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Synthesis and mesomorphic properties of some cyclohex-2-en-1-one derivatives

by V. S. BEZBORODOV*†‡, R. DABROWSKI§, J. DZIADUSZEK§,
G. SASNOVSKI† and V. F. PETROV¶

†Institute of Applied Physical Problems, Minsk 220064, Belarus
§Military University of Technology, 01-489 Warsaw, Poland
¶LCD R&D Group II, AMLCD Division, Semiconductor Business,
Samsung Electronics Co. Ltd, San #24 Nongseo-Lee, Kiheung-Eup, Yongin-Gun,
Kyungki-Do, Suwon, PO Box #37, 449-900, Korea

Mesomorphic properties of cyclohex-2-en-1-ones belonging to 14 different chemical structural types are compared and discussed. They were prepared by condensation of Mannich salts with 2-substituted acetoacetates or benzyl methyl ketones or acetylacetone in the presence of potassium hydroxide.

1. Introduction

Recently it has been reported that cyclohexenones are promising intermediates for the preparation of liquid crystalline compounds and also, but to a lesser extent, as components for liquid crystalline mixtures for display applications [1–11]. For example we showed that 3,6-disubstituted cyclohex-2-en-1-ones may be transformed in high yield into 2,5-disubstituted cyclohexanones [4] and then into difluorocyclohexanones or cyclohexane derivatives [10] or directly transformed in a 'one pot procedure' into chlorobenzene or chlorobiphenyl or chloroterphenyl derivatives [2]. They may also be used to synthesize optically active compounds with a chiral centre in the rigid core of the molecule [11]. Continuing our interest in liquid crystalline derivatives of cyclohex-2-en-1-one, we have synthesized some new 3,6-disubstituted cyclohex-2-en-1-ones (structures **1–14**) and investigated their mesomorphic properties; the results are summarized here, emphasizing structure-property relationships.
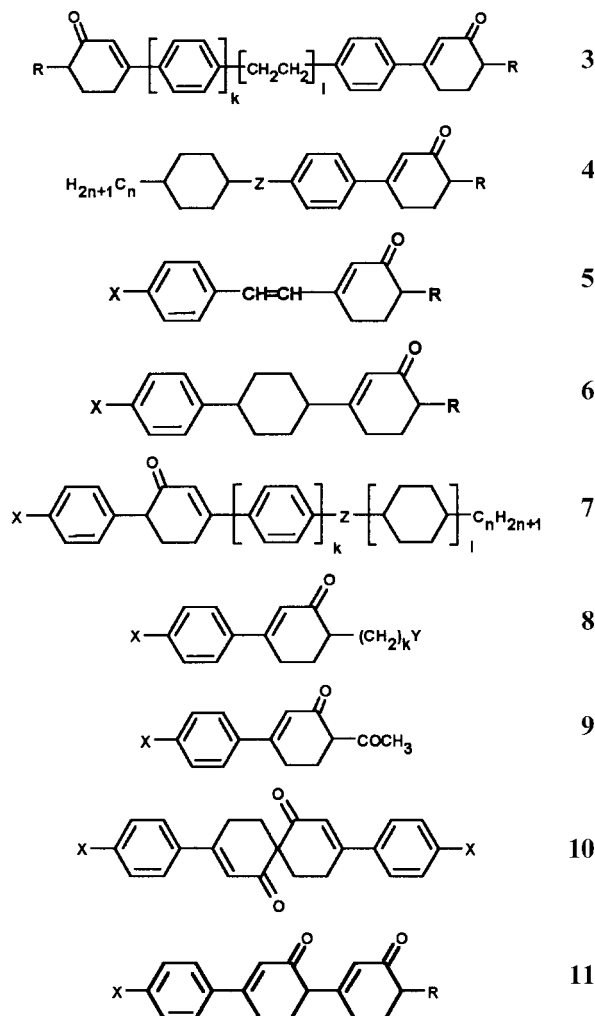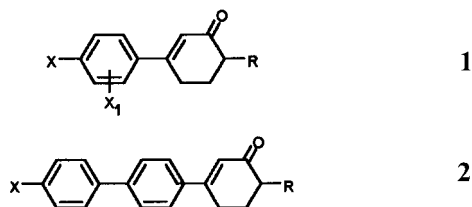
*Author for correspondence.
‡Present address: Samsung Display Devices Ltd, R&D Center, 575 Shin-Dong, Suwon City, Kyungki-Do 442-390, Korea.

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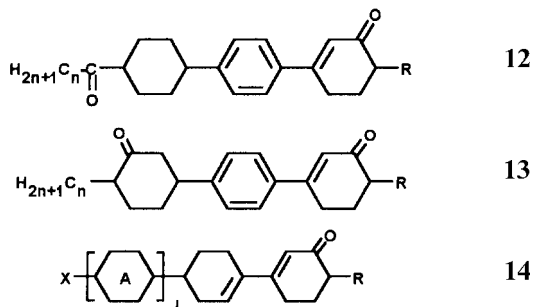
In the above structures, terminal substituents X and R are usually hydrogen or alkyl (C_nH_{2n+1}) or alkoxy ($C_nH_{2n+1}O$); terminal substituents X and lateral substituents X_1 are hydrogen and fluorine, Z is a single bond or $-CH_2CH_2-$, $k = 0$ or 1 and $l = 0$ or 1; Y is $-CN$, $-COOH$ or $-COOCH_3$ group.

2. Results and discussion
2.1. *Synthesis*

Compounds **1**–**6** (tables 1–6) have been synthesized in 50–80% yield by condensation of 2-substituted acetoacetates with Mannich salts: hydrochlorides of 4-phenyl substituted 2-*N,N*-dimethylaminopropiophenones (compounds **1**–**4**) or 4-substituted styryl 2-*N,N*-dimethylaminoethyl ketones (compounds **5**) or 2-*N,N*-dimethylaminoethyl *trans*-4-phenyl substituted cyclohexyl ketones (compounds **6**) in the presence of potassium hydroxide in boiling dioxane or diglyme [1, 10, 12] (scheme 1).

Under the same conditions 4-substituted benzyl methyl ketones with Mannich salts gave the compounds **7** in 60–75% yields (table 7), scheme 2.

The condensation of acetosuccinic, α-acetoglutaric or 2-(2-cyanoethyl)acetoacetic esters with the Mannich
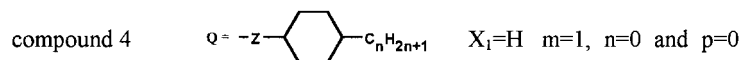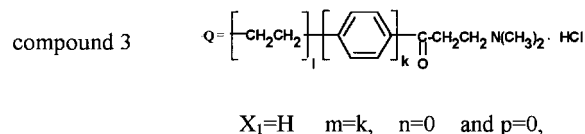
Table 1. Transition temperatures (°C) of 3-(4-substituted phenyl)-6-alkyl-, -6-(β-phenylethyl)- and 6-(β-cyclohexylethyl)-cyclohex-2-en-1-ones, formula **1**.

No.	X	X_1	R	Cr		SmA		N		I
1a	H	H	C_2H_5	•	33	—		—		•
1b	H	H	$C_{10}H_{21}$	•	51	—		—		•
1c	H_3C	H	C_4H_9	•	48	—		—		•
1d	H_5C_2	H	C_4H_9	•	48	•	(21)	—		•
1e	$H_{13}C_6$	H	C_3H_7	•	31	•	34	—		•
1f	$H_{11}C_6$[a]	H	C_4H_9	•	75	—		—		•
1g	$H_{11}C_6$[a]	H	C_5H_{11}	•	90	—		—		•
1h	H_5C_2O	H	CH_3	•	62	—		—		•
1i	H_5C_2O	H	C_3H_7	•	56	•	67	—		•
1j	H_5C_2O	H	C_4H_9	•	55	•	79	—		•
1k	H_5C_2O	H	C_5H_{11}	•	70	•	86	—		•
1l	H_7C_3O	H	C_5H_{11}	•	58	•	94	—		•
1m	H_9C_4O	H	CH_3	•	71	—		—		•
1n	H_9C_4O	H	C_3H_7	•	67	•	97	—		•
1o	H_9C_4O	H	C_4H_9	•	67	•	96	—		•
1p	H_9C_4O	H	C_5H_{11}	•	41	•	109	—		•
1q	H_5C_2O	H	C_3H_7	•	55	•	96	—		•
1r	H_5C_2O	H	C_5H_{11}	•	53	•	110	—		•
1s	$H_{13}C_6O$	H	C_5H_{11}	•	56	•	109	—		•
1t	$H_{19}C_9O$	H	C_5H_{11}	•	59	•	109	—		•
1u	$H_{21}C_{10}O$	H	C_5H_{11}	•	60	•	113	—		•
1v	H_5C_2O	H	$CH_2CH=CH_2$	•	71	—		—		•
1w	H_3CO	2-F	C_5H_{11}	•	48	—		—		•
1x	F_3CO	H	C_5H_{11}	•	37	—		—		•
1y	H_3C	H	$CH_2CH_2C_6H_5$	•	89	—		—		•
1z	H_3CO	3-F	$CH_2CH_2C_6H_5$	•	98	—		—		•
1a$'$	H_3CO	2-F	$CH_2CH_2C_6H_5$	•	78	—		—		•
1b$'$	F	H	$CH_2CH_2C_6H_5$	•	126	—		—		•
1c$'$	H		$CH_2CH_2C_6H_{10}C_3H_7$	•	89	—		—		•
1d$'$	H		$CH_2CH_2C_6H_{10}C_5H_{11}$	•	80	—		•	(78)	•
1e$'$	F		$CH_2CH_2C_6H_{10}C_3H_7$	•	87	—		•	101	•
1f$'$	F		$CH_2CH_2C_6H_{10}C_5H_{11}$	•	86	—		•	109·5	•
1g$'$	H_5C_2O	H	$CH_2CH_2C_6H_5$	•	94	•	(78)	—		•
1h$'$	F	2-F	$CH_2CH_2C_6H_{10}C_4H_9$	•	92	—		•	(89)	•
1i$'$	F	2-F	$CH_2CH_2C_6H_{10}C_5H_{11}$	•	96·5	—		•	(84)	•
1j$'$	H_3CO	3-F	$CH_2CH_2C_6H_{10}C_4H_9$	•	76	—		•	126	•

[a] Cyclohexyl.

Scheme 1. Reagents for preparation of compounds **1–6**.
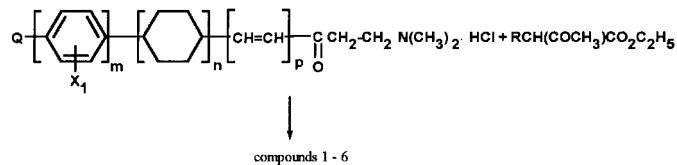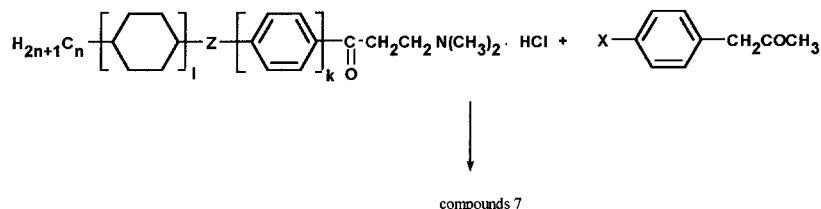
where: compound 1   Q=X,   m=1,   n=0   and p=0
       compound 2   Q=X, X_1=H m=2,   n=0   and p=0

compound 3

X_1=H   m=k,   n=0   and p=0,

compound 4 X_1=H m=1, n=0 and p=0

compound 5   Q=X, X_1=H m=1,   n=0,   and p=1
compound 6   Q=X, X_1=H m=1,   n=1,   and p=0

Scheme 2. Reagents for preparation of compounds **7**.

Table 2. Transition temperatures (°C) of 3-(4-substituted biphenyl-4′-yl)-6-alkylcyclohex-2-en-1-ones, formula **2**.

No.	X	R	Cr		SmA		N		I
2a	H	C_3H_7	•	119	•	(104)	—		•
2b	H	C_4H_9	•	110	•	116	—		•
2c	H	C_5H_{11}	•	101	•	120	—		•
2d	H	C_8H_{17}	•	89	•	130	—		•
2e	F	C_5H_{11}	•	89	•	114	•	141	•
2f	Br	C_5H_{11}	•	91	•	114	•	219	•
2g	H_3C	C_5H_{11}	•	117	•	179	—		•
2h	H_5C_2	C_5H_{11}	•	83	•	171	—		•
2i	H_5C_2	C_6H_{13}	•	94	•	191	—		•
2j	$H_{11}C_5$	C_2H_5	•	93	•	157	—		•
2k	H_5C_2O	C_3H_7	•	118	•	204	—		•

Table 3. Transition temperatures (°C) of 1,4-bis(6-alkyl-cyclohex-2-en-1-on-3-yl)benzenes, 4,4′-bis(6-alkyl-cyclo-hex-2-en-1-on-3-yl)biphenyls and dibenzyls, formula **3**.

No.	R	k	l	Cr		SmA		N		I
3a	$H_{11}C_5$	0	0	•	109	•	164	—		•
3b	H_3C	1	0	•	209	•	214	•	259	•
3c	$H_{11}C_5$	1	0	•	180	•	254	•	275	•
3d	$H_{11}C_5$	1	1	•	133	•	197	—		•

salts in dioxane in the presence of potassium hydroxide resulted in 3-(4-substituted phenyl)-6-(carboxymethyl)-cyclohex-2-en-1-ones, 3-(4-substituted phenyl)-6-(2-carb-oxyethyl)-cyclohex-2-en-1-ones or the corresponding

6-(2-cyanoethyl)cyclohex-2-en-1-ones (compounds **8**, table 8) in 30–50% yield.

3-Aryl-6-acetylcyclohex-2-en-1-ones (compounds **9**) were formed by the reaction of the Mannich salts with acetylacetone (table 9).

The condensation of equivalent quantities of the reagents of scheme 3 in benzene in the presence of potassium carbonate leads to the Michael reaction products (com-pounds **15** and **16**), which were partly transformed to
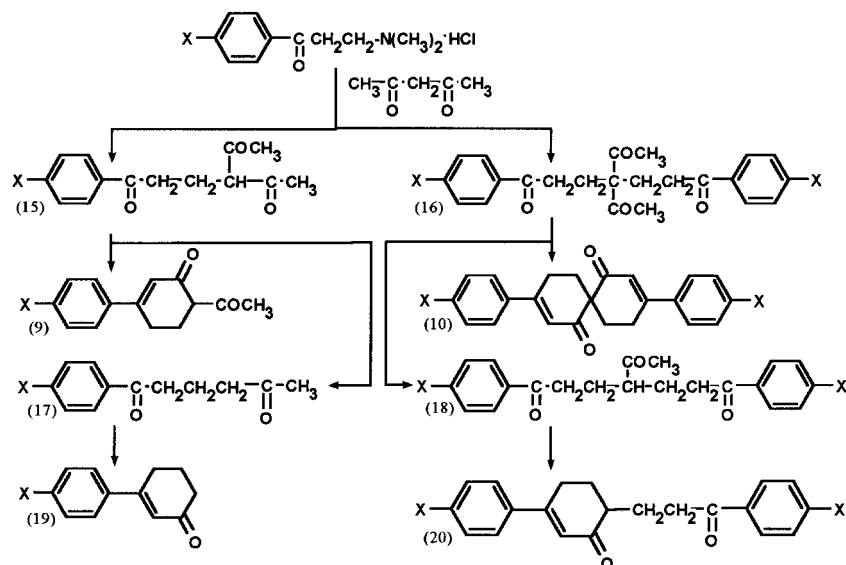
Scheme 3.   Reaction products of the condensation of Mannich salts with acetylacetone.

Table 4.   Transition temperatures (°C) of 3,6-disubstituted cyclohex-2-en-1-ones, formula **4**.

No.	n	Z	R	Cr		SmA		N		I
4a	2	—	C_3H_7	•	69	•	84	•	121	•
4b	2	—	C_5H_{11}	•	77	•	127	•	133	•
4c	3	—	C_3H_7	•	75	•	101	•	150	•
4d	3	—	C_4H_9	•	57	•	125	•	149	•
4e	3	—	C_5H_{11}	•	77	•	149	•	157	•
4f	3	—	C_6H_{13}	•	83	•	152	—		•
4g	5	—	C_2H_5	•	87	•	121	—		•
4h	5	—	C_4H_9	•	66	•	144	•	153	•
4i	5	—	C_5H_{11}	•	58	•	149	—		•
4j	3	—	$CH_2CH=CH_2$	•	84	—		•	102	•
4k	4	CH_2CH_2	C_2H_5	•	66	—		•	104	•
4l	3	CH_2CH_2	C_5H_{11}	•	71	•	131	•	139	•
4m	3	—	$CH_2CH_2C_6H_5$	•	117	•	170	—		•
4n	3	—	$CH_2CH_2C_6H_4OC_2H_5$	•	121	•	172	•	193	•
4o	3	—	$CH_2CH_2C_6H_{10}C_4H_9$	•	<20	•	243[b]	•	252	•
4p	3	—	$CH_2CH_2C_6H_{10}C_5H_{11}$	•	<20	•	248[c]	—		•
4q	3	—	$CH_2CH_2C_6H_{10}C_4H_9$	•	<20	•	222[d]	—		•
4r	4	CH_2CH_2	$CH_2CH_2C_6H_{10}C_4H_9$	•	71	•	226[e]	—		•
4s	4	CH_2CH_2	C_5H_{11}	•	91	•	143	—	185	•
4t	[a]	CH_2CH_2	C_5H_{11}	•	84	•	176	—		•

[a] 2-Fluoro-4-methoxyphenyl, instead of $H_{2n+1}C_n$ group in formula **4**.
[b] SmB → SmA at 174°C.
[c] SmB → SmA at 175°C.
[d] SmB → SmA at 161°C.
[e] SmB → SmA at 187°C.

the corresponding 3-(4-substituted phenyl)-6-acetyl-cyclohex-2-en-1-ones (compounds **9**, table 9) and the spiro bi-4-(4-substituted phenyl)-3-cyclohex-2-en-1-ones (compounds **10**, table 10). Under these conditions, a large amount of side products **19** and **20** were obtained.

Higher (40–50%) yields of the acetylcyclohex-2-en-1-ones (compounds **9**) can be achieved by the reaction of 2–3 equivalents of acetylacetone with one equivalent of the Mannich salt in boiling dioxane in the presence of potassium hydroxide.

Table 5. Transition temperatures (°C) of 3-(4-substituted styryl)-6-alkylcyclohex-2-en-1-ones, formula **5**.

No.	X	R	Cr		SmA		N		I
5a	HC_3O	C_5H_{11}	•	71	•	83	•	97	•
5b	H_5C_2O	C_4H_9	•	85	•	118	—		•
5c	H_5C_2O	C_5H_{11}	•	99	•	128	—		•
5d	F	C_5H_{11}	•	68	—		—		•
5e	H_5C_2O	C_6H_{13}	•	65	•	128	—		•
5f	Cl	C_5H_{11}	•	72	—		—		•
5g	H	C_4H_9	•	62	—		—		•
5h	H_5C_2O	$CH_2CH_2C_6H_5$	•	65	•	128	—		•
5i	$H_5C_6{}^a$	C_4H_9	•	75	•	89	—		•

^{a} Benzene ring.

Table 6. Transition temperatures (°C) of 3,6-disubstituted cyclohex-2-en-1-ones, formula **6**.

| No.	X	R	Cr		SmA		N		I
6a	H	C_3H_7	•	102	—		—		•
6b	H	C_5H_{11}	•	90	—		—		•
6c	H	C_9H_{19}	•	99	•	132	—		•
6d	H_7C_3	C_3H_7	•	90	—		•	104	•
6e	H_7C_3	C_5H_{11}	•	58·5	•	66	•	118	•
6f	H	$CH_2CH_2C_6H_{10}C_4H_9$	•	145	•	187	—		•
6g	^{a}	$CH_2CH_2C_6H_5$	•	56	—		—		•

^{a} CH_3 group instead of X-C_6H_4 in formula **6**.

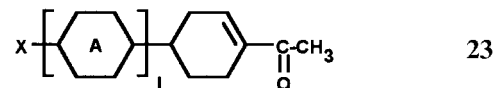Table 7. Transition temperatures (°C) of 3,6-disubstituted cyclohex-2-en-1-ones, formula **7**.

No.	n	l	k	Z	X	Cr		SmA		N		I
7a	4	0	1	—	C_6H_{13}	•	126	•	150	—		•
7b	6	0	1	—	C_4H_9	•	127	•	164	—		•
7c	6	0	1	—	C_6H_{13}	•	120	•	160	—		•
7d	5	0	2	—	H	•	125	•	175	•	189	•
7e	5	0	2	—	OCH_3	•	137	•	238	—		•
7f	5	1	1	—	F	•	148	•	157	•	200	•
7g ^{a}	5	1	1	—	OCH_3	•	116	•	173	•	224	•
7h	5	1	1	—	Cl	•	180	•	183	•	232	•
7i	5	1	1	—	OC_2H_5	•	127	•	222	—		•
7j	3	1	1	CH_2CH_2	OCH_3	•	122	•	135	•	193	•
7k	3	1	1	CH_2CH_2	F	•	125·5	•	140	•	175	•
7l	5	1	1	—	C_3H_7	•	105	•	220	—		•

^{a} Phase transition: SmB 134 SmA.

3-Aryl-6-acetylcyclohex-2-en-1-ones (compounds **9**) or *trans*-4-alkanoyl-1-(4-acetylphenyl)-cyclohexanes (compound **21**) or *trans*-2-alkyl-5-(4-acetylphenyl)cyclohexanones (compounds **22**) were used for the preparation

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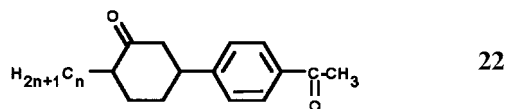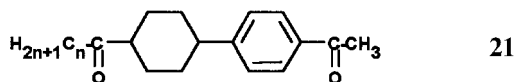
compounds **11**, **12** and **13**, respectively (tables 11–13), but the overall yields were low because the corresponding Mannich salts were isolated with difficulty. Contrary to the above mentioned compounds, 4-alkyl(aryl)-1-acetyl-cyclohex-1-enes (compound **23**) or *trans*-4-alkyl(aryl)-

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1-acetylcyclohexanes or 4-substituted acetophenones were formed from paraformaldehyde and dimethylamine

Table 8. Transition temperatures (°C) of 3,6-disubstituted cyclohex-2-en-1-ones, formula **8**.

No.	X	k	Y	Cr		SmA		N		I
8a	H_5C_2O	2	$COOCH_3$	•	102	•	(47)	—		•
8b	$H_{11}C_5C_6H_4$	2	CN	•	103	—		•	164	•
8c	tr-$H_{11}C_5C_6H_{10}$	2	CN	•	92	—		•	146	•
8d	H	1	COOH	•	146	—		—		•
8e	Cl	1	COOH	•	135	—		—		•
8f	H_3C	2	COOH	•	150	—		—		•
8g	H_3CO	1	COOH	•	170	—		—		•
8h	H_3CO	2	COOH	•	183	—		—		•
8i	H_5C_2O	1	COOH	•	157	—		—		•
8j	H_5C_2O	2	COOH	•	151	—		—		•
8k	$H_{21}C_{10}O$	2	COOH	•	117	•	123	—		•

Table 9. Transition temperatures (°C) of 3-(4-substituted phenyl)-6-acetylcyclohex-2-en-1-ones, formula **9**.

No.	X	Cr		SmA		I
9a	H	•	96	—		•
9b	H_3C	•	93	—		•
9c	H_3CO	•	103	—		•
9d	H_5C_2O	•	86	•	(67)	•
9e	H_9C_4O	•	79	•	(77)	•
9f	$H_7C_3C_6H_{10}$	•	99	•	156	•

Table 10. Transition temperatures (°C) of spirocyclohex-2-en-1-ones, formula **10**.

No.	X	Cr		SmA		I
10a	H_3C	•	84	—		•
10b	H_3CO	•	87	•	(71)	•
10c	H_5C_2O	•	140	•	(108)	•
10d	$H_{11}C_5C_6H_4$	•	163	•	197	•

Table 12. Transition temperatures (°C) of 3,6-disubstituted cyclohex-2-en-1-ones, formulae **12** and **13**.

No.	n	R	Cr		SmA		I
12a	2	C_5H_{11}	•	104	•	162	•
13a	4	C_2H_5	•	91	•	179	•
13b	4	C_5H_{11}	•	118	•	225	•

hydrochloride Mannich salts in 70–85% yield. Then their condensation with substituted acetoacetates led to 3,6-disubstituted cyclohex-2-en-1-ones (compounds **14**, table 14 or compounds **6**, table 6 or compounds **1**, **2**, **4**, tables 1, 2, and 4) in 60–70% yields.

2.2. *Mesomorphic properties*

The phase transition temperatures of the 3,6-disubstituted cyclohex-2-en-1-ones are given in tables 1–14.

As can be seen from table 1, the two-ring compounds **1** [3-(4-substituted phenyl)-6-alkylcyclohex-2-en-1-ones]

with a hydrogen or with two short alkyl chains in the terminal positions are not mesomorphic (compounds **1a**–**c**). Elongation of the alkyl chains to a total of six carbon atoms results in an appearance of a monotropic smectic A (compound **1d**) and then an enantiotropic smectic A phase (compound **1e**) [13, 14]. The change of the alkyl chain to a cyclohexyl ring increases the melting points and does not generate a mesophase (compounds **1f** and **1g**). The replacement of the alkyl group in the 1,4-phenylene fragment by an alkoxy group with the same or a similar number of carbon atoms increases the clearing temperatures (compare compounds **1d** and **1j**). These relations are typical for many other liquid crystalline homologous series [15, 16], but in this case the clearing points are higher. For example, the clearing points of 3-(4-ethoxyphenyl)-6-pentylcyclohex-2-en-1 (compound **1k**), 4-ethoxy-4′-pentylbiphenyl [20] and 4-ethoxyphenyl-1-*trans*-pentyl-cyclohexane [17] are 86°C, 81°C and 51°C, respectively. The ability of terminal chains to increase the clearing points (T_{cl}) in structures I ($X = H_5C_2O = $ const., $X_1 = $ H and $R = H_{2n+1}C_n$) and II ($X = H_{2n+1}C_nO$, $X_1 = $ H and

Table 11. Transition temperatures (°C) of 3-(4-substituted phenyl)-6-(6-alkylcyclohex-2-en-1-on-3-yl)-cyclohex-2-en-1-ones, formula **11**.

No.	X	R	Cr		SmA		N		I
11a	H_5C_2O	H_5C_2	•	91	•	112	—		•
11b	H_5C_2O	$H_{11}C_5$	•	92	•	130	•	154	•
11c	$H_7C_3C_6H_{10}$	$H_{11}C_5$	•	153	•	194	—		•

Table 13. Transition temperatures (°C) of cyclohexen-1-ylcyclohex-2-en-1-ones, formula **14**.

No.	X	A	l	R	Cr		I
14a	H_3C	—	0	$CH_2CH_2-C_6H_4-OC_2H_5$	•	26	•
14b	H_5C_2O	$-C_6H_4-$	1	C_5H_{11}	•	74	•

$R = H_{11}C_5 = $ const.) chosen from the compounds **1** presented in table 1 can be expressed by following orders:
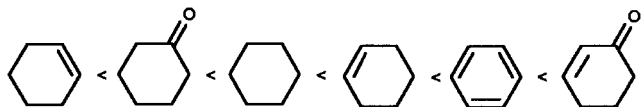
structure I

$$n = 1 < n = 3 < n = 4 < n = 5$$

structure II

$$n = 2 < n = 3 < n = 4 \approx n = 6 \approx 5 \approx n = 9 \approx n = 10$$

The clearing points and the smectic A phase range increase with the length of the alkyl or alkoxy chains for small n and are rather constant for large n. The odd–even alkyl chain effect is not seen. Interestingly, the replacement of the alkyl group attached to the cyclohex-2-en-1-one fragment by the alkenyl group with the same number of carbon atoms as in the compound **1i** creates the compound **1v** with no mesophase, but when the alkyl group is changed to the polar acetyl group the mesophase is maintained (compound **9d**, table 9). In the former case, the disappearance of the mesophase may have the same cause as that for the change of the hexyl chain to a cyclohexyl ring (**1f** and **1g**), namely increased steric hindrance.

The influence of the oxygen atom incorporated in the lateral position of the 1,4-cyclohexylene fragment on their mesogenic properties can be estimated by a comparison of the phase transition temperatures of the compounds **1** with their analogues with a cyclohexene ring instead of the cyclohexenone ring. For example, compound **1k** (table 1) has the phase transitions: Cr 70 SmA 86 I and its cyclohexene analogue Cr 79 (N 76) I [5]. This comparison shows that the introduction of oxygen atom as the lateral carbonyl group in the 1,4-cyclohexenylene fragment increases the clearing temperature and induces the smectic A phase, despite the bulk effect.

The effectiveness of the cyclohex-2-en-1-one ring in comparison to other rings incorporated into the molecular cores of the two-ring alkyl-alkoxy compounds **1** ($X = H_5C_2O$, $X_1 = H$ and $R = H_{11}C_5$) [1, 4, 17, 20] in increasing the clearing points is as follows:

This order shows that a flat conjugated structure is probably responsible for the high stability of the mesophases and that lateral dipole–dipole interactions, which are important for the stabilization of smectic phases, compensate in excess the steric repulsion of the lateral substituent in this case.

Further confirmation of these conclusions comes from comparison with the properties of compounds **5b**, **c** (table 5) having broader mesophase ranges and higher clearing points by about 50°. However the CH=CH bridge group between the benzene and cyclohex-2-en-1-one rings does not in the case of 3-(4-halogenostyryl)-6-alkylcyclohex-2-en-1-ones bring about the creation of a mesophase and these compounds, as well as the terminal hydrogen analogue, are not mesomorphic (compounds **5d**, **f** and **g**, table 5). This shows that the presence of an alkoxy group in the phenyl ring of structures **5** as well as **1**, is very important for the stability of the mesophases. Also the replacement of the alkoxy group by the unsubstituted benzene ring (compound **5i**) decreases the clearing point.

The compounds **2**—three ring analogues of **1**—also preserve the customary large differences between the clearing points of the alkyl and alkoxy derivatives (see compounds **2h** and **k**, table 2). The attachment of the second benzene ring to structure I (biphenyl moiety is formed) involves an increase of T_{SmA} by over 100°; compare compounds **1i** and **2h**. This is much more than for the case when these rings are attached at both sides of the cyclohexenone ring [13, 14]. For this reason such four ring compounds **7** (table 7) have only slightly higher clearing temperatures than the three ring compounds **2**.

The data (table 2) show that the effectiveness of the terminal substituents X for increasing T_{cl} in 3-(4-X-substituted biphenyl-4′-yl)-6-pentylcyclohex-2-en-1-ones (compounds **2**, $R = H_{11}C_5$) is:

$$H < F < C_2H_5 < CH_3 < Br$$

while in this structure, the influence of the cyclohex-2-en-1-one ring on the clearing points in comparison to other rings [4, 9, 19], in the case of $X = F$, is:
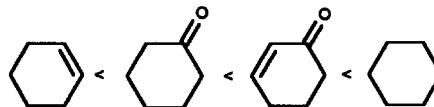
The replacement of one benzene ring in formula **2** by the cyclohexane ring gives structure **4** for $X = C_nH_{2n+1}$ and involves a decrease of T_{cl} as well as in mesophase range. Simultaneously, a nematic phase is created (compare compounds **4b**, table 4 and **2h**, table 2).

In structure **4** ($n = 3$, Z = single bond, $R = H_{11}C_5$) the observed relation is the following:
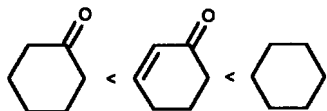
In the systems, increase of the alkyl chain length leads to the disappearance of the nematic phase, and the smectogenity of the compounds becomes more pronounced. For example, in the homologous series of 3-[4-(*trans*-4-propylcyclohexyl)phenyl]-6-alkylcyclohex-2-en-1-ones, the nematic phase disappears when the alkyl group is hexyl, see compound **4f**, table 4. The replacement of the alkyl group attached to the cyclohex-2-enone fragment by the alkenyl group with the same number of carbon atoms (compound **4j**, table 4) decreases the clearing point and only the nematic phase is observed, while the replacement of the alkyl group C_nH_{2n+1} attached to the *trans*-1,4-cyclohexane ring by $C_nH_{2n+1}CO$ group increases the clearing temperature (compound **12a**). The introduction of the dimethylene bridge between the rings of the molecular core in the compounds **4** decreases the temperatures of the smectic–nematic as well as the nematic–isotropic transitions (compare compounds **4e** and **4l**).

Similar relations are also observed for the four ring compounds listed in table 7. The replacement of the 1,4-phenylene fragment by the *trans*-1,4-cyclohexylene fragment (compare compounds **7e** and **7g**) involves a decrease of the clearing temperature, creates a nematic phase, but simultaneously creates a smectic B phase at lower temperature.

The effectiveness of the terminal groups X in the 3-[4-(*trans*-4-pentylcyclohexyl)phenyl]-6-(4-X-substituted phenyl)cyclohex-2-en-1-ones chosen from the compounds listed in table 7 (formula **7** for $n = 5$, $k = 1$, $l = 1$ and Z = single bond) in increasing the clearing points and the nematic range ΔT_N was observed and the order is as follows:

$$T_{cl} \quad F < C_3H_7 < OC_2H_5 < OCH_3 < Cl$$

$$\Delta T_N \quad F < Cl < OCH_3$$
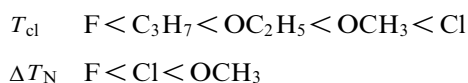
The results of the investigations of the phase transitions for the different classes of 3,6-disubstituted cyclohex-2-en-1-ones presented above in tables 1–13 show that they often have high thermal stability and a broad range for the smectic phases, and in some cases

the nematic phase is also observed. The cyclohexenone ring does not by itself preserve a high stability of mesophase as an internal feature, and the phase stability depends strongly on the other kinds of ring associated with it—see the comparison of the compounds below:
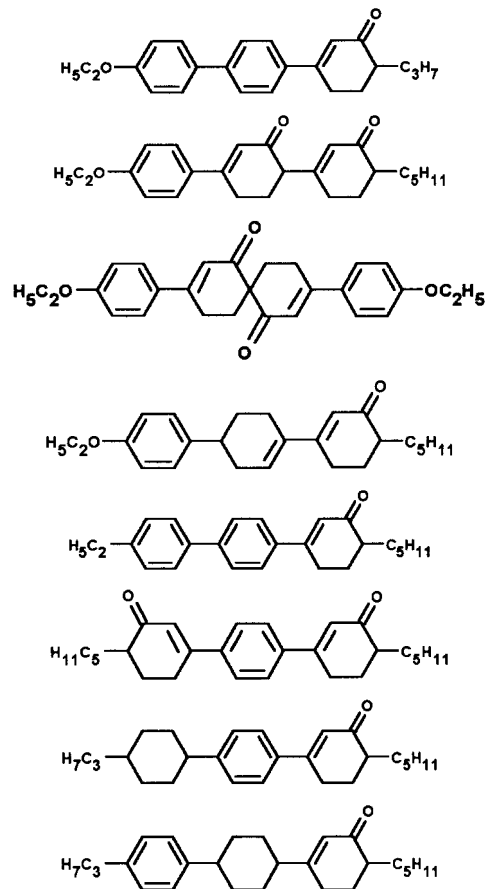
Compounds **2k**, **2h** and **4e** with one cyclohex-2-en-1-one ring linked directly to an aromatic core have higher clearing points and stability of the smectic phases than compounds **6e** or **14b**, wherein a cyclohexane or cyclohexene ring separates the cyclohexenone and benzene rings. The same is observed for compounds with two cyclohexenone rings; compound **3a** with two cyclohexenone rings surrounding the benzene ring, in spite of two terminal alkyl groups, has a higher clearing point than compound **11b** with these rings side by side. Spiro compound **10c** shows a smectic A phase, but with low thermal stability.

In the case of compound **14b**, mesophases are not observed at all. This results not only from breaking the conjugation, but also from the shape of this molecule which is less linear than **6e**.

The exchange of an aromatic ring in structure **2h** for a cyclohexane ring involves the creation of the nematic phase. Its range is broader for compound **6e** than **4e**.

For further examples see tables 4 and 6. A broad range for the nematic phase appears for

Compounds with the cyclohexyl and cyclohexanonyl moieties are strong smectogens and exhibit more ordered B and E phases [4]. Introducing the second carbonyl group (see compounds **12a** and **13a,b**, table 12) cancels the nematic phases existing for structures **4**.

The data presented in tables 1, 2 and 7 reveal that 3-(4-substituted phenyl)-6-alkylcyclohex-2-en-1-ones, 3-(4-substituted biphenyl-4′-yl)-6-alkylcyclohex-2-en-1-ones and 3,6-di-(4-substituted phenyl)cyclohex-2-en-1-ones are broad smectic A ranges in the case of terminal dialkyl or alkyl-alkoxy substitution, while terminal halogeno substitution results in the appearance of the nematic phase (compounds **1c′**, **1d′**, **2e** and **2f**). 3-(4-Substituted biphenyl-4′-yl)-6-(2-cyanoethyl)cyclohex-2-en-1-ones are strong nematogens (compounds **8b** and **8c**, table 8). The presence of the polar groups in the terminal position of the molecules enables the formation of nematogens with a cyclohexenone moiety.

3. Experimental

3,6-Disubstituted cyclohex-2-en-1-ones were made by the following general procedures. A mixture of 0·2 mol of Mannich salt, 0·21 mol of 2-substituted acetoacetate [or substituted benzyl methyl ketone or acetylacetone (in the last case, 0·6 mol)] potassium hydroxide and 200 ml of 1,4-dioxane was heated under reflux for 4–5 h. Upon cooling 100 ml of 20% sulphuric acid were added, the mixture was diluted with 150 ml benzene; the organic phase was separated and washed with dilute potassium hydroxide and water, dried with anhydrous magnesium sulphate and filtered through a layer of aluminium oxide. The residue obtained after evaporation was recrystallized from isopropyl alcohol. The yields were 50–70%.

The structures of the compounds were consistent with the analytical data, including IR, ^{1}H NMR and mass spectrometry. Phase transition temperatures given in tables 1–13 were measured using a 'Linkam' heating stage in conjunction with a polarizing PZO microscope. In the case of the presence of more ordered phases (B or E), differential scanning calorimetry ('Setaram' DSC'92) was also used.

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