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Analytical algorithms for ligand cone angles calculations. Application to triphenylphosphine palladium complexes

Algorithmes analytiques pour le calcul des angles coniques de ligands. Application à des complexes palladium triphénylphosphine

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ABSTRACT

We defined the smallest enclosing cone angle as the Tolman cone angle for null atomic spheres radii. Then we provide a simple analytical algorithm to compute the smallest enclosing cone at fixed apex, which works in the case of unsymmetrical ligand. We applied it to compute ligand cones for a family of triphenylphosphine palladium complexes, and we showed that both the angle of the cone and its resulting solid angle strongly correlate with the Tolman cone angle, thus suggesting that there is no more need for atomic radii. We also defined the best cone of fixed apex fitting a population of unit vectors. We proposed a simple analytical algorithm to compute it, which is proved to work in any *d*-dimensional Euclidean space. We defined the conicity index κ to evaluate quantitavely the pertinence of the best fitting cone. We used this best fit cone to define a mean ligand cone, and thus a mean cone angle and a mean cone axis. We applied it to our family of triphenylphosphine palladium complexes and we observed that the axis of the individual cones deviated from the mean cone axis by at most 13.2°. The observed conicity index was small ($\kappa = 0.0177$), indicating a very good fit for the whole family of complexes.

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RÉSUMÉ

Nous définissons l'angle du plus petit cône englobant comme étant l'angle conique de Tolman à rayons atomiques nuls. Puis, nous fournissons un algorithme analytique simple de calcul du plus petit cône englobant à apex fixé, qui fonctionne dans le cas des ligands non symétriques. Nous l'appliquons aux cônes de ligands pour une famille de complexes palladium triphenylphosphine et nous montrons qu'à la fois l'angle du cône et l'angle solide qui en résulte sont fortement corrélés avec l'angle conique de Tolman, suggérant ainsi qu'il n'y a plus besoin des rayons atomiques. Nous définissons aussi le meilleur cône moyen d'apex fixé pour une population de vecteurs unitaires. Nous proposons un algorithme analytique simple pour le calculer, que nous prouvons être valide dans tout espace euclidien *d*-dimensionnel. Nous définissons l'indice de conicité κ pour évaluer quantitativement la pertinence du meilleur cône. Nous utilisons ce meilleur cône pour définir un cône moyen de ligand, et donc un angle moyen de cône et un axe moyen de cône. Nous l'appliquons à notre famille de complexes palladium triphenylphosphine et nous

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observons que les axes individuels des cônes dévient de l'axe moyen de cône d'au plus 13,2°. L'indice de conicité observé est faible $(\kappa = 0,0177)$, indiquant un très bon ajustement à l'ensemble de la famille de complexes.

1. Introduction

Ligand cone angles were introduced by Tolman to measure the size of phosphine derivatives and other phosphorus ligands [1]. This size is the solid angle defined by the smallest angle cone having its apex lying at 2.28 Å from the phosphorus atom and circumscribing the ligand atoms, usually modelled by spheres. The solid angle, expressed in steradians, is $\theta = 2\pi(1 - \cos\alpha)$, where α is the angle between the generatrix of the cone and its axis (see general definitions in Section 3.1). In the case of symmetric ligands PR$_3$, the Tolman cone angle is easy to compute because its axis is in the direction of the mean of the three vectors defined by the P–R bonds. Then, given the radius of the spherical ligands, α is retrieved by elementary geometry calculus. This approach has to be refined for unsymmetrical ligands such as MPR$_1$R$_2$R$_3$ and more generally for MXR$_1$R$_2$R$_3$, where M = H or is a metal atom, and X = P, N, CH, or is any atom having a tetrahedral hybridisation such as sp^3 or sd^3. It was pointed out that even symmetrically substituted bulky phosphines may offer unsymmetrical conformations [2]. The difficulty of the calculation arises (i) when the spheres radii are unequal, and (ii) when the X–R$_i$ bonds are not symmetrically arranged around the M–X axis. Tolman approximated θ as $(\hat{\theta}_1 + \hat{\theta}_2 + \hat{\theta}_3)/3$, where $\hat{\theta}_i$ is the acute angle between the directions of the X–R$_i$ bond and of the M–X bond [3,4]. This method was criticized because the obtained values may not reflect the properties of the ligand, particularly when the substituent groups differ greatly [5]. It seems that few geometric tools are available to measure steric effects in organometallic chemistry, and that could explain why ligand cone angles were much used in this field [6–9], Recently, Bilbrey et al. [10–12] proposed an analytic solution to the ligand cone angle calculation.

It was also proposed to measure the steric size of ligands and substituents by the solid angle generated by the union of the atomic spheres [13], rather than the one generated by their enclosing cone. This approach gives rise to an analytical calculation of the solid angle, provided that the intersections of more than two spheres could be neglected [13]. There is a non-linear relationship between the cone angle and the solid angle, which was measured quantitavely [14]. To evaluate the importance of sphere overlaps, an exact analytical calculation of sphere intersections was done with the ASV freeware [15] using the atomic radii recommended by Gavezzotti [16], and showed that intersections between 6 or 7 atoms are commonly observed in organic molecules [15,18]. These atomic radii are sometimes slightly larger than those given by Bondi [17], but it is recalled that an increase in the sphere radii does not guarantee an increase of the van der Waals surfaces. Running ASV on a database of 70 diverse ligands showed that neglecting the intersections of more than two atoms induced a mean error on van der Waals surface calculations of 249%, and that neglecting the intersections of more than three atoms led to a mean error of 87%, and neglecting the ones of more than four atoms led to a mean error to 16%, the maximal observed error in this case being 37% [18]. Despite that van der Waals surfaces are not used in ligand solid angles calculations, these numbers show the importance of atomic spheres overlaps.

An improved ligand solid angle algorithm was proposed, which takes into account spheres intersections of orders 3 and 4 [19], but it needs a complex numerical integration. Recently, Bilbrey et al. [12,20] proposed an analytic solution to the solid angle calculation, based on the decomposition of the solid angle contributions between those due to spherical polygon parts and those due to the resulting truncated spherical sectors parts. This algorithm, implemented by the authors in their Mathematica FindSolidAngle package, is effective for the simple geometrical arrangements expected to be encountered in chemistry. However, it is not specified how it works in general. E.g., the detection of potential multiple connected components got by projection at the surface of the unit sphere is not evoked, the solid angle subtended by an internal spherical polygon may be not void and may even be not unique, etc. The detection and the management of such situations let the algorithm rather difficult to implement.

The impact of conformational variations was evoked early [21], leading to use weighted average cone angles [22], while it was considered that this problem was overcome by the use of the solid angle methodology [23]. At the same time, Müller and Mingos noticed also that the Tolman cone angle definition does not take into account the variations due to conformational changes [24,25], and they used the atomic centers of the ligand atoms rather than their van der Waals spheres. Then they applied their algorithm to perform statistics on thousands of phosphine structures found in the Cambridge Crystallographic Data Base [26], and observed a variation in cone angles for specific ligands, which is much larger than had previously been suspected.

This slight change in the ligand cone angle calculation, that we retain here (see Fig. 1) offers two other major advantages: (i) the cone angle can be generalized to complex polyatomic ligands R$_i$ via the calculation of the fixed apex minimal cone enclosing any desired number of atoms, and (ii) this calculation can be done analytically, as shown in Section 3 of the present paper. We emphasize that this generalization allows us to model molecular shapes and structural fragments with cones although it is usual to work with spherical models. Despite that is easy to compute spherical shapes, the spherical model was shown