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Liquid Crystal Properties of Methyl Substituted Stilbenes

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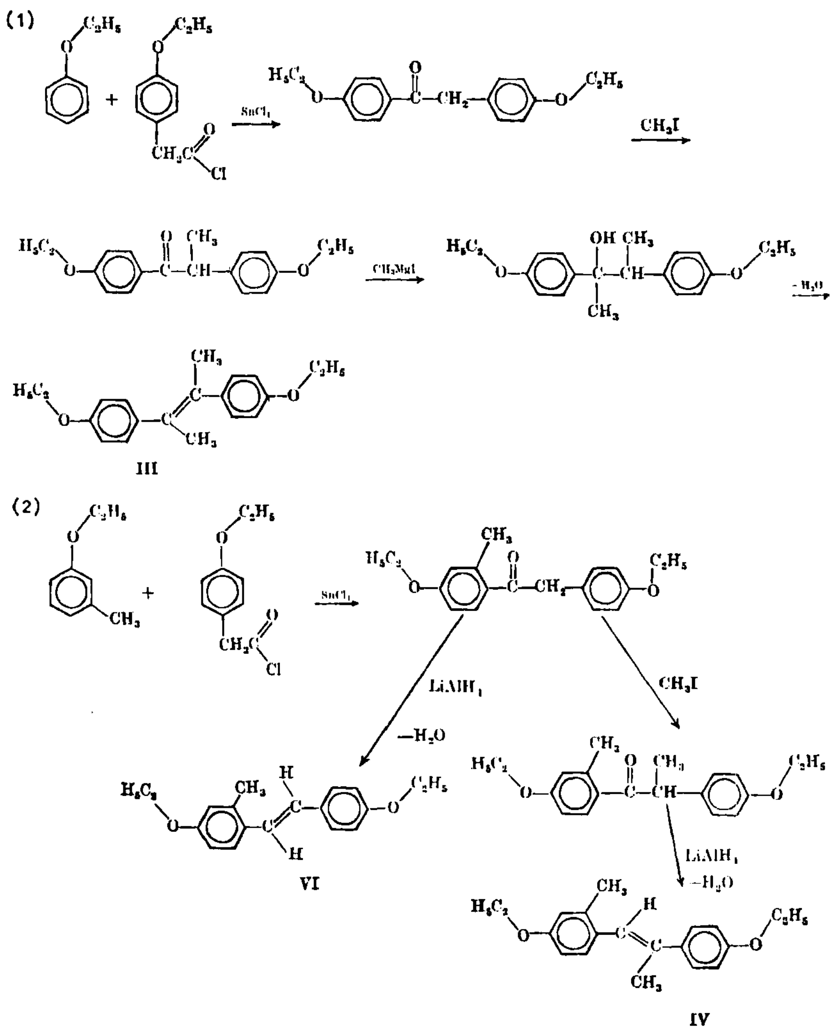
Abstract—A series of mono- and di-substituted trans-stilbenes were prepared and their nematic clearing point temperatures observed. There was found to be a direct relationship between the increase in molecular breadth and the lowering of this nematic clearing point temperature. The effect of twisting the stilbenes out of coplanarity does appear to produce a lowering of the nematic clearing point but, the overriding feature is simply the intermolecular separation.

1. Introduction

It has recently been shown⁽¹⁾ that in a series of 4,4′-dialkoxy substituted stilbenes the introduction of substituent groups into the molecule in the ortho or the α-positions decreases the melting points of these compounds and reveals the presence of suspected liquid crystal phases. Such substitutions will have two major effects on the geometry of the molecule, first the coplanarity will be disrupted,⁽²⁾ and second the overall breadth will be increased. It has been suggested⁽³⁾ that the existence of mesomorphic properties in the geometrically similar benzylideneanilines is due to a twist in the aniline ring out of the C—N=C—C plane, and recent calculations⁽⁴⁾ have indicated this twist to be as much as 55°. It thus becomes of interest to determine whether the appearance of the liquid crystal phase in the stilbenes was due to this twisting or was simply the result of the increased intermolecular separations caused by the bulky substituents. With the object of clarifying this point we have prepared a series of mono- and di-methyl substituted 4,4′-dialkoxy stilbenes.

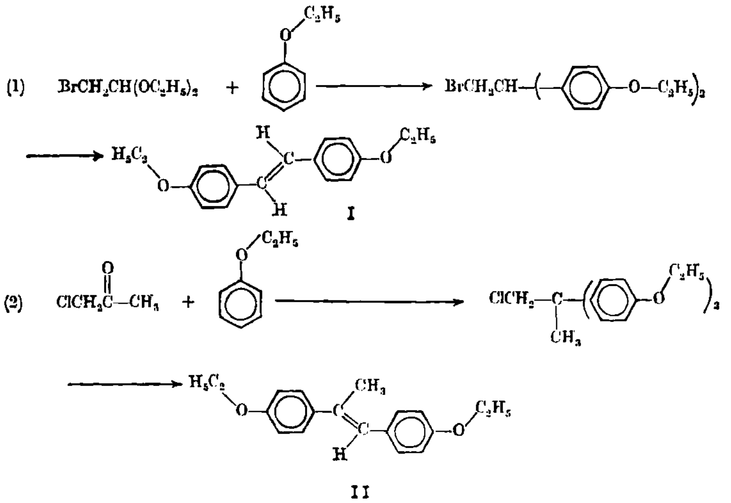
Scheme I



2. Results and Discussion

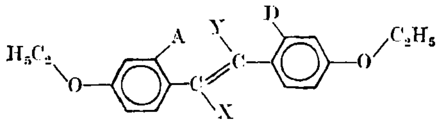
A series of methyl substituted 4,4'-dialkoxy stilbenes was synthesized. The compounds with their melting points and nematic clearing points are summarized in Table 1.

Scheme II



The syntheses were carried out by two general methods, (1) the Friedal–Crafts condensation of a phenylacetyl chloride with an ethoxybenzene to prepare the phenyl benzylketone then, treatment as outlined in Scheme I, to give compounds III, IV, and VI, (2) reaction of 2-bromodiethylacetal or chloroacetone with phenetole or *m*-ethoxytoluene as outlined in Scheme II to give compounds I, II, and V.

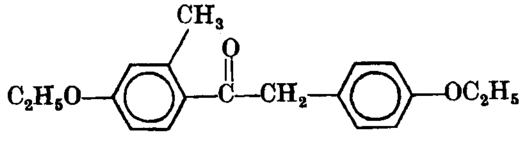
TABLE 1



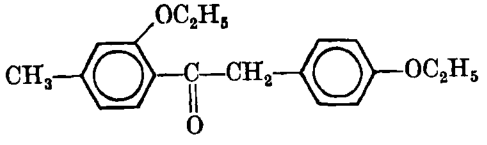
No.	A	X	Y	D	Melting Point °C	Nematic → isotropic Clearing point °C
I	H	H	H	H	209	(189)
II	H	CH_3	H	H	106	121
III	H	CH_3	CH_3	H	157	(77)
IV	CH_3	H	CH_3	H	98	(66)
V	CH_3	H	H	CH_3	142	(52)
VI	CH_3	H	H	H	113	(105)

The initial Friedel–Crafts condensation of *p*-ethoxyphenacetyl chloride with *m*-ethoxytoluene gave two isomers, one melting at 74–75 °C, the other at 45–47 °C. The NMR spectra of these compounds indicated the two structures A and B arising from a condensation of the acid chloride either ortho or para to the ethoxy group in *m*-ethoxytoluene.

A

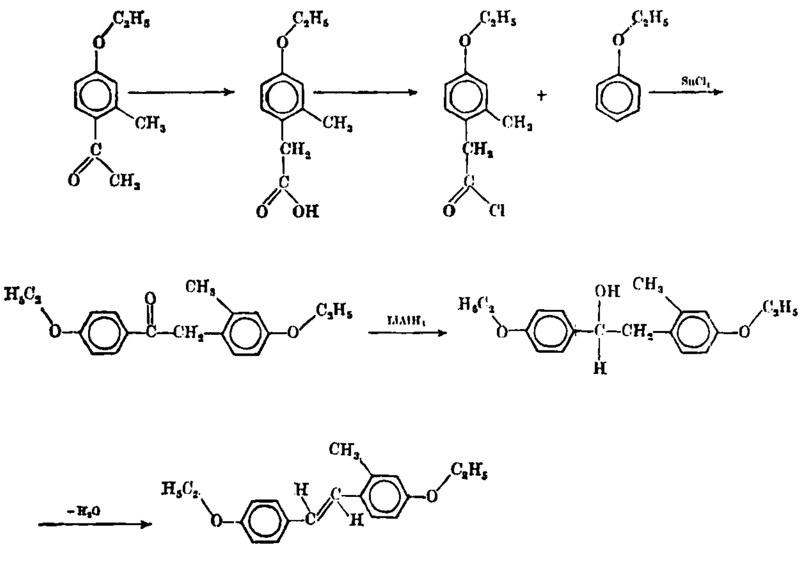


B



In order to identify correctly each of these isomers it was necessary to carry out an unequivocal synthesis of 4,4′-diethoxy-2-methylstilbene. Starting from 4-ethoxy-2-methylacetophenone the reaction sequence is as shown in Scheme III.

Scheme III



The stilbene isolated in this manner was identical with that isolated when starting from the ketone melting at 45–47 °C. Thus, this isomer has the configuration A, and isomer B melts at 74–75 °C.

With the exception of the α-methyl derivative (II) all the stilbenes have monotropic mesophases. Only in I and IV could the mesophase be observed by super cooling, and even here only with great difficulty because of the tendency to crystallize. It was thus found necessary to obtain the nematic clearing points using the method of binary mixtures(5) for compounds III, V, and VI.

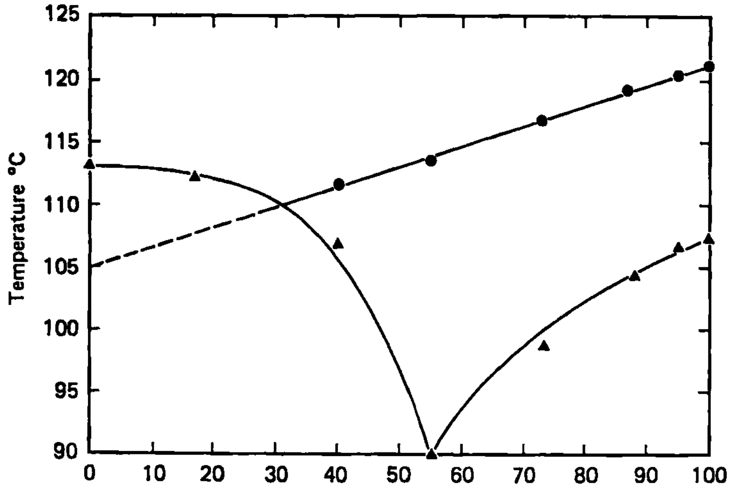


Figure 1. Mole percent of 4,4′–diethoxy-α-methylstilbene in 4,4′–diethoxy-2-methylstilbene.

Figure 1 shows a typical phase diagram for a mixture of 4,4′-diethoxy-α-methylstilbene and 4,4′-diethoxy-2-methylstilbene.

If the enantiotropic mesophase observed in the α-methyl derivative was due solely to a twisting of the benzene rings out of coplanarity, then one would expect the unsubstituted stilbene to show only a normal melting point with no mesophase. The fact that this compound has been shown to possess a monotropic nematic mesophase(6) is evidence against such a twisting mechanism being the sole cause of the appearance of liquid crystallinity in the stilbenes. It could, of course, still be a major factor in lowering the stability of the mesophase. This is evidenced by the large drop of 67 °C in the nematic clearing point from 189 °C in I, to 121 °C in II.

Molecular models indicate that the combination of an ortho methyl group with an α-hydrogen is sterically equivalent to an α-methyl and ortho hydrogen. Models also show that in the case of the substitution on the benzene ring the molecule is considerably broader than if the substitution is between the rings. Thus, if the primary effect on the stability of the mesophase is simply the greater intermolecular distance created by the substituents, then substitution on the benzene ring should have a more pronounced destabilization effect on the mesophase than does the same substitution in the α-position. Examination of the nematic clearing points in Table 1 shows that this is indeed the case. The order of greatest effectiveness in destabilization of the mesophase is *o,o′*-dimethyl, > α,*o′*-dimethyl > α, α′-dimethyl > *o*-methyl > α-methyl. Models show that this is also the order in which the substituents increase the molecular breadth.

In summary, it seems that, although steric effects in the stilbenes cause a twisting of the molecule out of coplanarity and this may in turn lower the stability of the mesophase, this is not the predominate factor affecting this stability. The primary effect is simply the intermolecular distance between the molecules caused by increasing the bulk of the lateral substituents.

3. Experimental

Determination of transition temperatures.

The mesophases were measured using a Leitz Ortholux POL Polarizing Microscope equipped with a Mettler FP2 Hot Stage Controller. In monotropic compounds which exhibited a tendency to crystallize rapidly the powder technique was employed.(7) In the cases where no amount of super-cooling would allow the observation of a liquid crystal phase, use was made of phase diagrams of binary mixtures. Small samples of the individual components were accurately weighed into a test tube and heated to fusion. A sample of this solution was then placed on a microscope slide and allowed to crystallize. The transitions reported are the temperatures at which the solid or the mesophase has completely disappeared. The solid → nematic transitions are shown by *o* and the nematic to isotropic transitions by *Δ*. In cases such as VI when the monotropic nematic clearing point is observable by means of super-cooling, the two methods give identical nematic clearing points to within a degree.

MATERIALS

4,4′-Diethoxystilbene(8) and 4,4′-diethoxy α-methylstilbene(9) were prepared by known methods as shown in Scheme II.

4,4′-Diethoxydesoxybenzoin: *p*-Ethoxyphenacetyl chloride was prepared from 12.9 g of *p*-ethoxyphenylacetic acid by treatment with 10 ml of thionylchloride. This acid chloride in 75 ml of benzene, was heated with 37.6 g of phenetole in 25 ml of benzene. A solution of 28 ml of anhydrous stannic chloride in 30 ml of benzene was added dropwise, the reaction mixture stirred at room temperature for 12 hours, and then it was poured into dilute hydrochloric acid. The benzene layer was separated, water washed, and the benzene was removed. The residue was recrystallized twice from ether by cooling in an acetone-dry ice bath. Ten grams of colorless crystals melting at 107–108 °C were obtained. The NMR spectrum indicated exclusive reaction in the para position of phenetole.

NMR (100 MHz) ($CDCl_3$) δ 1.2–1.4 (m 6 CH_3 of C_2H_5O)
3.9–4.1 (m 6 CH_2 of C_2H_5O and CH_2) 6.6–8.2 (m 8 aromatic)
Calcd. for $C_{18}H_{20}O_3$; C, 76.02; H, 7.08.
Found: C, 75.71; H, 6.98.

α-(4-Ethoxyphenyl)-4-ethoxy-2-methylacetophenone: The Friedel–Crafts acetylation of *m*-ethoxytoluene with *p*-ethoxyphenacetyl chloride by the above procedure gave an oil which distilled over a range of 200–330 °C at 0.05 mm pressure. Fractional crystallization of the oil from an acetone–ethanol mixture by cooling in a Dry-Ice–acetone bath gave two colorless solids, one melting at 74–75 °C, the other at 45–47 °C. Thin layer chromatography established the purity of these compounds and combustion analysis confirmed that they were isomers.

NMR of 74–75 °C isomer (100 MHz) ($CDCl_3$) δ 1.3–1.6 (d of t 6 CH_3 of C_2H_5O) 2.32 (s 3 CH_3) 3.8–4.2 (m 4 CH_2 of C_2H_5O) 4.22 (s 2 CH_2) 6.6–7.6 (m 7 aromatic)

NMR of 45–47 °C isomer (100 MHz) ($CDCl_3$) δ 1.3–15 (d of t 6 CH_3 of C_2H_5O) 2.5 (s 3 CH_3) 3.9–4.2 (m 6 CH_2 of C_2H_5O) 4.10 (s–2 CH_2) 6.6–7.8 (m 7 aromatic)

Calcd. for $C_{19}H_{22}O_3$: C, 76.48; H, 7.43.

Found: (m 74–75 °C.) C, 76.59; H, 7.44 (m 45–47 °C) C, 76.40; H, 7.33.

4-*Ethoxy*-2-*methylphenylacetic acid*:(10) A mixture of 37 g of 4-ethoxy-2-methylacetophenone, 27 g of morpholine, and 10 g of sulphur was heated to reflux overnight with stirring. The reaction mixture was poured into a solution of 2 ml of benzene in 98 ml of ethanol, and the solid thiomorpholide filtered. This was hydrolysed by heating in 1 liter of 10% potassium hydroxide solution for four hours. This solution was then cooled, ether extracted, the aqueous phase made acidic with hydrochloric acid, and the precipitate filtered and dried. Ten grams of 4-ethoxy-2-methylphenylacetic acid melting at 87–88 °C was recovered.

Calcd. for $C_{16}H_{14}O_3$: C, 68.02; H, 7.26.

Found: C, 67.45; H, 7.15.

NMR ($CDCl_3$) (100 MHz) δ 1.38 (t 3 CH_3 of C_2H_5O) 3.57 (s 2 CH_2), 3.98 (q 2 CH_2 of C_2H_5O), 6.6–7.2 (m 3 aromatic).

α-(4-*Ethoxy*-2-*methylphenyl*)-4-*ethoxyacetophenone*: 4-Ethoxy-2-methylphenylacetic acid was converted to the acid chloride by heating 29.4 g in 100 ml of benzene with 36 g of thionyl chloride and 10 drops of pyridine. The reaction was allowed to continue until no further evolution of hydrochloric acid was observed. The benzene and excess thionyl chloride were removed on a roto-evaporator and the residual acid chloride treated with 18.0 g of phenetole in 75 ml of benzene. A solution of 138 g of anhydrous stannic chloride in 75 ml of benzene was added dropwise and the mixture stirred overnight at room temperature. The crude reaction mixture was poured into dilute hydrochloric acid and ice, then ether extracted. The ether phase was separated, water washed, dried and the ether was evaporated. The white solids that remained were recrystallized from ethanol to yield 8.5 g of α-(4-ethoxy-2-methylphenyl)-4-ethoxyacetophenone melting at 107–109 °C.

NMR (CDCl$_3$) (100 HMz) δ 1.1–1.4 (m 6 CH$_3$ of C$_2$H$_5$O) 2.06 (s 3 CH$_3$), 3.7–4.0 (m 6 CH$_2$ of C$_2$H$_5$O and CH$_2$) 6.4–7.9 (m 7 aromatic).

4,4'-*Diethoxy*-2-*methylstilbene*: Prepared as in Scheme I. A solution of 3 g of α-(4-ethoxy-2-methylphenyl)-4-ethoxyacetophenone in 100 ml of ether was reduced in the normal manner with a solution of 4.0 g of lithium aluminum hydride in 100 ml of ether. The resultant alcohol was dehydrated without purification by heating under vacuum with 3.0 g of sodium bisulfate. The stilbene, m 110 °C, was isolated and purified by recrystallization from petroleum ether. The spectral properties of this compound (NMR and IR) were identical to those of the stilbene prepared from the condensation product melting at 45–47 °C obtained in the Friedal–Craft reaction between *m*–ethoxytoluene and *p*-ethoxyphenacetyl chloride.

Prepared as in Scheme III α-(4-ethoxyphenyl)-4-ethoxy-2-methylacetophenone was reduced with lithium aluminum hydride by the standard method in anhydrous ether. The oily alcohol was isolated and used without further purification. It was dehydrated by heating with sodium bisulfate under a 1 mm vacuum in a sublimation apparatus. The colorless solid that sublimed was recrystallized twice from petroleum ether. It melted at 113 °C.

Calcd. for C$_{19}$H$_{22}$O$_2$: C, 80.81; H, 7.85
Found: C, 80.95, H, 7.87.
NMR (CDCl$_3$) (100 MHz) δ 1.31 (t 6 CH$_3$ of C$_2$H$_5$O) 2.35 (s 3 CH$_3$) 4.0 (q 4 CH$_2$ of C$_2$H$_5$O), 6.6–7.5 (m 9 aromatic and ethylenic).

4,4'-*Diethoxy*-2-*methyl*-α-*methylstilbene*: A solution of sodium ethoxide was prepared by dissolving 2.0 g of sodium metal in 50 ml of absolute ethanol. Fifteen grams of methyl iodide and 2.0 g of α-(4-ethoxyphenyl)-4-ethoxy-2-methylacetophenone were added, and the reaction was refluxed overnight on a steam bath. The ethanol was evaporated from the reaction mixture and the residue poured into water and ether extracted. The ether phase was separated, water washed, dried and evaporated. A dark oil weighing 1.7 g remained. The NMR spectrum was indicative of methyl substitution alpha to the ketone. (A multiplet at 1.2–15 δ represents 9 protons and a quartet at 4.44 represents 1 proton.) This oil was used for the next step without further purification. It was dissolved in 25 ml of anhydrous ether and treated with a solution of 2.0 g of lithium aluminum hydride in 100 ml of ether. After refluxing for 45 min the reaction was worked up in the usual manner and the residual oil dehydrated by heating with 2.0 g of sodium bisulfate under 1 mm vacuum. The white solid that remained was recrystallized from petroleum ether and 0.1 g of 4,4′-diethoxy-2-methyl-α-methylstilbene melting at 98 °C was obtained.

NMR ($CDCl_3$) (100 MHz) δ 1.38 (t 6 CH_3 of C_2H_5O) 2.04 (s-3 CH_3), 2.20 (s-3 CH_3), 3.8–4.2 (m-4 CH_2 of C_2H_5O), 6.6–7.5 (m 7 aromatic and ethylenic)
Calcd. for $C_{20}H_{24}O_2$: C, 81.04; H, 8.16
Found: C, 80.97, H, 8.00.

4,4′-Diethoxy-2,2′-dimethylstilbene: A solution of 6.1 g of *m*-ethoxytoluene and 5.0 g of 2-bromodiethylacetal in 10 ml of glacial acetic acid was cooled to 0° with stirring. A mixture of 10 g of concentrated sulfuric acid and 5 g of acetic acid was added dropwise to this solution, keeping the temperature below 20 °C. The reaction mixture was allowed to stir for three hours, was poured into water, and ether extracted. The ether phase was washed with aqueous sodium carbonate solution, dried and evaporated. The residue was treated with 50 ml of amyl alcohol and refluxed for 12 hours. The solids were filtered and recrystallized twice from ethanol, and then twice from petroleum ether. They weighed 2.0 g and melted at 142–143 °C.

NMR ($CDCl_3$) (100 MHz) δ 1.3–1.5 (t 6 CH_3 of C_2H_5O), 2.36 (s 6 CH_3) 3.9-4.1 (q 4 CH_2 of C_2H_5O), 6.7–7.5 (m 8 aromatic and ethylenic).
Calcd. for $C_{20}H_{24}O_2$: C, 81.04; H, 8.16.
Found: C, 80.91; H, 8.13.

1-(4-*Ethoxyphenyl*)-2-(4-*ethoxyphenyl*)-1-*propanone*: A solution of

12.4 g of 4,4'-diethoxydesoxybenzoin in 200 ml of absolute ethanol was stirred with a solution of sodium ethoxide prepared from 4.6 g of sodium in 100 ml of ethanol and 30 g of methyl iodide. After stirring 12 hours at room temperature the reaction mixture was treated with an additional 2.4 g of sodium in 50 ml of ethanol and 17 g of methyl iodide and heated to reflux for three hours. The ethanol was removed from the reaction mixture and the residual oil obtained after ether extraction was recrystallized from methanol. The NMR spectrum indicated that the low melting solids were 1-(4-ethoxyphenyl)-2-(4-ethoxyphenyl)-1-propanone.

NMR ($CDCl_3$) (100 MHz) δ 1.1–1.6 (m 9 CH_3 of C_2H_5O and CH_3), 3.8–4.1 (m 4 CH_2 of C_2H_5O), 4.5–4.7 (q 1 CH), 6.7–8.0 (m 8 aromatic).

This crude product was used directly in the next reaction.

4,4'-Diethoxy-α,α'-dimethylstilbene: A solution of 5.4 g of crude 1-(4-ethoxyphenyl)-2-(4-ethoxyphenyl)-1-propanone in 100 ml of ether was added slowly to a solution of the Grignard reagent prepared from 1.5 g of magnesium and 10.5 g of methyl iodide in 50 ml of anhydrous ether. The reaction mixture was heated to reflux for two hours and hydrolysed by pouring into 200 ml of dilute sulphuric acid. The ether phase was separated, washed, dried and evaporated. The residual oil was dehydrated by heating with 3.0 g sodium bisulfate in a 1 mm vacuum. The crystalline solid was sublimed and then recrystallized twice from petroleum ether. It weighed 0.7 g and melted at 157–158 °C.

NMR ($CDCl_3$) (100 MHz) δ 1.3–1.5 (t 6 CH_3 of C_2H_5O), 1.90 (s 6 CH_3), 3.9–4.2 (q 4 CH_2 of C_2H_5O), 6.8–7.3 (m 8 aromatic).

Calcd. for $C_{20}H_{24}O_2$: C, 81.04; H, 8.16.
Found: C, 80.91; H, 8.21.

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