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ELECTRONIC STRUCTURE AND REACTIVITY OF THIONES AND SELENONES IN THE HETEROAROMATIC SERIES

V. P. Litvinov, A. A. Guliev,
I. A. Dzhumaev, and I. A. Abronin

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Quantum mechanical calculations were carried out for a series of thieno- and selenophenodihetero-2-thiones and selenones using the semiempirical SCF MO LCAO method and the CNDO/2 valence approximations with complete optimization of geometric parameters. The data obtained in this way was used to determine the reactivity of the compounds in processes leading to the formation of corresponding heterofulvalenes.

The synthesis of charge transfer complexes (CTC) based on tetrathiafulvalenes and tetraselenafulvalenes [1] constitutes a major achievement of the past few years in the preparation of organic substances displaying electronic conductivity similar to metals (so-called "organic metals"). Several superconductors based on these compounds are known [2-4]. Heterofulvalenes condensed with benzene or, in particular, heteroaromatic rings could also serve as prospective donor compounds in CTC. The introduction of additional heteroatoms of different natures into these systems would permit one to systematically and delicately vary the structural characteristics of the CTC, which, in turn, determine whether their phase transition properties are of the semiconductor—conductor or conductor—superconductor type.

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow.
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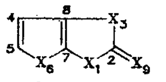
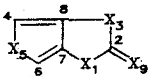
TABLE 1. Calculated and Experimental Geometric Parameters for Thiophene and Selenophene

Compound	Basis	Bond length, Å			Angle, deg		
		12	23	34	215	123	234
Thiophene	*sp*	1,86	1,33	1,44	86	113	114
	spd	1,69	1,38	1,45	132	78	137
	exp. acc. to [5]	1,71	1,37	1,42	92	112	113
Selenophene	*sp*	2,09	1,33	1,44	80	113	118
	spd	1,87	1,38	1,45	126	79	137
	exp. acc. to [6]	1,85	1,37	1,43	88	112	115

In the present paper we present the results of quantum mechanical calculations on isomeric thieno- and selenopheno-1,3-dihetero-2-thiones and selenones (I-IV).



Ia-h, IIIa-h



IIa-f, IVa-f

I X_9=S; III X_9=Se; I, III a X_1, X_3, X_6=S; b X_1, X_3=S; X_6=Se; c X_1=S; X_3, X_6=Se; d X_3=S; X_1, X_6=Se; e X_1, X_3, X_6=Se; f X_1, X_6=S; X_3=Se; g X_6=S; X_1, X_3=Se; h X_3, X_6=S; X_1=Se; II X_9=S; IV X_9=Se; II, IV a X_1, X_3, X_5=S; b X_1, X_3=S; X_5=Se; c X_1=S; X_3, X_5=Se; d X_1, X_3, X_5=Se; e X_1, X_5=S; X_3=Se; f X_5=S; X_1, X_3=Se

The goal of these calculations was to determine the structural parameters of the compounds, which are missing in the literature, and also their electronic structures, which influence their reactivity to give the corresponding heterofulvalenes.

One of the principal problems in calculating the geometric parameters of compounds containing Period III and IV atoms is the choice of the basis set (sp- vs. spd-). In order to resolve this difficulty the geometric parameters of thiophene and selenophene were calculated using both of these basis sets.

The calculated C–X and C–C bond lengths and bond angles, as well as the experimental values (for thiophene and selenophene) are presented in Table 1. As seen in Table 1, the C–X bond lengths using the spd-basis set are in better agreement with the experimental values (the calculated C–C bond lengths are satisfactory using either the sp- or spd-basis sets); the bond angle calculations, however, are completely unsatisfactory using the spd-basis set. The calculated bond angles using the sp-basis set, on the other hand, differ from the experimental values by no more than 8°. For this reason, further calculations were carried out using the sp-basis set.

The calculated values for the geometric parameters of the compounds under investigation are presented in Table 2. These results indicate that all of the compounds are planar. Furthermore, these results agree with calculations for Ia and IIa using the MINDO/3 method, in which the problem of nonplanar distortion was specifically addressed [7]. According to this method, the heteroaromatic fragments retain to a large extent their individual characteristics, regardless of the nature of the heteroatom, the properties of atoms attached to it, or the method of annelation; in all cases their structural parameters are very close to those for the individual heterocycles. Replacement of a S atom with a Se atom increases the corresponding bond length with carbon by 0.25 Å, and also changes the valence angles (compare I and III, II and IV, as well as *a* and e, Table 2). A pronounced change in valence angles also accompanies a change in the mode of annelation – from a formal double bond with the aromatic heterocycle (I, III) to a formal single bond with the aromatic heterocycle (II, IV).

The C–X_9 bond length does not depend on the nature of the other heteroatoms in the condensed heterocycles I-IV, but is determined only by the nature of X_9 (S vs. Se). For their part the structural parameters for the condensed heterocycle fragment are also independent of the nature of X_9 (compare values for I and III or II and IV, *a*-h, respectively, Table 2). This leads one to propose that the structural parameters compiled in Table 2 for the cyclic fragments could be employed in calculations of the corresponding heterofulvalenes.

TABLE 2. CNDO/2 Optimized Geometric Parameters for Compounds I-IV

Compound	Bond length, Å										Valence angle, deg									
	67	56	78	45	48	17	38	12	23	29	567	678	456	548	487	176	384	217	238	129
Ia	1,86	1,86	1,33	1,33	1,43	1,85	1,87	1,83	1,83	1,75	90	111	113	113	117	125	114	91	96	121
Ib	2,09	2,10	1,32	1,33	1,43	1,84	1,88	1,83	1,83	1,75	80	110	113	116	122	126	113	91	95	121
Ic	2,10	2,10	1,32	1,33	1,43	1,85	2,12	1,83	2,06	1,74	81	109	113	115	123	123	112	96	90	120
Id	2,09	2,10	1,32	1,33	1,43	2,07	1,88	2,07	1,83	1,74	80	110	112	116	121	128	117	87	100	124
Ie	2,10	2,10	1,32	1,33	1,43	2,08	2,12	2,07	2,06	1,74	81	109	112	116	122	125	115	92	95	124
If	1,86	1,86	1,32	1,33	1,43	1,85	2,10	1,83	2,06	1,74	87	111	113	112	118	123	113	96	89	120
Ig	1,86	1,86	1,32	1,33	1,43	2,08	2,11	2,07	2,06	1,74	87	111	113	113	117	124	116	91	94	123
Ih	1,85	1,86	1,32	1,34	1,43	2,08	1,87	2,06	1,84	1,74	86	112	113	113	116	127	118	87	99	124
IIIa	1,85	1,86	1,33	1,34	1,43	1,85	1,87	1,82	1,82	1,99	86	111	113	112	117	126	114	92	96	121
IIIb	2,09	2,10	1,32	1,33	1,43	1,84	1,88	1,82	1,82	1,99	80	110	113	115	122	127	113	92	95	122
IIIc	2,10	2,10	1,32	1,33	1,43	1,85	2,12	1,82	2,05	1,99	81	109	113	115	123	124	112	97	90	120
IIId	2,09	2,10	1,32	1,33	1,43	2,08	1,88	2,06	1,82	1,99	80	110	112	116	121	128	117	88	100	125
IIIe	2,09	2,10	1,32	1,33	1,43	2,08	2,12	2,06	2,05	1,98	81	109	112	116	122	125	115	92	96	123
IIIf	1,86	1,86	1,33	1,34	1,43	1,85	2,11	1,82	2,05	1,99	87	111	113	112	118	123	113	96	90	120
IIIg	1,86	1,86	1,32	1,33	1,43	2,08	2,11	2,06	2,05	1,98	87	111	113	112	117	125	116	92	95	123
IIIh	1,85	1,86	1,33	1,34	1,43	2,08	1,87	2,06	1,85	1,99	86	112	113	113	116	127	118	87	99	124

	Bond length, Å										Valence angle, deg									
	56	45	67	48	78	17	38	12	23	29	456	567	548	678	487	176	384	217	238	129
IIa	1,86	1,86	1,33	1,33	1,43	1,87	1,87	1,83	1,83	1,75	90	108	108	117	117	127	127	96	96	122
IIb	2,10	2,10	1,32	1,32	1,43	1,88	1,88	1,82	1,82	1,75	83	108	108	121	121	123	123	96	96	122
IIc	2,10	2,10	1,32	1,32	1,43	1,88	2,11	1,83	2,06	1,74	83	109	108	122	120	121	124	101	91	121
IId	2,10	2,10	1,32	1,32	1,43	2,11	2,11	2,06	2,06	1,74	83	108	108	121	121	122	122	96	96	124
IIe	1,86	1,87	1,33	1,32	1,43	1,87	2,10	1,83	2,06	1,74	90	109	108	118	116	124	127	100	91	121
IIf	1,87	1,87	1,33	1,33	1,43	2,11	2,11	2,06	2,06	1,74	89	109	109	116	117	125	126	95	97	124
IVa	1,86	1,86	1,33	1,33	1,43	1,87	1,87	1,82	1,82	1,99	90	108	108	117	117	127	127	96	96	122
IVb	2,10	2,10	1,32	1,32	1,43	1,88	1,88	1,82	1,82	1,99	83	108	108	121	121	124	124	97	97	123
IVc	2,10	2,10	1,32	1,32	1,43	1,88	2,11	1,82	2,05	1,99	83	109	108	120	121	121	124	102	92	125
IVd	2,10	2,10	1,32	1,32	1,43	2,12	2,12	2,05	2,05	1,98	83	108	108	212	121	122	122	96	96	124
IVe	1,86	1,87	1,33	1,32	1,43	1,87	2,11	1,82	2,05	1,99	90	109	108	118	116	125	127	101	91	121
IVf	1,87	1,87	1,33	1,33	1,43	2,11	2,11	2,05	2,05	1,98	90	108	108	117	117	125	125	96	96	124

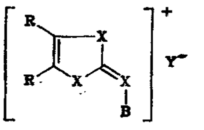
TABLE 3. Calculated Quantum Mechanical Properties of Compounds I-IV

Compound	$-E_{tot}$, eV	$q_{C_{(2)}}$	$q_{X_{(9)}}$	Δq_{XC}	$-E_{XC}$, eV
Ia	2165,647	0,179	−0,259	0,438	22,29
Ib	2117,542	0,179	−0,259	0,438	22,27
Ic	2069,277	0,166	−0,247	0,413	22,65
Id	2069,155	0,168	−0,250	0,418	22,61
Ie	2020,955	0,157	−0,236	0,393	22,97
If	2117,368	0,166	−0,247	0,413	22,69
Ig	2069,059	0,156	−0,236	0,392	22,98
Ih	2117,270	0,167	−0,249	0,416	22,63
IIa	2165,902	0,182	−0,261	0,443	22,29
IIb	2117,882	0,182	−0,260	0,442	22,25
IIc	2069,584	0,172	−0,248	0,420	22,59
IIe	2021,341	0,163	−0,235	0,398	22,98
IIf	2117,597	0,171	−0,249	0,420	22,65
IIg	2069,339	0,163	−0,236	0,399	22,96
IIIa	2117,875	0,185	−0,321	0,506	18,41
IIIb	2069,772	0,185	−0,321	0,506	18,39
IIIc	2021,480	0,174	−0,311	0,485	18,71
IIId	2021,363	0,175	−0,314	0,489	18,67
IIIe	1973,133	0,164	−0,303	0,467	19,00
IIIf	2069,571	0,174	−0,312	0,486	18,71
IIIg	2021,232	0,164	−0,303	0,467	19,02
IIIh	2069,478	0,175	−0,314	0,489	18,70
IVa	2118,135	0,189	−0,322	0,511	18,43
IVb	2070,118	0,190	−0,321	0,511	18,41
IVc	2021,793	0,180	−0,312	0,492	18,71
IVe	1973,522	0,171	−0,301	0,472	19,01
IVf	2069,804	0,179	−0,313	0,492	18,72
IVg	2021,526	0,173	−0,303	0,476	19,02

The calculated quantum mechanical characteristics of the compounds under investigation are presented in Table 3; these include their total energies, E_{tot}, the charges on atoms, $q_{C(2)}$ and $q_{X(9)}$, the charge difference, Δq_{XC}, which characterizes the polarity of the C—X bond, and also the two-center component of the energy, E_{XC}, related to the C_2—X_9 bond, which to a large extent is a measure of the bond strength.

As can be seen from the E_{tot} values, the type II or IV isomers are more stable than the corresponding isomers of type I or III. Furthermore, the heteroatom in position 9 exerts a greater stabilizing influence on the system than in any other position; the nature of the heteroatom in the heteroaromatic fragment is the next most important factor influencing the stability of these compounds (compare E_{tot} for IIIa, Ib, If, and Ih, or IVa, IIb, and IIf). In this respect heterofulvalenes condensed with a heteroaromatic residue should be more promising than those connected to other substituents due to the increased stabilization of the fulvalene fragment. The nature and position of the heteroatoms in the heterofulvalene fragment exert a much smaller effect on the stabilization of the system. The above analysis is valid only for systems containing an equivalent number of atoms of various types, i.e., for classical isomers, In order to analyze the relative stabilities of molecules with varying numbers of S or Se atoms it would be necessary to utilize thermodynamic parameters obtained using the MINDO/3 or MNDO methods; these parameters have not been calculated yet for Se.

At the present time one of the general routes for the synthesis of heterofulvalenes based on I-IV would involve initial desulfurization or deselenation followed by dimerization of the intermediate carbenes. The initial phase of this reaction is usually carried out by treatment with an agent that forms a complex with the $C_{(2)}$—$X_{(9)}$ bond, for instance, CH_3I or $P(OCH_3)_3$ [8]; the complex A then loses X. In such cases the counterion Y^- is localized predominantly on $C_{(2)}$, which carries the most positive charge (Table 3).



A

The principal factor affecting the ease of complex formation with a desulfurizing (or deselenizing) reagent will be the polarity of the $C_{(2)}$—$X_{(9)}$ bond, characterized by the charge difference between the two atoms (Δq_{XC}); an increase in the bond polarity should enhance complex formation. The strength of the bond (as measured by the magnitude of E_{XC}) will also affect the reaction; a decrease in bond strength should increase the reactivity toward complex formation. Our analysis indicates that there is a linear dependence between the values of Δq_{XC} and E_{XC}; this relationship is described by Eq. (1) for compounds I and II, and by Eq. (2) for compounds III and IV:

$$\Delta q_{SC}=0.0178E_{SC}+1.869 \qquad (r=0.990); \tag{1}$$

$$\Delta q_{SeC}=0.0152E_{SeC}+1.659 \qquad (r=0.973). \tag{2}$$

The different regression analysis (equation) for the $C_{(2)}-S_{(9)}$ bond vs. the $C_{(2)}-Se_{(9)}$ bond is probably related to the above-mentioned imbalance in parametrization of the thermodynamic characteristics calculated via the CNDO/2 method. In addition, as seen in Eqs. (1) and (2), and also in Table 3, the C–Se bond is consistently more polar and less stable than the C–S bond. The structures of the condensed fragments, and in particular the nature of the atoms in them, also affect both the polarity and strength of the $C_{(2)}-X_{(9)}$ bond. As a result, the most polar and least stable $C_{(2)}-X_{(9)}$ bonds are found in compounds of type *a* or b, which contain S atoms in the heterofulvalene fragment. Replacement of one S atom with a Se atom in this fragment decreases the polarity and increases the strength of the $C_{(2)}-X_{(9)}$ bond; replacement of both S atoms enhances this tendency by an equal amount, 0.2 eV for Δq_{XC}, and 0.3 for E_{XC} for each Se atom in position 1 or 3.

The values of Δq_{XC} are smaller for compounds of type I or III than for type II or IV compounds, despite practically equivalent values of E_{XC}.

The analysis of the calculated characteristics of the $C_{(2)}-X_{(9)}$ bonds leads to the following conclusions pertinent to the synthesis of S- and Se-containing heterofulvalenes:

1) the formation of heterofulvalenes from selenones III and IV should be more facile than from the corresponding thiones I and II;

2) tetrathiafulvalenes should be obtained under kinetically milder conditions than tetraselenafulvalenes.

The first conclusion has been verified in laboratory practice; the preparation of a heterofulvalene was achieved by the conversion of a thione to a selenone followed by deselenation [9]. The accuracy of the second conclusion can be verified only indirectly. For example, a selenium analog could not be obtained under conditions which sufficed for the synthesis of bis(ethylenedithio)tetrathiafulvalene [10].

In summary, the calculated properties described in this paper have been applied in the formulation of rules governing the synthesis of S- and Se-containing heterofulvalenes.

EXPERIMENTAL

The calculations were carried out using the SCF MO LCAO method with the CNDO/2 valence approximations [11] (parameters described in [12] were used for Se) with complete optimization of geometric parameters; the program used was a modified GEOMO (QCPE no. 290) on an IBM EC-1060 computer. The accuracy of the geometric optimization was 0.005 Å for the bond lengths and 0.5° for the bond angles.

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PYRYLOCYANINES.

21.* UNSYMMETRICAL α-PYRYLO- AND α-PYRIDOCYANINES

I. M. Gavrilyuk, A. A. Ishchenko,
M. A. Kudinova, and A. I. Tolmachev

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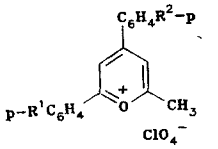
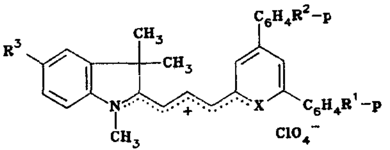
(2-Pyrylo)- and (2-pyrido)(indo)trimethinecyanines containing both electron donor and electron acceptor substituents in the heterocyclic rings have been synthesized. It has been shown that the 4,6-diphenyl-2H-pyran nucleus confers less basicity (electron donor characteristics) than the 1,3,3-trimethylindoline segment. It has also been shown that the introduction of substituents to the heterocyclic residues of unsymmetrical dyes allows one to manipulate their electronic asymmetry over a wide range up to a change in the distribution of charge from one ring to another.

The pyran ring constitutes one of the largest and most important groups, in a practical sense, of polymethine dyes, namely, the pyrylocyanines. Nevertheless, up to this time, the electron donating ability of the heterocyclic residues in these dyes has not been addressed in the literature. On the basis of the work in [2], which has appeared in a monograph [3], the 4,6-diphenyl-2H-pyran residue would be expected to exhibit more electron donating ability than the 1,3,3-trimethylindoline residue; on the other hand, on the basis of [4], just the opposite is predicted. In order to resolve this controversy, the present work describes, in analogy with [5-7], the properties of unsymmetrical dyes containing both electron donating and electron withdrawing substituents in the heterocyclic residues. This approach is well suited to accomplish the stated goal, inasmuch as the introduction of substituents does not alter the structural characteristics or conformation of the dye. Consequently, any change in the electron donating properties of the heterocyclic residues will depend only on the electronic nature of the substituents.

The unsymmetrical (2-pyrylo)(indo)trimethinecyanines IIa-f were synthesized via the condensation of nitro- and methoxy-substituted pyrylium salts Ia-d with 1,3,3-trimethyl-2-formylmethyleneindoline or its 5-nitroderivative. In addition, in order to elucidate analogous mechanisms for substituted (2-pyrido)(indo)trimethinecyanines, the compounds IIIa-f were prepared by treatment of the dyes IIa-f with methylamine.



Ia-d



IIa-f, IIIa-f

I–III a $R^1=NO_2$; c, d, f $R^1=OCH_3$; b, d, f $R^2=OCH_3$; e, f $R^3=NO_2$; II X=O; III X=NCH_3; if not specified, R^1, R^2, R^3 =H

The following parameters have been evaluated for solutions of the synthetic dyes (except IIIa, which could not be isolated in analytically pure form) in both the weakly polar solvent

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*For Communication No. 20, see [1].

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