Computational and Theoretical Chemistry 964 (2011) 25–31

Contents lists available at ScienceDirect

Computational and Theoretical Chemistry

journal homepage: www.elsevier.com/locate/comptc

# A computational study of the conformation of heterocyclic systems related to biphenyl

Ibon Alkorta *, José Elguero

*Instituto de Química Médica, CSIC, Juan de la Cierva, 3, E-28006 Madrid, Spain*

ARTICLE INFO

*Article history:*
Received 19 October 2010
Received in revised form 22 November 2010
Accepted 25 November 2010
Available online 27 November 2010

*Keywords:*
*N,N′*-linked
Pyrrole
Carbazole
Pyridinium
Pyridine
DFT

ABSTRACT

The conformation of nine *N,N′*-linked heterocycles including pyrrole, carbazole, 4*H*-1,2,4-triazole, pyrazole, pyridinium and 4-pyridone has been explored (minima and transition states) at the B3LYP/6-31G(d) level. Besides, six conformationally restricted molecules belonging to the same series have been calculated.



## 1. Introduction

Biphenyl (**1**), like benzene, methane, acetylene, pyridine, furan, ... is one of the paradigmatic molecules of organic chemistry. The rotation about the CC single bond that links both phenyl rings is related to atropisomerism [1,2], to rotational barriers [3,4] and to problems of conjugation between aromatic rings [5–7]. As Johansson and Olsen pointed out "From an electronic structure point of view, biphenyl is a surprisingly challenging molecule. Especially, pinpointing the energetics of the internal rotation around the central C–C bond connecting the two benzene units has proven problematic" [6].

Theoretical papers on biphenyl are very numerous and we will cite only a few recent ones. According to Hosoya [5], biphenyl can be considered as consisting of two unlinked aromatic rings. The same conclusion was reached by Taubert et al. [7]. The experimental barriers around the planar and perpendicular conformations were for the first time accurately reproduced by Johansson and Olsen [6]. Several ab initio methods were used by Grein to calculate the dihedral angle and energy barriers of biphenyl [8]. Prampolini et al. [9] analyzed the potential energy surface of biphenyl.

This compound has served as a test for different methodologies such as "quantum fidelity" [10] and Electronic Polarization from the Internal Continuum (EPIC) [11]. Many papers reported theoretical studies of substituted biphenyl derivatives, for instance, oligophenyl cruciforms [12] and ferroelectric biphenyl derivatives [13].

The replacement of the phenyl rings of biphenyl by heteroaromatic rings (including aromatic tautomers) results in a very large collection of compounds that we have illustrated with some examples in Scheme 1.

A survey of the literature [14] lead to Table 1.

Especially interesting is the publication of Bachrach and Stück [15a]. These authors described nanohoops formed by heteroaromatic rings, like pyridine, linked in a 1,4′ fashion. In these structures, a distortion of the *ipso* carbon was observed, distortion that was reduced by interaction between the nitrogen lone pair and the opposite *ortho* hydrogen.

The present paper reports in the first section the conformational study of the 10 compounds of Scheme 2, that include some examples of the empty cases of Table 1, N–N,6–6 and N–N,5–6, as well as a discussion of the literature results on N–N,5–5 compounds.

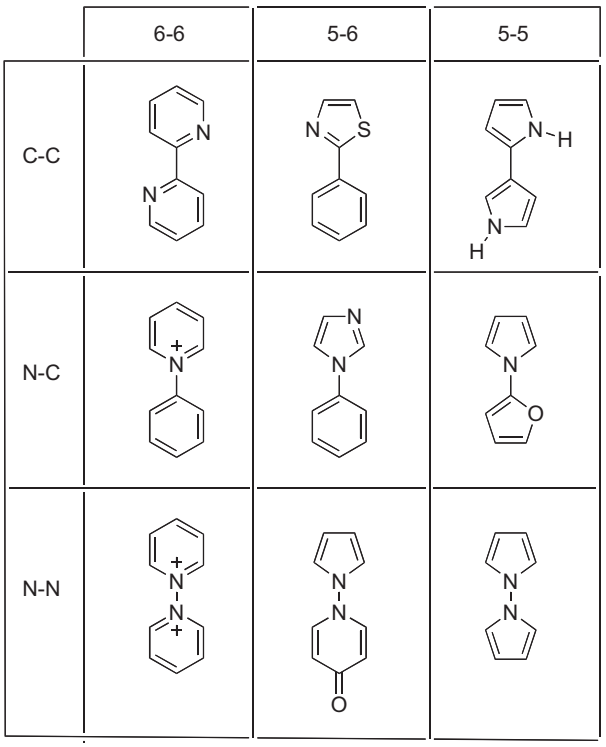
## 2. Results and discussion

### 2.1. Conformational analysis of the compounds of Scheme 2

All these compounds have in principle two barriers, one planar ($\theta = 0°$) and one perpendicular ($\theta = 90°$), save in those cases where the minimum is either planar or perpendicular. The planar barrier results from the interaction of the *ortho* (*alpha*) CH atoms, i.e., is of steric origin. The perpendicular one is due to the loss of conjugation and is of electronic origin.

* Corresponding author.
*E-mail address:* ibon@iqm.csic.es (I. Alkorta).
*URL:* http://www.iqm.csic.es/are/ (I. Alkorta).

2210-271X/$ - see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.comptc.2010.11.030




**Scheme 1.**

The most recent and accurate calculations of biphenyl (**1**) reproduce fairly well the torsion angle and the rotational barriers. Johansson and Olsen [6] calculated at CCSD(T) level a $\theta = 39°$ while the experimental value is $(44.4 \pm 1.2)°$ [23] as well as barriers in excellent agreement with the experimental values, $TS_0 = (6.0 \pm 2.1)$ and $TS_{90} = (6.5 \pm 2.0)$ kJ mol$^{-1}$ [24]. Taubert et al. [7] obtained the same value of $\theta = 39°$ at the B3LYP/def2-TZVP. The discrepancy with the experimental value can be assigned to vibrational and temperature effects [6,7].

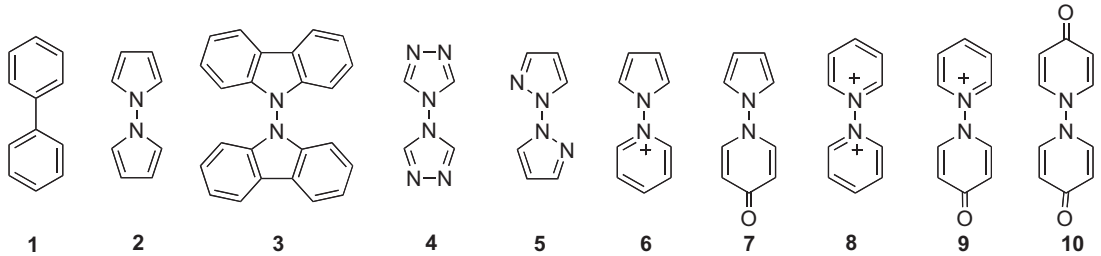
In 1972 Galasso and Trinajstic [17a] studied by the EHT (Extended Hückel) method the conformation of 1,1′-bipyrrole (**2**) concluding that the minimum energy conformation corresponds to a dihedral angle of around 48° and that the planar TS is higher in energy than the perpendicular one. Some of us reported in 1984 [22a] the MNDO calculations of 4,4′-bi-1,2,4-triazole (**4**) and of 1,1′-bipyrazole (**5**). In the case of **4** the minimum corresponds to $\theta = 90°$ (in the solid state, $\theta = 91.9°$) and the barrier through the planar conformation amounts to 27.5 kJ mol$^{-1}$. Since both **2** and **4** have four CH bonds pointing towards the N–N bond, it was expected that the minima were similar and not 48° and 90°, respectively. Compound **5** has its minimum at $\theta = 107.8°$ closer to the *anti* conformation (N atoms at positions 2 and 2′ on opposite sides) than to the *syn* one. The calculated rotational barrier were 28.7 kJ mol$^{-1}$ for $\theta = 0°$ and 7.7 kJ mol$^{-1}$ for $\theta = 180°$. In 2004, Ögretir and Tokay calculated all possible bipyrazoles (CC, NC and NN) [17b] at the MNDO, AM1 and PM3 semiempirical levels. Their MNDO calculations of **5** do not agree with those of our group; with the three methods they found that the *syn* isomer ($\theta = 56.8°$) was more stable than the *anti* one ($\theta = 128.7°$) by 3.4 kJ mol$^{-1}$. Ortí et al. [22b] calculated at the HF/STO-3G and HF/4-31G levels the conformation of **2**; the minimum corresponds to the orthogonal structure ($\theta = 90°$) and the barrier through the planar state ($\theta = 0°$) to 21.3 kJ mol$^{-1}$ (STO-3G) and 43.8 kJ mol$^{-1}$ (4-31G). Finally, Dey and Lightner [22c] reported the X-ray structure of **2** (refcode LISVIT) [25] and carried out molecular mechanics calculations: the experimental value has $\theta = 78.7°$ and the calculated one $\theta = 90°$. They calculated the rotational barrier about a planar TS but the geometry of the pyrrole rings has sp$^3$ nitrogen atoms which does not make much sense. No calculations of **3** have been reported but its X-ray structure is known (refcode PEDTAT) [24,26] as well as that of **4** (refcode TAZTAZ) [24,27]. The structure of the 4,4′-derivative of **8** has been determined (refcode ZETSAS) [24], $\theta = 84.7°$ (AM1 calculations, $\theta = 84.7°$) [21].

Our results at the B3LYP/6-31G(d) level are reported in Tables 2 (energetic aspects and aromaticity) and 3 (geometries).

For all the heterocyclic compounds in all conformations, the sum of the angles around the nitrogen atoms, $\Sigma\alpha$, is 360.0°, thus, the *ipso* carbon distortion reported for nanohoops was not

**Table 1**
Theoretical calculations on the nine types of structures of Scheme 1.

| X–X | Rings | Examples | No. of refs. and reference | |
|---|---|---|---|---|
| C–C | 6–6 | 2,2′-Bipyridine, 1,8-di(3′-pyridyl)naphthalene | 16 | [15] |
| C–C | 5–6 | Phenylthiazole, 2-pyridylbenzimidazole | 3 | [16] |
| C–C | 5–5 | Bithienyl, furylpyrrole, bifuran | 10 | [17] |
| N–C | 6–6 | *N*-Phenylpyridone, *N*-naphthylpyridinium | 2 | [18] |
| N–C | 5–6 | *N*-Arylazoles, sydnones, propellenes | 12 | [7,16a,19] |
| N–C | 5–5 | Pyrazolylpyrazoles | 3 | [17b,20] |
| N–N | 6–6 | – | 1 | [21] |
| N–N | 5–6 | – | 0 | |
| N–N | 5–5 | 1,1′-Bipyrrole, *N,N′*-biazoles | 4 | [17a,17b,22] |




**Scheme 2.**