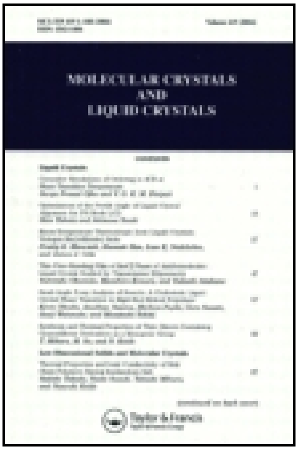

Molecular Crystals and Liquid Crystals

Chemical Structure and Reentrant Behavior

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Chemical Structure and Reentrant Behavior

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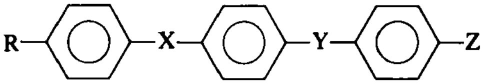
Several homologous series of chemically related compounds were synthesized. The influence of the terminal polar group and of the length of the conjugated system on the reentrant phenomenon was studied.

In 1979 Hardouin *et al.*[1] reported the first pure substance exhibiting a reentrant nematic phase (and a reentrant S_A phase) at atmospheric pressure: 4-(4′-*n*-octyloxybenzoyloxy)benzylidene-4′-cyanoaniline. By greater or lesser modifications of this molecule, a number of new substances with stable or metastable reentrant phases were then synthesized in quite a short time.[2–10]

The liquid crystalline substances possessing reentrant phases can be assigned the general formula‡



Z in all cases is a cyano group. With one exception X is a —COO— group, and the substituents R are alkyl, alkyloxy, or alkanoyloxy groups. The influence of R on the formation of reentrant phases was studied by Nguyen Huu Tinh *et al.*[7] Y can be —CH=CH—, —C≡C—, —N=N—, —CH=N— or —COO—; in a few cases Y is absent.

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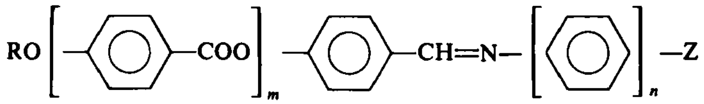
‡ Hitherto only two two-ring compounds are known to exhibit monotropic reentrant nematic phases.[5,11]

Sigaud *et al.*[12] studied the role of Y and the influence of the length of the conjugated part of the molecule on the reentrant phenomenon.

Now we present comparative investigations of several homologous series with special emphasis on the connection between the terminal polar group Z and the length of the conjugated part of the molecule on the occurrence of reentrant phases.

Starting from the general formula



m, *n* and Z were varied (see Table I).

The compounds of series **2** and **3** differ from that of **1** by the introduction of a methylene or CH_2CH_2 moiety, respectively, between the cyano group and the benzene ring. The clearing temperatures of the substances **2** and **3** are about 40–60°C lower than those of series **1** (see Tables II–IV). This fact is obviously the result of the interrupted mesomerism between the aromatic ring system and the polar substituent. It is interesting that for series **2** and **3**, the members with identical R show about the same clearing temperatures; furthermore, the tendency to form smectic phases decreases from **1** to **3**, i.e., with increasing distance of the polar cyano group from the benzene ring (Tables II–IV). In homologous series **2** and **3**, reentrant nematic phases could not be found. The continuous change of the transition temperatures S_A–N almost certainly excludes the occurrence of a metastable reentrant nematic phase.

When the mesomerism between the cyano group and the aromatic ring is favored by introducing an ethenyl group (series **4**), the transition temperatures

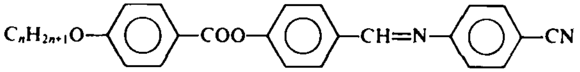
TABLE I

Compound No	*m*	*n*	Z	Ref.	Table
1a-g[a]	1	1	CN	8, 9, 10	II
2a-g	1	1	CH_2—CN		III
3a-e	1	1	CH_2—CH_2—CN		IV
4a-e[a]	1	1	CH=CH—CN	13	V
5a-d	1	1	NO_2		VI
6a-e	1	1	F, Cl, Br, $CONH_2$, SCN		VII
7a-f	1	2	CN		VIII
8a-e[a]	0	2	CN	14	IX
9	0	1	CH_2—CN		IX
10a-e	0	1	CH_2—CH_2—CN		X
11a-f[b]	0	1	CH=CH—CN		XI

[a] Reentrant nematic phases in pure substances.

[b] Reentrant nematic phases in binary mixtures of homologous substances.

TABLE II[a]

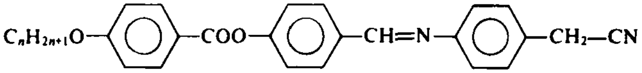


Ref. 8-10

Compound No	*n*	Cr	N_{re}	S_C	S_A	N	Is
1a	4	· 137.5	—	—	(· 101)	· 299	·
1b	5	· 122	—	—	(· 102)	· 280	·
1c	6	· 115	—	—	(· 84)	· 272	·
1d	7	· 115	—	—	(· 68)	· 265	·
1e	8	· 108	· 152	—	· 198	· 255	·
1f	9	· 97	(· 94)	—	· 224	· 247	·
1g	10	· 100	(· 66	· 79)	· 232	· 242	·

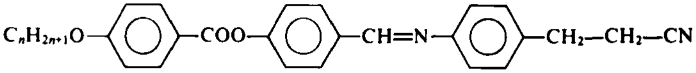
[a] Transition temperatures in this and all subsequent Tables are in °C.

TABLE III



No	*n*	Cr	S_C	S_A	N	Is
2a	4	· 153.4	(· 119	· 129)	· 242	·
2b	5	· 132	—	· 156.5	· 229	·
2c	6	· 145.5	—	· 170	· 225	·
2d	7	· 117.5	—	· 177	· 220	·
2e	8	· 130	—	· 186	· 213	·
2f	9	· 116	—	· 191	· 207	·
2g	10	· 118	—	· 197	· 203	·

TABLE IV



No	*n*	Cr	S_A	N	Is
3a	4	· 123.5	(· 104)	· 248	·
3b	5	· 127.5	· 144	· 234	·
3c	6	· 126.5	· 157.5	· 229	·
3d	7	· 126	· 169	· 219.5	·
3e	8	· 122.5	· 178.5	· 216.5	·

and the clearing temperatures strongly increase, obviously because of the increase of the polarizability anisotropy (see Table V). The heptyloxy derivative possesses a stable reentrant nematic phase; compared with other substances, the transition temperature N_{re}–S_A is relatively high (169°C). It is remarkable that in the higher homologues S_C phases occur. In a binary mixture of the C_7 and C_8 homologues, the enantiotropic S_C–N_{re} transition was observed with decreasing temperature.[13]

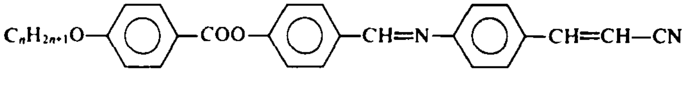
The exchange of the cyano group for other strong polar substituents such as —NO_2, —Br, —Cl, —F, —$CONH_2$ or —SCN gives compounds **5** and **6** (Tables VI–VII), which do not show reentrant phases. This result agrees with the liquid crystalline behavior of analogous 4-*n*-alkyloxybenzoyloxystilbenes.[12] In the case of the SCN, F, Cl, and Br derivatives, the highly ordered smectic low temperature phase is S_E.

As seen from series **4**, the increased length of the conjugated part of the molecule leads to a relatively high transition temperature N_{re}–S_A. For this reason an additional aromatic ring was introduced into the basic molecule. Although in the resulting four-ring compounds **7** (Table VIII), the length of the conjugated part able to undergo mesomerism is only slightly increased in comparison with the compounds of series **4**, no reentrant phases could be found, but large regions of S_A and S_B phases were observed.

When in the molecule **7**, the benzoyloxy group is removed, the 4-*n*-alkyloxybenzylideneamino-4′-cyanobiphenyls **8** result; one member of this series shows a stable reentrant nematic phase and additionally two smectic low-temperature phases S_B and S_E[14] (see Table IX).

In the series of two-ring compounds **9–11**, the liquid crystalline behavior is distinctly influenced by a variation of the polar group Z. In the substances of series **9**, no liquid crystalline phases could be observed. This is obviously due to the fact that the cyano group forms an angle with respect to the molecular

TABLE V

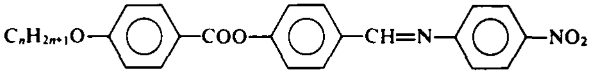


Ref. 13

No	*n*	Cr	N_{re}	S_C	S_A	N	Is
4a	6	· 137	—	—	(· 134)	· 337	·
4b	7	· 138.5	· 169	—	· 278	· 328	·
4c	8[a]	· 120	—	· 132	· 300	· 320	·
4d	9	· 116	—	(· 115)	· 307	· 316	·
4e	10	· 117	—	(· 109)	· 310	· 313	·

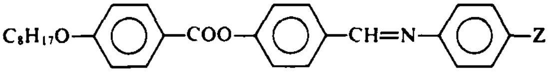
[a] Immediately before crystallization (93°C) a transition to an additional smectic phase was observed.

TABLE VI



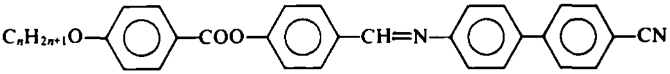
No	n	Cr	S_A	N	Is
5a	5	• 135.5	(• 117)	• 272	•
5b	6	• 139	• 192	• 265	•
5c	7	• 127	• 288.5	• 255	•
5d	8	• 131	• 245	• 251	•

TABLE VII



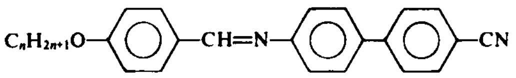
No	Z	Cr	S_E	S_A	N	Is
6a	—F	• 97	(• 89)	• 181	• 204	•
6b	—Cl	• 115	• 127	• 220.5	• 234	•
6c	—Br	• 105.5	• 140	• 231	• 239	•
6d	—$CONH_2$	• 233	—	• 249	• 265	•
6e	—SCN	• 105	(• 94)	• 213	—	•

TABLE VIII

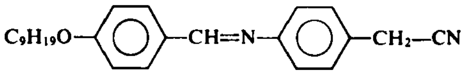


No	n	Cr	S_B	S_A	N	Is
7a	4	• 133	• 144	• 246	• >360	•
7b	5	• 166	(• 152)	• 269	• >360	•
7c	6	• 131	• 154	• 282	• >360	•
7d	7	• 95	• 160	• 326	• >360	•
7e	8	• 117	• 162	• 330	• >360	•
7f	9	• 95	• 163	• 338	• >360	•

TABLE IX


Ref. 14

No	*n*	Cr	S_E	S_B	N_{re}	S_A	N	Is
8a	5	· 119	(· 76)	· 120	—	—	· 299	·
8b	6	· 92		· 111	—	—	· 280	·
8c	7	· 73	· 95	· 111	· 140	· 212	· 273	·
8d	8	· 68	· 100	—	—	· 243	· 267	·
8e	9	· 76	· 99	—	—	· 249	· 258	·

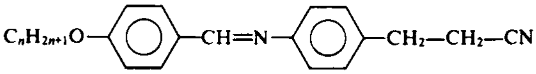

Cr 99 Is

long axis. The members of the series **10** show metastable nematic phases and (or) S_A phases (Table X), but neither in the pure compounds nor in binary mixtures of these compounds could a reentrant nematic phase be detected.

The introduction of a cyanoethenyl group into the two-ring compounds gives rise to a strong increase of the transition temperatures, so that the liquid crystalline ranges are unusually large for two-ring compounds (series **11**, see Table XI). The same result was reported for analogous azo-compounds.[15] Similarly to some members of series **4**, the heptyloxy compound of series **11** show a metastable S_C phase. In the pure compounds of series **11**, no reentrant phases occur, but in binary mixtures of the C_6 and C_7 homologues, both a polymorphism N S_A N_{re} and N S_A S_C N_{re} could be observed.

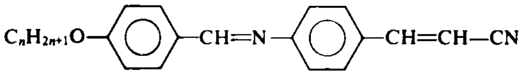
A comparison of several homologous series shows that molecules with three benzene rings constitute the optimal situation for formation of reentrant phases at atmospheric pressure. Furthermore, we can conclude from our results that the conjugation between the cyano group and the aromatic ring favors the occurrence of stable reentrant phases as can be seen from series **4**. On the other hand, by the interruption of conjugation between the terminal cyano group and the aromatic part of the molecule, by introduction of one or two methylene groups, the reentrant phenomenon disappears. This finding is in contrast to the behavior of the two-ring compounds, where the cyanoethylphenyl compounds show a comparable or stronger tendency to form reentrant phases in binary mixtures than do the corresponding cyanophenyl compounds.[11] For example, 4-(2′-cyanoethyl)phenyl 4′-*n*-nonyloxybenzoate, contrary to the behavior of the corresponding cyanophenyl compound, forms a metastable reentrant nematic phase immediately before crystallization.[11]

TABLE X



10a	6	· 72	—	(· 71)	·
10b	7	· 77.5	—	(· 69)	·
10c	8	· 79.5	—	(· 76.5)	·
10d	9	· 84	(· 71.5	· 72)	·
10e	10	· 84.5	(· 80)	—	·

TABLE XI



No	*n*	Cr	S_C	S_A	N	Is
11a	5	· 104	—	—	· 203	·
11b	6	· 77	—	—	· 199	·
11c	7	· 81.5	—	· 174	· 191.5	·
11d	8	· 96	(· 54)	· 181	· 188.5	·
11e	9	· 94	—	· 187	—	·
11f	10	· 95	—	· 186	—	·

In agreement with Sigaud *et al.*,[12] we found that the introduction of other polar groups such as —NO_2, —Br, —Cl, or —F causes the reentrant phases to disappear.

The occurrence of reentrant phases is extremely sensitive to the molecular structure. In a few series, only one member is able to exhibit reentrant phases at atmospheric pressure. In other series, the hypothetical transition temperatures for the reentrant phases are too low to be detected. However, in mixtures of neighboring members, the reentrant phases are sometimes stabilized to such an extent that they can be observed.

As shown by X-ray investigation,[16,17] the reentrant phenomenon is the result of molecular associations. It is remarkable that also in other cases with pronounced association behavior—in the case of cubic mesophases[18,19]—unusual phase sequences occur. In all other cases up to now, the general rule of phase sequences[20] is valid.

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