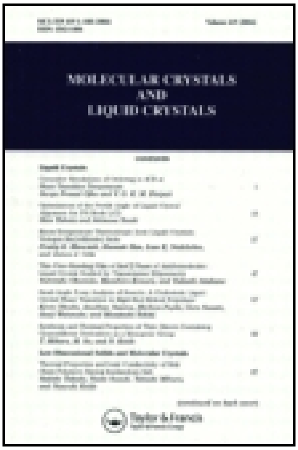

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Mesomorphic Properties of a Homologous Series of Aryl β-Diketones and a Few Related Derivatives

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A new homologous series of nine [1-(*p*-*n*-alkylbiphenyl)3-(phenyl)propane]1,3-diones have been prepared and their mesomorphic properties studied. The first four homologues in the series exhibit the classical nematic phase and a smectic phase, the next five showing only a smectic phase. The optical textures, miscibility and the X-ray data establish that the smectic phase is of the A_1 type. This is perhaps the first instance of a β-diketone exhibiting a nematic as well as a smectic A_1 phase. In addition, a few similar isomeric β-diketones have also been synthesized to study the terminal substituent effect on the mesomorphic properties.

Keywords: *β-diketone, smectic A phase, isomerism, substituent effect.*

INTRODUCTION

The liquid crystalline properties of compounds having a β-diketone group have been investigated only relatively recently. The first report of such a compound was on 1,3-di(*p*-*n*-decylphenyl)propane 1,3-dione prepared by Godquin-Giroud and Billard.[1] Subsequently,[2] they prepared a few more similar β-diketones and concluded that only such compounds having more than eighteen carbon atoms in the side chains exhibit a mesophase. Through optical and miscibility studies they also tentatively identified the mesophase as smectic E.

Recently, Ohta *et al.*[3,4,5] have also prepared a number of β-diketones including some of the compounds reported[2] earlier. The texture exhibited by these compounds has not been conclusively identified by them though they state that it is similar to that reported[1,2] by the French workers.

We have prepared a homologous series of β-diketones incorporating a biphenyl moiety and report here their properties. Through optical, miscibility and X-ray studies, the nature of the smectic phase has been established. We have also synthesised a few isomeric compounds to study the terminal substituent effect in some of these β-diketones.

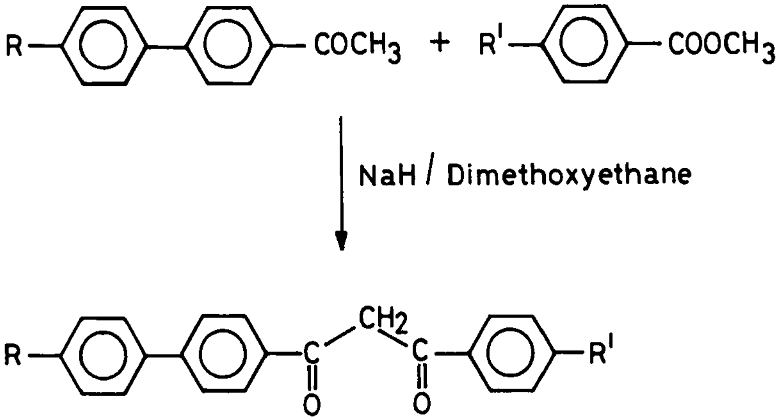
EXPERIMENTAL

4-*n*-Alkyl-4′-acetylbiphenyls were prepared in three steps; (i) by Friedel-Crafts acylation reaction on biphenyl using the appropriate *n*-acyl halide, (ii) reduction of the resulting ketone by the Wolff-Kishner method, and (iii) by Friedel-Crafts acylation of the 4-*n*-alkylbiphenyl using acetyl chloride. Commercial methyl benzoate was distilled prior to use. Methyl *p*-methoxybenzoate, methyl *p*-cyanobenzoate and methyl *p*-*n*-decylbenzoate were all obtained by the esterification of their respective acids using methanol. 4-cyano-4′-acetylbiphenyl was prepared from 4-bromobiphenyl in two steps: first, by the Friedel-Crafts acylation using acetyl chloride and secondly by replacing the bromine atom by a cyano group using cuprous cyanide in boiling N,N-dimethylformamide.

All the β-diketones were prepared according to the general scheme shown in Figure 1 and described for [1-(*p*-*n*-hexylbiphenyl) 3-(phenyl)propane]1,3-dione.

[1-(*p*-*n*-Hexylbiphenyl)3-(phenyl)propane]1,3-dione

A mixture of 4-*n*-hexyl-4′-acetylbiphenyl (12 mmol) and methylbenzoate (12 mmol) in dry 1,2-dimethoxyethane (60 ml) was stirred under an atmosphere of dry nitrogen. To this solution was added sodium hydride (25 mmol) dispersed in paraffin oil and the mixture was refluxed for four hours and stirred at room temperature overnight. The mixture was then cooled in ice and water (5 ml) was added carefully followed by dilute hydrochloric acid until it was acidic. The semisolid so obtained was extracted into ether (100 ml), washed with water (3 x 50 ml) and dried (Na_2SO_4).



1. $R = C_nH_{2n+1}$; $R' = H$.

2. $R = n\text{-}C_{10}H_{21}$; $R' =$ a) $-OCH_3$, b) $-CN$.

3. $R =$ a) $-H$, b) $-OCH_3$, c) $-CN$; $R' = n\text{-}C_{10}H_{21}$ ·

FIGURE 1 General route for the preparation of β-diketones.

Removal of solvent afforded a pale yellow solid which was chromatographed and crystallized from acetonitrile several times. Yield 40%, m.p. 93°C; IRν(cm^{-1}) 1600, 1590, 1230, 805 and 770; NMR (CDC1$_3$)δ 0.9(*t*,3H,—C$\underline{H}_3$), 1.1–2.0(m, 8H, 4×—C$\underline{H}_2$), 2.66(*t*,2H,ar C$\underline{H}_2$), 4.6(S, 0.07H, Keto C$\underline{H}_2$), 6.9 (S, 0.96H, —C=C$\underline{H}$—),16.9(S, 0.96H, enol OH), Enol: Keto = 0.96:0.07.

Found: C, 84.38; H, 7.29% $C_{27}H_{28}O_2$ requires
C, 84.49; H, 7.17%

The transition temperatures were determined using a Leitz Laborlux 12 POL polarizing microscope equipped with a Mettler FP52 heating stage and a FP5 controller, as also from thermograms recorded on a Perkin-Elmer, Model DSC-2 differential scanning calorimeter. The purity of the ligands was checked by thin layer chromatography, spectral data and microanalytical data. The infrared and electronic absorption spectra were recorded on a Shimadzu IR-435 and a Hitachi U-3200 spectrophotometers respectively. The PMR spectra were recorded on a Bruker WP80SY spectrometer. The X-ray data were obtained using the flat film technique with CuK$_\alpha$ radiation from a Carl-Zeiss Jena bent quartz crystal monochromator.

RESULTS AND DISCUSSION

The transition temperatures of homologous series [1-(*p*-*n*-alkylbiphenyl)3-(phenyl)propane]1,3-diones are given in Table I. As can be seen all the nine compounds exhibit mesophases. Compounds 1, 2 and 3 exhibit monotropic nematic and smectic

TABLE I

Transition temperatures (°C) and heats of transitions (K cals/mole) of a series of [1-(*p*-*n*-alkylbiphenyl)3-(phenyl) propane] 1,3-diones(1), *n* = 4 to 12

Compound No.	*n*	K		S$_A$		N		I
1	4^a	·	118 6.62	·	(81)	·	85	·
2	5^a	·	110.5 5.22	·	(88)	·	(94)	·
3	6^a	·	93^b 2.81	·	(91.2)	·	(91.3)	·
4	7^a	·	95.5	·	96	·	96.4	·
5	8	·	90 6.78	·		–	94.5 0.99	·
6	9	·	81 5.12	·		–	99 0.97	·
7	10	·	67 7.52	·		–	101 0.87	·
8	11	·	74.5 8.73	·		–	99.5 0.87	·
9	12	·	72 5.64	·		–	97 1.19	·

K: Crystal; S$_A$: Smectic A phase; N: nematic phase, and I: isotropic phase.
[a] The heats of the N → I and S$_A$ → N could not be measured.
[b] A solid–solid transition was observed.

phases while compound 4 shows enantiotropic smectic and nematic phases, though over a narrow range. The remaining homologues show only an enantiotropic smectic phase and have a fairly wide mesophase range.

The smectic phase exhibited by these compounds show a fan-shaped texture and aligns homeotropically rather easily. In order to conclusively establish the nature of this phase, miscibility as well as X-ray studies were undertaken. The miscibility diagram for compound 7 (Table I) and 4-biphenylyl-4″-*n*-dodecyloxybenzoate[6,7] which is known to be smectic A is shown in Figure 2. It is clear from this diagram

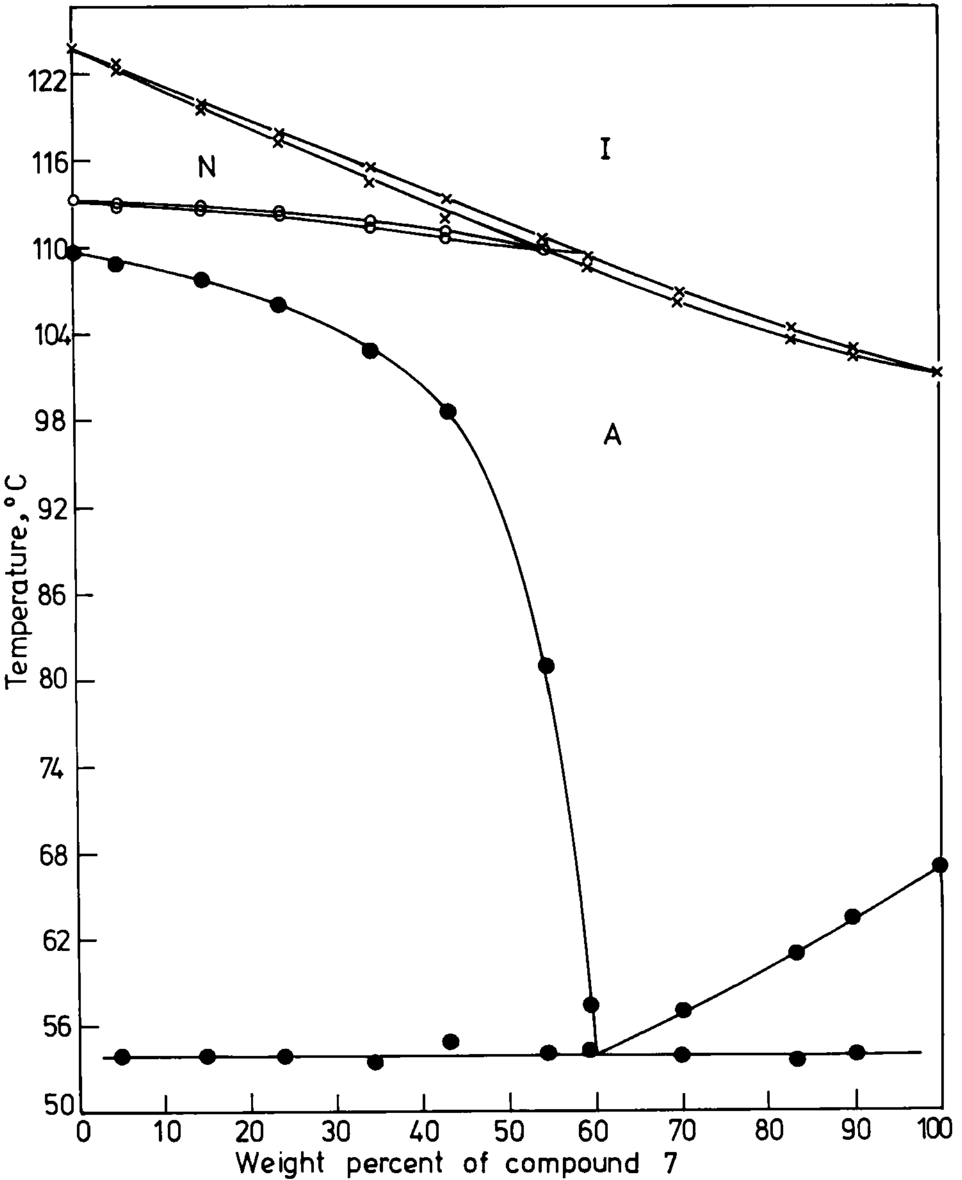
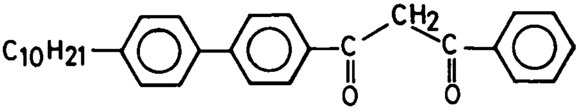


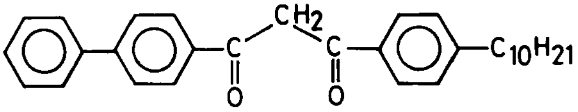
FIGURE 2 Binary phase diagram of a mixture of [1-(*p*-*n*-decylbiphenyl) 3-(phenyl)propane]1,3-dione (Compound 7) and 4-biphenylyl-4″-*n*-dodecyloxybenzoate.

1



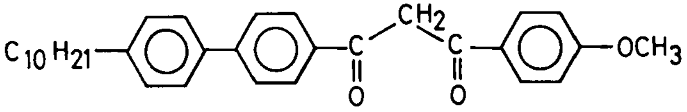
K67 S_A101 I

3a



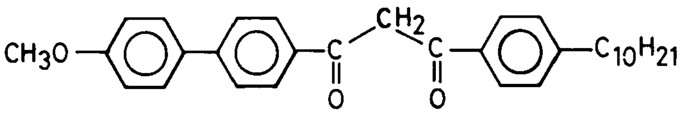
M.P. 89.5

2a



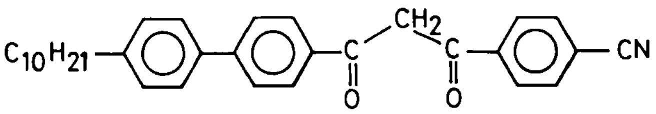
M.P. 113–114

3b



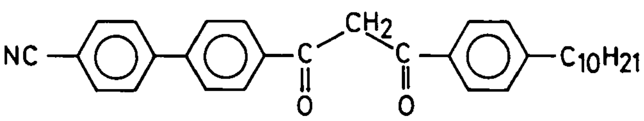
M.P. 127.5

2b



K126.5 S_A139 I

3c



K119.5 S_A 123.5 I

FIGURE 3 Chemical structure and transition temperatures (°C) of isomeric β-diketones.

that the smectic phase of compound 7 is continuously miscible over the entire composition range confirming that the phase is of the A type.

The X-ray data was obtained on compound 7. The sample was taken in a sealed Lindemann capillary tube and aligned by slowly cooling it in a magnetic field of strength 4 KG. The measured layer spacing in the smectic A phase of the compound is 29.1 ± 0.1 Å. This is approximately equal to the molecular length measured using Dreiding stereo-models. These β-diketones exist as tautomers, the enol form being present to a larger extent as indicated by the NMR spectra. However, the molecular lengths of the keto and enol forms are about the same. The layer spacing remained constant in the entire temperature range of the smectic A phase. It is clear that the smectic A phase exhibited by these compounds is monolayer.

In all the above β-diketones there is only one terminal substituent, which is the *n*-alkyl chain. In order to study the effect of terminal substituents, a few similar β-diketones were prepared and are shown in Figure 3 with their melting points and transition temperatures. Compound 1 has a fairly wide mesophase range of 34°. When this compound is terminally substituted with a methoxy group (compound 2a), the melting point goes up and it becomes non-mesomorphic. However, when a cyano group is inserted terminally (compound 2b), the melting point is again raised but the mesophase (smectic A phase) is retained. This behavior is not surprising since on substituting a terminal hydrogen in a mesogenic compound by another group, usually the melting point is raised and further the mesophase of the substituted compound becomes generally, though not always, thermally more stable.[8]

In Figure 3, compounds 1 and 3a are isomeric. When the *n*-decyl chain is on the biphenyl moiety, it is mesomorphic and when the same chain is on the phenyl ring, the compound becomes non-mesomorphic. Similarly compounds 2a and 3b are isomeric and both are non-mesomorphic. However, compounds 2b and 3c are isomeric and mesomorphic. It is therefore clear that assessing the relative efficiency of the terminal groups for the formation of liquid crystals is difficult in these β-diketones.

Acknowledgments

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