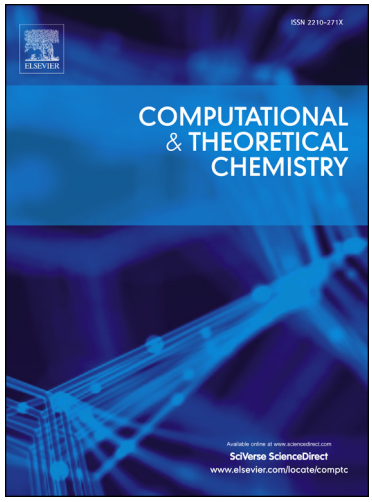

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Jesús Gálvez, José I. López Sánchez, Antonio Guirado

PII: S2210-271X(15)00259-5
DOI: http://dx.doi.org/10.1016/j.comptc.2015.06.020
Reference: COMPTC 1854

To appear in: *Computational & Theoretical Chemistry*

Received Date: 19 May 2015
Revised Date: 17 June 2015
Accepted Date: 21 June 2015

Please cite this article as: J. Gálvez, J.I. López Sánchez, A. Guirado, Computational study of the rotational pathways of the amino group in 2-chloroaniline, azines and formamide: one or two rotational barriers?, *Computational & Theoretical Chemistry* (2015), doi: http://dx.doi.org/10.1016/j.comptc.2015.06.020

Computational study of the rotational pathways of the amino group in 2-chloroaniline, azines and formamide: one or two rotational barriers?

Jesús Gálvez,[a,*†], José I. López Sánchez[b‡], and Antonio Guirado,[b]

[a]Departamento de Química Física, [b]Departamento de Química Orgánica,

Facultad de Química, Universidad de Murcia,

Campus de Espinardo, 30071 Murcia, Apartado 4021, Spain

Abstract

Rotation of the amino group in five different molecular systems, 2-aminopyridine, 2-aminopyrimidine, 2-chloroaniline, N-methylamino-1,3,5-triazine, and formamide, has been studied at B3LYP/6-311++G(2d,2p), MP2/6-311++G(2d,2p), and CCSD(T)/6-311++G(2d,2p)//B3LYP/6-311++G(2d,2p) levels of density functional, MP2, and coupled cluster theories. To this end, detailed rotation energy profiles for the above amino systems were obtained in two different ways: 1) by computing the energy-values as a function of only one torsion angle; and 2) by taking into account that the pyramidal nature of the NH_2 group changes as rotation progresses so that energy profiles should be defined by two torsion angles. In the first case, saw-toothed energy profiles exhibiting two rotational barriers were always obtained. Conversely, by using two torsion angles as reaction coordinates smooth pathways were found where a rotation cycle can be completed passing only through the lowest energy barrier. Implications of these conflicting pathways are discussed.

Keywords: amino group, rotational pathways, rotational barriers

[†]Corresponding author; e-mail: jgalvez@um.es

[‡]Present address: Dirección de Investigación, Universidad Internacional SEK Campus Miguel de Cervantes. Alberto Einstein, Carcelén, Quito (Ecuador)