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Imidazo [2, 1-*b*]-1,3,4-thiadiazoles

A new class of liquid-crystalline compounds†

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A series of new liquid-crystalline compounds called imidazo [2,1-*b*]-1,3,4-thiadiazoles has been synthesized. The new compounds contain alkyl, aryl, trans-alkylcyclohexyl groups in positions 2,6 and lateral Br- and CN-substituents in position 5 of the heterocyclic fragment. The new mesogens normally have a wide mesophase range and a high thermal stability (T_{CI} ~ 300° C). The mesophase type depends significantly on the nature and position of the substituents, in particular the cyclohexane ring. Some chemical, physico-chemical and spectral properties of the new compounds have been investigated. The results are compared with the corresponding characteristics of their aromatic and heterocyclic analogues.

1. Introduction

There are comparatively few works dealing with the investigation and synthesis of substituted imidazo [2,1-*b*]-1,3,4-thiadiazoles. The search of new biologically active compounds and medications has increased interest in these compounds [1, 2]. This practically planar and rigid heteroaromatic system [3] may also exist as a fragment of liquid-crystalline compounds. Because of the availability of four heteroatoms and two condensed heterocycles with different π-conjugation these compounds must have interesting physico-chemical liquid-crystalline properties.

2. Experimental

We have obtained new mesogens, imidazo [2,1-*b*]-1,3,4-thiadiazoles (I) containing alkyl-, trans-alkylcyclohexyl- and aryl-substituents in positions 2 and 6, using thiosemicarbazide, organic acid chlorides and various α-bromoketones [4] as starting materials according to the reaction scheme I.

3. Results

The spectral properties of compounds (I) have been investigated. There is a characteristic valency vibration band of C_5–H in the range 3100–3115 cm^{-1}. In the ^{1}H N.M.R. spectra C_5 protons have a chemical shift in the range 7·3–8·03 ppm and the C_5 atom signal in the ^{13}C N.M.R. spectra is in the 110–108 ppm range. The I.R. and N.M.R. data indicate the aromatic character of the C_5–H bond.

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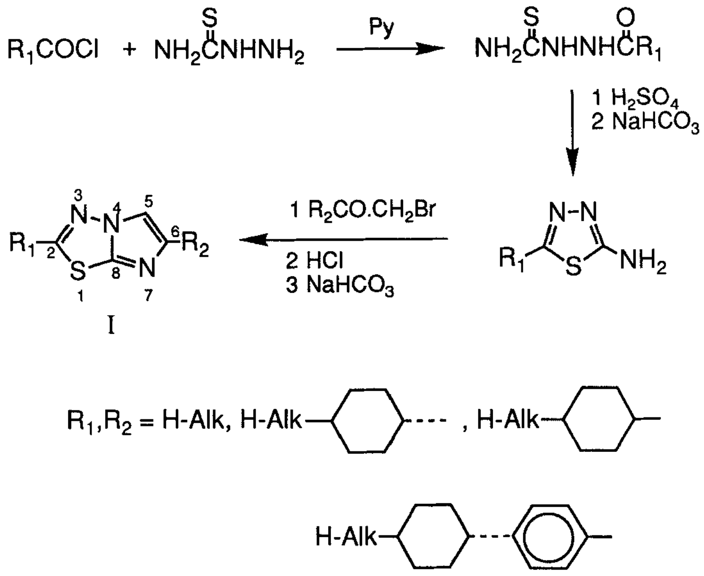
† Presented at the Twelfth International Liquid Crystal Conference, 15–19 August 1988, University of Freiburg F.R. Germany.



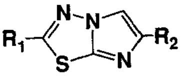
Scheme I.

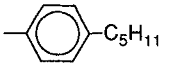
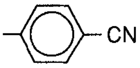
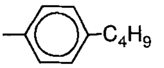
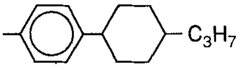
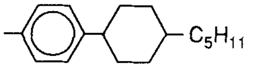
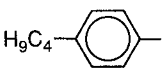
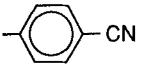
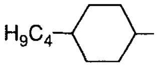
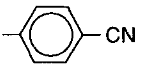
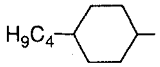
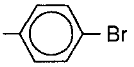
As we expected from the molecular structure, compounds (I) are characterized by relatively high melting points (above 100° C) and a tendency to form smectic phases (see table 1). This obtains because of the availability of four heteroatoms with a non-divided electron pair, molecular polarisation due to the electron displacement from thiadiazoles to the imidazole part, all of which makes strong intermolecular interactions possible.

Alkyl-aryl substituted compounds (see I a,b table 1) are neither mesomorphic nor monotropic; increase of the length of the alkyl substituent results in smectic characteristics (I c) over a narrow temperature range. Addition of one more cyclic fragment (1,4-phenelene or trans-1,4-disubstituted cyclohexylene) leads to the mesophase stability increasing by up to 100° C (compounds I d–o, see tables 1 and 2). The introduction of a phenylcyclohexane fragment causes a still greater increase in the mesomorphic range and in this case decomposition of the compound starts below the clearing temperature (about 300° C, see table 2, compounds I p–u).

The quality and quantity of the modification in the mesomorphic characteristics on the arrangement of the cyclohexane substituent, in the imidazole or thiadiazole part of the heterocylic ring (irrespective of whether the substituent is directly bound to the heterocyclic fragment or is a part of the phenylcyclohexane) is of special interest. Introduction of cyclohexane into the thiadiazole part (R_1) leads to a reduction of the melting points, while the clearing points remain practically the same (compare compounds I l,n with compounds I i,k, compounds I s,t and I p–r). The cyclohexane fragment of the R_2 substituent (the imidazole part of a molecule) causes a smaller change of the melting temperatures, but a greater depression of the clearing temperatures (cf. compounds I m,o and Ii,l). The presence of the alicyclic fragment both in R_1 and R_2 substituents results in a depression of both melting and clearing temperatures (cf. pairs I o–I i–n and I u–I s–t). Introduction of a saturated ring into the imidazole part of the molecule at the same time leads to the occurrence (cf. I m,o) and strong predominance of a nematic phase (cf. I p,q) as compared to analogues

Table 1. Transition temperatures, of the imidazo [2,1-*b*]-1,3,4-thiadiazoles (I a–I h).



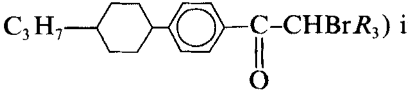
Code	R_1	R_2	
I a	C_5H_{11}		C [89·4°C] S_A C 95·6°C I
I b	C_5H_{11}		C 119·2°C I
I c	C_9H_{19}		C 98·1°C S_A 100·8°C I
I d	C_5H_{11}		C 145°C S_A 153°C N 221°C I
I e	C_2H_5		C 155°C N 220·6°C I
I f			C 157°C S_A 197°C N 274°C I
I g			C 172·5°C N 278°C I
I h			C 149·2°C S_A 229°C N 246·3°C I

containing this fragment in the thiadiazole part (cf. I l, I s–u). This effect may be explained both by electronic factors (the reduced conjugation on replacing the benzene ring with cyclohexane) and geometric factors (the low deviation from planarity in the imidazole part of the molecule [3] is enhanced by the non-planar cyclohexane ring). The 0·3 Å increase of the intermolecular separation in the mesophase (compare X-ray data for compounds I o and I n) could support the geometric interpretation.

Table 3 lists the transition temperatures of the imidazo thiadiazoles and their aromatic and heterocyclic analogues. The data in table 3 show that not only are the melting points of the new liquid-crystalline substances (I) higher than those of the benzene and tetrazine derivatives but their clearing points are also.

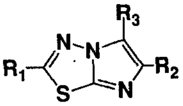
Substituents R_3 (alkyl, II a–e; bromo, III a–e; cyano, IV a–d) were inserted into position 5 of the heterocyclic fragment in order to reduce the melting points and to increase the intermolecular separations, causing the nematic range of the compounds (I). The temperature characteristics of mesogens (II)–(IV) are shown in table 4.

Introduction of a lateral substituent (Scheme I, using aryl-α-bromoalkylketones



$C_3H_7-C_6H_{10}-C_6H_4-\underset{\displaystyle \overset{\|}{O}}{C}-CHBrR_3$) increases the intermolecular separations, causing

Table 2. Dependence of mesomorphic properties of the imidazo [2,1-b]-1,3,4-thiadiazoles on the position of the cyclohexane ring.



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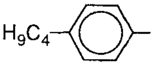
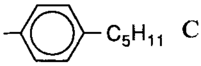
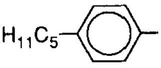
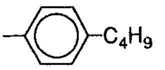
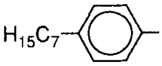
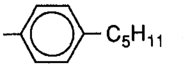
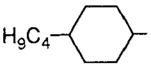
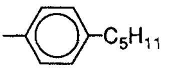
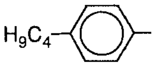
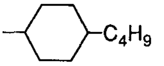
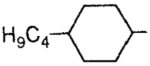
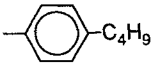
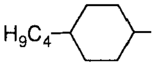
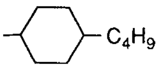
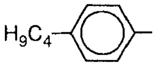
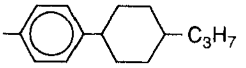
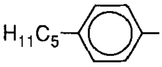
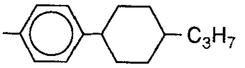
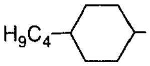
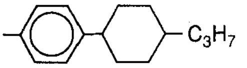
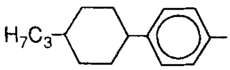
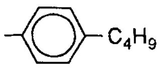
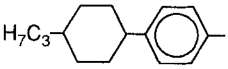
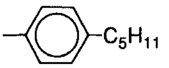
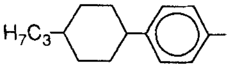
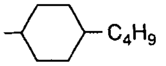
Ii			C 147°C S_A 243·2°C I
Ij			C 140·5°C S_A 240°C N 242·5°C I
Ik			C 113°C N 243°C I
Il			C 102·7°C N 244°C I
Im			C 114·5°C S_A 151·5°C N 195·8°C I
In			C 115°C N 236°C I
Io			C 103°C S_A 164°C N 177·5°C I
Ip			C 209·5°C S_A 212·5°C N 290°C I (decomp)
Iq			C 186·5°C S_A 203·9°C N 298°C I (decomp)
Ir			C 190°C S_A 260°C N 290°C I (decomp)
Is			C 156·6°C N 292°C I (decomp)
It			C 156°C N 298°C I (decomp)
Iu			C 126·5°C N 273°C I

Table 3. Transition temperatures of compounds (I) and their aromatic and heterocyclic analogues

$R_1 - X - R_2$

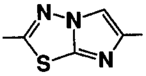
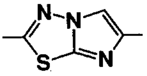
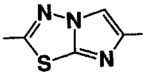
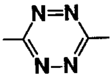
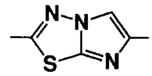
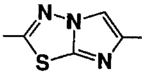
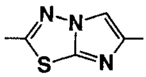
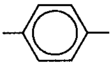
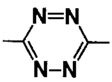
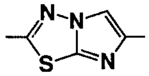
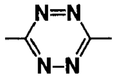
R_1	X	R_2							
C_5H_{11}		C_6H_4CN					C	119°C	I
C_5H_{11}		C_6H_4CN			C	22·5°C	N	35°C	I
C_2H_5		$C_6H_4C_6H_{10}C_5H_{11}$			C	155°C	N	220·6°C	I
C_2H_5		$C_6H_4C_6H_{10}C_5H_{11}$	C	34°C	S_A	146°C	N	164°C	I
C_5H_{11}		$C_6H_4C_6H_{10}C_3H_7$	C	145°C	S_A	153°C	N	221°C	I
†$C_5H_{11}C_6H_{10}$		$C_6H_4C_3H_7$	C	29°C	S_A	160°C	N	170	I
C_5H_{11}		$C_6H_4C_6H_{10}C_3H_7$	C	69°C	S_A	147·5°C	N	170·5°C	I
$C_4H_9C_6H_{10}$		$C_6H_4C_5H_{11}$	C	102·7°C	S_A	244°C	I		
$C_5H_{11}C_6H_{10}$		$C_6H_4C_4H_9$	C	20°C	S_A	160°C	N	170·5°C	I
$C_4H_9C_6H_{10}$		C_6H_4CN					C	278°C (decomp)	I
$C_4H_9C_6H_{10}$		C_6H_4CN			C	120°C	N	202°C	I
$C_4H_9C_6H_{10}$		$C_6H_{10}C_4H_9$	C	103°C	S_A	164°C	N	177·5°C	I
†$C_5H_{11}C_6H_{10}$		$C_6H_{10}C_3H_7$	C	41°C	S_A	156°C	N	160°C	I
$C_4H_9C_6H_{10}$		$C_6H_{10}C_4H_9$	C	56°C	S_A	108°C	N	128°C	I

Table 3 (*continued*).

R_1	X	R_2							
†$C_4H_9C_6H_{10}$		$C_6H_4C_6H_{10}C_3H_7$	C	190°C	S_A	260°C	N	290°C (decomp)	I
$C_5H_{11}C_6H_{10}$		$C_6H_4C_6H_{10}C_3H_7$	C	55°C	S_A	255°C	N	312°C	I
$C_4H_9C_6H_{10}$		$C_6H_4C_6H_{10}C_3H_7$	C	111°C	S_A	178°C	N	270°C (decomp)	I

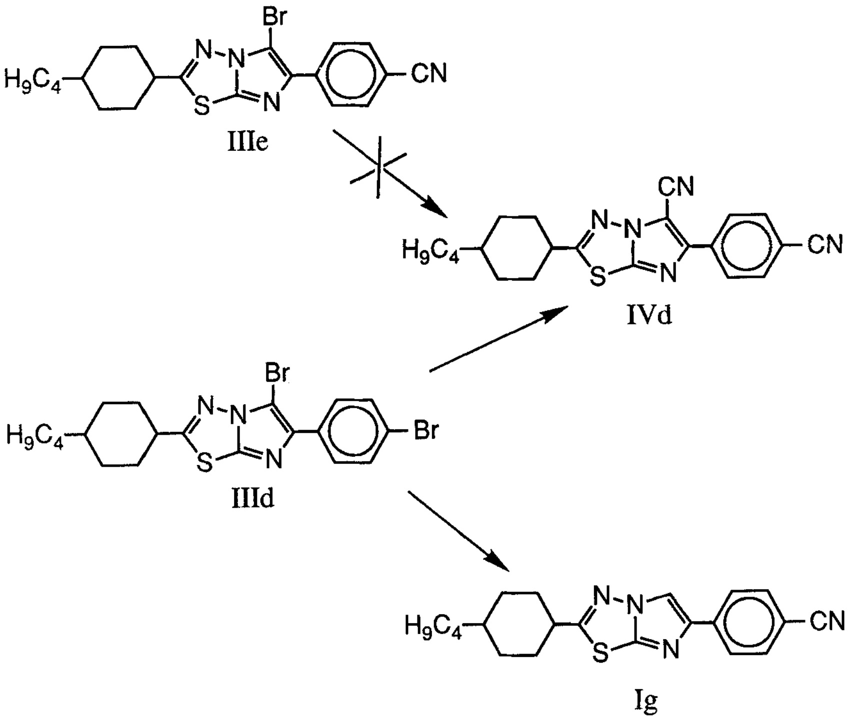
† These compounds were synthesized purposely; data shown here differ from those published formerly [6].

the disappearance of the smectic phase in compounds (II) and a drop in the melting and clearing temperatures. The X-ray data, however, do not show a sharp change in the mesophase structure for compounds (II a,b) except for compound (II c). The existence of a bulky lateral substituent ($R_3 = C_5H_{11}$) accounts for the essential change in the type of the molecular packing for the mesophase. In addition to the reflection corresponding to the medium intermolecular separation of 5·6 Å, compound (II c) also gives one more reflection corresponding to 15 Å. In addition, the repeat distance along the director is significantly lower than for the other members of this series (20 Å instead of the usual 28–29 Å). The low intensity of this reflection indicates a low molecular correlation along the director. Such a diffraction pattern is rather uncommon for a nematic phase.

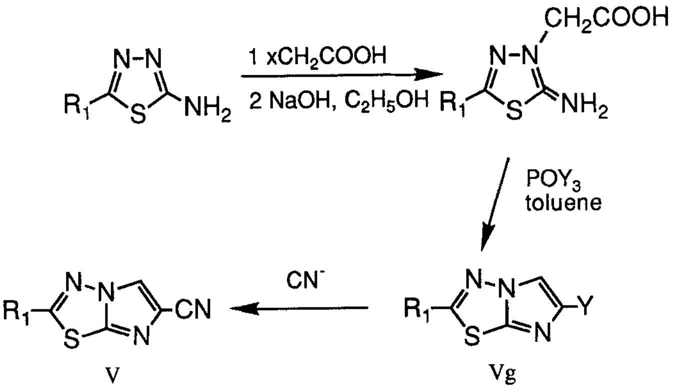
The same variations in the transition temperatures are observed for the imidazo [2, 1-*b*]-1,3,4-thiadiazoles obtained by bromination of compounds (I) in acetic acid (III a–e) and by cyanation of the latter with CuCN(IV a–d). The reactivity of (I) and (III) depends essentially upon the type of R_2 substituent. Compound (III e) (with the electron acceptor benzonitrile R_2 substituent) was obtained only by bromination in boiling acetic acid, but replacement of the halogen by a nitrile group in (III e) using CuCN (in DMF) was not successful.

The dinitrile (IV d) was obtained from the corresponding dibromide (III d) with CuCN in N-methylpyrrolidone according to scheme II. Compound (I g), unsubstituted in position 5, was obtained as a by-product. This was isolated by chromatography and its structure was proved by complete coincidence of its I.R. spectra with those of a control sample. The noted thermal disproportionation is a common feature of high temperature (III a)-type bromides. Calorimetric analysis of such compounds shows that together with the common endothermic signals, the characteristic of phase transitions in the temperature range 185–190° C, a strong exothermic signal occurs with an energy release of 971 kJ/mol which demonstrates the occurrence of a chemical reaction.

The self-polarization of the imidazo [2,1-*b*]-1,3,4-thiadiazole molecule should be evident in the dielectric properties of the liquid crystals. We have also investigated the influence of some substituents on the dielectric properties of compounds (I)–(IV) [9]. We have attempted the synthesis of compounds with the common formula (V), using a new cyclization procedure (see scheme III) in order to investigate the influence of the molecular structure of imidazo [2,1-*b*]-1,3,4-thiadiazole on the dielectric



Scheme II.



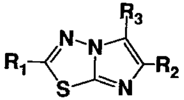
Scheme III.

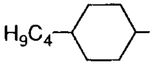
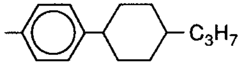
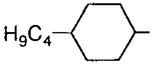
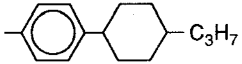
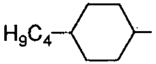
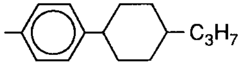
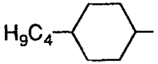
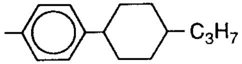
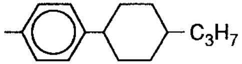
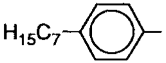
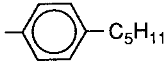
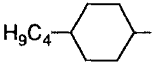
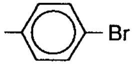
properties. Unfortunately the compounds obtained are not liquid crystals. Dielectric data were measured in mixtures with azoxy compounds within the temperature range, calculated from

$$T_{\mathrm{meas}} = 0{\cdot}95((273/\mathrm{K}) + T_{\mathrm{Cl}}) - (273/\mathrm{K}),$$

where T_{meas} is the temperature of the current experiment and T_{Cl} is the clearing temperature of the mixture. Dielectric data were measured at 1 kHz frequency. The average values of the dielectric anisotropy are shown in table 5.

Table 4. Transition temperature of the imidazo [2,1-b]-1,3,4-thiadiazoles (II)–(IV).



Code	R_1	R_2	R_3							
II a			CH_3			C	166·8°C	N	280°C (decomp)	I
II b			C_2H_5			C	168·5°C	N	285°C (decomp)	I
II c			C_5H_{11}			C	122°C	N	167°C	I
III a			Br	C C C	136·9°C 155·9°C 210–212°C	S_A S_A S_A	245°C	N	287°C (decomp)	I
III b	$H_{11}C_5$—		Br			C	99·5°C	N	159·5°C	I
III c			Br	C	109·6°C	S_A	162·3°C	I		
III d			Br			C	145·7°C	N	167·8°C	I

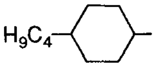
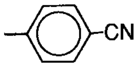
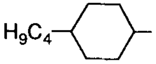
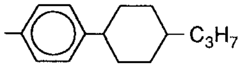
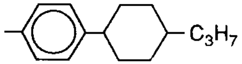
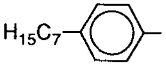
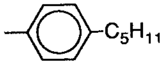
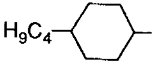
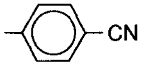
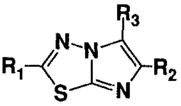
IIIe			Br			C	169·3°C	N	219·9°C	I
IVa			CN	C	121·5°C	S_A	124·7°C	N	292·5°C (decomp)	I
IVb	$H_{11}C_5$—		CN					C	149·5°C	I
IVc			CN			C	117°C	N	141°C	I
IVd			CN	C	(90°C)	S_A	124·3°C	N	138°C	I

Table 5. Average values of $\Delta\varepsilon$ for the imidazo [2,1-*b*]-1,3,4-thiadiazoles.



Code	$\Delta\varepsilon$	Code	$\Delta\varepsilon$
I b	30·9	V f	9·6
I f	36·8	I o	3·2
I g	33·5	I n	2·9
III e	24·8	I e	2·15
IV d	25·05	II b	3·3
III d	8·35	IV a	2·4

The dielectric permittivity anisotropy of (I b) is 30·9. This is much greater than for the carbocyclic analogue such as 4-*n*-pentyl-4′-cyanobiphenyl, having at the same temperature $\Delta\varepsilon$ equal to 11·6. Such a significant increase in $\Delta\varepsilon$ can only be related to the replacement of the aromatic carbocycle by the easily polarized heterocyclic fragment. This, combined with benzonitrile electron-acceptor substituent R_2 results in a major increase in the molecular dipole moment. Inserting the phenyl substituent into the thiadiazole part of the molecule (compound I f) increases the length of the conjugated chain still further, thus increasing the molecular dipole moment and $\Delta\varepsilon$. Compound (I g) is an example of the fact, that the lowering of the polarization anisotropy by replacement of the cyclohexane ring with a phenyl leads to some decrease of the dielectric anisotropy. Inserting a lateral polar substituent (Br, CN) at an angle of 80° to the long molecular axis causes a considerable reduction of $\Delta\varepsilon$ (see compounds III e, IV d). We explain this in terms of a decrease of the longitudinal component of the dipole moment due to the rearrangement of the electron density, as well as by the growth of the perpendicular component of the dipole moment. Changing the nitrile group in compound (IV d) for a less polar substituent (e.g. bromo) causes a considerable reduction of the dielectric anisotropy (III d). As suggested by the structure, the dielectric anisotropy of compound (V) is rather high. For example, for the bromide (V f) $\Delta\varepsilon$ is comparable with that for the cyanobiphenyls.

Thus, using both known and new methods of synthesis, a new class of liquid-crystalline compounds, the imidazo [2,1-*b*]-1,3,4-thiadiazoles, has been obtained. Their transition temperatures, spectra, physico-chemical and chemical properties have been comprehensively investigated.

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