

Optically Induced Kerr Constants for Pure Liquids: Homologous Series of *n*-Alkanes, 1-Alkenes, and 1-Alkynes

Neil J. Harrison and Barry R. Jennings^{*,†}

J. J. Thomson Physical Laboratory, Reading University, Reading, UK

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The optical Kerr effect, also known as laser-induced birefringence, has been measured for some 21 pure liquids which variously comprise three homologous liquid series of the *n*-alkanes, 1-alkenes, and 1-alkynes. Birefringence has been induced using nanosecond pulses of laser light at 1064-nm wavelength and detected at 442-nm wavelength. For all liquids, a quadratic dependence was obtained for the observed birefringence upon the inducing laser beam electric vector amplitude. Analysis of the data in terms of the Kerr constants shows that for the *n*-alkanes the effect is linearly proportional to the carbon chain length. For the 1-alkenes and 1-alkynes the responses are relatively independent of the carbon chain length and appear to be determined by π -bonding characteristics.

I. Introduction

The nonlinear optical properties of organic molecules have been the subject of many theoretical¹⁻⁵ and experimental⁶⁻¹⁰ investigations over the past two decades. These studies have been prompted by a 2-fold objective. The first is to seek novel organic compounds which might have nonlinear optical properties approaching those of the presently available inorganic crystals. The second is to understand better the structure-related molecular processes that give rise to these effects. The relative simplicity of pure liquid structures is the obvious starting point for such studies.

The optical Kerr effect (OKE) is one of a number of nonlinear optical effects. The conventional electric Kerr effect (EKE) involves the application of a direct or alternating current electric field to a medium so as to induce an optical birefringence which can be detected using a low powdered probe light beam. The OKE is achieved in an optically isotropic substance by the interaction of the electric vector in an intense light beam with the component molecules of the substance. Optically induced birefringence is therefore the high-frequency counterpart of the more widely known EKE.

With the advent of recent laser technology and the generation of high-intensity optical pulses of increasingly better beam definition with respect to polarization states, mode structure control, and temporal and spatial profiles, the OKE shows potential for studying high-frequency polarization processes in media. Furthermore, the fast switching characteristics of laser pulses indicates effects which can be harnessed as high-speed optico-optical switch and shutter mechanisms of use in device physics.

Following on from earlier studies in this research group on pure liquids,^{11,12} the present study was undertaken with the specific objective of investigating the role of carbon-carbon σ - and π -bonds in the OKE and hence in the nonlinear optical properties of simple organic molecules. Although several recent investigations have been reported on the study of π -bonds in organic molecules,^{13,14} the majority solely have involved highly conjugate organic molecules consisting of multiple double or triple bonds. Typical examples are the polyacetylenes and polyenes. The intention of this work was to investigate the role of lone double or triple bonds. The results presented herein are the first nanosecond OKE results to be published for the 1-alkenes and 1-alkynes. The three series of the *n*-alkanes, 1-alkenes, and 1-alkynes were selected as they allow comparisons between molecules having carbon-carbon single

(one σ -bond), double (one σ -bond plus one π -bond), and triple (one σ -bond plus two π -bonds) bonds located in the terminal groups of the molecules. Helfin et al.⁶ have observed a difference in third harmonic generation for *cis* and *trans* isomers of short chain polyenes. Hence molecules with terminal π -bonds were chosen as they exhibit no *cis-trans* isomerism.

II. Theoretical Background

The optical Kerr effect was first predicted by Buckingham in 1956.¹⁵ More extensive and complete theoretical descriptions were later developed as summarized by Kielich.¹⁷⁻¹⁹ The advent of the high-powered ruby laser enabled the effect first to be observed experimentally by Mayer and Gires in 1964.¹⁶ Recently a review has been published of the various experimental techniques and optical arrangements used to date to measure the effect. This constitutes a comprehensive overview of the field.²⁰ A compendium of all reported values of the optical Kerr constant for liquids has also been published recently.²¹

When an electric field is applied to an isotropic medium, the medium generally becomes birefringent. This is measured by the change in polarization state of a weak linearly polarized laser beam which probes the medium and is initially polarized at an azimuthal angle of 45° relative to the inducing field direction. The birefringence renders the probe beam elliptically polarized as a phase retardation is introduced into one of the two orthogonal linearly polarized generators of the ellipse. For a sample of length *l*, this phase shift δ relates to the birefringence (Δn) induced in the sample by

$$\Delta n = \frac{\lambda_p}{2\pi l} \delta \quad (1)$$

where λ_p is the probe beam wavelength.

It is assumed that the aligning electric field is unidirectional in the applied or inducing laser beam. Then, the birefringence Δn is defined relative to the refractive indices n_{\parallel} and n_{\perp} which are those for the medium parallel and perpendicular to the inducing electric field direction. Then

$$\Delta n = n_{\parallel} - n_{\perp} \quad (2)$$

Conventional optical arrangements for measuring Δn are reviewed in ref 22.

The quantification of the OKE response of a pure liquid to an inducing laser beam of wavelength λ_i has been achieved by defining an optical Kerr constant, B_o , analogous to the well-established electrical Kerr constant. This optical Kerr constant is defined

* To whom correspondence should be addressed.

† Also Research and Development Director, ECC International Ltd., John Keay House, St. Austell, Cornwall, U.K.

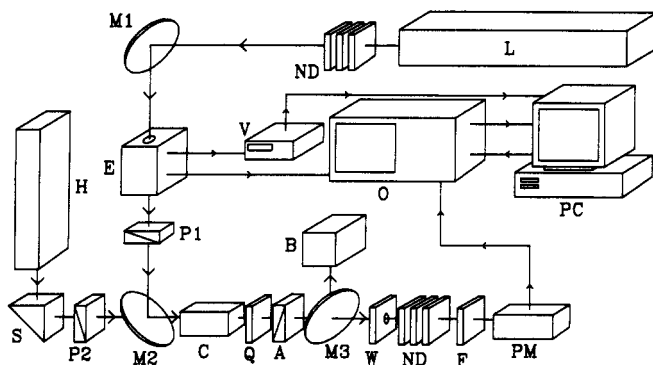


Figure 1. Schematic diagram of the apparatus used to measure the optical Kerr effect in pure liquids. L, inducing Nd:YAG laser; ND, neutral density filters; M1, M2, M3, dichroic mirrors; E, energy meter; V, voltmeter; H, HeCd laser; P1, P2, polarizers; S, probe beam steering prisms; C, sample cells; Q, quarter wave plate; A, analyzer; B, beam dump; W, slit; F, narrow band filter; PM, photomultiplier; O, digitizing oscilloscope, and PC, instrument controller.

by

$$B_0 = \frac{\Delta n}{\lambda_p \langle E \rangle^2} = \frac{\delta}{2\pi l \lambda_p \langle E \rangle^2} \quad (3)$$

where E is the equivalent, unidirectional electric field amplitude in the inducing laser beam. It should be noted that this constant varies with the wavelengths of both the inducing and the measuring probe beams. It is also extremely sensitive to the precision with which the equivalent field strength $\langle E \rangle$ can be estimated. As it must be inferred from aspects of the experimental design and a theoretical analysis of the system used, it is probably the source of greatest uncertainty in calculating B_0 values. This topic has been discussed elsewhere.²¹ Because of this, many workers publish not only their estimates for B_0 , but also quote data relative to measured values of the same parameter for benzene. Hence

$$B_{\text{rel}} = B_0 / B_{\text{benzene}} \quad (4)$$

Although not so analyzed in this study, in the case of isotropic systems such as pure liquids, the optical Kerr constant can be related to components of the third-order susceptibility of these media. Specifically expressed,²¹

$$B_0 = \frac{2\pi}{n\lambda_p} (\chi_{1212}^{(3)} + \chi_{1221}^{(3)}) \quad (5)$$

where $\chi_{ijkl}^{(3)}$ are the relevant components of the susceptibility tensor $\chi^{(3)}$ under these wavelength conditions.

III. Experimental Section

A schematic diagram of the apparatus is shown in Figure 1. The inducing laser was a Lumonics HY400 Nd:YAG laser capable of delivering pulses of 10–20 ns duration and of 5–30 mJ power, operated at a wavelength of 1064 nm. Care was taken to ensure the selection of a strict TEM₀₀ mode for this beam. The probe beam laser was a low-power 16 mW continuous working Omnichrome model 456X helium cadmium laser operating at 442-nm wavelength. All polarizing devices were of high quality with extinction crossing ratios of 10^{−5}. The reflecting mirrors were also carefully chosen both for their reflection and transmission characteristics at the relevant optical wavelengths and for their positioning so as to steer the inducing and probe beams along a coincident path through the sample. The birefringence was induced as a fast transient which was captured by a fast response, high-efficiency, multidynode photomultiplier (EMI type 9816B) connected to a Hewlett Packard 54111D 1 gigasample per second digitizing oscilloscope. The oscilloscope was used to simultaneously capture the laser pulse profile as recorded by the

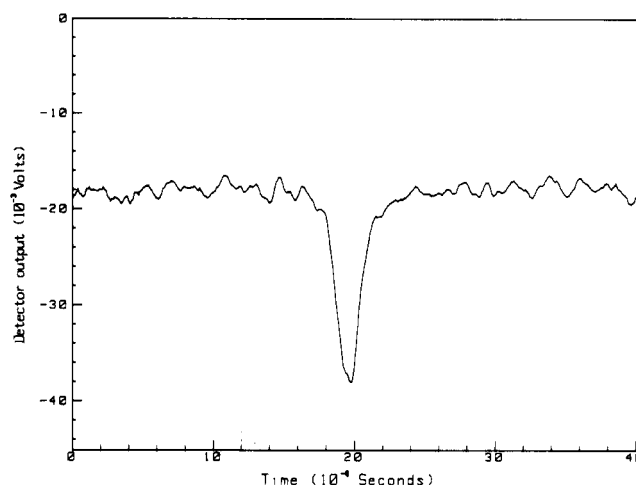


Figure 2. Representative transient response of the laser-induced birefringence. Data for octyne, with an inducing laser pulse of 26 mJ at 1.064- μm wavelength.

transmission energy meter. Full details of the apparatus and its method used have been given elsewhere.¹²

All samples used were the best commercially available grade. No further purification was attempted apart from filtering through a 0.2- μm filter into the sample cell.

IV. Results and Discussion

Figure 2 shows a typical detector trace of the induced effect for liquids in each class studied. The relative freedom of the trace from noise is noteworthy. Simultaneous recordings of the inducing pulse were recorded and analyzed to estimate the equivalent field strength. In this work the following equation was used

$$\langle E \rangle^2 = A(2 - Q) \frac{J}{R^2 \tau} \{1 - e^{-(R/\omega)^2}\} \quad (6)$$

where A is a constant given by

$$A = 1/2 (\mu_0 / \pi^3 \epsilon_0)^{1/2} \quad (7)$$

Here J is the inducing laser beam energy of which the fraction Q is absorbed during passage through the sample length l . The radius of the inducing beam is taken as R , which corresponds to that radius across the beam corresponding to the position where the spatial energy profile has fallen to e^{-1} of the maximal value at the beam axis. The similar parameter for the probe beam is ω , while τ is the temporal full width at half-maximum interval for the inducing beam. The parameters μ_0 and ϵ_0 are the free-space constants.

Graphs of the variation of the induced birefringence with the inducing field strength are plotted in Figure 3 for n -octane, 1-octene, and 1-octyne. In all cases, the data confirm a Kerr-law behavior with $\Delta n \propto \langle E \rangle^2$ as predicted through eq 3. From the slopes of these graphs, values of B_0 have been estimated for all samples. Simultaneous measurement of B_{benzene} has enabled values of B_{rel} to be evaluated. All data are listed in Table I. The error in each reading is typically of the order of $\pm 5\%$. The results for the n -alkanes are presented in Figure 4. These data have previously been reported elsewhere¹² and are included for comparison purposes.

Examination of Figure 4 clearly shows a linear relationship between B_{rel} and the number of carbon atoms in the molecule for the n -alkane series. This observation is in close agreement with that reported by Blaszcak and Gauden using the same experimental method.⁸ Such linearity is thought to be a reflection of the behavior of the σ -bond. In a σ -bond the electrons are generally well localized and cannot readily be displaced along the molecule.

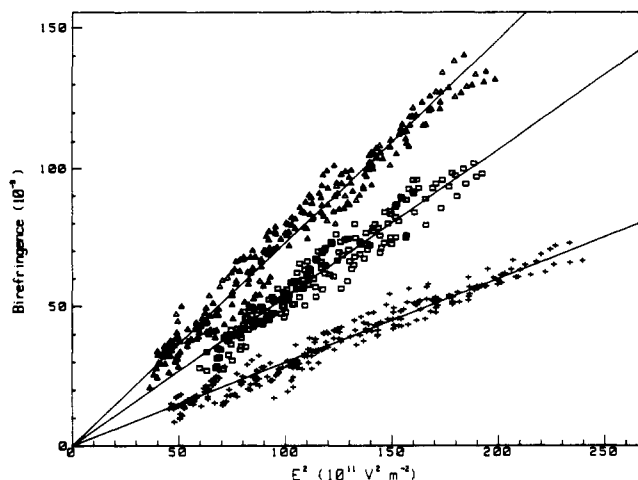


Figure 3. Field strength dependence of the induced birefringence data for *n*-octane, 1-octene, and 1-octyne are represented by crosses, squares, and triangles, respectively.

TABLE I: Optically Induced Kerr Constants for Liquids^a

pure liquid	B_{rel}	B_0 (10^{-14} V ⁻² m)
<i>n</i> -pentane	0.102	0.052
1-pentene	0.332	0.171
1-pentyne	0.432	0.222
<i>n</i> -hexane	0.136	0.070
1-hexene	0.287	0.148
1-hexyne	0.359	0.183
<i>n</i> -heptane	0.149	0.077
1-heptene	0.332	0.171
1-heptyne	0.374	0.192
<i>n</i> -octane	0.171	0.088
1-octene	0.290	0.149
1-octyne	0.392	0.201
<i>n</i> -nonane	0.170	0.087
1-nonene	0.333	0.171
1-nonyne	0.397	0.204
<i>n</i> -decane	0.206	0.106
1-decene	0.323	0.166
1-decyne	0.346	0.178
<i>n</i> -undecane	0.211	0.108
1-undecene	0.324	0.167
<i>n</i> -dodecane	0.233	0.120

^a Values are estimated to within $\pm 5\%$. Relative values are made against a value of 0.514×10^{-4} V⁻² m for benzene. All data are for an inducing beam wavelength of 1064 nm and a measuring beam of 442 nm.

In such cases, the carbon-carbon bonds can be regarded as independent polarizable units, adding vectorially and linearly to the overall induced dipole and hence to the optical Kerr constant of the molecule.

The results for the 1-alkenes are presented in Figure 4. cursory examination indicates that these liquids have a somewhat constant OKE value of $B_{rel} = 0.32$ within the molecular carbon chain lengths studied. It is tempting to assume that this result indicates the predominant behavior of π -bonding in these cases. Contributions from the alkyl chain appear to be insignificant or reduced even for the longer chain members of the series. It is of interest to note that, in the case of the second-order hyperpolarizability, Levine and Bethea⁵ have reported that π -electrons are an order of magnitude more effective than those associated with σ -bonding. Also Etchepare et al.²³ have showed that for conjugated molecules, the electronic contribution dominates the optical Kerr response on the picosecond time scale.

However, on the nanosecond time scale reorientational phenomena appear to be of greater importance. Altman et al.⁹ have reported a factor of some 30 times greater response from nanosecond rather than picosecond pulses with large organic

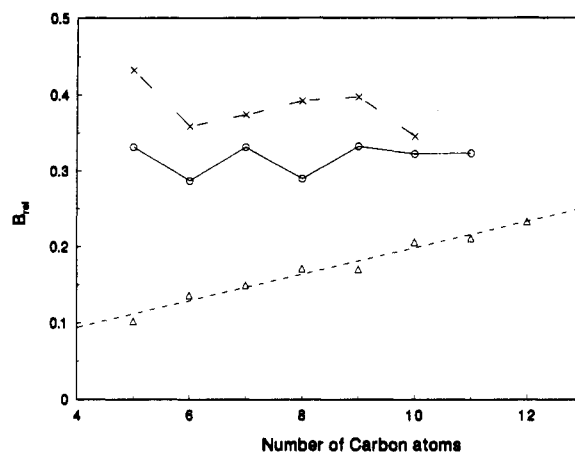


Figure 4. Variation of B_{rel} with number of carbon atoms in the series. Data for the *n*-alkanes (triangles), 1-alkenes (circles), and 1-alkynes (crosses).

molecules while Blaszcak and Gauden⁸ have estimated that with small saturated organic molecules the electronic contribution was of the order of 30% of the total on the nanosecond time scale. For the longer chain lengths, the contributions due to the saturated alkyl chain should become of increasing importance. No such trend is seen in the present study however for members up to 1-undecene. Work is currently in hand to extend the measurements to higher members of the 1-alkene series.

Figure 4 also shows the results for the 1-alkynes. The graph clearly shows a similar behavior to that of the 1-alkenes with a mean value of $B_{rel} = 0.38$. This is only about 20% higher than the corresponding value for 1-alkenes indicating that the second π -bond associated with the alkyne structures is not as effective as the single π -bond in contributing to the nonlinear polarizability.

There are several conclusions that can be drawn from these results. Firstly, and in general, the data on these liquids indicate that the contribution of a π -bond to the high-frequency polarizability is much greater than that of the σ -bond on the nanosecond time scale, in agreement with the previous findings by Levine and Bethea.⁵ This must be partially due to the ability of the electrons in a π -bond to be delocalized along part of the molecular backbone. The results for both the 1-alkenes and the 1-alkynes show no indication of any significant contribution from the alkyl tail, which would manifest itself as a steadily increasing effect with increasing alkyl chain length. Further investigations are required on liquid members of these series with even longer alkyl chain lengths.

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References and Notes

- (1) Rustagi, K. C.; Ducing, J. *Opt. Commun.* **1974**, *10*, 258.
- (2) Oudar, J. L.; Chemla, D. S. *Opt. Commun.* **1975**, *13*, 164.
- (3) Garito, A. F.; Teng, C. C.; Wong, K. Y.; Zamani-Khamiri, O. *Mol. Cryst. Liq. Cryst.* **1984**, *106*, 219.
- (4) Beraton, D. N.; Onuchic, J. N.; Perry, J. W. *J. Phys. Chem.* **1987**, *91*, 2696.
- (5) Levine, B. F.; Bethea, C. G. *Appl. Phys. Lett.* **1974**, *24*, 445.
- (6) Helfin, J. R.; Wong, K. Y.; Zamari-Khamiri, O.; Garito, A. F. *Phys. Rev.* **1988**, *B38*, 1573.
- (7) Huijts, R. A.; Hesselink, G. J. L. *Chem. Phys. Lett.* **1988**, *156*, 209.
- (8) Blaszcak, Z.; Gauden, P. *J. Chem. Soc., Faraday Trans. 2* **1988**, *8*, 239.
- (9) Altman, J. C.; Elizondo, P. J.; Lipscomb, G. F.; Lytel, R. *Mol. Cryst. Liq. Cryst.* **1988**, *157*, 515.
- (10) Albert, I. D. L.; Ramasesha, S. Photochemistry and photoelectrochemistry of organic and inorganic molecular thin films. *Proc. SPIE-Int. Soc. Opt. Eng.* **1991**, *1436*, 179.
- (11) Coles, H. J.; Jennings, B. R. *Philos. Mag.* **1975**, *32*, 1051.
- (12) Harrison, N. J.; Jennings, B. R. *Meas. Sci. Technol.* **1992**, *3*, 120.
- (13) Guha, S.; Frazier, C. C.; Porter, P. L.; Kang, K.; Finberg, S. E. *Opt. Lett.* **1989**, *14*, 952.

- (14) Kanbara, H.; Kobayashi, H.; Kubodera, K. *IEEE Photonics Tech. Lett.* **1989**, *1*, 149.
- (15) Buckingham, A. D. *Proc. Phys. Soc.* **1956**, *B69*, 344.
- (16) Mayer, G.; Gires, F. *C. R. Acad. Sci., Paris* **1964**, 2039.
- (17) Kielich, S. *Acta Phys. Pol.* **1966**, *30*, 683.
- (18) Kielich, S. *Acta Phys. Pol.* **1968**, *34*, 1093.
- (19) Kielich, S. *Chem. Phys. Lett.* **1968**, *1*, 675.
- (20) Tyson, D. G.; Jennings, B. R. *J. Phys. D: Appl. Phys.* **1991**, *24*, 645.
- (21) Harrison, N. J.; Jennings, B. R. *J. Phys. Chem. Ref. Data* **1992**, *21*, 157.
- (22) Fredericq, E.; Houssier, C. *Electric Dichroism and Electric Birefringence*; Clarendon Press: Oxford, 1973.
- (23) Etchepare, J.; Grillon, G.; Migus, A.; Martin, J. L.; Hamoniause, G. *Appl. Phys. Lett.* **1983**, *43*, 406.