



Imidazole derivatives as the organic precursor of ZnO nano particle

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ABSTRACT

*N*₁-Hydroxy-2,4,5-trisubstituted imidazoles were synthesized starting from 1,2-diketones. The crystal structure of 4,5-dimethyl-2-(3-nitrophenyl)-1*H*-imidazol-1-ol has been determined. An unusual intermolecular hydrogen bonding through the association of water molecule has been reported. These imidazole derivatives can be thought of as the organic precursor for the synthesis of zinc oxide nano particles.

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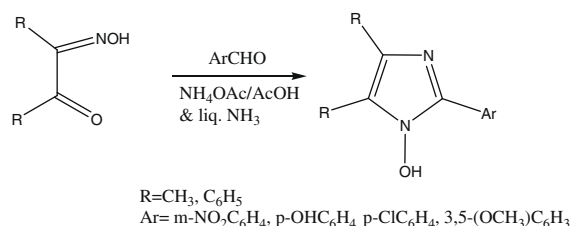
The imidazole ring is found in highly significant biomolecules, amino acids and alkaloids, which have been shown to exhibit interesting biological activities such as antimicrobial, anticryptococcal, and inhibition of nitric oxide synthase and cytotoxic activities.¹ Molecular recognition through fluorescence sensing has attracted much attention in recent times.² A significant number of imidazole derivatives were being reported to be implemented in electronic devices, optoelectronic devices, etc.³ In continuation of our search for suitable sensing element to sense urea or thiourea⁴ we have synthesized *N*₁-hydroxy-2,4,5-trisubstituted imidazoles⁵ (Scheme 1).

¹H NMR data⁶ is in accordance with that of the desired structure. A lot of work has been reported with respect to the imidazole derivatives but exact structural feature of the said compound was not provided. Thus we report here in the crystal structure of *N*₁-hydroxy-2-(*m*-nitrophenyl)-4,5-dimethyl imidazole.

We have started our work with an intention of synthesizing the imidazole derivative and to study the reactivity of these imidazole derivatives. The study of X-ray crystallographic analysis revealed the co-crystallization of these imidazoles with water (Fig. 1) even though the crystal is being grown from DMSO and the nitrogen of the imidazole get protonated forming quaternary nitrogen without any counter ion. Further analysis of the data has revealed that the water molecule is responsible for the intermolecular hydrogen bond and thus results in an array of imidazole molecules with the help of the hydrogen bonding (Fig. 2).

McCann and co-workers⁷ have reported that in the process of complexation, the neutral *N*-hydroxyimidazole ligands have tauto-

merized and are in the zwitterion form with the uncoordinated imidazole imine *N*-atom being protonated and the oxime O-atom deprotonated. Further, the solvate water molecule makes three hydrogen bonds to the protonated amine, the oxime O-atom and to a perchlorate O-atom. Furthermore, the intramolecular proton transfer in an aqueous medium is quite high, that has been proposed by the theoretical calculation using SCRF models⁸ for prototropic tautomerism of imidazolone in an aqueous solution. Thus, our finding is well established with reference to the works^{7,8} and we herein report that it is not during the complexation the imidazole imine nitrogen get protonated⁸ rather the ligand structure itself is associated with the zwitterion form. Furthermore the stabilization of the protonated amine is so high that during the process of synthesis liquid NH₃ is used which is unable to remove this proton. It emphasizes that the nucleophilicity of the nitrogen is quite high. The delocalization of the charge within the imidazole is quite evident with respect to the behavior of the imidazole nucleus. The solvate water molecule form three hydrogen bonds to the protonated amine, the oxime O-atom and the nitro group O-atom resulting in the self-assembly (Fig. 2).



Scheme 1. Synthesis of Imidazole derivatives.

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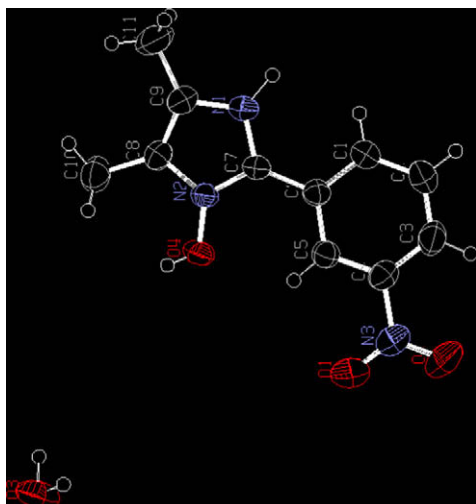


Figure 1. Single crystal structure of 4,5-dimethyl-2-(3-nitrophenyl)-1H-imidazol-1-ol.

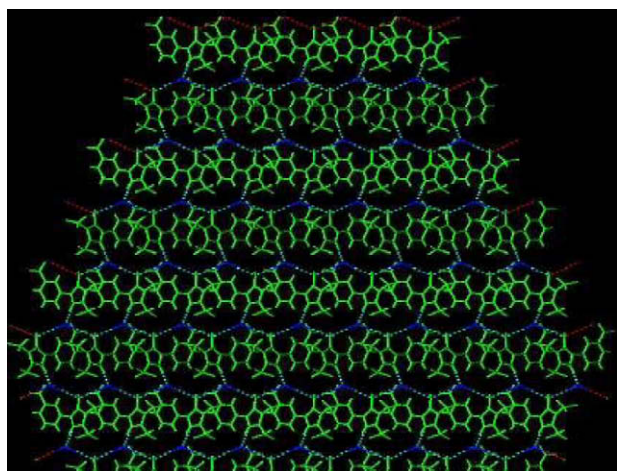
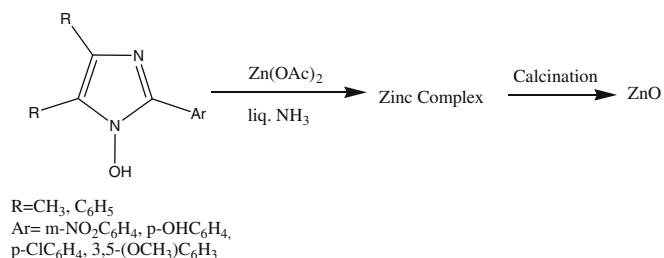


Figure 2. Self-assembled crystal structure of 4,5-dimethyl-2-(3-nitrophenyl)-1H-imidazol-1-ol.

This delocalization of the charge is quite significant and thus can be thought worthy to be used as Organic Laser, as it is quite evident that the water bridge that is existing, is corresponding to the metastable state. The charge balance could nicely be explained through the extensive delocalization of the charge over the quaternary nitrogen.

The water bridge also opens up much opportunity to synthetically tune the molecule and get appropriate result. In this context, the recent finding of Zeolite Imidazolate Framework (ZIF)⁹ is noteworthy.



Scheme 2. Preparation of ZnO nano particles.

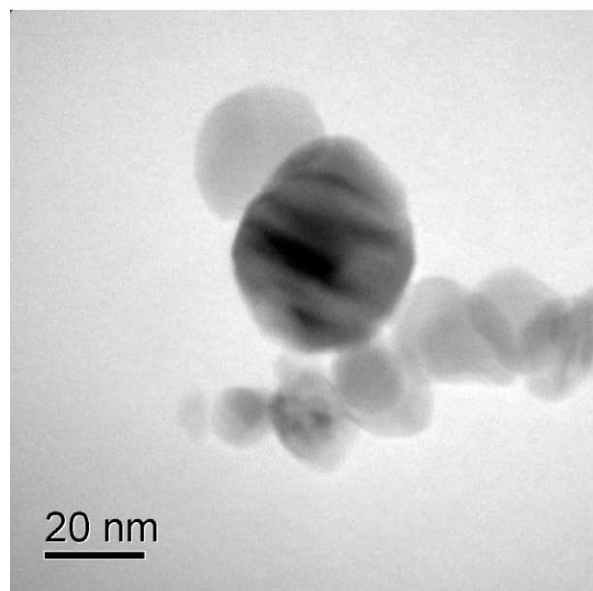
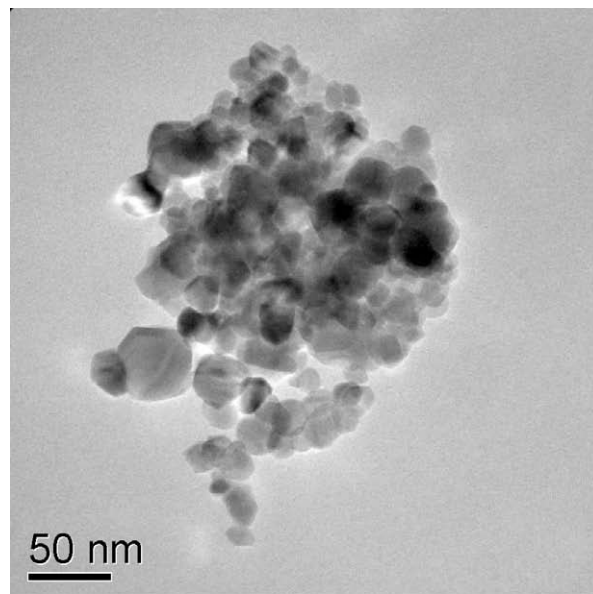


Figure 3. TEM picture of ZnO nano particle.

The structural feature of the hydroxy imidazole derivative provides an excellent groove with the hydroxyl, nitro group and the nitrogen atom for the metal ions to bind in. The complex can be thought as a probable precursor for the preparation of metal oxide nano particles. Thus, we have prepared the zinc oxide nano particles from the zinc complex of the imidazole derivatives⁵ (Scheme 2). The zinc complexes were subjected to calcination.¹⁰

The calcined zinc complex of *N*₁-hydroxy-2-(*m*-nitrophenyl)-4,5-dimethyl imidazole, is shown to be having pure ZnO, whereas the zinc oxide nano particles obtained from the *N*₁-hydroxy-2-(*m*-hydroxyphenyl)-4,5-dimethyl imidazole and *N*₁-hydroxy-2-(*p*-hydroxyphenyl)-4,5-dimethyl imidazole contain trace amount of carbon in the nano size as evident from the XRD analysis. TEM picture of zinc oxide nano particles (Fig. 3) obtained from *N*₁-hydroxy-2-(*m*-nitrophenyl)-4,5-dimethyl imidazole seems to be all spherical and free from any carbon as expected from the XRD-data.

Thus, we report herein the unusual hydrogen bonding in case of *N*₁-hydroxy-2-(*m*-nitrophenyl)-4,5-dimethyl imidazole with the solvent assistance. This also helps in the self-assembly of the imidazole molecules in a regular order forming an interesting water

bridge in between. Further, the delocalization of the charge is quite interesting and can open up an opportunity to be utilized as organic laser. Also, these imidazole derivatives can also be utilized as the organic precursors to prepare the metal oxide nano particles as depicted by the formation of zinc oxide nano particles.

Further, the zinc oxide nano particles formed show very good fluorescence behavior as expected and can be explored upon for some electronic activity after suitable doping.

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References and notes

1. Luca, L. De. *Curr. Med. Chem.* **2006**, *13*, 1.
2. Louis, C.; Bazzi, R.; Bridot, J. L. *Chem. Mater.* **2005**, *17*, 1673; Blazquez, M. T.; Muniz, F. M.; Saez, S.; Simon, L. M.; Alonso, A.; Raposo, C.; Lithgous, A.; Alazar, V.; Moran, J. R. *Heterocycles* **2006**, *69*, 73; Costa, P. G. S.; Oliveira, E.; Lodeiro, C.; Raposo, M. M. *Sensors* **2007**, *7*, 2096.
3. Fang, Z.; Wang, S.; Zhao, L.; Xu, Z.; Ren, J.; Wang, X.; Yang, Q. *Mater. Lett.* **2007**, *61*, 4803.
4. Chetia, B.; Iyer, P. K. *Tetrahedron Lett.*, **2006**, *47*, 8115; *ibid*, 2007, *48*, 47.
5. Synthesis of *N*₁-hydroxy-2,4,5-trisubstituted imidazoles: General procedure: To a mixture of diacetyl monoxime (0.01 mol) in acetic acid (20 mL) were added aromatic aldehyde (0.01 mol) and ammonium acetate (4 g). The mixture was stirred for 24 h. The resulting mixture was diluted with water (20 mL) and neutralized with liquor ammonia. The precipitate was filtered out and recrystallized from ethanol to give the pure product (92% yield). Synthesis of the Zinc Complex: General Procedure: To the imidazole derivative (0.001 mol) in methanolic ammonia medium saturated solution of zinc acetate (0.0025 mol) in methanol (20 mL) was added dropwise with stirring. After the complete addition the mixture was allowed to stir for additional 1 h. After removal of the solution the requisite solid was obtained (78% yield).
6. ¹H NMR (400 MHz, Perkin Elmer, DMSO-*d*₆, TMS standard) data: (a) 4,5-dimethyl-2-(3-nitrophenyl)-1*H*-imidazol-1-ol: δ 1.9 (dd, 3H); 2.3 (dd, 3H), 3.2 (s, 1H), 7.8–8.7 (m, 4H, ArH), mp 196–200 °C; (b) 4,5-dimethyl-2-(4-hydroxyphenyl)-1*H*-imidazol-1-ol: δ 1.9 (dd, 3H); 2.3 (dd, 3H), 3.2 (s, 1H), 6.8 (m, 2H, ArH), 7.3 (m, 2H, ArH) decomposed at 120 °C.
7. Abuskhuna, S.; McCann, M.; Briody, J.; Devereux, M.; Kavanagh, K.; Kayal, N.; McKee, V. *Polyhedron* **2007**, *26*, 4573.
8. Sanchez-Migallon, A.; de la Hoz, A.; Lopez, C.; Claramunt, R. M.; Infantes, L.; Motherwell, S.; Shankland, K.; Nowell, H.; Alkorta, I.; Elguero, J. *Helv. Chim. Acta* **2003**, *86*, 1026.
9. Phan, A.; Doonan, C. J.; Uribe-Romo, F. J.; Knobler, C. B.; O'Keeffe, M.; Yaghi, O. M. *Acc. Chem. Res.* **2010**, *43*, 58.
10. For determining isothermal weight loss, studies were done in the temperature range of 473–673 K. Known amount of the sample was taken inside a silica crucible and was introduced into a muffle furnace having provision for step wise increase in temperature. The samples were heated to the desired temperature for 2 h, then cooled to 473 K in the furnace and kept inside desiccators. All the weights were measured by a digital electronic balance AFCOSET-180A with an accuracy of ±0.1 mg. The total weight loss of a sample at a particular temperature was calculated as given below:

$$\% \text{ Weightloss} = \frac{100(w_1 - w_2)}{w_1}$$

*w*₁ = Weight of the sample before heating.

*w*₂ = Weight of the sample after heating.