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Mesomorphic Oxadiazoles with Terminal Cl-Substituent

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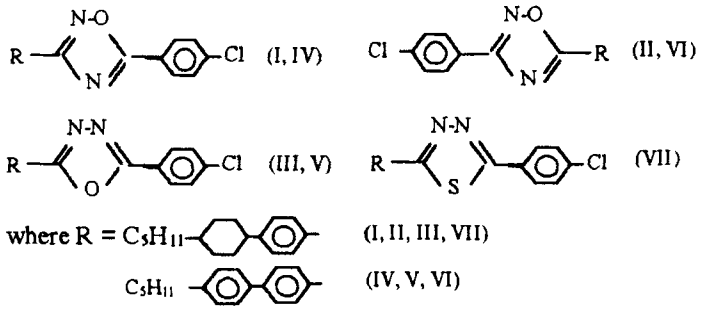
New liquid crystalline oxadiazoles containing terminal Cl-group and phenylcyclohexane fragment together with their biphenyl analogues have been synthesized and investigated by DSC and polarizing microscopy. There is a direct dependence of results obtained on the central heterocyclic structure and the character and position of the substituent related to the asymmetrical heterocyclic unit.

Keywords: oxadiazole; isomer; mesomorphic transition; DSC

INTRODUCTION

Due to the various types of isomerism[1] liquid crystalline oxadiazoles are extremely interesting objects for investigation of interrelations "structure-mesomorphic properties". It was the aim of our previous work concerning liquid crystalline properties of these five-membered heterocycles[1-5]. Now a series of new oxadiazoles (I-VI) with terminal Cl-substituent were synthesized.



The structure of these compounds represents all possible isomeric types. Two types are caused by the different combination of three heteroatoms (1,2,4-oxadiazoles I,II,IV,VI and 1,3,4-oxadiazoles III,VI). If the positions of two different substituents related to the heterocycle are changed there are present two different isomers called reversed structures.

EXPERIMENT

The synthesis of the oxadiazoles (I-VI) was performed by the usual ways described in the papers [2,6].

The transition temperatures were measured using both thermocontrollers Mettler FP-51 and Linkam, a Leitz polarizing microscope connected with a Grundig/Polaroid recording system, and via DSC-method, by means of a Perkin-Elmer apparatus. The enthalpies of phase transitions were determined. The results obtained by both methods are presented in Table 1.

Computer calculations were made by using the program with dynamic allocation of memory version 1.00: AMPAC - IBM PC.

TABLE 1 Microscopy and DSC observations of p-Cl-containing oxadiazoles

N	Microscopy		DSC				Mesophase interval,		
	Phase transition	T, °C	Phase transition	T, °C	H, J/g,	Scan. rate, °C/min	ΔT_{sm}, °C	ΔT_{nem} °C	ΔT, °C
I	C_1-C_2 (?)	102.6	C_1-C_2 (?)	98.28	7.68	5.0	-	118	118
	C_2-N	106.8	C_2-N	107.38	57.58	- " -			
	N-I	222.6	N-I	225.31	0.54	- " -			
II	C-S	89-91	C-S	91.53	52.4	5.0	78	64	142
	S-N	161.9-165	S-N	169.41	0.23	- " -			
	N-I	229.3	N-I	232.95	1.08	- " -			
III	C-S	153.1-154.3	C-S	156.68	37.97	5.0	14	28	42
				160.75	47.90	2.0			
	S-N	173.5	S-N	171.12	0.97	5.0			
				171.04	1.47	2.0			
	N-I	200	N-I	199.21	0.43	5.0			
				199.87	0.49	2.0			

TABLE 1 (continued)

IV	C_1-C_2(?)	89.7-91.5	C_1-C_2(?)	91.15	35.84	5.0	66	61	127
	C_2-S	97.1-100	C_2-S	98.59	63.92	- " -			
	S-N	161.7	S-N	165.06	0.60	- " -			
	N-I	222.8	N-I	226.06	1.68	- " -			
V	C-S_1	118-123	-	-	-	5.0	68	-	68
	S_1-S_2(B?)	133.7-137	-	-	-	5.0			
			C-S_2	136.34	-	1.0			
	S_2-S_3(A?)	140.7-142.5	C-S	140.2	44.13	5.0			
			S_2-S_3	141.53	-	1.0			
	S_3-I	201.3-203	S-I	208.24	7.34	5.0			
				209.2	-	1.0			
VI	C-S	115.5-117	C-S	115.46	46.46	2.0	106	12	118
	S-N	222	S-N	220.77	6.83	- " -			
	N-I	232-233	N-I	233.0	1.5	- " -			

RESULTS AND DISCUSSION

As seen from Table 1 the parameters of the new mesogens obtained by DSC method and polarizing microscopy are mostly similar. Some differences observed could be caused by the following reasons.

1. The high viscosity of the investigated mesogen compounds leads to the dependence of their physical parameters on the scanning rate (compounds III, V). For the compound V possessing the only smectic polymorphism, at higher scanning rates the DSC couldn't detect the transitions between the extremely viscous smectic phases which were observed by the polarizing microscopy. To reveal this kind of transition it is possible to apply the image processing analysis[7, 8], which is particulary useful in conditions where the transition is very smooth, implying only a small texture change inside the mesophase. It will be the subject of our future work.

2. The appreciable thermal decomposition at the temperatures above 220°C also causes some change in the mesomorphic characteristics of oxadiazoles investigated. Therefore the first DSC cooling run and the second heating run for the high temperature transitions are not reproducible.

In some new Cl-containing oxadiazoles (I, IV) DSC showed one additional peak inside the crystal region which can be interpreted either like a crystal-crystal transition or a reorganization of the crystalline form, as discovered earlier in the case of o-Cl- containing isomers[4]. In the cooling run from the isotropic phase such a peak did not appear and it was absent also

in the second heating run as well. This behaviour characterizes this class of heterocyclic mesogens.

As seen from Table 1, both the transition temperatures and the types of mesophase in the new oxadiazoles are determined by the structure of the heterocyclic unit and by the character and position of the substituent in either the oxazolic or the diazolic part as well. The mesogens with a *trans*-1,4-cyclohexylene unit have an obvious, nematogenic character compared with biphenyl analogues (see pairs I-IV, IV-VI, III-V). As it was observed in our previous works[2,3] this nematogenic role is most significant when the unit is located in the position 3 of the 1,2,4-oxadiazolic ring (see pair I-II).

Isomers with asymmetric central heterocyclic unit (I, II, IV, VI) are characterized by the lower melting points and broader temperature interval of the mesophase (120-140°C) than 1,3,4-oxadiazoles (III, IV) (42-68°C). The first ones also demonstrate the predominance of the nematic phase.

The essential difference in the mesomorphic behaviour of 1,2,4- and 1,3,4-oxadiazoles could be connected both with geometric factors (the linearity of the molecules) and also with electronic factors (the polarizability of the whole molecule). However, numerical calculations performed on the molecular models of the isomeric 1,2,4- and 1,3,4-oxadiazoles demonstrate that the difference in their molecular geometry is small. Only 1,3,4-thiadiazole (VII) possesses the most linear molecule due to the atomic radius of sulphur atom which is greater than the oxygen. Therefore the mesophase thermostability (C 120 S 237 N 254 I) is greater then the one of the oxadiazolic analog (III).

The significant role of electronic factors in mesomorphic behaviour was confirmed also by comparison of the pairs with the reversed structures (I-II, IV-VI). The asymmetrical 1,2,4-oxadiazole is a polarized structure with electronic localization on the diazolic C_3-atom of the ring[9]. The electronacceptor substituent at the diazolic C_3-atom participates in the electron delocalization, which is expected to lead to an increase of both the polarizability anisotropy and the mesophase thermostability. In fact we have actually seen these effects by comparing isomers I-II, IV-VI with an electronegative p-chlorophenyl substituent.

CONCLUSION

1. All possible isomeric oxadiazoles with p-chlorophenyl and p-(*trans*-4-amylcyclohexyl)phenyl substituents were synthesized and investigated by microscopy and DSC methods. The enthalpies of their mesomorphic transitions were determined.
2. It was shown again that the mesomorphic behaviour of such types of substances is determined mostly by electronic factors than by geometric ones. The computer models of isomeric oxa- and thiadiazoles were constructed.
3. The additional transitions inside the crystal region observed by DSC in the first heating run and their disappearance in the cooling run and in the second heating run is characteristic of this type of compounds.
4. The difference between DSC and visual data concerning smooth smectic-smectic transitions is caused by the high viscosity of these heterocyclic mesogens and needs an additional investigation by the image processing method.

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