文章编号：1006-9941(2011)06-0743-02

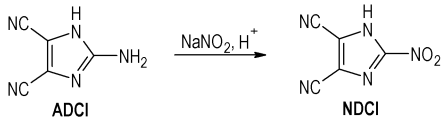
# One-pot Synthesis of 2-Nitro-4,5-dicyano-1*H*-imidazole

**XU Cheng**[1], **BI Fu-qiang**[1], **FAN Xue-zhong**[1], **LI Ji-zhen**[1], **WANG Bo-zhou**[1], **GE Zhong-xue**[1], **LIU Qing**[1], **ZHANG Guo-fang**[2]
(1. *Xi'an Modern Chemistry Research Institute, Xi'an* 710065, *China*; 2. *Key Laboratory of Applied Surface and Colloid Chemistry, Ministry of Education/School of Chemistry & Chemical Engineering, Shaanxi Normal University, Xi'an* 710062, *China*)

In the last few decades, nitroimidazoles have been investigated mostly due to their properties as antibiotics, radiosensitizers and anti-protozoans[1-3]. Recently these nitroimidazoles, such as 2, 4-dinitroimidazole, 1-methyl-2, 4, 5-trinitroimidazole and their energetic salts, have attracted renewed attention for their favorable explosive performance as well as improved safety characteristics[4,5]. Because of the activity of cyano group, 2-nitro-4, 5-dicyano-1*H*-imidazole (NDCI) could be used as an intermediate in the synthesis of novel energetic materials containing nitroimidazole moiety.

NDCI has been synthesized by the procedure given by Yixin Lu and coworkers[6], where the diazotization reaction and the Sandmeyer reaction were separately achieved. NDCI was obtained by adding a solution of sodium nitrite to 2-diazo-4, 5-dicyanoimidazole which was generated by diazotization of 2-amino-4, 5-dicyano-1*H*-imidazole (ADCI) with sodium nitrite in water-hydrochloric acid and collected by filtration. Dry 2-diazo-4, 5-dicyanoimidazole was so sensitive to shock that its separation may cause explosion[7].

In order to develop a simple and safe synthetic method, a one-pot synthesis of NDCI was accomplished without the treatment of shock-sensitive 2-diazo-4, 5-dicyanoimidazole intermediate (Scheme 1). The transformation of ADCI to NDCI was achieved by direct reaction of 2-diazo-4, 5-dicyanoimidazole, which was generated in a mixture of sodium nitrite and ADCI in mineral acid *in situ* at low temperature, with the excess nitrite anion in the reaction mixture.




**Scheme 1** The synthetic route of NDCI

The synthetic method was as follows: to mixture of sodium nitrite 10.455 g, 150 mmol, 2-amino-4,5-dicyano-1*H*-imidazole (2.058 g, 15 mmol) in 24 mL $H_2O$, the mineral acid was added dropwise at low temperature. The mixture was heated slowly to 40 ℃, kept for 4 h, and extracted with ethyl acetate. The extract was evaporated to dryness and purified by flash column chromatography (ethyl acetate as eluent). Yield 90.5%. $^{13}$C NMR (DMSO-$d_6$, 125 MHz), $\delta$: 114.18 (2C), 119.23 (2C), 156.82 (1C); $^{15}$N NMR (DMSO-$d_6$, 50 MHz), $\delta$: 263.31, 268.61, 360.73; IR (KBr, cm$^{-1}$), $\nu$: 3474, 3384, 3303 (N—H), 2250 (C≡N), 1689 (N—H), 1550($NO_2$, asym.), 1397($NO_2$, sym.).

The IR spectrum in KBr of NDCI showed the N—H stretching at 3303 cm$^{-1}$. The broad and intense band at 2250 cm$^{-1}$ may be assigned to the stretching vibration of the C≡N bond. Two bands at 1550 and 1397 cm$^{-1}$ indicate the presence of nitro groups in the compound. In the $^{13}$C NMR spectrum of NDCI in DMSO-$d_6$ solution (125 MHz), the two signals at 114.18 and 119.23 correspond to the carbon of cyano groups and the 4-, 5-carbon of the imidazole ring, while a signal at 156.82 is ascribed to the 2-carbon of the imidazole ring. The $^{15}$N NMR spectrum showed a signal at 263.31 which can be assigned to the nitrogen of the cyano groups. The signal at 268.61 and 360.73 can be ascribed to the nitrogen of the imidazole ring. A total of three signals appeared in the $^{13}$C or $^{15}$N NMR spectrum confirms the symmetrical nature of the molecule, where the proton is delocalized over the imidazole ring. This structure assignment is also confirmed by its single-crystal X-ray diffraction analysis. In addition, the X-ray analysis showed the presence of rich intermolecular hydrogen bonds in the crystal structure of NDCI (Fig. 1)

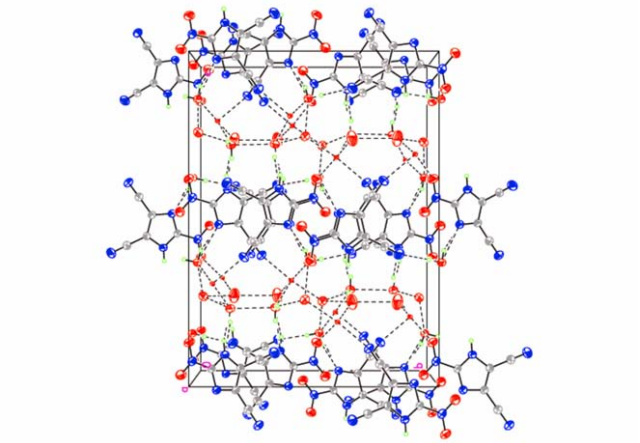


**Fig. 1** The packing diagram of NDCI

In summary, using ADCI and large excess sodium nitrite as the raw materials, the one-pot synthesis of NDCI was reported, which has advantages of safety and simple operation, and its molecular structure was characterized by IR, $^{13}$C NMR, $^{15}$N NMR and X-ray diffraction analysis.

**Key words**: organic chemistry; 2-nitro-4, 5-dicyano-1*H*-imidazole; synthesis; characterization

**CLC number**: TJ55; O62 **Document code**: A
**DOI**: 10.3969/j.issn.1006-9941.2011.06.031

**Received Date**: 2011-08-08; **Revised Date**: 2011-09-29
**Project Supported**: the National "973" project (No. 613740102)
**Corresponding Author**: BI Fu-qiang (1982 - ), male, engineer, research field: the synthesis and properties of energetic materials. e-mail: bifuqiang@gmail.com

**References:**

[1] Breccia A, Cavalleri B, Adames G E. Nitroimidazoles chemistry, pharmacology and clinical applications, nato advanced study institutes series[M]. Série A 42, New York: Plenum Press, 1982.

[2] Boyer J H. Organic nitrochemistry. series 1. nitroazoles. the C nitroderivatives of five membered N and N, O heterocycles[M]. New Jersey: Wiley-VCH Publisher, 1986.

[3] Nair M D, Nagarajan K. Nitroimidazoles chemotherapeutic agent[J]. *Prod Drug Res*, 1983, 27: 163 -165.

[4] LIU Hui-jun, CAO Duan-lin, LI Yong-xiang. Progress in 2, 4-dinitroimidazole[J]. *Chinese Journal of Energenic Materials*, 2005, 13(4): 269 -272.

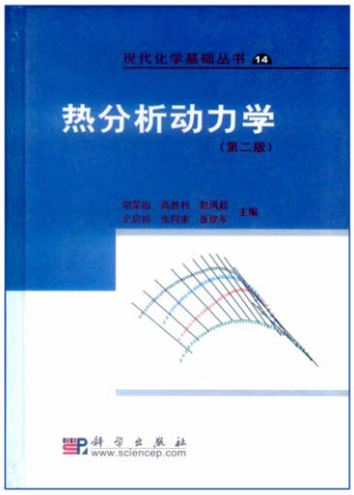
[5] Jin Rai Cho, Kwang Joo Kim, Soo Gyeong Cho. Synthesis and characterization of 1-methyl-2, 4, 5-trinitroimidazole (MTNI)[J]. *J Heterocyclic Chem*, 2001, 38: 141 -147.

[6] Lu Yixin, Just George. Stereoselective synthesis of dithymidine phosphorothioates using d-xylose derived chiral auxiliaries[J]. *Tetrahedron*, 2001, 57(9): 1677 -1687.

[7] Sheppard W A, Webster O W. Hydrogen cyanide chemistry. V. Diazodicyanoimidazole and dicyanoimidazole halonium ylides[J]. *Journal of the American Chemical Society*, 1973, 95(8): 2695 -2697.

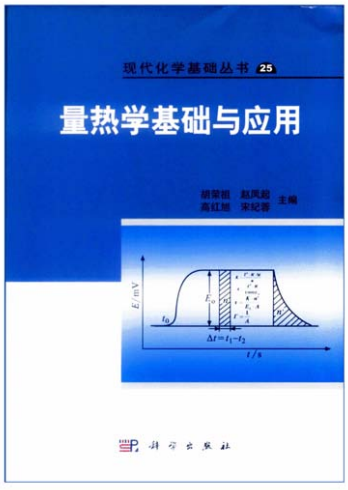
读者·作者·编者

# 《热分析动力学》、《量热学基础与应用》出版




"十一五"国家重点图书出版规划项目《现代化学基础丛书》(14):热分析动力学(第二版)(胡荣祖,高胜利,赵凤起,史启桢,张同来,张建军主编),(25):量热学基础与应用(胡荣祖,赵凤起,高红旭,宋纪蓉主编),已于2008年1月和2011年10月相继在科学出版社出版。

《丛书》(14):以热分析动力学方程为主线,汇集了近60年来国内外热分析动力学研究的学术成果。全书内容共13章。首先,回顾了热分析动力学理论、方法和技术;两类动力学方程和三类温度积分式的数学推导。其次,系统地总结了近60年发展起来的用微、积分法处理热分析曲线的成果。第三,涉及最概然机理函数的推断;动力学补偿效应;非线性等转化率的微、积分法。第四,阐述了一级及经验级数自催化分解反应动力学参数的数值模拟;诱导温度与诱导时间的关系;等温热分析曲线分析法;等温和非等温结晶过程DSC曲线分析法。第五,扼要地论述了非等温条件下热爆炸临界温度和临界温升速率的估算方法。书中编入了143道源自最新文献的习题,书末附有简明答案。该书55.8万字,售价68元。




《丛书》(25):以热效应准确度量和热动谱定量描述、解析与应用为主线,汇集了近70年来国内外量热学研究的学术成果。全书内容共24章,阐述了微量热学的技术基础——热电效应,量热原理,基线移位后热动谱峰面积的计算,热导式微热量计的性能检定,量热系统的可靠性,热动力学的基础理论,溶解/反应过程的动力学和热力学,熔化/凝固过程热流曲线的分析方法,热化学循环的设计,聚合/生成/稀释/结晶/生物代谢/振荡反应过程热动谱的解析和参数的数值计算,正负离子水合焓的估算,热力学参量比热容和热物性参量热导率的测定方法,热爆炸临界温度、热点起爆临界温度、撞击感度(特性落高)、放热系统热感度的估算,含能材料对爆轰区热作用的温度响应,小药量含能材料热安全性的评估。书中还编入了303道源自最新文献的习题,书末附有简明答案。该书83.7万字,售价98元。

《丛书》(14)和(25)可作为高校物理化学、分析化学、化学热力学、物理无机/物理有机化学、高分子物理化学、材料物理化学专业的硕士和博士研究生的教材,也可供科研院所的科技工作者及从事热化学、热力学、热分析研究的专业科技人员参考。