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AGRONOMSKI FAKULTET U ČAČKU

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FACULTY OF AGRONOMY
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AROMATICITY OF ROESKY'S KETONE

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Abstract The polythiazyl polymer $(SN)_x$ is an intrinsic electric polymeric conductor at room temperature and superconductor at temperatures close to absolute zero, having diverse applications in chemistry and chemical technology. In this work, electronic properties of the compounds with a $(SN)_2$ unit enclosed in the ring stricture were examined. Namely, the aromaticity of Roesky's ketone and its isomers was investigated by means of current density maps, multicentre delocalization indices (MCI) and nucleus-independent chemical shifts indices (NICS). The relative stability of the studied compounds was compared based on the calculated BLYP and CASSCF energies.

Keywords: ketone, aromaticity, NICS, multicentre delocalization index, current density maps

Introduction

Stating from the discovery of the metallic properties of polymeric $(SN)_x$ in the early 1970s (Walatka Jr., Labes and Perlstein, 1973)compounds containing $(SN)_2$ fragments have been the subject of interest of theoretical and experimental chemists. In the polymer $(SN)_x$ the sulfur and nitrogen atoms donate two π-electrons and one π-electron, respectively, making these compounds electron-rich and very reactive. The polythiazyl polymer $(SN)_x$ is a unique material being the only example of an intrinsic electric polymeric conductor at room temperature and superconductor at temperatures close to absolute zero. It also exhibits the behaviour of a quasi one-dimensional metal with the conductivity along the polymeric chain three orders of magnitude greater than in the transverse direction. On the other hand, compounds with a $(SN)_2$ unit enclosed in the rings of different size are found to be stable. The cyclic systems containing a $(SN)_2$ unit have been much studied in the past (Gerratt *et al.*, 1996; Jung *et al.*, 2004). An intensive theoretical research has been performed in order to understand the electronic structure and bonding patterns in the S_2N_2 monocyclic molecule(Gerratt *et al.*, 1996; Jung *et al.*, 2004).The structure, aromaticity and reactivity of molecules containing $(SN)_2$ fragments involved in the five- and six-membered rings have also been examined (Van Droogenbroeck *et al.*, 2004). The most important among the molecules having $(SN)_2$ fragments involved within the five-membered ring is 5-oxo-1,3,2,4-dithiadiazole or Roesky's ketone (**1**).

In a series of recent papers, Blockhuys and coworkers have presented a detailed study of the structure, aromaticity and reactivity of Roesky's ketone and Roesky's sulfoxide(Van Droogenbroeck *et al.*, 2004). Since there is no unique definition of

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aromaticity, it is possible to measure the aromaticity through its different manifestations(Cyrański, 2005). There is a series of different aromaticity indices, namely energetic, geometric, electron delocalization, reactivity-based and magnetic indices(Cyrański, 2005). The fact that all these indices do not correlate mutually has resulted in the so-called multidimensional concept of aromaticity.

In the previous studies, the aromatic character of **1** has been examined by means of NICS(Schleyer *et al.*, 1996) and geometry parameters obtained from the optimized structures of these compounds. Although, the NICS index is one among the most popular aromaticity indices, the problem with NICS is that although usually a negative (or aromatic) NICS value reflects the existence of a ring current, there is no direct way to prove the existence of an underlying ring current. There are many examples showing that the NICS and ring current results do not agree. For this reason the calculated NICS-values were compared with the current density maps.

In the present study the current density maps were obtained by means of the BLYP functional using the diamagnetic-zero (DZ) variant of the continuous transformation of origin of current density (CTOCD) method(Keith and Bader, 1992). In the CTOCD-DZ method, also known as the ipsocentricmethod, the current density at each point in the molecule is calculated by choosing itself as the origin of the vector potential. The ipsocentric method enables a direct visualization of the induced current density, and of its deconposition into orbital contributions.

In order to assess the extent of electron delocalization in the studied molecules the multicentre delocalization index (MCI)(Giambiagi *et al.*, 2000) was employed. In the present work different constitutional isomers of Roesky's ketone were also included (Figure 1) in order to perform a more detailed analysis of the aromatic nature of molecules containing $(SN)_2$ fragments. This way, we aim to establish the nature of the aromaticity in terms of sustaining of a ring current and in terms of assessing cyclic electron delocalization for Roesky's ketone.

Theoretical methods

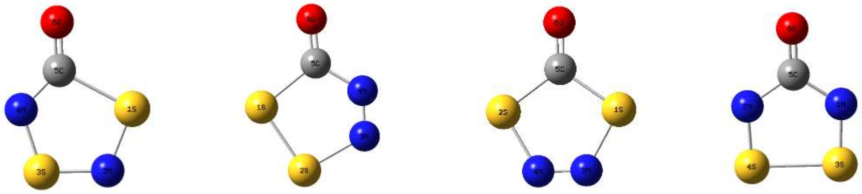
The structures of the molecules presented in Figure 1 were optimized at the BLYP/6-311+G(d,p) level of theory using the Gaussian 03 program(Frisch *et al.*, 2003).The single-point CASSCF(6,5)energy calculation with the same basis set was also performed. The NICS(Schleyer *et al.*, 1996) were obtained at the BLYP/6-311+G(d,p) level of theory through the gauge-including atomic orbital method (GIAO). The NICSwas calculated in the ring centre (NICS(0)), and 1Å above (NICS(1)) the ring centre. The *NICS* is a tensor, and its component along z-axis can also be used as aromaticity descriptor (NICS(1)zz).The MCI was calculated from the BLYP/6-311+G(d,p)NAO density matrix obtained from Natural Bond Orbital analysis(Reed, Curtiss and Weinhold, 1988).

The current density calculations were performed by the same level of theory BLYP/6-311+G(d,p). In all calculations a unit magnetic field perpendicular to the molecular plane was used and the calculated ring currents were plotted on a grid in the plane parallel to the molecular plane with a diatropic (aromatic) current represented by a counter clockwise circulation. The plotting planes were chosen to be 1Å above the molecular plane.

Calculations of MCI and ring currents were performed using in-house Fortran routines.

Results and discussion

The geometries of investigated molecules were obtained at the BLYP/6-311+G(d,p) level of theory. Roesky's ketone and its isomers are shown in Figure 1. The so-obtained geometries were used in the complete active space calculations (CASSCF) with the active space of 6 π-electrons and 5 π-molecular orbitals. The CASSCF calculations were used to predict stability order of the investigated molecules. The relative energies of the studied molecules are presented at Table 1. Both methods, BLYP and CASSCF, confirmed that **2** is the most stable molecule among the examined isomers. Both methods also agree on the order of stability in the given series of molecules.



1 **2** **3** **4**

Figure 1. Roesky's ketone (1) and its isomers

Different approaches were used to assess the aromaticity of the studied molecules. First of all, the studied molecules were found to be planar and all have 6 π-electrons coming from two SN fragments, plus 2 π-electrons coming from carbonyl CO group. Hückel's Rule states that every cyclic planar molecule that has 4n+2 π-electrons can be considered as aromatic. It is evident that the Hückel's Rule cannot give a straightforward answer of aromaticity in these molecules. Aromaticity is usually related to an electron delocalization. If a molecule has large electron delocalization, it can be aromatic. Quantitative description of electron delocalization is the MCI. The MCI values for the studied molecules were calculated and these results are presented in Table 1. The extent of cyclic electron delocalization in studied molecules is significant. Molecules **1** and **4** have the highest MCI values, which suggest a remarkable electron delocalization in these molecules. The problem with MCI is that it gives a measure of electron delocalization, but it still does not reveal whether the given ring is aromatic or antiaromatic. For instance, cyclobutadiene, the famous antiaromatic system, also has a significant value of MCI. For these reasons, the interpretation of the MCI as an indicator of aromaticity should be performed together with some other aromaticity indices, such as NICS or current density maps.

According to the NICS values there is significant aromatic character, as predicted by MCI values. Note that rings with negative NICS values qualify as aromatic, and the more negative the NICS, the more aromatic the rings. The data given in Table 1 reveal that all structural isomers of **1** have the aromatic character which varies from very pronounced in **4** to almost non-aromatic in **3**. Different NICS indices predict the same order of aromaticity character in the studied molecules. In addition, according to the MCI values **1** is more aromatic than **2**, whereas the NICS values predict reverse order of aromaticity. The NICS index measures the shielding calculated at the centre of a given ring, as a result of the ring currents in the molecule. In the case of non-symmetric current density distribution in **1** and **2** (Figure 2), the MCI values are more relevant index than the corresponding NICS. Therefore, it can be concluded that **1** has more pronounced aromatic character compared to **2**.

Table 1. Relative energies (in kJ mol-1) calculated at BLYP/6-311+G(d,p) and CASSCF(6,5)/6-311+G(d,p) levels of theory, MCI and NICS values of the studied molecules.

	1	**2**	**3**	**4**
BLYP	102.39	0.00	13.13	149.65
CAS	35.20	0.00	25.98	62.74
MCI	0.0465	0.0342	0.0313	0.0557
NICS(0)	-11.70	-16.34	-3.00	-19.42
NICS(1)	-7.69	-10.43	-3.45	-12.11
NICS(1)zz	-19.17	-24.78	-3.93	-29.18

The current density maps of the investigated molecules were examined (Figure 2). There is a significant diatropic circulation in molecules **1**, **2** and **4**. It is noticeable that the current density is the strongest in molecule **4**.

Based, on the MCI and current density maps results, the order of aromaticity in the studied molecules is the following: **4**>**1**>**2**>**3**. On the other hand, the order of stability is found to **2**>**3**>**1**>**4**. As can be seen, the aromaticity of the studied molecules is not related to their relative stability measured through the total energy of molecules.

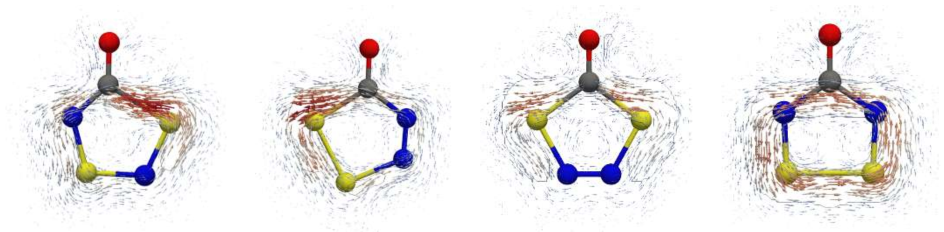

1 2 3 4

Figure 2. Current density maps; arrows coloured red represent strong, while blue arrows represent weak current density vectors.

One can consider that the obtained results as unexpected, and in disagreement with a "chemical intuition" which relates the aromaticity and thermodynamic stability. The presented results can be used as an instructive example how complex is the concept of aromaticity. According to the IUPAC definition, the aromaticity is *"the concept of* *spatial and electronic structure of cyclic molecular systems displaying the effects of cyclic electron delocalization, which provide for their enhanced thermodynamic stability (relative to acyclic structural analogues) and tendency to retain the structural type in the course of chemical transformations. A quantitative assessment of the degree of aromaticity is given by the value of the resonance energy. It may also be evaluated by the energies of relevant isodesmic and homodesmotic reactions"*(Minkin, 1999).It is worth noting that the resonance energy provides the measure of the thermodynamic stabilization coming from the cyclic electron delocalization effects. On the other hand, the relative energies given in Table 1 are based on the total energies of the studied molecules. The total energy of a molecule has all possible structural contribution of the given molecule (including the effects of cyclic delocalization, all kind of stains, etc.). For instance, different isomers **1** – **4**have the different cyclic delocalization stabilization effects, but also, they have different steric strain due to their cyclic structure with different bond angles (Table 2). The comparison of the steric stain in the given series of molecules is another intriguing topic, but this is not the aim of this work. To conclude, the total energies are not suitable to be used as aromaticity measure.

Table 2. Selected bond angles of the studied molecules.

1		**2**		**3**		**4**	
5C-1S-2N	96.06°	5C-4N-3N	122.85°	5C-1S-3N	96.46°	5C-1N-3S	121.54°
1S-2N-3S	112.69°	4N-3N-2S	117.00°	1S-3N-4N	119.36°	1N-3S-4S	92.61°
2N-3S-4N	109.20°	3N-2S-1S	94.75°	3N-4N-2S	119.36°	3S-4S-2N	92.61°
3S-4N-5C	117.46°	2S-1S-5C	94.59°	4N-2S-5C	96.46°	4S-2N-5C	121.54°
4N-5C-1S	106.59°	1S-5C-4N	110.81°	2S-5C-1S	108.46°	2N-5C-1N	111.71°

Conclusion

The polythiazyl polymer $(SN)_x$ found application in several diverse fields of chemistry and chemical technology, because these polymers were found to be electric polymeric conductor at room temperature and superconductor at temperatures close to absolute zero. In this work, the aromaticity of Roesky's ketone and its isomers, the compounds with a $(SN)_2$ unit enclosed in the ring stricture, were examined. Current density maps together with MCI indices were found to be suitable for measuring the aromaticity in the studied series. It was demonstrated that one can come to wrong conclusions if the aromaticity is measured only based on the values of NICS index.

It was found, contrary to a "chemical intuition", that the aromatic character of the studied molecules does not follow the trend of the relative stability measured through the BLYP or CASSCF energies. The obtained results can be used as an instructive example how complex is the concept of aromaticity. The total energy of a molecule is influenced by all possible structural details of the given molecule. In order to measure the energetic aspect of aromaticity, one should use the corresponding resonance energy which, by definition, assesses only the energetic effects of cyclic electron delocalization.

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