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Benzotriazol Type Liquid Crystals

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BENZOTRIAZOL TYPE LIQUID CRYSTALS

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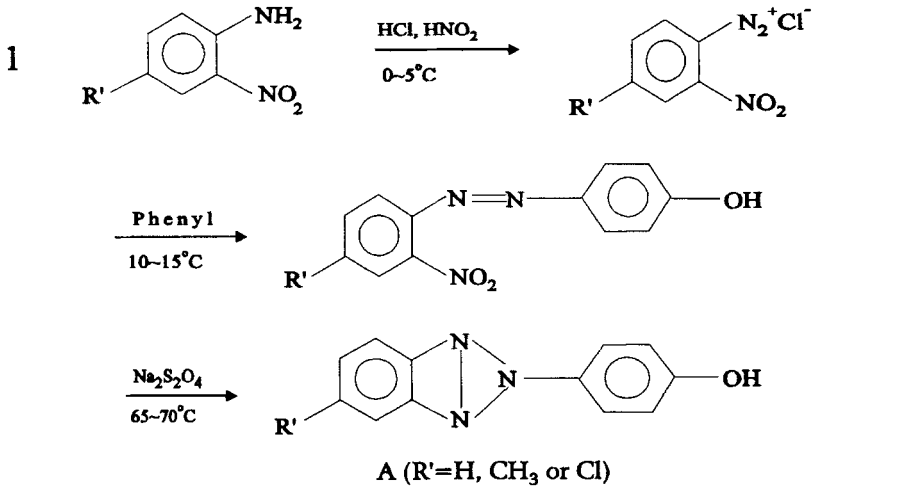
Abstract A new series of liquid crystals (LCs), benzotriazol type which have high absorptivities to ultraviolet (UV) light within the wavelength range from 290 to 350 nm were synthesized. Their syntheses and liquid crystalline properties are reported in this paper.

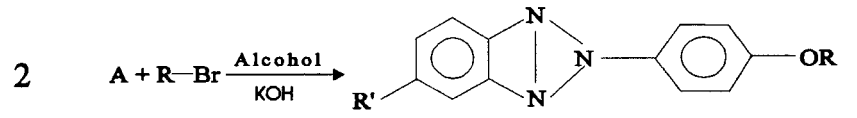
INTRODUCTION

Many types of liquid crystal materials have already been synthesized and most of them have been used in LC displaying devices. Many of them, however, shorten the service life of displaying components due to the decomposition or polymerization under sunshine for long periods of time. In order to improve the photo-stability, some UV-absorbents have been used in the materials of mixed liquid crystals to prolong their service life.[1]

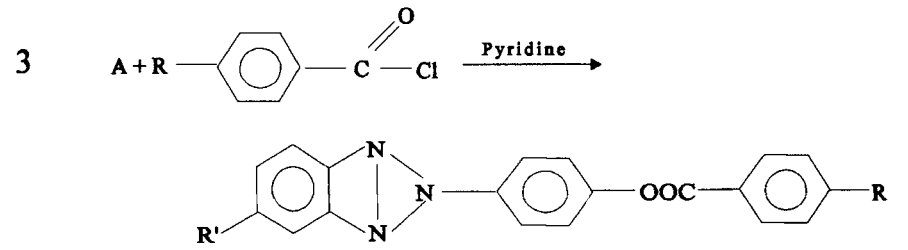
The benzotriazol type compounds have been widely used in many organic synthesized materials as UV-absorbents.[2] They can change photo-energy to thermal-energy and release it. Thus, the destruction to the molecular structure of the materials caused by UV-light is greatly improved by adding a small amount of UV-absorbents. The synthesis of benzotriazol type liquid crystals, however, has not been reported. This paper reports the syntheses and properties of this new series of liquid crystals. These materials have a strong UV absorption at 290-350 nm.[3] Therefore, the service life for displaying components can be extended by adding these new UV-absorbing liquid crystals.[4]



A (R'=H, CH_3 or Cl)



12MPT: R=n-$C_{12}H_{25}$, R'=CH_3
7ClPT: R=n-C_7H_{15}, R'=Cl



4PMPBZ: R'=CH_3, R=n-C_4H_9
4PHPBZ: R'=H, R=n-C_4H_9
5OPMPBZ: R'=CH_3, R=O(n-C_5H_{11})
7OPMPBZ: R'=CH_3, R=O(n-C_7H_{15})
5OPCPBZ: R'=Cl, R=O(n-C_5H_{11})
7OPCPBZ: R'=Cl, R=O(n-C_7H_{15})

SCHEME 1 Syntheses of Benzotriazol Type Liquid Crystals

EXPERIMENTAL

The synthetic routes used to prepare the reported compounds in this paper and their molecular structures are outlined in Scheme 1. All these compounds were prepared by the methods reported in reference 3. The intermediate A reacted with the corresponding acyl chlorides in toluene under the catalysis of pyridine to yield 4PHPBZ, 4PMPBZ, 5OPMPBZ, 7OPMPBZ, 7OPCPBZ and 7OPCPBZ; or reacted with the corresponding alkyl bromides in alcohol by using KOH as catalyst to yield 12MPT and 7ClPT, respectively (see Scheme 1.2 and 1.3). All products were recrystalized with alcohol until the clear point remained constant. The results of differential scanning calorimetry (DSC) analyses are shown in Table I (sensitivity: 5 mV/cm; the rate of increasing temperature: 2°C/min).

RESULTS AND DISCUSSION

The DSC analyses show that the eight compounds synthesized all have liquid crystalline phases (TABLE I).

TABLE I Temperature of Phase-transition

	Compounds	K-S(°C)	S-N(°C)	N-I(°C)
1	12MPT	74		77
2	7ClPT	94		101
3	4PHPBZ	114		155
4	4PMPBZ	159		191
5	5OPMPBZ	148		213
6	7OPMPBZ	126		200
7	5OPCPBZ	149	175	231
8	7OPCPBZ	115	190	216

The authors also synthesized the compound 7MPT in which the R terminal was n-heptyl and R' methyl (see Scheme 1) and did not find the existence of mesophase. The

cause of this behavior is that there is no strong polar group in the molecule. Therefore the liquid crystalline phase does not appear when the alkyl chain at the other terminal is not long enough. The narrow range of liquid crystalline phase was observed when the alkyl chain is long enough (e.g., when R is n-dodecyl, the range of the liquid crystalline phase is 3 °C). The mesophase range increased greatly when a strong polar group such as ester was introduced. When R' (CH_3) was replaced by Cl, the mesophase range increased obviously and the smectic phase appeared. For instance, the mesophase range of 5OPMPBZ was 148~213°C (65°C) and 7OPMPBZ 126~200°C (74°C), while 5OPCPBZ 149~231°C (82°C) and 7OPCPBZ 115~216°C (101°C) and smectic phases were observed at 175 and 190°C respectively. As mentioned above, 7MPT did not exhibit a liquid crystalline phase while 7ClPT did and the mesophase range was 94~101°C. When R' was H, the mesophase temperature was lower than that when R' was methyl. The K-N point of 4PHPBZ (R' = H) was 114°C while 4PMPBZ (R' = CH_3) 159°C.

The UV-absorption spectra of 12MPT, 5OPMPBZ and 4PMPBZ showed that each compound exhibited a strong absorption peak at the wavelength range of 290~350 nm.[3] The reason is that in the molecule, a benzotriazol group which has high UV absorptivity was bounded. The modification of the molecular structure did not change the ability of benzotriazol group to absorb the UV light. The clear point's decreasing and the appearance's yellowing of biphenyl liquid crystals under long period sunshine were improved significantly by adding a small amount of synthesized liquid crystals.[4]

This paper reports the primary experimental results of benzotriazol type compounds as both liquid crystal materials and UV-absorbents. When the terminal group R' is replaced by a strong polar group such as cyano group, an ideal temperature range of liquid crystal phase may appear.

Acknowledgement

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