Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

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Version of record first published: 29 Aug 2007.

To cite this article: Martin S. Beevers (1975): The Electro-Optical Kerr Effect in Solutions of the Nematogen N-(p-Methoxybenzylidene)-p-n-butylaniline, Molecular Crystals and Liquid Crystals, 31:3-4, 333-348

To link to this article: http://dx.doi.org/10.1080/15421407508082886

Mol. Cryst. Liq. Cryst., 1975, Vol. 31, pp. 333–348

Printed in Holland

The Electro-Optical Kerr Effect in Solutions of the Nematogen N-(*p*-Methoxybenzylidene)-*p*-*n*-butylaniline

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(*Received May 20, 1975; in final form July 23, 1975*)

The molecular Kerr constant has been measured for undiluted N-(*p*-Methoxybenzylidene)-*p*-*n*-butylaniline (MBBA) in the isotropic phase and also for MBBA in solution in benzene and carbon tetrachloride. The dependence of the molecular Kerr constant on concentration and temperature was studied. The anomalous optical properties manifested by pure MBBA in the isotropic phase were also found to be present in the solutions. De Gennes' theory was obeyed for undiluted MBBA and for concentrated solutions of MBBA in carbon tetrachloride. The infinite dilution molecular Kerr constant for MBBA in solution in benzene or carbon tetrachloride was readily interpreted in terms of modest anisotropies in the polarisability of the individual molecules.

INTRODUCTION

The wide range of electro-optical and magneto-optical phenomena manifested by mesophases or liquid-crystals has inspired many investigations on these materials. The reasons for the continuing interest in liquid-crystals are varied and too numerous to be cited here in full. From a practical viewpoint liquid-crystals have already made an impact in the field of optical display devices, which are now commercially available. The possibility of using certain liquid-crystals to indicate skin temperature has been demonstrated[1] and the role of liquid-crystals in the structure and function of biological systems has also been considered.[2] The use of liquid-crystals as anisotropic solvents, for studying compounds by nuclear magnetic reasonance[3–7] and electron spin resonance[8] is now well established. The high degree of order present at the molecular level in liquid-crystals provides an opportunity to study molecular interactions which are not dominated by geometrical constraints present in the solid phase.

In this investigation we are concerned with liquid-crystals of the nematic type in which the long axes of the molecules have a strong tendency to align parallel to one another so as to form an imbricated structure. If the long axis of a molecule in a liquid-crystal is chosen as a reference direction then nearest neighbouring molecules will have their long axes lying almost parallel to that of the reference molecule. Molecules which are far removed from the reference molecule will have no directional correlation with the latter. Between these two extremes there exists a gradual fall-off in the directional correlation of the long axis of the reference molecule with those of the surrounding molecules. This is a simplified interpretation of the distortion or continuum theory which is now widely used to interpret the physical properties of liquid-crystals.[9–11] Certain aspects of the continuum theory resemble those of the Kratky–Porod model used for interpreting the physical behaviour of rod-like polymer molecules.[12–13]

The electro-optical Kerr effect has recently been demonstrated to be an effective technique for studying pre-transitional behaviour of liquid-crystals in the isotropic phase.[14–19] The investigation reported here is concerned with the determination of the molecular Kerr constant of N-(*p*-methoxybenzylidene)-*p*-*n*-butylaniline (MBBA) in the undiluted state, and in solution in benzene and carbon tetrachloride. The effect of temperature on these systems has also been studied. One of the principal aims of the investigation was to see if the anomalous electro-optical behaviour observed in the isotropic phase of MBBA[14–19] was also present in solutions of MBBA in an inert solvent. In addition, by making measurements on dilute solutions of MBBA, information can be obtained concerning the electro-optical properties of individual molecules. This is an important aspect of the work, since it has been suggested that the electro-static polarisability ellipsoid of MBBA might be unusually anisotropic and that this may be an important factor in the formation of liquid-crystals in general.

The consequences of anomalous alignment and electro-hydrodynamic scattering in liquid-crystals in an electric field, due to anisotropies in the conductivity and/or permittivity have to be borne in mind.[20–23] We show that the general behaviour of the Kerr constant with temperature for undiluted MBBA agrees well with that found by other researchers using ac electric fields,[14–17] pulsed dc[18,19] and laser induced alignment.[24,25] In solutions of liquid-crystals in an inert solvent anomalous alignment is believed to contribute very little to the solution Kerr constant. Nakauchi *et al.*[26] using dc electric fields found that dynamic scattering did not occur in highly purified samples of MBBA. These workers placed emphasis on the removal of water, which they reduced to very low levels. All the materials used in the present study were thoroughly dried using activated zeolite. However, despite this precaution some electro-hydrodynamic scattering was still observed in undiluted MBBA, but diminished with increasing dilution for the solutions. In samples which exhibit light scattering in the presence of an electric field a continuous background of light of fluctuating intensity is super-imposed on the induced electrical birefringence. This leads to a loss in the accuracy with which the phase difference δ may be determined.

THEORY

When a liquid which transmits light is placed in a uniform electric field it becomes optically anisotropic. The magnitude of the induced anisotropy, measured as the refractive index Δn, for plane polarised light with its electric vector first parallel and then perpendicular to the direction of the applied electric field E, is given by the Kerr equation[27,28]

$$\Delta n = B \cdot \lambda \cdot E^2 \tag{1}$$

in which λ is the wavelength of the incident light and B is the Kerr constant. Experimentally, it is convenient to express the birefringence in terms of a measured phase difference δ which, in radians, is expressed as

$$\delta = 2\pi \cdot B \cdot l \cdot E^2 \tag{2}$$

where l is the optical path length between the electrodes.

From the point of view of the chemist a quantity more meaningful than B is the molecular Kerr constant,[27,28] defined in Equation (3)

$$_mK = 6 \cdot \lambda \cdot n \cdot B \cdot M/(n^2 + 2)^2(\varepsilon + 2)^2 d \tag{3}$$

where M, n, ε and d are respectively the molecular weight, refractive index, permittivity and density of the medium in question.[44] For solutions the molecular Kerr constant may be calculated using the alligation formula

$$_mK_{12} = {}_mK_1 \cdot f_1 + {}_mK_2 \cdot f_2 \tag{4}$$

where f is a molar fraction and the subscripts 1, 2 and 12 denote solvent, solute and solution respectively.

For solutions in which the refractive index, permittivity and density of the pure components only are known, the refractive index can be calculated by applying the Lorentz–Lorenz formula (Eq. 5) and assuming additivity of the molar refractions $[R]$ (Eq. 6).

$$[R] = (n^2 - 1)M/(n^2 + 2)d \tag{5}$$

$$[R]_{12} = [R]_1 f_1 + [R]_2 f_2 \tag{6}$$

A similar approach may be used to calculate the permittivities of the solutions using the Clausius–Mosotti relationship to calculate molar polarisabilities P (see Eqs. 7 and 8)

$$P = (\varepsilon - 1)M/(\varepsilon + 2)d \tag{7}$$

$$P_{12} = P_1 f_1 + P_2 f_2 \tag{8}$$

The densities of the solutions are calculated from the densities of the pure components at 298 K, assuming no change in volume on mixing.

EXPERIMENTAL

A diagram of the apparatus used to measure the phase difference δ is shown in Figure 1. A parallel, plane-polarised beam of monochromatic light is passed through the Kerr cell such that the plane of polarisation of the light is at an angle of 45° relative to the direction of the applied electric field. In the presence of an electric field the light leaving the cell is generally elliptically polarised. After passing through a suitably oriented quarter-wave retarder (de Senarmont compensator) the light can be extinguished by the analyser. The angular difference between the principal planes of the polariser and analyser is equal to $\delta/2$.

The design and the materials used in the construction of the Kerr cell resembled those used by other workers.[29] The cylindrical body of the cell and the two electrodes were made from stainless steel. The lower electrode was semi-circular in cross-section and made electrical contact with the cell wall, which was earthed. The upper electrode, also semi-circular in cross-section, had a smaller radius than the lower electrode and was electrically insulated from the cell wall by means of two Teflon plugs recessed into the upper surface of the electrode. The inter-electrode separation was 0.138 cm and was set by means of two glass spacers. The electrode assembly was held rigid in the cell by two screws which passed through the top of the cell and

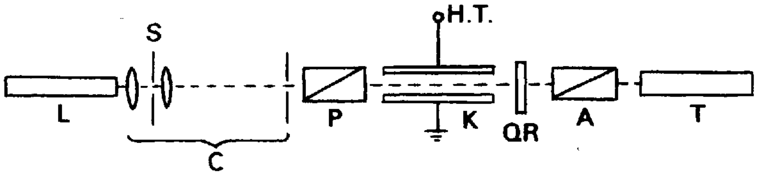

FIGURE 1 Diagram of apparatus used to measure the electro-optical Kerr effect. Principle components are: L, laser; C, collimating system consisting of two lenses, a slit S and a pinhole aperture; P, prism polariser; K, Kerr cell; QR, quarter-wave retarder; A, prism analyser; T, viewing telescope.

engaged the Teflon plugs in the upper electrode. The length of the electrodes was 7.45 cm and this was taken to be the effective optical path length between the electrodes. The windows of the cell consisted of two optical quality quartz discs which were carefully selected for their freedom from strain birefringence. Each window was secured to the cell by a steel retaining ring and three screws. A leak-proof seal was achieved using washers cut from low density polyethylene. The upper electrode was connected to the power supply via a steel spring seated in a Teflon plug which screwed into the wall of the cell. A Brandenberg model 707R power pack was used to supply the high tension voltage which was continuously variable in the range 0–15 kv. The temperature of the cell could be controlled to better than ±0.05 K by means of a close fitting water-jacket and a thermostatted water-bath. The water-jacket extended 4 cm beyond the windows of the cell in order to minimise temperature gradients. The light source was a Spectra Physics model 133 helium-neon laser emitting at a wavelength of 632.8 nm. The polariser and analyser were Glan-type prisms (Ealing Beck Ltd.) mounted in brass tubes. The analyser was set in a graduated circle which allowed rotations of 1 minute of an arc to be read with an accuracy of 0.5 minutes of arc. The quarter wave retarder was of mica (F. Wiggins and Sons Ltd.) mounted between glass discs and cleaved for use at 632.8 nm.

MATERIALS

A sample of the liquid-crystal MBBA (Eastman Kodak Ltd.) was twice fractionally distilled through a short Vigreux column at a pressure of about 0.5 mm of mercury. Only the fraction collected in the temperature range 451–453 K was considered suitable for use. All measurements made on undiluted MBBA and on solutions of MBBA in carbon tetrachloride were carried out using this sample which had a clearing temperature of 315.6 K. For measurements on solutions of MBBA in benzene, a fresh sample of MBBA was prepared by condensing equimolar quantities of anisaldehyde and para-*n*-butylaniline. The clearing temperature of this sample, after fractional distillation, was 318 K. The solvents, benzene and carbon tetrachloride, both of analytical grade, were further purified by fractional distillation. All materials were kept dry over 3A zeolite in tightly stoppered flasks. Solutions of MBBA were made up gravimetrically and were prepared as quickly as possible to minimise contamination. The solutions were rendered free of dust by filtering through a small-pore glass sinter. The components of the Kerr cell were thoroughly rinsed with dry solvent and air-dried before filling with fresh sample. When the cell was being reassembled care was taken to ensure that the hands of the operator did not touch parts of the cell which came into contact with the sample.

RESULTS

Undiluted MBBA and solutions of MBBA in carbon tetrachloride (0.15–3.95 mole litre^{-1}) were examined at temperatures between 283 K and 333 K. A series of solutions of MBBA in benzene (0.31–2.26 mole litre^{-1}) were also studied at temperatures of 293, 303, 313 and 323 K.

Typical plots of the measured phase difference δ as a function of the square of the applied electric field E^2 are shown in Figure 2. The two sets of data in this figure are for undiluted MBBA at 316 K and a solution of MBBA in carbon tetrachloride (1.58 mole litre^{-1}) at 283 K. In all the samples examined the phase difference δ was found to be directly proportional to E^2. Table I shows Kerr constant B_1 and B_{12} found for undiluted MBBA (4.19 mole litre^{-1}) and solutions of MBBA in carbon tetrachloride at various concentrations and temperatures. Presentation of the results in the form of molecular Kerr constants requires knowledge of the refractive index, permittivity and density of the medium under examination. Refractive

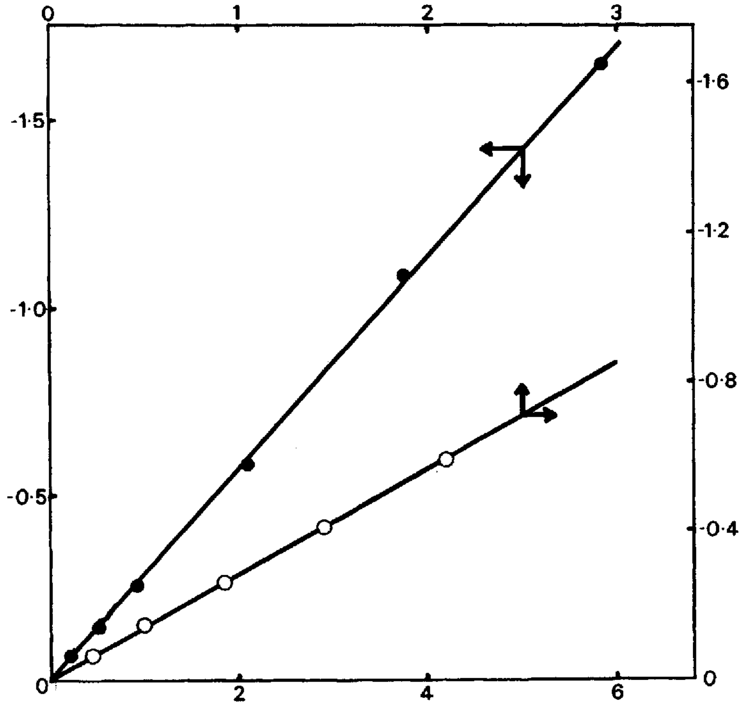

FIGURE 2 Phase difference as a function of the square of the applied electric field E^2 measured for undiluted MBBA at 316 K (●) and a solution of MBBA in carbon tetrachloride (1.58 mole litre^{-1}) at 283 K (○). Phase difference δ/radians. E^2/esu^2 cm^{-2} × 10^{-2}.

TABLE I

Concentration mole litre^{-1}	Experimental Kerr constants $B_{12} \times 10^8$ esu^{-2} cm for undiluted MBBA and solutions of MBBA in carbon tetrachloride at different temperatures					
	283	293	303	313	323	333	Other
0.154	1.84	1.80	1.76	1.74	1.71	—	—
0.288	2.22	2.35	2.43	2.66	2.68	—	—
0.548	—	3.12	3.60	3.47	3.63	—	—
1.10	1.15	1.71	2.84	3.63	4.45	—	—
1.58	−4.50	−1.79	−0.49	2.08	3.98	—	—
2.45	—	−33.1	−20.6	−12.9	−5.23	—	—
2.82	—	−64.0	−45.8	−26.7	−14.5	—	—
3.38	−272	−200	−129	−80.6	−58.1	−32.7	—
3.95	—	−1440	−550	−365	−254	-302^{318}	-3520^{288}
4.19	—	—	—	-6080^{316}	−985	−378	-525^{328}

indices and permittivities for the MBBA-benzene system at 298 K were taken from Maurel and Price[30] and were used in the calculation of molecular Kerr constants at other temperatures. Solution densities for MBBA in benzene were calculated from the densities of the pure components at 298 K using values of 1.12 g cm^{-3} for MBBA and 0.88 g cm^{-3} for benzene, and assuming no change in volume on mixing. For undiluted MBBA in the isotropic phase the refractive index,[31] permittivity[30] and density were taken to be 1.60, 4.87 and 1.12 g cm^{-3} respectively. These values were considered to be mean values in the temperature range 316–333 K covered in the measurements. Systematic errors incurred in the calculation of molecular Kerr constants for MBBA in the undiluted state, due to not allowing for changes in the refractive index, permittivity and density with temperature, are estimated to be less than 2%. The refractive index of solutions of MBBA in carbon tetrachloride were calculated from the refractive indices (MBBA 1.60; CCl_4 1.47) and densities (MBBA 1.12 g cm^{-3}; CCl_4 1.59 g cm^{-3}) of the pure components at 293 K using equations 5 and 6. Permittivities of solutions of MBBA in carbon tetrachloride were calculated from equations 7 and 8 using permittivities of 5.1 for MBBA[30] and 2.24 for carbon tetrachloride (The physical data for carbon tetrachloride at 293 K were taken from tables published by the National Bureau of Standards).

Systematic errors in the molecular Kerr constant determined for MBBA in solution in carbon tetrachloride due to not allowing for changes in the refractive index, permittivity and density with temperature are estimated to be approximately 5%. A check was made on the validity of the method used to calculate the refractive index and permittivity for solutions of MBBA in carbon tetrachloride. This was done by calculating the refractive index and permittivity for solutions of MBBA in benzene using Eqs. (5)–(8)

and the refractive indices and permittivities of the pure components[30] at 298 K, and comparing the values so obtained with those found experimentally.[30] Solution refractive indices calculated in the above manner were very close to those found experimentally, the discrepancy being less than 1% over the entire concentration range. Calculated solution permittivities were lower than the experimental values, the maximum difference being about 10% in the middle of the concentration range. We feel that these calculations justify the use of calculated refractive indices and permittivities in the evaluation of the molecular Kerr constant for MBBA in carbon tetrachloride.

In order to be able to determine the molecular Kerr constant ${}_mK_2$ for the solute MBBA in solution it is necessary to know the molecular Kerr constant of the solvent. Using the apparatus described here the molecular Kerr constants for benzene and carbon tetrachloride at 293 K were found to be $1.44 \pm 0.07 \times 10^{-12}$ and $6.10 \pm 0.30 \times 10^{-12}$ esu^{-2} cm^5 respectively. These values are in accordance with Kerr constants B and molecular Kerr constants ${}_mK$ found by other researchers.[27,29] To avoid ambiguity all references to molecular Kerr constants for MBBA in solution are to be interpreted as ${}_mK_2$'s the molecular Kerr constant for the solute (MBBA) calculated using Eq. (4). Figure 3 shows molecular Kerr constants for MBBA in the undiluted state and in solution in carbon tetrachloride at various concentrations and temperatures calculated from the Kerr constants B listed in Table I. The molecular Kerr constant for undiluted MBBA in the isotropic phase rapidly increases in magnitude as the temperature approaches the nematic-isotropic transition point. Dilution of the pure MBBA (4.19 mole litre^{-1}) with carbon tetrachloride depresses the nematic-isotropic transition temperature; T_c being 287 K for a 3.95 mole litre^{-1} solution. Further dilution eventually results in a change in sign of the molecular Kerr constant of MBBA. Thus for a 1.58 mole litre^{-1} solution at 306 K the molecular Kerr constant of MBBA is zero. For solutions in which the concentration is below 0.30 mole litre^{-1} the molecular Kerr constant is relatively insensitive to further dilution or to changes of temperature in the range 293–323 K. The infinite dilution molecular Kerr constant for MBBA in carbon tetrachloride at 293 K was found by extrapolation to be $1.20 \pm 0.10 \times 10^{-10}$ esu^{-2} cm^5.

Experimentally determined solution Kerr constants B_{12} and the corresponding molecular Kerr constants ${}_mK_2$ for MBBA in benzene at various concentrations and temperatures are presented in Table II. The infinite dilution molecular Kerr constant for MBBA in benzene at 293 K was found by extrapolation to be $1.0 \pm 0.1 \times 10^{-10}$ esu^{-2} cm^5, a value close to that found for MBBA in carbon tetrachloride.

The similarities in the critical behaviour of the static and dynamic proper-

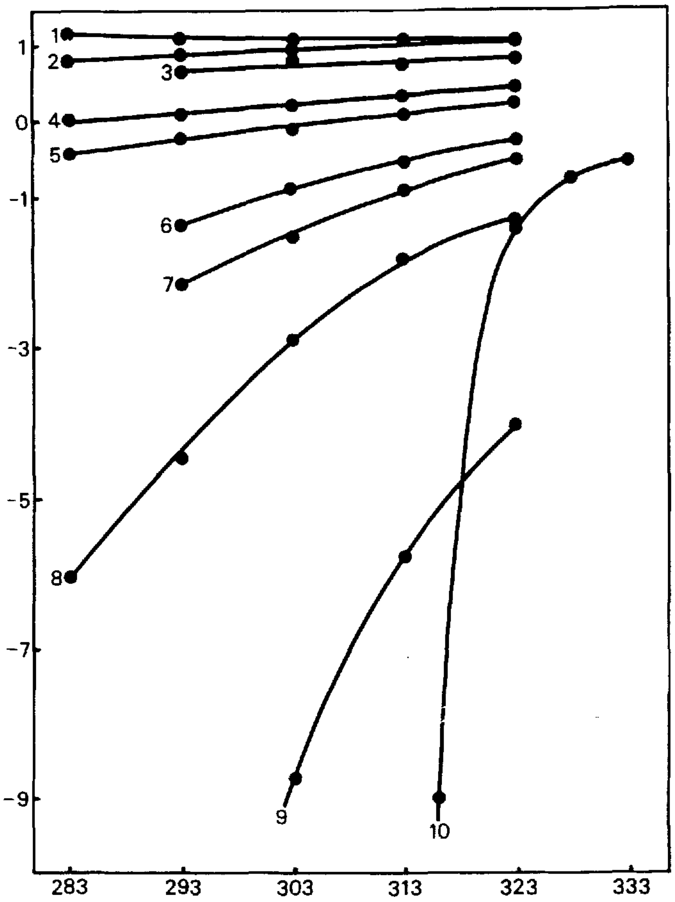

FIGURE 3 Molecular Kerr constants as a function of temperature for solutions of MBBA in carbon tetrachloride at concentrations of 0.15 (1), 0.29 (2), 0.55 (3), 1.10 (4), 1.58 (5), 2.45 (6), 2.82 (7), 3.38 (8) and 3.95 (9) mole litre^{-1} of solution. Also shown are molecular Kerr constants (÷10) for undiluted MBBA (10). Molecular Kerr constant $_mK$/cm^5 esu^{-2} × 10^{10}.

ties of nematic liquid-crystals and ferromagnetic materials (e.g., critical slowing) has led several investigators to interpret the macroscopic properties of liquid-crystals in terms of a critical index γ through the Curie–Weiss relationship and its analogous forms[38]

$$\chi = m(T - T^*)^{-\gamma} \tag{9}$$

The quantity χ can be a static property of the system such as the magnetic susceptibility or the intensity of scattered light, or it can be dynamic quantity such as a relaxation time.[39,40] The units of the constant of proportionality m, are determined of course by the nature of χ. T^*, the thermodynamic transition temperature is usually close to the clearing temperature T_c for the nematic-isotropic transition ($T_c - T^* \simeq 1$ K). For pure undiluted MBBA the inverse of the magnetic birefringence coefficient had been found to vary linearly with temperature.[41] A similar dependence on temperature has also been observed for the intensity of light scattering in the isotropic phase of MBBA.[41,42] In each instance the critical index γ was found to be close to unity, as predicted by the Meier–Saupe mean-field theory for liquid-crystals.[43]

TABLE II

	Experimental Kerr constants $B_{12} \times 10^8$ esu^{-2} cm and corresponding molecular Kerr constants ($_mK_2 \times 10^{12}$ esu^{-2} cm^5) for MBBA in solution in benzene at different temperatures			
Concentration mole litre^{-1}	293	303	313	323
0.31	5.97 (91.9)	5.87 (86.9)	5.92 (89.9)	5.87 (86.9)
1.04	8.11 (46.4)	8.96 (56.6)	9.23 (59.8)	9.60 (64.2)
1.41	8.04 (29.2)	9.10 (37.2)	9.88 (43.1)	10.60 (48.6)
1.88	2.77 (−6.4)	4.96 (4.40)	6.4 (11.5)	8.18 (20.3)
2.26	−8.21 (−44.6)	−2.94 (−24.9)	0.74 (−11.2)	3.69 (−0.12)

In Figure 4 the reciprocal of the molecular Kerr constant for MBBA is shown as a function of temperature for undiluted MBBA and for MBBA in solution in carbon tetrachloride at two concentrations. Also shown are results published by Johnston[17] and Filippini and Poggi[19] who employed alternating and pulsed dc electric fields respectively, to measure Kerr constants B for MBBA in the isotropic phase at various temperatures. For undiluted MBBA and the solution containing 3.95 mole litre^{-1} of MBBA the inverse of the molecular Kerr constant for MBBA varied linearly with temperature over a range of 15 K and 30 K respectively. For the more dilute solution (3.38 mole litre^{-1}) the temperature dependence of the molecular Kerr constant was found not be described by Eq. (9) and we conclude that orientational correlations between molecules of MBBA are drastically reduced by the presence of carbon tetrachloride at this concentration. The results for undiluted MBBA may be compared with those obtained by Johnston[17] and by Filippini and Poggi.[19] In all instances the inverse of the Kerr constant varies linearly with temperatures, i.e., $\gamma = 1$, and this aspect is clearly independent of the nature of the electric field used to measure the Kerr constant. However, the values of m, calculated from slopes of the curves in Figure 4 for undiluted MBBA differ significantly, with values of 0.93×10^{-8}, 1.21×10^{-8} and 1.59×10^{-8} esu^{-2} cm^5 K being obtained by this laboratory, Filippini and Poggi, and Johnston respectively.

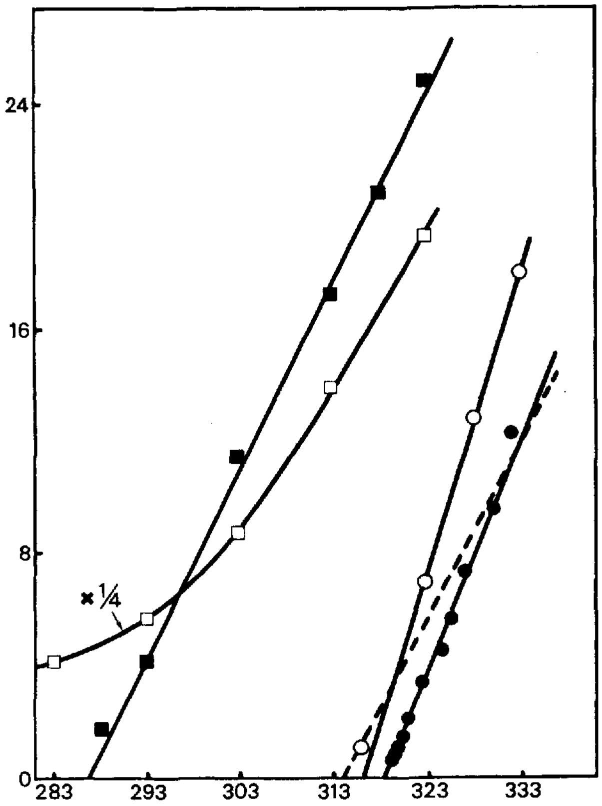

FIGURE 4 Inverse of the molecular Kerr constant as a function of temperature for undiluted MBBA (This laboratory, ○; Filippini and Poggi,[19] ●; Johnston, ---, calculated from Ref. 17 with $T^* = 313.9$ K and $m = -1.2 \times 10^{-9}$ V^{-2} cm K) and for solutions of MBBA in carbon tetrachloride (3.95 mole litre^{-1}, ■; 3.38 mole litre^{-1}, □). Kerr constant B published by Johnston, and by Filippini and Poggi were converted into molecular Kerr constants using Eq. (3) with ε, n and d values of 4.87, 1.60 and 1.12 g cm^{-3} respectively. Inverse molecular Kerr constant $-{}_mK^{-1}/\mathrm{cm}^{-5}\,\mathrm{esu}^2 \times 10^{-8}$.

DISCUSSION

From the results presented in this paper we see that the anomalous electro-optical properties observed in the isotropic phase of undiluted MBBA are also present in solutions of MBBA in benzene and in solutions of MBBA in carbon tetrachloride. The marked concentration and temperature dependence of the molecular Kerr constant of MBBA in solution is present to a substantial degree even in solutions containing large proportions of solvent. For a given temperature, dilution with an inert diluent drastically reduces the magnitude of the molecular Kerr constant of MBBA. As the dilution is continued the molecular Kerr constant of MBBA undergoes a change in its sign. For very dilute solutions the molecular Kerr constant is independent of the concentration. For MBBA in benzene and carbon tetrachloride at 293 K the infinite dilution molecular Kerr constant for MBBA is respectively 1.0×10^{-10} and 1.20×10^{-10} esu^{-2} cm^{5}. Given an experimental uncertainty of $\pm 10\%$ these two values may be regarded as identical. However, for the more concentrated solutions of MBBA in benzene and carbon tetrachloride a comparison of the molecular Kerr constants determined for MBBA at the same concentration and temperature reveals that those measured in benzene are the more positive. Bearing in mind that the molecular Kerr constant for the individual molecule is positive we conclude that on a volume basis benzene is more effective than carbon tetrachloride at disrupting association between molecules of MBBA. Thus, in undiluted MBBA and in solutions of MBBA in benzene and carbon tetrachloride association between molecules of MBBA leads to a negative Kerr constant, even though the individual molecules exhibit a positive Kerr effect. This type of behaviour, in which the Kerr constant of a solute undergoes a change in sign with dilution, has been observed in other systems.[14,28]

In simple non-polar liquids the change in the molecular Kerr constant with temperature is usually interpreted as a consequence of the T^{-1} dependence of the anisotropy term θ_1 of the molecular Kerr constant (see Eqs. 10–12). In polar liquids there is an additional dipolar term θ_2, which has a T^{-2} dependence. In the most dilute solutions of MBBA examined, the molecular Kerr constant for MBBA changes by only a few percent in the temperature range 283–323 K. This contrasts sharply with the nearly two orders of magnitude change in the molecular Kerr constant observed in undiluted MBBA, brought about by raising the temperature from 316 K to 333 K. Clearly, the very temperature sensitive molecular Kerr constant found in undiluted MBBA and in concentrated solutions of MBBA is a consequence of association between molecules of MBBA and is not due to competition between the anisotropy and dipolar components of the molecular Kerr constant.

The magnitude and sign of the molecular Kerr constant measured for MBBA in solution at infinite dilution can, in principle, be interpreted in terms of the semi-axes of the electrostatic and electro-optical polarisability ellipsoids of the molecule and the appropriate resolutes of the permanent dipole moment.[27,28] A complete discussion of the molecular Kerr constant in terms of the above mentioned parameters is only possible if the molar refraction and depolarisation factor of the molecule are known. The molar refraction for MBBA in dilute solution is relatively easy to measure and may also be calculated quite accurately using bond refractions. Unfortunately, the same cannot be said for the depolarisation factor, which to be of any use in this context should be measured for the molecule in the gas phase, since depolarisation factors depend very much on the physical state of the molecule. Other alternatives to the depolarisation factor such as the temperature dependence of the molecular Kerr constant or the frequency dependence of the molecular Kerr constant are respectively inaccurate and unavailable at the present time. Despite these difficulties useful comment can still be made concerning the significance of the magnitude and sign of the molecular Kerr constant for MBBA determined in solution at infinite dilution, the nearest we can approach to the gas phase situation.

As is generally the custom we assume that the electrical properties of the MBBA molecule can be adequately represented by an electrostatic polarisability ellipsoid. If the two phenyl groups are coplanar (see Refs. 32–34) then it is reasonable to assume that two axes of the polarisability ellipsoid, b_1 and b_2 lie in the plane of the molecule, with the third axis, b_3, being at right angles to the molecular plane. It also follows that the permanent dipole moment μ must lie in the plane of the molecule, with resolutes μ_1, μ_2 and μ_3 along the directions of the semi-axes b_1, b_2 and b_3 respectively. In the discussion which follows we will not attempt to define the directions of b_1, b_2, b_3, μ_1, etc. relative to the molecular geometry, but will restrict ourselves to considering only the interplay of these parameters as specified in Eqs. (10)–(12).

$$_mK = 2\pi N(\theta_1 + \theta_2)/9 \tag{10}$$

$$\theta_1 = [(b_1 - b_2)^2 + (b_2 - b_3)^2 + (b_3 - b_1)^2]/45kT \tag{11}$$

$$\theta_2 = [(\mu_1^2 - \mu_2^2)(b_1 - b_2) + (\mu_2^2 - \mu_3^2)(b_2 - b_3) + + (\mu_3^2 - \mu_1^2)(b_3 - b_1)]/45k^2T^2 \tag{12}$$

Calculations by Price[35] indicate that the polarisability ellipsoid of the MBBA molecule is oblate or disc shaped with the plane of the disc coinciding with the plane of the molecule. If this is the case then we may write $(b_1 = b_2) > b_3$. If the permanent dipole moment makes an angle ϕ with the semi-axis b_1 then we can also write $\mu_1 = \mu \cos \phi$, $\mu_2 = \mu \sin \phi$, $\mu_3 = 0$. These approximations allow equations 11 and 12 to be reduced to the following

$$\theta_1 = 2(b_1 - b_3)^2/45kT \tag{13}$$

$$\theta_2 = \mu^2(b_1 - b_3)/45k^2T^2 \tag{14}$$

We note that θ_2 will always be positive provided that $b_1 > b_3$ since the dipolar component depends on the square of the dipole moment. From measurements on dilute solutions of MBBA we know $b_1 + b_2 + b_3$, μ and $_mK$ to be 9.83×10^{-23} cm^3, 2.2 D and 1.20×10^{-10} esu^{-2} cm^5 respectively.[30] It is then quite simple to solve for b_1 and b_3 using Eqs. (10), (13) and (14); b_1

being 3.41 × 10^{-23} cm^3 and b_3 being 3.00 × 10^{-23} cm^3 at 300 K. Substitution of b_1 and b_3 into Eqs. (13) and (14) leads to values of 0.18 × 10^{-34} and 2.57 × 10^{-34} esu^{-2} cm^5 for θ_1 and θ_2 respectively at 300 K. Admittedly the above analysis lacks rigour, but it illustrates that only modest anisotropies in the molecular polarisability are required to account for the magnitude and sign of the molecular Kerr constant measured for MBBA in solution at infinite dilution.

It is instructive, in the light of the proceeding discussion, to consider how molecules of MBBA, which have a positive Kerr constant can be juxtaposed to give a large negative Kerr constant, as is observed in undiluted MBBA in the isotropic phase and in sufficiently concentrated solutions. It has been suggested[30] that molecules of MBBA associate with their long axes in a random anti-parallel arrangement. Further, in the nematic phase of MBBA rotation about the short axis of the molecule is believed to be severely hindered[36] whereas rotation about the long axis is virtually free.[37] Application of an external electric field would be expected to perturb only the orientational distribution function of the resolute of the permanent dipole moment at right angles to the long axis of the molecule. Coupling of the electric field with the permanent dipole moment of the molecule in this manner would be expected to lead to large negative Kerr constants since cooperative motions of the molecules would result in the axis of minimum polarisability being oriented more or less normal to the direction of the applied electric field.[14,43] Raising the temperature or adding an inert diluent decreases the cooperative effects between the molecules of MBBA and the molecular Kerr constant becomes more positive as it approaches that of the individual molecules.

CONCLUSIONS

The anomalous electro-optical properties manifested by MBBA in the isotropic phase have also been found to persist in solutions of MBBA in benzene and carbon tetrachloride, even in solutions which contain large proportions of solvent. Using dc electric fields, de Gennes' theory[38] has been found to be obeyed in the isotropic phase of MBBA and also in a solution of MBBA in carbon tetrachloride in which the clearing temperature had been depressed by about 30 K relative to the undiluted liquid-crystal.

The infinite dilution molecular Kerr constant for MBBA in an inert non-polar solvent has been shown not to be anomalous and that it is readily interpreted in terms of modest anisotropies in the polarisability of the individual molecules. The large negative Kerr constants observed in the isotropic phase of MBBA are interpreted as a consequence of

1) antiparallel alignment of the long axis of the molecules,

2) a large energy barrier restricting rotation about the short axis of the molecule,

3) virtually free rotation about the long axis of the molecule and

4) highly cooperative motions of the molecules in an electric field with almost no change in the degree of short range order.

Acknowledgements

The author wishes to acknowledge the close collaboration with G. Williams at all stages of this work. J. V. Champion and G. H. Meeten are thanked for the loan of certain pieces of equipment in the early stages of this study and also for their helpful advice. Stimulating discussions with M. Davies and A. H. Price are also acknowledged. H. Jolly is thanked for the construction of the Kerr cell.

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