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# Experimental determination of molecular polarizability anisotropy of nematogens by depolarized Rayleigh light scattering

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The anisotropy of molecular polarizability $\Delta\alpha$ of several nematogens has been determined by depolarized Rayleigh light scattering. The experimentally determined values were found to be noticeably smaller than those obtained by MOPAC calculation. $\Delta\alpha$ values determined from order parameter $S$ and refractive indices show reasonably good agreement with those determined in the present experiment. This result warns us that $\Delta\alpha$ calculated by MOPAC, particularly at a finite wavelength, may be larger than the true value.

## 1. Introduction

For the display application of liquid crystals, nematogens with a large birefringence $\Delta n$ are sometimes required. $\Delta n$ becomes large when the order parameter $S$ and anisotropy of molecular polarizability $\Delta\alpha = \alpha_l - \alpha_s$ are large—$\alpha_l$ and $\alpha_s$ are the molecular polarizabilities parallel and perpendicular to the molecular long axis, respectively. Since components of the dielectric constant $\varepsilon$ parallel and perpendicular to the director, $\varepsilon_\parallel$ and $\varepsilon_\perp$, are given by [1]

$$\bar{\varepsilon}_\parallel = n_\parallel^2 = 1 + \frac{N(\bar{\varepsilon}+2)}{3\bar{\varepsilon}_0}\left(\bar{\alpha} + \frac{2}{3}S\Delta\alpha\right) \quad (1)$$

$$\bar{\varepsilon}_\perp = n_\perp^2 = 1 + \frac{N(\bar{\varepsilon}+2)}{3\bar{\varepsilon}_0}\left(\bar{\alpha} - \frac{1}{3}S\Delta\alpha\right) \quad (2)$$

then $\Delta n$ is given by [1]

$$\Delta n = \left[1 + \frac{N(\bar{\varepsilon}+2)}{3\varepsilon_0}\left(\bar{\alpha} + \frac{2}{3}S\Delta\alpha\right)\right]^{1/2} - \left[1 + \frac{N(\bar{\varepsilon}+2)}{3\varepsilon_0}\left(\bar{\alpha} - \frac{1}{3}S\Delta\alpha\right)\right]^{1/2} \quad (3)$$

where $N$ is the number of molecules per unit volume, $\varepsilon_0$ is the permittivity of vacuum, and $\bar{\varepsilon}$ and $\bar{\alpha}$ are average values of $\varepsilon(=n^2)$ and polarizability $\alpha$,

$$\bar{\varepsilon} = \frac{2\varepsilon_\perp + \varepsilon_\parallel}{3} \quad (4)$$

$$\bar{\alpha} = \frac{2\alpha_s + \alpha_l}{3}. \quad (5)$$

To obtain materials having high $\Delta n$, molecules with high $\Delta\alpha$ have been designed by MOPAC calculation and synthesized [2, 3]. However, $\Delta n$ experimentally determined is always smaller than that obtained using calculated $\Delta\alpha$ and experimentally determined $S$ [2, 3]. This fact motivated us to determine $\Delta\alpha$ experimentally.

To obtain $\Delta\alpha$ experimentally, we made use of depolarized Rayleigh light scattering. This method was developed by Patterson and Flory [4]. As far as authors are aware however, there are no reports of measurements on liquid crystal molecules. In this paper, we apply the technique to determine $\Delta\alpha$ of nematogens and compare with $\Delta\alpha$ determined by MOPAC calculation

## 2. Principle

The incidence of light into molecular systems induces a dipole $p$ proportional to polarizability $\alpha$, and an electric field **E** in each molecule, resulting in the scattering of light. If the molecules are isotropic, the polarization state of scattered light is the same as that of the incident light. In anisotropic molecules, however, $\alpha$ is a tensor quantity,

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so that depolarized scattered light with a different polarization component from that of the incident light is emitted. The depolarized component is large for molecules with large anisotropy. Hence, the analysis of the depolarized scattered light gives the anisotropy of the molecular polarizability $\Delta\alpha$. This is the principle of the depolarized Rayleigh light scattering method.

Let us consider the scattering geometry shown in figure 1. Light linearly polarized along the $Z$ axis (vertical; V) is incident along the $Y$ axis, and induces a dipole in a molecular located at the origin; this causes light scattering. We observe $Y$-polarized (horizontal; H) scattered light at a distance $r$ from the origin in the $X$ direction. We consider a uniaxial molecule with a polarizability tensor

$$\alpha = \begin{bmatrix} \alpha_s & 0 & 0 \\ 0 & \alpha_s & 0 \\ 0 & 0 & \alpha_l \end{bmatrix}. \tag{6}$$

The induced dipole moment $\mathbf{p}$ is given by

$$\mathbf{p} = \alpha'\mathbf{E} \tag{7}$$

where $\alpha'$ is $\alpha$ at an arbitrary orientation and $\mathbf{E}$ is an electric vector of the incident light. The $Y$-polarized scattered intensity is proportional to the square of $p_Y$ averaged for random orientation, and is given by

$$I = \frac{16\pi^4}{r^2\lambda^4}\rho V p_{Y,\mathrm{ave}}^2 = \frac{16\pi^4}{r^2\lambda^4}\rho V(\alpha_l - \alpha_s)^2 E_Z^2, \tag{8}$$

where $V$ is a scattering volume, $\rho$ the number density of molecule and $\lambda$ the wavelength of light. $N$ in equations (1)–(3) and $\rho$ in equation (8) are connected by the relation, $N = N_A\rho/M$, where $N_A$ is the Avogadro number and $M$ is the molecular mass number. Since the scattered light intensity depends on $r$ and $V$, it is convenient to define the Rayleigh ratio $R$ by

$$R = \frac{Ir^2}{I_0 V} = \left(\frac{16\pi^4}{\lambda^4}\right)\left(\frac{\rho}{15}\right)(\Delta\alpha)^2 \tag{9}$$

where $I_0$ is the incident light intensity and the relation $\Delta\alpha = \alpha_l - \alpha_s$ is used.

Under our experimental conditions, liquid crystal molecules are dissolved in a solvent. Hence, corrections must be made by taking account of (1) scattering from the solvent, (2) the effect of an internal field and (3) intermolecular interaction. The correction for (1) is made by subtracting the contribution of the solvent $R^{\mathrm{solv}}$ from the overall contribution of the solution $R^{\mathrm{solu}}$,

$$\Delta R = R^{\mathrm{solu}} - R^{\mathrm{solv}}. \tag{10}$$

The effect of (2) was taken into account by using the Lorentz field, neglecting the effect of an anisotropic local field. Thus, the polarizability anisotropy of molecules dissolved in a solution of refractive index $n$ is given by $\{(n^2+2)/3\}\Delta\alpha$. Then, equation (10) is finally given by

$$\Delta R = R^{\mathrm{solu}} - R^{\mathrm{solv}} = \left(\frac{16\pi}{\lambda^4}\right)\left(\frac{n^2+2}{3}\right)^2\left(\frac{\rho}{15}\right)(\Delta\alpha_{\mathrm{app}})^2 \tag{11}$$

where $\Delta\alpha_{\mathrm{app}}$ is an apparent molecular polarizability anisotropy that contains the effect (3). To remove this effect, the dependence of $(\Delta\alpha_{\mathrm{app}})^2$ on number density must be obtained. $(\Delta\alpha)^2$ is finally obtained by extrapolating $(\Delta\alpha_{\mathrm{app}})^2$ to zero number density.

## 3. Experimental procedure

The experimental set-up for depolarized Rayleigh light scattering is schematically shown in figure 2. All the optics are placed in a dark box to detect the very weak scattered intensity. The light from a He-Ne laser (10 mW) was polarized by a Glan–Thompson prism, whose extinction

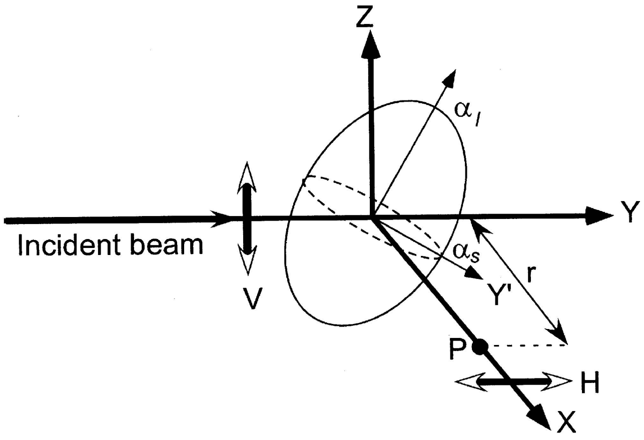

Figure 1. Optical geometry for depolarized Rayleigh light scattering.

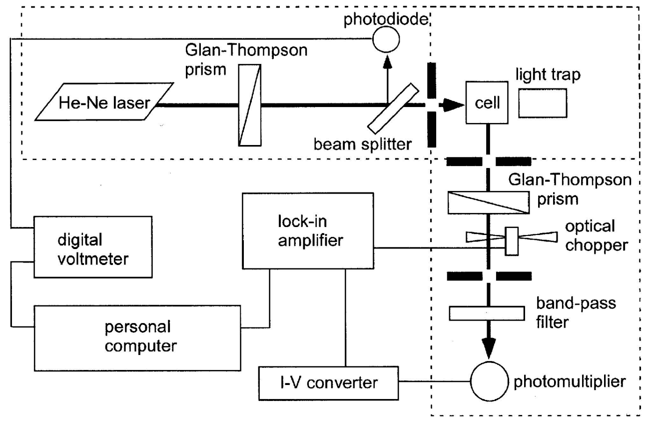

Figure 2. Experimental set-up for depolarized Rayleigh light scattering.

was better than 1 : $10^6$. The light scattered through another Glan–Thompson prism was detected by a photomultiplier and amplified by a lock-in amplifier. A band-pass filter with 10 nm half-width was used to avoid stray light and Raman scattering from the sample cell.

The structures of samples used are shown in figure 3. All of them except for 2CB and 4CB show only the nematic liquid crystalline phase. The compounds 3CPO2 and 5BP1 are supposed to have small anisotropy, since there is no strong polar group. In contrast, 6PA3 has a large anisotropy due to a large π-conjugated system [3].

The compounds were dissolved in $CCl_4$ and the solutions were introduced into a rectangular cuvette through a membrane filter (0.5 μm pore), great care being taken to measure accurately the density of solute and to avoid dust. The accurate determination of the Rayleigh ratio $R$ is generally not easy. Hence, $R$ values of the target compounds were determined by calibrating the scattered intensity of our samples, using the scattered intensity from benzene as a standard material whose $R$ is known, viz. $9.23 \times 10^{-6}\,\mathrm{cm}^{-1}$ for a polarized ($Z$-in, $Z$-out, W) scattering condition.

## 4. Experimental results and discussion

Figure 4 shows the reduced Rayleigh ratio $\Delta R$ as a function of solute number density for (*a*) 3CPO2, (*b*) 5BP1, (*c*) 6CB and (*d*) 6PA3. In all cases, the dependence is non-linear. This behaviour is the same as that in other molecules previously reported [4–6]. The non-linear behaviour indicates the effect of intermolecular interaction. $(\Delta\alpha_{\mathrm{app}})^2$ was determined using figure 4 and equation (11) and plotted as a function of the number density. The results shown in figures 5(*a–d*) show a linear dependence in all samples. The intersect at zero number density in figure 5 gives $(\Delta\alpha)^2$.

The $(\Delta\alpha)^2_{\mathrm{dRs}}$ values thus obtained are summarized in the table, where $(\Delta\alpha)^2_{\mathrm{MOPAC}}$ values obtained by MOPAC calculation [7] are also shown for comparison. In the MOPAC calculation, not only the same wavelength as in the experiment (633 nm, 1.96 eV) but also the infinite wavelength (0 eV) were used. The $(\Delta\alpha)^2_{\mathrm{dRs}}$ values are one-half or one-third the $(\Delta\alpha)^2_{\mathrm{MOPAC}}$ values at 1.96 eV.

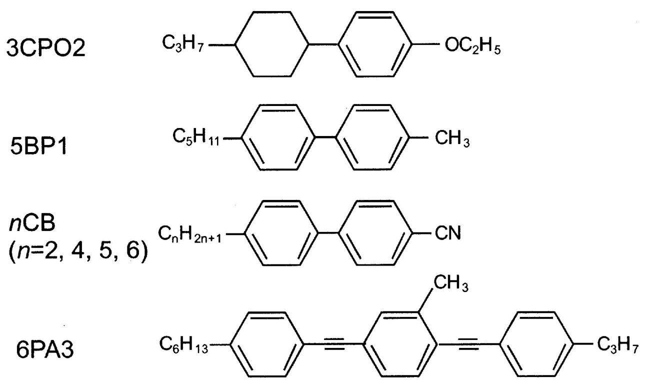

Figure 3. Samples used in the experiments.

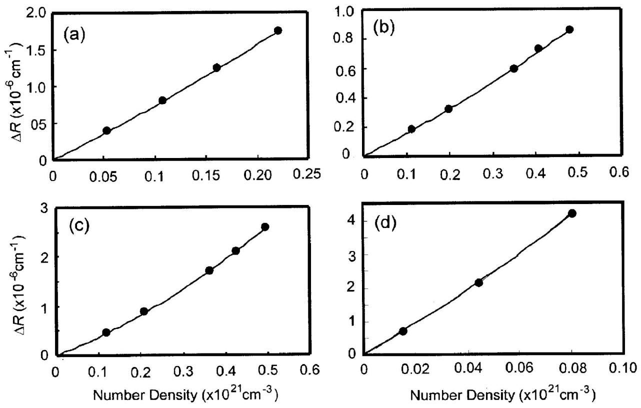

Figure 4. Reduced Rayleigh ratio $\Delta R$ as a function of number density for (*a*) 3CP2, (*b*) 5BP1, (*c*) 6CB and (*d*) 6PA3.

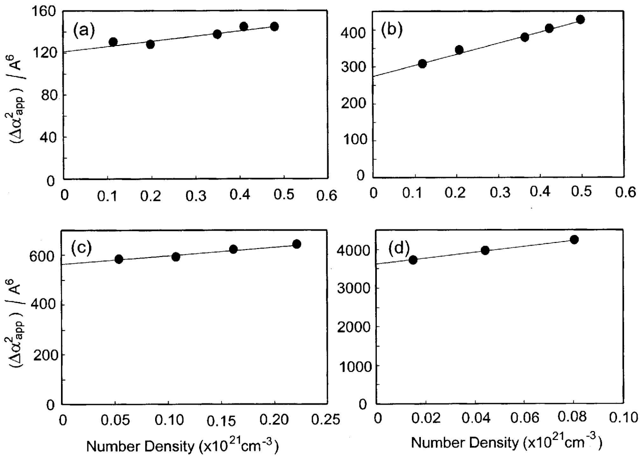

Figure 5. Apparent molecular polarizability anisotropy $(\Delta\alpha_{\mathrm{app}})^2$ as a function of number density for (*a*) 3CP2, (*b*) 5BP1, (*c*) 6CB and (*d*) 6PA3.

Table. Measured and calculated molecular polarizability anisotropy $(\Delta\alpha)^2_{\mathrm{dRs}}$ and $(\Delta\alpha)^2_{\mathrm{MOPAC}}$, for seven compounds. $(\Delta\alpha)^2_{nS}$ values calculated using $n$ experimentally determined and assuming the order parameter $S = 0.7$ are also shown for three compounds. They show better agreement with $(\Delta\alpha)^2_{\mathrm{dRs}}$ values than do $(\Delta\alpha)^2_{\mathrm{MOPAC}}$ values.

| | | $(\Delta\alpha)^2_{\mathrm{MOPAC}}/\mathrm{A}^6$ | | |
|---|---|---|---|---|
| | $(\Delta\alpha)^2_{\mathrm{dRs}}/\mathrm{A}^6$ | at 1.96 eV | at 0 eV | $(\Delta\alpha)^2_{nS}/\mathrm{A}^6$ |
| 3CPO2 | 121 | 287 | 217 | 71 |
| 5BP1 | 273 | 789 | 533 | |
| 2CB | 529 | 1090 | 743 | |
| 4CB | 570 | 1169 | 793 | |
| 5CB | 552 | 1196 | 812 | 547 |
| 6CB | 563 | 1223 | 828 | |
| 6PA3 | 3618 | 10 785 | 5930 | 5224 |

$(\Delta\alpha)^2_{\mathrm{MOPAC}}$ values at 0 eV give values closer to the experimental result, although the difference is still serious. However, the relative magnitudes of $(\Delta\alpha)^2$ for seven compounds show a similar trend both for $(\Delta\alpha)^2_{\mathrm{dRs}}$ and $(\Delta\alpha)^2_{\mathrm{MOPAC}}$, and both show good positive correlation, as shown in figure 6, where the points plotted in log-log scales are on straight lines of a slope of unity, as shown by the dotted lines. The intersections to the ordinate give average factors of the difference between experiment and MOPAC calculation: $(\Delta\alpha)^2_{\mathrm{MOPAC}} = 1.5\ (\Delta\alpha)^2_{\mathrm{dRs}}$ for 0 eV and $(\Delta\alpha)^2_{\mathrm{MOPAC}} = 2.5\ (\Delta\alpha)^2_{\mathrm{dRs}}$ for 1.96 eV.

In the calculation, we treat a single molecule, in vacuum, with its most stable molecular structure, while in the experiment, molecules are dissolved in solution and take various configurations. In this sense, it is rather surprising to find such a good correlation. In the present analysis, we use Vuks' model, in which anisotropic local field is neglected. The good correlation over a wide range of anisotropy of the refractive index shown in figure 6 implicitly reveals the validity of the Vuks' model.

We also examined the effect of solvent on the MOPAC calculation. According to the calculation made for molecules in $CCl_4$ ($\varepsilon = 2.228$ at 25°C), the solvent effect is negligible. Moreover, the effect cannot be seen even if we use a dielectric constant larger by a factor of 2.

It is found in both experimental and calculated results for *n*CB that $(\Delta\alpha)^2_{\mathrm{dRs}}$ scarcely depends on alkyl chain length, indicating that the polarizability is governed mainly by the polar group and its associated conjugation.

The right-hand column in the table shows $(\Delta\alpha)^2_{nS}$ values calculated using $n_{\parallel}(=n_e)$ and $n_{\perp}(=n_o)$ experimentally determined, and assuming the order parameter $S = 0.7$: Using these values, we can deduce $\bar{\alpha}$ and $\Delta\alpha$ using equations (1) and (2). Since the anisotropy of the macroscopic polarizability is proportional to $S$, the anisotropy of molecular polarizability is inversely proportional to $S$. Hence, if we use $S = 0.5$, we will have a molecular polarizability larger by 40%. For 5CB, a very good agreement between $(\Delta\alpha)^2_{nS}$ and $(\Delta\alpha)^2_{\mathrm{dRs}}$ is obtained. A more quantitative comparison, by taking account of the anisotropic local field and the dispersion of the refractive indices, and using an experimentally determined $S$, may lead to a better agreement in 3CPO2 and 6PA3. In particular, the effect of anisotropic local field [8] could be serious, although the estimation of $(\Delta\alpha)^2_{nS}$ was based on Vuks' model neglecting the local field anisotropy. The contribution of the local field factor $[(n^2+2)/3]^2$ has to be examined. However, a good correlation between measured and simulated molecular polarizabilities (figure 6) suggests that the effect is not so serious. At the present stage, however, we may conclude, by the comparison among these $(\Delta\alpha)^2$ values: the measured $(\Delta\alpha)^2_{\mathrm{dRs}}$ agrees more closely with $(\Delta\alpha)^2_{nS}$ expected from refractive index anisotropy, than does $(\Delta\alpha)^2_{\mathrm{MOPAC}}$ from MOPAC calculation.

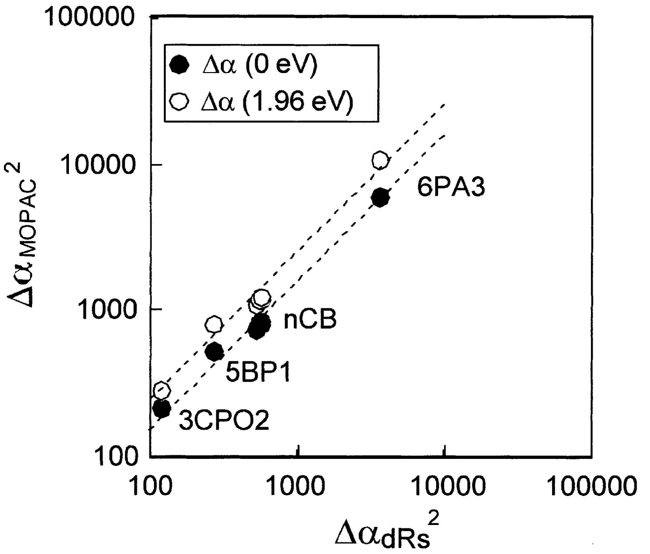

Figure 6. Correlation between molecular polarizability anisotropy values determined by depolarized Rayleigh light scattering and by MOPAC calculation in a log-log plot. The two dotted lines have a slope of unity for 0 eV and 1.96 eV.

## 5. Conclusion

Molecular polarizability anisotropy was determined experimentally by depolarized Rayleigh light scattering. The values agree with those expected from refractive index anisotropy. It is also concluded that molecular polarizability calculated using MOPAC always gives values larger than the true value.

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