

Discotic Liquid Crystalline Hydrazone Compounds: Synthesis and Mesomorphic Properties

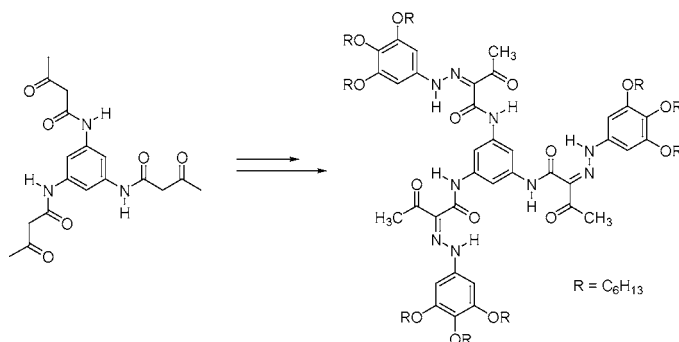
Min Ju Jeong,[†] Jun Ha Park,[†] Changjin Lee,[‡] and Ji Young Chang^{*,†}

School of Materials Science and Engineering and Hyperstructured Organic Materials Research Center, Seoul National University, Seoul 151-744, Korea, and Advanced Materials Division, Korea Research Institute of Chemical Technology, P.O. Box 107, Yusong, Taejeon 305-600, Korea

jichang@snu.ac.kr

Received February 24, 2006

ABSTRACT



1,3,5-Trisacetoacetamidobenzene with three 1,3-diketo groups was synthesized by the reaction of 1,3,5-triaminobenzene with diketene. Discotic hydrazone compounds were prepared by the diazo coupling reaction between 1,3,5-trisacetoacetamidobenzene and diazonium salts of 4-alkoxyphenylamines. The compounds existed in hydrazone forms exclusively, being stabilized by the intramolecular hydrogen bonds, and showed discotic nematic or columnar hexagonal mesophases.

Discotic liquid crystals are of great interest because of both their unique self-assembled structures and their potential applications in devices such as photovoltaic solar cells¹ and electroluminescent displays.² To induce the formation of discotic liquid crystalline phases, rigidity and planarity in the central part of the mesogenic molecule are essential. Typical discotic liquid crystalline compounds comprise aromatic rings such as benzene,³ triphenylene,⁴ and truxene⁵ as

core and peripheral alkyl chains. In recent years, disklike assemblies of molecules other than discotic ones have been studied considerably in an attempt to develop new types of core architecture. The driving forces for the self-assembly of a nondiscotic molecule to form a disklike structure include hydrogen-bonding,^{6–13} charge-transfer,^{14–16} and ionic interactions.^{17,18} Special attention has been given to intramolecular

[†] Seoul National University.

[‡] Korea Research Institute of Chemical Technology.

(1) Schmidt-Mende, L.; Fechtenkötter, A.; Mullen, K.; Moons, E.; Friend, R. H.; MacKenzie, J. D. *Science* **2001**, *293*, 1119.

(2) Christ, T.; Glusen, B.; Greiner, A.; Kettner, A.; Sander, R.; Stumpf, V.; Tsukruk, V.; Wendorff, J. H. *Adv. Mater.* **1997**, *9*, 48–52.

(3) Chang, J. Y.; Baik, J. H.; Lee, C. B.; Han, M. J.; Hong, S.-K. *J. Am. Chem. Soc.* **1997**, *119*, 3197.

(4) Boden, N.; Börner, R. C.; Bushby, R. J.; Cammidge, A. N.; Jesudason, M. V. *Liq. Cryst.* **1993**, *15*, 851.

(5) Lee, W. K.; Wintner, B. A.; Fontes, E.; Heiney, P. A.; Ohba, M.; Haseltine, J. N.; Smith, A. B. *Liq. Cryst.* **1989**, *4*, 87.

(6) Kato, T.; Frechet, J. M. J. *J. Am. Chem. Soc.* **1989**, *111*, 8533.

(7) Kato, T.; Kihara, H.; Uryu, T.; Fujishima, A.; Frechet, J. M. J. *Macromolecules* **1992**, *25*, 6836.

(8) Kumar, U.; Kato, T.; Frechet, J. M. J. *J. Am. Chem. Soc.* **1992**, *114*, 6630.

(9) Kawakami, T.; Kato, T. *Macromolecules* **1998**, *31*, 4475.

(10) Palmans, A. R. A.; Vekemans, J. A. J. M.; Fischer, H.; Hikmet, R. A.; Meijer, E. W. *Chem.—Eur. J.* **1997**, *3*, 300.

(11) Palmans, A. R. A.; Vekemans, J. A. J. M.; Hikmet, R. A.; Fischer, H.; Meijer, E. W. *Adv. Mater.* **1998**, *10*, 873.

hydrogen bonding, which has been shown to efficiently promote molecular ordering and stability in a liquid crystalline phase by allowing it to assume the shape of a large disk.^{10,11}

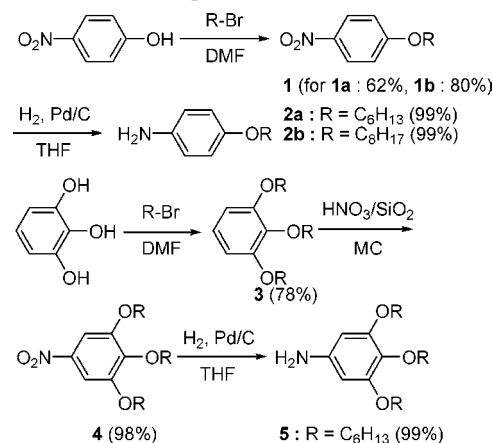
Hydrazone are generally prepared by the condensation reaction between a hydrazine and a carbonyl compound.¹⁹ They can also be obtained from an azo compound which has a labile proton at the position conjugated with an azo group because a hydrazone is a tautomer of an azo compound. Azo and hydrazone tautomerization has been extensively studied because the two tautomers show different optical properties such that certain hydrazone forms absorb light at longer wavelengths and have higher photoconductivity than their azo counterparts. Hydrazone have been investigated as potential charge-transport materials for organic photoconductors^{20–23} and nonlinear optical polymers.^{24–26} Hydrazone dendrimers have reportedly been used as hole-transport materials for electroluminescence devices.²⁷

In this paper, we report on the synthesis of discotic liquid crystalline hydrazone compounds by the azo coupling reaction of 1,3,5-trisacetoacetamidobenzene and diazonium salts of 4-alkoxyphenylamines. 1,3,5-Trisacetoacetamidobenzene having three 1,3-diketo groups was easily obtained by the reaction of 1,3,5-triaminobenzene with diketene.^{28,29} The stable disklike hydrazone structures were derived from the formation of six intramolecular hydrogen bonds around a benzene ring. Spectroscopic analysis showed that all of the N–H groups of the hydrazone units participated in hydrogen bondings so as to render the compounds more hydrophobic. Indeed, the compounds showed good solubility in low polar solvents such as toluene and chloroform. As

expected from their disklike structures, all of the hydrazone compounds showed liquid crystalline properties.

4-Alkoxyphenylamines (**2**) and 3,4,5-trisubstituted phenylamine (**5**) were prepared according to Scheme 1.

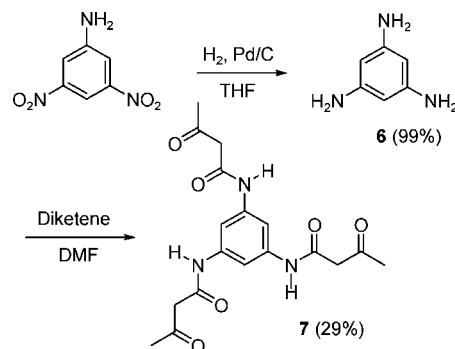
Scheme 1. Preparation of Aromatic Amines



A flexible alkyl group was introduced into the benzene ring by the reaction of 4-nitrophenol with 1-bromoalkane in DMF in the presence of potassium carbonate. The nitro group was reduced to the amino group by catalytic hydrogenation to give **2**. 3,4,5-Trisubstituted phenylamine (**5**) was prepared from 1,2,3-trihydroxybenzene in three steps. 1,2,3-Trisubstituted phenyl ether (**3**), obtained by the reaction of 1,2,3-trihydroxybenzene with 1-bromohexane under basic conditions, was nitrated using HNO₃ supported on SiO₂³⁰ and subsequently reduced by catalytic hydrogenation to produce 3,4,5-trisubstituted phenylamine (**5**).

1,3,5-Triaminobenzene (**6**) was prepared by the catalytic hydrogenation of 3,5-dinitroaniline. The amine was reacted with diketene in DMF, resulting in the formation of 1,3,5-trisacetoacetamidobenzene (**7**) having three 1,3-diketo moieties around the benzene ring (Scheme 2).

Scheme 2. Synthesis of 1,3,5-Trisacetoacetamidobenzene



The protons on the carbon between two carbonyl groups of **7** are easily removed under mild basic conditions,

(12) Percec, V.; Dulcey, A. E.; Balagurusamy, V. S. K.; Miura, Y.; Smidrkal, J.; Peterca, M.; Nummelin, S.; Edlund, U.; Hudson, S. D.; Heiney, P. A.; Duan, H.; Magonov, S. N.; Vinogradov, S. A. *Nature* **2004**, *430*, 764.

(13) Percec, V.; Dulcey, A. E.; Peterca, M.; Ilies, M.; Nummelin, S.; Sienkowska, M. J.; Heiney, P. A. *PNAS* **2006**, *103*, 2518.

(14) Demus, D.; Goodby, J.; Grat, G. W.; Spiess, H. W. *Handbook of Liquid Crystals*; Wiley-VCH: New York, 1998; Vol. 2B.

(15) Bengs, H.; Renkel, R.; Ringsdorf, H.; Baehr, C.; Ebert, M.; Wendorff, J. H. *Makromol. Chem., Rapid Commun.* **1991**, *12*, 439.

(16) Percec, V.; Glodde, M.; Bera, T. K.; Miura, Y.; Shiyonovskaya, I.; Singer, K. D.; Balagurusamy, V. S. K.; Heiney, P. A.; Schell, I.; Rapp, A.; Spiess, H.-W.; Hudson, S. D.; Duan, H. *Nature* **2002**, *419*, 384.

(17) Ujite, S.; Iimura, K. *Macromolecules* **1992**, *25*, 3174.

(18) Percec, V.; Cho, W.-D.; Ungar, G.; Yeardley, D. J. P. *Chem.—Eur. J.* **2002**, *8*, 2011.

(19) Norman, R. O. C.; Coxon, J. M. *Principles of Organic Synthesis*, 3rd ed.; Blackie Academic & Professional: New York, 1993.

(20) Gordon, P. F.; Gregory, P. *Organic chemistry in colour*; Springer: New York, 1987.

(21) Peters, A. T.; Freeman, H. S. *Colour chemistry*; Elsevier: New York, 1991.

(22) Waring, D. R.; Hallas, G. *The chemistry and application of dyes*; Plenum Press: New York, 1990.

(23) Peters, A. T.; Freeman, H. S. *Modern colorants*; Blackie Academic & Professional: London, U.K., 1995.

(24) Hayden, L. M.; Kim, W. K.; Chafin, A. P.; Lindsay, G. A. *Macromolecules* **2001**, *34*, 1493.

(25) Hayden, L. M.; Kim, W. K.; Chafin, A. P.; Lindsay, G. A. *Macromolecules* **2001**, *34*, 6152.

(26) Hayden, L. M.; Kim, W. K.; Chafin, A. P.; Lindsay, G. A. *J. Polym. Sci., Part B: Polym. Phys.* **2001**, *39*, 895.

(27) Nam, H.; Kang, D. H.; Kim, J. K.; Park, S. Y. *Chem. Lett.* **2000**, *11*, 1298.

(28) Kim, B. J.; Chang, J. Y.; Kim, C. H. *Polym. Bull.* **2001**, *46*, 285.

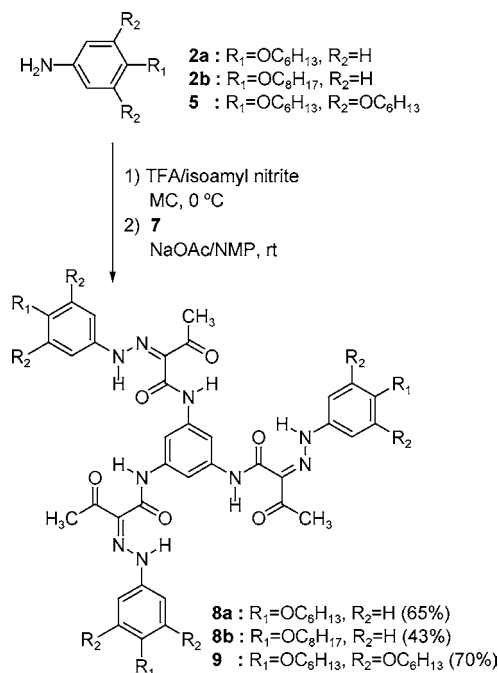
(29) Boese, A. B. *Ind. Eng. Chem.* **1940**, *32*, 16.

(30) Percec, V.; Ahn, C. H.; Bera, T. K.; Ungar, G.; Yeardley, D. J. P. *Chem.—Eur. J.* **1999**, *5*, 1070.

generating carbanions stabilized by resonance. These carbanions have good nucleophilicity and so can be used for nucleophilic substitution and addition reactions.³¹

The diazotization of aromatic amines **2** and **5** was performed using isoamyl nitrite and TFA in methylene chloride.³² The coupling reaction was carried out in situ, without isolating the diazonium salts, by adding a mixture of 1,3,5-trisacetoacetamidobenzene and sodium acetate in *N*-methyl-2-pyrrolidinone (NMP) (Scheme 3). The products

Scheme 3. Synthesis of Discotic Hydrazone Compounds



were isolated by column chromatography on silica gel and further purified by recrystallization from ethyl acetate/hexane to give yellowish powders.

The hydrazone structures of compounds **8a**, **8b**, and **9** were confirmed by ¹H NMR, ¹³C NMR, and FT-IR spectroscopy. In the ¹H NMR spectra obtained in CDCl₃, two peaks corresponding to the C=N–NH and CONH protons appeared at around 14.9 and 11.6 ppm, respectively, in addition to the peaks for the benzene ring protons and alkyl group protons. The peaks for the methine protons which were expected to be found in the azo tautomeric units were not observed. In the ¹³C NMR spectra measured in CDCl₃, the peaks for the C=N–NH carbons appeared at around 157 ppm. In the IR spectra, the C=O stretching vibration band of acetoacetamide at 1719 cm⁻¹ shifted to 1663 cm⁻¹, corroborating the participation of the carbonyl groups in the formation of intramolecular hydrogen bonds. The class of azo compounds having a β-keto group is known to exist

mainly in the hydrazone form, stabilized by intramolecular hydrogen bonding.^{20,33}

The hydrazone compounds showed good solubilities in less polar solvents such as chloroform, methylene chloride, and toluene but were insoluble in polar solvents including alcohols and DMSO. Compound **9** was soluble even in *n*-alkanes. It is noteworthy that 1,3,5-trisacetoacetamidobenzene (**7**), from which the core moieties of the hydrazone compounds were derived, showed poor solubilities in most organic solvents, probably because of the strong intermolecular interactions resulting primarily from the hydrogen bondings between the NH and carbonyl groups. This dramatic change in solubility is consistent with the proposed hydrazone structures having alkyl groups on the periphery, in which all of the carbonyl and NH groups are involved in forming intramolecular hydrogen bonds and thus are not available for intermolecular interactions.

The hydrazone structures were found to be extremely stable in the solution state. We examined the possible dissociation of the intramolecular hydrogen bonds, leading to the formation of the azo tautomer, by UV–vis spectroscopy. There are two types of acidic protons in the hydrazone compounds, i.e., the CONH protons of the amide groups and the C=N–NH protons of the hydrazone groups. In the UV absorption spectra of **8a** recorded in chloroform, methylene chloride, DMF, and THF, the maximum absorption occurred at 400, 398, 398, and 398 nm, respectively, showing that it was not influenced by the properties of the solvent. Even in the presence of a weak base, piperidine, no significant spectral changes were observed.

The liquid crystalline properties of the hydrazone compounds were investigated by differential scanning calorimetry (DSC) and polarizing optical microscopy (POM). Compounds **8** and **9** showed discotic nematic and hexagonal columnar mesophases, respectively. The transition temperatures and corresponding enthalpy changes are summarized in Table 1.

Table 1. Phase Transition Temperatures and Corresponding Enthalpy Values of Discotic Hydrazone Compounds^a

| compd | T, °C [ΔH, kJ/mol] | |
|-----------|---|--|
| | second heating | second cooling |
| 8a | FN 105, N _D 119 (0.2), I 156 (44.5), K 192 (49.4), I | I 117 (0.2), N _D 105, ^b FN |
| 8b | FN 69, ^b N _D 82 (0.1), I | I 79 (0.1), N _D 69, ^b FN |
| 9 | K 120 (11.3), Col _h 175 (1.7), I | I 159 (8.1), Col _h 93 (1.6), K |

^a Abbreviations: K = crystalline; N_D = discotic nematic mesophase; I = isotropic; FN = frozen nematic state; Col_h = columnar hexagonal mesophase. ^b Determined by POM.

The DSC analysis of compound **8a** showed an endothermic clearing transition at 192 °C (ΔH = 50.4 kJ/mol) on the first heating cycle. When cooled from the isotropic liquid

(31) March, J. *Advanced Organic Chemistry*, 4th ed.; John Wiley & Sons Inc.: New York, 1992.

(32) Colas, C.; Goeldner, M. *Eur. J. Org. Chem.* **1999**, 1357.

(33) Peters, A. T.; Freeman, H. S. *Colour Chemistry*; Elsevier: New York, 1991.

state to room temperature, compound **8a** exhibited a small exotherm at 117 °C with a ΔH of 0.2 kJ/mol, corresponding to the transition from the isotropic liquid to the liquid crystalline phase. In the POM study, birefringent *Schlieren* textures appeared at 117 °C and persisted to room temperature, without further crystallization (Figure 1). On the

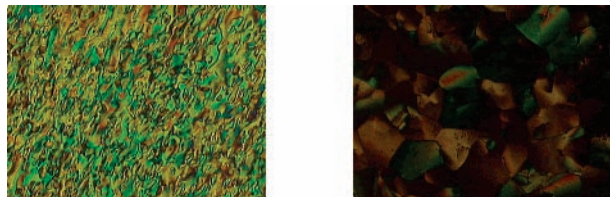


Figure 1. Polarizing optical photomicrographs of **8a** (left) and **9** (right) obtained at 110 °C and 157 °C, respectively, on cooling.

second heating cycle, this birefringent phase disappeared at 117 °C (the temperature far below its clearing transition temperature). At this premelt stage, crystallization could be induced by isothermal heating. In the second DSC heating run, compound **8a** exhibited an endotherm at 119 °C with a ΔH of 0.2 kJ/mol. An exothermic crystallization peak appeared at 156 °C with a ΔH of 44.5 kJ/mol, and an endothermic clearing transition peak was observed at 192 °C with a ΔH of 49.4 kJ/mol.

Compound **8b** showed a crystal to isotropic liquid transition at 167 °C with a ΔH of 0.5 kJ/mol on the first heating cycle. On cooling from the isotropic state to room temperature, a small exothermic peak appeared at 79 °C with a ΔH of 0.1 kJ/mol corresponding to the transition from the isotropic liquid to the liquid crystalline phase. The *Schlieren* texture was also observed under a polarizing optical microscope. On the second heating run, the endothermic isotropization was observed at 82 °C with a ΔH of 0.1 kJ/mol, but unlike in the case of compound **8a**, crystallization was not induced immediately by isothermal heating. This result is consistent with the low crystallinity of this compound, which showed a relatively small transition enthalpy in the first DSC heating run.

The structural analysis of the mesophases was performed using X-ray diffraction (XRD). After the textures were fully developed in their liquid crystalline states, the compounds

were quenched to room temperature and examined by XRD. In the small angle region, compounds **8a** and **8b** showed broad peaks with d -spacings centered at 23 and 27 Å, respectively, representing the lateral disk–disk distance in the discotic nematic structures. The peaks centered at a d -spacing of 3.7 Å in the wide angle region were assigned to the vertical disk–disk distance.

Compound **9** having a 3,4,5-trishexyloxy group as a tail formed an enantiotropic mesophase with a more ordered structure than that of compound **8**. In the DSC analysis, two endotherms appeared at 120 °C ($\Delta H = 11.3$ kJ/mol) and 175 °C ($\Delta H = 1.7$ kJ/mol), respectively, on the second heating run. A birefringent phase with mosaic textures was observed by POM between these two temperatures (Figure 1). In the XRD analysis, three peaks with d -spacings of 29.2, 17.1, and 14.6 Å, respectively, appeared in the small angle region. These d -spacings are in the ratio of 1:1/ $\sqrt{3}$:1/2, which is in good agreement with a hexagonal lattice. Wide angle XRD showed a peak with a d -spacing of 3.7 Å resulting from the stacking of the disks. When cooled from the isotropic melt, an exotherm appeared at 159 °C ($\Delta H = 8.1$ kJ/mol) and the compound began to show the same birefringent phase. The compound crystallized at 93 °C.

In conclusion, we prepared discotic liquid crystalline hydrazone compounds by the azo coupling reaction of 1,3,5-trisacetoacetamidobenzene and diazonium salts of 4-alkyloxyphenylamines. The hydrazone structures were found to be stabilized by the intramolecular hydrogen bonding between their N–H groups and the 1-keto groups. The amide N–H groups also formed hydrogen bonds with the 3-keto groups, yielding extended core structures. Considering both the ease with which acetoacetamides can be synthesized and the wide range of structures of amines, the approach described herein would be expected to be very useful in building large disk-shaped cores for discotic liquid crystalline assemblies.

Acknowledgment. This work was supported by the Ministry of Commerce, Industry, and Energy, Korea, and the Hyperstructured Organic Materials Research Center at Seoul National University.

Supporting Information Available: Experimental details and characterization data for new compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OL060479L