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The Ground-State Dipole Moments of *all-trans*- and 9-*cis*-Retinal

Anne B. Myers and Robert R. Birge*

Contribution from the Department of Chemistry, University of California, Riverside, California 92521. *Received October 24, 1980*

Abstract: The dipole moments of *all-trans*-retinal, 9-*cis*-retinal, acrolein, crotonaldehyde, and 2,4-hexadienal are determined from solution dielectric constant measurements by using a modification of the Onsager–Böttcher formalism. The salient feature of our procedure is the use of an ellipsoidal, rather than a spherical, solute cavity. The observed dipole moments of *all-trans*-retinal (5.26 ± 0.16 D) and 9-*cis*-retinal (4.86 ± 0.40 D) are larger than previously published values evaluated by using spherical cavity formalisms due to the importance of solute shape in determining the dielectric behavior of these solute molecules. The observed dipole moments of acrolein (3.07 ± 0.06 D) and crotonaldehyde (3.85 ± 0.06 D) are in better agreement with the vapor-phase values than previously reported solution values determined by using the Debye equation. The dipole moment of 2,4-hexadienal is observed to be 4.68 ± 0.08 D. A detailed error analysis is presented which demonstrates that uncertainties in the experimental determination of ϵ_2^∞, the solute dielectric constant for induced polarization, and the assignment of A_a, the solute ellipsoidal shape factor, are the greatest source of error in experimentally determining the dipole moments of the retinal isomers by using solution dielectric constant measurements.

The dipole moments of the retinal isomers have been calculated theoretically by several molecular orbital methods[1-3] and experimentally determined by using a variety of experimental techniques.[4-7] The values obtained by different theoretical methods vary widely: for example, calculated dipole moments for *all-trans*-retinal range from 2.65[1] to 8.10 D[2]. The dipole moment of *all-trans*-retinal has been experimentally determined by measurement of solution dielectric constants, but two separate investigations were not in agreement: Corsetti and Kohler's value of 4.59 D[6] is substantially higher than Bauer and Carl's value of 4.02 D[7]. Additionally, Bauer and Carl reported that the dipole moment of 11-*cis*-retinal is only 0.13 D lower than that of *all-trans*-retinal. This result is surprising in view of the fact that the predominant conformer of 11-*cis*-retinal in nonpolar solvents is believed to have a 12-*s*-*cis* geometry,[5] which should exhibit a much smaller dipole moment than *all-trans*-retinal.[2]

Corsetti and Kohler used the conventional Debye equation to calculate the dipole moment from their dielectric constant data, whereas Bauer and Carl used the Onsager equation. Both of these equations are based on theories which assume that the polar solute is surrounded by a spherical solvent cavity and that the solute is isotropically polarizable. These are reasonable assumptions for some molecules, but nearly planar, elongated molecules such as *all-trans*-retinal are far from the spherical and should be treated by a theory which takes molecular shape into account. Such theories have been developed by a number of authors,[8-14] and it has been shown that these formalisms generally calculate dipole moments which are closer to the vapor-phase values than those calculated by spherical cavity formalisms. Dipole moments of molecules, which are elongated in the direction of the dipole moment, tend to be underestimated when experimentally determined by using spherical cavity formalisms. *all-trans*-Retinal deviates from a spherical geometry more than the other isomers, so its dipole moment should be the most underestimated. Furthermore, if the other isomers, which are more nearly spherical, actually have smaller dipole moments than all-trans, these differences will not be properly reflected in experimental dipole moments determined by the conventional spherical cavity methods.

In this paper, we determine the dipole moments of *all-trans*- and 9-*cis*-retinal from dielectric constant data by using a modification of the Onsager–Böttcher formalism which takes solute cavity anisotropy into consideration. The same data are also analyzed by using the Debye equation and the spherical cavity Onsager equation, so that we can compare our results more readily with the previously published values. We also report the dipole moments of three of the shorter polyenals (acrolein, croton-

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aldehyde, and 2,4-hexadienal) for comparison.

Experimental Section

Dielectric constant measurements were made by using two different cells. The "large cell" consists of a stainless-steel parallel plate capacitor which fits inside a glass tube. The volume is ~10 mL and the capacitance in air is 115 pF. The "small cell", designed to allow measurements to be made on smaller volumes, consists of a stainless-steel rod which is held inside a slightly larger stainless-steel cylinder by using a tight-fitting Teflon stopper. The diameter of the inner rod is ~8 mm, the clearance between the inner rod and the cylinder wall is ~0.5 mm, and the height is ~8 cm. The volume is ~1.5 mL and the capacitance in air is 54 pF. The cell is filled by introducing solution through a syringe needle soldered into the bottom of the cell until a drop of solution emerges at the tip of a matching needle in the top of the cell. The cell is emptied, flushed with pentane, and dried between solutions. Measurements on acrolein (propenal), crotonaldehyde (*trans*-2-butenal), and *all-trans*-retinal were made in the large cell; measurements on crotonaldehyde, 2,4-hexadienal, *all-trans*-retinal, and 9-*cis*-retinal were made in the small cell. No systematic differences between the two cells were observed.

Capacitances were measured with a B & K Precision Model 820 Capacitance Meter (Dynascan Corp, chicago, Ill). The capacitance meter acts as a counter which measures the time required to charge the capacitor to a potential of 2.5 V and displays the capacitance to 0.1 pF. The spread in successive readings on the same solution is typically no more than ±0.2 pF in the small cell and ±0.1 pF in the large cell. The cells were initially calibrated with argon and five solvents ranging from pentane to benzene; thereafter, the calibration was checked before each day's experiments with at least two solvents. All measurements were made at ambient temperature (22–26 °C).

Measurements were taken at solute volume fractions up to 0.01–0.02 on all of the solutes except 9-*cis*-retinal, for which the maximum volume fraction was only 0.0024. Dielectric constants were measured at five or more concentrations in each solvent for the shorter polyenals. The retinal solutions were prepared from the most concentrated solution by successive dilutions, and three to five concentrations were used. Between 20 and 100 readings of the capacitance meter were taken at each concentration, the average and standard deviation were calculated, and the slope of a plot of dielectric constant against solute volume fraction was determined by weighted linear least squares.[15] When several sets of measurements were taken in the same solvent, the weighted mean[15] of the slopes was used in the dipole moment calculations.

Refractive indices at the sodium D line were measured with a Zeiss Model B refractometer. The calibration of the refractometer was checked with five solvents ranging from acetone to cyclohexane.

The solvents were spectroscopic or reagent grade and were stored under argon after opening. *all-trans*-Retinal (Eastman) and acrolein (propenal) (Eastman) were used without further purification. 9-*cis*-Retinal (Sigma) was recrystallized from petroleum ether (bp 20–40 °C) and hexane before use. The isomeric purity of the retinal isomers was determined to be greater than 98° by using HPLC. *trans*-Crotonaldehyde (*trans*-2-butenal) (Chemical Samples Co) and 2,4-hexadienal (Aldrich) were distilled immediately before use. All manipulations of the retinal isomers were carried out under dim red light.

Calculations

Dipole moments were calculated by a modification of the Onsager equation which treats the polar molecule as a polarizable dipole in the center of an ellipsodal solvent cavity.[14]

$$\mu_{\mathrm{OE}}^2 = \left\{\frac{\bar{a}_2^3 kT}{3[1 + (\epsilon_2^\infty - 1)A_\mathrm{a}]^2}\right\} \times \left\{\frac{[\epsilon_1 + (\epsilon_2^\infty - \epsilon_1)A_\mathrm{a}]^2(2\epsilon_1 + 1)}{[\epsilon_1 + (1 - \epsilon_1)A_\mathrm{a}]\epsilon_1^2}\right\}\left\{\left(\frac{\partial\epsilon}{\partial\phi_2}\right)_{\phi_2=0} + \frac{3\epsilon_1(\epsilon_1 - \epsilon_2^\infty)}{2\epsilon_1 + \epsilon_2^\infty}\right\} \quad (1)$$

The subscript 1 refers to the nonpolar solvent and the subscript 2 to the polar solute. A_a is the elliposidal shape factor, $\bar{a}_2$ is the average solute radius, ϵ_1 is the solvent dielectric constant, ϵ_2^∞ is the solute dielectric constant for induced polarization, and ϕ_2 is the volume fraction occupied by solute. The subscript on μ signifies *Onsager* theory, *ellipsoidal* cavity. This equation follows directly from eq 5.84 of ref 13 and the expressions for the spherical and ellipsoidal cavity reaction field factors and polarizabilities (eq 4.25, 5.63, 4.45, and 5.87 of ref 13). Equation 1 is derived and discussed in a separate paper.[14] We also calculated our dipole moments by using the spherical cavity Onsager equation (obtained from eq 1 by setting $A_\mathrm{a} = {}^1/_3$)

$$\mu_{\mathrm{OS}}^2 = \left[\frac{\bar{a}_2^3 kT}{(\epsilon_2^\infty + 2)^2}\right] \times \left[\frac{(2\epsilon_1 + \epsilon_2^\infty)^2}{\epsilon_1^2}\right]\left[\left(\frac{\partial\epsilon}{\partial\phi_2}\right)_{\phi_2=0} + \frac{3\epsilon_1(\epsilon_1 - \epsilon_2^\infty)}{2\epsilon_1 + \epsilon_2^\infty}\right] \quad (2)$$

and a form of the Debye equation[16]

$$\mu_{\mathrm{D}}^2 = \left[\frac{9\bar{a}_2^3 kT}{(\epsilon_2^\infty + 2)\,(\epsilon_1 + 2)}\right]\left[\frac{(\epsilon_2^\infty + 2)}{(\epsilon_1 + 2)}\left(\frac{\partial\epsilon}{\partial\phi_2}\right)_{\phi_2=0} + \epsilon_1 - \epsilon_2^\infty\right] \quad (3)$$

Values of A_a, the ellipsoidal shape factor, were taken from the tables in ref 14 which were calculated by using 40-point Gaussian quadrature. The axial ratios were estimated from molecular models, with the length of each axis taken to be the maximum length of the molecule (atoms plus van der Waals' radii) in each direction.

The average molecular radius, $\bar{a}_2$, is related to the cavity volume, V_2, by $V_2 = 4\pi\bar{a}_2^3/3$. The cavity volume is related to the density of the pure liquid by $V = M/dN_\mathrm{A}$, where M is the molecular weight, d is the density, and N_A is Avogadro's number, assuming the molecules occupy all available volume. This method was used to determine the cavity volumes of the shorter polyenals, which are liquids at the temperature of measurement. The cavity volumes of the retinal isomers, which are solids at room temperature, were determined from density measurements on solutions of *all-trans*-retinal in hexane. The volume occupied by the solvent was calculated from its weight, with the assumption that the solvent has the same density in dilute solutions as it does in the pure liquid; the remaining volume was assumed to be occupied by the known weight of the solute. The cavity volume, measured at 22 °C, was not corrected for thermal expansions between 22 and 26 °C. We did not have enough 9-*cis*-retinal to provide sufficient accuracy by using this method, so the cavity volume of this isomer was assumed to be equal to that of *all-trans*-retinal.

The solute dielectric constant for induced polarization, ϵ_2^∞, was set equal to the square of refractive index measured at the sodium D line. ϵ_2^∞ is actually slightly larger than n_2^2 because it includes the contribution of atomic as well as electronic polarization. However, the relative contribution of atomic polarization should be quite small for these molecules because of the large electronic polarizabilities associated with the extended π systems. The contribution of atomic polarization in these molecules should be considerably smaller than the 5% of the electronic polarization often used as a general estimate, so the error introduced by neglecting atomic polarization should be quite small. The refractive indices of the retinal isomers were determined from measurements on hexane and cyclohexane solutions by using

$$n_2^2 = \frac{2(\partial n^2/\partial\phi_2)n_1^2 + 3n_1^4}{3n_1^2 - (\partial n^2/\partial\phi_2)} \quad (4)$$

Equation 4 follows directly from eq 1 by setting $\epsilon_2^\infty = n_2^2$ and $\mu = 0$ (at optical frequencies, there is no contribution from atomic polarization or dipole orientation). We have shown previously that eq 4 gives better results for the solute refractive index than simple linear extrapolation of plots of n or n^2 against mole fraction.[14] The refractive index measurements on 9-*cis*-retinal are subject to fairly large uncertainties because of the low solute concentrations. Therefore, an alternative calculation of the dipole moment of 9-*cis*-retinal was made be setting ϵ_2^∞ equal to that of

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Table I. Experimental Parameters Used in Determining the Dipole Moments[a]

solute	ϵ_2^∞	$10^{23}\bar{a}_2^3$, cm^3	A_a	solvent	T, °C	ϵ_1	$\partial\epsilon/\partial\phi_2$
acrolein	1.960	2.65	0.23	hexane	23	1.885	13.27
				benzene	23	2.278	14.91
crotonaldehyde	2.061	3.28	0.19	cyclohexane	23	2.020	17.84
				benzene	24	2.276	17.67
2,4-hexadienal	2.356	4.27	0.14	cyclohexane	24	2.017	19.92
				benzene	23	2.278	19.75
all-trans-retinal	3.234	9.58	0.11	hexane	24	1.884	11.31
				cyclohexane	24	2.017	12.47
9-*cis*-retinal	3.234[b]	9.58	0.16	hexane	26	1.881	12.10
	3.702[c]			cyclohexane	26	2.013	10.27

[a] The parameters are defined in the text (see discussion following eq 1). [b] Assuming 9-*cis*-retinal and *all-trans*-retinal have equal polarizabilities. [c] Obtained from refractive index measurements on solutions of 9-*cis*-retinal in cyclohexane.

Table II. Comparison of Dipole Moments Calculated by Different Formalisms

solute	μ_{OE}[a]	μ_{OS}[b]	μ_D[c]
acrolein	3.07 ± 0.06	2.91 ± 0.06	2.89 ± 0.06
crotonaldehyde	3.85 ± 0.06	3.55 ± 0.08	3.50 ± 0.14
2,4-hexadienal	4.68 ± 0.08	4.12 ± 0.13	4.17 ± 0.18
all-trans-retinal	5.26 ± 0.16	4.55 ± 0.08	4.96 ± 0.08
9-*cis*-retinal	4.86 ± 0.40[d]	4.37 ± 0.37[d]	4.75 ± 0.41[d]
	4.69 ± 0.40[e]	4.21 ± 0.37[e]	4.71 ± 0.42[e]

[a] Calculated by using eq 1. [b] Calculated by using eq 2. [c] Calculated by using eq 3. [d] Calculated by assuming ϵ_2^∞ for 9-*cis*-retinal is equal to the value obtained for *all-trans*-retinal (3.234). [e] Calculated by using the ϵ_2^∞ value determined from refractive index measurements on solutions of 9-*cis*-retinal (ϵ_2^∞ = 3.702).

all-trans-retinal on the assumption that the polarizabilities of the two isomers should be very similar.

Solvent dielectric constants, liquid densities, and refractive indices for the shorter polyenals were taken from ref 17 and 18.

Results and Discussion

Table I lists the solvent and solute parameters and the experimental ϵ_2^∞ and $\partial\epsilon/\partial\phi_2$ values for the five molecules studied. Table II compares the experimental dipole moments calculated by our ellipsoidal cavity formalism (μ_{OE}), the spherical cavity Onsager equation (μ_{OS}), and the Debye equation (μ_D). The values in Table II are weighted means of the values obtained in the two solvents. Approximate error limits are based upon the uncertainties in the slopes of the plots of ϵ against ϕ_2, the estimated uncertainties in the concentrations and the calibration of the dielectric cells, and the differences between the dipole moments obtained in the two solvents.

The experimental vapor-phase dipole moments of acrolein and crotonaldehyde are available for comparison with our μ_{OE} values. Vapor-phase values for acrolein range from 3.04[19] to 3.11 D,[20] in good agreement with our value of 3.07 D. The vapor-phase dipole moment of crotonaldehyde is 3.70[21] –3.72 D,[22] somewhat lower than our μ_{OE} of 3.85 D. The corresponding solution values, calculated by the Debye equation (2.89–2.91 D for acrolein and 2.77–3.58 D for crotonaldehyde),[23] are considerably lower than the vapor-phase values. The large increase in the dipole moment on adding a methyl group to acrolein, an effect predicted by CNDO/2 molecular orbital calculations,[24] is due to methyl group induced resonant reorganization of the π system resulting in increased electron density at oxygen.[25] In contrast, the dipole moments of the aliphatic aldehydes are nearly independent of chain length. The dipole moment of 2,4-hexadienal has not been reported in the vapor phase. The published solution values of 3.96[26] and 3.98 D[27], calculated by using the Debye equation, are lower than our μ_D of 4.17 D and our μ_{OE} value of 4.68 D.

Our ellipsoidal cavity formalism yields dipole moments of 5.26 D for *all-trans*-retinal and 4.86 or 4.69 D (depending upon the choice of ϵ_2^∞) for 9-*cis*-retinal. The assumption of spherical cavities greatly reduces the calculated dipole moments; μ_{OS} is 0.71 D smaller than μ_{OE} for *all-trans*-retinal and about 0.5 D smaller for the more spherical 9-*cis*-retinal. The Debye equation also assumes spherical cavities, but it neglects the reaction field, which causes a larger induced dipole in a highly polarizable solute than that predicted by the Debye equation. μ_D is considerably larger than μ_{OS} for the latter reason and is approximately equal to μ_{OE} for 9-*cis*-retinal. The cavity shape effect predominates in *all-trans*-retinal, and μ_D is 0.3 D smaller than μ_{OE}.

The evaluation of the average cavity radius, $\bar{a}_2$, presents both experimental and theoretical difficulties. The cavity volume is generally determined from the density of the pure liquid at the temperature of measurement, but there are objections to procedures which allow the cavity volume to change with temperature.[10,11] The determination of the cavity volume of a solute from solution data requires the simplifying assumption that the average volume per solvent molecule does not change with solution composition, and it is experimentally difficult to accurately determine because the density differences to be observed are often quite small. Our $\bar{a}_2$ value for *all-trans*-retinal appears to be reasonable based on a comparison with the density of the shorter chain liquid analogue β-ionone. The density of β-ionone at 20 °C is 0.9462 g/mL,[18] while our data give the hypothetical liquid density of *all-trans*-retinal at 22 °C as 1.18 g/mL. Densities normally increase with increasing chain length, and retinal, with its long polyene chain, should have a higher density than β-ionone, which is dominated by the cyclohexene ring. Corsetti and Kohler[6] give their data in terms of mole fraction, which cannot be converted to volume fraction without knowledge of the solute cavity volume. However, by successive approximations, a value for $\bar{a}_2^3$ which is consistent with both their mole fractions and their densities can be obtianed. This approximate value of 9.2×10^{-23} cm^3 is within 5% of our value of 9.58×10^{-23} cm^3. Bauer and Carl[7] present their data only as a function of molarity, but the cavity volume can be estimated by inserting their calculated dipole moment back into the equation used to calculate it, which requires volume fractions. Their apparent value for $\bar{a}_2^3$ of 1.34×10^{-22} cm^3 is much larger than ours. Although their determination was made in methylcyclohexane, it is unlikely that there are significant differences between the cavity volumes in two saturated hydrocarbon solvents. The exact value of $\bar{a}_2^3$ is of little importance when the solute is measured by weight, because a change in the $\bar{a}_2^{-3}$ factor in eq 1 is nearly offset by the change in the denominator of $\partial\epsilon/\partial\phi_2$.

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Changes in $\bar{a}_2^3$ also affect the determination of ϵ_2^∞ from solution data by changing $\partial n^2/\partial\phi_2$ in eq 4, but the effect on μ_{OE} is fairly small whether ϵ_2^∞ changes with $\bar{a}_2^3$ or is held fixed (see below).

The assumption that *all-trans-* and 9-*cis*-retinal have the same solution volumes is questionable but was considered more accurate than attempting to measure densities of the more dilute 9-cis solutions. Calculations based on the effects of solvent and temperature on the electronic absorption spectra of 11-*cis*-retinal[28] indicate that the cavity radius of the 12-s-trans conformer is about 0.03 Å larger than the radius of the 12-s-cis conformer. If the difference between the cavity radius of *all-trans-* and 9-*cis*-retinal is of similar magnitude, the difference between the $\bar{a}_2^3$ values for the two isomers is less than 5%.

We obtain a solution refractive index of 1.798 for *all-trans*-retinal by application of eq 4 to our refractive index data. Corsetti and Kohler's data,[6] treated in the same manner, yield a considerably larger value of 1.938 if our cavity volume is assumed. (An even larger value of 2.110 is obtained under their assumption that n^2 is a linear function of mole fraction.) Bauer and Carl's value of n for *all-trans*-retinal is 1.73, measured with "dim red light" of unspecified wavelength.[7] Their method of calculation is not clear, but apparently they extrapolated a plot of refractive index against molarity to the pure solute value. It appears that the differences among various estimates for the refractive index of *all-trans*-retinal can be attributed to variations in both the experimental data and the method of calculation. It should also be noted that the true electronic polarizability is related to the refractive index extrapolated to infinite wavelength.[29] Molecules such as the retinal isomers, which absorb strongly at relatively long wavelengths, may have refractive indices which are substantially higher at the sodium D line than at infinite wavelength.

Equation 4 applied to our experimental data for 9-*cis*-retinal produces a refractive index of 1.924. The uncertainty in this number is considerably greater than the uncertainty in the all-trans value because of the low solute concentrations of the 9-cis solutions, and it does not seem reasonable that the polarizability of 9-*cis*-retinal should be much greater than that of *all-trans*-retinal. INDO–CISD molecular orbital calculations[30] indicate that the polarizabilities of the two isomers are nearly identical. Therefore, we have calculated the dipole moment of 9-*cis*-retinal in two ways: one with use of our experimental ϵ_2^∞ value of 3.702 and the other with use of the all-trans value of 3.234. Use of the more reasonable *all-trans*-retinal value reduces, but does not eliminate, the difference between the dipole moments of the two isomers.

Our experimental dielectric constant data for *all-trans*-retinal agree well with Corsetti and Kohler's data in hexane. When their data are converted from mole fraction to volume fraction by using our $\bar{a}_2$ value, their $\partial\epsilon/\partial\phi_2$ becomes 10.97, within 3% of our value of 11.31. Bauer and Carl's data in methylcyclohexane yield a $\partial\epsilon/\partial\phi_2$ of 10.98 if our molecular volume is assumed, while our value in cyclohexane is 12.47. Cyclohexane and methylcyclohexane have nearly identical polarizabilities, so the $\partial\epsilon/\partial\phi_2$ values in these two solvents are expected to be nearly equal. Our dipole moments measured in cyclohexane are larger than the dipole moments measured in hexane, which indicates that our $\partial\epsilon/\partial\phi_2$ value may be too large.

Bauer and Carl observed no change in the dielectric constant upon photoisomerizing solutions of *all-trans*-retinal to create a mixture of the all-trans, 13-cis, 9-cis, and 9,13-di-cis isomers. If we insert their data for *all-trans*-retinal into eq 1 by using their values of $\bar{a}_2^3$ (1.34×10^{-22} cm^3) and ϵ_2^∞ (2.993) and our A_a of 0.11, we obtain $\mu_{OE} = 5.00$, nearly 1 D higher than they calculate. The refractive index of the isomerized solution is not reported, but if we assume no change in ϵ_2^∞ or $\bar{a}_2$, hold $\partial\epsilon/\partial\phi_2$ fixed, and change A_a to the 9-*cis*-retinal value of 0.16, we obtain $\mu_{OE} = 4.79$ D. Simply altering the molecular geometry changes the calculated dipole moment by 0.21 D. Our data indicate that 9-*cis*-retinal may have a higher polarizability than all-trans, in which case the dipole moment of the 9-cis isomer would be reduced even further. It is important to realize that the observation of no significant change in the dielectric constant on isomerization does not necessarily imply that there is no significant change in the dipole moment. Solute shape and polarizability must also be considered.

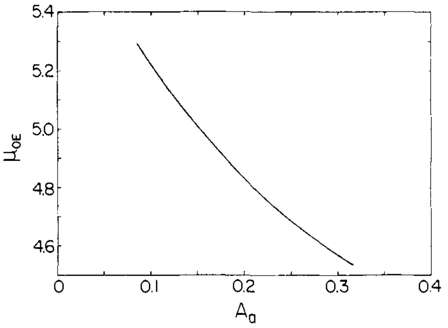

Figure 1. The dipole moment of *all-trans*-retinal calculated by using eq 1 as a function of A_a. All other parameters in eq 1 are set equal to those determined for *all-trans*-retinal in hexane (see Table I).

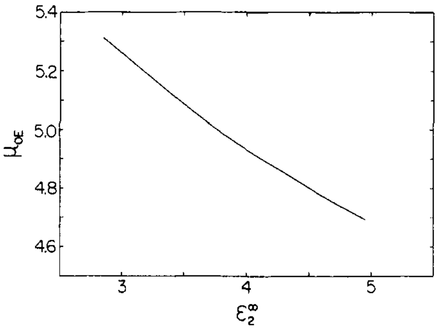

Figure 2. The dipole moment of *all-trans*-retinal calculated by using eq 1 as a function of ϵ_2^∞. All other parameters in eq 1 are set equal to those determined for *all-trans*-retinal in hexane (see Table I).

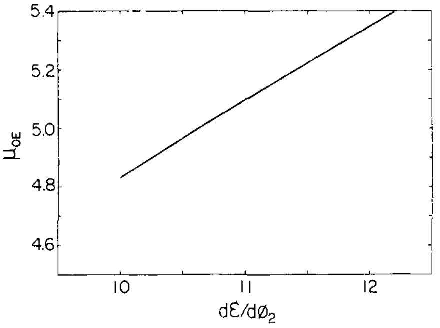

Figure 3. The dipole moment of *all-trans*-retinal calculated by using eq 1 as a function of $\partial\epsilon/\partial\phi_2$. The errors in $\partial\epsilon/\partial\phi_2$ are assumed to arise from errors in the measured dielectric constants or solute concentrations; the cavity radius is held fixed. All other parameters in eq 1 are set equal to those determined for *all-trans*-retinal in hexane (see Table I).

Determination of the dipole moment of 11-*cis*-retinal is complicated by the fact that it exists as an equilibrium mixture of the 12-s-cis and 12-s-trans conformers. Bauer and Carl, using the spherical cavity Onsager equation, obtained a difference of only 0.13 D between the dipole moments of 11-cis- and *all-trans*-retinal and concluded that the more polar 12-s-trans conformer must greatly predominate. Their conclusion is contradicted by the results of studies on the effect of external pressure on the electronic absorption spectrum,[5] which indicate a mole fraction of 0.35–0.48 for the 12-s-trans conformer in methylcyclohexane. Our ellipsoidal cavity formalism cannot be used to find the "average" dipole moment of a mixture of the 11-cis conformers because the two conformers have different A_a values, but Bauer and Carl's estimate of the difference between the dipole moments of all-trans and

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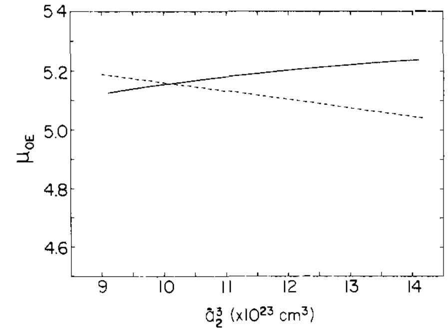

Figure 4. The dipole moment of *all-trans*-retinal calculated by using eq 1 as a function of $\bar{a}_2^3$. The dashed curve is obtained by varying only $\bar{a}_2^3$ and holding all other parameters constant. The solid curve is obtained by varying $\bar{a}_2^3$ and including the effects that variations in $\bar{a}_2^3$ have on $\partial\epsilon/\partial\phi_2$ and ϵ_2^∞. (ϵ_2^∞ is determined from solution refractive index measurements and it varies with the cavity radius through the $\partial\epsilon^2/\partial\phi_2$ term in eq 4.) Remaining parameters in eq 1 are set equal to those determined for *all-trans*-retinal in hexane (see Table I).

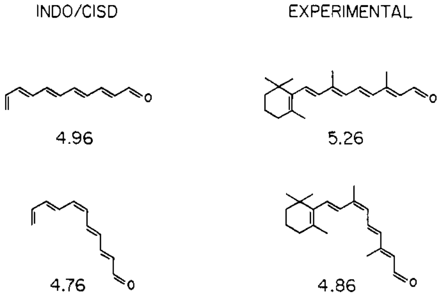

Figure 5. A comparison of theoretical (left) and experimental (right) dipole moments. The experimental values for *all-trans*-retinal (above) and 9-*cis*-retinal (below) are the μ_{OE} values given in Table II, with ϵ_2^∞ for 9-*cis*-retinal assumed to be equal to ϵ_2^∞ for *all-trans*-retinal. The theoretical values are taken from ref 30.

11-cis must be too small because the 11-cis isomer, in either conformation, is more spherical than *all-trans*-retinal. Furthermore, the relative contribution of the dipole moment to the dielectric constant will be greater for the 12-s-cis conformer than for the more polar but less spherical 12-s-trans conformer, making it even more difficult to obtain information about the relative populations of the conformers from dielectric measurements alone.

Dipole moments determined from solution dielectric data cannot be depended upon to be very exact, even when ellipsoidal cavity formalisms are used. The retinal isomers are particularly difficult to analyze because their large electronic polarizabilities are not accurately known and their molecular geometries are such that the cavity shapes cannot be determined unambiguously. Figures 1 through 4 illustrate the changes in the calculated dipole moment which result from altering the various parameters in eq 1. All of the parameters except the one to be varied are set equal to those determined for *all-trans*-retinal in hexane. Each figure demonstrates the effect on μ_{OE} of changes in one parameter (A_a, ϵ_2^∞, $\partial\epsilon/\partial\phi_2$, or $\bar{a}_2^3$) over a range of values which might reasonably be estimated or experimentally determined for use in dipole moment calculations on retinal isomers. The remaining parameters in eq 1, ϵ_1 and T, are normally known with sufficient accuracy that uncertainties in these parameters are insignificant sources of error. These figures underscore the importance of making accurate determinations of ϵ_2^∞ and A_a. Unfortunately, estimates of A_a for the same molecule can vary greatly depending upon whether or not the solute is allowed to rotate to define the cavity and whether average or maximum molecular dimensions are used. Dielectric constants can be determined with sufficient accuracy that errors in ϵ_2^∞ and A_a probably account for most of the error in dipole moment determinations on elongated polyenes like retinal.

Molecular orbital calculations on the polyene chain alone predict dipole moments of 4.96 D for the all-trans isomer and 4.76 D for the 9-cis isomer. These calculations were carried out by using the INDO-CISD formalism, an all-valence electron semiempirical molecular orbital theory including restricted single (~200) and double (~400) excitation configuration interaction.[30] The difference between the calculated and observed values are due in part to neglect of the methyl groups and the β-ionylidene ring; inclusion of the latter would increase the calculated dipole moments. The calculated dipole moments are, therefore, consistent with the observed values. The theoretical and experimental results are summarized in Figure 5.

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A MINDO/3 Theoretical Study on Structure, Fragmentation, and Scrambling Reaction in $C_6H_5^+$[1]

Mutsumi Tasaka, Michihiko Ogata, and Hiroshi Ichikawa*

Contribution from Hoshi College of Pharmacy, Shinagawa, Tokyo 142, Japan.
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Abstract: The structures, fragmentations, and scrambling reactions in the $C_6H_5^+$ system were examined by using the MINDO/3 method. The stable structures are the phenyl cation and its linear isomers. The activation energies of fragmentation from those ions were calculated. In the phenyl cation the cleavage that involves the β bond to the carbon atom with the formal cation requires lower energy than that of the α bond, indicating applicability of fragmentation rules in organic mass spectrometry to aromatic ring systems. The lowest activation energy for the loss of C_2H_2 from the phenyl cation is determined to be 108 kcal/mol. The calculated energies of interstructural conversions suggest a flexible nature of mutual conversion. One of the lowest energies for complete scrambling of carbon atoms in the phenyl cation was estimated to be less than 69 kcal/mol. This value is far lower than that of fragmentation, explaining complete scrambling of carbon atoms prior to the fragmentation of $C_6H_5^+$ ion which is produced from iodobenzene.

The fragmentation rules in organic mass spectrometry have developed from the relationship between geometrical structure, stability, and electronic structure of the system in both the initial and final states.[2] However, when it comes to the problem of

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