

Cr-F distance is shortened relative to the ground state and this results in a lengthening of the Cr-N bond length because of the reduction in the effective charge on the chromium. The ${}^2E_g \rightarrow {}^4B_{1g}$ luminescence spectrum of *trans*-[Cr(en)₂F₂]X (X = I, ClO₄) shows progressions in totally symmetric modes of 512 and 230 cm⁻¹ both of which occur strongly in the Raman spectrum. Comparison of the vibrational spectra of these compounds with those of *trans*-Cr(en)₂X₂⁺ (X = Cl, Br, I) and *trans*-Cr(py)₄F₂⁺ shows that the 512-cm⁻¹ band is essentially the α_{1g} Cr-F stretch so that the 230-cm⁻¹ mode must involve substantial α_{1g} Cr-N stretching character. Progressions involving other Raman-active modes in the range 450-600 cm⁻¹ were not detected.

These studies indicate that the totally symmetric modes in the range 280-320 cm⁻¹ in tris(ethylenediamine) complexes and at somewhat lower frequency in *D*_{4h} bis(ethylenediamine) complexes have substantial metal-nitrogen stretching character. They do not show that the totally symmetric modes in the range 450-600 cm⁻¹ do not involve a contribution from metal-nitrogen stretching character; indeed it would be difficult to explain the systematic variation of the frequency of these modes as the metal is changed^{4,5} without invoking some metal-ligand stretching character. In both studies progressions in a totally symmetric mode of ca. 500 cm⁻¹ would not have been detected if they were appreciably weaker than the observed progressions. It does seem probable however that the totally symmetric mode in the 220-320-cm⁻¹ region of ethylenediamine complexes has at least as much contribution from the metal-nitrogen stretching coordinate as the 450-600-cm⁻¹ mode. We attribute the difference between the hexammine and tris(ethylenediamine) complexes in part to the greater mass of the ethylenediamine ligand but chiefly to strong coupling between the Co-N modes and the internal ethylenediamine modes which occur in the same spectral region.

Acknowledgment. This work was supported by an SRC grant and studentship (to A.P.M.).

Registry No. Ethylenediamine, 107-15-3; cobalt, 7440-48-4; chromium, 7440-47-3.

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Twist Angle Calculations: Fact or Fantasy?

AIC40614R

Sir:

Descriptions of molecular structures are frequently given in terms of an idealized geometry. For example, in coordination chemistry a metal ion surrounded by six ligands is usually considered in terms of distortions from either an octahedral or trigonal-prismatic configuration. For bis(cyclopentadienyl)metal complexes, the relative orientation of the two five-membered rings is discussed in terms of the idealized "staggered" or "eclipsed" arrangements. In both these and many other cases, the deceptively simple problem arises of calculating the relative orientation of two approximately parallel plane faces. A variety of different methods have been used to calculate the so-called twist angle which, of course, ideally would be equivalent. However, in practice the value of the twist angle depends to a very large extent on the method of calculation. Since the difficulties involved in the twist angle calculation have not been presented nor apparently appreciated, we present the following discussion of this problem.

The calculation of the twist angle, ϕ , in octahedral complexes has been given in terms of the nonbonded contacts, s , the ligand bite, b , the metal ligand distances, a , and the distance between the two equilateral triangles, h .¹ However, the twist angle calculated by this method¹ is valid only if the two threefold faces are parallel, the metal atom lies on the line joining the centroids of the two faces, the three ligand bites are all equal, the six metal-ligand distances are all equal, and the nonbonded contacts are equal. Obviously, for the majority of octahedral complexes, one or more of these conditions will not hold, and then the twist angle will depend upon the choice of parameters used in the calculation. Problems with the idealized method have been discussed recently² with respect to the compression ratio for the two limiting cases. However, the effects of the deviations from ideality on the twist angle have not been considered.

The difficulties involved in calculating the twist angle between two n -fold faces can be appreciated by a consideration of the possibilities illustrated in Figure 1. In the general case we have two n -fold faces, face 1 and face 2, the centroids of which are C and C'. The faces need not be parallel but are inclined by an angle ω relative to each other. If a metal atom M is encompassed by the two faces, then the metal atom can be displaced by a distance Δ from the line defined by the two centroids C and C'. The twist angle ϕ_i can be calculated by a variety of methods and we shall define ϕ_i^n as the i th angle obtained from the n th method. We have considered the following six methods for computing: (1) the acute angle between the plane defined by L_i , C, and C' and the plane defined by L'_i , C, C'; (2) the angle between the projection of the metal-ligand vectors $M-L_i$ and $M-L'_i$ on face 1; (3) the angle between the projection of the metal-ligand vectors $M-L_i$ and $M-L'_i$ on face 2; (4) the angle between the projection of the metal-ligand vectors $M-L_i$ and $M-L'_i$ on a plane orthogonal to the line defined by the two centroids; (5) the angle between the metal-ligand vectors $M-L_i$ and $M-L'_i$ projected on a plane normal to the line defined by M-C; (6) the angle between the metal-ligand vectors $M-L_i$ and $M-L'_i$ projected on a plane normal to the line defined by M-C'. Since the problem of calculating twist angles is not limited to octahedral complexes, we have calculated the angles ϕ_i^n for both octahedral complexes as well as ferrocene derivatives. The results are tabulated in Table I. The compounds given in Table I were chosen to illustrate the types of deviations from ideality which we frequently encountered.

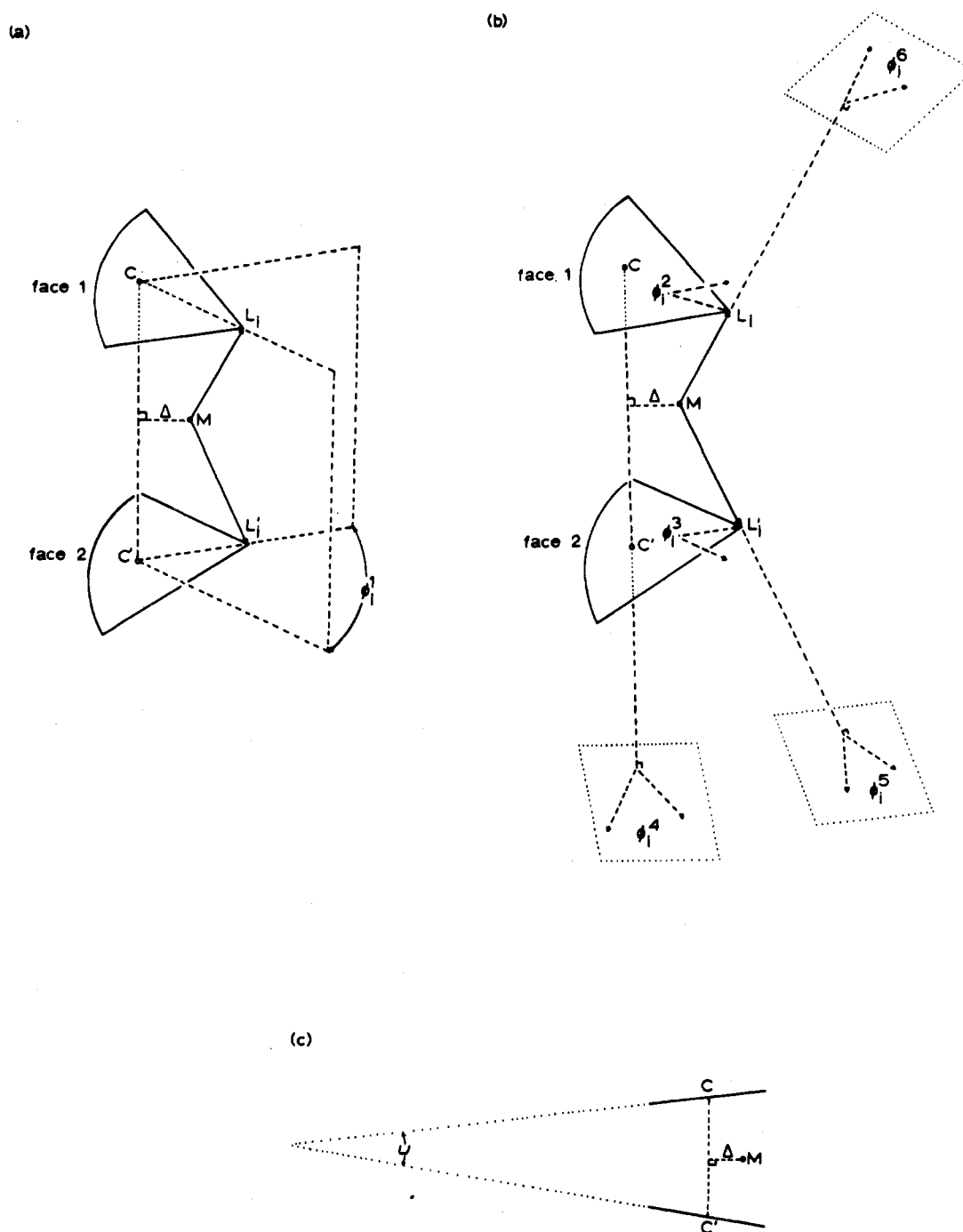


Figure 1. Schematic diagram illustrating the various methods used in calculating the twist angle ϕ^n between the two planes, face 1 and face 2. In all cases C and C' are the centers of the respective faces, Δ is the displacement of the metal M from the line joining the two centers, and L_i and L'_i are two atoms in the respective faces. In (a) the first method of calculating the twist angle, ϕ^1 , is shown as the dihedral angle between two planes. In (b) methods 2-6 are shown. The deviation of the two planes from being parallel is defined as ω and is illustrated in (c).

The results in Table I show the range of twist angles which can be calculated for a compound. The range in values is particularly pronounced if the rings deviate markedly from being parallel or if the metal atom has a large displacement from the line joining the two centroids. Because of the large range of values which can be calculated, a twist angle can usually be calculated which agrees with one's view of the geometry. However, a more uniform method of defining the twist angle would be most appropriate in discussing geometrical distortions.

Of the six methods used to calculate twist angles, numbers 2, 3, 5, and 6 define the angle relative to the other face. A definition of this type would appear to introduce asymmetry

in the molecular description. Indeed, some of the largest variations are found for methods 2, 3, 5, and 6. Method 4 defines the angle in terms of the metal atom vectors and the two centroids. However, if the metal is significantly displaced from the line between the two centroids (a large value of Δ), there are also large variations in the angle calculation. Therefore, we recommend that method 1 be used in calculating the twist angle in complexes involving two approximately parallel faces. The average twist angle, together with the deviation of the planes from being parallel, and the displacement of the metal from the line joining the two centroids would provide a complete description of the distortions in these molecules.

Table I. Twist Angle (ϕ_i^n , = deg) Calculations for Some π -Cyclopentadienyl and Octahedral Complexes^a

	<i>n</i>	C(1)C(8)	C(2)C(9)	C(3)C(10)	C(4)C(11)	C(5)C(12)	
1,1'-Tetramethylethyl- eneferrocene ³	1	10.4	10.3	10.8	9.7	10.4	
	2	9.6	34.5	43.2	19.6	15.5	
	3	7.5	16.2	14.3	42.0	32.0	
	$\omega = 23.2^\circ$	4	8.7	9.1	13.0	11.6	9.4
	$\Delta = 0.237 \text{ \AA}$	5	9.2	27.0	33.6	9.5	7.9
		6	8.7	9.1	7.8	32.8	26.6
	<i>n</i>	C(1)C(6)	C(2)C(7)	C(3)C(8)	C(4)C(9)	C(5)C(10)	
α -Keto-1,1'-tri- methyleneferrrocene ⁴	1	6.5	5.5	5.6	5.6	5.9	
	2	10.0	19.5	11.2	7.3	4.4	
	3	3.5	4.3	2.5	14.8	12.5	
	$\omega = 8.8^\circ$	4	6.1	5.5	6.0	5.8	5.6
	$\Delta = 0.087 \text{ \AA}$	5	8.5	13.7	8.7	1.9	0.0
		6	8.0	14.4	10.2	1.8	0.9
	<i>n</i>	C(9)C(1)	C(10)C(5)	C(6)C(4)	C(7)C(3)	C(8)C(2)	
Biferrocenyl ⁵	1	16.7	16.7	17.5	15.4	19.5	
	2	12.1	13.1	19.6	20.5	20.7	
	3	18.7	18.8	16.9	13.0	18.5	
	$\omega = 2.8^\circ$	4	17.0	17.0	17.3	15.2	19.4
	$\Delta = 0.022 \text{ \AA}$	5	18.1	15.5	15.4	15.4	21.5
		6	16.0	18.5	19.2	14.9	17.4
	<i>n</i>	S(1)S(1)'	S(2)S(3)	S(3)S(2)'	Other parameters		
Tris(<i>cis</i> -1,2-diphenyl- ethene-1,2-dithio- lato)vanadium(III) ⁶	1	3.5	4.7	4.7	$s = 3.065 (105) \text{ \AA}$		
	2	8.5	7.4	7.0	$s/h = 1.00 (3)$		
	3	8.5	7.0	7.4	$\phi(b, h, s)$ cannot		
	4	3.5	4.8	4.8	be computed		
	$\omega = 0.2^\circ$	5	3.5	3.9	5.6		
	$\Delta = 0.015 \text{ \AA}$	6	3.5	5.6	3.9		
	<i>n</i>	S(11)S(12)	S(3)S(2)	S(21)S(20)	Other parameters		
In(pmtc) ₃ ⁷	1	30.8	35.8	32.4	$s = 3.84 (8) \text{ \AA}$		
	2	27.6	37.6	33.4	$s/h = 1.44 (3)$		
	3	30.1	35.6	29.9	$\phi(b, h, s) = 38.6 (8)^\circ$		
	$\omega = 3.1^\circ$	4	31.0	35.8	32.2		
	$\Delta = 0.014 \text{ \AA}$	5	31.4	35.1	32.5		
		6	30.6	36.4	31.8		
	<i>n</i>	N(1)N(3)	N(5)N(2)	N(4)N(6)	Other parameters		
Cu(phen) ₃ ^{2+ 8}	1	55.8	50.2	51.3	$s = 3.18 (17) \text{ \AA}$		
	2	46.3	56.0	52.3	$s/h = 1.46 (8)$		
	3	48.1	49.9	57.0	$\phi(b, h, s) = 52.3 (31)^\circ$		
	$\omega = 6.3^\circ$	4	54.2	50.9	51.7		
	$\Delta = 0.052 \text{ \AA}$	5	54.0	48.2	54.4		
		6	54.7	53.4	48.9		
	<i>n</i>	O(1)O(2)	O(3)O(4)	O(6)O(7)	Other parameters		
Fe(acac) ₃ ⁹	1	58.6	54.8	54.6	$s = 2.81 (7) \text{ \AA}$		
	2	59.3	51.4	57.0	$s/h = 1.22 (3)$		
	3	60.9	56.7	50.0	$\phi(b, h, s) = 56.2 (24)^\circ$		
	$\omega = 5.7^\circ$	4	58.7	55.0	54.3		
	$\Delta = 0.010 \text{ \AA}$	5	58.1	55.5	54.6		
		6	59.3	54.6	54.0		

^a For each compound the twist angle calculated by the *n*th method is tabulated for the atom pairs L_iL_j' given in the table. The value of ω , the tip of the two planes from parallelism, is given, together with the displacement (Δ) of the metal atom from the line joining the two centroids. For the octahedral complexes the values of s , s/h , and $\phi(b, h, s)$ calculated from the values of b , h , and s are given at the side.

Acknowledgment. We wish to thank the Northeast Regional Data Center, State University System of Florida, for a grant of computer time and the National Cancer Institute, U.S. Public Health Service, for financial support through Grant Ca-12390.

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Received August 26, 1974