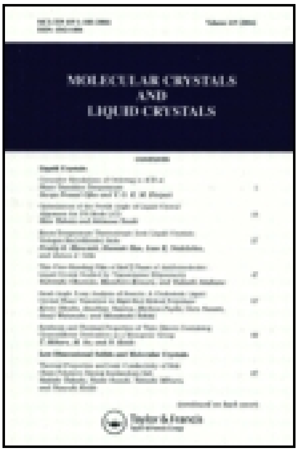

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The Synthesis and Liquid Crystal Properties of Certain 5,5″-Disubstituted 2,2′:5′,2″-Terthienyls

D. J. Byron [a], A. S. Matharu [a], R. C. Wilson [a] & G. Wright [a]

[a] Department of Chemistry and Physics, The Nottingham Trent University, Clifton Lane, Nottingham, NG11 8NS

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The Synthesis and Liquid Crystal Properties of Certain 5,5″-Disubstituted 2,2′:5′,2″-Terthienyls

D. J. BYRON, A. S. MATHARU*, R. C. WILSON and G. WRIGHT

Department of Chemistry and Physics, The Nottingham Trent University, Clifton Lane, Nottingham, NG11 8NS

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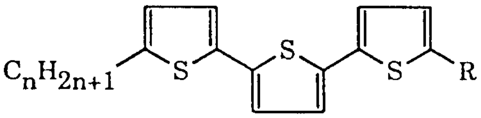
A preliminary account of the synthesis and liquid crystal properties of representative members of an homologous series of 5-alkanoyl-5″-alkyl-2,2′:5′,2″-terthienyls and the analogous 5,5″-di-alkyl-2,2′:5′,2″-terthienyls is given. The disposition of the three thiophene rings renders the molecular geometry sufficiently anisotropic that suitably substituted compounds are mesomorphic, and the liquid crystal transition temperatures of corresponding members of the two series are compared. The related 5,5′-disubstituted 2,2′-bithienyl derivatives are not mesomorphic.

INTRODUCTION

There is considerable interest in the liquid crystal properties of disubstituted thiophenes and bithienyls.[1–4] The mesogenic properties of these compounds are dependent on the geometrical anisotropy of the system which is determined by the relative disposition of the substituents and of the thiophene rings with respect to each other.

Here we report the results of preliminary work on analogous terthienyls, namely the synthesis and liquid crystalline properties of corresponding members of the homologous series of 5-alkanoyl-5″-alkyl-(**1**) and 5,5″-di-alkyl-2,2′:5′,2″-terthienyls (**2**).



R = $CO.C_mH_{2m+1}$ (1); C_nH_{2n+1} (2)

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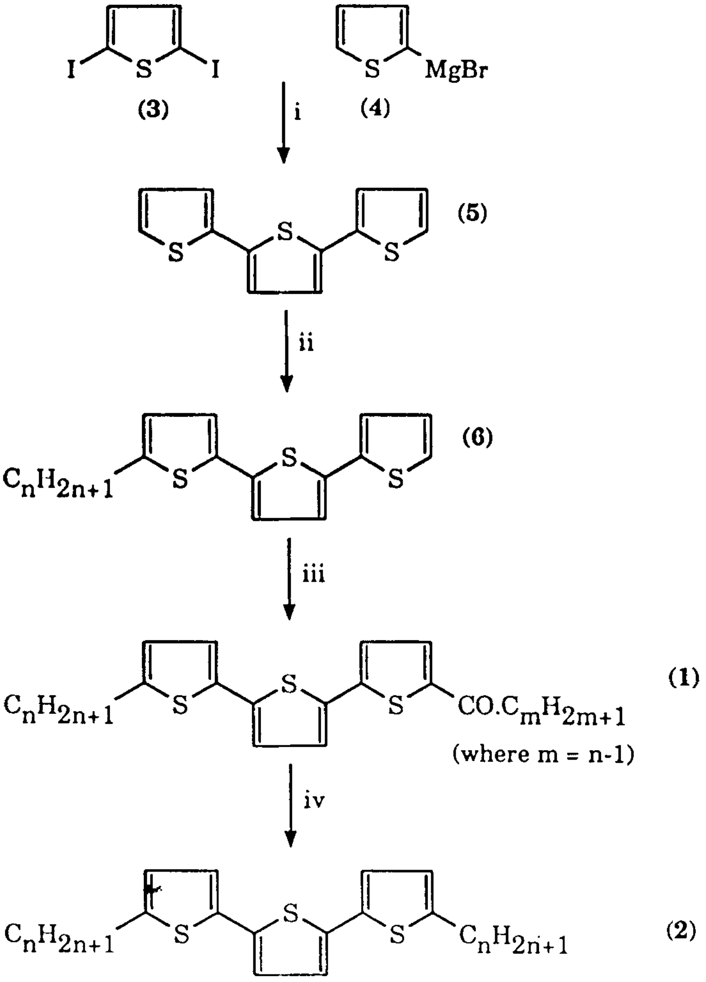
* Author for correspondence.



i. $[(C_6H_5)_2PCH_2CH_2CH_2P(C_6H_5)_2]NiCl_2$, ether, reflux.
ii. a. and iii. RCOCl, $TiCl_4$, CH_2Cl_2;
ii. b. and iv. $NH_2NH_2.H_2O$, KOH, diethylene glycol.

SCHEME 1

SYNTHESIS

The method of preparation of members ($n = 3 - 10$) of series (**1**) and the analogous members of series (**2**) is outlined in Scheme 1.

The Nickel-catalysed cross-coupling reaction[5] between 2, 5-diiodothiophene (**3**) and the Grignard reagent (**4**), derived from 2-bromothiophene, afforded 2,2′:5′,2″-terthienyl (**5**) in moderate yield. Friedel-Crafts acylation of compound (**5**) followed by Wolff-Kishner (Huang-Minlon) reduction of the resulting ketones gave the intermediate 5-alkyl-2,2′:5′,2″-terthienyls (**6**), and Friedel-Crafts acylation of the compounds (**6**) with the appropriate acid chloride then afforded the 5-alkanoyl-5″-alkyl-2,2′:5′,2″-terthienyls (**1**). Subsequent reduction of members of series (**1**) gave the corresponding 5,5″-di-alkyl-2,2′:5′,2″-terthienyls (**2**).

Structural confirmation of the identity of intermediates and final products was obtained by standard techniques. I.r. spectra were recorded for KBr discs with a Perkin-Elmer FT 1605 spectrophotometer and ^{1}H n.m.r. spectra were measured for solutions, in $CDCl_3$ with tetramethylsilane as internal standard with a JEOL FX60Q 270 MHz spectrometer. In each case the recorded spectra were consistent with the proposed structures.

RESULTS AND DISCUSSION

The disposition of the three thiophene rings of 2,2′:5′,2″-terthienyl (in the alternating 'up-down' manner shown in the text) is such that when suitable 5-and 5″-substituents are present the molecular geometry is sufficiently anisotropic to sustain mesomorphic behaviour. This is confirmed by our present studies of three members of the 5-alkanoyl-5″-alkyl-2,2′:5′,2″-terthienyls (**1**) and three members of the corresponding 5,5″-di-alkyl-2,2′:5′,2″-terthienyls (**2**). Thermodynamic data (determined with a Perkin-Elmer DSC7 instrument) for members ($n = 5, 7, 9$) of series (**1**) and (**2**) are listed in Tables I and II, respectively. Mesophases were identified and transition temperatures were determined by thermal optical microscopy.

All the members of series (**1**) are liquid crystalline: they exhibit either an S_A phase ($n = 5$), or both S_A and S_C phases ($n = 7, 9$). Reduction of the carbonyl group of members of series (**1**) results in a lowering of the melting point of the corresponding members of

TABLE I

Liquid crystal transition temperatures and enthalpies of transition for certain homologues ($n = 5, 7, 9$) of 5-alkanoyl-5″-alkyl-2,2′:5′,2″-terthienyls (**1**)[a]

n	m	C-S_C	C-S_A	S_C-S_A	S_C/S_A-I
5	4	–	137.2	–	163.0
			(15.57)		(6.36)
7	6	132.0	–	138.9	161.8
		(30.29)		(–)[b]	(12.22)
9	8	129.4	–	154.2	158.7
		(34.04)		(–)[b]	(13.12)

[a] For each compound the first row gives transition temperatures (°C) and the second row (in parentheses) gives enthalpies of transition (kJ mol^{-1}) on heating (DSC scan rate 10°C min^{-1}).

[b] The enthalpy of the second order S_C-S_A transition was too small to be evaluated.

TABLE II

Liquid crystal transition temperatures and enthalpies of transition for certain homologues ($n = 5, 7, 9$) of 5,5″-di-alkyl-2,2′:5′,2″-terthienyls (**2**)[a]

n	C-G	C-S_F	G-S_F	S_F-S_C	G/S_C-I
5	53	–	–	–	77
	(22.07)				(12.37)
7	55	–	78	83	89
	(19.31)		(3.92)	(0.99)	(10.21)
9	–	64	(62)[b]	91	95
		(29.74)	(10.49)[c]	(1.91)	(13.59)

[a] For each compound the first row gives transition temperatures (°C) and the second row (in parentheses) gives enthalpies of transition (kJ mol^{-1}) on heating (DSC scan rate 10°C min^{-1}).

[b] Monotropic transition.

[c] Enthalpy of transition on cooling.

series (**2**). In series (**2**), the lower homologue ($n = 5$) gives rise to a single mesophase which we believe to be a G phase, although the mosaic texture which forms on cooling the isotropic liquid forms *via* atypical, splinter-like lancets which give rise to angular, differently-sized mosaic areas. The higher homologues ($n = 7, 9$) give rise to S_C and S_F phases in addition to the G phase.

We have also investigated the analogous two-ring compounds, the 5,5′-disubstituted 2,2′-bithienyls, and found that they are not liquid crystalline. This is probably due to the molecular geometry being less conducive to mesophase formation when only two rings are present and to lower molecular polarisability of the bithienyl core. Comparison of the terthienyl compounds of series (**2**) with the analogous 4,4″-disubstituted 1,1′:4′,1″-terphenyls[6] shows that the presence of three thiophene rings considerably lowers the melting point (average melting point for members $n = 5, 7, 9$ is 57.3 °C—a reduction of 122.3°C) and mesophase thermal stability (average clearing point for members $n = 5,7,9$ is 87°C—a reduction of 114°C). The lowering of the thermal stability of the terthienyl relative to their terphenyl analogues may be attributed to the significant deviation from linearity within the terthienyl core which interferes with efficient molecular packing in the mesophases.[3]

Further investigation of the mesomorphic properties of 5,5″-disubstituted terthienyls and related three-ring heterocyclic compounds containing the bithienyl unit is in progress and will be reported in a future publication.

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