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Alkali induced chromics and stable single crystal of opened-ring form of a new spirooxazine

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Abstract

Stable single crystal of the opened-ring form of a new spirooxazine was synthesized. Its structure was confirmed by X-ray crystallographic analysis. Its alkali induced chromism and thermochromism in the alkali medium were studied. A new kind of organic thermochromic paint indicating temperature having different chromogenic temperatures is made by this new spirooxazine in the presence of different solvents and different amines.

Keywords: Single crystal; Spirooxazine; Pyridone; Thermochromic paint

1. Introduction

Photochromic organic compounds have widely been studied over the past decades because of their potential application in various photoactive devices such as optical memory, optical switches, displays and non-linear optics [1–5]. Spirooxazines (SO) are a type of well-known photochromic compounds that have been attracting much interest from the viewpoints of fundamental elucidation of photochemical reactions as well as from their potential applications to optical memories [6–12]. The photochromism of these molecules is due to the photocleavage of the spiro bond under UV irradiation, creating a deeply colored ring-opened photomerocyanine form (shown in Fig. 1) which absorbs in the visible spectral region and can be reverted back to the ring-closed form by visible-light irradiation or heating. But, in past decades, spirooxazine's application in memory is highly restricted by the short lifetime of the colored photomerocyanine species which reverts thermally to the ring-closed colorless spirooxazine form with a reaction half-time of $1–10^3$ s and an apparent activation energy of 14–30 kcal/mol [12]. Many theoretical studies about the ring-closing reaction dynamics [12–14] have been made and various methods stabilizing the photomerocyanine form [15–18] have been developed. For example, Wirnsberger et al. [18] doped photochromic spirooxazine dyes into the mesostructured materials, which are excellent hosts for stabilizing the photomerocyanine form of the photochromic dyes. Such host/guest nanocomposites combine the high stability of the inorganic host framework with the diversity of the guest dopants, leading to versatile optical properties for applications in e.g. ultra-high density photochromic devices. Since a number of isomers exist for the photomerocyanines, molecular orbital calculation and NMR-NOE experiments had been done to estimate the most stable structure of spironaphthoxazine which was described in the quinoidal form (TTC structure

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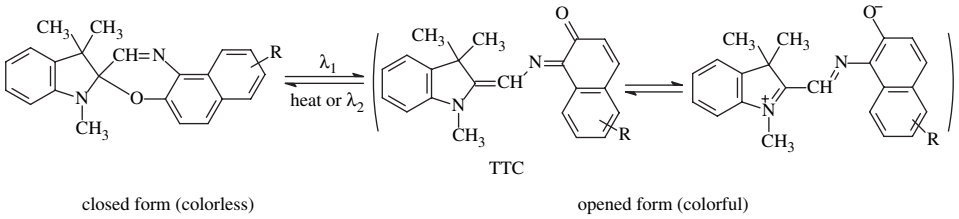


Fig. 1. Photochromism mechanism of a typical spironaphthoxazine.

shown in Fig. 1) [19]. From Fig. 1 we can understand that the poor thermal stability of the opened-ring form results from the exorbitant electronegative density of the oxygen atom on naphthalene ring. So the simplest method to improve the thermal stability of the opened-ring form of spironaphthoxazine should be one to reduce electronegative density of the oxygen atom by introducing electron-withdrawing groups or hetero atom to the naphthalene ring.

Pyridone derivatives are a kind of important heterocyclic compound [20]. There is not only nitrogen hetero atom, but also electron-withdrawing groups such as cyano group and carbonyl group on the rings. In this paper, we introduced a pyridone unit to synthesize a thermal stable opened-ring photomerocyanine form of spirooxazine (**Py-SO**) shown in Fig. 2 by reacting 1-ethyl-3-cyano-6-hydroxyl-4-methyl-5-nitroso-2-pyridone with 1,3,3-trimethyl-2-methyleneindolenine. A stable single crystal of the opened-ring form of this new spirooxazine was obtained and its structure was confirmed by X-ray crystallographic analysis. To our best knowledge, it is the first example of stable single crystal for the opened-ring merocyanine form of spirooxazine derivatives. The tunable chromism and thermochromism in the alkali medium were observed for this new spirooxazine, with which a new kind of organic thermochromic ink indicating chromomeric temperature is made in the presence of different solvents and different amines.

2. Experimental

IR spectra of the products were carried out on a Nicolet Magna-IR550 instrument using KBr tabulating. ^{1}H NMR spectra were measured on Brüker AVANCE 500 at 500 MHz in deuterium solvent with TMS as an internal reference. EI mass spectra (70 eV) were recorded on a HP5989A spectrometer. UV–vis absorption spectra were performed on a Varian Cray500 spectrophotometer. Fluorescence spectra were recorded on a Varian Cray Eclipse Fluorescence Spectrophotometer.

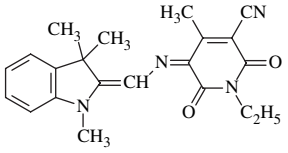


Fig. 2. Structure of **Py-SO** studied in this work.

2.1. Synthesis of 1-ethyl-3-cyano-6-hydroxyl-4-methyl-5-nitroso-2-pyridone

Two grams (0.05 mol) NaOH and 8.9 g (0.05 mol) 1-ethyl-3-cyano-6-hydroxyl-4-methyl-2-pyridone were dissolved in 85 ml water. The solution was cooled to 0–5 °C in ice-salt bath, and then 3.55 g (0.05 mol) $NaNO_2$ was added into it with stirring well. Sulfuric acid solution (containing 6.57 g sulfuric acid and 11.4 g ice-water) was stirred into the solution. During this procedure, the temperature of the mixture was maintained within 0–5 °C. Stir further for 1 h. Green solid was collected by filtration and washed with 200 ml water. The solid was recrystallized with ethanol to give 1-ethyl-3-cyano-6-hydroxyl-4-methyl-5-nitroso-2-pyridone in 90% yield, mp 144–146 °C.

2.2. Synthesis of target product ***Py-SO***

A mixture of 1,3,3-trimethyl-2-methyleneindolenine (3.46 g, 0.02 mol) and 1-ethyl-3-cyano-6-hydroxyl-4-methyl-5-nitroso-2-pyridone (4.14 g, 0.02 mol) in absolute ethanol (100 ml) was refluxed for 2 h with N_2 as protection. The mixture was cooled to room temperature. The precipitate solid was filtered and recrystallized with ethanol to give title compound **Py-SO** in 92% yield, mp 264–267 °C. ^{1}H NMR ($CDCl_3$) δ 1.23 (t, 3H, $J = 7.10$, 7.08 Hz, $-CH_2-CH_3$), 2.57 (s, 6H, $-C(CH_3)_2$), 3.76 (s, 3H, $-N-CH_3$), 4.04 (m, 2H, $-CH_2-CH_3$), 7.21 (d, 1H, $J = 7.72$ Hz, Ar–H), 7.34 (t, 1H, $J = 7.49$, 7.11 Hz, Ar–H), 7.47 (m, 2H, Ar–H), 9.65 (s, 1H, $-CH=N-$). MS m/z (rel. int.%) 363 (M^+, 23.73), 362 (73.76), 347 (13.24), 160 (7.95), 159 (100.00), 145 (7.69), 144 (22.53). IR (cm^{-1}) 3450, 2210, 1658, 1615, 1263.

2.3. X-ray crystallographic analysis

Preliminary experiment and data collection for X-ray crystal structure determination were performed on

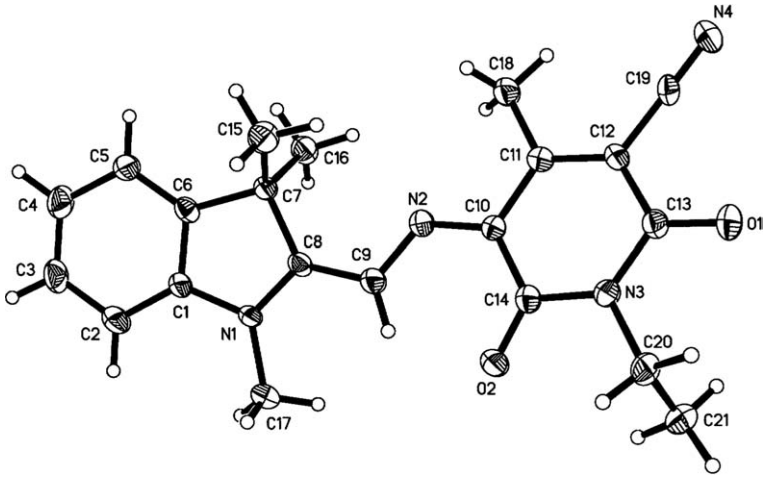


Fig. 3. Molecular diagram of target product **Py-SO**.

SMART 1000 diffractometer. The crystal size is 0.412 mm × 0.238 mm × 0.068 mm. Unit cell parameters indicated a triclinic space group P-1 with unit cell dimensions $a = 8.356(3)$ Å, $b = 9.510(3)$ Å, $c = 12.096(4)$ Å, $\alpha = 89.931(9)^\circ$, $\beta = 75.581(7)^\circ$, $\gamma = 81.927(9)^\circ$ and $Z = 2$. The crystal structure of **Py-SO** was resolved and refined using a full-matrix least squares procedure which resulted in final $R1$ and $wR2$ indices of 0.0774 and 0.1545, respectively.

3. Results and discussion

*3.1. Structure identification of target compound **Py-SO***

In general, when o-nitroso phenol derivatives reacted with 1,3,3-trimethyl-2-methyleneindolenine, white or yellow spirooxazines can be obtained [21,22]. But stable opened form of spirooxazine was obtained when we reacted 1-ethyl-3-cyano-6-hydroxyl-4-methyl-5-nitroso-2-pyridone with 1,3,3-trimethyl-2-methylene-indolenine in this paper. The target product **Py-SO** is a kind of blue crystal and the absorption peak of its ethanol solution is at about 553 nm, which showed no direct photochromism.

As it is fairly difficult to determine, experimentally, the structure of the opened form, X-ray crystallographic analysis was adopted. The molecular diagram of target product is shown in Fig. 3, and crystal packing structure in unit cell is shown in Fig. 4. From Figs. 3 and 4, we can see that the target **Py-SO** is the opened-ring form of spirooxazine, and exists in the diketone form other than ion form, because the bond length of O(2)–C(14) and O(1)–C(13) are 1.213 Å and 1.229 Å, respectively (shown in the Supporting Information). They are both double bond.

3.2. Alkali induced chromism

Compound **Py-SO** showed no photochromism, i.e. irradiation by visible light did not convert the colored solution to colorless one. However, there are some unique properties on chromism, one of which is alkali induced chromism. As shown in Figs. 5–7, it can be

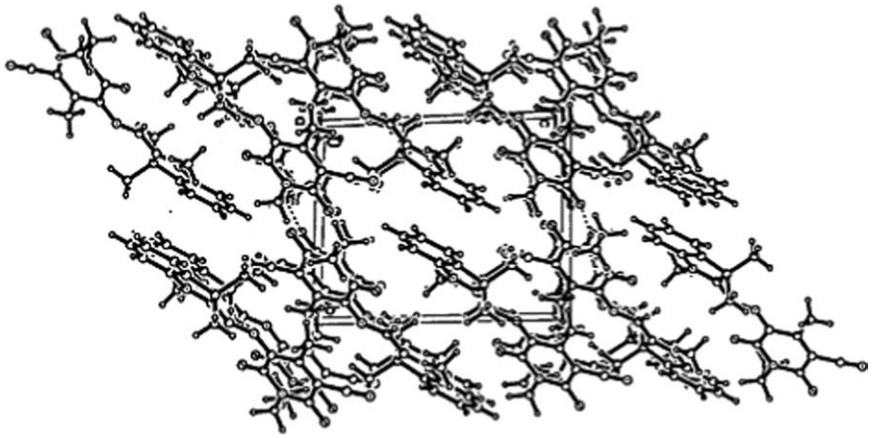


Fig. 4. Crystal packing structure in unit cell.

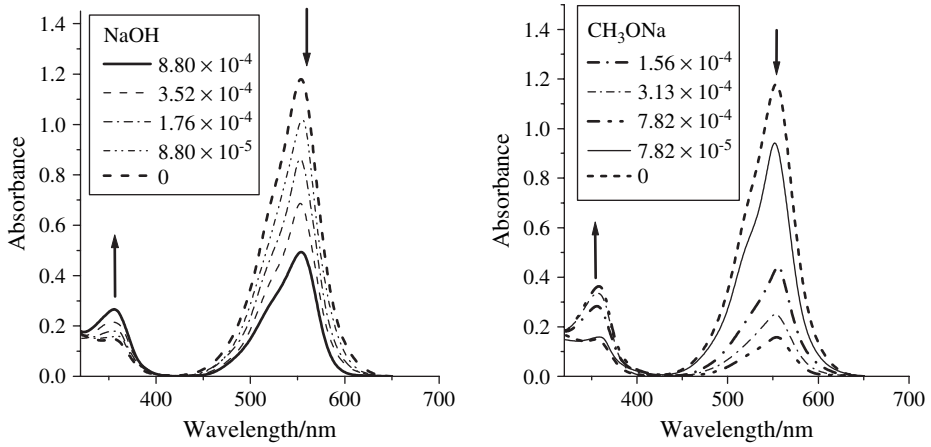


Fig. 5. The absorption spectral changes of **Py-SO** in DMF (20 °C) with the concentration variation of NaOH (left) and CH_3ONa (right).

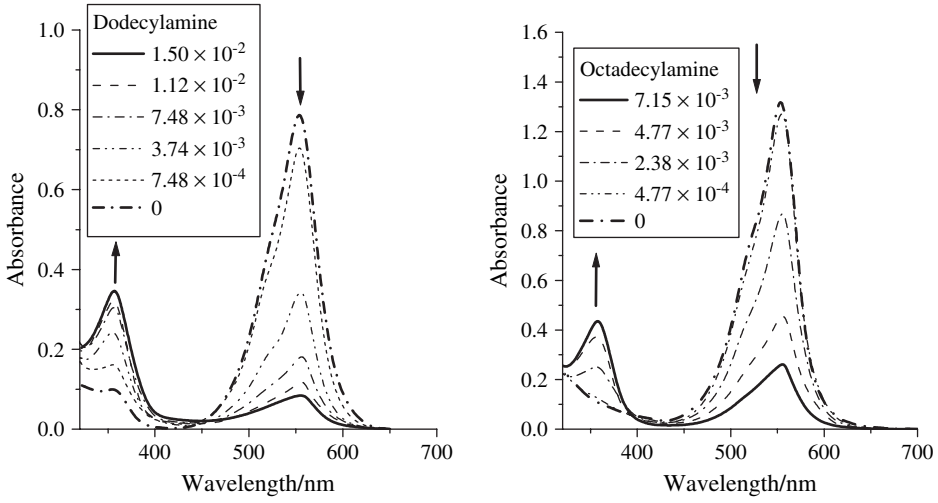


Fig. 6. The absorption spectral changes of **Py-SO** in DMF (20 °C) with the concentration variation of dodecylamine (left) and octadecylamine (right).

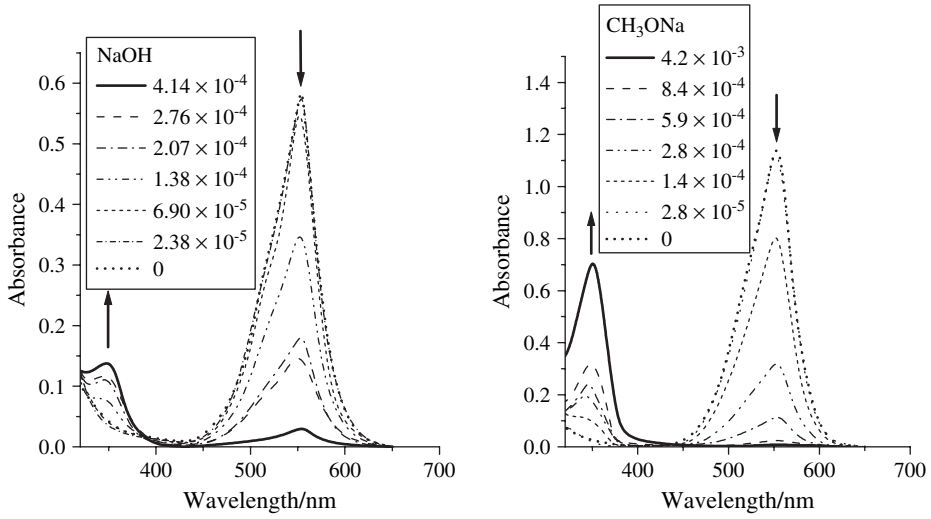
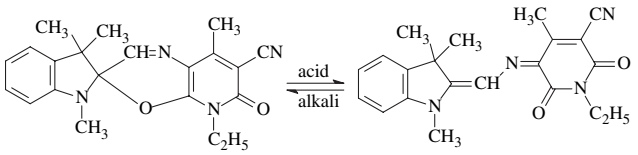


Fig. 7. The absorption spectra changes of **Py-SO** in ethanol (20 °C) with the concentration variation of NaOH (left) and CH_3ONa (right).



Scheme 1.

observed that the absorption intensity at 553 nm decreased and meanwhile the absorption at about 350 nm increased with the increase of the concentration of alkali, and this procedure is reversible when acid was added. This phenomenon results from the equilibrium between spirooxazine and its opened-ring form shown as in Scheme 1. The reason for this is evident, because it is well-known that spirooxazine converts to the opened-ring form in the presence of acid, and the opened-ring form can return to spirooxazine in the presence of alkali [23].

3.3. Thermochromism in alkali medium

Compound **Py-SO** shows thermochromism in alkali medium shown in Figs. 8 and 9. The absorption intensity at about 553 nm increased with the increase of temperature and meantime the absorption intensity at 350 nm decreased. This procedure is reversible when the temperature is decreased in the same system. This phenomenon also results from the equilibrium between spirooxazine and its opened form just like the alkali induced chromism. The phenomena might be explained as followed: spirooxazine forms a complex compound

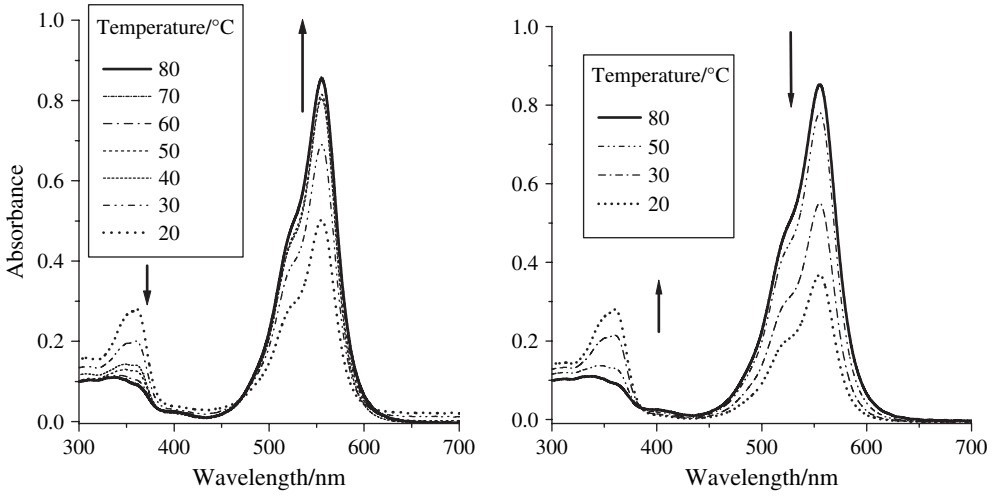


Fig. 8. The absorption spectral changes of **Py-SO** in DMF with the increasing temperature (left) and decreasing temperature (right) in the presence of dodecylamine (8.3×10^{-3} M).

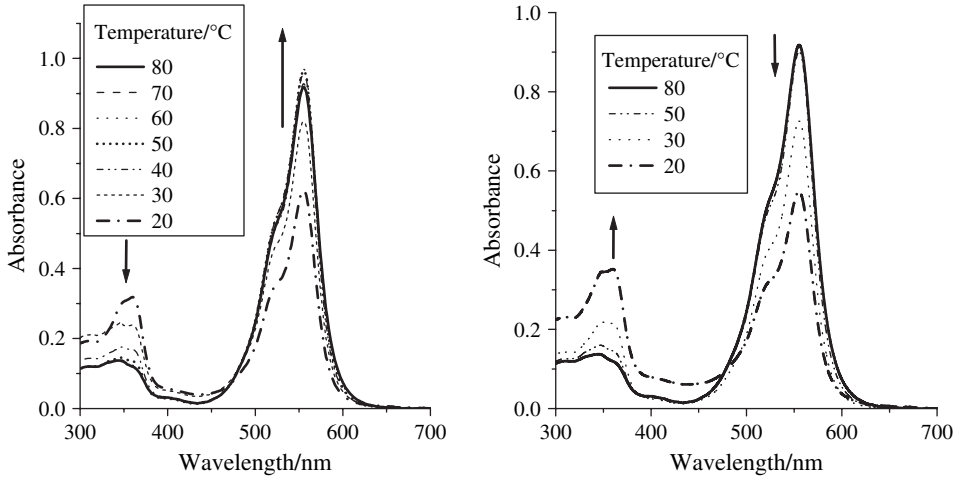
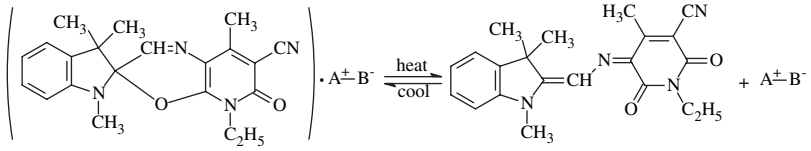


Fig. 9. The absorption spectral changes of **Py-SO** in DMF with the increasing temperature (left) and decreasing temperature (right) in the presence of octadecylamine (7.15×10^{-3} M).



Scheme 2.

with the alkali at low temperature. When temperature is increased, the complex compound is destroyed, and the spirooxazine converts to its opened-ring form, which is more stable than spirooxazine and deep colored. This procedure can be shown in Scheme 2.

4. Applications

One of the main applications of organic thermochromic compound is to make organic thermochromic paint indicating temperature [24,25]. Generally, organic thermochromic paint indicating temperature is made up of three components: leuco dye, ingrain agent and solvent [26–28]. Leuco dye is electron donor; ingrain agent is electron acceptor. Ingrain agents reported previously were organic compounds containing hydroxyl or carboxyl group mainly. The thermochromic mechanism is electron transfer reaction. Leuco dye gives its electron to ingrain agent with the interaction by means of the mixture of the solvent at higher temperature and changes its color, but leuco dye holds its electron and maintains its primary color at lower temperature since the interaction between leuco dye and ingrain agent was inhibited due to the solid solvent at lower temperature. Because the target product **Py-SO** in this study shows thermochromism in the alkali medium, a novel thermochromic paint indicating temperature can be made in a simple way.

As listed in Table 1, several thermochromic paints have different chromomeric temperature with the difference of solvent, amine and the ratio between them. The paints are colorless when temperature is lower than the chromomeric temperature and are red in color when temperature is higher than the chromomeric temperature. So we can obtain different thermochromic paints indicating temperature having different chromomeric temperature by changing the solvents and the amines.

5. Conclusion

Because there are strong electon-withdrawing group and nitrogen hetero atom on the pyridone ring, stable opened-ring form of a new spirooxazine was obtained by reacting 1-ethyl-3-cyano-6-hydroxyl-4-methyl-5-nitroso-2-pyridone with 1,3,3-trimethyl-2-methyleneindolenine. This new spirooxazine shows no photochromism, but takes place alkali induced chromism and the thermochromism in alkali medium. Based on these properties, a new kind of organic thermochromic paint indicating temperature having different chromomeric temperature was designed and prepared using the amines as ingrain agent.

Acknowledgements

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Table 1
Chromomeric temperature for thermochromism paints of different components (thermochromism compound **Py-SO**: 5×10^{-4} g; amine: 1 g)

Ratio (solvent/amine)		Solvent		
		1-Tetradecanol (°C)	1-Hexadecanol (°C)	1-Octadecanol (°C)
1	Dodecylamine	23–27	37–41	40–47
	Octadecylamine	40–53	43–56	50–60
1.5	Dodecylamine	24–29	37–39	42–50
	Octadecylamine	38–51	44–51	48–55
2	Dodecylamine	27–32	36–37	41–50
	Octadecylamine	36–46	43–48	52–58
2.5	Dodecylamine	29–33	36–39	43–52
	Octadecylamine	33–43	44–47	51–58
3	Dodecylamine	29–33	36–40	44–47
	Octadecylamine	34–40	44–47	52–57
4	Dodecylamine	30–37	39–43	45–53
	Octadecylamine	33–39	45–48	53–58

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