

Temperature Dependence of NMR Chemical Shifts and Flat PES of Furoxanes

Georgy E. Salnikov,^a Alexandr M. Genaev,^a Yuri A. Strelenko^b

^a Novosibirsk Institute of Organic Chemistry, Lavrentjeva, 9, 630090, Novosibirsk, Russia

^b Institute of Organic Chemistry, Leninsky prospect 47, 119991 Moscow B-334, Russia

Fax: (7-095) 135 5328

E-mail: strel@ioc.ac.ru

The structure of furoxanes was extensively studied both experimentally and theoretically. In particular, it was shown that the optimized O¹-N² bond length is very sensitive to the calculation method. We have found strong temperature dependence of the chemical shifts of the oxadiazole carbon and nitrogen atoms which cannot be described by the common techniques for rovibrationally averaged properties with harmonic and anharmonic force constants. Both these facts can be consequences of a flat PES along the O¹-N² distance coordinate. As this PES is asymmetric and some NMR chemical shifts exhibit strong changes with the movement along this coordinate, it should be possible to apply the approach proposed for the explanation of the temperature dependence of the ¹³C NMR chemical shifts in cyclobutenyl carbocations.

