Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Dichlorophosphanyl Isocyanate - Spectroscopy, Conformation and Molecular Structure in Gas Phase and Solid State

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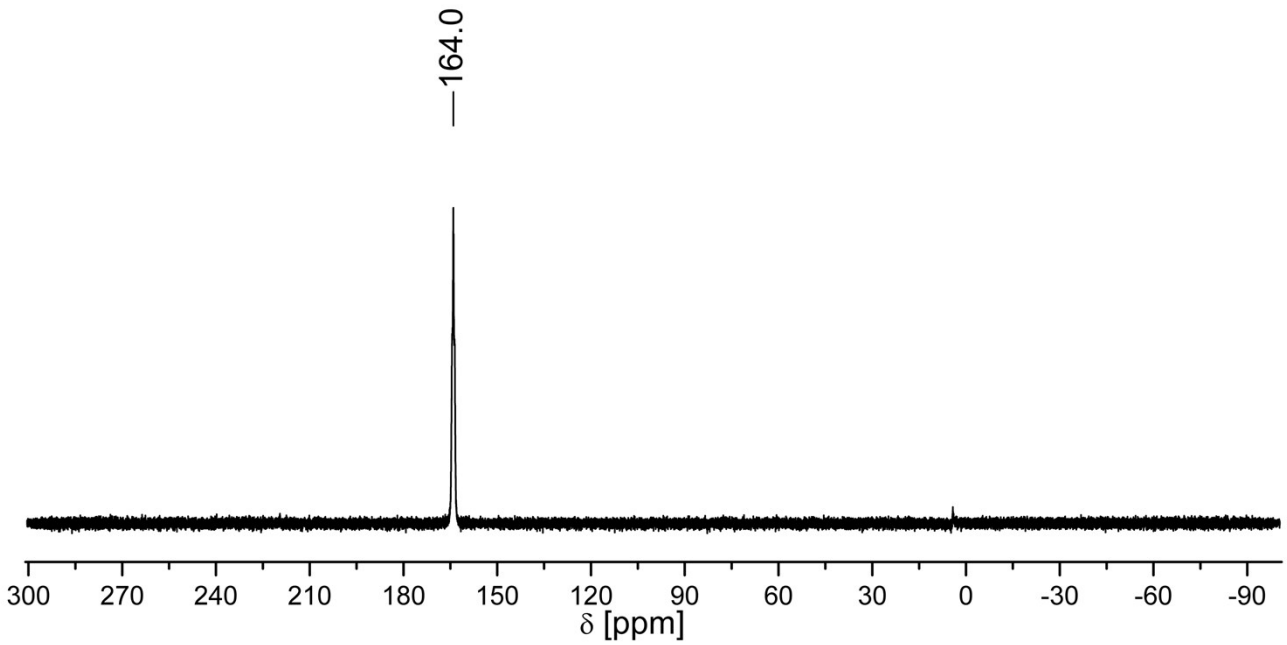

Figure S1. ^{31}P NMR spectrum of the dichlorophosphanyl isocyanate, Cl_2PNCO (242.9 MHz, CD_2Cl_2)

Table S1. Cartesian coordinates for the refined structure of Cl_2PNCO.

Cartesian coordinates of all atoms (Angstroms) in principal axes:

N	At	An	Mass	X	Y	Z
1	X	-1	0.00000000	0.400925137809	0.000000000000	1.651539280505
2	P	15	30.97376151	0.270874420710	0.000000000000	0.660031937627
3	Cl	17	34.96885271	1.274905541318	-1.550068673110	-0.198733286631
4	Cl	17	34.96885271	1.274905541318	1.550068673110	-0.198733286631
5	N	7	14.00307401	-1.097419500806	-0.000000000000	-0.273296211709
6	C	6	12.00000000	-2.278182904887	0.000000000000	-0.096810410627
7	O	8	15.99491462	-3.429122808464	-0.000000000000	-0.097281529714

Table S2. Full listing of structural parameters for the *syn* conformer of Cl_2PNCO. r_a, r_g, r_e values are given in Å. Errors correspond to one time standard deviation. For atom numbering see Table S1.

All internal geometrical parameters.

Errors are 1.000000 times standard deviations.

No.	Type	i	j	k	l	ra	rg	re	Error
1	stretch	1	2	0	0	1.00000	1.00000	1.00000	0.00000
2	stretch	2	3	0	0	2.04345	2.04501	2.03585	0.00020
3	stretch	2	4	0	0	2.04345	2.04501	2.03585	0.00020
4	stretch	2	5	0	0	1.66399	1.66734	1.65729	0.00096
5	stretch	5	6	0	0	1.20259	1.20294	1.19799	0.00033
6	stretch	6	7	0	0	1.15895	1.15929	1.15505	0.00033
7	bend	1	2	3	0			110.72900	0.00000
8	bend	1	2	4	0			110.72900	0.00000
9	bend	1	2	5	0			131.09192	0.15818
10	bend	3	2	4	0			99.36091	0.06337
11	bend	3	2	5	0			100.11272	0.08439
12	bend	4	2	5	0			100.11272	0.08439
13	bend	2	5	6	0			137.19684	0.22904
14	bend	5	6	7	0			171.47171	0.22904
15	torsion	1	2	5	6			180.00000	0.00000
16	torsion	3	2	5	6			129.24211	0.04696
17	torsion	4	2	5	6			-129.24211	0.04696
18	torsion	2	5	6	7			180.00000	0.00000

Table S3. Interatomic distances(r_a), mean square vibrational amplitudes (l) and vibrational corrections (corr) to equilibrium geometry in the optimized GED model of the *syn* conformer.[a] Gu indicates grouping of amplitudes for common refinement.

;A1	A2	Comm(ra)	l	Corr	A	Gu
O7	C6	1.158953	0.019820	-0.003900	0.000000	101
C6	N5	1.202593	0.020506	-0.004600	0.000000	101
N5	P2	1.663994	0.074612	-0.006700	0.000000	102
P2	Cl3	2.043446	0.056497	-0.007600	0.000000	103
P2	Cl4	2.043446	0.056497	-0.007600	0.000000	103
O7	N5	2.350435	0.045200	-0.003900	0.000000	103
C6	P2	2.671782	0.081904	-0.008100	0.000000	104
N5	Cl3	2.852256	0.083459	-0.010400	0.000000	105
N5	Cl4	2.852256	0.083459	-0.010400	0.000000	105
Cl3	Cl4	3.117253	0.091108	-0.012800	0.000000	105
O7	P2	3.794389	0.129915	-0.008900	0.000000	106
C6	Cl3	3.900389	0.165327	-0.012300	0.000000	106
C6	Cl4	3.900389	0.165327	-0.012300	0.000000	106
O7	Cl3	4.981279	0.208924	-0.013000	0.000000	107
O7	Cl4	4.981279	0.208656	-0.013000	0.000000	107

[a] All values in Å, corrections were calculated using SHRINK program from MP2/aug-cc-pVTZ and cubic force fields. The amplitudes were refined in groups by multiplying on the scale factors (one per group), which were treated as independent parameters.

Calculated Energies (in Hartrees) Atomic Coordinates (in Angstroms) for All Optimized Structures at the M06-2X/aug-cc-pVTZ Level of Theory.

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***syn* $Cl_2P(O)NCO$**

Zero-point correction= *0.017526*
Thermal correction to Energy= *0.024335*
Thermal correction to Enthalpy= *0.025279*
Thermal correction to Gibbs Free Energy= *-0.016407*
Sum of electronic and zero-point Energies= *-1429.903743*
Sum of electronic and thermal Energies= *-1429.896934*
Sum of electronic and thermal Enthalpies= *-1429.895990*
Sum of electronic and thermal Free Energies= *-1429.937676*

N	-0.80341600	1.13197800	0.00000000
P	0.82567700	0.67858700	0.00000000
O	-2.94309200	0.13198200	0.00000000
C	-1.88158700	0.58058700	0.00000000
Cl	0.82567700	-0.66594200	1.57941800
Cl	0.82567700	-0.66594200	-1.57941800

***gauche* $Cl_2P(O)NCO$**

Zero-point correction= *0.017544*
Thermal correction to Energy= *0.024349*
Thermal correction to Enthalpy= *0.025294*
Thermal correction to Gibbs Free Energy= *-0.016248*
Sum of electronic and zero-point Energies= *-1429.903613*
Sum of electronic and thermal Energies= *-1429.896808*
Sum of electronic and thermal Enthalpies= *-1429.895864*
Sum of electronic and thermal Free Energies= *-1429.937405*

N	1.03926100	-0.45113500	-0.17097100
P	-0.34878800	-0.05435700	0.71022400
Cl	-0.83146800	1.73775400	-0.20207300
Cl	-1.66983400	-1.30366000	-0.25231900
C	2.23302600	-0.30149600	-0.11620800
O	3.38512100	-0.19966500	-0.12933100