Measurement of Optical Anisotropies of Molecules in Solution by Light Scattering at 6328 Å

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Abstract: The intensity of depolarized Rayleigh-scattered light has been measured for a series of dilute solutions at 23°, using a specially constructed photometer equipped with a He–Ne laser source and a lock-in detection system. The scattering intensities have been related directly to the molecular optical anisotropies of benzene, naphthalene, quinoline, anthracene, and biphenyl, invoking the assumption of Bothorel, namely, that the effective field in solution is that of Lorentz. Contrary to earlier reports, agreement between optical anisotropy values calculated from Kerr constants and those calculated from scattered light intensities is excellent. Furthermore, it has been demonstrated for dichlorodimethylsilane that bond polarizabilities can be calculated and used to predict molecular optical anisotropies. Hence, the technique, which is highly sensitive and applicable to labile systems, can be applied to determine structures of molecules in solution or to investigate the electronic structure of molecules of known geometry.

The measurement of the depolarization of Rayleigh-scattered light[1] along with the measurement of Kerr constants and molecular refractions[2] allows the quantitative determination of optical anisotropies of gaseous molecules. In turn, knowledge of the optical anisotropy can be used to determine molecular structure since the anisotropy is often a rather strong function of bond angles and bond lengths. The molecular optical anisotropy, γ^2, has been described[3] in terms of the three nonzero components, α_{xx}, α_{yy}, and α_{zz} of the diagonalized molecular polarizability tensor. Hence, reference is often made to a molecular polarizability ellipsoid with semi-axes, α_{xx}, α_{yy}, and α_{zz}. Actually $\gamma^2 = {}^1/_2[(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{xx} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{yy})^2]$.

One of the better ways of calculating the diagonal elements is to use bond polarizability tensors.[2] Then by resolving the respective bond polarizability tensors into their principal components, and assuming that these components will be additive for an entire molecule, the principal components of the molecular polarizability tensor can be calculated. For simple molecules composed entirely of localized bonds, it is possible in principle to choose correctly between candidate structures, by comparing measured values of the light scattering depolarization with values computed for candidate structures using bond polarizability tensors.

Bond polarizability values, unfortunately, are not especially easy to obtain. Most attempts have involved the measurement of bond refractivities[2] or Raman vibrational scattering intensities.[4] Attempts to calculate bond polarizabilities using quantum mechanical principles have been unevenly successful. A Δ-function model[4,5] appears to merit serious consideration, since it has been used to calculate molecular polarizability values which compare favorably with experimental values for a wide variety of compounds. Undoubtedly, such calculations give bond polarizabilities with uncertainties as high as 10 to 20%. But, for many interesting systems, such certainty may be all that is needed.

Primarily because of experimental difficulties related to measuring the very small intensity values of the anisotropic Rayleigh scattering from gases, in recent years few studies have been made of gaseous systems. On the other hand, considerable interest has been shown in the anisotropic scattering from pure liquids[6] and solutions.[7] Magnitudes of the anisotropic scattering from solutions are relatively great and easily measured precisely, using either mercury arc or He–Ne laser illumination.

Bothorel[8] and others[9] have attempted to relate quantitatively the intensity of anisotropic Rayleigh scattering from solutions to the structures of solute molecules in solution. It has been reported,[10] however, that solute–molecule optical anisotropies are proportional to but not equal to gas phase values. Kerr constants, on the other hand, have been related by LeFevre[11] directly to gas and solute molecule anisotropies.

It is somewhat surprising that Kerr constants reportedly can be used to describe solute molecular optical anisotropies, but that light scattering anisotropies cannot be used in like fashion. This paper reports experimental work which demonstrates that it is possible in light scattering work to relate gas–molecule and solute–molecule optical anisotropies directly. Furthermore, the model of Lippincott[5] has been used to calculate bond polarizability tensors and to correctly describe the anisotropic scattering of solutions of dichlorodimethylsilane in cyclohexane. It follows that the light scattering method is highly sensitive to the geometries of dissolved molecules, and that it provides a practical means for studying the structures of dissolved molecules.

Experimental Section

The Light Scattering Apparatus. A schematic diagram of the photometer is shown in Figure 1. The entire apparatus was constructed on an optical bench made of 1-in. thick aluminum mounted

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(1) Lord Rayleigh, *Phil. Mag.*, **35**, 373 (1918).

(2) K. G. Denbigh, *Trans. Faraday Soc.*, **36**, 936 (1940).

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(4) T. V. Long and R. A. Plane, *J. Chem. Phys.*, **43**, 457 (1965).

(5) E. R. Lippincott and J. M. Stutman, *J. Phys. Chem.*, **68**, 2926 (1964).

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(10) M. J. Aroney, R. J. W. LeFevre, and J. D. Saxby, *Aust. J. Chem.*, **18**, 1501 (1965).

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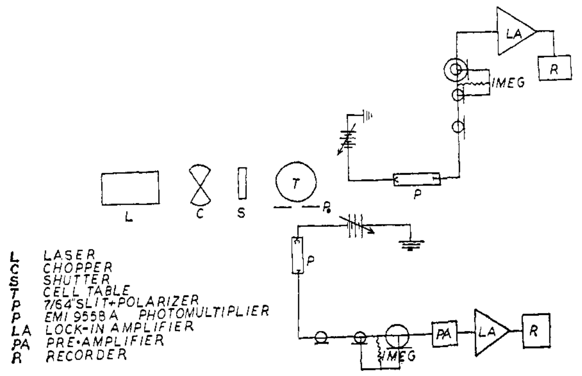

Figure 1.

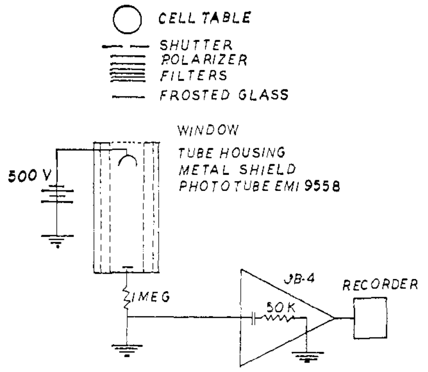

Figure 2.

on a heavy rubber pad to prevent vibration. The laboratory was air conditioned to allow all measurements to be made at temperatures controlled to 23 ± 1°. It was found that background noise was reduced if all electrical inputs were connected to one line source by means of an eight-membered socket box.

The source used was a standard 3-mW Spectra Physics Model 122 He–Ne laser. The 6328-Å light produced was chopped at 600 cps by a PAR Model BZ-1 variable-range mechanical light chopper. The chopper was also used to supply a square wave reference signal synchronous with the chopping. The polarization of the source was adjusted by means of a Spectra Physics Model 310 polarization rotator mounted directly on the laser housing.

Two separate detection systems were employed in making the depolarization measurements. One system shown in Figure 2 monitored the laser beam intensity at zero angle. Stability of the phototube signal was greatly enhanced if the beam of light impinging on the cathode was diffused by causing it to pass through an ordinary piece of frosted glass. An EMI 9558B photomultiplier tube housed in a shielded chamber, Model TE-104, purchased from Products for Research, Inc., initially amplified the reference signal. An applied potential of 500 V gave the most stable photocurrent.

After initial amplification by the photomultiplier, a PAR Model JB-4 lock-in amplifier tuned to a reference frequency of 600 cps further amplified the reference signal. A Hewlett–Packard Model 7100/7101 B two pen strip chart recorder measured the output signal. All connections from the power supply to the strip chart recorder were made with shielded cable and BNC connectors.

Measurement of the light scattered at 90° to the incident beam involved a detection system, Figure 3, analogous to that used for the scattered light at 0° angle. Initial amplification was achieved by an EMI phototube, but due to the low scattering intensities at 90°, the potential on this tube was raised to 900 V and the signal was preamplified by a PAR Model CR-4 low noise amplifier placed as close as possible to the phototube.

Since our studies involved the measurement of small depolarization ratios, the intensity of the vertically polarized scattered light exceeded that of the horizontally polarized component, often by as much as a factor of 20. It was found that greater precision could be achieved with the EMI photomultiplier tube if near equalization of the intensities of the vertically and horizontally polarized components was achieved by placing a 20X neutral filter in front of the photomultiplier tube when vertically polarized light was observed. To obtain reproducible measurements the filter had to be placed between the cell and the phototube. If placed in the incident beam in front of the scattering cell, precision was very poor.

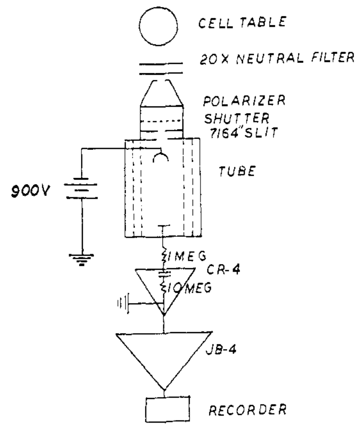

Figure 3.

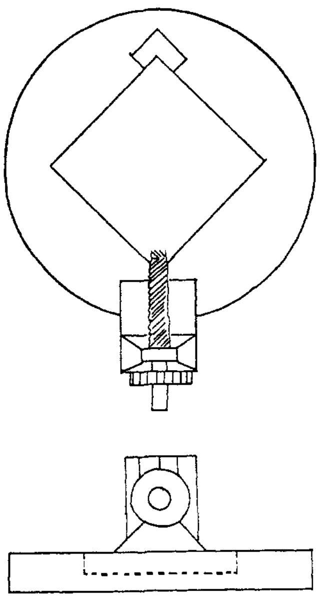

Figure 4.

A polarizer, a polaroid disk in a metal tube obtained from Phoenix Precision Instruments, Inc., was placed between the scattering cell and the phototube to allow separate measurement of the vertically and horizontally polarized components of the scattering light. The polarizer was calibrated by rotating it until the intensity of vertically polarized scattered light of a standard solvent was maximized. The vertically polarized components of the scattering from all solutions were measured with the polarizer locked in this position, and rotation by 90° allowed measurements of the horizontally polarized components.

A specially machined cell table, Figure 4, equipped with a high tension spring and a knurl knob, ensured reproducible positioning of the scattering cell. Since the same spring tension could be maintained throughout a measurement, the cell position could be reproduced with a high degree of precision.

All depolarization measurements were made using a 30 × 30 mm cell purchased from the Phoenix Instrument Company. This cell was painted on the outside, except for the entrance and exit slits, with a flat black paint to minimize reflection. Two other cells, also painted black, but having different geometries, were used to study reflection effects. The test cells, one of semihexagonal shape purchased from Phoenix, and a second one fabricated in the shape of a cross, gave depolarization ratios which varied by no more than 2% from square cell values, using pure benzene and cyclohexane. Values were almost identical with those reported at 6328 Å earlier by

Porto.[12] It is felt that the data indicate that reflections had been suppressed adequately.

Clarification of Solutions. The complete removal of the small particles of unwanted matter is essential if meaningful data are to be obtained. A Gelman Model 4280 pressure filtration funnel, equipped with a membrane filter, Type VCWPO4700, purchased from Millipore Corporation, freed solutions from dust, usually after three filtrations. Actually, it was found that a very few dust particles in the liquids did little harm. Due to the very small scattering volumes observed, the dust particles could be detected as spikes on the signal *vs.* time plots. However, as a general practice six or seven filtrations were performed on each solution and scattered light intensities were measured after each filtration. Intensity minima converged to a reproducible value varying only by 1-2%, after two to three filtrations.

Reagents. Spectro-grade benzene, cyclohexane, and carbon tetrachloride were purchased from Eastman Organics, Inc., and used with no further purification. Aromatics other than benzene were of analytical reagent grade and were distilled before use. Dichlorodimethylsilane purchased from Dow Corning Corporation was distilled before use. Tetraethyltin was bought from Alpha Inorganics and used without further purification.

Photometer Calibration. The Rayleigh ratios must be determined precisely for the various polarized components of the light scattered from solutions at 90° if correct values of the optical anisotropy are to be obtained. In this study, scattering from the pure solvents was used to calibrate the instrument. Turbidity values reported by Carr and Zimm[13] were used throughout. Since the very same cell was used for all scattering measurements, and since refractive index increments of solutions over solvents were very small, no scattering volume correction had to be made. Scattering intensity signals of a solvent and its solutions could be compared directly after correction by the Cabannes factor.

As a check on the standard method of calibration the turbidity increments for cyclohexane solutions of a compound of known molecular weight, tetra-*n*-butyltin, were measured and compared with increments predicted by the standard Debye equation

$$1/M = 1/571 = \frac{32\pi^3 n_0^2 \left(\frac{\delta n}{\delta c}\right) c^2}{3^4 N \tau^*}$$

where τ^* is the excess turbidity of solution minus solvent. Turbidity increments, τ^*, measured using the cyclohexane solvent as a standard, were systematically 30% higher than predicted. This lack of precise agreement is hardly grounds for total satisfaction, but it should be noted that photometers generally are calibrated for purposes of molecular weight determination by means of the scattering of standard polymer solutions rather than that of pure solvents. The effects of nonideal solution behavior should be somewhat reduced in that fashion. The fact that τ^* values for the standard solutions were high is very significant in itself, since if the standard solvent scattering signal did contain large components due to reflection, τ^* should be smaller and not larger than the theoretically calculated value. In brief, it is suggested that very large systematic errors due to calibration are unlikely, although at worst a systematic error as large as 20-30% could be possible. As usual in light scattering work the precision was much better than the accuracy. Scattered light relative intensities were reproducible to 1-2%.

Table I. Molecular Optical Anisotropies of Molecules Dissolved in Cyclohexane or CCl_4

Solute	Solvent	Concentration, M	Relative values of scattered light intensities R_{iv}	R_{ivs}	$\gamma^2 \times 10^{48}$ cm^6
Benzene	C_6H_{12}	0.10	1.22	0.13	10.3
Benzene	C_6H_{12}	0.25	1.22	0.35	11.5
Benzene	C_6H_{12}	0.32	1.22	0.44	11.5
Benzene	C_6H_{12}	0.33	1.22	0.53	12.5
Benzene	C_6H_{12}	0.44	1.22	0.65	11.5
Benzene	C_6H_{12}	0.50	1.22	0.79	12.5
Benzene	C_6H_{12}	0.10	1.00	0.15	12.6
Benzene	CCl_4	0.25	1.00	0.34	11.5
Benzene	CCl_4	0.40	1.00	0.61	12.6
Benzene	CCl_4	0.50	1.00	0.71	12.6
Benzene	CCl_4	0.60	1.00	0.89	13.6
Naphthalene	C_6H_{12}	0.053	0.999	0.441	79.5
Naphthalene	C_6H_{12}	0.11	0.999	0.901	78.4
Naphthalene	CCl_4	0.12	1.03	0.820	56.7
Naphthalene	CCl_4	0.20	1.03	1.59	67.2
Naphthalene	CCl_4	0.34	1.03	2.49	63.0
Naphthalene	CCl_4	0.50	1.03	3.63	63.0
Biphenyl	C_6H_{12}	0.10	1.28	0.810	61.7
Biphenyl	C_6H_{12}	0.20	1.28	1.78	68.0
Biphenyl	C_6H_{12}	0.30	1.28	2.52	64.9
Biphenyl	C_6H_{12}	0.40	1.28	3.11	64.9
Biphenyl	CCl_4	0.20	0.620	0.840	63.0
Biphenyl	CCl_4	0.40	0.620	2.28	64.0
Diphenylmethane	C_6H_{12}	0.10	0.760	0.270	34.5
Diphenylmethane	C_6H_{12}	0.25	0.760	0.570	31.9
Diphenylmethane	C_6H_{12}	0.40	0.760	0.990	32.4
Diphenylmethane	C_6H_{12}	0.60	0.760	1.41	32.4
Diphenylmethane	CCl_4	0.10	0.640	0.160	22.1
Diphenylmethane	CCl_4	0.25	0.640	0.370	21.0
Diphenylmethane	C_6H_{12}	0.60	0.640	1.01	24.1
Quinoline	C_6H_{12}	0.05	1.17	0.58	95.0
Quinoline	C_6H_{12}	0.10	1.17	1.22	104
Quinoline	C_6H_{12}	0.20	1.17	2.51	103
Quinoline	C_6H_{12}	0.30	1.17	3.70	103
Quinoline	C_6H_{12}	0.60	1.17	6.52	95.0
Quinoline	CCl_4	0.10	1.15	1.50	112
Quinoline	CCl_4	0.20	1.15	3.41	125
Quinoline	CCl_4	0.30	1.15	4.33	110
Quinoline	CCl_4	0.40	1.15	6.73	125
Quinoline	CCl_4	0.60	1.15	9.91	125
Tetraethyltin	C_6H_{12}	0.10	1.00	0.0043	0.418
Tetraethyltin	C_5H_{12}	0.20	1.00	0.0086	0.408
Tetraethyltin	C_6H_{12}	0.35	1.00	0.014	0.408
Tetraethyltin	C_6H_{12}	0.50	1.00	0.020	0.418
Dichlorodimethylsilane	C_6H_{12}	0.156	0.850	0.130	9.32
Dichlorodimethylsilane	C_6H_{12}	0.304	0.850	0.260	9.51
Dichlorodimethylsilane	C_6H_{12}	0.401	0.850	0.320	9.51
Dichlorodimethylsilane	C_6H_{12}	0.624	0.850	0.490	9.51

Calculation of the Molecular Polarizability Anisotropy

Values of the polarizability anisotropy were calculated according to the method of Bothorel.[3] Since the incident laser beam was vertically polarized, the calculations had to be modified accordingly. Actually no change had to be made in the equations of Bothorel at all, but in the calibration of the instrument it had to be noted that $R_v = 2R_u/(1 + P_u)$. R_u and R_v are the Rayleigh ratios for the solvents interacting with unpolarized and vertically polarized light, respectively. P_u is the depolarization ratio for unpolarized light. Using the Bothorel value for P_u and R_u, one obtains, for cyclohexane, that R_v equals 8.36×10^{-6} cm^{-1} at 5461 Å and 4.65×10^{-6} cm^{-1} at 6328 Å. For the horizontally polarized component of light scattered at 90° to the vertically polarized laser beam, the Rayleigh's constant is

$$R_{iv} = 4.65 \times 10^{-6}\left(\frac{P_v}{1 + P_v}\right) \text{cm}^{-1}$$

Since P_v equals 0.0304 for cyclohexane, R_{iv} equals 13.5×10^{-8} cm^{-1}.

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(12) R. Leite, R. Moore, and S. Porto, *J. Chem. Phys.*, **40**, 3741 (1964).

(13) C. I. Carr and B. H. Zimm, *ibid.*, **18**, 1616 (1950).

Table II. A Comparison of Anisotropy Values Measured in Different Laboratories[a]

Solute	Solvent	Bothorel, *et al.*	LeFevre, *et al.*	This study
Benzene	CCl_4	36[b]	14.5[c]	12.6
	C_6H_{12}	39.5[d]		12.0
Naphthalene	CCl_4	195[b]	97.0[c]	63
	C_6H_{12}			79
Diphenyl-methane	CCl_4	75.5[d]	28.1[e]	23
	C_6H_{12}			32
Quinoline	CCl_4	182[f]	99[g]	120
	C_6H_{12}			100
Biphenyl	CCl_4	208[h]	57.1[i]	63.5
	C_6H_{12}			65

[a] $\gamma^2 \times 10^{48}$ cm^6. [b] See ref 3. [c] See ref 10. [d] A. Unanué and P. Bothorel, *Bull. Soc. Chim. Fr.*, 2827 (1965). [e] R. J. W. LeFevre, M. Aroney, G. L. D. Ritchie, and A. N. Singh, *J. Chem. Soc.*, 5810 (1965). [f] P. Bothorel, A. Unanué, C. Gardere, N. P. Buu-Hoi, P. Jacquignon, and F. Perin, *Bull. Soc. Chim. Fr.*, 2920 (1966). [g] C. G. LeFevre, R. J. W. LeFevre, B. P. Rao, and M. R. Smith, *J. Chem. Soc.*, 1188 (1959). [h] A. Unanué and P. Bothorel, *Bull. Soc. Chim. Fr.*, 1640 (1966). [i] J. Y. H. Chau, C. G. LeFevre, and R. J. W. LeFevre, *J. Chem. Soc.*, 2666 (1959).

The value R_{iv} for carbon tetrachloride, calculated assuming $R_u = 5.88 \times 10^{-6}$ cm^{-1} at 5461 Å and that $P_v = 0.020$, is 12.28×10^{-8} cm^{-1}. The anisotropy value is calculated from the formula

$$1/\gamma^2 = \frac{32\pi^4 p(n^2 + 2)^2}{135\lambda^4 R_{ivs}}$$

p = number of molecules of solute per ml of solution, λ = wavelength of incident radiation in cm, n = refractive index of pure solvent at 6328 Å, and R_{ivs} = Rayleigh ratio of horizontally polarized light scattered from solution, minus R_{iv}. Typical anisotropy data appear in Table I.

Table II allows a comparison to be made between optical anisotropy values measured in this study, those determined by Bothorel by light-scattering using a mercury arc source, and those determined by LeFevre from Kerr constants.

A Calculation of the Optical Anisotropy of Dichlorodimethylsilane

If the molecular structure is to be established by means of the light scattering depolarization technique, bond polarizabilities must be either measured or calculated and then combined additively to give the molecular polarizability tensor. Lippincott has applied with considerable success a method of bond polarizability calculation based on a Δ-function model. It will be shown using Lippincott's method that bond polarizabilities can be calculated for dichlorodimethylsilane and combined to give the diagonalized molecular polarizability tensor. The molecular polarizability then can be used to predict the optical anisotropy. Calculated and measured values of the anisotropy can be compared to assess the applicability of the model.

Bond polarizability components, assuming a bond order of one, were obtained directly from the work of Lippincott and Stutman[5] for the Si–Cl bond: $\alpha_{\parallel} = 48.4 \times 10^{-25}$ cm^3, $\alpha_{\perp} = 13.3 \times 10^{-25}$ cm^3. Similar calculations applied to a $Si{-}CH_3$ group with a freely rotating methyl group gave $\alpha_{\parallel} = 55.5 \times 10^{-25}$ cm^3 and $\alpha_{\perp} = 28.4 \times 10^{-25}$ cm^3. Group polarizability component values then can be combined using the method of Smith and Mortensen,[14] assuming regular tetrahedral geometry, to calculate the principal components of the diagonalized polarizability tensor of dichlorodimethylsilane, *i.e.*, $\alpha_{xx} = 119.6 \times 10^{-25}$ cm^3, $\alpha_{yy} = 130.0 \times 10^{-25}$ cm^3, and $\alpha_{zz} = 124.6 \times 10^{-25}$ cm^3.

The resulting value of the anisotropy, γ^2, is 0.91×10^{-48} cm^6, a value well below the observed one of 9.5×10^{-48} cm^6. This seemingly poor agreement between measured and calculated values of γ^2 might at first glance appear to reflect unfavorably on the model used in the calculations. Yet, it must be noted that it is very likely that the bond order of Si–Cl is not in fact 1.0, but rather nearer 1.5 due to (p → d) π interactions. If the Si–Cl bond polarizability is calculated using a bond order of 1.4, $\alpha_{\parallel} = 66 \times 10^{-25}$ cm^3 and $\gamma^2 = 8.7 \times 10^{-48}$ cm^6. Then agreement between the calculated and measured values of the anisotropy is rather good. Very likely part of the difference between calculated and measured values is due to uncertainty in theory.

It should be apparent that the polarizability anisotropy is a sensitive measure of molecular geometry as well as of electronic structure. Assuming a square planar configuration for dichlorodimethylsilane the calculated value of the anisotropy increases dramatically to 41.6×10^{-48} cm^6, a value far in excess of the measured value in solution attributable to a tetrahedral structure.

Discussion

A glance at Table II shows that the molecular polarizability anisotropy values reported for several aromatic compounds in this study are very close to those of LeFevre, but substantially lower than those obtained by Bothorel. The systematically lower values of the anisotropy obtained for benzene in this study as compared to those of LeFevre suggest that the detection system may have been exposed to a small amount of reflection. The difference between the values measured in this study and those determined by Bothorel cannot be explained by such an effect. In fact, the small scattering volumes observed when laser illumination was used not only allowed dust to be detected readily and very likely reduced secondary scattering and convergence effects, but also must have reduced the reflections far below those normally observed in conventional systems. Only a tiny portion of the cell background could affect the sensing system because of the very small volume of solution subtended by the phototube optics. It can be concluded that reflection contributed only, at most, a few per cent to the scattering. The possibility of fluorescence was checked by inserting a Perkin-Elmer 582-1218 interference filter into the optical system. No significant amounts of fluorescence were noted. Background due to polarized Raman lines was neglected. It should be noted that the anisotropy of tetraethyltin is very small, as expected for a highly symmetrical molecule.

There are obvious advantages in being able to obtain the same values of the optical anisotropy from light scattering as from Kerr constants. The most obvious advantage is, of course, that the two techniques can be used to obtain the same type information, hence providing a valuable check on accuracy. Yet, perhaps

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(14) R. S. Smith and E. Mortensen, *J. Chem. Phys.*, **32**, 503 (1960).

most important, from the standpoint of this study, is the result that optical anisotropies measured by light scattering can be related directly to the bond polarizabilities and geometries of molecules. It follows that the light scattering technique can be used either to determine the geometries of molecules possessing well-characterized bonds or the electronic structure of bonds of molecules of known geometry.

Given the direct correlation between Kerr constant-based molecular optical anisotropies and those obtained from light scattering studies in solution, it will prove possible to investigate structurally, in detail, molecules as small as dichlorodimethylsilane. On the other hand much larger molecules can be studied as well. In theory, molecules of dimension up to $^1/_{20}$th of the wavelength of the incident light can be treated. Of course, it is expected that the technique will be most powerful for small molecules, since the optical anisotropy will vary more strongly for such systems as molecular geometry or electronic structure varies. It is anticipated that the light scattering technique will prove especially effective in the study of molecules undergoing rapid exchange processes in solution, that is, molecules usually inaccessible to either nmr or esr methods.

In summary, it has been demonstrated that by using a photometer equipped with a 6328-Å CW laser source the intensity of horizontally polarized Rayleigh-scattered light from solution can be measured precisely. Furthermore, using the equations derived by Bothorel it has proved possible to show that optical anisotropies of solute molecules measured from light scattering are very close in value to those derived from Kerr constants. In addition, it has been noted that a Δ-function model can be used to calculate bond polarizabilities, the resultant molecular polarizability tensors, and optical anisotropies for candidate structures. Since the optical anisotropy can vary substantially from one molecular geometry to another, unambiguous structural assignments can be made even though bond polarizabilities may not be known precisely.

Acknowledgment. Thanks are due Research, Inc. for generous support received during the early stages of this study. Much appreciated help also has been received from the National Science Foundation through Grant No. GP-5880. Valuable advice concerning construction of the photometer was generously given by Dr. J. L. Lundberg.

Resolution and Separation of the Stereoisomers of Tertiary Arsines by Means of Their Metal Complexes

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Contribution from the Ralph Forster and William Ramsay Laboratories, University College, London, England. *Received July 28, 1969*

Abstract: The two optical isomers of methylethylphenylarsine (MeEtPhAs) have been separated by fractional crystallization of the internal diastereoisomeric complex [PtCl(±)-MeEtPhAs(−)-stien]Cl (where (−)-stein = (−)-stilbenediamine). Methods are described for obtaining the two antipodes of the arsine from its complexes in high yield and high optical purity. The two dichloropalladium complexes containing the racemic and *meso* isomers of the ditertiary arsine, ethylene-1,2-bis(methylphenylarsine), have been chromatographically separated on silica gel. After decomposition of the complexes the two isomers can be distilled without interconversion. The structures of the two forms have been established by resolution of the dibenzyldiarsonium salt of the racemic compound. Certain physical data of the arsines and their complexes are recorded and discussed.

Simple dissymmetric tertiary arsines and phosphines are optically stable at room temperature. Hitherto these molecules have been obtained optically active either by electrolytic reduction[2] or, in appropriate cases, by nucleophilic displacement[3] reactions of the resolved quaternary salts.[4] In many cases these methods lead to some racemization of the phosphines or arsines, and in general are long and involved. In view of this, and because these optically active molecules play an important role in the elucidation of reaction mechanisms[5] and also because they may prove useful in the synthesis of asymmetric hydrogenation catalysts,[6,7] it seemed important to develop a simple and direct method for their resolution. Recently,[8] it was shown that methyl-*t*-butylphenylphosphine could be resolved through its platinum(II) complex; and although the free optically active phosphine was removed from the metal in solution, it was not isolated. Methods are reported here which are believed to be of considerable generality for the resolution of and the separation of the geometrical isomers of tertiary arsines. These methods, in essence, involve the formation of the metal complexes

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