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Sulfur-Nitrogen Rings: Relative Stabilities and Structures

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Abstract

Topological resonance energies (TRE) of some known and proposed sulfur-nitrogen rings and polycycles have been calculated as part of an attempt to understand structural and stability trends in this series of compounds. We have compared our results with those of similar calculations for aromatic hydrocarbons of comparable ring size and of the same number of pi electrons. Planar SN rings have TRE per electron (PE) values that are within the range of those of hydrocarbon annulenes. The TRE(PE) of planar SN rings generally decrease with larger numbers of pi electrons as is the case for hydrocarbon annulenes. But unlike the hydrocarbons, which for a given number of pi electrons show declining TRE(PE) as the rings get larger, the SN values seem to increase with ring size. Some polycyclic SN systems have greater TRE(PE) than do the corresponding monocycles. Our results suggest that several compounds that have not yet been reported experimentally should be stable.

Introduction

Over the past 20 years a number of planar, ring-shaped molecules and ions containing only the elements sulfur and nitrogen have been prepared and characterized [1–7]. These planar rings, shown in Fig. 1, have electronic structures that are formally related to those of aromatic hydrocarbons. We refer to the set of valence molecular orbitals (MOs) that are antisymmetric with respect to reflection in the molecular plane as pi orbitals. The sigma MOs are symmetric with respect to the molecular plane. We count pi electrons as two from each sulfur atom and one from each nitrogen with an appropriate adjustment for the total charge in the case of ions [4]. All other valence electrons belong to the sigma MO set. This apportionment of valence electrons between sigma and pi MOs is supported by the results of extended Hückel calculations [3] and, for those cases that have been reported, by *ab initio* SCF MO calculations [8–11]. With the exception of the radical cation $S_3N_2^+$, the planar SN rings have numbers of pi electrons that equal the quantity 4n + 2, the number of pi electrons required by the Hückel rule for aromatic hydrocarbons [12]. Compared to aromatic hydrocarbons, however, most of the SN rings are electron-rich, *i.e.*, they contain more pi electrons than the planar aromatic hydrocarbons of the same ring size. For example, $S_3N_3^-$ is a planar hexagon like benzene, but benzene has only 6 pi electrons while $S_3N_3^-$ has 10. Both 6 and 10 are 4n + 2 numbers. Sulfur and nitrogen contribute to the basis set AOs with lower or deeper Coulomb integrals than those for carbon and therefore the SN systems have MOs of lower energy than those for carbon systems. Consequently these inorganic systems can accommodate more electrons than the corresponding

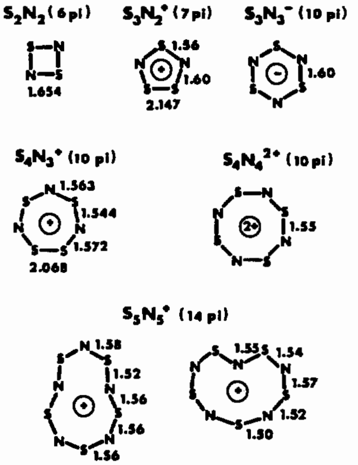

Fig. 1. Structures of known planar SN rings.

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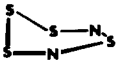
hydrocarbons. Waluk and Michl [13] have shown that MCD spectra of $S_3N_3^-$ and $S_4N_4^{2+}$ can be interpreted as arising from $\pi^*-\pi^*$ transitions of delocalized electrons in 'aromatic' systems using a model that was developed for 4n + 2 hydrocarbon annulenes.

There are at least three known SN compounds which, if they were planar, would have Hückel numbers of pi electrons but which are known to prefer nonplanar conformations or structures: S_4N_2 (1) is a half-chair rings [14, 15] $S_4N_5^-$ (2) has the cage structure of S_4N_4 but is capped by N^- bridging two sulfurs [16] and $S_6N_4^{2+}$ (3) is a loose dimer of $S_3N_2^+$ radical cations joined along the S–S edges of the five-membered rings in parallel planes [17, 18].



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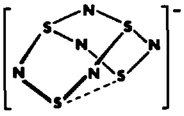

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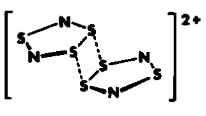


3

Three questions arise concerning SN compounds:

(i) Are the planar SN rings 'aromatic'?

(ii) What as yet unknown planar SN rings could one reasonably expect to be synthesized?

(iii) Why are some SN structures planar rings and others not if the Hückel 4n + 2 rule provides a criterion for exceptional stability in such systems?

In this paper we present provisional answers to these questions based on the results of topological resonance energy calculations.

Other authors have also considered general properties of $(AB)_n$ annulenes. Davies [19] and Haigh and Salem [20] have studied criteria for bond alternation in heterocyclic rings. Karadakov, Castaño, Fratev, and Enchev [21] have derived general formulas for resonance energies per electron for $(AB)_n$ rings.

Topological Resonance Energy [22, 23]

In simple Hückel theory the total pi energy E_π is the sum of orbital energies x_i multiplied by the number of electrons g_i (=2, 1, or 0) that occupy each MO i:

$$E_\pi = \sum_{i=1}^{N} g_i x_i$$

The resonance energy (RE) of a cyclic structure can be defined as the difference between the pi energy calculated for the cyclic structure and the pi energy of an appropriate acyclic reference structure:

$$\text{RE} = E_\pi(\text{cyclic structure}) - E_\pi(\text{acyclic reference structure}).$$

The characteristic polynomial of the cyclic structure can be obtained by means of Sachs' theorem which expresses the coefficients of the polynomial as functions of the numbers of unlinked edges and cycles that make up the structure [24, 25]. For an acyclic reference structure a well-defined characteristic polynomial can be obtained by omitting the cyclic contributions from the Sachs' theorem expressions for the polynomial coefficients for the cyclic structure [22]. If x_i^{ac} are the eigenvalues of such an acyclic polynomial, then the topological resonance energy (TRE) can be expressed as

$$\text{TRE} = \sum_{i=1}^{N} g_i(x_i - x_i^{ac}).$$

TRE values have been found to correlate very well with properties of aromatic hydrocarbons. For comparisons among molecules with different numbers of pi electrons it is necessary to compare the topological resonance energy per electron. TRE(PE), or TRE divided by the appropriate number of pi electrons [26]. The following ranges of TRE(PE), in units of the carbon resonance integral β, have been found useful in describing properties of planar cyclic hydrocarbon structures:

$\text{TRE(PE)} > +0.01$: aromatic

$-0.01 < \text{TRE(PE)} < +0.01$: nonaromatic

$\text{TRE(PE)} < -0.01$: antiaromatic

Very few calculations of TRE have been reported for inorganic systems [27]. Only experience with results such as those we report here can suggest whether these ranges might also be suitable for inorganic rings.

The results for sulfur–nitrogen rings described in the following section were obtained using these heteroatom parameters:

$\alpha_N = \alpha + 0.5\beta$;

$\alpha_S = \alpha + 1.0\beta$;

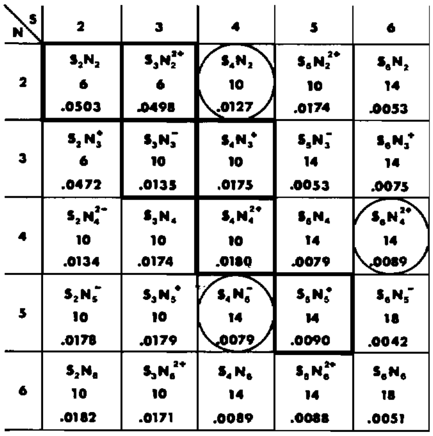
$\beta_{NS} = \beta_{SS} = \beta_{NN} = \beta$,

where α and β refer to Coulomb and resonance integrals, respectively, for carbon.

The equality of all resonance integrals was assumed because of our ignorance of how appropriate parameters should be chosen for SN systems; very little work has been reported on this problem, probably with good reason. But surely the equality of resonance integrals is appropriate for the symmetric systems $(SN)_n$, where all bonds are S–N and the structures obtained by experiment show that all bond lengths are equal or nearly so. There is some ambiguity in the selection of Coulomb integrals and this uncertainty and its implications will be discussed further on.

Results and Discussion

Figure 2 displays TRE(PE) values for a selection of real and hypothetical sulfur-nitrogen monocycles, each of which is assumed to contain the Hückel number of pi electrons indicated in the diagram. Entries enclosed in heavy squares are the known planar rings (Fig. 1), those in circles are known systems but which actually have the nonplanar structures **1**, **2**, or **3**. The others are unknown. The layout of Fig. 2 was suggested by a table prepared by Banister [1]. In selecting the hypothetical examples for this study we gave preference to cations rather than anions since four cationic rings have been characterized (including one dication) but only a single anion is known. Where two or more isomers are possible, the value of only the largest TRE(PE) appears in Fig. 2. For simplicity of comparisons we included the result for $S_3N_2^{2+}$ rather than for the known radical cation $S_3N_2^{+}$. Five of the six known planar rings turn out to have TRE(PE) values greater than the +0.01 minimum criterion for aromatic hydrocarbons. The sixth, $S_5N_5^{+}$, has a TRE(PE) of. 0.009, just below the aromatic threshold. Of the three known SN compounds that prefer nonplanar structures, only S_4N_2 has a TRE(PE) greater than +0.01, but only slightly greater, as a planar annulene. Apparently resonance energies for the three nonplanar examples are not sufficient to give them planar structures. The conformations of S_4N_2 and $S_3N_3^-$ have been discussed in more detail elsewhere [15, 28]. Figure 2 contains a number of unknown or hypothetical rings that are promising prospects for future synthesis because they have TRE(PE) values larger than the 0.01 threshold and larger than any of the know but nonplanar SN structures. Examples are $S_2N_3^+$ (**4**), S_3N_4 (**5**) and $S_2N_4^{2-}$ (**6**). Unlike any of the known planar rings, **4**–**6** have more nitrogen atoms than sulfurs.



N \ S	2	3	4	5	6
2	S_2N_2 6 .0503	$S_3N_2^{2+}$ 6 .0498	S_4N_2 10 .0127	$S_5N_2^{2+}$ 10 .0174	S_6N_2 14 .0053
3	$S_2N_3^+$ 6 .0472	$S_3N_3^-$ 10 .0135	$S_4N_3^+$ 10 .0175	$S_5N_3^-$ 14 .0053	$S_6N_3^+$ 14 .0075
4	$S_2N_4^{2-}$ 10 .0134	S_3N_4 10 .0174	$S_4N_4^{2+}$ 10 .0180	S_5N_4 14 .0079	$S_6N_4^{2+}$ 14 .0089
5	$S_2N_5^-$ 10 .0178	$S_3N_5^+$ 10 .0179	$S_4N_5^-$ 14 .0079	$S_5N_5^+$ 14 .0090	$S_6N_5^-$ 18 .0042
6	S_2N_6 10 .0182	$S_3N_6^{2+}$ 10 .0171	S_4N_6 14 .0089	$S_5N_6^{2+}$ 14 .0088	S_6N_6 18 .0051

Fig. 2. Topological resonance energies per electron (in units for β) for real and hypothetical monocycles.

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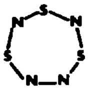


5

6

Figure 3 is a graph of TRE(PE) as a function of ring size for the $(SN)_n$ rings. These are the entries on the principal diagonal of the matrix of Fig. 2. Table I contains TRE(PE) values for monocyclic hydrocarbons [29]. Two trends are observable in these data. First, the TRE(PE) decreases with larger numbers of pi electrons. The TRE(PE) values for SN rings fall within the ranges for hydrocarbon annulenes. However, there is a significant difference that is a result of the electron-rich nature of the SN rings. Since they hold more pi electrons than hydrocarbon annulenes of the same size, these extra pi electrons fill MOs that are more antibonding than bonding, lowering the stabilities of the SN systems. For example, $S_3N_3^-$ has TRE(PE) in the 10 pi electron range, not within the 6-electron range with benzene. Of the symmetrical $(SN)_n$ rings featured in Fig. 3, only $S_3N_3^-$ and $S_4N_4^{2+}$ contain the same

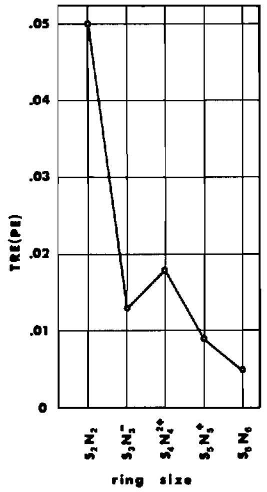


Fig. 3. Topological resonance energy per electron as a function of ring size for $(SN)_n$ annulenes containing a Hückel-number of pi electrons.

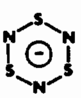
TABLE I. TRE(PE) for Planar Hydrocarbon Monocycles (in Units of β)[a].

Number of pi electrons	Range of ring size	Range of TRE(PE)
6	4–8	0.053–0.031
10	8–12	0.018–0.013
14	12–16	0.009–0.007
18	16–20	0.005–0.004

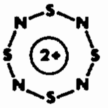
[a] Ref. 29.

numbers of pi electrons. The 'tooth' at $S_4N_4^{2+}$ reflects an increase in TRE(PE) with ring size for equal numbers of pi electrons to be discussed next.

The second trend for hydrocarbons is a general decline in TRE(PE) for larger rings with the same number of pi electrons. The SN rings show the opposite trend, increasing slightly with ring size for a given number of pi electrons. For example, the 10 pi-electron series $S_3N_3^-$ (7), $S_4N_3^+$ (8), and $S_4N_4^{2+}$ (9) shows an increase.


0.0135
7


0.0175
8


0.0180
9

For other examples, look at the isoelectronic segments of rows or columns of the matrix in Fig. 2. This increase in TRE(PE) with ring size for the same number of pi-electrons suggested that we consider the topological resonance energy per bond, TRE(PB). Figure 4 repeats Fig. 2 but with the total TREs divided by the number of ring bonds rather than the number of pi electrons and indeed the TRE(PB) shows a considerable degree of consistency among rings of different size but with the same number of electrons. Average values of TRE(PB) for given number of pi electrons: 6e, 0.0640; 10e, 0.0228; 14e, 0.0114; 18e, 0.0073.

N \ S	2	3	4	5	6
2	S_2N_2 6 .0755	$S_3N_2^{2+}$ 6 .0598	S_4N_2 10 .0212	$S_5N_2^{2+}$ 10 .0231	S_6N_2 14 .0088
3	$S_2N_3^+$ 6 .0566	$S_3N_3^-$ 10 .0225	$S_4N_3^+$ 10 .0250	$S_5N_3^-$ 14 .0084	$S_6N_3^+$ 14 .0117
4	$S_2N_4^{2-}$ 10 .0223	S_3N_4 10 .0249	$S_4N_4^{2+}$ 10 .0225	S_5N_4 14 .0123	$S_6N_4^{2+}$ 14 .0125
5	$S_2N_5^-$ 10 .0254	$S_3N_5^+$ 10 .0224	$S_4N_5^-$ 14 .0123	$S_5N_5^+$ 14 .0126	$S_6N_5^-$ 18 .0069
6	S_2N_6 10 .0228	$S_3N_6^{2+}$ 10 .0190	S_4N_6 14 .0125	$S_5N_6^{2+}$ 14 .0112	S_6N_6 18 .0077

Fig. 4. Topological resonance energies per bond (in units of β) for real and hypothetical monocycles.

SN rings of the same size and the same number of pi electrons but different atomic composition have very nearly the same TRE(PE). This can be interpreted as resulting from the truly topological nature of the TRE. Compare the examples with 10 pi electrons, $S_2N_4^{2-}$ (6), $S_3N_3^-$ (7), and S_4N_2 (10), on one of the diagonals perpendicular to the main diagonal of Fig. 2.


0.0134
6


0.0129
7


0.0127
10

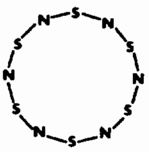
Nature apparently prefers an alternating order of different atoms around the ring as demonstrated by the structures of the known $(SN)_n$ annulenes: S_2N_2, $S_3N_3^-$, $S_4N_4^{2+}$, and $S_5N_5^+$. Indeed, the existing S_2N_2 isomer (11) with alternating S and N atoms has decidedly larger TRE(PE) than the unknown isomer (12) with adjacent pairs of S and N atoms.

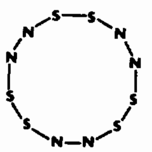

0.0503
11


0.0478
12

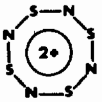
Ab initio calculations for S_2N_2 give puzzling conclusions. Collins and Duke [30] found that **11** is more stable than **12** by several hundred kcal/mol, a difference so large as to make their results questionable. Haddon and coworkers [31], using a more extensive basis set, reported that the unknown isomer **12** is more stable than the known structure **11** and that even the unknown chain structure SNNS has lower energy than **11**.

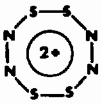
A smaller but still significant difference occurs for the pair of isomers (**13**, **14**) of the hypothetical S_6N_6 annulene.


0.0051
13


0.0031
14

But such differences do not always result. In the existing isomer of $S_4N_4^{2+}$, S and N atoms alternate with each other around the ring (**9**). The pair-wise alternating isomer (**15**) is unknown although it has almost exactly the same TRE(PE) as **9**.


0.0180
9


0.0181
15

Differences in TRE(PE) values probably do not provide grounds for discriminating between positional isomers of hypothetical $S_2N_4^{2-}$ (**16**, **6**).

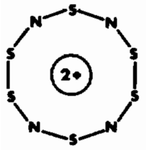
0.0127

16

0.0134

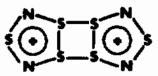
6

The loose dimer of five-membered rings in $S_6N_4^{2+}$ (**3**) suggested that we consider planar polycyclic structures containing five-membered rings. Comparison of monocyclic (**17**) and tricyclic (**3′**) structures for planar $S_6N_4^{2+}$ shows only a negligibly more stable arrangement for the polycyclic form.



0.0089

17

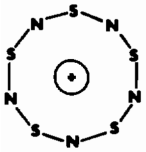


0.0091

3′

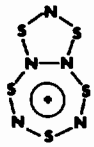
The bonding between the two monomers of $S_6N_4^{2+}$ has been variously described as a 2 electron-4 center bond [17], an electron-rich 6 electron-4 center bond [32], a pair of 3 electron bonds between pairs of opposing sulfurs [18], and a shift from net pi to approximately sigma bonding MOs [3].

Consider the monocyclic (**18**) and bicyclic (**19**, **20**) structures for $S_5N_5^+$. The TRE(PE) of the monocycle falls just short of the aromatic range while those of the two bicyclic structures exceed the criterion for aromaticity. The bicyclic or azulene-like structure **19**, with no transannular interactions between nitrogens, calls to mind the pear-shaped conformation of $S_5N_5^+$ which is the form apparently preferred in nature [33]. It is encouraging that **19** has a slightly larger TRE(PE) than **20** which has a ring closing sulfur–sulfur bond. The underlying sigma electronic structures of these systems do not permit a bond to close the five-membered rings as in **19** and **20** but the TRE results agree with conclusions based on calculated nonbonded transannular pi interactions that pear-shaped annulene conformations should be stabilized [34].



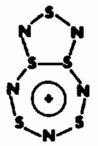
0.0090

18



0.0208

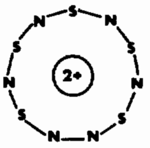
19



0.0193

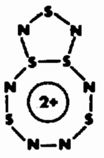
20

Compared to the hypothetical $S_5N_6^{2+}$ monocycle (**21**), bicyclic structures (**22**, **23**) with five-membered rings are clearly preferred.



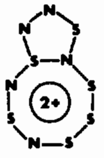
0.0088

21



0.0247

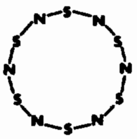
22



0.0240

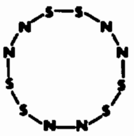
23

But among the four structures proposed below for the unknown S_6N_6, the monocycles (**13**, **14**) are much more stable than structures with five- and six-membered rings (**24**, **25**). The monocycles are in the nonaromatic range while the polycycles are antiaromatic.



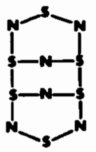
0.0051

13



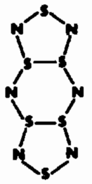
0.0031

14



−0.0099

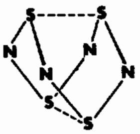
24



−0.0271

25

If S_4N_4 were planar its pi electrons would total 12, not a Hückel number. S_4N_4 is known to be a stable molecule of nonplanar cage structure (**26**). Weak bonds link pairs of sulfur atoms above and below the square plane of the nitrogens [35].



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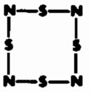
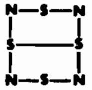
Consider the following hypothetical planar structures (**27**, **28**, **29**) for S_4N_4 assuming 12 pi electrons.



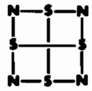
−0.0346

27



−0.0381

28

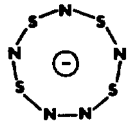


−0.0156

29

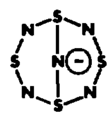
Although all are antiaromatic, as is appropriate for a number of electrons given by 4n rather than 4n + 2, the structure with two pairs of bonded sulfurs (**29**) is the least antiaromatic.

The nonplanar bicyclic ion $S_4N_5^-$ (**2**) has six-membered rings. Comparison of planar monocyclic (**30**) and bicyclic (**31**) forms shows the monocycle to be clearly more stable.



+0.0079

30

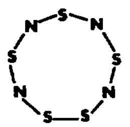


−0.0412

31

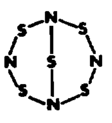
Bartetzko and Gleiter have given a molecular orbital based rationalization of the nonplanar bicyclic structure (2) of $S_4N_5^-$ [36].

The planar monocyclic structure (32) is much more stable than a planar, bridged or bicyclic arrangement (33) for the hypothetical S_5N_4.



+0.0079

32



−0.0380

33

Parameter-Dependent Results

There is a reasonable uncertainty about the relative weights of the Coulomb integrals for sulfur and nitrogen. The values we chose are those recommended by Streitwieser [37] and used by Johnson, Blyholder, and Cordes [38] in their calculation of the pi-electronic structure of $S_4N_3^+$. The order $\alpha_S < \alpha_N$ (both are negative quantitites) is based on the notion that since S contributes two electrons to the pi system while N furnishes only one, then a p AO on S must have a lower energy than a p AO on N. On the other hand, to reflect the fact that N is more electronegative than S, we should have chosen $\alpha_N < \alpha_S$. Valence state ionization potentials, which are routinely used as Coulomb integrals in extended Hückel calculations, produce the ordering $\alpha_N < \alpha_S$. Trsic, Laidlaw, and Oakley have given a particularly lucid discussion of this problem [39]. They conclude that no single parameterization scheme can be completely satisfactory for SN pi electron systems. If one is interested in obtaining the correct ordering of energy levels then one should choose $\alpha_S > \alpha_N$ but for the proper distribution of electron charge one needs to take $\alpha_S < \alpha_N$.

Uncertainties about heteroatom parameters such as those described above make the value of semiempirical calculations suspect unless one can demonstrate that the results are independent of specific parameter choices or that the outcome of the calculations is at least consistent with experimental results. Our choice of Coulomb parameters has three characteristics: i) α_S and α_N are both lower or deeper than α for carbon, ii) α_S and α_N are not equal, and iii) there is a sense or ordering of α_S and α_N values and for our work we took $\alpha_S < \alpha_N$. Each of these characteristics effects the results of the calculations. The fact that both α_S and α_N are deeper than α for carbon produces sets of molecular orbitals for SN systems that are lower in energy than those of the carbon systems of corresponding size, allowing the SN rings to accommodate a larger number of pi electrons. But this MO energy lowering has little effect on TRE. As we have seen our TRE values for SN rings fall within the same ranges as those for hydrocarbons with the same number of electrons. The sum of Coulomb integrals, one from each atom in the molecule, is a major component of the total pi electron energy. This should apply to both cyclic and corresponding acyclic reference structures, so that in the difference between total energies, the sums of Coulomb integrals must cancel, leaving the resulting TRE as determined from secondary effects produced by the arrangement of atoms of different kinds within the molecule. Perhaps it is not surprising that TRE values are relatively insensitive to the size and arrangement of Coulomb integrals in these systems.

Of the two remaining parameter characteristics, it turns out that the fact of the difference between α_S and α_N is more significant than the sense or order of that difference as the following examples show. Consider the isomers of S_2N_2 (**11** and **12**). The isomer with the structure of alternant S and N atoms (**11**) is well characterized; that with linked pairs of S and N atoms (**12**) is unknown. There is a considerable difference in calculated TRE(PE) between the two, decidedly favoring the known isomer. This preference is not a function of the sense of Coulomb parameter choice for S and N. An interchange of Coulomb integrals for S and N, or an interchange of labels of atoms, does not change these structures at all. Obviously the TRE difference between **11** and **12** would vanish if one set $\alpha_N = \alpha_S$. Therefore the preferred stability of **11** relative to **12** is determined by the difference between α_S and α_N and not by the sense of that difference.

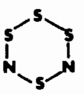
As a further example, consider the particular isomers of $S_4N_4^{2+}$ (**9**, **15**). The corresponding calculated values of TRE(PE) are essentially identical, not allowing one to discriminate the known isomer (**9**) from the unknown (**15**). In this case our inability to pick the correct isomer on the basis of TRE is not related to the sense of the Coulomb integrals used because interchange of S and N atoms would leave these structures unchanged.

Interchange of parameter values for S and N between $S_3N_2^{2+}$ (**34**) and $S_2N_3^+$ (**4**) would produce an interchange of TRE results for **34** and **4**. Therefore, the energy difference in this case is a result of the sense of Coulomb integral choice. Neither **4** nor **34** is known but **34** is related to the known radical cation $S_3N_2^+$.

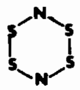

0.0498
34


0.0472
4

Consider the pairs of six-membered rings (**10**, **16** and **1**, **6**). Members of each of these $S_4N_2^{2-}$, S_4N_2 pairs are isoelectronic and bear a positive-negative relationship to each other; if sulfurs and nitrogens were interchanged or reversed each member of the pair would be converted into the other. For the **10**, **16** pair the TRE(PE) values are identical and those for the **1**, **6** pair differ by only 0.0008 β. We found similar results for seven- and eight-membered ring pairs. With the exception of the **4**, **34** pair, for which there is a sizable TRE(PE) difference, most such positive-negative pairs have insignificant TRE(PE) differences, suggesting that the calculated TRE values are generally insensitive to the sense chosen for S and N Coulomb integrals.


0.0127
10


0.0127
16


0.0126
1


0.0134
6

Conclusions

Calculations for the pi electron systems of sulfur-nitrogen rings reveal that many have TRE(PE) values that are comparable to those of aromatic hydrocarbons. In this sense, at least, SN rings can be said to be aromatic. Our results suggest that several as yet unreported cyclic systems have large enough TRE(PE) to make them targets for synthetic efforts. We found rather low TRE(PE) values for planar forms of known but nonplanar SN cyclic systems. The low TRE(PE) values in these cases were the result of the decline in this index with increasing numbers of pi electrons. Our results show a trend of increasing TRE(PE) with increasing ring size (but constant number of pi electrons), contrary to that found previously for planar monocyclic hydrocarbons. In some instances TRE results correctly chose the known isomer to be most stable; in others TRE values turn out to be essentially identical, yielding no ground to discriminate between isomers. However, in no instance did TRE values favor an unknown isomer over a known one. An analysis of TRE results for isomers and for iso-electronic pairs shows that generally these results are rather insensitive to the sense or order if not the difference between Coulomb integral choices for S and N. Planar, unsubstituted, polycyclic SN compounds are unknown but in several cases we found that by assuming transannular pi interactions we could increase the TRE(PE) values considerably compared to the symmetric or monocyclic forms. No general rules for such conformational preferences emerged from this study.

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