Comparison of the Dielectric Behavior of Several Schiff-Base and Phenyl Benzoate Liquid Crystals

R. T. Klingbiel,* D. J. Genova, T. R. Criswell, and J. P. Van Meter
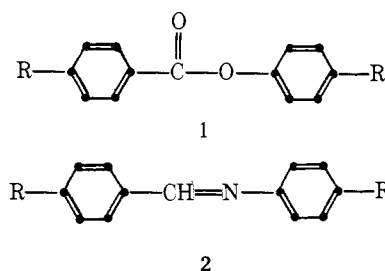
Contribution from the Research Laboratories, Eastman Kodak Company, Rochester, New York 14650. Received June 20, 1974

Abstract: The dielectric anisotropies of a number of terminally substituted Schiff-base and phenyl benzoate liquid crystals are reported. These permittivities are interpreted by use of the Onsager equation for the dielectric behavior of polar liquids. It is demonstrated how the effective dipole moment observed for oriented liquid crystals in fact represents an isotropic contribution as well as the anisotropic contribution, dependent upon the order parameter as previously described by Maier and Meier. Literature values for the group dipole moments are shown to permit quick estimation of the sign and magnitude of the dielectric anisotropy. Group moments, therefore, indicate the relative direction they would have with respect to the remaining structure if one is to optimize the sign and magnitude of the dielectric anisotropy.

Liquid crystalline materials are fluids that are anisotropic in their physical properties.[1] Their anisotropy occurs spontaneously, usually between the crystalline melting point, Tx, and a higher temperature, Tc, at which the fluid becomes isotropic. Several intermediate phases, or mesophases, may occur beween Tx and Tc; these various phases are classified according to the local symmetry of the anisotropy that the fluid possesses. The mesophase possessing the lowest symmetry is the nematic phase, which is locally uniaxial, with no translational correlation of molecular centers but rather a single preferred direction of molecular orientation. In principle, a biaxial nematic mesophase could exist, but these have not been observed to occur in the absence of any external orienting influence. Consequently, molecules forming a nematic mesophase are pictured to be rodlike in their orientation, with their long axes tending toward a mutual parallelism with each molecule remaining free to rotate about its long axis and free to translate as in an isotropic liquid. The intermolecular forces responsible for the mutual parallelism of the molecular long axes result in a long-range order, which has been the subject of a large number of studies.[2-7] One particularly illuminating experiment[8] has been the dielectric relaxation of nematic liquid crystals for an external electric field directed either parallel or perpendicular to the local optic axis. Maier and Meier[8] showed that the dielectric loss associated with dipolar reorientation about the molecular long axis (that is, when the electric field is perpendicular to the optic axis) occurred at frequencies comparable to isotropic liquids at the same temperature, namely ~10^{10} Hz. The loss associated with reorientation about the short axis, however, occurred at frequencies nearly three orders of magnitude lower. This unusually low loss frequency reflects the cooperative nature of the molecular orientation which results in an exceptionally high activation energy for a single molecule to undergo a dielectric reorientation.[9-13]

The static dielectric behavior of liquid crystals has also been of significant interest because of the importance of the dielectric anisotropy in describing the reorientation (and even disruption) of liquid crystals in the presence of electric fields. This description has been particularly useful for applications involving electrooptic devices.[14,15] The material parameter most generally used as a measure of utility for a particular liquid crystal is its dielectric anisotropy $\Delta\epsilon = \epsilon_\parallel - \epsilon_\perp$, where $\epsilon_\parallel$ is the dielectric permittivity parallel to the molecular long axis and $\epsilon_\perp$ is the permittivity perpendicular to the long axis. In actual measurements, $\parallel$ and $\perp$ usually refer to some external orientation direction, such as an orienting magnetic field. It is often assumed, but seldom verified, that the direction of external orientation is colinear with that of the molecular long axis, or local optic axis. This communication reports the observed dielectric anisotropy for a selected number of materials exhibiting a nematic mesophase. Two types of compounds are discussed, phenyl benzoates (**1**) and Schiff bases (**2**), where the terminal sub-

stituents R and R' have been selected so as to alter the dipolar character of the molecule. It is our purpose to demonstrate that the classical concept of group dipole moments can be useful in predicting optimum molecular structures to be sought in order for materials to have either a large positive or negative dielectric anisotropy.

Dielectric Permittivity

When a voltage V is applied across two parallel plate electrodes of unit area and separation d, an electric field **E** exists such that $|E| = V/d$. If a material is placed between the electrodes, an additional charge density σ (per unit area) develops at the plates as a result of the charge separation in the material induced by the electric field. A displacement field **D** is defined such that $|D| = 4\pi\sigma$. The dielectric permittivity, ϵ, is defined[16-18] as relating **D** and **E**.

$$\mathbf{D} = \epsilon\mathbf{E} \tag{1}$$

The charge separation manifest in the formation of σ can be described as an induced polarization, $\mathbf{p}_{ind}$, arising from a molecular polarizability α, where

$$\mathbf{p}_{ind} = \alpha\mathbf{E}_{eff} \tag{2}$$

Equation 2 actually defines the effective field $\mathbf{E}_{eff}$ that occurs within the material. In order to learn about the molecular quantity α from observed $\mathbf{p}_{ind}$, a good theory describing $\mathbf{E}_{eff}$ is required. The simplest description of $\mathbf{E}_{eff}$ was given by Mossotti, who calculated

$$\mathbf{E}_{eff} = [(\epsilon + 2)/3]\mathbf{E} \tag{3}$$

by assuming the surrounding medium "screened" a local region. Equation 3 leads to the Clausius–Mossotti relation

$$(\epsilon - 1)/(\epsilon + 2) = (4\pi/3)N\alpha \qquad (4)$$

for N molecules per unit volume. For materials not having a permanent dipole moment, ϵ is related simply to the refractive index for wavelengths far from an absorption band.

$$\epsilon = n^2 \qquad (5)$$

Debye[19] allowed for the effect of polar materials and showed that eq 4 could be put into the form

$$(\epsilon - 1)/(\epsilon + 2) = (4\pi/3)N(\alpha + p_{eff}) \qquad (6)$$

where

$$p_{eff} = \mu^2/3kT \qquad (7)$$

and μ is the permanent molecular dipole moment. Debye's results agree well with experiment for gases and dilute solutions of polar materials in nonpolar solvents. To attempt to describe condensed polar materials, Onsager[20] introduced a reaction field F such that

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi}{3}N\frac{\alpha + \mu^2}{3kT + F} \qquad (8)$$

where

$$F = 1 / \left(1 - \frac{2\epsilon - 2}{2\epsilon + 1}\frac{4\pi N\alpha}{3}\right) \qquad (9)$$

and by use of eq 4 and 5 expressed[18]

$$\mu^2 = \frac{9kT}{4\pi N}\frac{(\epsilon - n^2)(2\epsilon + n^2)}{\epsilon(n^2 + 2)^2} \qquad (10)$$

We shall interpret our results by use of eq 10.

Equations 1-10 apply to isotropic materials. The equations are considerably more complicated for anisotropic media, such as liquid crystals. Maier and Meier[21] treated the case of the nematic mesophase by incorporating into the Onsager theory the anisotropy of the material *via* the concept of the order of parameter S. The order parameter S was introduced by Maier and Saupe[3] to describe the average degree of orientation of the molecular long axis with respect to the local direction of preferred alignment, which for conceptual purposes may be assumed equivalent to the local optic axis. If the angle between the molecular long axis and the local optic axis is taken as θ, then S is defined as $[1 - \frac{3}{2}\overline{\sin^2\theta}]$, where the bar represents an ensemble average over all angles. It is seen that the parameter varies from one (representing complete order when θ equals zero for all molecules) to zero when the molecules are randomly oriented with all angles equally probable (*i.e.*, $\overline{\sin^2\theta} = \frac{2}{3}$). For S defined in this manner, Maier and Meier derived[21] the following expression for p_{eff}

$$p_{eff}^{1} = \frac{1}{3kT}[\mu^2(1 - S) + 3\mu_{\parallel}^2 S]\frac{3\bar{\epsilon}}{2\bar{\epsilon} + 1}F^2$$

$$p_{eff}^{2} = \frac{1}{3kT}[\mu^2(1 - S) + \frac{3}{2}\mu_{\perp}^2 S]\frac{3\bar{\epsilon}}{2\bar{\epsilon} + 1}F^2 \qquad (11)$$

$$\bar{\epsilon} = \frac{1}{3}(\epsilon_{\parallel} + 2\epsilon_{\perp})$$

The components $\parallel$ and $\perp$ refer to components parallel and perpendicular to the molecular axis, respectively. The superscript 1 represents the effective polarizability when the electric field is parallel to the optic axis, and 2 corresponds to the case of the field perpendicular to the optic axis. It should be noted that for complete disorder, *i.e.*, for the isotropic liquid, only the first term in the brackets remains, and p_{eff} reduces to the Debye term $\mu^2/3kT$ times a factor involving the Onsager reaction field. For complete order, *i.e.*, $S = 1$, all molecules are parallel to the optic axis and only one molecular component contributes to p_{eff}. In other

words, p_{eff} consists of an isotropic portion [weighted by $(1 - S)$] and a purely uniaxial portion (weighted by S).

It can be demonstrated that the effective μ^2 calculated from experiment by means of eq 10 corresponds to the bracketed term in eq 11. By writing $\mu^2 = \mu_{\perp}^2 + \mu_{\parallel}^2$ and substituting into eq 11, one arrives at the following identity.

$$\mu_{eff,\parallel}^{theory} = [\mu_{\perp}^2(1 - S) + \mu_{\parallel}^2(1 + 2S)]^{1/2}$$

$$\mu_{eff,\perp}^{theory} = [\mu_{\perp}^2(1 + (\frac{1}{2})S) + \mu_{\parallel}^2(1 - S)]^{1/2} \qquad (12)$$

If we are to express the molecular dipole moment components $\mu_{\perp}$ and $\mu_{\parallel}$ in terms of the group dipole moments of its substituents, we must consider the internal rotations of the substituents. We assume that each terminal substituent is free to rotate about the long axis of the molecule independently of any dipolar orientation of the remaining molecule. Therefore, the perpendicular components of each group rotate independently of one another and we may approximate

$$\mu_{\perp}^2 = \sum_i (\mu_{i,\perp}^2)$$

where i represents the ith substituent (including the central linkage). As the parallel components cannot orient independently, we must write

$$\mu_{\parallel}^2 = \left(\sum_i \mu_{i,\parallel}\right)^2$$

Equation 12 then becomes

$$\mu_{eff,\parallel}^{theory} = [\sum(\mu_{i,\perp}^2)(1 - S) + (1 + 2S)(\sum\mu_{i,\parallel})^2]^{1/2}$$

$$\mu_{eff,\perp}^{theory} = [\sum(\mu_{i,\perp}^2)(1 + (\frac{1}{2})S) +$$
$$(1 - S)(\sum\mu_{i,\parallel})^2]^{1/2} \qquad (13)$$

which we shall compare with the effective dipole moment calculated from the experimental ϵ and eq 14.

$$\mu_{eff,\parallel}^{exptl} = \frac{9kTM}{4\pi N_0\rho}\frac{(\epsilon_{\parallel} - \epsilon_x)(2\epsilon_{\parallel} + \epsilon_x)}{\epsilon_{\parallel}(\epsilon_x + 2)^2}$$

$$\mu_{eff,\perp}^{exptl} = \frac{9kTM}{4\pi N_0\rho}\frac{(\epsilon_{\perp} - \epsilon_x)(2\epsilon_{\perp} + \epsilon_x)}{\epsilon_{\perp}(\epsilon_x + 2)^2} \qquad (14)$$

M is the molecular weight, N_0 is Avogadro's number, and ρ is the density. Equation 14 follows from eq 10 when it is assumed that the dielectric permittivity of the polycrystalline solid, ϵ_x, approximates the square of the mean refractive index much as in isotropic media (see eq 5). We have thus ignored the influence of the optical birefringence on μ_{eff} as this contribution can be shown to represent only about 3% of the resulting computation. We also have had to assume that the density, ρ, is equivalent for all of our materials. For ease of computation we have selected $T = 0.98T_c$ in which case $S = 0.4$. It should be noted that the use of a single-order parameter is only an approximation of the order in nematic liquid crystals.[22,23]

Results

The measured permittivities, μ_{eff}^{exptl} and μ_{eff}^{theory}, for the phenyl benzoates are given in Table I and the corresponding Schiff-base data are presented in Table II. Table III lists the group dipole moments, μ_i, used to calculate μ_{eff}^{theory}. A summary of the procedure is exemplified in Figure 1 for 4-*n*-butyloxyphenyl 4'-*n*-pentyloxybenzoate. Note that the numerical computation of the right and left portions of Figure 1 are connected physically by the appropriate value of S at the experimental value of T.

It is obvious from Tables I and II that the sign and magnitude of the dielectric anisotropy of both phenyl benzoate

Table I. Dielectric Properties of Phenyl Benzoate Derivatives (Formula 1)

| Compd | | Transition temp, °C[a] | Dielectric permittivities | | | | | Effective dipole moments | | |
R	R'		T	$\epsilon_{\parallel}$	$\epsilon_{\perp}$	$\Delta\epsilon$	ϵ_x	$\mu_{eff,\parallel}$, exptl (theory)	$\mu_{eff,\perp}$, exptl (theory)	$(\mu_{\parallel}/\mu_{\perp})_{eff}$, exptl (theory)
C₃H₇	C₅H₁₁	15–19[b]	10.4	4.56	4.28	0.28	2.76	1.73 (1.77)	1.60 (1.96)	1.08 (0.90)
C₄H₉O	C₄H₉O	86–93[b]	85.4	5.14	5.38	−0.23	3.25	1.91 (2.21)	2.41 (2.73)	0.79 (0.87)
C₅H₁₁O	C₄H₉O	68–84[b]	78.5	5.12	5.32	−0.19	3.31	1.87 (2.21)	1.95 (2.73)	0.96 (0.87)
C₈H₁₇O	C₈H₁₇O	62.³72–90[b]	84.5	4.10	4.39	−0.29	2.49	2.36 (2.21)	2.54 (2.73)	0.91 (0.87)
CH₃O	C₅H₁₁	30–44[b]	38.3	5.70	5.59	0.11	2.80	2.18 (2.03)	2.15 (2.37)	1.01 (0.86)
C₅H₁₁	C₄H₉O	49–58[c]	48.7	4.44	4.73	−0.28	2.81	1.69 (1.99)	1.82 (2.37)	0.93 (0.84)
C₇H₁₅	CN	44–57[c]	49.9	26.70	9.25	17.50	2.52	6.50 (7.41)	3.57 (4.60)	1.82 (1.60)
C₅H₁₁O	CN	85–87 (77)[b]	71.8	27.80	11.66	16.13	2.73	6.41 (7.51)	3.95 (4.81)	1.62 (1.56)
CN	C₅H₁₁O	92–93 (90)[b]	88.0	10.60	6.04	4.56	2.54	4.01 (5.20)	2.75 (3.65)	1.45 (1.43)

[a] All temperature ranges are nematic unless indicated as s for smectic. Parentheses signify a monotropic transition. [b] J. P. Van Meter and B. H. Klanderman, *Mol. Cryst. Liquid Cryst.*, **22**, 271 (1973). [c] Compound prepared for this study.

Table II. Dielectric Properties of Schiff-Base Derivatives (Formula 2)

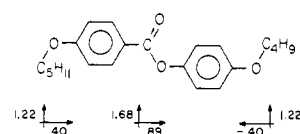| Compd | | Transition temp, °C[a] | Dielectric permittivities | | | | | Effective dipole moments | | |
R	R'		T	$\epsilon_{\parallel}$	$\epsilon_{\perp}$	$\Delta\epsilon$	ϵ_x	$\mu_{eff,\parallel}$, exptl (theory)	$\mu_{eff,\perp}$, exptl (theory)	$(\mu_{\parallel}/\mu_{\perp})_{eff}$, exptl (theory)
C₄H₉COO	C₄H₉COO	112–115[b]	112.7	4.20	4.96	−0.76	2.98	1.80 (2.07)	2.25 (2.92)	0.80 (0.71)
C₃H₇OCOO	C₃H₇OCOO	68–94[b]	87.4	4.30	4.15	0.15	2.83	1.96	1.86	
C₅H₁₁O	CN	64–97[c]	90.8	22.63	9.82	12.81	2.93	5.36 (6.89)	3.29 (4.43)	1.63 (1.55)
C₇H₁₅O	CN	65–89[c]	86.1	21.07	9.60	11.47	3.26	5.02 (6.89)	3.12 (4.43)	1.61 (1.55)
CN	C₅H₁₁O	79–105[c]	98.2	17.23	7.87	9.36	2.80	4.79 (5.77)	2.96 (3.86)	1.62 (1.49)
CN	C₇H₁₅O	63–103[c]	99.5	15.03	7.24	7.79	2.96	4.51 (5.77)	2.81 (3.86)	1.61 (1.49)
CH₃O	C₄H₉	20–46[d]	40.1	4.49	4.89	−0.40	3.48	1.31 (1.60)	1.98 (2.15)	0.67 (0.75)
C₂H₅O	C₄H₉	35–78[d]	73.8	4.37	4.50	−0.13	3.29	1.28 (1.60)	1.35 (2.15)	0.95 (0.75)
C₆H₁₃COO	C₂H₅O	94–120[c]	113.4	3.84	4.61	−0.77	2.89	1.57 (2.20)	2.06 (2.94)	0.75 (0.75)
C₂H₅COO	C₆H₁₃O	92–119[c]	110.8	3.84	4.57	−0.72	3.50	0.87 (2.20)	1.48 (2.94)	0.59 (0.75)
CH₃O	OOCCH₃	82–119[c]	101.5	5.68	6.60	−0.92	3.46	1.80 (2.84)	2.10 (3.11)	0.86 (0.91)
C₃H₇O	OOCCH₃	99–108[c]	100.2	5.54	5.94	−0.40	3.02	2.15 (2.84)	2.30 (3.11)	0.94 (0.91)
C₇H₁₅O	OOCCH₃	81–105[c]	97.3	5.08	5.33	−0.25	3.11	2.06 (2.84)	2.17 (3.11)	0.95 (0.91)

[a] All temperature ranges are nematic. [b] T. R. Criswell, B. H. Klanderman, and D. C. Batesky, *Mol. Cryst. Liquid Cryst.*, **22**, 211 (1973). [c] Compound prepared for this study. [d] H. Keller, B. Scheurle, R. Hatz, and W. Bartsch, *Angew. Chem., Int. Ed. Engl.*, **9**, 962 (1970).

Table III. Group Dipole Moments Used to Calculate the Theoretical Effective Dipole Moments

i	μ_i	μ_i	$\mu_{\parallel,i}$	$\mu_{\perp,i}$	Ref
Ph—C(=O)(O—Ph)		1.90	0.89	0.68	a
Ph—C(=H)(N—Ph)		1.57	0.40	1.51	b
Ph—CH₃		0.37	−0.37	0	c
Ph—CN		4.18	4.18	0	c
Ph—O(CH₃)		1.28	−0.40	1.22	c
Ph—O—C(=O)—CH₃		1.69	−0.69	1.54	c
Ph—C(=O)(H)		2.96	2.45	1.66	c

[a] R. J. W. LeFevre and A. Sundaram, *J. Chem. Soc.*, 3904 (1962). [b] W. F. Smith, *Tetrahedron*, **19**, 445 (1963). [c] V. Minkin, O. Osipov, and Y. Zhdamov, "Dipole Moments in Organic Chemistry," Plenum Press, New York, N. Y., 1970.

Figure 1. Example of computation of the theoretical and experimental effective molecular dipole moments.

and Schiff-base nematic liquids depend very much on the nature, location, and molecular length of the terminal substituents. For instance, clearly a negative dielectric anisotropy is not inherent to the phenyl benzoates.[24] Furthermore, the observed dielectric permittivity arises from an effective dipole moment whose magnitude is strongly affected by the "isotropic" portion of the effective polarizability.

For discussion purposes, data have been selected from Tables I and II and compared in Tables IV and V to emphasize particular trends. Table IV demonstrates the vector additivity of the parallel component of group dipole moments. When the alkoxy and cyano substituents are located so that their parallel dipolar components are directed similarly to that of the central linkage, then the net moment is greater than when the terminal substituents are reversed. One might expect the perpendicular components to be the same regardless of the location of the terminal substituents with respect to the central linkage. However, $\mu_{\perp}$ is observed to decrease significantly when $\mu_{\parallel}$ decreases. This decrease is due to the decreasing isotropic contribution to p_{eff}^2 in eq

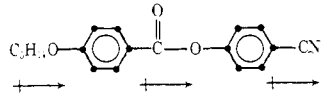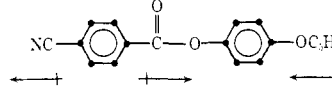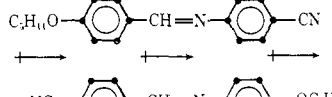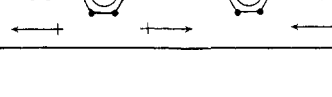**Table IV.** Vector Additivity of the Parallel Component of Group Dipole Moments
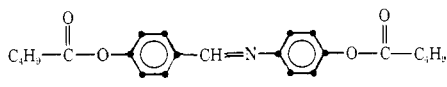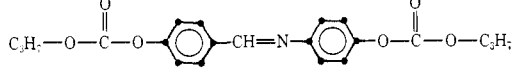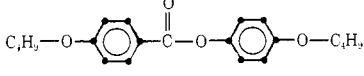
	Obsd			
	$\epsilon_\parallel$	$\mu_\parallel$	$\epsilon_\perp$	$\mu_\perp$
C_3H_7O—⟨○⟩—$\overset{O}{\overset{\|\|}{C}}$—O—⟨○⟩—CN	27.8	6.4	11.7	4.0
NC—⟨○⟩—$\overset{O}{\overset{\|\|}{C}}$—O—⟨○⟩—$OC_3H_7$	10.6	4.0	6.0	2.7
$C_5H_{11}O$—⟨○⟩—CH=N—⟨○⟩—CN	22.6	5.4	9.8	3.3
NC—⟨○⟩—CH=N—⟨○⟩—OC_3H_7	17.2	4.8	7.9	3.0

Table V. The Apparent Enhancement of the Parallel Dipole Moment Component Due to the Enhanced Total Dipole Moment

	μ Parallel component		
	Central linkage	Obsd	Theory
C_4H_9—$\overset{O}{\overset{\|\|}{C}}$—O—⟨○⟩—CH=N—⟨○⟩—O—$\overset{O}{\overset{\|\|}{C}}$—$C_4H_9$	0.40	1.80	2.07
C_3H_7—O—$\overset{O}{\overset{\|\|}{C}}$—O—⟨○⟩—CH=N—⟨○⟩—O—$\overset{O}{\overset{\|\|}{C}}$—O—$C_3H_7$	0.40	1.96	
C_4H_9—O—⟨○⟩—$\overset{O}{\overset{\|\|}{C}}$—O—⟨○⟩—O—$C_4H_9$	0.89	1.91	2.21

11. Therefore, one must conclude that rearrangement of terminal substituents affects $\epsilon_\perp$ *via* the change in the total dipole moment of the molecule.

Although the qualitative decrease in $\mu_\parallel$ of Table IV is explainable *via* internal compensation of the substituent dipole moments, the quantitative decrease in $\mu_\parallel$ is larger than expected from the group dipole moments given in Table III. For example, the data in Table IV would lead one to attribute a parallel dipolar component of 1.2 D for the ester linkage and 0.3 D for the benzylidene linkage, compared to 0.89 D for phenyl benzoate and 0.4 D for benzylideneaniline. The discrepancy is even more obvious when we examine the symmetric substitution demonstrated in Table V. We observe a central linkage contribution to $\mu_{eff,\parallel}$ nearly five times greater than expected for the Schiff bases and twice that expected for the phenyl benzoates. Again the explanation lies in the isotropic portion of p_{eff}^{1} as written in eq 11. In this case, it is $\mu_\perp$'s contribution to μ that is enhancing the effective dipole moment $\mu_{eff,\parallel}$ (see eq 12).

Conclusion

We have reduced our experimental dielectric permittivities to an effective molecular dipole moment *via* the Onsager equation. We have shown that this effective dipole can be simply interpreted in terms of an isotropic-like contribution and an anisotropic-like contribution, arising from the imperfect degree of order in the liquid crystal. We have shown that literature values of the substituent-group dipole moments allow one to predict the sign of the dielectric anisotropy. The lack of the material refractive index and density values has prevented a quantitative prediction of the dielectric permittivities *via* the group dipole moments. The ratio of the dipolar components is insensitive to these material parameters, however, and a comparison between theory and

experiment is acceptable, as is demonstrated in the last column of Tables I and II.

Experimental Section

The dielectric permittivities are calculated from the measure capacitance of a parallel plate capacitor containing liquid crystalline material oriented by means of an externally applied magnetic field. The apparatus is schematically represented in ref 13.

The cell consists of two 0.5 × 0.5 in. glass plates having an indium oxide conductive coating with a resistivity of 300 Ω per unit area (available as Nesatron from Pittsburgh Plate Glass Co., Pittsburgh, Pa.) and separated by 0.050-in. Teflon spacers. The cell and its holder are mounted to a thermostated block and jacketed to reduce heat loss. This assembly is then placed between two 6-in. pole faces of a 13-kG Varian electromagnet and oriented such that the magnetic field is either parallel or perpendicular to the applied electric field. The sample temperature is measured by means of a copper–constantan thermocouple made of 0.002-in. diameter wire to reduce conduction from the junction. The thermocouple makes contact to the glass electrodes *via* a heat-conducting grease. Temperature accuracy is approximately ±0.5°.

To the capacitor is applied a 10-kHz, 0.3-V peak-to-peak potential. The current flowing through an "active" area of approximately 1 cm² is collected and converted to a voltage by means of an operational amplifier having a large bandwidth and dynamic range. Fringe fields are minimized by surrounding the active area by a ground ring. The current-to-voltage converter output is fed to the input amplifier of a Model 220 Princeton Applied Research lock-in amplifier. The capacitive component of the cell current, which is 90° out of phase with the applied potential, is thus measured.

The permittivity is calculated from

$$\epsilon = (C_s - C_p)/(C_0 - C_p) \tag{15}$$

where C_s is the sample capacitance, C_0 the capacitance of the empty cell, and C_p the parasitic capacitance. The parasitic capacitance arises from two sources: (1) the physical arrangement of

leads, electronic components, stray field, etc.; (2) field fringing within the cell. The first contribution amounts to about 0.04 pF, as determined by physically removing the cell. The remaining 0.02-pF error is attributed to fringing and was determined by comparing the observed dielectric permittivity of Eastman white label toluene (ϵ = 2.394), chlorobenzene (ϵ = 5.592), ethyl acetate (ϵ = 5.982), and 1,1-dichloroethane (ϵ = 10.36) at 25° to the literature values 2.379, 5.621, 6.02, and 10.36, respectively. The typical value of C_0 was 12.5 to 15 pF. We therefore believe the reported permittivities to be accurate to within about 1%.

Summary

It is well known that electrooptical devices utilizing nematic liquid crystals require materials having either a large positive or negative dielectric anisotropy. We have demonstrated how the sign and magnitude of the anisotropy can be estimated easily from the group dipole moments associated with the terminal substituents and the central linkage in several phenyl benzoates and Schiff bases. We have further demonstrated how group dipole moment considerations quickly permit the best terminal location for a substituent. We have also emphasized how the isotropic portion of the effective dipole moment must be retained to understand properly the magnitudes of the observed dielectric permittivities.

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Structural Effects on Photophysical Processes in Saturated Amines. III[1]

Arthur M. Halpern[2]

Contribution from the Photochemistry and Spectroscopy Laboratory, Department of Chemistry, Northeastern University, Boston, Massachusetts 02115. Received December 28, 1973

Abstract: The vapor-phase absorption spectrum of 1-azabicyclo[3.3.3]undecane (ABCU) is reported between 35 and 49 kcm^{-1}. In this region, four distinct electronic transitions are identified and assigned as Rydberg $\leftarrow$ n on the basis of the quantum defect values. The (adiabatic) ionization potential of ABCU is reported, as are the oscillator strengths of the transitions. The vapor-phase fluorescence spectra of ABCU and an analogous cage amine, 1-azabicyclo[2.2.2]octane (ABCO), are presented. Partial vibrational analyses are performed for these spectra and comparisons are made with the respective $S_1 \leftarrow S_0$ transitions. Zero-pressure lifetime and quantum yield data are also reported, and these values are used to determine the respective radiative rate constants (k_R). For ABCO, the measured k_R value correlates very well with the value calculated from the Strickler-Berg relation. On the other hand, for ABCU, the agreement between the measured and calculated k_R values is rather poor, with the calculated value being about 0.6 that of the measured value. This discrepancy is discussed in terms of possible excited-state vibronic interactions affecting the transition moment. The measured k_R values are: 11×10^6 and $2.7_5 \times 10^6$ sec^{-1} for ABCU and ABCO, respectively. The zero-pressure quantum yield values reported are 1.0 for both amines.

The spectroscopic and photophysical properties of saturated amines have received remarkably little attention. Indeed, it is only recently that fluorescence from these compounds was reported.[3-6] This paper is one of a series dealing with the photophysical and spectroscopic investigations of saturated tertiary amines, and concerns, in particular, certain cage amines. The alkyl groups represented by the cage portion of such molecules can impose structural constraints upon the nitrogen atom. These effects may lead to rather striking characteristics in the electronic structure and the consequent excited state behavior.

In the saturated tertiary amines, where the chromophore is simply the nonbonding electron pair on the nitrogen atom, it is presumed that in the absence of steric and structural interference by the three alkyl groups, the configurationally relaxed excited singlet states are planar. This as-