

The stable inner salt 2,2-dimorpho-  
lino-2-ethylium-1-dithioateTakashi Fujihara,<sup>a\*</sup> Takeshi Ohba,<sup>a</sup> Akira Nagasawa,<sup>a</sup> Juzo Nakayama<sup>a</sup> and Kenji Yoza<sup>b</sup><sup>a</sup>Department of Chemistry, Faculty of Science, Saitama University, Shimo-Okubo 255, Saitama 338-8570, Japan, and <sup>b</sup>Nihon Bruker AXS KK, 21-5 Ninomiya 3-chome, Tsukuba, Ibaraki 305-0051, Japan  
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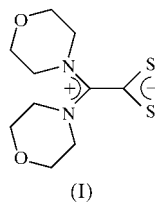
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The title compound, C<sub>10</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>S<sub>2</sub>, is considered to maintain an inner-salt structure in the crystal, where the planes of the carbenium and the thiocarboxylate moieties are nearly perpendicular to each other [77 (2)°], and the backbone C—C bond length [N<sub>2</sub>C—CS<sub>2</sub> 1.510 (2) Å] is significantly shorter than a normal C—C single-bond length.

## Comment

The bis(*N,N*-disubstituted amino)carbeniumdithiocarboxylates are a structurally interesting class of inner salts. They have been investigated with regard to their synthesis, structure and reactivity (Nakayama, 1993, 2000, 2002). Their thermodynamic stability apparently comes from localization of the positive and negative charges on the N—C—N and S—C—S moieties, respectively. The most remarkable structural characteristic of these compounds is that the planes of the CS<sub>2</sub> and CN<sub>2</sub> groups are almost perpendicular (Sheldrick *et al.*, 1980; Ziegler *et al.*, 1987; Borer *et al.*, 1989; Kuhn *et al.*, 1987; Nagasawa *et al.*, 1995; Nakayama *et al.*, 2000). We report here the characteristic molecular conformation of the title compound, (I), in the solid state (Fig. 1).



Selected bond lengths and angles are given in Table 1. The dihedral angle between the planes of the carbenium and thiocarboxylate moieties is close to being a right angle [77 (2)°], probably due to the above-mentioned localization of the charges. The attractive Coulombic interaction is reflected in the reduction of the C—C—S bond angles to about 114°, which also results in the shortening of the non-bonded

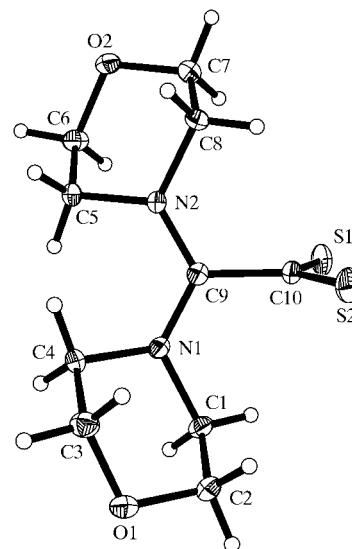


Figure 1

The molecular structure of the title compound, shown with 50% probability displacement ellipsoids and the atom-numbering scheme.

distances between the carbenium C atom and the S atoms [2.71 Å; sum of the van der Waals radii = 3.50 Å (Bondi, 1964)]. The shortened length of the N<sub>2</sub>C—CS<sub>2</sub> bond [1.510 (2) Å] would also be attributable to the Coulombic interaction. The two C—S distances are not significantly different, indicating that the negative charge is spread equally over these two S atoms. These distances are close to that expected for a C=S double bond rather than a C—S single bond (1.75 Å; Allen *et al.*, 1987). The average C—N bond length is 1.33 Å, which is slightly shorter than the common Csp<sup>3</sup>—Nsp<sup>3</sup> bond length of 1.36 Å (Allen *et al.*, 1987), indicating the contribution of the canonical structure. According to these results, the title compound is considered to maintain the inner-salt structure in the crystal. There is no significant contact among neighboring molecules.

These structural features were confirmed by a theoretical calculation using a natural bond orbital (NBO) analysis (Glendening *et al.*, 2001), with the fully optimized structure, and are consistent with the results obtained by GAUSSIAN98 (Frisch *et al.*, 2001), with a B3LYP/6-31G\* set of parameters. According to the NBO analysis, the σ\* orbital of the C9—C10 bond and the π\* orbital of the C9—N1 bond are occupied by 0.07 and 0.49 e, respectively, and the S atoms are principal lone-pair donors, providing an interaction energy of 31.8 kJ mol<sup>-1</sup> for the C9—C10 bond and 30.9 kJ mol<sup>-1</sup> for the C9—N1 bond. These electronic interactions of the sulfur lone pairs would contribute to the structural characteristics.

## Experimental

The title compound was synthesized according to the previously reported method of Nakayama & Akiyama (1992). Crystals suitable for X-ray diffraction were obtained by slow evaporation of a solution in acetonitrile at room temperature.

**Table 1**Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ).

C1—N1	1.476 (2)	C9—N1	1.329 (2)
C4—N1	1.475 (2)	C9—C10	1.510 (2)
C5—N2	1.480 (2)	C10—S1	1.6653 (18)
C8—N2	1.476 (2)	C10—S2	1.6699 (18)
C9—N2	1.328 (2)		
N2—C9—N1	122.62 (14)	C9—C10—S2	114.71 (12)
N2—C9—C10	118.53 (14)	S1—C10—S2	131.42 (10)
N1—C9—C10	118.85 (14)	C4—N1—C1	112.44 (13)
C9—C10—S1	113.87 (12)	C9—N2—C8	122.36 (14)

*Crystal data* $\text{C}_{10}\text{H}_{16}\text{N}_2\text{O}_2\text{S}_2$  $M_r = 260.37$ Orthorhombic, *Pbca* $a = 14.991 (1) \text{\AA}$  $b = 10.633 (1) \text{\AA}$  $c = 15.064 (1) \text{\AA}$  $V = 2401.2 (3) \text{\AA}^3$  $Z = 8$  $D_x = 1.441 \text{ Mg m}^{-3}$ Mo  $K\alpha$  radiation

Cell parameters from 4110

reflections

 $\theta = 2.7\text{--}31.0^\circ$  $\mu = 0.43 \text{ mm}^{-1}$  $T = 100 \text{ K}$ 

Plate, red

 $0.30 \times 0.27 \times 0.14 \text{ mm}$ *Data collection*Bruker CCD area-detector  
diffractometer $\varphi$  and  $\omega$  scansAbsorption correction: empirical  
(*SADABS*; Sheldrick, 1996) $T_{\min} = 0.882$ ,  $T_{\max} = 0.942$ 

18 623 measured reflections

3638 independent reflections

3021 reflections with  $I > 2\sigma(I)$  $R_{\text{int}} = 0.055$  $\theta_{\text{max}} = 31.0^\circ$  $h = -20 \rightarrow 20$  $k = -9 \rightarrow 15$  $l = -20 \rightarrow 21$ 

119 standard reflections

frequency: 740 min

intensity decay: none

*Refinement*Refinement on  $F^2$  $R[F^2 > 2\sigma(F^2)] = 0.045$  $wR(F^2) = 0.103$  $S = 1.09$ 

3638 reflections

209 parameters

All H-atom parameters refined

 $w = 1/[\sigma^2(F_o^2) + (0.0372P)^2 + 1.4616P]$ where  $P = (F_o^2 + 2F_c^2)/3$  $(\Delta/\sigma)_{\text{max}} < 0.001$  $\Delta\rho_{\text{max}} = 0.37 \text{ e \AA}^{-3}$  $\Delta\rho_{\text{min}} = -0.28 \text{ e \AA}^{-3}$ 

All H atoms were located from a difference Fourier map and refined isotropically [ $\text{C—H} = 0.89 (2)\text{--}0.99 (2) \text{\AA}$ ].

Data collection: *SMART* (Bruker, 1995); cell refinement: *SMART*; data reduction: *SHELXTL* (Sheldrick, 2001); program(s) used to

solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1383). Services for accessing these data are described at the back of the journal.

**References**

- Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.
- Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–451.
- Borer, L. L., Kong, J. V. & Oram, D. E. (1989). *Acta Cryst.* **C45**, 1169–1170.
- Frisch, M. J., Trucks, G. W., Schlegel, H. B., Scuseria, G. E., Robb, M. A., Cheeseman, J. R., Zakrzewski, V. G., Montgomery, J. A. Jr, Stratmann, R. E., Burant, J. C., Dapprich, S., Millam, J. M., Daniels, A. D., Kudin, K. N., Strain, M. C. *et al.* (2001). *GAUSSIAN98*. Revision A.11.1. Gaussian Inc., Pittsburgh, PA, USA.
- Glendening, E. D., Badenhoop, J. K., Reed, A. E., Carpenter, J. E., Bohmann, J. A., Morales, C. M. & Weinhold, F. (2001). *NBO*. Version 5.0. Theoretical Chemistry Institute, University of Wisconsin, Madison, Wisconsin, USA.
- Kuhn, N., Bohnen, H. & Henkel, G. (1987). *Z. Naturforsch. Teil B*, **49**, 1473–1480.
- Nagasawa, A., Akiyama, I., Mashima, S. & Nakayama, J. (1995). *Heteroatom Chem.* **6**, 45–49.
- Nakayama, J. (1993). *Sulfur Lett.* **15**, 239–245.
- Nakayama, J. (2000). *CACS Forum*, **20**, 7–20.
- Nakayama, J. (2002). *J. Synth. Org. Chem. Jpn.* **60**, 106–114.
- Nakayama, J. & Akiyama, I. (1992). *J. Chem. Soc. Chem. Commun.* p. 1552.
- Nakayama, J., Kitahara, T., Sugihara, Y., Sakamoto, A. & Ishii, A. (2000). *J. Am. Chem. Soc.* **122**, 9120–9126.
- Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Sheldrick, G. M. (2001). *SHELXTL*. DOS/Windows/NT Version 6.12. Bruker AXS Inc., Madison, Wisconsin, USA.
- Sheldrick, W. S., Shoenberg, A., Singer, E. & Eckert, P. (1980). *Chem. Ber.* **113**, 3605–3609.
- Siemens (1995). *SMART*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Ziegler, M. L., Weber, H., Nuber, N. & Serhadle, O. (1987). *Z. Naturforsch. Teil B*, **42**, 1411–1418.