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Rotational Spectroscopy of Organophosphorus Chemical Agents: Cresyl and Phenyl Saligenin Phosphate

Received 00th January 20xx,
Accepted 00th January 20xx

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DOI: 10.1039/x0xx00000x

www.rsc.org/chemcomm

Cresyl and phenyl saligenin phosphate have been probed in a jet expansion by broadband chirp-excitation microwave spectroscopy, revealing the most stable conformation and its structural properties. The rotational parameters offer a high-resolution univocal route for characterization of organophosphorous agents and a testbed for computational models.

Synthetic organophosphorous compounds (OPs, Scheme 1) are used as pesticides, pharmaceuticals, additives or warfare agents, mostly as pentavalent phosphate or phosphonate esters.¹ OPs are characteristically neurotoxic, with some of the G- and V-series nerve agents² producing lethal effects at very low dosages. Organophosphate poisoning is primary due to cholinergic toxicity,³ or irreversible inhibition of the enzyme acetylcholinesterase (AChE). AChE inhibition is caused by phosphorylation of the serine hydroxyl group at the catalytic triad site,⁴ and results in accumulation of acetylcholine at the muscarinic and nicotinic receptors in the central and peripheral nervous systems. Disturbances across the cholinergic synapses lead to severe multiorgan disfunctions and, eventually, death. Distinct paralytic conditions to AChE inhibition include organophosphorous ester-induced delayed neurotoxicity⁵ (OPIDN) and chronic neurotoxicity⁶ (OPICN).

The industrial and toxicological importance of phosphorous-containing organics justifies the development of structural and analytical methods for the investigation of these compounds. Microwave (MW) spectroscopy has been proposed as a powerful method for detection of organophosphates and chemical warfare agents,^{7,8} based on the extremely high resolution of the measured frequencies and specificity of the molecular rotation spectra, particularly appropriate for the analysis of isotopic species, multiconformational systems or complex mixtures in the gas

Scheme 1. Four coordinate phosphate insecticides and additives (left) vs phosphonate nerve agents (right, X = F, N(CH₃)₂, SR; R, R' = sidechain).

phase. Presently four G-series nerve agents (GA-tabun,⁹ GB-sarin,¹⁰ GD-soman,¹¹ GF-cyclo-hexylsarin¹²), one blister agent (HD-mustard gas⁷) and multiple simulants⁷ have been characterized by Suenram, Pate *et al.* in a MW database of chemical warfare agents, and instrument response and detection limits have been reported.^{7,8} The recent development of new broadband MW chirp excitation techniques,^{8,13} where a large band of the spectrum is accessed in a single experimental event, has significantly enhanced the capabilities of this technique for analytical purposes, only requiring as prerequisite the identification of molecular spectra of the pure compounds.

We report here a rotational and computational investigation of cresyl (CBDP, **1**, Scheme 2) and phenyl (PSP, **2**) saligenin phosphate. CBDP has been involved in OPIDN resulting from exposition to tri-o-cresyl phosphate (ToCP), either by poisoning or contamination with industrial products (as controversially proposed for the aerotoxic syndrome¹⁴). The toxicity of ToCP is related to its metabolic activation by conversion into CBDP *in vivo*.¹⁵ CBDP is an irreversible inhibitor of both AChE and butyrylcholinesterase (BChE),^{16,17} but it also affects carboxyl-

Scheme 2 CBDP or 2-(2-cresyl)-4H-1,3,2-benzodioxaphosphorin-2-oxide (**1**) and PSP (**2**), with atom numbering in the dioxaphosphorinane ring.

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† Electronic Supplementary Information (ESI) available: Experimental methods, rotational transitions and ab initio calculations. See DOI: 10.1039/x0xx00000x

Fig. 1 A (normalized) 2 GHz section of the MW spectra of CDBP vs. PSP (experimental details in ESI†).

esterases and the neuropathy target esterase¹⁸ (NTE). According to *in vitro* essays the specific affinity of CDBP for NTE would be the primary factor for OPIDN,¹⁴ confirming NTE as the second molecular target of metabolites of OPs.¹⁹ PSP is an analogue of CDBP differing in a single methyl group, known to similarly induce OPIDN by inhibition of NTE.²⁰

The present study will provide conformational, structural, energetic and spectroscopic parameters for both phosphates, additionally illustrating the extreme sensitivity of rotational spectra to minor, even isotopic, changes in molecular composition. No previous gas-phase spectroscopic investigations were available.

CBDP and PSP were specifically synthesized for this work according the procedures of Faria *et al.*²¹ The OPs were then probed in a jet expansion using chirp excitation Fourier-transform MW spectroscopy.^{8,13} Briefly, the samples were vaporized at temperatures of 110–150°C, pressurized with a light

inert carrier gas (Ne, 1 bar) and expanded near-adiabatically to form a supersonic jet. The estimated rotational temperature is ca. 2 K (vibrational temperatures below 210 K).²² The molecules in the jet were excited with a sequence of short (4 μ s) MW chirps covering the region 2–8 GHz, creating a rotational coherence or polarization of the molecular ensemble of electric dipoles. The transient (40 μ s decay time) decay emissions following sample excitation was recorded digitally and Fourier-transformed to obtain the frequency-domain spectrum. The resonance frequencies of the rotational transitions were measured with uncertainties smaller than 10 kHz ($\approx 10^{-7}$ cm⁻¹). A section of the spectrum, specific transitions and signal-to-noise values are illustrated in Figures 1 and S1–S2 (ESI†).

The experiment was guided by several computational models. Initially, a conformational search with molecular mechanics (MMMFs²³) and dedicated Montecarlo/low-mode search algorithms resulted in a set of 11 and 6 conformations for CBDP and PSP below 25 kJ mol⁻¹. All structures were reoptimized using *ab initio* (MP2²⁴) and density functional (B3LYP-D3(BJ)²⁵) molecular orbital calculations, which represent a moderate computational effort for these molecules with 18 (PSP) or 19 (CBDP) heavy atoms and one third period element. Two sets of triple- ζ basis sets were tested, including Alrichs' balanced functions (def2-TZVP²⁶) and a mixed scheme with Dunning's tight d-augmented correlation-consistent basis set (cc-pV(T+d)Z²⁷) for the phosphorous atom and cc-pVTZ for all other atoms. The quantum chemical calculations converged to four conformers in CBDP and two conformers for the smaller PSP. The calculation of the vibrational force field and centrifugal distortion constants used the same B3LYP and MP2 methods in the harmonic approximation because of computational efficiency and molecular size. The final energetic, structural, electric and rovibrational molecular properties are shown in Tables 1–2 and

Table 1 Rotational parameters of CBDP and comparison with the theoretical predictions (B3LYP-D3(BJ)/cc-PV(T+d)Z on P, cc-PVTZ for C, H, O). The experiment results correspond to the vibrational ground-state, while the *ab initio* predictions represent near-equilibrium values.

	Experiment	Theory			
		Isomer 1	Isomer 2	Isomer 3	Isomer 4
A / MHz ^a	553.85563(55) ^d	559.5 [1.0%] ^e	446.6 [-19.4%]	670.3 [21.0%]	475.4 [-14.2%]
B / MHz	310.11876(22)	303.6 [-2.1%]	428.0 [38.0%]	260.8 [-15.9%]	356.4 [14.9%]
C / MHz	243.71135(21)	240.2 [-1.4%]	293.2 [20.3%]	218.2 [-10.5%]	266.6 [9.4%]
κ	-0.57	-0.60	0.76	-0.81	-0.14
D_J / kHz	0.08429(67)	0.074	0.092	0.045	0.086
D_{JK} / kHz	-0.4053(36)	-0.37	-0.099	-0.29	-0.079
D_K / kHz	0.566(11)	0.58	0.030	0.59	0.033
d_1 / kHz	-0.02653(36)	-0.023	0.040	-0.0132	0.0193
d_2 / kHz	[0.0] ^e	-0.00053	-0.0057	-0.00040	-0.037
$ \mu_a $ / D	+ ^f	2.3	0.2	1.4	1.7
$ \mu_b $ / D	++	4.8	6.0	5.3	4.9
$ \mu_c $ / D	+	1.8	0.9	1.3	2.7
N^b	199				
σ / kHz	12.8				
ΔE / kJ mol ⁻¹ c		0.0	2.6	3.7	5.1
ΔG / kJ mol ⁻¹		0.0	3.3	3.5	5.0

^aRotational constants (A , B , C), Ray's asymmetry parameter (κ), Watson's S-reduction (I' representation) centrifugal distortion constants (D_J , D_{JK} , D_K , d_1 , d_2) and electric dipole moments (μ_a , $a = a, b, c$). ^bNumber of transitions (N) and rms deviation (σ) of the fit. ^cRelative energies corrected with the zero-point energy (ZPE), Gibbs energy (ΔG , 298 K, 1 atm). ^dStandard errors in units of the last digit. ^eValue fixed to zero. ^fPlus signs indicate qualitatively the spectral intensity. ^gRelative percentage deviation (experiment-theory)/theory.

Table 2 Rotational parameters of PSP and comparison with theoretical predictions.

	Experiment ^a	Theory	
		Isomer 1	Isomer 2
<i>A</i> / MHz	628.71995(18)	633.6 [0.8%]	851.7 [35.5%]
<i>B</i> / MHz	325.72580(17)	313.9 [-3.6%]	247.6 [-24.0%]
<i>C</i> / MHz	250.70121(22)	246.2 [-1.8%]	218.2 [-13.0%]
κ	-0.60	-0.65	-0.91
<i>D_J</i> / kHz	0.13153(61)	0.168	0.042
<i>D_{JK}</i> / kHz	-0.6760(10)	-0.86	-0.46
<i>D_K</i> / kHz	1.0241(19)	1.31	1.62
<i>d₁</i> / kHz	-0.04931(17)	-0.065	-0.0115
<i>d₂</i> / kHz	-0.00178(10)	-0.0029	-0.0003
$ \mu_a $ / D	+	2.0	1.4
$ \mu_b $ / D	++	4.3	5.0
$ \mu_c $ / D	+	2.2	0.7
<i>N</i>	163		
σ / kHz	6.2		
ΔE / kJ mol ⁻¹		0.0	2.0
ΔG / kJ mol ⁻¹		0.0	3.0

^aParameter definition and calculation level as in Table 1.

S1-S6 (ESI†). Experimental and theoretical methods are detailed in the ESI†.

Since molecular rotation spectra are extremely sensitive to the moments of inertia, different spectral simulations for all predicted isomers were generated with the four computational models. For both molecules all components of the electric dipole moment (μ_a , μ_b , μ_c in Tables 1-2) were predicted larger than zero, activating the three selection rules. Several quartets made of pairs of μ_b and μ_c rotational transitions were first identified for the two molecules, leading to the assignment of the spectrum. Iterative insertion of additional lines improved the fits and allowed the identification of new μ_a transitions. The experimental dataset finally comprised 199 individual rotational transitions for CDBP and 163 for PSP, spanning angular momentum quantum numbers $J=3-16$ (CDBP) and $J=6-18$ (PSP). The line intensities indicate magnitudes of the dipole moment components $\mu_b > \mu_c \approx \mu_a$. The observed frequencies were reproduced to measurement accuracy with Watson's semi-rigid rotor Hamiltonian,²⁸ resulting in the experimental rotational parameters of Tables 1 and 2. All rotational and quartic centrifugal distortion constants were accurately determined (except d_2 in CDBP). No additional isomers were detected, as remaining lines in the spectrum were not attributable to CDBP or PSP. Monosubstituted isotopic species were too weak for detection in natural abundance. All experimental frequency measurements and residuals for the fits of Tables 1-2 are presented in Tables S7 and S8 (ESI†).

A comparison of the experimental and predicted rotational parameters provided an unambiguous identification of the carrier of the spectrum for CDBP and PSP. For the two compounds the observations confirmed the detection of the global minimum (isomer 1), depicted in Figures 2 and S3-S5 (ESI†). Higher energy conformations, predicted within free energies of 3-5 kJ mol⁻¹ (B3LYP-D3(BJ)) or 1-6 kJ mol⁻¹ (MP2) are absent from the spectrum, either by being depopulated at ambient temperature or, alternatively, by collisional relaxation between conformational potential wells, as observed for low interconversion barriers in jet experiments.^{29,30} A direct comparison between experiment

Fig. 2 Conformational stability of CDBP and PSP according to B3LYP-D3(BJ) calculations in Tables 1-2 (see Figure S3, ESI, for additional views).

and theory would require a computation of anharmonic vibrational contributions. However, on assumption of minor (<1%) vibrational corrections³¹ the validity of the computational models can be assessed from the equilibrium values. The best agreement with the experiment was obtained with the dispersion-corrected B3LYP-D3(BJ)/cc-pV(T+d)Z calculations in Tables 1-2, with relative deviations in the rotational constants of 1.0-2.1% (CDBP) and 0.8-3.6% (PSP). The smaller basis set def2-TZVP behaves similarly (0.1-1.7% in CDBP, 1.2-2.5% in PSP), while the performance of MP2 was clearly worse (6-20%) for the two selected basis sets (Tables S1-S6, ESI†). Considering the relatively large size of CDBP and PSP, the intramolecular long-range dispersion interactions may be important for conformer stabilization. In that case, an overestimation of dispersion interactions with MP2 may explain why this method is not adequate for these compounds.

The conformational space of CDBP and PSP is dominated by the characteristic 1,3,2-dioxaphosphorinane six-membered ring. Previous studies in condensed phases using ³¹P-NMR³² or X-ray diffraction^{33,34} mostly addressed saturated phosphorinane rings, confirming that they normally occur as a distorted chair. However, the presence of the less common fused benzene ring

and the highly polarizable four coordinate phosphorous atom, with non-bonding electron pairs and unoccupied orbitals, is expected to favour stereoelectronic interactions and unconventional structural parameters. In CBDP and PSP the fused benzene ring produces the half-chair conformation for the most stable isomer 1 of both molecules, reminiscent of cyclohexene (P(2) and O(3) on different sides of the benzene plane). In the case of CBDP there is a second higher-energy near-boat dioxaphosphorinane conformation (isomers 2 and 4: P(2) and O(3) on the same side of the ring). The cresyl or phenyl groups add axial/equatorial possibilities and a two-rotor problem, and accordingly two isomers are predicted for each bicyclic conformation. Quantum chemical calculations show that in all cases the cresyl/phenyl rings are axial (equatorial phosphoryl P=O), the most common configuration for three/four coordinate phosphorinanes.^{32–35} The orientation of the cresyl/phenyl groups in the half-chair conformations is $\pm$ gauche, with the phenyl C $_{\alpha}$ staggered to the phosphoryl bond (CBDP: $\tau(\text{O}=\text{P}-\text{O}-\text{C}_{\alpha})=-63.7^{\circ}/+71.2^{\circ}$ in isomers 1 and 3). The cresyl/phenyl planes are anticlinal with respect to the phosphorous atom (CBDP: $\tau(\text{P}-\text{O}-\text{C}_{\alpha}-\text{C}_{\beta})=-129.8^{\circ}/+145.8^{\circ}$ in isomers 1 and 3). The orientation of the cresyl and phenyl ring planes in CBDP and PSP differs in ca. 7° , most probably because of a weak C-H $\cdots\pi$ intramolecular interaction in CBDP (present in the two half-chair conformations). Atomic coordinates for all predicted isomers are collected in Tables S9–S14 (ESI†).

A natural-bond-orbital (NBO³⁶) population analysis was carried out to identify the plausible stereoelectronic origin of the observed conformations, using B3LYP-D3(BJ)/def2-TZVP. Tables S15–S16 (ESI†) list the most relevant delocalizing interactions evaluated by a second-order perturbation analysis. In the global minimum of CBDP and PSP the main hyperconjugative interaction occurs between the lp_{σ} lone pair orbital at O(1) and the partially occupied lp_{σ}^* orbital of P(2), depicted in Figure S6. Four additional interactions involve other lp_{π} oxygen lone-pairs in O(7), O(8) and O(1) with the same lp_{σ}^* phosphorous orbital, reinforcing the P–O(1) bond and emphasizing the ability of phosphorous to engage in multiple intramolecular electronic interactions.³⁵

The gas-phase structural properties of CBDP and PSP can be compared to the only reported crystal structure of these compounds, available for PSP.³⁴ The condensed phase and the free molecule share the equatorial phosphoryl half-chair benzodioxaphosphorinane motif. However, the crystal structure shows differences of 4° – 5° with the gas-phase for the orientations of the phenyl plane and the phenyl C $_{\alpha}$ atom with respect to the phosphoryl group. Moreover, the phosphorinane half-chair is less flattened in the gas-phase by ca. 3° ($\tau(\text{O}(3)-\text{P}-\text{O}(1)-\text{C}(6))=-36.5^{\circ}$ > -33.2°), while still below the mean value (40° – 60°) in steroids²⁷. Because of the fused benzene ring the phosphorinane and phosphate bond distances are irregular (i.e., $r(\text{P}-\text{O})=1.549$ – 1.575), and larger for the gas phase (except O(3)–C(4)). Consequently, the crystal would reproduce the rotational constants with large relative deviations of 5.0–9.6%. A full comparison with the crystal is presented in Table S17 (ESI†).

The observation of PSP and CBDP organophosphorous compounds with rotational spectroscopy is notorious because of

their molecular size, and constitutes a proof-of-concept that high-resolution gas-phase methods can be applied structurally and analytically for the unambiguous characterization of organophosphorous agents, extending previous rotational work on pnictogen and calchogen^{37,38} organocompounds. In addition, the introduction of broadband chirp excitation rotational techniques^{8,13} contributes to this effort with fast, high throughput and high dynamic range methods, complementing previous frequency-scan techniques⁷ and common low-resolution spectroscopic or chromatographic methods.³⁹ Further rotational studies of organophosphates, present in a wide range of biological and industrial products, could be possible. Simultaneously, the availability of gas-phase rotational data represent a stringent test for quantum mechanical methods, as illustrated here by the deficiencies of MP2 model Chemistry to reproduce the experimental data for the selected basis sets. Progress towards more complex chemical targets will be necessary to exploit the synergy between rotational data and ab initio calculations.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We thank MICINN-FEDER (PGC2018-098561-B-C22) and JCyL (VA056G18) for funds.

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