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RESEARCH ARTICLE

SYNTHESISAND SPECTROPHOTOMETRIC STUDIES OF SOME NEW COUMARINDERIVATIVES.

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Abstract

The current study was designed to investigate the reactivity of 3-acetyl-6-bromocoumarintowards a variety of electrophilic and nucleophilic reagents such as aromatic aldehydes to give 3-cinnamoyl c**oumarin**s **2a,b**. The reaction of**2b** with guanidine hydrochloride gave 6-bromo-3-(substituted pyrimidine)coumarin-3-yl **3**. Other6-bromo-3-(substituted pyrimidine) coumarin-3-ylderivatives **5a** and **5b** were synthesized from treatment of **1** with thiosemicarbazide then treating the product **4** with active methylene compounds namely diethyl malonate and/or ethyl acetoacetate. Treating 4 with phenacyl bromide yielded the corresponding phenyl thiazole derivative **7**. Alkylation of **4** with acetic anhydride and/or benzoyl chloride yielded the corresponding diacetyl- and/or di benzoyl derivatives**6a,b**. The reaction of **4** with ethyl chloroacetate and/or chloro acetic acid in different media yielded two isomers **8a** and **8b**. The reaction of **1** with nitriles such as malononitrile and/or ethyl cyanoacetatefollowed by treatment with sulfur gave corresponding coumarin -3-y—thiophene derivatives **10a,b**. The structures of the newly synthesized derivatives were elucidated by means of microanalysis, IR, ^{1}H-NMR, ^{13}C-NMR and MS measurments. The UV-Vis absorption spectra of the various newly 3-substituted-6-bromo coumarin derivatives **1-10**were investigated in expectation of the shift to the longer wavelength region by the extension of the conjugated system. The absorption properties of the prepared compounds were investigated spectrophotometrically by dissolving in chloroform in the range 200-800 nm using 1cm quartz cells, showed good UV absorption properties and were discussed from the view point of the intermolecular charge transfer (ICT) between push- and pull-substituents.

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Introduction:-

Coumrines are simple organic molecules which constitute an important class of naturally occurring products and many of them exhibit versatile pharmacological and biological activities (Riveiro et al., 2008; Nolan et al., 2007;Hwu et al., 2008;Bondock et al., 2008;Ghate et al., 2003;Torres et al., 2006;Kontogiorgis et al., 2004; Soliman et al., 2018).

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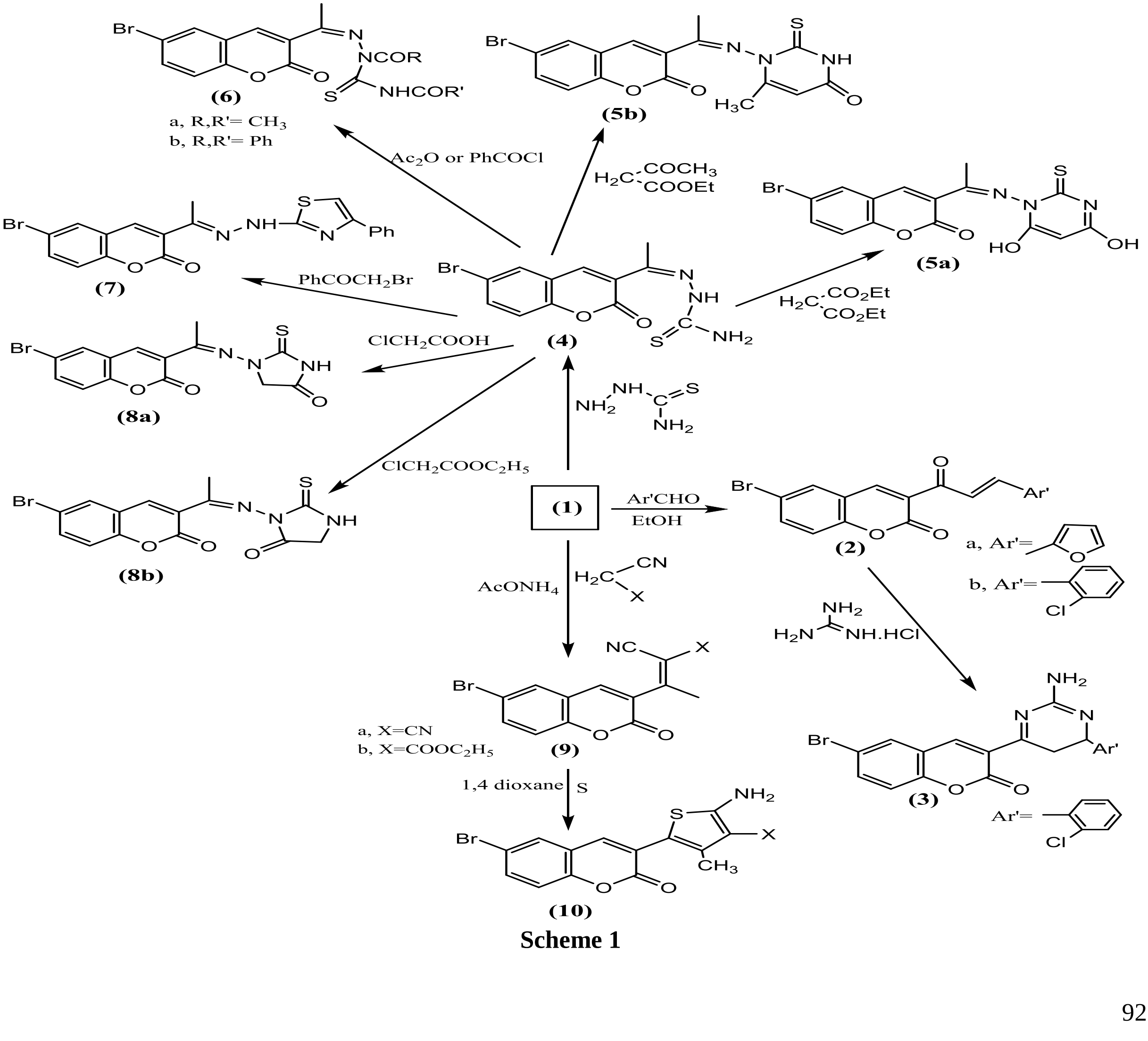
Moreover, they are characterized by their unique photochemical properties which make them useful in a variety of optical applications such as optical brighteners, laser dyes, non-linear optical chromophores, solar collector systems and organic light emitting diodes (LED). (Sharmaet al., 2003; Ranjith et al., 2010).

Coumarins substituted at some position with an electron-donating group or by lengthened π-conjugation are known to influence the fluorescent properties (Takadate et al., 1993). Coumarin itself is not fluorescent, but it exhibits intense fluorescence upon substitution by various functional groups at different positions (Kim et al., 2007;Turki et al., 2007).

The photophysical properties of coumarins were related to substitution at position 3- and/or 4-substitutuent in the parent molecule and in general electron-donating substituents tend to diminish it (Yao et al., 2011). In the same manner, biological activity as well as the therapeutic applications were based on different possibility of introducing substituents at either of the positions at C-3, C-4, C-6, C-7, C-8 and C-9 affected the physico-chemical properties and biological activity (Lee et al., 2006; Zhao et al., 2004).

In this study sixteen coumarin derivatives **(1-10)** substituted in position-3 with substituents of varying electron-withdrawing and/or electron-releasing, whereas in position-6 only one substituent of electron-donatingbromo (c.f. **Scheme 1**).

In the present investigation we examined in detail the absorption characteristics of the newly synthesized coumarin derivatives **(1-10)** from the viewpoint of the substituent effect in connection with two ICT in the coumarinskeleton and in terms of the 3D-geometrical structure in order to correlate the effect of the electron-withdrawing or electron-releasing substituents on the shape of the spectra and to gain some insight into their photo-physics.



Scheme 1

Experimental

General description of the experimental techniques

Melting points were measured in capillaries and were uncorrected. TLC was performed on precoated silica gel F-254 plates (0.025 nm; E.Merck), and products and starting materials were detected by viewing under UV light.Infrared spectra were recorded on Shimadzu IR-Prespige (KBr pellets).^{1}H-NMR and ^{13}C-NMR spectra**(Table1)** were recorded on a Varian NMR system 400 (400 MHz) with TMS as an internal standard using solutions in deuterated dimethyl sulfoxide. Low resolution mass spectra or high resolution mass spectra were obtained on Finnigan MAT-8430 instrument using electron impact ionization technique (70 eV). Microanalysis for C,H,N,S and Br were performed on Thermo Finnigan Elemental analyzer. Spectrophotometric measurements were recorded with Shimadzu 1601 UV/visible spectrophotometer in the range of 200-800nm using 1cm quartz cells and samples were dissolved in chloroform, their concentration being in the 10^{-5} m mol. rang.

Preparation of 3-acetyl-6-bromo coumarin 1

This compound was prepared from 5-bromosalicylaldehyde and ethylacetoacetate according to the method described in the literature(Al-Haiza et al., 2003). Crude product was recrystallized from ethanol as pale yellow crystals, m.p.177°C. IR (KBr, cm^{-1}): 3108, 1615, 1496 (CH aromatic); 1735 (C=O, lactone); 1678 (C=O, acetyl); 655 (C-Br). ^{1}H-NMR (DMSO-d$_6$): δ 2.22 (s, 3H, COCH$_3$); 6.64 (s,1H, C$_4$-H); 6.78 (s, 1H, C$_5$-H); 7.04 (d, 1H, C$_7$-H); 7.25 (d, 1H, C$_8$-H). HR-MS (EI$^+$) m/z 266.96.Calcd.for $C_{11}H_7O_3Br$; (267.08): C, 49.43; H, 2.62; Br, 29.69%. Found: C, 49.52; H, 2.71; Br, 30.05.

General synthetic method for the preparation of 2a,b.

A mixture of **1** (0.01mol.) and aromatic aldehydes namely, 2-furaldehyde (0.01 mol.) and/or 2-chlorobenzaldehyde (0.01 mol.) in 30 ml of absolute ethanol and few drops of piperidine (5 drops) was stirred at 0-5°C for 30 min., then refluxed for 6h. After cooling, the resulting precipitates were recrystallized from the proper solvents to give the coumarinyl chalcones **2a,b**.

6-Bromo-3-{3-(furan-2-yl)acryloyl} coumarin (2a). M.p.203°C, crystallized from pet.ether (b.p. 60-80°) as brown crystals. IR (KBr, cm^{-1}): 3010- 3100 (CH aromatic); 2865- 2982 (CH aliphatic); 1736 (C=O, lactone); 1676 (C=O, aroyl); 1608-1517 (aromatic C=C); 658 (C-Br). ^{1}H-NMR (DMSO-d$_6$): δ 6.81 (s,1H, C$_4$-H), 6.85 (s, 1H, C$_5$-H), 6.90-6.92 (m, 5H, Ar-H); 7.17 (d, 1H, CH$_\alpha$=CH); 8.14 (d, 1H, CH=CH$_\beta$). Anal.Calcd.for $C_{16}H_9O_4Br$ (345.15): C, 55.65; H, 2.60; Br, 23.18. Found: C, 55.69; H, 2.68; Br, 23.27. HR-MS (EI$^+$) m/z 344.97 (16.2%).

6-Bromo-3-{3-(2-chlorophenyl)acryloyl} coumarin (2b). M.p.192°C, crystallized from ethanol as yellow crystals. IR (KBr, cm^{-1}): 3000- 3100 (CH aromatic); 2855- 2990 (CH aliphatic); 1733 (C=O, lactone); 1678 (C=O, aroyl); 1602-1519 (aromatic C=C); 655 (C-Br). ^{1}H-NMR (DMSO-d$_6$): δ 6.82 (s,1H, C$_4$-H), 6.86 (s, 1H, C$_5$-H), 6.90-6.93 (m, 6H, Ar-H); 7.23 (d, 1H, CH$_\alpha$=CH); 8.21 (d, 1H, CH=CH$_\beta$). Anal.Calcd.for $C_{18}H_{10}O_3ClBr$ (389.63): C, 55.49; H, 2.59; Cl, 9.01; Br, 20.51. Found: C, 55.50; H, 2.60; Cl, 9.11; Br, 20.53. HR-MS (EI$^+$) m/z 389.96(1.1%), 389.95(9.73%).

Synthesis of 3-{2-amino-6-(2-chlorophenyl)-5,6-dihydropyrimidin-4-yl}-6-bromo-coumarin (3)

A mixture of **2b** (0.01mol.) and guanidine hydrochloride (0.01 mol.) in 30 ml of absolute ethanol containing freshly fused sodium acetate (0.03 mol.)was refluxed for 12h. After cooling, the resulting precipitate was collected, washed well with waterand recrystallized from ethanol to give**3**as yellow crystals, m.p.150°C.IR (KBr, cm^{-1}): 3275 (NH$_2$); 3090-2829 (CH aromatic, aliphatic); 1734 (C=O, lactone); 1628 (C=N); 1602-1595 (C=C); 654 (C-Br). ^{1}H-NMR (DMSO-d$_6$): δ 3.81 (d, 2H, CH$_2$-CH, pyrimidine), 4.62 (t, 1H, CH-CH$_2$ pyrimidine); 6.81(s,1H, C$_4$-H); 6.83 (s, 1H, C$_5$-H); 6.90-6.93 (m, 6H, Ar-H); 10.11 (s, 2H, NH$_2$, D$_2$O exchangeable). Anal.Calcd.for $C_{19}H_{13}O_2N_3ClBr$ (430.69): C, 52.99; H, 3.04; N, 9.76; Cl, 8.23; Br, 18.55. Found: C, 53.08; H, 3.13; N,9.85; Cl, 8.32; Br, 18.64. HR-MS (EI$^+$) m/z 430.99 (32.0%), 431.99 (5.2%).

Synthesis of 2-{1-(6-bromocoumarin-3-yl)ethylidene}hydrazine-1-carbothioamide (4)

A mixture of 3-acetyl-6-bromocoumarin **(1)** (0.01mol.) and thiosemicarbazide (0.01 mol.)(dissolved in 1ml of water) in 30 ml of acetic acidwas refluxed for 2h. After cooling, the solid product was collected, washed well with waterand recrystallized from ethanol to give**4** as yellow crystals, m.p.212°C.IR (KBr, cm^{-1}): 3300 (NH); 3230 (NH$_2$); 3080-2828(CH aromatic, aliphatic); 1734 (C=O, lactone); 1627 (C=N); 1601-1589 (C=C); 1249 (C=S); 655 (C-Br). ^{1}H-NMR (DMSO-d$_6$): δ 1.35 (s, 3H, CH$_3$); 4.041 (s, 1H, NH); 6.71 (s, 1H, C$_4$-H); 6.79 (s, 1H, C$_5$-H); 6.91-6.93 (m, 2H, Ar-H); 10.11 (s, 2H, NH$_2$, D$_2$O exchangeable). Anal.Calcd.for $C_{12}H_{10}O_2N_3SBr$ (340.20): C, 42.37; H, 2.96; N, 12.35; S, 9.42; Br, 23.49. Found: C, 42.46; H, 3.05; N,12.44; S, 9.51; Br, 23.58. HR-MS (EI^+) m/z 430.96 (4.5%), 341.97(1.1%).

Reaction of 2-{1-(6-bromocoumarin-3-yl) ethylidene}hydrazine-1-carbothioamide (4) with 1,3-dicarbonyl compounds. Formation of 5a, 5b

General procedure

A mixture of **4** (0.01mol.) and dicarbonyl compounds namely, diethyl malonate (0.01 mol.) and/or ethyl acetoacetate (0.01 mol.) in 25 ml of acetic acid was heated under reflux for 3h. After cooling, the products were diluted with water then filtered off, washed well with water andrecrystallized from the proper solvents as**5a** and **5b**.

6-Bromo-3-{1-(4,6-dihydroxy-2-thioxopyrimidin-1(2H)-yl)imino)ethyl}coumarin (5a). M.p.188°C, crystallized from ethanol as yellow crystals. IR (KBr, cm^{-1}): 3350 (OH); 3100-2828 (CH aromatic, aliphatic); 1735 (C=O, lactone); 1628 (C=N); 1605-1595 (C=C); 1241 (C=S); 655 (C-Br). ^{1}H-NMR (DMSO-d_6): δ 1.29 (s, 3H, CH_3); 4.49 (s, 1H, C_5-H, pyimimdine); 6.69 (s, 1H, C_4-H); 6.79 (s, 1H, C_5-H); 6.92-6.94 (m, 2H, Ar-H); 10.11, 10.14 (2xs, 2x1H, 2xOH).Anal.Calcd.for $C_{15}H_{10}O_4N_3SBr$ (408.23): C, 44.13; H, 2.47; N, 10.29; S, 7.85; Br, 19.57. Found: C, 44.22; H, 2.56; N,10.38; S, 7.93; Br, 19.66. HR-MS (EI^+) m/z 408.95 (4.5%), 409.95(1.1%).

1-{(1-(6-Bromocoumarin-3-yl) ethylidene) amino-6-methyl-2-thioxo pyrimidin-4(1H)-one (5b). M.p.194°C, crystallized from ethanol as yellow crystals. IR (KBr, cm^{-1}): 3375 (NH); 3010-2829(CH aromatic, aliphatic); 1734 (C=O, lactone); 1689 (C=O); 1626 (C=N); 1603-1589 (C=C); 1241 (C=S); 656 (C-Br). ^{1}H-NMR (DMSO-d_6): δ 1.29 (s, 3H, CH_3); 1.31 (s, 3H, CH_3); 5.81 (s, 1H, C_5-H, pyimimdine); 6.68 (s, 1H, C_4-H); 6.78 (s, 1H, C_5-H); 6.99-7.01 (m, 2H, Ar-H); 10.31 (s, 1H, NH, D_2O exchangeable).Anal.Calcd.for $C_{16}H_{12}O_3N_3SBr$ (406.25): C, 47.30; H, 2.98; N, 10.34; S, 7.89; Br, 19.67. Found: C, 47.39; H, 3.07; N,10.43; S, 7.98; Br, 19.76. HR-MS (EI^+) m/z 406.97 (4.5%), 406.98(1.1%).

Acylation of 2-{1-(6-bromocoumarin-3-yl) ethylidene}hydrazine-1-carbothioamide (4) with acetic anhydride, benzoyl chloride and phenacyl bromide. Formation of 6a, 6b and 7

A mixture of **4** (0.01mol.) and acetic anhydride (10 ml) in 10 ml of glacial acetic acid; or **4** (0.01mol.) and benzoyl chloride (0.01 mol.) in 20 ml of acetic acid or **4** (0.01mol.) and phenacyl bromide (0.01 mol.) in 30 ml of mixture of methanol-acetic acid (2:1; by volume) was refluxed for 4h. After cooling, the product that separated in each process was collected, washed well with water and recrystallized from the proper solvent to give**6a**, **6b** and **7**.

N-{1-acetyl-2-(1-(6-bromocoumarin-3-yl)ethylidene)hydrazine-1-carbonthionyl} acetamide (6a).M.p.208°C, crystallized from ethanol as yellow crystals.IR (KBr, cm^{-1}): 3322 (NH); 3000-2828 (CH aromatic, aliphatic);1736 (C=O, lactone); 1689 (C=O, acetyl); 1247 (C=S); 658 (C-Br).). ^{1}H-NMR (DMSO-d_6): δ 1.31 (s, 3H, CH_3); 2.99 (s, 3H, $COCH_3$); 3.21 (s, 3H, $COCH_3$); 6.69 (s, 1H, C_4-H); 6.71 (s, 1H, C_5-H); 6.99-7.11 (m, 2H, Ar-H); 10.11 (s, 1H, NH, D_2O exchangeable).Anal.Calcd.for $C_{16}H_{14}O_4N_3SBr$ (424.27): C, 45.30; H, 3.33; N, 9.90; S, 7.56; Br, 18.83. Found: C, 45.39; H, 3.42; N,9.99; S, 7.65; Br, 18.92. HR-MS (EI^+) m/z 424.99 (4.5%), 424.98 (4.4%).

N-{1-benzoyl-2-(1-(6-bromocoumarin-3-yl)ethylidene)hydrazine-1-carbonthionyl} benzamide (6b).M.p.188°C, crystallized from ethanol as brown crystals.IR (KBr, cm^{-1}): 3323 (NH); 3020-2889 (CH aromatic, aliphatic);1733 (C=O, lactone); 1705-1688 (C=O, aroyl); 1606-1589 (C=C); 1249 (C=S); 656 (C-Br).). ^{1}H-NMR (DMSO-d_6): δ 1.29 (s, 3H, CH_3); 6.67 (s, 1H, C_4-H); 6.73 (s, 1H, C_5-H); 7.02-7.13 (m, 2H, Ar-H); 11.12 (s, 1H, NH, D_2O exchangeable).Anal.Calcd.for $C_{26}H_{18}O_4N_3SBr$ (548): C, 56.93; H, 3.28; N, 7.66; S, 5.83; Br, 14.59. Found: C, 57.02; H, 3.37; N, 7.75; S, 5.92; Br, 14.68. HR-MS (EI^+) m/z 548 (4.5%), 548.31(1.2%).

6-Bromo-3-{1-(2-(4-phenyl thiazol-2-yl)hydrazineylidine) ethyl} coumarin (7).M.p.194°C, crystallized from pet.ether (b.p. 60-80°C) as brown crystals.IR (KBr, cm^{-1}): 3235 (NH); 3010-2882 (CH aromatic, aliphatic); 1735 (C=O, lactone); 1626 (C=N); 1602-1586 (C=C); 1125 (C-S); 655 (C-Br).). ^{1}H-NMR (DMSO-d_6): δ 1.29 (s, 3H, CH_3);6.67 (s, 1H, C_4-H); 6.78 (s, 1H, C_5-H); 6.95 (s, 1H, thiazole-H)); 7.01-7.89 (m, 7H, Ar-H); 10.13 (s, 1H, NH, D_2O exchangeable).Anal.Calcd.for $C_{20}H_{14}O_2N_3SBr$ (440.32): C, 55.56; H, 3.18; N, 9.54; S, 7.27; Br, 18.18. Found: C, 55.56; H, 3.27; N, 9.63; S, 7.36; Br, 18.27. HR-MS (EI^+) m/z 440 (16.2%), 440.99(4.5%); 441.0 (1.2%).

Alkylation of 2-{1-(6-bromocoumarin-3-yl) ethylidene}hydrazine-1-carbo-thioamide (4) with active methylene compounds. Formation of 8a, 8b

A mixture of **4** (0.01mol.) and either chloro acetic acid (0.01 mol.) in 20 ml of acetic acidcontaining freshly fused sodium acetate (0.03 mol.) was refluxed for 2h or/and ethyl chloro acetate (0.01 mol.) in 30 ml of methanolcontaining freshly fused sodium acetate (0.03 mol.)was refluxed for 6h.. After cooling, the product that separated from each process was collected, washed well with waterand recrystallized from ethanol to give **8a** as dark yellow crystals, m.p.162°C/ or **8b**as yellow crystals, m.p.190°C (mixed m.p. with **8a** showed depression).

1-{(1-(6-Bromocoumarin-3-yl) ethylidene) amino)-2-thioxo imidazolidin-4-one(8a).IR (KBr, cm^{-1}): 3235 (NH); 3000-2828 (CH aromatic, aliphatic); 1733 (C=O, lactone); 1687 (C=O); 1623 (C=N); 1601-1583 (C=C); 1249 (C=S); 654 (C-Br).). ^{1}H-NMR (DMSO-d_6): δ 1.37 (s, 3H, CH_3); 4.37 (s, 2H, N-CH_2-C=O);6.53 (s, 1H, C_4-H); 7.01 (s, 1H, C_5-H); 7.35-7.41 (m, 2H, Ar-H); 11.31 (s, 1H, CS-NH-CO) (D_2O exchangeable).Anal.Calcd.for $C_{14}H_{10}O_3N_3SBr$ (380.22): C, 44.23; H, 2.65; N, 11.05; S, 8.43; Br, 21.02. Found: C, 44.32; H, 2.74; N,11.14; S, 8.52; Br, 21.11. HR-MS (EI^+) m/z 380.96 (14.7%), 380.97 (1.1%).

3-{(1-(6-Bromocoumarin-3-yl) ethylidene) amino)-2-thioxo imidazolidin-4-one(8b).IR (KBr, cm^{-1}): 3230 (NH); 3000-2829 (CH aromatic, aliphatic); 1731 (C=O, lactone); 1689 (C=O); 1603-1583 (C=C); 1241 (C=S); 655 (C-Br).). ^{1}H-NMR (DMSO-d_6): δ 1.39 (s, 3H, CH_3); 4.09 (s, 2H, N-CH_2-C=O);6.54 (s, 1H, C_4-H); 7.04 (s, 1H, C_5-H); 7.40-7.50 (m, 2H, Ar-H); 10.12 (s, 1H, CS-NH-CO) (D_2O exchangeable).Anal.Calcd.for $C_{14}H_{10}O_3N_3SBr$ (380.22): C, 44.23; H, 2.65; N, 11.05; S, 8.43; Br, 21.02. Found: C, 44.29; H, 2.79; N,11.19; S, 8.53; Br, 21.19. HR-MS (EI^+) m/z 380.96 (4.5%), 380.97 (1.0%).

Reaction of 3-acetyl-6-bromocoumarin (1) with active nitrile compounds. Formation of 9a, 9b

To a dry solid of coumarin derivative**1** (0.01mol.), either malononitrile (0.01mol.) or ethyl cyanoacetate (0.01mol.) was added followed by ammonium acetate (0.03mol.). The whole reaction mixture was heated on a boiling water-bath for 8h then left to cool. The formed product was triturated with diethyl ether and the solid that formed was collected by filtration, washed well with water and dilute alcohol and recrystallized from the proper solvents as **9a** and **9b**.

2-{(1-(6-Bromocoumarin-3-yl) ethylidene} malononitrile (9a).M.p.228°C,crystalized from pet.ether (b.p. 40-60°C) as dark brown crystals . IR (KBr, cm^{-1}): 3110-2829(CH aromatic, aliphatic); 2222 (C≡N); 1737 (C=O, lactone); 1609-1588 (C=C); 655 (C-Br). ^{1}H-NMR (DMSO-d_6): δ 1.13 (s, 3H, CH_3); 6.57 (s, 1H, C_4-H); 6.81 (s, 1H, C_5-H); 7.12-7.23 (m, 2H,Ar-H).Anal.Calcd.for $C_{14}H_7O_2N_2Br$ (315.13): C, 53.36; H, 2.24; N, 8.89; Br, 25.36. Found: C, 53.45; H, 2.33; N,8.98; Br, 25.45. HR-MS (EI^+) m/z 315.61 (11.7%), 315.97(1.7%).

Ethyl-(E)-3-(bromocoumarin-3-yl)-2-cyanobut-2-enoate(9b).M.p.198°C, crystallized from ethanol as brown crystals.IR (KBr, cm^{-1}): 3020-2928 (CH aromatic, aliphatic); 2223 (C≡N); 1739 (C=O, lactone); 1679 (C=O, ester); 1605-1589 (C=C); 658 (C-Br). ^{1}H-NMR (DMSO-d_6): δ 1.24 (s, 3H, CH_3); 2.76 (t, 3H, CH_3 ester); 3.47 (q, 2H, CH_2 ester); 6.73 (s, 1H, C_4-H); 7.01 (s, 1H, C_5-H); 7.11-7.23 (m, 2H, Ar-H).Anal.Calcd.for $C_{16}H_{12}O_4NBr$ (362.18): C, 53.06; H, 2.34; N, 3.87; Br, 22.06. Found: C, 53.15; H, 3.43; N,3.96; Br, 22.15. HR-MS (EI^+) m/z 362.00 (17.3%), 363.00(1.3%).

General procedure for the synthesis of thiophene derivatives 10a,b

To a solution of either **9a** (0.01mol.) or **9b** (0.01mol.) in 1,4-dioxane (30ml) containing the catalytic amount of triethyl amine (1ml, 0.01mol.) was added sulfur (0.32g, 0.01mol.) and the reaction mixture was heated under reflux for 30 min. then left to cool at room temperature overnight. It was then poured onto ice/water, stirred well and the solid product formed was collected,washed well with water then dilute alcohol and recrystallized from the proper solvents as **10a** and **10b**.

2-Amino-4-(6-bromocoumarin-3-yl)-5-methyl thiophene-3-carbonitrile(10a).M.p.168°C,crystalized from pet.ether (b.p. 60-80°C) as brown crystals . IR (KBr, cm^{-1}): 3233 NH_2; 3009-2920 (CH aromatic, aliphatic); 2222 (C≡N); 1738 (C=O, lactone); 1605-1588 (C=C); 659 (C-Br). ^{1}H-NMR (DMSO-d_6): δ 1.01 (s, 3H, CH_3); 6.71 (s, 1H, C_4-H); 6.91 (s, 1H, C_5-H); 7.06-7.13 (m, 2H, Ar-H),11.10 (s, 2H, NH_2) (D_2O exchangeable).Anal.Calcd.for$C_{15}H_9O_2N_2SBr$ (361.21): C, 49.86; H, 2.49; N, 7.75; S, 8.86; Br, 22.16. Found: C, 49.95; H, 2.58; N,7.84; S, 8.95; Br, 22.25. HR-MS (EI^+) m/z 361.95 (16.2%), 363.95(0.4%).

2-Amino-4-(6-bromocoumarin-3-yl)-5-methylthiophene-3-ethylcarboxylate(10b).M.p.230°C,crystalized from pet.ether (b.p. 60-80°C) as brown crystals.IR (KBr, cm^{-1}): 3339 (NH$_2$); 3010-2828 (CH aromatic, aliphatic); 2230 (C≡N); 1739 (C=O, lactone); 1687 (C=O, ester); 1605-1589 (C=C); 655 (C-Br). ^{1}H-NMR (DMSO-d$_6$): δ 1.31 (s, 3H, CH$_3$); 1.59 (t, 3H, CH$_3$); 4.21 (q, 2H, CH$_2$ ester); 6.71 (s, 1H, C$_4$-H); 6.91 (s, 1H, C$_5$-H); 7.12-7.25 (m, 2H, Ar-H); 11.11 (s, 2H, NH$_2$) (D$_2$O exchangeable).Anal.Calcd.for $C_{17}H_{14}O_4NSBr$ (408): C, 50.24; H, 3.43; N, 3.43;S, 7.84; Br, 19.907. Found: C, 50.33; H, 3.52; N,3.54; S, 7.93;Br, 19.99. HR-MS (EI$^+$) m/z 408.98 (11.31%), 409.08(1.37%).

Results and Discussion:-

3-Acetyl-6-bromocoumarin **1**is an efficient starting material for the synthesis of 6-bromo-3-functionalized coumarin derivatives **(2-10)**. It is easily obtained from the interaction of 5-bromo salicylaladehyde and acetoacetic ester by means of Kneovenagel condensation using piperidine as a catalyst (Al-Haiza et al., 2003).

The relevant absorption data in chloroform are summarized in **Table 2**. The absorption spectra are shown in **(Figs.1-8)** with 3D-geometrical structure **(Figs. 9-18)**. The inductive polarization of the σ skeleton **(Figs. 20-29)** and the atomic charges for every derivative are in **(Tables 2-19)**.

Table 1:-^{13}C-NMR data* of the newly synthesized compounds (1, 2a, 3,4, 5a, 5b, 7, 8a, 10b)

Comp. No.	^{13}C-NMR (DMSO-d6) values; 400MHz
1	29.9 (CH$_3$); 118.4 (CH-9); 120.1 (C-7-Br); 124.9 (C-5); 130.7 (CH-6); 134.9 (CH-8); 137.8 (CH-4); 136.2 (C-3); 151.1 (C-10); 159.8 (C-2-O); 199.1 (C=O)
2a	113.1 (CH-4, furyl); 114.1 (CH-3, furyl); 118.9 (CH-9); 120.3 (C-7-Br); 124.9 (C-5); 129.9 (CHα); 130.9 (CH-6); 134.5 (CH-8); 136.2 (C-3); 138.9 (CHβ); 143.9 (CH-5, furyl); 147.7 (CH-4); 152.4 (C-10); 152.9 (C-2, furyl); 159.8 (C-2-O); 184.7 (C=O)
3	34.9 (CH$_2$-CH-pyrimidine); 48.9 (CH-CH$_2$-pyrimidine); 119.2 (CH-9); 120.3 (C-7-Br); 125.8 (C-5); 127.4, 128.3, 129.7, 130.1 (CH-phenyl); 131.7 (CH-6); 133.7 (C-Cl); 134.9 (CH-8); 136.2 (C-3); 137.8 (CH-4); 140.7 (C-1 phenyl); 152.9 (C-10); 153.9 (C-2-NH$_2$,pyrimidine); 159.9 (C-2-O).
4	14.3 (CH$_3$); 118.4 (CH-9); 120.1 (C-7-Br); 124.7 (C-5); 134.7 (CH-8); 133.7 (CH-4); 136.3 (C-3); 150.2 (C-10); 155.9 (C=N); 159.7 (C-2-O); 181.6 (C=S)
5a	14.5 (CH3); 58.7 (CH-C-pyrimidine); 119.2 (CH-9); 120.3 (C-7-Br); 125.5 (C-5); 130.9 (CH-6); 134.5 (CH-8); 135.3 (CH-4); 136.7 (C-3); 152.1 (C-10); 155.9 (CH3-C=N); 159.7 (C-2-O); 163.1 (N=C-OH-pyrimidine); 179.3 (C=S); 182.3 (N-C-OH-pyrimidine)
5b	15.0 (CH$_3$-C); 16.9 (CH$_3$-pyrimidine); 104.2 (CH-pyrimidine); 119.1 (CH-9); 120.2 (C-7-Br); 125.3 (C-5); 130.3 (CH-6); 133.7 (CH-4); 136.7 (C-3); 152.1 (C-10); 155.9 (CH$_3$-C≡N); 156.7 (CH$_3$-C=N); 159.7 (C-2-O); 161.7 (NH-C=O-pyrimidine); 175.5 (C=S)
7	14.7 (CH$_3$-C); 106.1 (CH-5-thiazolyl); 118.9 (CH-9); 120.2 (C-7-Br); 124.7 (C-5); 127.8, 128.9, 128.7, 129.9 (CH-phenyl); 130.7 (CH-6); 133.0 (C-1-phenyl); 134.1 (CH-4); 134.9 (CH-8); 135.1 (C-3); 137.7 (C-3); 150.7 (C-4-thiazolyl); 152.2 (C-10); 159.7 (C-2-O); 171.3 (C-S-thiazolyl)
8a	14.9 (CH$_3$-C); 62.7 (N-CH$_2$-CO); 119.2 (CH-9); 120.1 (C-7-Br); 125.2 (C-5); 130.3 (CH-6); 134.1 (CH-4); 134.8 (CH-8); 136.1 (C-3); 152.1 (C-10); 155.9 (CH3-C=N); 159.7 (C-2-O); 175.7 (C=O, imidazolyl); 179.3 (C=S, thioimidazolone)
10b	15.7 (CH$_3$); 15.2 (CH$_3$); 61.3 (CH$_2$); 119.2 (CH-9); 120.1 (C-7-Br); 125.9 (C-5); 125.9 (C-4, thiophene); 126.9 (C-3, thiophene); 130.7 (CH-6); 134.8 (CH-8); 135.1 (C-3); 136.7 (C-2, thiophene); 137.1 (CH-4); 152.1 (C-10); 159.9 (C-2-O); 161.3 (C=O ester); 165.7 (C-S)

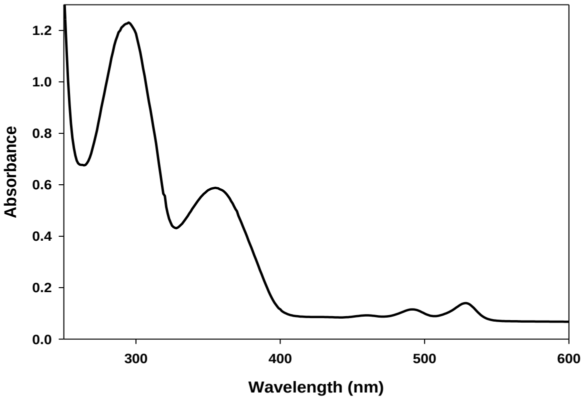
***** Whereδ in ppm.

From the above data of ^{13}C-NMR for a variety of the prepared compounds it is clear that there is a slight shift of the values of some carbons: such as methyl group of compound **1** and the methyl groups of compounds **(5a, 5b, 7, 8a, 10b)**. While for the values of the C=O at position-2 in the benzopyrone ring, its values were around 159.7 to 159.9 ppm, while the value of C=O for compound 10b showed a remarkable shift to the downfield with a value of 161.3 ppm. Similarly, for the substituent C-Br at the position -6 of the benzopyrone ring it showed a values for the ester (C=O)around 120.1-120.3.

Table 2:-UV-Vis absorption of compounds 1-10.

Compd. No.	λ_{max}/nm in $CHCl_3$	Compd. No.	λ_{max}/nm in $CHCl_3$
1	299; 354	**6b**	281
2a	284	**7**	275; 350
2b	299; 354	**8a**	296; 355
3	312; 315; 350	**8b**	298; 325; 355
4	275; 314; 348	**9a**	248
5a	299; 360	**9b**	288; 355
5b	305; 370	**10a**	250
6a	298; 360	**10b**	260; 338

It is clear from the UV absorption results at **Table 2** that 3-acetyl-6-bromo coumarin**(1)** with both electron-donating at the 6-position and an electron-withdrawing group at the 3-position develop the intramolecular charge transfer (ICT) between push- and pull- substituents in the ground and the excited states (Takadate et al., 1995; Murata et al., 2005). Due to this **1** showed two λ maximum at 299 and 354 nm. As we observed there were significant change in the λmax as for compounds **2a**, **3**, **4**, **5b**, **6b**, **7**, **8b**, **9a**, **9b** ,**10a** and **10b**. We tried to correlate the UV absorption of each compound with the 3D- geometrical structure and the distribution of the electronegativity on theatoms for all the tested compounds. Thus, the absorption maxima (λmax), **Fig. 1**, its 3D-geometrical structure, **Fig. 2**the electronic charges of compound **1**, **Fig. 3**and the atomic charges are listed in **Table 3**. Although the Hammett substituent constants are commonly used for the estimation of reactivity and there is no theoretical connection between $\sigma_p$constants and absorbance, these parameters appear to be suitable and easily available to represent the total electronic effects in the ground state because of the absorption of coumarins based upon the typical ICT between push- and pull- substituted coumarins correlated to the Hammett constants. As shown in **Fig.1**the absorption spectrum of compound **1** is influenced by a substituent at position 3 (acetyl group). The λmax value shows two absorption bands at 299 and 354 nm.



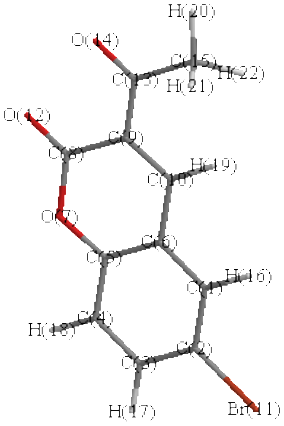


Fig.1:-Absorption spectra of compound 1 Fig.2: The 3D-geometrical structure of1

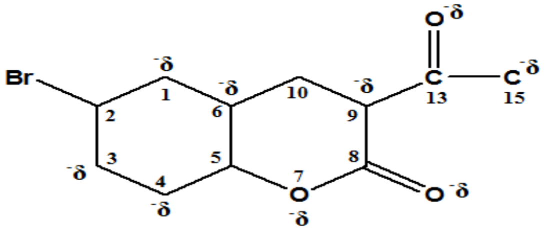


Fig. 3:-The electronic charges of compounds 1

Table 3:-The atomic charges on compound 1

Atom	Charge (Huckel)	Atom	Charge (Huckel)
C(1)	-0.107195	**O(12)**	-0.615503
C(2)	0.0875172	**C(13)**	0.457359
C(3)	-0.0610226	**O(14)**	-0.574395

C(4)	-0.0930942	**C(15)**	-0.175909
C(5)	0.0238654	**H(16)**	0.0222724
C(6)	-0.0119612	**H(17)**	0.0248909
O(7)	-0.0285719	**H(18)**	0.0279933
C(8)	0.54158	**H(19)**	0.0228145
C(9)	-0.0803952	**H(20)**	0.0417989
C(10)	0.0973871	**H(21)**	0.0613984
Br(11)	0.0630137	**H(22)**	0.0613675

As it is observed from **Table 3**, the highest electronegative charges are present on [O,12 -0.615503] and [O,14 -0.574395] while the highest positive charge is at [C,8 0.54158] and [C,13 0.457359]. Therefore, it can be expected that the ICT character of coumarin derivative (1) primarily reflects its absorbance .

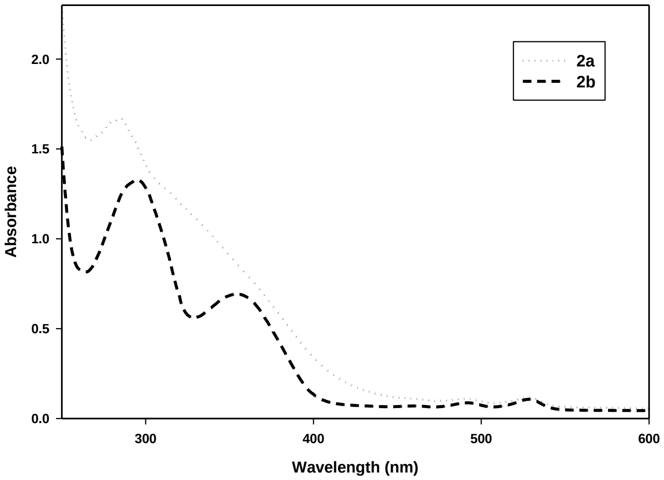
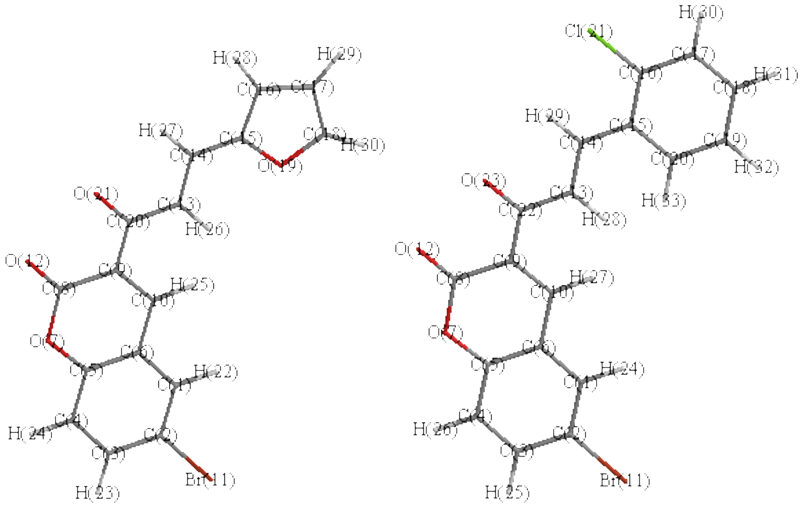


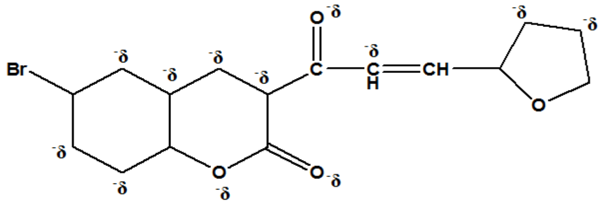
Fig.4:*Absorption spectra of compounds 2a,2b*



(2a) **(2b)**

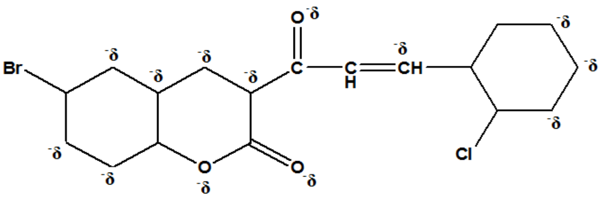
Fig. 5a **Fig. 5b**

Figs.5a,b:-The 3D-geometrical structure of compounds 2a and 2b



(2a)

Fig. 6a



(2b)

Fig. 6b

Figs.6a,b:-The electronic charges of compounds 2a and 2b

Table 4a:-The atomic charges on compound 2a

Atom	Charge (Huckel)	Atom	Charge (Huckel)
C(1)	-0.11045	**C(16)**	-0.122074
C(2)	0.0874404	**C(17)**	-0.150097
C(3)	-0.0649166	**C(18)**	0.141426
C(4)	-0.0932079	**O(19)**	0.0656799
C(5)	0.23473	**C(20)**	0.378142
C(6)	-0.0109829	**O(21)**	-0.686058
O(7)	-0.029664	**H(22)**	0.0222751
C(8)	0.536553	**H(23)**	0.0248908
C(9)	-0.0571234	**H(24)**	0.0279902
C(10)	0.0690654	**H(25)**	0.0316751
Br(11)	0.0630585	**H(26)**	0.0351671
O(12)	-0.613711	**H(27)**	0.025877
C(13)	-0.138844	**H(28)**	0.0247182
C(14)	0.0557416	**H(29)**	0.0268626
C(15)	0.207476	**H(30)**	0.0183606

Table 4b:-The atomic charges on compound 2b

Atom	Charge (Huckel)	Atom	Charge (Huckel)
C(1)	-0.110156	**C(18)**	-0.0094039
C(2)	0.0874896	**C(19)**	-0.0913171
C(3)	-0.0642052	**C(20)**	-0.0277727
C(4)	-0.0931761	**Cl(21)**	0.118783
C(5)	0.235419	**C(22)**	0.381883
C(6)	-0.0109786	**O(23)**	-0.677923
O(7)	-0.029493	**H(24)**	0.022275
C(8)	0.536863	**H(25)**	0.0248908
C(9)	-0.0573418	**H(26)**	0.0279903
C(10)	0.0712333	**H(27)**	0.0316905
Br(11)	0.063137	**H(28)**	0.0472693
O(12)	-0.613215	**H(29)**	0.0227831
C(13)	-0.143607	**H(30)**	0.0246128
C(14)	0.075879	**H(31)**	0.0249511
C(15)	-0.0146362	**H(32)**	0.0249585
C(16)	0.200138	**H(33)**	0.0330388
C(17)	-0.112061		

As shown in **Fig. 4** the λ max values of 3-acryloyl coumarins**2a** and **2b** are quite different from each other. For the 3-substituted coumarin**(2a)** the λmax value shifted to a shorter wavelength 284 nm, thus, indicating the decrease of the pull-character and increase in the push character (2-furyl). In contrast, the absorption spectrum of **2b** differed markedly as compared with that of **2a**. A drastic increase is observed for **2b** substituted with electron-donating group, i.e. 2-chlorophenyl as compared with **2a** with an electron-withdrawing furan ring. Theλmax value of **2b** has shown two values at 295 and 354nm. If we examine this absorption values from the view point of the substituent effect in accordance with the ICT in the coumarin skeleton, we find an electron- donating group at 6-position and an electron-withdrawing group at 3-position i.e. carbonyl attached to an electron-donating group i.e. ethylenic linkage joined to the 2-chlorophenyl. Thus, the introduction of such conjugated system into the coumarin skeleton would make it possible to absorb at a longer wavelength. This is quiteclear from the study of the 3D-geometrical structure, Figs. 5a,b and the electronic charges at Figs. 6a,b.

The absorption spectra of the three different pyrimidine derivatives **3**, **5a** and **5b**in chloroform are shown in **Fig. 7**; their 3D-geometrical structure are shown in **Figs. 8a-c** respectively; their atomic charge values are listed in **Tables 5a-c** and the distribution of the atomic charges on the atoms are shown in **Fig. 9a-c** respectively. As shown in **Fig. 7**, the differences in substituents in the 3-position of coumarin and in the pyrimidine itself affected the absorbance properties of these derivatives. The shape of the absorption bands of **5b** around 300 and 370 nm is markedly different from that of **3** and **5a**. Compound **5b** with an oxo-, and a methyl group at 4-, and 6-position in the pyrimidine ring. Has also a small shoulder band at 280 nm and another shoulder at 365 nm, whereas compound**3** has a small shoulder at 312 nm and two splitting absorption bands at 315 and 350 nm; and compound **5a** had two splitting absorption bands at 299 and 360 nm respectively, as shown in **Fig. 7**. Such differences in the substituents wheather for the coumarin ring or for the pyrimidine ring were frequently observed in aromatic heterocyclic rings. The λmax values of the pyrimidine derivatives shifted to longer wavelengths in the order **5b**>**5a**>**3** with decreasing absorbance.

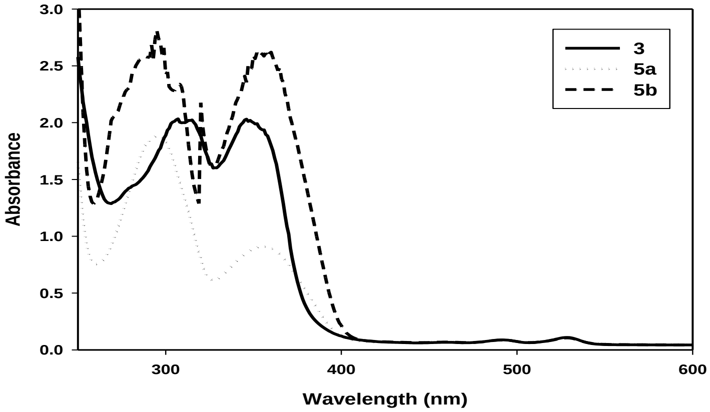
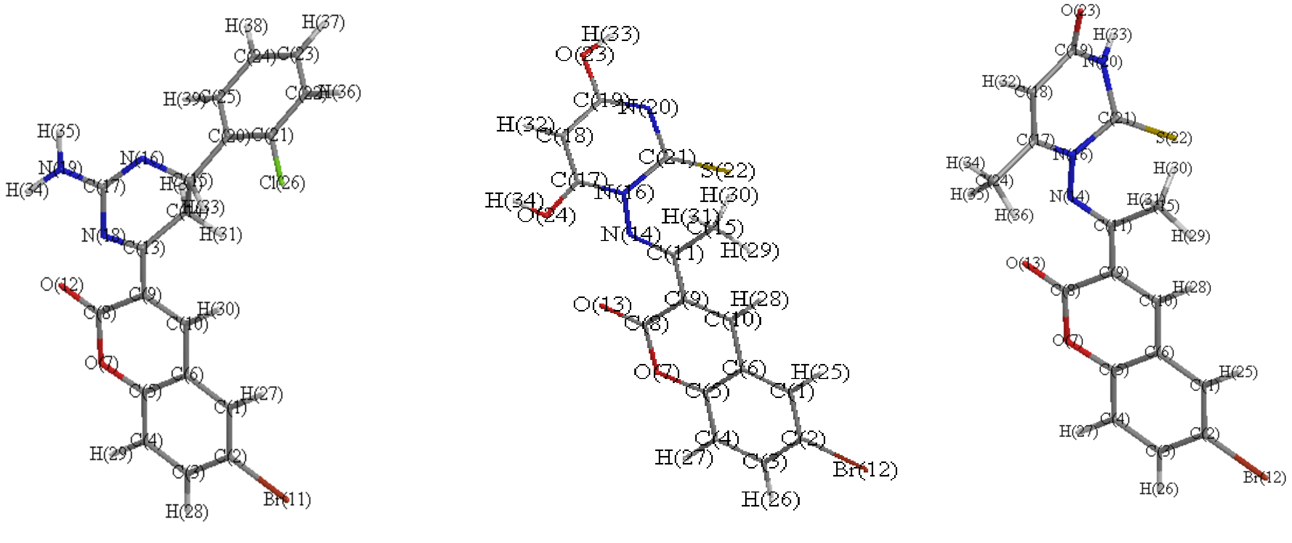


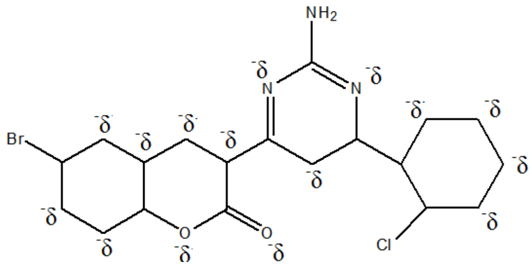
Fig.7:-Absorption spectra of thepyrimidine derivatives3,5a,5b



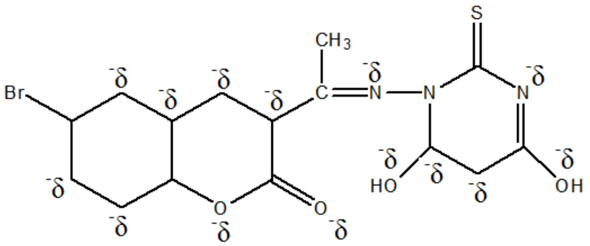
(3) **(5a)** **(5b)**

Fig. 8a **Fig. 8b** **Fig. 8c**

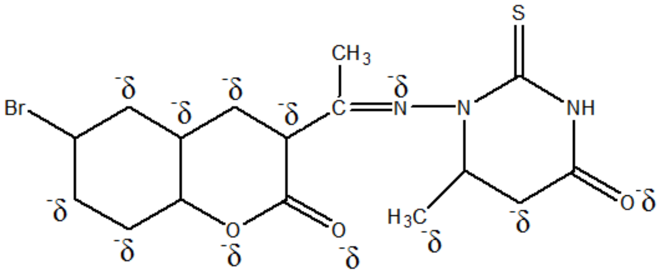
Figs.8a-c:-The 3D-geometrical structure of the pyrimidine derivatives3, 5a and 5b



(3)
Fig. 9a



(5a)
Fig. 9b



(5b)
Fig. 9c

Figs.9a-c:-The electronic charges of the pyrimidine derivatives 3, 5a and 5b

Table 5a:-The atomic charges on compound 3

Atom	Charge (Huckel)		Atom		Charge (Huckel)
C(1)	-0.125065		**C(21)**		0.138177
C(2)	0.0862908		**C(22)**		-0.118526
C(3)	-0.0895761		**C(23)**		-0.0581649
C(4)	-0.0945644		**C(24)**		-0.0097407
C(5)	0.211186		**C(25)**		-0.073938
C(6)	-0.00695849		**Cl(26)**		0.0756535
O(7)	-0.0347845		**H(27)**		0.0222743
C(8)	0.540592		**H(28)**		0.024892
C(9)	0.00920941		**H(29)**		0.0279973
C(10)	-0.00560257		**H(30)**		0.0202521
C(11)	0.329862		**H(31)**		0.0386436
Br(12)	0.0620156		**H(32)**		0.0479099
O(13)	-0.612991		**H(33)**		0.0146354
C(14)	-0.117398		**H(34)**		0.0910529
C(15)	0.0912645		**H(35)**		0.0920319
N(16)	-0.705527		**H(36)**		0.0247048
C(17)	0.389091		**H(37)**		0.0250286
N(18)	-0.380718		**H(38)**		0.0251298
N(19)	0.102104		**H(39)**		0.0250785
C(20)	0.00847715				

Table 5b:-The atomic charges on compound 5a

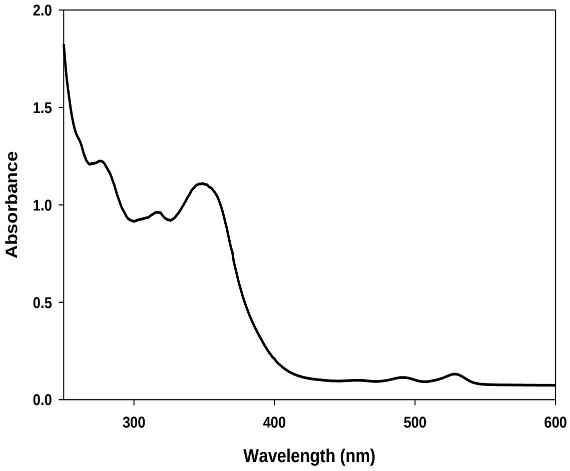
Atom	Charge (Huckel)	Atom	Charge (Huckel)
C(1)	-0.311162	**C(18)**	-0.371439
C(2)	0.0826467	**C(19)**	0.331091
C(3)	-0.280638	**N(20)**	-0.433181
C(4)	-0.193345	**C(21)**	0.0994015
C(5)	0.151311	**S(22)**	0.772409

C(6)	-0.0431207	**O(23)**	-0.293831
O(7)	-0.193489	**O(24)**	-0.273038
C(8)	0.316841	**H(25)**	0.0222669
C(9)	-0.255329	**H(26)**	0.0248917
C(10)	-0.474853	**H(27)**	0.0279911
C (11)	0.137205	**H(28)**	0.0366395
Br (12)	0.0601401	**H(29)**	0.0553327
O(13)	-0.750288	**H(30)**	0.236671
N(14)	-0.0879357	**H(31)**	0.0452898
C(15)	0.0955997	**H(32)**	0.0340528
N(16)	0.706505	**H(33)**	0.209231
C(17)	0.306387	**H(34)**	0.209745

Table 5c:-The atomic charges on compound 5b

Atom	Charge (Huckel)	Atom	Charge (Huckel)
C(1)	-0.308019	**C(19)**	0.341065
C(2)	0.0827121	**N(20)**	0.125678
C(3)	-0.277456	**C(21)**	0.191869
C(4)	-0.1906	**S(22)**	0.887579
C(5)	0.15086	**O(23)**	-0.774595
C(6)	-0.041456	**C(24)**	-0.146238
O(7)	-0.189924	**H(25)**	0.0222675
C(8)	0.323217	**H(26)**	0.0248918
C(9)	-0.246447	**H(27)**	0.0279905
C(10)	-0.474761	**H(28)**	0.036846
C(11)	0.112878	**H(29)**	0.0459786
Br(12)	0.0601665	**H(30)**	0.306063
O(13)	-0.749243	**H(31)**	0.0311497
N(14)	-0.145524	**H(32)**	0.0293343
C(15)	0.207109	**H(33)**	0.101309
N(16)	0.679334	**H(34)**	0.0391953
C(17)	0.0507678	**H(35)**	0.0499017
C(18)	-0.432751	**H(36)**	0.0488498

We examined in detail the absorption characteristic of thecoumarin derivative**(4)** from the viewpoint of the substituent effect in connection with the ICT in the coumarin skeleton and postulated that the ICT from an eletron-donating at 6-position to an electron-withdrawing lactone carbonyl group at the 2-position as well as the introduction of a conjugated system into the coumarin skeleton at position 3 would make it possible to absorb the UV in a different wavelength region. As shown in **Table 2** three absorption peaks at λmax 275, 314 and 348 nm as shown in **Fig. 10**.



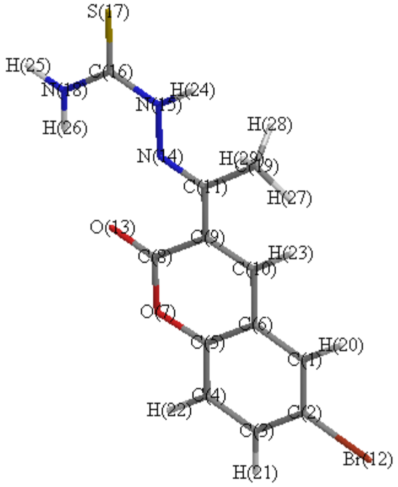


Fig.10:-Absorption spectra of compound4Fig.11: The 3D-geometrical structure of 4

The 3D-geometrical structure of **4**, **Fig. 11**; the electronic charges on the atoms, **Fig. 12** and the atomic charges in **Table 6** explain the effect of the ICT to shift the absorption shift to the given values in **Table 2**.

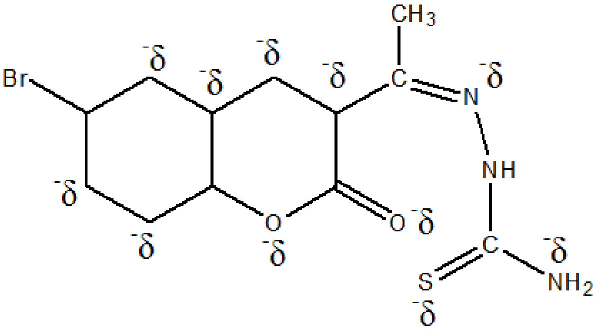


Fig.12:-The electronic charges of compound 4

It is clear from the above structure of the coumarin derivative (4) that the introduction of such conjugated system into the coumarin skeleton would make it possible to influence the absorption of such compound.

Table 6:-The atomic charges on compound 4

Atom	Charge (Huckel)	Atom	Charge (Huckel)
C(1)	-0.150316	**C(16)**	0.289853
C(2)	0.0861106	**S(17)**	-0.616851
C(3)	-0.116657	**N(18)**	-0.00629009
C(4)	-0.09868	**C(19)**	-0.217982
C(5)	0.191445	**H(20)**	0.0222685
C(6)	-0.000590249	**H(21)**	0.0248917
O(7)	-0.0481222	**H(22)**	0.0279907
C(8)	0.535433	**H(23)**	0.03674
C(9)	-0.0228509	**H(24)**	0.0731446
C(10)	-0.143293	**H(25)**	0.0989737
C(11)	0.0555343	**H(26)**	0.100811
Br(12)	0.0617842	**H(27)**	0.0599689
O(13)	-0.604728	**H(28)**	0.048721
N(14)	-0.131672	**H(29)**	0.0486968
N(15)	0.400977		

The absorption maxima (λmax) as listed in **Table 2** agreed well with ^{13}C-NMR as the presence of long chain conjugated system in coumarin skeleton tends to shift the absorption wavelength region. Thus, the λmax value of 6a showe the values 298 and 360 nm as a result of the presence of an electron-withdrawing to acetyl groups in the side chain. As shown in the absorption spectrum of 6b, it showed a shift of the λmax to a lower value of 281 nm and abroad peak. As a result of the substituent effect in connection with the ICT in the coumarin skeleton with one from the electron-donating group at the 6-position and the long conjugated electron-withdrawing group at the 3-position which would make it possible to shift the absorption properties. It should be also noted that the annulation possibly affected the absorption properties of the coumarin derivative **(6b)**.

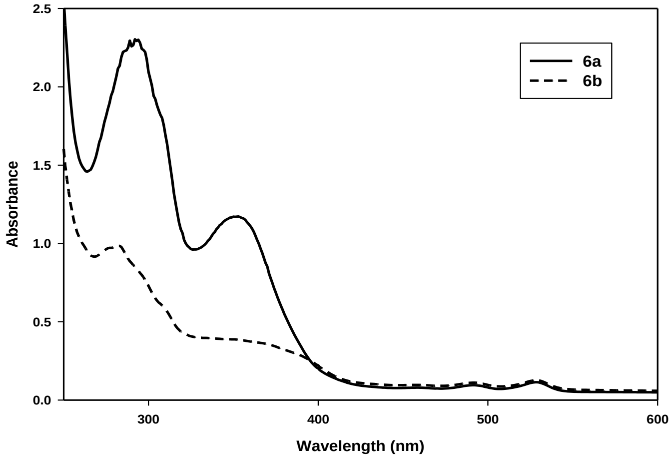
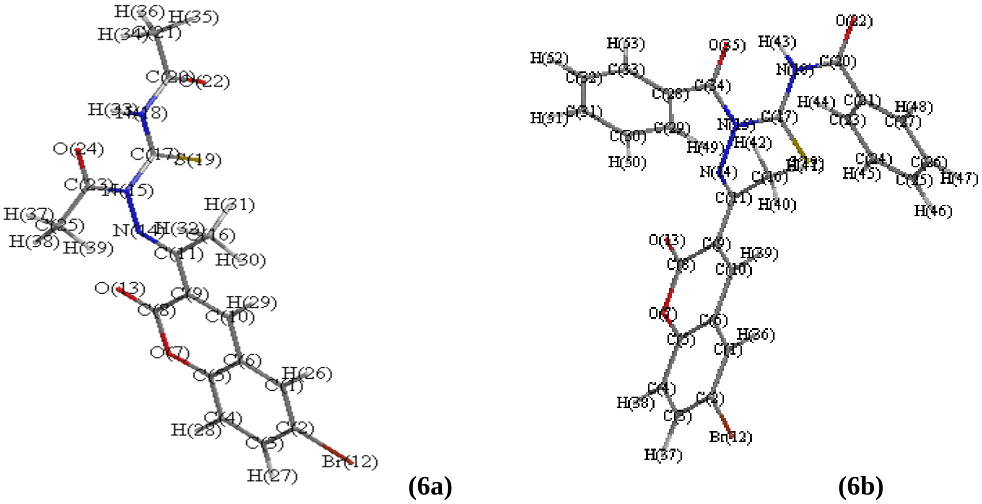


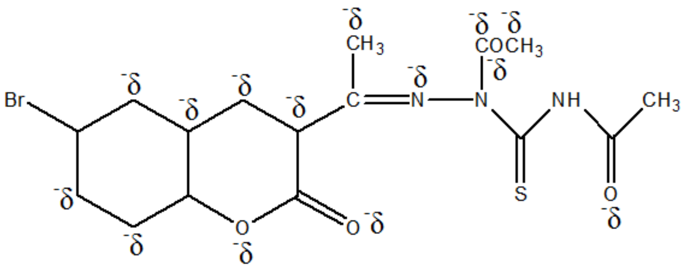
Fig.13:-Absorption spectra of compounds6a and 6b



(6a) **(6b)**

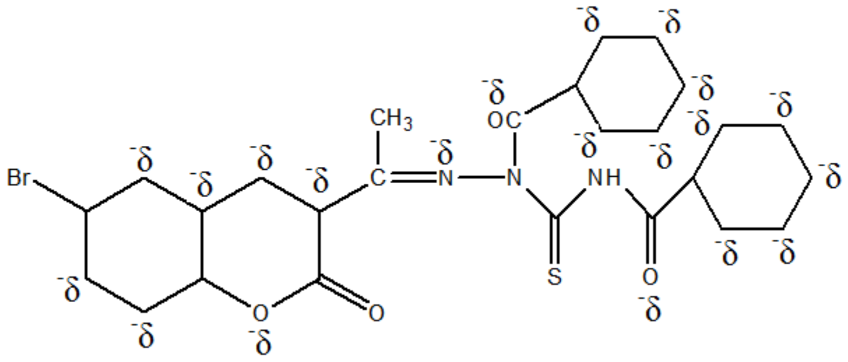
Fig. 14aFig. 14b

Figs.14 a,b:-The 3D-geometrical structure of compounds 6a and 6b



(6a)

Fig. 15a



(6b)

Fig. 15b

Figs.15a,b:-The electronic charges of compound 6a and 6b

Table 7a:-The atomic charges on compound 6a

Atom	Charge (Huckel)	Atom	Charge (Huckel)
C(1)	-0.223644	**C(21)**	-0.168353
C(2)	0.0847743	**O(22)**	-0.527822
C(3)	-0.192043	**C(23)**	0.332851
C(4)	-0.141796	**O(24)**	-0.767331
C(5)	0.175577	**C(25)**	-0.180472
C(6)	-0.0262885	**H(26)**	0.0222687
O(7)	-0.114042	**H(27)**	0.0248919
C(8)	0.452366	**H(28)**	0.0279909
C(9)	-0.148798	**H(29)**	0.0367368
C(10)	-0.278685	**H(30)**	0.0608166
C(11)	0.165596	**H(31)**	0.0534115
Br(12)	0.0611505	**H(32)**	0.0538613
O(13)	-0.66436	**H(33)**	0.122425
N(14)	-0.114914	**H(34)**	0.0436567
N(15)	0.584123	**H(35)**	0.058538
C(16)	-0.218275	**H(36)**	0.0585124
C(17)	0.253515	**H(37)**	0.0439381
N(18)	0.271191	**H(38)**	0.055881
S(19)	0.226193	**H(39)**	0.0563905
C(20)	0.440165		

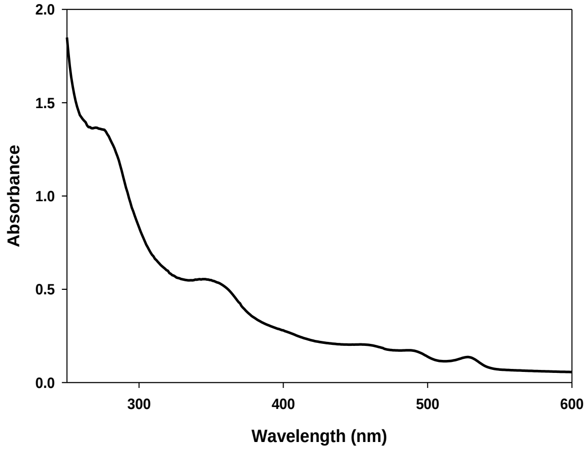
Table 7b:-The atomic charges on compound 6b

Atom	Charge (Huckel)	Atom	Charge (Huckel)
C(1)	-0.309449	**C(28)**	0.0613199
C(2)	0.0830272	**C(29)**	-0.107089
C(3)	-0.280412	**C(30)**	-0.0332056
C(4)	-0.188969	**C(31)**	-0.0532303
C(5)	0.149824	**C(32)**	-0.0340803
C(6)	-0.0438014	**C(33)**	-0.0422777
O(7)	-0.188562	**C(34)**	0.33607
C(8)	0.350284	**O(35)**	-0.793954
C(9)	-0.264691	**H(36)**	0.0222683
C(10)	-0.474465	**H(37)**	0.0248918
C(11)	0.175735	**H(38)**	0.0279911
Br(12)	0.0602791	**H(39)**	0.0367251
O(13)	-.0735765	**H(40)**	0.0606454

N(14)	-0.222822	**H(41)**	0.0537528
N(15)	0.626405	**H(42)**	0.0875406
C(16)	-0.236328	**H(43)**	0.12173
C(17)	0.232519	**H(44)**	0.0196973
N(18)	0.263935	**H(45)**	0.0263062
S(19)	1.00736	**H(46)**	0.0251999
C(20)	0.454628	**H(47)**	0.0262531
C(21)	0.223041	**H(48)**	0.020519
O(22)	-0.789434	**H(49)**	0.0805186
C(23)	0.113992	**H(50)**	0.0243616
C(24)	-0.0501794	**H(51)**	0.0251641
C(25)	-0.0227694	**H(52)**	0.0255612
C(26)	-0.0608999	**H(53)**	0.0209637
C(27)	0.0641413		

Since the absorption of coumarinof the UV radiation is related to the ICT between push- and pull-substituents in the molecule. As the introduction of conjugated systems into the coumarin skeleton affects the absorption and would make it possible to absorb in a different wavelength region, it is clear that coumarin derivative **7** showed two λmax 275 and 350 nm which is quite different from the absorption of the coumarin derivative **(1)**, this might be due to the introduction of a heterocyclic moiety with a phenyl ring to the conjugated chain at position-3 in the coumarin skeleton and would make it possible to shift the λmaxto a lower or higher value.

The ICT from the electron-donating group at position-6 to the electron-withdrawing at position-3 and the electron-withdrawing lactone carbonyl group at the 2-position contributed to the absorbance intensity.



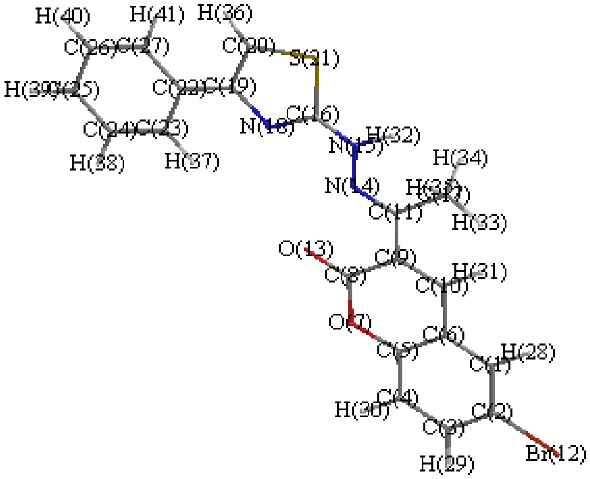


Fig.16:-Absorption spectra of compound7Fig.17: The 3D-geometrical structure of 7

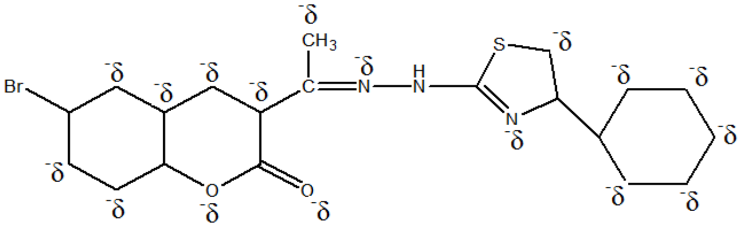


Fig.18:-The electronic charges of compound 7

Table 8:-The atomic charges on compound 7

Atom		Charge (Huckel)		Atom		Charge (Huckel)
C(1)		-0.181498		**C(22)**		0.0546073
C(2)		0.0858124		**C(23)**		-0.0883906
C(3)		-0.150679		**C(24)**		-0.026914

C(4)		-0.106882		**C(25)**		-0.0864682
C(5)		0.17155		**C(26)**		-0.0292531
C(6)		-0.00703369		**C(27)**		-0.0885063
O(7)		-0.0656555		**H(28)**		0.0222662
C(8)		0.540082		**H(29)**		0.0248915
C(9)		-0.0467028		**H(30)**		0.0279907
C(10)		-0.258865		**H(31)**		0.0367046
C(11)		0.0145949		**H(32)**		0.0536307
Br(12)		0.0603196		**H(33)**		0.0576535
O(13)		-0.603196		**H(34)**		0.0480015
N(14)		-0.107965		**H(35)**		0.0479824
N(15)		0.588424		**H(36)**		0.0310787
C(16)		0.201268		**H(37)**		0.0230572
C(17)		-0.215113		**H(38)**		0.0251426
N(18)		-0.534208		**H(39)**		0.0251684
C(19)		0.0491362		**H(40)**		0.025045
C(20)		-0.24004		**H(41)**		0.028142
S(21)		0.593585				

The structural isomerism in compounds**8a** and **8b** causes a slight difference in the ICT which in turn causes a slight shift in the absorption values and intensely. Thus, the absorption maxima of **8a** (λmax) showed values of 298 and at 355 nm, while the λmax of **8b** showed slight shift to a higher value 298 and shoulder at 355 nm respectively. The ^{13}C-NMR chemical shifts of **8a** and **8b(Table 1)**correlated to this shift in the absorption values. The decrease in the value of λmax for compound **(8a)** from **(8b)** may be attributed to the structure –N-CH_2-CONH in **8a** whereasthe structure at **(8b)**is –N-CO-CH_2NH, thus this difference in the arrangement might disturb the push-pull π-electron system.

The absorption spectra of the two isomers 8a and 8b in chloroform are shown in **Fig. 19** and their values are summarized in **Table 2**. As predicated the arrangement of the atoms in the imidazolinone-2-thioxo affected the value and shape of absorption of **8a** from **8b**. The shape of absorption band of **8b** from around 298 to 355 nm is markedly different from that of **8a**. Compound 8b with arrangement of the atoms is –N-CO-CH_2-NHC=S had three peaks and two small shoulder bands at around 250-310 nm, whereas compound 8a had two splitting absorption bands at 296 and 355 nm as shown in Fig. 19 and in which the arrangement of the atoms is N-CH_2-CO-NH-C=S. This difference in the shape and value of absorption may be due to this quite different arrangement.

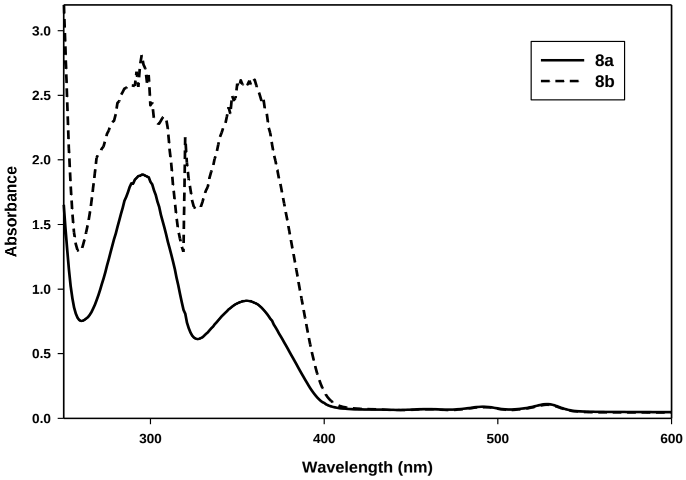
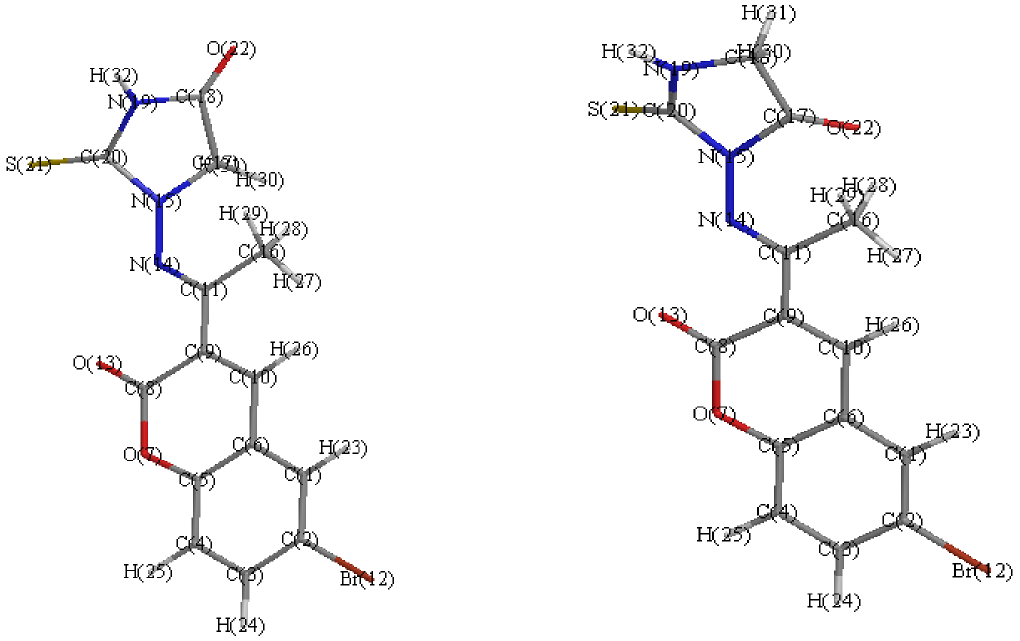


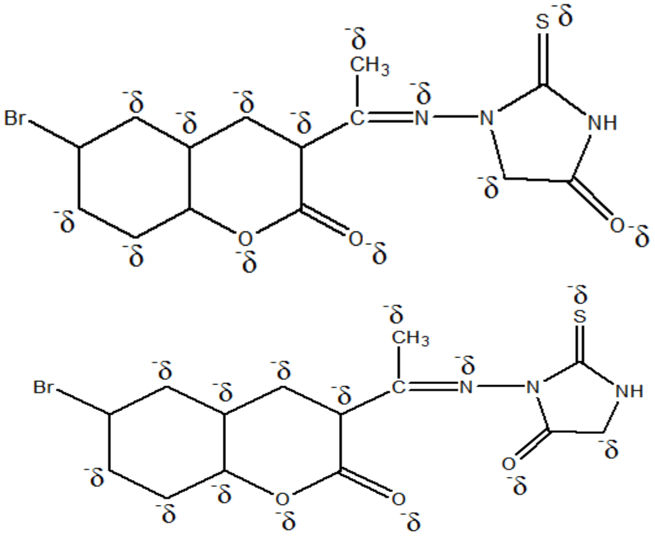
Fig.19:-Absorption spectra of compounds 8a and 8b



(8a) **(8b)**

Fig. 20aFig. 20b

Figs.20a,b:-The 3D-geometrical structure of compounds 8a and 8b



(8a)(8b)

Fig. 21aFig. 21b

Figs.21a,b:-The electronic charges of compounds 8a and 8b

Table 9a:-The atomic charges on compound 8a

Atom		Charge (Huckel)		Atom		Charge (Huckel)
C(1)		-0.187266		**C(17)**		-0.119385
C(2)		0.0856932		**C(18)**		0.459463
C(3)		-0.156516		**N(19)**		0.151732
C(4)		-0.112355		**C(20)**		0.320705
C(5)		0.173753		**S(21)**		-0.394262
C(6)		-0.0113855		**O(22)**		-0.679045
O(7)		-0.072776		**H(23)**		0.0222697
C(8)		0.530712		**H(24)**		0.0248924

C(9)		-0.0677608		**H(25)**		0.0279909
C(10)		-0.251511		**H(26)**		0.0367588
C(11)		0.0666177		**H(27)**		0.0596153
Br(12)		0.0615203		**H(28)**		0.0969244
O(13)		-0.605056		**H(29)**		0.0440078
N(14)		-0.0871128		**H(30)**		0.113501
N(15)		0.549567		**H(31)**		0.0495272
C(16)		-0.228279		**H(32)**		0.0974574

Table 9b:-The atomic charges on compound 8b

Atom		Charge (Huckel)		Atom		Charge (Huckel)
C(1)		-0.145901		**C(17)**		0.35555
C(2)		0.0862101		**C(18)**		-0.00592473
C(3)		-0.111206		**N(19)**		0.0391762
C(4)		-0.0982421		**C(20)**		0.316057
C(5)		0.196234		**S(21)**		-0.427539
C(6)		-0.0067666		**O(22)**		-0.534174
O(7)		-0.0463912		**H(23)**		0.0222686
C(8)		0.5351		**H(24)**		0.0248916
C(9)		-0.028543		**H(25)**		0.0279905
C(10)		-0.118691		**H(26)**		0.0367988
C(11)		0.100705		**H(27)**		0.0549504
Br(12)		0.0618579		**H(28)**		0.151626
O(13)		-0.607286		**H(29)**		0.026545
N(14)		-0.18147		**H(30)**		0.0380903
N(15)		0.501305		**H(31)**		0.031467
C(16)		-0.309998		**H(32)**		0.0936592

We examined in detail the 3D-geometrical structures of each of compounds **8a** and **8b(Fig.20a, 20b)** as well as the electronic charge values for each one (atom, charge, Hückel) **Tables 9a** and **9b** and we found a drastic differences in values for compound **8a** [C-1 -0.187266]; [C-3 -0.156516]; [C-4 -0.112355]; [C-6 -0.0113855]; [O-7 -0.072776]; [C-9 -0.0677608]; [C-10 -0.251511]; [O-13 -0.605056]; [N-14 -0.0871128]; [C-16 -0.228279]; [C-17 -0.119385]; [S-21 -0.394262]; [O-22 -0.679045].

For compound **8b** [C-1 -0.145901]; [C-3 -0.111206]; [C-4 -0.0982421]; [C-6 -0.0067666]; [O-7 -0.0463912]; [C-9 -0.028543]; [C-10 -0.118691]; [O-13 -0.605056]; [N-14 -0.18147]; [C-16 -0.309998]; [C-18 -0.00592473]; [S-21 -0.427539]; [O-22 -0.534174]. We found that for each corresponding atom in these two isomers, the value of the charge atom (Hückel) is quite different. This difference in that parameterappears to be suitable to explain the difference in the ICT as well as the push-pull in each of the two isomers, which is in agreement with differences in the ^{13}C-chemical shifts for each isomer **(Table 1)**.

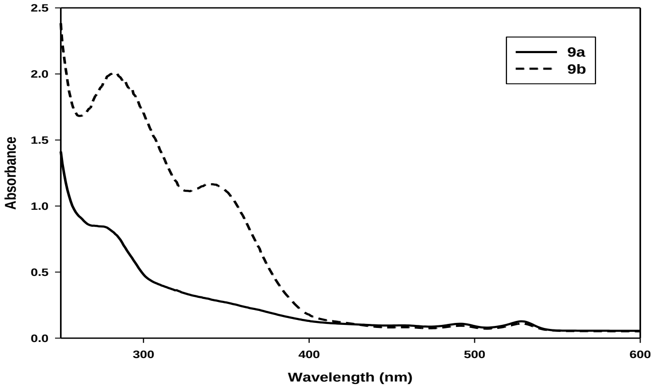
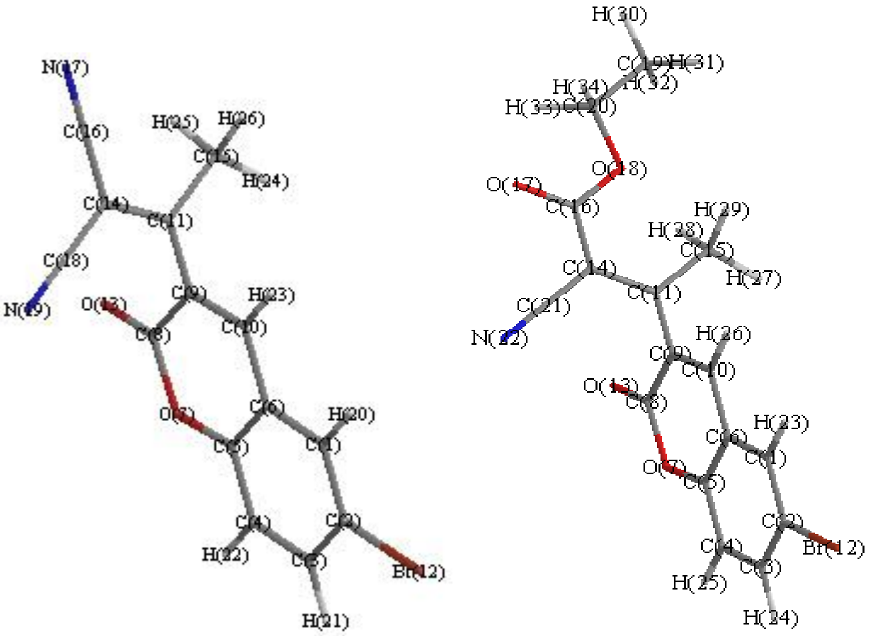


Fig.22:-Absorption spectra of compounds 9a and 9b

The absorption spectrum of 3-substituted coumarin**9a** differed markedly from the absorption spectrum of **1** .A drastic decrease in the value of λmax of the former from that of **1**. The comparison of the two substituents, which contain an electron-withdrawing groups at the 3-position i.e. cyanoethylidene for **9a** and an acetyl for **1**.The prominent decrease in **9a** of λmax value 248 nm is 51 nm may be attributed to the presence of two cyano groups at the substituent in position-3, where the push-pull π-electron system and the bromine at 6-position must cause such distinct difference in the absorption spectrum.

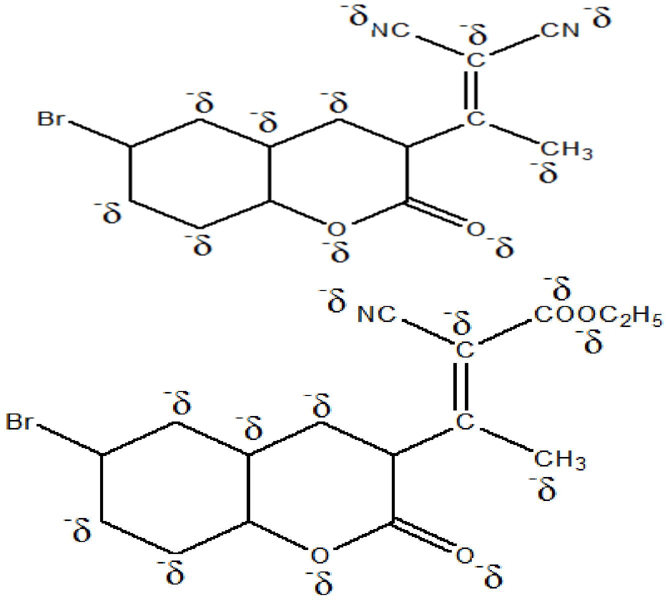


(9a) **(9b)**

Fig. 23aFig. 23b

Figs.23a,b: The 3D-geometrical structure of compounds 9a and 9b

There is also a quiet difference in the value of λmax for 9a which showed a value of 248 nm in the shape of a boarded band, while the absorption maxima for 9b showed λmax at 288 and 355 nm.



(9a)(9b)

Fig. 24aFig. 24b

Figs.24a,b:-The electronic charges of compounds 9a and 9b

This difference in the value of the shape and absorption is in agreement with the electronic charges **(Figs. 24a, 24b)** and the atomic charges (Hückel) **(Tables 10a, 10b)**.

Table 10a:-The atomic charges on compound 9a

Atom		Charge (Huckel)		Atom		Charge (Huckel)
C(1)		-0.132162		**C(14)**		-0.109746
C(2)		0.082158		**C(15)**		-0.121923
C(3)		-0.0993221		**C(16)**		0.391327
C(4)		-0.0947218		**N(17)**		-0.566814
C(5)		0.201508		**C(18)**		0.390599
C(6)		-0.00264064		**N(19)**		-0.566878
O(7)		-0.031715		**H(20)**		0.0222879
C(8)		0.550827		**H(21)**		0.0248927
C(9)		0.0618906		**H(22)**		0.0248927
C(10)		-0.036765		**H(23)**		0.0166579
C(11)		0.377534		**H(24)**		0.0378938
Br(12)		0.0620138		**H(25)**		0.0607915
O(13)		-0.609548		**H(26)**		0.0597967

Table 10b:-The atomic charges on compound 9b

Atom		Charge (Huckel)		Atom		Charge (Huckel)
C(1)		-0.132142		**O(18)**		-0.155357
C(2)		0.082162		**C(19)**		-0.146161
C(3)		-0.100057		**C(20)**		0.184002
C(4)		-0.0947895		**C(21)**		0.367827
C(5)		0.2009		**N(22)**		-0.561898
C(6)		-0.00238361		**H(23)**		0.0222878
O(7)		-0.0314084		**H(24)**		0.248928
C(8)		0.551848		**H(25)**		0.0279988
C(9)		0.0639771		**H(26)**		0.016653
C(10)		-0.0391424		**H(27)**		0.0327431
C (11)		0.358796		**H(28)**		0.0630318
Br (12)		0.0620184		**H(29)**		0.0618147
O(13)		-0.60874		**H(30)**		0.043139
C(14)		-0.135647		**H(31)**		0.04091478
C(15)		-0.118353		**H(32)**		0.0408996
C(16)		0.585865		**H(33)**		0.0130931
O(17)		-0.735311		**H(34)**		0.0130988

The absorption spectrum of **10a** differed markedly as compared to 3-substituted coumarin**1**. The λmax value of **10a** was shifted to a shorter wavelength with a value of250 nm, i.e. it shifted to a shorter wavelength region by a value of 49 nm. This prominent decrease may be attributed to the increase in the electron-withdrawing ability at the 3-position which confirms that the ICT from the bromine at the 6-position to a substituent such as thiophene moiety containing a cyano group at the 3-position of the coumarin skeleton greatly contributes to the absorption wavelength. In contrast, the absorption spectrum of coumarin derivative**10b**differed markedly with a drastic decrease in itsλmax for it was 260 and 338nm. This decrease in absorption by 49 nm for **10a**and of 39, 16 nm for **10b** may be attributed to the non-equivalent push-pull π-electron systems between a bromo atom at the 6-position and a thiophene moiety containing a cyano/or ethoxy carbonyl substituents, attached to position-3 of the coumarin skeleton.

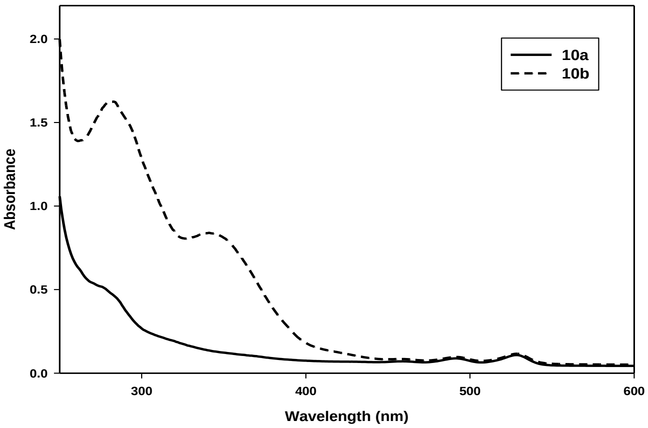
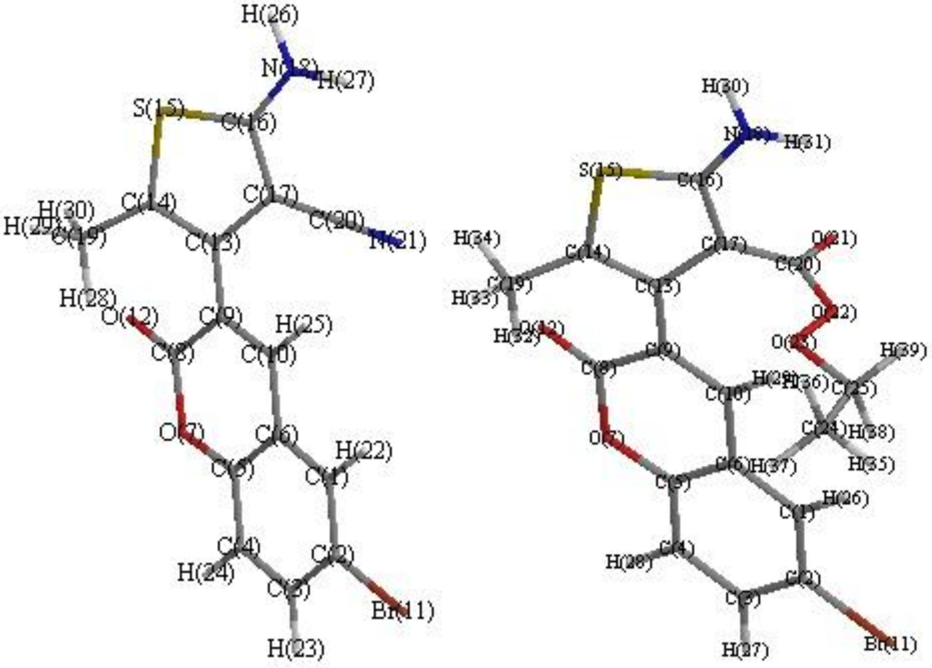


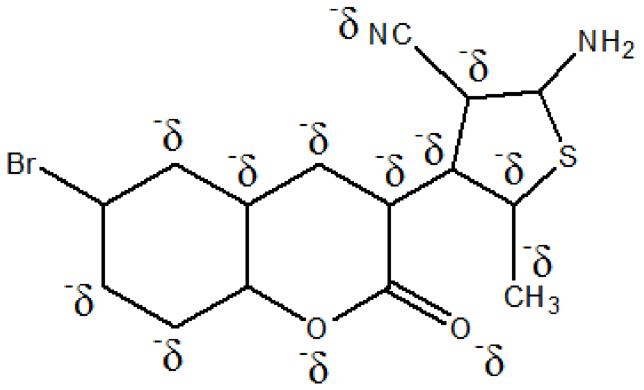
Fig.26:-Absorption spectra of compounds 10a and 10b

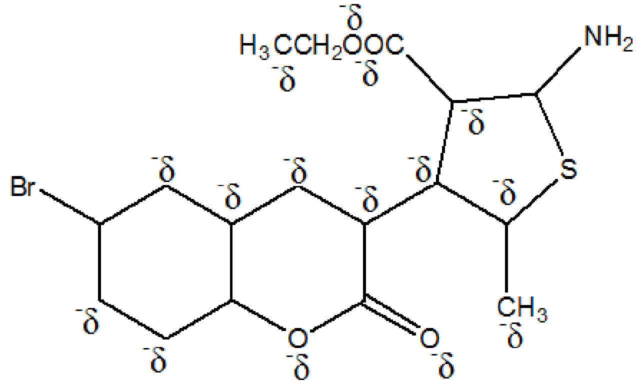


(10a) **(10b)**

Fig. 27aFig. 27b

Figs.27a,b:-The 3D-geometrical structure of compounds 10a and 10b





(10a)(10b)

Fig. 28aFig. 28b

Figs.28a,b:-The electronic charges of compounds 10a and 10b

Table 11a:-The atomic charges on compound 10a

Atom		Charge (Huckel)	Atom		Charge (Huckel)
C(1)		-0.0172618	**C(16)**		0.185962
C(2)		0.0809684	**C(17)**		-0.315107
C(3)		-0.141162	**N(18)**		0.146747
C(4)		-0.119384	**C(19)**		-0.244487
C(5)		0.183359	**C(20)**		0.33784
C(6)		-0.00164162	**N(21)**		-0.667969
O(7)		-0.0124352	**H(22)**		0.0222981
C(8)		0.352646	**H(23)**		0.0248936
C(9)		-0.0218841	**H(24)**		0.027983
C(10)		-0.0234347	**H(25)**		0.0409085
Br(11)		0.0596293	**H(26)**		0.0951379
O(12)		-0.260596	**H(27)**		0.0954076
C(13)		-0.080908	**H(28)**		0.222913
C(14)		-0.0785942	**H(29)**		0.043149
S(15)		0.508479	**H(30)**		0.0347272

Table 11b:-The atomic charges on compound 10b

Atom		Charge (Huckel)		Atom		Charge (Huckel)
C(1)		-0.172062		**O(21)**		-0.726274
C(2)		0.0809424		**O(22)**		0.0679545
C(3)		-0.140501		**O(23)**		-0.181191
C(4)		-0.119491		**C(24)**		-0.143909

C(5)		0.183944		**C(25)**		0.16834
C(6)		-0.00086332		**H(26)**		0.0223628
O(7)		-0.124899		**H(27)**		0.024894
C(8)		0.350937		**H(28)**		0.0279832
C(9)		-0.018227		**H(29)**		0.0495549
C(10)		-0.240854		**H(30)**		0.0951614
Br(11)		0.0596301		**H(31)**		0.0952985
O(12)		-0.258047		**H(32)**		0.223266
C(13)		-0.0799844		**H(33)**		0.041085
C(14)		-0.140058		**H(34)**		0.032253
S(15)		0.505781		**H(35)**		0.0425332
C(16)		0.134522		**H(36)**		0.0408521
C(17)		-0.39003		**H(37)**		0.0408371
N(18)		0.0771427		**H(38)**		0.0117381
C(19)		-0.241548		**H(39)**		0.011581
C(20)		0.589342				

Conclusion:-

We have prepared a variety of 6-bromo-3-substituted coumarin derivatives containing either conjugated substituents or heterocyclic nuclei at the 3-position by simple one pot reactions. The structures of the newly synthesized derivatives were elucidated by their IR, ^{1}H,^{13}C-NMR and mass spectra measurements. The UV/Vis absorption of these compounds were investigated in accordance with their ^{13}C-NMR as well as 3D-geometrical structures in order to correlate the relation of the different substituents with their absorption and to throw a more precise information on the effect of the ICT on the absorption. In future, the study of computer calculations of substituent effects in the excited state may enable the absorption characteristics to be predicted more precisely.

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