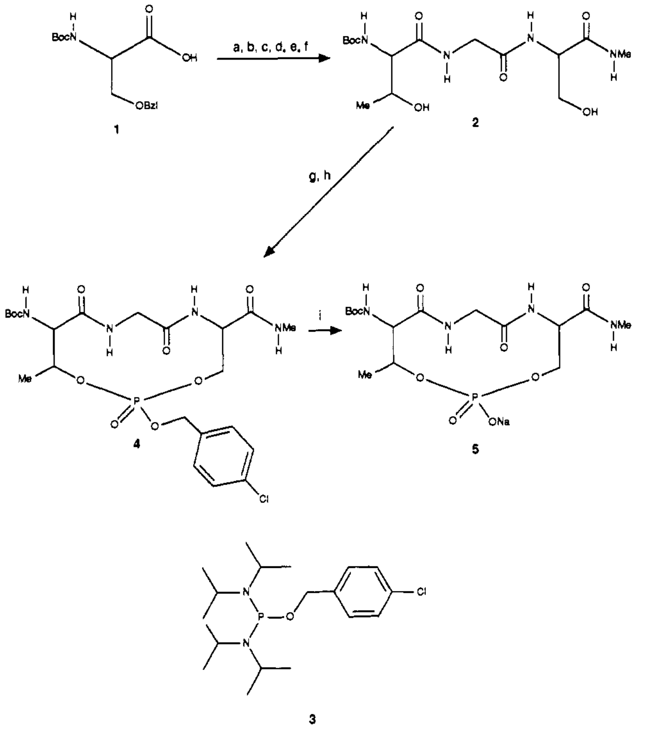
Scheme I[a]



[a] (a) Isobutyl chloroformate, 4-ethylmorpholine, H_2NMe (82%). (b) TFA, CH_2Cl_2, Et_3N. (c) Isobutyl chloroformate, 4-ethylmorpholine, Boc-Gly-OH (step b + step c, 82%). (d) TFA, CH_2Cl_2. (e) DCC, HOBt, Boc-Thr(OBzl)-OH, 4-ethylmorpholine, (step d + step e, 89%). (f) Pd/C, MeOH, H_2 (90%). (g) **3** (2 equiv), 1*H*-tetrazole, MeCN. (h) *t*-BuOOH (step g + step h, 30%). (i) Pd/C, *t*-BuOH, H_2O, NaOAc (1.2 equiv), H_2, Sephadex LH-20 (92%).

could be separated by short-column chromatography, were formed in a ratio of 15:1 in 32% total yield.[20] Hydrogenolysis of the 4-chlorobenzyl group under buffered[21] conditions afforded the sodium salt of the cyclic phosphopeptide **5** in 92% yield.

The NMR data of **5** are shown in Table I. The ^1H NMR spectra of **5** and **4**[20] display very sharp signals, indicative of conformers engaged in a fast equilibrium or perhaps even the presence of a single conformer in this solvent. Comparison of the ^1H NMR data of **5** with those obtained by Live and Edmondson[7] for the serine–threonine phosphodiester linkage in *Azotobacter* flavodoxin shows that the α-CH of threonine in **5** has a chemical shift (4.18 ppm) similar to that of the corresponding proton in *Azotobacter* flavodoxin (4.0 ppm). Van Boom et al.[11] found that in serylthreonyl phosphate the α-CH of threonine resonates at 3.70 ppm. However, a striking difference in chemical shift values, as compared to those obtained by Live and Edmondson,[7] was observed for the β-C protons of the serine residue in **5**: 4.07 and 4.30 ppm, as opposed to 3.4 and 3.7 ppm in *Azotobacter* flavodoxin. These chemical shift values found for **5** are in agreement with those earlier obtained[11] for serylthreonyl phosphate: 4.14 and 4.22 ppm.

In conclusion, the described method for the introduction of a phosphodiester linkage leading to a cyclic phosphopeptide provides a versatile approach for the synthesis of other cyclic phosphopeptides. Conformational analysis[15] of these types of molecules may reveal how the phosphodiester linkage affects the structure of the macrocycle.

In addition, via this approach, other phosphate-containing nonpeptide macrocycles[12] can be synthesized possibly possessing interesting structural features and binding properties.[12,13]

Acknowledgment. We thank A. W. M. Lefeber for recording some of the NMR spectra. We thank one of the referees for drawing our attention to ref 9.

Registry No. 1, 23680-31-1; **2**, 123639-57-6; **3**, 109915-25-5; **4** (diastereomer 1), 123621-78-3; **4** (diastereomer 2), 123673-04-1; **5**, 123621-79-4; BOC-Ser(BZl)-NHMe, 90013-41-5; BOC-Gly-OH, 4530-20-5; BOC-Gly-Ser(Bzl)-NHMe, 123621-80-7; BOC-Thr(Bzl)-OH, 15260-10-3; BOC-Thr(Bzl)-Gly-Ser(Bzl)-NHMe, 123621-81-8.

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[20] A satisfactory explanation for the observed diastereoselectivity cannot be offered at this time. In addition, it is not clear which diastereomer of the phosphotriester **4** is formed. The NMR data of the diastereomer **4** formed in excess: ^1H NMR (CD_3OD) δ 1.35 (d, Thr-C^4H_3, $J_{HH,vic} = 6.4$ Hz), 1.52 (s, Boc), 2.78 (s, N(H)CH_3), 3.80 (d, Gly-C^2H_a, $J_{HH,gem} = 16.6$ Hz), 4.04 (d, Gly-C^2H_b), 4.28 (ddd, Ser-C^3H_a, $J_{HH,vic} = 2.8$ Hz, $J_{HH,vic} = 11.2$ Hz, $J_{PH} = 10.3$ Hz), 4.42 (ddd, Ser-C^3H_b, $J_{HH,vic} = 2.8$ Hz, $J_{PH} = 10.8$ Hz), 4.42 (t, Thr-C^2H, $J_{HH,vic} = J_{PH} = 2.1$ Hz), 4.73 (q, Ser-C^2H, $J_{PH} = 2.8$ Hz), 4.96 (d, 4-Cl-benzyl, PhCH_2, $J_{PH} = 8.8$ Hz), 5.32 (dq, Thr-C^3H, $J_{PH} = 6.4$ Hz), 7.28 (s, 4-Cl-benzyl, aromatic part); ^{13}C NMR (CD_3OD) 18.0 (Thr-C^4), 26.6 (N(H)CH_3), 44.7 (Gly-C^2), 53.3 (Ser-C^2, $J_{PC} = 4.4$ Hz), 60.1 (Thr-C^2, $J_{PC} = 10.3$ Hz), 70.3 (Ser-C^3, $J_{PC} = 5.9$ Hz), 79.7 (Thr-C^3, $J_{PC} = 4.4$ Hz), 171.7, 172.6, and 174.4 (Ser-C^1, Gly-C^1, and Thr-C^1), 28.6, 81.4, and 157.7 (Boc), 69.9 (4-Cl-benzyl, PhCH_2, $J_{PC} = 5.9$ Hz), 129.7, 130.8, 135.5, 135.7 (4-Cl-benzyl, aromatic part); ^{31}P NMR −0.15.

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Reaction Volumes of Excited-State Processes: Formation and Complexation of the $Pt_2(P_2O_5H_2)_4{}^{4-}$ Excited State

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Reaction and activation volumes are usually determined for thermal processes by measuring the effect of pressure on chemical equilibria or rates.[1,2] Interpretation of this volume information often provides valuable structural and mechanistic insight into ground-state processes. However, this methodology is much less amenable to the study of excited-state processes, where generally only activation volumes can be obtained.[3,4] Partial molar volumes of short-lived species are not readily determined by using conventional methodologies. Consequently, our understanding of excited state processes is limited, in part, by our inability to construct reaction volume profiles involving excited states. In this regard, we wish to report the use of photoacoustic calorimetry (PAC) to measure the reaction volume and enthalpy for the formation and complexation of the excited state of $Pt_2(P_2O_5H_2)_4{}^{4-}$. This information can be used to estimate partial molar volumes and structural changes of the excited state.

Photoacoustic calorimetry measures the volume changes of a chemical system following photoexcitation.[5] The amplitude and time evolution of these changes are determined by deconvolution of the experimental acoustic waveforms. Details of this method have been previously reported.[6,7] These volume changes result

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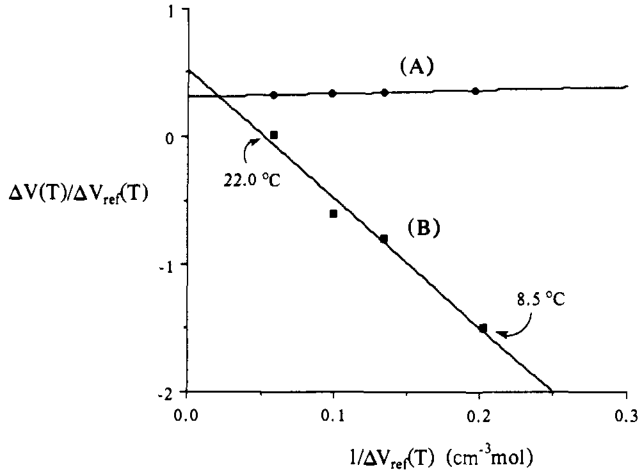

Figure 1. Plot of the total volume changes observed upon excitation (365 nm) of $Pt_2(P_2O_5H_2)_4^{4-}$ in water versus the volume change of a calibration compound, $FeCl_3$, at various temperatures (T = 8.5, 11.1, 13.5, and 22.0 °C): (A) 0 M $TlNO_3$ and (B) 0.01 M $TlNO_3$.

primarily from thermal expansion of the solvent and photochemical reaction volume changes.[5] These two contributions can be separated and analyzed to yield both reaction enthalpy *and* volume information.[8]

The $Pt_2(P_2O_5H_2)_4^{4-}$ complex has been extensively studied.[9] Photoexcitation of $Pt_2(P_2O_5H_2)_4^{4-}$ populates the long-lived $^3A_{2u}$ triplet state ($\cong$10 μs), via highly efficient intersystem crossing ($\phi_{isc} \cong 1$) from the initially formed $^1A_{2u}$ singlet state.[9,10] Irradiation of $Pt_2(P_2O_5H_2)_4^{4-}$ in water produces a single volume change ($\tau \leq 10$ ns), $\Delta V(*Pt_2)$, which reflects the formation of the $^3A_{2u}$ triplet state.[11] In the presence of Tl^+ ions, the $^3A_{2u}$ triplet state forms a long-lived 1:1 triplet exciplex ($\cong$10 μs).[12] Irradiation of $Pt_2(P_2O_5H_2)_4^{4-}$ with added $TlNO_3$ also produces a single volume change ($\tau \leq 10$ ns), $\Delta V(*Pt_2Tl^+)$, which now reflects the formation of the triplet exciplex.[11] The decay of either $*Pt_2$ or $*Pt_2Tl^+$ to the $^1A_{1g}$ ground state is not time-resolved under our experimental conditions.

The PAC volume change observed upon excitation of $Pt_2(P_2O_5H_2)_4^{4-}$, with or without added $TlNO_3$, is temperature dependent. The volume change, $\Delta V(T)$, is comprised of a temperature-dependent thermal expansion volume change, $\Delta V_{th}(T)$, and an assumed temperature-independent reaction volume change, ΔV_{rx}, and can be analyzed by using the equation[8]

$$\Delta V(T)/\Delta V_{ref}(T) = \Delta V_{th}(T)/\Delta V_{ref}(T) + \Delta V_{rx}/\Delta V_{ref}(T)$$

The volume changes are normalized by the thermal volume change of a calibration compound, $\Delta V_{ref}(T)$, which undergoes rapid nonradiative decay to its ground state after excitation.

Table I. Reaction Enthalpy and Volume Data Determined by PAC upon Photoexcitation of $Pt_2(P_2O_5H_2)_4^{4-}$[a–c]

excited state	ΔH (kcal/mol)	ΔV_{rx} (cm^3 mol^{-1})
$*Pt_2$	54.5 (1.0)[d]	0.5 (0.3)
$*Pt_2Tl^+$[e]	46.0 (4.3)	−10.6 (0.9)

[a] In water, 365-nm excitation, argon degassed, OD ≅ 0.8, 8.5–22.0 °C. [b] Average of six variable-temperature experiments. [c] See ref 8 and 11 for experimental details. [d] Values in parentheses are $\pm 1\sigma$. [e] 0.01–0.02 M $TlNO_3$ added.

In Figure 1, the normalized total volume changes of $Pt_2(P_2O_5H_2)_4^{4-}$, with and without added $TlNO_3$, are plotted versus $1/\Delta V_{ref}(T)$ at various temperatures.[13] The $\Delta V_{th}(T)/\Delta V_{ref}(T)$ term is a constant, i.e., $\Delta V_{th}(T)$ and $\Delta V_{ref}(T)$ exhibit the same temperature dependence. The reaction enthalpy, ΔH, is determined from the relationship $\Delta H = (1 - \Delta V_{th}(T)/\Delta V_{ref}(T))(E_{h\nu}/\Phi_{ex})$, where $\Delta V_{th}(T)/\Delta V_{ref}(T)$ is the y-intercept of the plot, Φ_{ex} is the quantum yield for formation of the excited state, and $E_{h\nu}$ is the photon energy. The slope of the plot yields the reaction volume, ΔV_{rx}. The experimental results are given in Table I.

The PAC reaction enthalpy for formation of $*Pt_2$, 54.5 kcal/mol, is in reasonable agreement with that determined from spectroscopic measurements, ≅58 kcal/mol.[10] In addition, the reaction enthalpy for formation of the $*Pt_2Tl^+$ excited state, 46.0 kcal/mol, is similar to that estimated from photophysical studies, ≅49 kcal/mol.[12,14] The lower PAC values may be due, in part, to competing absorption by the initially formed excited state within the laser pulse.[15] The difference in the reaction enthalpies for formation of the two excited states, −8.5 kcal/mol, yields the enthalpy of complexation of the $*Pt_2$ excited state with Tl^+ ion.

The reaction volume change can in general be considered to consist of two major contributions: a structure volume change, ΔV_{str}, due to changes in bond lengths and angles, and a solvation volume change, ΔV_{solv}, due to changes in the surrounding medium.[1,2] An important part of ΔV_{solv} is from changes in electrostriction, i.e., the interaction of an ion or dipole with the dielectric.

A negligible reaction volume change is observed by PAC upon excitation of Pt_2 to $*Pt_2$. The $^1A_{1g}$ ground state and the $^3A_{2u}$ triplet state, $*Pt_2$, should intereact similarly with the solvent so the ΔV_{solv} contribution should be small for this photoprocess, i.e., $\Delta V_{rx} \cong \Delta V_{str}$.[12] This suggests the partial molar volume of the $^1A_{1g}$ ground and $^3A_{2u}$ triplet state are approximately equal. However, resonance Raman, absorption, and emission studies indicate that photoexcitation of $Pt_2(P_2O_5H_2)_4^{4-}$ to the $^3A_{2u}$ triplet state results in a significant reduction in the Pt–Pt bond length, 0.21 Å.[10,16] This observation may appear surprising with regard to the PAC results

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(11) The photoacoustic apparatus has been previously described.[8] Excitation of the argon degassed samples is by a nitrogen-pumped dye laser (365 nm), and detection employs a ~0.5 MHz transducer. Similar results are obtained at several wavelengths and $Pt_2(P_2O_5H_2)_4^{4-}$ concentrations (0.2–0.8 OD). A thermostated acoustic cell with a Haake 80 circulating bath (±0.1 °C) is employed for the temperature studies, 5–25 °C. Na_2CrO_4 or $FeCl_3$ are used as the calibration compounds. $K_4Pt_2(P_2O_5H_2)_4$ is prepared by the literature procedure[22] and recrystallized before use.

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(14) Unfortunately, the temperature effect on the equilibrium constant of the reaction, $*Pt_2 + Tl^+ \rightleftharpoons *Pt_2Tl^+$, has not been measured so ΔH is not known. However, with use of the experimental $\Delta G = -6.0$ kcal/mol[12] and an estimated $\Delta S = -10$ cal mol^{-1} °C^{-1},[24] $\Delta H \cong -9.0$ kcal/mol, at 25 °C. Reaction entropies for organic exciplex formation in nonpolar solvents can vary from −10 to −25 cal mol^{-1} °C^{-1}. However, it is unclear if these are reasonable values to estimate ΔS for the formation of the $*Pt_2Tl^+$ complex in water. In fact, desolvation effects in water may have a significant effect on the reaction entropy.[25] In fact, desolvation effects in water may have a significant effect on the reaction entropy.[25] However, in light of the often observed empirical correlation between reaction volumes and entropies,[1] the negative reaction volume observed for complex formation suggests a negative reaction entropy.

(15) This absorption produces higher energy excited states which undergo rapid nonradiative relaxation. This effectively increases the magnitude of $\Delta V(T)$ and hence decreases the enthalpic, ΔH, and reaction volume, ΔV_{rx}, values. By using the known excited-state energies, an approximate correction can be applied to the ΔV_{rx} values. The corrected values are ≤5% greater than those reported in Table I. The PAC experiments were performed at various excitation wavelengths (365–380 nm) with the lowest laser energies possible to reduce the two photon events.

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given that photoexcitation of coordination compounds, which undergo very small isotropic changes (0.01 Å) in their van der Waals radii, produces reaction volume changes readily detectible by PAC.[8b] The small observed reaction volume change is potentially explained by the following: (i) the bond length reduction is not isotropic but rather anisotropic which results in only a small reaction volume change; (ii) compensating increases in other bond lengths in the excited state occur such that the ground- and excited-state volumes are similar; and (iii) the surrounding water molecules do not fill the void created by the compressed excited state, i.e., the excited state is not significantly hydrated.

In contrast, a large reaction volume decrease is observed by PAC upon excitation of $Pt_2(P_2O_5H_2)_4^{4-}$ in the presence of Tl^+ ions, presumably due to formation of the $^*Pt_2Tl^+$ exciplex.[17] The difference in reaction volumes between the formation of $^*Pt_2$ and $^*Pt_2Tl^+$, -11.1 cm^3 mol^{-1}, yields the reaction volume for complexation of the $^*Pt_2$ state with Tl^+ ion. Assuming ΔV_{solv} is negligible,[18] a Tl–Pt bond length of ~2.6 Å is suggested by molecular mechanics calculations to account for this structural reaction volume decrease.[19] This bond length is similar to that observed for axial substituents in Pt(III)–Pt(III) complexes and also is significantly less than the combined van der Waals radii of the two metals, 3.7 A,[20] indicating an appreciable interaction between $^*Pt_2$ and Tl^+.

Reaction volumes for excimer and exciplex formation can also potentially be obtained via pressure measurements.[21] However, this approach is limited in that the excited state and complex must be luminescent, and the requisite analysis involves numerous assumptions. Consequently, PAC provides a simple alternative method for measuring reaction volumes for excited-state complexation in cases where pressure studies may or may not be possible. In this regard, PAC may be particularly well-suited for the detection of triplet exciplexes, where often only indirect measures of their properties are available.

In conclusion, PAC yields reaction enthalpy, reaction volume, and potentially kinetic information about photoprocesses involving both luminescent and nonluminescent short-lived excited states. The reaction volume data can be related to structural changes in the excited state which may provide insight into excited-state reaction dynamics. Further PAC studies will examine other excited-state complexation processes.

Acknowledgment. This work was supported by the National Science Foundation (CHE-8713720), the Research Corporation, and the donors of the Petroleum Research Fund, administered by the American Chemical Society. We thank Prof. Kevin Peters and Dr. Gary Snyder for updated computer programs and D. Pensak for the molecular volume subroutine.

Registry No. $Pt_2(P_2O_5H_2)_4^{4-}$, 85565-26-0; $TlNO_3$, 10102-45-1.

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(17) In contrast, the addition of a noncomplexing salt, KNO_3 (0.02 M), has no effect on the experimental ΔH and ΔV_{rx} values.

(18) The magnitude of ΔV_{solv} for exciplex formation is difficult to estimate. The photoprocess involves partial desolvation of both Pt_2 and the Tl^+ ion in order to form the complex. Although ΔV_{solv} values for ion pair formation have been measured,[25] none are known for inorganic exciplex formation in water.

(19) Energy minimization of $Pt_2(P_2O_5H_2)_4^{4-}$, $^*Pt_2$, and $^*Pt_2Tl^+$ structures was done by using MODEL (Version 2.94). The Pt–Pt bond length was fixed at 2.92, 2.71, and 2.71 A for $Pt_2(P_2O_5H_2)_4^{4-}$, $^*Pt_2$, and $^*Pt_2Tl^+$, respectively. The volumes of the energy-minimized structures were determined by using an adapted subroutine to the MODEL program.[26] The Pt–Tl bond length was fixed at several positions, 2.0–5.0 A, and the volume of each energy-minimized structure determined.

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The Solvent Effect on the Electronic Nature of 1,3-Dipoles: An ab Initio SCRF Study

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The controversy about the electronic nature of 1,3-dipoles[2] has received much attention, both experimental and theoretical,[3] over the last two decades. Recently, Kahn, Hehre, and Pople[4] used ab initio molecular orbital theory in a novel way to investigate a series of 22- and 24-electron 1,3-dipoles. They used the difference between the restricted Hartree–Fock (RHF) and unrestricted Hartree–Fock (UHF) total energies for a given molecule as a measure of the degree of diradical character. Recent advances in the molecular orbital theory of macroscopic solvent effects suggested that it should now be feasible to investigate the solvent effect on the electronic nature of 1,3-dipoles by combining the self-consistent reaction field (SCRF) approach[5–7] with Hehre and Pople's UHF/RHF criterion to gain some insight into the nature of 1,3-dipoles in solution. We now report results for a series of 24-electron 1,3-dipoles in three solvents, *n*-hexane, methanol, and water. Since Kahn, Hehre, and Pople found no RHF → UHF instability for 22-electron 1,3-dipoles, these were not included in this study.

The 6-31G*[8] basis set was used throughout, and the geometries used for the "solution" calculations were those obtained by optimization at RHF/6-31G* or UHF/6-31G* in vacuo.[4] Table I shows the energy differences between the UHF and RHF calculations. The fact that the UHF wave functions do not collapse to RHF when the latter is more stable is surprising as the RHF solution must also be the true UHF solution. Geometry effects

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(7) Tomasi's SCRF procedure using spherical cavities around the atoms[6] was installed in the Convex version of Gaussian 82 (Binkley, J. S.; Whiteside, R. A.; Raghavachari, K.; Seeger, R.; DeFrees, D. J.; Schlegel, H. B.; Frisch, M. J.; Pople, J. A.; Kahn, L. "Gaussian 82"; Carnegie-Mellon University: Pittsburgh, PA, 1982). The SCF/self-polarization iterations were continued until the total energy in the solvent had converged within 10^{-8} hartrees. The dispersion energy was not included in the solvent effect calculations. The sphere radii used for the atoms were 20% larger than the van der Waals radii (hydrogen, 1.44 Å; carbon, 1.92 Å; nitrogen, 1.80 Å; oxygen, 1.68 Å). The solvent effect calculations were carried out at 298.15 K with the following values for the solvent diameter, σ (Å; taken from the following: Pierotti, R. A. *Chem. Rev.* **1976**, *76*, 17) and for the density, d (g/cm^3), thermal expansion coefficient, α, and dielectric constant, ϵ (all taken from the following: Riddick, J. A.; Bunger, W. B.; Sahano, T. K. *Organic Solvents*; Wiley: New York 1986; Vol. 2). The total energies in solution given below include the electrostatic interaction energy and the cavity energy.

solvent	σ	d	α	ϵ
n-hexane	5.94	0.654 84	0.001 391	1.8799
methanol	3.71	0.786 37	0.001 196	32.66
water	2.77	0.997 05	0.000 257	78.36

(8) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213. Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Pople, J. A. *J. Chem. Phys.* **1982**, *77*, 3654.

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