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Twist Angle Definitions

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Sir:

Recently, Dymock and Palenik[1] have commented on the question of the proper definition of the twist angle for coordination polyhedra which can be considered to consist of two "equivalent" polygons. To illustrate their point they have made calculations for and comparison of six definitions of the twist angle applied to seven polyhedra and have recommended that their definition 1 be used in preference to the others. However, they have not considered the possible definitions in any complete and systematic manner, nor have they considered the reasons for calculating twist angles. We wish to present a more systematic set of definitions, which includes the six definitions of Dymock and Palenik as a subset, and to point out that the selection of the appropriate definition depends upon the use to be made of the information.

The twist angle of a pair of equivalent ligand atoms, L_i and L_i', may be defined as the difference between their ϕ coordinates in a suitably defined polar coordinate system. The polar coordinate system may be defined by selecting a direction for the polar axis and a point through which the polar axis is to pass. Consideration of the nature of the polyhedra of the type of interest here suggests six "natural" possible choices for the direction of the polar axis: (1) the vector from the centroid of the "lower" polygon to the centroid of the "upper" polygon, (2) the vector from the metal ion to the centroid of the upper polygon, (3) the vector from the centroid of the lower polygon to the metal ion, (4) the normal to the upper polygon, (5) the normal to the lower polygon, and (6) the normal to the "midplane" of the polyhedron [i.e., the plane defined by the midpoints of the lines between pairs of "equivalent" ligand atoms] and four "natural" possible choices of the point: (1) the metal ion, (2) the centroid of the upper polygon, (3) the centroid of the lower polygon, and (4) the centroid of the polyhedron. In these terms we may identify any particular twist angle as $\phi^i{}_{jk}$, where i $(1-n)$ identifies the ligand atoms L_i, j (1–6) identifies the direction of the polar axis, and k (1–4) identifies the point through which the polar axis passes. Among these 24 twist angle definitions, some are, by definition, identical. Thus, $\phi^i{}_{14} \equiv \phi^i{}_{13} \equiv \phi^i{}_{12}$, $\phi^i{}_{22} \equiv \phi^i{}_{21}$, and $\phi^i{}_{33} \equiv \phi^i{}_{31}$. If the polyhedron has any symmetry, further identities may arise. In the ideal case of a polyhedron consisting of two equilateral, parallel polygons whose centroids lie on their mutual normal (e.g., a regular octahedron), with the metal ion lying at the centroid of the polyhedron, all 24 twist angles are identical. The six twist angles considered by Dymock and Palenik are $\phi^i{}_{12}$, $\phi^i{}_{41}$, $\phi^i{}_{51}$, $\phi^i{}_{11}$, $\phi^i{}_{21}$, and $\phi^i{}_{31}$, respectively.

We have calculated the twist angles for the seven polyhedra selected by Dymock and Palenik. Several errors occur in their Table I. We are unable to identify the angles listed as $\phi^6{}_i$ for α-keto-1,1'-trimethyleneferrocene. For In(pmtc)_3, $\phi^3{}_2$ should be 38.6°. Most of our values for $\text{Cu(phen)}_3{}^{2+}$ differ very slightly from those in the table, in such a manner as to suggest that they probably used coordinates for ligand atom N(2) which are slightly different from those given by Anderson.[2] The values in the table for Fe(acac)_3 have been calculated using ligand atoms O(1), O(3), and O(6) as face 1 and O(2), O(4), and O(5) (misnumbered O(7)) as face 2 although, to be consistent with the treatment of the other three six-coordinate complexes, face 1 should be O(1), O(5), and O(6) and face 2 should be O(2), O(4), and O(3).

In considering which definitions are most useful we can, as pointed out by Dymock and Palenik, dismiss the axis directions 2, 3, 4, and 5 on the basis of their asymmetry, although in special cases these values might be of interest. Perhaps it should be emphasized here that the "twist angle" becomes less significant as the two polygons become less nearly parallel. Similarly, passing the polar axis through the centroid of one of the polygons (points 2 and 3) gives twist angles of lesser uniformity and significance. Thus we are left with four definitions. We may use the line joining the two polygon centroids (axis 1) or the line normal to the midplane of the polyhedron (axis 6) as the direction of the polar axis. For six of the seven cases selected by Dymock and Palenik and for seven out of eight additional M(acac)_3 complexes which we have examined, axis 1 gives less variation of the twist angles than axis 6 (mean of the ranges for 15 cases 2.0° vs. 3.8°). Therefore, except for cases in which there is some other basis for decision, we suggest (in agreement with Dymock and Palenik) that the line joining the centroids of the polygons should be, in general, selected as the direction for the polar axis. Comparing the two choices for the "origin" of the polar coordinate system, we find that the centroid of the polyhedron (as would be expected) gives slightly less variation of the twist angles than the metal ion (mean of ranges for the 15 cases 1.9° vs. 2.1°). However, these are coordination polyhedra, in which the metal ion plays a central role, and we therefore suggest that the metal ion is generally a more appropriate origin. For example, such a coordinate system is the appropriate one for any quantum mechanical calculations involving metal ion orbitals. We therefore recommend that, if only one definition of twist angle is to be used, it be our $\phi^i{}_{11}$ ($\phi^4{}_i$ of Dymock and Palenik). In general, in order to maximize "fact" and minimize "fantasy", one should (a) use twist angles only when they are appropriate, (b) carefully consider which definition is most useful, and (c) define precisely the definition used, e.g., by defining the "axis" and "origin" as illustrated above.

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References and Notes

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