

Synthesis and Structure of Bis(dialkylamino)carbeniumdithiocarboxylates

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Received 20 September 1994

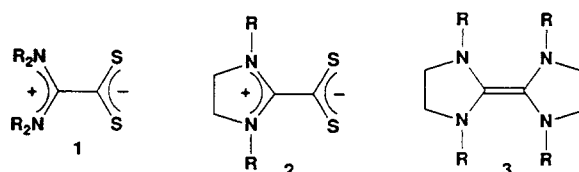
ABSTRACT

2-Chloro and 2-phenoxy substituted 1,1-bis(diethylamino)ethylenes (**4a** and **4c**) react with elemental sulfur at room temperature to give the inner salt, bis(diethylamino)carbeniumdithiocarboxylate (**1a**), in excellent yields with extrusion of hydrogen chloride and phenol, respectively, thus providing a new and convenient synthesis of the structurally interesting inner salt. X-ray single crystal structure analysis of **1a** reveals that the N–C–N and S–C–S planes are nearly vertical to each other with a dihedral angle of 82.0° and that the positive and negative charges are delocalized over the N–C–N and S–C–S moieties, respectively. Results of solid-state ¹³C NMR of **1a** are also briefly described.

INTRODUCTION

Bis(dialkylamino)carbeniumdithiocarboxylates such as **1** and **2** are a structurally interesting, unique class of inner salts. Their thermodynamic stability is probably due to delocalization of the positive charge over the N–C–N grouping and that of the negative charge over the S–C–S moiety. The first synthesis of the carbeniumdithiocarboxylates was attained by reaction of peraminoethylenes **3** with carbon disulfide, which produces a series of cyclic derivatives **2** in excellent yield [1]. Nearly contemporaneously with this report, preparation of **1** by

reaction of 1,1-bis(dialkylamino)ethylene with elemental sulfur was communicated [2]. The thermolysis of 1,3-bis(4-methoxyphenyl)-2-trichloromethylimidazolidine in the presence of carbon disulfide also produces a cyclic derivative **2** (R = 4-MeOC₆H₄), with elimination of chloroform [3]. We report here a convenient synthesis and the X-ray diffraction analysis of **1** [4]. The new synthesis involves the reaction of 2-chloro or 2-phenoxy substituted 1,1-bis(dialkylamino)ethylenes with elemental sulfur.



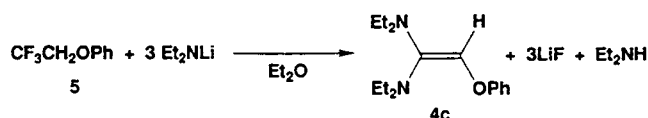
RESULTS AND DISCUSSION

Preparation of Starting Materials

1,1-Bis(diethylamino)- and 1,1-bis(dipropylamino)-2-chloroethylenes (**4a** and **4b**) are easily obtainable by treatment of trichloroethylene with lithium diethylamide and lithium dipropylamide, respectively [5]. The known compound, 1,1-bis(diethylamino)-2-phenoxyethylene (**4c**) [6], was prepared in a new way. Thus, treatment of phenyl 2,2,2-trifluoroethyl ether (**5**) [7] with 3 equivalents of lithium diethylamide affords 1,1-bis(diethylamino)-2-phenoxyethylene (**4c**) in 28% yield. This is in marked contrast with the fact that treatment of the sulfide and selenide analogs of **5** with lithium diethylamide gives 1-diethylamino-2-phenylthioacetylene and 1-diethylamino-2-phenylselenoacetylene, respectively [8,9].

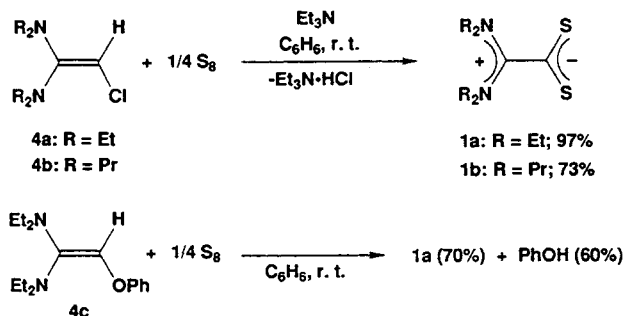
Dedicated to Prof. Shigeru Oae on the occasion of his seventy-fifth birthday.

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Preparation of the Inner Salts 1

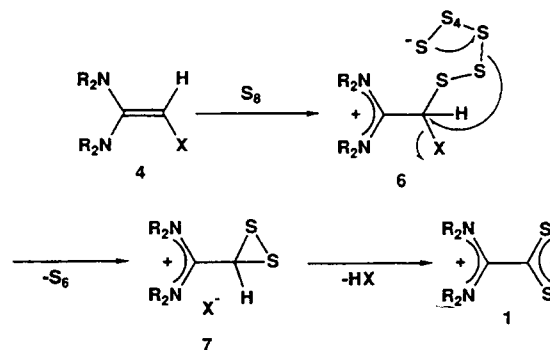
A mixture of **4a**, elemental sulfur, and triethylamine in benzene was stirred at room temperature. The mixture turned red gradually with deposition of triethylamine hydrochloride. Chromatographic workup of the mixture after stirring for 8 hours gave bis(diethylamino)carbeniumdithiocarboxylate (**1a**) in 97% yield. Addition of triethylamine is necessary to remove the hydrogen chloride that is liberated along with the progress of the reaction; the reaction carried out in the absence of triethylamine produces **1a** in low yield. In a similar way, the enediamine **4b** reacted with sulfur to give the carbeniumdithiocarboxylate **1b** in 73% yield. Treatment of the phenoxy substituted enediamine **4c** with sulfur also gave **1a** in 70% yield along with phenol (60%), thus suggesting that not only chloride but also phenoxide ion can function as the leaving group. In this case, addition of triethylamine is not required to improve the yield of **1a**.



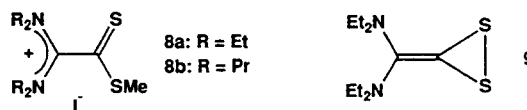
The initial step of the present reaction probably involves the electrophilic attack of elemental sulfur (cyclooctasulfur) on the strongly nucleophilic carbon of the enediamines **4** to give betaine intermediates **6**. Then, compounds **6** extrude S_6 (cyclohexasulfur) with simultaneous carbon-sulfur bond formation leading to the three-membered ring compound **7** with loss of X^- ($\text{X} = \text{Cl}, \text{OPh}$). Deprotonation of **7** would give rise to the final products **1** [10].

Properties and Structure of **1a** and **1b**

Both **1a** and **1b** are thermally stable, red crystalline compounds that are soluble in common organic solvents. They quickly react with methyl iodide to give quantitatively the carbenium iodides **8a** and **8b** that carry a dithioester functional group.



SCHEME 1



Compound **1a** shows UV-Vis peaks at 270 (ϵ 8400), 368 (10,800), and 435 nm (260) in CH_2Cl_2 . In the ^{13}C NMR solution spectrum (CDCl_3), the carbenium and dithiocarboxylate carbon signals of **1a** appear at δ 166.7 and 236.3, respectively. We have also determined the solid-state CPMAS ^{13}C NMR spectrum of **1a**, in which the carbenium and dithiocarboxylate carbons appeared at δ 171.1 and 237.9, respectively (Figure 1). Thus, no dramatic difference of the chemical shift values between a solution in CDCl_3 and in the solid state was observed, although a small lower field shift was brought about in the solid state. Incidentally, separations between carbenium and carbenium carbon signals are 69.3 and 66.8 ppm in CDCl_3 and in the solid state, respectively. At the present stage, it seems difficult to discuss what these observations tell us about the difference of the structure of **1a** between solutions and in the solid state. In the IR spectra, strong absorptions are observed at 1563 cm^{-1} for **1a** and 1555 cm^{-1} for **1b**. These absorptions, which would be ascribable to the C-N stretchings [3], are characteristic of these types of inner salts.

The structure of **1a** was also examined by X-ray single crystal structure analysis. Figure 2 shows a stereoscopic view of two crystallographically independent molecules of **1a** in an asymmetric unit. Bond angles and lengths data are given in Table 1. The most characteristic structural feature of **1a** is that the S-C-S and N-C-N planes are nearly vertical to each other with a dihedral angle of 82.0° (Figure 3). Thus, contribution of a canonical structure such as **9** is excluded, at least in the crystalline state. The bond lengths between dithiocarboxylate and carbenium carbons, C1A-C2A and C1B-C2B, are 1.47 and 1.51 Å, respectively. A slight shortening of these bonds compared to the common C-C single bond lengths can be attributed to

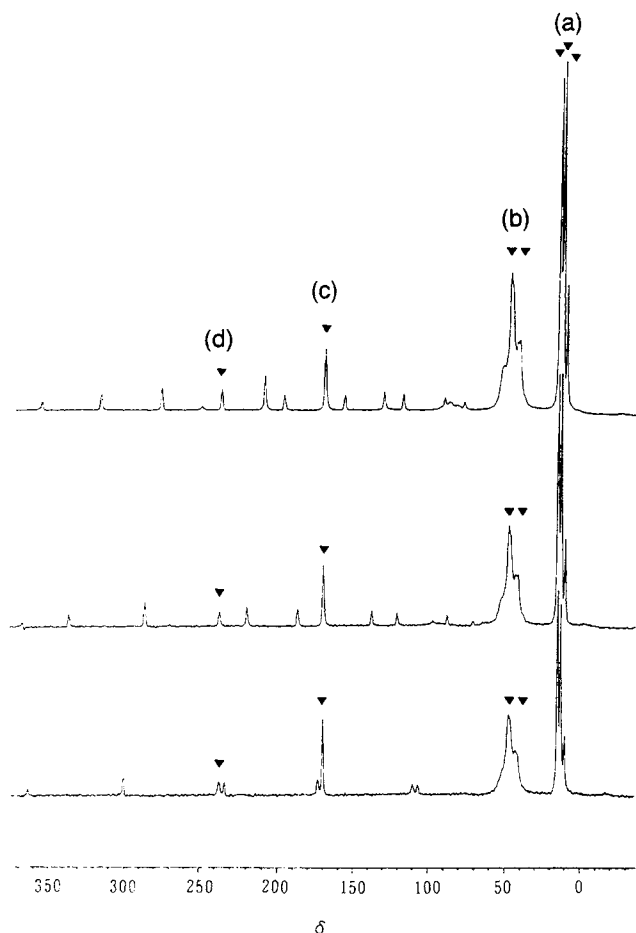


FIGURE 1 Solid-state CPMAS ^{13}C NMR of **1a**. Spinning rate: top, 4 KHz; middle, 5 KHz; bottom, 6 KHz. **a**: Methyl $\delta = 11.1, 13.9, 15.9$; **b**: methylene $\delta = 42.7, 48.9$; **c**: carbenium $\delta = 171.1$; **d**: dithiocarboxylate $\delta = 237.9$.

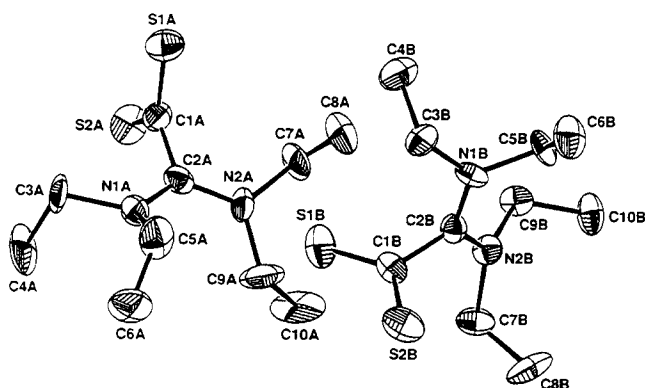


FIGURE 2 Stereoscopic view of two crystallographically independent molecules of **1a** in an asymmetric unit.

TABLE 1 Bond Angles and Lengths for **1a**

Bond	Angles ($^\circ$) ^a	Bond	Length (\AA) ^a
C2B–N1B–C3B	121(1)	S1B–C1B	1.68(1)
C2B–N1B–C5B	120(1)	S2B–C1B	1.67(1)
C3B–N1B–C5B	119(1)	N1B–C2B	1.32(2)
C2B–N2B–C7B	120(1)	N1B–C3B	1.49(2)
C2B–N2B–C9B	121(1)	N1B–C5B	1.50(2)
C7B–N2B–C9B	115(1)	N2B–C2B	1.34(2)
S1B–C1B–S2B	129.2(8)	N2B–C7B	1.53(2)
S1B–C1B–C2B	114.2(9)	N2B–C9B	1.47(2)
S2B–C1B–C2B	116.6(9)	C1B–C2B	1.51(2)
N1B–C2B–N2B	124(1)	C3B–C4B	1.53(2)
N1B–C2B–C1B	118(1)	C5B–C6B	1.56(2)
N2B–C2B–C1B	118(1)	C7B–C8B	1.51(2)
N1B–C3B–C4B	108(1)	C9B–C10B	1.53(2)
N1B–C5B–C6B	109(1)	S1A–C1A	1.68(1)
N2B–C7B–C8B	109(1)	S2A–C1A	1.67(1)
N2B–C9B–C10B	114(1)	N1A–C2A	1.37(2)
C2A–N1A–C3A	119(1)	N1A–C3A	1.53(2)
C2A–N1A–C5A	123(1)	N1A–C5A	1.56(2)
C3A–N1A–C5A	114(1)	N2A–C2A	1.34(2)
C2A–N2A–C7A	120(1)	N2A–C7A	1.47(2)
C2A–N2A–C9A	123(1)	N2A–C9A	1.48(2)
C7A–N2A–C9A	117(1)	C1A–C2A	1.47(2)
S1A–C1A–S2A	129.4(8)	C3A–C4A	1.53(2)
S1A–C1A–C2A	113(1)	C5A–C6A	1.47(2)
S2A–C1A–C2A	117.2(9)	C7A–C8A	1.56(2)
N1A–C2A–N2A	122(1)	C9A–C10A	1.35(3)
N1A–C2A–C1A	118(1)		
N2A–C2A–C1A	120(1)		
N1A–C3A–C4A	109(1)		
N1A–C5A–C6A	114(1)		
N2A–C7A–C8A	107(1)		
N2A–C9A–C10A	114(2)		

^aValues in parentheses are estimated standard deviations in the least significant digits.

the coulombic effects. The carbenium carbon–nitrogen bond lengths, C2A–N1A, C2A–N2A, C2B–N1B, and C2B–N2B, are 1.37, 1.34, 1.34, and 1.32 \AA , respectively. These bond lengths are rather closer to those of common C=N double bonds (1.30 \AA) rather than to those of C–N single bonds (1.47 \AA), which is indicative of the delocalization of the positive charge of **1a** over the N–C–N moiety. The av-

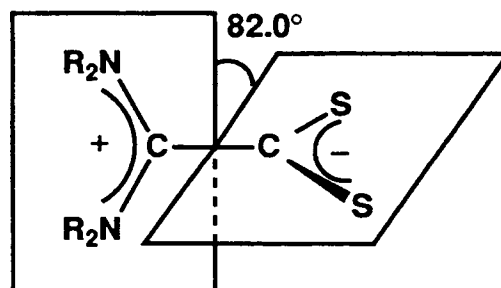


FIGURE 3

erage bite angle of S–C–S (129°) is larger than that of N–C–N (123°), probably due to the larger size of sulfur compared with nitrogen. The dithiocarboxylate carbon–sulfur bond lengths, C1A–S1A, C1A–S2A, C1B–S1B, and C1B–S2B, are 1.68, 1.67, 1.68, and 1.67 Å, respectively. These values reveal that two C–S bonds of **1a** are equivalent and have nearly equal bond lengths, with delocalization of the negative charge over the S–C–S moiety. These results are in harmony with those obtained with the crystal structure analysis of the cyclic compound **2** (R = Ph) [3]. Thus, it is concluded that the structure of these types of inner salts can best be expressed in the structural formulas such as **1** and **2**.

EXPERIMENTAL

General Procedures

Melting points were determined in open capillary tubes on a Mel-Temp melting point apparatus and are uncorrected. ^1H NMR spectra were recorded on a JEOL FX-90Q spectrometer (90 MHz) or a Bruker AM-400 spectrometer (400 MHz) with Me_4Si as an internal standard; ^{13}C NMR spectra were also taken on the above instruments (22.5 and 100.6 MHz), with reference to the center of CDCl_3 (77.0). The solid-state ^{13}C NMR spectrum of **1a** was determined on a Bruker AM-400 spectrometer (100.6 MHz). Infrared spectra were determined on a Hitachi 270-50 infrared spectrophotometer. Mass spectra were obtained at 70 eV on a Shimadzu QP-1000 spectrometer or a JEOL DX-303 spectrometer. UV-Vis spectra were recorded on a Shimadzu UV-160A spectrophotometer. Elemental analyses were performed by the Chemical Analysis Center of Saitama University. Silica gel used for column chromatography was 70-230 mesh ASTM, Merck 7734 Kiesel Gel.

1,1-Bis(diethylamino)-2-phenoxyethylene (4c). To a stirred and cooled (-50°C) solution of 3.99 g (22.7 mmol) of phenyl 2,2,2-trifluoroethyl ether and 5.30 g (72.6 mmol) of diethylamine in 60 mL of ether was added dropwise 43.7 mL (72.6 mmol) of a 1.66 M hexane solution of BuLi under argon. The mixture was warmed to room temperature slowly and stirred for 3 hours. The resulting insoluble material was filtered off and the filtrate was evaporated under reduced pressure. The brown residual oil was distilled to give 1.07 g (28%) of **4c**, bp $100^\circ\text{C}/0.15$ mm Hg; ^1H NMR (CDCl_3 , 400 MHz) δ 0.97 (t, $J = 7.2$ Hz, 6H), 1.04 (t, $J = 7.2$ Hz, 6H), 2.98 (m, 8H), 5.41 (s, 1H), 6.92 (m, 1H), 7.01 (m, 2H), 7.26 (m, 2H); ^{13}C NMR (CDCl_3 , 100.6 MHz) δ 11.82 (q), 13.34 (q), 42.37 (t), 43.25 (t), 114.97 (d), 116.00 (d), 120.66 (d), 129.23 (d), 144.00 (s), 159.16 (s); MS, m/z 262 (M^+).

Bis(diethylamino)carbeniumdithiocarboxylate (1a) from 4a and Sulfur. A mixture of 3.09 g (15.0 mmol)

of **4a**, 2.09 g (8.2 mmol as S_8) of elemental sulfur, and 5.58 g (75.0 mmol) of triethylamine in 200 mL of benzene was stirred at room temperature for 8 hours. The resulting crystalline precipitate of triethylamine hydrochloride (1.93 g, 94%) was removed by filtration and the filtrate was evaporated under reduced pressure. The crystalline residue was chromatographed on a column of silica gel (200 g). The column was first eluted with hexane to remove excess sulfur and then with $\text{CH}_2\text{Cl}_2/\text{EtOAc}$ (95/5) to give 3.40 g (97%) of **1a**, mp 98°C ; red needles (from hexane); results by ^1H NMR (CDCl_3 , 400 MHz) δ 1.32 (t, $J = 7.2$ Hz, 12H), 3.59 (q, $J = 7.2$ Hz, 8H); by ^{13}C NMR (CDCl_3 , 100.6 MHz) δ 12.64 (q), 46.49 (t), 166.65 (s), 236.20 (s); by solid ^{13}C NMR (100.6 MHz) δ 13.92, 48.9, 171.1, 237.9; by IR (KBr) 1050, 1563 cm^{-1} ; by UV-Vis (CH_2Cl_2) λ_{max} (ϵ) 270 (8400), 368 (10,800), and 435 nm (260); by MS, m/z 232 (M^+). Anal. calcd for $\text{C}_{10}\text{H}_{20}\text{N}_2\text{S}_2$: C, 51.68; H, 8.67; N, 12.05; found: C, 51.67; H, 8.47; N, 12.10.

The Dithiocarboxylate 1a from 4c and Sulfur

A mixture of 460 mg (1.76 mmol) of **4c** and 240 mg (0.94 mmol as S_8) in 25 mL of benzene was stirred at room temperature for 4.5 hours. The mixture was extracted with 5 mL of 1M NaOH. The aqueous layer was acidified with 1M hydrochloric acid, saturated with NaCl, and extracted with 10 mL of CH_2Cl_2 . The CH_2Cl_2 extract was dried over MgSO_4 and evaporated to give 102 mg (62%) of phenol. The original organic layer was washed with water, dried over Na_2SO_4 , and evaporated. The crystalline residue was chromatographed on a column of silica gel to give sulfur and 283 mg (70%) of **1a**.

Bis(dipropylamino)carbeniumdithiocarboxylate (1b) from 4b and Sulfur

A mixture of 262 mg (1.0 mmol) of **4b**, 141 mg (0.55 mmol as S_8) of sulfur, and 527 mg (5.2 mmol) of triethylamine in 15 mL of benzene was stirred at room temperature for 5 hours. The resulting precipitate was collected by filtration to give 85 mg (62%) of triethylamine hydrochloride, and the filtrate was evaporated under reduced pressure. The residue was subjected to silica gel column chromatography. Elution with hexane gave excess sulfur and then, with $\text{CH}_2\text{Cl}_2/\text{EtOAc}$ (95/5), 210 mg (73%) of **1b**, mp $104.5\text{--}106^\circ\text{C}$; red needles (from cyclohexane); results by ^1H NMR (CDCl_3 , 90 MHz) δ 0.97 (t, $J = 7.5$ Hz, 12H), 1.77 (m, 8H), 3.46 (t, $J = 7.3$ Hz, 8H); by ^{13}C NMR (CDCl_3 , 22.5 MHz) δ 11.01 (q), 20.76 (t), 53.68 (t), 170.14 (s), 236.29 (s); by IR (KBr) 1054, 1556 cm^{-1} ; by UV-Vis λ_{max} (ϵ) 225 (123,000), 271 (5860), 369 nm (7800); by MS, m/z 288 (M^+). Anal. calcd for $\text{C}_{14}\text{H}_{28}\text{N}_2\text{S}_2$: C, 58.28; H, 9.78; N, 9.71; found: C, 58.24; H, 9.50; N, 9.63.

TABLE 2 Crystallographic Data for 1a

Chemical formula	C ₁₀ H ₂₀ N ₂ S ₂
Formula weight	232.4
Crystal habit	red plate
Crystal size	0.11 × 0.25 × 0.30 mm
Crystal system	monoclinic
Space group	C2/c
Unit cell dimensions	
a (Å)	26.339(8)
b (Å)	7.838(6)
c (Å)	26.397(8)
β (deg)	90.50
V (Å ³)	5449(5)
Z	16
Density: (calcd) (g cm ⁻³)	1.133
Absolute coefficient: μ (cm ⁻¹)	3.6
Diffractometer used	Rigaku AFC-5
X-ray source	sealed tube
Monochromator	graphite
Radiation: (Å)	Mo K _α : 0.71073
Temperature: T (K)	298
Data collection speed (deg/min)	5.0
Scan type	θ-2θ
Scan range	2° < 2θ < 60°
Standard reflections	3 every 150 reflections
Reflections collected	4882
Reflections observed	1543 (F > 3.0 σ(F))
Octants	+h, +k, ±l
Internal consistency: R _{int}	0.0458 for 103 reflections
Number of parameters varied	254
Residuals ^a : R; R _w	0.107; 0.114
Goodness of fit: S ^b	2.591

^aR = Σ||F_o| - |F_c|| / Σ|F_o|, R_w = [Σw(|F_o| - |F_c||)² / Σw|F_o|²]^{1/2}, where w = 1/[σ(F_o)² + (0.020F_o)²].

^bS = [(Σw(|F_o| - |F_c||)² / n_{data} - n_{par}]^{1/2}.

Carbenium Salts **8a** and **8b** by Methylation of **1a** and **1b**.

Excess methyl iodide was added to a stirred solution of **1a** or **1b** (1 mmol) in 5 mL of CH₂Cl₂. After the addition, the mixture was stirred for several minutes and evaporated under reduced pressure. The residual solid was triturated with benzene to give pure **8a** or **8b** nearly quantitatively. **8a**, mp 112.5–114°C; results by ¹H NMR (CDCl₃, 400 MHz) δ 1.38 (t, J = 7.2 Hz, 12H), 2.96 (s, 3H), 3.75 (q, J = 7.2 Hz, 8H); by ¹³C NMR (CDCl₃, 100.6 MHz) δ 13.54 (q), 20.64 (q), 48.44 (t), 163.84 (s), 215.33 (s); by IR (KBr) 1102, 1456, 1589, 2896, 2976 cm⁻¹. Anal. calcd for C₁₁H₂₃N₂IS₂: C, 35.29; H, 6.19; N, 7.48; found: C, 35.15; H, 6.00; N, 7.35. **8b**, mp 60–62°C;

results by ¹H NMR (CDCl₃, 90 MHz) δ 1.01 (t, J = 7.3 Hz, 12H), 1.77 (m, 8H), 3.05 (s, 3H), 3.61 (t, J = 7.5 Hz, 8H); by ¹³C NMR (CDCl₃, 22.5 MHz) δ 10.85 (q), 20.19 (t), 20.93 (q), 54.73 (t), 165.67 (s), 215.40 (s). Anal. calcd for C₁₅H₃₁N₂IS₂: C, 41.85; H, 7.26; N, 6.51; found: C, 41.74; H, 7.08; N, 6.43.

X-Ray Diffraction Analysis of 1a. A crystal grown in ether was dried and anchored on a glass fiber with a cyanoacrylate glue, and the X-ray diffraction measurement was carried out in air at 25°C. The crystallographic data are given in Table 2.

ACKNOWLEDGMENTS

The authors thank Drs. K. Satoh (Niigata University) and T. Nishioka (Institute for Molecular Science) for valuable assistance with the X-ray structural analysis and the Institute for Molecular Science for usage of an X-ray diffractometer. This work was partially supported by Grant-in-Aid for Scientific Research No. 05453028 from the Ministry of Education, Culture and Science, Japan.

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