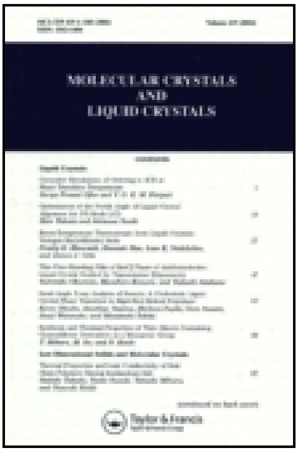


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Rod-like Liquid Crystals of Organic Transition Metal Complexes 2[1]: The Effect of the Introduction of Branched Alkyl Chains to Bis(dithiobenzoato)nickel(II) on the Mesomorphism

Kazuchika Ohta [a] , Yasue Morizumi [a] , Hiroshi Ema [a] , Tetsuya Fujimoto [a] , Iwao Yamamoto [a] & Tosio Sakurai [b]

[a] Department of Functional Polymer Science, Faculty of Textile Science and Technology, Shinshu University, Ueda, 386, Japan

[b] Department of Science, Faculty of Education, Shinshu University, Nagano, 380, Japan

To cite this article: Kazuchika Ohta , Yasue Morizumi , Hiroshi Ema , Tetsuya Fujimoto , Iwao Yamamoto & Tosio Sakurai (1992): Rod-like Liquid Crystals of Organic Transition Metal Complexes 2[1]: The Effect of the Introduction of Branched Alkyl Chains to Bis(dithiobenzoato)nickel(II) on the Mesomorphism, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 214:1, 151-159

To link to this article: http://dx.doi.org/10.1080/10587259208037289

Mol. Cryst. Liq. Cryst., 1992, Vol. 214, pp. 151–159
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

Rod-like Liquid Crystals of Organic Transition Metal Complexes 2^1: The Effect of the Introduction of Branched Alkyl Chains to Bis(dithiobenzoato)nickel(II) on the Mesomorphism

KAZUCHIKA OHTA, YASUE MORIZUMI, HIROSHI EMA, TETSUYA FUJIMOTO and IWAO YAMAMOTO

Department of Functional Polymer Science, Faculty of Textile Science and Technology, Shinshu University, Ueda 386, Japan

and

TOSIO SAKURAI

Department of Science, Faculty of Education, Shinshu University, Nagano 380, Japan

(Received April 16, 1991; in final form November 22, 1991)

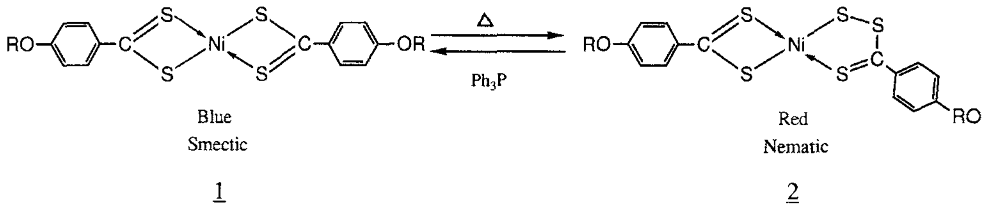
Branched alkyl chain-substituted complexes, bis(1-ethylpentoxydithiobenzoato)nickel(II), 1b, and bis(2-ethylhexyloxydithiobenzoato)nickel(II), 1c, have been synthesized and their liquid crystalline properties were characterized. In comparison with the straight alkyl chain-substituted complex, bis(*n*-pentoxydithiobenzoato)nickel(II), 1a, the branching effects could be observed as follows:

1) Their m.p.s and c.p.s are lowered significantly.
2) Complex 1b becomes to be not mesogenic.
3) Complex 1c shows only a smectic C phase, whereas complex 1a shows smectic H and C phases.

From the crystal structure analysis of the *n*-pentoxy derivative (1a), it could be considered that these branching effects appear more strongly in the 1-branched chain derivative 1b than in the 2-branched chain derivative 1c.

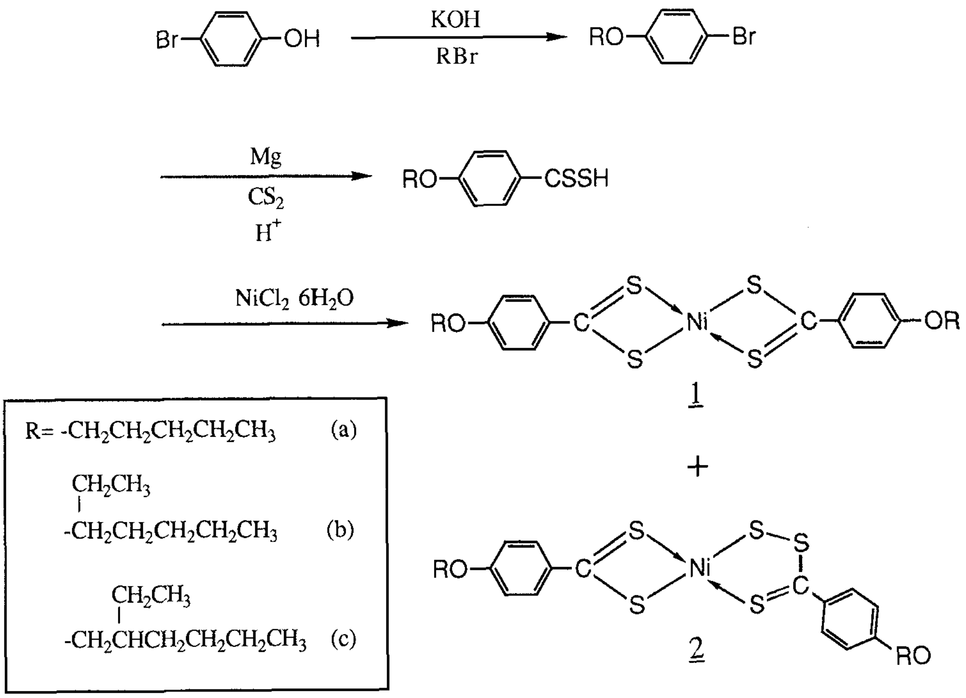
INTRODUCTION

We have already reported that bis(*p*-*n*-alkoxydithiobenzoato)nickel(II) complexes (abbreviated as (CnO—DTB)$_2$Ni: n = 4,8) are smectogens and show a very dense blue color, and that, when these complexes are heated, they transform into nematogens and show a very dense red color (Scheme I): these nematogens were analyzed to be (*p*-*n*-alkoxydithiobenzoato)(*p*-*n*-alkoxyperthiobenzoato)nickel(II) (abbreviated to (CnO—DTB)(CnO—PTB)Ni, n = 4,8) 2^1. The blue smectic phases of the bis-form 1 and the red nematic phase of the perthio-form 2 have potential application in display, but the melting and clearing points are very high



$R=C_n+H_{2n+1}$, n=4,8

SCHEME I Reversible transformation between complexes 1 and 2.



SCHEME II Synthetic route for complexes 1 and 2.

(e.g., m.p. = 145°C, and c.p. = 242°C for (C_4O—DTB)(C_4O—PTB)Ni[1]). Thereby, it is desired for application that these color complexes exhibit their mesophases at lower temperatures.

We thought that if we introduce branched alkyl chains to the complexes, 1 and 2, the order of molecular arrangement might decrease to give their liquid crystalline phases at lower temperature regions. Therefore, complex 1 and 2 with the branched side chains (b, c in Scheme II) have been prepared here.

It was found that the m.p. and c.p. of these complexes with branched chains (1b, 1c, 2b, 2c) are lower than those of complexes with straight chains (1a, 2a). Furthermore, it was found that the branched alkyl chains strongly affect the appearance and disappearance of the liquid crystalline phases. Judging from the crystalline structure of the 1a complex, it can be inferred that the 1-ethylpentyl group (b) more strongly weakens the interactions between the complexes than the 2-ethylhexyl group (c). In this report, we describe these effects of the branched chains on the mesomorphism.

EXPERIMENTAL

Synthesis

The synthetic route of the bis(*p*-alkoydithiobenzoato)nickel(II) derivatives, 1a–c is illustrated in Scheme II. The detailed synthetic procedures are almost the same as those of the bis(*p*-*n*-alkoxydithiobenzoato)nickel(II) complex reported previously.[1] Since only the purification method is different, it is described as follows.

For 1a–c complexes, the violet powder was filtered from the mixture of the complexing reaction. This crude product was washed sufficiently with ethanol using a Soxhlet apparatus. After that the residue was recrystallized from chloroform and a mixture of chloroform/ethanol for 1a and 1b–c, respectively. The colors of these crystals after recrystallization were violet (1a), blue (1b), and green (1c), respectively (see Table I). On the other hand, all solutions of 1a–c in chloroform showed a blue color.

It has been previously reported that the perthio-form 2 can be prepared by heating the bis-form 1[1] as shown in Scheme I. However, it was revealed here that these perthio-forms of 2a–c exist as the by-product in the filtrate of the Soxhlet in 3.6–9.6 percent yields. After those filtrates were evaporated, the purification was carried out by recrystallization from *n*-hexane for 2a and by column chromatography for 2b–c (silica gel, CCl_4, 2b: $R_f = 0.29$, 2c: $R_f = 0.21$).

TABLE I

Elemental analysis data, yields, crystalline shapes, and colors for 1a–c and 2a–c

Compound	Elemental analysis Found (Calcd.) %		Yield (%)	Crystalline shape	Color
	C	H			
1a	53.63(53.29)	5.63(5.58)	68.6	strip-like(K_1)	violet*1
1b	56.66(56.81)	6.45(6.49)	26.1	powder	blue *1
1c	57.97(57.89)	6.81(6.86)	51.2	powder	green*1
2a	50.61(50.37)	5.31(5.27)	6.2	needle-like	dark red-violet
2b	—	—	3.6	I.L.*2	red
2c	—	—	9.6	I.L.*2	red

*1 See the text.

*2 I.L. = isotropic liquid

In Table I are summarized elemental analysis data, yields, crystalline shapes, and colors of these 1a–c and 2a–c complexes.

1a: ^{1}H-NMR(CDCl$_3$, TMS) δ(ppm) 8.04–6.88(m, 8H, Ph) 4.05(t, 4H, OCH$_2$) 1.57(m, 12H, CH$_2$) 0.94(t, 6H, CH$_3$), IR(KBr) ν(cm^{-1}) 2950, 2880(CH$_2$) 1600, 1510(Ph) 1320, 1280, 1260(OPh)

2a: ^{1}H-NMR(CDCl$_3$, TMS) δ(ppm) 7.73–6.59(m, 8H, Ph) 3.90–3.81(m, 4H, OCH$_2$) 1.49(m, 12H, CH$_2$) 0.90(m, 6H, CH$_3$), IR(KBr) ν(cm^{-1}) 2950, 2880(CH$_2$) 1600, 1510(Ph) 1320, 1280, 1260 (OPh) 550, 530, 480 (S–S)

1b: ^{1}H-NMR(CDCl$_3$, TMS) δ(ppm) 7.27(q, 8H, Ph) 4.22(t, 2H, CH) 1.78–1.25(m, 16H, CH$_2$) 0.91(t, 6H, CH$_3$), IR(KBr) ν(cm^{-1}) 2940(CH$_2$) 1590, 1260, 1160, 1025(Ph) 970, 943, 825, 760(OPh)

1c: ^{1}H-NMR(CDCl$_3$, TMS) δ(ppm) 7.37(q, 8H, Ph) 3.91(d, 4H, OCH$_2$) 1.55–1.25(m, 18H, CH$_2$) 0.93(t, 12H, CH$_3$), IR(KBr) ν(cm^{-1}) 2930, 2570, 1900(CH$_2$) 1580, 1500, 1455, 1425(Ph) 1375(CH$_3$) 1240, 1155, 1110, 965, 940, 825(OPh)

Preparation of Single Crystals of 1a

The 1a complex was supersaturated in chloroform/*n*-hexane and the solvent was allowed to spontaneously evaporate in the atmosphere for two months. The size of the single crystal for the X-ray structural analysis was 0.20 mm × 0.20 mm × 1.00 mm.

Measurements

Phase transition behaviors of these compounds synthesized were observed with a polarizing microscope equipped with a heating plate controlled by a thermoregular, Mettler FP 80 and FP 82, and measured with a differential scanning calorimeter, Rigaku Thermoflex TG-DSC. X-ray diffraction on the powder was used to establish the identification of the mesophases of the present compounds. The patterns were obtained with Cu-Kα radiation with a hand-made heating plate controlled by a thermoregulator.[2] Single crystal diffraction data were collected at room temperature using a Rigaku AFC-5S four-circle diffractometer with Mo-Kα radiation.

RESULTS AND DISCUSSION

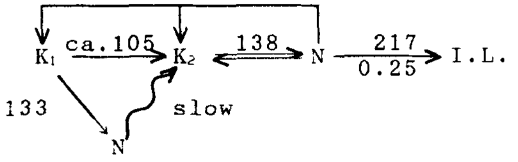
The phase transition temperatures and enthalpy changes of 1a–c and 2a–c complexes are summarized in Table II.

bis-form (1a–c)

The virgin crystals of 1a show a crystal-crystal phase transition at 187°C, and a crystal-smectic phase transition at 198°C. Although it is difficult to observe the latter transition by using a polarizing microscope, it shows stickiness when the cover glass was pressed. All reflections of the X-ray diffraction powder pattern of this smectic phase at 210°C could be assigned to the spacings in a monoclinic lattice of a S$_H$ phase (footnote in Table II). This assignment agrees with that of the other derivatives in the same series in the previous paper.[1] When the S$_H$ phase was heated

TABLE II

Phase transition temperatures (T) and enthalpy changes (ΔH) of 1a–c, and 2a–c

Complex	$\text{Phase}^{a} \xrightarrow[\Delta H(\text{kJ/mol})]{T(^{\circ}\text{C})} \text{Phase}$
	↝ relaxation
1a	$K_1 \xrightarrow[3.3]{187} K_2 \xrightarrow[1.0]{198} S_H{}^{*1} \xrightarrow[16.1]{224} S_C \xrightarrow{\text{ca.}231} \text{I.L.(decomp.)}$
2a	
1b	$K \xrightarrow[16.1]{104} \text{I.L.}$
2b	I.L. at r.t.
1c	$K \xrightarrow[16.1]{140} S_C{}^{*2} \xrightarrow{162} \text{I.L.(decomp.)}$
2c	I.L. at r.t.

[a] Phase nomenclature: K = crystal, S = smectic phase, N = nematic phase, and I.L. = isotropic liquid.

*1 X-ray analysis data of the S_H at 210°C: a = 11.1Å, b = 6.16Å, c = 19.6Å, β = 120.9°

*2 X-ray analysis data of the S_C at 140°C: c = 19.6Å

further, it transformed into another smectic phase at 224°C. This smectic phase gave a schlieren texture. This texture also agrees with that of the smectic C phase of the other derivatives in the previous paper.[1] The S_C phase transformed into an isotropic liquid (I.L.) at ca. 231°C, and it decomposed immediately. The decomposition contains the transformation from the bis-form 1a to the perthio-form 2a, which has been established in the previous work.[1]

The 1b complex gave no liquid crystalline phase but only a melting point at 104°C. The crystals of the 1c complex melted into an S_C phase at 140°C and it cleared into an I.L. phase at 162°C with fast decomposition (by changing into the perthio-form), the same case as the 1a complex.

Thus, the introduction of a side chain (b, c) to the complexes 1, made their m.p.s and c.p.s remarkably lower. Moreover the branched chain in b induces complex 1b to become non-mesogenic, while that in c induces complex 1c to have no S_H phase.

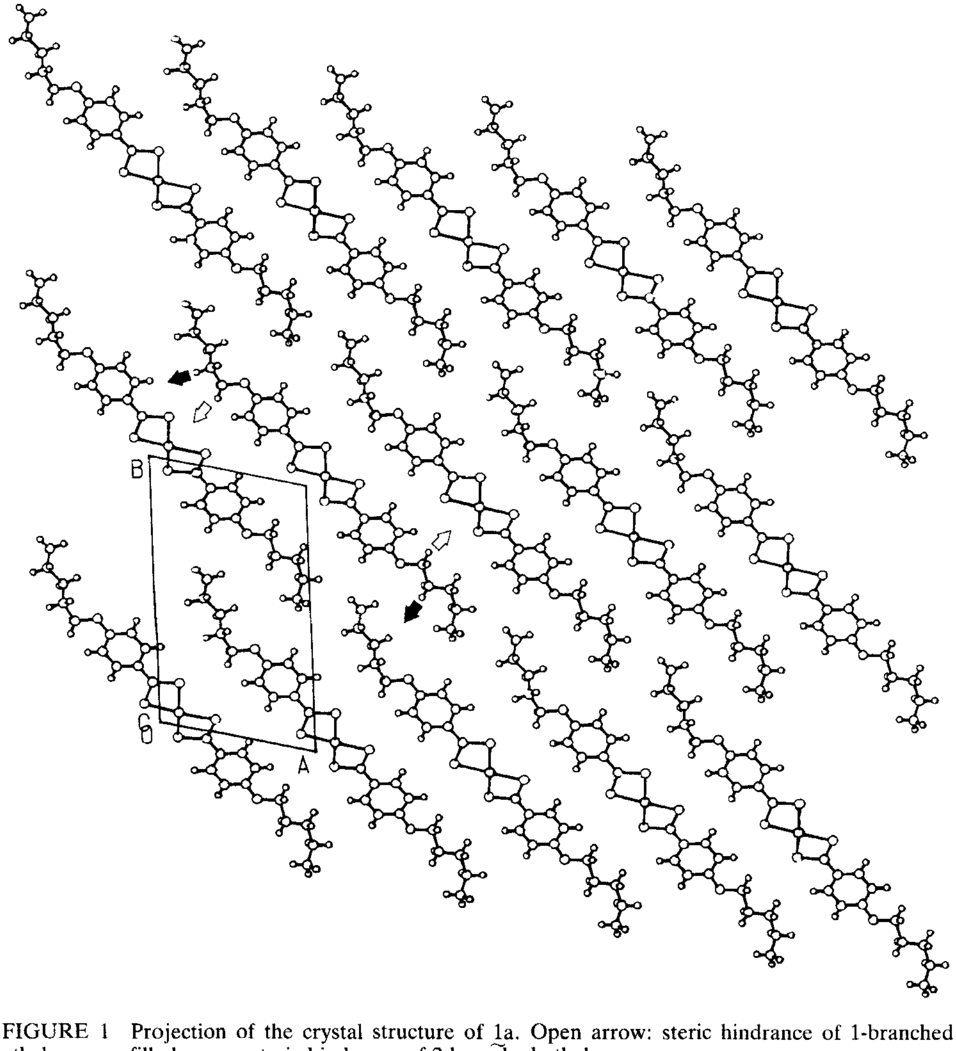


FIGURE 1 Projection of the crystal structure of 1a. Open arrow: steric hindrance of 1-branched ethyl groups, filled arrow: steric hindrance of 2-branched ethyl groups.

TABLE III

Experimental conditions for the structure determination and crystal structure data of 1a

Crystal system	Triclinic
Lattice Parameters	a = 9.956(5) Å b = 7.939(2) Å c = 16.72(1) Å α = 94.77(3) degrees β = 96.97(3) degrees γ = 102.68(6) degrees
Space Group	$P\bar{1}$
Z value	2
F(000)	510
mu(Mo-Kα)	$10.97 cm^{-1}$
Radiation	Mo-Kα (λ = 0.71069 Å) Graphite-monochromated
Temperature	23 °C
2-θ (max)	60.0 degrees
Number of reflections measured	1971
Number of free parameters	280
R(F)	0.056
Rw(F)	0.076
Goodness of Fit Indicator	1.68
Maximum Shift in Final Cryst	7.85
Volume of the unit cell	1272(1) $Å^3$
d calc.	$1.33 g/cm^3$
Diffractometer	Rigaku AFC5S

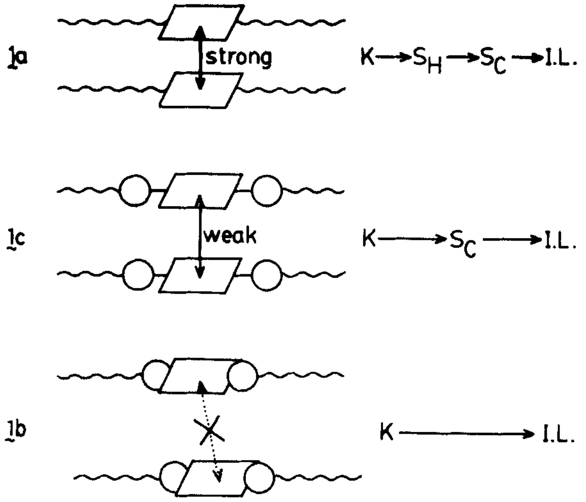


FIGURE 2 Possible reason for the absence of any mesophases in 1b and disappearance of the smectic H phase in 1c. The circles indicate the enhanced excluded volume effects of the ethyl groups in the branched chains.

Monoperthio-form (2a–c)

The virgin crystals of 2a are dark red-purple rods (K_1). When they were heated, a crystal-crystal phase transition to blue K_2 crystals was observed at ca. 105°C. These blue K_2 crystals melted into the very thick red nematic (N) phase, showing a schlieren texture. This texture is the same as that of the (C_nO—BTB)(C_nO—PTB)Ni, $n = 4, 8$ complex previously reported.[1] When the N phase was cooled, it crystallized into a mixture of crystals, K_1 and K_2. When it was heated again from r.t. at the heating rate of ≥10°C/min., only the K_1 crystals melted into the N phase at 133°C and then this N phase recrystallized slowly into the K_2 crystals by using the remaining K_2 crystals as the seeds. On further heating, these K_2 crystals melt again into the N phase at 138°C and the N phase cleared into a deep-red I.L. at 217°C. Thus, the monoperthio-form 2a having *n*-pentoxy chains has a N phase and shows unusual double melting behavior via the N phase. This behavior could be observed also for the (C_nO—BTB)(C_nO—PTB)Ni, $n = 4, 8$ complexes as previously reported.[1] On the other hand, both of the branched-chain-substituted complexes 2b, 2c have no N phases but the I.L. phases at r.t.

These branching effects could be summarized as follows:

1) Their m.p.s and c.p.s are lowered significantly.
2) Complex 1b is not mesogenic.
3) Complex 1c shows only a smectic C phase, whereas the complex, 1a, shows smectic H and C phases.

Figure 1 shows the projection of the crystal structure of the 1a complex. The crystal data are summarized in Table III. From this structure, we consider the effects of the branch in the wing group. It is obvious from Figure 1 that the molecules tilt to the layer. This fact corresponds to the S_H and S_C mesophases in which the molecules tilt to the layer. Moreover, it is apparent from Figure 1 that two alkyl chains of the molecule extend asymmetrically and they interdegitate slightly even in the crystalline state. Since the excluded volume effect is enhanced by rotating ethyl groups, the intermolecular force is weakened. When 1-ethyl groups are introduced into the straight alkyl chains (side chain b: open arrow in Figure 1), the ethyl groups are quite close to the rigid core complex parts. The branched alkyl chains no sooner start to rotate at high temperatures than complex 1b melts into the I.L. On the other hand, when 2-ethyl groups are introduced into the straight alkyl chains (side chain c: filled arrow in Figure 1), the ethyl groups are not so close to the core complex parts as in the case of the 1-ethyl groups. When the alkyl chains start to rotate, complex 1c does not clear into the I.L. but melts into the S_C mesophase. Figure 2 shows a schematic explanation of this reason.

CONCLUSION

Ethyl side chains were introduced into bis(dithiobenzoato)nickel(II) complexes (the 1-ethylpentoxy group (b) and the 2-ethylhexyloxy group (c)) and their liquid crystalline properties were characterized. In comparison with the *n*-pentoxy group (a) substituted derivative, the branching effects could be observed as follows:

1) Their m.p.s and c.p.s are lowered significantly.
2) Complex 1b is not mesogenic.
3) Complex 1c shows only a smectic C phase, whereas complex 1a shows smectic H and C phases.

From the crystal structure of the *n*-pentoxy derivative (1a), it could be considered that these branching effects appear more strongly in the 1-branched chain derivative 1b than in the 2-branched chain derivative 1c.

References

1. Part 1: K. Ohta, H. Ema, Y. Morizumi, T. Watanabe, T. Fujimoto and I. Yamamoto, *Liq. Cryst.*, **8**, 311 (1990).
2. H. Ema, Master thesis, Shinshu University, Ueda, Chap. 7, 1988.