Indian J. Phys. **78A** (3), 381-383 (2004)

Note

AN INTERNATIONAL JOURNAL
IJP A

X-ray diffraction studies of 8-(-2-azothiazolyl-)-7-hydroxy 4-methyl coumarin

P P Hankare*, A H Jagtap, L V Gavali, P S Battase and S R Naravane

Department of Chemistry, Shivaji University
Kolhapur-416 004, Maharashtra, India

E-mail : p_hankare@rediffmail.com

Received 8 May 2003, accepted 28 July 2003

Abstract : Ligand 8-(-2-azothiazolyl-)-7 hydroxy 4-methyl coumarin was synthesized by condensing 2-aminothiazole and 7-hydroxy 4-methyl coumarin. Purified sample has been subjected to X-ray diffraction to elucidate structural information. Structure of the sample is found to be tetragonal belonging non-primitive system. Strain broadening effects are also examined and discussed.

Keywords : X-ray diffraction, azo substituted coumarin, strain broadening.

PACS No. : 61.10.Nz

Coumarin compounds are found to be of great importance due to their fascinating useful properties like fluorescence, biological activity, coordinating abilities *etc*. Coumarin derivatives have been found to exhibit antibiotic, anti fungal, anticoagulating and plant growth regulating properties [1-3]. Azo coumarins were recommended as potential carcinostats [4]. Thiazolyl azocoumarins show antifungal antibacterial activities along with fluroscence properties [5, 6].

Thiazole derivatives have attracted considerable attention by Chemists since many of them have been used in medicinal therapy [7,8]. Derivatives of thiazole have been widely used as antibacterial [9], antifungal [10], anticancer [11] and antihelmintic [12] agents. It is known that the activity of many enzymes depends upon the interaction of thiazole group with transition metal ion. It is therefore of considerable interest and importance to know the detail about coordinating behaviour of ligands containing this important functional group, we have synthesized one such ligand 8-(-2 azothiazolyl-) 7-hydroxy 4-methyl coumarin and examined for structural properties.

All chemicals used were of AR grade. Ligand was prepared by diazotisation of 2-aminothiazole (1g, 0.01 mole) using conc. HCl and $NaNO_2$ following the method reported earlier [13] and consequently coupled with 7-hydroxy 4- methyl coumarin (1.76g, 0.01 mole) dissolved in 15 ml of aqueous 2N NaOH. Reaction mixture was stirred for 1 h at 0°C and then allowed to warm slowly at room temperature. Brick red precipitate formed was filtered, washed with water and recrystallised from ethanol. Purity of the product was checked by TLC (Thin layer chromatography).

Colour, yield, melting point and elemental analysis are as follows :

Brick red, yield 72%, M.P. – 189°C UV –39370 cm^{-1} and 44843 cm^{-1} ($\pi \rightarrow \pi^*$ organic moiety), 30487 cm^{-1} ($\pi - \pi^*$ of C = O group) and 23310 cm^{-1} (– N = N–), IR- 3478 cm^{-1} (ν OH), 1625 cm^{-1} ν (N = N), Thiazole viabration [1377 cm^{-1} (C = N), 1459 cm^{-1} (C = S)], 1678 cm^{-1} [ν (C = O)], 1212 cm^{-1} ν (C = O).

$C_{13}H_9O_3N_3S$, C: 54.34%, H: 3.15% N: 14.62%, S: 11.16% found C: 55.10 %, H: 3.27, N: 14.37%, S: 10.97%.

Structure of the ligand was tentatively fixed as given in Figure 1 on the basis of elemental analysis, IR, UV and ^{1}HNMR spectral studies.

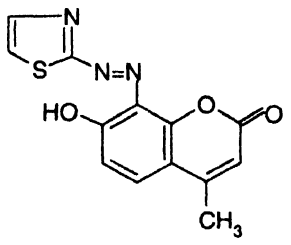

Figure 1. Structure of ligand.

* Corresponding Author

XRD (X-ray diffraction) spectra were recorded on Philips PW 3710 diffractometer attached to a digitized computer alongwith graphical assembly in which CuKα radiation source connected with tube Cu-Ni 25 kV/20 mA was used.

X-ray diffractogram of 8-(-2-azothiazolyl-)-7-hydroxy 4-methyl coumarin is shown in Figure 2. The XRD pattern shows fourteen reflections between 10° and 100° (2θ) with maxima at $2\theta = 26.75°$ corresponding to a value of $d = 3.3305$ Å.

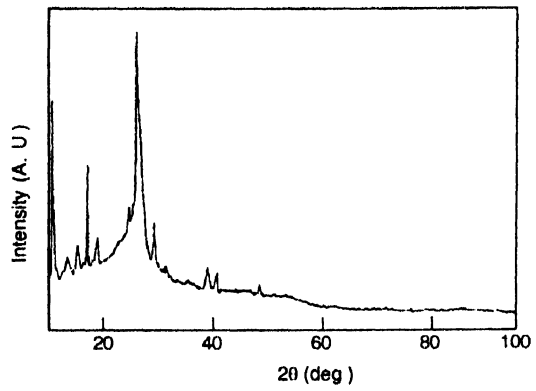

Figure 2. X-ray diffractogram of Ligand

Indexing of spectrogram with respect to the prominent peaks have been carried out by using computer software which uses an interactive method for analysis of powder diffraction data and having indexing program of version 2.3 named as Powdmult, prepared by E.Wu of School of Physical Sciences, Flinder University of South Australia.The indexing is confirmed on the basis of correction obtained between observed and calculated d and Q values and having symmetry constraints [14]. This method also yielded *hkl* (miller indices) values. Relative intensities corresponding to the prominent peaks have been calculated (Table 1).

Table 1. XRD data of 8 - (-2 azothiazolyl-) -7 hydroxy 4- methyl coumarin.

Peak No.	2 θ degree	d (Å) observed	d (Å) calculated	Q_{obs}	Q_{cal}	h k l	RI (%)
1	11.25	7.8586	7.8586	0.0162	0.0162	0 0 3	37.5
2	13.82	6.4025	6 4025	0.0243	0.0243	1 0 1	5 14
3	17.45	5.0180	5.0775	0.0397	0.0387	1 0 3	33.1
4	19.22	4.5963	4.6131	0.0478	0.0469	1 1 1	11 1
5	24.19	3.5673	3.6766	0.0785	0.0739	1 1 1	14.7
6	26.75	3.3305	3.3302	0.0901	0.0902	1 1 5	100
7	27.85	3.1935	3.2013	0.0980	0.0975	2 0 2	33.5
8	29.71	2.9952	3.0048	0.1114	0.1107	1 0 7	24.3
9	32.14	2.8018	2.7824	0.1273	0.1291	2 1 3	7.14
10	38.43	2.3443	2.3404	0.1819	0.1825	2 2 1	7.57
11	39.02	2.3005	2.3066	0.1889	0.1879	2 2 2	11.3
12	40.65	2.2184	2.2175	0.2031	0.2033	3 0 0	10.8
13	43.57	2.0828	2.0755	0.2306	0.2321	3 0 4	15.7
14	48.26	1.8877	1.8842	0.2806	0.2816	1 0 12	5.59

Experimental density was determined by using specific gravity method which further enabled to calculate volume of unit cell. Number of atoms per unit cell n was calculated by using the equation (ρ = nM/NV) and was found to be 2 With this number, theoretical density was fixed.

Other parameters such as pore fraction, packing fraction, particle size, radius of atom were then calculated. Space group and point group of ligand were noted from International Table for X-ray crystallography [15]. All these values are presented in Table 2.

Table 2. X-ray parameters of 8 - (-2 azothiazolyl-) -7 hydroxy 4- methyl coumarin.

Structure	Tetragonal
Space group	I4/mmm
Laue group	4/m
Point group	4/mmm
Symmetry of lattice	Non primitive
Lattice parameters	$a = b = 6.6525$ Å
	$c = 23.5758$ Å
Bond angles	$\alpha = \beta = \gamma = 90°$
Vol of unit cell	1043,37 Å^3
Density ρ (Experimental)	0.4571 gr/cc
Density ρ (Theoretical)	0 4456 gr/cc
Pore fraction	0 0251
Thickness of particle	232 Å

Comparison of the value of d and Q reveals a good agreement between the calculated and observed values of d and Q, on the basis of assumption of tetragonal structure. Structure yields values for lattice constants and cell volume as $a = b = 6.6525$ Å, $= 23.5758$ Å and $V = 1043.37$ Å^3 respectively. These values were further refined by using weight fraction method. Refined parameters were used for finding out Space group and Laue group. In conjunction with such cell parameters, the condition [16,17] such as $a = b \neq c$ and $\alpha = \beta = \gamma = 90°$ required for the sample to be tetragonal were tested and found to be satisfactory Hence, it is concluded that structure of the present ligand is tetragonal.

Particle size of the sample was calculated by using an equation $t = 0.9\ \lambda / B \cos\theta$. These parameters can distinguish between natural particle size and particle size due to broadening effect [18]. This was done by calculating full width at half maximum (B) corresponding to its Bragg's θ and thereby computing cos and sin values.

The nature and behaviour of these values for present ligand are shown graphically in Figure 3. A plot of parameter $B\cos\theta$ against $\sin\theta$ was observed to be a straight line parallel to $\sin\theta$ (*i.e.* x) axis indicating an absence of any strains caused by inhomogeneous lattice distortions and compositional

fluctuations. Hence, present sample seems to be homogeneous with respect to the particle size distribution.

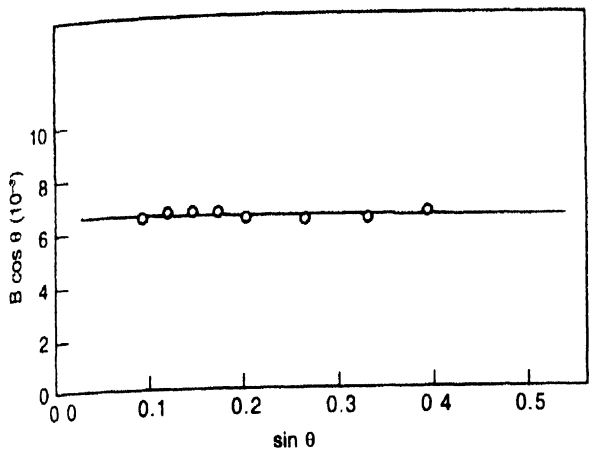

Figure 3. Analysis of Homogeneity.

References

[1] B Kalluraya, A M Shoney and Shalini Isdoor *Indian J Heterocyclic Chem* **11(2)** 59 (2001)

[2] El Sayed, A M Allah and D A Abd *Phosphours Sulphur Silicon and Related Elements* **170** 75 (2001)

[3] A M Mandour, M Ahmed, M I Nassar and Z Bazza *Egypt J Pharm Sci* **36** 71 (1995)

[4] V S Jolly and J P N Singh *J Indian Chem Soc* **IVIII** 527 (1989)

[5] A El Ansary, E M Abbas and M M Omav *Kolorisztikai Ertesitia* **6** 164 (1987)

[6] B Kalluraya, P V Isloor and Rai B Ganesh *J. Indian Council of Chemists* **16** 26 (1999)

[7] M Akabar Ali and S E Livingstone *Coordination Chem. Rev* **13** 101 (1974)

[8] R J Sundberg and R B Martin *Chem Rev* **74** 471 (1974)

[9] N H Bhavsar, A V Kasture and K R Desai *Asian J Chem.* **11** 165 (1999)

[10] S G Wadodkar and A V Kasture *J Indian Chem Soc.* **61** 374 (1984)

[11] H C Gerg and R A Sharma *J Pharm Soc.* **59** 348 (1970)

[12] B C Sharma *Bull Chem. Soc. Jpn* **40** 2422 (1967)

[13] H H Hovind *The Anal Rev* **100** 769 (1975)

[14] R T Pattar, K R Chowkimath and V G Tulasigiri *Indian J Phys.* **73A** 343 (1999)

[15] J D H Donney and David Haker *Tables of Space & Group Criteria, Crystallographiques Naturalist Canadien* **67** p33 and p160 (1940)

[16] B D Cullity *Elements of X-ray Diffraction* (Massachusetts · Addison - Wesley) (1956)

[17] H S Peiser, H P Rookshy, A J C Wilson *X-ray Diffraction by Polycrystalline Material* (London Institute of Physics) (1956)

[18] P P Hankare, L V Gavali and S S Chavan *Indian J Phys* **76A** 587 (2002)