Table V. Product Compositions for the Decomposition of Methyl Orthobenzoate in the Presence of Aqueous Solutions of Methoxyamine[a]

Methoxyamine (*M*)[b]	pH	Acetate (*M*)	f_e[c]
0.005	4.59	0	0.980
0.010	4.59		0.960
0.015	4.58		0.892
0.025	4.58		0.859
0.05	4.58		0.757
0.005	4.57	0.001	0.980
0.010	4.57		0.960
0.015	4.58		0.933
0.025	4.58		0.907
0.050	4.59		0.790
0.005	4.55	0.0025	1.0
0.010	4.56		0.933
0.015	4.56		0.927
0.025	4.57		0.866
0.050	4.58		0.778
0.005	4.50	0.010	1.0
0.010	4.53		0.947
0.015	4.53		0.927
0.025	4.55		0.878
0.050	4.57		0.764
0.005	4.50	0.10	0.994
0.010	4.51		0.960
0.015	4.51		0.932
0.025	4.51		0.906
0.050	4.53		0.798
0.005	4.55	0.25	1.0
0.010	4.55		0.994
0.015	4.55		0.954
0.025	4.56		0.927
0.05	4.57		0.811

[a] At several concentrations of acetate buffer at 25° and ionic strength 0.50 *M*. [b] Total amine. [c] Fraction of methyl orthobenzoate yielding methyl benzoate as determined by the hydroxylamine-ferric chloride method.

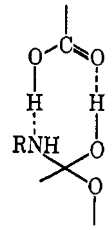
be made owing to the lack of rate constants for the reactions of amines with the dialkoxycarbonium ions.

While the transition from carboxylic ester to dialkoxycarbonium ion is sufficient to change the sensitivity of the reaction to amine basicity, the transitions from one to another of the dialkoxycarbonium ions studied here are insufficient to provide clear evidence for such an effect. The various values of β are all near 0.4. Multiple structure-reactivity relationship considerations indicate that values of β ought to be related to values of polar substituents constants, σ, for these reactions as follows[20]

$$\frac{\sigma_i}{\beta_i - \beta_0} = C$$

From the available data, one can conclude only that the value of *C* must be small.

Acetate, phosphate, and carbonate buffers, among others, have been observed to affect the partitioning of the tetrahedral intermediate formed during the hydrolysis of imidates.[21] It has been suggested that the influence of these buffers on the product distributions is the consequence of bifunctional catalysis of these buffers in which the neutral carbinolamine and buffer interact in the following way



Presumably, the addition of an amine to the dialkoxycarbonium ion generated during the ortho ester hydrolysis yields a similar tetrahedral intermediate with the exception that neither oxygen atom has a dissociable proton. Thus, the mechanism depicted above ought to be impossible in our system. The failure to observe any influence of an acetate buffer (Table V) on the product distribution during ortho ester aminolysis thus provides mild supporting evidence for this formulation.

(20) (a) E. H. Cordes and W. P. Jencks, *J. Amer. Chem. Soc.*, **84**, 4319 (1962); (b) W. P. Jencks, *Progr. Phys. Org. Chem.*, **2**, 63 (1964).

(21) (a) G. L. Schmir and B. A. Cunningham, *J. Amer. Chem. Soc.*, **87**, 5692 (1965); (b) B. A. Cunningham and G. L. Schmir, *ibid.*, **88**, 551 (1966); (c) R. K. Chaturvedi and G. L. Schmir, *ibid.*, **90**, 4413 (1968); (d) G. L. Schmir, *ibid.*, **90**, 3478 (1968).

The Role of *p*-Phenylene Groups in Nematic Liquid Crystals[1]

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Abstract: Many compounds forming nematic mesophases contain *p*-phenylene units. It is shown that these perform a dual function, providing rigid linear groupings and contributing to the polarizability of the molecule. These conclusions are based on a comparison with compounds where benzene rings are replaced by cyclohexane or bicyclo[2.2.2]octane.

Liquid crystals form a state of matter intermediate between crystalline solids and isotropic liquids;[3,4] such mesophases behave mechanically as liquids but differ from normal liquids in that the molecules in them are oriented, having lost two degrees of rotational free-

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(1) This work was supported by grants from the Air Force Office of Scientific Research (Grant No. GF-AFOSR-1050-67) and from the Robert A. Welch Foundation.

(2) Robert A. Welch Predoctoral Fellow, 1965.

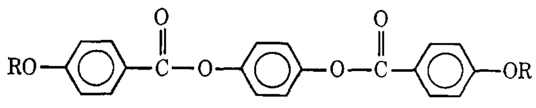
(3) G. W. Gray, "Molecular Structure and the Properties of Liquid Crystals," Academic Press, New York, N. Y., 1962.

(4) (a) G. H. Brown and W. G. Shaw, *Chem. Rev.*, **57**, 1049 (1957);

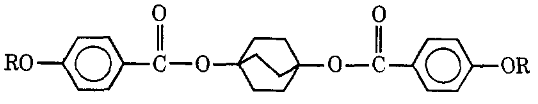
dom. Such orientation is favored by a rod-shaped geometry, and the large majority of compounds forming liquid crystals[5] are indeed rod shaped, having rigid linear structures enforced by the presence of 1,4-phenylene units. In the mesophase the molecules are oriented parallel to one another.

Much work has been reported[3,4] on the influence of molecular structure on the tendency to form mesophases, but most of this has been concerned with the role of the terminal groups in the molecule and with the effect of lateral substituents. The role of the benzene rings has remained uncertain. Obviously the 1,4-phenylene group provides an ideal unit for building up rigid linear molecules; it is, however, also possible, as Gray has suggested,[3] that an important feature may be the high polarizability of the π electrons in benzene, this leading to strong intermolecular van der Waals forces that should help to stabilize the mesophase.

We became interested in this problem in connection with studies of liquid crystals as solvents. The anisotropy of liquid crystals could have obvious applications to spectroscopy; for this purpose, however, it would clearly be preferable to have compounds free from unsaturated or aromatic groupings since these show strong light absorption in the ultraviolet region. We therefore decided to study the effect of replacing benzene rings in a typical liquid crystal, *p*-phenylene dianisate (I),[6] by two analogous saturated groups, *viz.* 1,4-bicyclo[2.2.2]octylene and *trans*-1,4-cyclohexylene. Here we report the preparation and properties of the four esters II–V containing bicyclooctane units, and a series of esters VI derived from *trans*-1,4-dihydroxycyclohexane. The esters Ia–g have also been reinvestigated for comparison.



I



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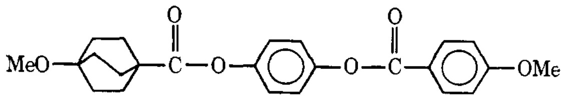
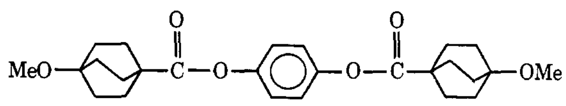
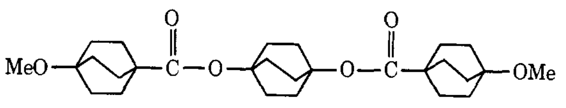


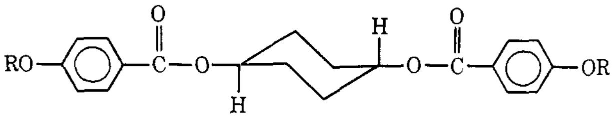
III



IV



V



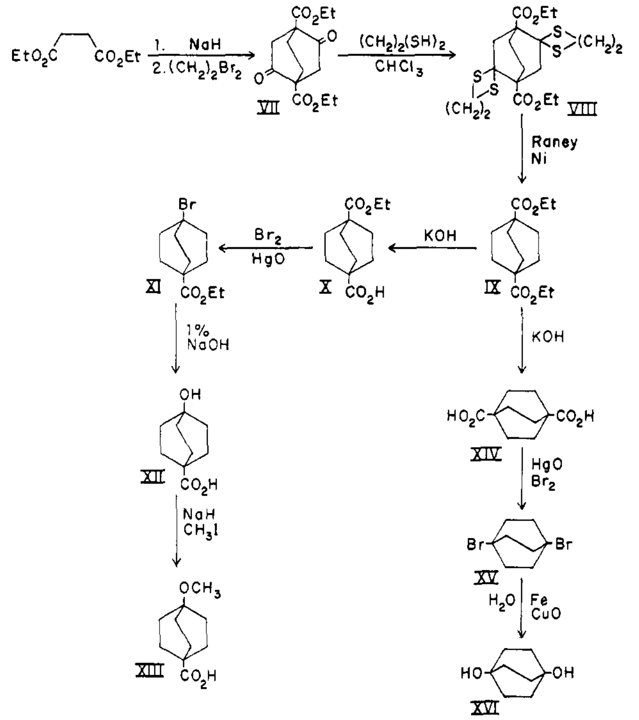
VI

a, R = CH_3
b, R = C_2H_5
c, R = n-C_3H_7
d, R = n-C_4H_9
e, R = n-C_6H_{13}
f, R = n-C_7H_{15}
g, R = n-C_8H_{17}

Experimental Section

Melting point determinations were made using a Thomas Hoover capillary melting point apparatus and a Leitz Ortholux II polarizing microscope fitted with a heating stage. All melting points are corrected. Elemental microanalyses were performed by Alfred Bernhardt Microanalytical Laboratories and Galbraith Laboratories. The syntheses of 4-methoxybicyclo[2.2.2]octane-1-carboxylic acid (XIII) and of 1,4-dihydroxybicyclo[2.2.2]octane (XVI) are outlined in the following chart.

Chart I



Diethyl succinate was converted to 1,4-dicarbethoxy-2,5-diketobicyclo[2.2.2]octane (VII) by the method of Holtz and Stock.[7] Ketone groups were reduced by conversion to thioketals followed by desulfurization with Raney nickel.[8] The resulting diester IX was then converted in three steps to the hydroxy acid XII by Roberts' method[8] and this to 4-methoxybicyclo[2.2.2]octane-1-carboxylic acid (XIII) by the method of Holtz and Stock.[7]

Bicyclo[2.2.2]octane-1,4-dicarboxylic Acid (XIV). A solution of potassium hydroxide (33 g) and IX (37 g) in ethanol (400 ml) was boiled under reflux for 12 hr, then cooled, diluted with water (500 ml), and acidified with dilute hydrochloric acid. The thick white precipitate was collected and washed with ethanol and ether giving XIV (26.0 g, 90%) as a white powder, mp >350° (lit.[9] mp 422° dec).

(b) V. A. Usol'tseva and I. G. Chistyakov, *Russ. Chem. Rev.*, **32**, 495 (1963); (c) D. Chapman, *Science*, **65**, 32 (1965); (d) A. Saupe, *Angew. Chem. Intern. Ed. Engl.*, **7**, 97 (1968).

(5) W. Kast in "Landolt-Bornstein," Vol. II, Part 2a, 6th ed, Springer-Verlag, Berlin, 1960, p 266.

(6) M. J. S. Dewar and J. P. Schroeder, *J. Org. Chem.*, **30**, 2296 (1965).

(7) H. D. Holtz and L. M. Stock, *J. Am. Chem. Soc.*, **86**, 5183 (1964).

(8) J. D. Roberts, W. T. Moreland, Jr., and W. Frazer, *ibid.*, **75**, 637 (1953).

(9) J. C. Kauer, R. E. Genson, and G. W. Parshall, *J. Org. Chem.*, **30**, 1431 (1965).

Table I. Physical Properties of 1,4-Bicyclo[2.2.2]octylene *p*-Alkoxybenzoates (II)

Compd	Yield, %	Nematic range, °C	Calcd, % C	Calcd, % H	Found, % C	Found, % H
IIa	13.2	185–269	70.23	6.38	70.26	6.52
IIb	29.0	171–273	71.21	6.90	70.89	6.88
IIc	43.5	161–236	72.08	7.35	72.15	7.41
IId	57.1	152–221	72.85	7.74	72.87	7.78
IIe	46.8	141–190.5	74.15	8.42	73.92	8.36
IIf	55.6	124–176	74.71	8.71	74.52	8.67
IIg	27.1	119–171	75.21	8.97	74.98	8.98

Table II. *trans*-1,4-Cyclohexylene *p*-Alkoxybenzoates (VI)

Compd	Crystallized from	Yield, %	Nematic range, °C	Calcd, % C	Calcd, % H	Found, % C	Found, % H
VIa	Dioxane	69.6	197[a]	68.74	6.29	68.63	6.11
VId	Acetone	60.0	129–157	71.77	7.74	71.73	7.64
VIe	EtOAc–hexane	49.3	122–136	73.25	8.45	73.12	8.36

[a] Mp, monotropic nematic mesophase, 195°.

1,4-Dibromobicyclo[2.2.2]octane (XV). A solution of bromine (13.2 g) in 1,2-dibromoethane (100 ml) was added slowly with vigorous stirring to a mixture of XIV (8.3 g), red mercuric oxide (12.9 g), and 1,2-dibromoethane (300 ml) at 75°. Stirring at 75° was continued for 12 hr and the mixture then filtered. The solid was washed with ether and benzene. The combined filtrates were washed with dilute sodium bisulfite, dilute sodium hydroxide, and water, and then dried (Na_2SO_4). Evaporation and sublimation at 120° (2 mm) gave XV (5 g, 44%) as white rhombic crystals, mp 248–249° (lit.[10] mp 256–258°). The nmr spectrum in chloroform-*d* showed a sharp singlet at τ 7.63.

Anal. Calcd for $C_8H_{12}Br_2$: C, 35.86; H, 4.51; Br, 59.63. Found: C, 35.59; H, 4.44; Br, 59.56.

1,4-Dihydroxybicyclo[2.2.2]octane (XVI).[11] A mixture of XV (9.3 g), cupric oxide (7.5 g), iron powder (3 g), and water (70 ml) was heated in an autoclave at 215° for 24 hr. The mixture was filtered, the filtrate evaporated, and the residue sublimed at 130° (1 mm), yielding XVI (3.1 g, 65%) as white crystals, mp 281–282° (lit.[11] mp 282–283°).

Anal. Calcd for $C_8H_{14}O_2$: C, 67.57; H, 9.92. Found: C, 67.75; H, 9.96.

Additional diol was obtained from Dr. J. C. Kauer at E. I. du Pont de Nemours, Inc.

***p*-Phenylene Di-4-methoxybicyclo[2.2.2]octane-1-carboxylate (IV).** A mixture of thionyl chloride (100 ml) and XIII (6.0 g) was heated under reflux for 2 hr and then distilled. The acid chloride (5.66 g, 85%) was collected at 94–96° (0.7 mm). A solution of hydroquinone (1.0 g) in dry pyridine was added to one of the acid chloride (5.66 g) in dry pyridine (20 ml). After stirring for 18 hr at room temperature, water (100 ml) was added, and the white precipitate washed with sodium bicarbonate solution and recrystallized three times from acetone, yielding XVII (0.5 g, 13%) as white needles, mp 208–209°.

Anal. Calcd for $C_{26}H_{34}O_6$: C, 70.56; H, 7.74. Found: C, 70.36; H, 7.65.

1,4-Bicyclo[2.2.2]octylene Di-4-methoxybicyclo[2.2.2]octane-1-carboxylate (V). A solution of XVI (0.57 g) in dry pyridine (20 ml) was added over 30 min to a refluxing solution of 4-methoxybicyclo-[2.2.2]octyl-1-carbonyl chloride (3.5 g) in dry benzene (20 ml) and heated continued for 24 hr. V was isolated by addition of water, extraction with chloroform, and washing with sodium bicarbonate solution. It crystallized from aqueous acetone in white needles (1.2 g, 63%), mp 294–295°.

Anal. Calcd for $C_{28}H_{42}O_6$: C, 70.86; H, 8.92. Found: C, 70.72; H, 9.06.

***p*-Hydroxyphenyl Anisate.** A solution of *p*-anisoyl chloride (34.0 g) in dry pyridine (100 ml) was added slowly (3 hr) to one of hydroquinone (22.0 g) in dry pyridine (100 ml) and the mixture was stirred for 24 hr. Water was then added and the white precipitate (diester) filtered. The filtrate was acidified with dilute HCl and collected and crystallized first from aqueous ethanol and then from aqueous acetone, giving *p*-hydroxyphenyl anisate (10.2 g, 20.9%) as white needles, mp 150–152°.

Anal. Calcd for $C_{14}H_{12}O_4$: C, 68.85; H, 4.95. Found: C, 68.68; H, 4.96.

4-(4′-Methoxybenzoxy)phenyl 4-Methoxybicyclo[2.2.2]octane-1-carboxylate (III). A solution of *p*-hydroxyphenyl anisate (0.9 g) in dry pyridine (25 ml) was added slowly to a refluxing solution of the acid chloride of XIII (1.5 g) in dry benzene (25 ml) and heating continued for 18 hr. III was isolated by addition of water and extraction with chloroform; after washing with sodium bicarbonate solution, it crystallized from acetone–water in small white flakes (0.96 g, 65%), mp 189°, nematic → liquid, 221°.

Table III. Transition Temperatures for *p*-Phenylene *p*-Alkoxybenzoates (I)

Compd	Transition temp, °C
Ia	solid $\xrightarrow{213}$ nematic[a] $\xrightarrow{297}$ isotropic
Ib	solid $\xrightarrow{226}$ nematic $\xrightarrow{287}$ isotropic
Ic	solid $\xrightarrow{175}$ nematic $\xrightarrow{249}$ isotropic
Id	solid $\xrightarrow{153}$ nematic[b] $\xrightarrow{241}$ isotropic
Ie	solid $\xrightarrow{121}$ nematic[b] $\xrightarrow{211}$ isotropic
If	solid $\xrightarrow{121}$ nematic[b] $\xrightarrow{198}$ isotropic
Ig	solid $\xrightarrow{118}$ nematic $\xrightarrow{192}$ isotropic

[a] Lit. values 222°, 300°.[6] [b] Dewar and Schroeder (personal communication) have confirmed these revised values (*cf.* ref 13a).

Anal. Calcd for $C_{24}H_{26}O_6$: C, 70.23; H, 6.38. Found: C, 70.54; H, 6.40.

***p*-Alkoxybenzoic Acids.** Ethyl *p*-alkoxybenzoates were prepared from ethyl *p*-hydroxybenzoate and the appropriate alkyl halides, and the esters saponified to the corresponding acids, by the method of Gray and Jones.[12] The properties of the acids agreed with those reported.

1,4-Bicyclo[2.2.2]octylene Di-*p*-alkoxybenzoates (IIa–g). A solution of 1,4-dihydroxybicyclo[2.2.2]octane (0.041 mole) and the appropriate *p*-alkoxybenzoyl chloride (0.041 mole) in dry pyridine (75 ml) was stirred for 24 hr at room temperature. The reaction mixture was then poured onto ice and acidified with dilute hydrochloric acid, and the ester isolated with chloroform, washed with sodium bicarbonate solution, treated with Norit, and recrystallized from acetone. The properties of the pure products are presented in Table I.

***trans*-1,4-Cyclohexylene Di-*p*-alkoxybenzoates (VI).** A solution of *trans*-1,4-dihydroxycyclohexane[13] (0.03 mole) and the appropriate *p*-alkoxybenzoyl chloride (0.07 mole) in dry pyridine (100 ml) was stirred at room temperature till reaction was complete, then poured onto ice (50 g) and acidified. The solid was collected, washed with water, stirred 6 hr with 5% sodium bicarbonate solution (250 ml), washed with ethanol, and recrystallized from a suitable solvent. The properties of the pure compounds are listed in Table II.

***p*-Phenylene Esters of *p*-Alkoxybenzoic Acid (Ia–g).** The esters were prepared by the method of Dewar and Schroeder.[6,14] Their transition points are recorded in Table III.

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(10) J. Kopecky and J. Smejkal, *Tetrahedron Letters*, **40**, 3889 (1967).

(11) J. C. Kauer, U. S. Patent 3,255,254 (1960); *Chem. Abstr.*, **60**, 14407*d* (1960).

(12) G. W. Gray and B. Jones, *J. Chem. Soc.*, 4179 (1953).

(13) L. N. Owen and P. A. Robins, *ibid.*, 320 (1949).

(14) M. J. S. Dewar and R. S. Goldberg, to be published.

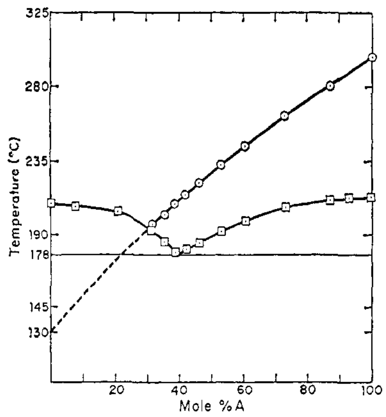

Figure 1. The phase diagram of the system of *p*-phenylene dianisate (A) and *p*-phenylene di-4-methoxybicyclo[2.2.2]octane-1-carboxylate.

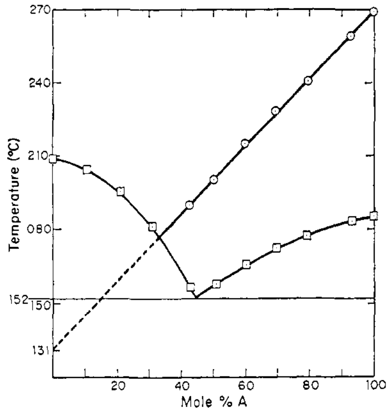

Figure 2. The phase diagram of the system of 1,4-bicyclo[2.2.2]-octylene dianisate (A) and *p*-phenylene di-4-methoxybicyclo[2.2.2]-octane-1-carboxylate.

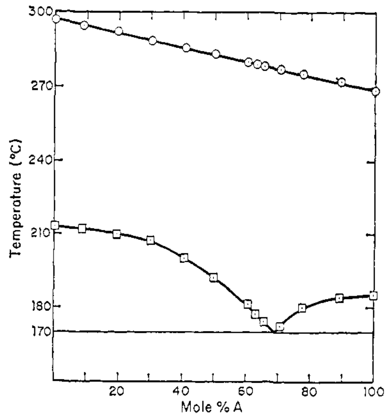

Figure 3. The phase diagram of the system of 1,4-bicyclo[2.2.2]-octylene dianisate (A) and *p*-phenylene dianisate.

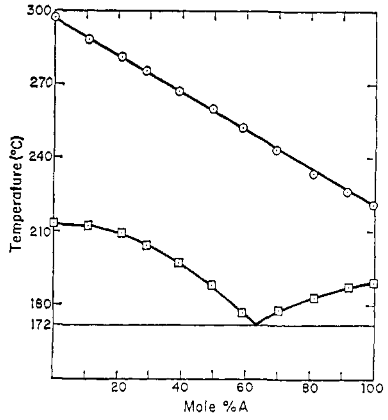

Figure 4. The phase diagram of the system of 4-(4′-methoxybenzoxy)phenyl 4-methoxybicyclo[2.2.2]octane-1-carboxylate (A) and *p*-phenylene dianisate.

Phase Diagrams. Mixtures of the two components in known proportions were prepared by fusion and rapid cooling. The transition temperatures were measured both with the polarizing microscope and with the capillary melting point apparatus. The transitions reported are the temperatures in which solid or mesophase had completely disappeared. In the phase diagrams ⊡ denotes the solid to nematic transition and ⊙ denotes the nematic to isotropic liquid transition.

Results and Discussion

If the benzene rings in I played only a geometrical role, one would expect the (nematic → liquid) transition temperatures to be little affected by replacement of benzene by bicyclooctane (BCO), for both groups are linear and have similar widths (benzene, 5.0 Å; BCO, 4.9 Å; measured with Courtauld atomic models), the only difference being that benzene is flatter (thickness 2.7 Å *vs.* 4.5 Å). This is clearly not the case. Thus replacement of the central benzene ring in Ia by BCO (IIa) leads to a decrease of 28° in the transition temperature, while replacement of a terminal ring (III) lowers the transition temperature by 76°. Similar decreases were also observed in the other pair of homologs of Ia and IIa; thus the transition temperature of IIf was less than that of If by 22°.

In the case of IV, the depression of the transition temperature was so great that no mesophase was observed. The transition temperature could, however, be estimated from binary phase diagrams by the method of Bogojawlensky and Winogradow.[15] Figures 1 and 2 show phase diagrams for the binary systems Ia–IV and IIa–IV. The visible portions of the nematic–liquid transition lines are only slightly curved, and the extrapolations indicated lead to very similar estimates (130°, 131°) for the transition temperature of IV. While this procedure is known to be unreliable, the hidden portions of transition lines often showing unexpected bends;[16] the extrapolation in this case is supported by the concordant results from two different systems, and by the fact that the corresponding transition lines in the analogous systems Ia–IIa (Figure 3) and Ia–III (Figure 4) are staight. The values obtained are less by 167° than that for Ia. This is approximately twice the difference between Ia and III, implying that the effects of the two BCO units in IV on the transition temperature are additive.

In the case of V, the transition temperature could neither be observed nor estimated, for V failed to give homogeneous melts with any of the analogs I–IV. Presumably the transition temperature of V must be even lower than that of IV; if additivity holds, as it apparently does in the case of III and IV, the transition temperature of V must be close to 100°.

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(15) A. Bogojawlensky and N. Winogradow, *Z. Phys. Chem.*, **64**, 228 (1908); R. Walter, *Ber. Deut. Chem. Ges.*, **58**, 2303 (1925).

(16) See, *e.g.*, J. S. Dave and M. J. S. Dewar, *J. Chem. Soc.*, 4305 (1955).

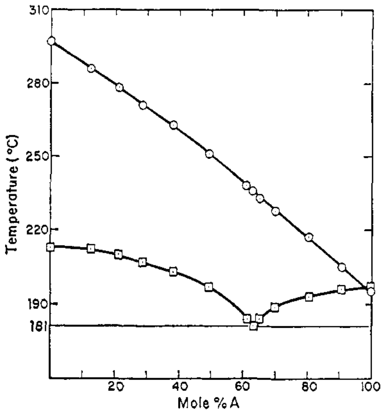

Figure 5. The phase diagram of the system of *trans*-1,4-cyclohexylene dianisate (A) and *p*-phenylene dianisate.

These results indicate very clearly that the benzene rings in I do play some role other than a purely geometrical one, presumably by enhancing the anisotropy of the intermolecular forces and so increasing the tendency to adopt an ordered arrangement of molecules. This special role of benzene must depend on its aromatic nature, *i.e.*, the presence of polarizable π electrons. An increase in polarizability should of course lead to increased intermolecular attraction by dispersion forces, and the π electrons could also act by resonance interactions with adjacent electromeric groups (*viz.* RO– and –COO– in I), leading to increased polarity and enhanced intermolecular dipole–dipole attractions. In either case the terminal rings in I would be expected to play a major part, for enhanced polarity and/or polarizability at the ends of a linear molecule should have a greater effect in making intermolecular forces anisotropic than would a corresponding change in the middle.

It is difficult to predict which of the two effects of the benzene ring should be the more important, but analogy seems to suggest that it is enhanced polarity that counts. Thus the boiling points of benzene (80°) and cyclohexane (81°) are almost identical, whereas that of anisole (154°) is much higher than that of methoxycyclohexane (133°).

While the aromaticity of the benzene rings in I is certainly an important factor in stabilization of the mesophase, the rigid linear geometry of the 1,4-phenylene group seems to play a still more important role. This is shown very clearly by a comparison of the esters II derived from 1,4-dihydroxybicyclooctane with the analogous esters (VI) derived from *trans*-1,4-dihydroxycyclohexane. The bonds to the central ring in VI must be essentially collinear on an average, given that the diequatorial chair conformation must be very strongly favored; however, the chair conformation of cyclohexane is much less rigid than BCO, so a given ester VI is more flexible than its analog II. The decrease in rigidity leads to a dramatic decrease in the nematic → liquid transition temperature. Indeed, in VIa the transition is observed only as a monotropic transition at 195°, below the melting point (197°), and lower by no less than 75° than the transition temperature for IIa. The difference between IIa and VIa is thus about three times the difference between IIa and Ia, implying that a rigid linear geometry is more essential to mesophase formation than the presence of aromatic groups. Similar differences are observed between the other sets of homologs; thus the difference between IId and VId (64°) is about three times that (20°) between Id and IId, and the difference between IIe and VIe (55°) is about three times that (20°) between Ie and IIe. Incidentally the transition temperature of VIa was confirmed by a study of the phase diagram for mixtures of Ia and VIa (Figure 5); the nematic → liquid transition line extrapolates to the monotropic transition observed in supercooled VIa.

Regarding the original purpose of this investigation, *i.e.*, the synthesis of liquid crystals transparent in the ultraviolet region, our results, while not immediately successful, seem to provide a good lead. It is clearly essential to have a rigid linear geometry, and for this the BCO unit, or perhaps some aza analog of it, seems by far the most hopeful choice. It will, however, be necessary to compensate in some way for the loss of terminal polarity when benzene rings in a typical liquid crystal are replaced by saturated groups. Up till now the commonest terminal groups in liquid crystals have been alkoxy; these apparently are not sufficiently polar in the case of saturated systems. It is interesting to note that the only all-saturated liquid crystals at present known are certain cholesterol derivatives in which the terminal groups are also weakly polar, and these mesophases are again relatively unstable.

One possible application of the esters described here may be to glpc. It has been shown[17] that liquid crystals form excellent substrates for the separation of position isomers, and the esters I were developed for this purpose; our analogs II may not only be superior in certain cases, due to the presence of an aliphatic central section, but mixtures of them with I may also be of value in view of the greater length of the mesophase. Thus the nematic phase for a eutectic mixture of Ia and IIa exists over a range of 110°, whereas the ranges for the pure components are 84° in each case.

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