Photochemistry in the Electronic Ground State. I. Vapor Phase Irradiation of Organic Compounds by Continuous Wave Carbon Dioxide Gas Laser

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Abstract: Limonene and isoprene were irradiated at various pressures by means of a continuous wave CO_2 laser. The results show that it is possible under controlled conditions to obtain reactions in the electronic ground state under nonequilibrium conditions. The possibility of carrying out reactions obeying symmetry selection rules of thermal reactions and having thermodynamic and kinetic properties of photochemical reactions by means of infrared laser light is discussed.

Since laser sources have been developed, many experiments established the fact that saturation of excited states (electronic as well as vibrational) may be obtained by optical pumping.[3-9]

In a gas mixture, under conditions of intense monochromatic infrared (ir) radiation, at controlled pressure, a situation may be achieved where the electromagnetic energy pumping exceeds collisional relaxations. In such a system the energy distribution among the mixture components is a function of their absorption coefficients and may differ considerably from the Boltzmann type distribution of energy which is specific to isothermal conditions.

If the mixture components are chemically interconvertible, a steady state may be achieved where the ratio among interacting compounds is a function of the absorption coefficient of the monochromatic ir radiation, rather than on the equilibrium constant K defined by eq 1 where A and B are the interconvertible gas mixture components.

$$K = [\mathrm{A}]/[\mathrm{B}] \qquad (1)$$

The nearest analog to the latter system is one where the mixture components are kept simultaneously at different temperatures. The thermodynamic conditions are similar to those of a system which is subject to monochromatic ultraviolet (uv) or visible light, which is absorbed preferably by one of the components. The difference is that the latter system undergoes reactions in electronic excited states which, according to symmetry selection rules, very often leads to products different from those obtained in ground state reactions.[10] On the other hand, ir light under the previously mentioned conditions may lead to vibrationally excited states in the electronic ground state, the vibrationally excited molecules may undergo reactions which are indistinguishable in nature from thermal reactions from a symmetry selection rule point of view, but the ratio between starting material and product will not depend on the free-energy difference but on the absorption coefficient as it is in an ordinary photochemical reaction.

The purpose of the present study was to test the feasibility of using monochromatic infrared radiation to induce photochemical reactions in the electronic ground state.

The ir absorption spectrum of most organic compounds starts above 2.5 μ (4000 cm^{-1}) with energies less than 14.3 kcal/einstein, so that single photon processes are rendered impossible for most organic reactions. Laser light seems to be the only monochromatic source that may fulfill the requirement of more than a single photon transition. We have studied the possibility of irradiating organic compounds in the gas phase by continuous wave (cw) ir laser to obtain stepwise photon absorption. By taking advantage of the long radiative lifetime of vibrational states, it was possible to study the collisional lifetime by controlling the pressure of the system. The simplest cw laser operating at high intensities is the CO_2 gas laser. Attempts to irradiate compounds at medium pressure (50–700 Torr) using a CO_2 laser are reported in the literature.[11-16] In all previous cases emission of uv or visible light or chemical reactions ceased upon reduction of pressure.

Results and Discussion

A. Irradiation at Low Pressures. 1-Limonene (**1**) was irradiated at 2 Torr in a 4-m long irradiation cell by means of a 5-W beam at 10.6 μ (943 cm^{-1}) obtained from a CO_2 laser. The starting material recovered after irradiation retained its original optical activity, but vapor phase chromatographic (vpc) separation

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(2) Taken in part from the Ph.D. thesis of R. M. J. Loewenstein. to be submitted to the Feinberg Graduate School of the Weizmann Institute of Science. Rehovot.

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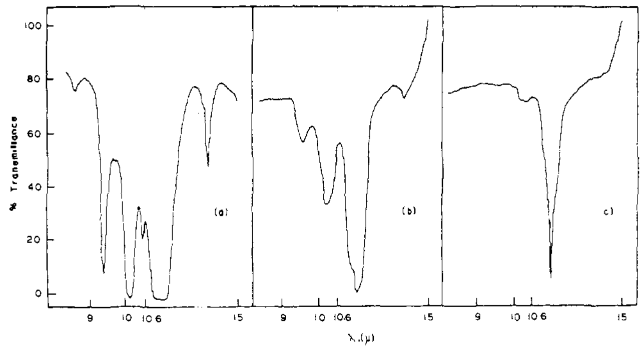
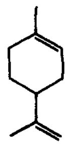


Figure 1. The infrared spectrum of isoprene: (a) in liquid phase in a 0.1-mm cell; (b) in gas phase at 73.5 Torr in a 10-cm cell; (c) in gas phase at 14.2 Torr in a 10-cm cell.

showed the presence of many cleavage products. Coupling the vpc column with a mass spectrometer facilitated identification of some of the products, the main one being isoprene (**2**). Isoprene could be formed by a retro-Diels–Alder reaction, which, according to symmetry selection rules, is allowed only in the electronic ground state.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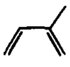
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The energy of activation is estimated to be greater than 60 kcal/mol,[17] far above the 2.7 kcal/einstein corresponding to 10.6-μ wavelength of irradiation. Other products were benzene, toluene, ethylbenzene, methylethylbenzene and isomers of allocimene, dihydrolimonene, and low molecular weight compounds which could be formed by further cleavage of isoprene (**2**) or from the cleavage of limonene (**1**) to form aromatic compounds. There is no indication of the electronic state involved in the formation of compounds other than isoprene (**2**), but also in these reactions, activation energies far exceed the 2.7 kcal/einstein supplied by the CO_2 laser in a single photon process and may reach the value of 100 kcal/mol when carbon–carbon single bonds are cleaved.[18] Multiple photon transitions are highly improbable by a 5-W continuous beam, and, moreover, the reaction shows no sensitivity toward fluctuations in light intensity of about 15% which should strongly influence a multiple photon reaction. In spite of the fact that the temperature measured was 25°, it may be argued that the reaction obtained was an ordinary thermal reaction where the ir beam just replaced a hot element. A study of the pressure dependence of the reaction provided an answer to this argument. Since the vapor pressure of l-limonene at room temperature is only 2 Torr, we chose to study the irradiation of isoprene, the vapor pressure of which is about 600 Torr at room temperature. The ir spectrum of isoprene is shown in Figure 1. It is seen from the figure that a broad absorption exists at 10.6 μ (943 cm^{-1}), the nature of which does not change significantly upon increase of pressure, and it retained its main characteristics even in the liquid phase.[19]

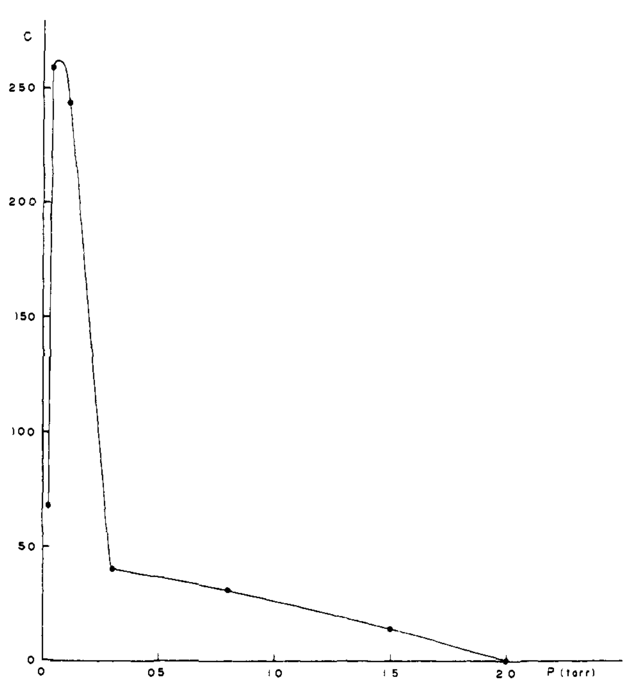

Figure 2. Plot of the total amounts of products (C) in arbitary units, obtained by iradiation of isoprene at low pressure *vs.* the pressure (p).

The products obtained from irradiation at 1 Torr were identical with the mixture obtained by irradiation of limonene (**1**),[20] but limonene (**1**) itself was not detected. Although small molecular weight products like C_2H_2, C_4H_4, and C_4H_6 can be formed directly from excited isoprene (**2**), higher molecular weight compounds may appear *via* a vibrationally excited dimer of isoprene (**2**) generated in a high vibrational state; it could not readily be deactivated due to the relatively low frequency of collisions and therefore underwent further cleavage. At pressures above 3 Torr no detectable amounts of products were formed. Upon reduction of pressure the amount of products increased, until a maximum value was reached at 0.05 Torr, whereas with further reduction of pressure the amount of products decreased. In Figure 2 the variation of the total amount of products (C) is plotted *vs.* the variation of pressure (p) at constant beam intensity and after 1 hr of irradiation.

In the following discussion we shall try to analyze the pressure dependence of various excited states of a light absorbing material, which is subject to intense monochromatic radiation.

Expansion of the Beer–Lambert equation to low-pressure conditions gives eq 2 where I_0 represents the

$$I = I_0(1 - \epsilon l p) \qquad (2)$$

intensity of radiation incident on the absorbing species at pressure p, I the light intensity transmitted through the cell of length l, and ϵ the extinction coefficient. The quantity of light absorbed $I_0 - I = E$ is given by eq 3.

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[17] H. Kwart and K. King, *Chem. Rev.*, **68**, 415 (1968).

[18] K. Tarama in "Handbook of Organic Structural Analysis," Y. Yukawa, Ed., W. A. Benjamin, New York and Amsterdam, 1965, pp 537–540.

[19] There is a finite absorption but no maximum.

[20] High-temperature pyrolysis of isoprene and other conjugated dienes has been shown to give similar products: *cf.* E. Gil-Av, J. Shabtai, and F. Steckel, *J. Chem. Eng. Data*, **5**, 98 (1960); J. Shabtai and E. Gil-Av, *Isr. J. Chem.*, **1**, 231 (1963)

$$E = I_0\epsilon l p \qquad (3)$$

Later in Figure 4 it will be shown that this equation is valid for isoprene at pressures below 30 Torr. From Landau and Teller's[21] equation (eq 4, where K is constant), it is seen that the rate of collisional relaxation is

$$p\tau \propto \exp(K/T^{1/3}) \qquad (4)$$

proportional to the pressure. According to these data we can write eq 5 for the rate of formation of singly excited isoprene. Here A^* represents the concentration

$$\mathrm{d}A^*/\mathrm{d}t = I_0\epsilon p - A^*K_1P - K_2A^* - A^*\epsilon_1I_0 \qquad (5)$$

of molecules excited by one photon, K_1 = rate constant for collisional relaxation, K_2 = rate constant for unimolecular relaxation, and ϵ_1 = absorption coefficient of A^* for the excitation by an additional photon to the state A^{**}.

Assuming that a steady state is achieved we derive eq 6. Knowing that K_2 is very small compared with K_1,[22]

$$A^* = I_0\epsilon p/(K_2 + K_1p + \epsilon_1I_0) \qquad (6)$$

and as long as collisional relaxations are much faster than two photon excitations, eq 6 is reduced to eq 7.

$$A^* = I_0\epsilon/K_1 \qquad (7)$$

At very low pressures, as K_1p becomes smaller, the latter considerations may become invalid, and a slight pressure dependence may appear. Due to the minor dependence of A^* on pressure, the fraction of excited molecules in the total mixture increases as the pressure decreases. This effect will lead to a pressure dependence of the apparent absorption coefficient and finally to saturation. Upon saturation A^* equals the concentration which corresponds to $p/2$.

In this case A^* is linearly reduced with reduction of pressure. Assuming now that part of A^* is further excited by absorption of photons, then with similar considerations we obtain eq 8 for the concentration of A^{**}.

$$A^{**} = A^*\epsilon_1I_0/(K_4p + K_5 + I_0\epsilon_2) \qquad (8)$$

At pressures where A^* is pressure independent A^{**} increases with a reduction of pressure. At lower pressures, where saturation conditions for A^* are achieved, A^* becomes pressure dependent, and K_4p may approach the value of $K_5 + I_0\epsilon_2$. Finally, A^{**} reaches a maximum value, and with a further reduction of pressure A^{**} is reduced. Applying the same treatment to the absorption of additional photons will show a sharper dependence on pressure, with a maximum near the saturation conditions. From this treatment it is seen that qualitatively the experimental results (see Figure 2) fit into a scheme where a successive absorption of photons is responsible for the observed reaction. A more detailed treatment is impossible since the exact mechanism of the reaction is unknown. The negligible dependence upon light intensity shows that the experiment takes place very near to saturation conditions, possibly also in higher levels of excitation.

In further experiments we have introduced various inert gases to the reacting gas. Addition of helium at pressures exceeding the pressure of isoprene decreased the rate of formation of all compounds with molecular weights larger than isoprene but did not influence the formation of low molecular weight products even at a pressure of 20 Torr. Similar results were obtained with argon, but product formation was totally inhibited with nitrogen at a pressure of 10 Torr, independent of the partial pressure of isoprene. The relationship between He and N_2 is the inverse from what is expected from their thermal conductivities which are 3.43×10^{-4} and 5.78×10^{-5} cal cm^{-1} sec^{-1} deg^{-1}, respectively.[23]

This experiment excludes the possibility of an isothermal reaction, because, if the optical energy pumping did not exceed collisional relaxations, then the laser beam would act as a hot wire in the irradiation cell, and deactivation by an inert gas will be in accordance with its thermal conductivity. On the other hand if eq 5–8 are valid, then deactivation will depend on the vibrational deactivation constants, and the nitrogen diatomic molecule should be more efficient than He which cannot vibrate. Moreover, isoprene itself is most efficient due to matching of all energy levels.[24]

In our discussion we have neglected the fact that due to the nonharmonic character of vibrational modes, successive absorption of photons may be forbidden. It should be emphasized that in the relatively complex molecules involved in the reaction, absorption by many modes may be responsible for the measured absorption at 10.6 μ (as is already seen from the broad nature of the band). Since the reactive state that we try to achieve is analogous to a state where the compounds with preferred absorption coefficients are at a higher temperature, it is not essential to direct all the irradiating energy which is necessary to cleave a specific bond at that bond itself.[25–29] Even if the energy is distributed among the various modes in the molecule, the probability of bond cleavage increases. It may also be argued that the energy which is stored in the absorbing modes is redistributed in all the other modes, so that the absorbing mode acts as a window through which the electromagnetic energy of the laser beam is pumped into the molecule while being itself raised no more than a single or perhaps a few steps above the vibrational ground state. This model can be tested by emission experiments from the absorbing compound. Such emission experiments appear in the literature.[11–16] In most cases emission appears not only from the band which was primarily excited by absorption of the laser light but also from other levels including levels with much higher energies than those supplied by the laser beam. Furthermore, Robinson, Woodward, and Barnes[11] described an experiment where simple organic compounds under the influence of 10.6 μ radiation emitted light from all the vibrational levels which appear in the absorption spectrum and also found that the total intensity of the light emitted depended on the absorption coefficient at 10.6 μ.

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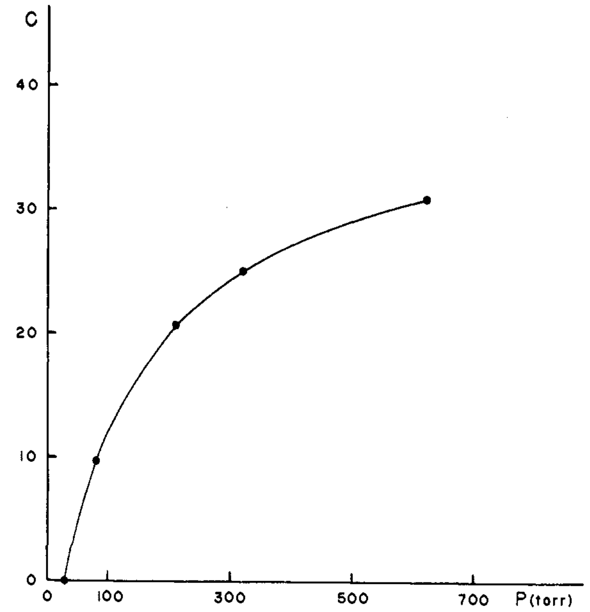

Figure 3. Plot of the total amounts of products (*C*) in arbitary units, obtained by irradiation of isoprene at high pressure *vs.* the pressure (*p*).

From this discussion one may draw the following conclusions. 1. Electronic ground state reactions can be induced by absorption of ir radiation. 2. Stepwise excitation may lead to reactions with energies of activation far above the energy/einstein of the incident radiation. 3. Nonequilibrium states may be achieved by the influence of the incident ir monochromatic light. 4. Product formation depends upon the vibrational lifetime which may in itself be controlled by the partial pressure of either the reacting material or that of an inert gas that may be introduced separately.

Most organic compounds have a considerable absorption at the wavelength of 10.6 μ used in these experiments. When laser sources will be available with sufficient intensity at other specific wavelengths, it will be possible that photochemistry in the electronic ground state may be introduced in those cases where selection rules prevent the desired product formation through electronic excited states.

B. Irradiation at High Pressures. It is obvious that earlier reports of reactions of organic compounds employing 10.6-μ laser beam irradiation at higher pressures$^{8-16}$ are completely different from the reactions reported above. In order to study the difference we have also carried out irradiation of isoprene at higher pressures.

Between the pressures 3–30 Torr no product formation was detected at a beam intensity of about 30 W; further increases of pressure led to the formation of three dimeric products.^{30,31} The total product formation after 20 min of irradiation as a function of pressure is shown in Figure 3. Unlike the experiments carried out at lower pressures, the total amount of products was sensitive to both variations in beam intensity as well as pressure. The data in Figure 3 can be interpreted as follows. At 30 Torr most of the light is not absorbed. This is seen in Figure 4A, where the amount

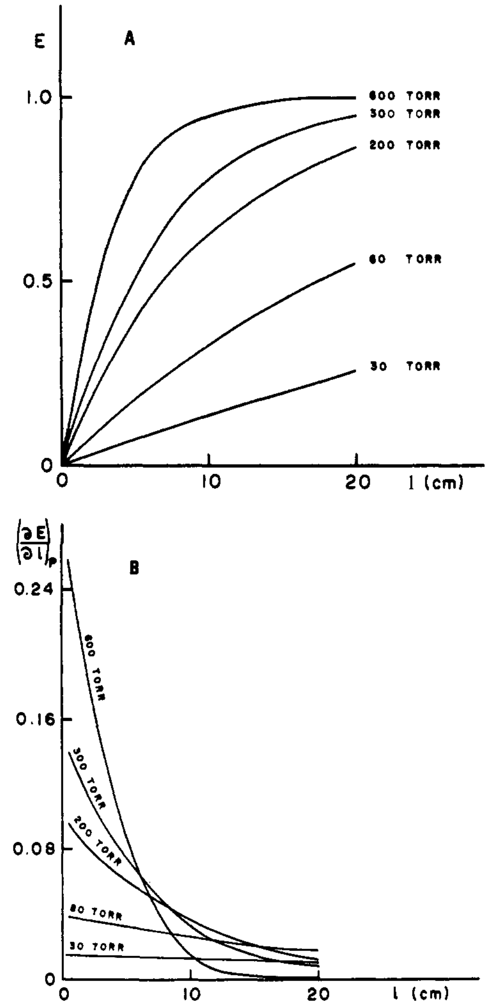

Figure 4. (A) Plot of *E vs. l*. (B) Plot of $(\partial E/\partial l)_p$ *vs. l*.

of light absorbed (*E*) (eq 9) is plotted *vs.* the path length

$$E = I_0(1 - e^{-\epsilon l p}) \qquad (9)$$

on the beam in the 15-cm cell. In Figure 4B, $(\partial E/\partial l)_p$ (eq 10) is plotted *vs. l*. This derivative is propor-

$$(\partial E/\partial l)_p = I_0 \epsilon p e^{-\epsilon l p} \qquad (10)$$

tional to the amount of light absorbed by unit volume of gas at point *l* in the beam cross section. From Figure 4B it is seen that at a pressure of 30 Torr $(\partial E/\partial l)_p$ hardly changes with *l*. At this pressure the experimental conditions may be compared with those of a hot wire surrounded by a cold isothermal cylinder.^{32} Also, at the same and higher pressures the thermal conductivity is pressure independent,^{33} and, neglecting heat losses by convection, the amount of heat conducted to the walls is proportional to the length of the wire.

From Figure 4A it is seen that the amount of light absorbed in the 15-cm irradiation cell increases considerably with pressure, while Figure 4B shows that at higher pressures $(\partial E/\partial l)_p$ becomes very large at the cell entrance but then falls off sharply with *l*. In the analogous hot wire experiment this is equivalent to a shortening of the wire while pumping more power into

(30) The exact structure cannot be deduced from the mass spectrum.

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(32) R. C. L. Bosworth, "Heat Transfer Phenomena," Associated General Publications PTY, Ltd., Sydney, Wiley, New York, N. Y., 1952, p 35.

(33) Reference 32, p 32.

it. In this case the thermal losses will decrease while the temperature will rise considerably. It is clear that under the conditions described the reaction at the higher pressures can be explained by an ordinary thermal process where the laser beam merely acts as a heat source.

The most important question in our discussion is whether the reaction rate of a substance in a gas mixture is dependent on the light absorbed by other components in the gas mixture. In a 15-cm cell we have irradiated successively two gas mixtures with the following constitutions: the first sample consisted of pure isoprene at 272 Torr; and the second sample 110 Torr isoprene, 58 Torr *trans*-butene, and 110 Torr pentane.[34] Both mixtures had the same optical density and approximately the same heat content and the same thermal conductivity.

Since the rate of an isothermal dimerization is given by eq 11 where V is the rate of dimerization, K = rate

$$V = K[\mathrm{M}]^2 \qquad (11)$$

constant, and [M] = the concentration of the monomer, we have divided the total amount of dimers obtained in each experiment by the square of the partial pressure of isoprene in that experiment. The rate constants obtained in this manner and expressed in arbitrary units are 55.8 and 56.2 for mixtures 1 and 2, respectively. The same rate constant is obtained for the dimerization of isoprene in experiments 1 and 2, in spite of the fact that in experiment 1 all the light was absorbed by isoprene and in experiment 2 most of the light was absorbed by *trans*-butene.

It is evident from the latter experiment that isoprene reached the same temperature in the two separate experiments, where it absorbed different fractions of light. No differentiation of temperatures among mixture components according to their absorption coefficients takes place at pressures above 30 Torr and with a beam of 30-W intensity, in contrast to what we assume for the same compounds at pressures below 3 Torr.

Similar reactions induced by a CO_2 laser and carried out at pressures above 30 Torr were reported by other authors.[11-16] In an interesting study of the unimolecular decomposition of BCl_3,[8] it was found that at a pressure of 150 Torr, the rate of reaction depended on the 25th power of the laser intensity. This dependence was reduced to the fifth power at a pressure of 375 Torr and to the second power at a pressure of 675 Torr. This behavior was related by the authors to a cascade excitation through collisions of excited molecules which competed with their collisional deactivation.

If our interpretation is considered, then increasing the pressure will lead to an elevation of temperature. Equation 12 represents the rate of decomposition of

$$-\mathrm{d}[\mathrm{BCl_3}]/\mathrm{d}t = [\mathrm{BCl_3}]Ce^{-\Delta E/KT} \qquad (12)$$

BCl_3 as a function of temperature, where C is a constant, T absolute temperature, and ΔE energy of activation. Since all the light is absorbed by the sample, then I, the light intensity, represents the rate of accumulation of thermal energy. The thermal conductivity to the walls by the gas is given by eq 13.[23] After a steady state is

$$\mathrm{d}Q/\mathrm{d}t = K(T - 298) \qquad (13)$$

obtained, the temperature at a specific point in the cell is given by eq 14, where D is constant.

$$T = 298 + DI \qquad (14)$$

Equation 12 is reduced to

$$-\mathrm{d}[\mathrm{BCl_3}]/\mathrm{d}t = [\mathrm{BCl_3}]Ce^{[-\Delta E/(298+DI)K]} \qquad (15)$$

The B–Cl bond cleavage occurs at temperatures where $DI > 298$, and eq 15 will be very sensitive to I. As we have shown above, D increases with pressure, and at high pressures as $K(298 + D) \gg \Delta E$, dependence of eq 15 on I vanishes, as was observed by the authors.

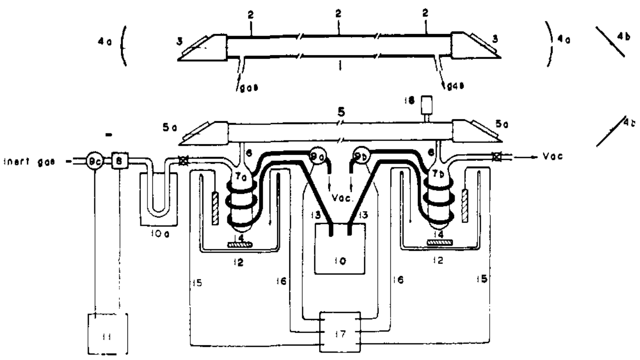

Figure 5. The irradiation system: (1) laser discharge tube; (2) electrodes; (3) Brewster angle sodium chloride windows: (4) mirrors, (a) the laser mirrors, (b) mirrors for folding the beam into the cell: (5) irradiation cell, with Brewster angle sodium chloride windows (5a): (6) capillary entrances; (7) material tubes; (8) thermistor (Veco 531); (9) magnetic valves; (10) liquid air containers; (11) inert gas controlling system; (12) vessels containing mixtures of isopentane and methylcyclohexane as thermal fluid; (13) metallic spiral tubes; (14) magnetic stirrers: (15) heaters; (16) thermocouples; (17) temperature controlling system: (18) McLeod gauge.

Experimental Section

Materials. All materials were first purified by distillation and then repeatedly by preparative vpc on a 20 ft × 3/8 in. column packed with 30% SE-30 coated on 30-60 mesh Chromosorb W until analytical vpc (capillary column 120 m × 0.02 in. coated with SE-30 on a Varian Aerograph 1200 gas chromatograph equipped with a flame ionization detector) indicated no impurities. The same analytical vpc technique was used for the quantitative estimation of the irradiation products. In order to analyze the products, the gas chromatograph was coupled with a Hitachi Perkin-Elmer RMU6 mass spectrometer.

Laser. The cw CO_2-N_2-He laser used (Figure 5) consisted of a 3-m long discharged tube with two Brewster angle sodium chloride windows and a cavity consisting of two concave mirrors at 4-m distance. The output coupling was achieved by a 6-mm hole in one of the mirrors.

Irradiation Cells. A 15-cm and a 4-m cell were used for the high-pressure and low-pressure experiments, respectively (Figure 5). The cells contained two control systems.

A. A System for Adjusting the Pressure of the Organic Compounds Which Were Irradiated (Figure 5). This was based on the dependence of the pressure on the temperatures of the compounds in tube 7a and tube 7b (*vide infra*). System 17 then controlled separately the temperatures of the compounds in the above tubes by switching on and off either the magnetic valves (9a and/or 9b) to let the flow of liquid air through the metallic spiral tubes (13a and/or 13b) or each of the electric heaters (15a and/or 15b) to adjust the temperatures measured by thermocouples (16a, b).

B. A System for Controlling the Pressure of the Inert Gas. A control unit (11) switched on and off the magnetic valve (9c) according to the temperature of a thermistor (Veco 531) (8). Since the heat flow from the thermistor (8) to the walls of the system is a function of the total pressure, therefore the temperature of the thermistor (operated at 12 V) depends on the pressure. A cold trap (10a) isolated the thermistor from the organic compounds.

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[34] The pressure extinction coefficients of *trans*-butene and isoprene are 15 × 10^{-4} and 5 × 10^{-4}, respectively: pentane is completely transparent.

Irradiation Experiments. In each experiment 100 ml of the purified organic compound was placed in one of the tubes (7a or 7b). During irradiation, the compound was distilled from one tube to the other by keeping the distillation tube at a somewhat higher temperature than the receiver tube. When the distillation was complete the temperature difference between the tubes was reversed and the distillation repeated in the opposite direction. Reversals of direction of distillation were repeated until the end of the irradiation. The pressure of the vapors in the cell was adjusted by controlling the temperature at both tubes, 7a and 7b.

The inert gases which were added in some experiments flowed through the cell slowly at a controlled pressure. After 1 hr of irradiation the products and the remaining starting material were collected in one tube and analyzed. The relative quantities of the products were then estimated by the peak areas of the gas chromatogram.

Central Linkage Influence upon Mesomorphic and Electrooptical Behavior of Diaryl Nematics. A General Proton Magnetic Resonance Method Employing a Lanthanide Shift Reagent for Analysis of Isomeric Azoxybenzenes

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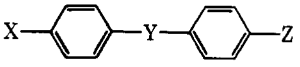
Contribution from the Air Force Materials Laboratory (AFML/LPH), Wright-Patterson Air Force Base, Ohio 45433, and Wright State University, Dayton, Ohio 45431. *Received April 1, 1971*

Abstract: The influence of the central linkage on the mesomorphic and electrooptical behavior of diaryl structures with low-temperature nematic potential is examined. The nematic to isotropic transitions for a wide variety of diaryl structures exhibit a parallel behavior for center linkage variation within a homologous series. No corresponding parallelism for the crystal to nematic transitions is present. The relative ordering of nematic thermal stability for 15 central linkages is examined for the 4-*n*-butyl-4′-methoxydiaryl derivatives. Low-temperature diaryl nematic systems are possible with a wide variety of central linkages. Several of these systems are examined with regard to the influence of the central linkage upon their ability to light scatter when electrically activated. Application of a new lanthanide shift reagent, tris(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionato)-europium(III), [Eu(fod)$_3$], to determine isomeric distributions of several unsymmetrical azoxybenzene mixtures is described. Upfield shifts are observed for protons on the 4,4′ substituents. This anomaly is discussed in terms of the expression for the pseudocontact interaction.

The majority of reported[2] nematic mesophases occur at substantially elevated temperatures. Recent discoveries utilizing the nematic mesophase as an anisotropic solvent for spectroscopy[3] and as a substrate exhibiting an important electrooptical response[4] have placed increasing importance on the development of room temperature nematic activity. Within the diaryls, whether as single compounds[5] or mixtures,[6] this search has been primarily restricted to anils. We were concerned with the influence of the central linkage upon diaryl structures with low temperature nematic potential.



A structural problem related to the assignment of oxygen in unsymmetrical diaryls with an azoxy central linkage arose. The presence of a formal negative charge on oxygen makes azoxybenzenes relatively strong Lewis bases and susceptible to structural elucidation *via* lanthanide shift reagents. Both the emergence[7] of shift reagents as tools for structure determination and the recent disclosures[8] related to the polarizing and structural influence of central linkages upon mesomorphic activity within the diaryls prompted us to report our results.

Results

The relative ordering of nematic thermal stability for 15 central linkages is shown in Table I and the effect of central linkage variation within a homologous series in Figure 1. The results of the influence of the central

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