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On the Optical Activity of Ketones Perturbed in Front Octants

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Abstract: The octant rule has been widely applied to interpret the optical activity of asymmetric ketones in the 3000-A region. However, very little data is available to ascertain if the sign of the Cotton effect should really change when a substituent is shifted from a back octant to the corresponding front octant. In the present note we review within the one-electron theory different models for the optical activity of the n–π^* transition in ketones. It is shown that some of these models predict an octant rule, others a quadrant rule, depending on the influence of the substituents and on the symmetry of mixing orbitals. In reality one must expect a superposition of octant rule and quadrant rule behavior. To decide theoretically and unambiguously which of these different possibilities is predominant requires more accurate wave functions than have been used until now. Although the octant rule has proved its usefulness when applied to ketones perturbed in rear octants, it must be applied with caution to front-octant perturbations. In the latter case the sign of the Cotton effect predicted by the octant rule is opposite to the sign predicted by the quadrant rule.

The "octant rule"[2] has been widely applied to interpret the optical activity of asymmetric ketones in the 3000-A region. It is well established that the optical activity at this wavelength is mainly due to the n → π^* transition, under the perturbing influence of an appropriate environment. The "octant rule" states that "the sign of the contribution which a given perturbing atom at point $P(x,y,z)$ makes to anomalous rotatory dispersion (of the ketone) will vary as the sign of the product (xyz) of its coordinates." There are thus three perpendicular planes where the contribution to the rotatory dispersion should vanish. The point of intersection of these planes is assumed to lie on the C–O axis, between the two atoms. As was already pointed out in footnote 4 of the original paper,[2] two of the planes are symmetry planes of the isolated keto group, but the third one which bisects the C–O bond is not. It is not strictly a plane and is related to the second nodal surface of the π^* orbital. From a symmetry viewpoint one may therefore question the existence of this latter surface in relation to the sign of the Cotton effect.

There is, as yet, little data on the rotatory dispersion of ketones perturbed by substituents located in front octants.[3] One cannot, at present, experimentally prove or disprove the correctness to the octant rule for these cases. The prediction that the sign of the optical activity should change as the substituent moves along the z axis and passes the region between the C and O atom remains a hypothesis. Based on the one-electron theory of optical activity[4] we want to reconsider the simplest quantum mechanical models for the optical activity of ketones in the 3000-A region, with particular attention to the change of sign along the bond axis.

Rotational Strength

The rotational strength of the n–π^* transition is given by the expression

$$R_{n\pi^*} = Im\{\langle n|\vec{r}|\pi^*\rangle\langle\pi^*|\vec{m}|n\rangle\} \qquad (1)$$

In the unperturbed ketone the electric dipole component $\langle n|\vec{r}|\pi^*\rangle$ is zero and hence also $R_{n\pi^*}$. The magnetic moment $\langle\pi^*|\vec{m}|n\rangle$ lies along the C–O axis. In the asymmetrically perturbed ketone n and π^* mix with other orbitals in such a way as to lead to a nonvanishing component of the electric transition moment along the C–O axis. In general this may be expressed as

$$n' = n + \varphi_1 + \delta_1 D \qquad (2a)$$

$$\pi^{*\prime} = \pi^* + \varphi_2 + \delta_2 D \qquad (2b)$$

φ_1 and φ_2 are appropriate linear combinations of atomic wave functions centered on the C and O atom of the keto group, while D refers to orbitals belonging to external substituents, δ_1 and δ_2 being coefficients. We note that

$$\pi^* = C_{\pi^*,C}2p_{x,C} + C_{\pi^*,O}2p_{x,O};\ n \equiv 2p_{y,O}$$

The matrix element of the electric transition moment becomes

$$\langle n'|\vec{r}|\pi^{*\prime}\rangle = \langle n|\vec{r}|\varphi_2\rangle + \langle\varphi_1|\vec{r}|\pi^*\rangle + \delta_2\langle n|\vec{r}|D\rangle + \delta_1\langle D|\vec{r}|\pi^*\rangle \qquad (3)$$

The first two terms represent transitions within the keto group itself, whereas the latter two terms correspond to charge-transfer components.

Depending on the nature of the asymmetric environment the perturbation leading to optical activity may be considered either (i) as an electrostatic "distortion" of the keto orbitals due to incomplete shielding of the nuclei of the substituents, or (ii) as a mixing of the keto orbitals with the external substituent orbitals due to overlap effects. The relative magnitude of the four terms in expression 3 will then of course depend on the

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[1] Most of this work was carried out while the author was at CIBA Ltd., Basel, Switzerland.

[2] W. Moffitt, R. B. Woodward, A. Moscowitz, W. Klyne, and C. Djerassi, *J. Am. Chem. Soc.*, 83, 4013 (1961).

[3] C. Djerassi and W. Klyne, *J. Chem. Soc.*, 2390 (1963).

[4] W. J. Kauzmann, J. E. Walter, and H. Eyring, *Chem. Rev.*, 26, 339 (1940).

relative importance of i and ii, as well as on the geometric properties governing the matrix elements of the electric dipole operator. We may assume, throughout our work, that the magnitude of $\langle\pi^{*\prime}|\vec{m}|n'\rangle$ remains little affected by changes in the asymmetric environment.

Cases with Negligible Charge Transfer

I. Electrostatic Perturbation. We shall not make any further assumptions on the analytic form of the perturbing potential V_D arising from the substituent D than that it decreases monotonically toward infinity and that it has the same sign throughout space.

(a) We shall first assume that the main effect of V_D is the admixture of higher C- and O-centered atomic orbitals φ_2 to π^*. If the isolated keto group is of symmetry C_{2v}, then π^* transforms like B_1, whereas n transforms like B_2. To allow for a nonvanishing component of the electric dipole transition moment along the z axis φ_2 must itself transform like B_2, because z transforms like A_1. Consequently, φ_2 may be, for instance, a linear combination of p_y or of d_{yz} orbitals. Moscowitz[5] has considered the case where $\varphi_1 = 0$, $\delta_1 = 0$, $\delta_2 = 0$, and $\varphi_2 = \lambda_{2,O}3d_{yz,O} + \lambda_{2,C}3d_{yz,C}$. By first-order perturbation theory and neglecting integrals between orbitals on different atoms

$$\lambda_{2,O} = C_{\pi^*,O}\langle 2p_{x,O}|V_D|3d_{yz,O}\rangle/\Delta E_O$$

$$\Delta E_O \approx E(2p_{x,O}) - E(3d_{yz,O})$$

$$\lambda_{2,C} = C_{\pi^*,C}\langle 2p_{x,C}|V_D|3d_{yz,C}\rangle/\Delta E_C$$

$$\Delta E_C \approx E(2p_{x,C}) - E(3d_{yz,C})$$

From (3) it is immediately apparent that the relative sign of $\langle n'|\vec{r}|\pi^{*\prime}\rangle$, depending on the position of the substituent, is given by the signs and relative magnitudes of $\lambda_{2,O}$ and $\lambda_{2,C}$. As was shown by Moscowitz and as may be seen in Figure 1, this situation indeed leads to an octant rule. The rotational strength vanishes on the surface bisecting the C–O bond and containing all points where

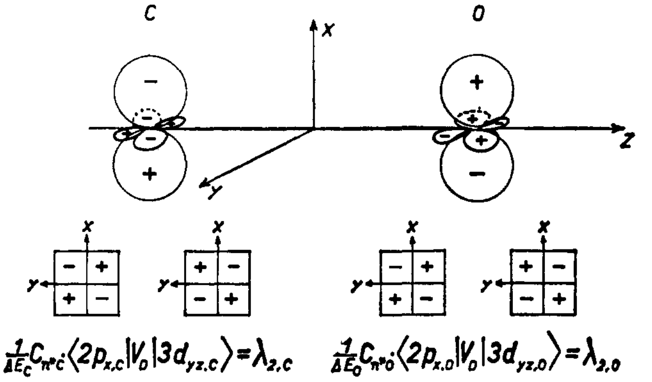

Figure 1. The π^* orbital and the small $3d_{yz}$ components which the perturbation adds to it. Between the two atoms $\langle n'|\vec{r}|\pi^{*\prime}\rangle$ changes sign. The signs of $\lambda_{2,C}$ and of $\lambda_{2,O}$ before and behind the C and O atom, respectively, are indicated.

$$\lambda_{2,O}\langle n|\vec{r}|3d_{yz,O}\rangle = -\lambda_{2,C}\langle n|\vec{r}|3d_{yz,C}\rangle$$

On the other hand, as $\langle n|\vec{r}|3p_{y,O}\rangle = 0$, the admixture of $3p_y$ orbitals to π^* is certainly of much lesser importance in making the n–π^* transition electric dipole allowed. However, it is interesting to note that such a mechanism would not lead to an octant rule, but to a quadrant rule instead.

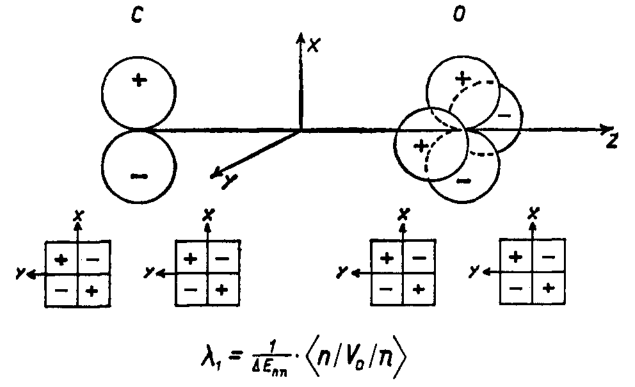

Figure 2. The π and n orbital. The sign of $\langle n'|\vec{r}|\pi^{*\prime}\rangle$ is in this case determined by the sign of λ_1, as indicated.

(b) The admixture of a contribution of type π to the n orbital through the influence of the perturbation V_D cannot be considered to be negligible. This mechanism was already considered by Schellman and Oriel in their study of the Cotton effect in helical polypeptides due to the n–π^* transition.[6] We set $\varphi_1 = \lambda_1\pi$, *i.e.*

$$n' = n + \lambda_1\pi,\ \lambda_1 = \langle n|V_D|\pi\rangle/\Delta E_{n\pi},\ \Delta E_{n\pi} = E_n - E_\pi$$

from which follows $\langle n'|\vec{r}|\pi^{*\prime}\rangle \approx \lambda_1\langle\pi|\vec{r}|\pi^*\rangle$. Both the strength of the π–π^* transition and the relative magnitude of the denominator $\Delta E_{n\pi}$—as compared with ΔE_O or ΔE_C, in spite of the fact that only rough estimates of these latter quantities are possible—speak in favor of n–π mixing. We notice that the sign of $R_{n\pi^*}$ is fixed by the sign of λ_1, which transforms like the sign of the product of the orbitals n and π (see Figure 2).

It becomes apparent that there is no plane bisecting the C–O axis on which $R_{n\pi^*}$ vanishes. Consequently we are, in this case, led to a quadrant rule, as Schellman and Oriel noted.

II. Overlap Perturbation. We consider a ketone perturbed by an s-type orbital. The orbital D of the substituent, which overlaps and consequently mixes with the keto orbitals n and π, is considered for simplicity to be nodeless and to resemble an s function in the way in which it interacts. Matrix elements of the perturbation are assumed to be proportional to the corresponding overlap integrals. Of course λ_1 vanishes to first order, but to second order one finds

$$n' = n + \lambda'_1\pi$$

and

$$\lambda_1' = \frac{\langle n|H_D|D\rangle\langle D|H_D|\pi\rangle}{\Delta E_{nD}\Delta E_{n\pi}} \approx \mu^2\frac{S_{nD}S_{D\pi}}{\Delta E_{nD}\Delta E_{n\pi}}$$

μ being a constant of proportionality. The product $S_{nD}S_{D\pi}$ transforms again like the product of the wave functions nπ and leads accordingly to a quadrant rule for $R_{n\pi^*}$.

It is interesting that the sign of $R_{n\pi^*}$ also depends on

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(5) A. Moscowitz, *Advan. Chem. Phys.*, 4, 67 (1962).

(6) J. A. Schellman and P. Oriel, *J. Chem. Phys.*, 37, 2114 (1962); J. A. Schellman, *ibid.*, 44, 55 (1966).

Table I. Determination of the Sign of $R_{n\pi^*}$ by the Charge-Transfer Model in Three Regions of Space Following the z Axis. Behind C and before O, $R_{n\pi^*}$ Tends to Have the Same Sign. $P_C \equiv 2p_{z,C}$, $P_O \equiv 2p_{z,O}$, $C_{\pi^*,O} \equiv C_O$, $C_{\pi^*,C} \equiv C_C$

x	y	$C_C\langle P_C\|D\rangle$	$C_O\langle P_O\|D\rangle$	$\langle n\|\vec{r}\|D\rangle$	$\delta_2\langle n\|\vec{r}\|D\rangle$	$\langle n\|D\rangle$	$C_C\langle P_C\|\vec{r}\|D\rangle$	$C_O\langle P_O\|\vec{r}\|D\rangle$	$\delta_1\langle \pi^*\|\vec{r}\|D\rangle$	$R_{n\pi^*}$
Location of D. Space in back of C: $\|\langle P_C\|D\rangle\| > \|\langle P_O\|D\rangle\|$										
+	+	+	−	−	−	+	−	+	−	−
+	−	+	−	+	+	−	−	+	+	+
−	+	−	+	−	+	+	+	−	+	+
−	−	−	+	+	−	−	+	−	−	−
Space between C and O: Region where $\|\langle P_C\|D\rangle\| \approx \|\langle P_O\|D\rangle\|$										
+	+	+	−	−	Undet	+	+	+	+	+
+	−	+	−	+	Undet	−	+	+	−	−
−	+	−	+	−	Undet	+	−	−	−	−
−	−	−	+	+	Undet	−	−	−	+	+
Space in front of O: Region where $\|\langle P_C\|D\rangle\| < \|\langle P_O\|D\rangle\|$										
+	+	+	−	+	−	+	+	−	−	−
+	−	+	−	−	+	−	+	−	+	+
−	+	−	+	+	+	+	−	+	+	+
−	−	−	+	−	−	−	−	+	−	−

ΔE_{nD}. This might furnish a rough explanation for the fact that substituents D with different ionization potentials (for instance, fluorine and chlorine) may lead to a rotational strength of different sign in the same quadrant. Of course, this conclusion rests upon the assumption that the influence of a halogen atom may be described by an s-type perturbation and presupposes that our Hückel-type energies ΔE_{nD}, $\Delta E_{n\pi}$ may be significantly correlated with the ionization potential of the substituent.

As the overlap perturbation discussed here is of second order, one may assume it to be less important than the first-order electrostatic effect. Such a comparison requires a detailed estimate of $\langle n|V_D|\pi\rangle$ *vs.* $\mu^2 S_{nD}S_{D\pi}/\Delta E_{nD}$ for a particular case. This lies beyond the scope of this present work.

Cases with Predominant Charge Transfer

The idea that it is essentially a charge-transfer component which is responsible for the optical activity of the 3000-A carbonyl band has been discussed in a general way by Mason[7] and applied by both Mason and Moscowitz and co-workers[8,9] to unsaturated ketones. With this model the sign of the rotational strength is not only determined by the sign of coefficients in the wave function, *i.e.*, δ_1 and δ_2, but also by the transformation properties of the projections of the vectors $\langle D|\vec{r}|\pi^*\rangle$ and (or) $\langle n|\vec{r}|D\rangle$ onto the z axis, *i.e.*, onto $\langle n|\vec{m}|\pi^*\rangle$. The rotational strength for the n–π* transition is given by the expression

$$R_{n\pi^*} = Im\{[\delta_2\langle n|\vec{r}|D\rangle + \delta_1\langle D|\vec{r}|\pi^*\rangle]\langle n|\vec{m}|\pi^*\rangle\}$$

with

$$\delta_2 = \langle \pi^*|H_D|D\rangle/\Delta E_{\pi^*D} \approx \mu\{C_{\pi^*,O}\langle 2p_{z,O}|D\rangle + C_{\pi^*,C}\langle 2p_{z,C}|D\rangle\}/\Delta E_{\pi^*D}$$

$$\delta_1 = \langle n|H_D|D\rangle\Delta E_{nD} \approx \mu\langle n|D\rangle/\Delta E_{nD}$$

We shall here not be concerned with unsaturated ketones and we assume, as in the cases with negligible charge transfer, that the wave function of D is of idealized simplicity (s type), namely, that the relative sign of the overlap integrals $\langle 2p_{y,O}|D\rangle$ and $\langle 2p_z|D\rangle$ are solely determined by the signs of n and $2p_z$, respectively, and the position of the substituent orbital D. The sign of the projection of $\langle n|\vec{r}|D\rangle$ onto z is then given by the sign of the product of the overlap integral $\langle n|D\rangle$ and the projection of the position vector $\vec{r}_{OD}$ onto z, $\vec{r}_{OD}\vec{k}$ (see Appendix). Similar considerations are applicable to $\langle D|\vec{r}|\pi^*\rangle$. The sign of $R_{n\pi^*}$ is best assessed with help of Table I. Following the z axis, space is subdivided into a part in back of the C atom, a part between the C and O atoms, and a part in front of the O atom. In the part of space in back of the C atom the matrix elements between D and 2 $p_{z,C}$ predominate. In front of O we find a region where the relative sign of $R_{n\pi^*}$ is determined by the sign of the matrix elements between D and $2p_{z,O}$. One must, of course, remember that $C_{\pi^*,C}$ and $C_{\pi^*,O}$ have opposite signs. It must also be noted that since $\langle 2p_{z,O}|D\rangle$ will in general be smaller than $\langle 2p_{z,C}|D\rangle$ at comparable distances, there may be some points even in front of O where $C_{\pi^*,C}\langle 2p_{z,C}|D\rangle$ is the dominating term in δ_2. Nevertheless, the general conclusion is that both $\delta_2\langle n|\vec{r}|D\rangle$ and $\delta_1\langle \pi^*|\vec{r}|D\rangle$ tend to have the same sign in back of C and in front of O. We do not, therefore, have an octant rule, but again, rather a quadrant rule with undetermined signs (depending on the relative magnitude of the different terms contributing) for $R_{n\pi^*}$ in the intermediate region. The absolute signs of $\delta_2\langle n|\vec{r}|D\rangle$ and $\delta_1\langle \pi^*|\vec{r}|D\rangle$ are chosen arbitrarily, but they are irrelevant to our argument.

Conclusions

Within the framework of the simplest one-electron theory we critically compare different mechanisms to explain the optical activity of ketones. As we have seen, the influence of the substituent(s) may be viewed as an electrostatic or as an overlap effect.

If we consider the ketone as a symmetric chromophore perturbed by an asymmetric environment, we may be led to an octant rule or to a quadrant rule. Schellman and Oriel showed that from a group theoretical point of view quadrant rule behavior is more fundamental. On the other hand, Moscowitz has had considerable success in correlating a model based on π^*–$3d_{yz}$ mixing—and consequently predicting an octant rule—with experi-

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[7] S. F. Mason, *Mol. Phys.*, **5**, 343 (1962); *Quart. Rev.* (London), **17**, 20 (1963).

[8] K. Mislow, M. Glass, A. Moscowitz, and C. Djerassi, *J. Am. Chem. Soc.*, **83**, 2771 (1961).

[9] A. Moscowitz, K. Mislow, M. Glass, and C. Djerassi, *ibid.*, **84**, 1945 (1962).

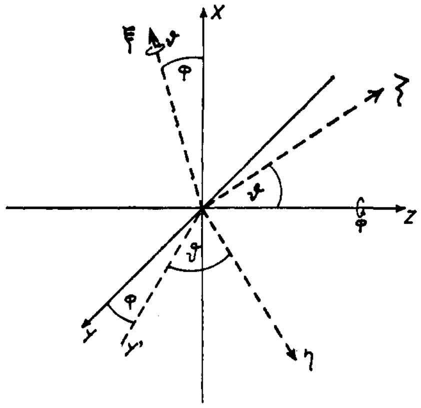

Figure 3. The transformation of x, y, z to ξ, η, and ζ.

mental data for saturated ketones. However, in all compounds examined the perturbation was in back octants.

The optically active ketone may also be viewed as an inherently dissymmetric system, in which the keto orbitals mix with the substituent orbitals, leading to charge-transfer transitions. Such an approach was followed, even for saturated ketones, by Mason. In the present note we have also examined this model from the point of view of front-octant perturbations. Within our simplifying assumptions the model favors a quadrant rule. However, the result depends strongly on the relative magnitude of certain overlap integrals.

A possible superposition of quadrant rule and octant rule behavior may lead to a situation where a substituent has a strong influence on the rotational strength if it is located in, say, back octants, but a relatively small effect if it is in front octants.

An unambiguous prediction of the optical activity of asymmetric ketones requires detailed calculations based on more accurate wave functions than the ones that have been used until now. It might be of great interest to have additional data on ketones perturbed in front octants. This experimental evidence might help in refining the theory.

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Appendix

We wish to prove that the sign of the projection of $\langle \mathrm{n}|\vec{r}|\mathrm{D}\rangle$ onto the C–O axis (z axis) depends on the position of the substituent D in the same way as the sign of the product of the overlap integral $\langle \mathrm{n}|\mathrm{D}\rangle$ and the projection of the position vector $\vec{r}_{\mathrm{OD}}$ onto that axis. We consider two coordinate systems x,y,z and ξ,η,ζ centered in the O atom and having unit vectors $\vec{i}$, $\vec{j}$, $\vec{k}$ and $\vec{\xi}$, $\vec{\eta}$, $\vec{\zeta}$, respectively. These unit vectors are related by the equations

$$\vec{\xi} = \cos\phi\,\vec{i} + \sin\phi\,\vec{j}$$

$$\vec{\eta} = -\sin\phi\cos\vartheta\,\vec{i} + \cos\phi\cos\vartheta\,\vec{j} + \sin\vartheta\,\vec{k}$$

$$\vec{\zeta} = \sin\phi\sin\vartheta\,\vec{i} - \cos\phi\sin\vartheta\,\vec{j} + \cos\vartheta\,\vec{k}$$

It is assumed that $\vec{\zeta}$ coincides with $\vec{r}_{\mathrm{OD}}$. Thus the position of the substituent D with respect to the keto group is characterized by the Eulerian angles ϕ and ϑ. The angle ϕ goes from 0 to 2π and corresponds to a counterclockwise rotation about the z axis, the angle ϑ has the range 0 to π and refers to a similar rotation about the ξ axis (see Figure 3).

It is convenient to look at $\langle \mathrm{n}|\vec{r}|\mathrm{D}\rangle$ not in the dipole vector, but in the dipole velocity form $\langle \mathrm{n}|\vec{p}|\mathrm{D}\rangle$. In the ξ,η,ζ system one may write

$$\langle \mathrm{n}|\vec{p}|\mathrm{D}\rangle = c[n_\xi a\vec{\xi} + n_\eta a\vec{\eta} + n_\zeta b\vec{\zeta}]$$

where

$$a \equiv \langle 2\mathrm{p}_\xi|\partial/\partial\xi|\mathrm{D}\rangle \equiv \langle 2\mathrm{p}_\eta|\partial/\partial\eta|\mathrm{D}\rangle; \quad b \equiv \langle 2\mathrm{p}_\zeta|\partial/\partial\zeta|\mathrm{D}\rangle$$

and c is a constant. n_ξ, n_η, and n_ζ are the projections of $2\mathrm{p}_{y,\mathrm{O}}$, *i.e.*, the n orbital, onto the axes ξ, η, and ζ. Matrix elements such as $\langle 2\mathrm{p}_\xi|\partial/\partial\eta|\mathrm{D}\rangle$ vanish because of the assumed s symmetry of D. We find $n_\xi = \sin\phi$, $n_\eta = \cos\phi\cos\vartheta$, $n_\zeta = -\cos\phi\sin\vartheta$; consequently

$$\langle \mathrm{n}|\vec{p}|\mathrm{D}\rangle = c[\vec{i}\{\sin\phi\cos\phi\sin^2\vartheta\,(a-b)\} + \vec{j}\,\{a - \cos^2\phi\sin^2\vartheta\,(a-b)\} + \vec{k}\,\{\cos\phi\sin\vartheta\cos\vartheta\,(a-b)\}]$$

Looking at the $\vec{k}$ component, it is easy to verify that the sign of the product $\cos\phi\sin\vartheta\cos\vartheta$ changes in the same way, according to the position of the substituent D, as the sign of the product $\langle \mathrm{n}|\mathrm{D}\rangle(\vec{r}_{\mathrm{OD}}\vec{k})$.