A Non-symmetric Disordered Tetramer: The Unusual Structure of 3(5)-ethyl-5(3)-phenyl-1*H*-pyrazole in the Solid State

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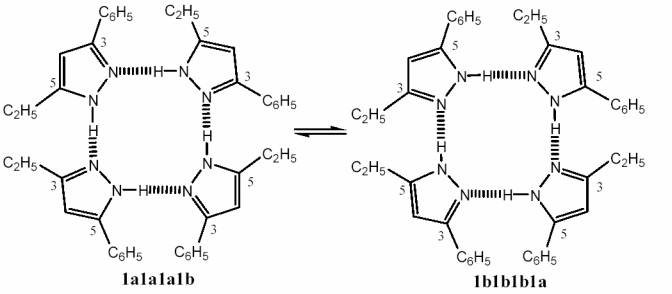
In a systematic exploration of 3,5-disubstituted pyrazoles for crystal engineering purposes, we prepared the still unknown 3(5)-ethyl-5(3)-phenyl-1*H*-pyrazole **1**.[1] Its X-ray structure has been determined: it is a hydrogen-bonded tetramer of a new type formed by three tautomers 5-ethyl-3-phenyl-1*H*-pyrazoles of class **a**, and one tautomer 3-ethyl-5-phenyl-1*H*-pyrazole of class **b**.



The 3(5)-ethyl-5(3)-phenyl-1*H*-pyrazole tetramer.

The NH protons are disordered even at low temperature, so there are two questions that could be asked: Is the disorder static or dynamic (SSPT)? What are the proportions of both tetramers **1a1a1a1b**/**1b1b1b1a** (either static mixture or dynamic equilibrium)? We have tried to answer these questions by a combination of DFT calculations, analysis of the X-ray geometries and ^{13}C and ^{15}N CPMAS NMR. For this last purpose, the [$^{15}N_2$]-labelled derivative of **1** was prepared.

[1] Torres V., Cornago P., Claramunt R. M., Loshkin V., Samat A., Pinilla E. , Torres M. R., in progress: 3(5)-ethyl-5(3)-phenyl-1*H*-pyrazole **1**, yellow-reddish solid of m.p. 80.1 ºC.

Keywords: hydrogen bonding, pyrazoles, supramolecular architectures