Thematic Section: Quantum-Chemical Research. **Full Paper**
Subsection: Organic Chemistry. *The Reference Object Identifier* – ROI: jbc-01/20-61-1-9
The Digital Object Identifier – DOI: 10.37952/ROI-jbc-01/20-61-1-9
Submitted on January 8, 2020.

Investigation of the nature of hydrogen bonds in 3,5-dimethylpyrazole

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Keywords: pyrazole, hydrogenlinked motifs, hydrogen bonds, supramolecular structure.

Abstract

Compounds containing a pyrazole fragment in their structure are part of many medicines and have a wide range of bioactivity (for example, antimicrobial, anti-tuberculosis, etc.), and are also successfully used for the development of various synthetic anti-tumor agents. Interest in them is also caused by the presence of hydrogen bonds, which are the main motive for self-organization of molecules. A theoretical study of the nature of hydrogen bonds in various hydrogen-bound motifs in 3,5-dimethylpyrazole was performed using the DFT/B3LYP/6-31G(d,p) method. The results obtained indicate the possible existence of dimeric, trimeric, and tetrameric cyclic forms. Geometric and energy parameters of hydrogen bonds N-H···N are determined and the energies of donor-acceptor interaction in possible forms of self-organization of the molecules of the studied compound are calculated. It has been established that the hydrogen bond (H-bond) is the result of the interaction of a hybrid unshielded pair of a nitrogen atom of one molecule and a loosening natural orbital between the nitrogen atoms of one molecule and the hydrogen of another molecule (σ* N-H). The formation of the binding σ-orbital of the H-bond indicates the predominance of covalent interaction in the hydrogen bond. The study and analysis of the results showed that the formation of supramolecular systems of 3,5-dimethylpyrazole most likely structures are trimers and tetramers.

References

[1] J.-M. Lehn. Toward self-organization and complex matter. *Science.* **2002**. Vol.295. No.5564. P.2400-2403.
[2] A.F. Pozharsky. Supramolecular chemistry. Part 2. self-Organizing molecules. *Soros education journal.* **1997**. No.9. P.40-47. (russian)
[3] C. Foces-Foces, A. Echevarría, N. Jagerovic, I. Alkorta, J. Elguero, U. Langer, O. Klein, M. Minguet-Bonvehí, H.H. Limbach. A solid-state NMR, X-ray diffraction, and ab initio computational study of hydrogen-bond structure and dynamics of pyrazole-4-carboxylic acid chains. *J. Am. Chem.Soc.* **2001**. Vol.123. P.7898-7906.
[4] L. Pauling. The Nature of the Chemical Bond, 3rd Ed. *Cornell University Press, Ithaca, NY.* **1960**. 644p.
[5] R.H. Gillette, A. Sherman. The Nature of the Hydrogen Bond. I. Association in Carboxylic Acids. *J. Am. Chem. Soc.* **1936**. Vol.58. P.1135-1139.
[6] C.A. Coulson, U. Danielson. Ionic and covalent contributions to the hydrogen bond. I, II. *J. Ark. Fysik*. **1954**. Vol.8. P.239-255.
[7] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, Jr.J.A. Montgomery, T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, Li X., J.E. Knox, H.P. Hratchian, J.B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W.

Chen, M.W. Wong, C. Gonzalez, J.A. Pople. Program package Gaussian 03, Revision B.04. *Gaussian Inc.: Pittsburgh, PA*. **2003**.
[8] G.A. Zhurko, G.A. Zhurko. Chemcraft v. 1.4 beta. http://www.chemcraftprog.com.
[9] J.P. Castaneda, G.S. Denisov, S.Yu. Kucherov, V.M. Schreiber, A.V. Shurukhina. Infrared and ab initio studies of hydrogen bonding and proton transfer in the complexes formed by pyrazoles. *J. Mol. Struct.* **2003**. Vol.660. No.1-3. P.25-40.
[10] T. Steiner. The Hydrogen Bond in the Solid State. *Angew. Chem. Int. Ed.* **2002**. Vol.41. P.4876.
[11] T.N. Coleen, J.L. Croix, J.M. Galbraith. Hydrogen bonding from a valence bond theory perspective: the role of covalency. *Phys. Chem. Chem. Phys.* **2018**. Vol.20. No.32. P.20963-20969.