[G015]

B3LYP study of electrical properties of the series of compound with formula Ph-(C$_{2+n}$N$_{4-n}$H$_n$)-Ph as candidates to electron conducting materials

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Abstract

The present communication reports a study on the variation of some structural and electronic properties related with electron conduction for the series of compounds represented by the formula Ph-(C$_{2+n}$N$_{4-n}$H$_n$)-Ph, n=0-4. Properties such as planarity, aromaticity, band gap, and adiabatic electron affinity were analyzed from a theoretical perspective as a function of the number of nitrogen atoms in the molecular structure.

1. Introduction

A great variety of compounds based on π-conjugated moieties has been studied as candidates for charge conducting materials due to their desirable chemical and electrical properties such as narrow HOMO-LUMO energy gaps, low intramolecular reorganization energies in electron-hole transport processes, chemical and thermal stability or high persistence length [1-4]. So far, π-conjugated polymers have been exploited mainly as *p*-type materials, giving rise to a somewhat unbalanced development causing differences in the efficiency between the hole- and electron-transporting materials [3].

The attractive properties described for 2,3-diphenyl-*s*-tetrazine and some related compounds led us to consider this compound and its derivatives as candidates for *n*-type conducting materials. In this sense, it has been reported that 2,5-diphenylpyrazine, 3,6-diphenyl-1,2,4-triazine and 2,3-diphenyl-s-tetrazine are reversible to the reduction and show low potentials which increase with the number of nitrogen atoms (-2.03, -1.89 and -1.24 V, respectively) [5,6]. Also, the existence of π-stacking interactions and weak intermolecular H-bonds between N and H-C of neighboring 2,3-diphenyl-s-tetrazine molecules allows to retain a planar conformation in the solid state [7-9] which favors the aromaticity and electric conductivity.

This hence focuses on the series of compounds represented in scheme 1. Our main aim is the study of the variation of some electronic properties related with the electron

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conduction as a function of the number of nitrogen atoms in the central ring. Some of these properties, the planarity and aromaticity, were studied through the dihedral angles $\tau_1(X_1\text{-}C_6\text{-}C_7\text{-}C_8)$ and $\tau_2(X_2\text{-}C_3\text{-}C_9\text{-}C_{10})$, and inter-ring bond distances $C_6\text{-}C_7$ and $C_3\text{-}C_9$ (see scheme 1 for atom numbering). The electronic excitation energy was studied by means of Time Dependent DFT (TD-DFT). Finally, the analysis the geometrical and electronic structure of anionic states (polarons) was essential to understand the changes occurred during the charge injection process and how these changes affect the studied properties.

$X = C, N$
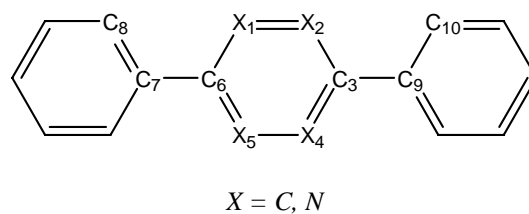
Scheme 1. Formula of the series of studied compounds showing the bond labelling scheme (hydrogen atoms have been omitted for simplicity)
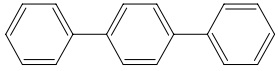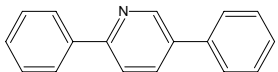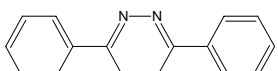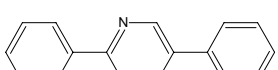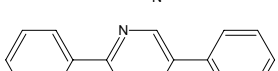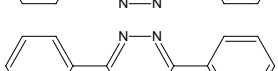
2. Computational Details

Gaussian03 (revision E.01) [10] running on a eight node Sun Fire X2200 Linux cluster and a Sun X4600 server has been employed for all the theoretical calculations. B3LYP [11,12] was the method employed for the optimization of geometries and calculation of energies. 6-31+G* basis set with diffuse *sp*-functions on heavy atoms was employed in order to obtain a more precise calculation of energy-related properties on open-shell systems [13]. The study of the electronic transitions was carried out by means of time dependent B3LYP (TD-B3LYP) on the corresponding geometries calculated at the same level and employing the 6-31+G* basis set.

3. Result and Discussion

3.1. Geometric Properties

Table 1 collects the calculated values for the dihedral angles $\tau_1(X_1\text{-}C_6\text{-}C_7\text{-}C_8)$ and $\tau_2(X_2\text{-}C_3\text{-}C_9\text{-}C_{10})$, and the inter-ring bond distances $C_6\text{-}C_7$ and $C_3\text{-}C_9$. As can be seen, 2,3-diphenyl-s-tetrazine is the only planar compound of the series. The rest of compounds show two different, non-planar conformers, with the phenyl groups in the same or different plane except 3,6-diphenyl-[1,2,4]triazine wherein one of the phenyl groups is near coplanar with the triazine ring (see figure 1). Thus, the dihedral angle τ_i diminishes, from 40° to 0°, as the number of nitrogen atoms increases due to the concomitant diminution of the steric hindrances between the H atoms linked to different rings. On the other hand, the inter-ring distances decrease from 1.484 Å, for the [1,1';4',1'']terphenyl, to 1.476 Å, for 2,3-diphenyl-s-tetrazine, due to the planarity favors the conjugation and enhancement of the double-bond character of the interring bonds.

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Table 1. Dihedral angles $\tau_1(X_1\text{-}C_6\text{-}C_7\text{-}C_8)$ and $\tau_2(X_2\text{-}C_3\text{-}C_9\text{-}C_{10})$, and interring bond distances $C_6\text{-}C_7$ and $C_3\text{-}C_9$ calculated at the B3LYP/6-31+G* level of theory.

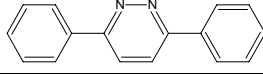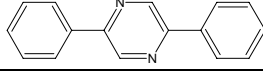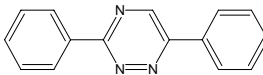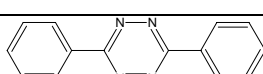| Compound	Conformer	$d_{interrings}$ / Å	τ_i / degrees
	1	1.4843	40.2
	2	1.4857	39.7/-39.7
	1	1.4825/1.4876	20.3/39.5
	2	1.4825/1.4875	20.0/-39.0
	1	1.4845	22.0
	2	1.4844	21.7/-21.7
	1	1.4822	21.1/23.0
	2	1.4831	20.5/-19.6
		1.4795/1.4805	22.2/1.4
		1.4763/1.4767	0.0
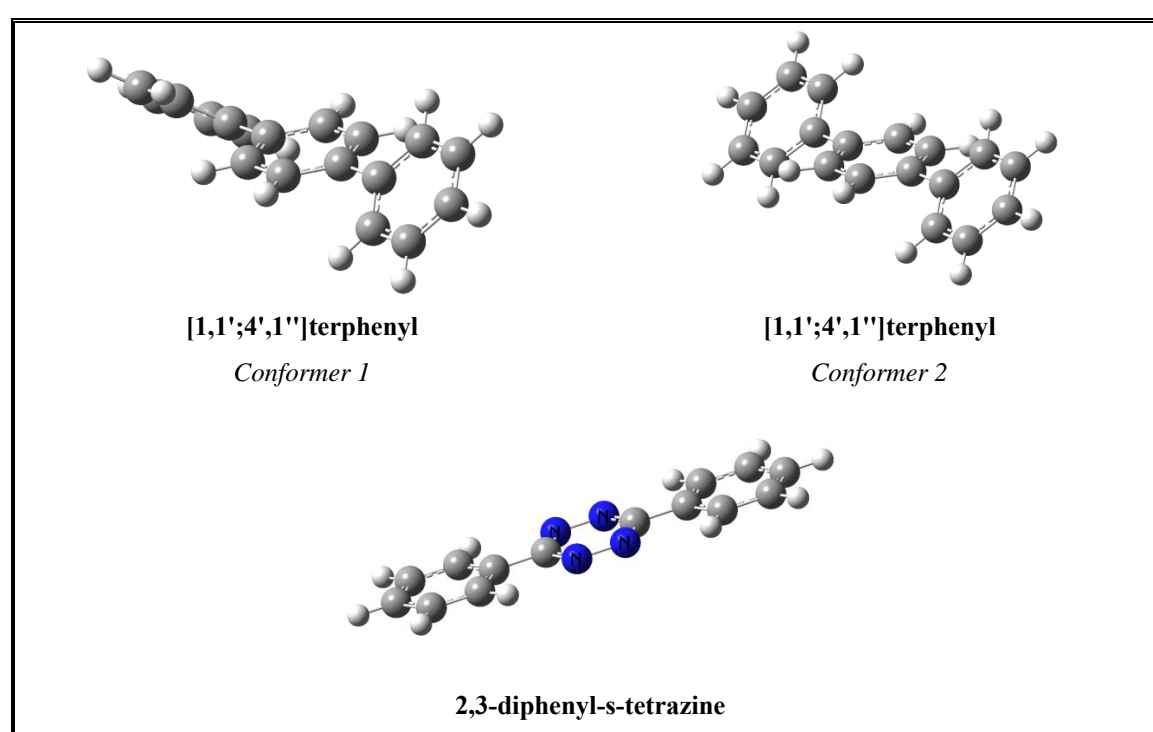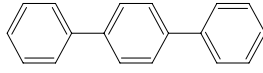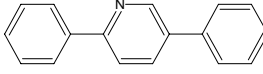
Figure 1. T the two conformers obtained for [1,1';4',1"]terphenyl and the planar structure calculated for 2,3-diphenyl-s-tetrazine.

3.2. Electronic Properties

A fundamental property of conducting polymers is the band gap between the valence and conduction bands, which must be narrow. On the other hand, when a monomer is studied as candidate to build a conducting polymer, the potentially interesting electronic transitions are those involving narrow energy gaps, high oscillator strength (*f*) and having a final molecular orbital (MO) completely delocalized over the molecule backbone. In table 2, the energy of those potentially interesting electronic transitions appears for each compound. In the case of [1,1';4',1"]terphenyl, the least energetic transition is that

corresponding to HOMO→LUMO. Both MOs are entirely delocalized over the whole molecule (see figure 2) and f shows a considerably high value. Furthermore, the energy of the HOMO→LUMO transition decreases as the number of N atoms increases. Nevertheless, the presence of the N atoms distorts the symmetry of the HOMO and LUMO orbitals causing a worse overlapping between both MOs and minor f values. In this sense, HOMO→LUMO transition becomes smaller for 3,6-diphenyl-[1,2,4]triazine (f = 0.0036), for which the HOMO orbital has a high non-bonding character and is mainly localized over the central ring of the molecule (see figure 2). Besides, HOMO-1→LUMO and HOMO-1→LUMO+1, with $f \geq 0.2$, are transitions which must be taken into account for 3,6-diphenyl-[1,2,4]triazine. Likewise, HOMO-1→LUMO+1 transition is the least energetic transition with a considerably high f value (1.05) calculated for 2,3-diphenyl-s-tetrazine. Both MOs are completely delocalized over the whole molecule, while HOMO and LUMO are localized on the central tetrazine ring. Thus, bearing in mind the low f value of HOMO-1→LUMO transition (0.2) for 3,6-diphenyl-[1,2,4]triazine, it seems that 2,5-diphenyl-pyrazine and 2,3-diphenyl-s-tetrazine are the compounds with the most suitable electronic transitions as concerns their possible use in conducting polymers.

Table 2. Electronic transition energies and adiabatic electron affinities calculated at the B3LYP/6-31+G* level of theory.
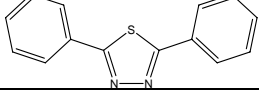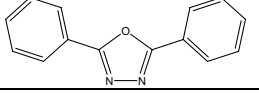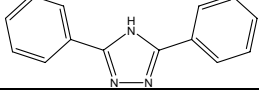
Compound	Conformer	Energy Gap / eV	f	Main component of the transition (% contribution)	AEA / eV
	1	4.33	0.8933	HOMO→LUMO (87%)	0.32
	2	4.32	0.8790	HOMO→LUMO (87%)	0.32
	1	4.12	0.8492	HOMO→LUMO (83%)	0.55
	2	4.14	0.8998	HOMO→LUMO (85%)	0.55
	1	4.10	0.9145	HOMO→LUMO (86%)	0.75
	2	4.11	0.9130	HOMO→LUMO (83%)	0.75
	1	3.85	0.7791	HOMO→LUMO (85%)	0.84
	2	3.85	0.7564	HOMO→LUMO (78%)	0.85
		3.73	0.2009	HOMO-1→LUMO (56%)	1.02
		4.03	0.6887	HOMO-1→LUMO+1 (51%)	
		3.91	1.0514	HOMO-1→LUMO+1(64%)	1.50
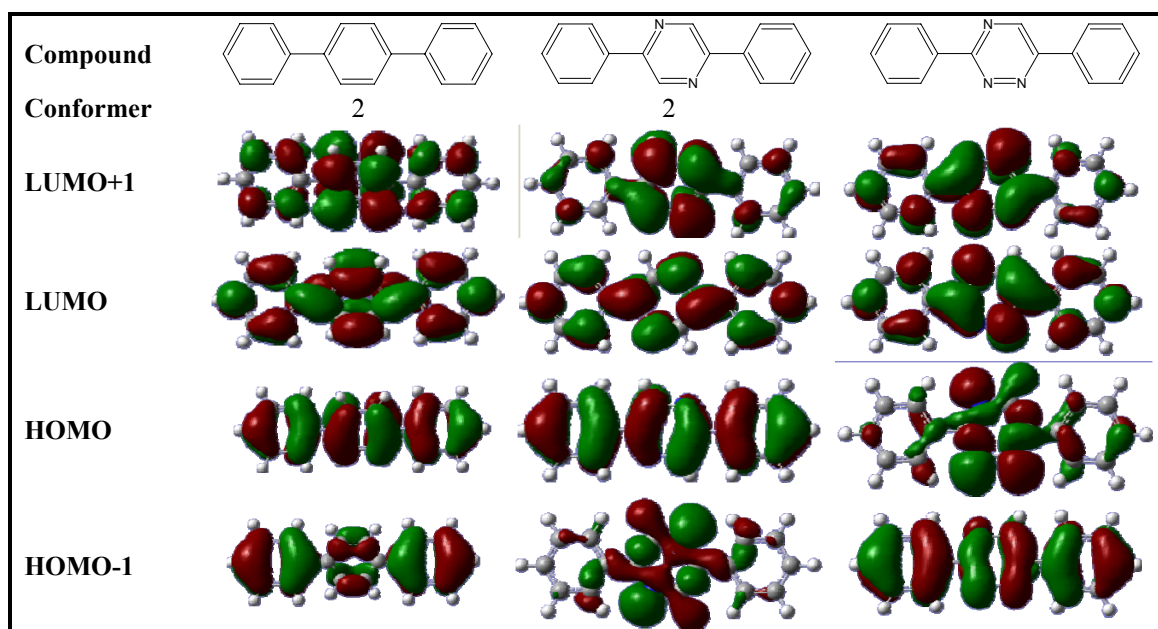
Figure 2. Representation of the frontier molecular orbitals for [1,1';4',1"]terphenyl, 2,5-diphenyl-pyrazine, and 3,6-diphenyl-[1,2,4]triazine.

Table 2 also shows the adiabatic electron affinity (AEA) calculated for each one of the studied compounds. High electron affinities are needed in order to get efficient charge injection [3]. As it can be seen, the AEA increases monotonously with the number of nitrogen atoms from 0.33 eV, for [1,1';4',1"]terphenyl, to 1.50 eV, for 2,3-diphenyl-s-tetrazine. With only N atom in the structure the calculated values are comparable to those calculated for other compounds with a higher number of N atoms such as 3,5-diphenyl-4*H*-[1,2,4]triazole and 3,5-diphenyl-4*H*-[1,2,4]oxadiazole (see table 3).

Table 3. Adiabatic electron affinities calculated at the B3LYP/6-31+G* level for other related diphenyl compounds [3].

Compound			
AEA / eV	0.96	0.68	0.42

Finally, the calculated AEA also gives an idea about the stability of the radical ion molecule towards quenching caused by molecular oxygen [3]. The calculated AEA for the molecular oxygen is 0.59 eV at the B3LYP/6-31+G* level of theory while the experimental electron affinity has been determined by photoelectron spectroscopy to be 0.448 ± 0.006 eV [3,14]. Thus, those compounds with more than one nitrogen atom in the central ring should be more effective against oxygen quenching.

4. Conclusions

In this work, the variation of the some structural and electronic properties related with the electron conduction, in the series of compounds represented in the scheme 1, was studied. It has been concluded that both the planarity and aromaticity increase with the

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number of N atoms in the central ring. On the other hand, the band gap is reduced while electron affinity increases with the number of N atoms. Also, from AEA calculations it could be inferred than those of the studied compounds with more than one N atom in the central ring should not be affected by oxygen quenching.

Acknowledgments

References

[1] S. Özen, C. Atilgan, G. Sonmez, J. Phys. Chem. C **111**, 16362 (2007).

[2] T. Yasuda, T. Imase, Y. Nakamura, T. Yamamoto, Macromolecules **38**, 4687 (2005).

[3] E. Jansson, P. H. Jha, H. Ågren, Chem. Phys. **330**, 166 (2006).

[4] J. M. Granadino-Roldán, A. Garzón, G. García, T. Peña-Ruiz, M. P. Fernández-Liencres, A. Navarro, M. Fernández-Gómez, J. Chem. Phys. **130**, 234907 (2009).

[5] T. Troll, Electrochimica Acta. **27**, 1311 (1982).

[6] K. Pieterse, J. A. J. M. Vekemans, H. Kooijaman, A. L. Spek, E. W. Meijer. Chem. Eur. J. **24**, 6 (2000).

[7] N. A. Ahmed and A. I. Kitaigorodsky, Acta Cryst. **B28**, 739 (1972).

[8] L. Infantes, M. F. Mahon, L. Male, P. R. Raithby, S. J. Teat, J. Sauer, N. Jagerovic, J. Elguero, S. Motherwell, Helvetica Chimica Acta. **86**, 1205 (2003).

[9] N. S. Oxtoby, A. J. Blake, N. R. Champness and C. WilsonGhosh, Cryst. Eng. Comm. **5**, 82 (2003).

[10] Frisch M J et al. Gaussian 03 Revision E.01, Gaussian Inc., Wallingford CT, 2004.

[11] A. D. Becke, J. Chem. Phys. **98** 5648 (1993).

[12] C. Lee, W. Yang, R. G. Parr, Phys. Rev. **B37**, 785 (1988).

[13] J. B. Foresman, A. E. Frisch, Exploring Chemistry with Electronic Structure Methods, 2nd ed. Pittsburg: Gausssian, Inc.

[14] K. M. Ervin, I. Anusiewicz, P. Skurski, J. Simons, W. C. Lineberger, J. Phys. Chem. A **107**, 8521 (2003).