Supporting Information

On the Role of Heteroatoms into Aromatic Rings. Insights from 10π Main Group Elements Heterorings [(EH)₂S₂N₄]^q (E=C, P, B, Si, Al and q=0,-2).

A. G. Papadopoulos^b, N. D. Charistos^{b, *}, A. Muñoz-Castro^{a,*}

^a Grupo de Química Inorgánica y Materiales Moleculares, Universidad Autonoma de Chile, El Llano Subercaseaux 2801, Santiago, Chile.

^b Aristotle University of Thessaloniki, Department of Chemistry, Laboratory of Applied Quantum Chemistry, Thessaloniki 54 124, Greece.

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I) Theoretical analysis of the Chemical Shift for1,5,2,4,6,8-Dithiatetrazocine.

NMR spectroscopy has been employed to evaluate experimentally the aromatic character of aromatic hydrocarbon rings, where the exocyclic hydrogen exhibits diatropic shifts denoting a deshielding from olefinic hydrogens^[S1]. Such technique represents a valuable tool for assessing the chemical environment of a certain probe nucleus within structure. In addition, the magnetic response at the nuclei, which account for usual NMR experiments, can be conveniently generalized through the space leading to a graphical representation of the short-and long-range magnetic behavior driven by the presence of induced currents^[S2-S4] (*vide supra*).

The characterized ¹H-NMR peaks for the aromatic hydrogen in the $(CH)_2S_2N_4$ ring are downfield in comparison to the respective values in benzene, suggesting a more aromatic character in the former structure. The calculated values of δ agree well with the experimental data (Exp. 9.7 and 7.33 ppm for (CH)₂S₂N₄ and benzene^[S5, S6] respectively), denoting values of 9.82 for (CH)₂S₂N₄ and 7.48 ppm for benzene, obtained as $\delta_{ij} = \sigma^{TMS} - \sigma_{ij}^{[S7]}$ (Table S1). The calculated variation of the ¹H-NMR shift exhibits a downfield of 2.34 ppm. In order to exploit the information given from such tensor (σ_{ij} , *i*,*j*=1,2,3), to gain a better understanding of the variation of δ_{ij} , we provide a graphical representation describing the three principal components (eigenvalues) of the diagonalized tensor in its own principal axis system $(PAS)^{[S8-S11]}$ (Figure S1). Here, σ_{ij} is oriented in the molecular frame which describes the orientation, magnitude and sign of such response, relevant parameters that are reduced to a single value when the isotropic chemical shift is usually employed^[S8-S11]. The principal components of the shielding tensor at the nuclei are designed by σ_{11} , σ_{22} and σ_{33} according to $\sigma_{11} \le \sigma_{22} \le \sigma_{33}$ [S8], reserving the *x*, *y* and *z* suffices for the through-space representation of the magnetic response (vide infra)^[S12]. For benzene and (CH)₂S₂N₄, the most shielded component (σ_{33}) is aligned to the C-H bond (Figure S1) and σ_{22} is contained in the ring plane, whereas σ_{II} is oriented out-of-plane. Such component, accounts mainly for the deshielding shift observed in ¹H-NMR for the exocyclic protons of (CH)₂S₂N₄, due that is the more influenced component of the deshielding region outside of the ring resulting from the aromatic character, in line to the previously described by Fowler and coworkers^[S13].



Figure S1. Graphical representation of the shielding tensor depicting the three main axes under its own PAS (see text).

Molecule	$\delta_{iso}{}^{TMS}$	
Benzene	7.5 (7.33) ^a	
1	5.4	
2- C	9.8 $(9.7)^b$	
2-В	6.3	
2-Si	6.8	
2-Al	5.0	

Table S1. ¹H-NMR (ppm) calculated at BP86/TZ2P.

^aExperimental values in parentheses from reference S6.

^bExperimental values in parentheses from reference S5.

II) Magnetic response of π -, σ - and core subsets of electrons

In order to gain a better understanding of the contribution from σ - and π -levels, the zz component of the induced magnetic field has been separated in terms of π , σ and core electrons. As observed from Figure S2, the induced field involving core electrons mainly exhibits a shielding response inside the ring with a complementary deshielding region in the outer part. Despite the different number of inner electrons for S and E (E = P, Si, Al) in comparison to carbon, the diatropic response of core orbitals presents very small differentiation among the series of molecules, with NICS(0)_{core,zz} values ranging from - 9.3ppm in **2-P** to -11.2ppm in **2-Si**, when the corresponding value for **1** is -10.5ppm (Table 2 in manuscript).

Moreover, the response given from the σ orbitals exhibits a central deshielding response, with a shielding region around the ring contour, similarly to benzene as has been previously depicted by Merino and coworkers^[S1]. Additionally an external deshielding region can be observed, which diminishes in **2-Si** and **2-AI**. This deshielding response inside the ring can be attributed to the more localized nature of the $n\sigma$ orbitals contained in the ring-plane. Through the series, an enhanced response is observed for the **2-Si** and **2-AI**, which exhibit similar NICS(0)_{$\sigma,zz}$ values with **1** (20.0ppm, 19.2ppm and 21.1ppm respectively), while the paratropic response is slightly reduced in **2-C** and **2-B**, exhibiting NICS(0)_{$\sigma,zz} values at 16.3ppm and 17.3ppm respectively. Interestingly,$ **2-P** $presents the weakest paratropic response from its <math>\sigma$ electrons, with its NICS(0)_{$\sigma,zz} value being less than half of$ **1** $, at 10.1ppm. The reduced paratropic contributions from <math>\sigma$ orbitals of **2-C** and **2-P** are responsible for their high total NICS(0)_{zz} values, which are almost equal to**1** $. From Chart S1 it is clear that the <math>\pi$ -magnetic response is much stronger and long-ranged with regard to the response of the σ -system.</sub></sub></sub></sub>

Concerning the magnetic field induced from the π -electrons, it remains similar within the series, where a strong and long-range shielding response is observed inside and above the ring, with a complementary outer deshielding region (Figure S2). This term is relevant in order to recall the Pople's ring current model, where only the π orbitals contribution to the magnetic response should be taken into account. Hence, from the π -contribution to the zz

component, the aromatic behaviour of the studied series is confirmed denoting the high similarity between the homo- and heteroatomic counterparts. Thus the aromatic character is in agreement to the early Pople's model^[S14], retaining a large aromatic character for the series composed by 10π -electrons heterorings.

Although all systems present long-range shielding response from their π -electrons, which is representative of aromaticity, the magnitude and the range of this effect differentiates among the molecules under study. This differentiation is clearly illustrated in B_z^{ind} profiles of the π system (Chart S1), where it is shown that the diatropic response of the π -system decreases through the series from 2-C to 2-Al, with the NICS(0)_{$\pi,zz} values$ ranging from -43.0ppm in the former down to -22.0ppm in the latter, while the corresponding value for 1 is -49.0ppm. From B_z^{ind} profiles it is shown that the differentiation of the π -response holds until approximate 4Å above the ring where all curves meet, and the magnetic response diminishes at a distance about 6Å. Thus, although the heterocycles present pronounced π -aromatic character due to their 10 π electrons, the aromaticity decreases as the electronegativity of E(E= C, P, B, Si, Al) is reduced from 2-C to 2-Al.</sub>



Figure S2. π -, σ - and core contributions to the out-of-plane component of the induced magnetic field.



Chart S1. B_z^{ind} (ppm) profiles of σ - and π -electrons above ring centers.

III) Magnetic response under different choice of origins

The magnetic response of Dithiatetrazocine was calculated with two different origins of the Cartesian axes (Figure S3): (A) the origin is the center of symmetry, and (B) the origin is at the carbon atom position. The through-space magnetic response of CMOs within the GIAO scheme is dependent on the choice of the origin (Figure S4), while their sum (total response) is independent of the chosen origin. However for symmetrical molecules, the through-space magnetic response is transposed towards the chosen origin (Figure S4.B) in such a way that the average response of two symmetrical chosen origins (with regard to the center of symmetry of the molecule), is equal to the magnetic response when the origin is the center of the molecule (center of symmetry), as shown in Figure S5. In this sense the average of the magnetic responses for distributed origins throughout the whole space is equal to the magnetic response when the origin is the center of symmetry of the molecule. Hence, the choice of the origin should be the center of symmetry in order to have legitimate maps of the magnetic response that correspond to the symmetry of the molecule.

For the molecules under study (D_{2h}) the total- π magnetic response is independent of the choice of origin due to symmetry, as shown in Figure RC2. CMO-NICS_{zz} values at the center of the molecule (center of symmetry) are also independent of the origin for molecules with center of symmetry, as shown in Table S2. It should be noted that GIAO components (gauge, dia, occ-occ, occ-unocc) and NICS tensor components (iso, xx, yy) at ring center are also equal for origins A and B.

Therefore the choice of origin does not influence the conclusions of the manuscript and another origin would reproduce the same CMO-NICS_{zz} values, CMO-NICS_{zz} profiles and total- π maps. CMO maps would not be valid as they would not correspond to the symmetry of the molecule.



Figure S3. Two different origins of Cartesian axes in Dithiatetrazocine.

MO	Svm	Type	Α	В
17	A.g	σ	-11.8	-11.8
18	B3.u	σ	-11.7	-11.7
19	B2.u	σ	-10.7	-10.7
20	B1.g	σ	-5.4	-5.4
21	A.g	σ	-4.7	-4.7
22	B2.u	σ	1.1	1.1
23	B3.u	σ	-5.9	-6.0
24	B1.g	σ	-5.9	-5.9
25	A.g	σ	-8.3	-8.3
26	B3.u	σ	-2.6	-2.6
27	B1.u	π1	-10.5	-10.5
28	B2.g	π2	-10.6	-10.6
29	B2.u	σ	-0.9	-0.9
30	B3.g	π3	-8.6	-8.6
31	A.g	σ	-2.9	-2.9
32	A.g	σ	15.3	15.4
33	B2.u	σ	25.8	25.8
34	A.u	π4	-7.1	-7.1
35	B3.u	σ	27.7	27.7
36	B1.g	σ	17.4	17.4
37	B1.u	π5	-6.1	-6.1
Total σ			16.5	16.5
Total π			-43.0	-43.0

Table S2. CMO-NICS $(0)_{zz}$ (BP86/TZ2P) at ring centers of Dithiatetrazocine for origins A and B.



Figure S4. CMO-NICS $_{zz}$ maps (BP86/TZ2P) of Dithiatetrazocine for origins A and B.



Figure S5. The average of the magnetic response of π_5 for two symmetrical origins with respect to the center of symmetry is equal to the magnetic response of π_5 when the origin is the center of symmetry.

IV) GIAO components analysis

To further investigate the origins of the varying magnetic behaviour of $2b_{lu}$ (π_3) and b_{2g} (π_3) orbitals, the out-of-plane component of shielding tensor at ring centers (equal to NICS(0)_{zz}) was analysed according to GIAO formalism, as a summation of four components: $\sigma^{total} = \sigma^{dia} + \sigma^{gauge} + \sigma^{occ-occ} + \sigma^{occ-unocc}$. The first two terms are related to the ground state and their magnitudes depend on the choice of the origin of the vector potential^[S15, S16]. The $\sigma^{occ-occ}$ term describes diatropic contributions arising from interactions between occupied orbitals. The last term, $\sigma^{occ-unocc}$, which is gauge independent, is related to excited states and describes paratropic contributions of rotationally allowed excitations from occupied to unoccupied orbitals induced by the magnetic perturbation^[S16]. This term is symmetry allowed within the corresponding point group, when the triple direct product of the irreducible representations of the interacting occupied and unoccupied orbitals with the rotational axis around the field direction, contains the totally symmetric representation^[S15]. In addition, the magnitude of $\sigma^{occ-unocc}$ term depends on the energy difference and the spatial overlap between occupied and rotated unoccupied interacting orbitals.

In Table S3, the GIAO components of b_{2g} (π_3) orbital are presented. Within the series of heterocycles, the terms that differentiate significantly is the σ^{gauge} , decreasing from -8.4ppm in **2-C** down to -3.8 in **2-AI**, and $\sigma^{occ\text{-unocc}}$ term, which presents increasing paratropic contributions, starting from -0.3ppm in **2-C** up to 6.4ppm in **2-AI**. The $\sigma^{occ\text{-unocc}}$ term seems to be the governing factor of NICS(0)_{zz} of b_{2g} (π_3), as these terms are inversely proportional (R²=0.99, Chart S2). The values of $\sigma^{occ\text{-unocc}}$ term arise exclusively from excitations of b_{2g} (π_3) to LUMO $2b_{3g}$ (π_6), which is symmetry allowed, as the corresponding triple direct product within D_{2h} point group, contains the totally symmetric representation: $\Gamma^{occ} \times \Gamma^{rot} \times \Gamma^{unocc} = \Gamma^{b2g} \times \Gamma^{b1g} \times \Gamma^{b3g} = A_g$. The energy difference between b_{2g} (π_3) and $2b_{3g}$ (π_6) decreases through the series from 6.47eV in **2-C** down to 3.82eV in **2-AI**, as b_{2g} (π_3) is destabilized and $2b_{3g}$ (π_6) is stabilized (Figure 3 from the main manuscript), allowing the rotational excitations to increase their paratropic contributions.

		J_{2g} and J_{3g} (LO	100)			
GIAO components			NICS	٨٢		
	gauge	dia	0CC-0CC	occ-unocc	NIC5 ₂₂	
1'	-7.1	1.3	-4.7	-0.1	-10.5	7.96
2-C	-8.4	1.1	-2.9	-0.3	-10.6	6.47
2-P	-7.3	1.2	-2.5	1.2	-7.5	5.14
2-B	-6.6	1.0	-3.2	1.0	-7.9	4.88
2-Si	-6.0	1.0	-2.4	3.7	-3.7	4.41
2-Al	-3.8	0.8	-2.6	6.4	0.8	3.82

Table S3. GIAO components, total NICS_{zz} values (ppm) of b_{2g} (π 3) orbital at ring center and energy gap Λ F (eV) between b_{2g} and b_{2g} (LUMO)



Chart S2. Correlation of NICS(0)_{zz} versus $\sigma^{occ-unocc}$ term for b_{2g} (π_3) orbital.

In Table S3, the GIAO components of $2b_{1u}$ (π_5) orbital are presented. For this orbital no significant contributions arise from $\sigma^{occ\text{-unocc}}$ term, as is expected for π -HOMO of aromatic molecules^[S16]. The term that differentiates significantly within the series of heterocycles is $\sigma^{occ\text{-occ}}$, decreasing from -9.0ppm in **2-C** down to -5.8ppm in **2-AI**. The magnitude of this term arises exclusively from interactions between $2b_{1u}$ (π_5) and a_u (π_4). The energy difference between these orbitals increase through the series of heterocycles, starting from 0.7eV in **2-C** up to 2.2eV in **2-AI** (Figure 3, Table 4 from the main manuscript), leading to weaker diatropic contributions from occupied orbitals interactions.

and energy gap ΔE (eV) between b_{1u} and a_u (π_4)						
GIAO components				NICS	٨F	
	gauge	dia	осс-осс	occ-unocc		
1'	5.9	-0.1	-15.2	0.5	-8.9	0.5
2-C	3.6	0.0	-9.0	-0.7	-6.1	0.7
2-P	3.0	0.1	-7.4	-0.3	-4.6	1.2
2-В	5.7	-0.1	-8.7	0.3	-2.9	1.3
2-Si	3.9	-0.2	-6.6	0.6	-2.3	1.9
2-Al	5.7	-0.9	-5.8	1.4	0.4	2.2

Table S4. GIAO components, total NICS_{zz} values of b_{1u} (HOMO) orbital at ring center and energy gap ΔE (eV) between b_{1u} and a_u (π_a)

Consequently, the destabilization of $2b_{1u}$ (π_5) and b_{2g} (π_3) orbitals with major contributions from p_z of E (E= C, P, B, Si, Al) plays an important role in the lowering of aromaticity through the series of 10π heterocycles, as it reduces the diatropic contributions from occupied-occupied orbital interactions in the $2b_{1u}$ (π_5), while it increases paratropic contributions from occupied-unoccupied interactions in b_{2g} (π_3).

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