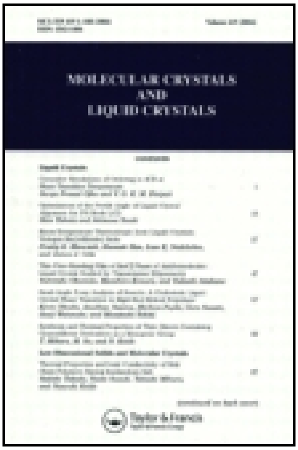

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

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The Synthesis of Ferroelectric Liquid Crystal Materials

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The Synthesis of Ferroelectric Liquid Crystal Materials

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Six compounds with the general structure

$$R—PH—PH—COO—PH—O—CH_2—CH(CH_3)—OR'$$

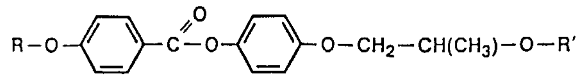
were synthesized, where R is a *n*-alkyl or *n*-alkoxy group of seven to twelve carbon atoms, R′ is an alkyl group of three to five carbon atoms, and PH is a phenyl ring. The synthesis procedure is discussed and structural assignments were confirmed by proton- and carbon-13 NMR spectroscopy. The liquid crystal behavior of these compounds was evaluated by DTA and polarized microscope. We discovered that all of them have liquid crystal phases and five out of six have a smectic C* phase with a wide temperature range. The identification of the smectic C* phase was confirmed by observing the response of liquid crystal to an applied train of square pulses with alternating polarity.

Mixtures of these compounds were also prepared and found to be useful as fast switching ferroelectric materials with a suitable temperature range.

INTRODUCTION

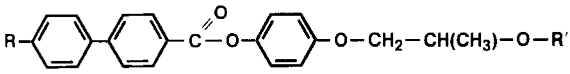
In 1975 R. B. Meyer[1,2] predicted theoretically, and then proved experimentally that chiral smectic C liquid crystal were ferroelectric. A few years later a bistable, fast-switching, electrooptic light valve using this ferroelectric liquid crystal was produced by N. A. Clark and S. T. Lagerwall.[3] Considerable interest in the synthesis of new smectogens suitable for applications of this nature has continued since then. However, the material must meet many requirements to become suitable for electrooptic applications. As pointed out by J. W. Goodby and T. M. Leslie[4] the materials should exhibit a high spontaneous polarization, have a wide temperature range, have a long helical pitch length, be stable, exhibit a smectic A phase on cooling from the isotropic liquid for alignment purposes, and have a very low viscosity. It is not easy to make a compound having all these properties. For practical use, what is needed is a liquid crystal material that operates at room temperature and has at least a 50°C temperature range.

Recently D. M. Walba[5] synthesized a series of compounds having for formula:



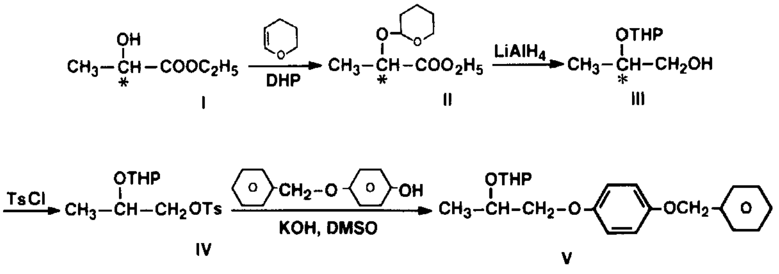
wherein R is a lower alkyl of one to three carbon atoms, and R′ is an alkyl of nine to twelve carbon atoms. These compounds exhibit high polarization and have a fast switching speed but their smectic C phases are monotropic and the temperature range is too low and narrow (around 25–35°C).

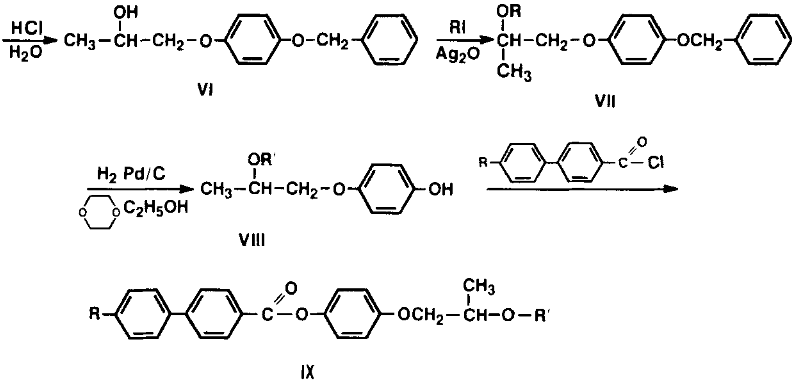
We felt that by increasing the length of the rigid part of the molecule we might increase the thermal stability of the compound and widen the temperature range. Therefore, another phenyl ring was inserted and a series of compounds were synthesized having the following formula:



SYNTHESIS

D. M. Walba[5] has reported a good route for the synthesis of 2-alkoxypropoxy phenol. But in order to use this method for larger preparations and to minimize the risk of racemization we think this route should be modified. The synthesis pathway is shown below:





The method reported by R. G. Ghirardelli[6] was used with a few modifications to synthesize the Tosylate IV.

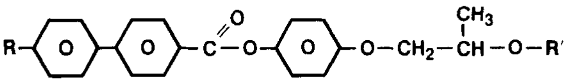
The tetrahydropyranyl ether protection reaction was almost quantitative and the product can be used directly. The hydride reduction went very well with high yield. Although the tosylate was not pure, it could be used in the next step without purification. In order to minimize the risk of racemization and fire hazard, the strongly basic and extremely flammable sodium hydride used by Walba was not used. The etherification reaction with potassium *p*-phenoxyphenolate was followed by an acid hydrolysis to remove the THP protection group and a pure compound VI was obtained after recrystallization. The Williamson reaction with alkyl iodide went smoothly using silver oxide as the base (VI–VII). The solubility of compound VII in ethanol was low, and according to M. E. Neubert et al.,[7] tetrahydrofuran cannot be used as a solvent in the hydrogenolysis reaction. Therefore, 30% dioxane in ethanol was used as solvent, whereby the reaction goes well at room temperature.

The 4-*n*-alkoxy-biphenyl-4′-carboxylic acid was obtained by acid catalysed hydrolysis of commercially available liquid crystals such as M-27 from BDH. The acid was converted to an acid chloride and the final ester was made by a procedure reported by J. C. Liang and R. Hubbard.[8]

RESULTS

Six compounds were thus synthesized; their structure and thermal data are summarized in Table I. The transition temperatures were obtained on cooling from the isotropic liquid and the thermograms shown in Figure 1, by heating the crystals in a DTA.

TABLE I



Tek#	R	R′	I-SmA	SmA-SmC*	SmC*-SmF(?)	Sm(?)-Cryst
2133	nonyl	propyl	129.7 C	89.0 C	82.5 C	80.8
2134	nonoxy	propyl	159.8	137.0	45.0	
2139	nonoxy	butyl	148.6	128.2	55.4	
2140	nonoxy	pentyl	144.5	123.6	77.1	
2141	octoxy	butyl	154.0	112.7	89.5	
2142	octoxy	pentyl	150.5	112.8	92.2	

(1) Transition from SmF to a more ordered smectic (-G) phase?

Interestingly, we found that all of the alkoxybiphenyl esters have a smectic C* phase with a fairly wide temperature range of about 50°C and can be switched quickly. They also have the desirable S_A above the Sc. However, the alkylbiphenyl ester has only a very narrow smectic phase.

Figure 2 shows the microscopic textures of different phases using Tek #2140 as an example.

We prepared many mixtures using these compounds in order to produce a material which has the ferroelectric Sm-C* phase at room temperature. As an example, the mixture Tek #LK-11 showed this phase from 8°C to 55°C. Tek #LK-11 could be aligned by using the rubbed nylon alignment method of Patel et al.[9] Its response time as measured optically was found to be about 200 μsec with ± 15V square wave as the driving voltage. The polarization P of this mixture was measured by the triangular wave method of K. Miyasato et al.[10] The results of our measurements as a function of temperature are shown in Figure 3. At room temperature $P = 11.5$ nC/m.

EXPERIMENTAL METHODS

The compounds were purified on a Water's 500A preparative chromatograph using a silica gel column. The pure products were identified by their proton and carbon 13 NMR spectra obtained on a

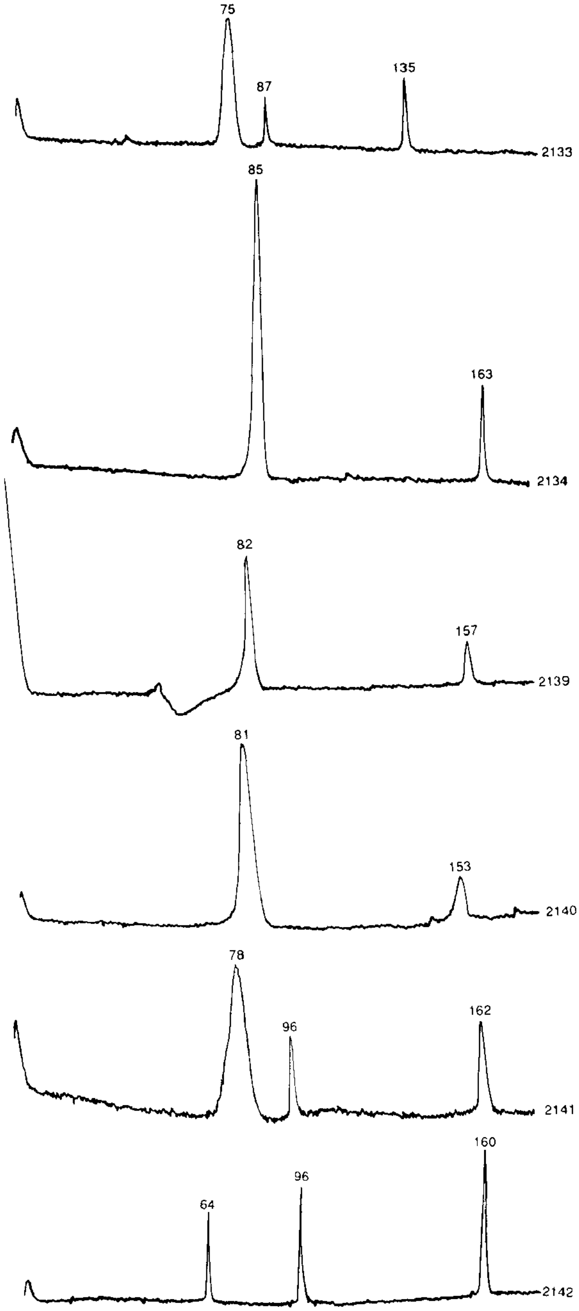


FIGURE 1 D. T. A. thermograms. (All data collected at first heating.)

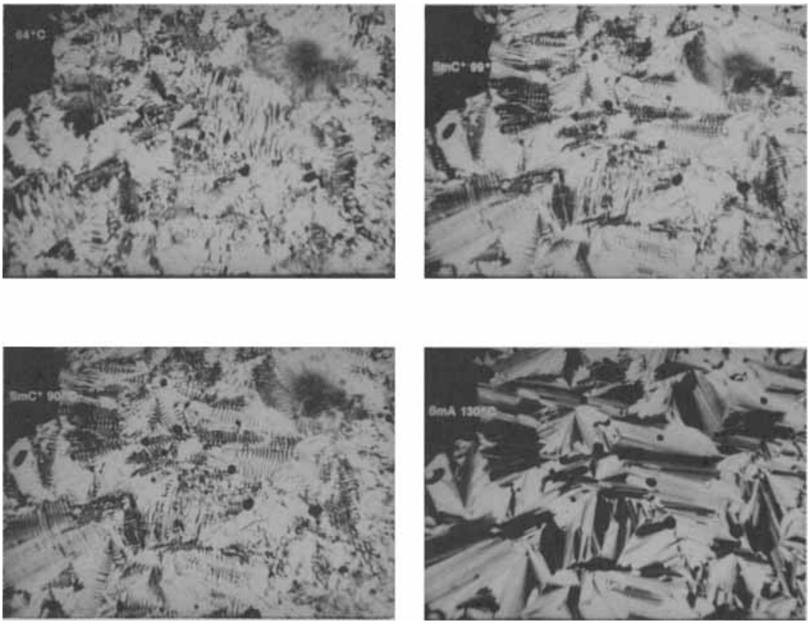


FIGURE 2 Photomicrographs of 2140 (textures observed on cooling).

JEOL FX-900 Spectrometer and by IR spectroscopy. The purity of the final products were checked on a Perkin-Elmer series 10 analytical HPLC instrument.

Using compound Tek #2139 as an example, the general synthesis procedure used is described as follows:

2-Terahydropyranyloxy propanol III. S-(-)-ethyl lactate (16 g = 0.135 mol) and 3,4-dihydro-2H-pyran (23 g = 0.273 mol) was mixed with 4 drops of concentrated hydrochloric acid at room temperature. Since the mixture might overheat, a water bath was needed occasionally to keep the temperature under 30°C. After about an hour, cooling was no longer needed and the mixture was stirred overnight. A few pellets of sodium hydroxide were added and the mixture was stirred for 30 minutes. It was then filtered and the filtrate concentrated in a vacuum to remove excess dihydropyran. The residue was dissolved in 120 ml of tetrahydrofuran and a 1M solution of lithium aluminum hydride in ether (90 ml = 0.08 mol) added dropwise. The mixture was stirred overnight at room temperature, decomposed by adding water and extracted with ether. The ether solution was washed

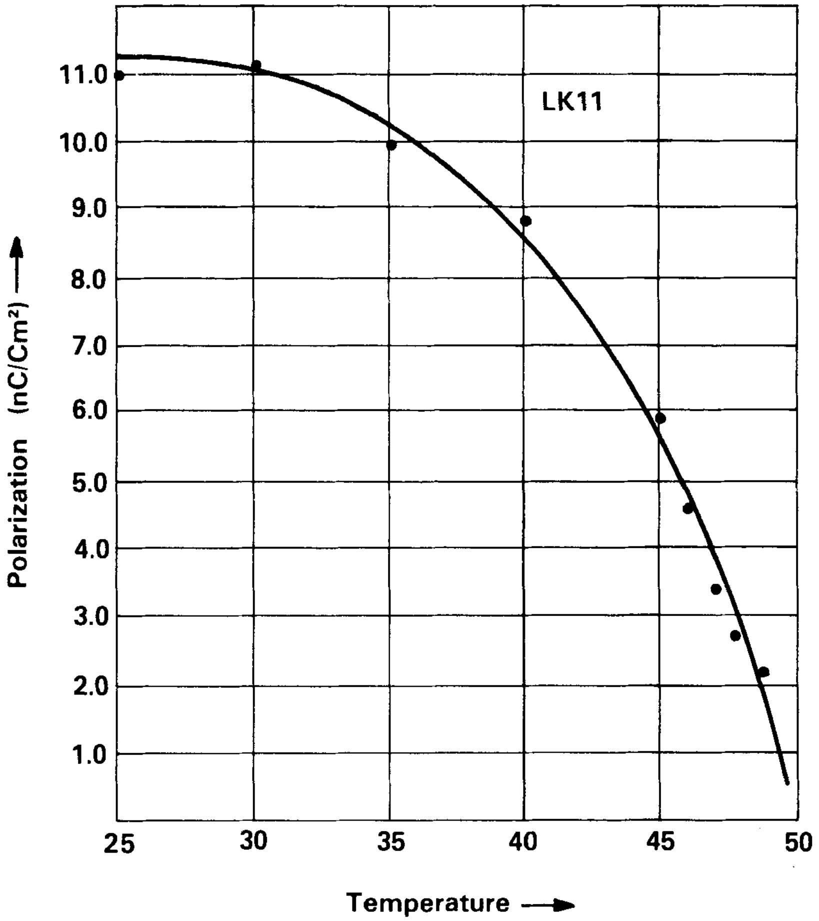


FIGURE 3 Polarization of LK-11.

by water, dried over anhydrous magnesium sulfate and concentrated in a vacuum. The residue (20.5 g) could be used in the next step without further purification.

1-(4-Benzyloxy-phenoxy)-2-propanol VI. The crude product described above (20 g), was dissolved in a mixture of 100 ml toluene and 15 ml pyridine. A solution of *p*-toluenesulfonyl chloride (32g. = 0.168 mol.) in 100 ml of toluene was added dropwise while cooling in an ice bath. Sodium hydroxide (12 g) was added after stirring for 3 hours, and then the mixture poured onto ice and extracted with toluene. The toluene layer was washed with water, dried over anhydrous magnesium sulfate and concentrated in a vacuum. The residue (30 g) could be used without further purification. A solution of potassium hydroxide (85% 1.5 g = 0.0227 mol) in 10 ml water was added to a solution of 4-benzyloxyphenol (4.5 g = 0.0225 mol) in 120 ml toluene. This mixture was refluxed for 2 hours using a Dean–Stark trap. About ⅔ of the toluene was then distilled and a solution of the above crude tosylate (7.5 g, a quarter of the total 30 gi.e. equivalent to 0.03375 mol) in 100 ml. DMSO was added. The reaction mixture was stirred overnight while the temperature was kept at about 100°C. This mixture was poured onto ice and extracted with methylene chloride. The organic extract was washed with water, dried over anhydrous magnesium sulfate, filtered and the filtrate concentrated in a vacuum. The residue was added to a solution of 170 ml of ethanol, 40 ml water, 10 ml hydrochloric acid with 2 g activated charcoal. This mixture was refluxed for 1.5 hours, filtered while hot and the filtrate concentrated in a vacuum to dryness. A yellowish solid was obtained which could be recrystallized from ethanol–water to give 4 g of white crystals (yield 69.9% based on 4-benzyloxyphenol or 45.9% based on the ethyl lactate used). A carbon-13 NMR spectrum, Figure 4 showed that this material is the pure alcohol VI.

2-Butyloxypropoxyphenol VIII. Benzyloxyphenoxypropan-2-ol (2.7 g = 0.0105 mol) was mixed with 50 g butyl iodide, and 10 g silver

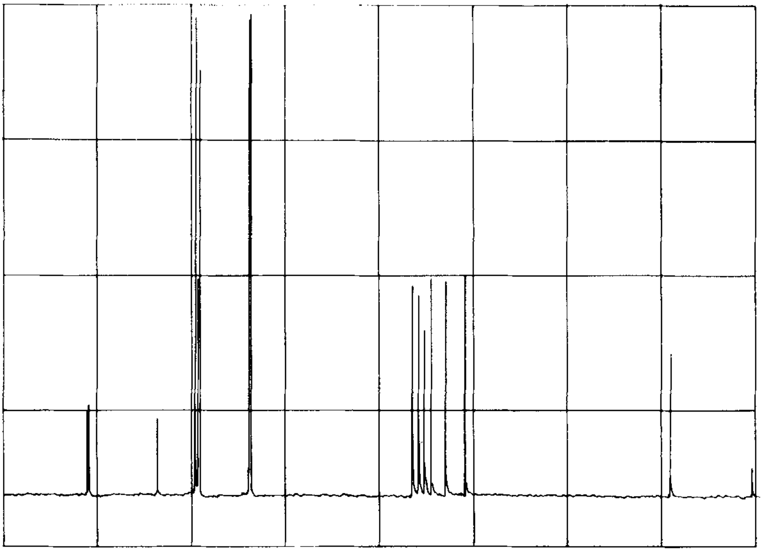


FIGURE 4 Carbon 13-NMR spectrum of benzyloxyphenoxy-2-propanol.

oxide. The mixture was heated to 110°C for 12 hours with stirring, filtered and the filtrate vacuum distilled to recover the excess butyl iodide. The residue was dissolved in dioxane-ethanol (1:3) and hydrogenolyzed with 0.75 g 10% Pd/C at 55 psi for 17 hours. This mixture was filtered and the filtrate concentrated in a vacuum. The residue was recrystallized with hexane to give 1.64 g white crystals (yield 69.7%). The carbon-13 NMR spectrum (Figure 5) shows that this is the pure phenol VIII.

2-Butyloxypropoxyphenyl p-*4'*-n-*nonyloxyphenylbenzoate (Tek #2139) IX.* *p*-4-*n*-Nonyloxyphenylbenzoic acid (made by acidic hydrolysis of commercially available M27 from BDH) (0.85 g) was dissolved in 40 ml toluene, to which thionyl chloride (10 ml) was added. This mixture was refluxed four hours and then concentrated in a vacuum. The residue was dissolved in 20 ml toluene, and 2-butyloxypropoxyphenol (0.49 g = 0.0022 mol) was added. Pyridine (2 ml) was added dropwise into the reaction mixture with stirring. Stirring was continued for 17 hours at room temperature. After dilution with toluene this mixture was washed with 10% hydrochloric acid, twice with water, dried over anhydrous magnesium sulfate, filtered and the filtrate concentrated to dryness in vacuum. The residue was dissolved in a mixture of ethyl acetate-methylene chloride-hexane (1:3:3) and injected into a normal phase preparative HPLC column using the same solvent system as the mobile phase. The compound corresponding to the major peak was separated and re-

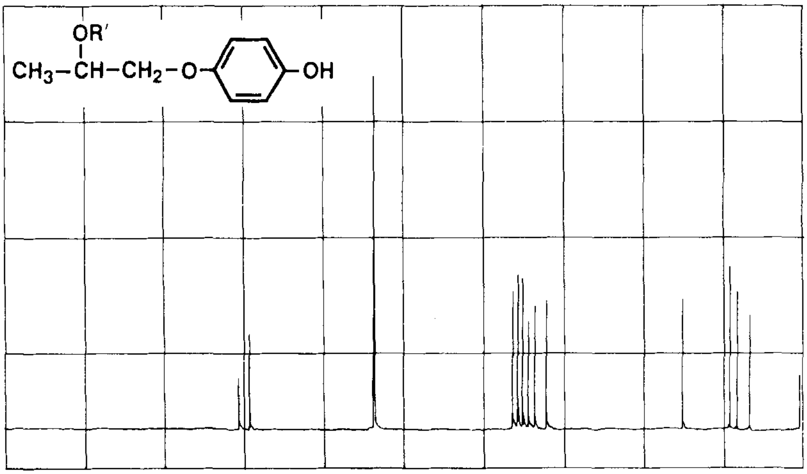


FIGURE 5 Carbon 13-NMR spectrum of 2-butyloxypropoxyphenol.

crystallized from methanol containing a small amount of tetrahydrofuran. Pure white crystals (0.46 g) were obtained. The carbon 13 NMR spectrum (Figure 6) shows that this is the pure ester IX.

The study of phase transitions of these newly synthesized compounds

The phase diagram of the compounds was determined by optical microscopy and confirmed by thermograms taken on a Perkin-Elmer DTA 1700 differential thermal analyzer with a system 7/4 controller (Figure 1). The material was filled in glass cells with transparent ITO electrodes on both sides and 1.5 μm photoresist spacers. These cells with electrical contacts were placed inside a Mettler FP84 oven and the temperatures were controlled with a precision of ±0.1°C. The liquid crystalline phases were identified by observing the characteristic texture under a polarizing microscope. The identification of the smectic C* phase was confirmed by observing the response of liquid crystal to an applied train of square pulses with alternating polarity.

Acknowledgments

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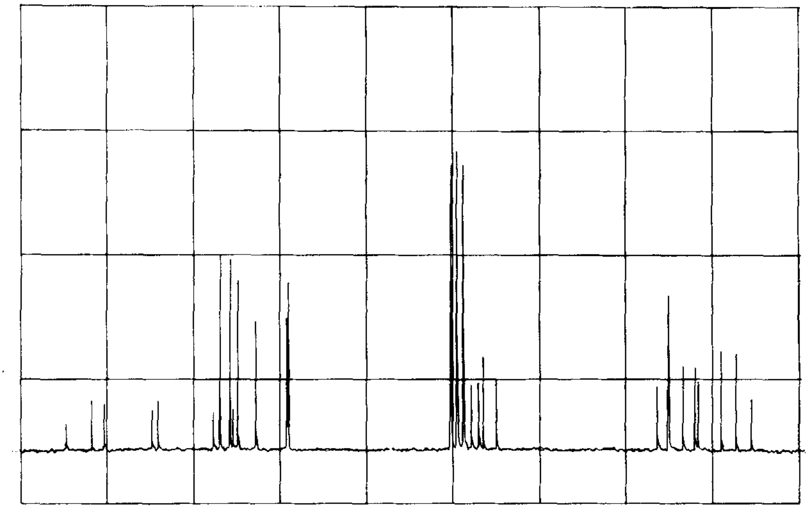

FIGURE 6 Carbon 13-NMR spectrum of Tek #2139.

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