This article was downloaded by:
On: *26 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Mesogenicity of 4-alkanoyl-4'-alkyloxybiphenyl derivatives

Toshinori Tanase[a]; Shinichi Yano[a]
[a] Department of Chemistry, Faculty of Engineering, Gifu University, Gifu, Japan

To cite this Article Tanase, Toshinori and Yano, Shinichi(1992) 'Mesogenicity of 4-alkanoyl-4'-alkyloxybiphenyl derivatives', Liquid Crystals, 12: 2, 297 — 303

To link to this Article: DOI: 10.1080/02678299208030398

URL: http://dx.doi.org/10.1080/02678299208030398

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

LIQUID CRYSTALS, 1992, VOL. 12, NO. 2, 297–303

Mesogenicity of 4-alkanoyl-4′-alkyloxybiphenyl derivatives

by TOSHINORI TANASE and SHINICHI YANO*
Department of Chemistry, Faculty of Engineering,
Gifu University, Yanagido, Gifu 501–11, Japan

(*Received 6 November 1991; accepted 6 February 1992*)

Phase transitions of 4-alkanoyl-4′-alkyloxybiphenyl were studied by differential scanning calorimetry and optical microscopy. 4-Acetyl-4′-alkyloxybiphenyl homologues (number of carbon atoms, of *n*, 4′-alkyloxy group is 4–10) showed S_E phases with good thermal stability, while 4-propionyl-4′-alkyloxybiphenyl homologues ($n=4$–10) and 4-pentanoyl-4′-decyloxybiphenyl showed S_A phases with good thermal stability. Moreover changes in the thermal stability by substitution of bulky Br, Cl or CH_3 substituents into the alkanoyl groups were studied for the previously mentioned three homologues. The substitution at the α-position of the alkanoyl group was found to strikingly lower the thermal stability.

1. Introduction

The terminal groups of liquid-crystalline compounds are known to govern the type of liquid crystal phase and its thermal stability. From this viewpoint, the relationships between chemical structure of terminal groups and mesogenicity have been studied extensively but studies on compounds having alkanoyl terminal groups have proven to be unexpectedly rare. Very recently, however, a few ferroelectric liquid crystal compounds containing alkanoyl groups as terminal groups have been reported [1–3]. The carbonyl groups of the alkanoyl groups have been found to enhance the spontaneous polarization in the ferroelectric phase. The straightforward but fundamental study on mesogenicity of various mesomorphic compounds having alkanoyl terminal groups should give much important information on the molceular design of new meso-compounds. This work deals with the mesogenicity of 4-alkanoyl-4′-alkyloxybiphenyl derivatives in order to clarify the relationships between chemical structure of terminal alkanoyl groups and mesogenicity. We discuss how the substitution of Br, Cl and CH_3 groups into the alkanoyl group affects the mesogenicity. The chemical structures of the compounds used here are shown in table 1.

2. Experimental

2.1. *General syntheses of compounds*

4-Alkyloxybiphenyls were prepared by refluxing a mixture of alkyl bromide (0·410 mol), 4-hydroxybiphenyl (0·353 mol) in ethanol (500 ml) and 13 M KOH (50 ml) solution for 48 h. The crude crystals were obtained by neutralizing the reaction solution by 6 M HCl. The crude crystals were purified by washing the crude crystals with 2 M KOH and water, giving a yield of 90 per cent. 4-Alkanoyl-4′-alkyloxybiphenyls (AA_n) were synthesized according to a standard Friedel Crafts procedure [4, 5]. The crude crystals were purified by recrystallizations from ether and were judged to be fully purified by thin layer chromatography and DSC. For example, for 4-acetyl-4′-heptyloxybiphenyl (AA_7); ^1H NMR: δ 0·9 ppm (3 H, t, H_a), 1·5 ppm (10 H, m, CH_2),

---

* Author for correspondence.

Table 1. The chemical structures of the compounds used.

4-Alkanoyl-4′-n-alkyloxybiphenyl derivatives (R-biphenyl–OC_nH_{2n+1}) R	Symbol of compound
$CH_3C(O)$–	AA_n
$BrCH_2C(O)$–	α-Br–AA_n
$ClCH_2C(O)$–	α-Cl–AA_n
$BrClCHC(O)$–	α-Br– Cl–AA_n
$CH_3CH_2C(O)$–	PA_n
$CH_3CHBrC(O)$–	α-Br–PA_n

4-Pentanoyl-4′-decyloxybiphenyl derivatives (R-biphenyl-$OC_{10}H_{21}$) R	Symbol of compound
$CH_3CH_2CH_2CH_2C(O)$–	PD
$CH_3CH_2CH_2CH(CH_3)C(O)$–	α-Me-PD
$CH_3CH_2CH(CH_3)CH_2C(O)$–	β-Me–PD
$(CH_3)_2CHCH_2CH_2C(O)$–	γ-Me–PD
$CH_3CH_2CH_2CHBrC(O)$–	α-Br–PD
$CH_3CH_2CH_2CBr(CH_3)C(O)$–	α-Br–α-Me–PD
$CH_3CH_2CH(CH_3)CHBrC(O)$–	α-Br–β-Me–PD
$(CH_3)_2CHCH_2CHBrC(O)$–	α-Br–γ-Me–PD

2·8 ppm (3 H, s, H_g), 4·0 ppm (2 H, t, H_b), 7·0 ppm (2 H, d, H_c) 7·6 ppm (2 H, d, H_d), 7·7 ppm (2 H, d, H_e), 8·0 ppm (2 H, d, H_f); IR: 3000, 1700, 1610, 1300, 1280, 1020, 800 cm^{-1}.

Bromo-substituted compounds were prepared by substitution of a Br atom into the alkanoyl group of 4-alkanoyl-4′-alkyloxybiphenyl (AA_n) synthesized as described previously [6–8]. For example, in the bromination of AA_4, a mixture of CuBr (12·0 g, 0·054 mol), ethyl acetate (30 ml) and AA_4 (8·0 g, 0·027 mol) in chloroform (50 ml) was refluxed for about 24 h. After the residue (CuBr and $CuBr_2$) was eliminated by filtering, the crystals were obtained by concentrating the filtrate. The crystals, separated by column chromatography (Waco gel-200, chloroform), were fully purified by recrystallizations from 2-propanol, giving a yield of 2·6 g (25 per cent). All compounds were judged to be fully purified by thin layer chromatography and DSC. ^1H NMR: 0·9 ppm (3 H, t, H_a), 1·6 ppm (4 H, m, CH_2), 4·0 ppm (2 H, t, H_b), 4·5 ppm (2 H, s, H_g), 7·0 ppm (2 H, d, H_c), 7·5 ppm (2 H, d, H_d), 8·0 ppm (2 H, d, H_f). IR: 3000, 1700, 1610, 1300, 1280, 1020, 800, 680 cm^{-1}.

2.2. *Characterization of compounds*

Phase transition temperatures and their entropy changes were obtained by use of a differential scanning calorimeter (Seiko-Denshi Co., SSC-5000) at a heating/cooling rate of 5 K min^{-1}. The texture of each mesophase was determined by optical polarizing microscopy (Nikon, Optiphoto-Pol, XTP-11) equipped with a Mettler FP 82 hot stage at a heating/cooling rate of 5 K min^{-1}.

3. Results and discussion

3.1. *Phase behaviour of 4-alkanoyl-4′-n-alkyloxybiphenyl derivatives*

Mesomorphic phase transition temperatures and entropy changes for a series of 4-alkanoyl-4′-alkyloxybiphenyl derivatives are listed in table 2. Figures 1 and 2 show the phase transition temperatures plotted against the carbon number, *n*, of the 4'-alkyloxy group for 4-acetyl-4'-alkyloxybiphenyl (AA_n) and 4-propionyl-4'-alkyloxybipehnyl (PA_n) derivatives, respectively. For 4-acetyl-4'-alkyloxybiphenyls (AA_n, $n = 3$–10), the $n = 3$ compound showed no mesophase but the $n = 4$–10 compounds have a smectic E (S_E) phase. The S_E phase was characterized by the appearance of a mosaic S_E texture from microscopic observations between crossed polarizers. Conversely the 4-propionyl-4'-alkyloxybiphenyls (PA_n) ($n = 4$–10) have a smectic A (S_A) phase which showed a focal conic texture on heating and a fan texture on the cooling between cross polarizers. For the AA_n series, the length of the 4'-alkyloxy group (*n*) does not much influence the thermal stability of the mesophase, when *n* is larger than 4. The AA_3 compound shows a high melting point of 430 K which could veil a mesophase. For the 4-haloalkanoyl-4'-alkyloxybiphenyls, clearly the halogen-substitution of the alkanoyl group lowers the mesomorphic phase transition temperature. For the α-monohalo-AA_n series, the S_E—I transition temperatures (T_{S_EI}) are lower than those of the AA_n series, and the S_A phase appears when *n* is larger than 6. This decrease of T_{S_EI}/T_{S_AI} must be caused by the increase in molecular breadth caused by the halogen atom; the larger decrease for the bromo-substituent is due to the larger van der Waals radius of Br, compared with that of the chloro-substituent.

It has been reported that α-substitution of an alkanoate group by a methyl group strikingly decreases the nematic thermal stability in several compounds; for example, in alkyl 4-(4-substituted benzylideneamino)cinnamates[9] and alkyl 4-[4-(4-substituted

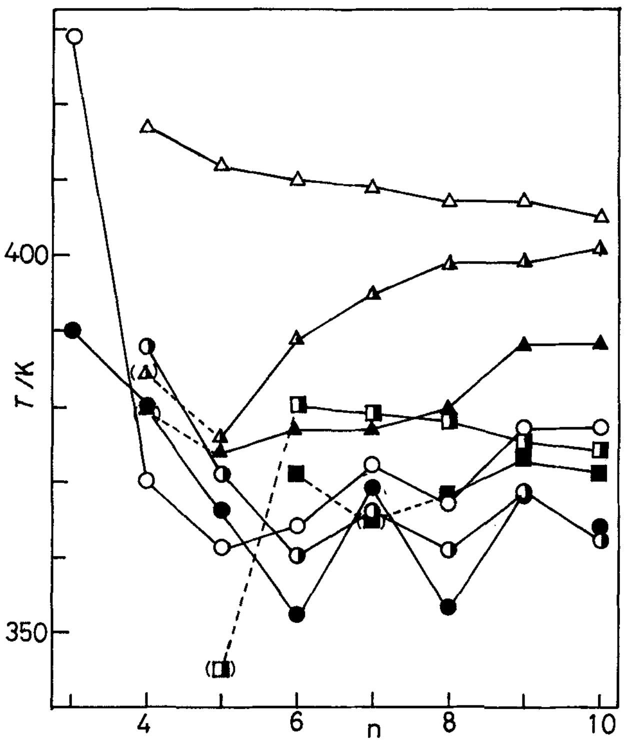

Figure 1. Plots of phase transition temperature versus carbon number, *n*, of the 4'-*n*-alkoxy group for 4-acetyl-4'-alkyloxybiphenyl derivatives. AA_n: ○, $C–S_E$; △, $S_E–I$. α-Cl–AA_n: ◑, $C–S_E/C–S_E$; ◨, $S_E–S_A$; ◮, $S_A–I$. α-Br–AA_n: ●, $C–S_E/C–S_A$; ■, $S_E–S_A$; ▲, $S_A–I$. ( ) denotes data on cooling.

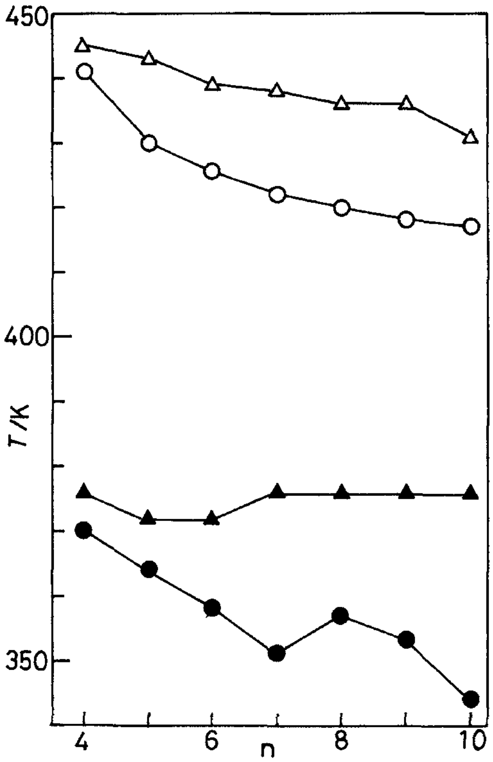

Figure 2. Plots of phase transition temperature versus carbon number, *n*, of the 4′-alkyloxy group for 4-propionyl-4′-*n*-alkyloxybiphenyl derivatives. PA_n: ○, C–S_A; △, S_A–I. α-Br–PA_n: ●, C–S_A; ▲, S_A–I.

benzylideneamino)-benzoyloxy]benzoates [10]. Previously we reported that the α-halo-substitution largely decreases the mesogenicity of a cholesteryl *n*-propionate [11]. Moreover we determined the structure of a cholesteryl ω-monohydrofluoropentanoate crystal by X-ray diffraction [12]. The ω-monohydrofluoroalkanoate group was found to bend from the molecular axis by a *gauche* transformation around the C_α–C_β bond, which causes the big decrease in the thermal stability of the mesophase. In mesomorphic compounds having a carbonyl group as the terminal group, it seems to be a general rule that bulky substituents at the α-position markedly decrease the mesogenicity.

As the length of the alkyloxy group (*n*) increases, the values of T_{S_EI} gradually decrease for AA_n homologues, while in the α-halo–AA_n homologues, T_{S_AI} values gradually increase and approach towards the values of T_{S_EI} for the AA_n series, as seen in figure 1. For the α-Cl–AA_n homologues, T_{S_AI} the values almost reach the T_{S_EI} values of the AA_n series, when *n* is 10. These results suggest that the long 4′-alkyloxy group compensates for the steric contribution of the halogen atom in the 4-haloacetyl group to the mesogenicity. However, this effect by the 4′-alkyloxy group appears to be relatively small for the α-Br–PA_n series (see figure 2).

Phase transition parameters of the α-Br–α-Cl–AA_n homologues are also listed in table 2. The dihalo-substitutions of the acetyl groups decrease the mesogenicity much more, as can easily be understood.

Table 2. Phase transition temperatures (K) and entropy changes (J K^{-1} mol^{-1}) of 4-alkanoyl-4′-*n*-alkyloxybiphenyl homologues.

Sample	*n*	*C*		S_E		S_A		I
AA_n	3	●	—		—		390/75	●
	4	●	370/27	●	—		417/42	●
	5	●	361/61	●	—		412/42	●
	6	●	364/64	●	—		410/43	●
	7	●	372/89	●	—		409/53	●
	8	●	367/82	●	—		407/38	●
	9	●	377/104	●	—		407/43	●
	10	●	377/107	●	—		405/47	●
α-Br–AA_n	3	●	—		—		390/72	●
	4	●	380/71	●	—		(379/37)	●
	5	●	366/44	●	—		374/38	●
	6	●	352/49	●	371/20	●	377/15	●
	7	●	369/105	●	365/16	●	377/13	●
	8	●	353/67	●	368/18	●	380/16	●
	9	●	368/92	●	373/21	●	389/16	●
	10	●	364/93	●	371/19	●	389/17	●
α-Cl–AA_n	4	●	388/64	●	—		(383/35)	●
	5	●	371/74	●	(345/)	●	(376/)	●
	6	●	360/53	●	380/22	●	389/9	●
	7	●	366/75	●	379/21	●	395/11	●
	8	●	361/75	●	378/20	●	399/12	●
	9	●	368/97	●	375/19	●	399/14	●
	10	●	362/113	●	374/21	●	401/15	●
α-Br–α-Cl–AA_n	7	●	—		368/145	●	(329/)	●
	8	●	—		341/36	●	344/61	●
	9	●	—		341/34	●	351/122	●
	10	●	—		338/41	●	339/79	●
PA_n	4	●	—		441/21	●	445/23	●
	5	●	—		430/18	●	443/26	●
	6	●	—		423/18	●	438/25	●
	7	●	—		422/18	●	438/25	●
	8	●	—		420/19	●	436/26	●
	9	●	—		418/18	●	433/26	●
	10	●	—		417/19	●	431/27	●
α-Br–PA_n	4	●	—		370/55	●	376/22	●
	5	●	—		364/53	●	372/20	●
	6	●	—		358/54	●	372/20	●
	7	●	—		351/80	●	376/22	●
	8	●	—		357/54	●	376/16	●
	9	●	—		353/86	●	376/22	●
	10	●	—		344/87	●	376/24	●

C, S_E, S_A and I denote crystalline, smectic E, smectic A and isotropic liquid phases, respectively. ( ) denotes monotropic transition.

3.2. *Phase transition of 4-pentanoyl-4′-decyloxybiphenyl derivatives* (*PD derivatives*)

Table 3 shows phase transition parameters of the PD derivatives. The substitution of Br/Me at the α-position of the 4-pentanoyl group clearly decreases the mesogenicity. The mesomorphic phase transitions of Me–PD compounds are very interesting. Figure 3 shows plots of mesomorphic phase transition temperatures versus the position of methyl-substitution, where ω denotes the unsubstituted *n*-pentanoyl group. Both the values of T_{S_AI} and T_{CS_A} decrease more, as the methyl-substituted position in the pentanoyl group approaches the C=O group, i.e. in the order ω→γ→β→α. The α-methyl-substitution reduces the thermal stability of the S_A phase more than that by α-Br-substitution (see table 3). This phenomenon might be caused by a difference in polarity between the methyl and Br substituents; in the S_A phase, a lateral intermolecular interaction may be strengthened by the polar Br substituent but may be weakened by the non-polar methyl substituent. The methyl-substitution of the α-Br–PD derivatives also depends on the substitution position; the melting point (T_m) is lower in the order of ω→γ→β→α but all α-Br–Me–PD compounds show no enantiotropic mesophase.

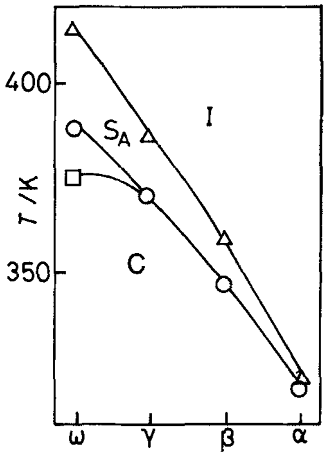

Figure 3. The change of phase transition temperature versus the position of methyl-substitution of the pentanoyl group for 4-pentanoyl-4′-*n*-decycloxybiphenyl. ω denotes PD and □ T_{CS_E} (see table 3).

Table 3. Phase transition temperatures (K) and entropy changes (JK^{-1} mol^{-1}) of 4-pentanoyl-4′-*n*-dodecyloxybiphenyl derivatives.

Sample	C		S_A		I
PD	●	†		414/29	●
α-Me–PD	●	320/100	●	322/19	●
β-Me–PD	●	347/108	●	359/25	●
γ-Me–PD	●	371/99	●	386/21	●
α-Br–PD	●	368/100	●	(351/21)	●
α-Br–α-Me–PD	●	—		318/140	●
α-Br–β-Me–PD	●	—		351/93	●
α-Br–γ-Me–PD	●	—		361/106	●

C, S_A and I denote crystalline, smectic A and isotropic liquid phases, respectively. ( ) denotes monotropic transition.

† PD showed C 375 K S_E 378 K S 388 K S_A 414 K I phase transitions.

4. Conclusion

The 4-alkanoyl-4′-alkyloxybiphenyl derivatives show smectic E or A phases with good thermal stability. Halo- or methyl-substitution of the *n*-alkanoyl group decreases the thermal stability. The magnitude of the decrease depends on the position of the substitution; especially α-substitution markedly decreases the thermal stability.

References

[1] Yoshisawa, A., Nishiyama, I., Furukawa, M., Hirai, T., and Yamane, M., 1989, *Jap. J. appl. Phys.*, **28**, L1269.

[2] Nishijima, I., Yoshisawa, A., Furukawa, M., and Hirai, T., 1989, *Jap. J. appl. Phys.*, **28**, L2248.

[3] Kobayashi, S., Ishibashi, S., and Tsuru, S., 1990, *Molec. Crystals liq. Crystals Lett.*, **7**, 105.

[4] Mcphee, W. D., and Kingsberg, E., 1963, *Org. Synth.*, **4**, 900.

[5] Farona, M. F., and White, J. F., 1971, *J. Am. chem. Soc.*, **93**, 2826.

[6] Helfrich, B. and Schaefer, W., 1941, *Org. Synth.*, **1**, 147.

[7] Thayer, K. F., 1941, *Org. Synth.* **1**, 12.

[8] Fusan, R. C., and Walker, J. T., 1943, *Org. Synth.*, **2**, 169.

[9] Gray, G. W., and Harrison, K. J., 1971, *Molec. Crystals liq. Crystals*, **13**, 37.

[10] Matsunaga, Y., and Miyajima, N., 1990, *Molec. Crystals liq. Crystals*, **178**, 157.

[11] Yano, S., Nabata, Y., and Aoki, K., 1981, *Molec. Crystals liq. Crystals*, **70**, 163.

[12] Sato, T., and Yano, S., 1987, *Molec. Crystals liq. Crystals*, **144**, 179.