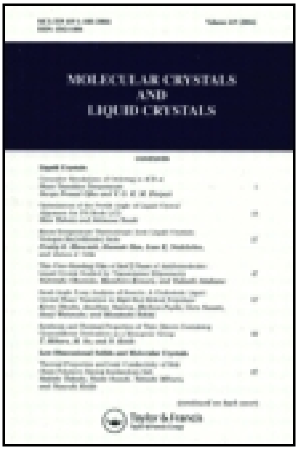

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Synthesis and Mesomorphic Properties of Schiff Base Esters p - n - Octadecanoyloxybenzylidene- p -Cyano-, p -Hydroxy-, p - Nitro, And p -Carboxyanilines

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SYNTHESIS AND MESOMORPHIC PROPERTIES OF SCHIFF BASE ESTERS *p*-*n*-OCTADECANOYLOXYBENZYLIDENE-*p*-CYANO-, *p*-HYDROXY-, *p*-NITRO, AND *p*-CARBOXYANILINES

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Synthesis and mesomorphic behaviors of p-*n-octadecanoyloxybenzylidene-*p-*substituted-anilines, $C_{17}H_{35}COOC_6H_4CH{:}NC_6H_4$-R, where R* = p-*CN,* p-*OH,* p-*NO_2, and* p-*COOH were reported. The physical properties as well as the chemical formulations of these compounds were derived from microanalysis and spectroscopic methods (FTIR, ^{1}H NMR and ^{13}C NMR). Phase transition temperatures and the thermal parameters were obtained from differential scanning calorimetry (DSC). The texture observation was performed under polarizing optical microscopy (POM) attached with Mettler hot stage. All the compounds are thermotropic liquid crystals except* p-*n-octadecanoyloxybenzylidene-*p-*nitroaniline. While the compounds containing R* = p-*CN and* p-*OH exhibit smectic phases, the one consisting of* p-*COOH shows nematic and smectic characteristics. The investigation upon the existence as well as the dissociation of intermolecular hydrogen bonding at various temperatures in different phases has also been inferred from the FTIR analysis.*

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Keywords: thermotropic liquid crystal; nematic; smectic; terminal substituents; intermolecular hydrogen bonding

INTRODUCTION

Compounds containing two unsaturated rings with terminal substituents or multiple substituents are the smallest molecules capable of showing mesogenic properties [1]. The typical examples of these compounds are Schiff base esters made up of an ester-linkage at one terminal and the different substituents residing at the other end along the long molecular axis. Over the past few years, the studies of low molar mass mesogens comprising these Schiff base esters have been documented, wherein the influence of terminal alkyl chain upon the liquid crystalline properties [2,3] and the possibility of enhancing the rigidity of core system of Schiff bases through metal complexes formation [4,5] have been claimed as two of the pathways to improve the mesogenic properties.

Sakagami and coworkers have studied the mesomorphic behavior of a homologous series of 4-(4-n-alkoxy-2-hydroxybenzylideamino)phenol [6]. They reported that the compounds of similar system with an alkoxy chain of C_{10} to C_{18} exhibit smectic phases wherein the intermolecular as well as intramolecular hydrogen bondings contribute greatly to the formation of the mesophases. It is well reported that the smectic mesophase can be easily introduced by increasing the terminal chain length. However, the mesophase of most of these compounds is not thermally stable.

In this paper, we report some Schiff base esters prepared from the esterification of 4-hydroxybenzaldehyde with n-octadecanoic acid (stearic acid) followed by condensation with various substituted anilines in which *para* position of aniline is occupied by CN, OH, NO_2, and COOH groups, respectively.

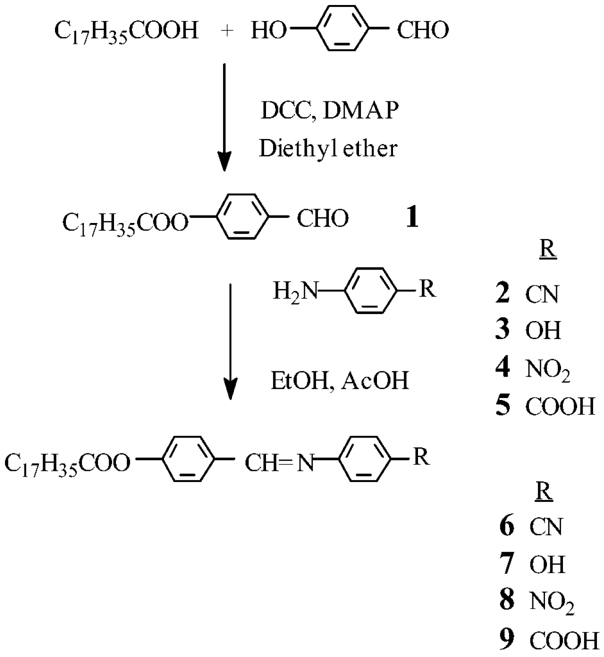
All compounds thus isolated were purified and characterized by microanalysis and spectroscopic methods (FTIR, ^{1}H NMR, and ^{13}C NMR) along with thermal analysis and texture observation using DSC and POM, respectively. Changes in the terminal polar substituents and the effect of the hydrogen bonding (H-bonding) on the mesophases are also discussed.

EXPERIMENTAL

4-Hydroxybenzaldehyde, 4-aminophenol, 4-aminobenzonitrile, 4-aminobenzoic acid, 4-dimethylaminopyridine (DMAP), and stearic acid were obtained from Merck (Germany). 4-Nitroaniline and dicyclohexylcarbodiimide (DCC) were purchased from Riedel-de Haen, Germany and Fluka Chemie, Switzerland respectively. All reagents were directly used without further purification.

Microanalyses were carried out on 2400 LS Series CHNS/O analyzers in The School of Chemical Sciences, Universiti Sains Malaysia. ^{1}H NMR and ^{13}C NMR were recorded on a JEOL JNM-GX-500 spectrometer 500 MHz with tetramethylsilane as internal standard. IR spectra were recorded using a Perkin-Elmer 2000-FTIR spectrophotometer. The infrared spectra used to determine the hydrogen bonding were recorded at different temperatures by the same spectrophotometer with a hot stage. Thin layer chromatography analyses were performed using aluminium-backed silica gel plates (Merck 60 F254) and were examined under UV light. Column chromatography was performed under gravity using Aldrich 100–200 mesh silica gel. Melting point of the synthesized compounds were measured by Gallenkamp melting-point apparatus.

The optical microscopy studies were carried out with an Olympus Vanox Tokyo Japan 200845 polarizing microscope equipped with a Mettler FP52 hot stage. The textures of the compounds were observed by using polarized



SCHEME 1 Synthetic routes towards the formation of intermediates and target compounds **1–9**.

light with crossed polarizers, with the sample in thin film sandwiched between glass slide and cover. The phase transition temperatures were determined by differential scanning calorimetry of Seiko DSC-10 at heating and cooling rates of 5°C/min and −5°C/min, respectively.

The syntheses of these Schiff base esters were carried out according to the reactions as summarized in Scheme 1.

Synthesis

Synthesis of n-octadecanoyloxybenzaldehyde, 1

This compound was synthesized according to the method described by Hassner and Alexanian [7]. Dicyclohexylcarbodiimide, DCC (0.41 g, 2×10^{-3} mole) and 4-dimethylaminopyridine, DMAP (0.02 g, 2×10^{-4} mole) were added to a stirred solution of 4-hydroxybenzaldehyde (0.24 g, 2×10^{-3} mole), stearic acid (0.57 g, 2×10^{-3} mole) and diethyl ether (50 mL). The mixture was stirred for 12 h at room temperature. The solution was filtered off and the filtrate washed with water (3 × 50 mL), 5% acetic acid solution (3 × 50 mL), and again with water (3 × 50 mL). The organic layer was dried (Na_2SO_4) and the solvent evaporated (yield 83%). m.p. 49–50°C IR (ZnSe), 1742 cm^{-1} (C=O of ester), 1695 cm^{-1} (C=O of aldehyde), 1221 cm^{-1}(C-O of ether). ^{1}H NMR ($CDCl_3$), 0.8–0.9 ppm (CH_3), 1.2 ppm (CH_2), 7.2–7.9 ppm (Ar-H), 10.0 ppm (CHO). ^{13}C NMR ($CDCl_3$), 14.1 ppm (CH_3), 29.1–29.7 ppm (CH_2), 122.3–155.5 ppm (Ar-C), 171.6 ppm (C=O of ester), 190.9 ppm (C=O of aldehyde).

Synthesis of p-n-octadecanoyloxybenzylidine-p-cyanoaniline, 6

In a round-bottom flask, a mixture of **1** (0.39 g, 1×10^{-3} mole), aminobenzonitrile (0.12 g, 1×10^{-3} mole) and ethanol (20 mL) with 2–3 drops of acetic acid was stirred for 4 h at room temperature. The precipitate obtained was filtered and recrystallized from ethanol (yield 63%). Elemental analysis: found, C 76.65, H 8.27, N 5.73: calculated (for $C_{32}H_{44}N_2O_2$) C 76.72, H 8.49, N 5.66. IR (KBr), 2230 cm^{-1} (C≡N), 1751 cm^{-1} (C=O of ester), 1627 cm^{-1}(C=N), 1202 cm^{-1}(C-O of ether). ^{1}H NMR ($CDCl_3$), 0.8–0.9 ppm (CH_3), 1.2–1.4 ppm (CH_2), 7.2–7.9 ppm (Ar-H), 8.3 ppm (CH=N). ^{13}C NMR ($CDCl_3$), 14.1 ppm(CH_3), 29.1–29.7 ppm (CH_2), 119.0 ppm (C≡N), 121.5–155.8 ppm (Ar-C), 161.1 ppm (C=N), 171.8 ppm (C=O of ester).

The preparation and characterization with the same procedures were carried out for compounds **7–9**. The analytical data obtained were summarized below as follows:

Synthesis of p-n-octadecanoyloxybenzylidine-p-hydroxyaniline, 7

Yield 59%. Elemental analysis: found, C 75.20, H 9.33, N 2.93: calculated (for $C_{31}H_{45}NO_3$) C 75.16, H 9.12, N 2.88. IR (KBr), 3383 cm^{-1} (OH), 1746 cm^{-1} (C=O of ester), 1624 cm^{-1} (C=N), 1213 cm^{-1} (C-O of ether). ^1H NMR ($CDCl_3$), 0.8–0.9 ppm (CH_3), 1.2 ppm (CH_2) 7.2–7.9 ppm (Ar-H), 7.9 ppm (CH=N). ^{13}C NMR ($CDCl_3$), 14.1 ppm (CH_3), 29.0–29.6 ppm (CH_2), 122.3–155.5 ppm (Ar-C), 155.5 ppm (C=N), 171.6 ppm (C=O of ester).

Synthesis of p-n-octadecanoyloxybenzylidine-p-nitroaniline, 8

Yield 53%. m.p. 49–50°C. Elemental analysis: found, C 76.07, H 8.79, N 2.35: calculated (for $C_{31}H_{44}N_2O_4$) C 76.00, H 8.76, N 2.55. IR (KBr), 1752 cm^{-1} (C=O of ester), 1601 cm^{-1} (C=N), 1695 cm^{-1}, 1351 cm^{-1} (NO_2), 1219 cm^{-1} (C-O of ether). ^1H NMR ($CDCl_3$), 0.8–0.9 ppm (CH_3), 1.2–1.3 ppm (CH_2), 7.2–7.9 ppm (Ar-H), 7.9 ppm (CH=N). ^{13}C NMR ($CDCl_3$), 14.1 ppm(CH_3), 29.1–29.7 ppm (CH_2), 122.3–155.5 ppm (Ar-C), 155.5 ppm (C=N), 171.6 ppm (C=O of ester).

Synthesis of p-n-octadecanoyloxybenzylidine-p-carboxyaniline, 9

Yield 56%. Elemental analysis: found, C 74.29, H 8.66, N 5.64: calculated (for $C_{31}H_{44}N_2O_4$) C 74.32, H 8.65, N 5.62. IR (KBr), 3493 cm^{-1} (OH), 1748 cm^{-1} (C=O of ester), 1683 cm^{-1} (C=N), 1211 cm^{-1} (C-O of ether). ^1H NMR ($CDCl_3$), 0.8–0.9 ppm (CH_3), 1.2–1.4 ppm (CH_2), 7.2–7.9 ppm (Ar-H), 8.4 ppm (CH=N). ^{13}C NMR ($CDCl_3$), 14.0 ppm (CH_3), 29.1–29.7 ppm (CH_2), 120.8–157.0 ppm (Ar-C), 160.5 ppm (C=N), 171.5–171.8 ppm (C=O of ester).

RESULTS AND DISCUSSION

Phase Transition Behavior and Liquid Crystallinity of *p*-n-octadecanoyloxybenzylidene-*p*-cyano-, *p*-hydroxy-, *p*-nitro, and *p*-carboxyanilines

The phase transitions and the texture of the compounds, especially at mesomorphic temperatures, were studied explicitly by using DSC and POM. The phase transition temperatures are summarized in Table 1. From Table 1, it is clearly shown that all the compounds except compound **8** exhibit the changes from crystal to mesophase and then isotropic over different temperatures. In order to determine the mesophases

TABLE 1 Transition Temperatures of Compounds **6**–**9** Upon Cooling Process

Compound	Transition	Temperature/°C	ΔT/°C	ΔH, J/g
6	Cr—SmA	66.5		
	SmA—I	106.8	40.3	65.7
7	Cr—SmC	108.0		
	SmC—I	124.7	16.7	80.9
8	Cr—I	48.3	—	75.5
9	Cr—N	91.8		
	N—SmC	106.4	15.0	64.3
	SmC—I	239.2	132.8	

Cr, crystal; SmA, smectic A; SmC, smectic C; I, isotropic.

in compounds **6**, **7**, and **9**, the texture observation on these compounds was carried out under POM, especially by the first and second cooling processes. The cooling scan upon compound **6** showed the presence of mesophase (Figure 1a) with broken fan-shaped texture. This feature is characteristic of the smectic-A as that reported in the literature [9]. The appearance of smectic-A phase is found to conform with the other aromatic compounds 4,4′-disubstituted phenylbenzoates as reported by Neubert and coworkers, even though the latter had shown smectic C phase rather than smectic A [9]. The presence of thermally stable mesomorphic Schiff base esters with the CN substituent can be ascribed to the ability of this compound to form bilayers as that reported for the compounds with OH substituent [8].

For compound **7**, a smectic schlieren texture (Figure 1b) similar to the texture reported in the literature [9] was again observed. However, for compound **9**, a nematic marbled texture (Figure 1c) was first observed when it was cooled down from the isotropic phase, and upon further cooling the texture characteristic of nematic phase has gradually changed to a phase identified as smectic C phase (Figure 1d).

One of the noticeable features is that the clearing temperature of compounds **7** and **9** are considerably higher than compound **6**. This piece of information is found to be in accordance with the increase in phase stability as that observed for *N*-[4-(4-n-alkoxybenzoyloxy)-2-hydroxybenzylidene]-hydroxyanilines, especially when the compound possesses polar OH group at *para* position [10]. The presence of *p*-OH and *p*-COOH substituents as those in the compounds reported by Sakagami [6] and Naoum [10] entailed the formation of lateral intermolecular H-bonding. In the earlier case, the presence of intermolecular H-bonding in *para*-substituted *N*-[4-(4-n-alkoxybenzoyloxy)-2-hydroxy-benzylidene]hydroxyaniline has led to the formation of dimeric associations [6]. Similarly, the higher transition temperatures possessed by 4-hexadecyloxyphenyl-4′-carboxybenzoate and

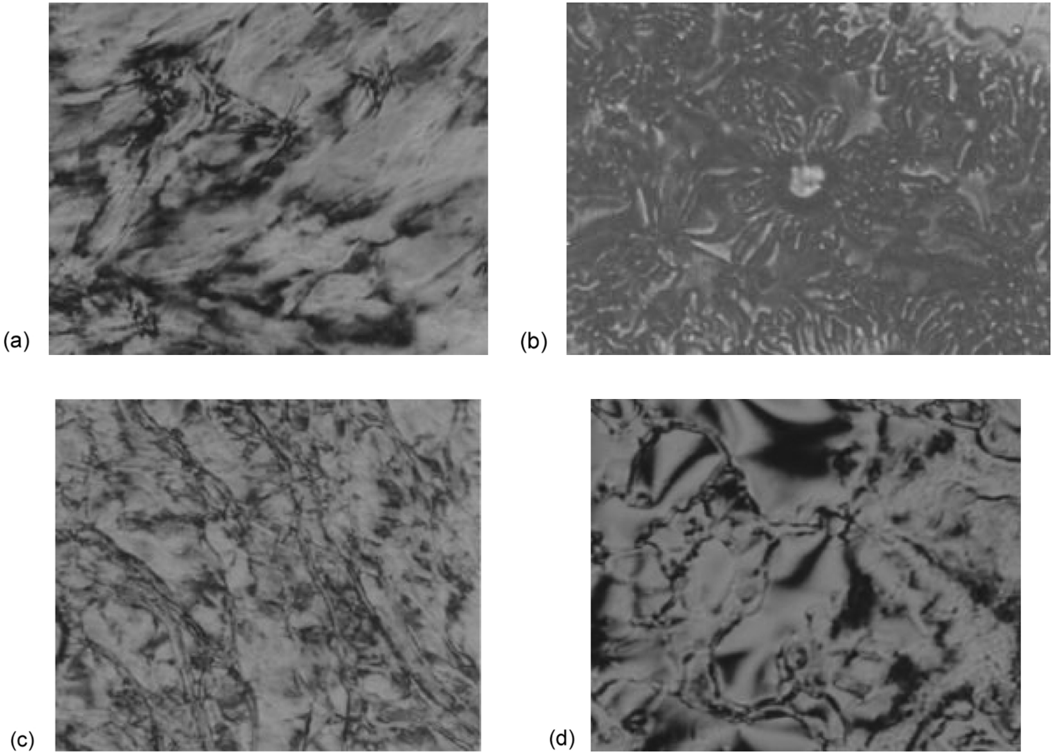


FIGURE 1 (a) Optical photomicrograph of compound **6** exhibiting broken fan-shaped texture. (b) Optical photomicrograph of compound **7** exhibiting schlieren texture. (c) Optical photomicrograph of compound **9** showing nematic phase. (d) Optical photomicrograph of compound **9** exhibiting schlieren texture (See Color Plate IV).

carboxyphenyl-4′-hexadecyloxybenzoate as reported by Naoum was attributed to the formation of linear dimeric molecules in the solid and liquid phases [10].

With this information we can postulate that the compounds **7** and **9** are also dimeric. The molecular structure for compound **9** with *p*-COOH, for example, has led to the formation of linear dimeric molecules, particularly in liquid phases. The existence of this dimeric molecule can be illustrated in Figure 2.

A further explanation with regards to the presence of intermolecular hydrogen bonding, particularly in the crystalline and mesophase of compounds **7** and **9**, is presented in the physical characterization by FTIR.

Physical Characterization

All the aromatic Schiff base esters thus obtained are found to be thermally stable and relatively resistant to hydrolysis.

The spectroscopic methods (FTIR, ^{1}H NMR, and ^{13}C NMR) have been employed to elucidate the structures of target compounds (**6**–**9**). FTIR data show that the diagnostic bands, which can be assigned to the stretching of cyano (C≡N), carbonyl (C=O), and imine (C=N) of compound **6,** were observed at the frequencies of 2230, 1751, and 1627 cm^{-1}, respectively. The bands appearing at 3482 and 3493 cm^{-1} in the spectra of compounds **7** and **9** can be ascribed to the presence of hydroxy (OH) group. A band assigned to the stretching of C=O of the ester linkage is also observable in the FTIR data of compounds **7** and **9**.

As for the present compound **7** existing as a crystal in ambient temperature, a broad peak assignable to the O-H stretching at 3383 cm^{-1} is found to be shifted to higher frequency 3482 cm^{-1} when the temperature was raised from room temperature to that above clearing point (Figure 3). In addition, the inspection from Figure 3 also shows that this peak is initially broadened but eventually forms a tangible shape peaking at higher frequency when the temperature was raised to clearing point. This observation could be ascribed to the occurrence of thermal motion when the compound undergoes isotropization process which reduces the intermolecular hydrogen bonding interaction as that reported for *p*-alkoxycinnamic acids [11]. A similar characteristic can also be inferred from the

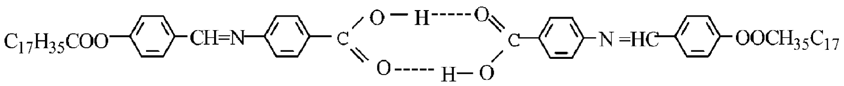


FIGURE 2 The proposed structure of linear dimeric molecule of compound **9**.

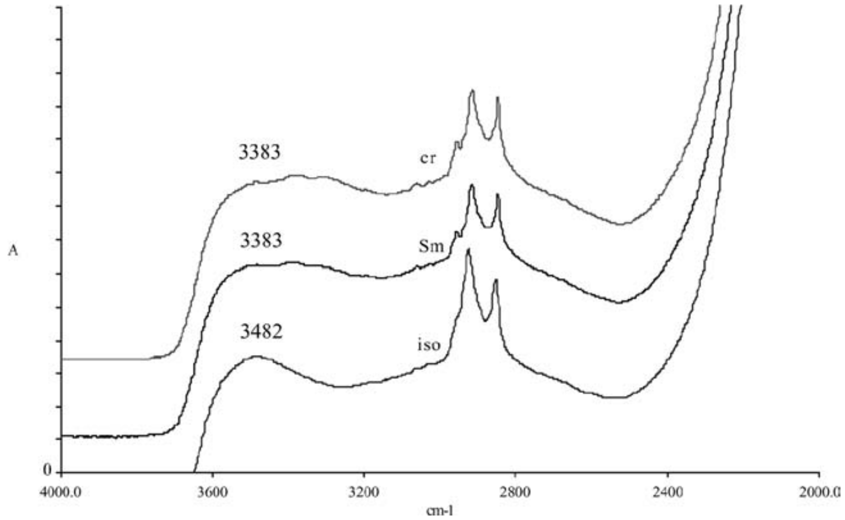


FIGURE 3 Observed IR spectrum—(a) isotropic at 140°C, (b) smectic C at 120°C, and (c) solid at 30°C—for compound **7**.

FTIR spectrum of compound **9**, wherein the transition from crystal to mesophase and then isotropic phase has resulted in the shift of O-H stretching frequency from 3493 cm^{-1} to 3504 cm^{-1} and finally 3536 cm^{-1}. This phenomenon could be ascribed to the same factor as that observed in compound **7**, wherein the increase in the O-H stretching frequency is due to the tendency for the compound to undergo dissociation of hydrogen bonding when it changes from crystal to mesophase or isotropic phase.

^{1}H NMR data of compound **6** showed that a peak due to the presence of azomethine proton (CH=N) was observable at the chemical shift $\delta = 8.3$ ppm. While a triplet assignable to the methyl group (CH_3) occurred at $\delta = 0.8$–0.9 ppm, the multiplet owing to the presence of methylene protons was observed within the range of $\delta = 1.2$–1.4 ppm. The structural information of **6** can also be inferred from the ^{13}C NMR data, wherein a peak ascribed to the carbon of ester carbonyl (-COO-) was observed at $\delta = 171.8$ ppm. The appearance of a peak at $\delta = 161.1$ ppm can be due to the presence of the carbon in imine group (C=N). An additional peak occurring at $\delta = 119.0$ ppm can be attributed to the presence of cyano ($C{\equiv}N$) group in compound **6**. The peaks with similar characteristic were also observed for compounds **7–9,** indicating the same molecular structures for these compounds as shown in Scheme 1.

The formulations and molecular structures of compounds **6–9** in Scheme 1 are also supported by the data obtained from microanalysis, wherein the percentages of C, H, and N from the analysis conform with the calculated values.

CONCLUSION

A series of Schiff base esters *p*-n-octadecanoyloxybenzylidene-*p*-cyano-, *p*-hydroxy-, *p*-nitro, and *p*-carboxyanilines has been successfully isolated. The physical properties, as well as their mesomorphic behavior, have been measured, wherein a noticeable feature pertinent to the intermolecular hydrogen bonding—particularly in compounds **7** and **9**—was highlighted. The FTIR analysis has further substantiated the inclination towards the formation of lateral intermolecular hydrogen bonding when the compounds exist at the temperature below the clearing point. The assessment by the FTIR has also revealed the dissociation of intermolecular hydrogen bonding due to the thermal motion.

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