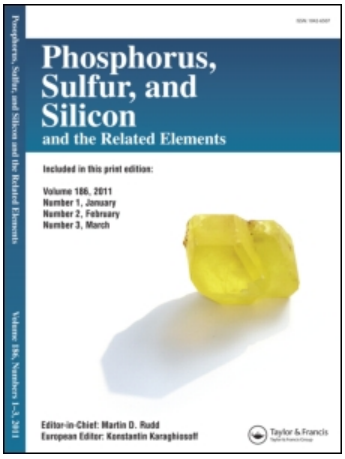

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THE CRYSTAL STRUCTURE AND ABSOLUTE CONFIGURATION OF ( )-O-METHYL-O-(α-NAPHTHYL)-S-METHYL PHOSPHOROTHIOLATE

Marian Mikołajczyk[a]; Piotr Kiełbasinski[a]; Anna Sut[a]; Janina Karolak-wojciechowska[b]; Michał Wieczorek[b]; Yurij T. Struchkov[c]; M. Y. Antipin[c]
[a] Department of Organic Sulphur Compounds, Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, Lodz, Boczna 5, Poland [b] Institute of General Chemistry, Technical University, Lodz, Zwirki 36, Poland [c] Institute of Organoelement Compounds, USSR Academy of Sciences, Moscow, USSR

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THE CRYSTAL STRUCTURE AND ABSOLUTE CONFIGURATION OF (+)-O-METHYL-O-(α-NAPHTHYL)-S-METHYL PHOSPHOROTHIOLATE[1]

MARIAN MIKOŁAJCZYK,* PIOTR KIEŁBASIŃSKI and ANNA SUT

Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, Department of Organic Sulphur Compounds, 90-362 Lodz, Boczna 5, Poland

and

JANINA KAROLAK-WOJCIECHOWSKA and MICHAŁ WIECZOREK

Institute of General Chemistry, Technical University, 90-924 Lodz, Zwirki 36, Poland

and

YURIJ T. STRUCHKOV and M. Y. ANTIPIN

Institute of Organoelement Compounds, USSR Academy of Sciences, 28 Vavilow Street, Moscow 117312, USSR

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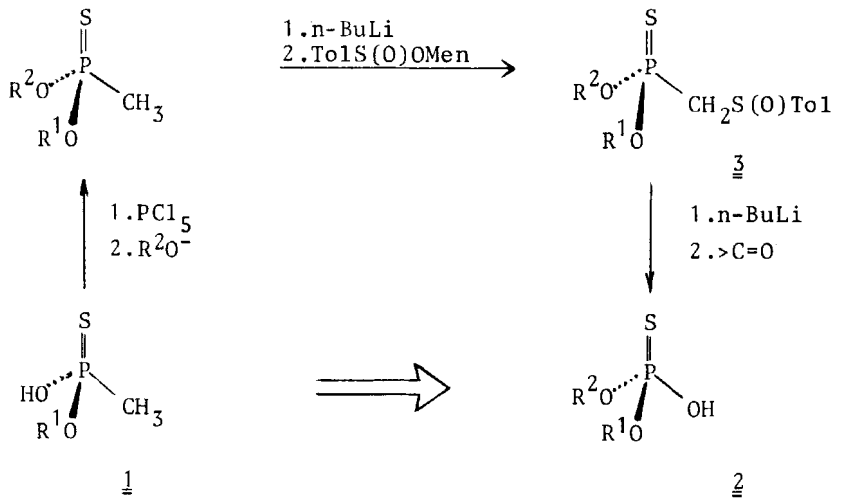
The structure of the title compound was solved by routine direct method and refined to R = 0.047 for 1422 independent reflections. The absolute configuration at phosphorus was found to be R. $C_{12}H_{13}O_3PS$, orthorombic, $P2_12_12_1$, a = 6.967(1), b = 10.600(2), c = 17.656(2) Å, z = 4, V = 1303.90 Å^3, D_c = 1.374 g·cm^{-3}, μ = 3.6 cm^{-1} (MoK_α).

INTRODUCTION

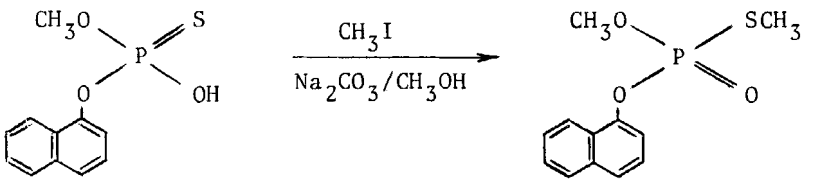
In the course of our studies on chiral thio-acids of phosphorus we developed recently a new method for the stereoselective conversion of chiral O-alkyl methanephosphonothioic acids (**1**) into the corresponding 0,0-dialkyl phosphorothioic acids (**2**).[2] In general, this method involves two principal steps. In the first step, thiophosphonic acids **1** are converted into α-phosphoryl sulfoxides **3** which, in the second step, are transformed into phosphorothioic acids **2** by means of the Horner-Wittig reaction. Scheme I shows the conversion of thioacids **1** into **2**. Since the absolute configuration of the starting phosphonothioic acids **1** as well as the stereochemical course of each reaction involved in the **1** → **2** conversion shown above are well-known,[3] this method makes also it possible to assign the absolute configuration for chiral phosphorothioic acids **2** formed.[4]

* To whom the correspondence should be addressed.



SCHEME 1

In this way we have assigned the R-chirality for (+)-O-methyl-O-(α-naphthyl) phosphorothioic acid **(4)**.



4, $[\alpha]_D = +13.3^{\circ}$

5, $[\alpha]_D = +48.17^{\circ}$ ($CHCl_3$, 0.82)

In view of the fact that this acid, in contrast to other chiral phosphorothioic acids, is easily resolved into its enantiomers[5,6] and that the acid (+)-**4** forms the crystalline (+)-S-methyl ester **5**[7] we decided to carry out the X-ray analysis of the latter compound in order to determine its absolute configuration and to confirm the assignment of the R-chirality for (+)-**4** deduced from chemical correlation.

RESULTS AND DISCUSSION

The structure and chirality of (+)-O-methyl-O-(α-naphthyl)-S-methyl phosphorothiolate **(5)** is shown in Figure 1. As it is seen from Figure 1, (+)-**5** has the absolute configuration R. Since the methylation of (+)-acid-**4** leading to (+)-ester-**5** does not involve any change of configuration at the phosphorus atom, the absolute configuration of (+)-**4** must also be R. This finding confirms the correctness of our assignment to this acid based on the chemical correlation.

The intramolecular bond distances and angles, uncorrected for thermal vibration, are given in Table 1. Bond distances and angles show no significant variation from

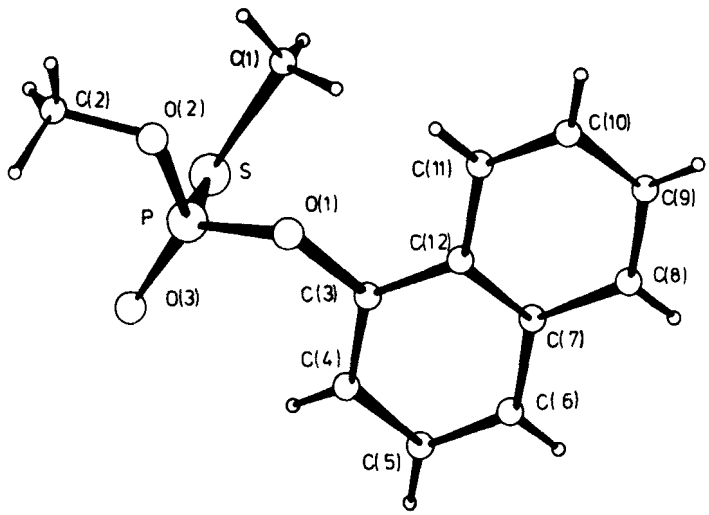


FIGURE 1 The drawing of (+)-O-methyl-O-(α-naphthyl)-S-methyl phosphorothiolate **(5)**.

the expected values. The molecular packing is determined only by van der Waals contacts.

EXPERIMENTAL

The crystal of (+)-**5**, $[\alpha]_D$ + 48.17° ($CHCl_3$, 0,82) in spherical shape (diameter 0.3 mm) was used for the data collection. Preliminary unit cell dimensions and systematic absences were derived from Weissenberg photographs, while accurate cell dimensions were obtained from diffractometer measurements by least squares refinement.

Crystal data: $C_{12}H_{13}O_3PS$, $M_r = 268.25$ a = 6.967(1), b = 10.600(2), c = 17.656(2) Å, $D_m = 1.405$ g·cm^{-3}, $D_c(z = 4) = 1.374$ g·cm^{-3}. Systematic absences: h00 when h is odd, OkO when k is odd and 001 when l is odd establish the space group $P2_12_12_1$.

Intensities were measured on SYNTEX-$P\bar{1}$ diffractometer with graphite-monochromatized Mo-K_α radiation. The θ-2θ scan technique was used. Of the 3158 hkl and $\bar{h}kl$ reflections measured, 2465 were considered as observed with $F \leqslant 3\sigma(F)$. The structure was solved and refined on the basis of 1422 independent reflections.

Structure determination and refinement. Multisolution tangent refinement with the SHELX-76 program[8] located all non-hydrogen atoms. The refinement was carried out by a full-matrix least-squares procedure. All H-atoms were located from different syntheses calculated during the anisotropic refinement of the non-hydrogen atoms. The positional parameters of the H-atoms were refined, while their isotropic temperature factors were kept as for their parent-carbon atoms. The weighting scheme employed was $w = 3.16/|\sigma^2(F) + 0.0002F^2|$, where the $\sigma(F)$ is the standard derivation of the observed amplitudes based on counting statistics. The final $R_w = \Sigma w^{1/2}||F_o| - |F_c||/\Sigma w^{1/2}|F_o|$ was 0.0422 with a conventional R of 0.0472. A conclusive difference map showed peaks $<0.28eA^{-3}$. The atomic fractional coordinates are given in Table 2 and 3. Anisotropic temperature factors for non-H-atoms are in Table 4. The atomic scattering factors were those of the SHELX system. All computation were performed on an ODRA 1305 computer.

The absolute configuration. In order to establish the absolute configuration of (+)-**5** the coordinates and anisotropic temperature factors were refined by least squares methods for both models (x, y, z) and

the enantiomer ($\bar{x}$, $\bar{y}$, $\bar{z}$) with the proper inclusion of anomalous scattering contribution for P and S atoms.

Final discrepancy indices $Rg = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$ are 0.0464 for model (x, y, z) and 0.0469 for model ($\bar{x}$, $\bar{y}$, $\bar{z}$). On the basis of Hamilton's $\mathcal{R}$-factor ratio,[9] model (x, y, z) has a probability of being correct at a significance level lower than 0.005 (99.5% probability).

The result was further confirmed when the method of Bijvoet, Peerdeman and Bommel was applied.[10] On the basis of the pairs (hkl-$\bar{h}$kl) of reflections there have been chosen 28 Bijvoet pairs showing a pronounced anomalous dispersion effect according the following criteria:[11]

$$|\Delta F_c| > 2\sigma(\Delta F_o)$$
$$|\Delta F_c| > [F_c(h) + F_c(-h)]/400$$

where

$$\Delta F_o = F_o(h) - F_o(-h)$$
$$\Delta F_c = F_c(h) - F_c(-h)$$
$$\sigma(\Delta F_o) = \{[\sigma(F_o(h))]^2 + [0.001F_c(h)]^2 + [\sigma(F_o(-h))]^2 + [0.001F_c(-h)]^2\}^{1/2}$$

Using the observed and calculated structure factors differences (ΔF_o and ΔF_c) (Table 5) the Bijvoet coefficient B and their e.s.d.'s $\delta(B)$ have been calculated.

$$B = \Sigma\Delta F_c\Delta F_o/\Sigma|\Delta F_c\Delta F_o|$$
$$\sigma(B) = (1 - |B|)[\Sigma(\Delta F_c\sigma(\Delta F_o))^2]^{1/2}/\Delta F_c\Delta F_o$$

The value of B = 0.98 with $\sigma(B) = 0.001$ indicated that the right enantiomer was chosen initially.

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Note: The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

The following data are deposited: Bond lengths (A) and their e.s.d.'s (Table 1); Bond angles (°) and their e.s.d.'s. Final atomic parameters ($\times 10^4$) and their e.s.d.'s for non-hydrogen atoms (Table 2). Atomic coordinates, isotropic temperature factors for the H-atoms with e.s.d.'s ($\times 10^3$) (Table 3). Anisotropic temperature factors ($A^2 \times 10^3$) in the form $\exp|-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2}2U_{23}klb^*c^* + 2U_{13}lhc^*a^* + 2U_{12}hka^*b^*)|$ (Table 4). The calculated and observed structure factors differences of reflection showing the accentuated effect of anomalous dispersion (Table 5). Observed and calculated structure factors for $C_{12}H_{13}O_3PS$.