## Notiz / Note

# Structure of the *cis* and *trans* Isomers of 2,4-Bis(diethylamino)-1,5-dimethyl-1,5,2,4-diazadiphosphorinan-6-one 2,4-Disulfide

**Igor V. Shevchenko, Axel Fischer, Peter G. Jones, and Reinhard Schmutzler***

Institut für Anorganische und Analytische Chemie der Technischen Universität Braunschweig,
Postfach 3329, D-38023 Braunschweig, Germany

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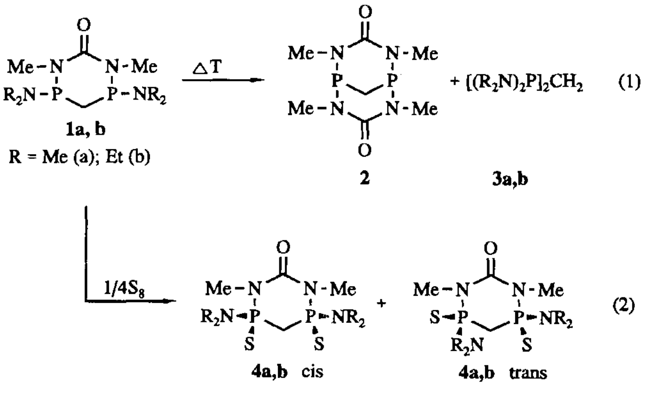
The 2,4-bis(dialkylamino)-1,5-dimethyl-1,5,2,4-diazadiphosphorinan-6-ones **1a** and **1b** (R = $CH_3$, **a**; $C_2H_5$, **b**) are thermally unstable and are transformed into the bicyclic species **2** when heated to 150°C (2 Torr). The reactions of **1a** and **1b** with elemental sulfur lead to the *P,P'*-disulfides **4a** and **4b** as a mixture of *cis* and *trans* isomers which are separated by column chromatography. Single-crystal X-ray structure determinations were conducted on compound **2** and on the *cis* and *trans* isomers of **4b**. The bicyclic compound **2** is found to display crystallographic twofold symmetry. Its structure is closely similar to that of the diphenyl analogue. For the *cis* and *trans* isomers of **4** almost ideal S–P···P–S torsion angles are observed. The isomers adopt different ring conformations.

Previously we described the synthesis and some chemical properties of the 2,4-bis(dialkylamino)-1,5-dimethyl-1,5,2,4-diazadiphosphorinan-6-ones **1a** and **1b** [alkyl = Me (**a**), Et (**b**)] which exist as *cis* and *trans* isomers, depending on the position of the dialkylamino substituents at phosphorus[1]. Compounds **1a** and **1b** were formed quantitatively (according to $^{31}P$-NMR evidence) but, after distillation in vacuo, the yield was substantially reduced. This is a result of the limited thermal stability of **1a** and **1b**, and heating the compounds to 150°C (2 Torr) leads to the bicyclic compound **2**. This observation is accounted for by the scrambling reaction (1). Whereas **2** was isolated as a colourless crystalline product whose physical data were in agreement with those previously described[2,3] the assumed formation of compounds **3a** and **3b** could not be experimentally confirmed.



Immediately after their preparation **1a** and **1b** are present as a 1:1 mixture of *cis* and *trans* isomers[1]. The *trans* isomer is thermodynamically more stable, and the *cis*/*trans* ratio at equilibrium is 1:9. The equilibration between *cis* and *trans* isomers and the high senstivity to moisture prevent a separation of the isomers. Sulfuration of **1a** and **1b** produces the disulfides **4a** and **4b**, which are substantially more stable to hydrolysis and do not undergo *cis-trans* isomerization. The *cis* and *trans* isomers could, therefore, be separated by column chromatography[1]. Since the isomers **4a** and **4b** (*cis*), and **4a** and **4b** (*trans*) are readily tractable crystalline compounds it was decided to study the X-ray crystal structure for a pair of *cis* and *trans* isomers in a representative case (**4b** *cis* and **4b** *trans*). This kind of structural comparison in such a system had not previously been possible.

## Single Crystal X-Ray Determinations of Compounds 2, 4b (*cis*), and 4b (*trans*)

Compound **2** exhibited crystallographic twofold symmetry (Figure 1), the symmetry axis passing through the carbon atom of the methano bridge (C4). The structure is closely similar to that of the related *N,N'*-dimethyl-*N,N'*-diphenyl compound[4] in which, however, the twofold symmetry is not crystallographically imposed.

Small differences are observed in the ring angles at the N(Me) atoms, 127.7 and 131.6(1)° in **2** but 132.6 and 132.4° in the related *N,N'*-dimethyl-*N,N'*-diphenyl compound[4]. Torsion angles of −7 and −16° about N1–C2 and C2–N2 illustrate the slight non-coplanarity of the five atoms P1, N1, C2, N2, and P1$^i$, which causes the slight magnetic inequivalence of the NMe groups.

## Compounds 4b *cis* and 4b *trans*

Figures 2 and 3 show the structures of **4b** *cis* and **4b** *trans*. The *cis* and *trans* isomers display similar bond lengths [maximum difference 179.7(2), 181.3(2) pm for P2–C2[5]]. However, there are major differences in some angles, e.g. 128.9(1), 120.5(1)° for P1–N1–C1. The latter angle seems unusually narrow, compared to the other chemically equivalent values of 131.8(1), 128.4(1)° for P2–N2–C1.

The ring conformation of the *cis* isomer is essentially half-chair, and the molecule possesses approximate non-crystallographic mirror symmetry (except for the conformation of the ethyl groups).

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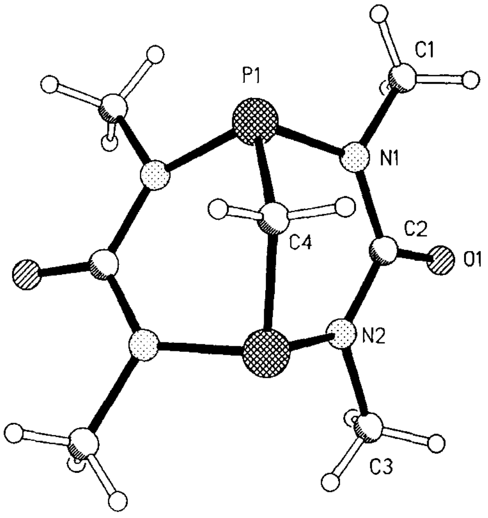

Figure 1. The molecule of compound **2** in the crystal. Radii are arbitrary, only the asymmetric unit is numbered; selected bond lengths [pm] and angles [°]: P1-N1 171.8(1), P1-C4 180.1(2), P1-N2$^{i}$ 172.9(2), O1-C2 122.1(2), N1-C1 147.4(3), N1-C2 137.8(2), N2-C2 138.4(3), N2-C3 147.2(3); N1-P1-C4 97.8(1), N1-P1-N2$^{i}$ 105.0(1), C4-P1-N2$^{i}$ 100.5(1), P1-N1-C1 117.0(1), P1-N1-C2 127.7(1), C1-N1-C2 114.8(1), C2-N2-C3 113.9(1), C2-N2-P1$^{i}$ 131.6(1), C3-N2-P1$^{i}$ 114.2(1), O1-C2-N1 120.7(2), O1-C2-N2 120.5(2), N1-C2-N2 118.8(1), P1-C4-P1$^{i}$ 112.6(1); symmetry operator (i): $1 - x, y, 1.5 - z$

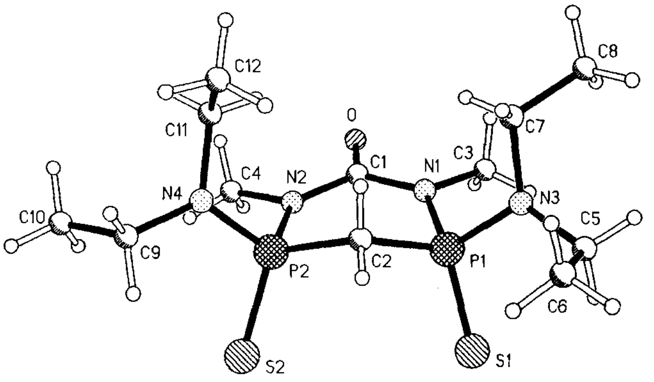

Figure 2. The molecule of the *cis* isomer of compound **4b** in the crystal. Radii are arbitrary, selected bond lengths [pm] and angles [°]: S1-P1 193.1(1), S2-P2 193.4(1), P1-N1 169.6(1), P1-N3 165.3(1), P1-C2 180.1(1), P2-N2 170.3(1), P2-N4 164.6(1), P2-C2 179.7(2), N1-C1 139.1(2), N2-C1 138.8(2), O-C1 122.3(2); S1-P1-N1 115.2(1), S1-P1-N3 113.6(1), N1-P1-N3 102.8(1), S1-P1-C2 115.9(1), N1-P1-C2 100.2(1), N3-P1-C2 107.5(1), S2-P2-N2 114.0(1), S2-P2-N4 113.6(1), N2-P2-N4 104.5(1), S2-P2-C2 115.8(1), N2-P2-C2 100.6(1), N4-P2-C2 106.9(1), P1-N1-C1 128.9(1), P2-N2-C1 131.8(1), N1-C1-N2 120.6(1), N1-C1-O 119.7(1), N2-C1-O 119.6(1), P1-C2-P2 116.5(1)

The *trans* isomer adopts an unusual conformation in which the four atoms N2, P2, C2, and P1 are almost coplanar, and the remaining atoms N1 and C1 lie on the same side of the plane so defined. The torsion angles S-P···P-S are almost ideally *cis* and *trans*, respectively (5, −179°).

The deviations of the ring nitrogen atoms from their substituent planes vary from the almost planar N2 (*cis* isomer) (2 pm) to the pyramidal N1 (*trans* isomer) (29 pm).

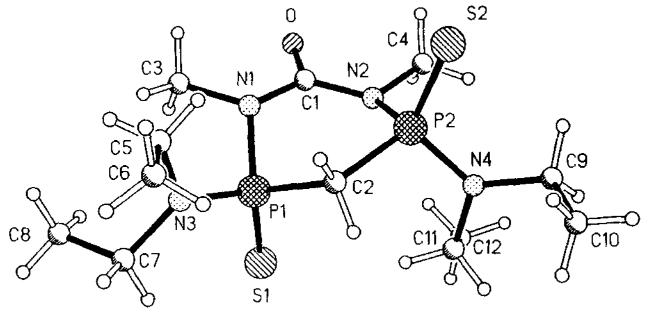

Figure 3. The molecule of the *trans* isomer of compound **4b** in the crystal. Radii are arbitrary, selected bond lengths [pm] and angles [°]: S1-P1 192.9(1), S2-P2 194.0(1), P1-N1 170.5(2), P1-N3 163.8(2), P1-C2 180.2(2), P2-N2 170.7(2), P2-N4 163.1(2), P2-C2 181.3(2), N1-C1 140.0(3), N2-C1 138.8(2), O-C1 121.4(2); S1-P1-N1 114.3(1), S1-P1-N3 114.1(1), N1-P1-N3 105.8(3), S1-P1-C2 115.6(1), N1-P1-C2 99.6(1), N3-P1-C2 105.9(1), S2-P2-N2 113.2(1), S2-P2-N4 113.1(1), N2-P2-N4 105.4(1), S2-P2-C2 113.1(1), N2-P2-C2 103.1(1), N4-P2-C2 108.2(1), P1-N1-C1 120.5(1), P2-N2-C1 128.4(1), N1-C1-N2 118.4(2), N1-C1-O 120.9(2), N2-C1-O 120.7(2), P1-C2-P2 117.9(1)

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## Experimental

All experiments were conducted with exclusion of air and moisture in sealed systems under dry nitrogen. Solvents were purified

Table 1. Crystallographic data

| Compound | **2** | **4b** (*cis*) | **4b** (*trans*) |
|---|---|---|---|
| Formula | $C_7H_{14}N_4O_2P_2$ | $C_{12}H_{28}N_4OP_2S_2$ | $C_{12}H_{28}N_4OP_2S_2$ |
| $M_r$ | 248.2 | 370.4 | 370.4 |
| Crystal habit | Yellow prism | Colourless prism | Colourless needle |
| Crystal size [mm] | 0.7 × 0.7 × 0.65 | 0.9 × 0.55 × 0.55 | 0.8 × 0.5 × 0.3 |
| Space group | $C2/c$ | $P\bar{1}$ | $P2_12_12_1$ |
| Cell constants: | | | |
| $a$ [pm] | 958.0(3) | 741.0(3) | 1064.5(5) |
| $b$ [pm] | 1211.5(3) | 1016.0(3) | 1191.9(4) |
| $c$ [pm] | 1017.5(3) | 1271.9(3) | 1448.4(6) |
| $\alpha$ [°] | 90 | 75.87(2) | 90 |
| $\beta$ [°] | 106.98(2) | 79.66(3) | 90 |
| $\gamma$ [°] | 90 | 87.98(3) | 90 |
| $V$ [nm$^3$] | 1.1294 | 0.9134 | 1.8378 |
| $Z$ | 4 | 2 | 4 |
| $D_x$ [Mg m$^{-3}$] | 1.459 | 1.347 | 1.339 |
| $F(000)$ | 520 | 396 | 792 |
| $\mu$ [mm$^{-1}$] | 0.36 | 0.46 | 0.47 |
| $2\Theta_{max}$ [°] | 55 | 55 | 55 |
| No. of reflections: | | | |
| measured | 1429 | 5070 | 8410 |
| independent | 1298 | 4231 | 4241 |
| $R_{int}$ | 0.014 | 0.019 | 0.017 |
| observed [$>4\sigma(F)$] | 1059 | 3850 | 3838 |
| $R$ | 0.032 | 0.028 | 0.027 |
| $wR$ | 0.039 | 0.037 | 0.031 |
| $g$ | 0.0002 | 0.0001 | 0.0002 |
| No. of parameters | 75 | 208 | 209 |
| $S$ | 1.8 | 2.5 | 1.2 |
| Max. $\Delta/\sigma$ | 0.014 | 0.002 | 0.001 |
| Max. $\Delta\rho$ [e pm$^{-3}$ · $10^6$] | 0.24 | 0.33 | 0.40 |

and dried according to the usual methods[6,7]. – NMR: Bruker AC 200 ($^1H$ at 200.1 MHz, $^{13}C$ at 50.3 MHz, $^{31}P$ at 81.3 MHz). Reference substances TMS ext. ($^1H$), $CDCl_3$ ($^{13}C$), and 85% $H_3PO_4$ ext. ($^{31}P$). High-field shifts were given negative, low-field shifts positive signs.

*Thermal Decomposition of* **1a** *and* **1b**, *Formation of* **2**: The compounds were prepared in situ by adding a solution of $(Me_2N)(Cl)PCH_2P(Cl)(NMe_2)$ (3.53 g; 15 mmol) or of $(Et_2N)(Cl)PCH_2P(Cl)(NEt_2)$ (4.37 g, 15 mmol) in 30 ml of $CH_2Cl_2$ to *N,N'*-dimethyl-*N,N'*-bis(trimethylsilyl)urea (3.49 g, 15 mmol), as previously described[1]. After the reaction mixture had been stirred at room temp. for 20 min the solvent was removed in vacuo (2 Torr). The remaining liquid product was heated to 150°C (2 Torr) for 15 min. The light yellow solid product thus formed was washed with ether, dried, and recrystallized from $CH_2Cl_2/(C_2H_5)_2O$ to give colourless crystals of **2** (0.34 g, 18%)[2,3]. – $^1H$ NMR ($CDCl_3$): $\delta$ = 2.03 [t, $^2J(PH)$ = 12.6 Hz, $PCH_2P$], 3.14 [d, $^3J(PH)$ = 11.6 Hz, NMe], 3.16 [d, $^3J(PH)$ = 11.6 Hz, NMe]. – $^{13}C$ NMR ($CDCl_3$) $\delta$ = 16.8 [t, $^2J(PC)$ = 11.0 Hz, $PCH_2P$], 38.5 [d, $^2J(PC)$ = 41 Hz, 2 NMe], 39.3 [d, $^2J(PC)$ = 11.0 Hz, 2 NMe], 152.9 [t, $^2J(PC)$ = 10.9 Hz, C=O]. – $^{31}P$ NMR ($CDCl_3$): $\delta$ = 86.9. – $C_7H_{14}N_4O_2P_2$ (248.2): calcd. N 22.58, P 24.96; found N 22.16, P 24.39.

The preparation of **4b** and **4b** was performed as described in ref.[1].

*X-Ray Crystal Structure Determinations* (Table 1): Crystals were mounted on glass fibres with inert oil and were transferred to the cold gas stream of a Siemens P3 diffractometer with a LT-2 low-temperature attachment. Data were collected using monochromated Mo-$K_\alpha$ radiation. Cell constants were refined from setting angles of ca. 50 reflections in the $2\Theta$ range 20–23°. Structures were solved by direct methods and subjected to full-matrix least-squares refinement on $F$ (program system Siemens SHELXTL PLUS). Hydrogen atoms were included using a riding model. For **4b** *trans*, which crystallizes in a non-centrosymmetric space group, an $\eta$ refinement gave an $\eta$ value of $-0.07(13)$, which indicates enantiomeric twinning. Weighting schemes of the form $w^{-1} = \sigma^2(F) + gF^2$ were employed. Complete data have been deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany. Any request for this material should quote a full literature citation and the reference number CSD-58096.

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[1] I. V. Shevchenko, M. V. Furmanova, V. P. Kukhar, R. Schmutzler, *Z. Naturforsch., Teil B*, **1992**, *47*, 258–262.

[2] F. Gol, G. Hasselkuß, P. C. Knüppel, O. Stelzer, *Z. Naturforsch., Teil B*, **1988**, *43*, 31–44.

[3] R. Neidlein, H.-J. Degener, *Arch. Pharm. (Weinheim, Ger.)* **1984**, *317*, 1053–1059.

[4] R. Neidlein, H.-J. Degener, A. Gieren, G. Weber, T. Hübner, *Z. Naturforsch., Teil B*, **1985**, *40*, 1532–1536.

[5] Values for **4b** (*cis*) are given first.

[6] Autorenkollektiv: *Organikum*, reprint of the 15th ed., VEB Deutscher Verlag der Wissenschaften, Berlin, **1977**, p. 783ff.

[7] D. D. Perrin, W. L. F. Armarego, *Purification of Laboratory Chemicals*, 3rd ed., Pergamon Press, Oxford, New York, Beijing, Frankfurt, Sao Paulo, Sydney, Tokyo, Toronto, **1988**.

[8] I. V. Shevchenko, A. Fischer, P. G. Jones, R. Schmutzler, *Chem. Ber.* **1992**, *125*, 1325–1332.

[9] J. F. Klebe, J. B. Busch, Jr., E. Lyons, *J. Am. Chem. Soc.* **1964**, *86*, 4400–4406.

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