Liquid Crystals
Publication details, including instructions for authors and subscription information:
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To cite this Article Ishizuka, Hidemi , Nishiyama, Isa and Yoshizawa, Atsushi(1995) 'Helical structures induced by laterally-connected chiral twin molecules', Liquid Crystals, 18: 5, 775 — 779
To link to this Article: DOI: 10.1080/02678299508036689
URL: http://dx.doi.org/10.1080/02678299508036689

LIQUID CRYSTALS, 1995, VOL. 18, NO. 5, 775–779

Helical structures induced by laterally-connected chiral twin molecules

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(Received 31 August 1994; accepted 27 October 1994)

A novel chiral twin material, (*R*)-bis[5-octyloxy-2-(4-octyloxyphenoxycarbonyl)phenyl] 3-methyladipate, has been prepared, where two mesogenic parts are connected laterally by a spacer possessing a chiral centre. A weaker helical structure, in particular in the chiral smectic C (S_C^*) phase, was found to be induced by the laterally-connected twin material than by the analogous terminally-connected twin material. If laterally-connected chiral twin molecules prefer to stay in the smectic layer structure so that the two mesogenic parts exist in the same smectic layer, the twist interaction between adjacent layers cannot be produced by direct correlation of motion and directions of two mesogenic parts. Thus, the helical structure in the S_C^* phase induced by laterally-connected chiral twin molecules becomes weak. An analogous laterally-branched 'monomeric' compound, (*S*)-5-octyloxy-2-(4-octyloxyphenoxycarbonyl)phenyl 3-methylpentanoate, has also been prepared, and the induced helical structures compared.

1. Introduction

Molecular configurations of chiral compounds as well as the structures at the chiral centre have been found to have substantial effects on chirality-dependent liquid crystalline properties. For instance, chiral twin materials where two mesogenic parts are linked terminally (see figure 1(*a*)) were found to produce stronger helical structures in the cholesteric (Ch) phase and, in particular, in the chiral smectic C (S_C^*) phase, than analogous chiral 'monomeric' materials (see figure 1(*b*)) [1,2]. The intercalation of the terminally-connected twin molecules in the smectic layer, where two mesogenic parts exist in neighbouring smectic layers, was proposed [1,2]. Since two mesogenic parts are connected by a chiral spacer, strong twist interaction can be produced between adjacent layers which induces the strong helical structure in the S_C^* phase. Laterally-connected chiral twin molecules (see figure 1 (*c*)), however, may prefer to exist so that the two mesogenic parts are in the same smectic layer. If this is the case, the twist interaction between adjacent layers cannot be produced by direct correlation of motion and directions of two mesogenic parts. Thus, the helical structure in the S_C^* phase induced by laterally-connected chiral twin molecules may be expected to be weaker than that induced by analogous terminally-connected chiral twin molecules.

In the present studies, a novel laterally-connected chiral twin compound, (*R*)-bis[5-octyloxy-2-(4-octyloxyphenoxycarbonyl)phenyl] 3-methyladipate (**MAB-8O8O-PCP**, see figure 2(*a*)), has been prepared and the liquid crystalline properties investigated for mixtures containing **MAB-8O8O-PCP**. Furthermore, the induced liquid crystalline properties have been compared to those induced by a related 'monomeric' compound, (*S*)-5-octyloxy-2-(4-octyloxyphenoxycarbonyl)phenyl 3-methylpentanoate (**MP-8O8O-PCP**, see figure 2(*b*)) or an analogous terminally-connected twin material, (*R*)-bis[4-(4-

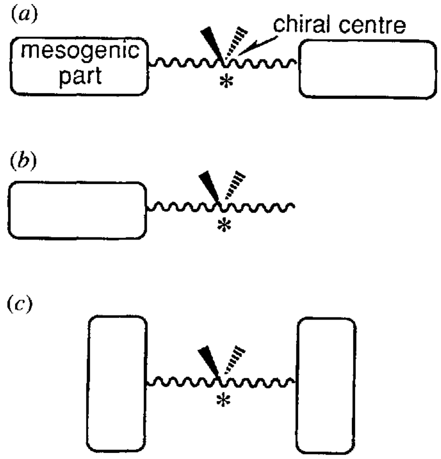

Figure 1. A schematic representation of a terminally-connected chiral twin molecule (*a*), an analogous chiral 'monomeric' molecule (*b*) and a laterally-connected chiral twin molecule (*c*).

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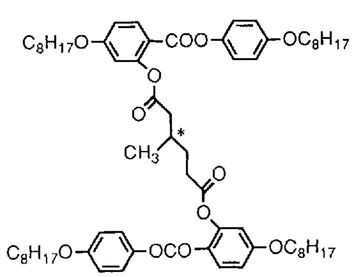
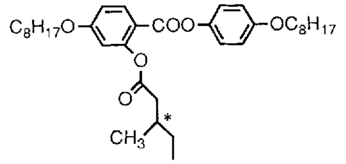
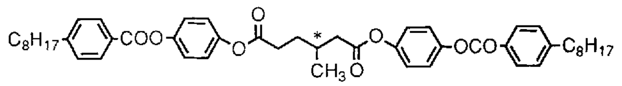


(a) MAB-8O8O-PCP



(b) MP-8O8O-PCP



(c) MAB-8-PHB

Figure 2. Structure of materials studied.

octylphenylcarbonyloxy)phenyl] 3-methyladipate [2] (**MAB-8-PHB**, see figure 2(*c*)).

2. Experimental

2.1. *General synthetic procedures*

The starting materials for the compounds presented in this paper were (*R*)-(+)-3-methyladipic acid (Aldrich Chemie, $[\alpha]_D^{21}$ +7·2°(*c* 5, MeOH)), (*S*)-(+)-3-methylpentanoic acid (Teikoku Chemical Industry Co., Ltd., $[\alpha]_D^{20}$ +6·9° (*c* 2·3, $CHCl_3$)), 4-octyloxyphenol (Kanto Chemical Co., Inc.) and 2,4-dihydroxybenzoic acid (Kanto Chemical Co., Inc.). The final products were obtained by esterification [3], using *N,N*′-dicyclohexylcarbodiimide (DCC) as esterification agent, 4-*N,N*-dimethylaminopyridine (DMAP) as catalyst, and dry dichloromethane as a solvent.

2.2. *Spectroscopic analysis*

The final esters were purified by column chromatography over Kieselgel 60 (70–230 mesh) silica gel (Merck, Darmstadt) and then recrystallized from ethanol or an ethanol–ethyl acetate mixture. The purities of the final products were checked by thin layer chromatography (Kieselgel 60 F254). Detection of products was achieved by UV irradiation ($\lambda = 254$ and 365 nm). The purities of the final compounds were also checked by reversed-phase high performance liquid chromatography, using a Waters ALC/GPC-244. Reversed-phase chromatography was carried out over octadecylsiloxane (7 μm particle size, 25 × 0·4 cm, ODS Lichrosorb RP-18 column) using methanol or water/methanol mixture (5/95, v/v) eluent. Detection of the eluting products was made using a Hewlett–Packard 1040A UV detector ($\lambda = 250$ and 260 nm). The structures of the final products were elucidated by a variety of spectral methods. Infrared (IR) spectroscopy was carried out using a SHIMAZU IR-435 infrared spectrophotometer. Proton nuclear magnetic resonance (^{1}H NMR) spectroscopy was carried out using a JEOL GSX-270 or HITACHI R-3000 FT nuclear magnetic resonance spectrometer. Mass spectrometry was carried out using a JMS-AX505H FD-MS or automated DI-MS. Specific rotations were measured using $CHCl_3$ solutions at 25°C in a Union PM-201 polarimeter. The analyses of the structures of the products and intermediates by spectroscopic methods were found to be consistent with the expected structures.

2.3. *Preparation of materials*

2.3.1. *4-Octyloxyphenyl 4-octyloxy-2-hydroxybenzoate*

To a solution of 2,4-dihydroxybenzoic acid (7·7 g, 0·05 mol) and 1-bromo-octane (10·39 g, 0·053 mol) in ethanol (70 ml) was added a solution of potassium hydroxide (10·34g) in water (40 ml). The resulting solution was heated under reflux for 10 h. After removal of ethanol, 2M-hydrochloric acid (80 ml) was added. The precipitate produced was redissolved in diethyl ether (50 ml × 3), and dried over anhydrous magnesium sulphate. After removal of the solvent, the residue was recrystallized from ethanol to obtain 2-hydroxy-4-octyloxybenzoic acid (2·71 g, 0·01 mol, 20 per cent). A solution of the obtained acid (1·70 g, 6·3 mmol) in dichloromethane (50 ml) was added gradually over about 5 h at room temperature to a solution of 4-octyloxyphenol (1·45 g, 6·5 mmol), *N,N*′-dicyclohexylcarbodiimide (1·61 g, 7·8 mmol), and 4-*N,N*-dimethylaminopyridine (0·07 g, 0·57 mmol), and the resulting solution was stirred at room temperature for 4 h. After filtration to remove precipitated materials, the solvent was removed by evaporation under reduced pressure. The product was purified by column chromatography (2:1) hexane–toluene) over silica gel. Yield 1·21 g (2·57 mmol, 41 per cent); ^{1}H NMR (270 MHz, solvent $CDCl_3$, standard TMS) δ 10·72 (1 H, s), 7·94 (1 H, d, $J = 8{\cdot}6$ Hz), 7·09 (2 H, d, $J = 8{\cdot}8$ Hz), 6·92 (2 H, d, $J = 8{\cdot}8$ Hz), 6·50 (1 H, d, $J = 8{\cdot}6$ Hz), 6·48 (1 H, s), 4·03 (2 H, t, $J = 6{\cdot}5$ Hz), 3·96 (2 H, t, $J = 6{\cdot}5$ Hz), 1·88–1·70 (4 H, m), 1·59–1·17 (20 H, m), 0·89 (6 H, t, $J = 6{\cdot}6$ Hz); IR (KBr) ν_{max}/cm^{-1} 3120, 2920, 2850, 1670, 1248, 1060; MS (*m/z*) 470[M$^+$], 249.

2.3.2. *(R)-Bis[5-octyloxy-2-(4-octyloxyphenoxycarbonyl)phenyl] 3-methyladipate*

To a solution of 4-octyloxyphenyl 4-octyloxy-2-hydroxybenzoate (0·75 g, 1·6 mmol), (*R*)-(+)-3-methyladipic acid (0·11 g, 0·69 mmol) and 4-*N,N*-dimethylaminopyridine (30 mg, 0·25 mmol) in dichloromethane (15 ml) was added *N,N*′-dicyclohexylcarbodiimide (0·33 g, 1·6 mmol), and the resulting solution was stirred at room temperature for 40 h. After filtration to remove precipitated materials, the solvent was removed by evaporation under reduced pressure. The product was purified by column chromatography (hexane dichloromethane 5/1, v/v) over silica gel, and recrystallized from ethanol ethyl acetate mixture (3/1, v/v). Yield 0·30 g (0·28 mmol, 41 per cent); ^{1}H NMR (270 MHz, solvent CDCl$_3$ standard TMS) δ 8·13 (2 H, d, $J = 8{\cdot}6$ Hz), 7·03 (4 H, d, $J = 9{\cdot}2$ Hz), 6·88 (4 H, d, $J = 9{\cdot}2$ Hz), 6·82 (2 H, d, $J = 8{\cdot}6$ Hz), 6·63 (2 H, s), 3·94 (8 H, m), 2·69–2·39 (4 H, m), 2·24–2·06 (1 H, m), 1·96–1·58 (6 H, m), 1·55–1·18 (44 H, m), 1·00 (3 H, d, $J = 6{\cdot}7$ Hz), 0·89 (12 H, t, $J = 6{\cdot}3$ Hz); IR (KBr) ν_{max}/cm^{-1} 2910, 2848, 1767, 1736, 1609, 1239, 1044; $[\alpha]_D^{25}$ + 3° ($c = 5{\cdot}0$, CDCl$_3$); MS (*m/z*) 1064[M$^+$]; Purity 98 per cent.

2.3.3. *(S)-5-octyloxy-2-(4-octyloxyphenoxycarbonyl) phenyl 3-methylpentanoate*

A solution of 4-octyloxyphenyl 4-octyloxy-2-hydroxybenzoate (0·70 g, 1·49 mmol), (*S*)-3-methylpentanoic acid (0·2 ml, 1·5 mmol) and 4-*N,N*-dimethylaminopyridine (0·02 g, 0·16 mmol) was added to *N,N*′-dicyclohexylcarbodiimide (0·41 g, 2·0 mmol), and the resulting solution was stirred for 4 days at room temperature. After filtration to remove precipitated materials, the solvent was removed by evaporation under reduced pressure. The product was purified by column chromatography (hexane toluene, 2/1, v/v) over silica gel and recrystallized from ethanol. Yield 0·49 g (0·863 mmol, 58 per cent); ^{1}H NMR (300 MHz, solvent CDCl$_3$, standard TMS) δ 8·13 (1 H, d, $J = 8{\cdot}7$ Hz), 7·03 (2 H, d, $J = 8{\cdot}7$ Hz), 6·88 (2 H, d, $J = 8{\cdot}7$ Hz), 6·83 (1 H, dd, $J = 8{\cdot}7$, 2·4 Hz), 6·60 (1 H, d, $J = 2{\cdot}4$ Hz), 4·01 (2 H, t, $J = 6{\cdot}2$ Hz), 3·93 (2 H, t, $J = 6{\cdot}6$ Hz), 2·61–2·34 (2 H, m), 2·06–1·93 (1 H, m), 1·88–1·69 (4 H, m), 1·49–1·16 (22 H, m), 0·99 (3 H, d, $J = 6{\cdot}6$ Hz), 0·89 (9 H, t, $J = 7{\cdot}4$ Hz); IR (KBr) ν_{max}/cm^{-1} 2910, 2850, 1759, 1736, 1610, 1237, 1048; $[\alpha]_D^{25}$ + 1·8° ($c = 5{\cdot}0$, CDCl$_3$), MS (*m/z*) 568 [M$^+$], 470, 249; Purity 99·2 per cent.

2.4. *Liquid crystalline properties*

The initial phase assignments and corresponding transition temperatures were determined by thermal optical microscopy using a Nikon OPTIPHOTO POL polarizing microscope equipped with a Mettler FP 82 microfurnace and FP 80 control unit. Samples were contained in cells (purchased from E.H.C., Japan) made with approximately 3 μm spacings with the inner surfaces coated with a polyimide and unidirectionally buffed. The heating and cooling rates were 2°C min^{-1}. Temperatures and enthalpies of transitions were investigated by differential scanning calorimetry (DSC) using a Seiko DSC 200 calorimeter. The materials encapsulated in aluminium pans were studied at a scanning rate of 2°C min^{-1} for both heating and cooling cycles. The helical pitch in the Ch phase was measured using a Cano wedge cell ($\tan\theta = 0{\cdot}0288$) for chiral nematic mixtures consisting of nematic host material, 4-*n*-hexyl-4′-cyanobiphenyl (6CB) (Merck Ltd, UK), and 2 per cent by weight of each chiral additive. The helical pitches in the S_C^* phases were measured for mixtures consisting of **Host A** and each chiral additive. **Host A** consists of several homologues of 5-alkyl-2-(4-alkoxyphenyl)pyrimidine. The S_C^* helical pitch was obtained directly by measuring the distance between the lines corresponding to the full pitch as seen by polarized light microscopy for a homogeneously aligned sample in a cell with 200 μm spacing. The helical twist senses in the S_C^* and Ch phases were measured at room temperature by using the contact method. The definition of the helical twist senses used in this article is the same as that made by Goodby [4]. The values of spontaneous polarization (P_S) were determined using a triangular wave method [5]. The direction of the P_S was determined directly from electric field studies combined with polarized light microscopy.

3. Results

3.1. *Liquid crystalline properties*

The transition temperatures and enthalpies of transition measured by DSC for the laterally-connected chiral twin material (**MAB-8O8O-PCP**), the laterally-branched chiral ‘monomeric’ material (**MP-8O8O-PCP**) and the terminally-connected chiral twin material [6] (**MAB-8-PHB**) are compared in table 1. **MAB-8O8O-PCP** and **MP-8O8O-PCP** were found to show no liquid crystal phases.

Next, 5 wt % of each chiral material was doped into **Host A**. The transition temperatures for the mixtures as well as those of **Host A**, determined by thermal optical microscopy, are compared in table 2. **MAB-8O8O-PCP** and **MP-8O8O-PCP** were found to have a stronger effect in destabilizing the liquid crystalline phases of **Host A** than **MAB-8-PHB**, and to produce coexistence of phases. These effects can be attributed to the quite different molecular configurations of the laterally-connected twin and the laterally-branched ‘monomeric’ materials compared with the rod shape of the host molecules. It should be noted that the addition of the laterally-branched ‘monomeric’ material has a stronger effect in destabilizing

Table 1. Phase transition temperatures (°C) and enthalpies of transition, in brackets, ΔH (kJ mol^{-1} determined for **MAB-8O8O-PCP, MP-8O8O-PCP** and **MAB-8-PHB.**

System	I		Ch		S_C^*		S_X†		Recryst.	m.p.
MAB-8O8O-PCP	•		•		•		•		•	98·3 (113·6)
MP-8O8O-PCP	•		•		•		•		•	32·8 (10·8)
MAB-8-PHB	•	140·6 (5·4)	•	113·2 (2·1)	•	110·2	•	108·7	•	116·6 (40·2)

† Smectic phase not characterized.

Table 2. Phase transition temperatures (°C) for **Host A** and mixtures (wt %) with each chiral material.

System	I		Ch		S_A		S_C^*		Recryst.	m.p.
Host A	•	68·5	•	65·2	•	49·8	•	0·8	•	2·0
MAB-8O8O-PCP (5%) + **Host A** (95%)	•	62·7 ~ 57·0	•	58·6	•	42·2	•	1·1	•	7·0
MP-8O8O-PCP (5%) + **Host A** (95%)	•	62·8 ~ 59·0	•	51·7 ~ 51·1	•	39·5	•	− 0·8	•	5·3
MAB-8-PHB (5%) + **Host A** (95%)	•	66·8	•	60·1	•	43·3	•	38·0	•	6·5

the smectic phases of **Host A** than the laterally-connected twin material.

3.2. *Pitch measurements*

The helical pitch values in the Ch phase determined for the chiral nematic mixtures consisting of **6CB** and 2 per cent by weight of each chiral material, and those in the S_C^* phases measured for **Host A** doped with each chiral material, as well as the helical twist senses in the Ch and S_C^* phases, are listed in table 3. The laterally-connected twin material (**MAB-8O8O-PCP**) was found to produce a much weaker helical structure in the S_C^* phase than the analogous terminally-connected twin material (**MAB-8-PHB**), **MAB-8O8O-PCP** produces a stronger helical structure in the Ch phase than **MP-8O8O-PCP**, but produces a weaker helical structure than **MAB-8-PHB**. The helical twist sense in the Ch phase of **MAB-8O8O-PCP** was found to be the same as that of **MAB-8-PHB**, and therefore the sense is consistent with the Gray–McDonnell rules [8].

Table 3. Helical pitches (μm) and helical twist senses in the Ch and S_C^* phases for the mixtures consisting of host materials and each chiral material.

	Ch		S_C^*	
Mixture	Pitch†	Sense	Pitch‖	Sense
MAB-8O8O-PCP	31	RH	Very long¶	— §
MP-8O8O-PCP	Very long‡	— §	Very long¶	— §
MAB-8-PHB	13	RH	15††	RH

† Determined for the chiral nematic mixtures consisting of **6CB** and 2 per cent by weight of each chiral material.

‡ Disclination lines were not observed in the Cano wedge.

§ Helical twist senses could not be determined due to the very small twisting power.

‖ Determined for the S_C^* mixtures consisting of **Host A** and 5 per cent by weight of each chiral material.

¶ Dechiralization lines corresponding to full pitch bands were not observed.

†† Determined for the S_C^* mixtures consisting of **Host A** and 1 per cent by weight of **MAB-8-PHB.**

3.3. *Spontaneous polarization studies*

The values of the spontaneous polarization (P_s) were measured for mixtures consisting of achiral **Host A** and 5 per cent by weight of each chiral dopant, i.e. **MAB-8O8O-PCP**, **MP-8O8O-PCP**, or **MAB-8-PHB**. The values of the P_s for the ferroelectric S_C^* phases, however, were too small to be detected, i.e. smaller than about 0·1 nC cm^{-2}, for all of the mixtures. Small P_s values have already been reported for some terminally-connected chiral twin materials [1, 7]. In spite of the small magnitude of the P_s values, the direction of the P_s was determined successfully by electric field studies when a d.c. field sufficiently large to produce one of the uniform states was applied to the samples. The direction of the P_s was found to be positive for the laterally-connected twin (**MAB-8O8O-PCP**)—the same as that of the terminally-connected twin (**MAB-8-PHB**) material, and this is due to the presence of the same chiral structure with the same absolute configuration in both twin materials. The direction of P_s was found to be negative for the laterally-branched 'monomeric' material (**MP-8O8O-PCP**), which has a similar chiral structure, but the opposite absolute configuration to the twin materials.

4. Discussion

Although the terminally-connected chiral twin material (**MAB-8-PHB**) was reported [2] to induce a strong helical structure in the S_C^* phase, the analogous laterally-connected chiral twin material (**MAB-8O8O-PCP**) was found to induce a weak helical structure in the S_C^* phase. The intercalation of terminally-connected chiral twin molecules in the smectic layers (see figure 3 (*a*)), which can increase correlation in motion and orientations of molecules between neighbouring layers, was proposed for producing twist interactions which induce strong helical structures. The experimental result that the laterally-connected chiral twin material (**MAB-8O8O-PCP**) induces a weak helical structure is quite consistent with the proposed model. This is because laterally-connected chiral twin molecules are expected to lie in the smectic layers in such a way that two mesogenic parts exist in the same smectic layer (see figure 3 (*b*)). If this the case, the chiral twin molecules cannot produce strong twist interactions between adjacent layers, and consequently, a weak helical structure is obtained. This hypothesis is also supported by the experimental result that the smectic phases for the host material doped with the laterally-connected twin material are more stable than those doped with the analogous laterally-branched 'monomeric' material (see table 2). This indicates that the laterally-connected twin molecules prefer to stay in the smectic layers more so than the laterally-branched 'monomeric' molecules.

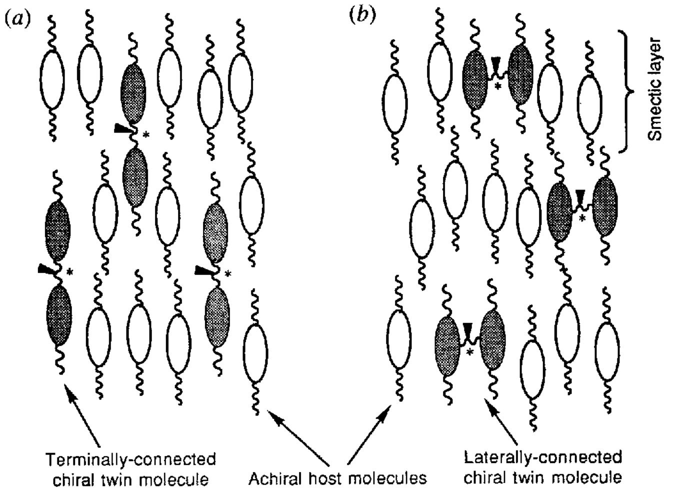


Figure 3. A schematic representation of possible models for smectic phases such as S_C^* phases consisting of the terminally-connected chiral twin molecules and S_C host molecules (*a*) and of laterally-connected chiral twin molecules and S_C host molecules (*b*).

5. Conclusions

A laterally-connected chiral twin material, (*R*)-bis-[5-octyloxy-2-(4-octyloxyphenoxycarbonyl)phenyl] 3-methyladipate, was found to induce a weak helical structure in the S_C^* phase. This experimental result is fully consistent with the proposed model for the strong helical structure in the S_C^* phase induced by terminally-connected chiral twin materials where chiral twin molecules are intercalated in the smectic layers and produce a strong twist interaction. This is because the laterally-connected chiral twin molecules are expected to occupy the smectic layers in such a way that two mesogenic parts exist in the same layer, so that they cannot produce strong twist interactions between adjacent layers.

Acknowledgments

We wish to thank Japan Energy Corporation for its support. We would like to thank Mr A. Yokoyama for useful discussions on the preparation of materials. We are also grateful to Miss A. Ono for DSC measurements, to Mr Matsuzaki, Mr Saitoh, Mr Arai and Mr Sasaya for spectroscopic analyses of the compounds, and to Miss N. Ise for pitch measurements.

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