Research Article

Crystal and Molecular Structure of 1,1-Bis(methylthio)-5-(4-chlorophenyl)-1,4-pentadien-3-one

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The 1,1-bis(methylthio)-5-(4-chlorophenyl)-1,4-pentadien-3-one compound crystallizes in the space group C2/c with unit cell parameters $a = 25.576(3)$ Å, $b = 8.0886(3)$ Å, $c = 14.145(2)$ Å, and $\beta = 108.6^\circ$. The structure was solved by direct methods and refined to an R-factor of 0.0593. Due to the steric interaction between the two methyl groups, one of the methylthio groups is in *cis* conformation with C11–C10 double bond and the other is in *trans* conformation. The cinnamoyl group on the carbonyl carbon atom effects more delocalization of the electrons within the molecule so that the structure is highly conjugated and planar.

1. Introduction

Cinnamoyl ketene dithioacetals are valuable intermediates in organic synthesis [1–4]. α -Oxoketene dithioacetals may be considered as highly functionalized α , β -unsaturated ketones which are potential precursors for the regioselective and stereoselective bond formation via 1,2 or 1,4 nucleophilic additions. Conformational studies on diacetyl ketene dithioacetals with bis(methylthio) methylene functionality show a slight twist about the carbon-carbon double bond with the two acyl groups having a highly twisted E,E-conformation. It is possible that the presence of a cross conjugating group like a styryl group near the carbonyl group could delocalize the electrons more efficiently thereby effecting conformational changes in the title compound.

2. Experimental

2.1. Synthesis. Sodium metal (0.45 g, 20 mmol) was dissolved in ethanol (20 mL) to which acetyl ketene dithioacetal (10.2 g, 5 mmol) in ethanol (10 mL) was added followed by para-chlorobenzaldehyde (10 mmol) (Scheme 1). The reaction mixture was stirred at 0–5°C for 4 hours. The solid

obtained was filtered and recrystallized from a mixture of hexane and ethyl acetate to give the title compound.

2.2. X-Ray Crystal Structural Studies. Yellow needle-shaped crystals of the compound were obtained by slow evaporation from acetone-ethyl acetate solution. The dimensions of the crystal used for data collection were $0.15 \times 0.12 \times 0.1$ mm. The compound crystallized in the monoclinic space group C2/c with unit cell parameters $a = 25.576(3)$ Å, $b = 8.088$ Å, $c = 14.145(2)$ Å, and $\beta = 108.6^\circ$. The intensity data were collected up to $2\theta_{\text{max}}$ of 135.86° by an Enraf-Nonius CAD-4 diffractometer using crystal monochromated CuK α radiation ($\lambda = 1.5418$ Å) in ω - 2θ mode. The usual precaution of checking the consistency of the intensities of three strong reflections periodically (every one hour) for monitoring the stability of the crystal during X-ray exposure was observed. The intensities were corrected for Lorentz, polarization, and absorption.

The structure was solved by direct methods using SHELXS-97 [5]. The top 17 peaks of the E-map formed the complete structure. The structure was refined using SHELXL-97 [5]. All hydrogen atoms were fixed by the program. Anisotropic refinement of the nonhydrogen atoms along

TABLE 1: Crystal data and structure solution details.

CCDC number	963549
Empirical formula	C ₁₃ H ₁₃ ClOS ₂
Formula weight	557.51
Wavelength	1.5418 Å
Crystal system, space group	Monoclinic, C2/c
Unit cell dimensions	$a = 25.576(3)$ Å, $b = 8.0886(3)$ Å, $c = 14.145(2)$ Å, $\alpha = 90^\circ$, $\beta = 108.68(1)^\circ$, $\gamma = 90^\circ$
Volume	$2772.1(6)$ Å ³
Z, calculated density	4, 1.336 Mg/m ³
Absorption coefficient	5.096 mm ⁻¹
$F(000)$	1184
Crystal size	0.15 × 0.1 × 0.1
Theta range for data collection	3.65 to 67.93°
Index ranges	−30 ≤ h ≤ 28, 0 ≤ k ≤ 9, 0 ≤ l ≤ 16
Reflections collected/unique	2517/2065
Goodness-of-fit on F^2	1.059
Final R indices [$I > 2$ sigma(I)]	$R_1 = 0.0593$, $wR_2 = 0.1659$
R indices [all data]	$R_1 = 0.0706$, $wR_2 = 0.1813$
Largest difference peak and hole	0.386 and −0.387 e [−] Å ^{−3}

SCHEME 1

with isotropic refinement of the hydrogen atoms using 2065 reflections with $I > 2\sigma(I)$ converged the R -factor to 0.0593.

3. Results and Discussion

The crystal data and structure solution details are given in Table 1. The bond lengths and bond angles for the nonhydrogen atoms are listed in Tables 2 and 3, respectively. The structure is more planar compared to our earlier reported structures having a dithiolane ring [6–10].

The bis(methylthio) group and the phenyl plane are inclined at an angle of only 12.35° which is less when compared to the angle between phenyl plane and the dithiolane plane in those structures (32° to 35°). The deviation of the atoms from the overall plane of the present molecule is less. The atoms C2, S1, and O1 are having deviations 0.226 Å,

FIGURE 1: ORTEP diagram of the molecule.

0.253 Å, and 0.224 Å from the molecular plane (Figure 1). The cinnamoyl group on the carbonyl carbon atom C9 effects more delocalization of electrons within the molecule. In the cinnamoyl part of the molecule, the C4–C7 [1.454 Å] and C8–C9 [1.323(5) Å] bond distances are comparable to the C_{sp2}–C_{sp2} single bond in coplanar conjugated double bonds. The chlorine atom attached to the phenyl ring lies in the ring plane as is evident from the torsion angle [Cl–C1–C2–C3 = $179.8(4)^\circ$].

The presence of the bis(methylthio) group as a donor and the cinnamoyl moiety as an acceptor about the double bond C10–C11 was expected to induce a “weak” push-pull character. The C10–C11 bond length [1.360(5) Å] is less than the corresponding average length [1.388 Å] found in structures having a dithiolane ring attached to C(10) carbon [6–10]. The angle S1–C11–S2 [$115.8(2)^\circ$] is greater than the corresponding angle [113.8°] in the dithiolane ring of these compounds. The observed intramolecular distance of 2.736 Å between O1 and S2 is longer compared to the average O–S distance [2.628 Å] in these compounds. This O1–S2 nonbonded distance is also larger than that reported in N-[bis(methylthio)methylene]cinnamamide and 3,3-bis(methylthio)-2-nitro-2-propene-1-nitrile structures [11, 12]. The S1–C12 bond is in *cis* [C12–S1–C11–C10 = $-8.9(3)^\circ$] conformation and S2–C13 in *trans* [C13–S2–C11–C10 = $177.8(3)^\circ$] with C11–C10. This may be due to the steric interaction between the two methyl groups.

The molecular stacking is due to Van der Waals interactions and C–H···Cl hydrogen bonding between the carbon atom of one of the methyl groups and the chlorine atom at the symmetry position $1/2 + x, -1/2 - y, 1/2 + z$. Similar C–H···Cl hydrogen bonding parameters are found in the literature [13]. There is intramolecular C–H···O interaction between C7–H7 and O1. The hydrogen bonding parameters are as in Table 4.

4. Conclusions

The title compound crystallized in the monoclinic space group C2/c. The bis(methylthio) group and the cinnamoyl

TABLE 2: Bond lengths (Å).

S1–C11	1.743(4)
S1–C12	1.786(5)
S2–C11	1.736(4)
S2–C13	1.793(4)
C1–C1	1.733(4)
O1–C9	1.233(4)
C1–C2	1.357(6)
C1–C6	1.371(5)
C10–C11	1.360(5)
C2–C3	1.380(6)
C3–C4	1.382(5)
C4–C5	1.383(5)
C4–C7	1.454(5)
C5–C6	1.369(5)
C7–C8	1.323(5)
C8–C9	1.466(5)
C9–C10	1.444(5)

TABLE 3: Bond angles in the title compound.

Bond angles (°)	
C11–S1–C12	104.7(2)
C11–S2–C13	105.0(2)
C2–C1–C6	121.0(4)
C2–C1–C1	119.0(3)
C6–C1–C1	120.1(4)
C1–C2–C3	119.6(4)
C2–C3–C4	121.0(4)
C3–C4–C5	117.8(4)
C3–C4–C7	119.6(4)
C5–C4–C7	122.6(3)
S2–C11–S1	115.8(2)
C6–C5–C4	121.5(3)
C5–C6–C1	119.2(4)
C8–C7–C4	128.0(3)
C7–C8–C9	123.3(3)
O1–C9–C10	122.6(3)
O1–C9–C8	121.2(3)
C10–C9–C8	116.3(3)
C11–C10–C9	124.5(3)
C10–C11–S2	121.4(3)
C10–C11–S1	122.8(3)

TABLE 4

D–H–A	Symm	H...A	D–A (Å)	D–H–A
C12–H12A–C1	$-1/2 + x, 3/2 - y, -1/2 + z$	2.767 Å	3.4971	133.44°
C7–H7...O1	—	2.520 Å	2.839(5)	100.39°

moiety in the title compound induce a “weak” push-pull effect about the double bond which is less compared to similar compounds having a cyclic ketene dithioacetal moiety. The steric

interaction between the two methyl groups affects the two sulphur-carbon bonds to be in *cis* and *trans* conformations, respectively, with the methylene bond.

Disclosure

Crystallographic data for the structural analysis of the title compound has been deposited with the Cambridge Crystallographic Data Centre (CCDC 963549). Copies of the data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, UK).

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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