

1437, 2174, 2951, and 3031  $\text{cm}^{-1}$ . The values 1437 and 3031  $\text{cm}^{-1}$  were used twice, for a total of 14 wavenumbers. The first three values in this list (below 600  $\text{cm}^{-1}$ ) were taken from Crowder (2), and the remaining values were taken from Moritz (6). The methyl thiocyanate molecule has seven atoms and therefore has 15 fundamental vibrational frequencies. Vapor state infrared frequencies are available for all 15 except for the methyl torsion, for which no experimental value is available, and the symmetric C—S—C stretch, for which the liquid state value is available. However, the methyl torsional frequency is not needed for calculation of the thermodynamic functions because the barrier to internal rotation has been determined from the microwave spectrum. Also, it is unlikely that the vapor state frequency for the C—S—C stretch would differ enough

from the liquid state value of 674  $\text{cm}^{-1}$  to affect the calculated thermodynamic properties appreciably, especially at the lower temperatures.

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## Condensation of Aromatic and Heterocyclic Aldehydes with Benzenediacetonitriles

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**A number of benzylidene-*p*-benzenediacetonitriles were prepared by base-catalyzed condensation of aromatic aldehydes with *p*-benzenediacetonitrile. Four products, substituted in the 4,4'-positions of the benzylidene groups, formed liquid crystals (mesomorphism) on melting. All were high melting solids. *m*-Substitution on the benzylidene groups lowered melting points and increased solubilities. Benzylidene-*m*-benzenediacetonitriles were lower melting and more soluble than the corresponding *p*-substituted compounds. The thermal stability of distyrylbenzene was lower than for the diphenyl ether fluids. A difunctional derivative was converted to a polymer.**

**A** STUDY of the properties of high melting and relatively heat stable materials led to an investigation of the condensation of aldehydes with aromatic acetonitriles. Of particular interest, because of relatively high molecular weight, were the distyrylbenzenes derived from the reaction of aromatic aldehydes with benzenediacetonitriles (Table I). The authors anticipated that potentially useful functional variants of  $\alpha,\alpha'$ -dibenzylidene-*p*-benzenediacetonitrile should be readily obtainable at moderate cost and that this structural system should have good thermal stability. For products with a given functionality, melting points and solubilities should be controlled by variation from the symmetrical *p*-benzenediacetonitriles to the less symmetrical *m*- and *o*-structures.

Several products related to those made in this study have been described previously. These are: the distyrylbenzene from *o*-benzenediacetonitrile and *o*-nitrobenzaldehyde (16) and the distyrylbenzenes from reaction of *p*-benzenediacetonitrile with *o*-chloro-, *p*-chloro-, 3,4-dichloro-, and 4-methoxybenzaldehydes (5). Also, a polymer has been prepared (12) by the condensation of terephthalaldehyde and *p*-benzenediacetonitrile, which on heating to 550°C. lost less than 30% of its weight and formed a stable polymeric residue. Utility of this polymer appears to be limited by its insolubility and infusibility.

There is little doubt that the condensation products of aromatic aldehydes with *m*- and *p*-benzenediacetonitrile obtained in this study are of the trans, trans configuration with respect to the stilbene grouping. The trans and cis

forms of  $\alpha$ -phenylcinnamionitrile were prepared (15), and the nitrile group of the isomer in which the phenyl substituents are trans was almost completely resistant to acid hydrolysis, whereas the cis form was readily hydrolyzed. Further, a number of cases (4, 11) have shown that the base-catalyzed condensation of aromatic aldehydes with phenylacetonitrile leads to trans products. Since the present materials were prepared by base-catalyzed condensations and since they were very resistant to acid hydrolysis, the trans structures seem assured.

The several  $\alpha,\alpha'$ -dibenzylidene-*p*-benzenediacetonitriles are high melting crystalline solids with limited solubilities in most common organic solvents. In the corresponding *m*-benzenediacetonitriles, the melting points are decreased 65° to 125°C., and the solubilities are increased greatly. The ease of preparation is reduced owing to the difficulties in isolation and owing to the fact that the driving force of having the product precipitate out, as in the case of the para compounds, is absent. A drop in melting point of 122°C. is shown between  $\alpha,\alpha'$ -dibenzylidene-*p*-benzenediacetonitrile (I), m.p. 255–6°C. and the *m*-isomer (II), m.p. 133–4°C. A striking difference in solubility is observed; in ethyl acetate at 25°C. the *p*-isomer is soluble to the extent of 0.06 gram per 100 ml., while the *m*-isomer is soluble to the extent of 2.3 grams per 100 ml. Similar increases in solubility were noted qualitatively for other solvents. Functionally varied *m*-benzenediacetonitriles showed similar changes in properties compared with the corresponding para compounds.

Table I. Formulas of Compounds and Numerical Designations

Number	R <sub>1</sub>	R <sub>2</sub>	Central Ring Substitution
I	H	H	<i>p</i>
II	H	H	<i>m</i>
III	OH	H	<i>p</i>
IV	H	OH	<i>p</i>
V	OH	H	<i>m</i>
VI	OH	OCH <sub>3</sub>	<i>p</i>
VII	OH	OCH <sub>2</sub> CH <sub>3</sub>	<i>p</i>
VIII	C <sub>2</sub> H <sub>5</sub> CO <sub>2</sub> —	H	<i>p</i>
IX	C <sub>4</sub> H <sub>7</sub> CO <sub>2</sub> —	H	<i>p</i>
X	Polycarbonate of III		
XI	CH <sub>3</sub> CO <sub>2</sub> —	OCH <sub>3</sub>	<i>p</i>
XII	CH <sub>3</sub> CO <sub>2</sub> —	OCH <sub>2</sub> CH <sub>3</sub>	<i>p</i>
XIII	HOCH <sub>2</sub> CH <sub>2</sub> O—	H	<i>p</i>
XIV	HOCH <sub>2</sub> CH <sub>2</sub> O—	H	<i>m</i>
XV		H	<i>p</i>
XVI			
XVII			

Of primary concern to the authors were hydroxy-substituted benzenediacylonitriles for use in the preparation of condensation polymers.  $\alpha, \alpha'$ -Bis-(*p*-hydroxybenzylidene)-*p*-benzenediacylonitrile (III) was a high melting (ca. 385°C.) yellow solid soluble in warm aqueous alkali and in dimethylformamide (DMF), slightly soluble in hot tetrahydrofuran (THF), and insoluble in the other common solvents tried.  $\alpha, \alpha'$ -Bis-(*m*-hydroxybenzylidene)-*p*-benzenediacylonitrile (IV) melted at 297–8°C. and was soluble in aqueous alkali and DMF but less soluble in THF.  $\alpha, \alpha'$ -Bis-(*p*-hydroxybenzylidene)-*m*-benzenediacylonitrile (V) melted at 288–90°C. and was soluble in acetone, DMF, THF, and pyridine. Thus, the solubilities of these three structures increased markedly in the order listed indicating less reduction of symmetry in going from *p*- to *m*-substitution on the benzylidene moiety than in changing from *p*- to *m*-substitution on the benzenediacylonitrile nucleus. Since  $\alpha, \alpha'$ -bis-(*p*-hydroxybenzylidene)-*p*-benzenediacylonitrile (III) was inconveniently high melting and insoluble, it was converted to the propionate (VIII) and butyrate (IX) by esterification with the corresponding anhydrides in the presence of pyridine. A polycarbonate (X) was prepared by an ester exchange reaction between  $\alpha, \alpha'$ -bis-(*p*-butyroyloxybenzylidene)-*p*-benzenediacylonitrile (IX) and diphenyl carbonate in hot diphenyl ether, phenyl butyrate being removed by distillation. The resin, which was insoluble and high melting (with decomposition), was characterized by its infrared spectrum and by analysis. No estimate of molecular weight was obtained.

To provide materials for the preparation of polyesters with high softening points as well as high thermal stability,  $\alpha, \alpha'$ -bis-(*p*-2-hydroxyethoxybenzylidene) derivatives of *p*- and *m*-benzenediacylonitrile (XIII and XIV) were made.

To provide an intermediate for making epoxy resins with high softening point and good thermal stability,  $\alpha, \alpha'$ -bis-[*p*-(2,3-epoxypropoxy)benzylidene]-*p*-benzenediacylonitrile (XV) was made. The product undoubtedly is a mixture of meso- and *dl*-forms with respect to the asymmetric epoxypropoxy groups. It showed a broad melting range and progressive decrease in solubility on recrystallization, as would be expected for such a mixture.

$\alpha, \alpha'$ -Di-(2-thenylidene)-*p*-benzenediacylonitrile (XVI) was prepared as a thermally stable antioxidant. Evaluation as an antioxidant in polyphenylether (14) high temperature fluids indicated that its solubility was limited, that it possessed some antioxidant activity as shown by reduction of viscosity increase, and that its heat stability was not quite as high as required as shown by a black deposit on metals suspended in the fluid.

A study was made to determine the thermal stability of *p*-distyrylbenzene (XVII) (6, 9), which is the generic backbone of the products of interest in this paper. The rate of thermal decomposition of *p*-distyrylbenzene was determined at 325° and at 400°C. by measuring the pressure increase in a closed glass cell using a nitrogen atmosphere. The sample weighed 0.5 gram, and the cell gas volume was 6.8 ml. At 325°C., the pressure increase was equivalent to 0.27 mmole of gas per minute per kg. of sample; at 400°C., 3.27 mmoles of gas per minute per kg. By extrapolating these data, assuming a linear relationship between the reciprocal of absolute temperature and the logarithm of the gas evolution rate, a decomposition point (2) of 270°C. (518°F.) was estimated. The product of the decomposition was a black insoluble resin and an acetone-soluble oil which, from its infrared spectrum, appeared to be mostly *trans*-stilbene contaminated with other unidentified materials. *p*-Distyrylbenzene does not compare favorably in thermal stability with the polyphenyl ethers, which have decomposition points in the range of 800°F. (2, 13, 14).

Several of the products studied displayed mesomorphism (liquid crystallinity) (3, 7, 10). Only the nematic phase was found. For example,  $\alpha, \alpha'$ -bis(*p*-2-hydroxyethoxybenzylidene)-*p*-benzenediacylonitrile (XIII) was observed to melt at 237° to 241°C. to a fluid, turbid melt which became clear at 289° to 290°C. Mesomorphism, which is exhibited by certain compounds with relatively linear, rigid molecules bearing polar groups, is interpreted as a state of matter between crystalline solids and isotropic liquids. On melting such a compound, the linear molecules attain freedom of movement in certain directions but are constrained to be parallel because of mutually attractive forces. The turbidity appears to be due to the presence of a large number of small domains, the parallel molecules in a given domain showing anisotropic optical properties. To the eye, an agglomeration of such domains, randomly oriented, appears turbid. Products showing the phenomenon of liquid crystallinity may have interesting and potentially useful applications since it may be possible to conduct normally liquid phase reactions, such as polymerizations (1), in the mesomorphic media where the molecules are held in an orientation much more restricted than is obtainable in isotropic liquids. Recently, the use of liquid crystals as the stationary phases in gas-liquid chromatography has been described (8).

## EXPERIMENTAL

$\alpha, \alpha'$ -Dibenzylidene-*p*-benzenediacylonitrile (I). A solution of benzaldehyde (53 grams) and *p*-benzenediacylonitrile (39 grams) in 95% ethanol (325 ml.) was held at 45°C., while 7 ml. of a 15% solution of sodium ethoxide in ethanol was added. A precipitate formed and was collected, washed with water and ethanol, and dried, weight 80.2 grams, m.p. 250–4°C. Two recrystallizations from acetonitrile raised the melting point to 255–6°C. Anal. Calcd. for

$C_{24}H_{16}N_2$ : C, 86.7; H, 4.8; N, 8.4. Found: C, 87.1; H, 4.9; N, 8.6.

When I was recrystallized from acetic acid, brilliant yellow crystals were obtained. When recrystallized from acetonitrile, the brilliant yellow form crystallized first, but as the temperature dropped, this form disappeared as pale yellow crystals grew. Both the brilliant yellow and pale yellow forms dissolved in acetone to give colorless solutions. When the pale yellow crystals were heated, they changed to brilliant yellow.

**$\alpha, \alpha'$ -Dibenzylidene - *m* - benzenediacetonitrile (II).** A solution of 3.1 grams of *m*-benzenediacetonitrile and 4.2 grams of benzaldehyde in 30 ml. of ethanol was treated with a quantity of a 6% solution of sodium ethoxide in ethanol sufficient to give an indication of a pH of 12 on moistened indicator paper. During the addition, an oil separated which was redissolved by adding an additional 30 ml. of ethanol and warming. By cooling and scratching the walls of the vessel, a solid separated weighing 6.0 grams, m.p. 95–7°C. Two recrystallizations from ethanol gave 2.0 grams of white crystalline material, m.p. 133–4°C. Anal. Calcd. for  $C_{24}H_{16}N_2$ : C, 86.7; H, 4.8; N, 8.4. Found: C, 87.0; H, 5.0; N, 8.0.

**Condensation of Phenolic Benzaldehydes with *p*-Benzenediacetonitrile.** A 0.5-mole sample of the appropriate aldehyde and 39 grams (0.25 mole) of *p*-benzenediacetonitrile were dissolved in a mixture of 500 ml. of 1-propanol and 30 ml. of acetic acid in a flask fitted with a heating mantle, a stirrer, and a reflux system with provision for passing the returning condensate through a bed of anhydrous calcium sulfate. The reaction mixture was blanketed with nitrogen, and 50 ml. of piperidine was added. Heating and stirring were begun. The formation of a solid began in a few hours. After 24 hours, the mixture was cooled, and the precipitate was collected and washed with 1-propanol, then methanol.

**$\alpha, \alpha'$  - Bis - (*p* - hydroxybenzylidene) - *p* - benzenediacetonitrile (III).** This compound was prepared from *p*-hydroxybenzaldehyde and *p*-benzenediacetonitrile by following the directions given above, except that a 25% excess of the aldehyde was used. The product was obtained in 95% yield, based upon nitrile. The material decomposed slowly above 300°C. An estimated melting point of 385°C. was obtained by plunging fresh samples in capillaries into a heating melting point bath. Anal. Calcd. for  $C_{24}H_{16}N_2O_2$ : C, 79.1; H, 4.4; N, 7.7. Found: C, 78.6; H, 4.4; N, 7.1.

**$\alpha, \alpha'$  - Bis - (*m* - hydroxybenzylidene) - *p* - benzenediacetonitrile (IV).** This compound was prepared from *m*-hydroxybenzaldehyde and *p*-benzenediacetonitrile by following the above directions. A 76% yield of crude material, m.p. 287° to 297°C. was obtained. Recrystallization from 2-methoxyethanol raised the melting point to 297° to 298°C. Anal. Calcd. for  $C_{24}H_{16}N_2O_2$ : C, 79.1; H, 4.4; N, 7.7. Found: C, 79.3; H, 4.4; N, 7.8.

**$\alpha, \alpha'$  - Bis - (*p* - hydroxybenzylidene) - *m* - benzenediacetonitrile (V).** In a manner similar to the condensation of phenolic aldehydes with *p*-benzenediacetonitrile, 7.6 grams of *p*-hydroxybenzaldehyde, 3.0 grams of *m*-benzenediacetonitrile, 50 ml. of 1-propanol, 3.2 ml. of acetic acid, and 5 ml. of piperidine were heated together for 24 hours. No precipitate had formed. Upon cooling and scratching the inside of the vessel, very slow crystallization began, and after 40 hours of intermittent stirring, the solid was collected, weight 6.2 grams, m.p. 284–8°C. Recrystallization from ethanol, then from 2-methoxyethanol gave 1.5 grams of product softening at 288°C. and melting 289.5–90°C. Anal. Calcd. for  $C_{24}H_{16}N_2O_2$ : C, 79.1; H, 4.4; N, 7.7. Found: C, 78.9; H, 4.4; N, 7.8.

**$\alpha, \alpha'$  - Bis - (4-hydroxy - 3- methoxybenzylidene) - *p* - benzenediacetonitrile (VI).** This compound was prepared from vanillin and *p*-benzenediacetonitrile following the above directions, except that a 20% excess of the aldehyde was

used. (Caution: the precipitate is voluminous and may cause "bumping".) An 86% yield of crude material, melting 235° to 242°C. was obtained. Recrystallization from acetonitrile gave needles which softened at 236°C. and melted 241–3°C. Anal. Calcd. for  $C_{26}H_{20}N_2O_4$ : C, 73.6; H, 4.8; N, 6.6. Found: C, 73.6; H, 4.8; N, 6.9.

A 0.5-gram sample of VI was dissolved by heating in 70 ml. of 1,1,2-trichloroethane. The solution was quickly cooled to room temperature and allowed to stand for 18 hours. Platelets separated and were collected, weight 0.3 gram. The melting behavior was observed using a microscope with polarizing filters and a Kofler hot stage apparatus. The crystals melted at 233–5°C., and while the temperature was held at 236°C., the sample crystallized as needles. These needles melted at 240–3°C. There was no evidence of gas evolution.

A 1.4-gram sample of VI was dissolved in 70 ml. of 1,1,2-trichloroethane by heating and placed in a 60°C. oven for 18 hours. Needles crystallized and were collected, weight 1.1 grams. When this sample was heated a few needles melted at 235°C., but the bulk of the sample was unchanged until it melted at 240–3°C. Thus VI is dimorphous.

**$\alpha, \alpha'$  - Bis - (3-ethoxy - 4- hydroxybenzylidene) - *p* - benzenediacetonitrile (VII).** This compound was prepared from 3-ethoxy-4-hydroxybenzaldehyde and *p*-benzenediacetonitrile by following the directions given above. An 80% yield of material melting 216–21°C. was obtained. Two recrystallizations from acetonitrile gave needles which on drying to equilibrium weight (160°C. in vacuum over  $P_2O_5$  for 3 hours) lost 8.4% of their weight. Loss of 1 mole of acetonitrile per mole of VII should produce a weight loss of 8.1%. The dried product melted 221–2°C. Anal. Calcd. for  $C_{25}H_{24}O_4N_2$ : C, 74.3; H, 5.4; N, 6.2. Found: C, 74.3; H, 5.5; N, 6.0.

**$\alpha, \alpha'$  - Bis - (*p* - propionyloxybenzylidene) - *p* - benzenediacetonitrile (VIII).** A stirred suspension of 124 grams of  $\alpha, \alpha'$ -bis-(*p*-hydroxybenzylidene)-*p*-benzenediacetonitrile (III) in a mixture of 500 ml. of propionic anhydride and 5 ml. of pyridine was heated while distillate was removed (100 ml. per hour) through a fractionating column and replaced with 5% pyridine in propionic anhydride. After 1.25 hours, a clear solution was obtained. Heating was continued an additional 1.25 hours, and then the mixture was allowed to cool slowly. The yellow-orange needles thus obtained were washed with acetic anhydride, acetic acid, then methanol. After drying they weighed 145 grams, m.p. 232–3.5°C. Recrystallization from chloroform or 1,1,2-trichloroethane gave crystals melting to the turbid nematic mesomorphic state at 232.5–3.5°C. and the clear isotropic liquid at 305–6°C. The nematic phase was confirmed using a hot stage microscope with polarizing filters. Anal. Calcd. for  $C_{30}H_{24}N_2O_4$ : C, 75.6; H, 5.1; N, 5.9. Found: C, 76.0; H, 5.4; N, 6.3.

**$\alpha, \alpha'$  - Bis - (*p* - butyroyloxybenzylidene) - *p* - benzenediacetonitrile (IX).** A 36.4-gram sample of  $\alpha, \alpha'$ -bis-(*p*-hydroxybenzylidene)-*p*-benzenediacetonitrile (III) was suspended in a mixture of 200 ml. of butyric anhydride and 2 ml. of pyridine and the mixture was heated to the boiling point for 1 hour. Cooling of the resulting solution caused the deposition of crystals which were collected and washed with acetic acid, methanol, and ether, weight 41.2 grams, m.p. 212–14°C. to a turbid melt which cleared at 290–2°C. Recrystallization of a sample from 1,1,2-trichloroethane yielded crystals melting to the turbid nematic mesophase at 214–14.5°C. and the clear isotropic liquid at 291–2°C. Anal. Calcd. for  $C_{32}H_{28}N_2O_4$ : C, 76.2; H, 5.6; N, 5.6. Found: C, 76.2; H, 5.5; N, 5.4.

**Poly- $\alpha, \alpha'$  - bis - (*p* - hydroxybenzylidene) - *p* - benzenediacetonitrile Carbonate (X).** A mixture of 10.1 grams of  $\alpha, \alpha'$ -bis - (*p* - butyroyloxybenzylidene) - *p* - benzenediacetonitrile (IX), 4.3 grams of diphenylcarbonate, 0.1 gram of sodium acetate, and 150 ml. of diphenyl ether was stirred

and heated in an apparatus equipped with an efficient fractionating column. As the temperature of the vapor at the top of the fractionating column dropped, indicating the concentrating of phenyl butyrate, distillate was removed, and fresh diphenyl ether was added to maintain the reaction volume. After 34 hours' heating, no depression of head temperature could be noted when operating at total reflux, and the precipitated solid was filtered from the hot reaction mixture and washed with ether. The yellow powder thus obtained weighed 7.3 grams and gave an infrared spectrum indicating the absence of the butyrate carbonyl group. The material was insoluble in boiling 1,1,2-trichloroethane, 2-methoxyethanol, and diphenyl ether. Only a portion of the solid was soluble in dimethylformamide. Anal. Calcd. for  $C_{25}H_{14}N_2O_3$ : C, 76.9; H, 3.6; N, 7.2. Found: C, 75.3; H, 3.7; N, 6.9.

**$\alpha,\alpha'$ -Bis-(4-acetoxy-3-methoxybenzylidene)-*p*-benzenediacetonitrile (XI).** A suspension of 5.0 grams of  $\alpha,\alpha'$ -bis-(4-hydroxy-3-methoxybenzylidene)-*p*-benzenediacetonitrile (VI) in 50 ml. of acetic anhydride was heated to 100°C., and 25 ml. of pyridine was added. The suspended solid began to dissolve, but after 2 minutes a precipitate suddenly formed and thickened the mixture. After 15 minutes, this solid was collected. Purification was begun by heating with 300 ml. of acetic acid. After cooling, the solid was removed and dried, weight 5.5 grams, m.p. 268–70°C. Recrystallization from 1,1,2-trichloroethane gave short yellow needles, m.p. 269–70°C. Anal. Calcd. for  $C_{30}H_{24}N_2O_6$ : C, 70.8; H, 4.8; N, 5.5. Found: C, 70.7; H, 4.7; N, 5.4.

**$\alpha,\alpha'$ -Bis-(4-acetoxy-3-ethoxybenzylidene)-*p*-benzenediacetonitrile (XII).** A 5-gram sample of  $\alpha,\alpha'$ -bis-(3-ethoxy-4-hydroxybenzylidene)-*p*-benzenediacetonitrile (VII) was dissolved in 50 ml. of hot acetic anhydride, and 0.5 ml. of pyridine was added to the solution. The solution was reheated to dissolve the precipitate, which began to form, then allowed to cool slowly. Crystals which formed were collected, weight 4.8 grams, m.p. 228–30°C. They were recrystallized from acetic anhydride, washed with diethyl ether, and dried, m.p. 228–9°C. Anal. Calcd. for  $C_{12}H_{22}N_2O_6$ : C, 71.6; H, 5.3; N, 5.2. Found: C, 72.1; H, 5.1; N, 5.3.

Microscopic examination showed that this product consisted of a mixture of rhombic crystals and of large poorly formed needles. After several minutes' exposure to ultraviolet light, the rhombic crystals showed brilliant blue-white fluorescence, while the needles showed only modest yellow fluorescence. On heating to 190°C., then cooling, all crystals fluoresced with the blue-white light. When heated slowly through the melting range using the hot stage microscope, both forms melted at 228–9°C. The melt then crystallized and remelted 230–1°C. Thus, XII is polymorphic.

**$\alpha,\alpha'$ -Bis-(*p*-hydroxyethoxybenzylidene)-*p*-benzenediacetonitrile (XIII).** *p*-2-Hydroxyethoxybenzaldehyde (58 grams) and *p*-benzenediacetonitrile (25.9 grams) were dissolved by warming in 300 ml. of 95% ethanol. This solution was stirred and held at 40°C. while a 3% solution of sodium ethoxide in ethanol was added cautiously until turbidity appeared in the reaction mixture. Addition of alkali was then stopped, and the reaction mixture was allowed to stand with occasional stirring for 2 hours. The thick mass then was filtered and the precipitate was washed with 600 ml. of ethanol, then 500 ml. of water. After drying, this material weighed 67.3 grams, m.p. 237–40°C. Recrystallization was accomplished by extracting this product with tetrahydrofuran in a Soxhlet extractor, and removing well-formed crystals from the distilling flask as necessary. Melting point behavior was studied, first with a capillary tube and oil bath. The sample melted to the turbid, fluid nematic mesophase at 239–41°C. The temperature was raised to 243°C., then cooled slowly. At 241°C. the sample cleared and finally crystallized at 238–7°C. Upon

slow reheating, the sample melted to a clear liquid at 241°C., then assumed the typical cloudy appearance a fraction of a degree higher. The transition from the nematic mesophase to the isotropic liquid occurred at 289–90°C. Examination of the melting behavior using the hot stage microscope confirmed the nematic mesophase but showed nothing analogous to the clear liquid condition below 241°C. observed with the capillary melting system. Anal. Calcd. for  $C_{28}H_{24}N_2O_4$ : C, 74.3; H, 5.3; N, 6.2. Found: C, 73.9; H, 5.2; N, 6.0.

**$\alpha,\alpha'$ -Bis-(*p*-2-hydroxyethoxybenzylidene)-*m*-benzenediacetonitrile (XIV).** To a solution of 7.8 grams of *m*-benzenediacetonitrile and 16.6 grams of *p*-2-hydroxyethoxybenzaldehyde in 50 ml. of 90% ethanol warmed to 40°C. was added 20 ml. of 3% sodium ethoxide in ethanol. Upon standing, the mixture gelled. The solid was collected with difficulty and washed with methanol, then recrystallized from methanol. The mixture of yellow and white solids thus obtained weighed 14.6 grams and melted at 176–7°C. Two recrystallizations from 1,1,2-trichloroethane gave 12.8 grams of yellow solid, m.p. 176–7°C. Anal. Calcd. for  $C_{28}H_{24}N_2O_4$ : C, 74.3; H, 5.4; N, 6.2. Found: C, 74.2; H, 5.4; N, 6.1.

***p*-(2,3-Epoxypropoxy)-benzaldehyde.** A mixture of 122 grams of *p*-hydroxybenzaldehyde, 277 grams of epichlorohydrin, and 50 ml. of benzene was heated in a flask equipped with a stirrer, dropping funnel, thermometer, and Dean-Stark trap. A 234-ml. aqueous solution containing 1.1 moles of potassium hydroxide was added from the dropping funnel to this boiling reaction mixture over a 4-hour period, while water was removed. At the completion of this time the excess epichlorohydrin was removed under vacuum. The residue was diluted with chloroform and the potassium chloride was removed by filtration. Washing of the chloroform solution, with dilute aqueous alkali, produced an emulsion which was broken by the addition of carbon tetrachloride. After the removal of all alkalinity by water washing, the solvents were evaporated and the residue was vacuum distilled. The fraction boiling from 110° to 137°C. at 0.15 mm. was collected (145 grams) and redistilled. A 17-gram forerun was removed; the main fraction (123 grams) distilled from 110° to 126°C. at 0.06 to 0.18 mm. and crystallized on cooling, m.p. 35–7°C. Anal. Calcd. for  $C_{10}H_{10}O_3$ : C, 67.4; H, 5.6. Found: C, 67.4; H, 5.8.

**$\alpha,\alpha'$ -Bis-[(*p*-(2,3-epoxypropoxy)-benzylidene)-*p*-benzenediacetonitrile (XV).** *p*-(2,3-Epoxypropoxy)-benzaldehyde (59.4 grams) and *p*-benzenediacetonitrile (26.0 grams) were dissolved in 500 ml. of 95% ethanol at 60°C. Then, 4 ml. of a 6% ethanolic solution of sodium ethoxide was added dropwise. In a few minutes, precipitation began. At ½ hour, an additional 3 ml. of the sodium ethoxide solution was added. At 2 hours, the precipitate was collected, washed with ethanol, water, and methanol, then dried. The crude product weighed 79.5 grams, m.p. 227° to 240°C. Bulk recrystallization was accomplished by extracting the crude product with 1,1,2-trichloroethane using a Soxhlet extractor, weight 65.7 grams, m.p. 238–40°C., clearing 254–8°C. For analyzing, the sample was recrystallized 3 times from 1,1,2-trichloroethane; solubility in the hot solvent decreased from 3 to 1.2%. This sample softened at 239°C., melted to the turbid nematic mesophase at 242–3°C., and to the clear isotropic liquid at 259–61°C. Anal. Calcd. for  $C_{30}H_{24}N_2O_4$ : C, 75.6; H, 5.1; N, 5.9. Found: C, 75.4; H, 5.1; N, 5.6.

**$\alpha,\alpha'$ -Di-(2-thenylidene)-*p*-benzenediacetonitrile (XVI).** An 11.2-gram sample of thiophene-2-carboxaldehyde and 7.8 grams of *p*-benzenediacetonitrile were dissolved in 65 ml. of warm 95% ethanol. One-half milliliter of a 15% solution of sodium ethoxide in ethanol was added to the reaction mixture. A precipitate formed rapidly which solidified the mixture, and more alcohol was added to allow stirring. After 30 minutes, the solid was collected, washed

thoroughly with ethanol, then water. After drying, the product weighed 16.5 grams and melted at about 265°C. Two recrystallizations from acetonitrile raised the melting point to 274–4.5°C. Anal. Calcd. for C<sub>20</sub>H<sub>12</sub>N<sub>2</sub>S<sub>2</sub>: C, 69.7; H, 3.5; N, 8.1; S, 18.6. Found: C, 69.7; H, 3.4; N, 8.0; S, 18.5.

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## Adsorption of Methane on Carbon at Temperatures to 121°C. and Pressures to 650 Atm.

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**Gas adsorption isotherms and isobars are presented for the methane-Spheron-6 system for six isotherms ranging from 37.8° to 121.1°C. Data were obtained utilizing a high pressure, constant temperature, volumetric apparatus at pressures up to 650 atm.**

CONDITIONS surrounding the production of large amounts of natural gas and the difficulties involved in separating the hydrocarbon components require continuing research in the area of gas adsorption at high temperatures and pressures. Gilmer and Kobayashi (4) have published data on adsorption of methane on silica at pressures up to 135 atm., while Frolich and White (3) report methane adsorption on carbon up to 140 atm. Both investigators report a Type I isotherm which agrees with other reports (1, 2, 5, 6) on carbon-methane adsorption.

This communication will report fundamental gas adsorption data at temperatures and pressures above the critical point of gas in the gas-solid system.

#### EXPERIMENTAL

**Materials.** Carbon black (Cabot Corp.), bearing the designation Spheron-6, served as the adsorbent for all isotherms. Density of the adsorbent was 1.8 grams per cc. Surface area of the solid was 123 sq. meters per gram, determined by the classical BET low temperature adsorption of nitrogen where monomolecular adsorption was assumed. The adsorbate was research grade methane having a stated purity of at least 99.65%. Helium was used to determine dead space volume.

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**Equipment and Methods.** The apparatus (Figure 1) was constructed of stainless steel. The volumetric system was composed of four thick-walled, constant volume cells. The adsorbent was enclosed in the high pressure cell, where

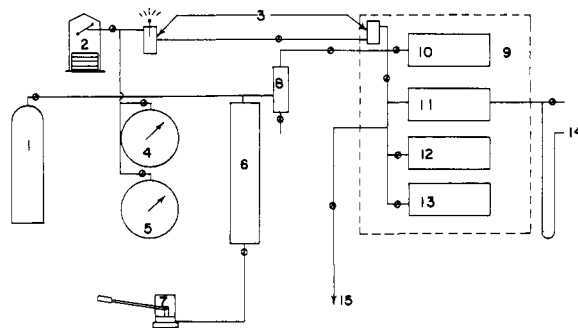


Figure 1. Flow diagram of hydraulic system

- |                         |                      |
|-------------------------|----------------------|
| 1. Gas cylinder         | 8. Trap              |
| 2. Dead weight gage     | 9. Air bath          |
| 3. Mercury level cell   | 10. H. p. cell       |
| 4. 15,000 P.s.i. gage   | 11. L. p. cell No. 1 |
| 5. 3,000 P.s.i. gage    | 12. L. p. cell No. 2 |
| 6. Pressure transmitter | 13. L. p. cell No. 3 |
| 7. Pressure pump        | 14. Manometer        |
|                         | 15. To vacuum system |