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Molecular Structure of 2,3–Dicyano–5,7,7–trimethyl–6,7–dihydro–1*H*–1,4–diazepine – Precursor of p*H*–Sensitive Porphyrazines

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Dedicated to Professor Olga G. Khelevina on the occasion of her Anniversary

Molecular structure of 2,3-dicyano-5,7,7-trimethyl-6,7-dihydro-1H-1,4-diazepine, which was recently used as precursor for pH-sensitive porphyrazine fluorophores (New J. Chem. 2020, DOI: 10.1039/d0nj04388e), was determined by single crystal X-ray diffraction analysis. The obtained structural data confirm the conclusions made on the basis of spectral study and quantum-chemical modelling and evidence that –N= and –NH– groups in 6,7-dihydro-1H-1,4-diazepine ring can be considered as pyridine- and pyrrole-type nitrogens, and the electronic lone pair of the latter is involved in formation of quasi-aromatic conjugated heterocyclic system.

Keywords: 1,4-Diazepines, crystal structure, X-ray diffraction analysis.

Молекулярная структура 2,3–дициано–5,7,7–триметил–6,7–дигидро–1*H*–1,4–диазепина – предшественника p*H*–чувствительных порфиразинов

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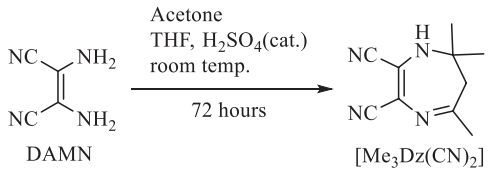
Молекулярная структура 2,3-дициано-5,7,7-триметил-6,7-дигидро-1H-1,4-диазепина, который был недавно использован в качестве предшественника в синтезе pH-чувствительных порфиразиновых флуорофоров (New J. Chem. 2020, DOI: 10.1039/d0nj04388e), установлена методом монокристального рентгено-структурного анализа. Полученные структурные данные подтвердили выводы, сделанные на основании спектральных измерений и квантово-химических расчетов, и показали, что –N= and –NH– группы в 6,7-дигидро-1H-1,4-диазепиновом фрагменте могут рассматриваться как атомы азота пиридинового типа и пиррольного типа, причём электронная пара –NH– группы вовлечена в образование квазиароматической сопряженной системы гетероцикла.

Ключевые слова: 1,4-Диазепины, кристаллическая структура, РСА.

Porphyrazines with annulated 1,4-diazepine rings (TDzPzs) were first reported two decades ago.[1,2] Now TDzPzs are actively studied as promising photosensitizers[3,4] and fluorescent sensors.[5,6] At the moment, porphyrazines containing 6*H*-, 6,7-dihydro-1*H*- and 4,5,6,7-tetrahydro-1*H*-1,4-diazepine fragments have been studied and described.[7-10] The spectral properties of corresponding macrocycles differ from each other. The study of struc-



Scheme 1

We have recently studied acid-base and photophysical properties of tetradiazepinoporphyrazines and their precursors containing 6,7-dihydro-1*H*-diazepine fragments.[6] We established using ^{1}H NMR UV-Vis spectroscopy that onlythe nitrogen atom of the imino group (–N=) can be protonated both in the case of porphyrazine and its precursor. The results of quantum chemical modelling also evidenced that the nitrogen atom of the imino group -N= has higher

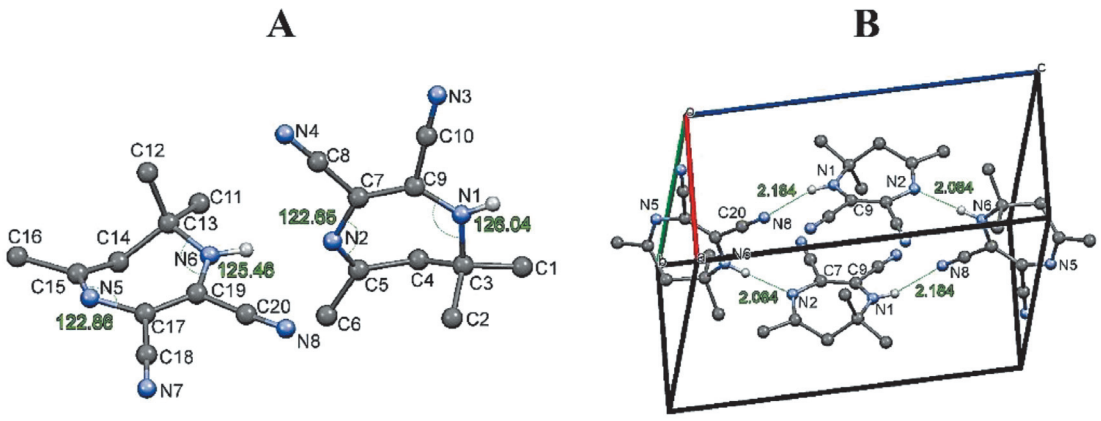


Figure 1. A – molecular structure of a single crystal of $[Me_3Dz(CN)_2]$; **B –** packing of molecules in a unit cell. Hydrogen atoms have been scattered for the sake of the picture.

tural and physicochemical features of dinitrile precursors is a fundamentally significant aspect that allows understanding of the peculiar physicochemical properties of target porphyrazines. Molecular structures of 2,3-dicyano-6*H*- and 4,5,6,7-tetrahydro-1*H*-1,4-diazepines have been previously described.[1,10,11] However, the molecular structure of the 6,7-dihydro-1*H*-type dinitrile precursors has not yet been identified.

The synthesis of 2,3-dicyano-5,7,7-trimethyl-6,7-dihydro-1*H*-1,4-diazepine and its analogs was proposed by R.V. Begland *et al*.[12] (Scheme 1). According to the procedure, diaminomaleonitrile participates in a cyclization reaction with the products of aldol condensation of ketones (for example, acetone, see scheme) in toluene or tetrahydrofuran in the presence of catalytic amounts of *p*-toluenesulfonic acid or concentrated sulfuric acid affording the corresponding 6,7-dihydro-1*H*-1,4-diazepine-2,3-dicarbonitrile.†

basicity than that of -NH- group. It was concluded that the latter can be considered as pyrrole-type nitrogen atom and its lone pair is involved in the formation of quasi aromatic conjugated system of heterocycle and does not participate in the acid-base interaction. In this work, we confirm these conclusions on the basis of single crystal X-ray diffraction study of 2,3-dicyano-5,7,7-trimethyl-6,7-dihydro-1*H*-1,4-diazepine $[Me_3Dz(CN)_2]$ and consider also the peculiarities of its packing in the unit cell.

Needle-like single crystals of $[Me_3Dz(CN)_2]$ suitable for X-ray diffraction analysis were obtained by slow evaporation at room temperature of its saturated solution. Triclinic crystal of $[Me_3Dz(CN)_2]$ belongs to symmetry space group P1, and the unit cell contains two independent molecules which have an "envelope" conformation (Figure 1, A).

In the molecular structure, the bond angles □CNC formed by nitrogen atoms N2 and N5 in the imino groups –N= are ~122.9°, and by N1 and N6 atoms in the –NH– groups are 125.5-126.0°. In both cases these values are characteristic for the sp^2-hybridization state. The almost planar heterocyclic fragments in one molecule include C3, N1, C9, C7 and N2 atoms and in another C13, N6, C19, C17, N5 (deviation < 0.01 Å). Carbon atoms C5 and C15 neighboring imino nitrogens N2 and N5 are deviated from these mean planes by 0.39 and 0.36 Å, respectively. The values of bond length N1C3, N6C13 (1.346, 1.349 Å), C9C7, C19C17 (1.384, 1.386 Å), C7N2, C17N5 (1.402, 1400 Å) and N2C5, N5C15 (1.290, 1287 Å) indicate that bonds in the N1C9C7N2 and N6C19C17N5 fragments are conjugated. These data evidence that the structure of the diazepine precursor contains both a pyridine type nitrogens (N2 and N5) and a pyrrole type nitrogens (N1 and N6) which are involved in forma-

† Synthesis of 2,3-dicyano-5,7,7-trimethyl-6,7-dihydro-1*H*-1,4-diazepine $[Me_3Dz(CN)_2]$. 2,5 g (23 mmol) of diaminomaleonitrile (DAMN), 5 mL (69 mmol) of acetone were suspended in 20 mL of THF or 1,4-dioxane and 5 drops of concentrated sulfuric acid or few crystals of *para*-toluene sulfonic acid was added to the reaction mixture. The brown solution was stirred for 3 days and filtered to remove black precipitate. The filtrate was evaporated and the resulting red material was recrystallized from boiling dichloromethane with activated coal. The resulting solution was cooled to room temperature and was placed in the freezer. Pure product was collected by filtration. Yield: 3.6 g (95%) as yellow needles; mp 182 °C (181–182 °C lit.[12]); IR (ATR) cm^{-1}: 3196(NH), 2875, 2778(CH), 2238, 2209(CN), 1619, 1550, 1372, 1315(H_3C–C–CH_3); ^{1}H NMR ($CDCl_3$) δ_H ppm: 5.27 (s, 1H, NH), 2.65 (s, 2H, CH_2), 2.29 (s, 3H, CH_3), 1.34 (s, 6H, H_3C–C–CH_3).

tion of conjugated quasi-aromatic system containing 6π electrons delivered by atoms of heterocyclic ring including electron pairs from the pyrrole-type nitrogens.

Another peculiar structural feature is a formation of two types of intermolecular hydrogen bonds between NH group in one molecule and imino group in another (N6H23…N2 – 2.084 Å) and between NH group and CN groups (N1H24…N8 – 2.183 Å) (Figure 1, B), which determine the crystal packing.

Thus, using X-ray structural analysis, the structure of 6,7-dihydro-1*H*-1,4-diazepine-2,3-dicarbonitrile was studied and it was found that nitrogen atoms of both imino (–N=) and amino (–NH–) groups are included into the conjugated quasi-aromatic system and can be considered as pyridine and pyrrole-type, respectively.

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