

Reversible Migrations of Nitro Group in a Methyltetramethoxycarbonylcyclopentadiene System

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Abstract—Quantum chemical calculations by the density functional theory method at the B3LYP/6-311++G** level have shown that 5-nitro-5-methyl-1,2,3,4-tetramethoxycarbonylcyclopentadiene (**1**) and 5-nitro-2-methyl-1,3,4,5-tetramethoxycarbonylcyclopentadiene (**2**) undergo interconversion by consecutive 1,5-sigmatropic shifts via the formation of an unstable isomer, 5-nitro-1-methyl-2,3,4,5-tetramethoxycarbonylcyclopentadiene (**3**), rather than through the NMR-detected 1,3-shift of the nitro group over the cyclopentadiene ring perimeter. According to calculations in the gas phase, isomer **3** is by ΔE_{ZPE} of 3.6 kcal/mol less stable than isomer **1**, while the activation barrier of the stepwise **1** → **2** process is 24.5 kcal/mol, which agrees well with NMR data (ΔG_{25C}^\ddagger , chlorobenzene, 26.5 kcal/mol).

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Acid-catalyzed rearrangements of derivatives of *N*-nitroaniline, *N*-nitroindazoles, triazoles, imidazoles, carbazoles, and aromatic nitro compounds including irreversible shifts of nitro group are widely used in organic synthesis [1]. The examples of reversible nitro group shifts are very few in number and are limited to migrations in the systems of substituted cyclopentadienes and benzenonium ions [2–5]. Similar structurally flexible cyclopolyenes can be considered as prototypes of molecular rotor motors due to reversible circular migrations of organoelement groups over the ring perimeter [6–10].

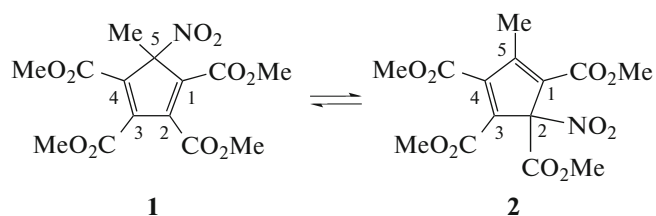
Experimental data on the migrations of nitro group in the ring of substituted cyclopentadienes provide no possibility to establish their exact mechanisms, which can be associated with 1,3- and 1,5-sigmatropic shifts of nitro group or dissociation via intermediate formation of a tight ion pair.

In this work, we studied possible reaction routes for nitro group migrations in the methyltetramethoxycarbonylcyclopentadiene system in the gas phase to establish the noted mechanisms by means of density functional theory (DFT) B3LYP/6-311++G(d,p) calculations.

Isomeric 5-nitro-5-methyl-1,2,3,4-tetramethoxycarbonylcyclopentadiene (**1**) and 5-nitro-2-methyl-1,3,4,5-tetramethoxycarbonylcyclopentadiene (**2**, Scheme 1) were synthesized by us previously [2] in a 0.55 : 0.45 ratio by the nitration of the corresponding cyclopentadiene with concentrated nitric acid in acetic anhydride at -50°C and were separated by low-temperature crystallization, while their crystal structure was proved by X-ray diffraction analysis.

We found by ^1H NMR that isomers **1** and **2** undergo interconversion in chlorobenzene at 80°C reaching the equilibrium ratio **1** : **2** = 0.85 : 0.15 in several minutes with activation barriers ΔG_{25C}^\ddagger 26.5 (**1** → **2**) and 25.4 (**2** → **1**) kcal/mol (Scheme 1).

According to ^1H NMR, the interconversion of isomers **1** and **2** occurs as a 1,3-shift of nitro group along the cyclopentadiene ring perimeter (Scheme 1). This process may be a result of the alternative rearrangement mechanism caused by consecutive 1,5-sigmatropic shifts of nitro group with intermediate forma-

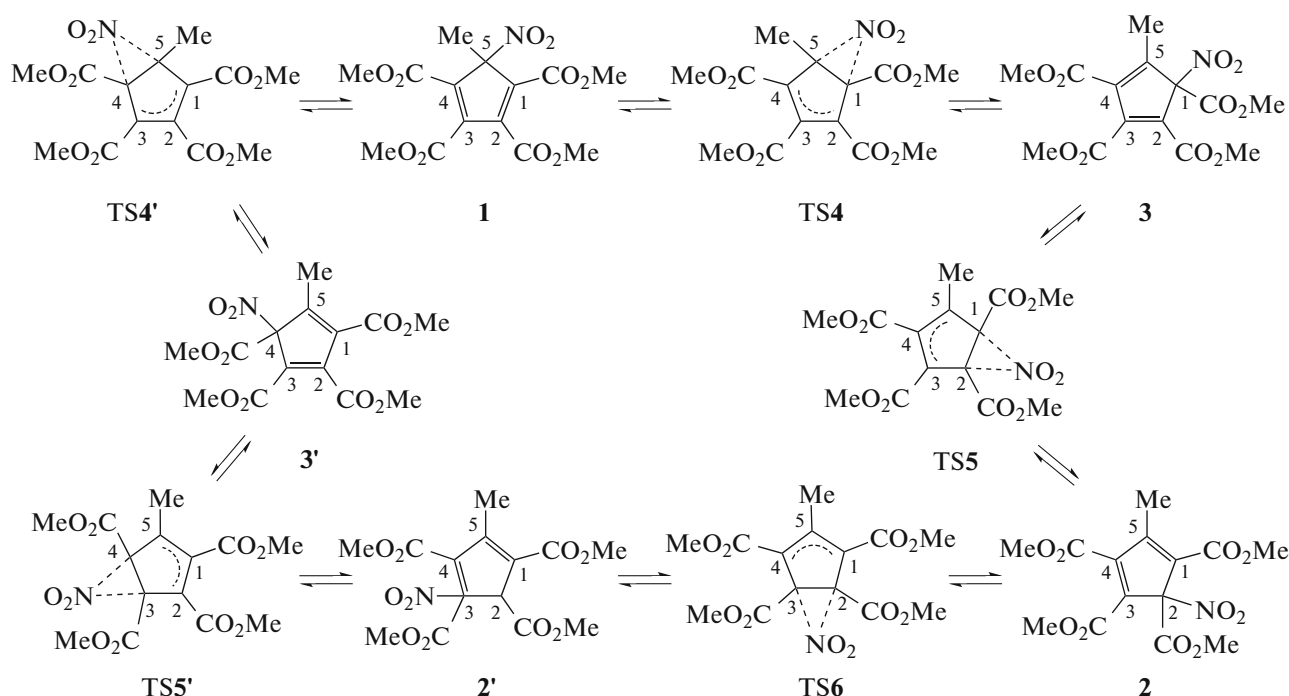


Scheme 1.

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Scheme 2.

tion of a less stable isomer, 5-nitro-1-methyl-2,3,4,5-tetramethoxycarbonylcyclopentadiene (**3**) (Scheme 2).

Quantum chemical calculations were performed by the DFT method [15] with the three-parameter B3LYP potential with the split-valence basis set 6-311++G(d,p) in the gas phase using the Gaussian-09 software package. All stationary points were identified by calculation of the Hessian matrix. Charges on atoms were calculated by the NBO scheme.

Table 1. Total (E_{total}) and relative energies of ground state structures **1–3** and transition states of sigmatropic shifts of nitro group **TS4–TS6** calculated by the B3LYP/6-311++G(d,p) method in the gas phase

Structure	E_{total} , au	ΔE_{ZPE} , kcal/mol	ω_1 , cm^{-1}
1	-1349.80181	0	31
1A	-1349.79968	1.3	19
2	-1349.79842	1.6	18
3	-1349.79546	3.6	29
TS4	-1349.76723	19.7	-273
TS5	-1349.75892	24.5	-323
TS6	-1349.76440	21.4	-244

E_{total} is the total energy, 1 au = 627.5095 kcal/mol; ΔE_{ZPE} is the relative energy corrected for the zero point energy; ω_1 , cm^{-1} is the lowest harmonic vibrational frequency or the value of the sole imaginary harmonic vibrational frequency; $E_{\text{ZPE}} = -1349.50911$ (**1**).

According to quantum chemical calculations in the gas phase, isomers **1–3** correspond to minima on the potential energy surface (PES). Isomers **1** and **2** are very close in stability ($\Delta E_{\text{ZPE}} = 1.6$ kcal/mol), while isomer **3** is less stable than **1** at $\Delta E_{\text{ZPE}} = 3.6$ kcal/mol (Table 1, Fig. 1, Scheme 2), which explains the lack of signals of isomer **3** in ^1H NMR spectra of nitromethyltetramethoxycarbonylcyclopentadiene owing to its low equilibrium content. The calculated geometrical parameters of structure **2** correspond to X-ray diffraction data [2]. 5-Nitro-5-methyl-1,2,3,4-tetramethoxycarbonylcyclopentadiene in the solid state has structure **1A** (Table 1, Fig. 1), which differs from **1** by the values of torsion angles of methoxycarbonyl substituents due to molecule packing effects in crystal, structure **1A** being energetically less favorable than **1** at $\Delta E_{\text{ZPE}} = 1.3$ kcal/mol.

Transition states **TS4–TS6** of symmetry C_1 corresponding to interconversions of isomers **1–3** through 1,5-sigmatropic shifts of the nitro group along the five-membered ring perimeter are localized on the reaction PES (Scheme 2, Fig. 2). Bond lengths between the migrating nitrogen atom and the carbon atoms of the five-membered ring in **TS4–TS6** are within 2.226–2.304 Å. The values of total charges on the nitro group (0e in **TS4**; 0.009e in **TS5**; and 0.017e in **TS6**) indicate the lack of charge separation between the migrant and the system, which is typical for sigmatropic shifts.

Transition states corresponding to 1,3-sigmatropic shifts of the nitro group and the dissociation process

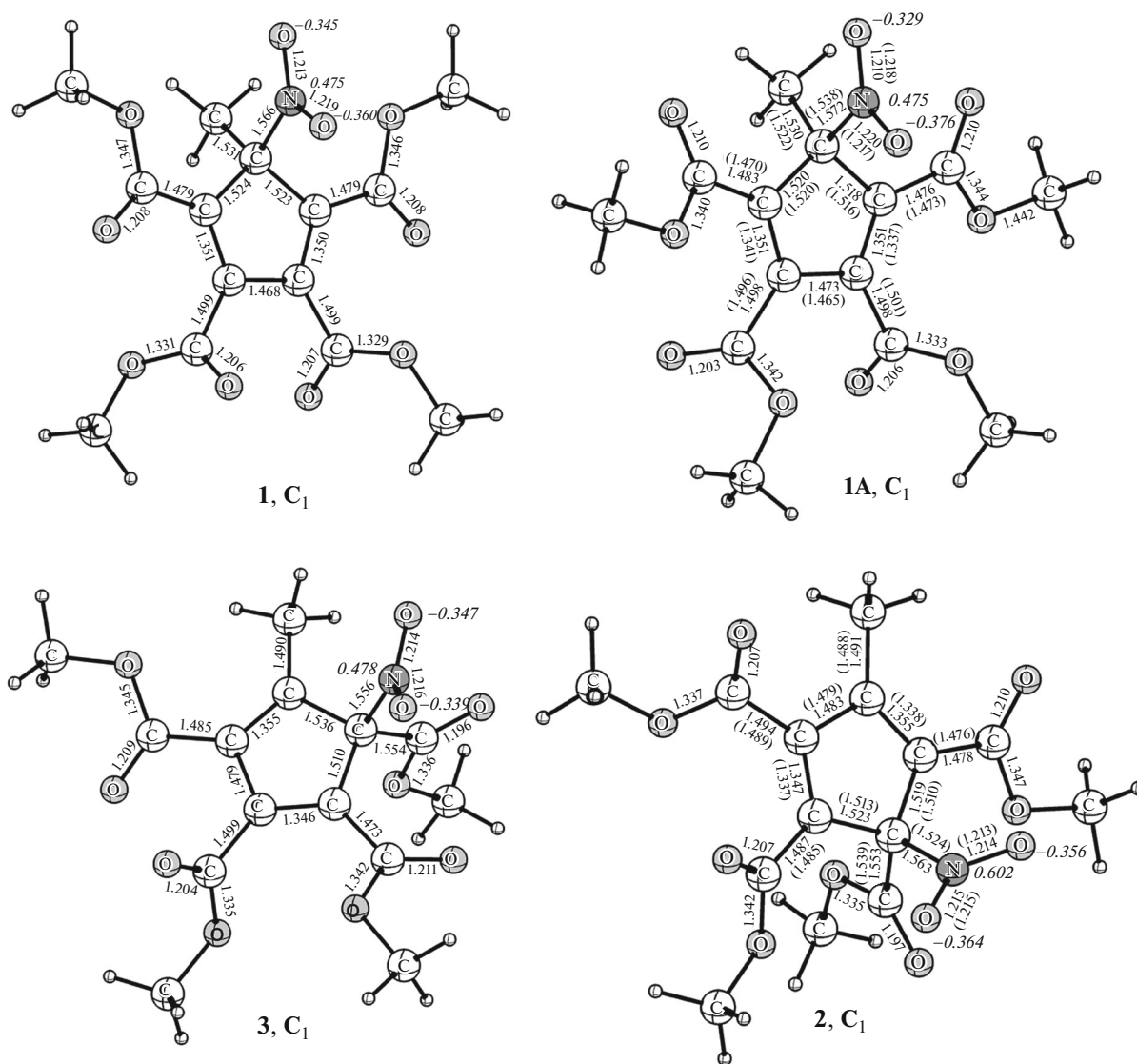


Fig. 1. B3LYP/6-311++G(d,p) geometrical parameters and charges (marked by italic) for ground state structures **1–3** and **1A** in the gas phase. Hereinafter, bond distances are given in angstroms. X-ray diffraction data for **1A** and **2** are shown in parentheses like in [2].

were not revealed on the PES, which indicates that these rearrangement mechanisms are impracticable.

The calculated energy barriers for the reversible consecutive 1,5-sigmatropic shifts of the nitro group along the five-membered ring perimeter are within ΔE_{ZPE}^\ddagger 16.1–22.9 kcal/mol (Table 1, Scheme 3).

Scheme 3 displays the energy profile of nitro group migrations over the methyltetramethoxycarbonylcyclopentadiene ring perimeter $\mathbf{1} \rightleftharpoons \text{TS4} \rightleftharpoons \mathbf{3} \rightleftharpoons \text{TS5} \rightleftharpoons \mathbf{2} \rightleftharpoons \text{TS6} \rightleftharpoons \mathbf{2}' \rightleftharpoons \text{TS5}' \rightleftharpoons \mathbf{3}' \rightleftharpoons \text{TS4}' \rightleftharpoons \mathbf{1}$ resulting in interconversion of isomers **1** and **2** through the formation of intermediate isomer **3**.

The experimental temperature-dependent ^1H NMR spectra of nitrocyclopentadienes **1** and **2** [2] reflect the overall process of consecutive 1,5-shifts of

nitro group; therefore, the energy difference between the most stable isomer **1** and the highest-energy **TS5** corresponds to the activation barrier of the stepwise $\mathbf{1} \rightarrow \mathbf{2}$ process and constitutes 24.5 kcal/mol according to calculations in the gas phase. Calculation data agree well with the ^1H NMR experiment for compounds **1** and **2** ($\mathbf{1} \rightarrow \mathbf{2}$, $\Delta G_{25\text{C}}^\ddagger$, chlorobenzene, 26.5 kcal/mol) and confirm the mechanism of 1,5-sigmatropic shifts of nitro group by Scheme 2 in accordance with the orbital symmetry conservation rules.

It is worth noting that, in cyclopolyene systems, the migrations of nitrogen-centered groups—aryldiazo group, iso(thio, seleno)cyanate groups, amidinyl groups, and N-phthalimido groups—proceed by dis-

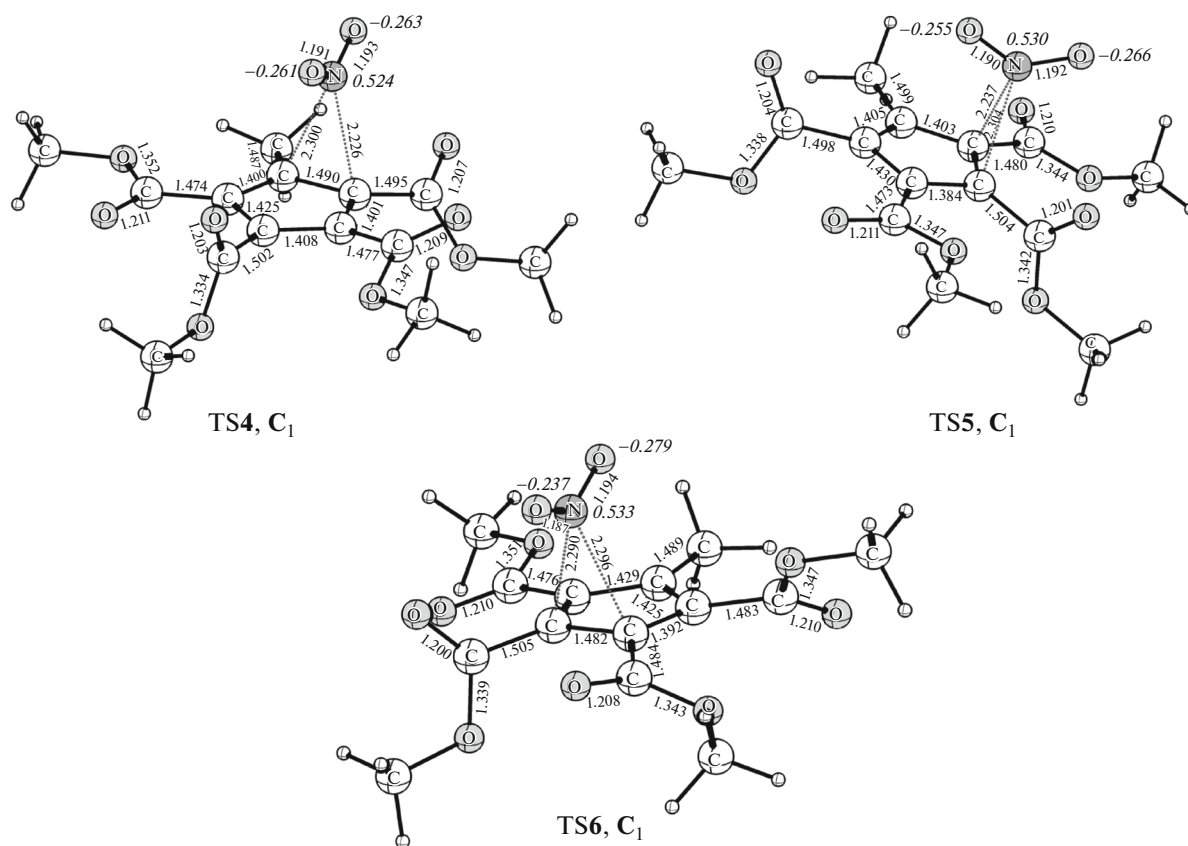
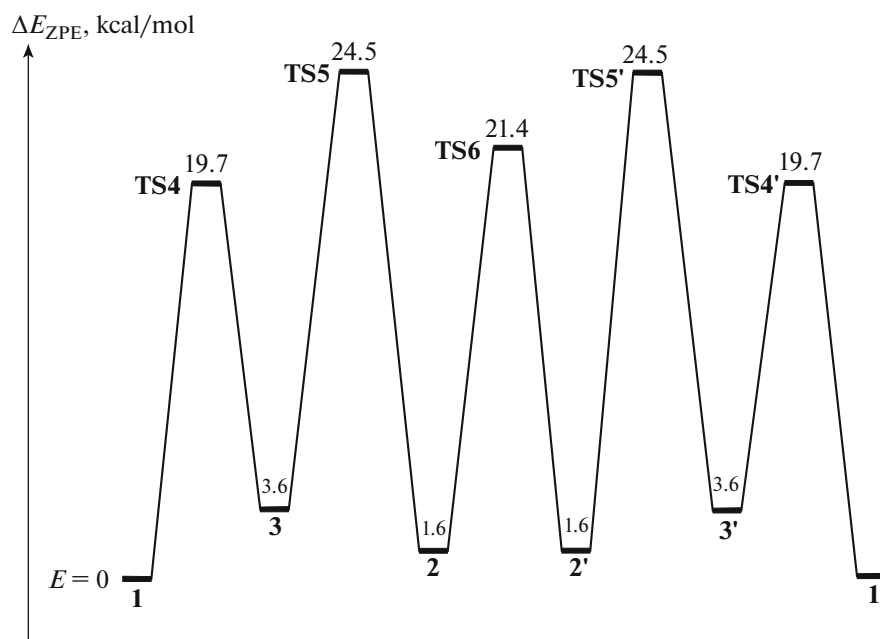


Fig. 2. B3LYP/6-311++G(d,p) geometrical parameters and charges (marked by italic) for transition state structures **TS4**–**TS6** for 1,5-shifts of nitro group in the gas phase.



Scheme 3.

sociation–recombination mechanisms via formation of tight ion pairs or 3,3-sigmatropic shift [11–14].

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REFERENCES

- Williams, D.L.H., in *The Chemistry of Amino, Nitroso, Nitro and Related Groups*, Patai S., Ed., Chichester: Wiley, 1996.
- Mikhailov, I.E., Kompan, O.E., Struchkov, Yu.T., Minkin, V.I., Dushenko, G.A., Klenkin, A.A., and Olekhovich, L.P., *Zh. Org. Khim.*, 1987, vol. 23, no. 5, pp. 1029–1038.
- Mikhailov, I.E., Dushenko, G.A., Zhdanov, Yu.A., Olekhovich, L.P., and Minkin, V.I., *Dokl. Akad. Nauk SSSR*, 1984, vol. 275, no. 6, pp. 1431–1434.
- Borodkin, G.I., Susharin, E.R., Shakirov, M.M., and Shubin, V.G., *Izv. Akad. Nauk, Ser. Khim.*, 1985, no. 12, pp. 2797–2800.
- Loktev, V.F., Korchagina, D.V., and Shubin, V.G., *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim.*, 1980, vol. 14, no. 6, p. 86.
- Gridnev, I.D. and Rosario, M.K.C., *Organometallics*, 2005, vol. 24, pp. 4519–4527.
- Bulo, R.E., Allaart, F., Ehlers, A.W., de Kanter, F.J.J., Schakel, M., Lutz, M., Spek, A.L., and Lammertsma, K., *J. Am. Chem. Soc.*, 2006, vol. 128, pp. 12169–12173.
- Erbas-Cakmak, S., Leigh, D.A., McTernan, C.T., and Nussbaumer, A.L., *Chem. Rev.*, 2015, vol. 115, no. 18, pp. 10081–10206.
- Minkin, V.I., Mikhailov, I.E., Dushenko, G.A., and Zschunke, A., *Usp. Khim.*, 2003, vol. 72, no. 10, pp. 978–1010.
- Dushenko, G.A., Mikhailov, I.E., Mikhailova, O.I., Minyaev, R.M., and Minkin, V.I., *Mendeleev Commun.*, 2015, vol. 25, no. 1, pp. 21–23.
- Dushenko, G.A., Mikhailov, I.E., Dorogan, I.V., Minyaev, R.M., Zschunke, A., and Minkin, V.I., *Mendeleev Commun.*, 1995, vol. 5, no. 6, pp. 213–215.
- Dushenko, G.A., Mikhailov, I.E., Zschunke, A., Reck, G., Schulz, B., and Minkin, V.I., *Mendeleev Commun.*, 1999, vol. 9, no. 6, pp. 222–225.
- Minkin, V.I., Mikhailov, I.E., Dushenko, G.A., Kompan, O.E., and Zschunke, A., *Russ. Chem. Bull.*, 1998, vol. 47, no. 5, pp. 884–894.
- Minkin, V.I., Mikhailov, I.E., and Dushenko, G.A., *J. Chem. Soc., Chem. Commun.*, 1988, no. 17, pp. 1181–1182.
- Foresman, J.B. and Frisch, E., *Exploring Chemistry with Electronic Structure Methods*, Pittsburgh: Gaussian, Inc., 1996.

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