Journal of Organometallic Chemistry, *478* (1994) 205–211

Solid angles I *. The radial profile

David White [a], B. Craig Tavener [a], Peter G.L. Leach [b] and Neil J. Coville [a]

[a] *Department of Chemistry, University of the Witwatersrand, Johannesburg, PO Wits 2050 (South Africa)*
[b] *Department of Mathematics and Applied Mathematics, University of Natal, King George V Avenue, Durban 4001 (South Africa)*

(Received February 9, 1994)

Abstract

The use of solid angles (Ω) has been extended to the calculation of the solid angle of a region of an atom or groups of atoms (*e.g.* ligands) as a function of distance from a common apex (*e.g.* a metal). This methodology permits the evaluation of a second dimension when describing the 'size' of a molecule as measured by cone or solid angles. This new measure is referred to as a radial profile. Radial profiles for some common ligands (*e.g.* 2,6-$Me_2C_6H_3NC$, ^tBuNC, $P(OMe)_3$, PPh_3 etc.) have been determined. A comparison of two radial profiles, corresponding to two ligands, permits a qualitative evaluation of the position of steric interaction between the two ligands.

Key words: Solid angles; Cone angles; Ligand size; Radial profile; Steric measurement

1. Introduction

Steric factors play an important role in determining the course of chemical reactions. The quantification of the steric factor is however a non-trivial problem and many attempts have been made to derive a general methodology for associating a steric size with an atom, group or ligand [1]. For example, the size of a ligand can be associated with a molecular volume [2] or a reactivity derived from chemical reactions [3], molecular mechanics calculations [4] or a cone [5] or solid angle [6] calculation. The various approaches have advantages and disadvantages associated with them, and their use is dependent on the problem to which they are assigned.

Recently we [7] and others [8] have explored the possibility of using the solid angle (Ω) as a measure of steric size for ligands and organic fragments. The solid angle is defined as the integral of the scalar product of the vector r with a vector element of surface divided by the cube of the magnitude of r

$$\Omega = \int_s \frac{r \cdot ds}{r^3}$$

More simply the solid angle is a measure of the "shadow" cast by an atom or group of atoms when placed relative to an apex atom, "a light source". For example if a metal atom is regarded as the apex then a

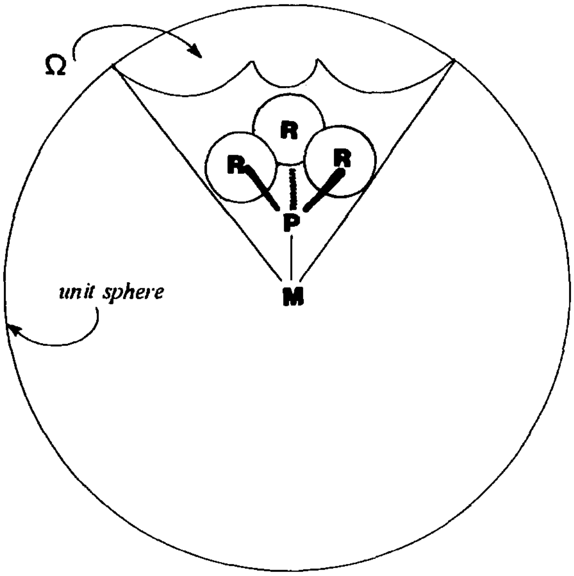

Fig. 1. Measurement of the solid angle (Ω) for a PR_3 ligand bonded to a metal, M. The solid angle corresponds to the "shadow" projected onto the inside of a unit sphere centred on the metal as apex.

Correspondence to: Professor N.J. Coville.
* For Part I, see ref. 7.

0022-328X/94/$7.00
SSDI 0022-328X(94)24628-V

PR_3 ligand attached to the metal will generate a solid angle, Ω, as depicted in Fig. 1. As can be appreciated the circumference of the shadow is irregular and reflects the actual shape of the ligand at its widest points. Numerical [8] and analytical [7] methodologies have recently become available which permit quantification of the 'shadow' area and hence of the steric size of the atom.

The solid angle, Ω, bears some resemblance to the well known Tolman cone angle, θ, [5] (*e.g.* as shown in Fig. 2(a) for a PR_3 ligand) especially when presented in the form of a ligand profile (angular profile) [9]. The ligand profile is a measure of the size of a group of atoms as a function of rotation about the axis between the apex (typically a metal) and the group of atoms (the ligand) (Fig. 2(b)). Thus the "cone" follows the contours of the group of atoms. The ligand profile can be represented in either cartesian [10] (Fig. 2(c)) or polar co-ordinates [11] (Fig. 2(d)). When represented in polar co-ordinates the difference between the steric size as measured by the ligand profile and the Tolman cone angle can readily be appreciated (Fig. 3). Presently, however, no methodology has been developed for quantifying the area encompassed by the ligand profile (*i.e.* the ligand size) using this approach. An equivalent measurement can be made using solid angles.

A shortcoming of the present approach is that it gives no indication of the radial distribution of the solid angle *i.e.* the variation of solid angle of an atom or group of atoms as a function of distance from an apex (*e.g.* a metal atom). Herein, we provide a procedure for determining the variation of the solid angle with distance from the apex. This variation of solid angle size with distance we refer to as a radial profile.

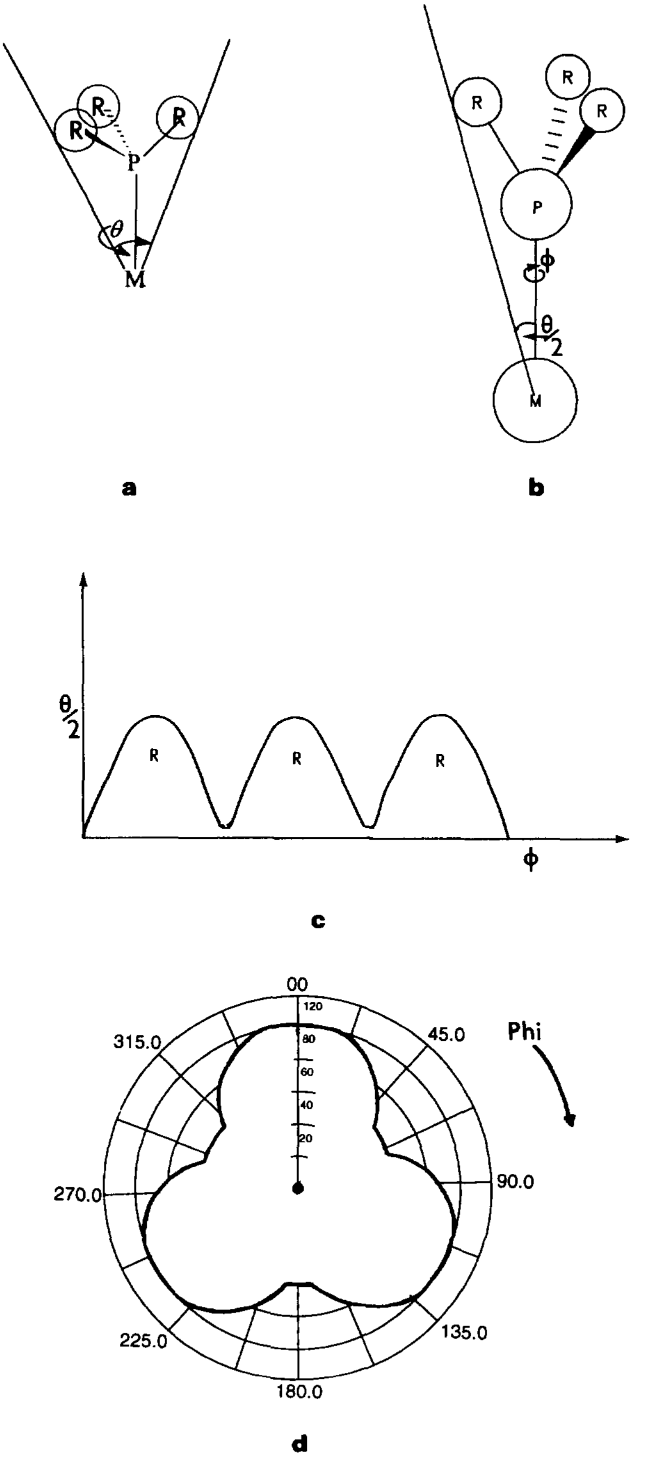

Fig. 2. (a) Measurement of Tolman Cone Angle (θ) for a PR_3 ligand; (b) measurement of a ligand profile for a PR_3 ligand attached to a metal, M. The half cone angle ($\theta/2$ is measured as a function of ϕ; (c) representation of the ligand profile in cartesian coordinates; (d) representation of the ligand profile in polar coordinates.

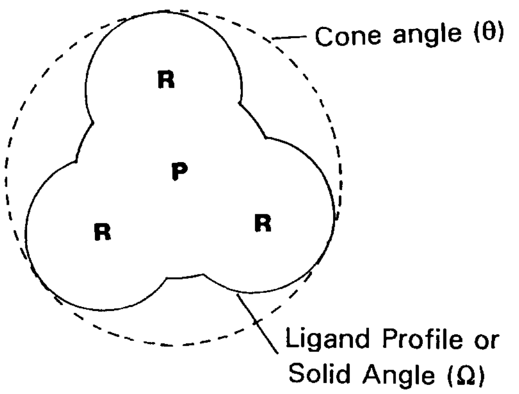

Fig. 3. A comparison of the cone angle (θ) and the ligand profile and solid angle (Ω) for a PR_3 ligand. The PR_3 ligand is viewed down the $M\text{-}PR_3$ axis.

2. Results and discussion

2.1. Radial profile measurement

The algorithm generated for calculating solid angles has been modified to permit calculation of a solid angle on an intersecting sphere at any distance from an apex. In this modification the solid angle measured is the "shadow" produced only by intersection of the atoms with the sphere at which the calculation is made.

Thus by using a range of spheres of different radii radiating out from an apex, a range of solid angles can be measured. Alternatively phrased, if a sphere of variable radius, r, is permitted to grow from the apex to beyond the atom(s) under consideration then solid angles can be measured at each radius. Let us consider a single atom placed a distance d from an apex (*e.g.* a metal atom). A sphere is allowed to grow outwards from the apex with radius $r_1, r_2, \ldots r_n$ (Fig. 4(a)). A sphere of radius r_f is the first radius to intersect the atom and a sphere of radius r_n is the final radius to intersect the atom. As the radius r increases from r_f to r_{max} the solid angle will increase; thereafter it will decrease until at r_n, $\Omega = 0$. The variation of Ω with distance as determined by the algorithm is shown graphically in Fig. 4(b).

The size of the intersection as a function of distance is also influenced by the distance of the atom from the apex. This dependence of Ω on distance ($\propto 1/d^2$) is related to the definition of the solid angle (see above). For example if an atom-apex distance is varied from d_1 to d_4 then the corresponding radial profile changes as shown in Fig. 5 (atom size is left constant).

Further examples to highlight the radial profile methodology are considered below.

(i) Two non-intersecting (identical) atoms (Fig. 6). Four cases are considered. In these four cases two atoms are shown relative to an apex in such a way that one atom remains at a constant distance from the apex, while the other atom is situated at a variable distance from the apex. Not unexpectedly, both the size and the shape of Ω varies in the four different cases. Figure 6(d) also highlights the effect of the distance of the atom from the apex on the measurement of Ω.

(ii) Two intersecting (identical) atoms. The result will be similar to the cases shown in Figs. 6(a)–6(d) but with the solid angles reflecting the overlap. Thus at each radius the solid angle will be calculated and the area of overlap taken into consideration [7].

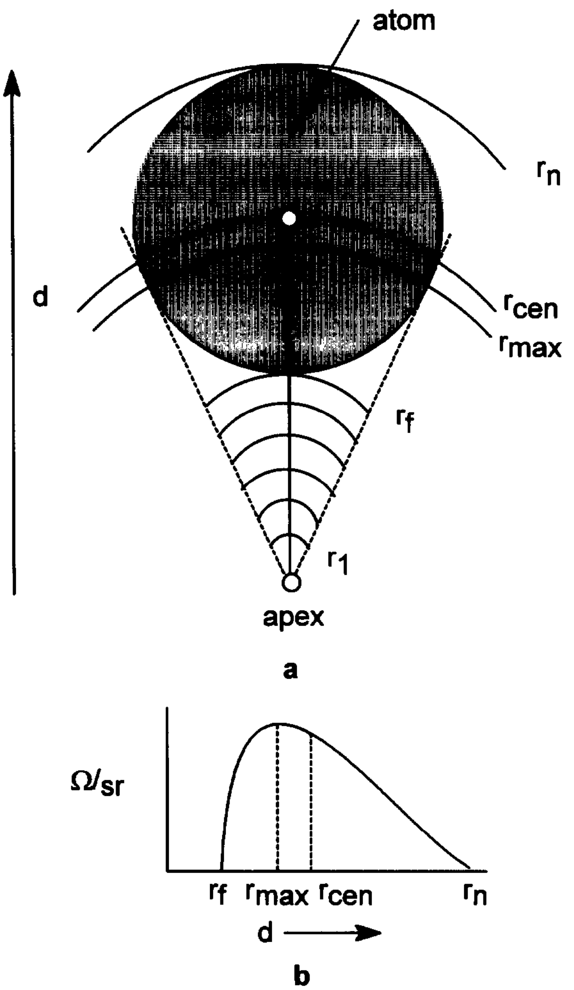

Fig. 4. (a) An atom (shaded) is placed a distance d from an apex. Spheres or radius r to r_n are then constructed from the apex; r_f corresponds to the radius of a sphere which first intersects the atom and r_n the radius of a sphere touching the outermost point of the atom. (b) The variation of Ω with d as determined by using the solid angle algorithm.

(iii) The many atom problem: intersecting and non-intersecting atoms with identical and different size atoms. These cases which are found in chemical structures (*e.g.* ligands or organic groups attached to metals) are readily dealt with by extension of the cases discussed above. An example, the measurement of the solid angle of a CH_3 group attached to a metal atom is described below. Three cases are encountered in determining Ω for CH_3 as a function of distance from a metal centre (Fig. 7(a)): the sphere intersects only one atom of the ligand (*e.g.* C); the sphere intersects two (or more) atoms which are overlapping; and the sphere intersects two (or more) non-overlapping atoms of the ligand (*e.g.* the three H atoms). If the sphere intersects more than two overlapping atoms, then these atoms are traversed in a pairwise manner, identical to the method used for the calculation of the total solid angle [7]. The radial profile for the methyl group is shown in Fig. 7(b).

The radial profiles for some commonly encountered ligands used in organometallic chemistry which were generated using the algorithm are shown in Fig. 8. In these examples a common M–P distance of 2.28 Å and

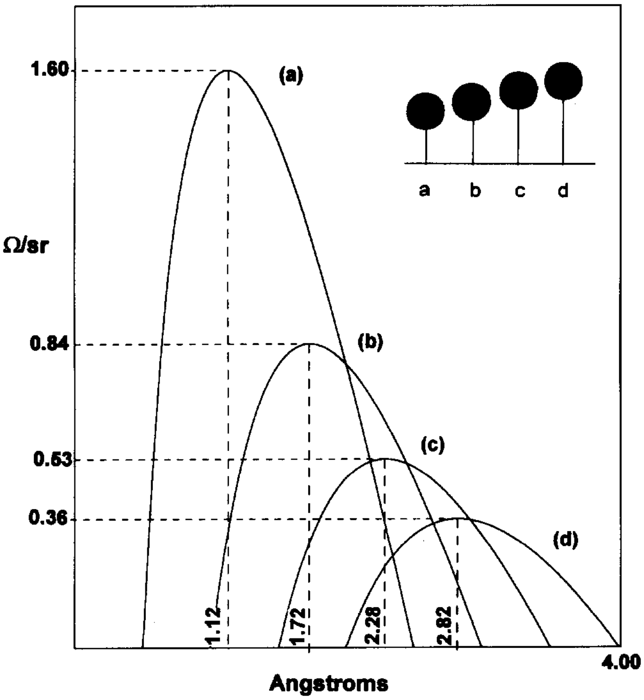

Fig. 5. Atom, radius 1.0 Å, placed at four different distances from an apex: (a) $d_1 = 1.5$ Å; (b) $d_2 = 2.0$ Å; (c) $d_3 = 2.5$ Å; (d) $d_4 = 3.0$ Å. Radial profiles for the four cases are shown.

a M–C(NR) distance of 1.80 Å have been chosen. The figures indicate the complex shapes of the ligands as a function of distance from the apex as well as the space (length, width) occupied by the ligand.

Some points to note from the data shown in Fig. 8 are given below.

(i) The radial profiles for the 2,6-$Me_2C_6H_3NC$-(xylNC) and ^tBuNC ligands do not differ dramatically from each other (Figs. 8(a) and 8(b)). The figures do reflect that the ^tBuNC ligand is wider than the xylNC ligand but that the latter extends out further in space from the apex. Since xylNC is a flat molecule two θ values are needed to describe its size whereas for Ω only one value is needed.

(ii) Figures 8(c) and 8(d) compare the radial profiles for two phosphite ligands. Here again the figures reflect the intuitive ligand sizes that would be expected with the P(O-*o*-tol)$_3$ ligand appearing larger and longer than the $P(OMe)_3$ ligand.

(iii) Figures 8(f), (g) and (h) correspond to PPh_3, P(*m*-tol)$_3$ and P(*p*-tol)$_3$ respectively. The radial profiles accurately reflect that the total solid angles are identical for all three ligands [1]. However, whereas the ligands are all equivalent at their widest point ($\Omega = 1.83$ at $d = 3.61$ Å) the difference is the ligands become noticeable at distances further from the metal corresponding to the meta and para ring positions.

(iv) Fig. 8(i) shows the radial profile of $P(CH_2C_6H_5)_3$, a bulky ligand which extends far out in space. Again the radial profile reflects this information.

(v) The ligand profiles for PMe_2Ph (Fig. 8(e)) and PPh_3 (Fig. 8(f)) indicates the radical effect that modification of ligand substituents can have on the radial profile.

Care is required in the use of radial profiles since the profiles represent a ligand size relative to an apex (metal). If the metal–ligand distance is increased, the absolute value for Ω will decrease but the general shape will remain near constant. It should also be noted that the total solid angle and the largest solid angle measured by the radial profile methodology do not necessarily have to be the same. This is highlighted by the date for the PPh_3 and PMe_2Ph ligands. Here Ω for $PMe_2Ph = 3.44$ and PPh_3 3.59 [1] while Ω max (radial profile) for $PMe_2Ph = 2.77$ and $PPh_3 = 1.83$ (Fig. 8). This difference arises from the way in which solid angles are measured — if there is a space between two atoms this space does not get incorporated in the measurement of the ligand width by the solid angle procedure.

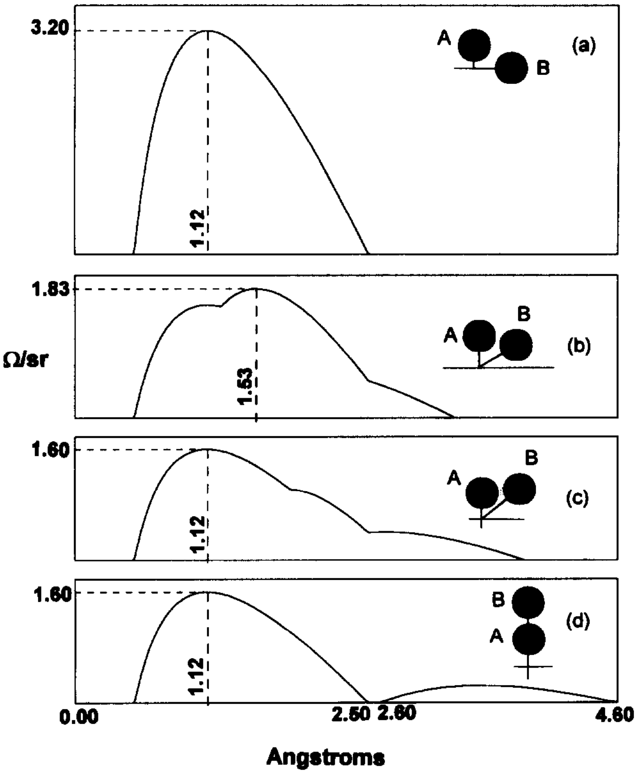

Fig. 6. Four possible orientations of two touching spheres relative to an apex. (Atom radii 1.0 Å and Atom A always 1.5 Å from apex; Atom B at variable distance from apex: (a) = 1.5 Å; (b) = 2.2 Å; (c) 2.8 Å; (d) 3.6 Å.

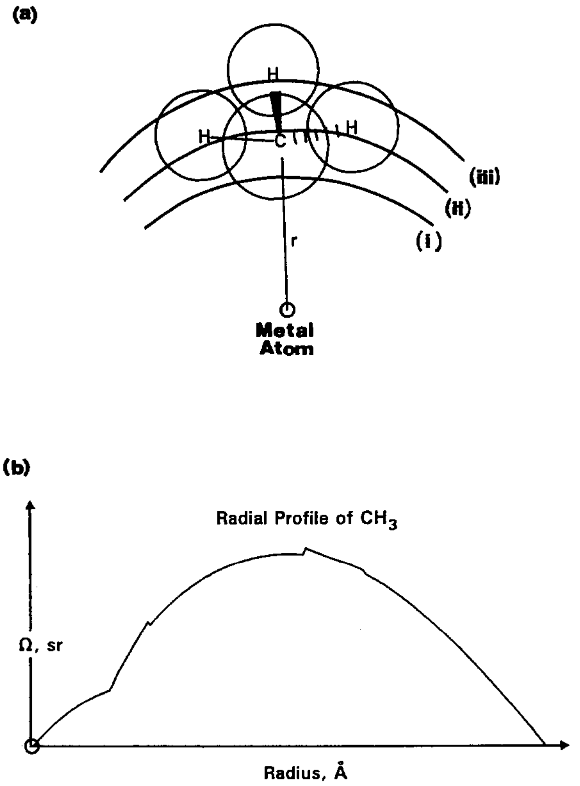

Fig. 7. (a) Measurement of the radial profile of a CH_3 group attached to a metal atom. (b) Radial profile for the methyl group.

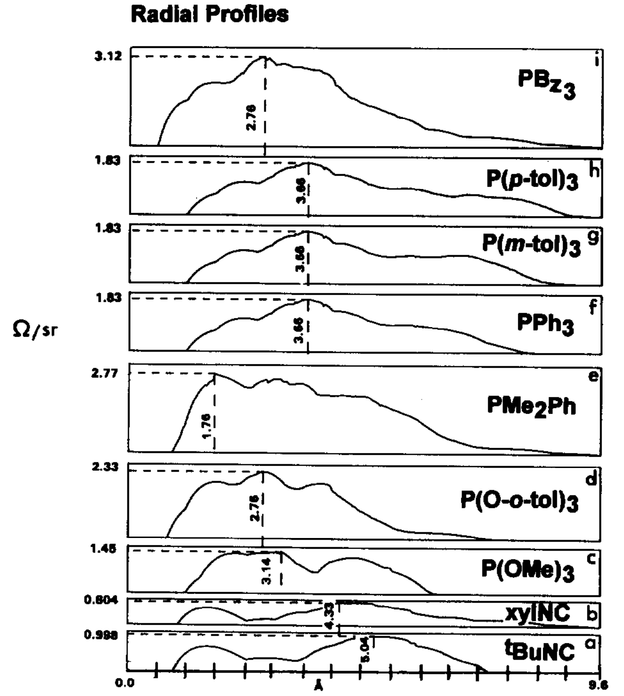

Fig. 8. Radial profiles for (a) ^tBuNC; (b) xylNC; (c) $P(OMe)_3$; (d) $P(O\text{-}o\text{-}tol)_3$; (e) PMe_2Ph; (f) PPh_3; (g) $P(m\text{-}tol)_3$; (h) $P(p\text{-}tol)_3$; (i) $P(CH_2C_6H_5)_3$.

2.2. The problem of two atoms attached to a common apex

To be of use to chemists the radial profile should provide information on the way in which two neighbouring atoms (or ligands) interact.

Let us consider the example of two identical non-overlapping atoms attached to an atom centred at the apex. Two extreme cases can be considered, as shown in Fig. 9. In both cases the radial profile is identical. This is consistent with solid angles being additive i.e. $\Omega_{AA} = \Omega_A + \Omega_A$ [7]. Thus no information is available on the relative positioning of atoms in space, provided they do not overlap. However when two radial profiles are compared, the potential regions of overlap can be ascertained. An example showing two methyl groups bound to a common apex (a metal atom) is shown in Fig. 10(a). When the radial profiles are superimposed, as shown in Fig. 10(b), the region of likely overlap, X, can readily be detected. It must also be remembered that if the atoms in a ligand are not tightly packed

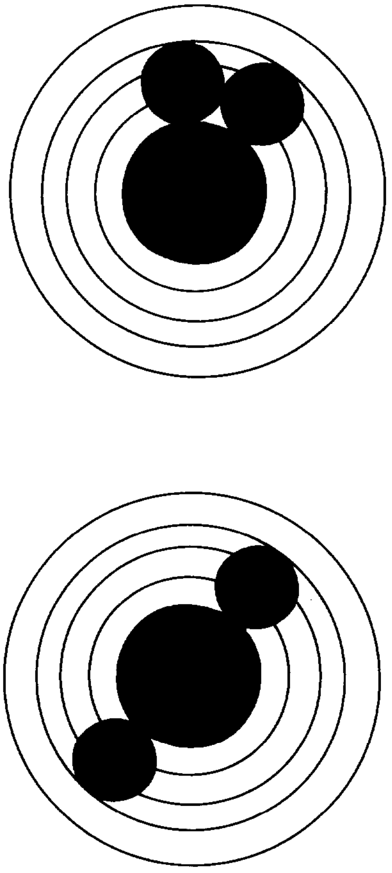

Fig. 9. Two possible arrangements of two non-intersecting atoms attached to a central atom. Spheres centred on the apex have been constructed and are represented in the diagram as circles of varying radii.

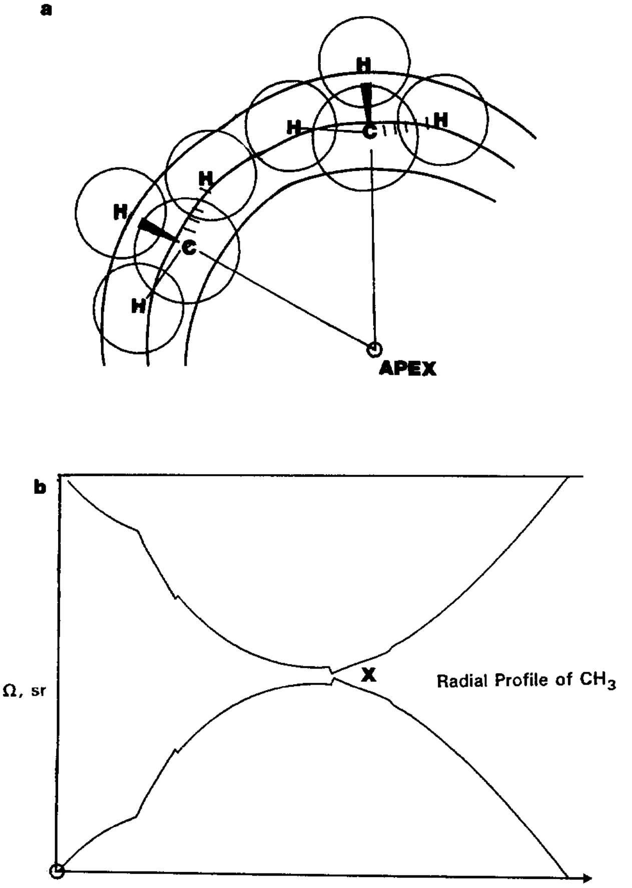

Fig. 10. (a) Two methyl groups attached to a common apex. (b) Comparison of the radial profile for the two methyl groups. Note that the point of closest interaction corresponds to X.

together, the point X may not correspond exactly with the two largest solid angle measurements associated with the ligands (see above).

Should the atoms overlap in space ($\Omega_{AA} < \Omega_A + \Omega_A$) then the radial profile methodology will provide a means of determining where the overlap has occurred. Quantification of this phenomenon will be dealt with in a separate publication.

Situations can be expected where the interaction of two groups not bonded to a common apex needs to be addressed. An example of this type was recently described by us [13] and is worth discussing further here.

Consider the problem of steric interaction between a ring substituent R′ on a cyclopentadienyl ring and a ligand eg. PR_3 attached to a metal as in (η^5-C_5H_4-R′)Fe(CO)I(PR_3) (Fig. 11).

To use the radial profile concept in this problem it is necessary to determine a common apex for both the R′ group and the PR_3 ligand. This is achieved by extending the vectors associated with the C_5H_4–R′ and M–PR_3 bonds back to a common origin, O, as is

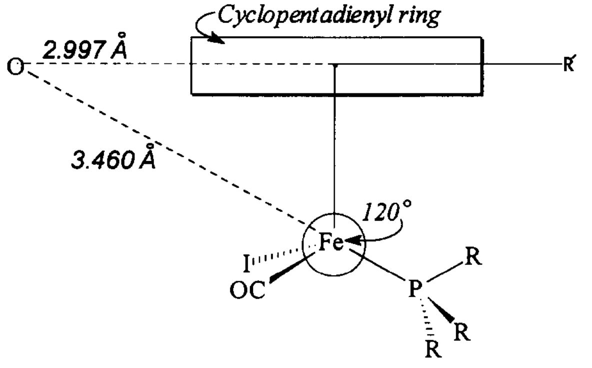

Fig. 11. Side view of (η^5-C_5H_4R')Fe(CO)(PR_3)I. Point O corresponds to the apex for measuring a radial profile for this molecule.

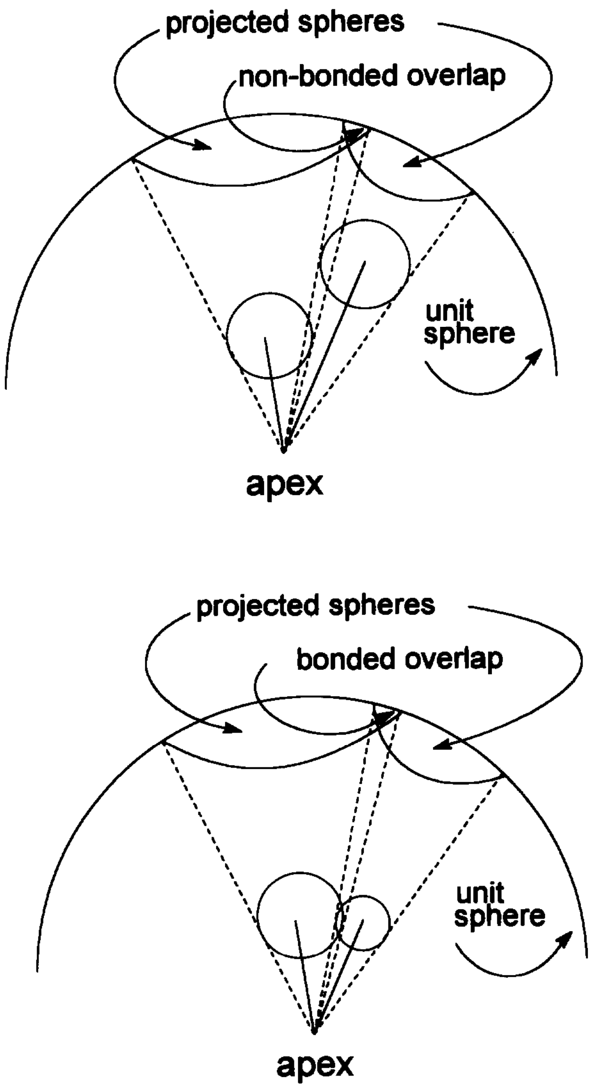

Fig. 12. (a) Solid angle measured when two atoms do not interact but their shadows overlap on the unit sphere. (b) Solid angle measured when two atoms do interact and their shadows overlap on the unit sphere.

shown in Fig. 11. This point of intersection can then be chosen as the apex to generate the radial profiles for the R′ and the PR_3 ligand.

As can be seen, the atoms in R′ and PR_3 lie a long way from the apex and since Ω drops off rapidly with distance (see above) the values for Ω will be very small. To enhance the size of Ω it is possible to enhance the scale on which Ω is plotted. Note that the choice of a common apex in the above problem permits a comparison of the sizes (Ω) of the ligands to be made. Again only a qualitative picture of the interaction can be achieved by this procedure.

Finally it is worth noting that the radial profile methodology can be used to differentiate between interacting and non-interacting atoms in the determination of a total solid angle. Consider the situation shown in Fig. 12. In both Figs. 12(a) and 12(b) the total solid angle indicates that overlap of atoms A and B has occurred, but the method of determination cannot necessarily differentiate between the two cases. However, when the radial profiles are used in conjunction with the total solid angle measurement no difficulty is encountered in establishing whether the solid angle measured is a result of bonding interactions or "shadow" overlap.

3. Conclusions

Extension of the solid angle concept to the measurement of atom, ligand, or organic group size as a function of distance from an apex (*e.g.* a metal) has been achieved. Radial profiles for any group of atoms can now be generated. A comparison of two radial profiles permits a qualitative evaluation of steric interaction between atoms or group of atoms in terms of distance from a common origin (the apex).

4. Experimental details

Details of an analytical procedure for measuring solid angles and of the method of determining the minimized structures of the ligands have been presented [7]. The program has now been modified to permit the measurement of radial profiles. The algorithm has been written into a computer program using high precision C [14]. Only a knowledge of atomic positions Van der Waals and covalent radii are needed as input for the radial profile and solid angle calculations.

Acknowledgements

We wish to thank the FRD and the University of the Witwatersrand for providing financial support for this project.

References

1 D. White and N.J. Coville, *Advances in Organometallic Chemistry, 36* (1994) 95.

2 A. Gavezzotti, *J. Am. Chem. Soc., 105* (1993) 5220.

3 R.W. Taft, in M.S. Newman (ed.), *Steric Effects in Organic Chemistry*, Wiley, New York, 1956, p. 556.

4 (a) M.L. Caffery and T.L. Brown, *Inorg. Chem., 30* (1991) 3907; (b) K.J. Lee and T.L. Brown, *Inorg. Chem., 31* (1992) 289; (c) T.L. Brown, *Inorg. Chem., 31* (1992) 1286

5 C.A. Tolman, *Chem. Rev., 77* (1977) 33.

6 A. Immirzi and A. Musco, *Inorg. Chim. Acta, 25* (1977) L41.

7 D. White, B.C. Taverner, P.G.L. Leach and N.J. Coville, *J. Comput. Chem., 14* (1993) 1042.

8 (a) M. Hirota, K. Sakakibara, T. Komatsuzaki and I. Akai, *Comput. Chem., 15* (1991) 241; (b) I. Akai, K. Sakakibara and M. Hirota, *Chem. Lett.*, (1992) 1317; C.T. Komatsuzaki, I. Akai, K. Sakakibara and M. Hirota, *Tetrahedron, 48* (1992) 1539; (d) R. Chauvin, and H.B. Kagan, *Chirality, 3* (1991) 242.

9 (a) G. Ferguson, P.J. Roberts, E.C. Alyea and M. Khan, *Inorg. Chem., 17* (1978) 2965; (b) D.H. Farrar and N.C. Payne, *Inorg. Chem., 20* (1981) 82.

10 E.C. Alyea, G. Ferguson and A. Somogyvani, *Inorg. Chem., 21* (1982) 1369.

11 J.D. Smith and J.D. Oliver, *Inorg. Chem., 17* (1978) 2585.

12 D.F. Mullica, S.L. Gipson, E.L. Sappenfield, C.C. Lin and D.H. Leschnitzer, *Inorg. Chim. Acta., 177* (1990) 89.

13 D. White, P. Johnston, I.A. Levendis, J.P. Michael and N.J. Coville, *Inorg. Chim. Acta., 215* (1994) 139.

14 B.C. Taverner, D. White, P.G.L. Leach and N.J. Coville, to be published.