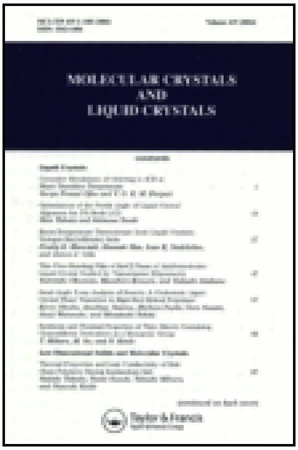

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Influence of Changes in the Central Core on the Mesomorphic Properties of 4,4′ -Dialkoxybenzalazines and Derivatives (II)

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Influence of Changes in the Central Core on the Mesomorphic Properties of 4,4′-Dialkoxybenzalazines and Derivatives (II)

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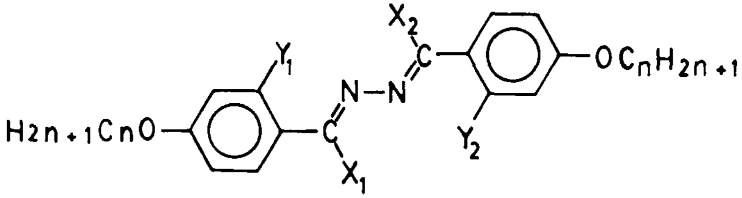
Two homologous series of benzalazines were synthesized, namely, the 4,4′-di-*n*-alkoxy-2-hydroxybenzalazines and 4,4′-di-*n*-alkoxybenzalazines, and their mesomorphic properties were studied.

All the prepared compounds of these series exhibit mesomorphism and some of them possess crystalline polymorphism also.

A comparative study of the mesomorphic properties of these series with those of 4,4′-di-*n*-alkoxy-2,2′-dihydroxybenzalazines and the analogous α,α′-dimethylbenzalazines was carried out in order to determine the influence of the central core on the mesomorphic properties.

INTRODUCTION

In previous papers[1,2,3] we described the synthesis and studied the mesomorphic properties of new series of compounds derived from diazines with general formula (I):



n=1-10,12,14,16,18

X_1 = or ≠ X_2 = H, CH_3

Y_1 = or ≠ Y_2 = H, OH

These studies were made in order to establish a relation between molecular structure and the mesogenic properties of the compounds, paying special attention to the geometry of the molecular central core.

In this paper, the synthesis and the mesogenic behaviour of two new series of compounds derived from benzalazine which were undertaken to complete these studies, are described. These are the

4,4′-di-*n*-alkoxy-2-hydroxybenzalazines, I(b), where $X_1 = X_2 =$ H and $Y_1 =$ OH, $Y_2 =$ H, and the

4,4′-di-*n*-alkoxybenzalazines, I(a), where $X_1 = X_2 =$ H and $Y_1 = Y_2 =$ H.

The former series was synthesized for the first time especially for this investigation, while the latter series is partly described in the literature[4] (for $n = 1 - 10$). Our experimental results, however, differ in some cases from the data reported in reference 4.

A comparative study of the mesogenic properties of these series with some of the others described in the above-mentioned papers has also been carried out, in order to study the influence of the hydroxyl group in position 2 of the aromatic ring and the different mesogenic behaviour observed between azines derived from ketones and azines derived from aldehydes.

EXPERIMENTAL

Synthesis

The method of synthesis used for the preparation of the compounds of series I(a) and I(b) is similar to that described in a previous paper.[1]

4,4′-di-*n*-alkoxybenzalazines (series I(a)) were prepared using the method used to prepare 4,4′-di-*n*-alkoxy-α,α′-dimethylbenzalazines and the 4,4′-di-*n*-alkoxy-2-hydroxybenzalazines (series I(b)) were prepared in the same way as the 4,4′-di-*n*-alkoxy-2-hydroxy-α,α′-dimethylbenzalazines.

In the latter case the conditions used for alkylation of the OH group in position 4 had to be modified and it was necessary to use the weaker base, $KHCO_3$, instead of K_2CO_3 and shorter reaction times, to avoid the alkylation of the OH group in position 2 in one of the benzene rings, taking place also.

Techniques

The melting points, transition temperatures and enthalpies were determined using a PERKIN-ELMER DSC-2 Differential Scanning

Calorimeter. The heating rate was 4°C/min. The apparatus was calibrated by measuring the known melting points and fusion enthalpies of benzoic acid (121.2°C, 33.9 cal/g) and indium (156.6°C, 6.8 cal/g).

The optical observations were made using a REICHERT-THERMOVAR HT-1 B11 Polarizing Microscope equipped with a heating stage.

The identification of products was carried out by the usual spectroscopic methods: UV (PERKIN-ELMER 200), IR (PERKIN-ELMER 283) and NMR (PERKIN-ELMER R-12-B).

The purity of all products was checked using the above-mentioned techniques and by thin-layer chromatography.

Textures observed

The mesophase textures were observed with a polarizing microscope using thin films of the sample mounted between a glass slide and a cover slip.

The mesophase textures observed were nematic (N) and smectic C (S_C) mesophases, identified because of their similarity to the descriptions of these textures made by Demus and Richter.[5]

RESULTS AND DISCUSSION

Effect of increasing terminal chain length of series I(a) and I(b) on mesomorphic behaviour

Transition temperatures and enthalpies and the mesophase type shown by the compounds of the two series: I(a), 4,4′-di-*n*-alkoxybenzalazines and I(b), 4,4′-di-n-alkoxy-2-hydroxy-benzalazines are listed in Tables I and II respectively.

Both types of compounds show very similar mesogenic behaviour. In series I(a), the compounds show a nematic phase when n = 1−9 and an S_C phase for n = 14,16,18. When n = 10,12, both a smectic C and a nematic phase are exhibited (see Figure 1).

Series I(b) shows similar properties except that the region where both S_C and N phases appear is n = 7−10 (see Figure 2).

The melting temperatures decrease from n = 2 onwards reaching a minimum when n = 6 in series I(a) and n = 9 in series I(b). The clearing temperatures gradually decrease from n = 2 onwards but no minimum was observed. Both series show the odd-even effect, the effect being more pronounced for shorter terminal chains.

TABLE I

Transition temperatures and enthalpies for 4,4′-di-*n*-alkoxybenzalazines (series I(a)).

n	Transition	Temperature °C	ΔH Kcal/mol
1	C - N	169.8	9.26
	N - I	182.8	0.38
2	C - N	172.6	10.46
	N - I	198.2	0.65
3	C_1 - C_2	103.0	2.22
	C_2 - N	158.9	8.11
	N - I	163.8	0.41
4	C_1 - C_2	99.3	3.93
	C_2 -N	146.3	7.60
	N - I	168.7	0.60
5	C - N	129.1	11.97
	N - I	149.4	0.35
6	C - N	126.8	14.02
	N - I	151.4	0.63
7	C_1 - C_2	94.0	5.80
	C_2 - N	130.9	8.58
	N - I	141.9	0.61
8	C_1 - C_2	93.0	6.21
	C_2 - N	131.0	8.87
	N - I	140.8	0.61
9	C_1 - C_2	79.8	5.99
	C_2 - C_3	83.2	1.53
	C_3 - N	125.8	8.80
	N - I	136.4	0.58
10	C_1 - C_2	78.9	7.57
	C_2 -S_C	123.2	8.16
	S_C - N	124.6	0.89
	N - I	135.5	0.83
12	C_1 - C_2	89.4	5.79
	C_4 - C_2^a	83.8	2.97
	C_2 - C_3	95.4	3.12
	C_3 - S_C	120.2	8.66
	S_C - N	127.8	1.81
	N - I	130.2	1.20
14	C_1 - C_2	92.4	4.04
	C_4 - C_2^a	88.0	1.90
	C_2 - C_3	105.9	5.89
	C_3 - S_C	119.0	9.66
	S_C - I	127.2	3.55
16	C_1 - C_2	99.4	6.51
	C_2 - C_3	111.2	7.42
	C_3 - S_C	118.0	11.74
	S_C - I	124.1	4.27
18	C_1 - C_2	103.7	7.72
	C_4 - C_2	101.0	7.24
	C_2 - C_3	116.6	9.87
	C_3 - S_C	118.2	12.25
	S_C - I	120.0	4.59

[a] Transition observed in the 2nd DSC scan.

TABLE II

Transition temperatures and enthalpies for 4,4′-di-*n*-alkoxy-2-hydroxybenzalazines. (Series I(b))

n	Transition	Temperature °C	ΔH Kcal/ mol.
1	C_1 - N	141.6	7.22
	C_2 - C_1+N	139.6	4.31
	C_1+N-N	142.2	2.92
	N - I	166.2	0.21
2	C - N	164.6	9.32
	N - I	193.8	0.44
3	C - N	139.0	7.40
	N - I	150.6	0.25
4	C - N	134.7	9.46
	N - I	164.6	0.45
5	C - N	134.2	11.01
	N - I	152.0	0.36
6	C_1 - C_2	96.2	1.59
	C_2 - N	116.2	9.75
	N - I	150.8	0.48
7	C - S_C	110.6	9.60
	S_C - N	116.4	0.47
	N - I	144.4	0.63
8	C_1 - C_2	94.9	5.61
	C_3 - C_2[a]	91.8	4.33
	C_2 - S_C	100.1	7.67
	S_C - N	126.0	0.66
	N - I	144.6	0.75
9	C - S_C	87.2	13.84
	S_C - N	127.6	1.47
	N - I	136.6	1.07
10	C_1 - C_2	68.0	0.87
	C_2 - S_C	89.8	10.14
	C_3 - S_C	82.8	9.96
	S_C - N	130.1	1.42
	N - I	134.9	1.04
12	C_1 - C_2	85.4	3.53
	C_2 - S_C	88.4	9.52
	S_C - I	128.9	2.39
14	C_1 - C_2	89.9	3.41
	C_2 - S_C	94.0	12.38
	S_C - I	129.1	3.54
16	C_1 - C_2	96.0	2.82
	C_3 - C_2[a]	91.2	2.07
	C_2 - S_C	101.0	10.31
	S_C - I	129.1	2.57
18	C_1 - C_2	98.4	0.54
	C_2 - S_C	103.0	15.90
	S_C - I	122.0	3.80

[a] Transition observed in the 2nd DSC scan.

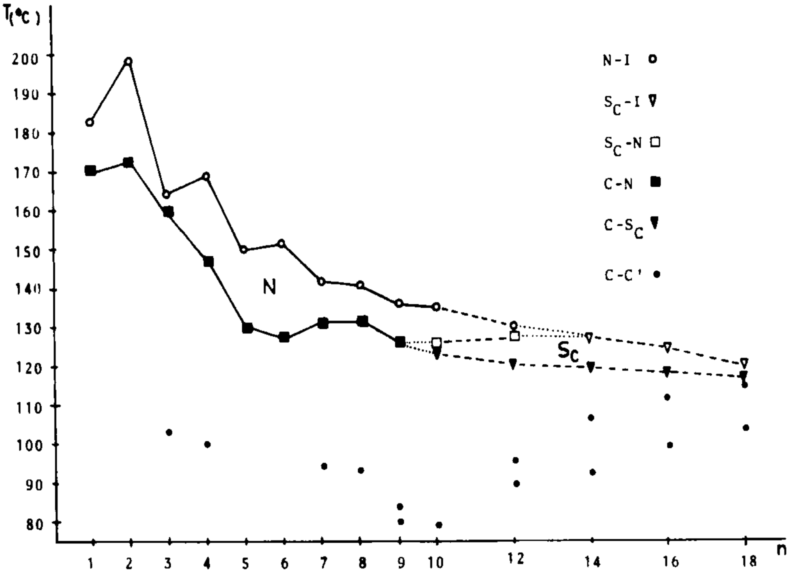


FIGURE 1 Transition temperatures as a function of alkyl chain length for 4,4′-di-*n*-alkoxybenzalazines.

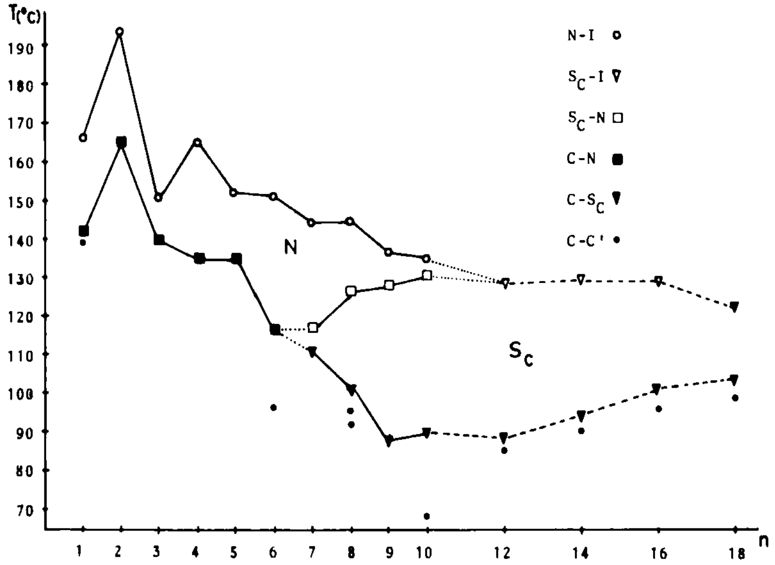


FIGURE 2 Transition temperatures as a function of alkyl chain length for 4,4′-di-*n*-alkoxy-2-hydroxybenzalazines.

As can be observed in Figures 1 and 2, most of the compounds of these series showed crystalline polymorphism (series I(a) when n = 3,4,7–10,12,14,16,18; series I(b) when n = 1,6,8,10,12,14,16,18). These solid state transitions were observed by optical microscopy.

Some examples of the melting cycles noted are:

$C_1 \rightleftarrows C_2 \rightleftarrows$ Mesophase n = 4,7,8 in series I(a)

n = 18 in series I(b)

$$\begin{tikzcd} C_1 \arrow[r] & C_2 \arrow[r, shift left] \arrow[d, shift left] & \text{Mesophase} \arrow[l, shift left] \\ & C_3 \arrow[u, shift left] & \end{tikzcd}$$

n = 8,16 in series I(b)

More information about these cycles can be obtained from the data gathered in tables I and II.

It should be pointed out that one of the principal diagreements obseved in our data for the compounds of series I(a) with respect to those in the literature (reference 4) corresponds to a crystal-crystal transition which is reported (for $n = 7 - 10$) as a crystal-smectic transition.

Influence of an OH group in the *ortho* position

Figures 3 and 4 show the melting points and N (or S_C)-I transition temperatures, respectively, for series I(a), 4,4′-di-*n*-alkoxybenzalazines, I(b), 4,4′-di-*n*-alkoxy-2-hydroxy-benzalazines and I(c), 4,4′-di-*n*-alkoxy-2,2′-dihydroxybenzalazines.[3]

Comparison of the three series shows different behaviour for temperatures at which the transitions appear and the subsequent mesomorphic properties with increase in terminal chain length.

While the lowest melting temperatures are shown by the compounds of series I(b), the highest melting temperatures correspond to compounds belonging to series I(a) when the terminal chains are long ($n \geqslant 7$), and to the compounds of series I(c) when the terminal chains are short ($1 \leqslant n \leqslant 6$).

The fact that compounds belonging to series I(b), with one OH group in the *ortho* position, show lower melting points than their homologues in the other two series, I(a) and I(c), can be attributed to the asymmetry of the molecular central core which constitutes a bigger steric hindrance to the regular order of the molecules in the solid state and therefore causes weaker forces of interaction in the solid.

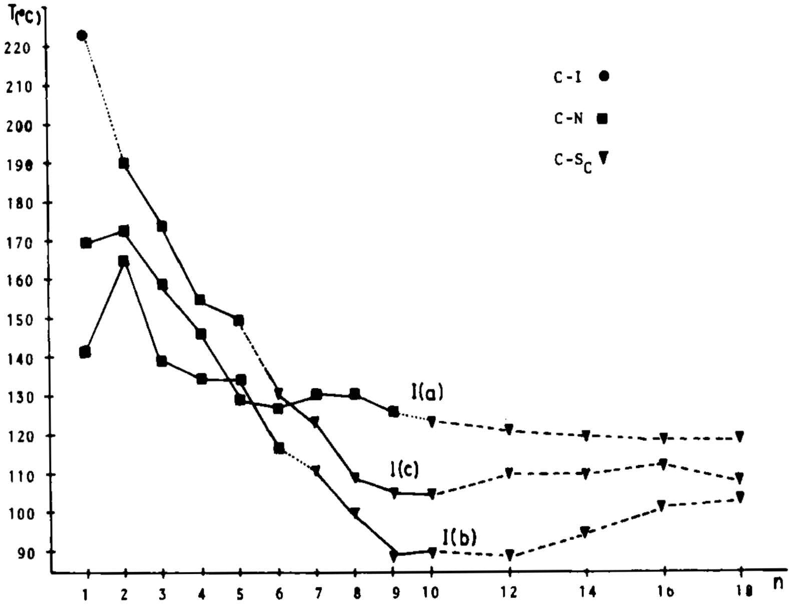


FIGURE 3 Crystal-mesophase transition as a function of alkyl chain length for three series of compounds I(a), I(b) and I(c).

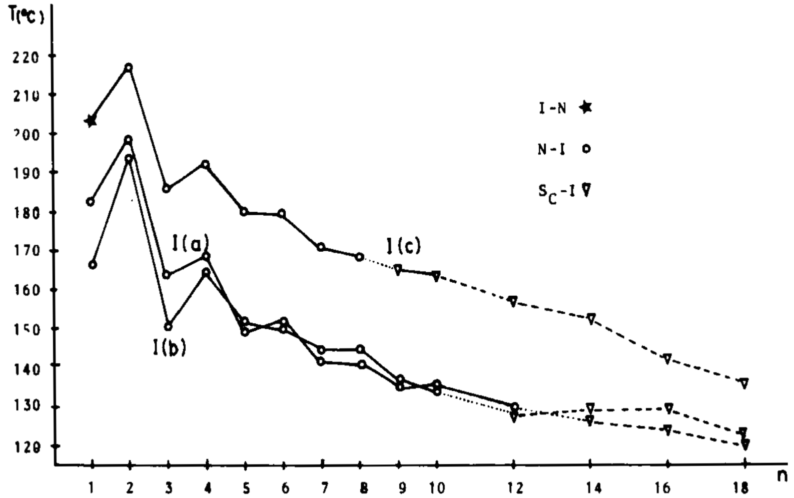


FIGURE 4 Mesophase-isotropic liquid transition as a function of alkyl chain length for three series of compounds I(a), I(b) and I(c).

An S_C mesophase appears in series I(c) when n = 5, in series I(b) when n = 7 and in series I(a) when n = 10. It is observed that the introduction of the hydroxyl group in the *ortho* position causes the S_C mesophase to appear for terminal chains of shorter length. This indicates an increase in the degree of molecular order which is favoured by the influence of the electronic parameters introduced by the hydroxyl group (increase in the polarizability).

The introduction of the hydroxyl group also influences the stability of the mesophases. Compounds of series I(a) and I(b) show very similar temperatures for the transition to the isotropic liquid (see Figure 4), while the corresponding temperatures for the compounds which belong to series I(c) are 25°C higher on average. It can therefore be assumed that the presence of a second OH group in an *ortho* position confers a high degree of stability on the mesophase, undoubtedly due to the increase in van der Waals forces which are in turn due to the increased anisotropy of the molecular polarizability.

It must be pointed out that the compounds of series I(a) and I(b) show similar temperatures for the transition to the isotropic liquid. This is because, in the mesophase, the molecules have greater freedom and so the influence of steric hindrance, caused by the asymmetry of the central core of the compounds of series I(b), is reduced. This gives rise to interaction forces of the same order and consequently the clearing points are similar.

Differences observed in the mesogenic behaviour between the two series of benzalazines described and the analogous derivatives of α,α′-dimethylbenzalazines.

Figure 5 shows the melting temperatures of the compounds of series I(a) 4,4′-di-*n*-alkoxybenzalazines, I(b) 4,4′-di-*n*-alkoxy-2-hydroxybenzalazines, I(a′) 4,4′-di-*n*-alkoxy-α,α′-dimethylbenzalazines[1] and I(b′) 4,4′-di-*n*-alkoxy-2-hydroxy-α,α′-dimethylbenzalazines,[1] and Figure 6 shows the clearing points of the compounds of series I(b) and I(b′).

If we compare the thermal data of compounds derived from benzalazines with homologous derivatives of ketazines it can be seen that, with some exceptions, the former melt at lower temperatures than the analogous derivatives of α,α′-dimethylbenzalazines (see Figure 5). We can also observe that the derivatives of benzalazine show a smectic C mesophase while the corresponding mesophase shown by the derivatives of ketazines is smectic A.

On the other hand, it should be emphasized that the compounds

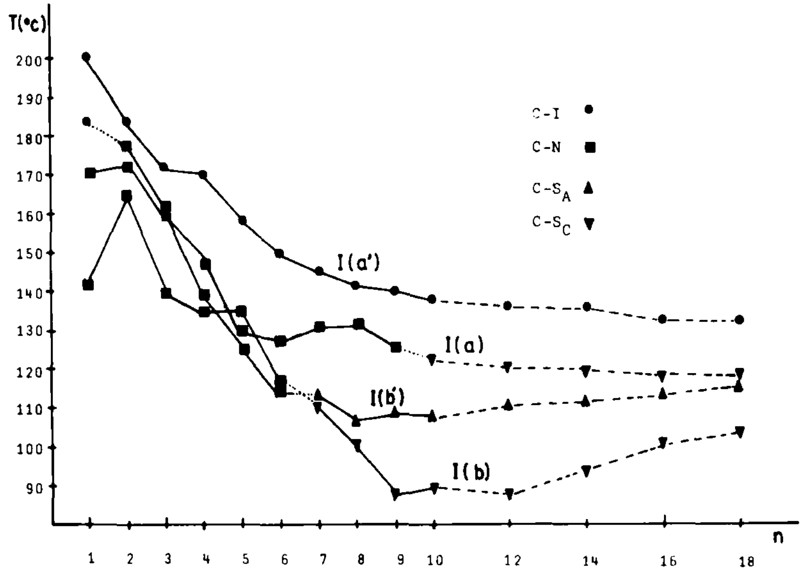


FIGURE 5 Crystal-mesophase transition as a function of alkyl chain length for four series of compounds I(a), I(a'), I(b) and I(b').

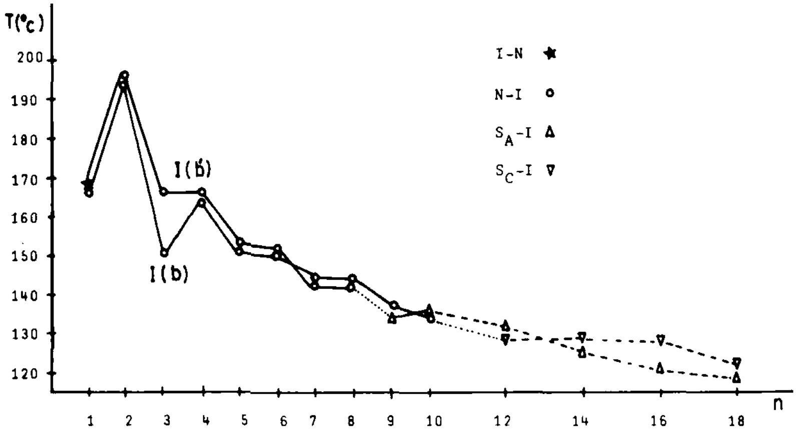


FIGURE 6 Mesophase-Isotropic liquid transition as a function of alkyl chain length for two series of compounds I(b) and I(b').

derived from ketazines with no hydroxyl group in the *ortho* position (series I(a'), show only a monotropic nematic mesophase for three members (n = 1,2,3), and the rest of the compounds of the series are not mesogenic whereas the homologous derivatives of benzalazines (series I(a)) are all enantiotropic mesogens, as described in this paper.

Also noteworthy is the fact that the temperatures of transition to the isotropic liquid of compounds derived from benzalazines (series I(b)) are slightly lower than the clearing temperatures of compounds derived from α,α'-dimethylbenzalazines (series I(b')) (see Figure 6).

CONCLUSIONS

An OH group in an *ortho* position of a benzene ring of benzalazines forms hydrogen bonds with the N atom of the azine central core. This increases the anisotropy of the molecular polarisability and hence increases the degree of molecular order causing the smectic phase to have increased stability and to appear for compounds with relatively short alkyl chains.

Compounds derived from benzalazines always show a smectic C mesophase whereas the compounds derived from α,α'-dimethyl-benzalazines always show smectic A mesophases.

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