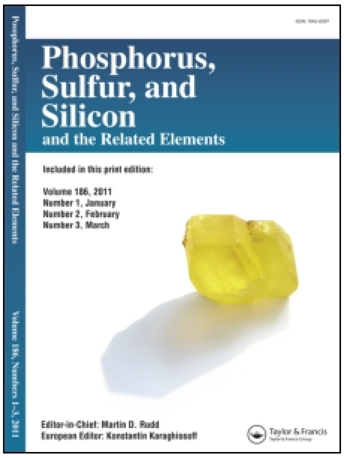

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Substitution Effect in NICS Values in Tropylium Ion Derivatives: An Ab Initio Study

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*Hartree–Fock (HF) and hybrid density functional theory (B3LYP) calculations were performed on tropylium ion and 19 of its mono- and diheteroatomic derivatives. The aromaticity in this class of compounds is evaluated based on the nucleus independent chemical shift (NICS) values. The NICS values are calculated at the center of the rings NICS (0) and at 1Å above the molecular plane NICS (1). The geometry optimization and NICS calculations were carried out at the HF/6–311+G** and at the B3LYP/6–311+G (2d, p) density functional level, respectively. These calculations in the effects of heteroatoms such as N, B, P, and Si are considered on aromaticity, molecular properties, NICS values, and structural parameters.*

Keywords Aromaticity; DFT; NICS; tropylium ion

INTRODUCTION

Aromaticity is among the most widely used concepts in chemistry.[1–9] Molecules with cyclic conjugated π-electron systems have specific magnetic properties different from other π-electron systems.[10] They have, in particular, a stronger diamagnetic susceptibility than expected from additive rules like those of Pascal,[11] a pronounced anisotropy of the susceptibility, and a deshielding of the protons attached to the ring carbons, as compared to noncyclic conjugated π-systems.[12] Their extra stabilization, special reactivity, and magnetic properties are associated with the cyclic delocalization of π-electrons. Aromatic compounds exhibit a diamagnetic ring current. Qualitatively, this ring current can be viewed

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as the migration of the influence of the magnetic field in NMR spectrometer.[13–15] The ring current effect is responsible for a large magnetic anisotropy in aromatic compounds. The chemical shift phenomenon can be treated on a quantitative basis by quantum-mechanical calculation of the chemical shift at the center of the rings. The value of the chemical shift at a point in the center of the ring can be calculated. These values are referred to as the nucleus independent chemical shift (NICS).[16–18] These values show excellent correlation with other manifestations of aromaticity. The index is defined as the negative value of the absolute magnetic shielding computed at ring's center.[19–22] It is based on a probe with no basis functions (bq), which is placed at or above the geometrical center of a conjugated ring. NICS values are calculated at the center of the rings and at 1Å above the molecular plane. Rings with highly negative values of NICS are quantified as aromatic by definition, whereas those with positive values are anti-aromatic.[23–28] The NICS (1) values are considered to better reflect the π-electron effects.[28–34]

We studied the effects of one and two heteroatoms (B, N, P, and Si) on the tropylium cation and on the change in the properties caused by these replacements in the ring current and aromaticity.

RESULT AND DISCUSSION

This study systematically evaluates the performance of NICS analysis in evaluating the aromaticity in tropylium ion (**1**) and a series that replaced mono- and diheteroatom with CH groups.

Mono-Substituted Tropylium Ion

When the boron was replaced and hydrogen eliminated, the electron density was focused inside the ring. So, the sigma effect in NICS (0) increased.

TABLE I NICS (0) and (1) Values Were Calculated by Ab Initio Study in B3LYP/6–311+G (2d, p) Level of Theory

	B	C	N	Si	P
NICS(0)	−7.7	−5.3	−4.7	−4.7	−5.3
NICS(1)	−9	−9.2	−9.1	−7.3	−8.9

TABLE II NICS (0) and (1) Value Compared by Tropylium Ion Designed

	σ	π
P	Meager negative effect	Meager negative effect
N	Negative effect	Non effect
B	Positive effect	Non effect
Si	Meager negative effect	Negative effect

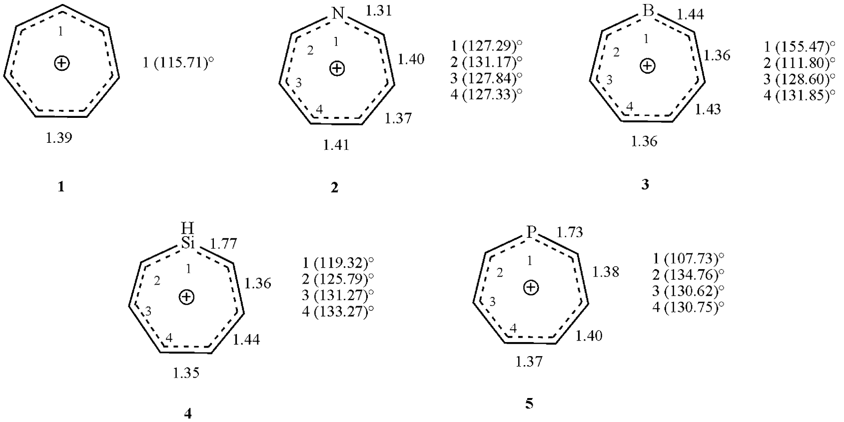
Reducing of aromaticity and ring current in NICS values involved negative effect of heteroatom, and increasing with positive effects.

In the aza derivative, because of withdrawing of electron and the small size of nitrogen, the electron density and resonance focused on nitrogen and NICS (0) decreased.

In the sila tropylium ion, by reducing of electronegativity and increasing size of Si and bond length (C-Si), we observed decreasing of value of NICS (0) and (1).

In the phospha tropylium ion, the value of NICS (1) in comparison with the tropylium ion decreased.

According to these results, which are given in Tables I and II, by increasing the size of heteroatom and increasing the value of electronegativity, we observe a decreasing of NICS values, which is shown Scheme 1.



SCHEME 1

TABLE III NICS (0) and (1) Values Were Calculated by Ab Initio Study in B3LYP/6–311+G (2d, p) Level of Theory

		NICS (0)	NICS (1)
N, N	1, 2	−4.7	−10.1
	1, 3	−4.0	−8.8
	1, 4	−3.9	−9.1
N, B	1, 2	−6.0	−8.0
	1, 3	−8.5	−9.9
	1, 4	−7.5	−8.9
N, Si	1, 2	−3.5	−6.2
	1, 3	−4.1	−7.4
	1, 4	−4.6	−7.3
N, P	1, 2	−3.9	−8.4
	1, 3	−4.4	−9.1
	1, 4	−4.4	−8.8
P, P	1, 2	−5.50	−9.49
	1, 3	−3.69	−8.10
	1, 4	−3.93	−7.78

Disubstituted Tropylium Ion

When two nitrogen atoms were replaced with CH groups, delocalization of the electron was decreased by focused electron density of ring on two heteroatoms, and NICS value decreased. That result is given Table III.

In the nitrogen and boron derivatives, nitrogen decreases aromaticity and boron increases it. Hence, the properties of these structures were between the tropylium ion and the boron tropylium ion.

When the nitrogen and phosphorous were replaced in tropylium ion, the NICS values are the same as in the mono nitrogen substituted ion. The effect of the phosphorous atom in aromaticity is meager.

By replacing nitrogen and silicon in the tropylium ion, the NICS values decreased. As a result, nitrogen decreased σ-portion in aromaticity and silicon decreased π-portion.

In two phosphorous atom derivatives, the aromaticity decreased because increasing of phosphorous size and bond length caused the ring structural disruption.

COMPUTATIONAL METHOD

Optimization of all species was carried out by the HF/6–311+G** level of theory. The GIAO/B3LYP/6–311+G (2d, p) method was used for the NICS calculations. NICS is the negative value of absolute magnetic shielding calculated at revealing point in or near an aromatic system. All calculations were performed by using the GAUSSIAN 98 suite of programs.[35]

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