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Nonbonded Bond Orders, Molecular Conformations, and Relative Stabilities of Sulfur-Nitrogen Rings and Chains

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In electron-rich pi-electron systems such as the planar sulfur-nitrogen rings and chains, pi-bond orders between nonbonded atoms are often large and positive. These quantities can be used to rationalize the observed conformations of such structures and assess the relative stabilities of rings *versus* chains. For chains, the end-end nonbonded bond order is a convenient measure of the extra stabilization attainable on ring formation. Qualitative molecular orbital theory can be used to explain the sizes of the nonbonded bond orders and to understand trends through series of compounds.

INTRODUCTION

In the simple Hückel theory of pi-electron sytsems, Coulson bond orders have been very useful quantities.[1] They are calculated as

$$p_{rs} = \sum_i n_i c_{ir} c_{is},$$

where p_{rs} is the bond order between atoms r and s, c_{ir} and c_{is} are the coefficients of AOs on atoms r and s, respectively, in the i-th MO Ψ_i and n_i is the number of electrons occupying Ψ_i. If the two coefficients c_{ir} and c_{is} in a particular molecular orbital have the same sign or phase, that term will make a bonding contribution to the sum in p_{rs}; if the coefficients are of opposite sign or phase their contribution will be antibonding. Normally, bond orders are calculated for pairs of atoms that are considered to be linked by chemical bonds but bond orders between nonbonded atoms are also interesting quantities and can often give qualitative insight into the problems of conformations of chains and rings and the relative stabilities of rings *versus* chains. In electron-rich inorganic pi-electron systems such as sulfur-nitrogen rings and chains[2-6] the calculated nonbonded pi bond orders are often positive and sizable, in some cases being as large or larger than bond orders between bonded pairs of atoms. The following examples serve to illustrate what can be learned from nonbonded bond orders.

In counting pi electrons in sulfur-nitrogen molecules and ions, we assume that each sulfur contributes two electrons while each nitrogen supplies only one, adding or subtracting electrons as appropriate to satisfy the total charge in the case of ions. For the Hückel calculations we used the heteroatom parameters recommended by Streitwieser[7] and used by Johnson, Blyholder, and Cordes[8] in their calculation of $S_4N_3^+$:

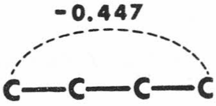
$$\alpha_S = \alpha + 1.0\beta;\ \alpha_N = \alpha + 0.5\beta;\ \beta_{SN} = \beta,$$

where α and β are the standard (carbon) Coulomb and resonance integrals, respectively.

RESULTS AND DISCUSSION

S_2N_2

Consider the end-end nonbonded bond orders in butadiene (**1**) and in the hypothetical chain SNSN (**2**). The strongly negative value for the C_4 system indicates no tendency for the chain to close to form a ring with 4 pi electrons. The positive value for SNSN is consistent with the fact that S_2N_2 is known to be a four-membered ring.[9,10] Figure 1 correlates MOs and orbital energies for the four-membered chain and ring. In the C_4 system only Ψ_1 and Ψ_2 are occupied. Look at the interaction between AOs on atoms 1 and 4 (end-end interactions) in the chain. This interaction is in-phase in Ψ_1 giving a positive term in the bond order sum. In Ψ_2 the end-end interaction is out-of-phase for a negative contribution to the bond order. Notice that an in-phase interaction stabilizes or lowers the energy of the MO; an out-of-phase interaction raises



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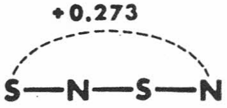

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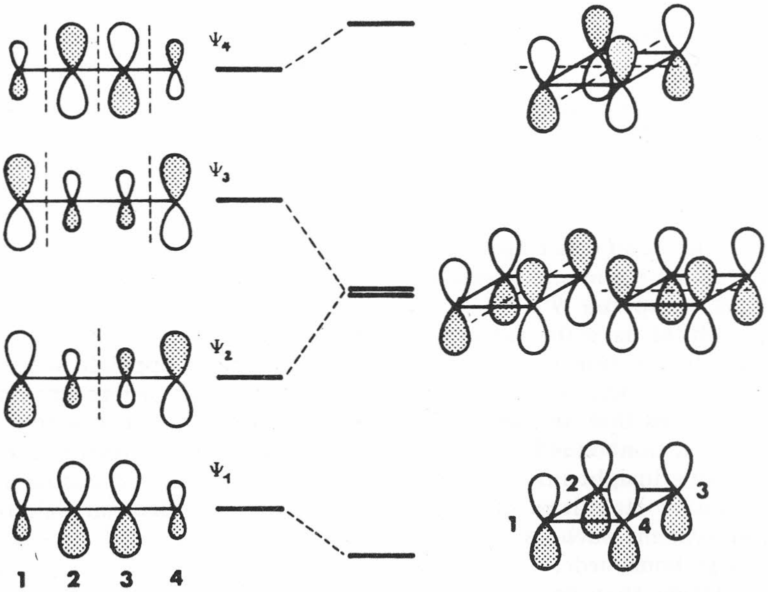


Figure 1. Correlation of MOs for the four-membered chain and ring. Relative energy levels shown are those of butadiene.

or destabilizes the energy. In the C_4 system the end-end interactions of the chain do not give a positive bond order, the lowering of the energy of Ψ_1 on cyclization is cancelled by the energy increase of Ψ_2, and no ring forms. S_2N_2 has 6 pi electrons and Ψ_3 is end-end in-phase giving a positive net bond order and a stabilization of the energy of Ψ_3 leading to ring closing. These conclusions are supported by the differences in pi energies (in units of β) for ring and chain that

TABLE I

Hückel pi-Electron Energies and the Stabilization Energy (Ring Minus Chain) for Butadiene and S_2N_2

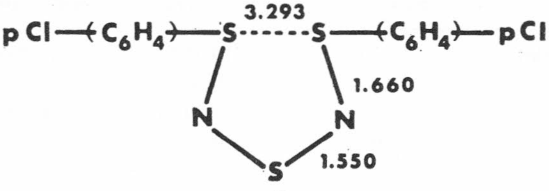
	C_4 (4e)	S_2N_2 (6e)
E_π (cycle)	4.000	8.531
E_π (chain)	4.472	7.774
ΔE_π	—0.472	+0.757
$\Delta E_\pi/n$	—0.118	+0.126

appear in Table I. For the purpose of comparing stabilization energies ΔE_π for systems of different sizes it will be necessary to introduce the energy difference or stabilization energy per electron $\Delta E_\pi/n$, where n is the number of pi electrons. For S_2N_2, $\Delta E_\pi/n = 0.757/6 = 0.126$.

Naturally, cyclization of the SNSN chain also involves the formation of a sigma bond between terminal S and N. In S_2N_2 there are 22 valence electrons subdivided as 6 pi electrons and 16 sigma electrons. The 16 sigma electrons would be allocated more advantageously among the four S—N single bonds and four lone pairs of the ring than as three S—N bonds and 5 lone pairs (or 4 lone pairs and two unpaired electrons) in the chain. It is important to remember that the sigma electronic structure also gives a strong push towards ring formation.

S_3N_2

The S_3N_2 system has 5 orbitals and 8 pi electrons. The compound $(p\text{-ClC}_6H_4)_2S_3N_2$ (**3**) contains a U-shaped-SNSNS-chain in a nearly planar molecule.[11] The



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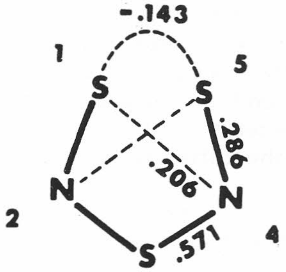
S - - S distance between ends of the SNSNS chain is 3.293 Å, considerably less than the S - - S van der Waals distance (3.70 Å) but much larger than a normal S—S single bond (2.06 Å). Is it a weak pi bond that holds the sulfurs close together?

The Hückel bond orders between nonbonded S and N atoms 1,4 and 2,5, shown in **4**, are nearly as large as those between the bonded pairs. The end-end nonbonded bond order (1,5) is negative. Therefore it is the bonding 1,4 and 2,5 interactions that are responsible for the U-shaped but noncyclic conformation of the SNSNS chain.



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It should be obvious that phase relationships govern everything here and these are easily understood from free-electron theory (the problem of the particle-in-a-one-dimensional box). With 8 pi electrons, orbitals are occupied through Ψ_4 (**5**). The 1,4 and 2,5 interactions in Ψ_4 are same-phase and are responsible for the positive nonbonded bond orders in (**4**). The AOs at the ends of the chain in Ψ_4 are of opposite phase and produce the negative end-end bond order. From Table II one can see that depopulation of Ψ_4 increases the stability of the ring relative to the chain. Although the 6-electron dication ring $S_3N_2^{2+}$ has not been reported, the 7-electron radical cation ring $S_3N_2^{+}$ is known.[12]

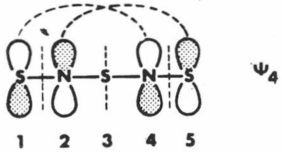

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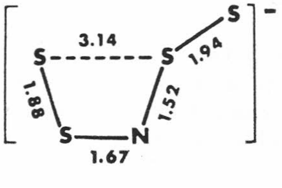
TABLE II

Comparison of Total pi-Electron Energies for Ring and Chain Structures for S_3N_2 Systems

	S_3N_2 (8e)	$S_3N_2^{+}$ (7e)	$S_3N_2^{2+}$ (6e)
E_π (cycle)	9.797	10.578	11.358
E_π (chain)	10.000	10.281	10.562
ΔE_π	—0.203	+0.297	+0.796
$\Delta E_\pi/n$	—0.025	+0.042	+0.133

S_4N^-

The ion S_4N^- (**6**) has a planar chain structure that has been described as sickle-shaped.[13]



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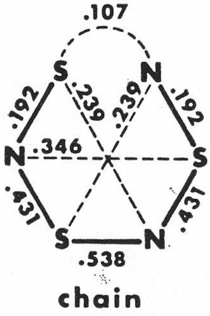
S_4N^- is isoelectronic with the -SNSNS-chain and the same pi orbitals apply. As in the S_3N_2 chain, 1,4 and 2,5 pi interactions would be expected to stabilize the U-shaped conformation. But chain conformations must be a compromise between effects involving the pi-system, the sigma-system, and crystal packing forces. Lone pair repulsions (represented in MO theory as linear combinations of lone pair-like AOs) might be reduced if the chain abandons the U-shape for the sickle in which only one 1,4 nonbonded pi interaction remains.

Gleiter and Bartetzko[14] have done MNDO calculations for S_4N^- in various conformations and have noted the 1,4 stabilizing effect of the pi MO Ψ_4 described above. They have pointed out similar 1,4 (or more generally: t, $t + 3$) interactions that influence but do not completely determine the conformations of the planar, 12 pi-electron systems $S_3N_2O_2$ and the hypothetical $S_4N_3^-$ ion. These authors do not explicitly discuss the sigma structure.

$S_3N_3^-$

The calculated pi bond orders for $S_3N_3^-$ (10 pi electrons) are shown below for chain (7) and ring (8) structures. Notice that in the chain the principal nonbonded bond orders (1,4; 2,5; 3,6) are larger than the smallest bond order between bonded atoms (1,2). Even the 1,6 end-end (more generally 1, Ω) nonbonded bond order is sizable, suggesting a tendency to cyclize. In the six-membered ring (8) the positive transannular bond orders equal the bond orders of the ring bonds. The ion $S_3N_3^-$ is known to be a planar ring[15].



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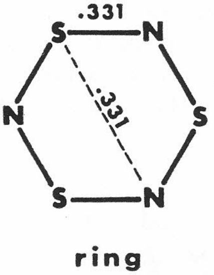

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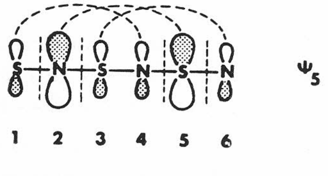
The HOMO of the hypothetical $S_3N_3^-$ chain is Ψ_5 (9). The number and placement of nodes are determined by symmetry (or near symmetry). In general, 2m electrons occupy m orbitals. The HOMO, Ψ_m, has $m - 1$ nodes. In Ψ_5 (9) all interactions between atoms t and $t + 3$ are in-phase and match the large positive nonbonded bond orders in (7). The 1,6 (end-end) AO interactions are also in-phase.



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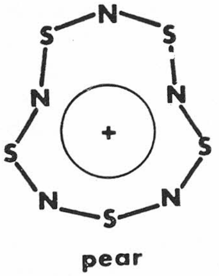
$S_5N_5^+$

The planar $S_5N_5^+$ ring is known in both pear-shaped[16] (**10**) and heart-shaped[17] (**11**) conformations. More pear-shaped than heart-shaped rings have been observed. No ring that approximates five-fold symmetry has been found. In the hypothetical $S_5N_5^+$ chain HOMO for 14 pi electrons would be Ψ_7 6 nodes. An even number of nodes means an in-phase interaction between chain ends. In Ψ_7 all t, $t + 3$ as well as some t, $t + 4$ interactions are in-phase. These are preserved on ring formation as the calculated pi-bond orders for chain (**12**) and ring (**13**) show.



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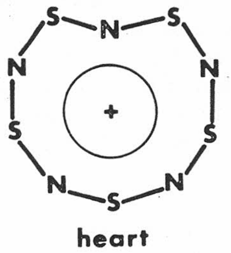

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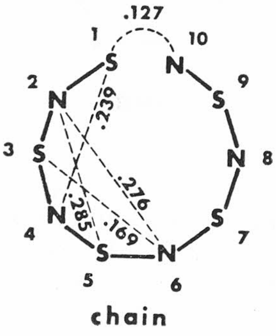

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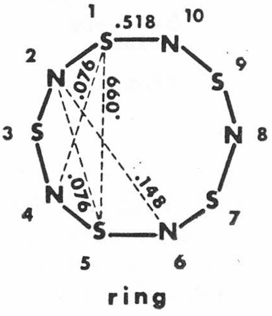

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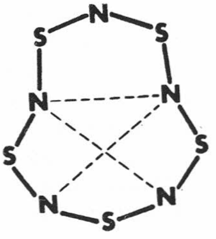
In the $S_5N_5^+$ ring, the largest of the positive transannular bond orders are the t, $t + 4$, N - - N interactions. The t, $t + 4$, S - - N interactions are smaller. Somewhat smaller but still positive are the t, $t + 3$ S - - N interactions.

To form a heart from the five-fold ring one could indent or form a cusp at either a sulfur or a nitrogen. Forming a nitrogen cusp would favor the N - - N transannular interactions which are stronger than S - - S. Indeed, this is what nature chooses to do in the $S_5N_5^+$ ring. The heart has only two such shortened N - - N distances (**15**) while the pear has three (**14**).



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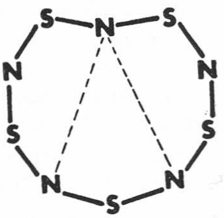

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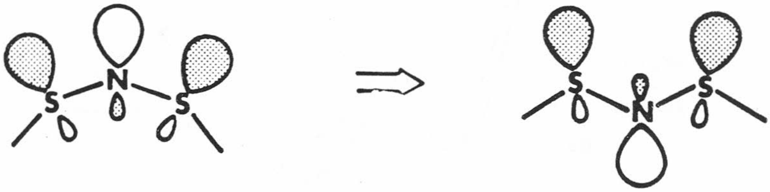
Table III counts the various transannular interactions that are favored by cusp formation. It would appear that pi-nonbonded interactions favor the pear conformation over the heart.

TABLE III

Transannular Interactions in the $S_5N_5^+$ Ring in Pear and Heart Conformations

Interaction *Type*	Number of interactions *Pear*	*Heart*
$t, t+4$; N --- N	3	2
$t, t+4$; S --- S	0	0
$t, t+3$; S --- N	4	2

Bartetzko and Gleiter[18] have performed extended Hückel calculations which indicate that the pear is more stable than the heart which in turn is more stable than the ring with full D_{5h} symmetry. They explain these conformational preferences on the basis of repulsions among exocyclic lone pairs. The particular MO involved is composed largely of lone pair orbitals of alternant phase around the ring. Indentation of the ring to form cusps relieves out-of-phase interactions among neighboring lone pairs (**16**) and lowers the energy.



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The heart-shaped conformation requires one such cusp; the pear-shaped form has two cusps.

Longer Chains, Larger Rings

We can generalize from the previous observations. Suppose we have a chain with $2m$ pi eletcrons. The HOMO will be Ψ_m which will have $m-1$ nodes. If m is even the end AOs of Ψ_m will have opposite phase and no ring will form. The cases in which m is odd (ring formation) require an odd number of pairs of electrons which could be expressed as $2m = 4n + 2$. Thus the Hückel $4n + 2$ rule arises as a requirement for stabilization by cyclization and not as a condition for filled configurations involving doubly degenerate orbitals as is often stated. This explains why inorganic rings of low symmetry still require $4n + 2$ pi electrons. Goldstein and Hoffmann came to similar conclusions in their study of symmetry, topology, and aromaticity.[19]

Figure 2 shows two measures of ring stability: $p_{1\Omega}$, the end-end nonbonded bond order, and $\Delta E_\pi/n$, the pi stabilization energy (ring-chain) per electron. These measures parallel each other remarkably for rings of different size. The examples shown in Figure 2 all contain $4n + 2$ pi electrons. The two indicies of relative stability, ΔE_π and $p_{1\Omega}$, are indeed related. The total energy of a pi-electron system can be given as[20]

$$E_\pi = \sum_{r=1}^{N} q_r \alpha_r + \sum_{r<s} 2p_{rs}\beta_{rs},$$

where α_r is the Coulomb integral for the AO on atom r and β_{rs} is the resonance integral between bonded atoms r and s, p_{rs} is the bond order between r and s and q_r is the charge density on atom r. Now consider the difference ΔE_π between such expressions for a ring and its corresponding chain. Individual terms in the expression for the chain can be paired with corresponding terms in the sums for the ring except for the ring closing term $2p_{1\Omega}\ \beta_{1\Omega}$ in the ring sum. In the difference ΔE_π all the paired terms approximately cancel, leaving ΔE_π approximately equal to $2p_{1\Omega}\ \beta_{1\Omega}$. Of course, $p_{1\Omega}$ for the end-end nonbonded bond order is not the same as that for the ring closing link in the ring, but they should have the same sign. Figure 2 shows that the relationship is surprisingly close.

Relative thermodynamic stability is determined by an energy difference such as ΔE_π, but $p_{1\Omega}$ is far more convenient to interpret since, as we have seen,

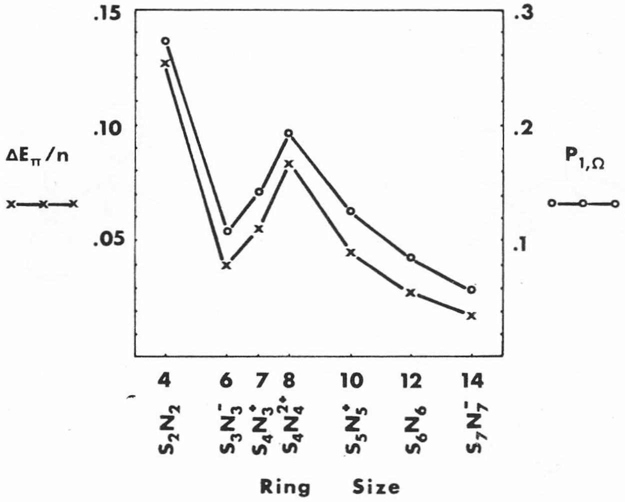


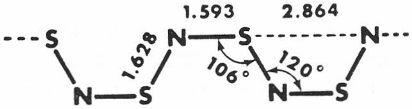
Figure 2. $\Delta E_\pi/n$ and $p_{1\Omega}$, two indicies of stability of the ring compared to the chain, parallel each other closely as a function of ring size.

its sign can be predicted from phase relationships between the AOs at the ends of the chain in the HOMO. Ring stability in Figure 2 declines for large rings, a result in accord with that found for normal hydrocarbon annulenes.[21] This result can be interpreted in terms of the $p_{1\Omega}$ index as a consequence of MO normalization.[22] As chains get longer, more AOs appear per MO but the squares of coefficients must still sum to unity for normalization. Therefore coefficients get smaller the longer the chain. Of course longer chains mean more occupied MOs which contribute more individual terms to the bond order sum. But for end-end $(1, \Omega)$ interactions the signs of the terms in the sum alternate causing the terms to cancel each other approximately. In $4n + 2$ chains the HOMO contributes the term that makes the $p_{1\Omega}$ sum positive and this term should get smaller for larger rings.

Conformations of chains are determined, at least in part, by interactions of the t, $t + 3$ type which tend to produce a coiled structure.

The $(SN)_x$ Polymer

The X-ray crystal structure of the $(SN)_x$ polymer (**17**) shows a planar chain.[10]



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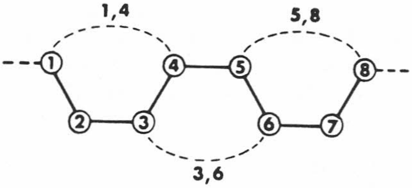
The nonbonded S - - N distance of 2.864 Å is long for a sulfur nitrogen single bond (1.75 Å) but short compared to the sum of van der Waals radii for S and N (3.35 Å). These nonbonded interactions are of the t, $t + 3$ type, where t is odd (**18**).



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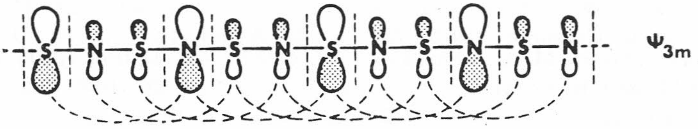
A generalized HOMO of the type required to produce t, $t + 3$ interactions for all t is shown in (**19**).



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Suppose $x = 2m$. Then $(SN)_x$ has $4m$ AOs and $6m$ pi electrons. The HOMO is Ψ_{3m} which has $3m - 1$ nodes. For long chains the ratio of number of nodes to number of AOs in the HOMO is 3 to 4. The representation (**19**) above meets this criterion.

Nonbonded pi interactions favor the kind of t, $t + 3$ interactions observed in the conformation of the $(SN)_x$ polymer. But these interactions cannot completely determine the chain conformation, otherwise the polymer would have a more coiled structure. Somehow lone-pair-lone-pair interactions along the chain must limit the coiling as they do in S_4N^- in a way to be described in another study.

SUMMARY

In this report we have shown how pi bond orders calculated between nonbonded atoms can be used to rationalize the conformations of planar electron-rich sulfur-nitrogen rings and chains. The end-end nonbonded bond order $p_{1\Omega}$ for a chain is related to the difference in pi energies ΔE_π between ring and chain. The signs of nonbonded bond orders are determined by the nodal properties of the highest occupied molecular orbital which in turn can be deduced from qualitative molecular orbital considerations. Therefore nonbonded bond orders provide an easily interpreted key to molecular properties.

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SAŽETAK

Nevezni redovi veza, konformacije molekula i relativne stabilnosti S—N prstena i lanaca

Benjamin M. Gimarc

Kod π-elektronskih sustava koji su bogati elektronima, kao što je to slučaj s planarnim prstenima i lancima sastavljenim od atoma sumpora i dušika, često se događa da su redovi π-veza veliki i pozitivni, čak i za atome koji nisu neposredni susjedi. S pomoću tih veličina mogu se racionalizirati opažene konformacije spomenutih spojeva kao i relativna stabilnost prstenastih struktura u odnosu na lance. U tu svrhu može se koristiti jednostavna kvalitativna MO-teorija. Ona je potpuno dovoljna da se odredi veličina neveznih redova veza i objasni trend promjena strukturnih karakteristika u nizu spojeva.