Pergamon

Tetrahedron 57 (2001) 8181–8184

TETRAHEDRON

Tub and boat–chair forms in a 1,3,2-dioxaphosphocin ring: do C–H···O interactions influence the conformations?

Sudha Kumaraswamy, K. Senthil Kumar, S. Raja and K. C. Kumara Swamy*

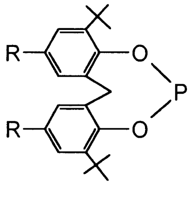
School of Chemistry, University of Hyderabad, Hyderabad 500 046, India

Received 13 March 2001; revised 28 June 2001; accepted 26 July 2001

Abstract—A boat–chair conformation is found for the same ring in the thiophosphite [CH_2\{6-*t*-Bu-4-Me-C_6H_2O\}$_2$]P(S)H (**2**), as revealed by X-ray structural analysis, whereas a tub conformation is found for the eight-membered 1,3,2-phosphocin ring in the phosphite [CH_2\{6-*t*-Bu-Me-C_6H_2O\}$_2$]P(O)H (**1**). Compound **1** exists as a weakly bonded dimer through C–H···O hydrogen bonding in the solid state. No discernible changes were observed in the ^{1}H NMR spectra in solution (C_6D_6) for the two compounds in the temperature range 25–70°C, suggesting that the structures are fairly rigid in solution. Optimisation of the structures using AM1 calculations suggests that a boat–chair conformation should be favoured for **1** in the absence of intermolecular interactions. © 2001 Elsevier Science Ltd. All rights reserved.

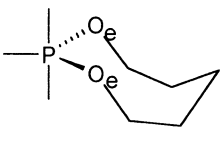
1. Introduction

In our investigations on the chemistry of cyclic phosphorus compounds, we have utilised the eight-membered 'phosphocin' ring system (**I**) quite extensively.[1] Although these eight-membered rings can be expected to be conformationally flexible, so far only two major conformers, the 'boat–chair' (**II**) and the 'tub' (**III**), are found in pentacoordinate compounds which have a trigonal bipyramidal geometry around phosphorus.[1d] In this connection it was of interest to investigate the conformational preferences of the same ring in systems where phosphorus has different environments. Herein, we report our observations on two (hydrido)phosphocin compounds [CH_2\{6-*t*-Bu-4-Me-C_6H_2O\}$_2$]P(O)H (**1**) and [CH_2\{6-*t*-Bu-4-Me-C_6H_2O\}$_2$]P(S)H (**2**) both of which contain the same eight-membered ring as in (**II**) or (**III**) but differ from each other only in the chalcogen X present at the P=X part. In the solid state (X-ray structure), **1** exists as a C–H···O bonded dimer, a situation which to our knowledge, has not been noted before in analogous systems. Compound **2** represents the first cyclic thiophosphite to be structurally characterised.



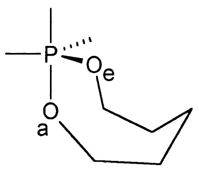
R = Me, *t*-Bu

(I)



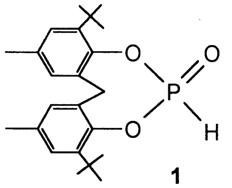
Boat-chair

(II)

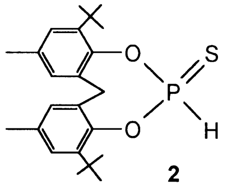


Tub

(III)



1



2

2. Results and discussion

Compounds **1** and **2** are prepared by treating the chloro precursor [CH_2\{6-*t*-Bu-4-Me-C_6H_2O\}$_2$]PCl (**3**) with H_2O and H_2S, respectively, in the presence of triethylamine; whereas **1** is the sole product in the reaction with H_2O, the salt $[Et_3NH]^+$[CH_2\{6-*t*-Bu-4-Me-C_6H_2O\}$_2$]P(S)(S)$^-$ (**4**) is also formed alongside **2** in the reaction with H_2S. It is likely that air oxidation of H_2S occurred, resulting in the formation of elemental sulphur which then oxidised **2** to yield **4**.

Surprisingly, the eight-membered ring in **1** has a 'tub' conformation (Fig. 1) in the solid state; the sulphur analogue **2**, in contrast, has a 'boat–chair' conformation (Fig. 2). There have been a few studies on the conformational features of analogous eight-membered rings in the solid state;[2–6] in a majority of cases the 'boat–chair' form is found.

In the light of the above, and in view of the fact that boat–chair conformations are well established for a variety of eight-membered ring systems, we carried out some semi-empirical calculations (AM1) on **1** and **2**. The boat–chair forms (chalcogen axial/equatorial: **VI** and **VII**) were more

---

Keywords: phosphocin ring; conformation; X-ray structures; C–H···O interactions.

* Corresponding author. Fax: +91-40-3012460; e-mail: kckssc@uohyd.ernet.in

PII: S0040-4020(01)00792-X

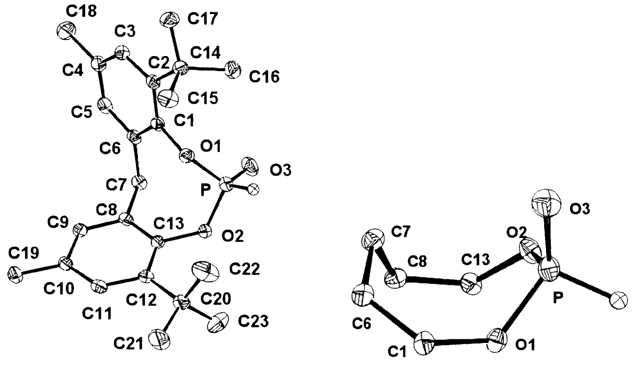


Figure 1. An ORTEP drawing of **1**. Also shown on the right side is the conformation of the eight-membered ring. Selected bond parameters: P–O(1) 1.572(2), P–O(2) 1.579(2), P–O(3) 1.453(2), P–H 1.30(2) Å; O(1)–P–O(2) 105.01(7)°.

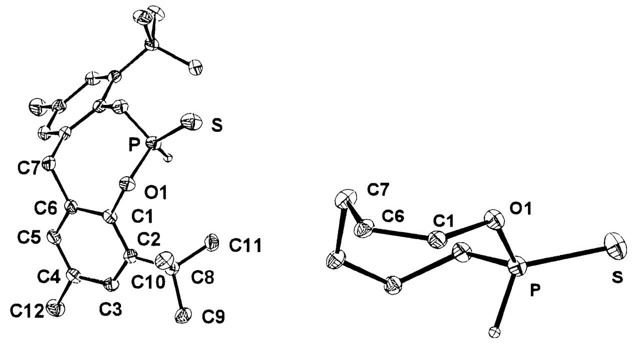
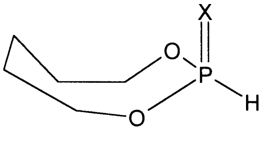
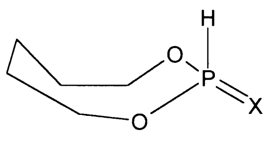


Figure 2. An ORTEP drawing of **2**. Also shown on the right side is the conformation of the eight-membered ring. Selected bond parameters: P–O(1) 1.585(2), P–S 1.906(2), P–H 1.36(3) Å; O(1)–P–O(1)′ 110.30(15)°.

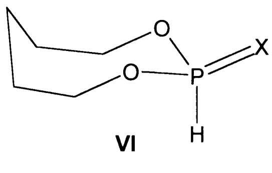
stable than the tub forms (chalcogen axial/equatorial: **IV** and **V**) in both cases by 12–20 kJ mol^{-1}. Although this is consistent with the structure of **2**, it is opposite to that observed for **1** in the solid state. To check this aspect further, we heated **1** at 150°C for 1 h and after cooling, crystallised the sample from hexane; the cell parameters obtained were identical to those observed before heating, proving that there was no change in structure. We also recorded the variable temperature ^{1}H NMR spectra in solution (C_6D_6) for **1** and **2** from 25 to 70°C and found no discernible change. The Ar–CH_AH_X protons appear as two well-separated doublets in **1** and **2** throughout the temperature range, suggesting the presence of a single conformational isomer in both the cases.



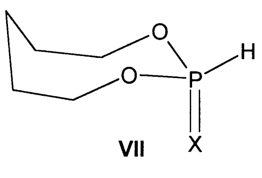
IV



V



VI



VII

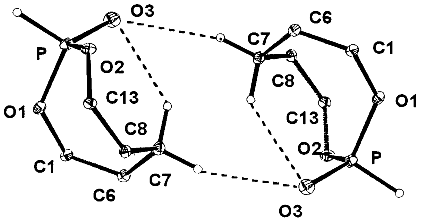


Figure 3. A diagram showing the C(–H)···O interactions leading to the dimer formation in **1**. Only non-hydrogen atoms are labelled. Relevant distances: O(3)–C(7) 3.333(3), O(3)–H(7A) 2.557(3), O(3)–C(7′) 3.528(3), O(3)–H(7B′) 2.700(2) Å [Symm. equiv.: 2−*x*, 1−*y*, −*z*].

Next we looked at the intermolecular interactions and found that **1** is in fact a dimer through weak C–H···O interactions involving the phosphoryl (P=O) oxygen and a hydrogen of the methylene group (Fig. 3). There is also intramolecular contact between the second hydrogen of the methylene group and the phosphoryl group. We believe that these features are responsible for the tub conformation observed in this molecule; no analogous dimer formation and intramolecular contacts were found in **2**. To our knowledge, such an inference has not been made in previous studies. Hence we looked for the presence of such features in two of our compounds, 2,2-N_4P_4\{[O-4,6-(*t*-Bu)$_2C_6H_2]_2CH_2$\}Cl_6·0.5$C_4H_8Cl_2$ (**5**) and $Cl_2P(O)N{=}P[(O\text{-}4\text{-}Me\text{-}6\text{-}t\text{-}BuC_6H_2)_2CH_2]Cl$ (**6**) reported recently.[1c] In **5**, C(7) does indeed have a close intramolecular contact with the N(=P) of the cyclophosphazene (3.175 Å; Fig. 4(a)) and the conformation of the dioxaphosphocin ring is tub; in **6**

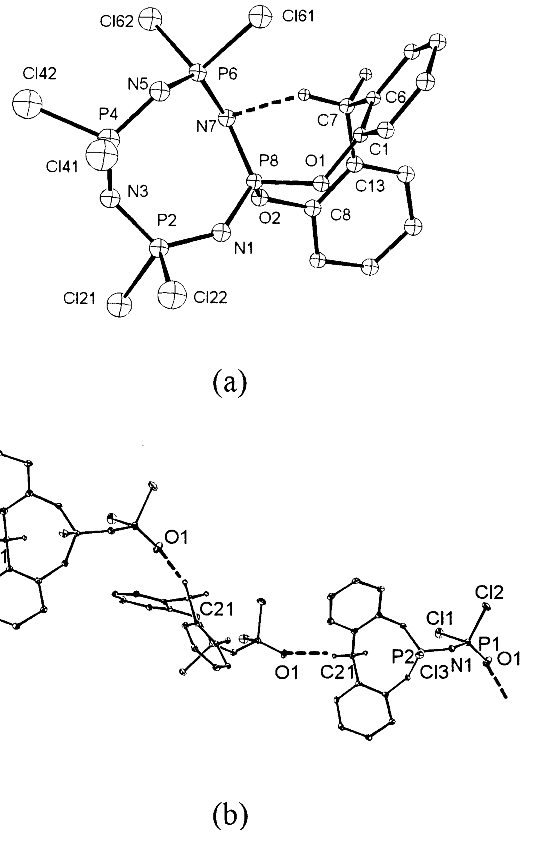


Figure 4. A diagram showing the C–H···O interactions in (a) 2,2-N_4P_4\{[O-4,6-(*t*-Bu)$_2C_6H_2]_2CH_2$\}Cl_6.0.5$C_4H_8Cl_2$ (**5**) [C(7)–N(7) 3.175 (3) Å] and (b) $Cl_2P(O)N{=}P[(O\text{-}4\text{-}Me\text{-}6\text{-}t\text{-}BuC_6H_2)_2CH_2]Cl$ (**6**) [C(21)–O(1) 3.384 Å]. Only selected atoms highlighting the C–H···O interactions are shown.

where the dioxaphosphocin ring has a boat–chair conformation, C(7) (labelled C(21) in Fig. 4(b)) has weak but clearly discernible intermolecular hydrogen bonded contacts with the phosphoryl oxygen of a different molecule (C···O 3.384 Å) leading to a chain structure. Thus it appears that subtle differences in weak hydrogen bonding leads to the conformational changes observed in the present study. The propensity of the phosphoryl oxygen to participate in H-bonding interactions is well known, but the involvement of a hydrogen atom connected to an sp^3 carbon as observed in **1** is an interesting feature to be noted in this emerging area of weak hydrogen bonding.[7]

3. Conclusions

We have ascribed the observation of a tub conformation for the dioxaphosphocin ring in **1** and a boat–chair conformation in **2** to the presence of weak C–H···O hydrogen bonding in **1**. Our AM1 calculations suggest that in the absence of other effects (like hydrogen bonding), a boat–chair conformation should be favoured over the tub for the eight-membered ring in **1**. Clarifications on these aspects may come through by a detailed analysis of C–H···O interactions and their effects on structural features in analogous heterocyclic compounds. In a broader perspective, it is likely that weak interactions do play a role in influencing structural features in the solid state.

4. Experimental

4.1. General

Chemicals were purchased from Aldrich/Fluka or local manufacturers; they were purified when required. H_2S were dried by passing through a P_2O_5 tower. Solvents were purified according to standard procedures.[8] ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on a Brucker 200 MHz spectrometer in $CDCl_3$ with chemical shifts (ppm) measured against $(CH_3)_4Si$ (^{1}H and ^{13}C) or 85% H_3PO_4 (^{31}P). IR spectra were recorded on a Perkin–Elmer 1310 spectrophotometer. Elemental analyses were carried out on a Perkin–Elmer 240C CHN analyser.

4.1.1. Preparation of 1. A mixture of water (0.045 g, 2.47 mmol) and triethylamine (0.25 g, 2.47 mmol) was added to a solution of $[CH_2\{6\text{-}t\text{-Bu-4-Me-}C_6H_2O\}_2]PCl$ (**3**)[6] (1.00 g, 2.47 mmol) in toluene (20 mL) and the mixture stirred for 24 h. Filtration followed by removal of solvent and recrystallisation of the residue from toluene–heptane afforded **1** as a crystalline solid (0.86 g, 90%). Mp 152°C. IR (cm^{-1}): 2446 (ν(PH)). ^{1}H NMR (C_6D_6): 1.42 (s, 18H, *t*-Bu-*H*), 2.32 (s, 6H, Ar–CH_3), 3.66 (d, J=14.6 Hz, 1H, CH_AH$_X$), 4.43 (d, J=14.6 Hz, 1H, CH$_A$$H_X$), 7.05, 7.07 (2s, 4H, Ar–*H*), 7.32 (d, J=730.0 Hz, 1H, P–*H*). ^{13}C NMR ($CDCl_3$) 20.98, 30.62, 34.65, 35.15, 127.11, 129.41, 131.95, 134.92, 140.75, 140.84, 145.30, 145.50. ^{31}P NMR ($CDCl_3$): 0.1. Anal. calcd for $C_{23}H_{31}O_3P$: C, 71.48; H, 8.08. Found: C, 71.46, H, 8.12.

4.1.2. Preparation of 2. Dry H_2S gas was bubbled for 0.5 h into a solution of **3** (0.745 g, 1.84 mmol) in hexane (40 mL); then Et_3N (0.19 g, 0.26 mL, 1.88 mmol) was added while still passing H_2S. After 1 h, addition of H_2S was stopped and the mixture stirred overnight at room temperature. The reaction mixture was then filtered, the precipitate washed with toluene and the washings added to the filtrate; the solution thus obtained was evaporated to dryness. The obtained solid was washed with hexane (4×5 mL), the washings were combined and the solvent slowly evaporated in air to give crystalline **2** (0.1 g, 14%), mp 166–168°C. IR (cm^{-1}): 2369 (ν(PH)). ^{1}H NMR (C_6D_6): 1.42 (s, 18H, *t*-Bu-*H*), 2.31 (s, 6H, Ar–CH_3), 3.58 (d, J=14.3 Hz, 1H, CH_AH$_X$), 4.52 (d, J=14.3 Hz, 1H, CH$_A$$H_X$), 7.05, 7.07 (2s, 4H, Ar–*H*), 8.08 (d, J=654.3 Hz, 1H, P–*H*). ^{13}C NMR ($CDCl_3$): 21.04, 30.85, 34.76, 35.60, 127.16, 129.25, 132.99, 135.01, 141.23, 141.34, 146.64. ^{31}P NMR ($CDCl_3$): 64.9. Anal. calcd for $C_{23}H_{31}O_2PS$: C, 68.63; H, 7.76. Found: C, 68.58, H, 7.65. The hexane insoluble part was found to be the salt $[Et_3NH]^+[CH_2\{6\text{-}t\text{-Bu-4-Me-}C_6H_2O\}_2]P(S)(S)^-$ (**4**) details of which will be reported separately.

X-Ray data were collected at 293 K using MoKα (λ=0.71073 Å) radiation and Enraf–Nonius Mach-3 diffractometer by mounting the crystal on a glass fibre. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 160845 and 160846. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.camb.ac.uk). Crystal data: **1**, emp. formula $C_{23}H_{31}O_3P$, formula wt 386.45, monoclinic, space group $P2_1/n$, a=13.576(2), b=9.617(6), c=17.080(3) Å, β=97.057(10)°, V=2213.0(16) Å^3, Z=4, density (calcd) 1.160 mg/m^{-3}, θ range 1.81–24.96°, reflns collected 4049, independent reflns 3883 [R(int)=0.0151], refinement-full-matrix least-squares on F^2, data/restraints/parameters 3883/0/256, GOOF 1.070, $R1[I>2\text{sigma}(I)]$=0.0400, $wR2$(all)=0.1287, largest diffusion peak and hole 0.186 and −0.301 e A^{-3}. **2**, emp. formula $C_{11.5}H_{15.5}OP_{0.5}S_{0.5}$, formula wt 201.25, monoclinic, space group $P2_1/m$, a=5.891(6), b=23.058(5), c=8.155(2) Å, β=93.314(10)°, V=1105.8(12) Å^3, Z=4, density (calcd) 1.209 mg/m^{-3}, θ range 1.77–24.96°, reflns collected 2173, independent reflns 1983 [R(int)=0.0115], refinement-full-matrix least-squares on F^2, data/restraints/parameters 1983/0/134, GOOF 1.089, $R1[\text{I}>2\text{sigma}(I)]$=0.0491, $wR2$(all)=0.1581, largest diffusion peak and hole 0.420 and −0.295 e A^{-3}.

4.1.3. AM1 calculations. Full optimisation by starting with X-ray co-ordinates for **1** and **2** was performed. In the optimisation, it was ascertained that the gradient norms were $\leq$5. The relative heats of formation in kJ/mol and gradient norms (given in parentheses) were as follows: (i) X=O (**IV**) −599.1(4.1), (**V**) −601.6(4.6), (**VI**) −615.5(4.9), (**VII**) −620.5 (5.1); (ii) X=S (**IV**) −243.9 (3.7), (**V**) −238.9 (4.2), (**VI**) −256.1(2.0), (**VII**) −256.1 (3.8).

Acknowledgements

We thank: (i) the Council of Scientific and Industrial Research (New Delhi) for financial support, (ii) University

Grants Commission (New Delhi; COSIST and SAP) for instrumental facilities and (iii) Department of Science and Technology (New Delhi) for setting up a National Single Crystal Diffractometer Facility at the University of Hyderabad. We also thank Dr T. P. Radhakrishnan (University of Hyderabad) for help in AM1 calculations.

References

1. (a) Said, M. A.; Kumara Swamy, K. C.; Chandra Mohan, K.; Venkata Lakshmi, N. *Tetrahedron* **1994**, *50*, 6989. (b) Said, M. A.; Pülm, M.; Herbst-Irmer, R.; Kumara Swamy, K. C. *J. Am. Chem. Soc.* **1996**, *118*, 9841. (c) Kumaraswamy, S.; Vijjulatha, M.; Muthiah, C.; Kumara Swamy, K. C.; Engelhardt, U. *J. Chem. Soc., Dalton Trans.* **1999**, 891. (d) Kumaraswamy, S.; Muthiah, C.; Kumara Swamy, K. C. *J. Am. Chem. Soc.* **2000**, *122*, 964.
2. (a) Reddy, C. D.; Reddy, R. S.; Reddy, M. S.; Krishnaiah, M.; Berlin, K. D.; Sunthankar, P. *Phosphorous Sulfur* **1991**, *62*, 1. (b) Holmes, R. R.; Prakasha, T. K.; Pastor, S. D. In *Phosphorus-31 NMR spectral properties in compound characterisation and structural analysis*, Quin, L. D., Verkade, J. G., Eds.; VCH: New York, USA, 1994 Chapter 3.
3. Goddard, J. D.; Payne, A. W.; Cook, N.; Luss, H. R. *J. Heterocycl. Chem.* **1988**, *25*, 575 and references cited therein.
4. Prakasha, T. K.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1992**, *31*, 3391 and references cited therein.
5. In the tricoordinated compound $[CH_2\{6\text{-}t\text{-Bu-4-Me-}C_6H_2O\}_2]P(OPh)$ where no phosphoryl oxygen is present, the eight-membered ring has the normal boat–chair conformation. See Litvinov, I. A.; Struckhov, Y. T.; Arbuzov, B. A.; Arshinova, R,P.; Ovodova, O. V. *Zh. Strukt. Khim.* **1984**, *25*, 118.
6. Sherlock, D. J.; Chandrasekaran, A.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1997**, *36*, 5082.
7. Selected references: (a) Davidson, M. G.; Goeta, A. E.; Howard, J. A. K.; Lamb, S.; Mason, S. A. *New J. Chem.* **2000**, *24*, 477. (b) Steiner, T. *Chem. Commun.* **1997**, 727. (c) Desiraju, G. R. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2311. (d) Desiraju, G. R.; Steiner, T. *The Weak Hydrogen Bond in Structural Chemistry and Biology*; OUP: Oxford, 1999. (e) Derewenda, Z. S.; Lee, L.; Derewenda, U. *J. Mol. Biol.* **1995**, *252*, 248.
8. Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*; Pergamon: Oxford, 1986.