

Rotational Disorder in 2-Piperidyl-5-nitro-6-methylpyridine: Structural Phase Transition and its Vibrational Characteristics

J. Lorenc¹, B. Palasek¹, J. Hanuza^{1,2}, M. Mączka², A. Waśkowska²

¹Department of Bioorganic Chemistry, Institute of Chemistry and Food Technology, Academy of Economics, 118/120 Komandorska Street, 53-345 Wrocław, Poland, ²Institute of Low Temperature and Structure Research, Polish Academy of Sciences, Okólna 2., 50-950 Wrocław, Poland.

2-piperidyl-5-nitro-6-methylpyridine is a novel compound among the pyridine-derivatives that has not yet been studied. The discussion of the vibrational spectra of this material has been based on the structure of this compound and DFT quantum chemical calculations.

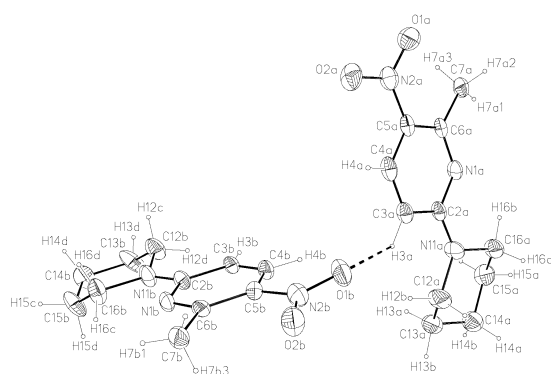


Fig. 1: Asymmetric unit of $C_{11}H_{15}N_3O_2$ in the low temperature phase. Displacement ellipsoids are drawn at the 30% probability level.

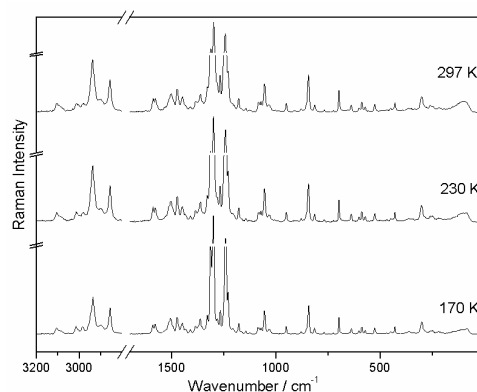


Fig. 2: The Raman spectra of $C_{11}H_{15}N_3O_2$ at 297, 230 and 170 K in the region $3200-30\text{ cm}^{-1}$

X-ray diffraction studies have shown that 2-piperidyl-5-nitro-6-methylpyridine, $C_{11}H_{15}N_3O_2$, undergoes structural phase transition at $T = 240\text{ K}$. The room temperature structure is tetragonal, space group $I4_1/a$, with the unit cell dimensions $a = 13.993(2)$ and $c = 23.585(5)\text{ Å}$. The pyridine ring takes *trans* conformation with respect to the piperidine unit. While pyridine is well ordered, the piperidine moiety shows apparent disorder resulting from a libration about linking N – C bond. The low temperature phase is monoclinic, space group $I2/a$. Contraction of the unit cell volume by 2.3% at 170 K enables the C – H...O linkage between the molecules of the neighbouring stacks. As result, the asymmetric unit becomes bi-molecular. The thermal librations of the piperidine and methyl groups become considerably reduced at 170 K and nearly fully reduced at about 100 K. The IR spectra and polarised Raman spectra agree with the X-ray structure and confirm the disorder effect on the piperidine ring.

The temperature dependence of IR and Raman modes shows clear changes at about 240, 200 and 100 K. For instance, a clear splitting is observed at 240 K for the following bands: $1472 \rightarrow 1472 + 1467$, $1431 \rightarrow 1434 + 1427$, $1164 \rightarrow 1176 + 1163\text{ cm}^{-1}$. These bands correspond to the vibrations of the methyl group coupled with the pyridine ring. The most pronounced changes are observed, however at about 100 K where the splitting of the following bands is observed: $2945 \rightarrow 2956 + 2944$, $2898 \rightarrow 2912 + 2893$, $1315 \rightarrow 1318 + 1308$, $1055 \rightarrow 1057 + 1052$, $1032 \rightarrow 1034 + 1026$, $907 \rightarrow 911 + 907$, $809 \rightarrow 816 + 812$, $725 \rightarrow 729 + 727$, $587 \rightarrow 588 + 584$, $214 \rightarrow 226 + 218 + 207\text{ cm}^{-1}$. Such effects agree with the structural changes induced by the temperature lowering, i.e. freezing of the methyl and piperidine units librational motions.