

in the preparation of compound **12**. 51% yield, mp 295-297 °C; ¹H NMR (DMSO-d₆) δ 12.7 (broad, 1H, NH), 10.5 (d, *J*=9 Hz, 1H, C₁₀-H), 9.0-7.7 (m, 3H, Ar-H), 8.6 (s, 1H, C₂-H), 4.3 (q, *J*=7.1 Hz, 2H, CH₂), 1.3 (t, *J*=7.1 Hz, 3H, CH₃); MS: *m/e* (relative intensity) 286 (M⁺, 47), 241 (100), 213 (12).

Ethyl 1-ethyl-5-fluoro-4-oxo-pyrido[2,3-g]quinoline-3-carboxylate (27). The reaction was carried out by the same method described in the preparation of compound **13**. 58% yield, mp 179-180 °C; ¹H NMR (CDCl₃) δ 10.8 (d, *J*=8.7 Hz, 1H, C₁₀-H), 9.0-7.5 (m, 3H, Ar-H), 8.5 (s, 1H, C₂-H), 4.5-4.3 (m, 4H, 2CH₂), 1.6-1.4 (m, 6H, 2CH₃); MS: *m/e* (relative intensity) 314 (M⁺, 9), 270 (11), 243 (100), 214 (15), 186 (4).

1-Ethyl-5-fluoro-4-oxo-pyrido[2,3-g]quinoline-3-carboxylic acid (6). The reaction was carried out by the same method described in the preparation of compound **5**. 83% yield, mp 291-294 °C; ¹H NMR (DMSO-d₆) δ 10.5 (d, *J*=8.7 Hz, 1H, C₁₀-H), 9.2 (s, 1H, C₂-H), 9.1-7.9 (m, 3H, Ar-H), 4.7 (q, *J*=7 Hz, 2H, CH₂), 1.5 (t, *J*=7 Hz, 3H, CH₃); MS: *m/e* (relative intensity) 286 (M⁺, 7), 243 (100), 214 (32), 186 (16).

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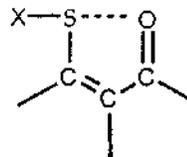
Intramolecular Sulfur-Oxygen Interaction. Structure of Dimethyl 1,3-dithiolan-2-ylidenemalonate

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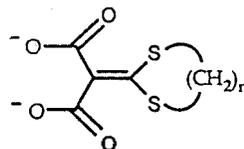
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Intramolecular interactions between sulfur and oxygen often occur in organic and inorganic compounds.^{1,2} This type of interaction (shorter than the sum of the van der Waals radii) plays an important role in controlling physicochemical properties such as structural conformation and reactivity.^{3,4} Such a strong sulfur-oxygen interaction is particularly favorable in the conjugated system of X-S-C=C=O with the following configuration and conformation.^{2,5} For the conjugat-



ed system, the planar conformation can be stabilized by the S...O interaction. The intramolecular interaction can be also affected by properties of the X group.⁵

Recently the authors are involved in a synthetic and structural works on platinum(II) complexes using sulfur-containing dicarboxylate ligands of the following structure and have shown that a variety of coordination modes (O,O', O,S-, and



S,S'-chelates) were formed depending on their dithioether ring size.⁶⁻⁸ In particular, 1,3-dithiolan-2-ylidene malonic acid (*n*=2) alkyl esters of the above system are commercialized compounds as horticultural fungicides or therapeutic agents for treating hepatic diseases.⁹ The platinum complex of 1,3-dithiolan-2-ylidenemalonate ligand exhibits exclusively O,O'-chelation probably due to remarkable decrease of sulfur basicity, which, in addition to the ring size effect, may be at

Table 1. Details of Crystallographic Data for Dimethyl-1,3-dithiolan-2-ylidenemalonate

formula	C ₈ H ₁₀ O ₄ S ₂
fw	234.28
temperature, K	293(2)
wavelength, Å	0.71073
crystal system	monoclinic
space group	P2 ₁ /a (no. 14)
a, Å	10.943(3)
b, Å	6.744(2)
c, Å	14.331(5)
β, deg	90.30(2)
V, Å ³	1057.7(6)
Z	4
d _{calc} , g/cm ³	1.471
absorption coefficient, mm ⁻¹	0.489
F(000)	488
crystal size, mm	0.30×0.30×0.25
theta range, deg	2.84-24.95
index ranges	0<h<12, 0<k<7, -16<l<16
independent reflections	1487[R(int)=0.000]
refinement method	full-matrix least-squares on F ²
data to parameter ratio	1486/127
GOF on F ²	1.124
final R indices [I>2σ (I)]	R ₁ =0.0508, wR ₂ =0.1521
R indices (all data)	R ₁ =0.0563, wR ₂ =0.1649
largest diff. peak and hole	0.230 and -0.445 e.Å ⁻³

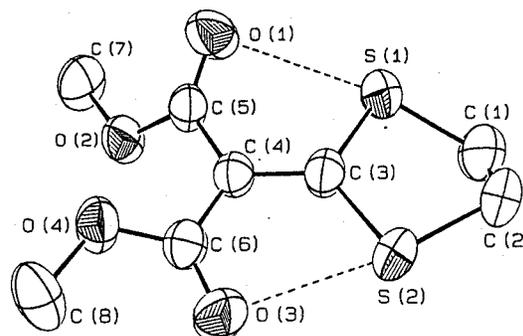
$R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$. $wR_2 = \{\sum w(F_o^2 - F_c^2)^2 / \sum wF_o^4\}^{1/2}$, where $w = 1/[\sigma^2 F_o^2 + (aP)^2 + bP]$, where $P = \{\text{Max}(F_o^2, 0) + 2F_c^2\} / 3$ and a, b were determined by the program.

least partly ascribable to the intramolecular S...O interaction of the ligand. Thus herein are reported the structure and its related properties of dimethyl 1,3-dithiolan-2-ylidenemalonate.

Experimental

Preparation and Measurements. Dimethyl 1,3-dithiolan-2-ylidenemalonate was prepared according to the literature procedure.¹⁰ The compound was recrystallized from acetone to obtain crystals suitable for X-ray crystallography. ¹H and ¹³C NMR spectra were recorded on a Varian Gemini-300 NMR spectrometer operating at 300.00 MHz (¹H) and 75.48 MHz (¹³C) in pulse mode with Fourier transform. The chemical shifts are relative to SiMe₄ (¹H and ¹³C) as an internal standard for both indicated nuclei.

The X-ray data were collected on an Enraf-Nonius CAD 4 automatic diffractometer with graphite-monochromated Mo Kα (λ=0.71073 Å) at ambient temperature. Unit cell dimensions were based on 25 well-centered reflections by using a least-square procedure. During the data collection, three standard reflections monitored every hour did not show any significant intensity variation. The data were corrected for Lorentz and polarization effects. Absorption effects were corrected by the empirical psi-scan method. The structures were solved by Patterson method (SHELXS-86), and were refined by full-matrix least squares techniques (SHELXL-93).¹¹ All

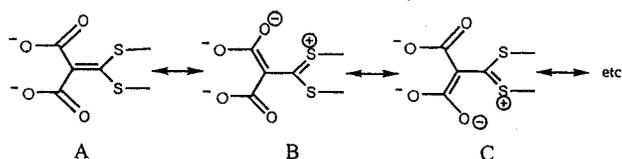
**Figure 1.** X-ray crystal structure and atomic labeling scheme of dimethyl 1,3-dithiolan-2-ylidenemalonate.**Table 2.** Bond Lengths (Å) and Angles (°) for Dimethyl-1,3-dithiolan-2-ylidenemalonate

S(1)-C(3)	1.744(4)	S(1)-C(1)	1.793(5)
S(2)-C(3)	1.745(4)	S(2)-C(2)	1.805(6)
O(1)-C(5)	1.194(5)	O(2)-C(5)	1.320(4)
O(2)-C(7)	1.446(5)	O(3)-C(6)	1.201(5)
O(4)-C(6)	1.327(4)	O(4)-C(8)	1.445(5)
C(1)-C(2)	1.485(10)	C(3)-C(4)	1.362(5)
C(4)-C(6)	1.474(5)	C(4)-C(5)	1.479(5)
C(3)-S(1)-C(1)	95.5(2)	C(3)-S(2)-C(2)	95.7(2)
C(5)-O(2)-C(7)	116.5(3)	C(6)-O(4)-C(8)	115.7(3)
C(2)-C(1)-S(1)	107.4(4)	C(1)-C(2)-S(2)	108.2(4)
C(4)-C(3)-S(2)	123.5(3)	C(4)-C(3)-S(1)	122.5(3)
S(2)-C(3)-S(1)	114.0(2)	C(3)-C(4)-C(6)	119.3(3)
C(3)-C(4)-C(5)	118.7(3)	C(6)-C(4)-C(5)	121.9(3)
O(1)-C(5)-O(2)	123.7(4)	O(1)-C(5)-C(4)	123.4(3)
O(2)-C(5)-C(4)	112.8(3)	O(3)-C(6)-O(4)	122.9(4)
O(3)-C(6)-C(4)	124.3(4)	O(4)-C(6)-C(4)	112.8(3)

non-hydrogen atoms were refined anisotropically and hydrogen atoms were added at calculated positions. Crystal parameters and procedural information corresponding to data collection and structure refinement are given in Table 1. Final atomic coordinates and isotropic thermal parameters are given in Supplementary Materials.

Results and Discussion

The molecular structure along with atomic labeling is shown in Figure 1, and relevant bond distances and angles are listed in Table 2. The C(3)-C(4) double bond (1.365(5) Å) is significantly longer than the normal double bond (1.33 Å).¹² The bond lengths of C(3)-S(1) (1.744(4) Å) and C(3)-S(2) (1.745(4) Å) are also shorter than that (1.82 Å) of a typically isolated C-S single bond.¹³ Furthermore, the C-C single bonds (C(4)-C(5), 1.479(5); C(4)-C(6), 1.474(5) Å) are shorter than that (1.54 Å) of ethane.¹² These bond lengths reflect the presence of the following resonance structures B and C etc. in the present compound containing sulfur atom in contrast to the analog without sulfur atom in which no resonance structure is allowed. In addition to the bond lengths, the atoms of S(1), C(3), C(4), C(5), O(1), S(2), C(6), and O(3) are almost in a plane supporting the contribution of the reso-



Scheme 1.

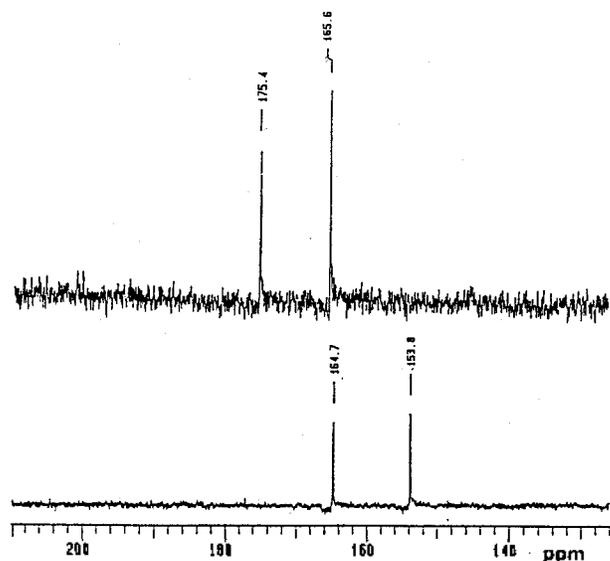


Figure 2. ^{13}C NMR spectra of dimethyl 1,3-dithiolan-2-ylidene-malonate (top) and diethyl isopropylidenemalonate (bottom) in the region of 140–200 ppm.

nance structures B and C etc. (supplementary materials). The most interesting observation is that the distances of $\text{S}(1)\cdots\text{O}(1)$ (2.80 Å) and $\text{S}(2)\cdots\text{O}(3)$ (2.70 Å) are much shorter than that of van der Waals radii (3.30 Å),¹⁴ which implies possible formation of the heteroaromatic 5-membered rings¹⁵ consisting of $\text{S}(1)$, $\text{C}(3)$, $\text{C}(4)$, $\text{C}(5)$, and $\text{O}(1)$, and of $\text{S}(2)$, $\text{C}(3)$, $\text{C}(4)$, $\text{C}(6)$, and $\text{O}(3)$. The $\text{S}\cdots\text{O}$ distances of the present compound are comparable to the corresponding distance (2.743(4) Å) in methyl-2-nitrobenzenesulfinate.²

Figure 2 shows ^{13}C NMR of the title compound measured in chloroform solution and compared with that of diethyl isopropylidenemalonate¹⁶ which is an analog without sulfur atoms. For $\text{C}=\text{O}$ group, ^{13}C resonance (175.4 ppm) of the title compound is deshielded by 10.7 ppm relative to that (164.7 ppm) of diethyl isopropylidenemalonate. The chemical shift of vinyl carbon atom adjacent to carbonyl group of the present compound and diethyl isopropylidenemalonate lies at 165.6 and 153.8 ppm, respectively. Such prominent differ-

ences of the chemical shifts between the two compounds indicate that the presence of sulfur atom strongly affect chemical environment of the title compound. Moreover, the ^{13}C NMR spectra indicate that the structure of the present compound is retained in solution.

In conclusion, the title compound is a rare example with two strong intramolecular $\text{S}\cdots\text{O}$ interactions in a molecule that seem to correlate with useful applicabilities. For a similar system, such an interaction should be considered in designing compounds that exhibit desirable biological activities.

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