δ $H_{(1nx)-(2nx)}$, and Free Energy Gaps, Δ $G_{(1nx)-(2nx)}$, in $kcalmol^{-1}$, Between Norbornadienes ($1_{nX}$) and Their Corresponding Quadricyclanes ($2_{nX}$); Where n = 1, 2, or 7 and X = N, P, and As**

| | B3LYP/6-311++G* | | | |
|---|---|---|---|---|
| nX (n = 1, 2, or 7) | $\Delta ZPE_{(1nx)-(2nx)}$ | $\Delta E_{(1nx)-(2nx)}$ | $\Delta H_{(1nx)-(2nx)}$ | $\Delta G_{(1nx)-(2nx)}$ |
| **1-N** | −12.72 | −12.55 | −12.55 | −12.86 |
| **1-P** | −23.40 | −23.17 | −23.17 | −23.56 |
| **1-As** | −24.07 | −23.83 | −23.83 | −24.20 |
| **2-N** | −32.35 | −32.21 | −32.21 | −32.48 |
| **2-P** | −8.65 | −8.50 | −8.50 | −8.85 |
| **2-As** | −6.41 | −6.29 | −6.29 | −6.60 |
| **7-N** | −19.50 | −19.29 | −19.29 | −19.69 |
| **7-P** | −25.75 | −25.56 | −25.56 | −25.89 |
| **7-As** | −29.63 | −29.41 | −29.41 | −29.77 |

system. Therefore, the extent of solar energy storage is the most for $\mathbf{1}_{1As}$ (–24.20 $kcalmol^{-1}$),$\mathbf{1}_{2N}$ (–32.48 $kcalmol^{-1}$), and $\mathbf{1}_{7As}$ (–29.77 $kcalmol^{-1}$) by replacing of heteroatoms at carbons $C_1$, $C_2$, or $C_7$ at the B3LYP/6-311++G(3df,2p) level, respectively. The highest calculated free energy gaps, Δ $G_{(1nx)-(2nx)}$, between $\mathbf{1}_{nX}$ and $\mathbf{2}_{nX}$, could be related to stability and/or instability of each $\mathbf{1}_{nX}$ and/or $\mathbf{2}_{nX}$. However, we could not conveniently compare the absolute energies for compounds with different molecular formulae. The stability and/or instability each of $\mathbf{1}_{nX}$ and/or $\mathbf{2}_{nX}$ may be described through comparison of their corresponding relative energies (Table I). By comparison of relative energies, one could conclude that the highest Δ $G_{(1nx)-(2nx)}$ (in where n = 1 or 7) is attributed to raise the stability of Gibbs free energy of $\mathbf{1}_{1X}$ and$\mathbf{1}_{7X}$ from X = N to X = As more than for $\mathbf{2}_{1X}$ and $\mathbf{2}_{7X}$, respectively (Figure 1a). While, the highest Δ $G_{(1nx)-(2nx)}$ (in where n = 2) is attributed to increase the stability of Gibbs free energy for $\mathbf{1}_{2X}$ from X = As to X = N more than for $\mathbf{2}_{2X}$ (Figure 1b). Increasing the stability of Gibbs free energy of $\mathbf{1}_{2X}$ from X = As to X = N is related to the instability of $\mathbf{1}_{2X}$ when X is P and As. The instability of $\mathbf{1}_{2X}$ with replacing of heavy atoms has been reported by Kutzelnigg[36]: "Single bonds between first row elements are weak and multiple bonds are strong, whereas for the second or higher row elements single bonds are strong and multiple bonds weak." Therefore, P and As atoms construct weak double bonds and lead to instability compounds of $\mathbf{1}_{2P}$ and $\mathbf{1}_{2As}$.



(a) (b)

**FIGURE 1** Reaction coordinate diagram for norbornadienes ($\mathbf{1}_{nX}$) and quadricyclanes ($\mathbf{2}_{nX}$): (a) n = 1, 7; (b) n = 2.

## CONCLUSION

DFT calculations were carried out to maximize the solar energy storage in the norbornadiene (**1**)/quadricyclane (**2**) system, through the exhange of mono-heteroatoms at $C_1$, $C_2$, or $C_7$ atoms of **1** and **2**, and calculating the corresponding energies at the B3LYP/6-311++G(3df,2p) level of theory. Free energy gaps between $\mathbf{1}_{nX}$ and $\mathbf{2}_{nX}$, $\Delta\ G_{(1nx)-(2nx)}$, or solar energy storage were the most for $\mathbf{1}_{1As}$ (–24.20),$\mathbf{1}_{2N}$ (–32.48), and $\mathbf{1}_{7As}$ (–29.77) in kcalmol$^{-1}$ from group V of the Periodic Table. The highest $\Delta\ G_{(1nx)-(2nx)}$ (in where n = 1 or 7) is attributed to an increase in the stability of Gibbs free energy of $\mathbf{1}_{1X}$ and$\mathbf{1}_{7X}$ from X = N to X = As more than for $\mathbf{2}_{1X}$ and $\mathbf{2}_{7X}$, respectively (Figure 1), while, the highest $\Delta\ G_{(1nx)-(2nx)}$ (in where n = 2) is attributed to increasing the stability of the Gibbs free energy for $\mathbf{1}_{2X}$ from X = As toward X = N more than for $\mathbf{2}_{2X}$.

## REFERENCES

[1] A. M. Helms and R. A. Caldwell, *J. Am. Chem. Soc.*, **117,** 358 (1995).
[2] W. Fub, K. K. Pushpa, and W. E. Schmid, *Photochem. Photobiol. Sci.*, **1,** 60 (2002).
[3] R. D. Bach, I. L. Schilke, and H. B. Schlegel, *J. Org. Chem.*, **61,** 4845 (1996).
[4] Y. Inadomi, K. Morihashi, and O. Kikuchi, *J. Mol. Struct.*, **434,** 59 (1998).
[5] R. R. Hautala, R. B. King, and C. Kutal, *Solar Energy: Chemical Conversion and Storage* (Humana Press, Clifton, NJ, 1979), p. 333.
[6] V. A. Bren, A. D. Dubonosov, V. I. Minkin, and V. A. Chernoivanov, *Russ. Chem. Rev.*, **60,** 451 (1991).
[7] A. Cox, *Photochemistry*, **30,** 389 (1999).

[8] P. Laine, V. Marvaud, A. Gourdon, J. P. Launnay, R. Argazzi, and C. A. Bignozzi, *Inorg. Chem*., **35,** 711 (1996).

[9] E. E. Bonfantini and D. L. Officer, *J. Chem. Soc., Chem. Commun*., 1445 (1994).

[10] S. Fraysse, C. Coudret, and J. P. Launay, *Eur. J. Org. Chem*., 1582 (2000).

[11] S. Takahashi, K. Samata, H. Muta, S. Machida, and K. Horie, *Appl. Phys. Lett*., **78,** 13 (2001).

[12] K. Horie, T. Nishikubo, K. Kinoshita, S. Morino, S. Machida, and S. Yamashita, *Jpn. Kokai Tokkyo Koho*, IP 10448727 A2 (1998).

[13] S. Morino, T. Watanabe, Y. Magaya, K. Horie, and T. Nishikubo, *J. Photopolymer. Sci. Technol*., **7,** 121 (1994).

[14] S. Morino and K. Horie, *ACS Symp. Ser*., **672,** 260 (1997).

[15] H. Nishino and Y. Inoue, *Jpn. Kokai Tokkyo Koho*, IP 2000086588 (2000).

[16] S. Miki, Y. Asako, and Z. Yoshida, *Chem. Lett*., **16,** 195 (1987).

[17] F. Strack, P. G. Jones, and R. Herges, *Eur. J. Org. Chem*., 2533 (1998).

[18] R. Herges and W. Reif, *Liebigs Ann. Chem*., 761 (1996).

[19] S. Nakatsuji, S. Takeuchi, T. Ojima, Y. Ogawa, H. Akutsu, and J. Yamada, *Mol. Cryst. Liq. Cryst. Sci. Technol. Sect. A*, **356,** 23 (2001).

[20] S. Takeuchi, Y. Ogawa, A. Naito, K. Sudo, N. Yasuoka, H. Akutsu, and S. Nakatsuji, *Mol. Cryst. Liq. Cryst. Sci. Technol. Sect. A*, **345,** 167 (2000).

[21] S. Nakatsuji, Y. Ogawa, S. Takeuchi, H. Akutsu, J. Yamada, A. Naito, K. Sudo, and N. Yasuoka, *J. Chem. Soc. Perkin Trans*. 2, 1969 (2000).

[22] M. E. Wright, G. D. Allred, R. B. Wardle, and L. F. Cannizzo, *J. Org. Chem*., **58,** 4122 (1993).

[23] T. Nagai, I. Takahashi, and T. Nishikuboy, *Chem. Lett*., **32,** 754 (2003).

[24] D. W. Rogers and F. J. McLafferty, *J. Phys. Chem. A*, **103,** 8733 (1999).

[25] K. Raghavachari, R. C. Haddon, and H. D. Roth, *J. Am. Chem. Soc*., **105,** 3110 (1983).

[26] M. Rosi and A. Sgamellotti, *Inorg. Chem*., **38,** 1520 (1999).

[27] M. Z. Kassaee and E. Vessally, *J. Mol. Struct. (Theochem)*, **716,** 159 (2005).

[28] M.Z. Kassaee, E. Vessally, and S. Arshadi, *J. Mol. Struct. (Theochem)*, **801,** 1200 (2006).

[29] C. Lee, W. Yang, and R. G. Parr, *Phys. Rev. B*, **37,** 785 (1988).

[30] A. D. Becke, *J. Chem. Phys*., **98,** 5648 (1993).

[31] M. J. Frisch et. al., GAUSSIAN 98, Revision A. 6, Gaussian Inc., Pittsburgh, PA (1998).

[32] C. Peng, P. Y. Ayala, H. B. Schlegel, and M. J. Frisch, *J. Comp. Chem*., **17,** 49 (1996).

[33] R. F. Hout Jr., B. A. Levi, and W. J. Hehre, *J. Comput. Chem*., **3,** 234 (1982).

[34] G. Rauhut and P. J. Pulay, *Phys. Chem*., **99,** 3093 (1995).

[35] A. D. Walsh, *Trans. Faraday Soc*., **45,** 179 (1949).

[36] W. Kutzelnigg, *Angewandte*, **84,** 1578 (1984).