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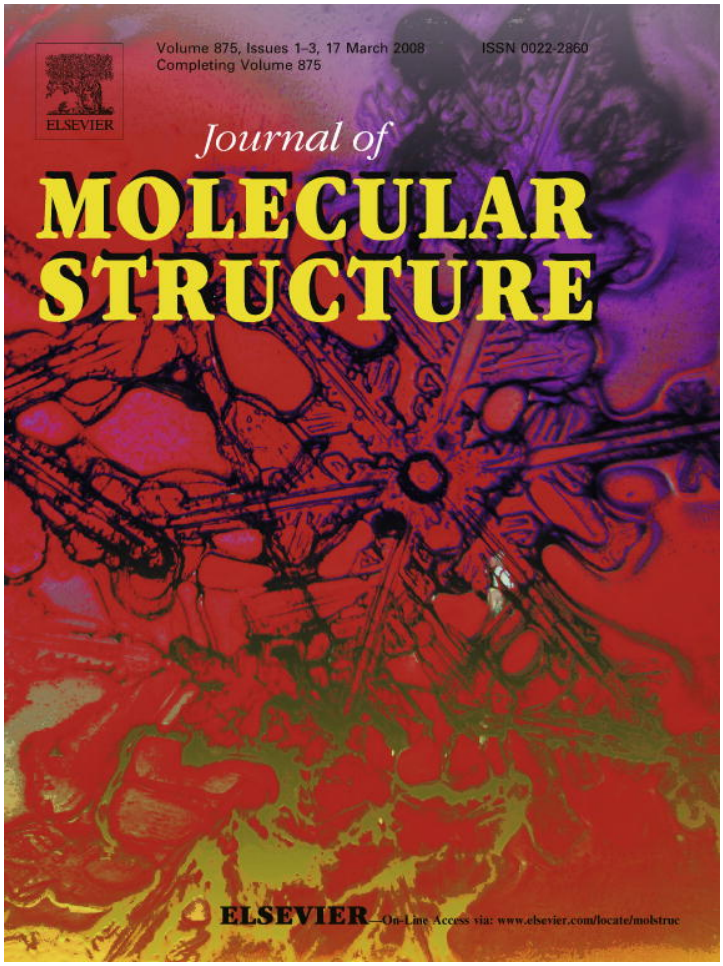

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DFT and MP2 ring puckering potential functions, vibrational analysis and comparison with experiment for 3-chloro-1,3-thiaphosphetane 3-oxide, 3-sulfide and 1,3-dithietane 1,1-dioxide

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Received 7 January 2007; received in revised form 17 April 2007; accepted 20 April 2007
Available online 29 April 2007

Abstract

The ring puckering in the four-membered 3-chloro-1,3-thiaphosphetane 3-oxide, its 3-sulfide derivative and 1,3-dithietane 1,1-dioxide hetero rings were investigated by DFT and ab initio MP2 calculations using a 6-311+G** basis set. From the calculations at both levels of theory the asymmetric ring puckering potential energy curves in the two phosphetanes were consistent with an almost single minimum that corresponds to a *pseudo-axial* configuration (P—Cl bond is in *axial* position) with a puckering angle of about 15–20°. In the case of the dithietane dioxide the symmetric ring puckering potential was consistent at the B3LYP level with a flat minimum that corresponds to a *planar* ring but at the MP2 level with a double minimum with a very low barrier of about 185 cal/mol to ring planarity. The potential functions that describe the ring puckering in the three molecules were derived at the B3LYP/6-311+G** and the MP2/6-311+G** levels of calculations. The vibrational wavenumbers were calculated and the potential energy distributions PED among the symmetry coordinates of the normal modes were computed for the stable conformers of each of the molecules. Complete vibrational assignments were provided on the basis of the calculated PED values. The experimental infrared and Raman spectra of the two phosphetane molecules were simulated and compared to the calculated ones.
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Keywords: DFT-B3LYP; Ab initio MP2; Ring puckering; Vibrational spectra and analysis; 3-Chloro-1,3-thiaphosphetane 3-oxide (3-oxo-3-chloro-1,3-thiaphosphetane) and 3-sulfide (3-thio-3-chloro-1,3-thiaphosphetane); 1,3-Dithietane 1,1-dioxide

1. Introduction

The structural stability of cyclobutane derivatives has been of interest for many years [1–12]. Rotational microwave and vibrational IR and Raman spectroscopic techniques, electron diffraction and ab initio calculations were all employed in these studies. The information obtained from the theoretical calculations and from the interpretation of the molecular spectra have provided better understanding of the nature of forces that control the ring stability in these four-membered ring compounds.

In an early study, we provided a comprehensive comparative study between experimental [9] and theoretical data of cyclobutanecarboxaldehyde [12]. We optimized the energies of all possible conformers of the molecule at both DFT-B3LYP and MP2 levels of theory by using four different basis sets namely 6-31G**, 6-311G**, 6-311+G** and 6-311++G** [12]. Only the smaller basis sets showed *gauche-equatorial* (*g-eq*) conformer and not the *trans-equatorial* (*g-eq*) form as the absolute minimum [12] as it was detected experimentally in the gaseous phase [9]. Furthermore, the four basis sets applied in the DFT calculations reproduced the measured rotational constants of the two

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doi:10.1016/j.molstruc.2007.04.030

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low energy *g-eq* and *t-eq* conformers of the molecule best [9] but was not the case in the MP2 calculations [12]. We concluded that extreme care must be taken in making the choice of basis sets in such relatively large molecules and when nonlinearities appear, larger basis does not imply better basis. Even in our moderate 6-311G** basis set total energy differences of conformers could not be fully trusted, neither on DFT nor on MP2 level. In this study the resulting spectra from energy derivatives reproduced experiment fairly well, within known limitations. We concluded that for spectra, MP2 appeared just to be a computationally more expensive replacement for DFT and yields results of about the same quality [12].

As a continuation of our interest in the structure of four-membered ring compounds we investigated 3-chloro-1,3-thiaphosphetane 3-oxide, its 3-sulfide and 1,3-dithietane 1,1-dioxide as the first molecules in a series of heterocyclic compounds. We carried out ab initio optimization of the energies for the *puckered* structures and the *planar* transition states of the molecules. From the data the relative conformational stability and the size of the ring puckering barrier were determined. Additionally, we calculated the vibrational wavenumbers of the low energy structures and made complete assignments for the normal modes by employing normal coordinate calculations. We used the calculated frequencies to make the plots of infrared and Raman spectra of the three molecules. The experimental vibrational spectra of the two phosphetane molecules were simulated and compared to the corresponding theoretical ones. The results of this work are presented herein.

Table 1
Calculated structural parameters, total dipole moment, and rotational constants of 3-chloro-1,3-thiaphosphetane 3-oxide (X = O) and 3-sulfide (X = S) at B3LYP/6-311+G** and MP2/6-311+G** levels

Parameter[a]	Oxide		Sulfide	
	B3LYP	MP2	B3LYP	MP2
Bond length (Å)				
$r(P_1{-}C_2{=}P_1{-}C_3)$	1.839	1.826	1.850	1.834
$r(S_4{-}C_2{=}S_4{-}C_3)$	1.859	1.837	1.857	1.835
$r(P_1{=}X_5)$	1.478	1.478	1.929	1.908
$r(P_1{-}Cl_6)$	2.085	2.050	2.103	2.062
$r(C_2{-}H_7{=}C_3{-}H_9)$	1.091	1.093	1.090	1.092
$r(C_2{-}H_8{=}C_3{-}H_{10})$	1.088	1.090	1.088	1.091
Bond angle (degree)				
$(C_2P_1C_3)$	88.0	86.9	86.9	85.9
$(C_2S_4C_3)$	86.9	86.2	86.6	85.9
(Ring-X_5)	136.1	137.6	136.9	138.0
(Ring-Cl_6)	109.8	108.2	107.5	106.4
$(X_5P_1Cl_6)$	114.1	114.2	115.6	115.6
$(H_7C_2P_1{=}H_9C_3P_1)$	110.9	110.4	110.9	110.3
$(H_8C_2P_1{=}H_{10}C_3P_1)$	115.2	115.4	115.2	115.4
$(H_7C_2H_8{=}H_9C_3H_{10})$	110.9	111.0	110.9	110.9
$(H_7C_2P_1S_4{=}H_9C_2P_1S_4)$	115.0	114.9	115.6	115.3
$(H_8C_2P_1S_4{=}H_{10}C_2P_1S_4)$	117.2	117.5	117.4	118.0
Puckering angle (β)	13.8	21.6	13.0	20.1
Dipole moment (Debye)				
μ_t	2.76	3.13	2.22	2.67
Rotational constants (MHz)				
A	2917	2896	2090	2216
B	1548	1649	1287	1307
C	1287	1339	957	987

[a] Calculated total energies (hartree) of the oxide are −1353.739791 and −1351.665736 and of the sulfide are −1676.704215 and −1674.238710 at B3LYP/6-311+G** and MP2/6-311+G** levels of theory, respectively.

2. Ab initio calculations

The GAUSSIAN 98 program [13] running on IBM RS/6000 Model S85 Unix Server, was used to carry out the DFT-B3LYP and the MP2 calculations with the extended 6-31G**, 6-311G** or 6-311+G** basis sets. The structural parameters of the axial and equatorial forms and the planar structure of 3-chloro-1,3-thiaphosphetane 3-oxide, 3-sulfide and 1,3-dithietane 1,1-dioxide were optimized by minimizing the energy with respect to the geometrical parameters. The calculated structural parameters, energies, total dipole moments and rotational constants of the molecules are given in Tables 1–3.

2.1. Ring puckering potential function

The ring puckering potentials were calculated for the three molecules. However, the details of the fits are the same in all three cases. So we report them here just for one of them, namely 3-oxo-3-chloro-1,3-thiaphosphetane.The ring puckering potential was calculated at 21 values of the ring puckering angle β between −50° and +50° in increments of 5°. The ring puckering angle is defined as the angle between the lines from the mid-point, X, between C_2 and C_3 to the phosphorus atom P_1 in the planar form and in the form with a puckering angle β (Fig. 1). In the calculations β was kept at a fixed value at each point and all the other geometrical parameters were optimized. The ring puckering coordinate, x, is defined as usual as the distance between $P_1(0)$ in the planar form and $P_1(\beta)$ in the puckered conformer (see Fig. 1 for atom numbering and the definition of both β and x).

The law of cosines gives the ring puckering coordinate x as follows:

$$x = \sqrt{R(0)^2 + R(\beta)^2 - 2 \cdot R(0) \cdot R(\beta) \cdot \cos\beta}$$

where, $R(0)$ is the distance $XP_1(0)$ in the planar conformer and $R(\beta)$ is the distance $XP_1(\beta)$ in the puckered one, where X as mentioned above is the mid-point of the line C_2C_3. x is given a positive sign when the puckering angle is positive and vice versa. $R(0)$ is 1.3144 Å in case of DFT and 1.3118 Å in case of MP2.

Then x is fitted to β/β_o as a power series, with β_o being the puckering angle in the calculated minimum of the potential (15° for DFT and 20° for MP2):

$$x = \sum_{k=0}^{N} X(k)\left(\frac{\beta}{\beta_o}\right)^k$$

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Table 2
Calculated structural parameters, total dipole moment, and rotational constants of 1,3-dithietane 1,1-dioxide at B3LYP/6-311+G** and MP2/6-311+G** levels

Parameter	B3LYP	MP2	
	Planar	Planar	Puckered
Bond length (Å)			
$r(S_1{-}C_2{=}S_1{-}C_3)$	1.840	1.820	1.820
$r(S_4{-}C_2{=}S_4{-}C_3)$	1.848	1.829	1.829
$r(S_1{=}O_5)$	1.460	1.453	1.453
$r(S_1{=}O_6)$	1.460	1.453	1.453
$r(C_2{-}H_7{=}C_3{-}H_9)$	1.088	1.090	1.091
$r(C_2{-}H_8{=}C_3{-}H_{10})$	1.088	1.090	1.090
Bond angle (degree)			
$(C_2S_1C_3)$	86.9	86.7	85.8
$(C_2S_4C_3)$	86.4	86.2	85.3
(Ring-O_5)	119.3	119.1	120.8
(Ring-O_6)	119.3	119.1	117.7
$(O_5S_1O_6)$	121.4	121.8	121.5
$(H_7C_2S_1{=}H_9C_3S_1)$	111.0	110.8	110.1
$(H_8C_2S_1{=}H_{10}C_3S_1)$	111.0	110.8	112.1
$(H_7C_2H_8{=}H_9C_3H_{10})$	112.4	112.3	112.4
$(H_7C_2S_1S_4{=}H_9C_2S_1S_4)$	117.1	117.3	116.7
$(H_8C_2S_1S_4{=}H_{10}C_2S_1S_4)$	117.1	117.3	117.5
Puckering angle (β)	0.0	0.0	18.5
Dipole moment (Debye)			
μ_t	3.24	3.79	3.93
Rotational constants (MHz)			
A	4697	4759	4795
B	1887	1926	1940
C	1869	1901	1908

The quality of the fit of x to the angle does not depend too much on the order N of the fit and the dependence is almost a linear one. The root mean square deviation, rms, of such fits decreases from 0.035 to 0.022 mÅ when going with N from 8 to 14 in case of DFT and from 0.034 to 0.004 mÅ in case of MP2. To be consistent with the potential fits, we list the parameters for the $N = 10$ case in for the three molecules in Tables 4 and 5.

As second step the ring puckering potential $V(x)$ is fitted to the relative energies of the conformers (relative to the minima at 15° and 20°, respectively):

$$V(x) = \sum_{k=0}^{N} V(k)\left(\frac{x}{x_o}\right)^k$$

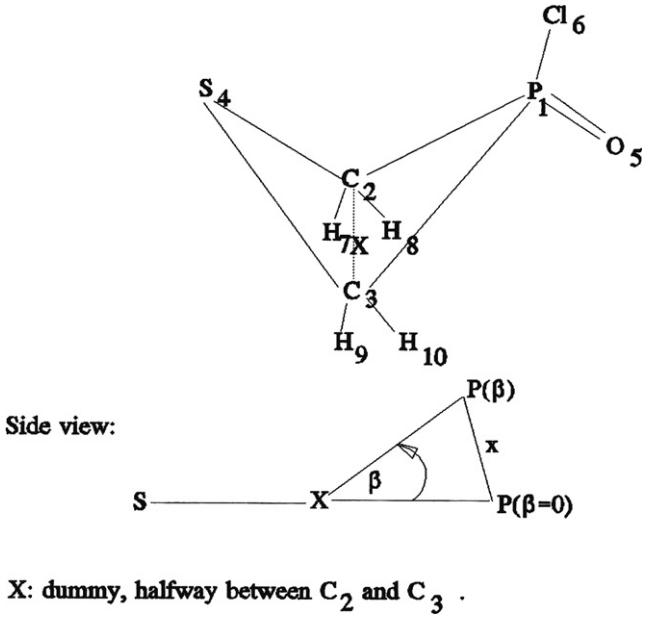

Fig. 1. Atom numbering as well as the definitions of ring puckering angle and coordinate in 3-chloro-1,3-thiaphosphetane 3-oxide and 3-sulfide (O═S) and 1,3-dithietane 1,1-dioxide (─POCl is ─SO_2).

where x_o is the coordinate for the minima, being 0.3445 Å ($\beta = 15°$) for DFT and 0.4578 Å ($\beta = 20°$) for MP2. In the case of DFT the rms of such a fit is 5.00 cal/mol at $N = 8$ and 1.57 cal/mol at $N = 8$ for MP2. Going from $N = 10$ to 14 in case of DFT the rms is between 3 and 4 cal/mol and between 0.1 and 0.7 cal/mol for MP2, however, the higher order potential constants for the fits of order 12 and 14 are negligible. Thus we restrict ourselves also here to the 10th order fits. Fig. 2 shows the potential curves and Tables 4 and 5 the fit parameters for the case $N = 10$.

For 3-chloro-1,3-thiaphosphetane 3-oxide the DFT curve has just one minimum and the plateux in the potential is much less obvious than for MP2. However, for our 6-311+G** basis set the DFT calculations show no warnings about large molecular orbital coefficients, while all MP2 calculations do with the maximum MO coefficients between 26 and 43. Since these coefficients are largest in the region in the center of the plot where the plateaux appears and indicate basis set linear dependences, we trust the DFT results more than the MP2 ones in this case.

Table 3
DFT-B3LYP and MP2 energies E (hartree) and energy differences ΔE (kcal/mol) between *planar* and *puckered* structures[a] of 1,3-dithietane 1,1-dioxide

Level	Planar			Puckered[b]		
	(β)	E	ΔE	(β)	E	ΔE
B3LYP/6-31G**	(0)	−1025.360314				
B3LYP/6-311G**	(0)	−1025.471195				
B3LYP/6-311+G**	(0)	−1025.478906				
MP2/6-31G**	(0)	−1023.618738	0.128	(17)	−1023.618942	0.000
MP2/6-311G**	(0)	−1023.772449	0.001	(4)	−1023.772450	0.000
MP2/6-311+G**	(0)	−1023.787586	0.185	(18)	−1023.787881	0.000

[a] β is ring puckering angle.
[b] The *puckered* structure was predicted to turn into the *planar* form upon completion of optimization.

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Table 4
The potential constants $V(k)$ (cal/mol) for the potential fits and the parameters $X(k)$ (in mÅ) for the $x(\beta)$ fits, both for order 10 for DFT and MP2 calculations of 3-chloro-1,3-thiaphosphetane 3-oxide and 3-sulfide

Molecule/k	DFT[a,c]		MP2[b,d]	
	$V(k)$	$X(k)$	$V(k)$	$X(k)$
3-Chloro-1,3-thiaphosphetane 3-oxide				
0	285.0	−0.026	1134.7	−0.004
1	−467.6	344.1	−1231.8	457.8
2	29.8	0.408	−437.2	0.027
3	78.4	−0.007	284.4	−0.642
4	81.7	0.036	272.9	0.357
5	1.4	−0.007	−4.8	0.233
6	−5.5	−0.001	−19.5	0.011
7	−0.3	0.001	−0.5	−0.046
8	0.5	0.003	2.6	−0.013
9	0.02	0	0.06	0.003
10	−0.01	0	−0.1	0.001
rms	3.79 cal/mol	0.033 mÅ	0.68 cal/mol	0.017 mÅ
3-Chloro-1,3-thiaphosphetane 3-sulfide				
0	207.2	−0.010	869.4	−0.001
1	−267.0	233.1	−986.1	464.3
2	15.9	0.141	−447.5	−0.140
3	32.6	−0.015	355.4	−0.785
4	14.2	0.012	235.8	0.671
5	−0.6	−0.002	−19.1	0.202
6	−0.4	0	−10.4	−0.146
7	0.02	0	1.0	−0.031
8	0.01	0	1.6	−0.018
9	0	0	−0.01	0.001
10	0	0	−0.08	−0.001
rms	2.77 cal/mol	0.023 mÅ	0.27 cal/mol	0.010 mÅ

[a] DFT-B3LYP total energy of the oxide at the minimum ($\beta = 15°$): −1353.7397813 hartrees.
[b] DFT-B3LYP total energy of the oxide at the minimum ($\beta = 20°$): −1351.6657188 hartrees.
[c] MP2 total energy of the sulfide at the minimum ($\beta = 10°$): −1676.7042020 hartrees.
[d] MP2 total energy of the sulfide at the minimum ($\beta = 20°$): −1674.2387095 hartrees.

Table 5
The potential constants[a] $V(k)$ (cal/mol) for the potential fits and the parameters $X(k)$ (in mÅ) for the $x(\beta)$ fits, both for order 14 for DFT and MP2 calculations of 1,3-dithietane 1,1-dioxide

k	DFT[b]		MP2[c]	
	$V(2k)$	$X(2k+1)$	$V(2k)$	$X(2k+1)$
0	1.1	1336.5	179.1	461.8
1	570.4	26.2	−443.6	−0.05
2	4116.6	−187.6	281.4	0.03
3	−765.7	780.5	−19.8	0.05
4	534.9	−1247.1	2.8	−0.01
5	−89.2	672.4	−0.1	0
rms	1.04 cal/mol	0.033 mÅ	0.19 cal/mol	0.016 mÅ

[a] Note that here all odd numbered potential constants $V(k)$ and all even numbered puckering coordinate constants $X(k)$ vanish.
[b] Total energy at the minimum ($\beta = 0°$): −1025.4789059 hartrees, puckering angles without dimensions are here $\beta/1°$, and puckering coordinates without dimensions are $x/1$ Å.
[c] Total energy at the minimum ($\beta = 20°$): −1023.7878719 hartrees.

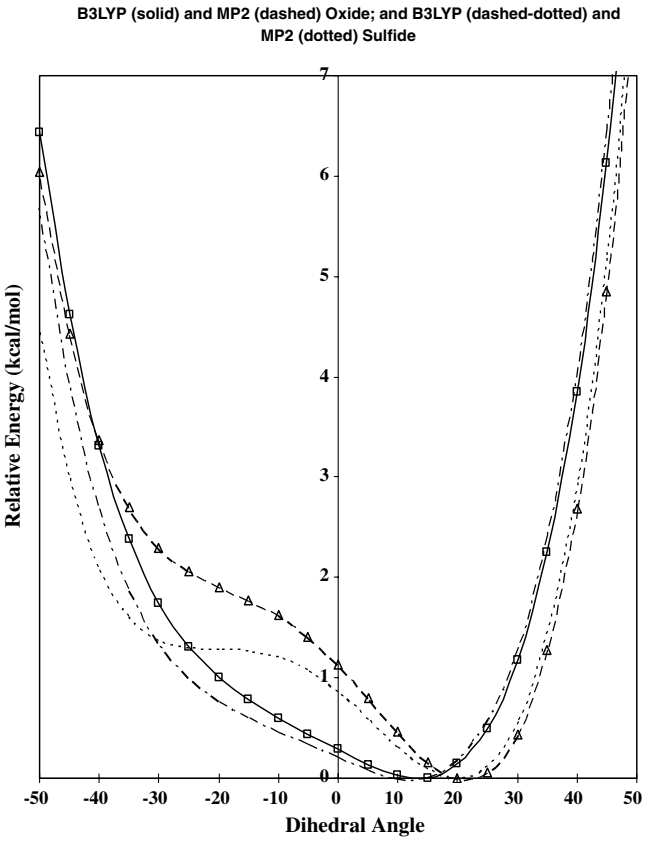

Fig. 2. The determined ring puckering potential functions for 3-chloro-1,3-phosphetane 3-oxide at B3LYP/6-311G** (solid line) and MP2/6-311G** (dashed line) and for 3-chloro-1,3-phosphetane 3-sulfide B3LYP/6-311G** (dashed-dotted line) and MP2/6-311G** (dotted line) levels, respectively.

In the case of the sulfide the results for the $N = 10$ fits are rather similar. Here $R(0)$ is 1.3352 Å for DFT and 1.3300 Å for MP2. Here the warnings appear again for all MP2 calculations with largest MO coefficients between 29 and 63, where at the plateux in the potential curve there is a local maximum of the largest coefficient. Thus also here we are inclined to trust DFT more than MP2. For the fit the rms is 2.76 cal/mol for DFT and 0.27 cal/mol for MP2 energies. In the case of the $x(\beta)$ fit the rms is 0.023 mÅ for DFT and 0.010 mÅ for MP2. The parameters of the fits are listed also in Table 4, atom numbering is given in Fig. 1 and plots of the fits in Fig. 2. The explicitly calculated points of minimum potential energy are in case of DFT at $\beta_o = 10°$ corresponding to $x_o = 0.2332$ Å and in case of MP2 at $\beta_o = 20°$ corresponding to $x_o = 0.4641$ Å.

In the final molecule, the symmetric 1,4-dithietane-1,1-dioxide, the variation of the largest MO coefficient is much less pronounced than in the former cases, namely only between 32 and 36, and thus more or less the largest coefficient is a constant here. Thus in this case MP2 can be trusted more than in the former ones, and probably also more than DFT, which has its problems with the centers of double well potentials. This is important here, because

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DFT gives the planar conformer as the absolute minimum, while MP2 yields a clear minimum around 20° puckering angle. While for MP2 everything is as above, in the DFT case because of the minimum values for β and x being at zero, we had to put artificially x_o to 1 Å and β_o to 1° to avoid divisions by 0. Note, that this fact makes also the DFT coefficients in the table comparatively large. The energies, however, are in both cases relative to the minimum, being at 20° and $x = 0.4619$ Å for MP2. In the MP2 case the barrier is only about 180 cal/mol, extremely low indeed. The plot of the calculated ring puckering potential energy curves of the dithietane molecule at DFT and MP2 levels of theory are shown in Fig. 3.

2.2. Vibrational wavenumbers and normal coordinate analyses

The optimized structural parameters of 3-chloro-1,3-thiaphosphetane 3-oxide and its 3-sulfide derivative and 1,3-dithietane 1,1-dioxide in their low energy structures were used to calculate the vibrational wavenumbers at the B3LYP/6-311+G** level of theory. Normal coordinate analyses were then carried out for the molecules as described previously [14,15]. The internal and the symmetry coordinates of each molecule are extracted from those reported earlier [12]. The potential energy distributions (PED) among the symmetry coordinates of all the normal modes of the molecules were calculated and given in Tables 6–8. Complete assignments of the fundamentals were proposed on the basis of the calculated PED values, infrared band intensities, Raman line activities, depolarization ratios and experimental infrared and Raman spectra of the two phosphetane molecules [16]. The calculated wavenumbers of the three molecules are listed in Tables 6–8.

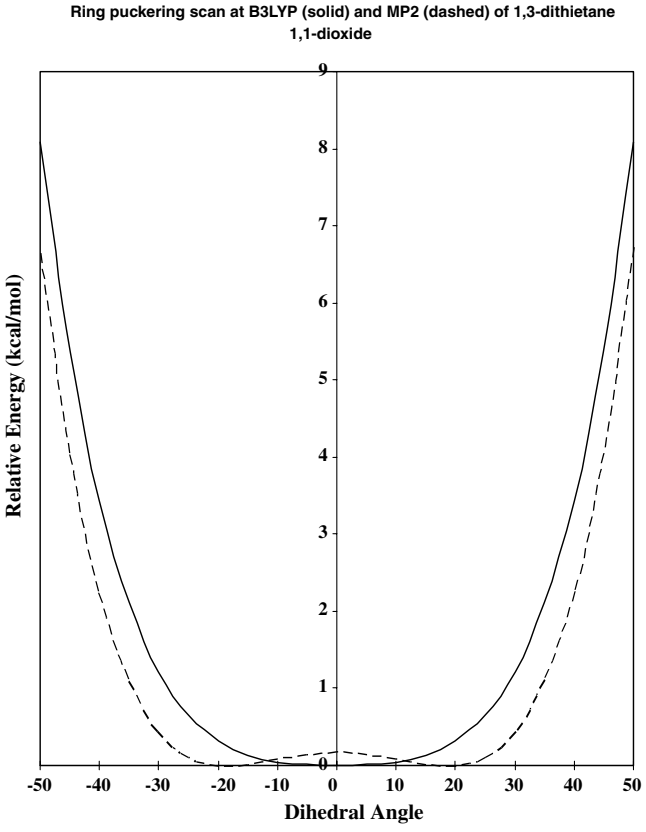

Fig. 3. The determined ring puckering potential functions for 1,3-dithietane 1,1-dioxide 3-oxide at B3LYP/6-311G** (solid line) and MP2/6-311G** (dashed line) levels, respectively.

2.3. Vibrational spectra

In order to obtain spectra from the experimental ones which are comparable with the theoretical spectra, we have replotted the experimental spectra together with the DFT ones. We obtained the wavenumbers and peak intensities for each line from the experimental spectrum, and in order to replot it we have assumed a constant line width $\Delta k = 10\ \mathrm{cm}^{-1}$ in both spectra. For the experimental one we assumed a Lorentzian line shape for each of the lines, j:

$$L_j(k) = \frac{A_j}{\pi}\frac{\Delta k/2}{(k-k_j)^2 + (\Delta k/2)^2}$$

where the peak heights I_j can be measured from the experimental spectra and thus:

$$I_j = L_j(k_j) = \frac{A_j}{\pi \Delta k/2}$$

$$A_j = \frac{1}{2} I_j \Delta k \pi$$

where I_j is the distance between the peak of the line and the base line of the experimental spectrum. The final spectra are then the superpositions of all experimental lines j:

$$T(k) = -\sum_j \frac{I_j(\Delta k/2)^2}{(k-k_j)^2 + (\Delta k/2)^2}$$

$$I(k) = \sum_j \frac{I_j(\Delta k/2)^2}{(k-k_j)^2 + (\Delta k/2)^2}$$

Transmittances $T(k)$ and intensities $I(k)$ are rescaled such that the largest absolute value of the transmittance or intensity is equal to unity. The theoretical and the experimental spectra, replotted as described are shown in Figs. 4 (infrared) and 5 (Raman) for the oxide and in Figs. 6 (infrared) and 7 (Raman) for the sulfide. Note, that different parts of the experimental spectra may have different factors of enhancement of transmittances and intensities in them.

Despite some differences in appearance, probably due to different enhancement factors in the experimental spectra, the agreement between experiment and DFT is quite satisfactory for the sulfide spectra (6 and 7), while in case of the oxide some lines seem to caoalesce in the DFT spectra which are well resolved in the experimental ones (4 and 5), however, also here the lines highest in intensity are quite well reproduced. For example the P═O (or P═S) and P─Cl stretching modes in the infrared spectra (Figs. 4 and 6) and

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Table 6
Calculated vibrational frequencies[a] (cm^{-1}) at B3LYP/6-311+G** level for 3-chloro-1,3-thiaphosphetane 3-oxide

Sym.	No.	Freq.	IR int.	Raman act.	Depol. ratio	Obs.		Obs./ calc.	PED
						IR	Raman		
A′	ν_1	3152	0.4	25.1	0.56	*2995*	*2991*	*0.95*	95% S_1 (CH_2 antisym. str.)
	ν_2	3081	4.4	231.4	0.08	*2930*	*2926*	*0.93*	95% S_2 (CH_2 sym. str.)
	ν_3	1462	9.7	13.6	0.62	*1398*	*1396*	*0.96*	100% S_5 (CH_2 def.)
	ν_4	1275	202.0	19.8	0.40	1265	1265	0.99	88% S_3 (P═O)
	ν_5	1174	6.7	5.6	0.08	*1130*		*0.99*	91% S_6 (CH_2 wag)
	ν_6	1030	18.5	5.2	0.55	*1010*	*1008*	*0.98*	95% S_7 (CH_2 twist)
	ν_7	872	42.8	1.4	0.16	870	865	1.00	86% S_8 (CH_2 rock)
	ν_8	764	23.6	35.2	0.07	780		1.02	74% S_9 (Ring breathing), 19% S_{10} (Ring def.)
	ν_9	649	19.6	1.2	0.22	655		1.01	93% S_{11} (Ring def.)
	ν_{10}	487	114.7	4.9	0.41	505	500	1.04	48% S_4 (P—Cl), 30% S_{10} (Ring def.), 15% S_{13} (POCl def.)
	ν_{11}	410	17.0	14.0	0.11		427	1.04	37% S_{10} (Ring def.), 35% S_4 (P—Cl), 15% S_9 (Ring breathing)
	ν_{12}	301	2.4	6.1	0.49				40% S_{14} (POCl rock), 30% S_{13} (POCl def.), 15% S_4 (P—Cl)
	ν_{13}	232	4.8	2.8	0.42				51% S_{13} (POCl def.), 23% S_{14} (POCl rock), 12% S_{10} (Ring def.)
	ν_{14}	79	4.9	1.5	0.75				80% S_{12} (Ring puckering), 20% S_{14} (POCl rock)
A″	ν_{15}	3153	0.1	102.1	0.75	*2995*	*2991*	*0.95*	95% S_{15} (CH_2 antisym. str.)
	ν_{16}	3080	4.1	17.0	0.75	*2930*	*2926*	*0.93*	95% S_{16} (CH_2 sym. str.)
	ν_{17}	1445	8.9	1.8	0.75	*1380*	*1380*	*0.96*	100% S_{17} (CH_2 def.)
	ν_{18}	1156	14.7	1.3	0.75	*1110*		*0.96*	96% S_{18} (CH_2 wag)
	ν_{19}	1018	0.1	1.2	0.75		*990*	*0.98*	96% S_{19} (CH_2 twist)
	ν_{20}	811	1.0	1.1	0.75	797		0.98	86% S_{22} (CH_2 rock)
	ν_{21}	746	18.7	1.2	0.75		772	1.03	63% S_{21} (Ring def.), 16% S_{20} (Ring def.)
	ν_{22}	665	4.7	10.6	0.75		667	1.00	78% S_{20} (Ring def.), 22% S_{21} (Ring def.)
	ν_{23}	327	24.7	3.2	0.75				80% S_{23} (POCl wag), 11% S_{21} (Ring def.)
	ν_{24}	212	0.1	3.2	0.75				85% S_{24} (POCl twist)

[a] IR intensities and Raman activities are calculated in km mol^{-1} and $A^{\circ 4}$ amu^{-1}, respectively.
[b] Observed wavenumbers are taken from infrared and Raman data of the liquid oxide in reference [16]. Italic denotes observed wavenumbers of the CH_2 modes obtained from data of the liquid sulfide [17].

the ring breathing and P—Cl stretching modes (Figs. 5 and 7) in the Raman spectra of the oxide and sulfide molecules are really produced rather well.

3. Discussion

The interesting structures and properties of 3-chloro-1,3-thiaphosphetane 3-oxide (3-oxo-3-chloro-1,3-thiaphosphetane), its sulfide [16,17] and 1,3-dithietane 1,1-dioxide [18] prompted our attention to investigate the heterocyclic ring puckering in these fascinating molecular systems. The stability of such hetero-ring molecules is controlled by two main forces, the ring strain that tend to keep the ring *planar* and the repulsive *n–n* interaction between the lone-pairs on the sulfur and the chlorine atoms (or the *n*–π interactions between the lone-pairs on the sulfur and the pi system of the carbonyl moiety) that tend to keep the ring *puckered*. The structure of 3-chloro-1,3-thiaphosphetane 3-oxide (3-oxo-3-chloro-1,3-thiaphosphetane) was investigated by electron diffraction and it was determined to exist with 80% axial phosphoryl group configuration and 20% equatorial [19]. The hetero ring in 3-chloro-1,3-thia-phosphetane 3-oxide was reported to be nearly flat with a ring puckering angle of about 10° [18]. The vibrational spectra of 3-chloro-1,3-thiaphosphetane 3-oxide and 3-sulfide were reported too [16,17].

In the present work, we are reporting complete potential functions that describe the ring puckering in these hetero-cyclic four-membered ring molecules. We also performed normal coordinate calculations to provide comprehensive vibrational assignments of the normal modes of the molecules. From the calculations at both levels of theory the ring puckering potential energy curves were consistent with a single minimum that corresponds to an *pseudo-axial* configuration of the ring (the P—Cl bond is in *axial* position) with a puckering angle of about 15–20° (Fig. 2). From full energy optimization the *pseudo-equatorial* form was predicted at both levels of theory to turn into the *pseudo-axial* conformation upon completion of calculation. In the case of the dithietane the symmetric ring puckering potential was consistent at the B3LYP level with a flat minimum that corresponds to a *planar* ring but at the MP2 level with a double minimum with a barrier of about 185 cal/mol to ring planarity and a puckering angle of about 18° (Fig. 3). We repeated the calculations at the two DFT-B3LYP and MP2 levels using 6-31G** and 6-311G** basis sets. The three DFT-B3LYP calculations predicted only one *planar* ring minimum (Table 3). This was not the case in the MP2 calculations as a result of large linear dependences of the basis sets functions especially when the diffuse functions are included in the 6-311+G** basis set (Table 3).

A similar situation was reported for 2,5-dihydrothiophen 1,1-dioxide *c*-$C_4H_6SO_2$ (3-sulfolene) where the microwave spectrum of the ground and five excited states of the ring puckering vibration showed that this vibration has a double minimum potential function with a very low barrier

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Table 7
Calculated vibrational frequencies[a] (cm^{-1}) at B3LYP/6-311+G** level for 3-chloro-1,3-thiaphosphetane 3-sulfide

Sym. No.		Freq.	IR int.	Raman act.	Depol. ratio	Obs.		Obs./calc.	PED
						IR	Raman		
A'	ν_1	3152	0.4	19.5	0.47	2995	2991	0.95	98% S_1 (CH_2 antisym. str.)
	ν_2	3084	3.8	207.9	0.07	2930	2926	0.95	98% S_2 (CH_2 sym. str.)
	ν_3	1458	6.3	15.0	0.67	1398	1396	0.95	100% S_5 (CH_2 def.)
	ν_4	1187	8.2	3.1	0.30	1130		0.95	97% S_6 (CH_2 wag)
	ν_5	1030	7.6	2.5	0.63		990	0.98	97% S_7 (CH_2 twist)
	ν_6	870	68.2	1.4	0.71	860	861	0.99	81% S_8 (CH_2 rock)
	ν_7	777	56.9	13.4	0.19	786	786	1.01	63% S_9 (Ring breathing), 18% S_3 (P═S)
	ν_8	717	95.6	38.9	0.11		*716*	*1.00*	45% S_3 (P═S), 20% S_{11} (Ring def.), 19% S_{10} (Ring def.), 14% S_9 (Ring breathing)
	ν_9	625	26.3	1.6	0.33				71% S_{11} (Ring def.), 18% S_3 (P═S)
	ν_{10}	452	87.5	7.4	0.56	485	*476*	*1.05*	61% S_4 (P─Cl), 25% S_{10} (Ring def.)
	ν_{11}	362	13.9	29.9	0.11		*377*	*1.04*	34% S_{10} (Ring def.), 30% S_4 (P─Cl), 15% S_3 (P═S), 14% S_9 (Ring breathing)
	ν_{12}	258	0.5	3.7	0.43				67% S_{14} (PSCl rock), 17% S_{12} (Ring puck.)
	ν_{13}	187	2.2	7.8	0.74				91% S_{13} (PSCl def.)
	ν_{14}	74	3.2	2.3	0.73				77% S_{12} (Ring puckering), 23% S_{14} (PSCl rock)
A''	ν_{15}	3153	0.2	100.8	0.75	2995	2991	0.95	97% S_{15} (CH_2 antisym. str.)
	ν_{16}	3083	4.3	6.2	0.75	2930	2926	0.93	98% S_{16} (CH_2 sym. str.)
	ν_{17}	1442	7.8	1.1	0.75	1380	1380	0.96	100% S_{17} (CH_2 def.)
	ν_{18}	1159	15.2	0.4	0.75	1110		0.96	98% S_{18} (CH_2 wag)
	ν_{19}	1032	0.1	1.3	0.75	1010	1008	0.98	96% S_{19} (CH_2 twist)
	ν_{20}	809	0.1	0.5	0.75				91% S_{22} (CH_2 rock)
	ν_{21}	719	3.9	2.4	0.75				72% S_{21} (Ring def.), 17% S_{20} (Ring def.)
	ν_{22}	670	4.1	9.8	0.75	673	671	1.00	81% S_{20} (Ring def.), 19% S_{21} (Ring def.)
	ν_{23}	250	6.0	4.2	0.75		268	1.07	93% S_{23} (PSCl wag),
	ν_{24}	193	0.5	4.2	0.75		*204*	*1.06*	94% S_{24} (PSCl twist)

[a] IR intensities and Raman activities are calculated in km mol^{-1} and $A^{\circ 4}$ amu^{-1}, respectively.
[b] Observed wavenumbers are taken from infrared and Raman data of the liquid sulfide in references [17]. Italic denotes observed wavenumbers of the Raman spectrum of the crystal [17].

Table 8
Calculated vibrational frequencies[a] (cm^{-1}) at B3LYP/6-311+G** level of *planar* 1,3-Dithietane 1,1-dioxide

Sym. No.		Freq.	IR int.	Raman act.	Depol. ratio	PED
A_1	ν_1	3091	3.2	217.0	0.10	100% S_2 (CH_2 sym. str.)
	ν_2	1459	3.5	12.7	0.68	100% S_5 (CH_2 def.)
	ν_3	1219	48.8	3.9	0.73	87% S_6 (CH_2 wag), 10% S_4 (SO_2 sym. str.)
	ν_4	1101	169.5	18.0	0.13	83% S_4 (SO_2 sym. str.), 12% S_6 (CH_2 wag)
	ν_5	760	3.9	42.1	0.06	71% S_9 (Ring breathing), 24% S_{10} (Ring def.)
	ν_6	643	16.3	3.9	0.08	87% S_{11} (Ring def.)
	ν_7	538	26.2	4.4	0.30	50% S_{13} (SO_2 def.), 37% S_{10} (Ring def.)
	ν_8	342	7.6	8.2	0.31	42% S_{13} (SO_2 def.), 36% S_{10} (Ring def.), 18% S_9 (Ring breathing.)
A_2	ν_9	3170	0.0	120.5	0.75	100% S_{15} (CH_2 antisym. str.)
	ν_{10}	1022	0.0	0.4	0.75	98% S_{19} (CH_2 twist)
	ν_{11}	854	0.0	1.9	0.75	95% S_{22} (CH_2 rock)
	ν_{12}	259	0.0	2.9	0.75	96% S_{24} (SO_2 twist)
B_1	ν_{13}	3169	1.2	0.4	0.75	100% S_1 (CH_2 antisym. str.)
	ν_{14}	1313	231.8	9.0	0.75	94% S_3 (SO_2 antisym. str.)
	ν_{15}	1014	6.7	9.6	0.75	94% S_7 (CH_2 twist)
	ν_{16}	886	4.6	0.3	0.75	89% S_8 (CH_2 rock)
	ν_{17}	322	0.6	0.5	0.75	82% S_{14} (SO_2 twist)
	ν_{18}	33	9.6	1.0	0.75	91% S_{12} (Ring puckering)
B_2	ν_{19}	3091	4.4	0.6	0.75	100% S_{16} (CH_2 sym. str.)
	ν_{20}	1444	3.8	0.7	0.75	100% S_{17} (CH_2 def.)
	ν_{21}	1170	11.6	0.7	0.75	98% S_{18} (CH_2 wag)
	ν_{22}	756	25.9	0.8	0.75	63% S_{21} (Ring def.), 27% S_{23} (SO_2 wag)
	ν_{23}	678	13.4	13.5	0.75	84% S_{20} (Ring def.), 16% S_{21} (Ring def.)
	ν_{24}	402	26.4	6.2	0.75	73% S_{23} (SO_2 wag), 21% S_{21} (Ring def.)

[a] IR intensities and Raman activities are calculated in km mol^{-1} and $A^{\circ 4}$ amu^{-1}, respectively.

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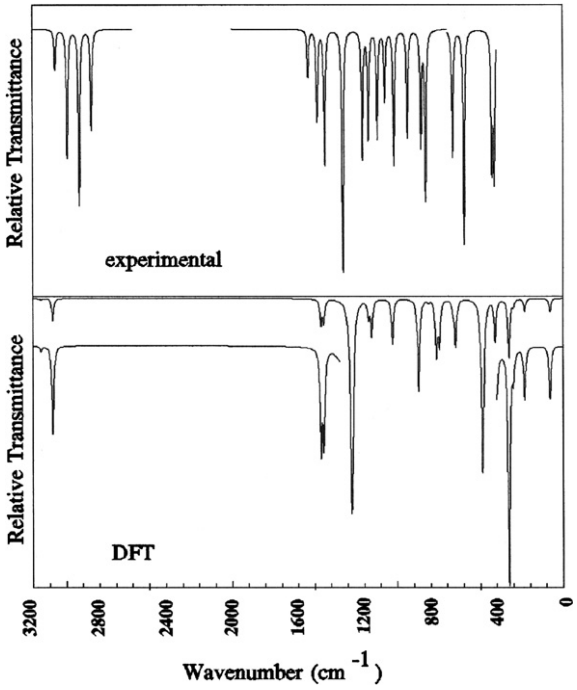

Fig. 4. Simulated experimental (upper) and theoretical infrared spectra of 3-chloro-1,3-thiaphosphetane 3-oxide.

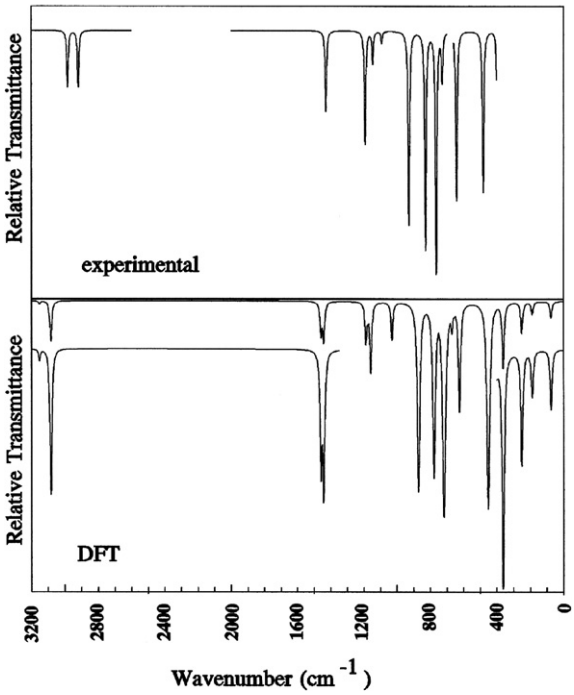

Fig. 6. Simulated experimental (upper) and theoretical infrared spectra of 3-chloro-1,3-thiaphosphetane 3-sulfide.

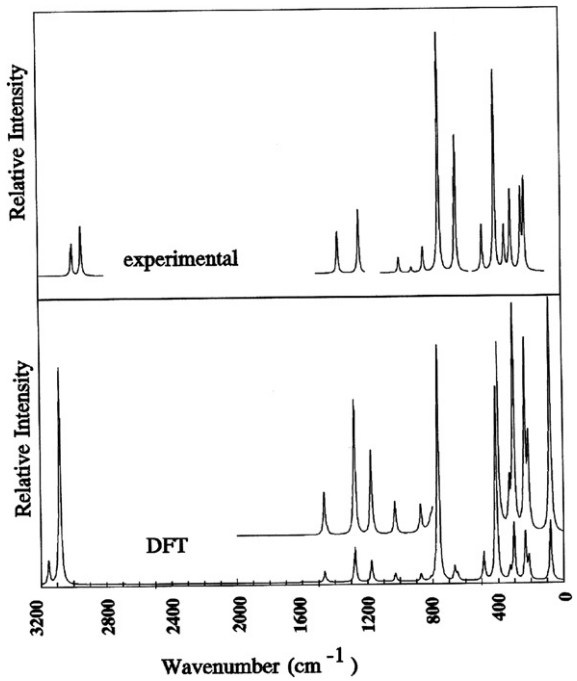

Fig. 5. Simulated experimental (upper) and theoretical Raman spectra of 3-chloro-1,3-thiaphosphetane 3-oxide.

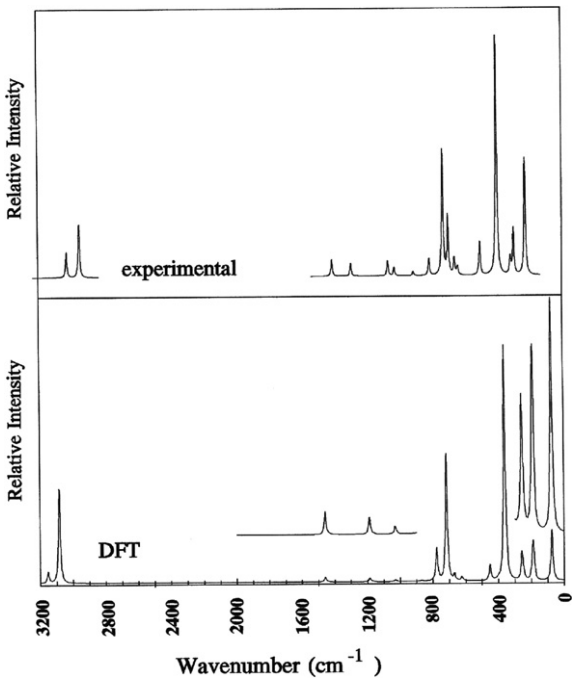

Fig. 7. Simulated experimental (upper) and theoretical Raman spectra of 3-chloro-1,3-thiaphosphetane 3-sulfide.

of about 100 cm^{-1} (286 cal/mol) to planarity of the ring [20]. Since the four-membered dithietane ring is more strained than the five-membered dihydrothiophen ring it should posses a more *planar* structure as its ground state [20]. Therefore, we adopted the *planar* C_{2v} structure of 1,3-dithietane 1,1-dioxuide and calculated its vibrational wavenumbers at the B3LYP-6-311+G** level of theory (Table 8). Also we calculated the frequencies of the C_s puckered structure of 3-chloro-1,3-thiaphosphetane 3-oxide and 3-sulfide molecules at the same level of calculations (Tables 6 and 7).

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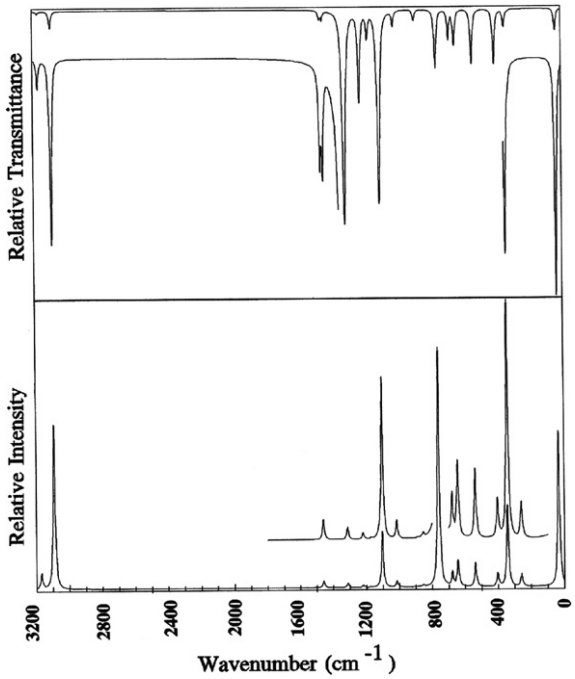

Fig. 8. Calculated infrared (upper) and (lower) spectra of 1,3-dithietane 1,1-dioxide.

The two phosphetane molecules in their *puckered* structures have C_s symmetry and their 24 vibrational modes span the irreducible representations: 14 A' and 10 A''. The A' modes should be polarized whereas the A'' modes be depolarized in the Raman spectra of the liquid. The dithietane molecule in its *planar* structure has C_{2v} symmetry and its 24 vibrational modes span the irreducible representations: 8 A_1, 4 A_2, 6 B_1 and 6 B_2. We provided reliable vibrational assignments for the normal modes of the molecules on the basis of calculated PED values, infrared line intensity, Raman activities, depolarization ratios and experimental data of the oxide and sulfide as shown in Tables 6 and 7.

In the following discussion we will only concentrate on the assignments of the intense spectral features that characterize each of the three molecules with high PED values. In the 2800–3200 cm^{-1} spectral region two bands with medium intensity were observed at about 2995 and 2930 cm^{-1} (95% PED) in the infrared spectra of the oxide and the sulfide thiaphosphetanes are assigned to the CH_2 stretching modes (Tables 6 and 7). The observed bands at 1265 and 712 cm^{-1} with moderately strong intensity in the infrared spectra of liquid oxide and sulfide can be assigned to the P═O (88% PED) and P═S (45% PED) stretching modes, respectively (Figs. 4 and 6 and Tables 6 and 7).

The most intense lines below 1000 cm^{-1} spectral region observed at 780 and 505 cm^{-1} in the Raman spectra of the oxide can be assigned with confidence to the ring breathing (74% S_9) and P─Cl (48% S_4) stretching modes, respectively (Fig. 5). These two modes were observed in the same spectrum of the sulfide at 786 cm^{-1} (63% S_9) and 485 cm^{-1} (61% S_4), respectively (Fig. 7 and Table 7). The lowest wavenumber calculated at 79 cm^{-1} (80% S_{12}) and 74 cm^{-1} (77% S_{12}) in the spectra of the oxide and sulfide is the ring puckering mode (Tables 6 and 7).

For 1,3-dithietane 1,1-dioxide the main characteristic modes are the two SO_2 stretching modes, the ring puckering and the ring breathing modes. The antisymmetric and symmetric SO_2 stretching modes were predicted, respectively, at 1313 cm^{-1} (94% S_3) and 1101 cm^{-1} (83% S_4) in the spectrum of the molecule (Table 8). Additionally the ring breathing and puckering modes were calculated at 760 cm^{-1} (71% S_9) and 33 cm^{-1} (91% S_{12}). It is interesting to notice that the ring breathing mode was calculated to have the greatest Raman activity as expected below 900 cm^{-1} spectral region in the hetero-dithietane ring (Fig. 8 and Table 8).

Acknowledgement

The authors gratefully acknowledge the support of this work by King Fahd University of Petroleum and Minerals through Grant CY/Rotation/309.

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