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Complexes between Formaldehyde and Boron Trihalides. An ab Initio Study

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Abstract: The complexes between formaldehyde and boron trihalides have been theoretically studied at several levels of calculation. The nature of the interaction and the relative acid strength of boron trihalides have been discussed. The effect of complexation on the molecular geometry, molecular spectra, and reactivity has also been considered.

Introduction

Complexation of carbonyl compounds by Lewis acids plays an important role in many catalytic processes in organic chemistry. These include catalyzed Diels-Alder reactions,[1] aldol condensations,[2] and several photochemical reactions.[3]

The drastic effects that the activation by Lewis acids produce in the mechanism of these reactions make necessary the knowledge of the structure and properties of such complexes. In the last years, several experimental studies have shown that complexation by Lewis acids produces important modifications on UV,[3c,4] IR,[4,5] and NMR[3c,d,6,7] spectra of carbonyl compounds. In spite of all this information, few experimental data are available on the equilibrium geometries of these complexes.[3b,8-10]

This kind of compound has also been the object of theoretical studies.[9,11-16] Complexes with boron trifluorides have been studied by means of semiempirical[9,11,13] as well as ab initio methods.[15,16] All these studies show a preference for a bent coordination mode of BF_3, in good agreement with the X-ray diffraction structure of the benzaldehyde-BF_3 complex.[9]

Chart I

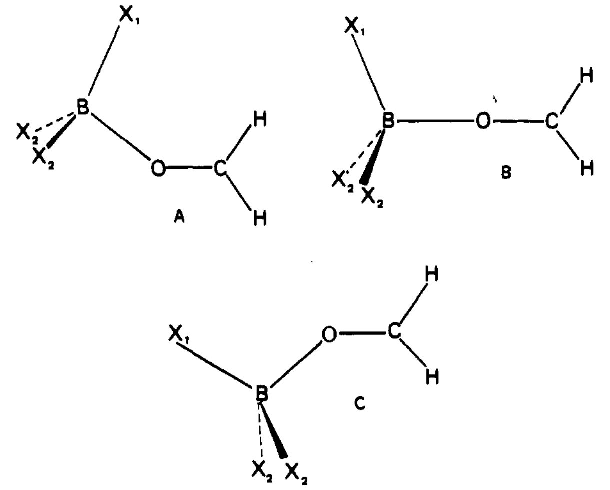

Table I. Relative Energies (kcal/mol) for Different Structures[a] of Formaldehyde-BX_3 Complexes

	A	B	C
BH_3[b]	0	7.7	1.25
BF_3	0	9.1	2.6
BCl_3	0	10.5	0.9

[a] See Chart I. [b] Reference 16.

Another important aspect of the activation of carbonyl compounds by Lewis acids is the relationship between the relative strength of Lewis acids and the effects they produce in the structure and reactivity of the carbonyl compounds. Several experimental data[17] suggest that the Lewis acid strength of boron trihalides follows the order $BF_3 < BCl_3 < BBr_3$. This trend is the opposite of that expected from electronegativity arguments. For carbonyl compounds the only experimental data regarding the relative strengths of boron trihalides are based on the variation of chemical shifts in NMR spectra,[6] this result confirming the same acidity scale. From a theoretical point of view, only BF_3 complexes have been studied and no attempt to explain the relative strength of the interaction between carbonyl compounds and the series of boron trihalides has been done.

The purpose of the present paper is to do a systematic theoretical study of the structure and properties of the complexes of formaldehyde with boron trihalides. We have considered the complexes of formaldehyde with BF_3, BCl_3, and BBr_3 at several levels of

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Table II. Computed and Experimental Geometries of Boron Trihalides

compd	basis set	B–X, Å	compd	basis set	B–X, Å
BF_3	3-21G	1.328	BBr_3	3-21G	1.933
	MIDI-3	1.338		MIDI-3	1.935
	6-31G*	1.301		HW1	1.957
	exp[a]	1.310		3-21G(*)	1.892
BCl_3	3-21G	1.771		MIDI-3(*)	1.895
	MIDI-3	1.774		HW2	1.924
	HW1	1.771		HW3	1.918
	3-21G(*)	1.747		exp[b]	1.87
	MIDI-3(*)	1.743			
	HW2	1.742			
	6-31G*	1.745			
	HW3	1.737			
	exp[b]	1.72			

[a] Reference 26a. [b] Reference 26b.

calculation. The nature of the interaction between formaldehyde and boron trihalides has been analyzed and the relative strength of the boron trihalides has been discussed. The effect of complexation on molecular geometry, molecular spectra, and reactivity of formaldehyde has also been considered.

Method of Calculation

The molecular geometries of formaldehyde, boron trihalides, and the studied complexes have been fully optimized through ab initio SCF calculations. The computations have been carried out with the 3-21G,[18] MIDI-3,[19] and 6-31G*[20] basis sets. For Cl and Br, the 3-21G(*) and MIDI-3(*) basis sets, which include d polarization functions,[19,20d] have also been employed.

For Cl and Br the effective core potentials (ECP) of Hay and Wadt[21] have also been used to replace the internal electrons, while a double-ζ expansion has been used for the valence shell. The basis sets that use ECP will be denoted by HW*n*, where *n* is 1, 2, or 3. For $n = 1$ the 3-21G basis set is used for the first and second period atoms. When $n = 2$ the basis set of the halogen atom is increased with d functions with the same exponents as the 3-21G(*) basis set. Finally, for $n = 3$ 6-31G* is used for the first and second row atoms, while d functions on Cl and Br are also included.

Electron correlation has been included through second order Møller–Plesset perturbation theory.[22] Only the valence electrons have been correlated. These calculations have been done at the RHF geometries. The calculations have been carried out with the GAUSSIAN-86,[23] MONSTERGAUSS,[24] and GAMESS[25] programs.

Results and Discussion

We will first discuss the different ways in which boron trihalides can coordinate to formaldehyde. The considered structures are represented in Chart I. The geometry of each structure has been optimized at the RHF/3-21G level for the BF_3 and BCl_3 complexes. The relative energies of these complexes are presented in Table I along with the results corresponding to the formaldehyde–BH_3 complex.[16] One can observe that in all cases **A** is the most stable structure. However, the energy difference with **C** is small. These two structures correspond to different conformations resulting from rotation around the B–O bond. However, both structures can also be connected through the linear **B** structure, which corresponds to the transition state of the **A** → **C** inversion process.[9,16] Structure **A** is the only one that will be considered in the following discussion.

Geometries of the Complexes. Tables II and III present the most important geometrical parameters obtained for the boron trihalides and formaldehyde and its complexes.

The optimized distances corresponding to boron trihalides are in excellent agreement with the experimental values. The relative error is in all cases smaller than 5%. For formaldehyde an excellent accordance is also observed, specially with the 3-21G and MIDI-3 basis sets.

Let us now analyze the geometries of the complexes. The results obtained for the BF_3 complex are analogous to those reported by LePage and Wiberg.[16] The 3-21G and MIDI-3 basis sets give a reasonable value for the B–O bond length, when it is compared with the experimental value, 1.591 Å, corresponding to the benzaldehyde–BF_3 complex.[9] However, with the more extended 6-31G* basis set the obtained value seems too long. Complexation involves a geometry distortion of formaldehyde and boron trifluoride: the C=O bond length slightly increases, while the BF_3 moiety suffers an important pyramidalization, as shown by the values of $\angle OBX_1$ and $\angle OBX_2$ bond angles and by the lengthening of the B–F bonds.

The complexes with BCl_3 and BBr_3 present smaller B–O bond lengths than the formaldehyde–BF_3 complex at all levels of calculation. This suggests that BCl_3 and BBr_3 form stronger complexes with formaldehyde than BF_3. The distortion of both addends is also more important: the C=O bond length and the pyramidalization of the BX_3 moiety are greater in the BCl_3 and BBr_3 complexes. Here, it is to be noted that the $\angle OBX_1$ bond angle is greater than the $\angle OBX_2$ bond angle, while in the BF_3 complex the situation was inversed. The $\angle BOC$ bond angle also changes, its value being about 8–9° greater than that in the BF_3 complex.

Regarding the relative strength of the BCl_3 and BBr_3 complexes, the results are dependent on the level of calculation. 3-21G leads to a slightly stronger complex for BCl_3 than for BBr_3, while MIDI-3 and the use of ECP for the halogen atoms predict that BBr_3 forms the strongest complex. As mentioned above, the experimental acid strength of Lewis acids increases in the order $BF_3 < BCl_3 < BBr_3$. The theoretical results agree with this ordering only when MIDI-3 or basis sets with ECP are used.

For the BCl_3 complex all electron calculations and ECP calculations lead to almost the same geometries. The introduction of d functions over Cl (3-21G(*), MIDI-3(*), and HW2) and over Cl and second period elements (6-31G* and HW3) produces the same effect in both cases, i.e., a lengthening of the B–O bond length and a minor degree of geometry distortion of the addends. However, for BBr_3, the use of ECP leads to an important shortening of the B–O bond length.

Energetics. The formation energies of the formaldehyde–BX_3 complexes computed at different levels of calculation are presented in Table IV. One can observe that these values are greatly dependent on the level of calculation. For the BF_3 complex, the 3-21G and MIDI-3 basis sets overestimate the complexation energy, while the 6-31G* and the MP2/6-31G* values seem more reasonable.[3c,16]

Regarding the BCl_3 and BBr_3 complexes, the results obtained with all electron basis sets are very similar to those obtained with ECP for Cl and Br. In both cases the magnitude of the computed complexation energy diminishes when the size of the basis set is increased and the inclusion of electron correlation produces an important stabilization of the complex.

According to the above-mentioned generally accepted Lewis acidity scale, the formation energy of formaldehyde–BX_3 complexes should increase in the order $BF_3 < BCl_3 < BBr_3$. The

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Table III. Selected Geometric Parameters[a] for Formaldehyde and Formaldehyde–BX_3 Complexes

		bond lengths, Å				bond angles, deg		
compd	basis set	C–O	B–O	B–X1	B–X2	∠COB	∠OBX1	∠OBX2
H_2CO	3-21G	1.207						
	MIDI-3	1.208						
	6-31G*	1.184						
	exp[b]	1.230						
$H_2CO–BF_3$	3-21G	1.225	1.683	1.376	1.358	123.5	99.8	103.3
	MIDI-3	1.227	1.687	1.387	1.368	123.8	100.1	103.1
	6-31G*	1.191	2.211	1.318	1.308	122.0	93.4	95.4
$H_2CO–BCl_3$	3-21G	1.232	1.602	1.895	1.845	131.3	105.5	104.1
	MIDI-3	1.232	1.634	1.865	1.834	131.5	105.2	103.2
	HW1	1.232	1.601	1.892	1.846	132.0	105.6	104.1
	3-21G(*)	1.229	1.644	1.847	1.811	131.2	105.2	103.2
	MIDI-3(*)	1.228	1.687	1.817	1.795	131.0	104.5	102.1
	HW2	1.229	1.650	1.840	1.805	131.5	105.7	103.1
	6-31G*	1.205	1.651	1.832	1.810	129.0	106.5	102.7
	HW3	1.205	1.659	1.822	1.799	128.7	106.3	102.6
$H_2CO–BBr_3$	3-21G	1.230	1.604	2.060	2.012	131.9	106.6	103.3
	MIDI-3	1.233	1.606	2.060	2.015	133.6	106.8	103.3
	HW1	1.232	1.588	2.095	2.045	133.4	106.8	104.2
	3-21G(*)	1.229	1.656	1.991	1.959	130.9	104.9	102.3
	MIDI-3(*)	1.231	1.642	1.986	1.959	132.2	106.0	102.9
	HW2	1.230	1.622	2.034	1.999	133.2	106.3	103.6
	HW3	1.207	1.611	2.022	1.995	130.1	108.0	103.2

[a] See Chart 1 for numeration. [b] Reference 26b.

Table IV. Formation Energies (kcal/mol) of the Formaldehyde–BX_3 Complexes

	Lewis acid		
level of calculation	BF_3	BCl_3	BBr_3
RHF/3-21G	-25.5	-22.9	-18.0
RHF/MIDI-3	-25.2	-21.1	-18.4
RHF/HW1		-22.6	-20.7
RHF/3-21G(*)		-15.4	-11.2
RHF/MIDI-3(*)		-13.7	-14.9
RHF/HW2		-14.5	-14.1
RHF/6-31G*	-7.2	-2.7	
RHF/HW3		-2.1	-2.8
MP2/6-31G*	-7.0	-7.1	
MP2/HW3		-6.0	-8.0

Table V. Charge Transfer (au) to the Lewis Acid in Formaldehyde–BX_3 Complexes

	Lewis acid		
basis set	BF_3	BCl_3	BBr_3
3-21G	0.167	0.281	0.265
MIDI-3	0.165	0.232	0.261
HW1		0.279	0.283
3-21G(*)		0.244	0.211
MIDI-3(*)		0.192	0.216
HW2		0.242	0.237
6-31G*	0.035	0.234	
HW3		0.230	0.253

Table VI. Orbital Energies (au) for the Equilibrium Geometries of Boron Trihalides

orbital	basis set	BF_3	BCl_3	BBr_3
a_2''	3-21G[a]	0.4150	0.0490	0.0275
	6-31G*[b]	0.2092	0.0805	0.0539
e''	3-21G[a]	-0.6656	-0.4998	-0.4399
	6-31G*[b]	-0.6768	-0.4875	-0.4313

[a] HW1 is used for BCl_3 and BBr_3. [b] HW3 is used for BCl_3 and BBr_3.

Table VII. Orbital Energies (au) for the Equilibrium Geometry of Formaldehyde

orbital	basis set	*E*
b_2	3-21G	-0.4329
	6-31G*	-0.4354
a_1	3-21G	-0.6369
	6-31G*	-0.6528

Table VIII. Computed Wavenumber[a] for the C=O Stretching Vibration of Formaldehyde and Formaldehyde–BX_3 Complexes

	$\bar{\nu}$, cm^{-1}
H_2CO	1916
$H_2CO–BF_3$	1837
$H_2CO–BCl_3$	1800
$H_2CO–BBr_3$	1796

[a] Computed with the 3-21G basis set for H_2CO and $H_2CO–BF_3$ and with HW1 for $H_2CO–BCl_3$ and $H_2CO–BBr_3$.

results presented in Table IV show that this is not always the case. As a matter of fact, the correct ordering for the BF_3/BCl_3 couple is only attained at the MP2/6-31G*//6-31G* level of calculation and with an energy difference of only 0.1 kcal/mol. For the BCl_3/BBr_3 couple the experimental ordering is already obtained at the RHF level with MIDI-3(*) and HW3. The inclusion of electron correlation increases the energy difference.

These results show that the computed complexation energies are greatly dependent on the level of calculation. It is well-known that the use of truncated basis sets leads to the so called basis set superposition error. This error is supposed to diminish when the size of the basis set is increased. However, explicit correction of this error does not necessarily give more reliable results.[16,26]

The values presented in Table IV show that the computation of reliable complexation energies requires a high level of calculation, at least MP2/6-31G*//6-31G*, which in most cases involves a huge computational effort. However, other aspects, such as complex geometries, can be described at a lower computational cost.

Analysis of the Interaction. Formaldehyde and boron trihalides form typical donor–acceptor complexes. A certain degree of electronic charge transfer between the Lewis base moiety and the Lewis acid moiety is produced. Table V presents the magnitude of this charge transfer computed from the Mulliken population analysis for the studied complexes. One can observe that there is a close relationship between the magnitude of the charge transfer, the value of the B–O bond length, and the degree of geometry distortion of both fragments (see Tables II and III). The stronger the Lewis acid, the greater should be the charge transfer. With all basis sets, the BCl_3 complex involves a greater charge transfer than the BF_3 complex. However, for the

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Table IX. Orbital Energies (au) for Formaldehyde and Formaldehyde–Y Complexes

orbital	basis set		Y			
			BF_3	BCl_3	BBr_3	H^+
π^*	3-21G[a]	0.1475	0.0447	0.0033	−0.0010	−0.1951
	6-31G*[b]	0.1459	0.1110	0.0398	0.0290	−0.1858
n	3-21G[a]	−0.4329	−0.5452	−0.5964	−0.6332	−0.8312
	6-31G*[b]	−0.4354	−0.4766	−0.5781	−0.6253	−0.8434
π	3-21G[a]	−0.5267	−0.6387	−0.6942	−0.6968	−0.8959
	6-31G*[b]	−0.5402	−0.5764	−0.6746	−0.6847	−0.9075

[a] HW1 is used for BCl_3 and BBr_3. [b] HW3 is used for BCl_3 and BBr_3.

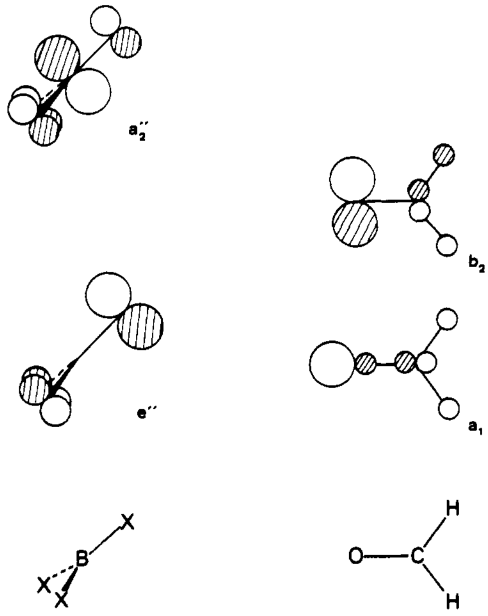

Figure 1. Molecular orbitals of BX_3 and formaldehyde which intervene in the interaction between both fragments.

BCl_3/BBr_3 couple 3-21G and 3-21G(*) do not agree with the correct acidity scale.

These results can be rationalized in terms of molecular orbital interactions. Figure 1 schematically represents the molecular orbitals of formaldehyde and BX_3 that intervene in these interactions. The most important interaction takes place between the two occupied molecular orbitals of formaldehyde, a_1 and b_2, which represent the two oxygen lone pairs, and the LUMO of BX_3, a_2''. This kind of interaction leads to a ∠BOC bond angle of 120–130°, which is the situation that allows a maximum overlap between the LUMO of BX_3 and both formaldehyde occupied orbitals.

Tables VI and VII show the computed energies for the molecular orbitals presented in Figure 1. These orbital energies allow us to understand the relative strength of boron trihalides as Lewis acids. As a matter of fact, the energy of the LUMO of BX_3 decreases when going from BF_3 to BBr_3, thus favoring the interaction with the formaldehyde donor orbitals.

The BX_3 e″ occupied orbital also plays a role in the interaction. For BCl_3 and BBr_3 this orbital can interact in a repulsive way with the b_2 orbital of formaldehyde, since they have similar energies. On the contrary, for BF_3, this e″ orbital is much lower in energy, so that its interaction with b_2 is very weak. This repulsive interaction can be related to the values of the ∠BOC bond angle in the complexes. The obtained values increase in the order $BF_3 < BCl_3 < BBr_3$ (see Table III), which agrees with the energy ordering of the e″ orbitals. As the interaction with the e″ orbital becomes important, the ∠BOC angle increases to minimize the repulsive interaction. This fact produces an increase in the overlap between the LUMO of BX_3 and the a_1 orbital of formaldehyde and so a more important lengthening in the C=O bond, since this orbital is bonding with respect to this bond. The repulsive interaction with the e″ orbital of BX_3 also plays a role in the relative values of the $\angle OBX_1$ and $\angle OBX_2$ angles. This interaction scheme can also be applied to the formaldehyde–BH_3 complex.[16] In this case the ∠BOC, $\angle OBX_1$, and $\angle OBX_2$ angles have similar values to those corresponding to the BF_3 complex, since in BH_3 there is no e″ orbital.

The weakening of the C=O bond in the complex leads to a variation of the values of the frequency associated with the C=O stretching vibration. Table VIII presents the values for this wavenumber computed for formaldehyde and its complexes with boron trihalides. Complexation produces an important diminution of this wavenumber, the degree of diminution being related to the strength of the complexing Lewis acid. The computed shift in the wavenumber for the formaldehyde–BF_3 complex, 79 cm^{-1}, is in excellent agreement with experimental values.[3f,4] For instance, shifts of 70–85 cm^{-1} have been reported for aromatic aldehydes.[4]

The interaction between molecular orbitals of the donor and acceptor fragments allows us to understand the main features of formaldehyde–BX_3 complexes. Other kinds of interactions seem to play a less important role. For example, a purely electrostatic interaction would lead to a linear B–O–C arrangement, since the dipole moment of formaldehyde lies along the C=O bond axis.[12] Moreover, from an electrostatic point of view, the Lewis acidity scale for boron trihalides should be $BF_3 > BCl_3 > BBr_3$, in contradiction with experimental evidence and with the theoretical results discussed above.

Interactions involving the formaldehyde π orbitals do not seem to be important, since the acceptor orbital of the BX_3 moiety with the appropriate symmetry lies too high in energy. However, the energies of these π orbitals noticeably change through complexation as can be seen in Table IX, where the energies of the most important molecular orbitals centered on the formaldehyde moiety are presented. For sake of comparison, protonated formaldehyde has also been included. One can observe that the energy of the nonbonding n orbital diminishes because of the complexation. This stabilization is more important the stronger is the Lewis acid. The interaction scheme discussed above allows us to interpret this fact since this orbital is one of the donor orbitals of formaldehyde (b_2) that intervenes in the interaction with the Lewis acid. π and π^* orbitals are also stabilized through the complex formation. Here, the stabilization is mainly due to the electric field produced by the Lewis acid that perturbates the π charge distribution of formaldehyde.[28] This stabilization is also related to the acid strength.

The π orbital of formaldehyde is mainly centered in the oxygen atom, while the π^* orbital is centered in the carbon atom. For this reason the stabilization of the π orbital is more important and the energy different between π and π^* orbitals increases. This fact can be related to the calculated blue shift in the π–π^* transition of the formaldehyde–H_2O complex.[29] The great stabilization of the n orbital of formaldehyde leads to an augmentation of the energy separation between this orbital and the π^* orbital. This fact qualitatively agrees with the experimentally observed blue shift in the n–π^* transition for carbonyl compounds under Lewis acid complexation.[3d,4]

The fact that boron trihalides produce the same effect on π orbitals that H^+ does favors the idea that these effects are mainly of electrostatic nature, since for H^+ there is no orbital capable of interaction with the π orbitals of formaldehyde.

The electric field of the Lewis acid produces a polarization in the π electron system as can be seen in Table X, where the atomic

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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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