

Intramolecular Interactions in Anisole, Thioanisole, and Selenoanisole. Application of Natural Bond Orbitals Method

V. M. Bzhezovskii and E. G. Kapustin

Institute of Organic Chemistry, Ukrainian Academy of Sciences, Kiev, 02094 Ukraine

Received August 2, 2000

Abstract—Calculations of molecules PhXMe (X = O, S, Se) in MP2(f)/6-31G(d) approximation were performed. The stationary points on the potential energy surface were determined and identified. The anisole molecule is planar with a barrier to rotation ΔH^\ddagger 7.78 kJ mol⁻¹. In thioanisole and selenoanisole (ΔH^\ddagger 3.08 and 10.25 kJ mol⁻¹ respectively) the energy minimum corresponds to an orthogonal form. Analysis of relation between intramolecular interactions and conformational structure of the molecules in question was performed by the method of natural bond orbitals. In X atoms one lone electron pair is a hybrid orbital with the following fraction of s-component: 38–45% (O), 66–68% (S), and 73–74% (Se). The second lone electron pair is virtually pure p_z-AO.

Anisole, thioanisole, and selenoanisole are traditional objects for the study of interaction between atoms O, S, and Se and an aromatic ring. Different electronegativity (EN) of the heteroatoms and also the capability of their lone electron pairs (LEP) to be in resonance interaction with the π -system result in significant distinctions in the physico-chemical characteristics and reactivity of these compounds. Experimental and some theoretical results of investigation of aromatic compounds containing elements from chalcogens subgroup were summed up in [1–3]. The signs of n,π -interaction in anisole, thioanisole, and selenoanisole were detected by virtually all physico-chemical methods, for instance, photoelectron [4, 5], X-ray emission [6–8], UV, IR [9–13], NMR [6, 7, 14, 15] spectroscopy and dipole moment measurements [16, 17]. As a rule the experimental methods provide a possibility of estimating only relative energies of n,π -interaction in isostructural anisoles, such as the values of level splitting in the photoelectron spectra [1, 3, 4], parameters of IR [9] or ¹³C NMR [13, 14] spectra. The spectrophotometric studies of charge-transfer complexes (CTC) also only permit characterization of general trends in the changes in HOMO energy [1, 3]. Similarly may also be regarded the values of resonance constants from the correlation analysis that describe the changes in shielding of ¹⁹F nuclei in the NMR spectra of a series of para-fluorosubstituted benzenes, or are obtained from the other spectral parameters or from reactivity data [18, 19]. In most cases such results evidence

overall properties of substituents (with the prevalence of resonance characteristics), and they correspond to efficient (averaged) conformation of the molecule. It was established that the n,π -interaction in the isostructural anisoles decreased in the substituents series: OMe > SMe > SeMe > TeMe. The energetical characteristics of the n,π -interaction were estimated by thermochemical methods (measurement of combustion heats and enthalpy of complex formation) [2]. Data on results of measurements of combustion heats for the series of isostructural anisoles are not available. By complex formation procedure the energy of n,π -interaction in anisole is estimated as 25.9, and in thioanisole as 15.5 kJ mol⁻¹ [2]. However it cannot be stated definitely that the values contain only the energy of the n,π -interaction since essentially the discussed figures correspond to the enthalpy of complex formation which is affected by quite a number of factors [2]. For instance, it was strange that the energies of n,π -interaction for diphenyl ether and dimethoxy-substituted benzenes turned out to be significantly greater than the respective interaction in anisole ([2], kJ mol⁻¹): (Ph)₂O 36.8, 1,4-(MeO)₂C₆H₄ 53.6, 1,3-(CH₃O)₂C₆H₄ 66.5, and Ph₃P 29.7. The efficiency of n,π -interaction essentially depends not only on the electronic nature of the heteroatom but also on the angle between the symmetry axis of the p-component of the LEP orbital and the symmetry axis of the p _{π} -orbital of the closest carbon atom of the unsaturated moiety, i.e., on the conformation of the molecule. On qualitative level the conformational

Table 1. Total energy ($-E_{\text{tot}}$, a.u.) of molecules PhXMe (X = O, S and Se)

Compound	φ , deg						
	0	15	30	45	60	75	90
PhOMe	345.6831291	.6827475	.6817110	.6804153	.6796587	.6795371	.6795188
PhSMe	668.3024735	.3025569	.3027167	.3029312	.3033128	.3035414	.3035681
PhSeMe	2668.4157576	.4158972	.4162850	.4169517	.4180682	.4192233	.4196979

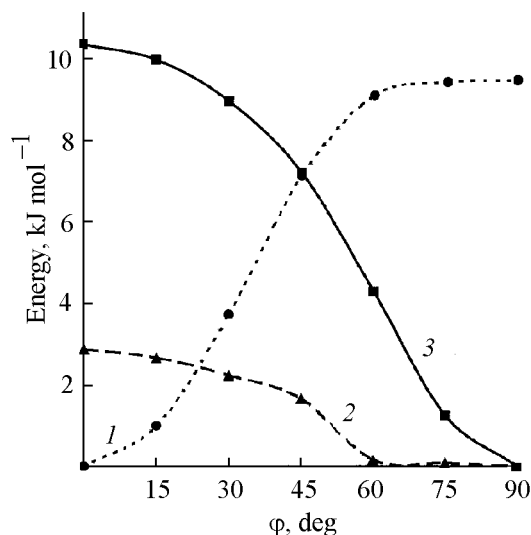
influence on n, π -interaction were demonstrated by ^{13}C NMR [6, 14, 15], photoelectron [1, 4, 5], X-ray emission [6, 7], IR and UV [9–13] spectroscopy in the studies of compounds PhXAlk (X = O, S, Se; Alk = Me, Et, *i*-Pr and *t*-Bu) where the molecular conformation varied due to the change in spatial parameters of alkyl groups. In the early works great attention was directed to the participation of the vacant d -orbitals of the atoms from the third and lower periods in the formation of the chemical bonds [20–22]. However the modern quantum-chemical studies show that the d -orbitals mostly play some role in polarization, and even here the antibonding σ -orbitals may be better electron acceptors [23–26].

Thus the available experimental data do not provide complete quantitative information on LEP of O, S, and Se atoms and on their interaction with the aromatic ring in the isostructural anisoles. The modern quantum-chemical methods give such opportunity. The goal of this investigation is the analysis of intramolecular interactions in the molecules of anisole, thioanisole, and selenoanisole proceeding from nonempirical quantum-chemical calculations with accounting for correlation energy in MP2(f)/6-31G(d) approximation followed by transformation of the obtained canonical molecular orbitals by means of the method of natural bond orbitals (NBO) into orbitals corresponding to common chemical terms (bond, core orbital, lone electron pair). The calculations provided quantitative characteristics of hybridization, energy, and occupancy of LEP of O, S, and Se atoms, the energy values of their resonance coupling with the antibonding π^* -orbitals of the ring, and the natural charges on the atoms.

Nonempirical quantum-chemical calculations were carried out in approximation of Møller–Plesset perturbation theory of the second order (MP2) [27, 28] with the use of software GAUSSIAN 98W (Revision A.7) [29]. Correlation correction was taken into account for all orbitals: MP2(f). In all calculation was used doubly split basis set 6-31G(d) with six-lobe

sd -functions [30]. We used standard convergence criteria for density matrix and energy gradient. The calculations were performed in the range of changes of the torsion angle φ (between the planes of the benzene ring and bonds $\text{C}_{sp^2}\text{-S-C}_{sp^3}$) from 0 to 90 degrees with a step of 15 degrees. The refining of positions of stationary points (minimum and maximum points) on the potential function of internal rotation of fragments around the bonds $\text{C}_{sp^2}\text{-X}$ was done with complete optimization of the geometrical parameters, including the torsional angle φ . The nature of the stationary points was identified by solving oscillatory problems. The analysis of occupancy of the wave functions was carried out in the framework of formalism of NBO method [31–33] with the use of software NBO Version 3.1 (link 607, GAUSSIAN 98W) [34].

The decisive contribution into the solution of numerous problems related to the nature of intramolecular interactions make the data on the spatial structure of molecules.



Potential functions of internal rotation around bonds $\text{C}_{sp^2}\text{-X}$ in molecules of anisole (1), thioanisole (2), and selenoanisole (3).

Table 2. Optimized values of bond angles (deg) and bond lengths (Å) in molecules PhXMe (X = O, S and Se)

Compound	φ	CXC angle	CCX angle	$l(C_{sp^2}-X)$	$l(C_{sp^3}-X)$	$\Sigma l(C_{Me}-H)/3$
PhOMe	0	116.79	124.86	1.371	1.422	1.093
	45	115.24	123.04	1.377	1.427	1.093
	90	111.94	119.68	1.385	1.429	1.094
PhSMe	0	102.58	124.61	1.770	1.802	1.091
	45	100.80	122.43	1.775	1.810	1.091
	90	98.56	120.26	1.781	1.813	1.091
PhSeMe	0	100.36	124.02	1.905	1.941	1.090
	45	98.29	121.86	1.908	1.949	1.090
	90	95.98	120.08	1.910	1.951	1.090

In the anisole molecule in the minimum point of the total energy (φ 0 deg) (Table 1, figure) the matrix of second derivatives (Hesse matrix) possesses only positive eigenvalues, and in the maximum point (90 deg) one negative eigenvalue (-45.56 cm^{-1}). The corrections for the energy of zero oscillations (here and hereinafter with account taken for the scaling factor 0.9661 [35]) amount to 0.1299839 (φ 0) and 0.1293386 Hartree/particle (φ 90 deg). The barrier to rotation including correction for the zero oscillations energy is 7.78 kJ mol^{-1} .

The planar conformation of anisole was proved by direct structural studies: gas-phase electron diffraction [36, 37] and microwave spectroscopy [38].

Complete optimization of thioanisole geometry shows that to the energy minimum corresponds a conformation with φ 85.64 deg ($E_{\text{tot}} -668.3035682 \text{ a.u.}$), where the Hesse matrix possesses only positive eigenvalues. The correction for the zero oscillations energy amounts to 0.1263533 Hartree/particle. The principal maximum is located at the torsional angle φ 0 deg. The Hesse matrix has at this point a single negative eigenvalue (-29.86 cm^{-1}), and the correction for the zero oscillations energy is 0.1264325 Hartree/particle. The barrier separating the planar and nonplanar (close to orthogonal) forms including the corrections for zero oscillations energy amounts to 3.08 kJ mol^{-1} . Hesse matrix for the structure with φ 90 deg has one negative eigenvalue (-30.05 cm^{-1}). The barrier separating two nonplanar forms, at φ 90°, is estimated as purely formal value of 0.02 J mol^{-1} close to the calculation error. At room temperature the barriers to rotation of about 2.5 kJ mol^{-1} correspond to free rotation of fragments [39]. The value we obtained (3.08 kJ mol^{-1}) is close to this figure. If the accounting for the correlation energy is increased to the MP(SDQ) level the barrier to rotation in thioanisole would decrease to 2.2 kJ mol^{-1} [40].

Consequently, the situation in thioanisole is intermediate: free rotation around the bond $C_{sp^2}-S$ or restrained rotation with a low barrier and large amplitude of fragments motion in a potential well with a wide bottom. The molecule corresponds to the type of conformationally nonrigid structures, and the experimental conditions may shift the conformational equilibrium. This reasoning is supported by the results of the gas-phase electron diffraction studies [41]: the apparent conformation of thioanisole was estimated as having φ of 45 ± 10 deg. That means the free rotation around the bond $C_{sp^2}-S$. The calculation of the selenoanisole molecule shows that in the minimum point (φ 90 deg) the Hesse matrix has only positive eigenvalues, and at the maximum point (φ 0 deg) it has one negative value (-34.16 cm^{-1}). Corrections for zero energy oscillations are 0.1254259 and 0.1253892 Hartree/particle respectively. The barrier to rotation including the corrections for the zero oscillations energy is equal to $10.25 \text{ kJ mol}^{-1}$.

It should be noted that the above result does not qualitatively agree with the data on the selenoanisole conformation obtained by gas-phase electron-diffraction. The latter evidenced nonplanar conformation of the molecule but with smaller φ (40 ± 13 deg) [29] providing a possibility of free rotation of fragments around the $C_{sp^2}-\text{Se}$ bond.

As seen from Table 2 the bond angles CXC decrease in the series anisole > thioanisole > selenoanisole, but the bond angles CCX weakly depend on the heteroatom nature. Bond lengths $C_{sp^2}-X$ and $C_{sp^3}-X$ as should be expected grow in the series anisole < thioanisole < selenoanisole. The length of $C_{sp^2}-X$ bond in each molecule is shorter than that of $C_{sp^3}-X$ bond. With growing φ , i.e. at transition from the more strained planar conformation to the less strained orthogonal one the bond angles CXC and CCX get smaller, and bond lengths $C_{sp^2}-X$ and

Table 3. Hybridization degree (s_n , %), energy (E_n , eV), occupancy (P_n , e) and energy of n, π^* -interaction ($E_{n, \pi}$, kJ mol⁻¹) of LEP of O, S and Se atoms in molecules PhXMe

X	Parameter	φ , deg						
		0	15	30	45	60	75	90
O	s_n^1	40.9	40.7	40.2	39.5	38.5	38.8	45.0
	s_n^2	0.0	0.3	1.4	3.1	5.3	5.9	0.0
S	s_n^1	66.0	66.0	66.1	66.2	66.6	67.8	68.0
	s_n^2	0.0	0.1	0.3	0.7	0.9	0.5	0.0
Se	s_n^1	72.6	72.6	72.7	72.9	73.2	73.7	74.1
	s_n^2	0.0	0.1	0.3	0.5	0.6	0.3	0.0
O	E_n^1	-21.42	-21.37	-21.22	-20.99	-20.71	-20.72	-21.89
	E_n^2	-13.03	-13.10	-13.31	-13.66	-14.13	-14.28	-13.17
S	E_n^1	-20.99	-20.98	-20.95	-20.92	-20.94	-21.05	-21.14
	E_n^2	-9.22	-9.24	-9.29	-9.36	-9.40	-9.34	-9.26
Se	E_n^1	-22.12	-22.11	-22.09	-22.07	-22.09	22.18	-22.25
	E_n^2	-8.64	-8.66	-8.70	-8.75	-8.78	-8.74	-8.68
O	P_n^1	1.94076	1.94050	1.93958	1.93745	1.93332	1.92778	1.92321
	P_n^2	1.83212	1.83583	1.84672	1.86419	1.88456	1.90081	1.90926
S	P_n^1	1.95307	1.95305	1.95286	1.95223	1.95119	1.95009	1.94952
	P_n^2	1.84065	1.84460	1.85596	1.87290	1.88963	1.90096	1.90515
Se	P_n^1	1.95916	1.95916	1.95913	1.95882	1.95816	1.95738	1.95688
	P_n^2	1.86078	1.86426	1.87442	1.88937	1.90397	1.91316	1.91631
O	$E_{n, \pi}^1$	0.0	0.0	0.0	4.7	8.8	17.3	30.1
	$E_{n, \pi}^2$	146.9	139.5	118.9	88.4	54.4	25.9	0.0
S	$E_{n, \pi}^1$	0.0	0.0	0.0	2.3	3.9	5.7	6.6
	$E_{n, \pi}^2$	104.0	96.8	77.4	50.3	26.5	7.8	0.0
Se	$E_{n, \pi}^1$	0.0	0.0	0.0	0.0	2.2	3.1	3.6
	$E_{n, \pi}^2$	81.1	75.4	59.6	37.8	18.6	5.0	0.0

C_{sp^3} -X increase. The calculated geometrical parameters are in fair agreement with the results obtained by gas-phase electron diffraction studies [36, 37, 41, 42].

With the use of formalism of NBO method we carried out successive transformation of the initial nonorthogonal sets of canonical MO into natural atomic orbitals (NAO), natural hybrid orbitals (NHO), natural bond orbitals (NBO), and natural localized molecular orbitals (NLMO) [31–33]. These results provide a possibility of interpreting quantum-chemical results (Table 3) in keeping with the classical Lewis representation of molecular structures.

A different hybridization of LEP in the atoms from chalcogen group was established by photoelectron spectroscopy. The highest σ -orbital in all isostructural anisoles is an orbital belonging to one of LEP of heteroatom [1, 3, 4]. In thioanisole and selenoanisole the HOMO is characterized by large contribution from the second LEP originating from n, π -interaction. These orbitals are very dissimilar in energy ($\Delta E >$

2 eV). In anisole the highest σ -orbital and MO with a large contribution from the second LEP of oxygen (third orbital) are less different in energy ($\Delta < 0.5$ eV). The concepts of nonequivalence of orbitals of LEP in atoms O, S, and Se characterized by σ and π -symmetry are widely applied to interpretation of formation mechanism of charge transfer complexes [1–3], of stereoelectronic nature of anomer effect and stereoselective formation of hydrogen bonds [43], to explanation of conformational distortion of n, π -interaction observed in ¹³C NMR spectroscopy [15], of LEP effect on direct coupling constants ¹³C–¹³C and ¹³C–¹H [44, 45] etc.

It was possible with the use of NBO analysis to characterize quantitatively the hybridization of LEP of O, S, and Se atoms. In keeping with the results obtained (Table 3) one LEP (n^1) is a hybrid orbital, and the other (n^2) is a virtually pure p -orbital. The contribution from the s -component in the hybrid LEP n^1 grows in the series O \ll S $<$ Se. It should be

noted that the deformation electron density distribution charts obtained by X-ray diffraction study show relatively uniform electron density distribution in the region of LEP of O and S atoms [43, 46]. This may be due to a fact that theoretical considerations are related to static situation and equilibrium nuclear configuration, and the experiment registers the dynamic pattern of electron density distribution averaged over all possible configurations [47]. Consequently the thermal "erosion" of the deformation electron density may hamper observation of fine difference in the hybridization of LEP in heteroatoms.

The hybrid LEP n^1 with respect to energy is situated a lot deeper than n^2 . The energy of the non-hybridized LEP n^2 grows in the series $O < S < Se$, and energy characteristics of the hybrid LEP n^1 are affected besides the principal quantum number also by hybridization degree. In the planar anisole conformation the E_n^1 value at oxygen atom is slightly deeper than the values E_n^1 at S atom in any thioanisole conformation. The deepest position with respect to energy belongs to E_n^1 at Se atom. The LEP n^2 belonging to O, S, and Se considerably stronger differ in energy. The n^2 orbital of oxygen is notably deeper situated with respect to energy than the n^2 orbitals of S and Se.

The occupancy of n^1 by O, S, and Se atoms is higher than that of n^2 (Table 3), and by O it is significantly more sensitive to conformational changes than by S and Se. The occupancy of LEP n^2 depending on conformation alters in wider range than the occupancy of LEP n^1 . The increase in occupancy of the nonhybridized LEP n^2 at O, S, and Se atoms with transition from planar to orthogonal conformation is due to the distortion of the n, π -conjugation and consequently to the greater localization of LEP on the heteroatom. However the hybrid LEP n^1 are also sensitive to conformation: with growing φ the occupancy decreases. The larger range of changes in P_n^1 for O atom as compared to those of S and Se atoms apparently may be due to higher fraction of p -component in the hybrid orbital of LEP n^1 of oxygen.

We already mentioned that experimental methods provide mainly relative evaluation of n, π -conjugation. The quantitative estimations obtained by measuring the heat evolution at complexing require application of various empirical rules accounting for inductive, hyperconjugation, and steric effects, and numerous other factors [2]. Therefore the most informative way for study of interaction between LEP of heteroatoms and unsaturated fragments on orbital

level consists in theoretical approaches. Analysis of donor-acceptor interaction in the formalism of NBO method is performed by means of perturbation theory. Diagonal elements of NBO Fock matrix are regarded as unperturbed part, and nondiagonal elements as perturbation. Therewith are analyzed all possible interactions between occupied (donor) and unoccupied (acceptor) natural orbitals, and the energy of the interactions is evaluated. The $E_{n,\pi}$ values quantitatively characterize the donor-acceptor interaction of LEP n^1 and n^2 of O, S, and Se with antibonding π^* -orbitals of the aromatic ring, thus the efficiency of n, π -conjugation in anisole, thioanisole, and selenoanisole. In the planar conformation the hybrid LEP n^1 of O, S, and Se virtually do not interact with the π^* -orbitals of the ring whereas the resonance interaction of LEP n^2 is maximal: 146.9 (O), 104.0 (S), and 81.1 (Se) kJ mol^{-1} . With growing torsional angle φ the interaction of n^2 with the π^* -orbitals of the ring sharply decreases, but at similar conformations (save orthogonal) the interaction of LEP n^2 with aromatic ring in anisole molecule is always stronger than in thioanisole and selenoanisole. It is interesting that calculated in the corresponding approximations for the vinyl methyl chalcogenides of the general formula $\text{CH}_2=\text{CHXMe}$ in planar *s-cis*- and *s-trans*-conformations the energy of interaction of nonhybridized LEP of O, S, and Se atoms with the π^* -orbitals of the double bond is always higher: 182 (O), 139 (S) and 109 (Se) kJ mol^{-1} in the *s-cis*-form, and 155 (O), 120 (S) and 95 (Se) kJ mol^{-1} in the *s-trans*-form [48].

In the molecules $\text{CH}\equiv\text{CXMe}$ the nonhybridized LEP interacts with only one of the antibonding π^* -orbitals of the triple bond. The energy of this interaction $132(\text{Se}) < 159(\text{S}) < 192(\text{O}) \text{ kJ mol}^{-1}$ [49] is significantly higher than the energy of the corresponding interaction between LEP of the heteroatoms in question with a double bond and an aromatic ring. In the orthogonal conformation in the isostructural analogs LEP n^2 of the O, S, and Se atoms actually does not interact with the ring by the resonance mode. However in nonplanar conformations (starting with $\varphi \approx 45^\circ$) appears a resonance interaction of hybrid LEP n^1 with the π^* -orbitals of the aromatic ring; therewith the LEP n^1 of oxygen are more efficiently involved into the resonance interaction than those of sulfur and selenium. These distinctions are especially clear in the orthogonal conformation. Thus the oxygen atom to a certain extent conserves the possibility of the resonance interaction with the aromatic ring in the orthogonal conformation ($E_{n,\pi}^2$ 30.1 kJ mol^{-1}), but with S (6.6) and Se (3.6 kJ mol^{-1}) atoms the resonance interaction is

Table 4. Natural charges (q , a.u.) on atoms in molecules PhXMe ($X = O, S, Se$)

φ , deg	qX	qC_i	$\Sigma qC_o/2$	$\Sigma qH_o/2$	$\Sigma qC_m/2$	$\Sigma qH_m/2$	qC_p	qH_p	qC_{Me}	$qH_{Me}/3$
PhOMe										
0	-0.5306	0.3061	-0.2880	0.2427	-0.2298	0.2361	-0.2515	0.2358	-0.3095	0.2092
45	-0.5489	0.2990	-0.2768	0.2430	-0.2306	0.2366	-0.2466	0.2362	-0.3037	0.2065
90	-0.5656	0.2896	-0.2675	0.2449	-0.2321	0.2372	-0.2403	0.2368	-0.2965	0.2037
PhSMe										
0	0.3038	-0.2060	-0.2483	0.2377	-0.2259	0.2376	-0.2420	0.2368	-0.8395	0.2483
45	0.2742	-0.2109	-0.2395	0.2411	-0.2257	0.2378	-0.2367	0.2374	-0.8266	0.2447
90	0.2507	-0.2171	-0.2324	0.2460	-0.2270	0.2391	-0.2310	0.2379	-0.8183	0.2421
PhSeMe										
0	0.3734	-0.2431	-0.2477	0.2371	-0.2257	0.2379	-0.2403	0.2370	-0.8838	0.2513
45	0.3461	-0.2492	-0.2405	0.2416	-0.2258	0.2386	-0.2355	0.2375	-0.8704	0.2479
90	0.3262	-0.2571	-0.2345	0.2469	-0.2267	0.2392	-0.2307	0.2379	-0.8626	0.2456

Table 5. Charge difference (Δq , a.u.) on the atoms of aromatic ring in molecules PhXMe ($X = O, S, Se$) and in unsubstituted benzene: $\Delta q = q(\text{PhXMe}) - q(\text{C}_6\text{H}_6)$

φ , deg	qC_i	$\Sigma qC_o/2$	$\Sigma qH_o/2$	$\Sigma qC_m/2$	$\Sigma qH_m/2$	qC_p	qH_p
PhOMe							
0	0.5411	-0.0530	0.0078	0.0053	0.0011	-0.0165	0.0008
45	0.5340	-0.0418	0.0080	0.0045	0.0016	-0.0116	0.0012
90	0.5246	-0.0325	0.0099	0.0029	0.0022	-0.0053	0.0018
PhSMe							
0	0.0290	-0.0133	0.0027	0.0091	0.0026	-0.0070	0.0018
45	0.0241	-0.0045	0.0061	0.0093	0.0028	-0.0017	0.0024
90	0.0179	-0.0026	0.0110	0.0080	0.0041	0.0040	0.0029
PhSeMe							
0	-0.0081	-0.0127	0.0021	0.0093	0.0029	-0.0053	0.0020
45	-0.0142	-0.0055	0.0066	0.0092	0.0036	-0.0005	0.0025
90	-0.0221	0.0005	0.0119	0.0083	0.0042	0.0043	0.0029

negligible. This statement is experimentally supported by the analysis of ^{13}C NMR spectra of compounds PhXBu-*t* that exist in the orthogonal or similar conformation [14, 15]. In the molecules of PhSBu-*t* and PhSeBu-*t* the shielding of the carbons in the *para*-position (128.1 ppm) is sufficiently close to that of carbon atoms in the unsubstituted benzene (128.5 ppm [50]) whereas in the PhOBu-*t* molecule the $^{13}\text{C}_p$ atom is significantly more shielded (122 ppm). The NBO-analysis indicates the existence of donor-acceptor interaction between LEP n^2 of O, S, and Se atoms

and antibonding π^* -orbitals of the C-H bonds in the methyl groups. They are estimated at about 29(O), 25 (S), and 17 (Se) kJ mol^{-1} and weakly depend on the molecular conformation.

Natural atomic orbitals (NAO) form an orthogonal set of AO encompassing the space of non-orthogonal basis functions. Natural occupancies obtained proceeding from NAO are always positive, and their sum is exactly equal to the number of electrons in the molecule. Therefore the natural charges

derived from the natural occupancies give better description of the electron density distribution in the molecule than the traditional Mulliken analysis [51]. Proceeding from the value of charges on atoms (Table 4) it is apparently possible to determine the direction of the bond moment. In anisole because of the higher electronegativity of oxygen compared to carbon the bond moment of $C_i \rightarrow O$ is directed to O atom, and on the C_i atom a deficit of electron density is observed, and on the O atom is present a high excess electron charge. In thioanisole and selenoanisole the bond moment $C_i \leftarrow X$ is directed to C_i atom, and on the latter is excess of electron density, and on atoms S and Se is deficit of electron density. Independent of conformation the bond moments in anisole of $C_i \rightarrow C_o$ and $C_m \rightarrow C_o$ are directed to ortho-carbons, and the bond moments of $C_m \rightarrow C_p$ are directed to para-carbon. A similar scheme of bond polarity can be deduced from the chemical shifts values in the ^{13}C NMR spectrum (δC_i 159.9, δC_o 114.0, δC_m 129.5, δC_p 120.6 ppm) [14, 15]. In all conformations of thioanisole the direction of bond moments in the aromatic ring coincides with that in anisole and with the results of ^{13}C NMR spectroscopy (δC_i 138.6, δC_o 126.1, δC_m 128.6, δC_p 124.5 ppm) [14, 15].

However the difference in charges on the atoms $C_i \rightarrow C_o$, $C_m \rightarrow C_o$ and $C_m \rightarrow C_p$ is smaller than in anisole. In selenoanisole in the conformations with φ 45 and 90 deg the bond moment of $C_i \leftarrow C_o$ is directed to C_i , the moment of bond $C_m \rightarrow C_o$ is directed to C_o , and bond moment of $C_m \rightarrow C_p$ to C_p . The signals in the ^{13}C NMR spectrum are located at δC_i 131.9, δC_o 128.7, δC_m 129.9, δC_p 125.6 ppm [15]. The moment of the bond $O \leftarrow C_{\text{Me}}$ is directed to oxygen, and the moments of bonds $S \rightarrow C_{\text{Me}}$ and $\text{Se} \rightarrow C_{\text{Me}}$ are directed to C_{Me} . The charge on C_{Me} atom increases in the series anisole < thioanisole < selenoanisole, and in the same order grows the shielding of C_{Me} (δ_{C} , ppm): 54.5(O) < 15.5(S) < 6.7 (Se) [14, 15]. The bonds $C_{\text{Me}} \leftarrow \text{H}$ in all the molecules in question are polarized in direction of C_{Me} . Note the large electron charge on the C_{Me} atoms in thioanisole and selenoanisole, and consequently a great charge difference between S or Se atoms and C_{Me} (1.1–1.3 a.u.), and also between C_{Me} and H (~1.1 a.u.). In anisole the charge difference between O and C_{Me} atoms (0.2–0.3 a.u.) and between C_{Me} and H (0.50–0.52 a.u.) is considerably smaller.

The effect of OMe, SMe, and SeMe groups on the electron density distribution in the aromatic moiety can be conveniently discussed comparing the difference in charge values on atoms in the molecules

in question and on the atoms in an unsubstituted benzene: $\Delta q = q(\text{PhXMe}_3) - q(\text{C}_6\text{H}_6)$ (Table 5). The quantum-chemical calculation of a molecule of unsubstituted benzene in MP2(f)/6–31G (d) approximation with subsequent NBO-analysis of the wave function shows that natural charges on every carbon in this molecule are equal to –0.2350 a.u., and on hydrogen atoms respectively 0.2350 a.u. The increase in the negative value Δq (or decrease in the positive value Δq) corresponds to the greater electron charge on the respective atom (C or H) compared to that in the unsubstituted benzene. In anisole the values $\Delta q C_i$ (0.52–0.54 a.u.) evidence a strong acceptor effect of OMe group on atoms C_i . In thioanisole and selenoanisole on C_i atoms exists an excess of electron density ($\Delta q C_i$ –0.01...–0.03 a.u.). In the planar anisole molecule the situation for interaction between LEP n^2 of oxygen with π^* -orbitals of the ring is the most favorable, therefore the values of Δq on C_o and C_p are the most negative. This is also reflected in the δC_o and δC_p values in the ^{13}C NMR spectrum (see above). In the orthogonal conformation of anisole the electron-donor effect of the OMe group is still transferred to the *ortho*- and *para*-positions of the ring as a result of the resonance interaction between the hybrid LEP n^1 and π^* -orbitals of the ring, as has been shown above. The donor effect of SMe group to the *ortho*- and *para*- positions of the aromatic ring is transferred only in close to planar conformations ($\varphi \approx 0$ –45 deg).

According to the potential function of internal rotation we constructed and to the results of electron diffraction studies [41] in the thioanisole molecule in the gas phase occurred free rotation around the C_{sp}^2 -S bond. Taking into account the difference in values between δC_o and δC_p in this molecule and δC in the unsubstituted benzene it is presumable that in solution the equilibrium is apparently shifted to the nearly planar conformations. The comparison of $\Delta q C_o$ values with the shielding of $^{13}\text{C}_o$ nuclei evidences that the selenoanisole exists in the orthogonal conformation, but the shielding of the $^{13}\text{C}_p$ nuclei is stronger than that of ^{13}C nuclei in the unsubstituted benzene. We cannot explain these distinctions. In the orthogonal conformation the SMe and SeMe groups produce on C_o and C_p an acceptor effect. The groups OMe, SMe, and SeMe exert an acceptor effect on the C_m and hydrogen atoms of the aromatic ring.

Thus the intramolecular interactions and electron density distribution in anisole, thioanisole, and selenoanisole depend on the electronegativity of heteroatoms and of conjugation between LEP of O, S, and

Se atoms with the π -system of the aromatic ring. The latter is significantly influenced by the conformation of the molecule. The research performed permitted obtaining on a common level of theoretical calculations quantitative characteristics of n,π -interaction between LEP of O, S, and Se atoms and antibonding π^* -orbitals of the aromatic moiety at varying molecular conformations, estimating the hybridization extent, orbital energies and occupancy of the LEP of heteroatoms, and also provided information on electronic effect of OMe, SMe, and SeMe groups and on the distribution of electron density in the molecules.

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