

terms of ring size): from Cu-O frequencies  $5 > 7 > 15 > 12 > 9 > 10 > 8 = 6$ ; from conductivities  $5 \gg 7 > 15 > 8 > 6 > 10 > 9 > 12$ . The two sequences are not identical but the odd-membered rings are generally more stable than the even-membered rings, excepting the C<sub>9</sub> ring.

Previous authors<sup>8,9</sup> have associated the ultraviolet absorption of metal chelates with the absorption by the ligand as perturbed by the metal ion. In some cases, there has been found a general correlation between  $\Delta\lambda_m$  and the stability of the respective metal chelates, where  $\Delta\lambda_m$  is the difference between  $\lambda_m$  of the chelate and chelating compound or enolate ion.<sup>9-12</sup> Consequently, it was hoped that the ultraviolet spectra would provide a measure of the relative stabilities of the chelates under study. Unfortunately, there are no significant differences in the  $\lambda_m$  values for these chelates in the ultraviolet region.

Absorption in the visible region by copper chelates is generally associated with d-d' excitation, and it has been shown<sup>13</sup> that one can expect  $\lambda_m$  to shift to the red with decreasing stability of the metal chelates. Such a correlation could not be tested here because the absorption bands in the visible region for the chelates 5-15 were too broad for quantitative assignments of  $\lambda_m$  values. Neither could deviations from Beer's law be used as a criterion of degree of dissociation in solution, *i.e.*, relative stability, because all of the chelates obey Beer's law within the concentration range that can be used for the absorption measurements.

From this study, the Cu-O bond infrared frequencies of the copper chelates of 2-acetylcyclanones indicate that their relative stabilities alternate with ring size, with the odd-membered rings being generally more stable than the even-membered rings.<sup>14</sup> This alternating effect can be added to several other physical properties of alicycles found to oscillate with ring size, such as (1) the enol contents of cyclanones,<sup>6</sup> (2)  $\lambda_m^{\text{H}_2\text{O}}$  in the ultraviolet region of the anions of nitrocyclanes,<sup>15</sup> (3) the nuclear magnetic resonance (nmr) chemical shifts for the vinyl protons in bromomethylenecyclanes,<sup>16</sup> (4) the half-wave potentials of bromocyclanes,<sup>17</sup> and (5) the carbonyl infrared frequencies of  $\alpha$ -nitrocyclanones.<sup>18</sup>

#### Experimental Section

**Preparation of Chelates.**—The 2-acetyl derivatives of eight cyclanones were prepared by BF<sub>3</sub>-catalyzed acetylations of the respective cyclanones following the method of Vogel.<sup>19</sup> The three smallest ketones were isolated: 2-acetylcyclopentanone, bp 65-68° (10<sup>-3</sup> mm) [lit.<sup>20</sup> bp 72-75° (8 mm)]; 2-acetyl-

cyclohexanone, bp 86-89° (5 mm) (lit.<sup>21</sup> bp 106-108° (14 mm)); 2-acetylcycloheptanone, bp 96-99° (10<sup>-3</sup> mm) [lit.<sup>22</sup> bp 107.5-110° (10 mm)]. The rest of the ketones were not isolated but converted directly into their copper chelates. All chelates were prepared by adding an excess of a saturated aqueous solution of copper acetate to an ether solution of a purified or crude ketone and the mixture was shaken for a few minutes. 2-Acetylcyclohexanone required the addition of a small volume of dilute ammonia to effect chelation. The precipitated chelates were filtered, washed with water, then with ether, dried in an oven at 90-100°, and recrystallized to constant melting point from tetrahydrofuran or ether. Their analyses are given in Table I.

**Infrared Spectral Measurements.**—Spectra for the chelates in the region 4000-200 cm<sup>-1</sup> were obtained using Perkin-Elmer Models 21 and 421 spectrophotometers. Nujol mulls were found to be suitable down to 650 cm<sup>-1</sup> using sodium chloride windows. The range where Nujol absorbs was examined by using hexafluorobutadiene solvent. Spectra below 700 cm<sup>-1</sup> were measured on the 421 grating instrument (to  $\pm 1$  cm<sup>-1</sup>) using Epolene C-3 film (Eastman Chemical Co.) and KBr windows. Essentially the same frequencies were obtained in the overlap region with Epolene C-3 and Nujol mulls but the intensity of the bands was much greater with the former.

**Ultraviolet-Visible Spectral Measurements.**—Ultraviolet-visible spectra of the chelates were measured with a Cary Model 14 recording spectrophotometer using matched quartz cells. The solutions were freshly prepared using tetrahydrofuran as a solvent in both regions.

**Conductivity Measurements.**—The conductivities were measured in 75% aqueous pyridine at 20° with a Wheatstone bridge assembly<sup>23</sup> and an oscilloscope for detecting zero current. The cell constant was determined using a standard KCl solution.

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### Molecular Order in the Nematic Mesophases of 4,4'-Di-*n*-hexyloxyazoxybenzene and Its Mixtures with 4,4'-Dimethoxyazoxybenzene

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The ordered, anisotropic nature of a mesomorphic liquid (liquid crystal)<sup>1,2</sup> appears to have an orienting effect upon solute molecules dissolved in it. Linear, rod-shaped solute molecules have been shown to have a less disruptive effect on nematic mesophases than bulky, nonlinear molecules, presumably because the former adapt more readily to the parallel molecular arrangement in the liquid crystal, being oriented with their long axes parallel to those of the solvent molecules.<sup>3</sup>

Such behavior suggested that mesomorphic solvents might display selectivity toward solutes on the basis

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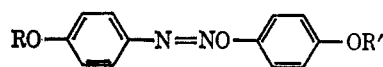
TABLE I  
RELATIVE RETENTION TIME OF *p*-XYLENE (*m*-XYLENE = 1.00) IN COLUMNS EMPLOYING  
Ib AND Ib-Ia MIXTURES AS STATIONARY LIQUID PHASES<sup>a</sup>

Stationary liquid phase		Column temperature, °C								
Compn, mole % Ib <sup>b</sup>	Nematic range, °C	65	70	75	80	85	90	95	105	110
100	81-129			<i>c</i>	1.07 <sup>d</sup>	1.06		1.05	1.05	1.04
73 <sup>e</sup>	77-125.5	<i>c</i>	1.07 <sup>d</sup>	1.07 <sup>d</sup>	1.06		1.05		1.04	
66	86.5-125.5				1.06 <sup>d</sup>	1.06 <sup>d</sup>	1.05		1.04	
39	107-124.5					1.05 <sup>d</sup>		1.05 <sup>d</sup>		1.03

<sup>a</sup> Retention times were corrected for column dead space in calculating these values. <sup>b</sup> The remainder was Ia, nematic range 119.5-135°. <sup>c</sup> Stationary liquid phase crystallized in attempting runs at this temperature. <sup>d</sup> This value was determined on the supercooled nematic melt at a temperature below the (solid-nematic) transition point. <sup>e</sup> Eutectic composition.

of molecular shape. This was demonstrated to be true by us<sup>4</sup> and, independently, by Kelker<sup>5</sup> through the use of nematic and smectic compounds as stationary liquid phases in gas-liquid partition chromatography. Separations of close-boiling *meta*- and *para*-disubstituted benzenes were achieved and the *para* isomer was invariably eluted last. The data are consistent with a selective affinity of the mesophase toward the more linear *para*-substituted molecules as a result of their fitting more readily into its parallel molecular alignment.

Our first publication on this subject<sup>4a</sup> included a study of 4,4'-di-*n*-hexyloxyazoxybenzene (Ib) and 4,4'-di-*n*-heptyloxyazoxybenzene (Ic) as mesomorphic station-



- Ia, R = R' = CH<sub>3</sub>  
 b, R = R' = *n*-C<sub>6</sub>H<sub>13</sub>  
 c, R = R' = *n*-C<sub>7</sub>H<sub>15</sub>  
 d, R = CH<sub>3</sub>, R' = *n*-C<sub>6</sub>H<sub>13</sub>  
 e, R = *n*-C<sub>6</sub>H<sub>13</sub>, R' = CH<sub>3</sub>

ary liquid phases with which excellent chromatographic separations of *m*- and *p*-xylene were obtained. Later, it was discovered that, due to the preparative method, the substances actually used were not pure Ib and c but, rather, mixtures of 4,4'-dialkoxyazoxybenzenes (I) in which some of the R substituents were CH<sub>3</sub> as well as *n*-C<sub>6</sub>H<sub>13</sub> or *n*-C<sub>7</sub>H<sub>15</sub>. The synthetic procedure was reduction of the appropriate 4-*n*-alkoxybenzene with methanolic sodium methoxide in the course of which some of the *n*-C<sub>6</sub>H<sub>13</sub> or *n*-C<sub>7</sub>H<sub>15</sub> groups were replaced by CH<sub>3</sub>. The resulting products undoubtedly contained, in addition to the desired Ib and c, compounds of the type illustrated by Id and e for the *n*-hexyl system and possibly 4,4'-dimethoxyazoxybenzene (Ia).<sup>6</sup>

Because of these findings, an examination of the solvent properties of pure Ib has been undertaken. Using this compound as the stationary liquid phase in a gas-liquid partition chromatographic column, the relative retention time of *p*-xylene (*m*-xylene = 1.00) was found to be 1.07 at 80°, exactly the same as the value observed earlier for mixture A under similar conditions.<sup>4a</sup>

This result was somewhat surprising. The selectivity of a liquid crystalline solvent toward solute mole-

cules on the basis of shape must depend on the orderliness of its parallel molecular arrangement. The mesophase of pure Ib would be expected to be more highly ordered than those of its mixtures with other components even if the latter were very similar to Ib in structure. Our data indicate that at 80° the mesophase of mixture A is as well ordered as that of pure Ib. In order to find out more about this phenomenon, the model system Ib-Ia, which roughly simulates the situation in mixture A, was selected for further study.

Determination of the phase transitions of known mixtures of Ib and a showed that these compounds form mixed nematic mesophases over all compositions. Pure Ib also displays a monotropic (nematic → smectic) transition at 74° but a smectic mesophase was not observed for any of the mixtures. The (nematic-isotropic) transition temperature *vs.* composition curve was found to be definitely concave upward, suggesting that these components do not form "ideal" mixed nematic mesophases as do the more similar Ia and 4,4'-diethoxyazoxybenzene (I, R = R' = C<sub>2</sub>H<sub>5</sub>) for which the transition curve is linear.<sup>7</sup> This apparent non-ideality increased our surprise at the identical selectivities of mixture A and pure Ib toward *m*- and *p*-xylene.

We proceeded next to an estimate of the relative degrees of molecular order in the nematic mesophases of Ib and Ib-Ia mixtures using their ability to separate *m*- and *p*-xylene in gas-liquid chromatography as the criterion. This is a difficult separation to achieve<sup>4a,8</sup> and, therefore, should be a sensitive test of regularity in the parallel molecular alignment of the mesophase. Chromatographic columns were prepared in which the stationary liquid phases were Ib and Ib-Ia mixtures containing 39, 66, and 73 mole % Ib. The relative retentions of *m*- and *p*-xylene in these columns were determined at several temperatures with the results shown in Table I.

It is evident on examining these data that addition of Ia to b disrupts the nematic mesophase very little. While there is a diminution of relative retention time (and, hence, molecular order) with increasing concentration of Ia at a given temperature, the decrease is extremely gradual. As expected, mesophase order decreases with increasing temperature at a fixed composition. Seeking further confirmation of the high order of the Ib-Ia mixed nematic mesophases, their

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selectivities toward two other *meta-para* isomer pairs, the dichlorobenzenes and methylanisoles, were determined. The relative retention times using Ib, the eutectic composition and a mixture containing 66 mole % Ib at temperatures in the lower parts of their nematic ranges are compared in Table II. The excellent selectivities of the mixed mesophases are apparent, in agreement with the data for the xylenes.

TABLE II  
RELATIVE RETENTION TIMES OF *p*-DICHLOROBENZENE AND  
*p*-METHYLANISOLE (*meta* ISOMER = 1.00) IN COLUMNS  
EMPLOYING Ib AND Ib-Ia MIXTURES AS  
STATIONARY LIQUID PHASES<sup>a</sup>

Compn of stationary liquid phase, mole % Ib <sup>b</sup>	Column temp., °C	Relative retention time	
		<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> Cl	<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub>
100	85	1.11	1.13
73	75	1.17	1.16
66	85	1.16	1.14

<sup>a</sup> Retention times were corrected for column dead space in calculating these values. <sup>b</sup> The remainder of the liquid phase was Ia.

If Ia causes little disruption of the Ib nematic mesophase, Id and e should cause even less since they are more similar to Ib structurally. In light of these results, it is reasonable that nematic mixture A had a high molecular order and displayed the same selectivity toward the xylene isomers as nematic Ib. By analogy, there is every reason to believe that the nematic mesophases of mixture B and pure Ic would exhibit very similar selectivities also.

The upward concavity observed for the (nematic-isotropic) transition curve in the Ib-Ia-phase diagram apparently reflects nonideality only at temperatures near that transition because our chromatographic data for mixtures at temperatures near their melting points certainly indicate a close approach to ideal behavior. It is planned to extend the chromatographic studies to higher temperatures in order to check this point.

The results of this preliminary investigation indicate that the selectivity of mesomorphic liquids toward solute molecules on the basis of shape is an excellent tool for estimating mesophase molecular order. Also, the high selectivity displayed by the Ia-Ib mixtures suggests a similar study of other mixed mesophase systems. The variety of possible mixtures

should provide a diversity and control of solvent properties which are impossible when one is limited to pure mesomorphic compounds. Both approaches are being explored.

#### Experimental Section

**Materials.**—4,4'-Dimethoxyazoxybenzene (Ia) was prepared by reduction of 4-nitroanisole with methanolic sodium methoxide.<sup>10</sup> After recrystallization from benzene, the product had mp 119.5°, (nematic-isotropic) transition temperature 135° (lit.<sup>11</sup> 118.5 and 135°). 4,4'-Di-*n*-hexyloxyazoxybenzene (Ib) was prepared by lithium aluminum hydride reduction of 4-*n*-hexyloxynitrobenzene<sup>12</sup> and was recrystallized from 95% ethanol. It had the following transition temperatures: (nematic → smectic) 74 (monotropic, on cooling the nematic melt), (solid → nematic) 81, and (nematic-isotropic) 129° (lit.<sup>13</sup> 72, 81, and 127°). The *meta*- and *para*-disubstituted benzenes which were used as chromatographic samples were commercial products and were not purified further. No major contaminants were detected in their gas-liquid partition chromatograms.

**Procedure and Apparatus.**—Mixtures of Ia and b were prepared by weighing the components accurately into a small beaker, melting, stirring to give an intimate blend, and cooling with stirring until solidification occurred. Phase transitions were determined on powdered samples in a Nalge-Axelrod melting point apparatus. In this instrument the sample, which is between cover glasses in an aluminum heating block, is illuminated by polarized light and viewed through a 25-power microscope with a rotatable analyzer in the eyepiece so that birefringence can be observed.

The chromatograms were obtained with an Aerograph Hy-Fi gas chromatograph, Model 600-D, using nitrogen as the carrier gas (flow rate 24 cc/min) and a flame ionization detector. The injection chamber was at 200° and the sample size was 0.5 μl of a 1% solution in carbon disulfide for all runs. The chromatographic columns were made from 3.2-mm o.d. and 1.8-mm i.d. annealed copper tubing and were 5 m in length. The packings for the columns were prepared from Chromosorb-W (60-80 mesh) as solid support and solutions of the stationary liquid phases in dichloromethane. All packing contained 15% liquid phase by weight and the total weight of packing in each column was 4.0 g. The relative retention values were found to be reproducible to a precision of ±0.5%.

**Registry No.**—Ia, 1562-94-3; Ib, 2587-42-02.

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