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A study of homologation and the occurrence of an $S_A-S_C-S_A$ sequence of phases in the 4-*n*-alkoxy-3-fluorophenyl 4-(5-*n*-alkyl-2-thienyl)benzoates

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A study of homologation and the occurrence of an $S_A-S_C-S_A$ sequence of phases in the 4-*n*-alkoxy-3-fluorophenyl 4-(5-*n*-alkyl-2-thienyl)benzoates

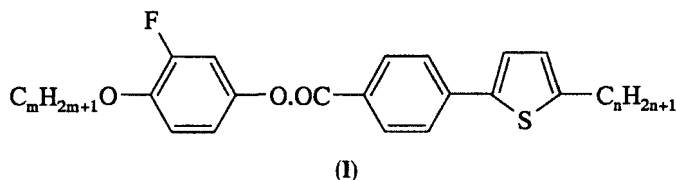
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Seventeen esters, derived from 4-*n*-alkoxy-3-fluorophenols and 4-(5-*n*-alkyl-2-thienyl)benzoic acids, have been prepared and their liquid crystal transition temperatures determined by thermal optical microscopy. On cooling the isotropic liquid, the $S_A-S_C-S_A$ sequence of phases reported for the octyloxy-octyl and octyloxy-nonyl esters has been observed for certain other homologues, principally members of the 4-(5-*n*-nonyl-2-thienyl)benzoates. For these compounds, the temperature range of occurrence of the intermediate S_C phase decreases as the length of the alkoxy chain increases (for the hexyloxy-nonyl to dodecyloxy-nonyl esters) and the S_C phase is absent for the tetradecyloxy-nonyl homologue.

1. Introduction

We recently reported [1] unusual smectic polymorphism shown by the octyl homologue of the 3-fluoro-4-*n*-octyloxyphenyl 4-(5-*n*-alkyl-2-thienyl)benzoates (I; $m = n = 8$), for which the observed sequence of phases on cooling the isotropic liquid is $S_A-S_C-S_3-S_E$. Subsequent investigation of additional members of this series (see figure 1) revealed [2] that the nonyl homologue has similar properties, and we presented X-ray diffraction and DSC evidence which supported that from optical microscopy pointing clearly to the conclusion that the S_3 phase is another phase with unstructured layers, which we believe to be a second S_A phase.



The characteristics of the textural changes occurring in the phase sequence $S_A-S_C-S_3$ are as follows. The bâtonnets that initially separate from the isotropic liquid develop into well defined focal-conic fans interspersed with homeotropic regions, typical of an S_A phase. On cooling to the S_A-S_C transition, the fans lose their well-defined appearance and the homeotropic regions give rise to the schlieren texture of an

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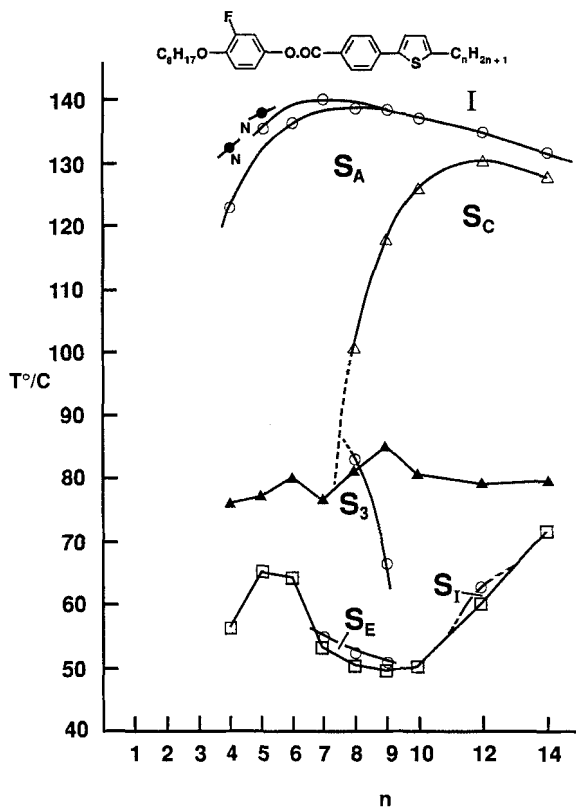


Figure 1. 3-Fluoro-4-*n*-octyloxyphenyl 4-(5-*n*-alkyl-2-thienyl)benzoates: transition temperatures against *n*, the number of carbon atoms in the alkyl group. (▲) indicates the melting point and (□) the crystallization temperature at a cooling rate of $4^{\circ}\text{C min}^{-1}$.

S_C phase (see plate 1*). On further cooling into the S_3 (second S_A) phase the schlieren areas disappear, becoming homeotropic once more, and the broken fans gradually recover their well-defined appearance (see plate 2*).

2. Results and discussion

We now report the results of the effect of homologation on liquid crystal behaviour in which we have included 17 other members of related series, namely the corresponding pentyloxy (I; $m=5$, $n=9$), hexyloxy (I; $m=6$, $n=7-10$), heptyloxy (I; $m=7$, $n=7-10$), nonyloxy (I; $m=9$, $n=7-10$, 12), decyloxy (I; $m=10$, $n=9$), dodecyloxy (I; $m=12$, $n=9$), and tetradecyloxy esters (I; $m=14$, $n=9$).

Initially, we prepared members of the hexyloxy, heptyloxy and nonyloxy series. The liquid crystal transition temperatures for these esters are listed in the table and are shown plotted against *n*, the number of C atoms in the alkyl group, in figures 2, 3 and 4.

These plots show a very close similarity to that for the octyloxy esters (see figure 1) previously discussed [2]. In particular, the homologues $n=8$ and 9 of the hexyloxy compounds, and $n=9$ of both the heptyloxy and nonyloxy esters also show the S_3 (second S_A) phase. The series differ in their behaviour on further cooling. Before

* For $n=9$ of the octyloxy homologue.

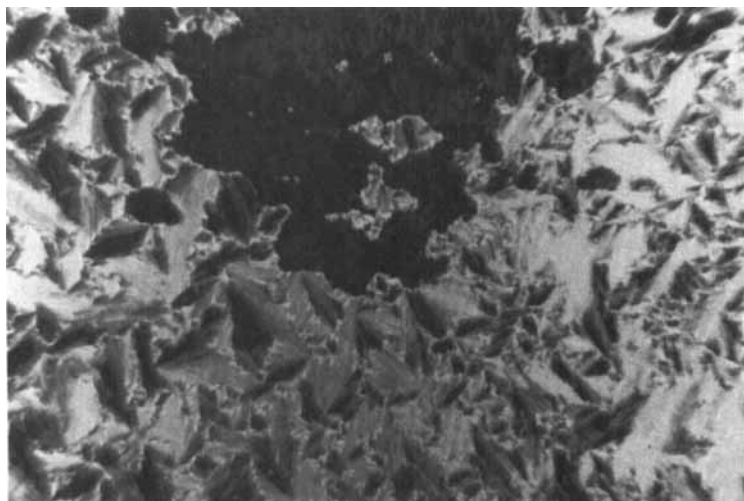


Plate 1. S_C phase of (I); $m=8$, $n=9$.

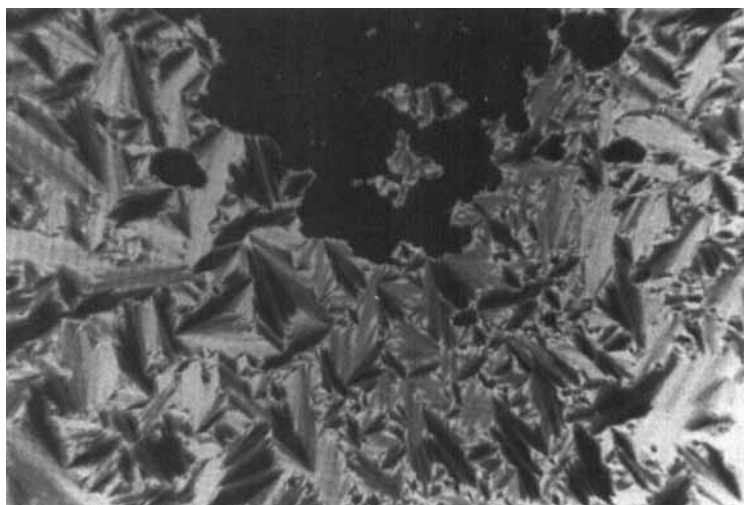


Plate 2. S_3 (second S_A) phase of (I); $m=8$, $n=9$, just before S_3-S_E transition.

crystallization, the homologues $n=7-10$ and $n=8$ and 9 , respectively, of the hexyloxy and heptyloxy series each give an S_E phase, and the member $n=10$ of the heptyloxy esters gives an S_I phase. In contrast, the nonyloxy esters do not give rise to higher order phases.

Conclusions that may be drawn from this work are:

- (i) the form of the plots of transition temperature against n (the length of the alkyl chain) for the hexyloxy to nonyloxy esters is, broadly, very similar;
- (ii) the occurrence of the S_3 (second S_A) phase is confined to the $n=8$, and principally, the $n=9$ homologues.

Transition temperatures for the 4-*n*-alkoxy-3-fluorophenyl 4-(5-*n*-alkyl-2-thienyl) benzoates.

		Transition temperature/ $^{\circ}\text{C}$ (a)						$S_{\text{A}}-\text{C}$ (b)
<i>n</i> -Alkoxy group	<i>n</i> -Alkyl group	$\text{C}-S_{\text{A}}$ $\text{C}-S_{\text{C}}^{\dagger}$	$S_{\text{A}}-\text{I}$	$S_{\text{C}}-S_{\text{A}}$	$S_{\text{3}}-S_{\text{C}}$ $S_{\text{I}}-S_{\text{C}}^{\dagger}$	$S_{\text{E}}-S_{\text{A}}^{\dagger}$ $S_{\text{E}}-S_{\text{C}}^{\dagger}$ $S_{\text{E}}-S_{\text{3}}^{\S}$	$S_{\text{I}}-\text{C}^{\dagger}$ $S_{\text{C}}-\text{C}^{\S}$ $S_{\text{3}}-\text{C}^{\parallel}$	
$\text{C}_5\text{H}_{11}\text{O}$	C_9H_{19}	86.4 \dagger	141.7	101.4		(60.8) \ddagger (c)	54 \dagger	
$\text{C}_6\text{H}_{13}\text{O}$	C_7H_{15}	71.5	142			(56.9) \dagger	56 \dagger	
	C_8H_{17}	77.5 \dagger	141	98	(75.1)	(53.2) \S	45 \dagger	
	C_9H_{19}	82 \dagger	140.5	111.2	(59)	(51.3) \S	49.5 \dagger	
	$\text{C}_{10}\text{H}_{21}$	78.8 \dagger	138	116.8		(50.4) \ddagger	49.5 \dagger	
$\text{C}_7\text{H}_{15}\text{O}$	C_7H_{15}	81	140				63	
	C_8H_{17}	84.1	138.6			(49.6) \dagger	48.5 \dagger	
	C_9H_{19}	89 \dagger	138.9	114.8	(65)	(48) \S	47 \dagger	
	$\text{C}_{10}\text{H}_{21}$	81 \dagger	138.5	123.2	(58.4) \dagger		54 \ddagger	
$\text{C}_9\text{H}_{19}\text{O}$	C_7H_{15}	86	137.4				60	
	C_8H_{17}	80.7	135				56	
	C_9H_{19}	92.7 \dagger	135.5	112	(73.3)		55 \parallel	
	$\text{C}_{10}\text{H}_{21}$	81.5 \dagger	134.2	122			59.8 \S	
	$\text{C}_{12}\text{H}_{25}$	82 \dagger	127.6	119			58.9 \S	
$\text{C}_{10}\text{H}_{21}\text{O}$	C_9H_{19}	87.7 \dagger	135	111.2	(74)		52.9 \parallel	
$\text{C}_{12}\text{H}_{25}\text{O}$	C_9H_{19}	93.3 \dagger	131.5	101.5	(83.8)		65.8 \parallel	
$\text{C}_{14}\text{H}_{29}\text{O}$	C_9H_{19}	97	128.5				71.2	

(a) Symbols have their usual meaning: C, crystal; I, isotropic liquid; N, nematic; S_{A} , smectic A, etc. Thus $\text{C}-S_{\text{A}}$ represents the temperature (m.p.) at which a transition from the crystalline solid to the smectic A phase occurs.

(b) Temperature of crystallization (at a cooling rate of approximately $4^{\circ}\text{C min}^{-1}$).

(c) Values in parentheses are for monotropic transitions.

We then prepared the $n = 9$ homologue of the pentyloxy, decyloxy, dodecyloxy, and tetradecyloxy esters (the transition temperatures for which are listed in the table) and found that except for the former and latter esters these compounds also give the S_{3} (second S_{A}) phase. Accordingly, the results for these esters have been incorporated into the plot shown in figure 5 which indicates, in a different manner to figures 1–4, the effect of homologation on liquid crystal behaviour in these series. In figure 5 the liquid crystal transition temperatures are plotted against m , the number of C atoms in the alkoxy group, for the nonyl homologue ($n = 9$) of each series, i.e. the plot shows the effects of varying the alkoxy group for a constant alkyl chain length. The main features of figure 5 are that with increasing alkoxy chain length, m :

- the points for the $S_{\text{A}}-\text{I}$ transition temperatures show an odd–even m alternation, with the curves falling gradually and the even m curve uppermost;
- odd–even m alternation of the $S_{\text{C}}-S_{\text{A}}$ transition temperatures also occurs, with the curves for both odd and even members rising to a maximum (at $m = 7$ and $m = 8$) and then falling;
- alternation in the opposite sense (even–odd m) of the $S_{\text{3}}-S_{\text{C}}$ transition temperatures occurs, the curves for both odd and even members rising continuously from their onset at $m = 6$ to the highest transition temperature observed at $m = 12$;

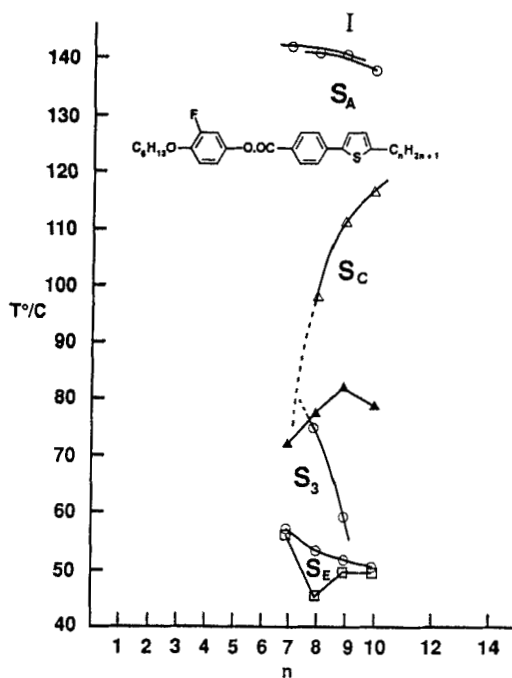


Figure 2. 3-Fluoro-4-*n*-hexyloxyphenyl 4-(5-*n*-alkyl-2-thienyl)benzoates: transition temperatures against *n*, the number of carbon atoms in the alkyl group. (▲) indicates the melting point and (□) recrystallization at a cooling rate of $4^{\circ}\text{C min}^{-1}$.

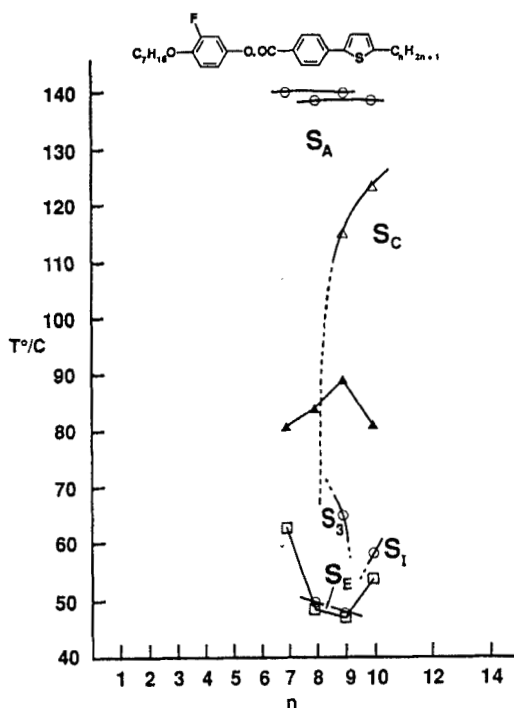


Figure 3. 3-Fluoro-4-*n*-heptyloxyphenyl 4-(5-*n*-alkyl-2-thienyl)benzoates: transition temperatures against *n*, the number of carbon atoms in the alkyl group. (▲) indicates the melting point and (□) recrystallization at a cooling rate of $4^{\circ}\text{C min}^{-1}$.

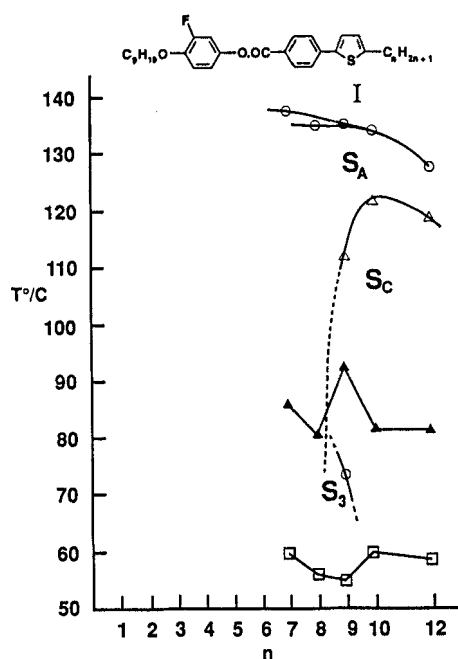


Figure 4. 3-Fluoro-4-*n*-nonyloxyphenyl 4-(5-*n*-alkyl-2-thienyl)benzoates: transition temperatures against *n*, the number of carbon atoms in the alkyl group. (\blacktriangle) indicates the melting point and (\square) recrystallization at a cooling rate of $4^{\circ}\text{C min}^{-1}$.

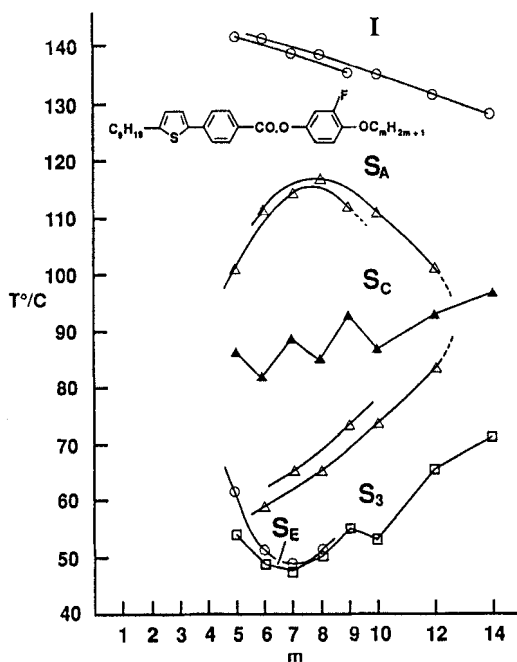


Figure 5. 3-Fluoro-4-*n*-alkoxyphenyl 4-(5-*n*-nonyl-2-thienyl)benzoates: transition temperatures against *m*, the number of carbon atoms in the alkoxy group. (\blacktriangle) indicates the melting point and (\square) recrystallization at a cooling rate of $4^{\circ}\text{C min}^{-1}$.

- (d) the temperatures of transition to S_E phases, for $m=5$ (S_E-S_A) and $m=6-8$ (S_E-S_3) fall to a minimum at $m=7$ and then rise;
- (e) the homologue $m=14$ gives only an S_A phase.

The most striking feature of figure 5 is the temperature range over which the S_C phase occurs. There is an overall reduction in the sequence 52.2° , 49.8° , 51.6° , 38.7° , 37.2° , 17.7°C as the alkoxy chain length increases from $m=6-10$, 12. For the homologue $n=14$, the S_C phase is absent, and the S_A phase continues, without interruption, into the temperature region of occurrence of the S_3 phase. This behaviour firmly indicates an affinity in identity between the S_A and S_3 phases. Indeed, this plot for the nonyl homologues strongly suggests that it is the S_C phase that is the deviant feature by the injection, over a well-defined temperature range, of tilting into otherwise orthogonal S_A layers.

3. Conclusion

This study of the effect of homologation on the liquid crystal properties of the 3-fluoro-4-*n*-alkoxyphenyl 4-(5-*n*-alkyl-2-thienyl)benzoates confirms our earlier conclusion [2] that the sequence of phases observed on cooling the isotropic liquid includes a second S_A phase, namely $I-S_A-S_C-S_A$. This behaviour is confined principally to the 4-(5-*n*-nonyl-2-thienyl)benzoates and, to a lesser extent, the octyl homologues. However, it is not clear how the molecular structure of these octyl and nonyl esters influences the stabilization of tilted unstructured layers within a relatively narrow temperature band above and below which orthogonal unstructured layers are favoured. As the length of the alkoxy chain of the phenyl moiety increases there is a decrease in the range of temperature over which the intermediate S_C phase occurs.

4. Experimental

The esters were prepared and characterized as described previously [2]. Thermal optical microscopy was carried out with a Vickers M75 polarizing microscope in conjunction with a Mettler FP 52 hot stage and FP 5 control unit. Thermal analysis was carried out with a Perkin-Elmer DSC 7 differential scanning calorimeter.

4.1. Preparation of materials

The 4-*n*-alkoxy-3-fluorophenyl 4-(5-*n*-alkyl-2-thienyl)benzoates were prepared as described previously and summarized in the earlier synthetic scheme [2]. Several 4-*n*-alkoxy-3-fluorophenols were required and these were obtained by the following method.

The appropriate *n*-alkyl bromide (0.047 mol) was added, dropwise, with vigorous stirring, to 4-bromo-2-fluorophenol (9.0 g, 0.047 mol) and anhydrous potassium carbonate (21.0 g, 0.115 mol) in dry acetone (80 ml). The reaction mixture was heated under reflux for 8 h, then cooled, poured into water, and extracted with ether. The extract was dried, the solvent removed, and the oily residue purified by distillation under reduced pressure affording the 4-*n*-alkoxy-3-fluoro-1-bromobenzene (90–95 per cent) as a pale straw coloured oil, b.p.s. (0.1–0.15 mm Hg): pentyloxy, 105° ; heptyloxy, 145° ; octyloxy, 140° ; decyloxy, 180°C ; dodecyloxy, 204° ; tetradecyloxy, 240°C .

The 4-*n*-alkoxy-3-fluoro-1-bromobenzene (0.031 mol) and an equimolar quantity of 1,2-dibromoethane (as an entrainer) in dry ether (100 ml) were added, dropwise, in an atmosphere of nitrogen, over 4 h to magnesium turnings (1.5 g, 0.062 g atom) under dry ether (10 ml). When the reaction was complete the solution of the Grignard reagent was transferred to a dropping funnel and added, slowly, with vigorous stirring, in an

atmosphere of nitrogen, over 30 min to trimethyl borate (0.065 mol) in dry ether at -78°C . The resulting slurry was left to stand overnight under nitrogen, and 4M-aqueous hydrochloric acid (100 ml) then added, with stirring. The layers were separated, the aqueous phase was discarded, and 30 per cent hydrogen peroxide (20 ml) added, dropwise, with stirring, over 15 min, to the organic phase at 0°C . Stirring was continued for a further 15 min, whereafter the ether layer was separated, washed with 10 per cent aqueous iron(II) ammonium sulphate (200 ml) and then shaken with 4M-aqueous sodium hydroxide (100 ml) in two portions. Acidification of the alkaline solution released the phenol which, after extraction with ether, was distilled under reduced pressure and then crystallized from light petroleum (b.p. $40-60^\circ\text{C}$) affording the 4-*n*-alkoxy-3-fluorophenol (45-64 per cent) as an oil or white crystalline solid, m.p.s.: heptyloxy, $46-47^\circ$; octyloxy, $43.5-44.5^\circ$; decyloxy, $52.5-53.5^\circ$; dodecyloxy, $59-60^\circ$; tetradecyloxy, $66.5-67.5^\circ\text{C}$; pentyloxy, b.p. $145^\circ\text{C}/0.1$ mm Hg. Samples of 4-*n*-hexyloxy-, -octyloxy-, and -nonyloxy-3-fluorophenol were supplied by Merck Ltd.

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