Mesogenic Properties of Tricyclic 2,5-Di(4-alkoxybenzoyloxy)tropones. Increasing Smectic Thermal Stabilities by the Lateral Polar Carbonyl Group

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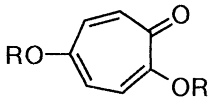
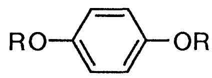
2,5-Di(4-alkoxybenzoyloxy)tropones showed similar mesogenic properties to the corresponding benzenoids. The tropone carbonyl group, which behaved as a polar lateral substituent, enhanced the thermal stability of the smectic phases and reduced that of the nematic phases when compared with those of the benzenoids. The tropone carbonyl group induced an intermolecular attractive force.

A polar group in a lateral position caused a pronounced effect on mesophase types and transition temperatures although it depends on the size and the positioning. It has been rationalized in terms of a reduction in anisotropic polarisability and an increased axial separation of the molecules.[1] Recently, we prepared new liquid crystals[2] having a tropone core structure, in which the troponoids (**1**) with a benzyloxy group at C-2 showed a monotropic smectic A (S_A) phase, whereas the corresponding benzenoids did not.[3] Thus, the tropone carbonyl group enhanced the stability of mesophases. Here, we report the preparation and the mesogenic properties of tricyclic 2,5-di(4-alkoxybenzoyloxy)-tropones (**2**), in which the tropone carbonyl group enhanced the thermal stability of the smectic C (S_C) phases and reduced that of the nematic (N) phases when compared with the corresponding benzenoids.

Compounds **2** were prepared by esterification of 5-hydroxytropolone (**3**) with a corresponding aroyl chloride. Compounds **2** with the different side chain lengths at C-2 and C-5 were prepared with monoesterification of **3** and following esterification of the resulting 5-aroyloxytropolones (**4**). Phase transition temperatures were determined by a differential scanning calorimeter. The appearance of the mesogenic phases was identified on the basis of the observed microscopic texture.



1 $R = C_mH_{2m+1}$, $R' = CH_2C_6H_4OC_nH_{2n+1}$-*p*
2 $R = COC_6H_4OC_mH_{2m+1}$-*p*, $R' = COC_6H_4OC_nH_{2n+1}$-*p*
3 $R = R' = H$
4 $R = COC_6H_4OC_mH_{2m+1}$-*p*, $R' = H$



5 $R = COC_6H_4OC_mH_{2m+1}$-*p*, $R' = COC_6H_4OC_nH_{2n+1}$-*p*

The phase transition behaviors of **2** are summarized in Table 1 together with those of the corresponding benzenoids (**5**). The nematic-isotropic (N-I) transition temperatures decreased with increasing alkyl chain length. Replacement of the central benzene ring of **5** by a tropone ring leads to a decrease of 55 °C in **2a**, 31 °C in **2b**, 37 °C in **2c**, 26 °C in **2d**, 25 °C in **2e**, and 18 °C in **2f** in the N-I transition temperature, while the depression of the melting points was rather small and the S_C-N transition temperatures in **2** were higher than those of **5**; 28 °C in **2f**, 24 °C

Table 1. Transition temperatures (°C) of troponoids **2** and benzenoids **5**

			2				**5**			
	m	n	K	S_C	N	I	K	S_C	N	I
a	1	1	• 152		• 245[a]	•	• 222		• 300[b]	•
b	4	4	• 130		• 210	•	• 153		• 241[c]	•
c	4	6	• 116		• 189	•	• 117		• 226[c]	•
d	4	8	• 110		• 188	•	• 121		• 214[c]	•
e	6	6	• 125		• 188	•	• 124		• 213[c]	•
f	8	8	• 111	• 154	• 177	•	• 121.9	• 125.6	• 194.9[d]	•
g	10	10	• 104	• 171	• 175	•	• 126.7	• 146.6	• 181.7[d]	•
h	12	12	• 98	• 173	• 175	•	• 109.1	• 155.7	• 171.5[d]	•

[a] Decomposed. [b] M. J. S. Dewar and J. P. Schroeder, *J. Org. Chem.*, **30**, 2296 (1965). [c] S. A. Haut, D. C. Schroeder, and J. P. Schroeder, *J. Org. Chem.*, **37**, 1425 (1972). [d] Reference 4.

in **2g**, and 17 °C in **2h**.

It has been reported[4] that benzenoids **5** have a planar molecular conformation with maximum overlap of the p orbitals. In **2**, the C_2-O bond would twist to reduce the coplanarity between the tropone ring and the ester group, -COO- since the benzoyl group at C-2 should deviate from the mean plane of the tropone ring to migrate to the tropone carbonyl group in the mesophase, so-called [1,9] sigmatropy, as observed in the ^{13}C CPMAS spectra of 5-dodecyloxy-2-(4-dodecyloxybenzoyloxy)-tropone.[5,6] Twist around the C_2-O bond would reduce the overlap of the p orbitals of the molecule, which would decrease the mutual conjugation along the entire molecule to lower both melting points and the transition temperatures of the N phases. However, the thermal stabilities of S_C phases of **2** increased more than those of **5**. Consequently, the tropone carbonyl group played roles to increase the thermal stability of the S_C phases and to decrease that of the N phases.

Recently, Goodby and his coworkers have reported[7] that the lateral hydroxy group on an off-central position enhanced the thermal stability of the chiral S_C phase and Gray et al. have focused on the lateral fluoro-substituents, which ensured extremely high S_C phase stability.[8] Furthermore, it has been reported that the lateral carbonyl group of fluorenone decreased the S_A phase and increased the chiral S_C phase stability when compared with the fluorene series.[9] In the case of **2**, the tropone carbonyl group acted both to widen the molecular breadth and to induce an attractive force. The former dominated to depress the thermal stability in the N phases and the latter to enhance that of the S_C phases since the stability of the S phases is explained mainly in terms of the interaction of the cores of neighboring molecules.

Thus, the tropone carbonyl group induced an attractive force between the molecules to increase the thermal stability of the S_C phases and the [1,9] sigmatropy helped to form time-averaged liquid crystalline structures to induce dipole moment along with the longer molecular axis.[5,6] These properties are characteristic of troponoid systems.

References and Notes

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