

STRANGE AROMATIC MOLECULES

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Abstract - Aromaticity and localized π -orbitals in some interesting cyclic molecules are studied on the basis of CNDO/2 quantum chemical calculations. Very specific SS linkages are found in SN rings. Strong evidences call for a diagonal "n only" SS bond in $(SN)_2$. In contrast to the generally accepted view it is supposed that a double bond in $S(SN)_2^{2+}$ and a triple one in $S(SN)_3^+$ exists. Three-centre SNS bonds are formed and only a single lone pair is localized at each sulphur atom in all three molecules. Molecular geometry is discussed in terms of the localized π -orbitals. Localization yields two-centre NN and three-centre NCN π -orbitals in formazan. Delocalization is considerably larger in the cyclic, hydrogen-bonded form than in the corresponding linear structure reflecting the importance of cyclization in producing aromatic character. The steric arrangement of the novel hydrogen bond, found in 3-carboxymethylthio-1,5-diphenylformazan, is discussed. All investigated rings are moderately aromatic to about the same extent like pyrrole.

INTRODUCTION

Aromaticity has been the subject of numerous studies for more than 100 years. Though the significance of this concept is often questioned (for a review see Ref. 1) we feel that it has its place in chemistry, anyway. A proper definition of aromaticity should help the experimentalist in classifying and understanding diverse phenomena. Since some of the findings, like enlarged thermodynamic stability or anomalous magnetic behaviour, are often very different in nature a sound definition would need firm theoretical foundation.

It is often resonance energy, as defined within the frame of simple Hückel theory (see e.g. Refs. 2-6) which is used to estimate the measure of aromaticity. On the other hand, we feel, an analysis of localized molecular orbitals (see Note a) may shed more light on the intrinsic nature of

Note a. The abbreviation "MO" is used for molecular orbital throughout in this paper.

the problem. Localization of canonical MO-s, as obtained from the solution of the Hartree-Fock-Roothaan equations, helps much in understanding essential features of the chemical bond (see e.g. Refs. 7-8). The first steps to link localized MO-s and aromaticity were done by England and Ruedenberg (9-10). However, relatively few further studies have been done until now (11-13).

Recently it has been suggested (14) that orbital localizability can serve as a measure of aromaticity for certain classes of molecules. Through this the estimation and detailed analysis of (quasi)aromaticity in some strange systems like molecules with third-row atoms or cyclic, hydrogen-bonded structures becomes possible. In this work the theoretical basis is outlined first. Later on properties and composition of localized π -orbitals in $(SN)_2$, $S(SN)_2^{2+}$, $S(SN)_3^+$ and formazan, $HNNC(H)NNH_2$, are discussed.

THEORY

Localized MO-s were obtained within the CNDO/2 approximation (15) using the Edmiston-Ruedenberg localization procedure (16) as programmed by Tinland (17). ab initio calculations for such large systems as treated in this work would be too costly. However, as it was found by Kishner et al. (18) for nitrogen oxides, results of CNDO/2 calculations agree well with ab initio ones. Further it is known that for molecules with third-row atoms the CNDO/2 method overestimates d-orbital participation in MO-s (19). ab initio calculations for thiophene with STO-3G and STO-3G* bases were performed to check the reliability of the CNDO/2 method in estimating d-orbital participation in producing aromaticity (20). A qualitative agreement between both methods was achieved. This means that they are in accord in predicting thiophene to be moderately aromatic. Further, d-orbitals on sulphur are found to play an important role in determining aromaticity in both calculations.

Let us suppose that each functions, u_a , of the MO basis is centered at one of the atoms of the molecule. The i -th localized MO is written as a linear combination

$$\varphi_i = \sum_a c_{ia} u_a \quad (1)$$

Summation in Eq. (1) includes each basis functions. The localizability of φ_i to atom A is defined as follows

$$l_A^i = \sum_{a,b \text{ on A}} c_{ia} c_{ib} S_{ab} \quad (2)$$

with

$$S_{ab} = \int u_a^* u_b dv \quad (3)$$

Summation in Eq. (2) runs over basis functions, only, which are centered at atom A. Localizability to bond AB is given by the following expression

$$l_{AB}^i = l_A^i + l_B^i + \sum_a \text{on A} \sum_b \text{on B} c_{ia} c_{ib} S_{ab} \quad (4)$$

It is seen that, according to the normalization condition, the localizability to all atoms of the molecule $l_{AB\dots C}^i = 1$. In the zero differential overlap approximation S_{ab} is neglected thus (see Ref. 21)

$$l_A^i = \sum_a \text{on A} c_{ia}^2 \quad (5)$$

and

$$l_{AB}^i = l_A^i + l_B^i \quad (6)$$

Two-centre localizabilities, as given in Eqs. (4) and (6), can be used to estimate relative importance of a given Kekulé structure. Let us define L as the average localizability to a given structure (in %):

$$L = \frac{100}{n} (l^1 + l^2 + \dots + l^n) \quad (7)$$

Upper indices refer to π -orbitals localized to one- or two-centre bonds of the limiting structure.

The aromaticity index of monocyclic systems is defined as

$$A = 100 - L_{\max} \quad (8)$$

L_{\max} belongs to the maximally localizable Kekulé structure (see Ref. 14).

In subsequent sections the localized MO-s are used to characterize bonds. It is understood that no strict correspondence between both concepts exists. However, we feel, localized MO-s yield some useful informations on chemical bonding.

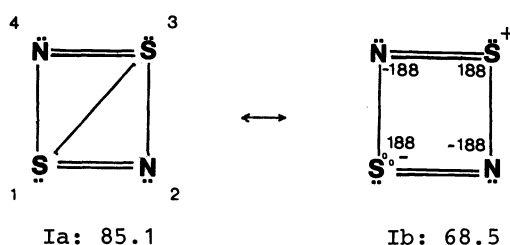
SN RINGS

Interesting examples for inorganic aromatic molecules are certain SN rings. For a recent review see (22). It is clear that for such systems discussion of aromaticity on the basis of simple Hückel theory may become impossible. Therefore more sophisticated methods, like CNDO/2, are needed.

The following structures were treated: $(SN)_2$, $S(SN)_2^{2+}$ and $S(SN)_3^+$. The rings are distinguished by roman numbers, I, II and III. The first and last molecules are observed experimentally (22). II is a model of the radical cation $S(SN)_2^+$. The results of Gillespie and coworkers (23) indicate that this latter has an aromatic sextet. Thus II, possessing three doubly occupied π -orbitals, is thought to be similar at least in aromatic character.

Localizability, as defined in Eqs. (5-6), exceeds 95 % for all two-centre σ -orbitals and lone pairs at sulphur atoms in all three molecules. Lone pairs at nitrogen atoms are considerably delocalized to neighbouring sulphur atoms mainly to their d-orbitals.

Table 1 includes the composition of π -orbitals in the investigated molecules. Certain similarities between corresponding orbitals in all three rings can be observed. SS orbitals are well localizable with a low d-orbital participation. SN orbitals are considerably delocalized to the neighbouring sulphur atom. d-orbitals play an important role especially in delocalization. As a result three-centre SNS orbitals are formed. The localizability to these three atoms exceeds 97.5 % in all cases. Similar situation has been found in N-sulphonyl-sulphimides, too (24). Aromaticity decreases with increasing ring size. For I,



II and III A is equal to 14.9, 11.7 and 10.3, respectively.

TABLE 1. Composition of localized π -orbitals in SN rings. d-characters are given in parentheses.

mol.	AB bond	l_{AB}	l_A	l_B	delocalization (l_C)
I	S^1N^2, S^3N^4	77.7	21.0(42.1)	56.7(0.0)	S^3, S^1 : 21.0(42.1)
	S^1S^3	100.0	50.0(0.9)	50.0(0.9)	--
II	S^4N^3, S^4N^5	84.1	26.0(36.0)	58.1(0.0)	S^2, S^1 : 13.7(51.6)
	S^1S^2	96.6	48.3(10.5)	48.3(10.5)	--
III	S^4N^3, S^6N^7	89.5	29.2(38.4)	60.3(0.0)	S^2, S^1 : 10.1(65.7)
	S^6N^5	81.3	18.2(50.2)	63.1(0.0)	S^4 : 18.2(50.2)
	S^1S^2	98.6	49.3(17.6)	49.3(17.6)	--

Let us study now SS bonds in detail. A strange " π only" bond between both sulphur atoms seems to exist in I. Note the low value of the L average localizability, defined in Eq. (2), for structure Ib and the perfect localizability of the S^1S^2 π -orbital. Limiting structures with $L < 80$ % are omitted here and in the following. π -type lone pairs are indicated by empty

circles. The isodensity contour map for this orbital is depicted in Fig. 1. Though the overlap between both atomic π -orbitals is relatively small it is definitely discernible.

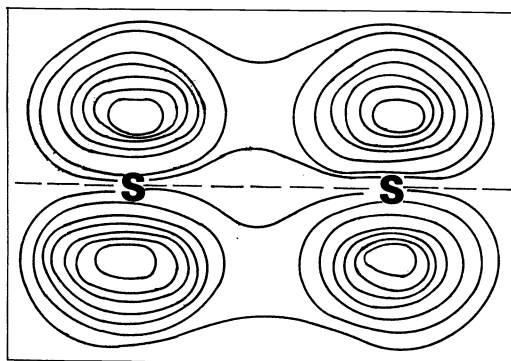
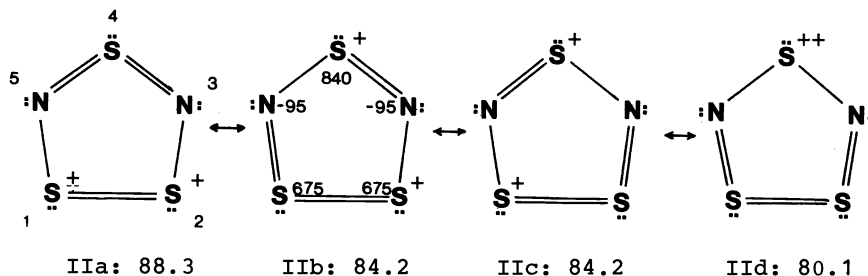


Fig. 1. Isodensity contour map for the localized SS π -MO in I. The lines (from the outermost to the innermost) correspond to electronic densities of 2, 5, 11, 16, 22, 27 and 32 $\text{C}.\text{mm}^{-3}$, respectively.

Experimental evidence for bonding is obtained from the approximate equality of SNS and NSN angles (90.4° and 89.6° see Ref. 22). In other SN rings SNS angles tend to be larger than NSN ones. For example in II $S^2N^3S^4\alpha = 120^\circ$, $N^3S^4N^5\alpha = 107^\circ$ (23) in III $S^2N^3S^4\alpha = 152^\circ$, $S^4N^5S^6\alpha = 135^\circ$ while $N^3S^4N^5\alpha = 119^\circ$ (22). Thus both sulphur atoms get closer than expected and a weak diagonal bond is formed in I. The SS distance, 2.34 Å, seems to be not large enough to make bonding impossible. Bannister and coworkers report on an SS bond length of 3.03 Å in $S_6N_4^{2+}$ the dimer of $S(SN)_2^+$ (25).

In accordance with the generally accepted view Gillespie and coworkers state that an SS single bond with two lone pairs on both sulphur atoms is formed in II. In contrary we stand for a double bond. Our CNDO/2 calculations indicate the existence of a SS π -orbital with an isodensity contour map very similar to that of Fig. 1. Further as it has been mentioned above only one single lone pair is attached each to S^1 and S^2 . The limiting structures, involving two separate lone pairs on both sulphur atoms, have a minor weight. Though the analogy of the SS π -bond with an ordinary CC one is rather far it is reflected in Fig. 1. Therefore, we feel, the limiting structures IIa-d can be amended to describe bonding in $S(SN)_2^{2+}$.



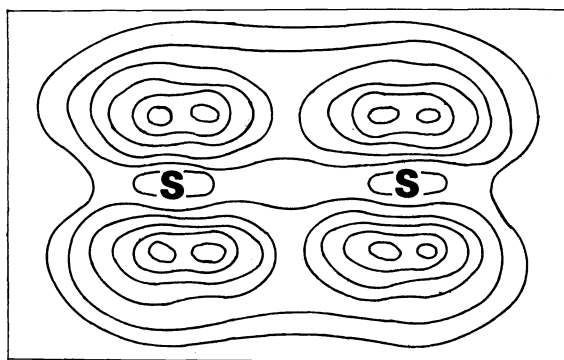
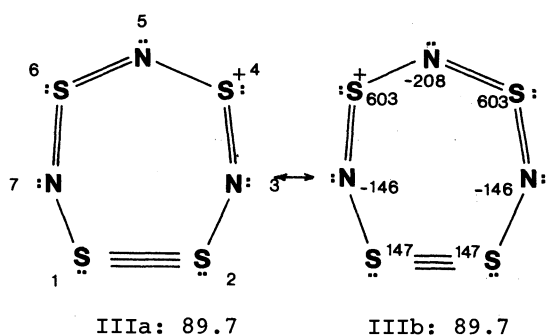


Fig. 2. Isodensity contour map for the localized SS "in-plane π -" MO in III. The lines (from the outermost to the innermost) correspond to electronic densities of 2, 5, 11, 16, 22 and 27 C.mmm^{-3} , respectively.

A more unorthodox situation is found in III. The ring is not a 10π but a 8π system with a triple bond between S^1 and S^2 . This is in contradiction to the suggestion of Roesky (22). According to our results three MO-s can be localized to the S^1S^2 atom pair. The first has a σ symmetry while the second π -type MO is perpendicular to the ring. The third localized orbital lies within the molecular plane and it has a negligible s-character. For an isodensity contour map see Fig. 2. It can be said that two π -bonds are formed which are perpendicular to each other. Consequently only one of them is part of the ring π -system. Note the relatively low value of the aromaticity index, $A = 10.3$. The reduced S^1S^2 distance (2.06 Å) can be treated as an experimental indication for the existence of a triple bond. This distance is compared with 2.14 Å in II, 2.20 Å in $\text{FSO}_2\text{NS(SN)}_2$ and 2.22 Å in $(\text{PF}_2\text{N})_3\text{S(SN)}_2$ (22).

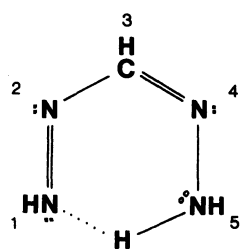
Characteristics of localized MO-s together with atomic net charges (the latter are given in millielectrons at structures Ib, IIb and IIIb) can be used to make qualitative predictions on bond distances. The difference in lengths of S^2N^3 (1.61 Å) and S^4N^3 (1.56 Å) bonds in II is understood considering the most important limiting structure IIa. Structure IIId, involving the reverse bond length ratio, has a minor weight, only. The delocalization of the N^3 lone pair is almost the same to S^2 and to S^4 (5.0 % and 5.8 %) thus

it has no influence on the relative magnitude of the bond lengths. The electrostatic force between both atoms of a bond is approximately proportional to the product of their net charges. This product for S^4N^3 (-0.081) indicates a stronger attraction than for S^2N^3 (-0.065). Thus electrostatic and delocalization effects are cumulated to make the S^4N^3 bond relatively shorter. The approximate equality of S^4N^3 and S^4N^5 bond lengths (1.55 Å and 1.57 Å) in III is explained in terms of the limiting structures IIIa-b and the product of net atomic charges (-0.088 and -0.125). Note that delocalization and electrostatic effects act against each other. Using the above arguments the S^2N^3 bond should be relatively long. This is not the case its length is 1.54 Å indicating that our model fails here. The aforementioned systematic difference in SNS and NSN bond angles is explained using valence shell repulsion theory (26). The reduced steric extension of the three-centre SNS bonds allows NSN angles to get smaller. Quantum chemistry yields here the argument for the formation of the three-centre bond.

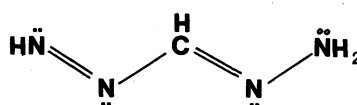
FORMAZAN

Let us study now quasiaromaticity on the formazan ring. As it has been suggested by Hutton et al. (27) 3-carboxymethylthio-1,5-diphenylformazan has an intramolecularly hydrogen-bonded, cyclic structure in chloroform solution. According to X-ray crystallographic studies the molecule has a completely different conformation in the solid state. A five-membered ring of atoms $N^1N^2C^3N^4H$ is formed. This is an interesting example where different conformers exist in solution and in the crystalline phase.

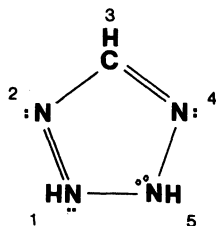
3-Carboxymethylthio-1,5-diphenylformazan was modelled by structures IV and V which differ in conformation, only. Further the related structures VI and VII were studied. VI can be treated as an ordinary aromatic ring. Note the existence of symmetry-related limiting structures in case of IV, VI and VII. Composition of localized π -orbitals, as obtained from CNDO/2 calculations, is given in Table 2. It is seen that N^1N^2 orbitals are well localizable. They are strongly polarized towards N^1 . Three-centre $N^2C^3N^4$ π -orbitals exist while the N^5 lone pair is delocalized to N^4 . σ -bonds of V and VI are well localizable (1 > 98 %). Hydrogen bonding in IV allows a considerable delocalization of the σ lone pair of N^5 (or N^1) to the proton. The bonds are strongly polarized (81.9 % to N^1 or to N^5). A three-centre $N^2C^3N^4$ π -orbital with negligible s-character is formed in VII. 29.3 % is localized both at N^2 and N^4 while C^3 has 37.5 %. The situation is reflected by the limiting structure VII which includes a positively charged nitrogen atom and the σ lone pair is absent. The aromaticity index of Eq. (8) is calculated for the compounds IV-VII. It is understood that for the linear structures V and VII A is a measure of delocalization and not of aromaticity. The following values are obtained: IV: 14.9, V: 5.1, VI: 20.2 and VII: 8.2. Delocalization is considerably higher for rings than for chains indicating that formation of a cyclic structure is essential in producing aromatic character.



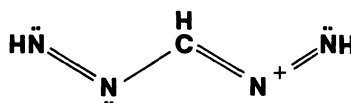
IV: 85.1



V: 94.9



VI: 79.8



VII: 91.8

TABLE 2. Composition of localized π -orbitals in molecules IV-VII

AB bond	mol.	l_{AB}	l_A	l_B	delocalization l_C
N^1N^2	IV	97.3	77.6	19.7	N^4 : 1.9
	V	96.9	53.1	43.8	N^4 : 1.8
	VI	92.5	72.2	20.3	N^4 : 5.9
	VII	97.5	65.1	32.4	N^4 : 1.4
C^3N^4	IV	80.4	62.3	18.1	N^2 : 18.1
	V	94.6	52.3	42.3	N^2 : 3.1
	VI	74.5	50.5	24.0	N^2 : 24.0
	VII	80.4	65.2	15.2	N^2 : 15.2
N^5 lp	IV	77.7	77.7	--	N^4 : 19.7
	V	93.2	93.2	--	N^4 : 4.4
	VI	72.5	72.5	--	N^4 : 19.7
N^4N^5	VII	97.5	65.1	32.4	--

Hutton and coworkers suggest that a novel intramolecular hydrogen bond between the formazan ring and the carboxylic proton in 3-carboxymethylthio-1,5-diphenylformazan is formed (27). They point out that "the arrangement most favoured sterically is that in which the -OH group of the side chain -SCH₂CO₂H points almost axially through the centre of the π -electron system

of the formazan ring". According to a simplified method (28) the electrostatic isopotential map for the unsubstituted formazan (IV) was constructed within the molecular plane. Fig. 3 shows two symmetrically positioned minima near N^2 and N^4 . It is known that local minima in the electrostatic isopotential map of a molecule coincide approximately with possible proton binding sites (29). Let us write the proton binding energy in an approximate form as $q^H \cdot V_{\min}$ where q^H denotes the (dimensionless) CNDO/2 net charge on the hydrogen atom, V_{\min} is the minimal value of the potential. In our case $q^H = 0.170$ (as calculated for acetic acid) $V_{\min} = 80 \text{ kcal.mol}^{-1}$. Thus the proton binds with an energy of $13.6 \text{ kcal.mol}^{-1}$ within the molecular plane. This is quite a strong bond so it is probable that, instead of a symmetric structure, an asymmetric one is formed where the proton is bound outside the ring. This statement could be verified by tracing the chirality of the molecule.

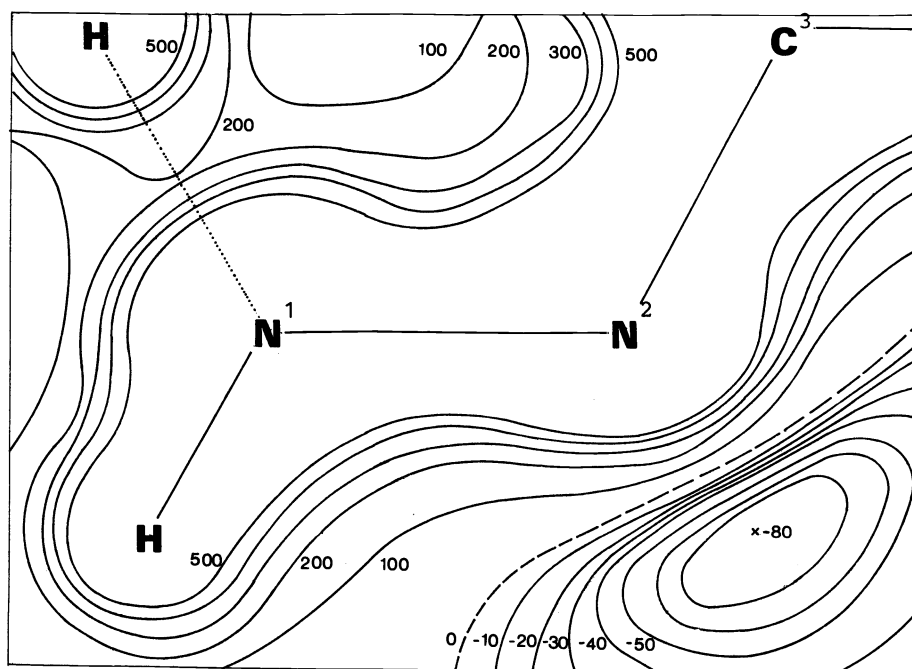


Fig. 3. Electrostatic isopotential map for formazan in the molecular plane (in kcal.mol^{-1}). Only one half of the mirror symmetric figure is shown.

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