Table X. Sum of Orbital Populations in the C and O p_π Orbitals of Formaldehyde and Formaldehyde–Y Complexes

	basis set	C	O
H_2CO	3-21G	0.779	1.221
	6-31G*	0.668	1.298
$H_2CO–BF_3$	3-21G	0.580	1.410
	6-31G*	0.608	1.358
$H_2CO–BCl_3$	HW1	0.531	1.455
	HW3	0.502	1.465
$H_2CO–BBr_3$	HW1	0.534	1.461
	HW3	0.491	1.482
$H_2CO–H^+$	3-21G	0.416	1.584
	6-31G*	0.362	1.609

π populations over the carbon and oxygen atoms of formaldehyde are shown. The π polarization also increases with the acid strength. This polarization, along with the stabilization of the π^* orbital of formaldehyde, will favor nucleophilic attack processes on the carbonyl group, in good agreement with experimental facts.

Concluding Remarks

The results obtained in this work show that boron trihalides follow the usual Lewis acidity scale when complexed with formaldehyde. BF_3 is predicted to be the weakest Lewis acid with all basis sets. The acid strengths of BCl_3 and BBr_3 are quite similar, but the correct ordering has only been obtained with the MIDI-3 basis set and with basis sets which use effective core potentials for Cl and Br.

The interaction between the donor and acceptor moieties of the complexes can be analyzed from molecular orbital considerations. The relative strength of the complexes is mainly determined by the LUMO energy of the boron trihalide. The proposed interaction scheme has been used to rationalize the effects produced by complexation on the molecular geometry as well as on the IR spectra of formaldehyde. Finally, the perturbation produced by the Lewis acid on the π electron system of formaldehyde allows one to understand the variation on its UV spectrum and the effect on its reactivity.

Phosphoryl Nitride Isomeric Dimers, Trimers, and Tetramers: $(NPO)_x$ (x = 2–4)

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Abstract: Ab initio quantum mechanical methods have been applied to eight stationary points on the $N_2O_2P_2$ potential energy hypersurface and in addition to the trimeric and tetrameric systems $(NPO)_3$ and $(NPO)_4$. The self-consistent field method was used in conjunction with a double-ζ plus polarization basis set, N, O (9s5p1d/4s2p1d), P (11s7p1d/6s4p1d). The global minimum for the dimer system is the experimentally unknown cyclodiphosphazene. Analogous structures for the trimer and tetramer are low-lying and should be synthesizable.

Introduction

Phosphoryl nitride (or phosphorus oxynitride) thin films and polymers, $(NPO)_x$, have been used for such diverse purposes as a passivating coating on InP surfaces[1] and a flame retardant in plastics manufacture.[2] The crystal structure of the solid is known,[3,4] and its electronic structure has been studied by X-ray photoemission spectroscopy and extended Hückel theory.[5] Recently the monomeric PNO molecule has been identified by matrix isolation spectroscopy,[6] and the lowest energy isomers PNO and NPO have been studied theoretically.[6-8] NPO is found to lie about 5 kcal/mol[6,8] above the global minimum PNO at the highest level of theory. Thus the two extremes of extended structures (solid, thin films, polymers), on the one hand, and the isolated monomer, on the other hand, have been studied, but to our knowledge the intermediate ground (dimers, trimers, and tetramers) of PNO or NPO has been studied very little[9] and not at all theoretically. We present here the results of the first ab initio theoretical studies of various isomers of the formula $N_2O_2P_2$ (atoms in alphabetical order and no chemical significance implied) and of the as yet unknown cyclotriphosphazene $(NPO)_3$ and a bis(cyclodiphosphazene) $(NPO)_4$.

Methods

All geometry optimizations and vibrational frequencies were obtained by using analytic first and second derivative methods, respectively, at the Hartree–Fock self-consistent field (SCF) level of theory. The double-ζ plus polarization (DZP) basis sets of Huzinaga[10] and Dunning[11] were used, with polarization function (i.e., d functions) exponents of N = 0.80, O = 0.85, and P = 0.50. Six d-like functions were used throughout. The PSI program[12] was used for all isomers except $(NPO)_4$, for which the GAUSSIAN 88 program[13] was run at the Cornell National Supercomputing Facility. For the tetramer only, the phosphorus d functions had orbital exponent $\alpha_d(P) = 0.37$.

For the dimers, configurations interaction involving all single and double excitations (CISD) has also been carried out. The CISD procedure held the 14 core-like (N 1s, O 1s, P 1s, 2s, $2p_x$, $2p_y$, $2p_z$) SCF molecular orbitals doubly occupied in all configurations. In addition, the

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[1] Furukawa, Y. *Jpn. J. Appl. Phys.* **1984**, *23*, 1157. Mikami, O.; Okamura, M.; Yamaguchi, E.; Hirota, Y.; Furukawa, Y. *Jpn. J. Appl. Phys.* **1984**, *23*, 1408.

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[13] GAUSSIAN 88, Frisch, M. J.; Head-Gordon, M.; Schlegel, H. B.; Ragavachari, K.; Binkley, J. S.; Gonzalez, C.; Defrees, D. J.; Fox, D. J.; Whiteside, R. A.; Seeger, R.; Melius, C. F.; Baker, J.; Martin, R. L.; Kahn, L. R.; Stewart, J. J. P.; Fluder, E. M.; Topiol, S.; Pople, J. A. Gaussian, Inc.: Pittsburgh, PA.

0002-7863/91/1513-4136$02.50/0

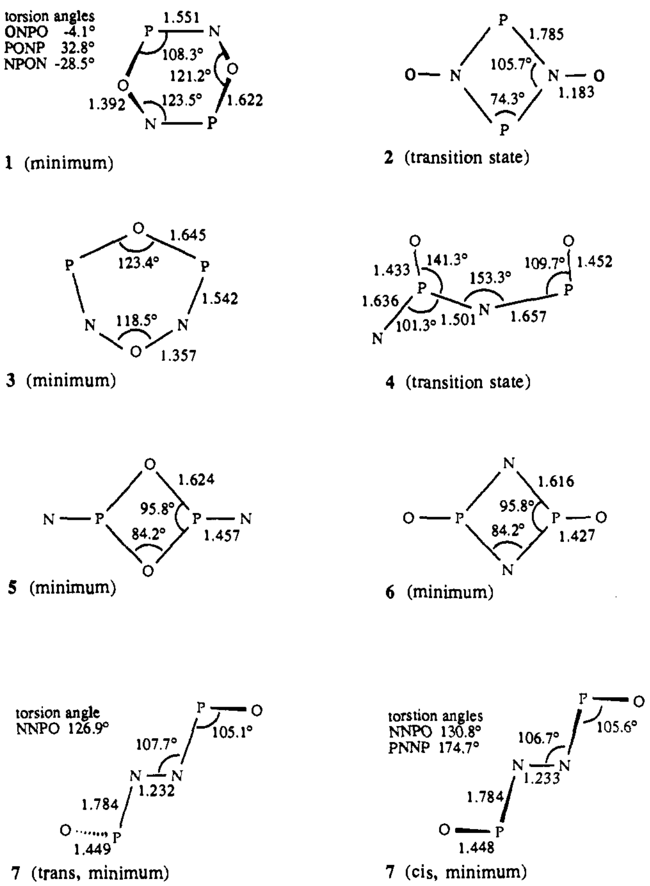
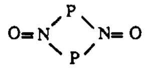
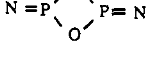
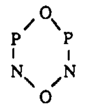
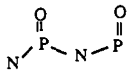
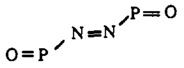
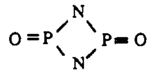


Figure 1. Theoretical DZP SCF geometries for stationary points of $N_2O_2P_2$. The vibrational character for each structure is also indicated. All bond distances are in Å.

Table I. DZP SCF Total Energies (in hartrees) for $N_2O_2P_2$ Isomers and Energies Relative to Two Separated PNO Monomers in kcal mol^{-1}

	Structure	Total Energy	Relative Energy
2		-939.82410	+54.0
5		-939.94741	-23.3
1		-939.96115	-31.9
3		-939.97619	-41.4
4		-939.98557	-47.3
7		-940.04851 (cis) -940.04770 (trans) -940.04629 (planer)	-86.8 -86.3 -85.4
6		-940.07391	-102.7

six highest lying virtual orbitals were deleted from the CISD procedure. In the lowest point group considered (C_2), the CISD wave function for the dimer includes 370 883 configurations.

Results and Discussion

A. Dimers. We investigated eight distinct structures with the formula $N_2O_2P_2$. The geometries of the theoretical stationary points are given in Figure 1. The total energies and energies relative to two (global minimum) PNO monomers are given in Table I. The eight structures may be divided into three types: PNO dimers, NPO dimers, and mixed dimers.

Structures **1** and **2** are PNO dimers. An open chain PNO dimer O=N—P=P—N=O rearranges to the ring **1** at the DZP SCF level of theory. The ring structure **2** is higher in energy than two separated PNO monomers and has an imaginary vibrational frequency leading to dissociation. This leaves only ring **1** as a viable isomer for the direct dimerization of the PNO molecule observed by Ahlrichs, Schunck, and Schnöckel.[6] Ring **1** may be considered both a PNO and an NPO dimer; thus, one might observe rearrangement through this ring to other structures that are NPO dimers. The P–N bond distance in ring **1** is quite short, 1.551 Å, shorter than the experimental bond found in the related cyclotriphosphazene, $(F_2PN)_3$ (1.570 Å).[14] A constrained planar variant of **1** was also considered and found to be a transition state. The low imaginary vibrational frequency (85i cm^{-1}) indicates that the potential energy hypersurface is very flat with respect to out-of-plane motions.

The mixed PNO–NPO ring **3** is a genuine minimum on the potential energy hypersurface but lies at a relatively high energy. In experiments in which NPO is initially formed, it is likely that NPO–NPO dimerization, which is strongly favored energetically (see below), will be preferred. The NPO dimers considered here are structures **4–7**. Both the acyclic structure **4** and the ring structure **5** are at high energy and will not be discussed in detail. The acyclic structure **4** has an imaginary frequency leading to the out-of-plane motion of the oxygen atoms. According to Trinquier,[16] this structure should rearrange to the cyclodiphosphazene **6** with a small energy barrier. The ring **5** appears in the Gmelin handbook,[9] but it is a high-energy structure, and it is unlikely that this isomer, rather than the cyclodiphosphazene **6**, would be formed.

By far the lowest energy of any of the dimers is the cyclodiphosphazene, isomer **6**. At the DZP SCF level of theory, structure **6** is predicted to lie 15.9 kcal/mol below structure **7** (cis, see discussion below). The DZP CISD total energies for **6** and **7** are −940.807 32 and −940.778 33 hartrees, respectively. Thus CISD increases the energy difference between **6** and **7** to 18.2 kcal/mol.

A related cyclodiphosphazene with the formula $[N(iPr)_2PN]_2$ was first reported by Baceiredo, Bertrand, Majoral, Sicard, Jaud, and Galy[15] in 1984. An X-ray diffraction structure determination revealed a planar four-membered ring with ring P–N distances of 1.65 Å, an NPN angle of 95.0°, and a PNP angle of 85.0°. These are quite similar to the theoretical structural parameters predicted here for $(NPO)_2$: PN = 1.616 Å, NPN = 95.8°, and PNP = 84.2°. Bertrand and co-workers also observed the IR spectrum, leading to vibrational frequencies, which they assigned to P=N and P–N stretches at 1131 and 964 cm^{-1}, respectively. The full set of theoretical frequencies for the $(NPO)_2$ cyclodiphosphazene ring **6** is given in Table II. In earlier theoretical work on another related system, Trinquier reported ab initio investigations of the model cyclodiphosphazene $(H_2PN)_2$.[16] He concluded that least-motion head-to-tail dimerization is thermally forbidden, but nonleast-motion dimerization should be allowed as well as photochemical generation. This analysis suggests the possibility of forming and trapping the $(NPO)_2$ structure **6**, if one

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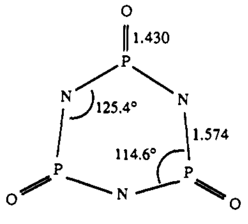
Table II. Theoretical DZP SCF Vibrational Frequencies (cm^{-1}) and Infrared Intensities (km mol^{-1}) for the Global Minimum (**6**) Cyclodiphosphazene $(NPO)_2$

	assignment	frequency	intensity
ω_1	PO stretch (a_g)	1572	0
ω_2	PO stretch (a_u)	1517	676
ω_3	PN stretch (b_{3u})	1131	354
ω_4	PN stretch (a_g)	1085	0
ω_5	PN stretch (b_{2u})	964	184
ω_6	PN stretch (b_{1g})	808	0
ω_7	ring bending (a_g)	605	0
ω_8	ring pucker (b_{1u})	571	138
ω_9	PO in-plane bending (b_{1g})	411	0
ω_{10}	PO out-of-plane bending (b_{3g})	404	0
ω_{11}	PO in-plane bending (b_{3u})	337	35
ω_{12}	ring out-of-plane mode (b_{1u})	165	17



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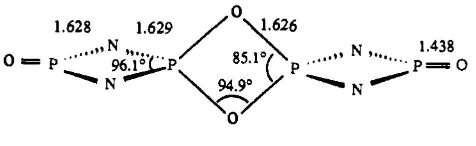

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Figure 2. Theoretical DZP SCF minimum energy geometry for the cyclotriphosphazene $(NPO)_3$ and stationary point for bis(cyclodiphosphazene) $(NPO)_4$. All bond distances are in Å. The trimer (**8**) and tetramer (**9**) total energies are −1410.230 98 and −1880.178 65 hartrees, respectively.

can produce the NPO monomer, perhaps via the gas-phase reaction of PN with oxygen.

The noncyclic dimer **7** is the second lowest energy $N_2O_2P_2$ isomer. The constrained planar structure has two imaginary vibrational frequencies that lead to cis and trans out-of-plane structures. Optimization leads to dihedral angles of 130.8° (cis) and 126.9° (trans). The energy lowering accompanying this optimization is small, less than 1 kcal mol^{-1} for both the trans and cis structures. Trinquier[16] investigated a similar isomer for the related $(H_2PN)_2$ molecule and found it to be 10.4 kcal mol^{-1} below the cyclodiphosphazene at the DZP SCF level. The P–N bond length in structure **7** is quite long, perhaps indicating a tendency toward dissociation to $N_2 + 2PO$.

B. Trimer and Tetramer. Because the cyclophosphazenes are of both practical and theoretical interest, we extended the present study of NPO cyclophosphazenes beyond the dimer. We have optimized the structures of the cyclotriphosphazene **8** and a bis(cyclodiphosphazene) isomer **9**. These are shown in Figure 2. The DZP SCF dissociation energy per monomer is much greater for the cyclotriphosphazene **8** (76 kcal mol^{-1}/monomer) than the cyclodiphosphazene **9** (56 kcal mol^{-1}/monomer), as one might expect for the less strained six-membered ring. Note that the dissociation energies just given refer to the NPO monomer, which is predicted to lie 3.4 kcal/mol above PNO with the DZP SCF method. The tremendous energetic driving force (240 kcal mol^{-1}) toward forming the cyclotriphosphazene **8** from three NPO monomers argues strongly that it should be formed given NPO fragments. The theoretical vibrational frequencies and infrared intensities of the cyclotriphosphazene **8** are given in Table III and should provide a distinctive pattern for identification of this species.

Table III. Theoretical DZ SCF Vibrational Frequencies in cm^{-1} and Infrared Intensities in km mol^{-1} for the Cyclotriphosphazene $(NPO)_3$, i.e., Structure **8**[a]

	assignment	frequency	intensity
ω_1	PO stretch (e′)	1328	1007
ω_2	PO stretch (a_1')	1214	0
ω_3	PN stretch (a_2')	1102	0
ω_4	PO, PN combination stretch (e′)	1086	3
ω_5	PN stretch (e′)	725	159
ω_6	PN stretch (a′)	640	0
ω_7	OPN bend (a_2')	522	0
ω_8	ring out-of-plane bending (a_2'')	496	276
ω_9	ring and PO out-of-plane (e″)	371	0
ω_{10}	PO in-plane bending (a_1'')	363	0
ω_{11}	in-plane ring bending (e′)	363	42
ω_{12}	PO out-of-plane bending (e′)	265	15
ω_{13}	ring out-of-plane bending (e″)	162	0
ω_{14}	ring out-of-plane bending (a_1'')	146	32

[a] Structure **8** has a D_{3h} equilibrium geometry.

Although it is thermodynamically strongly favored compared to three isolated PNO (the global minimum for the triatomic species) molecules, the cyclotriphosphazene **8** might still be kinetically unstable with respect to some sort of polymerization. The Mulliken population analysis of the DZ SCF wave function for the cyclic trimer **8** indicates a large positive charge on the phosphorus (+1.89) and large negative charges on the N (−1.22) and O (−0.67). The structure of solid phosphoryl nitride has tetrahedrally coordinated phosphorus atoms. These can be modeled by end-on coordination as in the bis(cyclodiphosphazene) **9** shown in Figure 2. The dimerization of dimers is favored by an additional 19.3 kcal mol^{-1}. The tetramer structure **9** is interesting for the near equality of the three independent bond lengths in the rings.

While it may be possible to capture the dimeric global minimum **6** experimentally, one reviewer has expressed the strong conviction that collision with another monomer will form the trimer almost without fail. As this is far more likely than collision with another dimer, it is not certain what role the tetramer may actually be called upon to play in the laboratory. The most remarkable feature of tetramer is its fascinating structure.

Concluding Remarks

The lowest energy species of the formula $N_2O_2P_2$ was found to be the cyclodiphosphazene, structure **6**. The theoretical vibrational frequencies and IR intensities for both the cyclodiphosphazene $(NPO)_2$ and the cyclotriphosphazene $(NPO)_3$ are presented in hopes of facilitating experimental identification of these compounds.

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Registry No. 6, 133100-45-5; **8**, 133100-46-6; **9**, 133100-47-7.