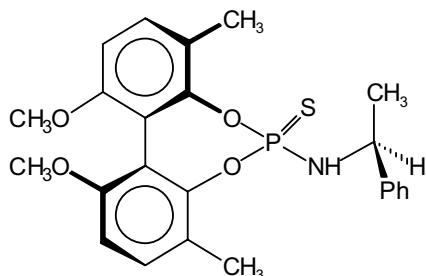


[o.m12.p7] Structure and stability of a bridged biphenyl: an X-ray and theoretical study. A. Forni, G. Casalone, CNR – Centro per lo Studio delle Relazioni tra Struttura e Reattività Chimica, via Golgi 19, I-20133 Milano, Italy.
Keywords: ortho-substituted biphenyl; conformation; transition state.

Structure of an axially chiral biphenyl, (*S,M*)-dibenzo[*d*,*f*][1,3,2]dioxaphosphin-6-amine-1,11-dimethoxy-4,8-dimethyl-*N*-(1-phenylethyl)-6-sulfide¹



was determined by X-ray diffractometry and by theoretical (semiempirical AM1 and ab-initio RHF) calculations in the gas phase. A relevant feature of the ortho-substituted biphenyls is the extent of molecular distortion around the inter-ring bond, which can be quantified through the interplanar dihedral angle. If the distortion of non-bridged biphenyls is mainly due to overcrowding between the ortho substituents, in the presence of a single or double bridge between the ortho positions, the interplanar dihedral angle is considerably influenced by the nature of the bridge(s).

In the solid state, crystal-packing forces may also contribute to the molecular distortion. In both ortho unsubstituted² and substituted³ biphenyls with no bridges, intermolecular interactions play generally a substantial role in determining the geometry of the molecule. In the title compound, the value of the interplanar dihedral angle, 49.93(9)°, was reproduced within a few degrees at all levels of theory, indicating a weak influence of the lattice forces on the biphenyl distortion.

The stability of the title compound was analyzed at theoretical level by calculating the torsional potential around the inter-ring bond and by locating the transition state for the isomerization process. A relatively low rotation barrier of 23.3 kcal/mol was obtained.

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[o.m12.p8] Steric and Electronic studies of Palladium bis-Phosphine Catalysts. P.A. Champkin, M.R.J. Elsegood, W. Clegg, Dept. of Chemistry, Bedson Building, University of Newcastle Upon Tyne, Newcastle Upon Tyne, NE1 7RU. U.K.

Keywords: catalysis, charge density, synchrotron.

The production of catalytic compounds is a huge area worked on by many of today's synthetic chemists. Of these catalytic compounds there is a great deal of interest within the area of Homogeneous catalysis. These catalysts are of great importance in Industry, as the chosen compounds' efficiency may prove to be the success of a given chemical process.

Many Homogenous catalysts incorporate a Transition metal centre and of these a number contain bridging organic backbone ligands. Here we find that bridging di-phosphine ligands are a good choice, as by altering the organic backbone as well as the groups on phosphorus we can alter the steric and electronic properties of the ligand. We are working on Palladium based chelating bis-phosphines that give polyketone or methylpropionate, depending on subtle changes in the R groups on phosphorus or changes in the organic backbone. I hope to be able to present steric and electronic analyses on a number of these compounds, with the aim of pointing out trends in catalytic efficiency.

The steric analyses will be derived from observations I have made after collecting data sets on many of these compounds here in Newcastle on our SMART, along with data freely available on the Cambridge Structural Database (CSD).

The electronic aspect of the analyses will be from that of a number of Charge Density data sets also collected on the SMART and using XD for multipole charge density refinement. I also hope to be able to present some of the first 2nd row Transition metal compounds studied using a new extended version of XD, these datasets will have been collected at the Synchrotron source in Daresbury.