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# Conformation and structure of dichlorophosphoryl isocyanate in the gaseous and solid phase

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Dedicated to Professor Bernt Krebs on the Occasion of his 80th Birthday

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#### **KEYWORDS**

Isocyanate – phosphorus – gas electron diffraction – vibrational spectroscopy – X-ray diffraction – molecular structure - conformation

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#### Abstract

The conformational properties and the molecular structure of dichlorophosphoryl isocyanate, Cl<sub>2</sub>P(O)NCO, have been studied by combining vibrational spectroscopy (IR and Raman), gas-phase electron diffraction (GED), X-ray crystallography (XRD), and quantum-chemical calculations. Computationally, two conformers of  $C_s$  symmetry with the P=O bond being in *syn-* or *anti*-configuration relative to the NCO group are predicted to be close in energy (ca. 2 kJ mol<sup>-1</sup>). Experimentally, both gas-phase and matrix-isolation IR spectra of Cl<sub>2</sub>P(O)NCO suggest the presence of a single conformer, which was determined to be the energetically more favorable *syn-*conformer. This was also found to exist in the solid state by low-temperature XRD. However, the molecule in the solid state is significantly distorted from ideal  $C_s$  symmetry with an O–P–N–C dihedral angle of 38.1(1)° due to intermolecular C···O contacts (2.881(4) Å). In the gas phase, the GED analysis suggests that the molecule exists predominantly as *syn-*conformer but with dynamic behaviour about the two minimum structures (*syn* and *anti*).

#### Introduction

Covalent isocyanates R–NCO are versatile reagents in synthetic and materials chemistry.<sup>1</sup> For example, toluene diisocyanate and methylene diphenyl isocyanate have been widely used in industry for manufacturing of flexible and rigid polyurethane products as thermoplastic elastomers and thermoset resins.<sup>2</sup> Chemically, isocyanates are not only reactive towards alcohols and amines but also unstable due to self-additions and trans-condensations. This is particularly the case for simple  $\alpha$ -oxo-isocyanates such as acyl isocyanates (RC(O)–NCO),<sup>3</sup> sulfinyl isocyanates (RS(O)–NCO),<sup>4</sup> and sulfonyl isocyanates (RS(O)<sub>2</sub>–NCO),<sup>5</sup> most of which undergo facile oligomerization or polymerization reactions in the condensed phase at room temperature. Therefore, the fundamentally important conformational and structural properties of these compounds remained attracting theoretical and experimental interest in the recent few decades.

As another class of  $\alpha$ -oxo-isocyanates, phosphoryl isocyanates (R<sub>2</sub>P(O)-NCO) have been used for the synthesis of phosphorylated urethanes and ureas, and some physiologically active ones find applications as insecticides and drugs.<sup>6</sup> Similar to the synthesis of phosphorus(III) isocyanates,<sup>7</sup> most phosphoryl isocyanates can be easily prepared from phosphoryl halides and silver isocyanate. However, in contrast to

other  $\alpha$ -oxo-isocyanates, only very few simple phosphoryl isocyanates have been isolated and structurally characterized. Recently, the vibrational spectroscopy and solid-state structure of the simplest phosphoryl isocyanate F<sub>2</sub>P(O)NCO have been reported.<sup>8</sup> According to the quantum-chemical calculations, two energetically similar conformers of F<sub>2</sub>P(O)NCO ( $\Delta E_{cal} = 4.4 \text{ kJ mol}^{-1}$ , CBS-QB3) are expected to coexist, but instead, only the lower-energy conformer with the P=O bond being in *syn*-configuration to the NCO group was ascertained in the solid state by low-temperature X-ray crystallography. The preference of a single conformation has also been observed in other phosphorus(III) isocyanates F<sub>2</sub>PNCO<sup>9</sup> and Cl<sub>2</sub>PNCO,<sup>7</sup> but instead, two conformers have been observed for the isoelectronic azides F<sub>2</sub>PN<sub>3</sub>.<sup>10</sup> Very recently, the complex conformational landscape of triallyl phosphate has been explored by combining matrix-isolation IR spectroscopy and density functional theory (DFT) calculations, and more than 50 conformers have been identified.<sup>11</sup>

Continuing our interest in the synthesis and characterization of simple isocyanates<sup>7,9</sup> and azides,<sup>7,12</sup> herein, we report a first-time full characterization of dichlorophosphoryl isocyanate, Cl<sub>2</sub>P(O)NCO, by combining vibrational spectroscopy, gas-phase electron diffraction (GED), X-ray crystallography (XRD), and quantum-chemical calculations. Prior to this study, this isocyanate has been only characterized by IR spectroscopy in the gas phase.<sup>13</sup>

#### **Experimental Section**

#### **Sample preparation**

Dichlorophosphoryl isocyanate,  $Cl_2P(O)NCO$ , was synthesized by the reaction of  $PCl_5$  with urethane (EtOC(O)NH<sub>2</sub>) according to literature.<sup>13</sup> The volatile part of the reaction mixture was distilled by passing through three cold traps held at -20, -100 and -196 °C. Pure  $Cl_2P(O)NCO$  was retained in the first trap. The quality of  $Cl_2P(O)NCO$  was checked by gas-phase IR spectroscopy and <sup>31</sup>P NMR spectroscopy (singlet, -11.9 ppm, reference to external standard H<sub>3</sub>PO<sub>4</sub>).

#### Vibrational and NMR spectroscopy

Gas-phase IR spectra were measured in an IR gas cell (optical path length 20 cm, Si windows, 0.5 mm thick), which was fitted into the sample compartment of the FT-IR instrument (Bruker, Tensor 27).

Raman spectra of the liquid were recorded on a Bruker-Equinox 55 FRA 106/S FT-Raman spectrometer using a 1064 nm Nd:YAG laser (200 mW) with 200 scans at a resolution of 2 cm<sup>-1</sup>. Matrix IR spectra were recorded on an FT-IR spectrometer (Bruker 70v) in a reflectance mode by using a transfer optic. A KBr beam splitter and a liquid-nitrogen-cooled MCT detector were used in the spectral region of 4000–600 cm<sup>-1</sup>. For each spectrum, 200 scans were collected at a resolution of 0.5 cm<sup>-1</sup>, The gaseous Cl<sub>2</sub>P(O)NCO was mixed with neon (1:1000) in a 1-L stainless-steel container, the Cl<sub>2</sub>P(O)NCO/noble gas mixture was deposited (2 mmol h<sup>-1</sup>, 1.5 h) onto the cold matrix support (2.8 K, Rh-plated Cu block) in a high vacuum (~10<sup>-8</sup> mbar), using a closed-cycle helium cryostat (Sumitomo Heavy Industries, SRDK-408D2-F40H) inside the vacuum chamber. For the IR spectra measurement, the cryostat was horizontally rotated ( $\pm$ 180°) to irradiate the matrix-isolated sample with the IR beam.

#### **Quantum-chemical calculations**

A potential energy surface scan was performed on the MP2 *ab initio* level of theory as well as based on several density functional theories with varying Dunning-type or Pople basis set by rotating both isocyanate groups around the P–N bond. Subsequent optimisations of the minimum structures were performed on the respective combination of method and basis set including the calculation of vibrational frequencies to assure true minima. All calculations were performed using the GAUSSIAN09 quantum-chemical program at the version D.01.<sup>14</sup>

#### Gas-phase electron diffraction experiment

The electron diffraction patterns were recorded on the heavily improved Balzers Eldigraph KD-G2 gasphase electron diffractometer at Bielefeld University. Experimental details are found in the Supporting Information (Table S1). Instrumental details are reported elsewhere.<sup>15</sup> Electron diffraction patterns were measured on the Fuji BAS-IP MP 2025 imaging plates, which were scanned by using calibrated Fuji BAS.1800II scanner. Intensity curves (Figure 1) were obtained by applying the method described earlier.<sup>16</sup> Sector function and electron wavelength were refined using carbon tetrachloride diffraction patterns,<sup>17</sup> recorded in the same experiment as the substances.



**Figure 1**. Experimental (O) and model (-) molecular scattering intensities and differences for long (upper curves) and short (lower curves) nozzle-to-detector distances for Cl<sub>2</sub>P(O)NCO.

#### Gas-phase electron diffraction structural analysis

The structural analysis was performed using the UNEX program.<sup>18</sup> All refinements were performed using two intensity curves simultaneously (Figure 1), one from the short and another from the long nozzle-todetector distance. These were obtained by averaging intensity curves measured in independent experiments obtained at the same camera distance. The anti- and syn-conformers were assumed to be of Cs symmetry while for all the other pseudo-conformers  $C_1$  symmetry was used. The differences between values of parameters refined in the same group were kept fixed at the values taken from the MP2/aug-cc-pVTZ calculations. In order to calculate start values for amplitudes of vibrations and curvilinear corrections used in the gas-phase electron-diffraction refinements, analytical quadratic and numerical cubic force fields were calculated for all pseudo-conformers employing the MP2/aug-cc-pVTZ approximation. The bond lengths, angles and dihedrals as well as amplitudes of vibration were refined in the same groups among the conformers. The input potential was initially taken form MP2/aug-cc-pVTZ calculations and then refined without any restrictions during the refinement steps. Between each pair of the ten pseudo-conformers used explicitly by setting up individual z-matrices, ten pseudo-conformers were taken in to the refinement, whose geometries were interpolated between the respective pairs of pseudo conformers. The mean square amplitudes and vibrational corrections to the equilibrium structure were calculated with the SHRINK program.19

#### X-Ray crystallography

A single crystal of dichlorophosphoryl isocyanate was grown *in situ* at 235 K and cooled to 218 K at a rate of 1 K h<sup>-1</sup>. The single crystal was measured on a Rigaku SuperNova diffractometer using Mo-K $\alpha$  radiation

 $(\lambda = 0.71073 \text{ Å})$  at 100.0(1) K. Using Olex2,<sup>20</sup> the structure was solved with the Superflip<sup>21</sup> structure solution program using charge flipping and refined with the ShelXL<sup>22</sup> refinement package using leastsquares refinements. All atoms were refined anisotropically. Crystal Data:  $(M = 159.89 \text{ g mol}^{-1})$ : monoclinic, space group  $P2_1/c$  (no. 14), a = 7.18096(14) Å, b = 11.17462(18) Å, c = 6.58354(11) Å,  $\beta = 11.17462(18)$  Å, c = 11.17462(18) Å, c = 11102.0804(18)°, V = 516.593(16) Å<sup>3</sup>, Z = 4,  $\mu$ (Mo K $\alpha$ ) = 1.442 mm<sup>-1</sup>,  $\rho_{calc} = 2.056$  g cm<sup>-3</sup>, 28035 reflections measured (5.802°  $\leq 2\Theta \leq 59.972°$ ), 1493 unique ( $R_{int} = 0.0547$ ,  $R_{sigma} = 0.0140$ ) which were used in all calculations. The final  $R_1$  was 0.0208 for 1475 reflections with  $I > 2\sigma(I)$  and  $wR_2$  was 0.0583 for all data. CCDC 1579328 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif.

#### Discussion

#### Quantum chemical calculations

For the determination of possible conformers of Cl<sub>2</sub>P(O)NCO existing, several energy profiles for the rotation of the isocyanate group around the P–N bond were calculated. The results of the energy curves are shown in Figure 2. The used combinations of methods and basis sets for determining the potential shoed trustworthiness in previous examinations of the rotational barrier of isocyanantes and azides bound to phosphorus (vide infra).



**Figure 2**. Potential energy scan for the rotation of the isocyanate group around the P–N bond on different levels of theory: a – PBEO/aug-cc-pVTZ, b – MP2/aug-cc-pVTZ, c – MP2/6-311G(2df), d – B3PW91/aug-cc-pVTZ.

All four energy curves confirm the existence of two minima. The first and lowest in energy with a dihedral angle  $\phi$ (OP–NC) of 0° is the *syn*-conformer whereas the second occupies a dihedral angle of 180° and is therefore called *anti*. Both conformers are depicted in Figure 3. Although all four methods show the same tendency in the conformers, some differences occur among the calculations. For example the combination of the *ab initio* perturbation theory MP2<sup>23</sup> and the Pople-type basis set 6-311G(2df)<sup>24</sup> show a very shallow progression around the minimum of the *anti*-conformer and the two maxima in the energy curve ( $\Delta E(\max-\min_{anti</sub>) \approx 0.3 \text{ kJ mol}^{-1}$ ). However, the combination of the Dunning-type basis set aug-cc-pVTZ<sup>25</sup> and MP2 results in a relative low minimum of the *anti*-conformer ( $\Delta E(\max-\min_{anti</sub>) \approx 0.8 \text{ kJ mol}^{-1}$ ). Furthermore, a high-energy barrier for the transition from the *syn* to the *anti*-conformer with about 3 kJ mol<sup>-1</sup> is found in the B3PW91<sup>26</sup>/aug-cc-pVTZ calculation.



Figure 3. Optimized minimum structures of dichlorophosphoryl isocyanate.

**Table 1.** Calculated relative differences in total energy ( $\Delta E$ , kJ mol<sup>-1</sup>), Gibbs free energy ( $\Delta G$ , kJ mol<sup>-1</sup>) between the *anti*- and *syn*-conformers and the relative abundance of the *anti*-conformer in the gas-phase at 298 K.

| method             | $\Delta E$ | $\Delta G$ | anti |
|--------------------|------------|------------|------|
| HF/cc-pVTZ         | 4.6        | 2.69       | 26%  |
| B3PW96/cc-pVTZ     | 2.6        | 1.8        | 32%  |
| PBE0/cc-pVTZ       | 1.9        | 1.3        | 37%  |
| MP2/cc-pVTZ        | 2.0        | 2.3        | 28%  |
| HF/6-311G(2df)     | 4.4        | 1.7        | 33%  |
| B3PW96/6-311G(2df) | 2.5        | 1.6        | 35%  |
| PBE0/6-311G(2df)   | 1.9        | 1.4        | 36%  |
| MP2/6-311G(2df)    | 1.8        | 2.1        | 30%  |

In Table 1 some calculated differences in the total energy ( $\Delta E$ ) as well as the thermodynamically corrected Gibbs Free Energy ( $\Delta G$ ) are given. The abundancies of the *anti*-conformer were calculated based on  $\Delta G$ values for free molecules. It becomes clear that in the row of the cc-pVTZ calculations the Hartree-Fock<sup>27</sup> and the MP2 calculation set the same trend of about 26% and 28% of the *anti*-conformer, respectively, while the density-functional calculations predict the *anti*-conformer to be energetically preferred (32% and 37%). Regarding the calculations using the 6-311G(2df) basis set the calculation show lower energy differences between the two conformers.

Table 2. Calculated geometrical parameters on different levels of theory.

|                         | HF/cc-pVTZ |       | MP2/co | c-pVTZ | PBE0/cc-pVTZ |       |  |
|-------------------------|------------|-------|--------|--------|--------------|-------|--|
| parameters <sup>a</sup> | syn        | anti  | syn    | anti   | syn          | anti  |  |
| <i>r</i> (P=O)          | 1.436      | 1.431 | 1.467  | 1.463  | 1.479        | 1.475 |  |
| r(P-N)                  | 1.640      | 1.632 | 1.664  | 1.659  | 1.678        | 1.673 |  |
| r(P–Cl)                 | 1.999      | 2.007 | 2.006  | 2.015  | 2.036        | 2.045 |  |
| r(N=C)                  | 1.202      | 1.195 | 1.225  | 1.223  | 1.224        | 1.222 |  |
| r(C=O)                  | 1.128      | 1.130 | 1.165  | 1.165  | 1.168        | 1.168 |  |
| ≰(Cl–P–Cl)              | 103.5      | 103.3 | 103.0  | 102.8  | 103.1        | 103.0 |  |
| ≰(O=P–N)                | 116.5      | 114.8 | 117.4  | 114.6  | 117.5        | 114.0 |  |
| ≰(P–N–C)                | 132.1      | 141.1 | 129.5  | 133.7  | 133.1        | 137.5 |  |
| ≰(N=C=O)                | 175.7      | 176.4 | 174.2  | 175.7  | 174.4        | 174.8 |  |

<sup>a</sup> Distances *r* in Å, angles and dihedral angles in deg. <sup>b</sup>

In comparison to the analogous phosphorus(III) compound  $Cl_2PNCO^7$  the determination of possible conformers in this case is more convincing and unambiguous. In the previous case of dichlorophosphanyl isocyanate different levels of theory suggested different conformers to be stable and it was not even clear which conformer was the global minimum. This indicates an interaction of the phosphoryl moiety P=O with the isocyanate group. The fluorinated analogue F<sub>2</sub>P(O)NCO<sup>8</sup> only showed a very shallow minimum for the *anti*-conformer on an energy curve calculated at the B3LYP/6-311+G(3df) level of theory. This implies that the fluorine atoms also affect the conformational properties, which can be attributed to steric reasons because the shorter P–F bond brings the fluorine atoms closer to the isocyanate group. The higher barrier of rotation of about 5 kJ mol<sup>-1</sup> also adds to this fact. Moreover, the more electronegative fluorine atom can diminish the conjugation effects among the phosphoryl and the isocyanate groups by withdrawing electron density. Calculated structural parameters at different levels of theory are listed in Table 2. Along the series HF, MP2 and PBE0 in general all the bond lengths increase, whereas most of the angles remain more or less unchanged. However, the angle  $\neq$ (P–N–C) and in particular its variance between both conformers are larger in the HF calculation ( $\Delta = 9^\circ$ ). The angle  $\neq$ (N=C=O) is in all cases predicted to be about 175°. Regarding the effects of the conformation on the isocyanate group, the differences among the conformers are negligible, as they get smaller by performing calculations at DFT or *ab initio* level. The parameters varying most among the conformers are the angles  $\neq$ (O=P–N) and  $\neq$ (P–N–C) is widened by up to nine degrees in the *anti*-conformer (HF) and by about four degrees in the other calculations.

#### **Vibrational Spectra**

The IR (gas-phase and Ne-matrix) and Raman (liquid) spectra of  $Cl_2P(O)NCO$  are shown in Figure 4. To aid the assignment, calculations of the IR spectra for the two conformers (*syn* and *anti*) B3LYP/6-311+G(3df) were performed and the results are collected in Table 3.

In the IR spectra, the observed strongest bands at 2290 cm<sup>-1</sup> (gas phase) and 2288.6 cm<sup>-1</sup> (Ne-matrix), belong to the antisymmetric stretching vibration of the NCO group ( $v_{as}$ (NCO)), which appears as a very weak band at 2283 cm<sup>-1</sup> in the Raman spectrum. The band position is red-shifted comparing to that of F<sub>2</sub>P(O)NCO (gas-phase IR: 2309 cm<sup>-1</sup>, Ar-matrix IR: 2306.9 cm<sup>-1</sup>, liquid Raman: 2307 cm<sup>-1</sup>),<sup>8</sup> but it is blue-shifted compared to that of OP(NCO)<sub>3</sub> (liquid IR: 2265 cm<sup>-1</sup>).<sup>28</sup> These shifts coincide with the electronegativity order F > Cl > NCO. The NCO symmetric ( $v_s$ (NCO)) and P=O ( $v_{PO}$ ) stretching vibrations in the Ne-matrix locate at 1417.5 and 1312.5 cm<sup>-1</sup>, respectively. It is noteworthy that in the Raman spectrum of the liquid the P=O stretching vibration shifts to 1292 cm<sup>-1</sup>, indicating the presence of intermolecular interactions including the phosphoryl oxygen atom in the condensed phase. The P–N stretching vibration ( $v_{PN}$ ) in Cl<sub>2</sub>P(O)NCO (747.1 cm<sup>-1</sup>, Ne-matrix) is slightly lower in frequency than that

in  $F_2P(O)NCO$  (751.8 cm<sup>-1</sup>, Ar-matrix).<sup>8</sup> The in-plane and out-of-plane deformation modes of the NCO group in the Ne matrix are observed at 629.7 and 611.5 cm<sup>-1</sup>, and the asymmetric and symmetric stretching vibrations of the CIPCI units in the liquid state occur at 597 and 517 cm<sup>-1</sup>, respectively.



**Figure 4.** Upper trace: IR spectrum of  $Cl_2P(O)NCO$  isolated in a Ne-matrix at 2.6 K (absorbance *A*, resolution: 0.5 cm<sup>-1</sup>) the frequency of  $CO_2$  is marked by asterisk (\*). Middle trace: IR spectrum of gaseous  $Cl_2P(O)NCO$  at 300 K (transmission *T*, resolution: 2 cm<sup>-1</sup>). Lower trace: Raman spectrum of liquid  $Cl_2P(O)NCO$  at 300 K (Raman intensity *I*, resolution: 2 cm<sup>-1</sup>).

#### Solid-state structure

As the isocyanate  $Cl_2P(O)NCO$  is a liquid at room temperature, a suitable crystal was grown *in situ* by generating manually a crystal seed at 235 K and subsequently slowly chilling to 100 K. The crystallographic details can be found in the Experimental Section. Figure 5 shows the molecular structure of  $Cl_2P(O)NCO$  in the solid state and structural parameters are listed in Table 4.

Table 3. Calculated and Experimental Vibrational Frequencies (cm<sup>-1</sup>) and Intensities of Cl<sub>2</sub>P(O)NCO.

| Calculated $(I_{\rm IR})[I_{\rm Ra}]^a$   |   | Observed <sup>b</sup>   | Mode <sup>c</sup>   |  |  |
|---|---|---|---|--|--|
| 631/2   | anti  | IR<br>Gas phase   | No Motrix   | Raman  |  |
| $\frac{5 \text{ m}}{2362 (1576) [5]}$ $\frac{2362 (1576) [5]}{1469 (129) [34]}$ $\frac{1313 (146) [14]}{728 (163) [2]}$ $\frac{632 (139) [1]}{616 (45) [<1]}$ $\frac{616 (45) [<1]}{580 (236) [2]}$ $\frac{506 (61) [21]}{372 (18) [6]}$ $\frac{350 (6) [3]}{282 (2) [3]}$ $\frac{234 (1) [1]}{192 (<1) [2]}$ $\frac{85 (<1) [2]}{24 (<1) [3]}$ | $\begin{array}{c} 2367 (1449) [5] \\ 1488 (136) [27] \\ 1329 (166) [16] \\ 713 (213) [2] \\ 621 (31) [<1] \\ 620 (44) [1] \\ 569 (254) [2] \\ 489 (39) [24] \\ 348 (3) [5] \\ 347 (6) [4] \\ 321 (21) [1] \\ 238 (1) [<1] \\ 196 (<1 [2]) \\ 72 (2) [3] \\ 23 (<1) [3] \end{array}$ | 2290 vs<br>1421 w<br>1319 m<br>744 m<br>618 m<br>597 m<br>517 w | 2288.6 vs<br>1417.5 m<br>1312.5 s<br>747.1 s<br>629.7 m<br>611.5 s<br>603.5 s | 2283 vw<br>1425 w<br>1292 m<br>740 vw<br>520 vs<br>381 m<br>362 m<br>299 vw<br>247 vw<br>205 m | $ \begin{array}{l} \nu_{as}(NCO) \\ \nu_{s}(NCO) \\ \nu(PO) \\ \nu(PN) \\ \delta_{i.p.}(NCO) \\ \delta_{o.o.p.}(NCO) \\ \nu_{as}(CIPCI) \\ \nu_{s}(CIPCI) \\ \delta(OPN) \end{array} $ |

<sup>*a*</sup> B3LYP/6-311+G(3df) calculated IR intensities (km mol<sup>-1</sup>) in parentheses and Raman intensities (Å<sup>4</sup> amu<sup>-1</sup>) in square brackets. <sup>*b*</sup> Band positions and intensities: vs very strong, s strong, m medium strong, w weak, vw very weak and br broad. <sup>*c*</sup> Tentative assignments were made according to the vibrational displacement vectors of the *syn* Cl<sub>2</sub>P(O)NCO.

The most remarkable difference to the calculations is the deviation from ideal  $C_s$  symmetry. The isocyanate group occupies a *gauche*-conformation regarding the P=O bond with a dihedral angle of 38.1(2)°, defined by the angle of torsion for P1-N1-C1-O1. This deviation has nearly no effect on the non-symmetrical P–Cl bonds, which are within experimental error of the same length (1.987(1) and 1.985(1) Å), but slightly different O2-P1-Cl angles of 112.4(1) and 114.3(1) for Cl1 resp. Cl2.

| Table 4. | Structural | parameters <sup>a</sup> | of ( | $Cl_2P(0)$ | D)N | CO | and | related | mol | lecu | les in | the soli | d state. |
|----------|------------|-------------------------|------|------------|-----|----|-----|---------|-----|------|--------|----------|----------|
|----------|------------|-------------------------|------|------------|-----|----|-----|---------|-----|------|--------|----------|----------|

|                         | r(P=O)   | r(P-N)   | r(N=C) <sup>b</sup> | r(C=O) <sup>b</sup> | r(P–X)            | ≰(OPN)   | ≰(PNC) / | ≰(NCO) / | ≰( <i>X</i> –P– <i>X</i> ) | <i>φ</i> (OP–NC) / | φ(XP–NC) /     |
|-------------------------|----------|----------|---------------------|---------------------|-------------------|----------|----------|----------|----------------------------|--------------------|----------------|
|                         |          |          |                     |                     |                   |          | ≰(PNN)   | ≰(NNN)   |                            | $\phi$ (OP–NN)     | $\phi(XP-NC)$  |
| Cl <sub>2</sub> P(O)NCO | 1.455(1) | 1.623(1) | 1.213(2)            | 1.149(2)            | 1.987(1)/1.985(1) | 118.4(1) | 135.2(1) | 174.1(1) | 103.6(1)                   | -38.1(2)           | 161.7(1) (Cl1) |
| Cl <sub>2</sub> PNCO    |          | 1.688(2) | 1.202(2)            | 1.160(2)            | 2.054(1)/2.049(1) |          | 136.1(2) | 174.6(2) | 99.9(1)                    |                    | 121.3(2)       |
| F <sub>2</sub> P(O)NCO  | 1.438(2) | 1.615(2) | 1.216(3)            | 1.146(3)            | 1.519(2)/1.517(2) | 119.9(1) | 132.5(2) | 174.2(3) | 99.4(1)                    | -18.9(5)           |                |
| $F_2P(O)N_3^b$          | 1.442(2) | 1.639(2) | 1.225(3)            | 1.113(3)            | 1.525(2)/1.527(2) | 120.1(1) | 117.3(2) | 173.4(3) | 98.6(1)                    | -0.2(3)            |                |
| $F_2P(O)N_3{}^b \\$     | 1.447(2) | 1.638(2) | 1.247(3)            | 1.117(3)            | 1.523(2)/1.526(2) | 120.1(1) | 118.6(2) | 172.4(3) | 99.0(1)                    | -0.7(3)            |                |

<sup>a</sup> Distances r in Å, angles and dihedral angles in deg. <sup>b</sup> In this case two crystallographically independent molecules were found

The asymmetric molecular structure is a consequence of the formation of dimers in the solid state (Figure 6). In these dimers the two monomers are linked by P=O···C contacts at 2.789(1) Å which is below the sum of their van der Waals radii ( $\Sigma(C,O) = 3.22$  Å). The related angle is 128.1(1)° ( $\measuredangle$ P=O···C). These

dimers are linked by contacts of at 2.929(1) Å building layers perpendicular to the a axis as shown in Figure 6, the related angle is 137.7(1)° ( $\measuredangle$ P=O···C) This interaction between the electron-rich oxygen atom and the most electropositive carbon atom is also found in the solid state structure of the fluorinated analogue<sup>8</sup>. Hence, in F<sub>2</sub>P(O)NCO a trimeric species is formed with longer P=O···C contacts (2.881(4) and 3.087(4) Å). Solid-state contacts in the phosphanyl isocyanate<sup>7</sup> are established via the isocyanate oxygen and the carbon atom of the adjacent molecule with 2.887(2) Å forming polymeric chains. In the extended solid-state structure the layers are packed to a three-dimensional network by  $\sigma$  hole contacts of Cl2 to an oxygen atom from an isocyanate group of the next sheet, the P1–Cl(2)···O(1) contact is 3.306(1) ) Å, the angle at Cl2 is 160.0(1)°, see Figure 7.

Parameters of comparable substances in the solid state are listed in Table 3. A well-established indication of the electronegativities<sup>29</sup> of the atoms or groups connected to the phosphoryl moiety is the P–O bond. As the electronegativity increases in the row F, Cl, NCO, N<sub>3</sub> the shortest P–O bond is found in difluoroisocyanate followed by difluoroazide and the longest bond is found in the substance under investigation. On the contrary, the P–N bond elongates along the following series:  $F_2P(O)NCO$ ,  $Cl_2P(O)NCO$ ,  $F_2P(O)N_3$ ,  $Cl_2PNCO$ . This might indicate that the azide group favours less conjugation to the phosphoryl moiety. Between both phosphoryl isocyanates the bonds N=C and C=O do not vary much but in the phosphanyl isocyanate the N=C bond is by 0.01 Å slightly shorter whereas the C=O bond is slightly longer by the same magnitude. The P–Cl bond is shorter in the phosphoryl isocyanate that the azide reason the Cl–P–Cl angle is tighter in the phosphorus(III) compound. The angle at the nitrogen atom P–N–C or P–N–N is larger in the isocyanate compounds.



Figure 5. Molecular structure of dichlorophosphoryl isocyanate in the solid state. a shows the numbering, b the view along the P–N bond. Displacement ellipsoids are depicted with 50% probability.



**Figure 6**. Aggregation to layers of  $Cl_2P(O)NCO$  by  $O\cdots C$  contacts in the solid state, view approximately along the crystallographic a-*axis*. Thick stippled lines for the contacts with 2.789(1) Å, thin ones for 2.929(1) Å.

Among these three isocyanates the largest angle is found in the phosphanyl isocyanate and the shortest in  $F_2P(O)NCO$ . The N–C–O angle is in all three isocyanates about 174.3° within the error limits, whereas the corresponding N–N–N angle in the azide is slightly smaller.

Table 5. Structural parameters of the gas-phase structure of Cl<sub>2</sub>P(O)NCO and related molecules.

|                      | r(P=O)   | r(P-N)   | r(N=C)   | <i>r</i> (C=O) | r(P-X)    | ≰(OPN)   | ≰(PNC)   | ≰(NCO)   | <i>≰</i> ( <i>X</i> –P– <i>X</i> ) |
|----------------------|----------|----------|----------|----------------|-----------|----------|----------|----------|------------------------------------|
| $Cl_2P(O)NCO, r_g$   | 1.442(1) | 1.646(1) | 1.212(1) | 1.157(1)       | 1.995(1)  | 118.3(2) | 135.8(2) | 175.3(2) | 102.8(1)                           |
| $Cl_2PNCO, r_g$      |          | 1.667(3) | 1.203(1) | 1.159(1)       | 2.045(1)  |          | 137.2(6) | 171.5(6) | 99.4(2)                            |
| $F_2P(O)N_3, r_{h1}$ | 1.437(4) | 1.657(2) | 1.251(3) | 1.130(2)       | 1.5316(6) | 118.9(3) | 117.8(5) | 172(2)   | 98.8(3)                            |
| $F_2PN_3, r_{h1}$    |          | 1.716(3) | 1.247(3) | 1.127(3)       | 1.572(2)  |          | 117.7(5) | 177(1)   | 96.4(2)                            |
| $F_2$ PNCO, $r_a$    |          | 1.683(6) | 1.256(6) | 1.168(5)       | 1.563(3)  |          | 130.6(8) |          | 97.9(8)                            |

<sup>a</sup>Distances *r* in Å, angles and dihedral angles in deg. <sup>b</sup> For the azides the analogous parameters are given.

Concerning the conformation in the solid state, the azide compound with a dihedral angle  $\phi$ (OP–NN) of  $-0.2(3)^{\circ}$  and  $-0.7(3)^{\circ}$  is closest to an ideal *syn*-conformation in the solid state while the isocyanates deviate more from  $C_s$  symmetry. The fluorine analogue adopts a dihedral angle  $\phi$ (OP–NC) of 18.9(5)° and the dichloride a larger one of 38.1(1)°. This reflects the higher flexibility of the isocyanate group and the conformational stability caused by the fluorine atoms.



Figure 7. Packing of Cl<sub>2</sub>P(O)NCO in the solid state. View approximately along the crystallographic *c*-axis.

#### **Gas-phase structure**

The structure of free molecules of Cl<sub>2</sub>P(O)NCO was determined by gas-phase electron diffraction. A dynamic model<sup>7,30</sup> was used to describe the molecular structure, because neither a **static** one- nor a two-conformer model resulted in a satisfactory agreement with the experimental data. Especially in the region between 4 and 5 Å in the radial distribution curve where mainly the distances between the isocyanate oxygen atom and the atoms bound to phosphorus are mapped. The dynamic model was set up using ten different pseudo-conformers with a dihedral angle  $\phi$ (OP–NC) being varied over a range starting at  $\phi$ (OP–NC) = 0° (*syn*) to  $\phi$ (OP–NC) = 180° (*anti*) with steps of 20°. For all pseudo-conformers, distinct cubic force fields were calculated at the MP2/aug-cc-pVTZ. The starting potential was taken from the MP2/aug-cc-pVTZ calculation. For modelling the potential during the refinement, three parameters were used and refined. As the potential was refined without any restrictions, it is

possible that the model can result in static one or two conformer models or in models with less dynamic character than the one set up at the start of the refinement. The refined model resulted in overall a disagreement factor  $R_f$  of 2.47%. The final radial distribution curve is depicted in Figure 8 also containing some labelled interatomic distances of the *syn*-conformer, which is lowest in energy.



**Figure 8.** Experimental (circles  $\circ$ ) and model (continuous line –) radial distribution functions of Cl<sub>2</sub>P(O)NCO. The difference curve is shown below. Vertical bars indicate interatomic distances of the *syn*-conformer (lowest in energy), selected ones are labelled.

The potential described by these three parameters deviates from quantum-chemically predicted potential. Both are depicted in Figure 9. By comparison of the both dynamic models for the Cl<sub>2</sub>PNCO and the here examined Cl<sub>2</sub>P(O)NCO it is evident that in the phosphorus(V) compound a more local dynamic model, is describing the composition in the gas phase. The term local dynamic means that not the full range of the dynamic parameter (here  $\phi$ (OPNC)) is necessary to describe the gas-phase composition but pseudo conformers close to the minimum structures are used for modelling the gas-phase structure. The usage of the local dynamic model implies that the phosphoryl moiety in Cl<sub>2</sub>P(O)NCO is stabilizing both conformers observed in the gas phase and that the isocyanate group is less flexible that in the phosphorus(III) analogue. Thus, the gas-phase structure was described by using the two minimum conformers and additionally pseudo conformers, Because of the local dynamic

description of the gas phase structures in here,  $Cl_2P(O)NCO$  seems to be more related to the azides  $F_2PN_3$  and  $F_2P(O)N_3$ , as these compounds show a local dynamic behaviour as well in the gas phase.



Figure 9. Potential a) calculated at the (MP2/aug-cc-pVTZ) level of theory and b) refined against experimental scattering intensities.

In Table 5 gas-phase structural parameters of related molecules are listed. The effect of the introduction of an oxygen atom and the resulting higher oxidation state of the phosphorus atom is a decreasing bond length to the other atoms at phosphorus. In the isocyanates, the P–N bond is shortened by 0.02 Å to 1.646(1) Å and the P–Cl bond is 0.05 Å shorter in the phosphoryl compound. The same tendency is seen for the azides. However, only minor changes are observed in the pseudo-halide moieties. The bond lengths are the same within experimental error, whereas the N=C bond is slightly longer in phosphoryl isocyanate. Interestingly the deviation from linearity in the pseudo halides cannot be correlated to the oxidation state of the central phosphorus atom. In general it is to be mentioned that the angle  $\alpha$ (NCO) was often described as a parameter hard to determine, thus, in some cases it is not even reported<sup>31</sup> or treated as a fixed parameter.<sup>32</sup> Anyhow, in the here examined case contributions from interatomic scattering of the isocyanate oxygen and the chlorine made it possible to determine this angle with reasonable accuracy.

#### Conclusions

Dichlorophosphoryl isocyanate,  $Cl_2P(O)NCO$ , was synthesized and fully characterized. The molecular conformation and structure was examined by means pf gas-phase electron diffraction, vibrational spectroscopy in different phases and in the solid state by X-ray diffraction. The applied theoretical methods all suggest the *syn*-conformer to be the most stable one besides an *anti*-conformer, as the barrier for interconversion was calculated to be between 2 and 3 kJ mol<sup>-1</sup>. A dynamic model was used in the gas-phase structure refinement. The resulting abundances of the different pseudo conformers show that the isocyanate group is vibrating close to the computationally determined minima. In the solid state dimers are formed via C···O contacts, which build layers in the crystal phase.

#### **Conflicts of interest**

There are no conflicts to declare.

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