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The oxadiazole as a structural fragment in liquid crystals

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This paper examines in some detail the effect of introducing the oxadiazole fragment into the molecular core of liquid crystals on their physico-chemical properties. The results of this study are compared with those obtained for other molecular fragments, and are rationalized in terms of existing theories.

1. Introduction

The design and synthesis of liquid crystalline 3,5-disubstituted 1,2,4-oxadiazole and 2,5-disubstituted 1,3,4-oxadiazole derivatives have been the subject of considerable research in recent years because of their promising physico-chemical properties [1–14]. Obviously, there is a relationship between the molecular structure of these compounds and their properties. On the other hand, the clear description and understanding of the driving force of these phenomena are still lacking, and for this purpose we present the results of estimating the effect on physico-chemical properties of introducing the 1,2,4-oxadiazole-3,5-diyl and 1,3,4-oxadiazole-2,5-diyl into the molecular core of liquid crystals, and comparing them with results obtained for other well known molecular fragments.

2. Mesomorphic properties

It has been reported that the introduction of 1,3,4-oxadiazole-2,5-diyl into the molecular core of two-ring amino- and nitro-phenyl derivatives produced no mesophase [15]. As can be seen from table 1, inserting 1,2,4-oxadiazole-3,5-diyl in the molecular core of three-ring nitro derivatives shows more pronounced effect on their mesomorphic properties. So far, the introduction of 1,2,4-oxadiazole-3,5-diyl with its oxygen atom pointed toward the nitrophenyl fragment, as a middle ring in the molecular core of three-ring nitro derivatives, gives rise to smectic and nematic phases with moderate thermostabilities (compound **1-1**); in comparison, the corresponding 3,5-disubstituted 1,2,4-oxadiazole derivative with reversed structure (its oxygen atom is pointed toward the pentylphenyl fragment) exhibits higher melting point and smectic thermostability, narrower smectic and nematic ranges, and lower nematic thermostability (compound **1-2**, table 1). These results reveal that the effect on mesomorphic properties depends on the positions of the heteroatoms. The replacement of the pentyl group by the butoxy group in compounds **1-1** and **1-2** to obtain compounds **1-3** and **1-4**, respectively, results in the opposite influence of the positions of the 1,2,4-oxadiazole-3,5-diyl's heteroatoms on mesomorphic properties, with lower nematic thermostability recorded for compound **1-3** (having the oxygen atom of its 1,2,4-oxadiazole-3,5-diyl pointed toward the nitrophenyl fragment) compared with that of compound **1-4** which incorporates the 1,2,4-oxadiazole-3,5-diyl with reversed structure. These results show the importance of terminal substituents. Such an insertion of the 1,3,4-oxadiazole-2,5-diyl into the same molecular core (compound **1-5**, table 1) further increases the crystal–smectic and smectic–isotropic phase transition temperatures and leads to the disappearance of the nematic phase, in comparison with compound **1-4**.

2.1. *System (1) (see the scheme)*

It is convenient to express the effect of introducing the oxadiazole fragments into the molecular core of three-ring nitro (and other) derivatives by the orders (shown

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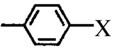
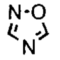
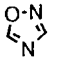
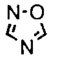
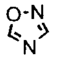
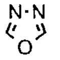
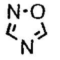
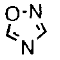
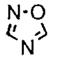
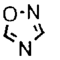
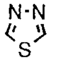
Table 1. Physico-chemical properties of liquid crystals: $H_{2n+1}C_n(O)_k$ –A–BX

Compound No.	*k*	*n*	*A*	*B*	*X*	Phase transitions/°C	$\Delta\varepsilon$[a]	Ref.
1-1	0	5			NO_2	Cr 73 Sm 106 N 119 I	11.5	[2]
1-2	0	5			NO_2	Cr 100 Sm 114 N 117 I	17.6	[2]
1-3	1	4			NO_2	Cr 106 N 116 I		[2]
1-4	1	4			NO_2	Cr 140 Sm 142 N 150 I		[2]
1-5	1	4			NO_2	Cr 165 Sm 175 I		[4]
1-6	1	4			NO_2	Cr 139 Sm 168 I		[4]
1-7	0	4			NO_2	Cr 91 I	3.7	[2]
1-8	0	4			NO_2	Cr 71 N (70) I	6.7	[2]
1-9	0	4			CN	Cr 100 N (99) I	5.8	[1]
1-10	0	4			CN	Cr 114 N (93) I	10.4	[1]
1-11	0	4			CN	Cr 132 N 202 I		[16]
1-12	0	4			CN	Cr 124 N 228 I		[17]

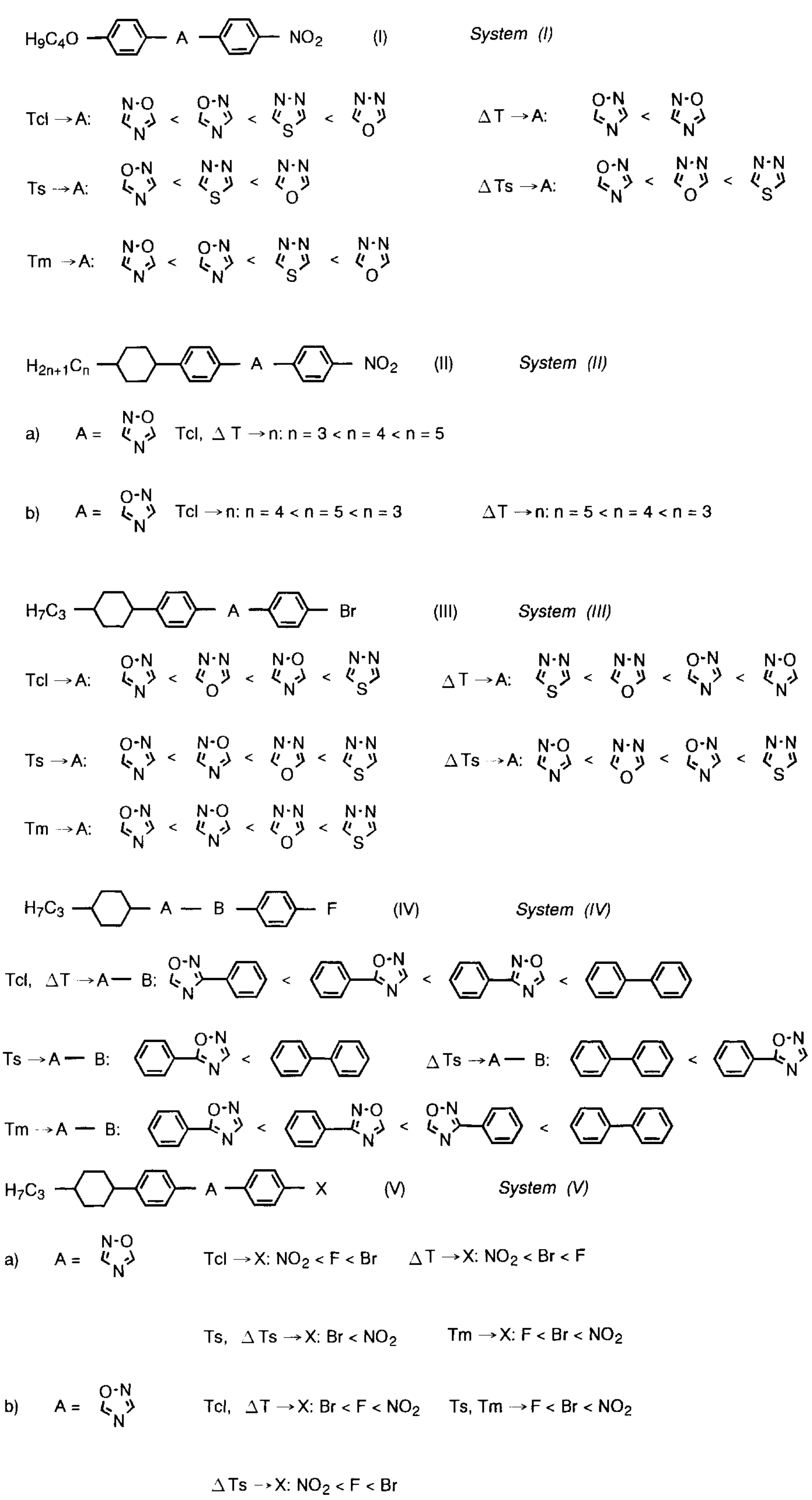
[a] Extrapolated from the 5 wt % solution in a mixture of cyano derivatives at 20°C.

in the scheme) of increasing clearing temperatures (T_{cl}) (nematic–isotropic or smectic–isotropic), nematic ranges (ΔT), smectic thermostabilities (T_s) (smectic–nematic or smectic–isotropic), smectic ranges (ΔT_s), and melting temperatures (T_m) (crystal–nematic or crystal–smectic) depending on the fragment *A* (compounds **1-3–1-6**, table 1).

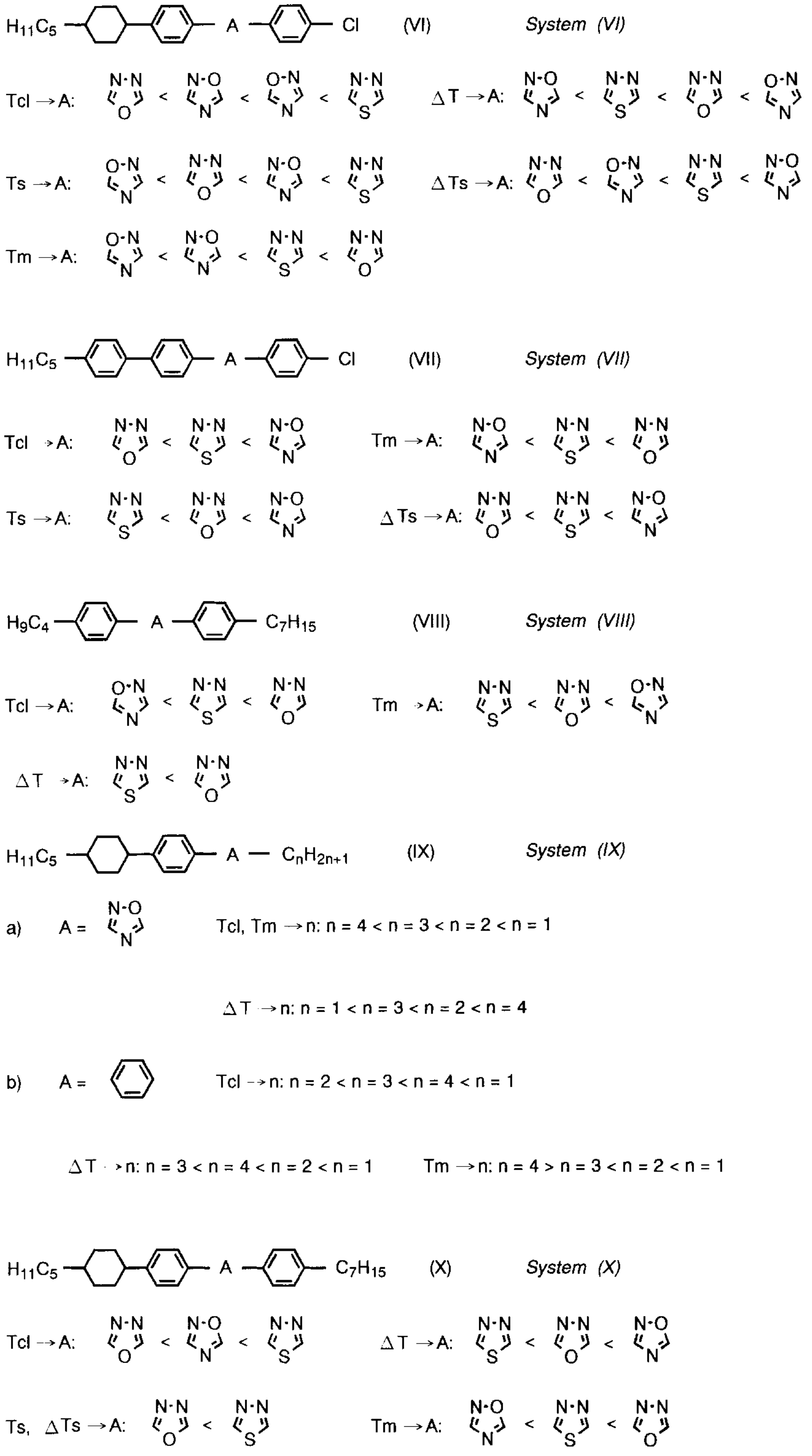
The above results and the thermal data presented in table 1 show that the introduction of the 1,3,4-oxadiazole-2,5-diyl into the molecular core of the system (I) produces liquid crystals with the highest clearing (smectic thermostability) and melting points, while inserting the 1,2,4-oxadiazole-3,5-diyl with its oxygen atom pointed toward the nitrophenyl fragment, gives liquid crystals exhibiting only the nematic phase and with the lowest clearing and melting points among the compounds of system (I). The introduction of the 1,2,4-oxadiazole-3,5-diyl with reversed structure (its oxygen atom pointing toward the butoxyphenyl fragment) results in the lowest smectic thermostability and narrowest smectic and nematic ranges. Thus the effect of introducing the oxadiazole fragment into the molecular core of three-ring nitro derivatives depends on the positions of the oxadiazole's heteroatoms.

The replacement of the 1,4-phenylene by the *trans*-1,4-cyclohexylene, and the butoxy group by the butyl group in compounds **1-3** and **1-4**, to obtain compounds **1-7** and **1-8**, respectively, leads to a less pronounced effect of introducing the 1,2,4-oxadiazole-3,5-diyl in these compounds. These changes result in the disappearance of the mesophase in compound **1-7**, having the oxygen atom of its 1,2,4-oxadiazole-3,5-diyl pointing toward the nitrophenyl fragment, and the creation of the monotropic nematic phase with decreased melting point in compound **1-8** which incorporates the 1,2,4-oxadiazole-3,5-diyl with reversed structure.

The corresponding cyano derivatives show the opposite influence of the positions of their 1,2,4-oxadiazole-3,5-diyl's heteroatoms; higher monotropic nematic efficiency and lower melting temperature are observed for



Scheme. List of structural systems.



Scheme. (*continued*).

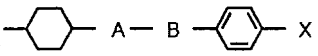
compound **1-9** (having the oxygen atom of its 1,2,4-oxadiazole-3,5-diyl pointing toward the cyanophenyl fragment) compared with those of compound **1-10** (possessing the 1,2,4-oxadiazole-3,5-diyl with reversed structure). These results again demonstrate the importance of the structure of the terminal substituents. As can be seen from table 1, the corresponding other 5- and 6-membered ring cyano derivatives (compounds **1-11**, **1-12**) exhibit significantly higher nematic thermostabilities and increased melting temperatures in comparison with those of the 1,2,4-oxadiazole-3,5-diyl cyano derivatives **1-9** and **1-10**. Similarly decreased nematic thermostabilities have been found for four-ring 1,2,4-oxadiazole-3,5-diyl cyano derivatives, compared with those of the corresponding four-ring pyrimidine-2,5-diyl and pyridine-2,5-diyl cyano derivatives (compounds **2-9** and **2-10**, **2-11** and **2-12**, table 2). For the melting points of the 1,2,4-oxadiazole-3,5-diyl cyano derivatives, both a decrease (compounds **2-9** and **2-10**) and an increase (compounds **2-11** and **2-12**) were recorded.

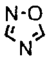
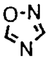
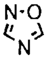
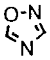
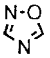
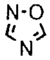
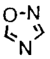
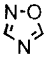
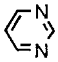
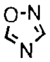
2.2 *System (II)*

The thermal data presented in table 2 reveal that the effect of introducing the 1,2,4-oxadiazole-3,5-diyl into the molecular core of four-ring nitro derivatives depends on their alkyl chain length. Among the propyl and butyl derivatives, the lower clearing points are observed for compounds having the 1,2,4–oxadiazole-3,5-diyl's oxygen atom pointed toward the nitrophenyl fragment, in comparison with those of the corresponding derivatives incorporating the 1,2,4-oxadiazole-3,5-diyl with reversed structure (compounds **2-1** and **2-2**, **2-3** and **2-4**). For the pentyl derivatives the opposite situation is found (compounds **2-5** and **2-6**). In other words, the positions of the 1,2,4-oxadiazole-3,5-diyl's heteroatoms inserted in the molecular core of four-ring nitro derivatives (compounds **2-1–2-6**) influence their odd–even effect (see the scheme).

In the case of smectic thermostability, lower values are recorded for the butyl and pentyl derivatives having the 1,2,4–oxadiazole-3,5-diyl's oxygen atom pointed toward the nitrophenyl fragment, than for those of the corresponding derivatives with reversed structure (compounds **2-3** and **2-4**, **2-5** and **2-6**). For the propyl derivatives the opposite situation is found (compounds **2-1** and **2-2**). Interestingly, the melting temperatures are lower for compounds of system (II) having the 1,2,4-oxadiazole-3,5-diyl's oxygen atom pointed toward

Table 2. Physico-chemical properties of liquid crystals: $H_{2n+1}C_n$



Compound No.	*n*	*A*	*B*	*X*	Phase transitions/°C	$\Delta\varepsilon^a$	Ref.
2-1	3			NO_2	Cr 115 Sm 140 N 204 I	9.7	[2]
2-2	3			NO_2	Cr 122 Sm 125 N 258 I	12.5	[2]
2-3	4			NO_2	Cr 126 Sm 148 N 222 I		[2]
2-4	4			NO_2	Cr 129 Sm 153 N 244 I		[2]
2-5	5			NO_2	Cr 119 Sm 169 N 256 I		[2]
2-6	5			NO_2	Cr 121 Sm 176 N 247 I		[2]
2-7	5			NO_2	Cr 138 Sm 236 I	6.1	[2]
2-8	5			NO_2	Cr 140 Sm 230 N 244 I	13.1	[2]
2-9	5			CN	Cr 172 N 252 I		[1]
2-10	5			CN	Cr 187.3 N> 360 I		[18]
2-11	3			CN	Cr 170 Sm 180 N 255 I		[1]
2-12	3			CN	Cr< 30 Sm> 300 I		[19]

[a] Extrapolated from the 5 wt % solution in a mixture of cyano derivatives at 20°C.

the nitrophenyl fragment than for the corresponding derivatives with the reversed structure (compounds **2-1** and **2-2**, **2-3** and **2-4**, **2-5** and **2-6**).

Replacing the 1,4-phenylene by the *trans*-1,4-cyclohexylene in compounds **2-5** and **2-6** to obtain compounds **2-7** and **2-8**, respectively, changes the dependence of the clearing points and smectic thermostabilities on the positions of the 1,2,4-oxadiazole-3,5-diyl's heteroatoms and keeps the same dependence of the melting points (compounds **2-5** and **2-6**, **2-7** and **2-8**, table 2). These results show that the effect of introducing the 1,2,4-oxadiazole-3,5-diyl into the molecular cores of four-ring nitro derivatives depends on their structures.

It has been shown that insertion of the 1,2,4-oxadiazole-3,5-diyl into the molecular core of a two-ring perfluorobutylphenyl derivative produced no mesophase [1]. The introduction of this fragment into the molecular core of three- and four-ring derivatives having halogenated terminal substituents shows the more pronounced effect on their mesomorphic properties recorded in tables 3, 4 and 6. As can be seen from table 3, introducing the 1,2,4-oxadiazole-3,5-diyl into the molecular core of three-ring derivatives having halogenated terminal substituents, results in the creation of the monotropic nematic phase (compounds **3-1** and **3-2**; **3-5** and **3-6**; **3-10**) or disappearance of the mesophase (compounds **3-3** and **3-4**, **3-7** and **3-8**; **3-9** and **3-11**). It also results in decreased melting points (compounds **3-1** and **3-2**, **3-3** and **3-4**, **3-5** and **3-6**, **3-7** and **3-8**) compared with those of the corresponding other 6-membered ring derivatives. Among three-ring derivatives having halogenated terminal groups presented in tables 3 and 6, only the 3,5-disubstituted 1,2,4-oxadiazole derivative incorporating the terminal perfluorobutyl group exhibits the enantiotropic narrow nematic and wide smectic phases, possibly due to the enhanced ability of the perfluoroalkyl derivatives to form smectic phases compared with that of the corresponding alkyl derivatives (compounds **6-7** and **6-10**, table 6, see also [27]).

From comparison of the phase transition temperatures of compounds **1-3–1-5** and **3-9–3-11** having the nitro and bromo terminal groups (tables 1 and 3), respectively, we can see the different dependences of their mesomorphic properties on the positions of the oxadiazole's heteroatoms, resulting in the highest clearing points recorded for the 2,5-disubstituted 1,3,4-oxadiazole

Table 3. Mesomorphic properties of liquid crystals: $H_{2n+1}C_n(0)_k$–A–B––X

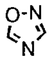
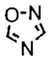
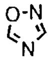
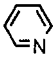
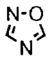
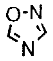
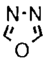
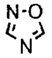
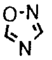
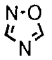
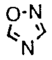
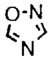
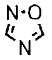
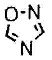
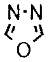
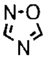
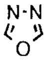
Compound No.	*n*	*k*	*A*	*B*	*X*	Phase transitions/°C	Ref.
3-1	3	0			$OCHF_2$	Cr 53 N (44) I	[1]
3-2	3	0			$OCHF_2$	Cr 82 Sm 121.1 N 169.4 I	[20]
3-3	3	0			F	Cr 91 I	[1]
3-4	3	0			F	Cr 98.3 N 153.4 I	[21]
3-5	5	0			F	Cr 53 N (42) I	[1]
3-6	5	0			F	Cr 100 N 153 I	[22]
3-7	5	0			F	Cr 60 I	[1]
3-8	5	0			F	Cr 150 Sm (126) I	[17]
3-9	4	1			Br	Cr 143 I	[4]
3-10	4	1			Br	Cr 125 N (100) I	[2]
3-11	4	1			Br	Cr 130 I	[4]

Table 4. Mesomorphic properties of liquid crystals: $H_{2n+1}C_n$–A–B–K––X

Compound No.	*n*	*A*	*B*	*K*	*X*	Phase transitions/°C	Ref.
4-1	3				Br	Cr 110 Sm 120 N 228 I	[1]
4-2	3				Br	Cr 85 Sm 117 N 180 I	[1]
4-3	3				Br	Cr 122 Sm 152 N 214 I	[5]
4-4	3				Br	Cr 140 Sm 185 N 245 I	[5]
4-5	3				F	Cr 90 N 210 I	[3]
4-6	3				F	Cr 75 Sm 100 N 200 I	[3]
4-7	3				F	Cr 102 N 199.5 I	[1]
4-8	3				F	Cr 140 SmA 147 N 301 I	[23]
4-9	5				Cl	Cr 105 Sm 225 N 228 I	[4]
4-10	5				Cl	Cr 90 Sm 169 N 232 I	[4]
4-11	5				Cl	Cr 157 Sm 170 N 200 I	[4]
4-12	5				Cl	Cr 120 Sm 237 N 254 I	[4]
4-13	5				Cl	Cr 91 Sm 226 I	[4]
4-14	5				Cl	Cr 141 Sm 204 I	[4]
4-15	5				Cl	Cr 115 Sm 190 N 210 I	[4]

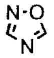
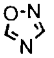
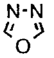
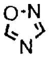
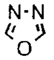
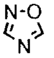
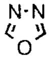
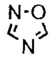
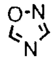
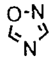
nitro derivative **1-5** (among compounds **1-3–1-5**) and 3,5-disubstituted 1,2,4-oxadiazole bromo derivative **3-10** (among compounds **3-9–3-11**). These again show the importance of the terminal substituents.

2.3. *System (III)*

As expected, the introduction of the oxadiazole fragment into the molecular core of four-ring halogeno-substituted derivatives presented in table 4 gives a more pronounced effect on phase transition temperatures, compared with the corresponding three-ring derivatives. For bromo derivatives it can be expressed by the following orders of thermal efficiency (compounds **4-1–4-4**, table 4).

These results reveal that the introduction of the 1,2,4-oxadiazole-3,5-diyl with its oxygen atom pointed toward the bromophenyl fragment, into the molecular core of system (III), results in the formation of liquid crystals exhibiting moderate melting and clearing points, smectic thermostability, broadest nematic and narrowest smectic ranges. Inserting the 1,2,4-oxadiazole-3,5-diyl with reversed structure gives liquid crystals with the lowest melting and clearing points, and lowest smectic thermostability among the compounds of system (III). Introduction of the 1,3,4-oxadiazole-2,5-diyl into the same molecular core creates the smectic phase with increased thermostability and moderate range, and leads to the formation of the nematic phase with moderate

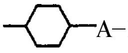
Table 5. Mesomorphic properties of liquid crystals: $H_{2n+1}C_n(O)_p$–A–B–K–$(O)_tC_mH_{2m+1}$

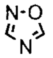
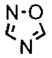
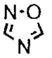
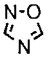
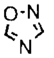
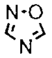
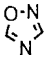
Compound No.	*n*	*p*	*A*	*B*	*K*	*t*	*m*	Phase transitions/°C	Ref.
5-1	6	1			—	0	9	Cr 37.7 N 38.1 I	[1]
5-2	6	1			—	0	9	Cr 33 SmB 64 SmC 81.5 I	[24]
5-3	4	1				1	7	Cr 93 N (84) I	[2]
5-4	4	1				0	7	Cr 92 N (83) I	[4]
5-5	4	1				0	7	Cr 45 Sm 90 N 110 I	[4]
5-6	4	0				0	7	Cr 53 I	[4]
5-7	4	0				0	7	Cr 42 N 70 I	[4]
5-8	4	0				0	7	Cr 40 Sm 61 N 67 I	[4]
5-9	4	0				0	7	Cr 35 I	[4]
5-10	4	0				0	7	Cr 40 Sm 65 I	[4]
5-11	4	0				1	7	Cr 30 N 34.5 I	[2]
5-12	4	0				1	7	Cr 38 N (33) I	[2]
5-13	2	0				1	7	Cr 39 I	[2]
5-14	2	0				1	7	Cr 93 Sm 117 I	[2]
5-15	5	0				0	4	Cr 44 I	[1]

range and thermostability. The replacement of the 1,3,4-oxadiazole-2,5-diyl by the 1,3,4-thiadiazole-2,5-diyl in system (III) produces liquid crystals with the highest melting point, highest nematic and smectic thermostabilities, and broadest smectic and nematic ranges among the compounds of this system.

2.4. *System (IV)*

For four-ring fluoro derivatives presented in table 4, the effect of introducing the 1,2,4-oxadiazole-3,5-diyl and its position in the molecular cores of compounds **4-5–4-8** on their mesomorphic properties is as shown in the scheme. These results show that by inserting the 1,2,4-oxadiazole-3,5-diyl with its oxygen atom pointed toward the phenylcyclohexane fragment, into the molecular core of the system (IV) liquid crystals are obtained with lower melting point, lower nematic thermostability, narrower nematic range, and an additional smectic phase, compared with those of the corresponding derivative having the oxygen atom of its 1,2,4-oxadiazole-3,5-diyl pointed toward the fluorophenyl fragment (compounds **4-5** and **4-6**). Moving the 1,2,4-oxadiazole-3,5-diyl close to the propylcyclohexyl fragment (compound **4-7**) sufficiently increases the melting point, leads to the disappearance of the smectic phase, creates the narrowest range nematic phase, and slightly decreases the clearing point, in comparison with those of compound **4-6**. The corresponding 1,4-phenylene derivative **4-8** exhibits higher nematic and smectic thermostabilities (as was observed for three-ring fluoro derivatives presented in table 3) than those of the 3,5-disubstituted 1,2,4-oxadiazole derivatives **4-5–4-7**.

Table 6. Mesomorphic properties of liquid crystals: $H_{11}C_5$A–B–X.

Compound No.	*A*	*B*	*X*	Phase transitions/°C	Ref.
6-1			CH_3	Cr 85 N 119 I	[1]
6-2			CH_3	Cr 98 Sm 123 N 178 I	[25]
6-3			C_2H_5	Cr 49 N 87 I	[1]
6-4			C_2H_5	Cr 34 Sm 146 N 164 I	[22]
6-5			C_3H_7	Cr 45.5 N 82 I	[1]
6–6			C_3H_7	Cr 29 Sm 160 N 170 I	[26]
6-7			C_4H_9	Cr 45 N 74.5 I	[1]
6-8			C_4H_9	Cr 122 I	[1]
6-9			C_4H_9	Cr 20 Sm 160 N 170.5 I	[26]
6-10			C_4F_9	Cr 33 Sm 58.6 N 59 I	[1]
6-11			C_4H_9	Cr 14 N 29 I	[1]

2.5. *System (V)*

The different orders of thermal efficiency shown in the scheme for system (V) (compounds **2-1**, **4-1**, **4-5**; and **2-2**, **4-2**, **4-6**; tables 2, 4) show that the introduction of the 1,2,4-oxadiazole-3,5-diyl into the molecular core of four-ring derivatives can influence the efficiency of the terminal groups.

2.6. *System (VI)*

The thermal data collected in table 4 show the effect of introducing the oxadiazole fragments into the molecular core of four-ring chloro derivatives (compounds **4-9–4-12**) on their phase transition temperatures; this is expressed by the orders of thermal efficiency shown in the scheme. These results show that the introduction of the 1,2,4-oxadiazole-3,5-diyl with its oxygen atom pointed toward the phenylcyclohexane fragment, into the molecular core of system (VI) produces liquid crystals with the lowest melting point, broadest nematic range with moderate thermostability, and narrowest smectic range with moderate thermostability, among the compounds of this system. The corresponding derivative having the 1,2,4-oxadiazole-3,5-diyl with its oxygen atom pointed toward the chlorophenyl fragment (compound **4-9**) exhibits a higher melting temperature, a nematic phase with narrowest range and decreased thermostability, and a smectic phase with the broadest range and moderate thermostability. Insertion of the 1,3,4-oxadiazole-2,5-diyl gives liquid crystals with the highest melting point, lowest nematic thermostability with moderate range, and narrowest smectic range with moderate thermostability. Replacing the 1,3,4-oxadiazole-2,5-diyl by the 1,3,4-thiadiazole-2,5-diyl in system (VI) results in the formation of liquid crystals showing the highest nematic and smectic thermostabilities—as was found for the system (III)—and moderate ranges for the compounds of this system.

2.7. *System (VII)*

From table 4, it follows that the replacement of the *trans*-1,4-cyclohexylene by 1,4-phenylene in compounds **4-10**, **4-11**, **4-12** to obtain compounds **4-13**, **4-14**, **4-15**, respectively, results in a different dependence of their mesomorphic properties on the positions of the oxadiazole's heteroatoms, consistent with the orders of thermal efficiency (compounds **4-13–4-15**, table 4) shown in the scheme. These results show that the introduction of the 1,2,4-oxadiazole-3,5-diyl with its oxygen atom pointed toward the chlorophenyl fragment, into the molecular core of system (VII), produces a liquid crystal (compound **4-13**) exhibiting the highest clearing temperature (smectic thermostability), while the corresponding 2,5-disubstituted 1,3,4-oxadiazole derivative **4-14** exhibits the lowest clearing point, among the compounds of this system. As in the case of four-ring nitro derivatives (see table 2), the effect on phase transition temperatures of introducing the oxadiazole fragment into the molecular cores of four-ring chloro derivatives depends on their structures (see systems VI and VII).

From table 5 it follows that the introduction of the 1,2,4-oxadiazole-3,5-diyl into the molecular core of weakly polar two-ring hexyl-nonyloxy derivatives produces liquid crystals exhibiting only a nematic phase with very low efficiency, in contrast to the corresponding pyridine-2,5-diyl derivatives showing very rich and highly efficient polymorphism (compounds **5-1** and **5-2**).

Interestingly, introducing the 1,2,4-oxadiazole-3,5-diyl as a middle ring in the molecular core of three-ring butoxy-heptyloxy derivative **5-3** leads to the formation of a monotropic nematic phase, while introducing this fragment into the molecular core of the corresponding butoxy-heptyl derivative **5-4** and butyl-heptyl derivative **5-6** slightly decreases the melting temperature and monotropic nematic thermal efficiency, this results in the disappearance of the mesophase, respectively. These results show that the effect on mesomorphic properties of introducing the 1,2,4-oxadiazole-3,5-diyl into the molecular core of three-ring weakly polar derivatives depends on the structure of their terminal substituents.

2.8. *System (VIII)*

As in the case of the strongly polar CN and NO_2, and moderately polar $OCHF_2$, F, Cl, Br derivatives considered above, the effect of introducing the oxadiazole fragment into the molecular core of three-ring weakly polar derivatives strongly depends on the positions of its heteroatoms, resulting in increasing the nematic (compounds **5-4** and **5-5**, **5-6** and **5-7**) and the smectic (compounds **5-4** and **5-5**) thermostabilities, and decreasing the melting points (compounds **5-4** and **5-5**, **5-6** and **5-7**) observed for the 2,5-disubstituted 1,3,4-oxadiazole derivatives, in comparison with those of the corresponding 3,5-disubstituted 1,2,4-oxadiazole derivatives presented in table 5. These can be expressed by the orders of thermal efficiency for butyl-heptyl derivatives **5-6–5-8** shown in the scheme.

These results and the phase transition temperatures of compounds **5-6–5-8** presented in table 5 show that the replacement of 1,3,4-oxadiazole-2,5-diyl by 1,3,4-thiadiazole-2,5-diyl in system (VIII) results in the appearance of the smectic phase, and decreases the melting point, nematic range and thermostability. The highest melting point is recorded for the corresponding 3,5-disubstituted 1,2,4-oxadiazole derivative **5-6** among the compounds of this system.

Similar results have been found for other weakly polar three-ring derivatives: (a) the disappearance of the mesophase for the 3,5-disubstituted 1,2,4-oxadiazole derivative **5-9**, (b) the appearance of only a smectic phase in the corresponding 2,5-disubstituted 1,3,4-oxadiazole derivative **5-10**, (c) the creation of the low efficient nematic phase for derivative **5-11** having the oxygen atom of its 1,2,4-oxadiazole-3,5-diyl pointed toward the heptyloxyphenyl fragment; and (d) the appearance of a monotropic nematic phase with decreased thermostability for the corresponding derivative **5-12** incorporating the 1,2,4-oxadiazole-3,5-diyl with reversed structure.

The thermal data collated in table 5 reveal that, moving the 1,2,4-oxadiazole-3,5-diyl from the middle position in the molecular core of the non-mesomorphic three-ring ethyl-heptyl derivative to the position close to the ethyl group, creates the smectic phase with moderate thermostability (compounds **5-13** and **5-14**). The effect of introducing the 1,2,4-oxadiazole-3,5-diyl as a central fragment in the molecular cores of three-ring butyl-pentyl derivatives depends on their structures, resulting in the low thermally efficient nematic phase recorded for compound **6-11** incorporating two *trans*-1,4-cyclohexylene fragments, and the disappearance of the mesophase for the corresponding 3,5-disubstituted 1,2,4-oxadiazole derivative **5-15** having the *trans*-1,4-cyclohexylene and 1,4-phenylene fragments (see tables 5 and 6).

2.9. *System (IX)*

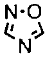
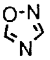
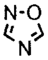
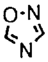
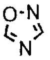
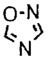
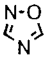
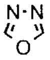
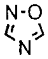
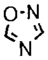
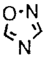
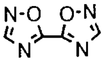
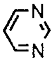
The phase transition temperatures of compounds **6-1** and **6-2**, **6-3** and **6-4**, **6-5** and **6-6**, **6-7** and **6-9** presented in table 6, and the orders of thermal efficiency obtained for the system (IX) (see the scheme) show that the introduction of the 1,2,4-oxadiazole-3,5-diyl, as an outer ring in the molecular core of weakly polar three-ring dialkyl derivatives, results in a significant decrease in the nematic thermostabilities, disappearance of the smectic phases and an effect on the terminal alkyl group efficiency, in comparison with those of the corresponding 1,4-phenylene derivatives. The influence of the positions of the 1,2,4-oxadiazole-3,5-diyl's heteroatoms incorporated in the molecular core of three-ring pentyl-butyl derivatives is shown in table 6, revealing the nematic character of the mesophase for compound **6-7** having the oxygen atom of its 1,2,4-oxadiazole-3,5-diyl pointed toward the butylphenyl fragment, in comparison with the non-mesomorphic behaviour of the corresponding compound **6-8** having the 1,2,4-oxadiazole-3,5-diyl with reversed structure.

2.10. *System (X)*

As expected, the introduction of the oxadiazole fragment into the molecular core of the four-ring dialkyl derivatives presented in table 7 leads to more pronounced mesomorphic properties in comparison with those observed for the three-ring dialkyl derivatives considered above.

For example, introducing the 1,2,4-oxadiazole-3,5-diyl with its oxygen atom pointed toward the propylphenyl fragment (compound **7-1**) creates liquid crystals exhibiting only a nematic phase with low melting and high clearing temperatures. A similar insertion of the 1,2,4-oxadiazole-3,5-diyl with reversed structure increases the melting and clearing points, and creates the smectic phase (compound **7-2**). Moving the 1,2,4-oxadiazole-3,5-diyl close to the propyl group increases the melting and clearing temperatures, and smectic thermostabilities (compounds **7-1** and **7-3**, **7-2** and **7-4**), leading to the disappearance of the nematic phase in compound **7-4**. Interestingly, compounds **7-3** and **7-4** show a similar dependence of their mesomorphic behaviour on the positions of the 1,2,4-oxadiazole-3,5-diyl heteroatoms (excepting the melting points) as was observed for compounds **7-1** and **7-2**. Similar results have been found for four-ring dipentyl derivatives; lower melting and clearing temperatures, and lower smectic thermostability are seen for compound **7-6** (having the 1,2,4-oxadiazole-3,5-diyl inserted between the pentylcyclohexyl and pentylbiphenyl

Table 7. Mesomorphic properties of liquid crystals: $H_{11}C_5$–A–B–K–L–M–C_nH_{2n+1}.

Compound No.	*A*	*B*	*K*	*L*	*M*	*n*	Phase transitions/°C	Ref.
7-1					—	3	Cr 48 N 187 I	[1]
7-2					—	3	Cr 53 Sm 98 N 193 I	[1]
7-3					—	3	Cr 78 Sm1 148 Sm2 210 N 230 I	[3]
7-4					—	3	Cr 75 Sm 155 SmB 187 SmA 239 I	[3]
7-5					—	5	Cr 68 Sm 163 N 194 I	[2]
7-6					—	5	Cr 67 Sm 79 N 159 I	[2]
7-7					—	3	Cr 37 Sm 65 N 173 I	[1]
7-8					—	7	Cr 67 N 175.5 I	[2]
7-9					—	7	Cr 80 Sm 145 N 156 I	[4]
7-10					—	7	Cr 78 Sm 175 N 185 I	[4]
7-11						3	Cr114 N 265 I	[3]
7-12						3	Cr 113 N 285 I	[3]
7-13						3	Cr 51 Sm1 101 Sm2 171.5 N 274 I	[3]
7-14						3	Cr 156 Sm 169 N 320 I	[1]
7-15					—	3	Cr 119.4 Sm 186.5 N 323 I	[28]

fragments) than for the corresponding compound **7-5** (having the 1,2,4-oxadiazole-3,5-diyl moved to the position close to the pentylphenyl fragment).

The introduction of the 1,2,4-oxadiazole-3,5-diyl into the molecular core of the four-ring pentyl-propyl derivative in the position close to the pentylcyclohexyl fragment significantly reduces the melting and clearing temperatures, and the smectic thermostability (compound **7-7**) in comparison with those of the corresponding pyrimidine-2,5-diyl derivative **7-15**.

The effect of introducing the oxadiazole fragments into the molecular core of four-ring pentyl-heptyl derivatives is shown in table 7 and is expressed by the orders of thermal efficiency (compounds **7-8–7-10**) shown in the scheme. These results, and the data on the phase transition temperatures for compounds **7-8–7-10** presented in table 7, reveal that the introduction of the 1,2,4-oxadiazole-3,5-diyl into the molecular core of system (X) produces a liquid crystal (compound **7-8**) exhibiting only a nematic phase with the lowest melting point, broadest range and moderate thermostability. The corresponding 2,5-disubstituted 1,3,4-oxadiazole derivative (compound **7-9**) exhibits the highest melting temperature, lowest nematic thermostability and an additional smectic phase with the lowest range and thermostability among the compounds of the system (X).

Similar results showing the effect of the 1,2,4-oxadiazole-3,5-diyl fragment and its heteroatoms positions in the molecular core of five-ring weakly polar derivatives are given in table 7, for compounds **7-11–7-13**. The introduction of the 1,2,4-oxadiazole-3,5-diyl as a central fragment in the molecular core of five-ring pentyl-propyl derivatives results in the appearance of the nematic phase; higher clearing and lower melting points are recorded for compound **7-12** (having the oxygen atom of its 1,2,4-oxadiazole-3,5-diyl pointed toward the pentyl group) than for the corresponding derivative **7-11** (having the 1,2,4-oxadiazole with reversed structure). Moving the 1,2,4-oxadiazole-3,5-diyl to the position close to the pentylcyclohexyl fragment decreases the melting and clearing temperatures and creates a broad range smectic phase (compounds **7-12** and **7-13**).

It has been shown that the introduction of two 1,2,4-oxadiazole-3,5-diyl fragments as the central group in the molecular core of a four-ring dibutyl derivative does not produce a mesophase [1], however increasing the number of the rings in the molecular core up to 6 in the pentyl-propyl derivative, by inserting two 1,2,4-oxadiazole-3,5-diyl fragments as a central group (compound **7-14**, table 7), finally gave pronounced mesomorphic behaviour with a high clearing point. As before, the positions of the oxadiazole heteroatoms and its position in the core have a marked effect on mesomorphic properties.

The decreased thermal efficiency observed for oxadiazole derivatives compared with other derivatives can be explained in terms of increased distortion of molecular linearity [1, 12, 29, 30–32,], leading to unfavourable molecular packing and consequent loss of thermal efficiency [33]. Indeed the electronic structure of the oxadiazole fragment [1, 31, 32, 34, 35], which is influenced by the positions of its heteroatoms, plays a very important role in the intra- and inter-molecular interactions which in turn may affect the molecular packing [33].

Similar results have been obtained for other liquid crystalline oxadiazole derivatives [1–14, 29, 36, 37].

3. Static dielectric properties

The relationship between the dielectric anisotropy $\Delta\varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp}$, where $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ are, respectively, dielectric constants parallel and perpendicular to the nematic director **n**, and the molecular structure of liquid crystals, is described by the theory of Maier and Meier [38]:

$$\Delta\varepsilon = NhF/\varepsilon_0[\Delta\alpha - F\mu^2/kT(1 - 3\cos^2\beta)]S \qquad (1)$$

where $h = 3\varepsilon^*/(2\varepsilon^* + 1)$, $\varepsilon^* = (\varepsilon_{\parallel} + 2\varepsilon_{\perp})/3$; $\Delta\alpha = (\alpha_{\parallel} - \alpha_{\perp})$ is the polarizability anisotropy; F is the cavity reaction field; μ is the dipole moment; β is the angle between the molecular long axis and the dipole moment and N is the number of molecules per unit volume; S is the order parameter.

Tables 1 and 2 present the dielectric properties of some oxadiazole derivatives extrapolated from the data of their 5% solutions in a mixture of cyano derivatives at 20°C [1, 2]. One can see that the introduction of the 1,2,4-oxadiazole-3,5-diyl in the molecular core of liquid crystals results in a diversity of dielectric properties, because the positions of the heteroatoms in the 1,2,4-oxadiazole-3,5-diyl, and its related dipole moment, considerably affect the magnitude and the direction of the total dipole moment. For example, when the longitudinal component of the dipole moment of the 1,2,4-oxadiazole-3,5-diyl coincides with that for the terminal NO_2 or CN groups, $\Delta\varepsilon$ increases (compounds **1-2**, **1-8**, **1-10**, **2-8**; tables 1, 2); in the opposite case $\Delta\varepsilon$ decreases (compounds **1-1**, **1-7**, **1-9**, **2-7**; tables 1, 2), in an agreement with equation (1).

Resonance effects also contribute significantly to polarizability anisotropy and consequently to the dielectric anisotropy of compounds **1-2**, **1-8**, **1-10** and **2-8**, where the electron density is more easily donated into the nitro-(cyano)aryl system in comparison with that of the corresponding compounds **1-1**, **1-7**, **1-9** and **2-7** where the electron density is first repelled from the nitro(cyano)aryl rings.

4. Conclusion

Systematic studies on the effect on physico-chemical properties of introducing the oxadiazole fragment into the molecular core of a variety of liquid crystals have been performed. The information here presented may lead to a better understanding of the nature of liquid crystals and their use for various applications.

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