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Synthesis and Liquid Crystal Properties of some Acetylene Derivatives†

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Abstract—A series of *p*-alkoxyphenyl acetylenedicarboxylates has been prepared which allows a direct comparison to be made between the triple bond and the *para*-phenylene ring as central groups. The acetylene derivatives are found to have phase transitions some 60–100° below those of the corresponding *para*-phenylene compounds; however, they also exhibit much lower nematic stability. Since both central groups are rigid and linear with respect to substituents, effects due to the electronic and geometric structure of the triple bond are discussed as contributing factors to mesophase instability.

Several acetylene derivatives containing one or more methylene groups near the center of the molecule were also prepared but none exhibited mesomorphic behavior.

1. Introduction

Many compounds which form nematic mesophases contain a *para*-substituted benzene ring as the central group. The contribution of this ring to mesophase stability appears to lie in its rigidity, linearity, and polarizable π-electron density.⁽¹⁾ A recent study by Dewar and Goldberg⁽²⁾ also arrived at this conclusion.

The carbon-carbon triple bond is another group which also possesses rigidity, linearity, and polarizable π-electron density. It offers the further advantage of being more transparent in the ultraviolet region than a *para*-phenylene ring.

2. Results

We have prepared a series of symmetrical *p*-alkoxyphenyl esters of butynedioic acid which has the triple bond as the central group and

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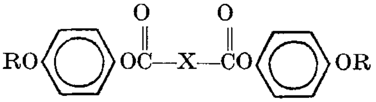
which allows comparison with the corresponding all-benzenoid compounds. Transition temperature data for the acetylene series and the *para*-phenylene series⁽³⁾ are given in Table 1.

TABLE 1 Transition Temperatures of Some *p*-Alkoxyphenyl Acetylenedicarboxylates and *p*-Alkoxyphenyl Terephthalates



	X				
	—C≡C—(a)		—(b)		
R(c)	m.p. or crystal-nematic pt., °C	N—I, °C	crystal-nematic pt., °C		N—I, °C
CH_3	148–150	—	211		281
C_2H_5	121–122	—	221		278
C_3H_7	134	134(d)	205		240
C_4H_9	91.5	99.5	189		235
C_5H_{11}	89	89(d)	167(e)	175(f)	213
C_6H_{13}	89	89(d)	162(e)	176(f)	207
C_7H_{15}	85	82(d)	153(g)		188

(a) All acetylenic compounds gave correct elemental analyses. (b) Ref. 3. (c) All alkyl groups are normal. (d) Monotropic transition. (e) Crystal-smectic transition. (f) Smectic-nematic transition. (g) Dewar, M. J. S. and Goldberg, R. S., *J. Org. Chem.*, **35**, 2711 (1970). In footnote 12, a private communication from J. L. Fergason reports a monotropic smectic phase for this compound.

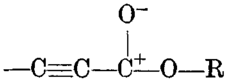
3. Discussion

A striking feature evident from comparison of the data is the substantially lower transition temperatures of the acetylene compounds. The nematic-isotropic transitions are more than 100° *lower* than those of the corresponding all-benzenoid derivatives, while comparable melting or crystal-nematic points of the acetylenic esters range from 61 to 99° lower. Thus, the acetylenic linkage appears to be a potentially useful group in the search for compounds which are mesomorphic at room temperature.⁽⁴⁾

The nematic ranges exhibited by the acetylenic esters are considerably shorter and of lower thermal stability(1) than those of the comparison series. Since both groups are rigid and linear with respect to substituents, the observed differences must be attributed to variations related to the electronic structure and geometry of the triple bond and the *para*-phenylene ring.

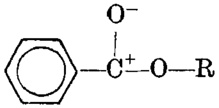
Group polarizability is an important factor in mesophase stability. A significant difference which affects the polarizability is the length of the triple bond in comparison to the distance between *para*-carbon atoms in benzene derivatives. The triple bond in disubstituted alkynes has an average length of 1.21 Å,(5) whereas the distance between *para*-carbons in benzene is more than twice as great, 2.97 Å.(6) For unsaturated organic molecules, polarizability increases with the number of π-electrons and with the larger volume in which the electrons may delocalize. The four π-electrons of the triple bond are constrained to a relatively small volume compared to a benzene derivative, thus leading to a lower polarizability. In addition, the shorter length of the triple bond compared to the *para*-carbon distance in a benzene derivative leads to a decrease in the length of the molecule with a corresponding decrease in molecular anisotropy. Both of these factors will lead to a decrease in mesophase stability.(1,7)

The π-electron density distribution in the acetylenic bond approximates a cylindrical electron cloud with the two sp-hybridized carbons being more electronegative than the sp^2-hybridized carbons of the benzene ring, due to the large amount of s-character. Hence, dipolar structures such as



$$-C\equiv C-\overset{O^-}{\overset{|}{C^+}}-O-R$$

and



which tend to stabilize mesophase formation(1,7) will be less favorable for the acetylene derivatives. A similar conclusion is reached upon considering resonance stabilization of the positive charge in the dipolar structures.

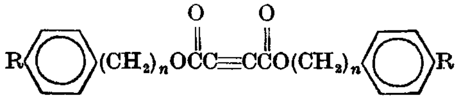
All of the acetylenic esters in Table 1 are colorless, crystalline solids. In general, the triple bond is much more transparent in the ultraviolet than is an aromatic ring. For example, the longest wavelength absorption maximum in 2-octyne is at 222.5 nm (ϵ 160).(8) The UV characteristics of these compounds are exemplified by the data for *p*-butoxyphenyl acetylenedicarboxylate in tetrahydrofuran, λ_{max} 258 (ϵ 41,000), with no end absorption above 300 nm.

The *p*-butoxy derivative in its mesomorphic state between transparent glass electrodes was found to exhibit dynamic scattering,$^{(9)}$ a property characteristic of the nematic state.

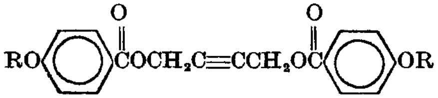
PREPARATION OF OTHER ACETYLENE DERIVATIVES

Several other derivatives of acetylenedicarboxylic acid and of 2-butyne-1, 4-diol containing one or more CH_2 groups were prepared, Table 2. None exhibited mesomorphic behavior.

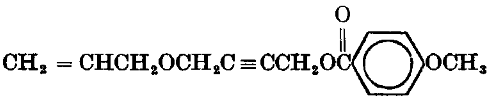
TABLE 2 Some Non-mesomorphic Acetylenic Esters Prepared in the Present Study$^{(a)}$



R	*n*	m.p., °C
H	1	(b)
H	2	47.5–48.5
H	3	91.0–92.0
Cl	1	86.0–87.0
CH_3O	2	53.5–54.5



R	m.p., °C
C_2H_5	108.5–109.5
C_4H_9	108.0–109.0
C_5H_{11}	81.5–82.5

	m.p., °C
$C_7H_{15}OCH_2C{\equiv}CCH_2OC_7H_{15}$	−14– −12
	98.0–98.5

(a) All compounds gave correct elemental analyses. (b) Viscous liquid, purified by molecular distillation.

In general, the introduction of methylene groups near the center of a molecule may cause significant deviations from linearity, which leads to a decrease in mesophase stability.$^{(10)}$

Experimental Section

Mesophases were identified with an AO Spencer polarizing microscope equipped with a variable temperature stage designed in these laboratories.(11) The thermometer used in the microscopic measurements was calibrated with Fisher " Thermetric " standards. For mesomorphic substances, the temperatures reported are those at which the solid or mesophase has just disappeared.

Microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn.

The acetylenic esters were all prepared by the following method: acid-catalyzed reaction of the alcohol or phenol with the diacid in benzene. The water formed in the reaction was separated in a Dean-Stark trap. A typical procedure is given below.

PREPARATION OF ACETYLENEDICARBOXYLIC ACID

We found the following procedure to be much more economical of time and money than that given in " Organic Syntheses ".(12)

A slurry of 15 g of the monopotassium salt of acetylenedicarboxylic acid (Aldrich Chem. Co.) in 80 ml of water is acidified with 50% H_2SO_4 to pH 1–2, while cooling the reaction in an ice bath. The mixture is then extracted with five 40 ml portions of ether. The combined ether extracts were distilled to give as residue a viscous oil (the hydrated diacid). This was placed in a 500 ml round bottom flask together with 200 ml of benzene. The benzene-water azeotrope is distilled off followed by removal of the remaining benzene under vacuum. The anhydrous diacid remaining in the flask is a white powder, m.p. 179–180° (dec); lit.(12) m.p. 175–176°.

PREPARATION OF *p-n*-BUTOXYPHENYL ACETYLENEDICARBOXYLATE

Acetylenedicarboxylic acid is not soluble in benzene, but was found to dissolve in an excess of the phenols and alcohols used in the esterfications. Hence, only enough benzene is added to azeotrope off the water formed during the reaction.

A mixture of *p-n*-butoxyphenol (6.64 g, 0.04 mole), acetylenedicarboxylic acid (1.14 g, 0.01 mole), and 5 ml of dry benzene were placed in a round bottom flask fitted with a Dean-Stark trap and reflux condenser. Conc. H_2SO_4 (0.5 ml) was added and the reactants refluxed for 14 hr, during which time the theoretical amount of water was collected. The reaction mixture was cooled and 50 ml of ether added. The ether solution was washed twice with 25 ml portion of satd NaCl solution, then with two 25 ml portions of 10% $NaHCO_3$ solution, and one 25 ml portion of ice-cold water. The solution was dried (Na_2SO_4), filtered, and the ether evaporated to yield a pale yellow solid. Two recrystallizations from ethanol afforded white crystals of *p*-*n*-butoxyphenyl acetylenedicarboxylate, 3.0 g, 73% yield, K 92 N 99.5 I.(13)

Anal. Calc. for $C_{24}H_{26}O_6$: C, 70.23; H, 6.38; Found: C, 70.20; H, 6.35.

Acknowledgement

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