

## 2,2'-Biimidazole의 합성 및 구조분석

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## Synthesis and Characterization of 2,2'-Biimidazole

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**요 약:** 2,2'-Biimidazole은 glycol과 ammonium 용액을 반응하여 합성하였다. 2,2'-biimidazole의 정확한 화학적 구조는 *trans* ( $C_{2h}$ ) 또는 *cis* ( $C_{2v}$ )형 중 하나로 발표되었다. 본 실험은 2,2'-biimidazole의 화학 구조를 규명하기 위하여 FTIR과 Raman Spectrum의 서로 상호보완작용을 이용하여 분석하였으며, 그 외  $^1\text{H}$ ,  $^{13}\text{C}$  NMR, computer molecular modeling도 사용하였다. 2,2'-biimidazole의 구조는 FTIR과 Raman 스펙트럼을 비교 분석한 결과 *cis* ( $C_{2v}$ ) 보다는 *trans* ( $C_{2h}$ )로 판명되었다. 이 결과는 computer molecular modeling과 X-ray crystallography<sup>1</sup>의 실험 결과와 일치한다. 본 연구는 pyridine nitrogen을 함유한 chelating 성질을 지닌 2,2'-biimidazole의 구조 규명에 좋은 증거로 사료된다.

**Abstract:** The 2,2'-Biimidazole was synthesized by the reaction between glycol and ammonium solution. The correct solid structure of 2,2'-biimidazole in this method reported either *trans* ( $C_{2h}$ ) or *cis* ( $C_{2v}$ ) form. In this study, the correct structure of 2,2'-biimidazole was analysed by both FTIR and Raman spectroscopy using mutual exclusion properties of them. Also, it was analysed by  $^1\text{H}$  and  $^{13}\text{C}$  NMR and computer molecular modeling. The structure of 2,2'-biimidazole found to be *trans* ( $C_{2h}$ ) than *cis* ( $C_{2v}$ ) by comparison between FTIR and Raman Spectra. This results agree with computer molecular modeling and x-ray crystallography.<sup>1</sup> This study provide good evidence for identifying structural orientation of the 2,2'-biimidazole containing pyridyl nitrogen.

**Key words:** 2,2'-biimidazole, chelating compound

### 1. INTRODUCTION

Several mono-nuclear and binuclear metal complexes have been reported.<sup>1</sup> Other studies have shown that the acidity of NH protons increases substantially on coordination and that the ligand is a strong  $\pi$ -donor. The strong chelating ability of bidentate ligands containing the group  $-\text{N}=\text{C}=\text{N}-$  is considered to result from  $d_{\pi}-p_{\pi}$  binding from the transition metal to ligand.<sup>2,3</sup> This  $\pi$ -binding imparts

some aromatic character to chelate ring. The structure of 2,2'-biimidazole and its derivatives are very important because of its chelating properties.

2,2'-biimidazole has served as an intermediate to biologically active nitro-2,2'-biimidazole.<sup>4-6</sup> Since then, it has received much attention due to the metal ion coordination capacity of this conjugated bidentate ligand and because it represents one of few diimine ligands containing two five membered heterocyclic rings.<sup>2</sup> The term 2,2'-biimidazole implies

two five-membered heterocyclic imidazole rings bonded together at the carbons numbered 2; each ring consists of a tertiary nitrogen and an imino group. The imino nitrogen, also called "azole" or "pyrrole", possesses two electrons in the unhybridized 'p' orbital which contribute to the  $\pi$ -electron cloud while the tertiary nitrogen ("pyridine nitrogen"), which is designated as position 3, contains a lone pair of electrons in a hybrid orbital and a single electron in the 'p' orbital which is donated to the  $\pi$  cloud. Each of the three carbon atoms contribute a 1pz electron to the molecular orbital. The presence of the acidic pyrrol and basic pyridine nitrogens in the biimidazole ( $pK_a=4.57$ ) accounts for its amphoteric behavior.<sup>2</sup>

The preparation of 2,2'-biimidazole from the reaction of glyoxal with ammonia was first published by Debus in 1858.<sup>7</sup> He reported that the product had typical characteristics of aldehyde and ammonia, therefore he named it "glyoxaline". Although he established the correct composition of biimidazole, a structural formula was not proposed. In 1976, Duranti and Balsamini synthesized 2,2'-biimidazole by reaction of 2,2'-bi [2-imidazoline] with hexamethyldisilazane to form a soluble adduct.<sup>8</sup> More recently, it has been prepared by reaction of bis-methylimidate with aminoacetaldehyde dimethylacetal in acid to give the bis-N-(2,2-dimethoxyethyl acetamide) dihydrochloride which in turn is reacted with p-toluene sulfonic acid to yield 2,2'-biimidazole.<sup>9</sup> Wyss recognized the amphoteric nature and great chemical stability of this compound but failed to report the correct structure.<sup>10</sup> It was Ban-

berger who furnished the most convincing evidence for two possible structures of 2,2'-biimidazole as shown in Fig. 1.<sup>11</sup>

## 2. EXPERIMENTS

### 2.1. Preparation of 2,2'-biimidazole

The synthesis was based on the method of Debus.<sup>7</sup> Equal volumes of a 29% solution of ammonium hydroxide and a 40% solution of glyoxal were combined with stirring. The formed crude 2,2'-biimidazole was recrystallized from boiling water. The final product was a light fluffy white power.

### 2.2. Analysis method of 2,2'-biimidazole

Infrared absorbance spectra of the compound, using a KBr matrix were obtained using a Perkin-Elmer model 1750 FTIR under a dry air purge in the 4000-450  $\text{cm}^{-1}$  region. Raman spectra were obtained using a Spex 1403, 0.85 m double monochromator equipped with photon counting electronics, a cooled Hammamatsu R928 multi-alkali photomultiplier tube, interfaced with an IBM-XT computer. The laser excitation source at 488 nm, was a Coherent Ar<sup>+</sup> (Innova 90-5) laser; typical laser power was 200 mW. Benzene was used for frequency calibration. Spectral resolution was 5  $\text{cm}^{-1}$  and the scattered radiation was observed 90° to the incident beam. NMR spectra were obtained with either a VARIAN EM360 or a JEOL JNM-FX100 spectrometer with a switchable proton-carbon probe. The solid <sup>13</sup>C NMR spectra were obtained using a VXR-200 Fourier transform nuclear magnetic resonance spectrometer.

Molecular modeling of 2,2'-biimidazole was measured the minimum energy by "quanta" program (Silicon Graphic Co.). Tetramethylsilane (TMS) was used as an internal standard for the proton spectrum while the solvent (hexamethylphosphoramide) was used as reference for <sup>1</sup>H NMR spectrum at room temperature.

## 3. RESULTS AND DISCUSSION

The solution preparation of 2,2'-biimidazole from

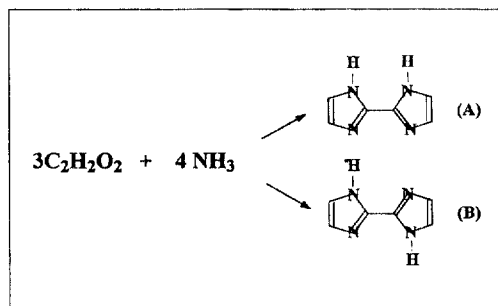


Fig. 1. Two Possible Structures of 2,2'-Biimidazole in Solid State.

Table 1. Elemental Analysis of 2,2'-biimidazole

Elements	Calculation	Found
C	53.73	53.77
N	41.79	41.57
H	4.48	4.48

aqueous ammonia and 40% glyoxal resulted in 15-20% yield of the product. The results of elemental analysis for 2,2'-biimidazole are shown in Table 1. Its composition with theoretical values was in agreement with previous reported values.<sup>2</sup>

The proton NMR (Fig. 2) spectrum consists of 2 singlets at 13.13 and 6.92 ppm. The first peak at 13.13 ppm is broad and assigned to the pyrrole type N-H while the ring hydrogen of C(4) and C(5) are equivalent due to rapid exchange of the N-H in solu-

tion. Around 2-3 ppm are solvent (hexamethylphosphoramide) peaks. The tautomeric character of 2,2'-biimidazole which involves the rapid proton transfer from one nitrogen to an imino nitrogen and makes the C(4) and C(5) proton equivalent on the NMR scale. Also the intermolecular hydrogen bonding of 2,2'-biimidazole and thereafter the rapid chemical exchange cause the broadening of the absorption of the imino hydrogen.

The solid <sup>13</sup>C NMR spectrum of the 2,2'-biimidazole is dominated 3 peaks by the broad peaks 126.7 and 119.7 ppm for two aromatic carbon and one single peak at 139.2 ppm for center carbon respectively. The around 75 and 200 ppm were side bands (Fig. 3).

The solid state structural features of 2,2'-biimi-

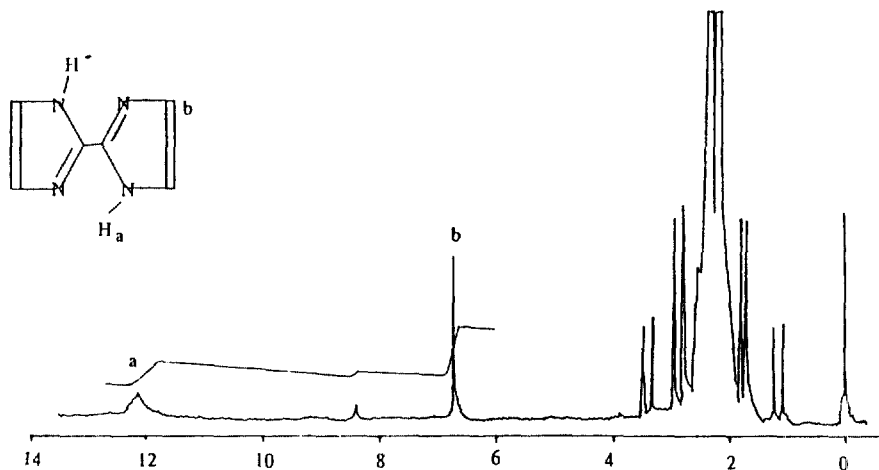


Fig. 2. Proton NMR of 2,2'-Biimidazole in Hexamethylphosphoramide at Room Temperature.

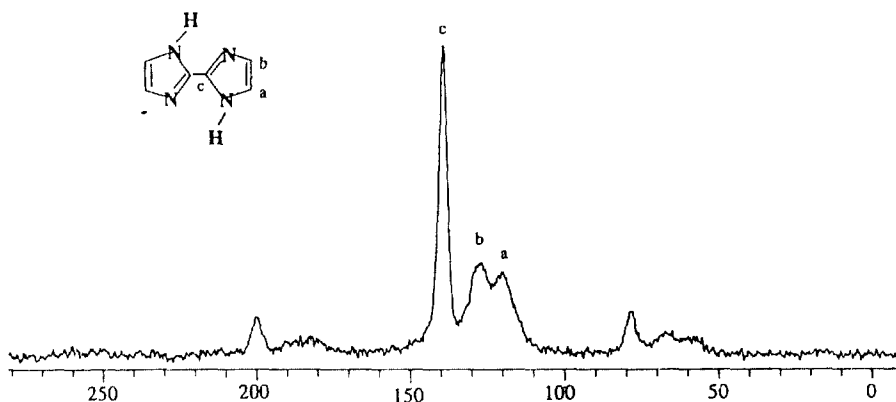


Fig. 3. Solid C-13 NMR Spectrum of 2,2'-Biimidazole.

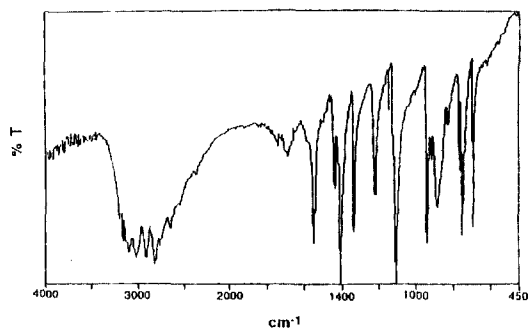


Fig. 4. FTIR Spectrum of 2,2'-Biimidazole.

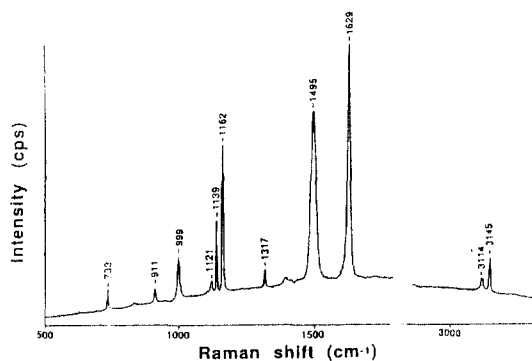


Fig. 5. Raman Spectrum of 2,2'-Biimidazole.

dazole were considered using a comparison of FTIR and Raman spectra (Fig. 4 and 5). Table 2 also shows the FTIR and Raman spectral assignments. The FTIR spectrum is dominated by a broad absorption from 3200 to 2500  $\text{cm}^{-1}$  that is assigned to unsymmetrical intermolecular N-H hydrogen bonding and two possible aromatic C-H stretching frequencies. The FTIR and Raman spectra may assigned empirically by comparison with that of imidazole.<sup>2,12-14</sup> The comparison of 2,2'-biimidazole of FTIR and Raman spectra can be used in-part to account for its structure in the solid state. The frequencies for the -N=C-N- stretching in both the FTIR and Raman spectra provide good evidence for discerning *cis* and *trans* orientation of the 2,2'-biimidazole pyridyl nitrogen. If the structure was *cis* {Fig. 1(A)}, Raman and IR spectra can have quite similar appearances like as for molecular possessing little or no symmetry.<sup>13,14</sup> However, for molecules with a center of symmetry, vibrational transitions that are allowed in the infrared are forbidden in the

Table 2. Raman and FTIR Spectral Assignments for 2,2'-Biimidazole

Assignments	Wavenumber ( $\text{cm}^{-1}$ )	
	FTIR	Raman
Intermolecular N-H Stretching	2500-3500	
C-H Stretching		3145
		3114
C=C Stretching	1545	
C=N		1629
		1436
N-H Bending	1334	1495
C-H Stretching	1217	1163
		1139
Imidazole in-plane	1104	999
C-H Bending	919	911
Imidazole out-of-plane		
Ring Bending	886	733

Raman effect and vice versa. This complementarity derives from the rule of mutual exclusion. The FTIR and Raman spectra assignment in Table 1 are not identical. Therefore, the structure of 2,2'-biimidazole is strongly expected to be the *trans* {Fig. 1(B)} isomer. These results are consistent with the *trans* pyridyl nitrogen arrangement found in reported X-ray crystallographic studies of 2,2'-biimidazole.<sup>1</sup>

The crystal structure of 2,2'-biimidazole has been determined by X-ray crystallography.<sup>1</sup> In the crystalline state of 2,2'-biimidazole, the five atoms in each ring are coplanar within 1.423 but the two rings are rotated 4.6° about in the central C(2)-C(2') bond. After metal binding, two rings are rotated 3.8°.

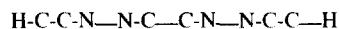


Fig. 6. Molecular Modeling of 2,2'-Biimidazole (Side View).

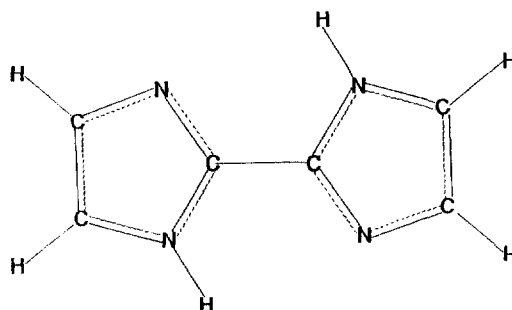


Fig. 7. Molecular Modeling of 2,2'-Biimidazole (Front View).

The molecular molding of 2,2'-biimidazole is shown in Fig. 6 and 7. The comparison of 2,2'-biimidazole conformation energy can be used in-part to account for its structure in the solid state. The results of the minimum energy molecular modeling of 2,2'-biimidazole predicts the *trans* structure to be predominant. These results are consistent with *trans* imidazole nitrogen arrangement found in reported X-ray crystallography,<sup>1</sup> and Raman and FTIR spectroscopies of 2,2'-biimidazole. The intermolecular hydrogen bonding of 2,2'-biimidazole makes it highly insoluble in solvents except in acidic or strong basic solvents. The high melting point above 300°C may be attributed to this type of association as well. In this study, the correct solid structure of 2,2'-biimidazole was identified as *trans* form.

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