

Ethyl 3-[1-(5,5-dimethyl-2-oxo-1,3,2-dioxaphosphorin-2-yl)propan-2-ylidene]carbazate: a combined X-ray and density functional theory (DFT) study

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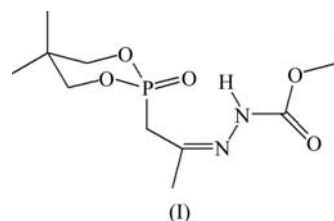
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In the title compound, C₁₁H₂₁N₂O₅P, one of the two carbamate N atoms is involved in the C=N double bond and the H atom of the second N atom is engaged in an intramolecular hydrogen bond with an O atom from the dimethylphosphorin-2-yl group, which is in an uncommon *cis* position with respect to the carbamate group. The cohesion of the crystal structure is also reinforced by weak intermolecular hydrogen bonds. Density functional theory (DFT) calculations at the B3LYP/6-311++g(2d,2p) level revealed the lowest energy structure to have a *Z* configuration at the C=N bond, which is consistent with the configuration found in the X-ray crystal structure, as well as a less stable *E* counterpart which lies 2.0 kcal mol⁻¹ higher in potential energy. Correlations between the experimental and computational studies are discussed.

Comment

Phosphyldiazones are considered excellent reagents in heterocyclic synthesis [e.g. phosphopyrazoles (Ben Akacha *et al.*, 1988; Aboujaoude *et al.*, 1985), pyrazoles (Bondion & Legrand, 1983), phosphonated diazaphospholine oxides (Baccolini *et al.*, 1980; Ben Akacha *et al.*, 1991), *etc.*]. However, to the best of our knowledge, the synthesis and molecular structures of this class of compounds have been presented without using X-ray crystal structure analysis. We have succeeded in the synthesis of the title compound, (I), a member of this class of reagents. As part of our co-operative effort on the development and structural studies of this kind of molecule, we report the synthesis and X-ray crystal structure of (I), supported also by density functional theory (DFT) calculations.

In compound (I) (Fig. 1), there is one P atom bonded to three O atoms and a –CH₂– group, with the shortest P–O bond distance corresponding to the double bond. The other two O atoms, O2 and O3, are also bonded to two –CH₂– groups, and all belong to the widely studied dimethylphosphorin-2-yl entity [e.g. Setzer *et al.* (1985); Hassen *et al.* (2003)]. In this entity, the six-membered ring adopts a chair conformation, with puckering parameters (Cremer & Pople, 1975; Spek, 2009) $\varphi = 6.8(7)^\circ$, $\theta = 159.2(2)^\circ$ and $Q = 0.505(2)$ Å. On the other hand, the molecule contains two N atoms, one of them involved in the C=N double bond and the second belonging to the carbamate group, which is in an uncommon *cis* position with respect to the dimethylphosphorin-2-yl group despite the steric hindrance between them. Atom H2 is involved in an intramolecular N2–H2···O1 hydrogen bond, which may induce the *cis* conformation. The cohesion of the crystal structure is also reinforced by weak intermolecular C–H···O hydrogen-bond interactions (Table 1), and the molecules are linked into chains running along the [010] axis (Fig. 2).



In order to gain more insight into the molecular structure of (I), the geometries of the *Z* and *E* forms were optimized by means of DFT [B3LYP/6-311++g(2d,2p)] computational methods performed using the GAUSSIAN03 program package (Frisch *et al.*, 2003). The optimized molecular structure of the stable *Z* form is similar to that obtained from the X-ray crystal structure, with the exception of the direction of the puckering of the six-membered ring. The potential energy

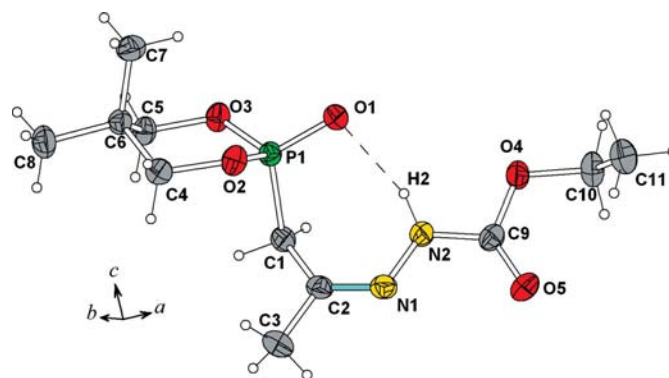


Figure 1

The molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. The intramolecular hydrogen bond is denoted by a dashed line.

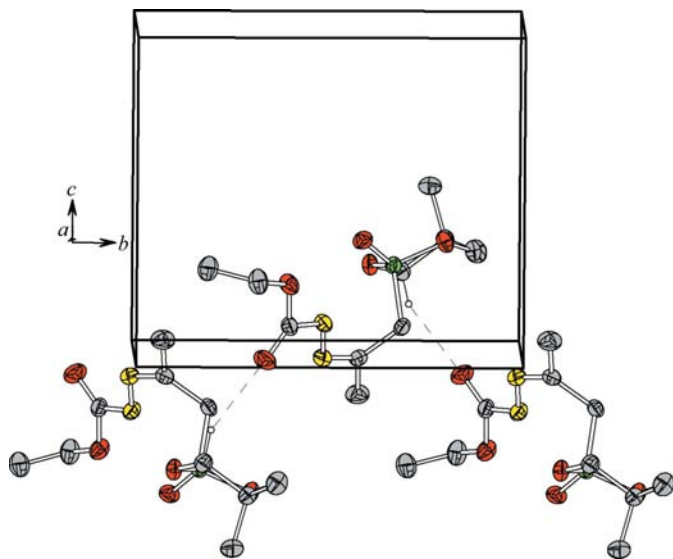


Figure 2

A partial packing view of (I), showing the chain along [010] generated by intermolecular hydrogen-bond interactions (dashed lines). H atoms not involved in these interactions have been omitted for clarity.

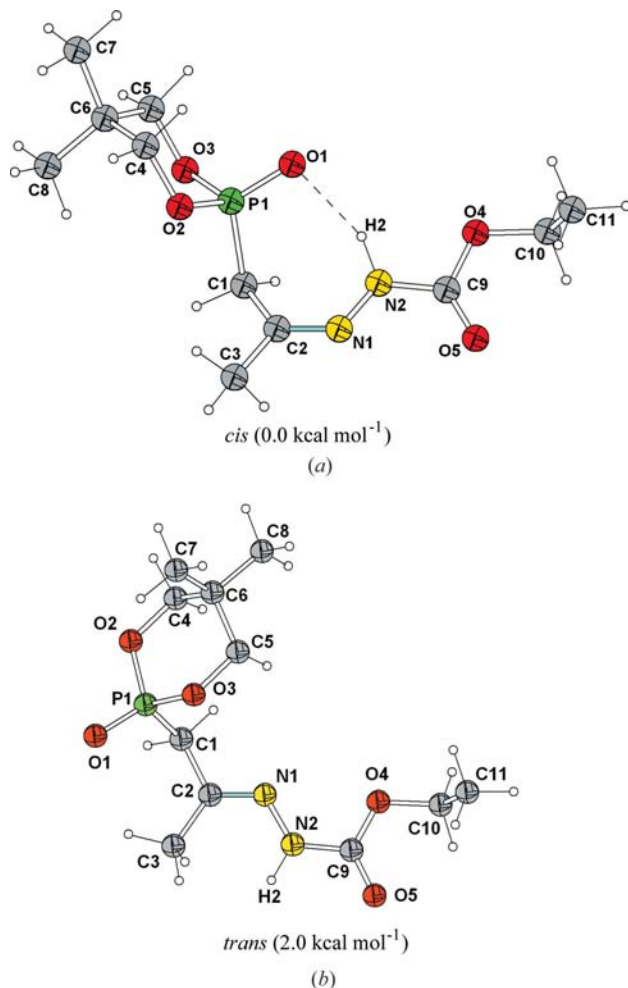


Figure 3

The DFT-optimized molecular structures of (I) and their relative energies. Atom labelling is the same as in Fig. 1.

difference between the two forms is $2.0 \text{ kcal mol}^{-1}$ ($1 \text{ kcal mol}^{-1} = 4.184 \text{ kJ mol}^{-1}$), indicating the stability of the *Z* form (Fig. 3). This stability can be attributed to the existence of the intramolecular $\text{N2-H2} \cdots \text{O1}$ hydrogen bond, which is absent in the *E* counterpart, despite the long theoretical $\text{O1} \cdots \text{N2}$ distance of 5.41 \AA , thus excluding a significant electronic lone-pair repulsion between these two atoms in the *E* form.

Some experimental and optimized geometric parameters of the *Z* configuration are summarized in Table 2. The sums of the angles around atom C2 in the experimental configuration and in the optimized one are close to 360° , in agreement with the sp^2 hybridization. The experimental N2-N1=C2-C1 torsion angle is 4.48° and the optimized one is -5.52° . We can attribute the small differences between the calculated and observed geometric parameters to the fact that the theoretical calculations were carried out with isolated molecules in the gaseous phase. It should be emphasized that the ^{31}P NMR spectrum at 298 K indicates that an equilibrium between the two forms is possible in solution; both *Z* and *E* isomers were found, with an *E/Z* ratio of 0.40/0.60. As for the case of the phosphonylhydrazone series (Ben Akacha *et al.*, 1999), the equilibrium also depends on temperature. Thus, at 328 K the equilibrated content of the *Z* isomer decreases to 0.50.

In conclusion, the experimental X-ray diffraction and theoretical DFT studies of (I) have revealed the same configuration at the C=N bond. The preferential *cis* conformation is likely determined by intramolecular hydrogen bonds in the crystal structure.

Experimental

The title compound was prepared by the reaction of an equimolar amount of phosphoallene and ethyl carbazate in chloroform, following previously reported procedures (Ayed *et al.*, 1985; Ben Akacha *et al.* 1988, 1999). To a solution of 5',5'-dimethyl-2'-oxo-1',3',2'-dioxaphosphorinylpropadiene (0.05 mol) dissolved in chloroform (100 ml), a solution of ethyl carbazate (0.05 mol) in chloroform (10 ml) was added dropwise at room temperature and the mixture was refluxed for 6 h. After cooling, the solution was concentrated *in vacuo* and the crude product was crystallized from dimethyl sulfoxide, giving colourless crystals of (I) in 70% yield (Salah *et al.*, 2009).

For the *Z* form, ^{31}P NMR (CDCl_3): δ 18.16; ^{13}C NMR (CDCl_3): δ 155.10 ($-\text{C=O}$), 145.13 ($-\text{C=N}$), 75.82 ($^2J_{\text{CP}} = 6.79 \text{ Hz}$, $-\text{CH}_2-\text{O}-$), 61.62 ($\text{CH}_3-\text{CH}_2-\text{O}-$), 29.32 ($^1J_{\text{CP}} = 131.3 \text{ Hz}$, $-\text{CH}_2-\text{P}$), 32.52 ($^3J_{\text{CP}} = 3 \text{ Hz}$, $-\text{C}-\text{CH}_2-\text{O}-$), 21.70 [$\text{CH}_3(e)-$], 21.47 [$\text{CH}_3(a)-$], 16.16 ($\text{CH}_3-\text{C=N}$), 14.55 ($\text{CH}_3-\text{CH}_2-\text{O}-$); ^1H NMR (CDCl_3): δ 19 (H-N), 3.68–4.05 ($-\text{CH}_2-\text{O}-\text{P}$), 4.25 ($-\text{O}-\text{CH}_2-\text{CH}_3$), 3.01 ($^2J_{\text{HP}} = 21 \text{ Hz}$, $\text{P}-\text{CH}_2-$), 2.14 ($^4J_{\text{HP}} = 3 \text{ Hz}$, $\text{CH}_3-\text{C=N}$), 1.13 [$\text{CH}_3(e)-\text{C}-\text{CH}_2-\text{O}-$], 1.00 [$\text{CH}_3(a)-\text{C}-\text{CH}_2-\text{O}-$]. For the *E* form, ^{31}P NMR (CDCl_3): δ 19.52; ^{13}C NMR (CDCl_3): δ 155.10 ($-\text{C=O}$), 145.13 ($-\text{C=N}$), 76.19 ($^2J_{\text{CP}} = 6.79 \text{ Hz}$, $-\text{C}-\text{CH}_2-\text{O}-$), 61.79 ($\text{CH}_3-\text{CH}_2-\text{O}-$), 35.10 ($^1J_{\text{CP}} = 131.3 \text{ Hz}$, $-\text{CH}_2-\text{P}$), 32.69 ($^3J_{\text{CP}} = 3 \text{ Hz}$, $\text{C}-\text{CH}_2-\text{O}-$), 21.22 [$\text{CH}_3(e)-$], 21.04 [$\text{CH}_3(a)-$], 16.15 ($\text{CH}_3-\text{C=N}$), 14.56 ($\text{CH}_3-\text{CH}_2-\text{O}-$); ^1H NMR (CDCl_3): δ 8.12 (H-N), 3.84–4.08 ($-\text{CH}_2-\text{O}-\text{P}$), 4.28 ($-\text{O}-\text{CH}_2-\text{CH}_3$), 3.05 ($^2J_{\text{HP}} = 21 \text{ Hz}$, $\text{P}-\text{CH}_2-$), 2.04 ($^4J_{\text{HP}} = 3 \text{ Hz}$, $\text{CH}_3-\text{C=N}$), 1.14 [$\text{CH}_3(e)-\text{C}-\text{CH}_2-\text{O}-$], 1.04 [$\text{CH}_3(a)-\text{C}-\text{CH}_2-\text{O}-$].

Crystal data

$C_{11}H_{21}N_2O_5P$	$V = 738.7 (4) \text{ \AA}^3$
$M_r = 292.27$	$Z = 2$
Monoclinic, $P2_1$	Mo $K\alpha$ radiation
$a = 7.235 (2) \text{ \AA}$	$\mu = 0.20 \text{ mm}^{-1}$
$b = 10.823 (4) \text{ \AA}$	$T = 293 \text{ K}$
$c = 9.545 (3) \text{ \AA}$	$0.30 \times 0.20 \times 0.18 \text{ mm}$
$\beta = 98.78 (2)^\circ$	

Data collection

Enraf–Nonius CAD-4 diffractometer	1697 independent reflections
Absorption correction: ψ scan (North <i>et al.</i> , 1968)	1601 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.879$, $T_{\max} = 0.940$	$R_{\text{int}} = 0.025$
2510 measured reflections	2 standard reflections every 120 min
	intensity decay: 1%

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.028$	1 restraint
$wR(F^2) = 0.080$	H-atom parameters constrained
$S = 1.08$	$\Delta\rho_{\text{max}} = 0.24 \text{ e \AA}^{-3}$
1697 reflections	$\Delta\rho_{\text{min}} = -0.12 \text{ e \AA}^{-3}$
176 parameters	

Table 1

Hydrogen-bond geometry (\AA , $^\circ$).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N2-H2\cdots O1$	0.86	2.05	2.865 (3)	158
$C4-H42\cdots O5^i$	0.97	2.45	3.380 (3)	161

Symmetry code: (i) $-x, y + \frac{1}{2}, -z$.

All H atoms attached to C or N atoms were fixed geometrically and treated as riding, with C–H = 0.96 (methyl) or 0.97 \AA (methylene) and N–H = 0.86 \AA , with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C methylene or N})$ or $1.5U_{\text{eq}}(\text{C methyl})$. Owing to the low Friedel-pair coverage of 11.56%, the absolute structure could not be reliably determined, so the Friedel pairs were merged.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1995); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 1998); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Table 2

Selected experimental and optimized bond lengths (\AA).

Bond	X-ray diffraction data	DFT-optimized Z conformation
C1–C2	1.520 (3)	1.519
C2–N1	1.286 (3)	1.277
N1–N2	1.394 (3)	1.374
P1–C1	1.810 (3)	1.803
P1–O1	1.4745 (18)	1.477
P1–O3	1.5797 (18)	1.608
P1–O2	1.5736 (17)	1.609
N2–C9	1.372 (3)	1.382
N2...O1	2.865 (3)	2.976
H2...O1	2.05	2.032

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DN3143). Services for accessing these data are described at the back of the journal.

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