

## Nuclear Magnetic Resonance Study of 4-Substituted NN-Linked Bi(Heterocycles)

AMIR SULTAN AFRIDI

Department of Chemistry, Govt. Postgraduate College Bannu, Pakistan.

(Received 20th October 1980)

We have recently reported the preparation of a number of NN-linked bi(heterocycles)<sup>1,2</sup> from dehydroacetic acid and lutidone with N-aminoheterocycles. Although NN-linked bi(heterocycles) are potentially useful as synthetic intermediates, only a few compounds belonging to this class have been reported. They include NN-bipyrrolys<sup>3,4</sup>, NN-biimidazolyls,<sup>5,6</sup> and NN-biquinolonyls.<sup>7</sup> Subsequently, the preparation of a number of new NN-linked bi(heterocycles) and their cations have been reported.<sup>8</sup>

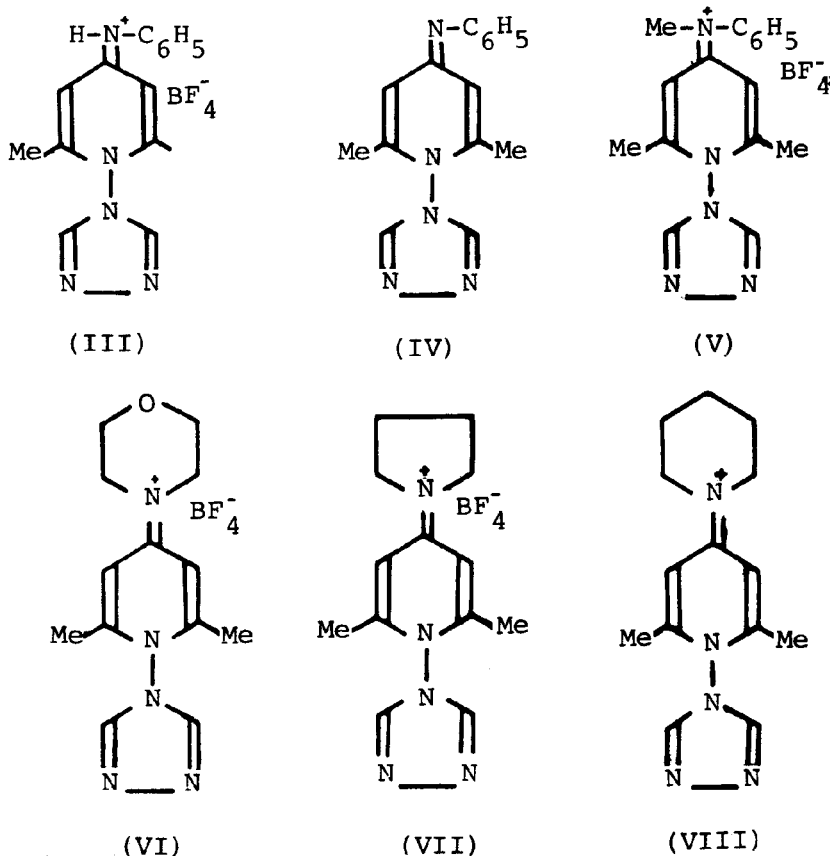
Although, in our previous studies, we have reported the preparation of NN-linked bi(heterocycles) and their reactions with various nucleophiles at 4-position, but less

attention has been paid to the n.m.r spectra of these compounds (III-VIII). The effect of temperature on the n.m.r spectra of these compounds is described here.

## Materials and Methods

2,6-dimethyl-1-(1,2,4-triazol-4-yl)-4-pyridone (II) was prepared by heating dehydroacetic acid (I)<sup>9</sup> and 4-amino-1,2-triazole<sup>10</sup> in pyridine (20 ml) under reflux. After cooling, the solid which separated was recrystallized from ethanol to give 2,6-dimethyl-1-(1,2,4-triazol-4-yl)-4-pyridone (II). (65% yield).

2,6-dimethyl-4-phenylamino-1-(1,2,4-triazol-4-yl)



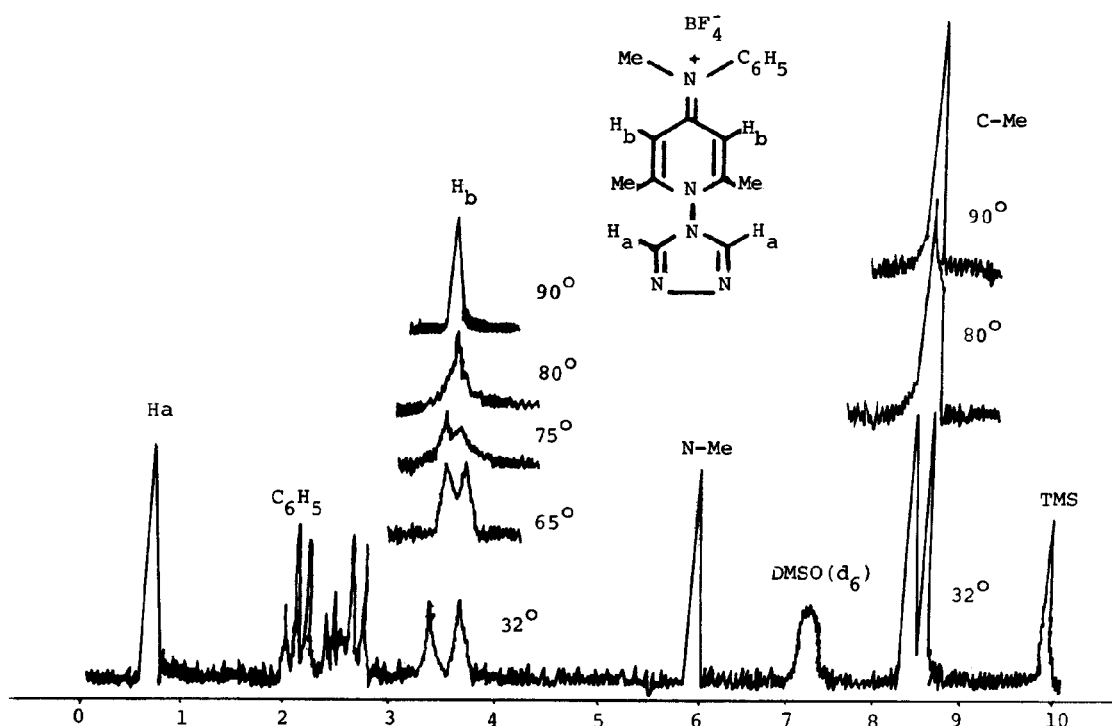
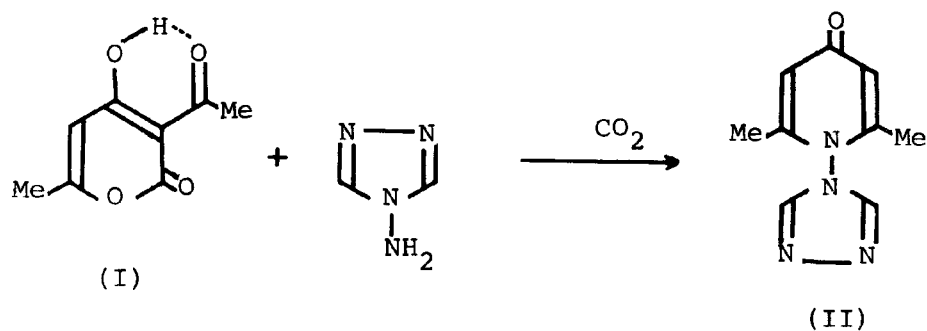


Figure 1

pyridinium tetrafluoroborate (III) was prepared by the reaction of (II) at room temperature with phosphoryl chloride. The resulting solid product was washed with ether and then stirred with tetrafluoroboric acid at room temperature. Aniline was then added to the solid and stirred in ethanol. The solid which separated was recrystallized from ethanol to give compound (III) (70% yield).

In a similar manner compound (II) during reaction with N-methyl aniline, morpholine, pyrrolidine and piperidine gave compounds (V, VI, VII, and VIII) respectively.

2,6-dimethyl-4-phenylimino-1-(1,2,4-triazol-4-yl)-

4-pyridone (IV) was prepared by heating (III) in ethanol at 50°C with potassium hydroxide. After suitable work-up the solid product was recrystallized from ethanol to give compound (IV) in 60% yield. All these compounds are soluble in trifluoroacetic acid and  $(\text{CD}_3)_2\text{SO}$  hence these solvents were used for n.m.r spectra (60 and 100 MHz) with tetramethyl silane as an internal reference. The n.m.r spectra of these compounds were run at 30 to 90°C (Figure 1-3).

In compounds (VI, VII and VIII) when the substituents at 4-position are symmetrical, then the n.m.r signals for the two similar CH as well as for the similar two

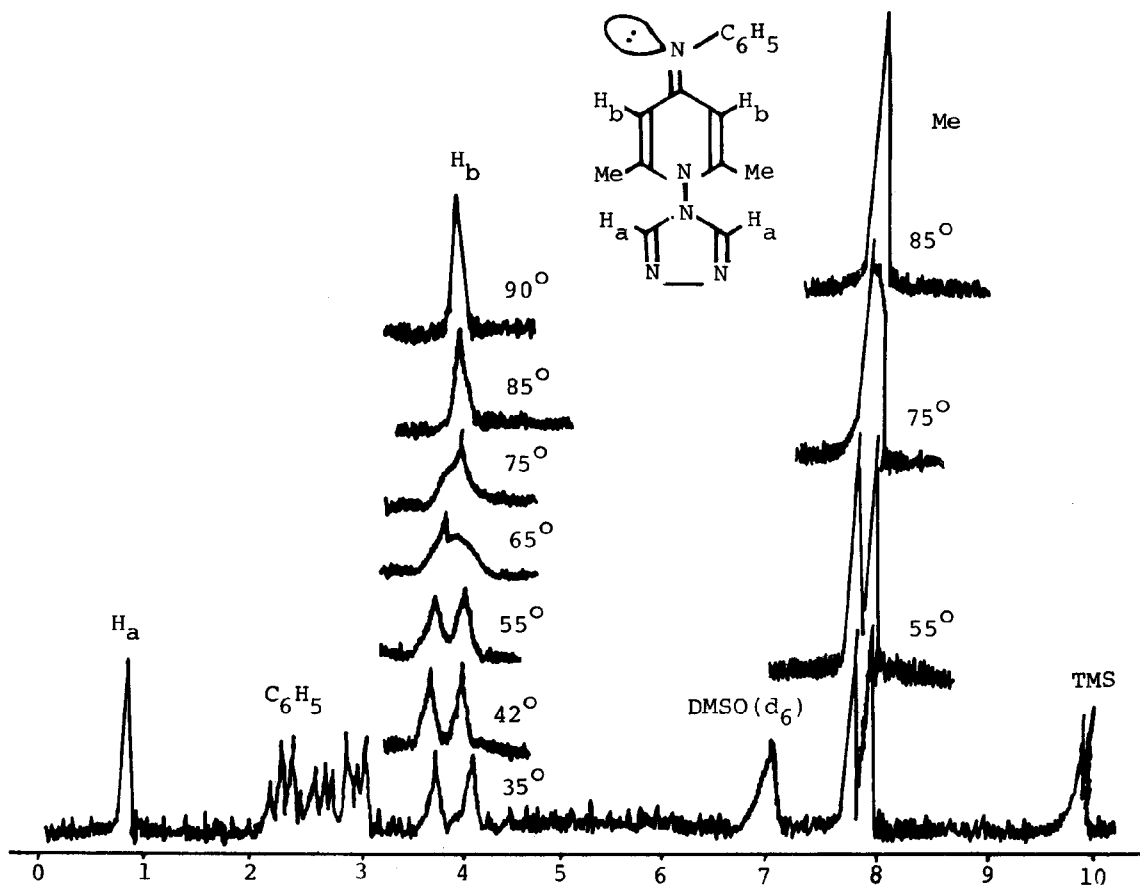


Figure 2

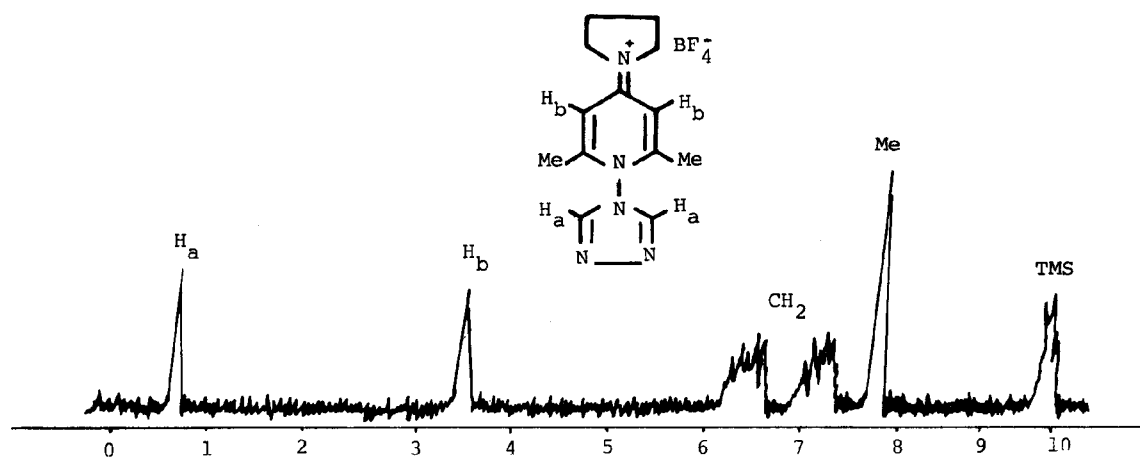


Figure 3

