

## Structures of Alkali Metal Pseudohalides: LiOCP, NaOCP, LiSCP, NaSCP

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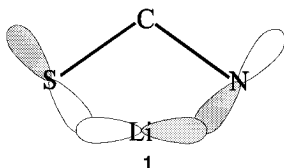
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The equilibrium geometries of LiOCP, NaOCP, LiSCP, and NaSCP were calculated at the MP2 and QCISD/6-311G\* levels of theory. It was found that all four have  $\pi$ -type cyclic conformers. In case of the former two, this form is the most stable isomer, whereas in LiSCP and NaSCP, no other conformations but the cyclic exist. Vibrational frequencies and ionization energies were calculated to facilitate vapor phase identification. Semiempirical quantum chemical and molecular mechanics simulations were also undertaken to study their behavior in solutions; they are expected to dissociate, and the resulting pseudohalide anions are linear. Thus the existence of the  $\pi$ -complex cannot be demonstrated in solution.

## Introduction

In our previous works<sup>1–3</sup> we demonstrated the existence of a new isomeric form of pseudohalides: the  $\pi$ -complexes. In these molecules the substituent atom is bonded to the two end atoms of the pseudohalide group, which becomes bent: a four-atom ring is formed (see e.g. LiSCN, structure 1). The bond



was explained by the interaction of the pseudohalide  $\pi$ -system with the empty p orbital of the substituent atom. Similar complexes were shown to exist by IR spectroscopy in a noble gas matrix between alkali metal cations and  $\text{CO}_2^-$ , where the alkali metal atom is situated between the two oxygens.<sup>4</sup> The existence of the complex  $\text{Li}^+\text{CO}_2^-$  with  $C_{2v}$  symmetry is questionable. While this complex could not be identified by infrared spectroscopy in a noble gas matrix,<sup>5</sup> it was observed by ESR spectroscopy in the same medium.<sup>6</sup>

Similarly, the molecules MNC (M = Li, Na, K) were shown to exist as stable T-shaped  $\pi$ -complexes both by calculations<sup>7</sup> and by microwave spectroscopy.<sup>8</sup> However, the electronic structure of these molecules is quite different from that presented

in structure 1, as the chemical bond is formed between the alkali p orbital pointing toward the CN group and the in-plane  $\pi$  orbital of the CN group. As the stabilities of the three lowest energy isomers in MNC are different by less than 20 kJ/mol and the transition states between them are also low-lying, none of these states will be proper eigenstates of the system.<sup>7</sup> This may also be the situation for the  $\pi$ -complex of  $\text{NaN}_3$ .<sup>1</sup>

The  $\pi$ -complexes show an increasing tendency of formation in the series NCO,  $\text{N}_3$ , NCS and with the size of the substituent atom.<sup>1</sup> We have so far found two examples by ab initio calculations (LiNCS and NaNCS) where the  $\pi$ -complex is the global minimum on the potential energy surface. In NaNCS, the cyclic form is between 12 and 16 kJ/mol more stable than the linear and thus it appears likely that sodium rodanide, if exists, is a tetraatomic ring in the vapor phase.

On the basis of the previous discussion and the literature, it appears likely that if the nitrogen atom in the pseudohalide group is replaced by the heavier phosphorus, the stability of the  $\pi$ -complex further increases. This may provide the possibility of synthesizing such compounds. The aim of this work was to investigate the feasibility of this idea by calculating the PCO and PCS derivatives of lithium and sodium. A further question arises as to whether the  $\pi$ -complex, however stable it might be in the vapor phase, could also exist in the condensed phase. Thus an intended aim was also to estimate the structure in solution.

Only the alkyl and hydrogen derivatives of the substituted PCO and PCS compounds are known so far. The first phosphaketene, *t*-BuPCO, was synthesized in 1983.<sup>9</sup> This compound dimerizes above  $-60^\circ\text{C}$ , similarly to the analogous phosphatioketene.<sup>10</sup> Both compounds may be stabilized by introducing bulky substituent groups.<sup>11</sup> The unstable HPCO was identified and studied by infrared spectroscopy in an argon matrix at low temperature.<sup>12</sup> The equilibrium geometries of XPCO, XPCS, XOCP, XSOP (where X = H,  $\text{CH}_3$ ) have been calculated at the ab initio HF and MP2 levels.<sup>13</sup>

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**Table 1.** Geometries of the Stable Pseudohalide Isomers (Å; deg)<sup>a</sup>

molecule <sup>b</sup>	XC	XO	PC	CO	XCO	XCP	PCO
LiOCP (l)		1.6485	1.5799	1.2505	0.0	180.0	180.0
		1.6538	1.5873	1.2542	0.0	180.0	180.0
LiOCP (r)	1.9458	1.9384	1.6082	1.2250	71.29	94.21	165.19
	1.9389	1.9695	1.6145	1.2314	72.99	93.12	166.10
NaOCP (l)		2.0178	1.5897	1.2397	0.0	180.0	180.0
		2.0246	1.5954	1.2446	0.0	180.0	180.0
NaOCP (r)	2.3317	2.4349	1.6205	1.2112	80.06	90.68	170.70
	2.3244	2.4653	1.6234	1.2196	81.76	90.22	171.99

molecule <sup>b</sup>	XC	XS	PC	CS	XCS	XCP	PCS
LiSCP (r)	2.0270	2.2974	1.5913	1.6546	76.48	93.39	169.80
	2.0109	2.3259	1.6082	1.6422	78.38	91.62	169.99
NaSCP (r)	2.4021	2.6715	1.593	1.6539	80.08	94.72	174.80
	2.3824	2.7015	1.6098	1.6412	82.13	93.09	175.22

<sup>a</sup> Geometries at the QCISD/6-311G\* (always on top) and MP2/6-311G\* (below) levels of theory. <sup>b</sup> l and r in parentheses mean the linear and cyclic isomers, respectively.

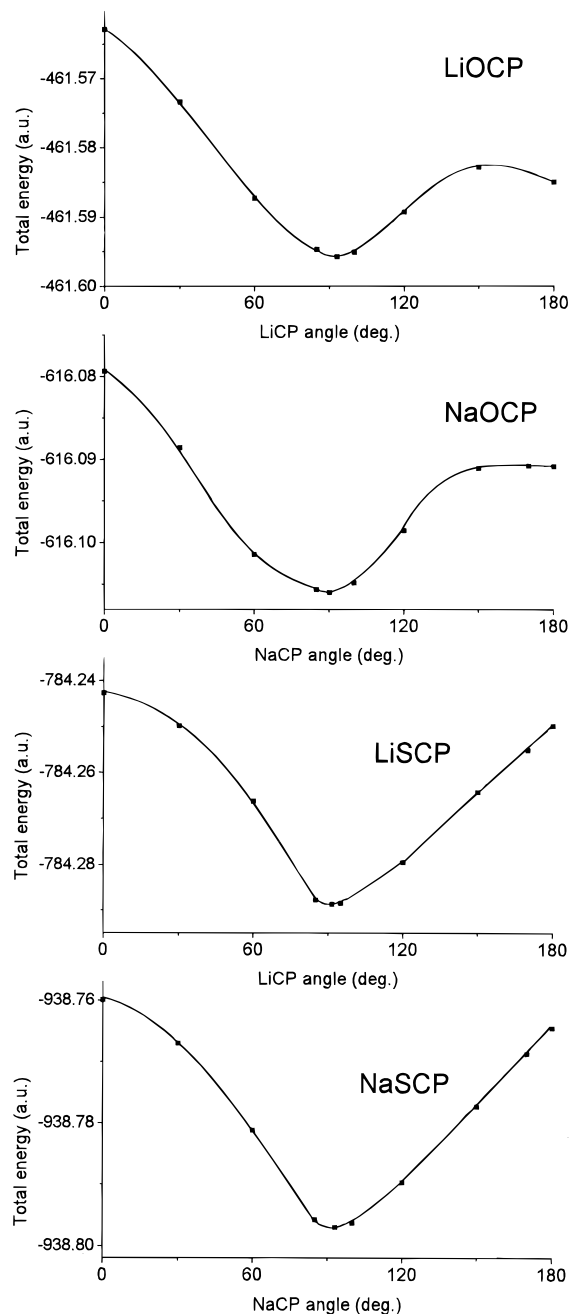
### Calculations

Ab initio calculations in this work were performed using the Gaussian-92<sup>14</sup> quantum chemistry package with a 6-311G\* basis set. Equilibrium geometries were obtained by the gradient method at the full QCISD/6-311G\* level. Bending potential energy surfaces were calculated by varying the LiCP and NaCP angles and optimizing all other geometrical parameters at each point at the MP2/6-311G\* level. This procedure ensures that the interaction of all vibrations is being explicitly taken care of. Harmonic vibrational frequencies were calculated at the equilibrium geometries at the MP2/6-311G\* level to ensure that the calculated equilibrium conformations are genuine minima on the potential energy surface. In order to ensure that the ionic forms of the molecules investigated are properly described, some calculations were carried out using diffuse functions (MP2/6-311+G\*) and a larger basis set (MP2/6-311+G(2d,f)) as well.

In order to estimate bulk behavior of  $\pi$ -complexes, the geometry of dissolved LiPCS was simulated using semiempirical methods and molecular mechanics. In calculations using an MNDO Hamiltonian,<sup>15</sup> molecules were arranged in a droplet with the XFIT algorithm.<sup>16</sup> Solvation was represented with the inclusion of 64 water molecules around an LiPCS  $\pi$ -complex. Additionally, molecular mechanics calculations on 214 water molecules around LiPCS and with the inclusion of periodic boundary conditions were also performed with the MM+ method using AM1 charges on all atoms and the default force parameters.<sup>17</sup> Because of the geometry dependence of charge, the optimization was performed in iterative steps; i.e. single-point AM1 calculations and MM+ optimization steps followed each other until the rms gradient was less than 0.1 kJ/(Å mol).

### Results and Discussion

The calculated equilibrium structures of the studied molecules are given in Table 1. Figure 1 shows the change in the potential energy as a function of the alkali metal atom (X) position with respect to the PCO and PCS groups. These were produced by varying the XCP angle with the rest of the geometry being optimized at all points.



**Figure 1.** Potential energy diagram for the migration of the Li and Na atoms between the two ends of the PCO and PCS groups. The XCP angle (X = Li, Na) was varied, and the rest of the geometry was fully optimized at each point of the curve (at the MP2/6-311G\* level).

According to the QCISD/6-311G\* calculations, both LiOCP and NaOCP have two stable isomers: one linear and one cyclic. This may seem odd in comparison with the nitrogen-containing pseudohalides where there are two low-energy linear forms, the cyanates and isocyanates. The situation is essentially different if a methyl group is attached to OCP and SCP groups: neither the linear nor the cyclic form exists. The frame becomes strongly bent.<sup>13</sup> While CH<sub>3</sub>PCO is more stable than CH<sub>3</sub>OCP, of the sulfur isomers CH<sub>3</sub>SCP is more stable. In linear LiOCP and NaOCP molecules, the calculated CO bond lengths are 1.24–1.25 Å, definitely shorter than that in the analogous methyl derivative (1.302 Å<sup>13</sup>) or in CH<sub>3</sub>OCN (1.293 Å<sup>18</sup>).

One surprising aspect of the calculated structures is that in both LiOCP and NaOCP the global minimum is the cyclic

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**Table 2.** Calculated Vibrational Frequencies and Intensities<sup>a</sup>

LiOCP lin.	1805 (1126)	975 (7)	638 (83)	456 (1)	88 (71)	
	$\nu_{\text{asOCP}}$	$\nu_{\text{sOCP}}$	$\nu_{\text{LiO}}$	$\delta_{\text{OCP}}$	$\delta_{\text{LiOC}}$	
LiOCP ring	1815 (653)	838 (10)	714 (117)	445 (52)	462 (3)	217 (14)
	$\nu_{\text{CO}}$	$\nu_{\text{OCP}}$	$\nu_{\text{LiC}}$	$\delta_{\text{OCP}}$	$\gamma_{\text{OCP}}$	$\delta_{\text{ring}}$
LiSCP ring	1429 (421)	587 (59)	645 (80)	373 (16)	333 (9)	253 (7)
	$\nu_{\text{asSCP}}$	$\nu_{\text{sSCP}}$	$\nu_{\text{LiC}}$	$\delta_{\text{SCP}}$	$\gamma_{\text{SCP}}$	$\delta_{\text{ring}}$
NaOCP lin.	1823 (1146)	886 (89)	354 (64)	464 (2)	32 (21)	
	$\nu_{\text{asOCP}}$	$\nu_{\text{sOCP}}$	$\nu_{\text{NaO}}$	$\delta_{\text{OCP}}$	$\delta_{\text{NaOC}}$	
NaOCP ring	1850 (734)	821 (8)	581 (22)	469 (6)	277 (42)	111 (2)
	$\nu_{\text{CO}}$	$\nu_{\text{OCP}}$	$\nu_{\text{NaC}}$	$\delta_{\text{OCP}}$	$\gamma_{\text{OCP}}$	$\delta_{\text{ring}}$
NaSCP ring	1407 (510)	604 (23)	461 (34)	257 (31)	337 (13)	137 (2)
	$\nu_{\text{asSCP}}$	$\nu_{\text{sSCP}}$	$\nu_{\text{NaC}}$	$\delta_{\text{SCP}}$	$\gamma_{\text{SCP}}$	$\delta_{\text{ring}}$

<sup>a</sup> Frequencies in  $\text{cm}^{-1}$  and intensities (in parentheses) in  $\text{km/mol}$ . Obtained by 6-311G\*/MP2 calculations.

**Table 3.** Comparison of the Results of Geometry Optimizations with Different Methods on LiPCS<sup>a</sup>

method	LiC	PC	CS	LiCS	PCS
QCISD/6-311G*	2.0270	1.5913	1.6546	76.48	169.85
MP2/6-311G*	2.0109	1.6082	1.6422	78.38	169.99
MP2/6-311+G*	2.0107	1.6090	1.6420	78.32	169.95
MP2/6-311+G(2d,f)	2.0163	1.6042	1.6342	79.13	171.42
HF/6-311G*	2.0796	1.5581	1.6257	75.26	171.45
MNDO	2.240	1.466	1.602	68.16	175.60
MNDO soln <sup>b,e</sup>	>4	1.452	1.544		180.00
MM+ <sup>c</sup>	2.610	1.662	1.622	98.98	179.02
MM+ soln <sup>d,e</sup>		1.606	1.658		179.89

<sup>a</sup> Bond lengths in angstroms; bond angles in degrees. <sup>b</sup> Calculated for 64 water molecules around an LiPCS  $\pi$ -complex. <sup>c</sup> Using AM1 charges; see text. <sup>d</sup> Calculated for 214 water molecules around an LiPCS  $\pi$ -complex considering periodic boundary conditions. <sup>e</sup> The molecule dissociates on solution to  $\text{Li}^+$  and  $\text{PCS}^-$ .

$\pi$ -complex (28.4 and 40.0 kJ/mol below the linear form). Furthermore, the linear forms are not even expected to exist: the potential barriers from the linear side are 5.7 and 1.5 kJ/mol, respectively, which are of the order of the energies of the  $\delta_{\text{XOC}}$  deformation vibrations (88 and 32  $\text{cm}^{-1}$ , respectively; see Table 2.).

In LiSCP and NaSCP, the importance of the cyclic form is even more striking. As can be seen from Figure 1, the linear isomers do not even appear on the potential energy surface. In order to test the adequacy of the basis set used, further calculations for the linear and cyclic isomers of LiSCP were carried out with a larger basis set. However, no linear form could be found and the optimum geometrical data for the cyclic isomer did not vary considerably using the MP2/6-311+G\* and MP2/6-311+G(2d,f) levels of theory (Table 3). Therefore all the conclusions in the following were drawn from calculations with the 6-311G\* basis. We also performed calculations to prove or disprove the existence of other topologically possible isomers as minima on the potential surface. On using relative stabilities for the [CLiNO] potential surface,<sup>19</sup> the analogues of lithium fulminate, carbonitrene, isofulminate, and oxazirine were also studied, where the oxygen atom is replaced by a sulfur and the nitrogen by a phosphorus atom. None of the above are, however, real isomers at the MP2/6-311G\* level, and thus the potential surfaces [CLiPS] and [CNaPS] have only one stable minimum, the cyclic  $\pi$ -complex.

All of the  $\pi$ -complexes, studied so far, are planar molecules. On formation of the complex between the linear PCO group and the alkali metal atom, the PC bond length increases whereas the CO length slightly decreases while the entire pseudohalide group bends. The central pseudohalide angles in PCO and PCS derivatives of 165–170 and 170–175°, respectively, are somewhat greater than those in NCO (164–168°) and NCS (165–170°) analogues.

**Table 4.** Calculated Ionization Energies (eV)<sup>a</sup>

LiOCP lin.	7.50 ( $\pi$ )	11.95 ( $\sigma$ )	15.15 ( $\pi$ )	19.23 ( $\sigma$ )
LiOCP ring	8.25, 8.78	13.03	15.90, 16.27	18.90
NaOCP lin.	6.84 ( $\pi$ )	11.43 ( $\sigma$ )	14.47 ( $\pi$ )	18.22 ( $\sigma$ )
NaOCP ring	7.63, 7.97	12.50	15.42, 15.59	18.45
LiSCP ring	8.02, 8.61	12.84	12.28, 12.78	16.11
NaSCP ring	7.51, 7.88	11.80	12.16, 12.35	15.70

<sup>a</sup> Calculated with a 6-311G\* basis using Koopmans' theorem.

The calculated harmonic vibrational frequencies are summarized in Table 2. These values reflect the structural differences expected between the linear and cyclic forms. In linear pseudohalides, the deformation vibration,  $\delta_{\text{MOC}}$ , is a low-frequency one (88 and 32  $\text{cm}^{-1}$ ). In contrast, the lowest frequency vibrations of the cyclic complexes are the ones corresponding to the torsional motions of the alkali metal atoms, and thus the potential curves in Figure 1 depict these vibrations well. The frequencies of the torsional vibrations are more strongly dependent on the alkali metal atoms than on the pseudohalide group. The torsional vibrational frequencies for LiNCS, LiOCP, and LiSCP are 196,<sup>1</sup> 217, and 253  $\text{cm}^{-1}$ , respectively, whereas the corresponding values for NaNCS, NaOCP, and NaSCP are 139,<sup>1</sup> 111, and 137  $\text{cm}^{-1}$ . Therefore the zero-point energies, which fall in the range 0.6–1.6 kJ/mol, are negligible compared to the barrier height.

A better method to prove the existence of the cyclic form of these molecules by experiment might be gas-phase UV photoelectron spectroscopy. The calculated ionization energies (using Koopmans' theorem) are listed in Table 4. As can be seen, the photoelectron spectra of the linear and cyclic forms of LiOCP and NaOCP are expected to be strikingly different.

The above observations and ref 1 show that a number of  $\pi$ -complexes correspond to well-defined minima on the potential energy surface and some of them are even global minima. Thus, if these molecules existed in the vapor phase, they could be observed by spectroscopic methods.<sup>1</sup> However it is yet unknown if they do exist there and thus lower level calculations were performed to attempt to simulate their behavior in aqueous solutions. LiPCS was chosen as an example where the  $\pi$ -complex form is the only minimum. First, the MNDO method was employed. Solutions were modeled by 64 water molecules arranged in close fit around the  $\pi$ -complex. Although periodic boundary conditions were not applied in these calculations, the diameter of the droplet increased by less than 10% as a result of the calculations. The results of MNDO geometry optimizations (see Table 3) indicated unambiguously that the molecule dissociates on solution to  $\text{Li}^+$  and  $\text{PCS}^-$ . As the lithium gradually moves away from the  $\text{PCS}^-$  moiety during optimization, the PCS angle gradually increases to finally reach 180°. In order to include periodic boundary conditions and a larger ensemble of molecules, molecular mechanics calculations were invoked. First, it can be seen for a single LiPCS molecule in Table 3 that the geometry is reasonably well represented by

the MM+ method, considering that the applied bond parameters were not optimized. Nevertheless, the MM+ optimization on the solution also resulted in the Li<sup>+</sup> ion leaving the rest of the molecule (>4 Å). (Obviously, greater interatomic distances are not expected in molecular mechanics calculations, even if a molecule dissociates.) The appropriate energy gain on dissociation can be calculated from the energy difference between first using the gas-phase structure in an optimized water shell and then co-optimizing LiPCS and water. This energy was calculated to be ~300 kJ/mol. Thus it can be seen from the above discussion that both semiempirical and molecular mechanics calculations predict that  $\pi$ -complexes will dissociate on solution and hence cannot be detected as such by spectroscopic methods.

Additionally, molecular dynamics simulations on an isolated LiPCS molecule were also carried out, using an MM+ force field. These calculations were performed using different heating rates with and without bath relaxation. These showed that dissociation of an isolated LiPCS molecule would take place above ~1200 K. This value of course is hypothetical, as it stems from a simplified model and neglects all interactions between molecules. It is however likely that if LiPCS molecules

enter the vapor phase as isolated molecules (i.e.  $\pi$ -complexes), they would be fairly stable there and could possibly be observed.

### Conclusions

High-level ab initio calculations in this work demonstrated that the molecules LiPCS and NaPCS should only exist as tetraatomic rings in the vapor phase. As a result, they should be ideal candidates for providing proof for the existence of the  $\pi$ -complex form, which had been shown to be a new and often predominant isomer for a number of pseudohalides.<sup>1</sup> Although their examination in the solution phase does not appear to be feasible, they are expected to be stable above their melting points. It is hoped that this work will induce experimental effort, especially by vapor phase electron diffraction, MW, and IR and UV photoelectron spectroscopy or possibly in a noble gas matrix to identify this isomer.

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