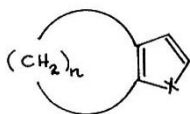


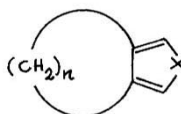
## GRAPHICAL STUDY OF POSITIONAL ISOMERS

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Structurally closely related heteroconjugated molecules (e.g., I and II) are named positional isomers<sup>1</sup> because they differ formally only in the position of a heteroatom.

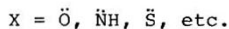


I



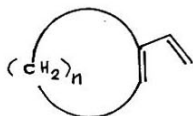
II

$$n = \begin{cases} 4m + 2 \\ 4m \end{cases}$$

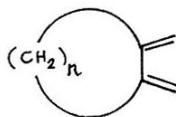


This difference in the position of a heteroatom causes dramatic changes in physical and chemical properties among the positional isomers belonging to the same set<sup>2</sup>. The order of relative stabilities of members of a particular set of positional isomers may be predicted by examining the topological factors determining the stability of the underlying "parent" hydrocarbon (e.g., Ia and IIa) obtained by deleting heteroatoms (donating two  $\pi$  electrons)

and bonds incident to them.



Ia

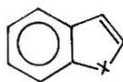


IIa

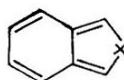
We have postulated<sup>3</sup> that the topological factors which are responsible for the stability of "parent" hydrocarbons are also to great extent determining the stability of the related heterocycles. The topological factors<sup>4,5</sup> which enter the expression for  $\Pi$ -electron energy (in Hückel theory) are the number of atoms ( $N$ ), the number of bonds ( $\vee$ ), the number and the type of rings ( $n_i$ ,  $i=4, 6, 8, \dots$ ), branching of a molecular skeleton ( $D_i$ ,  $i=1, 2, 3$ ) and the algebraic structure count ( $ASC=K^+ - K^-$ , where  $K^+$  and  $K^-$  are the Kekulé structures of different parity<sup>6,7</sup>). Positional isomers, however, differ only in their ASC values;  $N$ ,  $\vee$ ,  $n_i$ , and  $D_i$  values being identical. Thus, the evaluation of ASC is sufficient for predicting the stability order of the isomers<sup>8,9</sup>. The ASC values can be obtained either in a way described by Herndon<sup>8</sup> or by Cvetković et al.<sup>10</sup>

### Examples

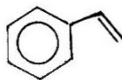
(1)



III



IV



IIIa



IVa

$$K^+(\text{IIIa}) = 2; K^-(\text{IIIa}) = 0$$

$$\text{ASC}(\text{IIIa}) = 2$$

$$K^+(\text{IVa}) = 1$$

$$\text{ASC}(\text{IVa}) = 1$$

Prediction of the stability order: III > IV.

This prediction is confirmed in the case of some known compounds<sup>2</sup>: indole-isoindole, benzofuran-isobenzofuran, benzothiophene-isobenzothiophene, etc.

(2)



V



VI



Va



VIa

$$K^+(\text{Va}) = 1; K^-(\text{Va}) = 1$$

$$\text{ASC}(\text{Va}) = 0$$

$$K^+(\text{VIa}) = 1$$

$$\text{ASC}(\text{VIa}) = 1$$

Stability prediction: V < VI.

In some known cases this prediction is fully confirmed. For example, diphenyl derivative of thieno[c]cyclobutadiene (VII<sub>I</sub>) is reported<sup>11</sup> while neither thieno[b]cyclobutadiene (VII) or its derivatives are known yet.

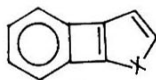


VII

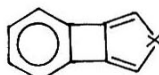


VIII

(3) Interesting prediction is reached for molecules IX and X.



IX



X



IXa



Xa

$$K^+(IXa) = 2; K^-(IXa) = 1$$

$$ASC (IXa) = 1$$

$$K^+(Xa) = 2; K^-(Xa) = 0$$

$$ASC (Xa) = 2$$

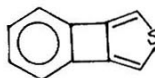
Stability prediction: IX < X.

The experimental findings are in accord with this prediction. For example, 2-thianorbiphenylene (XI<sub>I</sub>) is prepared (stable white crystalline solid)<sup>12</sup> whereas 1-thianorbiphenylene (XI) is still unknown compound.

We have studied with this method a number of sets of positional isomers and in all studied cases the qualitative agreement with experimental findings is obtained. Furthermore, the available MO calculations support our graphical results.



XI



XII

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