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Crystal structure analysis of Methyl-1-methyl-8-nitro-3-phenyl-1,2,3,9b-tetrahydrothiochromeno [4,3-b]pyrrole-3a(4H)-carboxylate

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Abstract: The title compound, $C_{20}H_{20}N_2O_4S$, has been synthesized and characterized by X-ray crystallography. The structure is solved in monoclinic with space group C2/c with a = 22.368(3)Å, b = 8.1187(10)Å, c = 20.185(3)Å , β = 94.472(6)°, V = 3654.4(9) Å^3, Z = 8. The pyrrole ring adopts an envelope conformation with C9 atom at the flap, deviating from the mean plane defined by the plane of the other ring atoms by 0.708Å. Crystal data were collected using BRUKER SMART APEX II CCD X-ray diffractometer. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares procedures to the final R_1 of 0.040 using SHELXL programs.
Key Words: Pyyrole, thiochromene and crystal structure.

Introduction

Pyrrole derivatives are of considerable synthetic importance due to their extensive use in drug discovery[1] which is linked to their pharmacological activity such as antiinflammatory[2], cytotoxicity[3] and their use in the treatment of hyperlipidemias[4] and as antitumour agents[5]. Against this background, the X-ray analysis of the title compound has been carried out to study its structural aspects.

Experimental

X-ray Structure Determination

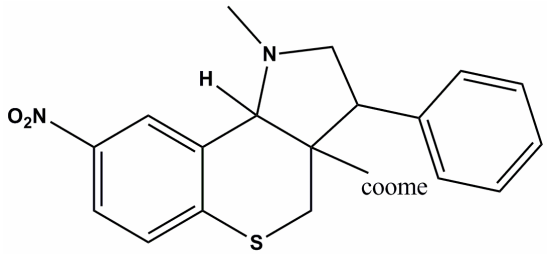
Single crystal of the compound suitable for x-ray diffraction was obtained by slow evaporation method. Three dimensional intensity data were collected on a Bruker[6] SMART APEX CCD Diffractometer using graphite monochromatized Mo-Kα radiation (λ= 0.71073 Å) at Department of chemistry, IIT, Chennai, India. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares procedures using the SHELXL programs[7]. All the non-hydrogen atoms were refined using isotropic and later anisotropic thermal parameters. The hydrogen atoms were included in the structure factor calculation at idealized positions by using a riding model, but not refined. Images were created with ORTEP-3[8]. The crystallographic data for the compound are listed in Table 1.

Table 1: Crystal data and structure refinement of the titled compound

Compound	**Parameters**
Empirical formula	$C_{20}\,H_{20}\,N_2\,O_4\,S$
Formula weight	384.44
Temperature	293(2) K
Wavelength	0.71073Å
Crystal system, space group	Monoclinic, C 2/c
Unit cell dimensions	a = 22.368(3)Å α = 90° b = 8.1187(10)Å β = 94.472(6)° c = 20.185(3)Å γ= 90°
Volume	3654.4(8) A^3
Z, Calculated density	8, 1.397 Mg/m^3
Absorption coefficient	0.207 mm^{-1}
F(000)	1616
Crystal size	0.30 x 0.25 x 0.20 mm
Theta range for data collection	1.83 to 25.00 deg.
Limiting indices	-26<=h<=26, -7<=k<=9, -24<=l<=24
Reflections collected / unique	11271 / 3217 [R(int) = 0.0406]
Completeness to theta = 25.00	100.00%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3217 / 0 / 246
Goodness-of-fit on F^2	1.044
Final R indices [I>2sigma(I)]	R1 = **0.0402**, wR2 = 0.1291
R indices (all data)	R1 = 0.0606, wR2 = 0.1393
Largest diff. peak and hole	0.729 and -0.633 $e.A^{-3}$

Synthesis of the compound

A solution of methyl (Z)-2-(((2-formyl-4-nitrophenyl)thio)methyl) -3-phenylacrylate (1 mmol) and sarcosine (1.2 mmol) in acetonitrile (10ml) was refluxed until the completion of the reaction as evidenced by TLC. The solvent was removed under vacuum. The crude product was subjected to column chromatography on silica gel (100-200 mesh) using petroleum ether-ethyl acetate (8:2) as eluent, which successfully provided the pure product as colorless solid. The product was dissolved in chloroform and heated for two minutes. The resulting solution was subjected to crystallization by slow evaporation of the solvent for 48 hours resulting in the formation of single crystals. The scheme diagram is given below.



Results and Discussion

The molecular structure of the title molecule is shown in Fig. 1. The pyrrole ring (N2/C9-C11) adopts an envelope conformation with C9 atom located at the flap position having asymmetry parameter[9] ΔCs = 3.2(2)Å and with the puckering parameters[10] q_2 =0.475(2)Å and ϕ_2 = 221.8(3)°. The thiopyran ring (S1/C6-C9) in the molecule very similar to a Half-chair conformation. The puckering parameters for this ring are q_2 = 0.362Å and ϕ_2 = 87.5(3)°. The thiopyran ring makes dihedral angles of 60.24(2) and 3.29(1)° with benzene and the phenyl rings, respectively. The pyrrole and phenyl rings with maximum deviations of 0.328 and -0.058Å, respectively, at atoms C10 and N1. The carboxylate group assumes an extended conformation, as can be seen from the C8-C19-O4-C20 torsion angle = -175.9(2)°. The mean plane of the pyrrole ring is inclined to the mean plane of the thiopyran ring by 69.88(2), 58.6(2) and 56.6(1)°, respectively.

A weak intramolecular C7---H7A...N2 interaction is also observed. The molecules at (x,1-y,-z) and (x,-y,-z) are linked by two sets of C2---H2...O3 and C20---H20C...O2 hydrogen bonds to form, centrosymmetric dimmer containing two $R^2_2(10)$ ring motifs (Fig 2 & Table 2). The selected bond lengths and angles are listed in table 3 and 4, respectively.

Table 2: Hydrogen-bond geometry [Å]

Distance (Å)				Angle (°)
C2---H2…03	0.93	2.57	3.326(3)	138.7
C4---H4…O3	0.93	2.48	3.324(3)	150.6
C20---H20C…O2	0.96	2.17	3.105(7)	164.6

Symmetry code: i) -x,1-y,-z, ii) -x,-y,-z

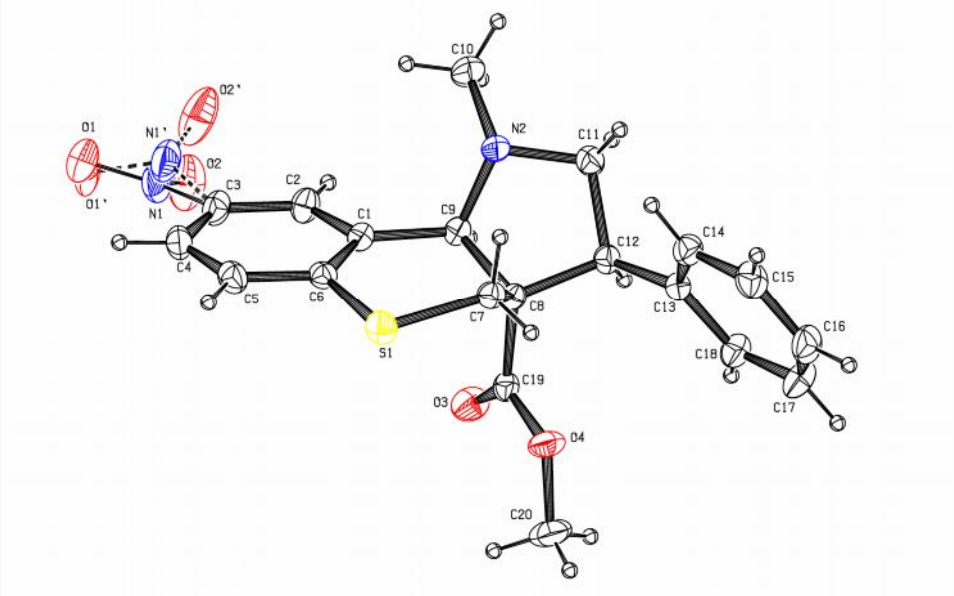


Fig.1. The molecular structure of the title compound, with the atom-numbering scheme. The displacement ellipsoids are drawn at 30% probability level.

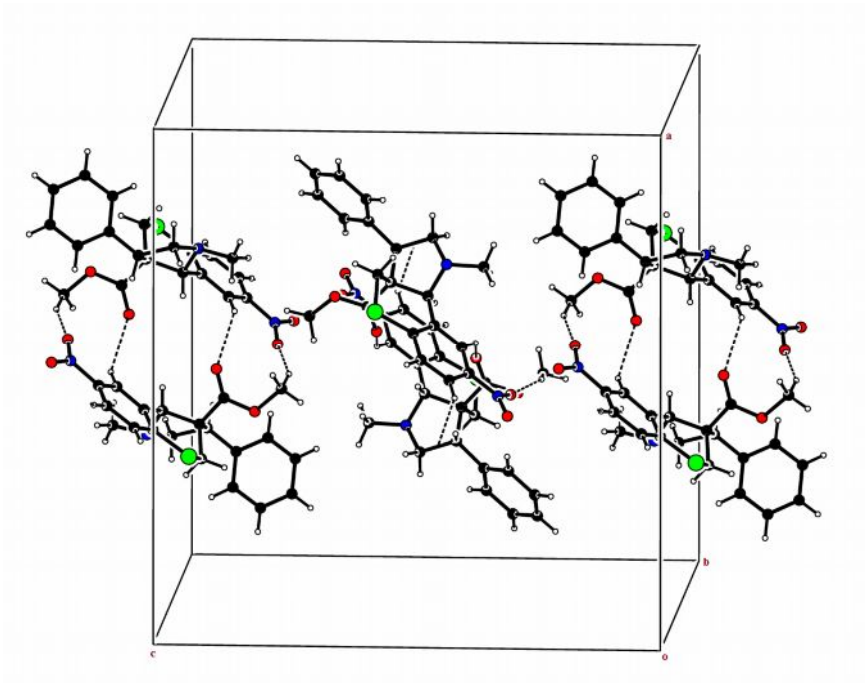


Fig.2. The crystal packing of the title compound, viewed along a axis. The molecules at (-x,1-y,-z) and (-x,-y,-z) are linked by two sets of C2---H2...O3 and C20---H20C...O2 hydrogen bonds to form, centrosymmetric dimmer containing two $R^2_2(10)$ ring motifs.

Table 3: Selected Bond lengths (Å)

Atom	Length
C(1)-C(2)	1.390(3)
C(1)-C(6)	1.403(3)
C(1)-C(9)	1.509(3)
C(2)-C(3)	1.382(4)
C(2)-H(2)	0.93
C(3)-C(4)	1.370(4)
C(3)-N(1)	1.465(4)
C(4)-C(5)	1.368(4)
C(4)-H(4)	0.93
C(5)-C(6)	1.397(3)
C(5)-H(5)	0.93
C(6)-S(1)	1.746(2)
C(7)-C(8)	1.525(3)
C(7)-S(1)	1.802(2)
C(7)-H(7A)	0.97
C(7)-H(7B)	0.97
C(8)-C(19)	1.520(3)
C(8)-C(9)	1.538(3)
C(8)-C(12)	1.574(3)
C(9)-N(2)	1.477(3)
C(9)-H(9)	0.98
C(10)-N(2)	1.456(3)
C(10)-H(10A)	0.96
C(10)-H(10B)	0.96
C(10)-H(10C)	0.96
C(11)-N(2)	1.472(3)
C(11)-C(12)	1.539(3)

Table 4: Selected Bond angles (º)

Atom	Angle
C(2)-C(1)-C(6)	117.6(2)
C(2)-C(1)-C(9)	118.7(2)
C(6)-C(1)-C(9)	123.7(2)
C(3)-C(2)-C(1)	120.4(2)
C(3)-C(2)-H(2)	119.8
C(1)-C(2)-H(2)	119.8
C(4)-C(3)-C(2)	122.2(2)
C(4)-C(3)-N(1)	118.6(2)
C(2)-C(3)-N(1)	119.2(3)
C(5)-C(4)-C(3)	118.2(2)
C(5)-C(4)-H(4)	120.9
C(3)-C(4)-H(4)	120.9
C(4)-C(5)-C(6)	121.2(2)
C(4)-C(5)-H(5)	119.4
C(6)-C(5)-H(5)	119.4
C(5)-C(6)-C(1)	120.3(2)
C(5)-C(6)-S(1)	115.46(19)
C(1)-C(6)-S(1)	124.08(18)
C(8)-C(7)-S(1)	113.28(16)
C(8)-C(7)-H(7A)	108.9
S(1)-C(7)-H(7A)	108.9
C(8)-C(7)-H(7B)	108.9
S(1)-C(7)-H(7B)	108.9
H(7A)-C(7)-H(7B)	107.7
C(19)-C(8)-C(7)	112.10(18)

Conclusion

The crystal structure analysis of a novel Pyrrole compound was studied using x-ray diffraction method. In the crystal, molecules are linked by two sets of C---H...O hydrogen bonds, to form, centrosymmetric dimmer containing two $R^2_2(10)$ ring motifs.

Acknowledgments

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