

Naphthyl azomesogens with lateral chloro groups[†]

A K PRAJAPATI*, H M PANDYA and N L BONDE

Applied Chemistry Department, Faculty of Technology and Engineering, M S University of Baroda, Kalabhavan, P O Box No 51, Vadodara 390 001, India
e-mail: akprajapati@yahoo.co.uk

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Abstract. A homologous series of azomesogens, 2''-[4-(4'-*n*-alkoxybenzoyloxy)-2-chlorophenylazo] naphthalenes, with lateral chloro groups was synthesised. All the homologues synthesized exhibit enantiotropic nematic mesophase. The mesomorphic properties of the present series are compared with other structurally related series to evaluate the effect of lateral chloro group and its position on mesomorphism.

Keywords. Azomesogens; lateral chloro group; nematic.

1. Introduction

A vast number of mesogenic naphthalene derivatives are reported in the literature,^{1,2} as naphthalene derivatives exhibit rich mesomorphism if properly designed. Wiegand³ reported a few mesogenic Schiff bases of 2,6-, 1,5- and 1,4-diaminonaphthalenes. Gray and Jones⁴ investigated liquid crystalline properties of different alkoxynaphthoic acids. Coates and Gray⁵ synthesized 4-*n*-alkyl/alkoxy phenyl esters of 6-*n*-alkyl/alkoxy naphthalene 2-carboxylic acid. Dave and others studied a variety of liquid crystalline naphthalene derivatives such as alkoxybenzoates of 1,5- and 1,4-dihydroxynaphthalene,⁶ esters of cholesterol⁷ and alkoxy naphthylidene Schiff's bases^{8–10} exhibiting smectic, nematic, and cholesteric mesomorphism. Malthete *et al*¹¹ synthesized tetra-acylated 1,4,5,8-tetrahydroxynaphthalene derivatives, which may be looked upon as "conjoined twin" mesogens. In the last decade, a significant number of research papers on naphthalene LC cores appeared in the literature.^{12–21} Recently the synthesis and mesomorphic properties of banana-shaped compounds derived from 2,7-dihydroxynaphthalene have also appeared in the literature.^{22,23} Previously we have reported^{24,25} the mesogenic homologous series of Schiff's base esters containing the naphthalene moiety and studied the effect of lateral thiol and methoxy

substituent on mesomorphism. We have also reported the synthesis of mesogenic homologous series of azomesogens without lateral substituent,²⁶ with lateral methyl²⁷ and chloro²⁸ groups and evaluated the effect of lateral methyl as well as chloro group on mesomorphism. Recently, we have reported²⁹ the mesogenic homologous series of azoesters containing two naphthalene nucleuses and studied the effect of naphthalene moiety on mesomorphism. We have also reported³⁰ mesogenic homologous series of Schiff's base cinnamates comprising a naphthalene moiety and investigated the effect of an ethylene linking group (cinnamoyl linkage) and naphthalene moiety on the mesomorphic properties of such molecules. As an extension of this work on naphthalene moiety, we have synthesized a new mesogenic homologous series of azoesters containing lateral chloro group to investigate the influence of the lateral chloro group and its position on mesomorphism.

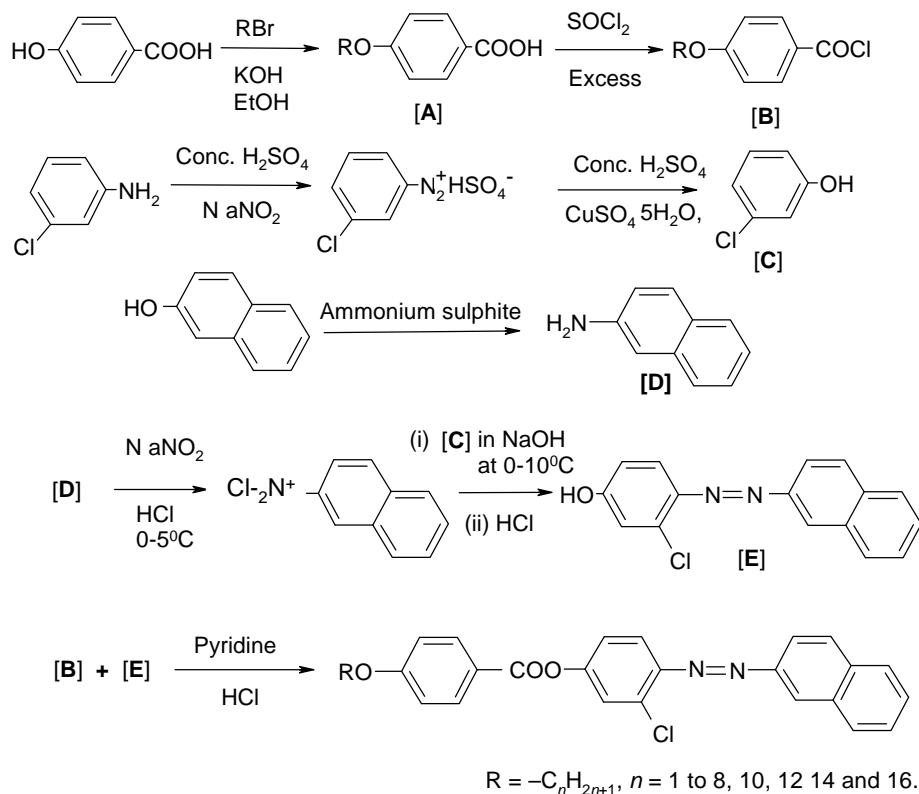
2. Experimental

2.1 Characterization

Microanalysis of the compounds was performed on a Coleman carbon–hydrogen analyzer and the values obtained are in close agreement with those calculated. IR spectra were determined as KBr pellets, using a Shimadzu IR-408 spectrophotometer. ¹H NMR spectra were obtained with a Perkin–Elmer R-32 spectrometer using tetramethylsilane (TMS) as internal reference standard. The chemical shifts are

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*For correspondence



Series 1

Scheme 1. Synthetic route to series 1.

quoted as *d* (parts per million) downfield from the reference. $CDCl_3$ was used as a solvent for all the compounds. Liquid crystalline properties were investigated on a Leitz Laborlux 12 POL microscope provided with a heating stage. The enthalpies of transitions reported as J/g, were determined from thermo grams obtained on a Mettler TA-4000 system, adopting a scanning rate of $5^\circ C/min$. The calorimeter was calibrated using pure indium as standard.

2.2 Synthesis

The synthetic route to series 1 and 2 is illustrated in scheme 1.

4-Hydroxybenzoic acid, the appropriate *n*-alkyl halides, $SOCl_2$, KOH, 2-naphthol, 3-chloro aniline, $NaNO_2$, $CuSO_4 \cdot 5H_2O$, anhydrous K_2CO_3 etc. were used as received. Solvents were dried and distilled prior to use.

2.2a 4-*n*-Alkoxybenzoic acids [A] and 4-*n*-alkoxybenzoyl chlorides [B]: These were synthesized by the modified method of Dave and Vora.³¹

2.2b 3-Chlorophenol [C]: Two similar methods^{32,33} are convenient for the synthesis of 3-chlorophenol. However the first method³² permits the use of copper sulphate pentahydrate after diazotization of 3-chloroaniline³³ and gives somewhat better yield.

A solution of (54 g) of 3-chloroaniline in 83 ml of conc. H_2SO_4 and 150 ml of water was cooled by addition of 250 g of ice and diazotized with 27.3 g of $NaNO_2$ in 54 ml of water. The filtered solution of the diazonium salt was added dropwise to a mixture of water (175 ml), sulphuric acid (170 ml, d 1.84), and copper sulphate pentahydrate (50 g) which was steam-distilled. The temperature of the diazotized solution was kept below $5^\circ C$ until immediately before the addition. Extraction of the distillate with ether, followed by distillation, gave the phenol (70% yield), b.p. $211^\circ C$, deliquescent yellow needles, m.p. $31^\circ C$ (reported³² m.p. $31-32^\circ C$).

2.2c 2-Aminonaphthalene [D]: The 2-aminonaphthalene was synthesized by following the method described in the literature.³⁴ A stream of sulphur dioxide was passed into 200 ml of cooled, concen-

trated ammonia solution (sp. gr. 0.88) until 50 g of gas was absorbed. This ammonium sulphite solution was placed together with 72 g of 2-naphthol in an autoclave provided with a stirrer and stirring adjusted at 260 rpm. The mixture was securely fastened in the cap and heated at 150°C with continuous stirring for 8 h. It was then allowed to cool with stirring. The reaction mixture was then removed from the apparatus diluted with the aid of about 250 ml of water and filtered on a Buckner funnel. The crude material was dissolved in a boiling mixture of 75 ml of concentrated hydrochloric acid and 200 ml of water, and then diluted with 500 ml of water. Five grams of decolourizing carbon was added, the solution boiled for 5 min, and filtered through a hot water funnel to remove any undissolved dinaphthylamine ($C_{10}H_7NHC_{10}H_7$). The hot filtrate was poured with stirring into a solution of 60 g of sodium hydroxide in 250 ml of water. It was ensured that the resulting slurry was alkaline to phenolphthalein, cooled with stirring to 20°C, filtered with suction, and washed with 1 l of cold water. It was then pressed well. The product was dried to constant weight at 50–60°C. Yield of 2-aminonaphthalene, m.p. 112°C (reported³⁴ m.p. 112–113°C) isolated as a light tan powder was 55%.

2.2d 2-(4*C*Hydroxy-2*C*chlorophenylazo) naphthalene [*E*]: 2-(4'-Hydroxy-2'-chlorophenylazo) naphthalene was synthesis by using conventional method of diazotization and coupling.³⁴ The dye was crystallized from ethanol till constant melting point was obtained. Yield: 68% m.p. 138°C. Elemental analysis: found C 68.06, H 3.23, N 9.46%, $C_{16}H_{11}N_2Cl$

requires C 68.21, H 3.55, N 9.94%. IR spectra of the compound show a broad peak of intermolecularly hydrogen bonded phenolic –OH between 3500 and 3100 cm^{-1} . –N=N– stretching vibrations are seen at 1605 cm^{-1} . Other signals are observed at 1500, 1465, 1380, 1230, 1150, 850, 686 (C–Cl) cm^{-1} .

2.2e 2²-[4-(4*C**n*-(Alkoxybenzoyloxy)-2-chlorophenylazo)naphthalenes (**1**): 2-(4'-Hydroxy-2'-chlorophenylazo) naphthalene (0.02 mol) was dissolved in dry pyridine (5 ml) and a cold solution of 4-*n*-alkoxybenzoyl chloride (0.02 mol) in dry pyridine was added with constant stirring in an ice bath. The mixture was allowed to stand overnight at room temperature. It was acidified with cold water and hydrochloric acid. The solid obtained was separated, dried and triturated by stirring for 30 min with 10% aqueous sodium hydroxide, and was then washed with water. The insoluble mass separated and crystallized several times from acetic acid till constant transition temperatures were obtained. Yield: 65 to 70%. Elemental analysis of all compounds of series **1** was found to be satisfactory and the compounds are listed in table 1.

IR spectrum (*n*-tetradecyloxy derivative): 2900, 1735 (–COO–), 1604, 1581 (–N=N–) 1510, 1470, 1400, 1220, 898, 850, 750, 690 (C–Cl cm^{-1}).

¹H NMR spectrum (*n*-tetradecyloxy derivative, 200 MHz): **d** 0.88 (*t*, 3H, –CH₃), 1.26–1.85 (*m*, 24H, 12 X –CH₂–), 4.05 (*t*, 2H, ArOCH₂), 7.00 (*d*, *J* = 9 Hz, 2H, ArH at C-3' and C-5'), 7.20–7.60 (*m*, 7H, ArH of naphthalene ring), 7.80–7.95 (*m*, 2H, ArH at C-5 and C-6), 8.00–8.15 (*m*, 2H, ArH at C-2' and C-6'), 8.50 (*s*, 1H, ArH at C-3).

Table 1. Elemental analysis for series **1** compounds.

Compound	R = –C _{<i>n</i>} H _{2<i>n</i>+1} n =	Formula	% Required (% found)		
			C	H	N
1	1	C ₂₄ H ₁₇ N ₂ O ₃ Cl	69.15 (69.24)	4.08 (3.81)	6.72 (6.57)
2	2	C ₂₅ H ₁₉ N ₂ O ₃ Cl	69.69 (69.71)	4.41 (4.67)	6.50 (6.45)
3	3	C ₂₆ H ₂₁ N ₂ O ₃ Cl	70.19 (70.06)	4.72 (4.92)	6.30 (6.21)
4	4	C ₂₇ H ₂₃ N ₂ O ₃ Cl	70.67 (70.55)	5.02 (4.86)	6.12 (6.37)
5	5	C ₂₈ H ₂₅ N ₂ O ₃ Cl	71.11 (71.42)	5.29 (5.38)	5.93 (6.06)
6	6	C ₂₉ H ₂₇ N ₂ O ₃ Cl	71.53 (71.26)	5.55 (5.58)	5.75 (5.92)
7	7	C ₃₀ H ₂₉ N ₂ O ₃ Cl	71.93 (72.17)	5.79 (5.84)	5.59 (5.54)
8	8	C ₃₁ H ₃₁ N ₂ O ₃ Cl	72.30 (71.95)	6.02 (6.37)	5.44 (5.24)
9	10	C ₃₃ H ₃₅ N ₂ O ₃ Cl	72.99 (72.73)	6.45 (6.66)	5.16 (5.18)
10	12	C ₃₅ H ₃₉ N ₂ O ₃ Cl	73.62 (73.46)	6.84 (6.85)	4.91 (4.82)
11	14	C ₃₇ H ₄₃ N ₂ O ₃ Cl	74.18 (74.38)	7.18 (7.26)	4.68 (4.77)
12	16	C ₃₇ H ₄₇ N ₂ O ₃ Cl	74.70 (74.86)	7.50 (7.21)	4.47 (4.80)

3. Results and discussion

Mesophases exhibited by series **1** compounds were identified by examining thin films of a sample sandwiched between a glass slide and a cover slip under a optical polarizing microscope. On cooling the isotropic liquid small droplets appeared which coalesce to classical schlieren (threaded) textures characteristic of the nematic phase.

Calorimetry is a valuable method for the detection of phase transitions. It yields quantitative results; therefore we may draw conclusions concerning the nature of the phases which occur during the transitions. In the present study, enthalpies of two derivatives of each series **1** were measured by differential scanning calorimetry. Data are recorded in table 2. Enthalpy values of the various transitions agree well with the literature³⁵ value.

3.1 Series **1** – 2²-[4(4*n*-alkoxybenzoyloxy) 2-chlorophenylazo]naphthalenes

All the twelve homologues synthesised exhibit enantiotropic nematic mesophase (table 3). It can be noticed from the plot of transition temperatures against the number of carbon atoms (figure 1) that crystal-mesophase transition temperatures decrease with increase in the length of terminal alkoxy chain with the exception of *n*-propyloxy, *n*-butyloxy and *n*-octyloxy derivatives. The N-I transition temperatures also decrease with increase in terminal alkoxy tail and exhibit the usual odd–even effect. However the odd–even effect of this series is not so pronounced. This is in agreement with the observation reported for such homologues series.³⁶

Table 4 shows the comparison of *N-iso* transition temperature, range (width) of nematic phase and molecular structure of representative compound **7** (*n* = 7) of the present series **1** and structurally related compounds **A**²⁸, **B**²⁶, **C**²⁷ and **D**²⁹ reported in the literature. The nematic mesophase range and the *N-iso* transition temperature of compound **7** are

Table 2. DSC data for series **1** compounds.

Series	<i>n</i> =	Transition	Peak temperature (°C)	ΔH	ΔS
1	12	Cr–N	91.6	22.90	0.0628
		N–I	152.5	1.17	0.0027
	14	Cr–N	92.2	45.07	0.1234
		N–I	139.6	1.05	0.0025

lower by 4.0°C and 47.0°C, respectively when compared with of compound **B**. The molecular structure of compound **7** differs from compound **A** only at the central aromatic core; compound **7** has lateral chloro group at the central benzene nucleus, whereas compound **B** has no lateral substituent at the central benzene nucleus. Thus compared with the molecule of compound **B**, the molecule of compound **7** has increased breadth due to the lateral chloro group on central benzene ring. Gray³⁶ has explained that increase in the breadth of the molecules reduces both nematic and smectic mesophase stability. It seems that the lateral chloro group not only increases the breadth of the molecule of compound **7** but also in-

Table 3. Transition temperatures (°C) of the series **1**.

R = –C_{*n*}H_{2*n*+1}

Compound	<i>n</i> =	Cr	N	I
1	1	• 103	• 216	•
2	2	• 98	• 215	•
3	3	• 107	• 204	•
4	4	• 135	• 205	•
5	5	• 95	• 188	•
6	6	• 94	• 179	•
7	7	• 92	• 171	•
8	8	• 95	• 165	•
9	10	• 92	• 158	•
10	12	• 89	• 153	•
11	14	• 89	• 150	•
12	16	• 87	• 148	•

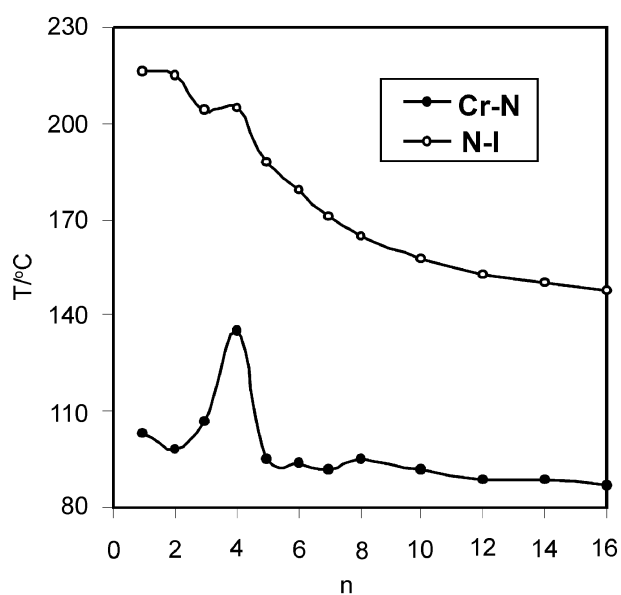
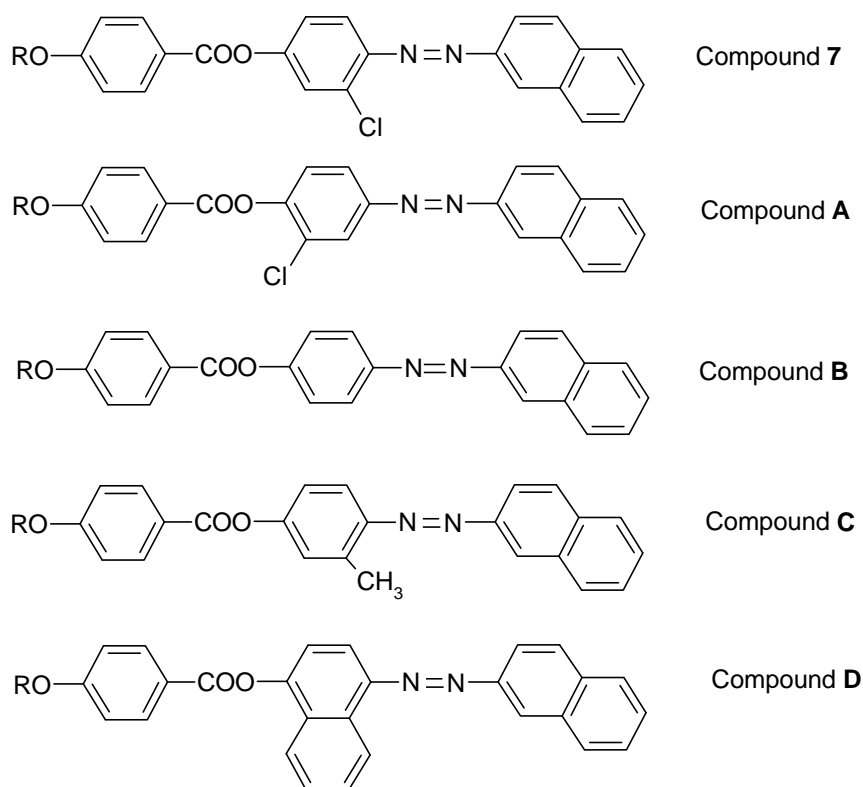


Figure 1. The phase behaviour of series **1**.

Table 4. The comparison of *N-iso* transition temperature ($^{\circ}\text{C}$) and the range of nematic phase between a representative compound **7** (C_7 homologue) of the present series **1** and structurally related compounds reported in the literature.

$\text{R} = -\text{C}_7\text{H}_{15}$, comparative molecular structure of the compounds **7**, **A**, **B**, **C** and **D**.

Compound	Cr	N	Iso	Mesophase range ($^{\circ}\text{C}$)	Commencement of smectic phase
7	• 92.0	• 171.0	•	79.0	–
A	• 111.0	• 186.0	•	75.0	–
B	• 135.0	• 218.0	•	83.0	C_{10}
C	• 86.0	• 147.0	•	61.0	–
D	• 111.0	• 144.0	•	33.0	–



creases the acoplanarity in the system due to steric interaction. Both these factors would eliminate the smectogenic tendencies as well as decrease the nematic mesophase range and the *N-iso* transition temperature for compound **7** reported in the present investigation. These agree well with the work reported by Prajapati²⁷ in which the mesogenic homologous series **C** with a lateral methyl group exhibits only nematic phase with low thermal stabilities compared to parent unsubstituted homologous series **B**.

Reference to table 4 indicates that the width of the nematic mesophase for compound **A** is 75.0°C and for compound **7** is 79.0°C , whereas *N-iso* transition temperature for compound **A** is 186.0°C and that

of compound **7** is 171.0°C . Gray³⁶ has explained that a compound which requires more thermal energy to disorganize the parallel molecular arrangement of the nematic melt is thermally more stable. As can be seen in table 4, more thermal energy has to be supplied to disorganize the parallel molecular arrangement of the nematic melt of compound **A**, as can be evidenced by the fact that the *N-iso* transition temperature is higher by 15.0°C , than for compound **7**. The higher *N-iso* transition temperature for compound **A** may be due to the presence of lateral chloro group *ortho* to the $-\text{COO}-$ central linkage. Probably the flexibility of the $-\text{COO}-$ central linkage compensates the steric hindrance and enables a

more compact packing of the molecules to stabilize the nematic. The range and thermal stability of the mesophase is a more important factor in relating mesomorphic behaviour to chemical constitution, since the chemical grouping gives rise to intermolecular attractions which in turn determine the mesophase range and thermal stability. One should remember too that the length of the mesophase is determined partly by the Cr-N transition temperature, which is lower for compound **7** compared to compound **A**. Therefore the nematic mesophase length for compound **7** is higher by 4.0°C than that of compound **A**.

Table 4 shows that the nematic mesophase range and the N-iso transition temperature for compound **7** are higher by 18.0°C and 24.0°C respectively, when compared to that of compound **C**. The difference in the molecular structure of both the compounds is only in the type of lateral substituent on the central benzene nucleus. Compound **7** has a lateral chloro group, whereas compound **C** has a lateral methyl group. Probably the increase in the polarizability of the compound **7** due to polar chloro group slightly overcomes the increased molecular separation caused by the lateral substituent. Therefore, the width of the nematic mesophase as well as the N-iso transition temperature of compound **7** becoming a little higher than that of compound **B**.

Table 4 further shows that the nematic mesophase range as well as N-iso transition temperature of compound **7** are higher by 46.0°C and 27.0°C respectively, when compared to that of compound **D**. The molecular structural difference between compounds **7** and **D** lies only at the central aromatic core; compound **7** has lateral chloro groups at the central benzene nucleus, whereas compound **D** has a naphthalene nucleus at the centre. This difference has significant influence on the nematic mesophase range as well as on N-iso transition temperature as can be seen in table 4. The stabilization of nematic phase in case of compound **7** is wide and perhaps the foregoing discussion would hold good for this behaviour.

From the above discussion the order of lateral group efficiency for nematic phase thermal stability can be derived for the compounds as under: $-H > 3-Cl > 2-Cl > -CH_3 >$ fused ring (1-4 substituted naphthalene moiety).

It agrees well with the order in lateral group efficiency for nematic phase obtained by Gray³⁶ for pure nematogenic rod-shaped molecules.

4. Conclusion

A new mesogenic homologous series of naphthyl azomesogens with lateral chloro groups was synthesized. The study indicated that the lateral chloro group adversely affects mesophase thermal stability. However, due to the polar nature of the chloro group, the effect is less pronounced compared to the lateral methyl group.

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