CHAPTER 4

CRYSTAL AND MOLECULAR STRUCTURE OF COUMARIN DERIVATIVES
This chapter deals with crystal structure analysis of two different compounds of coumarin derivatives.

1. Diethyl-dithiocarbamic acid 6-methyl-2-oxo-2H-chromen-4-ylmethyl ester

2. Diethyl-dithiocarbamic acid 6-chloro-2-oxo-2H-chromen-4-ylmethyl ester
4 Crystal and Molecular Structures of Coumarin derivatives.

4.1. Introduction

During the last twenty years, the study of the biological activities of coumarin derivatives has been the aim of many researchers [1-5]. Although most of the existing natural coumarins have been isolated from higher plants, some of them have been discovered in microorganisms, for example, aminocoumarin antibiotics: novobiocin, coumermycin A1 and chlorobiocin (produced by the actinomycete Streptomyces niveus) [6]. Synthetic coumarin derivatives have been obtained by chemical modification of the coumarin ring. Coumarins and their derivatives have attracted considerable attention due to their extensive biological activities such as antibacterial, antifungal, antiviral, anti-tubercular, anti-malarial, anticoagulant, anti-inflammatory, anticancer, antioxidant properties and so on. Numerous efforts including the separation and purification of naturally occurring coumarins from a variety of plants as well as artificial synthesis of coumarin compounds with novel structures and properties have been focusing on the research and development of coumarins as potential drugs. So far, some coumarins, for example, warfarin, acenocoumarol, armillarisin A, hymecromone and carbochromen have been approved for therapeutic purposes in clinic. More importantly, an increasing number of coumarin compounds have displayed great potency in the treatment of various types of diseases [7].

The coumarin-based natural products comprise a large class of substances found in a variety of sources, especially in green plants [8]. Natural and synthetic coumarin derivatives have been shown to possess a diverse array of pharmacological and biochemical properties. The anti-coagulation and anti-thrombotic activities of the coumarin derivative such as warfarin are well known [9]. Other activities such as anti-HIV and lipid-lowering effect have also been reported recently [10-13]. However, the most widely reported activities for coumarin derivatives are their anti-inflammatory and anti-cancer activities. For example, cloricromene, a semi-synthetic coumarin derivative, has been shown to inhibit TNFa production and protect against collagen-induced arthritis and DNBcolitis in animal models [14-16]. Other coumarin derivatives such as those isolated from P. pabularia and the 7-carbamate-substituted coumarins have also been shown to inhibit TNFa production [17, 18]. Coumarin derivatives with anti-cancer activities include aromatase inhibitors, carbonic
anhydrase inhibitors, and steroid sulfatase inhibitors [19-21]. Other coumarin-based anti-cancer compounds include the naturally occurring GUT-70 from C. brasiliense [22], 7-isopentenyloxycoumarin from H. lanatum [23], 5-oxygenated-6,7-methylenedioxyxoumarins from P. polystachyum [24] as well as the synthetic coumarin derivatives such as 7-hydroxycoumarin, 6-nitro-7-hydroxycoumarin, coumarin 3-(N-aryl) sulfonamides, and 3-bromophenyl 6-acetoxymethyl-2-oxo-2H-I-benzopyran-3-carboxylate [25-28].

Coumarin and its derivatives have been extensively studied due to their commercial applications in several fields. Moreover, this series of compounds has outstanding optical properties, including an extended spectral range, high quantum yields, superior photostability and good solubility in common solvents. So these compounds are widely used as laser dyes [29–30], nonlinear optical chromophores [31], fluorescent whiteners [32], as well as fluorescent labels and probes for physiological measurement [33–36]. Another feature of the coumarin derivatives is that photophysical and spectroscopic properties can be readily modified by the introduction of substituents in the coumarin ring, giving themselves more flexibility to fit well in various applications [37–40]. For example, electron-releasing substituents in 3- or 7- positions not only bring bathochromic shifts of the absorption edge towards long wavelength side, but also enhance band intensity (in absorption and fluorescence). Coumarin derivatives have attracted much attention due to their potential application for OLEDs [41–42]. Coumarins, chromones and flavones are widely distributed edible plant products, some of which are known to inhibit the induction of tumors by carcinogenic chemicals [43].

The crystal structure analyses of coumarin derivatives reveal several structural aspects which have attracted intense interest in recent years, because of their diverse pharmacological properties. Coumarins, an old class of compounds, are naturally occurring benzopyrane derivatives. The pharmacological and biochemical properties and therapeutic applications of simple coumarins depend upon the pattern of substitution. These include the latent structural asymmetry, the substituted fluoro group at C6 with respect to the coumarin ring, the diethyl-dithiocarbamic acid substitution at C4. Additionally these compounds provide essential molecular frameworks that predispose them to biological activity.
4.2. Crystal and molecular structure of Diethyl-dithiocarbamic acid 6-methyl-2-oxo-2H-chromen-4-ylmethyl ester (A10)

![Molecular Structure](image)

Fig. 4.1a

4.2.1. Introduction

The title molecule A10 (C$_{16}$H$_{19}$NO$_2$S$_2$), being a derivative of coumarin possessed wide-ranging biological properties. In addition to biological activities associated with 4-substituted coumarins, the groups linked at the C-4 methylene carbon have profound influence on their solid-state conformations. A single crystal X-ray diffraction analysis was carried out to establish the crystal as well as molecular structure and to understand the self-aggregation in terms of possible intermolecular interactions.

4.2.2. Experimental Procedure for the Preparation of A10

The title compound A10 was prepared in two stages as shown in Scheme 4A.

![Scheme 4A](image)

Scheme 4A

A mixture of diethyl dithiocarbamic acid 2 (1.53g, 10 mmol) and anhydrous potassium carbonate (1.38g, 10mmol) was stirred for 30 min in dry acetone (30 mL). To this, 4-bromomethyl-6-methyl-chromen-2-one 1 (2.67g, 10 mmol) was added and
the stirring was continued for 24h. Then, the resulting reaction mixture was poured to crushed ice. The separated solid was filtered and washed with 1:1 HCl (30 mL) and water. Then product A10 was recrystallised from ethanol to get pale yellow needles. [Compound (A10): Yield 80%; m.p. 155°C].

4.2.3. X-Ray Structure Analysis

The X-ray diffraction data were collected on a Bruker Smart CCD Area Detector System [44], using MoKα (0.71073Å) radiation for the crystal. Intensity data were collected up to a max of 27.00° for the compound in the ω–φ scan mode. The data were reduced using SAINT [44]. A total of 9079 reflections were collected, resulting in 3392 independent reflections of which the number of reflections satisfying $I>2\sigma(I)$ criteria were 2763. These were treated as observed. It was confirmed that the crystal belongs to monoclinic crystal system and the space group is $P2_1/c$. The structure was solved by direct methods and difference Fourier synthesis using SHELXS97 [45]. The positions of all non-hydrogen atoms were included in the full-matrix least-square refinement using SHELXL97 [45]. Anisotropic refinement using full-matrix least-square procedures was carried out for a few cycles until convergence was reached. All hydrogen atoms were located in difference Fourier maps and refined isotropically. The H atoms were placed at calculated positions in the riding model approximation (C—H 0.93Å); their temperature factors were set to 1.2 times those of the equivalent isotropic temperature factors of the parent atoms. All other non-H atoms were refined anisotropically. The R factor after final convergence was 0.0632 and the maximum and minimum values of residual electron density were 0.779 and −0.791 eÅ$^{-3}$. Molecular diagrams were generated using ORTEP [46]. The mean plane calculation was done using the program PARST [47].

4.2.4. Results and Discussion

Figure 4.1a shows the chemical diagram of compound A10. Table 4.1a summarizes the crystal data, intensity data collection and refinement details for the compound A10. The atomic coordinates of the nonhydrogen atoms with their equivalent temperature factors for the compound are presented in Table 4.2a anisotropic displacement parameters are given in Table 4.3a. The corresponding bond lengths and angles are given in Tables 4.4a. The torsion angles for the nonhydrogen atoms are listed in Table 4.5a. Table 4.6a shows the atomic coordinates and isotropic
temperature factors for the hydrogen atoms. The least-squares planes calculated using the programs PARST [47] are tabulated in Table 4.7a. The intra- and intermolecular hydrogen bonds including the weak interactions are listed in Table 4.8a.

![Fig: 4.2a](image)

**ORTEP diagram of compound A10, showing 50% probability displacement ellipsoids and the atom-numbering scheme.**

The compound 3a crystallizes in space group $P2_1/c$. In the title molecule, an intramolecular C–H…S hydrogen bond (Fig.4.2a) forms a pseudo-seven-membered ring with graph set $S(7)$, thus locking the molecular conformation and eliminating conformational flexibility. The two rings in the molecule are nearly coplanar. The dihedral angle between the least-squares plane of the phenyl and pyrone rings is 1.28(7)°, confirming the planarity of the coumarin moiety. The bond lengths and bond angles in the coumarin moiety of the molecule show a fair amount of agreement with some 4-substituted coumarin derivatives [48]. The heterocyclic ring is distorted by about 5°, but the phenylene moiety is nearly planar. The orientation of methyl ester group is characterized by torsion angles C(4)-C(11)-S(2)-C(12) of 80.2(2)°. The survey of the structure at a molecular level reveals usual geometrical parameters for the S–C bond of 1.785(3)Å.

### 4.2.5. Intermolecular Features

The packing of layers of molecules is stabilized by the presence of an intermolecular short contact of types C-H…O, C-H…N and C-H…S. The C-H…O interaction
generates centrosymmetric head to head dimers with packing motifs in accordance with Etter’s analysis are $R^{2}_{2}(8)$ along the crystallographic ‘$b$’-axis (Fig. 4.3a). The C-H…S interaction also forms dimers corresponding to graph set notation $R^{2}_{2}(22)$ (Bernstein et al., 1995) along ‘a’ axis (Fig. 4.3a).

Fig. 4.3a

**C-H…O and C-H…S dimers in A10 along crystallographic ‘b’-axis**

The C-H…O and C-H…N interactions links the molecules into chains along the crystallographic ‘$a$’-axis (Fig. 4.4a). Weak C–H…π intermolecular interactions further stabilizes the packing of the molecules in the crystal lattice (Fig. 4.5a). The C–H…π interactions involve the coumarin ring and the phenyl ring. The packing of layers of molecules is further stabilized by π-π stacking interactions (Fig. 4.6a) between the pyrone and phenyl ring with a shortest centroid-centroid distance of 3.718Å. The supramolecular aggregation in this structure is due to C–H…N, C–H…S, C-H…O, C–H…π and π-π stacking intermolecular interactions.
Fig. 4.4a

C-H...O and C-H...N dimers in A10 along crystallographic ‘a’-axis

Fig: 4.5a

A π-π interaction in A10 along ‘b’ axis
Fig. 4.6a

C–H…π interaction in A10 along ‘c’-axis
Table 4.1a

Summary of crystal data, intensity data collection and refinement of A10 compound

<table>
<thead>
<tr>
<th>Crystal data</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>C_{16}H_{19}NO_{2}S_{2}</td>
<td>D_{c} = 1.372Mgm^{-3}</td>
</tr>
<tr>
<td>M_r = 321.44</td>
<td>Mo Kα radiation 0.71073 Å</td>
</tr>
<tr>
<td>Monoclinic, P_{2}_{1}/c</td>
<td>θ = 2.64 – 27.00°</td>
</tr>
<tr>
<td>a = 7.8105(11)Å</td>
<td>μ = 0.346mm¹</td>
</tr>
<tr>
<td>b = 7.9975(11)Å</td>
<td>T = 293 (2) K</td>
</tr>
<tr>
<td>c = 25.198(4)Å</td>
<td>Needle, pale yellow</td>
</tr>
<tr>
<td>β = 98.753(2)°</td>
<td>0.18 × 0.16 × 0.16 mm</td>
</tr>
<tr>
<td>V = 1555.7(4)Å³</td>
<td></td>
</tr>
<tr>
<td>Z = 4</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Data collection</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Bruker SMART CCD area - detector</td>
<td>2763 reflections with I &gt; 2σ(I)</td>
</tr>
<tr>
<td>diffractometer</td>
<td>R_{int} = 0.0812</td>
</tr>
<tr>
<td>φ and ω scans</td>
<td>θ_{max} = 27.0°</td>
</tr>
<tr>
<td>Absorption correction: none</td>
<td>h = -9→ 9</td>
</tr>
<tr>
<td>9079 measured reflections</td>
<td>k = -7→ 10</td>
</tr>
<tr>
<td>3392 independent reflections</td>
<td>l = -32→ 31</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Refinement</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Refinement on F²</td>
<td>w = 1/[ σ²(Fo²) + (0.1797P)²</td>
</tr>
<tr>
<td>R[F² &gt; 2σ(F²)] = 0.0632</td>
<td>+3.4500P ]</td>
</tr>
<tr>
<td>wR(F²) = 0.2109</td>
<td>where P = (Fo² + 2F_c²)/3</td>
</tr>
<tr>
<td>S = 0.795</td>
<td>(Δ/σ)_{max} = 0.001</td>
</tr>
<tr>
<td>3392 reflections</td>
<td>Δρ_{max} = 0.779 e Å⁻³</td>
</tr>
<tr>
<td>193 parameters</td>
<td>Δρ_{min} = -0.791 e Å⁻³</td>
</tr>
<tr>
<td>H-atom parameters constrained</td>
<td></td>
</tr>
</tbody>
</table>

Programs used

Data collection: SMART (Bruker, 1998);
Cell refinement: SMART;
Data reduction: SAINT (Bruker, 1998);
Structure solution: SHELXS97 (Sheldrick, 2008);
Structure refinement: SHELXL97 (Sheldrick, 2008);
Molecular graphics: PLUTON (Speck, 1997); ORTEP-3 (Farrugia, 1997); CAMERON (Watkin et al., 1993); WinGX (Farrugia, 1999)

Data deposition

Crystallographic data for the structure reported here has been deposited with the Cambridge Data Centre. The deposition number is CCDC 877888.
Table 4.2a
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\AA^2 \times 10^3$) of A10.

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>U(eq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(1)</td>
<td>4869(4)</td>
<td>5120(4)</td>
<td>5913(1)</td>
<td>29(1)</td>
</tr>
<tr>
<td>C(2)</td>
<td>1533(4)</td>
<td>11825(4)</td>
<td>4668(1)</td>
<td>20(1)</td>
</tr>
<tr>
<td>C(3)</td>
<td>815(4)</td>
<td>10364(3)</td>
<td>4377(1)</td>
<td>19(1)</td>
</tr>
<tr>
<td>C(4)</td>
<td>1268(4)</td>
<td>8787(4)</td>
<td>5225(1)</td>
<td>20(1)</td>
</tr>
<tr>
<td>C(5)</td>
<td>3080(4)</td>
<td>6959(4)</td>
<td>5689(1)</td>
<td>20(1)</td>
</tr>
<tr>
<td>C(6)</td>
<td>2784(4)</td>
<td>8536(4)</td>
<td>5293(1)</td>
<td>20(1)</td>
</tr>
<tr>
<td>C(7)</td>
<td>4954(4)</td>
<td>9857(4)</td>
<td>5754(1)</td>
<td>20(1)</td>
</tr>
<tr>
<td>C(8)</td>
<td>3204(4)</td>
<td>9966(4)</td>
<td>5293(1)</td>
<td>20(1)</td>
</tr>
<tr>
<td>C(9)</td>
<td>2520(4)</td>
<td>8536(3)</td>
<td>5014(1)</td>
<td>17(1)</td>
</tr>
<tr>
<td>C(10)</td>
<td>558(4)</td>
<td>7258(3)</td>
<td>4224(1)</td>
<td>20(1)</td>
</tr>
<tr>
<td>C(11)</td>
<td>32(4)</td>
<td>8219(3)</td>
<td>3135(1)</td>
<td>19(1)</td>
</tr>
<tr>
<td>C(12)</td>
<td>-2856(4)</td>
<td>8089(4)</td>
<td>2612(1)</td>
<td>31(1)</td>
</tr>
<tr>
<td>C(13)</td>
<td>-3996(4)</td>
<td>9150(4)</td>
<td>2198(1)</td>
<td>22(1)</td>
</tr>
<tr>
<td>C(14)</td>
<td>-291(4)</td>
<td>7798(4)</td>
<td>1848(1)</td>
<td>29(1)</td>
</tr>
<tr>
<td>C(15)</td>
<td>2719(3)</td>
<td>11555(2)</td>
<td>5124(1)</td>
<td>20(1)</td>
</tr>
<tr>
<td>C(16)</td>
<td>1184(3)</td>
<td>13272(2)</td>
<td>4551(1)</td>
<td>25(1)</td>
</tr>
<tr>
<td>O(1)</td>
<td>-993(3)</td>
<td>8467(3)</td>
<td>2665(1)</td>
<td>19(1)</td>
</tr>
<tr>
<td>O(2)</td>
<td>2175(1)</td>
<td>8465(1)</td>
<td>3230(1)</td>
<td>21(1)</td>
</tr>
<tr>
<td>S(1)</td>
<td>-1118(1)</td>
<td>7577(1)</td>
<td>3660(1)</td>
<td>19(1)</td>
</tr>
<tr>
<td>S(2)</td>
<td>47(2)</td>
<td>19(1)</td>
<td>22(1)</td>
<td>-4(1)</td>
</tr>
</tbody>
</table>

Table 4.3a
Anisotropic displacement parameters ($\AA^2 \times 10^3$) of A10.

The anisotropic displacement factor exponent takes the form:

\[ -2\pi^2 \sum \sum U_{ij}(a_i^*a_j^*)(\mathbf{a}_i\cdot\mathbf{a}_j) \]

<table>
<thead>
<tr>
<th>Atom</th>
<th>U11</th>
<th>U22</th>
<th>U33</th>
<th>U23</th>
<th>U13</th>
<th>U12</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(1)</td>
<td>33(2)</td>
<td>25(2)</td>
<td>28(2)</td>
<td>5(1)</td>
<td>-1(1)</td>
<td>5(1)</td>
</tr>
<tr>
<td>C(2)</td>
<td>24(2)</td>
<td>19(1)</td>
<td>17(1)</td>
<td>1(1)</td>
<td>6(1)</td>
<td>0(1)</td>
</tr>
<tr>
<td>C(3)</td>
<td>33(1)</td>
<td>23(1)</td>
<td>17(1)</td>
<td>1(1)</td>
<td>1(1)</td>
<td>1(1)</td>
</tr>
<tr>
<td>C(4)</td>
<td>22(1)</td>
<td>17(1)</td>
<td>14(1)</td>
<td>-1(1)</td>
<td>4(1)</td>
<td>-2(1)</td>
</tr>
<tr>
<td>C(5)</td>
<td>27(2)</td>
<td>14(1)</td>
<td>18(1)</td>
<td>-2(1)</td>
<td>4(1)</td>
<td>-1(1)</td>
</tr>
<tr>
<td>C(6)</td>
<td>22(2)</td>
<td>20(1)</td>
<td>19(1)</td>
<td>2(1)</td>
<td>6(1)</td>
<td>1(1)</td>
</tr>
<tr>
<td>C(7)</td>
<td>27(2)</td>
<td>23(2)</td>
<td>17(1)</td>
<td>0(1)</td>
<td>2(1)</td>
<td>0(1)</td>
</tr>
<tr>
<td>C(8)</td>
<td>21(1)</td>
<td>20(1)</td>
<td>19(1)</td>
<td>-4(1)</td>
<td>2(1)</td>
<td>-2(1)</td>
</tr>
<tr>
<td>C(9)</td>
<td>25(1)</td>
<td>15(1)</td>
<td>18(1)</td>
<td>0(1)</td>
<td>5(1)</td>
<td>1(1)</td>
</tr>
<tr>
<td>C(10)</td>
<td>21(1)</td>
<td>16(1)</td>
<td>15(1)</td>
<td>0(1)</td>
<td>6(1)</td>
<td>-1(1)</td>
</tr>
<tr>
<td>C(11)</td>
<td>29(2)</td>
<td>15(1)</td>
<td>14(1)</td>
<td>1(1)</td>
<td>2(1)</td>
<td>0(1)</td>
</tr>
<tr>
<td>C(12)</td>
<td>25(1)</td>
<td>10(1)</td>
<td>21(1)</td>
<td>-4(1)</td>
<td>0(1)</td>
<td>-1(1)</td>
</tr>
<tr>
<td>C(13)</td>
<td>23(2)</td>
<td>24(1)</td>
<td>20(1)</td>
<td>2(1)</td>
<td>-3(1)</td>
<td>-4(1)</td>
</tr>
<tr>
<td>C(14)</td>
<td>23(2)</td>
<td>30(2)</td>
<td>39(2)</td>
<td>10(1)</td>
<td>4(1)</td>
<td>2(1)</td>
</tr>
<tr>
<td>C(15)</td>
<td>29(2)</td>
<td>18(1)</td>
<td>18(1)</td>
<td>4(1)</td>
<td>4(1)</td>
<td>0(1)</td>
</tr>
<tr>
<td>C(16)</td>
<td>47(2)</td>
<td>19(1)</td>
<td>22(1)</td>
<td>-1(1)</td>
<td>9(1)</td>
<td>-1(1)</td>
</tr>
<tr>
<td>O(1)</td>
<td>26(1)</td>
<td>11(1)</td>
<td>21(1)</td>
<td>-1(1)</td>
<td>2(1)</td>
<td>-2(1)</td>
</tr>
<tr>
<td>O(2)</td>
<td>36(1)</td>
<td>13(1)</td>
<td>24(1)</td>
<td>2(1)</td>
<td>1(1)</td>
<td>1(1)</td>
</tr>
<tr>
<td>N(1)</td>
<td>25(1)</td>
<td>15(1)</td>
<td>17(1)</td>
<td>-1(1)</td>
<td>3(1)</td>
<td>-1(1)</td>
</tr>
<tr>
<td>S(1)</td>
<td>21(1)</td>
<td>21(1)</td>
<td>22(1)</td>
<td>-3(1)</td>
<td>2(1)</td>
<td>-2(1)</td>
</tr>
<tr>
<td>S(2)</td>
<td>21(1)</td>
<td>18(1)</td>
<td>16(1)</td>
<td>-1(1)</td>
<td>1(1)</td>
<td>-2(1)</td>
</tr>
</tbody>
</table>
Table 4.4a
Bond lengths [Å] and angles [°] for non H-atoms of A10 with esds in parenthesis

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length 1</th>
<th>Angle 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(1)–C(6)</td>
<td>1.513(4)</td>
<td></td>
</tr>
<tr>
<td>C(2)–O(2)</td>
<td>1.215(4)</td>
<td></td>
</tr>
<tr>
<td>C(2)–O(1)</td>
<td>1.379(3)</td>
<td></td>
</tr>
<tr>
<td>C(2)–C(3)</td>
<td>1.446(4)</td>
<td></td>
</tr>
<tr>
<td>C(3)–C(4)</td>
<td>1.352(4)</td>
<td></td>
</tr>
<tr>
<td>C(4)–C(10)</td>
<td>1.450(4)</td>
<td></td>
</tr>
<tr>
<td>C(4)–C(11)</td>
<td>1.510(4)</td>
<td></td>
</tr>
<tr>
<td>C(5)–C(6)</td>
<td>1.386(4)</td>
<td></td>
</tr>
<tr>
<td>C(5)–C(10)</td>
<td>1.412(4)</td>
<td></td>
</tr>
<tr>
<td>C(6)–C(7)</td>
<td>1.404(4)</td>
<td></td>
</tr>
<tr>
<td>C(7)–C(8)</td>
<td>1.390(4)</td>
<td></td>
</tr>
<tr>
<td>C(8)–C(9)</td>
<td>1.375(3)</td>
<td></td>
</tr>
<tr>
<td>C(9)–C(10)</td>
<td>1.405(4)</td>
<td></td>
</tr>
<tr>
<td>C(11)–S(2)</td>
<td>1.798(3)</td>
<td></td>
</tr>
<tr>
<td>C(12)–N(1)</td>
<td>1.339(4)</td>
<td></td>
</tr>
<tr>
<td>C(12)–S(1)</td>
<td>1.666(3)</td>
<td></td>
</tr>
<tr>
<td>C(12)–S(2)</td>
<td>1.785(3)</td>
<td></td>
</tr>
<tr>
<td>C(13)–N(1)</td>
<td>1.469(4)</td>
<td></td>
</tr>
<tr>
<td>C(14)–C(1)</td>
<td>1.375(3)</td>
<td></td>
</tr>
<tr>
<td>C(12)–S(1)</td>
<td>1.666(3)</td>
<td></td>
</tr>
<tr>
<td>C(12)–S(2)</td>
<td>1.785(3)</td>
<td></td>
</tr>
<tr>
<td>C(13)–N(1)</td>
<td>1.469(4)</td>
<td></td>
</tr>
<tr>
<td>C(13)–C(14)</td>
<td>1.520(4)</td>
<td></td>
</tr>
<tr>
<td>C(15)–N(1)</td>
<td>1.476(4)</td>
<td></td>
</tr>
<tr>
<td>C(15)–C(16)</td>
<td>1.521(4)</td>
<td></td>
</tr>
<tr>
<td>O(2)–C(2)–O(1)</td>
<td>116.7(3)</td>
<td></td>
</tr>
<tr>
<td>O(2)–C(2)–C(3)</td>
<td>126.3(3)</td>
<td></td>
</tr>
<tr>
<td>O(1)–C(2)–C(3)</td>
<td>117.1(2)</td>
<td></td>
</tr>
<tr>
<td>C(4)–C(3)–C(2)</td>
<td>122.9(2)</td>
<td></td>
</tr>
<tr>
<td>C(3)–C(4)–C(10)</td>
<td>119.0(2)</td>
<td></td>
</tr>
<tr>
<td>C(3)–C(4)–C(11)</td>
<td>123.1(2)</td>
<td></td>
</tr>
<tr>
<td>C(10)–C(4)–C(11)</td>
<td>117.8(2)</td>
<td></td>
</tr>
<tr>
<td>C(5)–C(6)–C(7)</td>
<td>118.6(3)</td>
<td></td>
</tr>
<tr>
<td>C(5)–C(6)–C(1)</td>
<td>121.1(3)</td>
<td></td>
</tr>
<tr>
<td>C(7)–C(6)–C(1)</td>
<td>120.3(3)</td>
<td></td>
</tr>
<tr>
<td>C(8)–C(7)–C(6)</td>
<td>121.6(3)</td>
<td></td>
</tr>
<tr>
<td>C(9)–C(8)–C(7)</td>
<td>118.6(3)</td>
<td></td>
</tr>
<tr>
<td>O(1)–C(9)–C(8)</td>
<td>116.0(2)</td>
<td></td>
</tr>
<tr>
<td>O(1)–C(9)–C(10)</td>
<td>122.1(2)</td>
<td></td>
</tr>
<tr>
<td>C(8)–C(9)–C(10)</td>
<td>121.9(3)</td>
<td></td>
</tr>
<tr>
<td>C(9)–C(10)–C(5)</td>
<td>117.8(3)</td>
<td></td>
</tr>
<tr>
<td>C(9)–C(10)–C(4)</td>
<td>117.5(2)</td>
<td></td>
</tr>
<tr>
<td>C(5)–C(10)–C(4)</td>
<td>124.7(2)</td>
<td></td>
</tr>
<tr>
<td>C(4)–C(11)–S(2)</td>
<td>117.31(19)</td>
<td></td>
</tr>
<tr>
<td>N(1)–C(12)–S(1)</td>
<td>124.2(2)</td>
<td></td>
</tr>
<tr>
<td>N(1)–C(12)–S(2)</td>
<td>113.4(2)</td>
<td></td>
</tr>
<tr>
<td>S(1)–C(12)–S(2)</td>
<td>122.36(17)</td>
<td></td>
</tr>
<tr>
<td>N(1)–C(13)–C(14)</td>
<td>113.5(2)</td>
<td></td>
</tr>
<tr>
<td>N(1)–C(15)–C(16)</td>
<td>112.9(2)</td>
<td></td>
</tr>
<tr>
<td>C(9)–O(1)–C(2)</td>
<td>121.4(2)</td>
<td></td>
</tr>
<tr>
<td>C(12)–N(1)–C(13)</td>
<td>124.4(2)</td>
<td></td>
</tr>
<tr>
<td>C(12)–N(1)–C(15)</td>
<td>120.9(2)</td>
<td></td>
</tr>
<tr>
<td>C(13)–N(1)–C(15)</td>
<td>114.6(2)</td>
<td></td>
</tr>
<tr>
<td>C(12)–S(2)–C(11)</td>
<td>103.82(14)</td>
<td></td>
</tr>
<tr>
<td>Torsion angles [°] for non H-atoms of A10 with esds in parenthesis</td>
<td></td>
<td></td>
</tr>
<tr>
<td>---------------------------------------------------------------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O(2) – C(2) – C(3) – C(4)</td>
<td>-179.9(3)</td>
<td></td>
</tr>
<tr>
<td>O(1) – C(2) – C(3) – C(4)</td>
<td>-0.4(4)</td>
<td></td>
</tr>
<tr>
<td>C(2) – C(3) – C(4) – C(10)</td>
<td>0.3(4)</td>
<td></td>
</tr>
<tr>
<td>C(2) – C(3) – C(4) – C(11)</td>
<td>-178.4(3)</td>
<td></td>
</tr>
<tr>
<td>C(10) – C(5) – C(6) – C(7)</td>
<td>-0.8(4)</td>
<td></td>
</tr>
<tr>
<td>C(10) – C(5) – C(6) – C(1)</td>
<td>179.9(3)</td>
<td></td>
</tr>
<tr>
<td>C(5) – C(6) – C(7) – C(8)</td>
<td>1.5(4)</td>
<td></td>
</tr>
<tr>
<td>C(1) – C(6) – C(7) – C(8)</td>
<td>-179.2(3)</td>
<td></td>
</tr>
<tr>
<td>C(6) – C(7) – C(8) – C(9)</td>
<td>-0.6(4)</td>
<td></td>
</tr>
<tr>
<td>C(7) – C(8) – C(9) – C(10)</td>
<td>179.5(3)</td>
<td></td>
</tr>
<tr>
<td>C(7) – C(9) – C(10) – C(4)</td>
<td>-1.0(4)</td>
<td></td>
</tr>
<tr>
<td>C(1) – C(9) – C(10) – C(5)</td>
<td>-179.0(2)</td>
<td></td>
</tr>
<tr>
<td>C(8) – C(9) – C(10) – C(5)</td>
<td>1.6(4)</td>
<td></td>
</tr>
<tr>
<td>O(1) – C(9) – C(10) – C(4)</td>
<td>0.1(4)</td>
<td></td>
</tr>
<tr>
<td>C(8) – C(9) – C(10) – C(4)</td>
<td>-179.4(3)</td>
<td></td>
</tr>
<tr>
<td>C(6) – C(5) – C(10) – C(9)</td>
<td>-0.7(4)</td>
<td></td>
</tr>
<tr>
<td>C(6) – C(5) – C(10) – C(4)</td>
<td>-179.7(3)</td>
<td></td>
</tr>
<tr>
<td>C(3) – C(4) – C(10) – C(9)</td>
<td>-0.2(4)</td>
<td></td>
</tr>
<tr>
<td>C(11) – C(4) – C(10) – C(9)</td>
<td>178.6(2)</td>
<td></td>
</tr>
<tr>
<td>C(3) – C(4) – C(10) – C(5)</td>
<td>178.9(3)</td>
<td></td>
</tr>
<tr>
<td>C(11) – C(4) – C(10) – C(5)</td>
<td>-2.4(4)</td>
<td></td>
</tr>
<tr>
<td>C(3) – C(4) – C(11) – S(2)</td>
<td>-6.1(4)</td>
<td></td>
</tr>
<tr>
<td>C(10) – C(4) – C(11) – S(2)</td>
<td>175.2(2)</td>
<td></td>
</tr>
<tr>
<td>C(8) – C(9) – O(1) – C(2)</td>
<td>179.3(2)</td>
<td></td>
</tr>
<tr>
<td>C(10) – C(9) – O(1) – C(2)</td>
<td>-0.2(4)</td>
<td></td>
</tr>
<tr>
<td>O(2) – C(2) – O(1) – C(9)</td>
<td>179.9(3)</td>
<td></td>
</tr>
<tr>
<td>C(3) – C(2) – O(1) – C(9)</td>
<td>0.4(4)</td>
<td></td>
</tr>
<tr>
<td>S(1) – C(12) – N(1) – C(13)</td>
<td>173.4(2)</td>
<td></td>
</tr>
<tr>
<td>S(2) – C(12) – N(1) – C(13)</td>
<td>-6.2(3)</td>
<td></td>
</tr>
<tr>
<td>S(1) – C(12) – N(1) – C(15)</td>
<td>-6.0(4)</td>
<td></td>
</tr>
<tr>
<td>S(2) – C(12) – N(1) – C(15)</td>
<td>174.34(19)</td>
<td></td>
</tr>
<tr>
<td>C(14) – C(13) – N(1) – C(12)</td>
<td>97.7(3)</td>
<td></td>
</tr>
<tr>
<td>C(14) – C(13) – N(1) – C(15)</td>
<td>-82.8(3)</td>
<td></td>
</tr>
<tr>
<td>C(16) – C(15) – N(1) – C(12)</td>
<td>90.5(3)</td>
<td></td>
</tr>
<tr>
<td>C(16) – C(15) – N(1) – C(13)</td>
<td>-89.1(3)</td>
<td></td>
</tr>
<tr>
<td>N(1) – C(12) – S(2) – C(11)</td>
<td>177.7(2)</td>
<td></td>
</tr>
<tr>
<td>S(1) – C(12) – S(2) – C(11)</td>
<td>-2.0(2)</td>
<td></td>
</tr>
<tr>
<td>C(4) – C(11) – S(2) – C(12)</td>
<td>80.2(2)</td>
<td></td>
</tr>
</tbody>
</table>
### Table 4.6a

Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\AA^2 \times 10^3$) of V9

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>U(eq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H (1A)</td>
<td>4372</td>
<td>4906</td>
<td>6232</td>
<td>44</td>
</tr>
<tr>
<td>H (1B)</td>
<td>6110</td>
<td>5108</td>
<td>5998</td>
<td>44</td>
</tr>
<tr>
<td>H (1C)</td>
<td>4501</td>
<td>4273</td>
<td>5650</td>
<td>44</td>
</tr>
<tr>
<td>H (3)</td>
<td>7</td>
<td>10516</td>
<td>4070</td>
<td>23</td>
</tr>
<tr>
<td>H (5)</td>
<td>2636</td>
<td>5995</td>
<td>5048</td>
<td>24</td>
</tr>
<tr>
<td>H (7)</td>
<td>5778</td>
<td>8198</td>
<td>6253</td>
<td>27</td>
</tr>
<tr>
<td>H (8)</td>
<td>4873</td>
<td>10818</td>
<td>5930</td>
<td>24</td>
</tr>
<tr>
<td>H (11A)</td>
<td>112</td>
<td>6506</td>
<td>4473</td>
<td>23</td>
</tr>
<tr>
<td>H (11B)</td>
<td>1515</td>
<td>6692</td>
<td>4096</td>
<td>23</td>
</tr>
<tr>
<td>H (13A)</td>
<td>-3107</td>
<td>7244</td>
<td>2818</td>
<td>28</td>
</tr>
<tr>
<td>H (13B)</td>
<td>-3144</td>
<td>7625</td>
<td>2206</td>
<td>28</td>
</tr>
<tr>
<td>H (14A)</td>
<td>-3761</td>
<td>10040</td>
<td>2971</td>
<td>46</td>
</tr>
<tr>
<td>H (14B)</td>
<td>-5192</td>
<td>9285</td>
<td>2533</td>
<td>46</td>
</tr>
<tr>
<td>H (14C)</td>
<td>-3754</td>
<td>10450</td>
<td>2363</td>
<td>46</td>
</tr>
<tr>
<td>H (15A)</td>
<td>669</td>
<td>9890</td>
<td>2325</td>
<td>26</td>
</tr>
<tr>
<td>H (15B)</td>
<td>-1181</td>
<td>9880</td>
<td>1982</td>
<td>26</td>
</tr>
<tr>
<td>H (16A)</td>
<td>1291</td>
<td>7213</td>
<td>2049</td>
<td>43</td>
</tr>
<tr>
<td>H (16B)</td>
<td>691</td>
<td>8302</td>
<td>1538</td>
<td>43</td>
</tr>
<tr>
<td>H (16C)</td>
<td>-595</td>
<td>7026</td>
<td>1737</td>
<td>43</td>
</tr>
</tbody>
</table>

### Table 4.7a

Mean planes through various groups of atoms and deviations (Å) from the plane in A10.
The equation of the plane: $m_1X + m_2Y + m_3Z - D = 0$ where $m_1$, $m_2$, $m_3$ and $D$ are constant. Starred atoms are included in the plane calculations.

<table>
<thead>
<tr>
<th>Plane</th>
<th>m1</th>
<th>m2</th>
<th>m3</th>
<th>D</th>
<th>Atom</th>
<th>Deviations</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.833(9)</td>
<td>0.017(7)</td>
<td>-0.551(9)</td>
<td>-6.736(5)</td>
<td>C2*</td>
<td>-0.0034(3)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C3*</td>
<td>0.0005(2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C4*</td>
<td>0.0093(2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C10*</td>
<td>0.0077(2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C5*</td>
<td>-0.0072(3)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C6*</td>
<td>-0.0149(3)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C7*</td>
<td>0.0099(3)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C8*</td>
<td>0.0115(3)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C9*</td>
<td>0.0003(2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>O1*</td>
<td>-0.0072(2)</td>
</tr>
</tbody>
</table>
Dihedral angles formed by LSQ-Planes in A10.

<table>
<thead>
<tr>
<th>Plane1</th>
<th>Plane2</th>
<th>Angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenyl ring</td>
<td>Pyrone ring</td>
<td>1.28(7)°</td>
</tr>
</tbody>
</table>

Table 4.8a
Nonbonded interactions and possible hydrogen bonds in A10 (Å,°).
(D-donor; A-Acceptor; H-hydrogen)

<table>
<thead>
<tr>
<th>D–H...A</th>
<th>D–H</th>
<th>H...A</th>
<th>D...A</th>
<th>D–H...A</th>
</tr>
</thead>
<tbody>
<tr>
<td>C3–H3····S2</td>
<td>0.930 (3)</td>
<td>2.662(1)</td>
<td>3.112 (3)</td>
<td>110(2)</td>
</tr>
<tr>
<td>C8–H8···S11</td>
<td>0.930(3)</td>
<td>2.939(1)</td>
<td>3.654(3)</td>
<td>135(2)</td>
</tr>
<tr>
<td>C5–H5···O1ii</td>
<td>0.930(3)</td>
<td>2.677(2)</td>
<td>3.606(3)</td>
<td>177(1)</td>
</tr>
<tr>
<td>C1–H1C···O1ii</td>
<td>0.960(3)</td>
<td>2.803(2)</td>
<td>3.726(4)</td>
<td>161(2)</td>
</tr>
<tr>
<td>C15–H15A···N1iii</td>
<td>0.970(3)</td>
<td>2.872(2)</td>
<td>3.597(4)</td>
<td>132(2)</td>
</tr>
<tr>
<td>H8–C81iv</td>
<td>0.930(3)</td>
<td>3.217(6)</td>
<td>3.230(3)</td>
<td>132(1)</td>
</tr>
</tbody>
</table>

Symmetry code: (i) -x+1,-y+2,-z+1 (ii) x,+y-1,+z (iii) -x,+y+1/2,-z+1/2 (iv) -x+2,+y+1/2,-z-1/2
4.3. Crystal and molecular structure of Diethyl-dithiocarbamic acid 6-chloro-2-oxo-2H-chromen-4-ylmethyl ester (A11)

![Figure 4.1b](image)

4.3.1. Introduction

Coumarins represent a group of naturally occurring lactones, whose potential as anti-inflammatory, anti-microbial, anticancer and protease inhibiting agents has recently been reviewed. During the last twenty years, the study of the biological activities of coumarin derivatives has been the aim of many researchers [2-5]. Coumarin derivatives, such as warfarin and trioxsalen, have a variety of potent bioactivities, and are being used clinically for curing platelet coagulation and leucoderma, respectively [3]. In this study, an X-ray analysis of title compound A11 $C_{15}H_{16}ClNO_2S_2$ was undertaken in order to determine its crystal structure and inherent conformation.

4.3.2. Experimental Procedure for the Preparation of A11

![Scheme 4B](image)

A mixture of diethyl dithiocarbamic acid 2 (1.53g, 10 mmol) and anhydrous potassium carbonate (1.38g, 10mmol) was stirred for 30 min in dry acetone (30 mL). To this, 4-bromomethyl-6-chloro-chromen-2-one 1 (2.73g, 10 mmol) was added and the stirring was continued for 24h. Then, the resulting reaction mixture was poured to
crushed ice. The separated solid was filtered and washed with 1: 1 HCl (30 mL) and water. Then product A11 was recrystallised from ethanol to get pale yellow needles. [Compound (A11): Yield 80%; m.p.160°C].

4.3.3. X-Ray Structure Analysis

The X-ray diffraction data were collected on a Bruker Smart CCD Area Detector System [44], using MoKα (0.71073Å) radiation for the crystal. Intensity data were collected up to a max of 27.00° for the compound in the ω–ϕ scan mode. The data were reduced using SAINT [44]. A total of 8938 reflections were collected, resulting in 3323 independent reflections of which the number of reflections satisfying I>2 σ(I) criteria were 2735. These were treated as observed. It was confirmed that the crystal belongs to monoclinic crystal system and the space group is P21/n. The structure was solved by direct methods and difference Fourier synthesis using SHELXS97 [45]. The positions of all non-hydrogen atoms were included in the full-matrix least-square refinement using SHELXL97 [45]. Anisotropic refinement using full-matrix least-square procedures was carried out for a few cycles until convergence was reached. All hydrogen atoms were located in difference Fourier maps and refined isotropically. The H atoms were placed at calculated positions in the riding model approximation (C—H 0.93Å); their temperature factors were set to 1.2 times those of the equivalent isotropic temperature factors of the parent atoms. All other non-H atoms were refined anisotropically. The R factor after final convergence was 0.0474 and the maximum and minimum values of residual electron density were 0.949 and -0.484 eÅ³. Molecular diagrams were generated using ORTEP [46]. The mean plane calculation was done using the program PARST [47].

4.3.4. Results and Discussion

Figure 4.1b shows the chemical diagram of compound A11. Table 4.1b summarizes the crystal data, intensity data collection and refinement details for the compound A11. The atomic coordinates of the nonhydrogen atoms with their equivalent temperature factors for the compound are presented in Table 4.2b anisotropic displacement parameters are given in Table 4.3b. The corresponding bond lengths and angles are given in Tables 4.4b. The torsion angles for the nonhydrogen atoms are listed in Table 4.5b. Table 4.6b shows the atomic coordinates and isotropic temperature factors for the hydrogen atoms. The least-squares planes calculated using
the programs PARST [47] are tabulated in Table 4.7b. The intermolecular hydrogen bonds are listed in Table 4.8b.

Fig: 4.2b

ORTEP diagram of compound A11, showing 50% probability displacement ellipsoids and the atom-numbering scheme.

In the compound A11, (Fig.4.2b), the diethyl-dithiocarbamic acid moiety and chloro group is linked to coumarin derivative on the either sides. The X-ray crystal structure of the molecule reveals the coumarin moiety is planar with dihedral angle 1.28(7)° between the least-squares plane of the phenyl and pyrone rings. Bond lengths and bond angles in the coumarin moiety of A11 are typical for coumarin derivatives [48]. The coumarin molecule is effectively flat with a deviation between the components in 6-membered rings of 0.84°. The C3-C4 bond is conjugated to the carbonyl group, giving it a Michael acceptor function, characteristic of certain chemopreventive agents (48-51). The two C-O bonds in the coumarin ring (O1-C14 and O1-C2) are of unequal lengths, the one farthest from the carbonyl group (O1-C14) being shorter. The presence of an electron donating methyl group at C4 appears to affect the conjugated double bond system, so that the C= C bond in the coumarin ring has less double bond character. When the substituent is a CF3 group, with its strong electron withdrawing effect, this does not appear to be the case.
4.3.5. **Intermolecular Features**

The overall packing in the crystal provides a motif for binding of coumarins of this type. In the crystal structure, the molecule is stabilized by C-H…O, C-H…S and C-H…Cl interactions. The C-H…S hydrogen bonds links the molecules into dimers along ‘a’ axis (Fig. 4.3b). The packing motif of this dimer corresponds to Etter's descriptor, R$_2^2$(18). There are two C-H…O bonds with O2 acting as a bifurcated acceptor to C5-H15 and C1-H1A, connecting two molecules (Fig. 4.3b).

![Fig. 4.3b](image)

**The C-H…O and C-H…S interactions in A11, forming bifurcated H-bond and the dimers pattern**

The C-H…Cl interactions between C1 and Cl1 forms centrosymmetric head-to-head dimers corresponding to graph set notation of R$_2^2$(14), (4.4b). The supramolecular cohesion is further strengthened by π-π stacking interactions between coumarin rings of two molecules being separated by a distance of 3.361(2)Å (symmetry code: $\frac{1}{2}$-x, $\frac{1}{2}$ +y, $\frac{1}{2}$-z) (Fig. 4.5b).
Fig. 4.4b
The C-H…Cl interactions in A11, forming centrosymmetric dimers along ‘a’ axis

Fig. 4.5b
π-π stacking interaction in A11.
### Table 4.1b
Summary of crystal data, intensity data collection and refinement of A11 compound

<table>
<thead>
<tr>
<th><strong>Crystal data</strong></th>
<th><strong>Data collection</strong></th>
<th><strong>Refinement</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>C₁₅H₁₆ClNO₂S₂</td>
<td>Bruker SMART CCD area - detector</td>
<td>Refinement on $F^2$</td>
</tr>
<tr>
<td>$M_r$ = 341.86</td>
<td>diffractometer</td>
<td>$R[F^2 &gt; 2\sigma(F^2)] = 0.0474$</td>
</tr>
<tr>
<td>Monoclinic, $P_{2_1}/n$</td>
<td>$\varphi$ and $\omega$ scans</td>
<td>$wR(F^2) = 0.1666$</td>
</tr>
<tr>
<td>$a = 7.7713(11)\text{Å}$</td>
<td>Absorption correction: none</td>
<td>$S = 1.237$</td>
</tr>
<tr>
<td>$b = 7.9324(12)\text{Å}$</td>
<td>8938 measured reflections</td>
<td>3323 reflections</td>
</tr>
<tr>
<td>$c = 25.144(4)\text{Å}$</td>
<td>3323 independent reflections</td>
<td>192 parameters</td>
</tr>
<tr>
<td>$\beta = 98.546(3)^\circ$</td>
<td>All H-atom parameters refined</td>
<td>$w = 1/[\sigma^2(Fo^2) + (0.0919P)^2 + 0.0000P]$</td>
</tr>
<tr>
<td>$V = 1532.8(4)\text{Å}^3$</td>
<td>where $P = (Fo^2 + 2Fc^2)/3$</td>
<td>$(\Delta F)^{max} = 0.001$</td>
</tr>
<tr>
<td>$Z = 4$</td>
<td></td>
<td>$\Delta \rho^{max} = 0.949e\text{Å}^{-3}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\Delta \rho^{min} = -0.484e\text{Å}^{-3}$</td>
</tr>
</tbody>
</table>

#### Programs used
- **Data collection:** SMART (Bruker, 1998);
- **Cell refinement:** SMART;
- **Data reduction:** SAINT (Bruker, 1998);
- **Structure solution:** SHELXS97 (Sheldrick, 2008);
- **Structure refinement:** SHELXL97 (Sheldrick, 2008);
- **Molecular graphics:** PLUTON (Speck, 1997); ORTEP-3 (Farrugia, 1997); CAMERON (Watkin et al., 1993); WinGX (Farrugia, 1999)

#### Data deposition
Crystallographic data for the structure reported here has been deposited with the Cambridge Data Centre. The deposition number is CCDC 877887.
### Table 4.2b
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\AA^2 \times 10^3$) of A11.

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>U(eq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(1)</td>
<td>1356(4)</td>
<td>2865(3)</td>
<td>771(1)</td>
<td>19(1)</td>
</tr>
<tr>
<td>C(2)</td>
<td>1825(3)</td>
<td>-1757(3)</td>
<td>334(1)</td>
<td>20(1)</td>
</tr>
<tr>
<td>C(3)</td>
<td>1409(3)</td>
<td>-262(3)</td>
<td>623(1)</td>
<td>19(1)</td>
</tr>
<tr>
<td>C(4)</td>
<td>1755(3)</td>
<td>1314(3)</td>
<td>468(1)</td>
<td>18(1)</td>
</tr>
<tr>
<td>C(5)</td>
<td>2917(3)</td>
<td>3112(4)</td>
<td>-231(1)</td>
<td>20(1)</td>
</tr>
<tr>
<td>C(6)</td>
<td>3693(4)</td>
<td>166(4)</td>
<td>-759(1)</td>
<td>23(1)</td>
</tr>
<tr>
<td>C(7)</td>
<td>4057(4)</td>
<td>372(4)</td>
<td>-697(1)</td>
<td>21(1)</td>
</tr>
<tr>
<td>C(8)</td>
<td>3693(4)</td>
<td>166(4)</td>
<td>-759(1)</td>
<td>23(1)</td>
</tr>
<tr>
<td>C(9)</td>
<td>2937(3)</td>
<td>91(3)</td>
<td>-295(1)</td>
<td>20(1)</td>
</tr>
<tr>
<td>C(10)</td>
<td>2534(3)</td>
<td>1530(3)</td>
<td>16(1)</td>
<td>16(1)</td>
</tr>
<tr>
<td>C(11)</td>
<td>1891(3)</td>
<td>1886(3)</td>
<td>1857(1)</td>
<td>16(1)</td>
</tr>
<tr>
<td>C(12)</td>
<td>-446(4)</td>
<td>2048(4)</td>
<td>2430(1)</td>
<td>23(1)</td>
</tr>
<tr>
<td>C(13)</td>
<td>-1631(4)</td>
<td>522(4)</td>
<td>2397(1)</td>
<td>33(1)</td>
</tr>
<tr>
<td>C(14)</td>
<td>2498(4)</td>
<td>946(3)</td>
<td>2794(1)</td>
<td>21(1)</td>
</tr>
<tr>
<td>C(15)</td>
<td>3490(4)</td>
<td>2297(4)</td>
<td>3138(1)</td>
<td>29(1)</td>
</tr>
<tr>
<td>C(16)</td>
<td>4094(1)</td>
<td>5107(1)</td>
<td>29(1)</td>
<td>29(1)</td>
</tr>
<tr>
<td>O(1)</td>
<td>2587(2)</td>
<td>-3187(2)</td>
<td>448(1)</td>
<td>25(1)</td>
</tr>
<tr>
<td>N(1)</td>
<td>1325(3)</td>
<td>1644(3)</td>
<td>2328(1)</td>
<td>19(1)</td>
</tr>
<tr>
<td>Cl(1)</td>
<td>4057(4)</td>
<td>372(4)</td>
<td>-697(1)</td>
<td>21(1)</td>
</tr>
<tr>
<td>O(2)</td>
<td>1552(3)</td>
<td>-3187(2)</td>
<td>448(1)</td>
<td>25(1)</td>
</tr>
<tr>
<td>N(1)</td>
<td>1325(3)</td>
<td>1644(3)</td>
<td>2328(1)</td>
<td>19(1)</td>
</tr>
<tr>
<td>S(1)</td>
<td>3949(4)</td>
<td>2297(4)</td>
<td>3138(1)</td>
<td>29(1)</td>
</tr>
<tr>
<td>S(2)</td>
<td>224(1)</td>
<td>2565(1)</td>
<td>1337(1)</td>
<td>19(1)</td>
</tr>
</tbody>
</table>

U_{eq} = (1/3)\sum_{ij} U_{ij}(a_i \cdot a_j)

### Table 4.3b
Anisotropic displacement parameters ($\AA^2 \times 10^3$) of A11

The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2a_i^2U_{11} + ... + 2hka_i^bU_{ij} ]$

<table>
<thead>
<tr>
<th>Atom</th>
<th>U11</th>
<th>U22</th>
<th>U33</th>
<th>U23</th>
<th>U13</th>
<th>U12</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(1)</td>
<td>26(2)</td>
<td>17(1)</td>
<td>15(1)</td>
<td>-4(1)</td>
<td>5(1)</td>
<td>-2(1)</td>
</tr>
<tr>
<td>C(2)</td>
<td>18(1)</td>
<td>24(2)</td>
<td>17(1)</td>
<td>0(1)</td>
<td>1(1)</td>
<td>-1(1)</td>
</tr>
<tr>
<td>C(3)</td>
<td>22(1)</td>
<td>20(1)</td>
<td>15(1)</td>
<td>-2(1)</td>
<td>3(1)</td>
<td>1(1)</td>
</tr>
<tr>
<td>C(4)</td>
<td>14(1)</td>
<td>21(1)</td>
<td>16(1)</td>
<td>0(1)</td>
<td>1(1)</td>
<td>4(1)</td>
</tr>
<tr>
<td>C(5)</td>
<td>19(1)</td>
<td>19(1)</td>
<td>20(1)</td>
<td>1(1)</td>
<td>0(1)</td>
<td>0(1)</td>
</tr>
<tr>
<td>C(6)</td>
<td>19(1)</td>
<td>24(1)</td>
<td>19(1)</td>
<td>5(1)</td>
<td>1(1)</td>
<td>4(1)</td>
</tr>
<tr>
<td>C(7)</td>
<td>20(1)</td>
<td>32(2)</td>
<td>15(1)</td>
<td>0(1)</td>
<td>5(1)</td>
<td>0(1)</td>
</tr>
<tr>
<td>C(8)</td>
<td>19(1)</td>
<td>25(2)</td>
<td>25(2)</td>
<td>-3(1)</td>
<td>6(1)</td>
<td>0(1)</td>
</tr>
<tr>
<td>C(9)</td>
<td>16(1)</td>
<td>20(1)</td>
<td>23(1)</td>
<td>0(1)</td>
<td>2(1)</td>
<td>2(1)</td>
</tr>
<tr>
<td>C(10)</td>
<td>16(1)</td>
<td>17(1)</td>
<td>15(1)</td>
<td>1(1)</td>
<td>0(1)</td>
<td>0(1)</td>
</tr>
<tr>
<td>C(11)</td>
<td>19(1)</td>
<td>14(1)</td>
<td>16(1)</td>
<td>-2(1)</td>
<td>2(1)</td>
<td>1(1)</td>
</tr>
<tr>
<td>C(12)</td>
<td>22(2)</td>
<td>29(2)</td>
<td>20(1)</td>
<td>-3(1)</td>
<td>8(1)</td>
<td>5(1)</td>
</tr>
<tr>
<td>C(13)</td>
<td>21(2)</td>
<td>37(2)</td>
<td>42(2)</td>
<td>6(2)</td>
<td>5(1)</td>
<td>-2(1)</td>
</tr>
<tr>
<td>C(14)</td>
<td>24(2)</td>
<td>22(1)</td>
<td>15(1)</td>
<td>-1(1)</td>
<td>3(1)</td>
<td>2(1)</td>
</tr>
<tr>
<td>C(15)</td>
<td>36(2)</td>
<td>27(2)</td>
<td>20(2)</td>
<td>-1(1)</td>
<td>-4(1)</td>
<td>-1(1)</td>
</tr>
<tr>
<td>C(16)</td>
<td>33(1)</td>
<td>27(1)</td>
<td>27(1)</td>
<td>7(1)</td>
<td>9(1)</td>
<td>-4(1)</td>
</tr>
<tr>
<td>O(1)</td>
<td>31(1)</td>
<td>20(1)</td>
<td>24(1)</td>
<td>-2(1)</td>
<td>6(1)</td>
<td>-1(1)</td>
</tr>
<tr>
<td>O(1)</td>
<td>24(1)</td>
<td>19(1)</td>
<td>16(1)</td>
<td>-2(1)</td>
<td>5(1)</td>
<td>0(1)</td>
</tr>
<tr>
<td>N(1)</td>
<td>20(1)</td>
<td>21(1)</td>
<td>17(1)</td>
<td>2(1)</td>
<td>5(1)</td>
<td>2(1)</td>
</tr>
<tr>
<td>S(1)</td>
<td>18(1)</td>
<td>24(1)</td>
<td>21(1)</td>
<td>-2(1)</td>
<td>4(1)</td>
<td>1(1)</td>
</tr>
<tr>
<td>S(2)</td>
<td>19(1)</td>
<td>23(1)</td>
<td>17(1)</td>
<td>0(1)</td>
<td>4(1)</td>
<td>2(1)</td>
</tr>
</tbody>
</table>
Table 4.4b
Bond lengths [Å] and angles [°] for non H-atoms of A11 with esds in parenthesis

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length  [Å]</th>
<th>Angle  [°]</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(1) – C(4)</td>
<td>1.505 (3)</td>
<td></td>
</tr>
<tr>
<td>C(1) – S(2)</td>
<td>1.796 (3)</td>
<td></td>
</tr>
<tr>
<td>C(2) – O(2)</td>
<td>1.197 (3)</td>
<td></td>
</tr>
<tr>
<td>C(2) – O(1)</td>
<td>1.383 (3)</td>
<td></td>
</tr>
<tr>
<td>C(2) – C(3)</td>
<td>1.452 (4)</td>
<td></td>
</tr>
<tr>
<td>C(3) – C(4)</td>
<td>1.349 (4)</td>
<td></td>
</tr>
<tr>
<td>C(4) – C(10)</td>
<td>1.459 (4)</td>
<td></td>
</tr>
<tr>
<td>C(5) – C(6)</td>
<td>1.377 (4)</td>
<td></td>
</tr>
<tr>
<td>C(5) – C(10)</td>
<td>1.410 (4)</td>
<td></td>
</tr>
<tr>
<td>C(6) – C(7)</td>
<td>1.394 (4)</td>
<td></td>
</tr>
<tr>
<td>C(6) – Cl(1)</td>
<td>1.740 (3)</td>
<td></td>
</tr>
<tr>
<td>C(7) – C(8)</td>
<td>1.371 (4)</td>
<td></td>
</tr>
<tr>
<td>C(8) – C(9)</td>
<td>1.382 (4)</td>
<td></td>
</tr>
<tr>
<td>C(9) – O(1)</td>
<td>1.376 (3)</td>
<td></td>
</tr>
<tr>
<td>C(9) – C(10)</td>
<td>1.393 (4)</td>
<td></td>
</tr>
<tr>
<td>C(11) – N(1)</td>
<td>1.337 (3)</td>
<td></td>
</tr>
<tr>
<td>C(11) – S(1)</td>
<td>1.668 (3)</td>
<td></td>
</tr>
<tr>
<td>C(11) – S(2)</td>
<td>1.781 (3)</td>
<td></td>
</tr>
<tr>
<td>C(12) – N(1)</td>
<td>1.473 (3)</td>
<td></td>
</tr>
<tr>
<td>C(12) – C(13)</td>
<td>1.516 (4)</td>
<td></td>
</tr>
<tr>
<td>C(14) – N(1)</td>
<td>1.482 (3)</td>
<td></td>
</tr>
<tr>
<td>C(14) – C(15)</td>
<td>1.514 (4)</td>
<td></td>
</tr>
<tr>
<td>C(4) – C(1) – S(2)</td>
<td>117.13 (19)</td>
<td></td>
</tr>
<tr>
<td>O(2) – C(2) – O(1)</td>
<td>116.8 (2)</td>
<td></td>
</tr>
<tr>
<td>O(2) – C(2) – C(3)</td>
<td>126.4 (2)</td>
<td></td>
</tr>
<tr>
<td>O(1) – C(2) – C(3)</td>
<td>116.8 (2)</td>
<td></td>
</tr>
<tr>
<td>C(4) – C(3) – C(2)</td>
<td>122.9 (2)</td>
<td></td>
</tr>
<tr>
<td>C(3) – C(4) – C(10)</td>
<td>118.6 (2)</td>
<td></td>
</tr>
<tr>
<td>C(3) – C(4) – C(1)</td>
<td>123.1 (2)</td>
<td></td>
</tr>
<tr>
<td>C(10) – C(4) – C(1)</td>
<td>118.3 (2)</td>
<td></td>
</tr>
<tr>
<td>C(6) – C(5) – C(10)</td>
<td>119.1 (3)</td>
<td></td>
</tr>
<tr>
<td>C(5) – C(6) – C(7)</td>
<td>121.8 (3)</td>
<td></td>
</tr>
<tr>
<td>C(5) – C(6) – Cl(1)</td>
<td>120.1 (2)</td>
<td></td>
</tr>
<tr>
<td>C(7) – C(6) – Cl(1)</td>
<td>118.2 (2)</td>
<td></td>
</tr>
<tr>
<td>C(8) – C(7) – C(6)</td>
<td>119.6 (2)</td>
<td></td>
</tr>
<tr>
<td>C(7) – C(8) – C(9)</td>
<td>119.1 (2)</td>
<td></td>
</tr>
<tr>
<td>O(1) – C(9) – C(8)</td>
<td>115.7 (2)</td>
<td></td>
</tr>
<tr>
<td>O(1) – C(9) – C(10)</td>
<td>121.9 (2)</td>
<td></td>
</tr>
<tr>
<td>C(8) – C(9) – C(10)</td>
<td>122.4 (2)</td>
<td></td>
</tr>
<tr>
<td>C(9) – C(10) – C(5)</td>
<td>118.0 (2)</td>
<td></td>
</tr>
<tr>
<td>C(9) – C(10) – C(4)</td>
<td>118.2 (2)</td>
<td></td>
</tr>
<tr>
<td>C(5) – C(10) – C(4)</td>
<td>123.9 (2)</td>
<td></td>
</tr>
<tr>
<td>N(1) – C(11) – S(1)</td>
<td>124.0 (2)</td>
<td></td>
</tr>
<tr>
<td>N(1) – C(11) – S(2)</td>
<td>113.18 (19)</td>
<td></td>
</tr>
<tr>
<td>S(1) – C(11) – S(2)</td>
<td>122.77 (15)</td>
<td></td>
</tr>
<tr>
<td>N(1) – C(12) – C(13)</td>
<td>113.1 (2)</td>
<td></td>
</tr>
<tr>
<td>N(1) – C(14) – C(15)</td>
<td>112.9 (2)</td>
<td></td>
</tr>
<tr>
<td>C(9) – O(1) – C(2)</td>
<td>121.7 (2)</td>
<td></td>
</tr>
<tr>
<td>C(11) – N(1) – C(12)</td>
<td>124.3 (2)</td>
<td></td>
</tr>
<tr>
<td>C(11) – N(1) – C(14)</td>
<td>120.7 (2)</td>
<td></td>
</tr>
<tr>
<td>C(12) – N(1) – C(14)</td>
<td>115.1 (2)</td>
<td></td>
</tr>
<tr>
<td>C(11) – S(2) – C(1)</td>
<td>103.44 (13)</td>
<td></td>
</tr>
<tr>
<td>Torsion angles [°] for non H-atoms of A11 with esds in parenthesis</td>
<td></td>
<td></td>
</tr>
<tr>
<td>---------------------------------------------------------------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O(2) - C(2) - C(3) - C(4)</td>
<td>-179.8(3)</td>
<td></td>
</tr>
<tr>
<td>O(1) - C(2) - C(3) - C(4)</td>
<td>-0.9(4)</td>
<td></td>
</tr>
<tr>
<td>C(2) - C(3) - C(4) - C(10)</td>
<td>1.9(4)</td>
<td></td>
</tr>
<tr>
<td>C(2) - C(3) - C(4) - C(1)</td>
<td>-178.8(2)</td>
<td></td>
</tr>
<tr>
<td>S(2) - C(1) - C(4) - C(3)</td>
<td>-4.6(4)</td>
<td></td>
</tr>
<tr>
<td>S(2) - C(1) - C(4) - C(10)</td>
<td>174.65(19)</td>
<td></td>
</tr>
<tr>
<td>C(10) - C(5) - C(6) - C(7)</td>
<td>-1.5(4)</td>
<td></td>
</tr>
<tr>
<td>C(10) - C(5) - C(6) - Cl(1)</td>
<td>178.7(2)</td>
<td></td>
</tr>
<tr>
<td>C(5) - C(6) - C(7) - C(8)</td>
<td>1.4(4)</td>
<td></td>
</tr>
<tr>
<td>Cl(1) - C(6) - C(7) - C(8)</td>
<td>-178.8(2)</td>
<td></td>
</tr>
<tr>
<td>C(6) - C(7) - C(8) - C(9)</td>
<td>-0.5(4)</td>
<td></td>
</tr>
<tr>
<td>C(7) - C(8) - C(9) - O(1)</td>
<td>179.1(2)</td>
<td></td>
</tr>
<tr>
<td>C(7) - C(8) - C(9) - C(10)</td>
<td>-0.3(4)</td>
<td></td>
</tr>
<tr>
<td>O(1) - C(9) - C(10) - C(5)</td>
<td>-179.1(2)</td>
<td></td>
</tr>
<tr>
<td>C(8) - C(9) - C(10) - C(5)</td>
<td>0.1(4)</td>
<td></td>
</tr>
<tr>
<td>O(1) - C(9) - C(10) - C(4)</td>
<td>1.4(4)</td>
<td></td>
</tr>
<tr>
<td>C(8) - C(9) - C(10) - C(4)</td>
<td>-179.4(2)</td>
<td></td>
</tr>
<tr>
<td>C(6) - C(5) - C(10) - C(9)</td>
<td>0.7(4)</td>
<td></td>
</tr>
<tr>
<td>C(6) - C(5) - C(10) - C(4)</td>
<td>-179.8(2)</td>
<td></td>
</tr>
<tr>
<td>C(3) - C(4) - C(10) - C(9)</td>
<td>-2.1(4)</td>
<td></td>
</tr>
<tr>
<td>C(1) - C(4) - C(10) - C(9)</td>
<td>178.6(2)</td>
<td></td>
</tr>
<tr>
<td>C(3) - C(4) - C(10) - C(5)</td>
<td>178.4(2)</td>
<td></td>
</tr>
<tr>
<td>C(1) - C(4) - C(10) - C(5)</td>
<td>-0.8(4)</td>
<td></td>
</tr>
<tr>
<td>C(8) - C(9) - O(1) - C(2)</td>
<td>-179.7(2)</td>
<td></td>
</tr>
<tr>
<td>C(10) - C(9) - O(1) - C(2)</td>
<td>-0.4(4)</td>
<td></td>
</tr>
<tr>
<td>O(2) - C(2) - O(1) - C(9)</td>
<td>179.1(2)</td>
<td></td>
</tr>
<tr>
<td>C(3) - C(2) - O(1) - C(9)</td>
<td>0.1(4)</td>
<td></td>
</tr>
<tr>
<td>S(1) - C(11) - N(1) - C(12)</td>
<td>173.7(2)</td>
<td></td>
</tr>
<tr>
<td>S(2) - C(11) - N(1) - C(12)</td>
<td>-5.7(3)</td>
<td></td>
</tr>
<tr>
<td>S(1) - C(11) - N(1) - C(14)</td>
<td>-5.6(4)</td>
<td></td>
</tr>
<tr>
<td>S(2) - C(11) - N(1) - C(14)</td>
<td>175.02(19)</td>
<td></td>
</tr>
<tr>
<td>C(13) - C(12) - N(1) - C(11)</td>
<td>99.2(3)</td>
<td></td>
</tr>
<tr>
<td>C(13) - C(12) - N(1) - C(14)</td>
<td>-81.5(3)</td>
<td></td>
</tr>
<tr>
<td>C(15) - C(14) - N(1) - C(11)</td>
<td>90.0(3)</td>
<td></td>
</tr>
<tr>
<td>C(15) - C(14) - N(1) - C(12)</td>
<td>-89.3(3)</td>
<td></td>
</tr>
<tr>
<td>N(1) - C(11) - S(2) - C(1)</td>
<td>177.76(19)</td>
<td></td>
</tr>
<tr>
<td>S(1) - C(11) - S(2) - C(1)</td>
<td>-1.7(2)</td>
<td></td>
</tr>
<tr>
<td>C(4) - C(1) - S(2) - C(11)</td>
<td>79.1(2)</td>
<td></td>
</tr>
</tbody>
</table>
Table 4.6b
Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\AA^2 \times 10^3$) of A11

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>U(eq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H (1A)</td>
<td>654</td>
<td>3634</td>
<td>515</td>
<td>23</td>
</tr>
<tr>
<td>H (1B)</td>
<td>2468</td>
<td>3444</td>
<td>900</td>
<td>23</td>
</tr>
<tr>
<td>H (3)</td>
<td>868</td>
<td>-401</td>
<td>935</td>
<td>22</td>
</tr>
<tr>
<td>H (5)</td>
<td>2674</td>
<td>4122</td>
<td>-54</td>
<td>23</td>
</tr>
<tr>
<td>H (7)</td>
<td>4584</td>
<td>1784</td>
<td>-1277</td>
<td>26</td>
</tr>
<tr>
<td>H (8)</td>
<td>3956</td>
<td>-840</td>
<td>-935</td>
<td>28</td>
</tr>
<tr>
<td>H (12A)</td>
<td>-961</td>
<td>2898</td>
<td>2165</td>
<td>28</td>
</tr>
<tr>
<td>H (12B)</td>
<td>-376</td>
<td>2555</td>
<td>2793</td>
<td>28</td>
</tr>
<tr>
<td>H (13A)</td>
<td>-1763</td>
<td>52</td>
<td>2032</td>
<td>50</td>
</tr>
<tr>
<td>H (13B)</td>
<td>-2774</td>
<td>858</td>
<td>2481</td>
<td>50</td>
</tr>
<tr>
<td>H (13C)</td>
<td>-1123</td>
<td>-332</td>
<td>2655</td>
<td>50</td>
</tr>
<tr>
<td>H (14A)</td>
<td>3340</td>
<td>172</td>
<td>2662</td>
<td>25</td>
</tr>
<tr>
<td>H (14B)</td>
<td>1801</td>
<td>282</td>
<td>3019</td>
<td>25</td>
</tr>
<tr>
<td>H (15A)</td>
<td>4275</td>
<td>2883</td>
<td>2929</td>
<td>43</td>
</tr>
<tr>
<td>H (15B)</td>
<td>4170</td>
<td>1775</td>
<td>3455</td>
<td>43</td>
</tr>
<tr>
<td>H (15C)</td>
<td>2667</td>
<td>3106</td>
<td>3254</td>
<td>43</td>
</tr>
</tbody>
</table>

Table 4.7b
Mean planes through various groups of atoms and deviations (Å) from the plane in A11.
The equation of the plane: $m_1X + m_2Y + m_3Z - D = 0$ where $m_1$, $m_2$, $m_3$ and $D$ are constant. Starred atoms are included in the plane calculations.

<table>
<thead>
<tr>
<th>Plane</th>
<th>m1</th>
<th>m2</th>
<th>m3</th>
<th>D</th>
<th>Atom</th>
<th>Deviations</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-0.833(7)</td>
<td>0.034(6)</td>
<td>-0.551(5)</td>
<td>-1.585(7)</td>
<td>C3*</td>
<td>0.006(3)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C4*</td>
<td>-0.010(2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C10*</td>
<td>0.008(2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C9*</td>
<td>-0.002(2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>O1*</td>
<td>-0.001(2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C2*</td>
<td>0.001(2)</td>
</tr>
<tr>
<td>2</td>
<td>0.517(9)</td>
<td>-0.608(1)</td>
<td>-0.602(1)</td>
<td>2.731(9)</td>
<td>C5*</td>
<td>-0.005(2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C6*</td>
<td>0.007(2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C7*</td>
<td>-0.004(2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C8*</td>
<td>-0.003(2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C9*</td>
<td>0.001(2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C10*</td>
<td>0.001(2)</td>
</tr>
</tbody>
</table>
### Dihedral angles formed by LSQ-Planes in A11.

<table>
<thead>
<tr>
<th>Plane1</th>
<th>Plane2</th>
<th>Angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenyl ring</td>
<td>Pyrone ring</td>
<td>1.28(7)°</td>
</tr>
</tbody>
</table>

### Table 4.8e

Non bonded interactions and possible hydrogen bonds in A11 (Å,°)

*(D-donor; A-Acceptor; H-hydrogen)*

<table>
<thead>
<tr>
<th>D–H...A</th>
<th>D–H</th>
<th>H...A</th>
<th>D...A</th>
<th>D–H...A</th>
</tr>
</thead>
<tbody>
<tr>
<td>C5–H5··O2¹</td>
<td>0.950</td>
<td>2.689</td>
<td>3.633</td>
<td>172</td>
</tr>
<tr>
<td>C1–H1A··O2¹</td>
<td>0.990</td>
<td>2.628</td>
<td>3.244(3)</td>
<td>121</td>
</tr>
<tr>
<td>C8–H8··S1¹</td>
<td>0.950(0.003)</td>
<td>2.883(1)</td>
<td>3.610(3)</td>
<td>134(2)</td>
</tr>
<tr>
<td>C1–H1B··CL1¹ii</td>
<td>0.990(3)</td>
<td>2.889(1)</td>
<td>3.849(3)</td>
<td>163(2)</td>
</tr>
</tbody>
</table>

Symmetry code: (i) $x,y+1,z$ (ii) $-x+1,-y+1,-z$ (iii) $-x+1,-y,-z$
4.4 Summary

The two compounds \textbf{A10} and \textbf{A11} which are discussed in this chapter are Coumarin derivatives. In \textbf{A10} and \textbf{A11}, diethyl-dithiocarbamic acid is substituted at position 4. The methyl group and chloro group is substituted at position 6 to the coumarin moiety in \textbf{A10} and \textbf{A11} respectively.

In these two molecules, the coumarin moiety is planar with dihedral angle 1.28(7)° between the least-squares plane of the phenyl and pyrone rings. Bond lengths and bond angles in the coumarin moiety are typical for coumarin derivatives. The coumarin molecule is effectively flat with a deviation between the components in 6-membered rings of 0.84°. The C3-C4 bond is conjugated to the carbonyl group, giving it a Michael acceptor function, characteristic of certain chemopreventive agents. The supramolecular structures of \textbf{A10} and \textbf{A11} were investigated in terms of C-H...O, C-H...S, C-H...N and C-H...Cl intermolecular interactions. In \textbf{A10}, the C-H...O and C-H...S interactions generates dimers corresponding graph set motif R\textsuperscript{2}(8) and R\textsuperscript{2}(22) respectively where as C-H...N interactions forms chain of molecules. In \textbf{A11}, the C-H...S hydrogen bonds links the molecules into dimers and the two C-H...O interactions connects the two molecules through bifurcated bonds. The C-H...Cl interactions in \textbf{A11} generates centrosymmetric dimers with R\textsuperscript{2}(14) graph set notation. In addition, the supramolecular cohesion is further strengthened by π-π stacking and C-π interactions in both the compounds.

In conclusion, the two compounds discussed in these chapter posses diverse pharmacological properties and biological activities. A single crystal x-ray diffraction analysis was carried out to establish the crystal structure and to understand the self-aggregation in terms of possible intermolecular interactions.
Chapter 4

Coumarin Derivatives

References


