Dyes and Pigments, Vol. 32, No. 2, pp. 71–83, 1996
Copyright © 1996 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
PII: S0143-7208(96)00017-4 0143-7208/96 $15.00+0.00

Synthesis and Properties of Long and Branched Alkyl Chain Substituted Perylenetetracarboxylic Monoanhydride Monoimides

Yukinori Nagao,* Tadashi Naito, Yoshimoto Abe
& Takahisa Misono

Department of Industrial Chemistry, Faculty of Science and Technology,
Science University of Tokyo, Noda, Chiba 278, Japan

(Received and accepted 2 January 1996)

ABSTRACT

N-*Alkyl-3,4:9,10-perylenetetracarboxylic monoanhydride monoimides were prepared by the condensation of 3,4:9,10-perylenetetracarboxylic monoanhydride monopotassium salt with alkylamines (alkyl = decyl, lauryl, tetradecyl, cetyl, stearyl, etc.).* N-*Branched alkyl substituted perylenetetracarboxylic monoanhydride monoimides were prepared by the hydrolysis of* N,N′-*dialkyl-3,4:9,10-perylenebis(dicarboximide)s with potassium hydroxide. The absorption spectra of paint film, thermal stability and solubilities of these monoimides were investigated. Copyright © 1996 Elsevier Science Ltd*

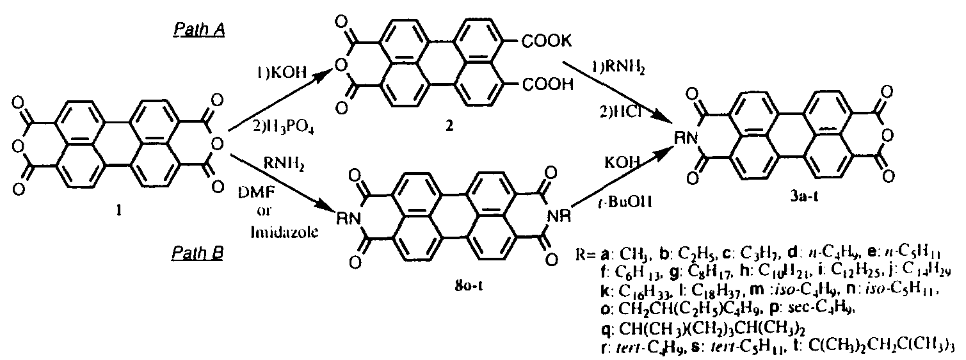
INTRODUCTION

In general, symmetrical 3,4:9,10-perylenebis(dicarboximide)s have excellent resistance to light, heat and solvents. Some of them are used as dyes, organic photoconductors in electrophotography,[1–4] and pigments for coloring plastics.[5–8] One characteristic of these compounds is reported to be their excellent heat resistance. Recently these compounds have become of interest as conductors in organic solar, laser dyes and fluorescent dyes.

We have previously prepared *N*-alkyl-3,4:9,10-perylenetetracarboxylic monoanhydride monoimide (alkyl = H, methyl, ethyl, propyl, butyl, etc.) **3a–g** and **3m** by condensation of 3,4:9,10-perylenetetracarboxylic dianhydride

---

*To whom correspondence should be addressed.



Scheme 1.

1 with alkylamines.[9,10] In this present paper, the synthesis of monoimides having a long alkyl chain (**3h–l**: alkyl = decyl, lauryl, tetradecyl, cetyl, stearyl, etc.), and the monoimides having a branched alkyl chain (**3h–t**), is described (Scheme 1). The absorption spectra of paint film, the thermal stability and the solubilities of these derivatives are also reported.

EXPERIMENTAL

Material and measurements

The dianhydride **1** and all alkylamines used were obtained commercially. Mass spectra were recorded on a Hitachi M-80A and JEOL JMS-SX102A mass spectrometer. Visible absorption spectra were recorded on a JASCO UVIDEC-610C, and IR spectra on a Hitachi 260-50 spectrometer. Thermal decomposition was measured with a Rigaku TG-8110 differential thermal micro balance at a heating rate of 10°C min^{-1} in air.

Paint film tests were carried out as follows: the prepared pigments (2.0 mg) and 2 ml of lacquer solution (containing 30 g of polymethyl methacrylate, 100 ml of tetrachloroethane and 10 ml of *O*-butylbenzylphthalate) were mixed using a mortar and painted on to a transparent plastic film over a constant area (15 × 50 mm).

Preparation of monopotassium salt (2) and monoimides (3a–n)

The preparations of 3,4:9,10-perylenetetracarboxylic acid monopotassium salt (**2**) and perylenetetracarboxylic monoanhydride monoimides were effected in a similar manner to that described by Tröster.[11]

Monopotassium salt **2**[11]

The dianhydride **1** (10.0 g), 3 molar ratio of 85% potassium hydroxide and 135 ml of water were heated with stirring to 90°C. 10% *ortho*-phosphoric acid was then added dropwise to the reaction mixture until the pH value was 5.5–6.5. After further stirring at 90°C, the precipitate was filtered, washed with water and dried to yield **2**.

Monoimides **3a–d**[11]

The monoimide **3a** was prepared as follows: a mixture of the monopotassium salt of 3,4:9,10-perylenetetracarboxylic monoanhydride **2** (5.0 g), a 10 molar ratio of 40% methylamine solution and 20 ml of water was heated at 90°C for 2 h with stirring. 25% aqueous potassium carbonate was added and the reaction mixture heated at 90°C for 1 h with stirring, filtered, and the residue washed with 2% potassium carbonate. The residue was stirred into hot 3.5% potassium hydroxide, insoluble symmetric substituted diimide removed, and the filtrate acidified with 20% hydrochloric acid. The final precipitate was filtered, washed with water and dried to give **3a** in 88.5% yield.

The monoimides **3b–d** were prepared in a similar manner by the reaction of **2** with the appropriate alkylamines. Yields of **3b–d** were 69.5, 75.4, 77.6 and 87.5%, respectively. IR and UV of **3a–d** were in accord with previous values.[9]

Monoimides **3e–n**[9,11]

Compound **3e** was prepared as follows: a mixture of the monopotassium salt of 3,4:9,10-perylenetetracarboxylic monoanhydride **2** (5.0 g), a 4.4 molar ratio of amylamine and 45 ml of water was stirred at room temperature for 4 h and heated at 90°C for 2 h with stirring. The reaction mixture was acidified with 10% hydrochloric acid and the resulting precipitate was filtered and washed with water to remove residual amine. The residue was stirred into hot 10% potassium hydroxide and to the mixture was added 8% potassium chloride to separate the precipitated potassium salt of **3e** and the symmetrical substituted diimide from soluble, unreacted **2**. The solid was stirred into water, insoluble symmetric substituted diimide removed, and the filtrate was acidified with 20% hydrochloric acid. The precipitate was filtered, washed with water and dried to give **3e** in 87.4% yield (4.5 g).

The monoimides **3f–n** were prepared in a similar manner by the reaction of **2** with the pertinent alkylamines using a H_2O-PrOH mixture as solvent, viz: (H_2O-PrOH(v/v)) = 2 (**3f** and **3g**), 1 (**3h** and **3i**), 0.5 (**3j**), 0.2 (**3k**), 0.1 (**3l**). The yields of **3f** and **3g** were 84.9 and 82.1%, respectively. IR and UV of **3e–g** and **3n** were in good agreement with previous data.[9]

N-Decyl-3,4:9,10-perylenetetracarboxylic monoanhydride monoimide (**3h**). Yield: 87.8%, MS (*m*/*z*): 531 (M^+). Calcd (%) for $C_{34}H_{29}NO_3$, C: 76.8, H: 5.5, N: 2.6; found (%), C: 76.7, H: 5.3, N: 2.3.

N-Lauryl-3,4:9,10-perylenetetracarboxylic monoanhydride monoimide (**3i**). Yield: 82.9%, MS (*m/z*): 559 (M^+). Calcd (%) for $C_{36}H_{33}NO_5$, C: 77.2, H: 5.9, N: 2.5; found (%), C: 77.2, H: 5.7, N: 2.2.

N-Tetradecyl-3,4:9,10-perylenetetracarboxylic monoanhydride monoimide (**3j**). Yield: 79.4%, MS (*m/z*): 587 (M^+). Calcd (%) for $C_{38}H_{37}NO_3$, C: 77.6, H: 6.4, N: 2.4; found(%), C: 77.4, H: 6.2, N: 2.2.

N-Cetyl-3,4:9,10-perylenetetracarboxylic monoanhydride monoimide (**3k**). Yield: 61.2%, MS (*m/z*): 615 (M^+). Calcd (%) for $C_{40}H_{41}NO_5$, C: 78.0, H: 6.7, N: 2.3; found(%), C: 77.7, H: 6.6, N: 2.1.

N-Stearyl-3,4:9,10-perylenetetracarboxylic monoanhydride monoimide (**3l**). Yield: 65.6%, MS (*m/z*): 643 (M^+). Calcd (%) for $C_{42}H_{45}NO_5$, C: 77.4, H: 7.0, N: 2.2; found(%), C: 77.9, H: 6.8, N: 1.9.

N-(3-Methylbutyl)-3,4:9,10-perylenetetracarboxylic monoanhydride monoimide (**3n**). Yield: 57.7%, MS (*m/z*): 461 (M^+). Calcd (%) for $C_{29}H_{19}NO_5$, C: 75.5, H: 4.2, N: 3.0; found(%), C: 75.3, H: 4.0, N: 2.7.

Preparation of bis(dicarboximide)s (8o–t) and monoimides (3o–t)

Bis(dicarboximide)s **8o–q**[12]

The bis(dicarboximide) **8o** was prepared as follows: the dianhydride **1** (2.5 g), 6 molar ratio of *sec*-butylamine and 30 ml of DMF were refluxed for 2 h with stirring, and the liquor then filtered. The residue was stirred into hot 1% aqueous potassium hydroxide and filtered to remove unreacted **1**. The precipitate was added to water, the mixture acidified with dilute hydrochloric acid and then filtered. The product was washed with water and dried to yield **8o**.

The bis(dicarboximide)s **8p–q** were prepared in a similar manner by the reaction of **1** with the appropriate alkylamine.

Bis(dicarboximide)s **8r–t**[13]

The bis(dicarboximide) **8r** was prepared by reaction of the dianhydride **1** (2.5 g) with a 5 molar ratio of *tert*-butylamine in 12.5 g of DMF at 160°C for 4 h with stirring. Hydrochloric acid was added to the cooled reaction mixture, which was then filtered. The residue was stirred into hot 1% aqueous potassium hydroxide and filtered to remove unreacted **1**. The precipitate was added to water, the mixture acidified with dilute hydrochloric acid and then filtered. The product was washed with water and dried to yield **8r**.

Bis(dicarboximide)s **8s–t** were prepared in a similar manner by the reaction of **1** with the corresponding alkylamines.

N,N′-Bis(2-ethylhexyl)-3,4:9,10-perylenebis(dicarboximide) (**8o**). Yield: 89.0%, MS (*m/z*): 614 (M^+).

N,N'-Bis(1-methylpropyl)-3,4:9,10-perylenebis(dicarboximide) (**8p**). Yield: 85.8%, MS (*m*/*z*): 502 (M^+).

N,N'-Bis(1,5-dimethylhexyl)-3,4:9,10-perylenebis(dicarboximide) (**8q**). Yield: 85.2%, MS (*m*/*z*): 614 (M^+).

N,N'-Bis(1,1-dimethylethyl)-3,4:9,10-perylenebis(dicarboximide) (**8r**). Yield: 64.5%, MS (*m*/*z*): 502 (M^+).

N,N'-Bis(1,1-dimethylpropyl)-3,4:9,10-perylenebis(dicarboximide) (**8s**). Yield: 50.4%, MS (*m*/*z*): 532 (M^+).

N,N'-Bis(1,1,3,3-tetramethylbutyl)-3,4:9,10-perylenebis(dicarboximide) (**8t**). Yield: 56.0%, MS (*m*/*z*): 614 (M^+).

Monoimides **3o–t**[14]

The monomimide **3o** was prepared from **8o** (1.3 g) by reaction with a 3 molar ratio of 85% potassium hydroxide and 50 ml of *tert*-BuOH at reflux for 0.5 h with stirring. The reaction mixture was acidified with 10% hydrochloric acid and the precipitate which formed was filtered and washed with water. The residue was stirred into hot 10% aqueous potassium hydroxide and 8% aqueous potassium chloride to precipitate the potassium salt of **3o** and unreacted **8o**. These were filtered and stirred in water to remove insoluble **8o**, and the filtrate acidified with 20% hydrochloric acid. The precipitate was filtered, washed with water and dried to yield **3o**.

Monoimides **3p–t** were prepared in a similar manner by the hydrolysis of **3p–t** with potassium hydroxide (**3p**: 0.5 h, **3q**: 0.5 h, **3r**: 1 h, **3s**: 0.5 h, **3t**: 1 h).

N-(2-Ethylhexyl)-3,4:9,10-perylenetetracarboxylic monoanhydride monoimide (**3o**). Yield: 48.3%, MS (*m*/*z*): 503 (M^+). Calcd (%) for $C_{32}H_{25}NO_5$, C: 76.3, H: 5.0, N: 2.8; found(%), C: 75.0, H: 5.0, N: 2.5.

N-(1-Methylpropyl)-3,4:9,10-perylenetetracarboxylic monoanhydride monoimide (**3p**). Yield: 51.8%, MS (*m*/*z*): 447 (M^+). Calcd (%) for $C_{28}H_{17}NO_5$, C: 75.2, H: 3.8, N: 3.1; found(%), C: 74.3, H: 3.1, N: 2.6.

N-(1,5-Dimethylhexyl)-3,4:9,10-perylenetetracarboxylic monoanhydride monoimide (**3q**). Yield: 40.9%, MS (*m*/*z*): 503 (M^+). Calcd (%) for $C_{32}H_{25}NO_5$, C: 76.3, H: 5.0, N: 2.8; found(%), C: 76.2, H: 5.0, N: 2.0.

N-(1,1-Dimethylethyl)-3,4:9,10-perylenetetracarboxylic monoanhydride monoimide (**3r**). Yield: 13.9%, MS (*m*/*z*): 447 (M^+). Calcd (%) for $C_{28}H_{17}NO_5$, C: 75.2, H: 3.8, N: 3.1; found(%), C: 74.1, H: 3.8, N: 3.3.

N-(1,1-Dimethylpropyl)-3,4:9,10-perylenetetracarboxylic monoanhydride monoimide (**3s**). Yield: 17.4%, MS (*m*/*z*): 461 (M^+). Calcd (%) for $C_{29}H_{19}NO_5$, C: 75.5, H: 4.2, N: 3.0; found(%), 74.2, H: 4.3, N: 4.2.

N-(1,1,3,3-Tetramethylbutyl)-3,4:9,10-perylenetetracarboxylic monoanhydride monoimide (**3t**). Yield: 48.4%, MS (*m*/*z*): 503 (M^+). Calcd (%) for $C_{32}H_{25}NO_5$, C: 76.3, H: 5.0, N: 2.8; found(%), C: 75.3, H: 4.1, N: 3.5.

RESULTS AND DISCUSSION

Preparation of monoimides 3h–l and 3n

Yields and spectral data of the *N*-alkyl-3,4:9,10-perylenetetracarboxylic monoanhydride monoimides **3h–l** prepared by the condensation of the monopotassium salt of 3,4:9,10-perylenetetracarboxylic monoanhydride **2** with alkylamines are listed in Table 1. Whilst the long alkyl chain substituted monoimides **3h–l** were obtained in good yield, the branched chain monoimide **3n** was obtained only in low yield.

In the visible spectra in 95% concentrated sulfuric acid, λmax was at 581 nm for the monoimides **3h–l** and **3n**, i.e. no change in λmax was apparent with different alkyl groups. The IR spectra of **3h–l** and **3n** showed anhydride $\nu_{C=O}$ at 1760–1770 and 1720–1740 cm^{-1} and imide $\nu_{C=O}$ at 1690–1700 and 1660–1655 cm^{-1}.

Preparation of 3o–t

The monoanhydride monoimide **3n** was prepared by condensation of the monopotassium salt of 3,4:9,10-perylenetetracarboxylic monoanhydride **2** with alkylamines (Method A), whilst compounds **3o–t** were prepared by hydrolysis of the *N*,*N*′-symmetrical dialkyl substituted 3,4:9,10-perylenebis(dicarboximides) **8o–t** with potassium hydroxide (Method B). Yield and spectral data of *N*,*N*′-symmetrical dialkyl substituted 3,4:9,10-pery-

TABLE 1
Yields and Spectral Data of **3h–l** and **3n**

Compound	R	Yield (%)	Color	IR[a] $\nu_{C=O}$ (cm^{-1})		UV-visible[b] (nm)
				Anhydride	Imide	
3h	n–$C_{10}H_{21}$	87.8	Reddish brown	1770, 1725	1700, 1660	581
3i	n–$C_{12}H_{25}$	82.9	Reddish brown	1770, 1725	1700, 1660	581
3j	n–$C_{14}H_{29}$	79.4	Reddish brown	1765, 1720	1695, 1655	581
3k	n–$C_{16}H_{33}$	61.2	Reddish brown	1765, 1725	1700, 1660	581
3l	n–$C_{18}H_{37}$	65.6	Reddish brown	1765, 1725	1695, 1660	581
3n	*iso*–C_5H_{11}	57.7	Brown	1755, 1720	1690, 1650	581

[a] KBr disk method.
[b] Solvent: conc. H_2SO_4.

TABLE 2
Yields and Spectral Data of Bis(dicarboximide)s **8o–t**

Compound	R	Yield (%)	Color	IR[a] $\nu_{C=O}$ (cm^{-1}) Imide	UV-visible[b] (nm)
8o	$CH_2CH(C_2H_5)(CH_2)_3CH_3$	89.0	Reddish brown	1690, 1650	600
8p	$CH(CH_3)CH_2CH_3$	85.8	Reddish brown	1695, 1650	598
8q	$CH(CH_3)(CH_2)_3CH(CH_3)_2$	85.2	Reddish brown	1690, 1645	611
8r	$C(CH_3)_3$	64.5	Brown	1695, 1655	594
8s	$C(CH_3)_2CH_2CH_3$	50.4	Brown	1690, 1655	596
8t	$C(CH_3)_2(CH_2)_2C(CH_3)_3$	56.0	Dark brown	1690, 1655	612

[a] KBr disk method.
[b] Solvent: conc. H_2SO_4.

lenebis(dicarboximide)s **8o–t**, prepared by the condensation of 3,4:9,10-perylenetetracarboxylic dianhydride (**1**) with alkylamines, are listed in Table 2. Compounds **8o–q** were obtained in good yield.

In 95% concentrated sulfuric acid, λmax was in the region 595–600 nm, the nature of the alkyl group having only minimal effect. The IR spectra showed imide $\nu_{C=O}$ at 1690–1700 and 1660–1655 cm^{-1}.

Yields and spectral data of the monoimides **3o–t** are listed in Table 3. Compounds **3r** and **3s** were obtained only in very low yield. Electronic

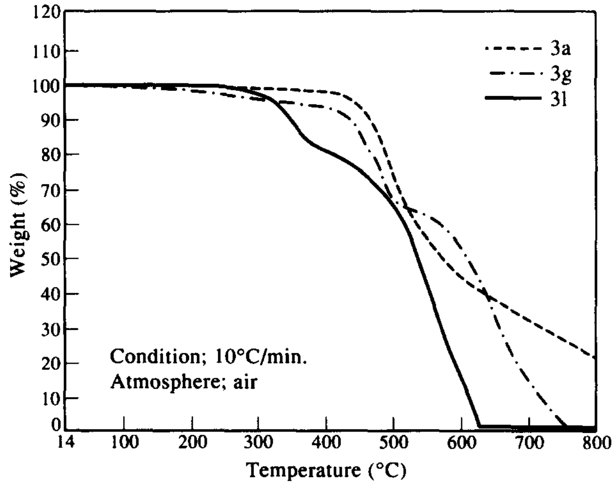


Fig. 1. TG curves of **3a**, **3g** and **3l**.

TABLE 3
Spectral Data of **3o–t**[a]

Compound	R	Yield (%)	Color	IR[a] $\nu_{C=O}$ (cm^{-1})		UV-visible[b] (nm)
				Anhydride	Imide	
3o	$CH_2CH(C_2H_5)(CH_2)_3CH_3$	48.3	Brown	1765, 1725	1695, 1650	582
3p	$CH(CH_3)CH_2CH_3$	51.8	Reddish brown	1765, 1730	1695, 1655	580
3q	$CH(CH_3)(CH_2)_3CH(CH_3)_2$	40.9	Brown	1765, 1720	1695, 1650	580
3r	$C(CH_3)_3$	13.9	Dark brown	1765, 1730	1695, 1660	579
3s	$C(CH_3)_2CH_2CH_3$	17.4	Dark brown	1750, 1720	1690, 1660	580
3t	$C(CH_3)_2(CH_2)_2C(CH_3)_3$	48.4	Reddish brown	1760, 1725	1690, 1670	579

[a] KBr disk method. [b] Solvent: conc. H_2SO_4.

TABLE 4
Thermal Decomposition Temperatures of Monoimides **3a–t**

Compound	R	T_{decomp}/°C	Compound	R	T_{decomp}/°C
3a	CH_3	468	**3k**	n–$C_{16}H_{33}$	327
3b	C_2H_5	475	**3l**	n–$C_{18}H_{37}$	316
3c	n–C_3H_7	476	**3m**	$CH_2CH(CH_3)_2$	443
3d	n–C_4H_9	449	**3n**	$(CH_2)_2CH_2(CH_3)_2$	442
3e	n–C_5H_{11}	439	**3o**	$CH_2CH(C_2H_5)(CH_2)_3CH_3$	319
3f	n–C_6H_{13}	417	**3p**	$CH(CH_3)CH_2CH_3$	449
3g	n–C_8H_{17}	429	**3q**	$CH(CH_3)(CH_2)_3CH(CH_3)_2$	366
3h	n–$C_{10}H_{21}$	352	**3r**	$C(CH_3)_3$	483
3i	n–$C_{12}H_{25}$	354	**3s**	$C(CH_3)_2CH_2CH_3$	452
3j	n–$C_{14}H_{29}$	325	**3t**	$C(CH_3)_2(CH_2)_2C(CH_3)_3$	292

spectra in 95% concentrated sulfuric acid showed λmax at 579–582 cm^{-1}. The IR spectra of **3o–t** showed imide $\nu_{C=O}$ at 1690–1700 and 1660–1655 cm^{-1} and anhydride $\nu_{C=O}$ at 1760–1770 and 1720–1740 cm^{-1}.

Properties of monoanhydride monoimides

The TG curves of the *N*-methyl-(**3a**), *N*-octyl-(**3g**) and *N*-stearyl-(**3l**) derivatives are shown in Fig. 1. All weight losses were exothermic, as shown by DTA curves. A one-step weight loss and the highest decomposition temperature was shown by **3a**. TG curves show a multi-step weight loss, except for **3a**. The initial slow weight losses of 36% (up to 530°C) for **3g** and 21% (up to 410°C) for **3l** correspond to degradation of each alkyl group. All

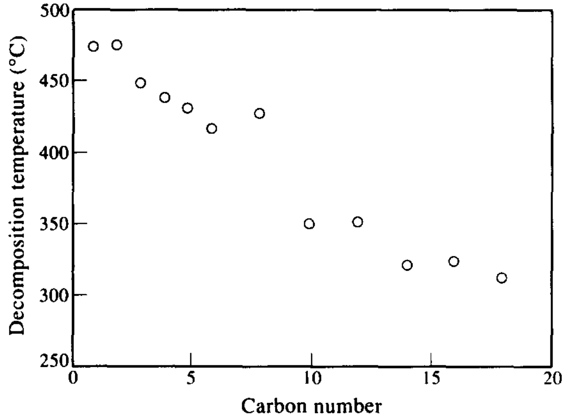


Fig. 2. Relationship between the thermal decomposition temperature and the carbon number of compounds **3a–t**.

TABLE 5
Solubility of **3a–t**[a,b]

Compound	R	Hexane	Benzene	CCl_4	$CHCl_3$	THF	Acetone	MeOH	DMSO
3a	CH_3	–	–	–	–	–	±	–	±
3b	C_2H_5	–	–	–	–	–	±	–	±
3c	n–C_3H_7	–	–	–	±	±	±	–	±
3d	n–C_4H_9	–	–	–	±	±	±	–	±
3e	n–C_5H_{11}	–	–	–	±	±	±	–	±
3f	n–C_6H_{13}	–	±	–	±	±	±	–	±
3g	n–C_8H_{17}	–	±	–	±	±	±	–	±
3h	n–$C_{10}H_{21}$	–	±	±	±	±	±	–	±
3i	n–$C_{12}H_{25}$	–	±	±	±	±	±	–	±
3j	n–$C_{14}H_{29}$	–	±	±	±	±	±	–	±
3k	n–$C_{16}H_{33}$	–	±	±	±	±	±	–	±
3l	n–$C_{18}H_{37}$	–	±	±	±	±	±	–	±
3m	$CH_2CH(CH_3)_2$	–	±	–	±	±	–	–	–
3n	$(CH_2)_2CH_2(CH_3)_2$	–	–	–	±	±	–	–	±
3o	$CH_2CH(C_2H_5)(CH_2)_3CH_3$	–	±	–	±	±	±	–	±
3p	$CH(CH_3)CH_2CH_3$	–	±	–	±	±	±	–	±
3q	$CH(CH_3)(CH_2)_3CH(CH_3)_2$	–	±	–	±	±	±	–	±
3r	$C(CH_3)_3$	–	±	–	±	±	±	–	±
3s	$C(CH_3)_2CH_2CH_3$	–	±	–	±	±	±	–	±
3t	$C(CH_3)_2(CH_2)_2C(CH_3)_3$	–	–	–	±	±	±	±	±

[a] +, Soluble; ±, less soluble; –, insoluble.
[b] At room temperature.

TABLE 6
Properties of Paint Film Colored with the Monoimides **3a–t**

Compound	R	Color	λmax (nm)	λedge (nm)
3a	CH_3	Red	477	728
3b	C_2H_5	Red	468	660
3c	n–C_3H_7	Red	486	700
3d	n–C_4H_9	Red	483	708
3e	n–C_5H_{11}	Red	490	710
3f	n–C_6H_{13}	Red	490	740
3g	n–C_8H_{17}	Red	488	688
3h	n–$C_{10}H_{21}$	Red	488	730
3i	n–$C_{12}H_{25}$	Red	488	722
3j	n–$C_{14}H_{29}$	Red	487	728
3k	n–$C_{16}H_{33}$	Red	487	730
3l	n–$C_{18}H_{37}$	Red	485	725
3m	$CH_2CH(CH_3)_2$	Red	476	736
3n	$(CH_2)_2CH_2(CH_3)_2$	Red	470	716
3o	$CH_2CH(C_2H_5)(CH_2)_3CH_3$	Reddish orange	485	738
3p	$CH(CH_3)CH_2CH_3$	Orange	495	715
3q	$CH(CH_3)(CH_2)_3CH(CH_3)_2$	Reddish orange	485	734
3r	$C(CH_3)_3$	Orange	484	698
3s	$C(CH_3)_2CH_2CH_3$	Orange	488	706
3t	$C(CH_3)_2(CH_2)_2C(CH_3)_3$	Orange	489	685

decompositions of the monoimides **3a–l** are considered to be initiated by the degradation of the *N*-alkyl substituents.

The initial temperatures of thermal decomposition of **3a–t** are shown in Table 4 and Fig. 2. The highest temperature is shown for **3r**. The longer alkyl and branched (C8) alkyl chain in the *N*-alkyl compounds appeared to lower the decomposition temperature, but shorter and branched (C4, C5) chains appeared to increase it. The lowering of decomposition temperature could be due either to decrease of intermolecular interaction or to initial decomposition of the alkyl substituent. If the former factor was operative, the branched (C4, C5) alkyl monoimides should show a decrease in the decomposition temperature because of their relatively bulky structure, but such a decrease was not observed. The decrease in decomposition temperature is thus due to the initial decomposition of the alkyl substituent.

The solubility of **3a–t** in various solvents is shown in Table 5. The highest solubility was observed for **3l** in the long alkyl chain and for **3p** in the branched alkyl chain derivatives. These results indicate that intermolecular interaction is decreased by a bulky alkyl group attached to the imide nitrogen atom.

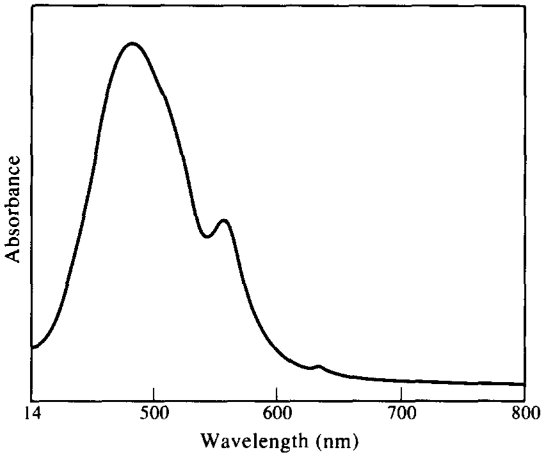


Fig. 3. Visible spectra of **3l**.

Paint film colored with the monoimides gave a pale red transparent color for **3a–t**. The properties of these films are shown in Table 6 for **3a–t**. Absorption spectra of paint films for **3l** are shown in Fig. 3. All λmax and λedge are listed in Table 6. In 95% concentrated sulfuric acid, the color was bluish purple for the monoimides **3a–l**, due to interaction between the solute and solvent. The difference in color of these imides in paint film and in solution appears to be relatable to the degree of π interaction or intermolecular overlap in the solids.[12] The branched alkyl substituted monoimides **3m–t** gave a brighter color than the long alkyl chain analogues **3a–l** because of the lower intermolecular interaction by bulky alkyl substituents.

REFERENCES

1. Wiedemann, W., Kalle A. G., *Ger. Offen.* 2237539 (1974).
2. Komiya, T. & Nishigaki, Y., Canon Inc., *Japan Kokai* 59037 (1975).
3. Murayama, T., Mitsubishi Chemical Industries, *Japan Kokai* 20344 (1978).
4. Kojima, A., Ohta, M., Sasaki, M. & Okuno, Z., Ricoh Inc., *Ger. Offen.* 2737516 (1978).
5. Yamada, M., Nippon Kayaku, *Japan Kokai* 37918 (1976).
6. Niwa, T. & Hirano, S., Mitsubishi Chemical Industries, *Japan Kokai* 128923 (1977).
7. Oki, S., Yamaguchi, I., Ooka, S. & Abe, Y., Dainichiseika Color and Chemicals, *Japan Kokai* 58551, 106745 (1978).
8. Haginoya, M. & Nagano, K., Dainippon Ink and Chemicals, *Japan Kokai* 10095 (1978).
9. Nagao, Y., Tanabe, Y. & Misono, T., *Nippon Kagaku Kaishi*, **4** (1979) 528.

10. Nagao, Y. & Misono, T., *Bull. Chem. Soc. Jpn.*, **544** (1981) 1191.
11. Tröster, H., *Dyes and Pigments*, **4**(3) (1983) 171.
12. Duff, J. M., Hor, A. M., Loutfy, R. O. & Melnyk, A. R., *Chemistry of Functional Dyes*. Mita Press, Tokyo, 1993, Vol. 2, p. 564.
13. Demmig, S. & Langhals, H., *Chem. Ber.*, **121** (1988) 225.
14. Kaiser, H., Lindner, J. & Langhals, H., *Chem. Ber.*, **124** (1991) 529.