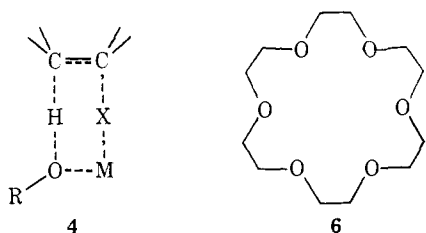


As in earlier studies,<sup>3</sup> Brown and Liu chose a solvent of low polarity to suppress competing solvolysis. However, marked effects of base association upon elimination orientation and stereochemistry in such solvents have recently been recognized.<sup>4-6</sup> Associated alkali metal-alkoxide ion bases exhibit large steric requirements<sup>5</sup> and stabilize syn elimination transition states by simultaneous coordination of the metal cation with the base and a neutral leaving group,<sup>4,6</sup> as depicted in 4. Both factors should favor exo-syn elimination from 1.

In order to assess the effect of base association upon the stereochemistry of eliminations from *exo*-2-norbornyl tosylate, reactions of 1 and its undeuterated analog 5 with the sodium salt of 2-cyclohexylcyclohexanol in triglyme in the presence of a sodium ion complexing agent<sup>7</sup> 18-crown-6,<sup>8</sup> 6, have been investigated.



A comparison of our results with those of Brown and Liu is presented in Table I. The appreciable amount of

**Table I.** Products from Reactions<sup>a</sup> of *exo*-2-Norbornyl Tosylate with the Sodium Salt of 2-Cyclohexylcyclohexanol<sup>b</sup> in Triglyme at 80°

Compound	18-Crown-6 present	% of total hydrocarbons <sup>c</sup>		
		2	3	Nortricyclene
5 <sup>d</sup>	No	99.5		0.5
1 <sup>d</sup>	No	98.0	0	2.0
5	Yes <sup>e</sup>	99.5		0.5
1	Yes <sup>e</sup>	70.0	27.2	2.8

<sup>a</sup> [ROT] = 0.1 M, [NaOR'] = 1.0 M. <sup>b</sup> A mixture of 70% *trans*- and 30% *cis*-2-cyclohexylcyclohexanol was used in the present investigation. <sup>c</sup> 60-65% yields of hydrocarbons were realized. <sup>d</sup> Reference 1. <sup>e</sup> 1.0 M 6 present.

3 formed from 1 in the presence of 6 reveals the importance of base association in producing the exclusive syn-exo elimination stereochemistry observed earlier.

Increase in the nortricyclene percentage from the deuterated compound presumably arises by decreased rate of 2 formation due to a primary deuterium isotope effect. On this basis, the relative product proportions indicate an isotope effect of 5-7 for syn-exo elimination from 1 promoted by the dissociated base.<sup>9</sup> If the rela-

tive proportions of 2 and 3 formed by reactions of the dissociated base with 1 are adjusted for an assumed isotope effect of 6 in the formation of 2, a relative propensity for syn-exo and anti-endo-H eliminations of approximately 15:1 may be calculated. This ratio contrasts with >100:1 for the associated base. These results clearly demonstrate the heretofore unrecognized importance of base association upon the stereochemistry of base-promoted  $\beta$  eliminations from norbornyl derivatives.

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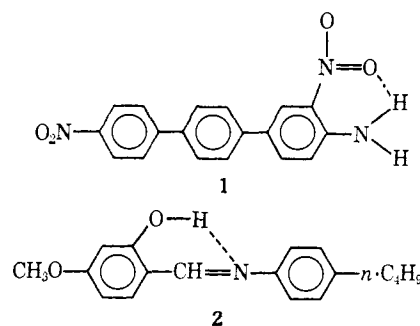
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### *p*-Phenylene Di-*p*-amino- and Di-*p*-hydroxybenzoate. Novel Mesomorphism of an Amine and a Phenol

Sir:

The molecular structural criteria for mesomorphism (liquid crystallinity)<sup>1-3</sup> are rigidity, rod shape, and polarity. Sometimes compounds that satisfy these criteria do not exhibit mesomorphism, phenols and amines being prime examples. In 1962, Gray<sup>4</sup> proposed that phenols had never been observed to be mesomorphic because intermolecular hydrogen bonding raises the melting point above the mesophase-isotropic liquid transition temperature and may also encourage the adoption of a nonlinear molecular arrangement. He further pointed out that, for the same reasons, primary or secondary amines are unlikely to be mesomorphic unless they are capable of intramolecular H bonding. To our knowledge, the only liquid crystalline primary amine (1)<sup>5</sup> and phenol (2)<sup>6,7</sup> presently described in



the literature have this capability. Accordingly, we were surprised to find that *p*-phenylene di-*p*-aminobenzoate (3, Z = NH<sub>2</sub>) and *p*-phenylene di-*p*-hydroxybenzoate (3, Z = OH) are mesomorphic. Their molecular

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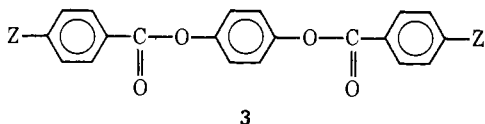
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structures, high melting points, and ir spectra strongly indicate exclusively intermolecular H bonding,<sup>8</sup> and yet both exhibit very stable mesophases.

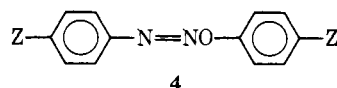
The diamine was prepared by hydrogenation of *p*-phenylene di-*p*-nitrobenzoate (3, Z = NO<sub>2</sub>)<sup>9,10</sup> with Adams catalyst in dioxane. *Anal.*<sup>11</sup> Calcd for C<sub>20</sub>H<sub>16</sub>N<sub>2</sub>O<sub>4</sub>: C, 68.96; H, 4.63; N, 8.04. Found: C, 68.80; H, 4.49; N, 7.84. It melts at 322.5° to a peculiar nematic<sup>12</sup> mesophase consisting of birefringent, schlieren-textured or striated zones in a predominantly homeotropic (pseudoisotropic) matrix. The compound's ir spectrum (KBr pellet) shows strong absorption bands at 3360 and 3380 cm<sup>-1</sup> (N-H stretch, intermolecular H bonding) and at 3433 and 3480 cm<sup>-1</sup> (N-H stretch, free NH<sub>2</sub>). On cooling the nematic melt, crystallization occurs at about 275°.

The diphenol was first synthesized from the diamine by tetrazotization followed by acid hydrolysis (transition temperatures: solid-nematic, 339°; nematic-smectic, 248°). *Anal.*<sup>11</sup> Calcd for C<sub>20</sub>H<sub>14</sub>O<sub>6</sub>: C, 68.57; H, 4.03. Found: C, 68.41; H, 4.10. The product is soluble in cold 5% aqueous NaOH solution and is converted to the known di-*n*-hexyloxy ether (3, Z = *n*-C<sub>6</sub>H<sub>13</sub>O) by reaction with *n*-hexyl bromide in the presence of K<sub>2</sub>CO<sub>3</sub> (transition temperatures: solid-nematic, 123°; nematic-isotropic, 211° (lit.<sup>13</sup> 124°, 213°)). A purer product was recently obtained in better yield by hydrogenolysis of *p*-phenylene di-*p*-benzyloxybenzoate (3, Z = C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>O) in dioxane over palladium on charcoal. This material melts at 340° to a nematic mesophase identical in appearance with that of the diamine. Its ir spectrum (KBr pellet) has a very strong absorption band at 3390 cm<sup>-1</sup> (O-H stretch, intermolecular H bonding). The melt supercools phenomenally. At 267°, there is a thermally reversible transition to a smectic<sup>12</sup> mesophase, unmistakable from its focal-conic texture. Crystallization does not commence until about 215°.

The thermal stabilities of the nematic mesophases are remarkable. Neither shows evidence of transition to isotropic liquid on heating to 360°, where marked decomposition (gas evolution) occurs. The stability of the diphenol's mesophases is further demonstrated by their resistance to crystallization on cooling over 120° below the melting point.<sup>14</sup> Our conclusion is that intermolecular H bonding is not a deterrent to mesomor-

phism in these compounds and, in consideration of the high mesophase stabilities, may even encourage it. We propose that this unusual behavior is associated with the particularly strong tendency of the *p*-phenylene di-benzoates (3) to be mesomorphic.<sup>10</sup> This propensity undoubtedly carries over to the diamine and diphenol. Under these circumstances, with the long molecular axes tending to be parallel, there are two available modes of intermolecular H bonding between NH<sub>2</sub> or OH groups that are compatible with mesomorphism. Lengthwise head-to-tail bonding would result in linear chains of molecules that are consistent with nematic mesomorphism. Sidewise bonding between adjacent parallel molecules is consistent with smectic mesomorphism. Molecular models indicate that lengthwise bonding is entirely reasonable but that sidewise bonding gives a crowded arrangement with aromatic rings on adjacent molecules facing one another in very close proximity. X-Ray diffraction data for the solids and the smectic mesophase would be helpful in appraising the validity of these hypothetical molecular arrangements, and we intend to obtain such information.

If this view is generally correct, other compounds with terminal NH<sub>2</sub> and OH groups should be mesomorphic. However, it appears that a backbone structure which is especially prone to give a parallel molecular alignment may be necessary; *e.g.*, although the *p,p'*-di-*n*-alkoxyazoxybenzenes (4, Z = *n*-alkoxy) are mesomor-



phic,<sup>2</sup> the corresponding diphenol (4, Z = OH) is not.<sup>15,16</sup>

**Acknowledgment.** We thank the University of North Carolina at Greensboro Research Council for financial support.

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## Nuclear Magnetic Resonance Spectroscopy. Carbon-13 T<sub>1</sub> Measurements of Cycloalkanes<sup>1</sup>

Sir:

The recent increase of interest in <sup>13</sup>C spin-lattice relaxation times<sup>2,3</sup> prompts us to report data on <sup>13</sup>C T<sub>1</sub>'s of cycloalkanes. These compounds have been chosen because (i), with only one nmr signal, they are ideal to study the reproducibility and the systematic

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