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1,3-Dimethylimidazolidiniodithioacetates; Stable Inner Salts Having a 1,4-Dipolar Structure

Juzo Nakayama,* Keiichi Akimoto, and Yoshiaki Sugihara
Department of Chemistry, Faculty of Science, Saitama University, Urawa, Saitama 338-8570, Japan

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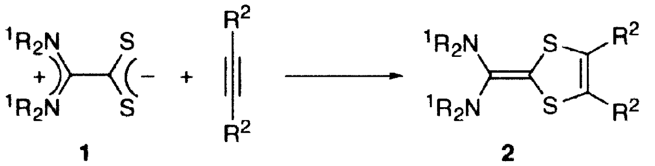
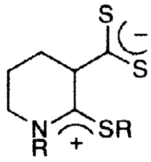
Abstract: Addition of carbon disulfide to 2-isopropylidene- and 2-methylene-1,3-dimethylimidazolidines gave the thermally stable, crystalline inner salts, 1,3-dimethylimidazolidiniodithioacetates (**10** and **12**), where carbenium ion and dithiocarboxylate parts are insulated by an sp^3 carbon atom. X-Ray diffraction analyses of these compounds and the reaction of **10** with DMAD are described.

The inner salts **1** serve as a typical 1,3-dipole, affording 1,3-dithioles **2** on reaction with alkynic 1,3-dipolarophiles.[1] Meanwhile, the inner salts such as **3** and **4** are assumed to be 1,4-dipoles,[2,3] where carbenium ion and dithiocarboxylate parts are insulated by an sp^3 carbon atom. These compounds are thermally labile, however, and evidences for their formation were provided by ^{1}H NMR spectra at low temperature and 1,4-dipolar cycloadditions with heterocummulenes.[3] Recently, we have reported the formation of a similar inner salt **6** by addition of **5** to carbon disulfide.[4] Although **6** was thermally stabler than expected, it could not be obtained in pure crystalline form because it existed as an equilibrium mixture with its dithioic acid tautomer **7** in the ratio 9:1 in $CDCl_3$ at 22 °C and is readily air-oxidized to the disulfide **8** via **7**. Therefore, 2-isopropylidene-1,3-dimethylimidazolidine (**9**),[5] where the corresponding methylene hydrogens are replaced by methyl groups and hence no foregoing equilibrium exists in the resulting adducts, was now chosen as the starting material. This led to the preparation of thermally stable, crystalline inner salts, which enabled their structure to be determined by X-ray diffraction analysis.



1 **2**



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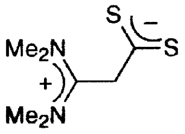

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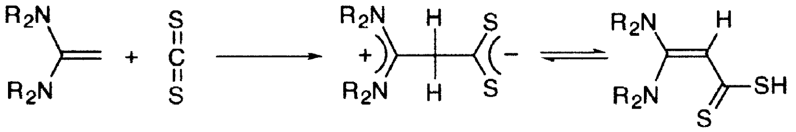
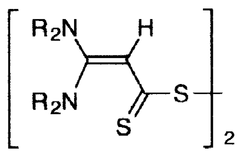


5 R,R = $CH_2(CH_2)_3CH_2$ **6** **7**



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Thus, stirring a mixture of **9**[5] and carbon disulfide in ether resulted in the separation of the expected inner salt **10**[6,7] in 92% yield as light orange powder. Recrystallization of the powder from a mixture of methanol and ether gave analytically pure, single crystals of **10**, which melted at 92-100 °C with some decomposition. The compound is rather thermally stable and storable at room temperature for a long time of period. In the ^{13}C NMR spectrum, the carbenium and dithiocarboxylate carbons of **10** appeared at δ 173.2 and 257.6, respectively, in agreement with the assigned structure.

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e-mail: nakaj@sacs.sv.saitama-u.jp fax: 81-48-858-3700

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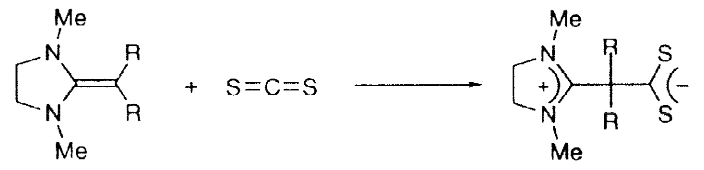


9 (R = Me); **11** (R = H) **10** (R = Me); **12** (R = H)

The molecular structure of **10** is shown in Fig. 1.[8] The imidazolidine ring of **10** is nearly planar as is evident from the torsion angles data. Thus, the carbenium ion center should be fully stabilized by conjugation with two sp^2 nitrogen atoms. In harmony with this prediction, the C5-N6 (1.33 Å) and C5-N9 (1.32 Å) bonds are much shorter than common C(sp^2)-N(sp^3) single bonds (1.416 Å).[9] The C-S bond length of the dithiocarboxylate (1.67 Å) is comparable with that of common C-S double bonds (1.671 Å).[9] The non-bonded distance of S1-C5 (2.89 Å) is shorter than the summation of the van der Waals radii of S and C (3.50 Å),[10] revealing the existence of intramolecular attractive interaction between the dithiocarboxylate sulfur and carbenium carbon atoms, which reflects an inner salt structure.

These data probably suggest that inner salts of the present type may become stable enough without methyl substituents, if their carbenium ion center is fully stabilized by conjugation as in the above system. Indeed, 2-methylene-1,3-dimethylimidazolidine **11**[5] smoothly reacted with carbon disulfide to give the inner salt **12**[6,7] as stable, orange crystals in 71% yield. The structural features of **12**, determinedby X-ray diffraction analysis, are similar to those of **10** (Fig. 2).[8]

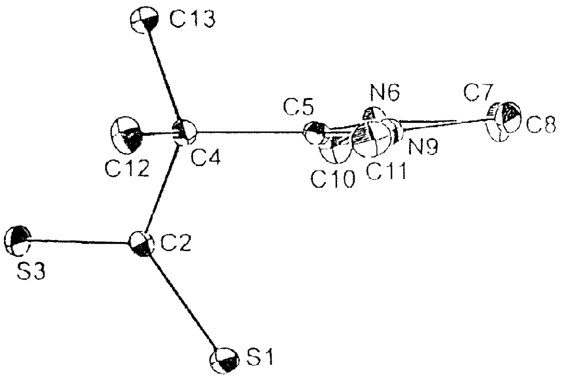


Figure 1: Molecular Structure of **10**.
Selected bond lengths (Å), angles (°), torsion angles (°), and non-bonded lengths (Å): C5-N6 1.330(2), C5-N9 1.323(2), C4-C5 1.529(2), C2-C4 1.557(2), S1-C2 1.676(2), S3-C2 1.671(1), C4-C5-N6 120.6(2), C4-C5-N9 128.5(2), C2-C4-C5 107.5(2), C4-C2-S1 115.3(2), S1-C2-S3 126.2(2), N6-C5-N9-C8 1.1(2), N9-C5-N6-C7 4.9(2), S1-N6 3.354(1), S1-N9 3.571(1), S1-C5 2.890(1).

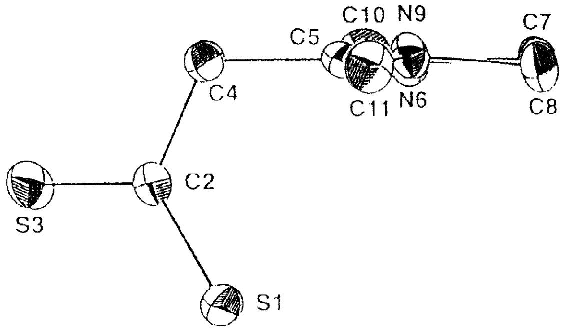
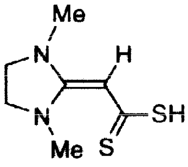


Figure 2: Molecular Structure of **12**.
Selected bond lengths (Å), angles (°), torsion angles (°), and non-bonded lengths (Å): C5-N6 1.313(1), C5-N9 1.324(1), C4-C5 1.488(1), C2-C4 1.524(1), S1-C2 1.675(1), S3-C2 1.674(1), C4-C5-N6 122.4(1), C4-C5-N9 125.5(1), C2-C4-C5 111.7(1), C4-C2-S1 116.3(1), S1-C2-S3 126.8(1), N6-C5-N9-C8 0.3(1), N9-C5-N6-C7 5.9(1), S1-N6 3.623(1), S1-N9 3.519(1), S1-C5 3.007(1).

As mentioned already, **6** existed as an equilibrium mixture with **7** in solution, which hampered its isolation in pure crystalline form. By contrast, in case of **12**, no dithioic acid form **13** was detected by ^{1}H NMR in harmony with its resistance to air-oxidation. Both methylene hydrogens and carbon signals adjacent to the dithiocarboxylate in **12** appeared at higher fields than those in **6** by 0.13 ppm (δ 4.44 vs. 4.57) and 6.6 ppm (δ 53.9 vs. 60.5), respectively.[4] These chemical shift data also indicate that the carbenium ion center in **12** is more effectively stabilized by conjugation with two nitrogen atoms than that in **6**, and hence the methylene hydrogens of **12** would be less acidic than those of **6**. The difference of the acidity is reflected in the rate of H-D exchange; the methylene hydrogens of **6** were completely replaced by deuterium within 5 min by addition of D_2O to its $CDCl_3$ solution,[4] whereas, in case of **12**, 1 h was required for 35% H-D exchange.

The inner salts **10** and **12** are easily methylated by iodomethane to give the carbenium iodides **14** and **15** quantitatively.[7,11]



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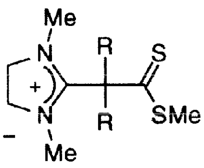
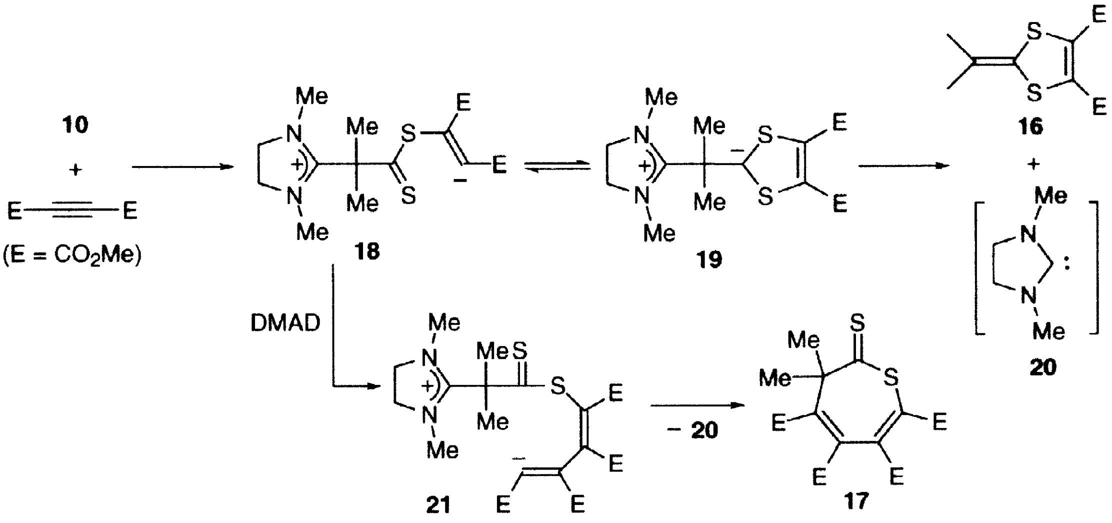


14 (R = Me); **15** (R = H)

The reaction of **10** with an equimolar amount of dimethyl acetylenedicarboxylate (DMAD) gave a 1,3-dithiole **16**[12] in 38% yield. No expected 1,4-dipolar cycloadduct was formed. In addition, the reaction with two molar amounts of DMAD gave an eight-membered dithiolactone **17**[7,13] in 86% yield along with **16** in 11% yield. The present reaction would be initiated by a Michael addition of **10** to DMAD which forms a betaine **18**. Ring closure of **18** gives another betaine **19**. Elimination of a carbene **20** from **19** would produce **16**. When two molar amounts of DMAD was used, the betaine **18** further reacts with DMAD to give a betaine **21**. An intramolecular S_N2 reaction of **21** on the quaternary carbon would produce the final product **17** with the carbene **20** acting as the leaving group. However, despite much effort, no products derived from the carbene **20**, including the dimeric product, could be isolated. Even the use of excess DMAD did not give the adduct[14] arising from **20** and DMAD. Attempted trapping of **20** by other reagents such as elemental sulfur,[15] methanol,[16] and carbon disulfide,[1a,17] was also unsuccessful; in some cases, complex mixtures formed at the sacrifice of the formation of **16** and **17**. In this connection, preparation of an inner salt, which yields a stable, isolable carbene[18] on reaction with DMAD, is under way to establish the above mechanism.



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6. **8**: mp 92-100 °C (decomp); ^{1}H NMR (270 MHz, $CDCl_3$, TMS): δ = 1.86 (s, 6H, CCH_3), 3.32 (s, 6H, NCH_3), 3.82 (s, 4H, CH_2); ^{13}C NMR (67.8 MHz, $CDCl_3$, TMS): δ = 31.4 (CH_3), 37.5 (CH_3), 51.8 (CH_2), 64.2 (C), 173.2 (NCN), 257.6 (SCS); FT-IR (KBr): 1572, 1528, 1399, 1377, 1283, 1066, 1041 cm^{-1}; UV/Vis (CH_3CN): $\lambda_{max}(\varepsilon)$ = 220 nm (13200), 241 nm (sh) (8500), 348 nm (14300). **12**: orange granules (from methanol-ether); mp 134-136 °C (decomp); ^{1}H NMR ($CDCl_3$): δ = 3.25 (s, 6H, NCH_3), 3.92 (s, 4H, NCH_2CH_2N), 4.44 (s, 2H, CH_2); ^{13}C NMR ($CDCl_3$): δ = 34.5 (CH_3), 50.0 (CH_2), 53.9 (CH_2), 165.3 (NCN), 241.2 (SCS); FT-IR (KBr):1620, 1574, 1410, 1363, 1296, 1182, 1084, 1051, 1024 cm^{-1}; UV/Vis (CH_3CN): $\lambda_{max}(\varepsilon)$ 219 nm (15000), 246 nm (sh) (9100), 345 nm (16000).
7. Satisfactory elemental analyses were obtained for all new compounds.
8. Crystal structure data for **10**: $C_9H_{16}N_2S_2$, M_r = 216.37, orthorhombic, Pcab (# 61), a = 11.559(4), b = 13.874(3), c = 14.081(3) Å, V = 2258.2(7) Å^3 , Z = 8, D_{calc} = 1.33 gcm^{-3}, μ(Mo K_α) = 8.689 mm^{-1}, T = 298 K. A yellow crystal with dimensions 0.26 x 0.25 x 0.22 mm was mounted on a Mac Science DIP3000 diffractometer equipped with a graphite monochrometer. Oscillation and nonscreen Weissenberg photographs were recorded on the imaging plates of the diffractometer by using Mo $K\alpha$ radiation (λ = 0.71073 Å) and the data reduction was made by the MAC DENZO program system. Intensity data of 3375 unique reflections were collected in the range of $0 \leq h \leq 16$, $0 \leq k \leq 19$, $0 \leq l \leq 19$. Cell parameters were determined and refined by using the MAC DENZO for all observed reflections. The structure was solved by direct methods using SIR[19] in the CRYSTAN-GM program system. The atomic coordinates and anisotropic thermal parameters of the non-H atoms were refined by full-matrix least squares[20] to minimize the functions, $\Sigma(|F_o|-|F_c|)^2$ for 2297 reflections with $I > 3\sigma(I)$. The final R, R_w, and GOF values are 0.050, 0.071, and 3.529, respectively. Residual electron density (eÅ^{-3}): min = -0.51, max = 0.57. Crystal structure data for **12**: $C_7H_{12}N_2S_2$ M_r = 188.32, triclinic, P1, a = 8.958(1), b = 9.408(1), c = 11.258(1) Å, β = 100.716(4) °, V = 932.24(17) Å^3 , Z = 4, D_{calc} = 1.34 gcm^{-3}, μ(Mo K_α) = 8.689 mm^{-1}, T = 153 K. A yellow crystal with dimensions 0.35 x 0.20 x 0.15 mm was used. Intensity data of 2385 unique reflections were collected in the range of $0 \leq h \leq 12$, $0 \leq k \leq 10$, $-16 \leq l \leq 15$. Solution and refinement were carried out for 2137 reflections. The final R, R_w, and GOF values are 0.033, 0.040, and 0.774, respectively. Residual electron density (eÅ^{-3}): min = -0.50, max = 0.26.
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11. **14**: yellow powder; mp 131.5-132.5 °C; ^{1}H NMR ($CDCl_3$): δ = 2.06 (s, 6H, CCH_3), 2.74 (s, 3H, SCH_3), 3.26 (s, 6H, NCH_3), 4.13 (s, 4H, NCH_2CH_2N); ^{13}C NMR ($CDCl_3$): δ = 19.9 (CH_3), 29.7 (CH_3), 37.8 (CH_3), 52.5 (CH_2), 59.5 (C), 168.2 (NCN), 238.1 (C=S). **15**: yellow powder; mp 144.0-144.5 °C; ^{1}H NMR ($CDCl_3$): δ = 2.73 (s, 3H, SCH_3), 3.23 (s, 6H, NCH_3), 4.06 (s, 4H, NCH_2CH_2N), 4.54 (2H, s, N_2CCH_2CS); ^{13}C NMR ($CDCl_3$): δ = 20.4 (CH_3), 34.8 (CH_3), 45.9 (CH_2), 50.4 (CH_2), 164.0 (NCN), 221.7 (C=S).
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13. **17**: yellow crystals; mp 96.5-98.0 °C (from ether-hexane); ^{1}H NMR ($CDCl_3$): δ = 1.41 (s, 6H, CH_3), 3.82 (s, 6H, 2 x CO_2CH_3), 3.86 (s, 3H, CO_2CH_3), 3.97 (s, 3H, CO_2CH_3); ^{13}C NMR ($CDCl_3$): δ = 23.6 (CH_3), 52.9 (CH_3), 53.2 (2 x CH_3), 53.5 (CH_3), 54.6 (C), 129.5 (2 x C), 129.8 (C), 160.2 (2 x C=O), 160.6 (C), 161.1 (C=O), 162.8 (C=O), 200.9 (C=S).
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