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Rotation of Polar Groups in Organic Compounds

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The problem of the intramolecular rotation of polar groups in organic compounds about a single bond was first attacked theoretically by Williams[1] on the assumption that such rotation is perfectly free. He obtained for the average electric moment of a molecule containing two similar polar groups rotating about a common axis the relation

$$\bar{\mu} = \sqrt{2}m \sin \vartheta \tag{1}$$

where m is the magnitude of the group moments and ϑ is the angle the moments make with the axis of rotation. To make this equation fit the experimental values for the ethylene dihalides, $X{\cdot}CH_2{\cdot}CH_2{\cdot}X$, it was necessary to assume considerable distortion of ϑ from the normal value for the tetrahedral carbon atom. This distortion was attributed to the repulsive forces between the polar groups.

It is more reasonable to suppose that any repulsive forces would result in a more or less pronounced restriction of the rotation of the groups. Meyer[2] treated the problem from this point of view. By taking into account the mutual potential energy of the group dipoles, he showed that on the classical theory the right member of equation (1) should be multiplied by the factor $(1 - X)$, where

$$X = \frac{\alpha/(kT) + \beta/(kT)^2 + \gamma/(kT)^3 + \dots}{m + n/(kT) + o/(kT)^2 + p/(kT)^3 + \dots} \tag{2}$$

In this equation, k is the Boltzmann constant, T is the absolute temperature and the coefficients are determined by the dimensions of the molecule. As pointed out by Greene and Williams,[3] this result means that to a second approximation the plot of molar polarization against the reciprocal of the absolute temperature should be a parabola rather than the straight line required by the theory of Debye[4] for molecules having a constant dipole moment. These authors and Zahn[5] have found that the results of measurements on the ethylene dihalides and on diacetyl, $CH_2{\cdot}CO{\cdot}CO{\cdot}CH_3$, in the vapor state are in agreement with this prediction.

Zahn and others[6] have suggested that in some cases, at least, it may be necessary to quantize the intramolecular rotation of polar groups. This should be particularly true with molecules in which the dipole interactions are comparatively large. Smyth, Dornte and Wilson[7] have investigated this quantization in the case of ethylene dichloride, and have shown that

(1) Williams, *Z. physik. Chem.*, **A138**, 75 (1928).

(2) Meyer, *ibid.*, **B8**, 27 (1930).

(3) Greene and Williams, *Phys. Rev.*, **42**, 119 (1932).

(4) Debye, "Polar Molecules," Chemical Catalog Company, Inc., New York, 1929, p. 37.

(5) Zahn, *Phys. Rev.*, **38**, 521 (1931); **40**, 291 (1932).

(6) *Cf.* Eyring, *ibid.*, **39**, 746 (1932).

(7) Smyth, Dornte and Wilson, THIS JOURNAL, **53**, 4242 (1931).

the energy levels are so close together that the quantum treatment should not constitute a significant improvement over Meyer's classical analysis. The method they followed would have involved the use of the so-called Mathieu functions in the actual calculation of the electric moment. The theory of these functions is in such a state of development that such calculations, carried to temperatures as high as 300°K., would necessitate an amount of tedious labor out of all proportion to the accuracy of the original assumptions or the results that might be obtained. It will be shown in the present paper that a simple change in the form of the potential energy function used avoids the introduction of the troublesome Mathieu functions, the easily handled Hermite functions entering in their place. The results obtained are entirely in accord with experimental observations and with the qualitative predictions of Smyth, Dornte and Wilson. The present calculations have been carried out for diacetyl rather than for ethylene dichloride, since the smaller moments of inertia of the rotating groups should lead to greater deviations from the classical theory.

Electric Moments.—Suppose m_1, m_2, represent the components of the rotating group moments perpendicular to the common axis of rotation, m_3 the sum of the components of all the group moments parallel to the axis, and φ the angle between m_1 and m_2. The square of the resultant moment of the molecule is given by

$$m^2 = m_1^2 + m_2^2 + m_3^2 + 2m_1m_2 \cos \varphi \tag{3}$$

The mean square moment of the molecules having intramolecular rotational energy ϵ_i is then

$$\bar{\mu}_i^2 = \int_0^{2\pi} m^2\psi_i^2 d\varphi \tag{4}$$

ψ_i is the normalized wave function corresponding to this energy level. It is assumed that the other modes of motion of the molecules or the groups within them have no appreciable effect on the rotation of the polar groups, or on the magnitudes or positions of the group dipoles. The mean square moment at any temperature is

$$\bar{\mu}^2 = \Sigma p_i \bar{\mu}_i^2 \, e^{-\Delta\epsilon_i/kT} / \Sigma p_i \, e^{-\Delta\epsilon_i/kT} \tag{5}$$

where $\Delta\epsilon_i = \epsilon_i - \epsilon_0$ and p_i is the quantum weight of the i^{th} state.

Potential Energy Function.—Following Smallwood and Herzfeld[8] and Smallwood,[9] the individual group moments have been assumed to lie along the valence bonds and to be located at the circumferences of the atoms involved. These assumptions differ somewhat from the model used by Meyer. Smyth, Dornte and Wilson have shown that the two methods of locating the group moments lead to values of the potential which are in qualitative agreement with each other in the case of ethylene dichloride.

Two dipoles, $m_1 = q_1d_1$, $m_2 = q_2d_2$, separated from each other by a

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(8) Smallwood and Herzfeld, THIS JOURNAL, **52**, 1919 (1930).

(9) Smallwood, *ibid.*, **54**, 3048 (1932).

distance D large compared to d_1 and d_2 have a mutual potential energy given by

$$V = (-m_1m_2/D^3)(2\cos\eta_1\cos\eta_2 - \sin\eta_1\sin\eta_2\cos\chi) \qquad (6)$$

Here η_1, η_2 are the angles between the dipoles and the line joining them, and χ is the angle between their projections in a plane perpendicular to this line. These quantities may be expressed as functions of the angle φ of equation (3); expansion of the resulting expression for V about the position of minimum potential energy, φ_0, gives

$$V = a_0 + a_2(\varphi - \varphi_0)^2 + a_4(\varphi - \varphi_0)^4 + \ldots \qquad (7)$$

where the coefficients are rather complicated functions of the molecular dimensions, etc. Their values for diacetyl and formic acid, HCOOH, are given in Table I; in each case the interactions included in the calculations and the value of φ_0 are indicated. The molecular dimensions and group moments used were those given by Smallwood.[9] Polarization effects were neglected. Smyth, Dornte and Wilson expanded the potential function for ethylene dichloride in a Fourier series, and in their calculations neglected the terms after the first two. The Fourier expansion for diacetyl is as follows

TABLE I

COEFFICIENTS (ERGS × 10^{14}) IN THE EXPANSION OF THE POTENTIAL ENERGY FUNCTION

Substance	a_0	a_2	a_4	a_6	Interactions included	φ_0
Diacetyl	17.7	7.17	−1.23	0.25	C:O—C:O; C:O—C·H; C·H—C·H	π
Formic acid	−40.7	9.19	−2.33	0.49	C:O—O·H; C·H—O·H	0

$$V = (30.82 + 13.11\cos\varphi + 0.28\cos 2\varphi + 0.27\cos 3\varphi + \ldots) \times 10^{-14}$$

Wave Equation.—The wave equation for the intramolecular rotation is separable by well-known methods. The equation involving the variable φ is found to be

$$\frac{d^2\psi}{d(\varphi - \varphi_0)^2} + \frac{8\pi^2 I}{h^2}\left[\epsilon - \Sigma a_{2j}(\varphi - \varphi_0)^{2j}\right]\psi = 0 \qquad (8)$$

I is the reduced moment of inertia, $I_1I_2/(I_1 + I_2)$, and $I_i = M_ir_i^2\sin^2\vartheta_i$, where M_i is the mass of the i^{th} rotating group, ϑ_i is the angle between the valence bond to this group and the axis of rotation, and r_i is the distance along the valence bond from the axis to the center of mass of the group. (The group is assumed to be symmetrical about the extension of the valence bond.)

In general, equation (8) has to be treated by approximate methods. For example, if the terms in the potential function for which $j > 1$ are small enough, they may be taken as perturbation terms, so that the wave equation for the unperturbed system is simply that of the torsional harmonic oscillator. If the interaction is sufficiently strong, the wave functions and energy values may be identified with those of the linear oscillator, since neglect of the actual system's periodic nature involves no appreciable error. The first approximation to the true proper functions and values may then be obtained by Schrödinger's method for non-degenerate systems.

Diacetyl.—Zahn[10] has made a careful experimental study of the temperature variation of the electric moment of diacetyl. He found the average value of $(\varphi - \varphi_0)$ to be about 30–40° at moderate temperatures. Calculation shows that even at 600°K. an average error of only 8% will be introduced into the variable part of the potential by neglecting the terms in $(\varphi - \varphi_0)^4$ and $(\varphi - \varphi_0)^6$, and the resulting expression agrees on the average to within 3% with the potential taken in the form $V = c_0 + c_1 \cos \varphi$, the form used by Smyth, Dornte and Wilson in their calculations with ethylene dichloride. To this approximation the wave functions are $\psi_n = (1/N_n)e^{-s^2/2}H_n(s)$, $n = 0, 1, 2, \ldots$, where N_n is the normalizing factor, H_n is the n^{th} Hermitian polynomial, and the variable s is defined by the relations $s = (\varphi - \pi)/a$ and $a^2 = h/2\pi \sqrt{1/2Ia_2}$. The functions ψ_n may be normalized in the same manner as for the linear harmonic oscillator since any contributions to the integrals $\int_{-\infty}^{+\infty} e^{-s^2} H_n^2(s)\,\mathrm{d}s$ corresponding to values of $(\varphi - \pi)$ for which $|\varphi - \pi| > \pi$ are negligible (for diacetyl, $s \approx 5(\varphi - \pi)$). The value of N_n is then $\pi^{1/4}\, 2^{n/2}\, (n!)^{1/2}$. The energy levels corresponding to these wave functions are $\epsilon_n = a^2a_2(2n + 1) + a_0$.

In the variable s, equation (3) for a symmetrical molecule with $m_1 = m_2$ and $m_3 = 0$ becomes

$$m^2 = m_1^2\left(a^2s^2 - \frac{a^4s^4}{12} + \frac{a^6s^6}{360} - \ldots\right) \tag{9}$$

The integrals involved in the calculation of $\overline{\mu}_i^2$ by equation (4) can be expressed very simply as follows

$$\int_{-\infty}^{+\infty} s^2\,\psi_i^2\,\mathrm{d}s = {}^1/_2(2i + 1)$$

$$\int_{-\infty}^{+\infty} s^4\,\psi_i^2\,\mathrm{d}s = {}^3/_4\,(2i^2 + 2i + 1)$$

$$\int_{-\infty}^{+\infty} s^6\,\psi_i^2\,\mathrm{d}s = {}^{15}/_8\,({}^4/_3i^3 + 2i^2 + {}^8/_3i + 1)$$

Using these relations we obtain $\overline{\mu}_i^2$ as a power series in i.

Since the constant a^2 is small, the energy levels are close together, and it is therefore permissible at temperatures not too low to calculate $\overline{\mu}^2$ by replacing the summations in equation (5) by integrals. This is most conveniently accomplished by noting that $i^n\,e^{-\beta i} \approx \int_{i-1/2}^{i+1/2} x^n\,e^{-\beta x}\,\mathrm{d}x$, so that

$$\sum_{i=0}^{\infty} i^n\,e^{-\beta i} \approx \int_{-1/2}^{\infty} x^n\,e^{-\beta x}\,\mathrm{d}x = \frac{(-1)^n\,e\beta/2}{\beta}\left[\frac{1}{2^n} - \frac{n}{\beta 2^{n-1}} + \frac{n(n-1)}{\beta^2\,2^{n-2}} - \ldots + (-1)^n\,\frac{n!}{\beta^n}\right]$$

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[10] Zahn, *Phys. Rev.*, **40**, 291 (1932).

In this way it is readily found, since $p_i = 1$ in the present case, that

$$\bar{\mu}^2 \approx m_1^2 \left[-\frac{a^4}{32} + \left(1 + \frac{5a^4}{576}\right)\frac{kT}{2a_2} - \frac{(kT)^2}{16a_2^2} + \frac{(kT)^3}{192a_2^3} - \dots \right] \quad (10)$$

The accuracy of this method of approximation was tested by numerical calculation for the rather unfavorable case for which $a_2 = 10^{-13}$ and $a^2 = 0.2$. It was found that the value of $\bar{\mu}$ at 200°K. calculated by equation (10) was only 1.5% lower than that obtained by direct evaluation of the summations in equation (5).

It is of interest to compare equation (10) with the results obtainable on the classical theory of Meyer. In cases where the dipole interaction is large, Meyer's method of calculation leading to equation (2) is very tedious because of the slow convergence of the expansion of $e^{-V/(kT)}$. However, when it is possible to write $V = a_0 + a_2(\varphi - \varphi_0)^2$, the calculations can be performed very simply in a different way. For diacetyl the mean square moment is given by

$$\bar{\mu}^2 = \frac{\int m^2 e^{-V/(kT)}\, d\vartheta}{\int e^{-V/(kT)}\, d\vartheta} = 2m_1^2 \left[1 - \frac{\int_{-\infty}^{+\infty} \cos\vartheta\; e^{-a_2\vartheta^2/(kT)}\, d\vartheta}{\int_{-\infty}^{+\infty} e^{-a_2\vartheta^2/(kT)}\, d\vartheta} \right]$$

where $\vartheta = \varphi - \pi$. No appreciable error is made in taking the limits of integration as $-\infty$ and $+\infty$ instead of $-\pi$ and $+\pi$, and the evaluation of the integrals is rendered very much easier. We thus obtain the expression

$$\bar{\mu}^2 = 2m_1^2\,[1 - e^{-kT/(4a_2)}] \quad (11)$$

To compare this with equation (10) we expand the exponential

$$\bar{\mu}^2 = m_1^2 \left[\frac{kT}{2a_2} - \frac{(kT)^2}{16a_2^2} + \frac{(kT)^3}{192a_2^3} - \dots \right] \quad (12)$$

The error caused by neglecting higher terms is about 5% or less at 300°K. The value of a^4 for diacetyl is approximately 0.002, so that equations (10) and (12) are practically identical for this molecule.

It is probable that similar agreement between the classical and wave-mechanical results at temperatures in the neighborhood of 300°K. would be obtained with molecules whose dipole interactions can only be given by expressions containing powers of $(\varphi - \varphi_0)$ up through the fourth or sixth. The treatment in such cases would obviously be very much more difficult. Calculations have been carried through for molecules having comparatively small interactions, such as hydroquinone, p-$C_6H_4(OH)_2$, and terephthalic aldehyde, p-$C_6H_4(CHO)_2$, and the results at temperatures above 200°K. differ in no respect from those obtained on the classical theory. The former substance was treated by perturbation methods, taking as zero order approximation the rotator with one degree of freedom. The potential function for terephthalic aldehyde was taken in the form $V =$

$c_0 + c_1 \cos \varphi$, so that the proper functions were constant multiples of the Mathieu functions of even order.[11,12]

The values of the root mean square moment of diacetyl calculated by equation (11) are plotted against the temperature in Fig. 1, along with the values determined experimentally by Zahn.[10,13] The excellent agreement between the calculated and observed values is to be considered as fortuitous in view of the uncertain nature of the molecular model used, the approximations made in the calculations and the complete neglect of polarization effects, which latter might be expected to be rather important because of the close approach of a carbonyl group to the hydrogens on the methyl group attached to the other central carbon atom at the position of minimum potential.

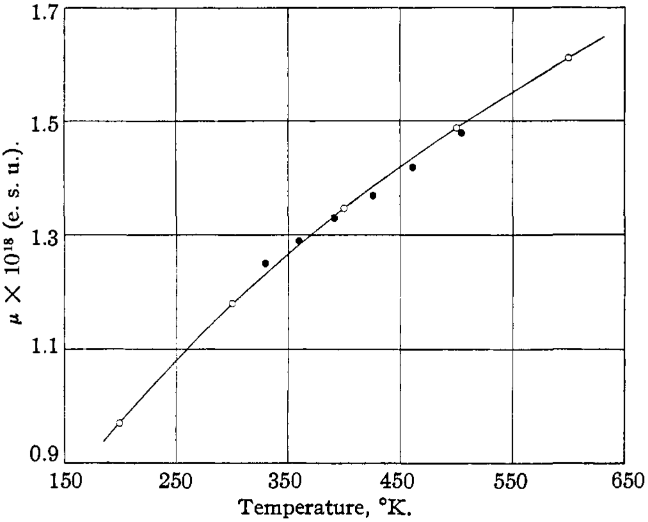

Fig. 1.—Electric moment of diacetyl: ○, calculated by equation (11); ●, observed by Zahn, Ref. 10, p. 293.

Formic Acid.—The term involving $(\varphi - \varphi_0)^4$ in the potential function for formic acid is rather large to be neglected, so that the above treatment was not employed. The resultant moment for this molecule was calculated on the classical theory, using Simpson's rule for the evaluation[14] of the

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(11) *Cf.* Whittaker and Watson, "Modern Analysis," Fourth ed., University Press, Cambridge, 1927, p. 404; Goldstein, *Trans. Cambr. Phil. Soc.*, **23**, 303 (1927); Condon, *Phys. Rev.*, **31**, 891 (1928).

(12) In this case the calculations involving the Mathieu functions were very much easier than they would be with diacetyl or ethylene dichloride since the value of the parameter q occurring in Mathieu's equation

$$(d^2\psi/dx^2) + (4\alpha - 16q\cos 2x)\psi = 0 \quad (x = {}^1/_2\varphi)$$

had the comparatively small value 8.05.

(13) These values reported by Zahn were not calculated by the method recommended by Greene and Williams, Ref. 3. However, this change would make no appreciable difference in the agreement between experiment and theory.

(14) These calculations were facilitated by the convenient table of values of e^{-x} given by Newman, *Trans. Cambr. Phil. Soc.*, **13**, 145–241 (1883).

integrals involved. The mean square moment is given by the relation

$$\bar{\mu}^2 = m_1^2 + m_2^2 + m_3^2 + 2m_1m_2 \frac{\int_0^{2\pi} \cos\varphi\, e^{-V/(kT)}\,d\varphi}{\int_0^{2\pi} e^{-V/(kT)}\,d\varphi} \quad (13)$$

The values of $\bar{\mu}^2$ calculated by this equation are listed in Table II. They fall on the curve

$$\bar{\mu}^2 \times 10^{36} = 1.370 + 3.62 \times 10^{-3}T + 2.9 \times 10^{-8}T^2 - 1.7 \times 10^{-9}T^3 \quad (14)$$

TABLE II

ELECTRIC MOMENT OF FORMIC ACID CALCULATED BY EQUATION (13)

T, °K.	200	300	400	500
$\bar{\mu}^2 \times 10^{36}$ (e. s. u.)	2.08	2.41	2.71	2.98
$\bar{\mu} \times 10^{18}$ (e. s. u.)	1.44	1.55	1.65	1.73

Equation (11) leads to values of $\bar{\mu}$ which range from 3 to 6% lower than those given in Table II.

Meyer[15] arrived at the conclusion that the carboxyl group should show no change of electric moment with temperature in the neighborhood of 300°K. However, he only carried his calculations through a first approximation, which, as he pointed out in discussing ethylene dichloride, is not sufficient in cases where the dipole interactions are large. He then compared the lower limit for the moment calculated in this way with the experimental values for formic[16] and benzoic[17] acids then available. The close agreement led him to believe that rotation is completely frozen out at ordinary temperatures. Zahn[18] has made a careful study of the temperature variation of the dielectric constant of formic acid vapor. He found that the apparent electric moment increases with the temperature, but he was able to account for the observed molecular polarizations by consideration of the partial association of formic acid into double molecules, with the assumption that the single and double molecules have *constant* moments equal to 1.51 and 0.99×10^{-18}, respectively. He used the equations given by Coolidge[19] to calculate the degree of association, and assumed that the constant part of the polarization is doubled on association.

The results in Table II indicate that the assumption of a constant moment for the single molecules is questionable. If one uses for $\bar{\mu}^2$ for the single molecules the values given by equation (14), and assumes a moment equal to zero for the double molecules, one obtains the molecular polarization in the form

$$P = (n_1 + 2n_2)A + n_1(\beta_0/T + \beta_1 + \beta_2 T + \beta_3 T^2) \quad (15)$$

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(15) Meyer, Ref. 2, p. 37.

(16) Wolf, *Physik. Z.*, **31**, 227 (1930).

(17) Williams, *ibid.*, **29**, 174 (1928).

(18) Zahn, *Phys. Rev.*, **37**, 1516 (1931).

(19) Coolidge, THIS JOURNAL, **50**, 2166 (1928).

where n_1, n_2 are the mole fractions of the single and double molecules, respectively. Zahn used the value 8.53 for A. The values of P calculated in this way are given in the second line of Table III. The experimental values of Zahn are listed in the third line.

TABLE III

MOLECULAR POLARIZATION OF FORMIC ACID

T, °K.	344.6	386.9	403.1	423.4
Calcd. by eq. (15) P, cc.	32.69	41.86	44.59	46.14
Observed	41.43	41.40	41.34	41.26

The trend of the calculated values indicates that the assumption of a zero moment for the double molecules is erroneous. The theoretical curve could be made to parallel the experimental curve by assuming a finite moment for the double molecules which *decreases* with increasing temperature. This would be the result of a gradual loosening of the forces holding the two formic acid units away from the anti-parallel position. However, attempts at a quantitative treatment of this effect would not be worth while because of the very limited information concerning the associated molecules.

In conclusion, the author wishes to express his appreciation of the very helpful discussions he has had with Prof. Henry Margenau of the Department of Physics during the course of this work.

Summary

1. In certain cases of strong dipole interaction between polar groups capable of rotation about a single bond in organic molecules, application of quantum methods to the study of the motion of these groups leads to practically the same results as those obtained on the classical theory at temperatures within the range of experimental observations. In one such case, diacetyl, the calculated values of the electric moment agree very well with experiment over a temperature range of 200°.

2. Classical calculations indicate that the electric moment of formic acid should show a considerable temperature variation, which is not in disagreement with experimental observations.

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