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Topological Resonance Energies of Thiocoumarins*

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Topological resonance energies of thiocoumarin, thiochromone, and related systems are reported. Theoretical predictions indicate that systems in which the benzene ring retains to great extent its aromatic structure are much more stable than the corresponding quinonoid isomers.

In the present note[1] the topological resonance energy, TRE, model[2-4] is applied to thiocoumarin, thiochromone, and related structures. All studied structures are given in Figure 1.

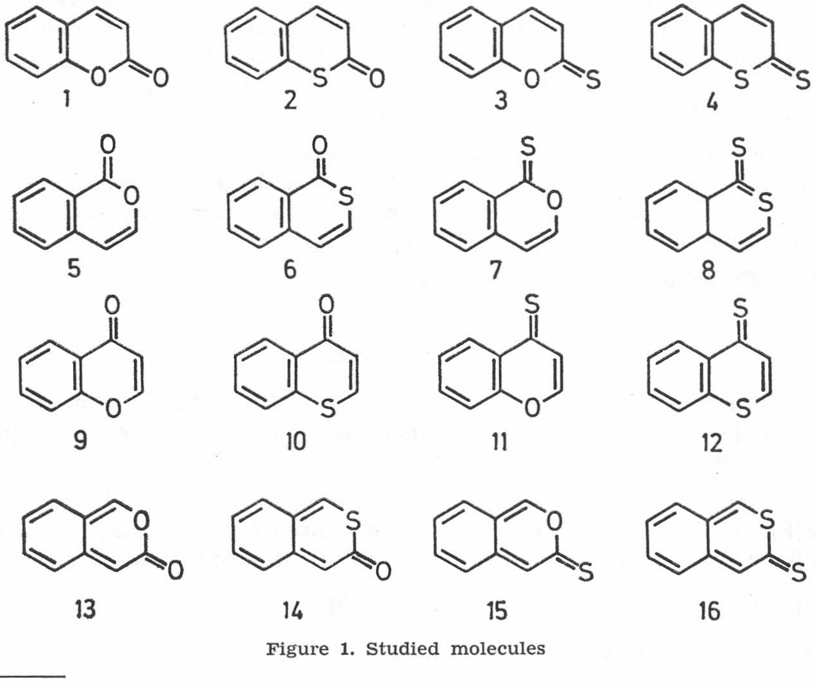

Figure 1. Studied molecules

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While coumarin (2H-1-benzopyran-2-one) is a molecule with a long and exciting history,[5-8] thiocoumarin has been studied to a much less extent.[9-11] Similarly, all thio systems in Figure 1 are also not well known molecules. This is surprising because thiocoumarin, thiochromone, their derivatives, and related structures have many interesting and useful physico-chemical, biological, and pharmaceutical properties and have found wide applications in chemical and pharmaceutical industry.[12-25]

Aromatic stability of coumarin, chromone (4H-1-benzopyran-4-one), and its derivatives has been discussed by a number of researchers.[1,6,26-29] However, there is no work, to our knowledge, in which the resonance energies of thiocoumarins are reported and their aromatic stabilities discussed. Therefore, we decided to study thiocoumarin, thiochromone, and related molecules by means of topological resonance energy approach which has shown previously, with certain limitations,[34] to be a quite reliable method for predicting aromaticity in various conjugated systems.[3,4,29-40]

Topological resonance energies of molecules 1—16 have been calculated using the following formula

$$\mathrm{TRE} = \sum_{j=1}^{N} h_j \, (x_j - x_j^{ac}) \qquad (1)$$

where x_j and x_j^{ac} represent the Hückel spectrum of a given molecule and the spectrum of the corresponding acyclic polynomial,[2,3] respectively, while h_j ($j = 1, 2, \ldots, N$) are the orbital occupancy numbers. N is the number of π centers in a given molecule. The parameters for heteroatoms are taken from work by Hess and Schaad.[41,42] Numerical work is carried out in a way described elsewhere.[43]

We have also calculated the TRE per electron, TRE(PE), values of thiocoumarins since we wanted to find out how these molecules compare to benzene. Because they are larger systems than benzene, we compared their TRE(PE) values to that one of benzene (TRE(PE) = 0.046).

TRE(PE) values are calculated from the formula,

$$\mathrm{TRE\,(PE)} = \frac{\mathrm{TRE}}{\mathrm{N}\,(\pi)} \qquad (2)$$

where $\mathrm{N}(\pi)$ is the total number of π electrons in the molecule. Note, for many heteroconjugated systems $\mathrm{N}(\pi) \neq \mathrm{N}$, because some π centers are populated with one π-electron, and others with two.

There are, of course, other possibilities open for normalizing TRE.[44,45] If TRE(PE) is accepted as a convenient normalised form of TRE, the threshold values for aromatic, non-aromatic, and anti-aromatic compounds are as follows:

(i) aromatic compounds: $\mathrm{TRE(PE)} > 0.01$

(ii) non-aromatic compounds: $\mathrm{TRE(PE)} = 0.00$

(iii) anti-aromatic compounds: $\mathrm{TRE(PE)} < -0.01$

Numerical values of TRE and TRE(PE) for thiocoumarins are reported in the Table.

TABLE I

Topological Resonance Energies of Thiocoumarins

Compound[a]	TRE	TRE (RE)	% of benzene character	Reference to the preparative work
1	0.2436	0.0203	44	6
2	0.2676	0.0223	49	11
3	0.2388	0.0197	43.5	14
4	0.2655	0.0221	48.7	10
5	0.2302	0.0192	42	7
6	0.2644	0.0220	48.5	12
7	0.2348	0.0195	43	11
8	0.2639	0.0220	48	11
9	0.2553	0.0213	46.9	9
10	0.2805	0.0234	51.5	9
11	0.2590	0.0216	47.5	9
12	0.2800	0.0233	50.7	10
13	0.0903	0.0075	16.5	
14	0.1005	0.0088	19	
15	0.0865	0.0072	15.9	
16	0.1161	0.0089	19.7	

[a] Compounds are listed in Figure 1.

From the Table we see that the thio-derivatives of coumarin (**1**), thiocoumarins, and thio-derivatives of chromone (**5**), thiochromones, are all aromatic compounds. Experimental evidence supports this result.[11] Therefore, *the substitution of oxygen by sulphur does not cause destabilization of the system.* However, the aromatic stability of thiocoumarins and thiochromones is only half that of the benzene ring stability. The meaning of this result is that the benzene ring in the thiocoumarins and thiochromones is distored to a certain extent.

Thio-derivatives of 3H-2-benzopyran-3-one (**14—16**) are much less stable than thio-derivatives of coumarin and chromone. While thiocoumarins and thiochromones are stable and have TRE(PE) values in the range of 0.019—0.023, compounds **14—16** should be much less stable with TRE(PE) values in the range 0.007—0.009. They are quinonoid structures in which the benzene ring is very much distorted. Therefore, it is not surprising that compounds **14—16** are not reported as yet.

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SAŽETAK

Topologijske rezonancijske energije tiokumarina

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Izračunane su topologijske rezonancijske energije tiokumarina, tiokromona i srodnih struktura. Teorijska predviđanja ukazuju na veću stabilnost struktura u kojima benzenski prsten zadržava svoju aromatičku strukturu u odnosu na odgovarajuće kinoidne izomere.