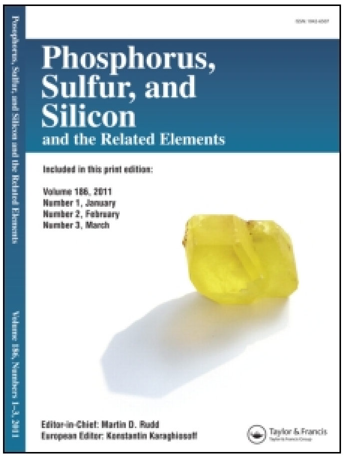

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New Type of Molecular Propellers with Acyclic Blades Stabilised by Phosphorus Atropoisomerism

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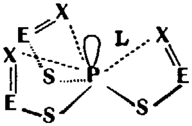
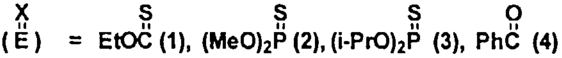
Here we report on a new type of chiral molecular propellers - trianhydrides of trithiophosphorous acid and organic thioacids.





$$(\overset{\overset{X}{\|}}{E}) = \mathrm{EtO}\overset{\overset{S}{\|}}{C}\ (1),\ (\mathrm{MeO})_2\overset{\overset{S}{\|}}{P}\ (2),\ (i\text{-PrO})_2\overset{\overset{S}{\|}}{P}\ (3),\ \mathrm{Ph}\overset{\overset{O}{\|}}{C}\ (4)$$

The detailed analysis of our previously obtained X-ray data[1-3] reveals that all three planar P-S-E=X fragments of these molecules are twisted around the P-S bonds by equal angles, i.e. all three dihedral angles (*lp*)-P-S-E (*lp* - phosphorus lone pair) are equal in sign and value. Thus, the molecules 1-4 adopt in crystals the form of a propeller with three identical blades, the phosphorus atom lying on the C_3 rotational axis.

Molecular propellers being an interesting class of molecular structures are nevertheless poorly explored. Molecules of this type have a central rotation axis C_n with n planar fragments twisted about their local axes by equal angles like the blades of a propeller. In the really existing organic molecular propellers the rigid aromatic fragments usually fulfil the role of blades [4-6]. The general stability of individual configuration in this molecules is provided by high barriers to internal rotation. The compounds **1-4** represent the scare if not the first example of molecular propellers with acyclic nonaromatic fragments as the propeller blades.

Propeller is a chiral system for which both left and right screws are possible, thus the blades can be twisted clockwise or counterclockwise with equal probability. So, two identical conformations about the P-S bonds can be realised in the compounds **1-4**: *ggg* or *-g-g-g* being mirror images of each other (Figure 1).

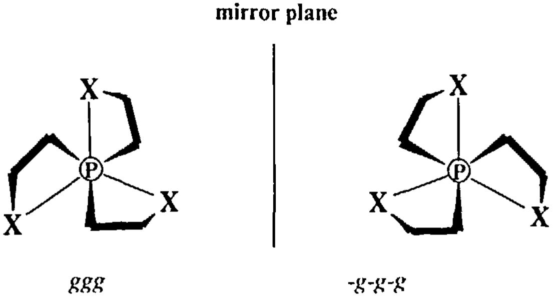
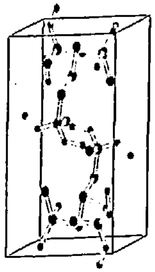


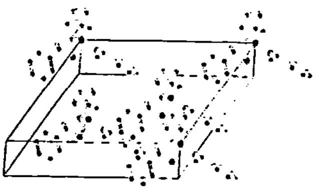
Figure 1. The enantiomeric relation of possible conformations of molecules (1-4)

As a rule, asymmetric organic molecules are crystallised as racemate with crystal unit cells containing both antipodes, compensating the asymmetry of each other. According to our X-ray data the compounds **1-3** are crystallised exactly in this way. For example, the compound **2** is crystallised in P1 centrosymmetric group with left and right propellers being related by the inversion operation (Figure 2a). The compound **4** is crystallised in R3 group containing three molecules in a unit cell with planar P-S-C(=O)Ph fragments twisted in the same direction in all the molecules (Figure 2b). This means that the crystals **4** contain the pure enantiomer. To best of our knowledge no mention has been made in literature prior to this communication of the isolation of spatial isomers resulting from hindered internal rotation around phosphorus bonds, although most of types of stereoisomerism are known in phosphorus chemistry.

a)



b)



It should be noted that molecules **1-4** possess the conformational rigidity and reveal the short 1,4-contact between the phosphorus (III) atom and the terminal heteroatom X, the P...X distance (L) being shorter than the sum of the van-der-Waals radii by 0.6-0.9 A. Possible reasons of such contacts are discussed by us elsewhere [1-3]. There are some grounds for believing that the molecules of this type hold their shape in going from crystal to solutions.[7] Hence, the enantiomerism of the compound **4** could possibly be observed by polarimetry methods provided that the two enantiomeric crystals were dissolved separately. Unfortunately, we did not succeed in separating mechanically two enantiomers of compound **4** in sufficient quantity.

In closing we would like to emphasise that (i) all the reported results are intimately connected with the phenomenon of phosphorus-centrical atropoisomerism; (ii) trianhydrides of trithiophosphorous acid and organic thioacids **1-4** belong to a class of organic molecular propellers, but differ from other known propellers by acyclic fragments constituting the blades; (iii) compound **4** is crystallised as a mixture of two types of crystals, each one consisting of pure enantiomers.

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