two resultant curves. In the case of the promoted states in eq 11 and Tables II and III one can, if one wishes, attribute the potential maxima described in earlier paragraphs to avoided crossings between repulsive and attractive LCAS potential curves. For example, for H_2 one has a strongly repulsive LCAS curve for $(1s \cdot 2p\pi)_g$ of eq 11 and a corresponding presumably moderately attractive curve for $(1s \cdot 3d\pi)_g$, and similarly for the analogous triplet H_2 and the corresponding singlet and triplet He_2 curves.[40] Thus for H_2 or He_2, avoided crossings of the separate potential curves of the two LCAS states,[36] which are required for the cases which correspond at small R to promoted Rydberg MO's, can be held responsible for the potential maxima in these cases.[41] Here the

ionic components which need to be admixed into the LCAS wave functions as R decreases are being ignored, but (as was pointed out above) because of a lack of orthogonality of the ionic and covalent wave functions the presence or absence of these ionic admixings does not change the qualitative characteristics of the potential curves.

The discussion in this section has shown that, for states which are Rydberg states near R_e, it is incorrect because of strong CM at large R values to think of the core and the Rydberg electron as following independent correlation curves as $R \rightarrow \infty$. However, there is no reason why these states need be thought of as ceasing to be Rydberg states at larger R values. Further, although a T and n^* value associated with a specific Rydberg MO lack meaning at large R values, an *ionization energy* can be defined at every R value. At intermediate R values, ionization involves a considerable internal rearrangement of structure which leaves the positive ion the same *as if* an electron had merely been removed from a nonbonding Rydberg MO, while as $R \rightarrow \infty$, the ionization energy becomes equal to the T for the excited atom in an LCAS function; these relations correspond to the *pseudo-correlation* of section 4.

(40) An interesting minor point, however, is that the $(1s^2 1s2p\sigma)_u$ and probably the $(1s^2 1s3d\pi)_g$ He_2 attractive curves are at first (at large R values) repulsive (cf. ref 4a), and become attractive only at smaller R values. This behavior can be correlated phenomenologically with the fact that the overlap integral S changes sign as R decreases in the cases of $S(2p\sigma_a, 2p\sigma_b)$ and $S(3d\pi_a, 3d\pi_b)$; the MO's $\sigma_u 2p$ and $\pi_g 3d$ involve negative overlap and so are antibonding at large R but attain positive overlap at smaller R, with $S = 1$ at $R = 0$. It is also of interest that the overlap for $\sigma_g 3d$ has positive maxima both at large R values and $(S = 1)$ at $R = 0$, but is smaller and even becomes slightly negative between, according to unpublished calculations by Dr. S.-I. Kwun in this laboratory.

(41) On the other hand, reference to Figure 1 of ref 3 for He_2 might suggest that *repulsive* LCAS's such as $(1s^2 1s2s)_g$ and $(1s^2 1s2p\pi)_u$, taken *alone*, tend to go, as R decreases, into MO states *with repulsive cores but unpromoted Rydberg MO's* $(1\sigma_g 1\sigma_u^2 2s$ and $1\sigma_g 1\sigma_u^2 3d\pi$, respectively), whereas the corresponding *attractive* LCAS's $(1s^2 1s2s)_u$ and $(1s^2 1s2p\pi)_g$ definitely correlate with MO states with *attractive cores* and the same

unpromoted Rydberg MO's $(1\sigma_g^2 1\sigma_u 2s$ and $1\sigma_g^2 1\sigma_u 2p\pi)$. There seems to be no theoretical reason for such correlations for the repulsive single LCAS Ψ's, and the explanation given in the text appears much more satisfactory.

Electric Moments and Internuclear Distances in Molecules Containing Both Fixed and Rotating Polar Groups

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Abstract: Equations are derived which give the components of a rotating vector in terms of the components of its axis of rotation, the angle between the axis and the rotating vector, and the angle of rotation. It is shown how these equations can be used to calculate the electric moments of molecules with rigid frameworks to which fixed and/or rotating polar groups are attached, for which the skeletal coordinates and angles are known or can be inferred, and in which either free rotation or certain conformations of a rotatable group are assumed. An expression is derived for the calculation of the distance between an atom in a rotatable group and some vicinal fixed atom. Examples of the use of the various expressions derived are given. It is concluded that dipole moment data may be helpful in providing evidence for the absence, but not for the presence, of free rotation in the types of molecules for which the relationships given are applicable.

In the investigation of reaction mechanisms, problems regarding the configurations of fairly large molecules with rigid frameworks are often encountered. Electric moment data have proved to be helpful in the solution of these problems in many instances.[1-7] For

simple molecules, they are often sufficient for immediate structural assignments, but as the molecular complexity increases, it often becomes necessary to use geometrical models from which theoretical moments are calculated in order to determine which particular configurations are consistent with the experimentally determined moments.

A systematic approach to the calculation of theoretical moments from assumed models for several bicyclic

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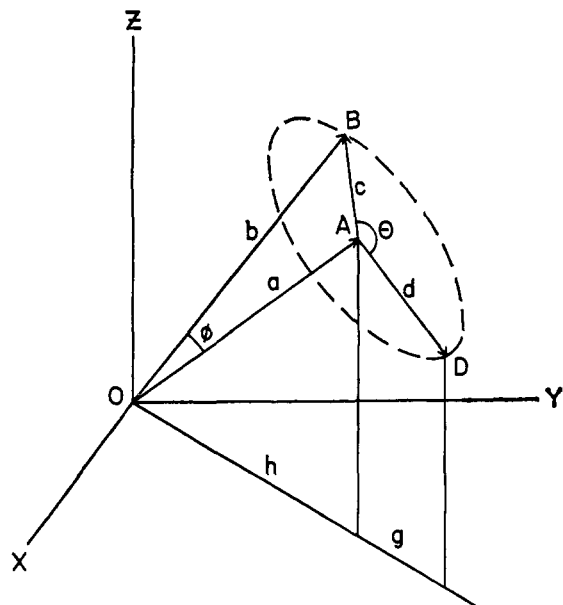
Figure 1. Coordinate system for rotating vector.

molecules has been presented by Wilcox.[8] This approach involves the use of vector algebra in the calculation of electric moments when the polar substituents are "fixed" groups, i.e., single atoms or groups of atoms whose symmetry axis coincides with the axis of rotation. For molecules containing "rotating" polar groups, i.e., groups for which the moment vector does not coincide with the axis of rotation, as well as fixed groups, it is necessary to modify the vector method in order to calculate theoretical moments. It is the purpose of this paper to show how this can be done using as a foundation the approach described by Wilcox. The results to be obtained are applicable to molecular systems with rigid frameworks in which, at least to a first approximation, it is useful to assume free rotation or some particular conformation of the rotatable group.

Components of a Rotating Vector. It is assumed at the outset that the geometry of the parent molecule is reasonably certain, and hence that one can calculate the rectangular coordinates of the atoms to which polar groups can be attached and the components of the unit vectors which describe the directions of the bonds at the various points of attachment, as illustrated by Wilcox.[8] The parent molecule itself may have a measured electric moment and will have one or more polar groups bonded to it. For a rotating group, the moment vector will enclose an angle ϕ with the bond vector about which it can rotate.

The x, y, and z contributions of the fixed moments are readily calculated,[8] but the contributions of the rotating moments must be expressed by equations which give the vector components for the ith rotatable group in terms of ϕ_i, θ_i (the angle of rotation), and the vector components of the axis about which rotation occurs.

The derivation of these equations is readily accomplished by reference to Figure 1, in which a represents the unit vector about which the vector b rotates, and ϕ is the angle between a and b. These vectors start at the origin and terminate in the fixed point A and the moving point B. The motion of B describes a circle upon

(8) C. F. Wilcox, Jr., J. Am. Chem. Soc., 82, 414 (1960).

which some arbitrary fixed point D is chosen. This circle is perpendicular to a, and thus the length of b is $1/\cos \phi$. Two vectors, c and d, are directed from A to B and D, respectively; they are equal in magnitude, and the angle between them is the angle of rotation θ. Since a is a unit vector, $b^2 = 1 + c^2$. With the coordinates of A, B, and D represented by (a_x, a_y, a_z), (b_x, b_y, b_z), and (d_x, d_y, d_z), respectively, the following relations may be written.

$$\mathbf{a} \cdot \mathbf{b} = a_x b_x + a_y b_y + a_z b_z = ab \cos \phi = 1 \quad (1)$$

$$\mathbf{c} \cdot \mathbf{d} = (b_x - a_x)(d_x - a_x) + (b_y - a_y)(d_y - a_y) + (b_z - a_z)(d_z - a_z) = c^2 \cos \theta \quad (2)$$

$$b^2 = b_x^2 + b_y^2 + b_z^2 = 1 + c^2 \quad (3)$$

Equations 1, 2, and 3 are to be solved for b_x, b_y, and b_z, the components of the rotating vector b. The coordinates of D must therefore be expressed in terms of c and the coordinates of A in order to eliminate d_x, d_y, and d_z from eq 2. This can be done readily by choosing the location of D at the lowest point on the circle and hence such that the normal from D to the x-y plane intersects the extension of the projection of a on this plane. It then follows from simple geometry that $d_z/a_z = d_y/a_y = 1 + g/h$, where $h = (a_x^2 + a_y^2)^{1/2}$ and g is the distance between the points at which the normals from A and D intersect the x-y plane. If ζ is defined as the angle between a and its projection on the x-y plane, it is also the angle between d and the normal from A; thus $a_z = \sin \zeta = g/c$, and $h = \cos \zeta = (a_z - d_z)/c$. We use these relations to obtain $d_x - a_x = ca_x a_z/h$; $d_y - a_y = ca_y a_z/h$; and $d_z - a_z = -ch$. Equation 2 can then be written, after rearrangement and simplication, as

$$a_x b_x + a_y b_y + a_z b_z - b_z/a_z = (hc/a_z) \cos \theta \quad (4)$$

The simultaneous solution of eq 1, 3, and 4 yields

$$b_x = a_x + [a_x a_z c \cos \theta \pm a_y c \sin \theta]1/h$$

$$b_y = a_y + [a_y a_z c \cos \theta \mp a_x c \sin \theta]1/h$$

and

$$b_z = a_z - hc \cos \theta$$

For θ increasing when c rotates in a clockwise direction as viewed from the origin, the signs in front of the second terms in the brackets are $-$ and $+$, respectively. Thus, when these components of b are converted to unit vector components (indicated by primes) by dividing each by $(1 + c^2)^{1/2}$, which is the same as multiplying by $\cos \phi$, there results, since $c \cos \phi = \sin \phi$

$$b'_x = a_x \cos \phi + [a_x a_z \sin \phi \cos \theta - a_y \sin \phi \sin \theta]1/h \quad (5)$$

$$b'_y = a_y \cos \phi + [a_y a_z \sin \phi \cos \theta + a_x \sin \phi \sin \theta]1/h \quad (6)$$

$$b'_z = a_z \cos \phi - h \sin \phi \cos \theta \quad (7)$$

Resultant Moment. An expression for the resultant electric moment, μ, of n rotating group moments can be obtained by combining the rotating vector com-

ponents in the usual manner

$$\mu^2 = (\sum_i^n m_i b'_{ix})^2 + (\sum_i^n m_i b'_{iy})^2 + (\sum_i^n m_i b'_{iz})^2 \quad (8)$$

in which the b' terms are given by eq 5, 6, and 7, and m_i is the scalar magnitude of the moment of the ith rotating group. For free rotation, the mean-square resultant $\langle \mu^2 \rangle$ is obtained by integrating

$$1/2\pi \int_0^{2\pi} \mu^2 d\theta \quad (9)$$

for all of the independent θ's. There results

$$\langle \mu^2 \rangle = \sum_i^n m_i^2 + 2\sum_{i \neq j}^n m_i m_j (a_{ix}a_{jx} +$$
$$a_{iy}a_{jy} + a_{iz}a_{jz}) \cos \phi_i \cos \phi_j \quad (10)$$

For a molecule with only fixed polar groups ($\theta = 0°$), the expression for the mean-square resultant is the same as eq 10 but, of course, with the two cosine factors replaced by unity.[9]

For the general case in which there are both fixed and rotating groups, it is desirable to have an expression for the resultant in which the contributions of the fixed and rotating groups are given separately. There will be, however, one cross-term between them, and, because of this, it is convenient to symbolize the total x, y, and z contributions of the fixed vectors as m_x, m_y, and m_z, which are defined as

$$\sum_k m_k a_{kx}, \sum_k m_k a_{ky}, \sum_k m_k a_{kz}$$

respectively, where m_k refers to the scalar magnitude of the kth fixed group moment and the a_k values are the components of the vector describing the direction of the kth group bond. The resultant of the fixed group moments will be symbolized by m; i.e., $m^2 = m_x^2 + m_y^2 + m_z^2$. For the sake of clarity, the indices i and j are used to refer to rotating and k to fixed groups. The mean-square electric moment for a molecule with both fixed and n rotating polar groups then can be written as

$$\langle \mu^2 \rangle = m^2 + \sum_i^n m_i^2 + 2\sum_i^n m_i(m_x a_{ix} + m_y a_{iy} +$$
$$m_z a_{iz}) \cos \phi_i + 2\sum_{i \neq j}^n m_i m_j (a_{ix}a_{jx} +$$
$$a_{iy}a_{jy} + a_{iz}a_{jz}) \cos \phi_i \cos \phi_j \quad (11)$$

In situations in which it is desired to calculate the dipole moment for some particular orientation of the rotating vector, the value of θ corresponding to this conformation may be substituted into eq 5, 6, and 7 along with the other necessary data to obtain the components of the group moment vector b'. These components may then be combined with those for any other polar groups in the usual manner to obtain the resultant moment of the molecule in the desired conformation. An example of this is given in a subsequent section.

Equations 9 and 10 resemble that derived by Eyring[10] a number of years ago for molecules in which there is

(9) It is perhaps worth noting that if the three b' terms are erroneously averaged for all θ between 0 and 2π before incorporation into eq 8, the result is identical with eq 10 except that the first term on the right comes out to be $\sum_i^n m_i^2 \cos^2 \phi_i$.

(10) H. Eyring, Phys. Rev., 39, 746 (1932).

free rotation about each of the valence bonds other than the terminal ones. The mode of derivation used here suffers in comparison with the simple elegance of Eyring's method, but yields expressions in a form which is more tractable to the type of analysis and the kind of molecules treated in this paper.

Internuclear Distances. There is often the question of whether free rotation is possible for a given molecular configuration or whether it is hindered as a result of steric repulsions or of special attractions (e.g., hydrogen bonding) between the atoms in the rotatable polar group and some fixed atom in the molecule. It is therefore desirable to be able to calculate how close a protruding atom in the rotating group can come to a nearby atom. This can be done with the aid of the components of the rotating vector given in eq 5, 6, and 7. When used for this purpose, the angle ϕ in these equations becomes the angle (designated by ϕ' to avoid confusion) between the axis of rotation and the line of length s drawn from the base of this axis (point O in Figure 1) to the nucleus of the protruding atom. If the coordinates of the nucleus at point O are represented by (x_2, y_2, z_2), the square of the internuclear distance S between the atom of interest in the rotating group and a nearby fixed nucleus can be written as

$$S^2 = (x_1 - x_2 - sb'_x)^2 + (y_1 - y_2 - sb'_y)^2 +$$
$$(z_1 - z_2 - sb'_z)^2 \quad (12)$$

in which x_1, y_1, and z_1 are the coordinates of the nearby nucleus;[11] s is calculated from a knowledge of the pertinent valency angle and bond distances; and the b' terms are those given by eq 5, 6, and 7.

Application of the condition for a minimum or maximum in S^2 with respect to θ yields two values of the angle of rotation θ'_m, differing by 180°, which can be calculated from the equation

$$\tan \theta'_m = \frac{a_x \Delta x - a_y \Delta y}{a_z E - \Delta z} \quad (13)$$

in which Δx, Δy, and Δz are $x_1 - x_2$, $y_1 - y_2$, and $z_1 - z_2$, respectively; a_x, a_y, and a_z have previously been defined (e.g., eq 1); and $E = a_x \Delta x + a_y \Delta y + a_z \Delta z$. By combining and rearranging eq 5, 6, 7, 12, and 13, one obtains the following expression for the maximum or minimum value of the square of the desired internuclear distance, S_m^2

$$S_m^2 = \Delta^2 + s^2 - 2s[E \cos \phi' \pm$$
$$(\Delta^2 - E^2)^{1/2} \sin \phi'] \quad (14)$$

in which $\Delta^2 = (\Delta x)^2 + (\Delta y)^2 + (\Delta z)^2$ and for which the minimum value obviously occurs when the sign in front of the last term is positive.

Range of Moment Values. In a manner completely analogous to that described above, an expression similar to eq 13 can be derived for the values of θ_m corresponding to maximum and minimum values of μ^2 for a molecule with a single rotating polar group

$$\tan \theta_m = \frac{a_x m_y - a_y m_x}{a_z F - m_z} \quad (15)$$

in which m_x, m_y, and m_z have the same meaning as in eq 11, and $F = a_x m_x + a_y m_y + a_z m_z$. The two values

(11) See ref 8 for a sample calculation of these coordinates.

of θ_m calculated with eq 15 will not, in general, be the same as those of θ'_m in eq 13.

The maximum and minimum values of μ^2 for a molecule with one rotating polar group and several fixed groups is then given by

$$\mu_m{}^2 = \langle \mu^2 \rangle \pm 2m_1(m^2 - F^2)^{1/2} \sin \phi \qquad (16)$$

in which $\langle \mu^2 \rangle$ is the free rotation value (see eq 17 below), m_1 is the magnitude of the rotating group moment, and the rest of the terms have been defined in preceding sections.

The quantity F in eq 15 and 16 will be recognized as the scalar product of the unit vector **a** and the vector which describes the direction of the resultant of all the fixed groups within the molecule; i.e., $F = m \cos \psi$, where ψ is the angle between **a** and the resultant. Hence $(m^2 - F^2)^{1/2} = m \sin \psi$. Thus we see that when the axis of rotation of the rotatable polar group is parallel to the direction of the resultant ($\psi = 0$ or $180°$), there is no difference between the maximum and minimum values of μ^2, and the moment of the molecule is the same regardless of whether rotation occurs or whether the rotatable group assumes some particular conformation. On the other hand, when the axis of rotation is perpendicular to the direction of the resultant, the difference between the maximum and minimum dipole moments will be greatest.

Sample Calculations. The use of some of the equations derived above will be illustrated for several molecules containing a single rotatable polar group, as well as one or more fixed groups. For such molecules eq 11 reduces to

$$\langle \mu^2 \rangle = m^2 + m_1{}^2 + 2m_1F \cos \phi \qquad (17)$$

1. Let us first calculate the free rotation values of μ for two isomeric alcohols, exo- and endo-norborneol. These are derivatives of norbornane (bicyclo[2.2.1]-heptane) for which the necessary skeletal coordinates and unit vector components have been deduced by Wilcox[8,12] and to which the OH groups are bonded, in the two possible configurations, to a carbon atom (designated as C_2) in one of the two-carbon bridges in the molecule. The data needed here are the x, y, and z vector components of the exo and endo bonds at C_2, which are $(+0.349, +0.842,$ and $+0.411)$[13] and $(+0.349, -0.115,$ and $-0.930)$, respectively; these are the components of the axes of rotation of the C–O–H group moment for the two isomers. The dipole moments of the two isomers have recently been remeasured[14] with presumably greater accuracy than in the original investigation.[4a] The new results are 1.63 and 1.66 D. for the exo and endo alcohols, respectively. The fact that these two results are identical within the limits of error and also in agreement with the moments

reported for several cycloalkanols[15] raises some interesting points. First, recent studies indicate that the parent hydrocarbon itself has a small moment in the range of 0.15[16] to 0.24 D.[14] These results are of interest in that they represent the largest moment values reported for a saturated hydrocarbon and suggest the possibility that internal angle strain causes changes in bond moments. Furthermore, if the effect is real, one would expect the moments of the two isomeric alcohols to be different. It is therefore pertinent to calculate the magnitude of the difference to be expected for the moments of the alcohols when the parent molecule is assumed to have a moment. In carrying out such a calculation, the question of the direction of this moment is also involved. It must be either upward or downward along the symmetry axis of the molecule, which passes through the center of the one-carbon bridge and through the midpoint of the line joining the bridge-head carbons. (This axis will be taken as having the direction of the z axis in Figure 1 and as having a positive direction from the midpoint up through the bridge.) Calculation of the root-mean-square (rms) values of μ with eq 17 gives some information relative to these points.

In using this equation, we will take 0.20 D. as the moment of norbornane, i.e., $m = m_z = \pm 0.20$ (since $m_x = m_y = 0$). The values of F are therefore $(+0.411) \cdot (\pm 0.20) = \pm 0.082$ and $(-0.930)(\pm 0.20) = \mp 0.186$ for the exo and endo alcohols, respectively; 1.6 D. and $63°$ are reasonable values for m_1 and ϕ.[7] For $m_z = +0.20$, the rms moments of the exo and endo isomers come out to be 1.65 and 1.53 D., whereas the corresponding values for $m_z = -0.20$ are 1.57 and 1.69 D. Since the uncertainty in the experimental values (1.63 and 1.66 D.) is no less than 0.1 D., and since it is possible that the rotation of the O–H group is somewhat restricted in both isomers, it is clear that no conclusion can be drawn as to the direction of the moment of the hydrocarbon. By the same token, however, it is also clear that the experimental data are not inconsistent with the possibility that the hydrocarbon itself has a moment of about 0.2 D.

2. An example involving steric effects is provided by the molecule, exo-2-hydroxy-syn-8-chlorodibenzobicyclo[3.2.1]octadiene,[17] whose dipole moment has been measured and for which a reasonable set of coordinates and unit vector components have been worked out.[7] The following data given in ref 7 are needed in the calculations: (a) the vector components of the exo bond at C_2 and of the syn bond at C_8, which are $(+0.530, +0.635, +0.562)$ and $(0.000, +0.850, +0.527)$, respectively; and (b) the measured dipole moment of the parent hydrocarbon (0.97 D.), which is assumed to be directed along the negative z axis, i.e., to have components of $(0, 0, -1)$.

Using 2.1 D. as the C–Cl group moment,[2] one calculates the contributions of the fixed groups to be $m_x = 0, m_y = (2.1)(0.850) = 1.78, m_z = (2.1)(0.527) - 0.97 = 0.14$, and hence $m^2 = 3.19$. The vector com-

(12) The structure of norbornane was derived by Wilcox from considerations of minimum strain in the internal bond angles, assuming 1.540 A as the length of all C–C bonds. The coordinates and angles he obtained agree quite well with those found by electron diffraction (V. Schomaker, et al., unpublished data kindly furnished by Dr. Saul Winstein). For example, the angle between the planes of the two-carbon bridges was assumed to be $109°$; the electron diffraction data yield a value of $110°$. The angles and nonbonded distances calculated from Wilcox's model are generally lower, by 2% or less, than the corresponding electron diffraction values.

(13) The z component is listed in ref 8 as 0.414 owing to a typographical error.

(14) P. Hirsjärvi and H. Krieger, Suomen Kemistislehti, **B37**, 140 (1964).

(15) A. L. McClellan, "Tables of Experimental Dipole Moments," W. H. Freeman and Co., San Francisco, Calif., 1963, pp 147, 215, 305.

(16) C. F. Wilcox, Jr., J. G. Zajacek, and M. F. Wilcox, J. Org. Chem., **30**, 2621 (1965). These authors report 0.15 D. by direct measurement; from the measured moments of various chloro derivatives they calculate that the moment of norbornane is essentially zero.

(17) The syn configuration is taken to be that in which the substituent group is on the same side of the one-carbon bridge as C_2.

ponents (a_x, a_y, a_z) of the axis about which the hydroxyl group may rotate are those given for the *exo* bond at C_2; thus $F = (0.635)(1.78) + (0.562)(0.14) = 1.21$. With 1.6 D. and 63° for m_1 and ϕ as before, the rms of the resultant is calculated with eq 17 as

$$\langle\langle\mu^2\rangle\rangle^{1/2} = [(3.19)(1.6)^2 +$$
$$2(1.6)(1.21) \cos 63]^{1/2} = 2.74 \text{ D.}$$

The observed moment for this compound (2.50 D.)[7] is in rather good agreement with this theoretical value, from which one might be tempted to infer that the OH group is relatively free to rotate.

There is a possibility, however, that the hydroxyl H might assume conformations in which it is either weakly hydrogen bonded to the *syn* Cl atom or repelled by it; hence it is of interest to calculate the minimum distance between these two atoms and the moments associated with this and the maximum distances. This can be done using the coordinates of C_2 and C_8 which have been calculated to be (1.35, 1.35, −0.742) and (0.00, 0.00, +0.969).[7] With 1.77 A as the C–Cl distance[18] and with the vector components of the *syn* bond at C_8, the coordinates of the Cl atom (x_1, y_1, and z_1 of eq 12) come out to be (0.00, 1.50, 1.90). The coordinates (x_2, y_2, z_2) in eq 12 are those of C_2; thus $\Delta x = -1.35$, $\Delta y = 0.15$, and $\Delta z = 2.64$. By means of eq 16 and using 1.92 A for s and 28.9° for ϕ' (calculated assuming C–O and O–H bond distances of 1.43 and 0.96 A and an oxygen valency angle of 105°[18]), one then obtains a minimum internuclear separation of 2.07 A, which is small enough or perhaps even too small for a hydrogen bond since the sum of the van der Waals radii of H and Cl atoms is 3.0 A.[18]

The value of the angle of rotation θ' corresponding to this minimum separation, calculated with eq 13, comes out to be either 156.5 or 336.5°. Since θ is chosen to be zero when the angle between the vector **b** and the +z axis is greatest, it is clear that the smaller angle is associated with the minimum separation when **b** points to the hydroxyl H atom. On the other hand, the C–O–H group moment vector is on the opposite side of the axis of rotation from the O–H bond vector; hence when **b** assumes the direction of the group moment, the value of θ to be used in computing the components of **b** according to eq 5, 6, and 7 will be 336.5° for the minimum and 156.5° for the maximum separation. When evaluated for $\phi = 63°$ and for the the components of **a** describing the direction of the *exo* bond at C_2, the components of **b'** turn out to be (+0.809, +0.412, −0.420) and (−0.327, +0.164, +0.930) for the minimum and maximum separation conformations, respectively. Vectorial combination of these components with the contributions of the C–Cl bond at C_8 and of the hydrocarbon itself yields

resultant moments of 2.81 and 2.66 D.[19] According to eq 16, the total range of μ values is from 1.93 to 3.36 D. There will therefore be two conformations of the hydroxyl H atom for which the calculated moments will equal that of the experimentally determined value of 2.50 D.; these are for the hydroxyl H being nearly at its minimum and maximum separations from the Cl atom. However, since the free rotation value is 2.74 D. and since the uncertainties in the calculated and observed moments are both about 0.1 D., it is clear that no definite conclusion can be drawn as to whether rotation is free or whether the rotatable group assumes some particular conformation.

3. An example of a molecule containing several rotatable groups is furnished by 1,3,5-trimethoxybenzene, whose moment is 1.8 D.[20] If the molecule is placed in a coordinate system so that the origin is at the center of the benzene ring and the y axis passes through C_1, the components of **a** for the three rotation axes are (0, 1, 0), ($\frac{1}{2}\sqrt{3}$, $-\frac{1}{2}$, 0), and ($-\frac{1}{2}\sqrt{3}$, $-\frac{1}{2}$, 0); these axes coincide with the three C–O bond vectors directed from C_1, C_3, and C_5, respectively. Incorporation of these components into eq 10 leads to 1.85 D. for the rms value of μ when the CH_3–O bond moment ($= m_i = m_j$) is taken to be 1.14 D.[21] and ϕ, the oxygen valency angle, is 110°.[21]

The good agreement between the calculated and the observed moments might lead one to infer that the methoxy groups are freely rotating. It would be unwise to conclude this, however, as the following calculation shows. If, instead of free rotation, the molecule were constrained to assume only those conformations in which the methyl groups are coplanar with the benzene ring, the calculated moment comes out to be essentially the same as the free rotation value. Of the eight coplanar conformers, two have zero moments and the other six have moments of 2.14 D. If all eight conformations are equally probable, the rms value of μ is 1.86 D., which is to be compared with the free rotation value of 1.85 D.[22]

It can be concluded from the illustrations given above that dipole moment data may be of use in ruling out the possibility of essentially free rotation of groups in molecules containing polar substituents, but not in providing evidence that it does exist.

(18) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, pp 226, 229, 260, 453.

(19) The angle between the C–Cl bond vector and b' would appear by inspection and indeed can be calculated to be greater for the conformer in which the H–Cl distance is a minimum. This would suggest that the moment of this conformer should be less than that of its opposite; actually it is greater. Hence, it should be recognized that erroneous conclusions can be drawn, even regarding which resultant is larger, when making superficial estimates of the resultant of several vectors in three-dimensional frameworks.

(20) J. W. Williams, *Physik. Z.*, **29**, 683 (1928).

(21) C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill Book Co., Inc., New York, N. Y., 1955, p 301.

(22) The agreement between the moment calculated for free rotation and that calculated for the planar conformations holds only for a valency angle of 110°.