CYCLIC ARYLENEAZACHALCOGENS: SYNTHESIS, VIBRATIONAL SPECTRA, AND π-ELECTRON STRUCTURES

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It is shown that a convenient general method for the synthesis of benzo-2,1,3-thiadiazole, its Se analog, their 4,5,6,7-tetrafluoro derivatives, and naphtho[1,8-c,d][1.2.6]thiadiazine is the reaction of the corresponding arylenediamines with chalcogen tetrahalides. A complete interpretation of the vibrational spectra of the synthesized compounds was obtained using the experimental shifts of the bands caused by the introduction of the ^{15}N *and* ^{77}Se *isotopes into the compositions of the molecules and calculations of the frequencies and forms of the normal vibrations within the stretching-force field approximation. The peculiarities of the π-electron structures of the molecules of these substances were established by means of an analysis of the force constants of the CC, CN, NS, and NSe bonds and quantum-chemical calculations by the MNDO method: 1) The group π orbitals of the NXN fragments (X = S, Se) interact effectively with the group π orbitals of the carbocycles; 2) the p AO of nitrogen and sulfur make the principal contribution to the π MO of different symmetries (*a_2 *and* b_1*, respectively), as a consequence of which their π overlapping with one another is small, and the chemical bond within the limits of the NSN group is best described in the form of* $(-\overset{-}{N}-\overset{+}{S}=N-)\longleftrightarrow(-N=\overset{+}{S}-\overset{-}{N}-)$; *resonance; the same is also valid for the NSeN group; 3) on the whole, the π MO display a tendency for localization in individual molecular fragments. All of these factors decrease the aromatic character of the molecules.*

According to [1-4], a paradoxical combination of aromatic and antiaromatic properties is characteristic of naphtho[1,8-c,-d:c',d']bis[1.2.6]thiadiazine (I) and its Se analog II. It is impossible to theoretically evaluate the aromatic character or antiaromatic character of these molecules from the sign and value of the Dewar resonance energy (DRE) [5]; however, the paradox is most likely an apparent one due to the imperfection of the criteria used in [1-4] – indirect spectroscopic data, for the interpretation of which, in particular, the physically inadequate [6] model of ring currents has been invoked. On the basis of a study of the electron structures of I and II by the methods of theoretical and experimental quantum chemistry it has been concluded that these compounds are nonaromatic substances that have a quinoid structure and that the reason for such a pronounced transformation of the π system of naphthalene is effective intramolecular interaction with the NXN groups (X = S, Se) [7, 8]. However, according to the data in [7, 8], the 3p AO of sulfur participate in the π MO of I, which contradicts the conclusion regarding the quinoid structure of its molecules drawn in the same studies. Thus, the π-electron structures of the molecules of I and II remain unclear.

In the present research, by means of quantum-chemical calculations by the MNDO method and vibrational (IR, Raman) spectroscopy we studied the π-electron structures of molecules of simpler compounds containing only one NXN fragment attached to a benzene or naphthalene ring – benzo-2,1,3-thiadiazole (III), its Se analog (IV), their 4,5,6,7-tetrafluoro derivatives (V and VI, respectively), and naphtho[1,8-c,d][1.2.6]thiadiazine (VII).

A convenient general method for the synthesis of III-VII is the reaction of the corresponding arylenediamines with chalcogen tetrahalides SF_4 (III, V, and VII) and $SeCl_4$ (IV and VI). In the presence of hydrogen halide acceptors (NaF for HF, pyridine for HCl) the reactions proceed rapidly and give the products in high yields. In the case of IV and VI this method makes it possible to readily introduce selenium isotopes (^{77}Se in the present research) into the composition of the molecule starting from elementary selenium, which by the action of chlorine is converted quantitatively to $SeCl_4$; this is also a merit of the synthesis.

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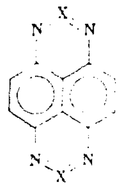
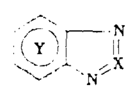
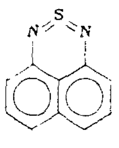

I-II


III-VI


VII

I, III, V X=S, II, IV, VI X=Se; III, IV Y=H, V, VI Y=F

Naptho[1,8-c,d][1.2.6]selenadiazine (VIII) and benzo-2,1,3-telluradiazole (IX) could not be synthesized via this method. The reaction of $SeCl_4$ with 1,8-naphthalenediamine (X) or of $TeCl_4$ with o-phenylenediamine under conditions similar to the conditions used to obtain IV and VI leads to unidentified, nonhomogeneous, dark products that are insoluble in the usual organic solvents, nonvolatile in vacuo, and unmeltable on heating to 200°C. This evidently constitutes evidence not so much regarding the limited possibilities of the synthetic approach used as it does regarding the inability of VIII and IX to exist under ordinary conditions. Although it has been previously reported [9] that VIII was obtained from X and SeO_2, the synthesis could not be reproduced [3]. 1H,3H-Naphtho[1,8-c,d][1.2.6]selenadiazine 2-oxide, attempts at the dehydration of which by several methods were unsuccessful, rather than VIII is also formed in the reaction of X with $SeOCl_2$ [3].

The complete absence of data on the corresponding acyclic compounds prevents calculation of the DRE of III-VII, and we therefore selected a method that uses the most important peculiarity of aromatic molecules, viz., the delocalized π MO, in which all of the ring atoms participate [5]. For III, V, and VII the MO were calculated by the MNDO method (see Table 1 and Fig. 1). A natural criterion of the quality of the calculations with respect to the structure of the MO is a comparison of the theoretical and experimental x-ray emission spectra of the molecules. The SK_β spectra have been measured for III and V [10], while experimental data are absent for VII. A comparison of the theoretical and experimental SK_β spectra of III and V reveals good correspondence (Fig. 1). Thus, the MNDO calculations adequately convey the structure of the MO of the compounds under consideration.

A comparison of the π MO of III, V, and VII with the π MO of benzene, 1,2,3,4-tetrafluorobenzene, naphthalene, and the hypothetical cis,cis-1,3-diaza-2-thiaallene (XI), which were also calculated by the MNDO method, provides evidence regarding the effective interaction of the group π orbitals of carbocycles with the group π orbitals of the NSN fragment, which leads to a significant change in the form and energy of the orbitals. For example, in III the energy splitting between the $2a_2$ and $1a_2$ MO (Table 1), which can be regarded, respectively, as the antibonding and bonding combinations of the highest occupied molecular orbital (HOMO) of XI (the nonbonding combination of the $2p_\pi$ AO of nitrogen) with the group orbital of the carbocycle, which correlates with the $1e_{1g}S$ MO of benzene, is 2.55 eV. In V, the $4a_2$ and $3a_2$ MO (Table 1), the splitting between which is 2.70 eV, correspond to these MO.

In the molecules of III, V, and VII the p AO of nitrogen and sulfur make contributions to different π MO: the 2p AO of nitrogen contributes primarily to the MO with a_2 symmetry, while the 3p AO of sulfur contributes only to the MO with b_1 symmetry. This is evidently due in part to the topology of the molecules (compare, for example, with the structure of the π MO of the cyclopentadienyl cation [11]) and reflects in part the specific characteristics of these compounds. Thus, in III, the 3p AO of sulfur participates in the $3b_1$ and $2b_1$ π MO (48 and 18%, respectively; see Fig. 1), to which the 2p AO of nitrogen virtually do not contribute. In turn, the 2p AO of nitrogen contribute to the $2a_2$ and $1a_2$ MO (10 and 29%, respectively, from each atom), in which the 3p AO of sulfur does not participate. The 3p AO of sulfur and the 2p AO of nitrogen enter only into the lowest-lying $1b_1$ π MO simultaneously with a contribution of 18% from each atom. Similarly, in V the 3p AO of sulfur contributes to the $5b_1$ and $4b_1$ π MO (40 and 21%, respectively; see Fig. 1), in which the 2p AO of nitrogen do not participate, while the 2p AO of nitrogen contribute to the $4a_2$ and $3a_2$ π MO (7 and 30%, respectively, from each atom), in which the 3p AO of sulfur does not participate. The p AO of nitrogen and sulfur participate simultaneously only in the low-lying $3b_1$ π MO with contributions, as in III, of 18% from each atom. In VII the 3p AO of sulfur makes a contribution to the $3b_1$ and $2b_1$ π MO (28 and 34%, respectively), in which a contribution of the 2p AO of nitrogen is absent, while the 2p AO of nitrogen contribute to the $3a_2$, $2a_2$, and $1a_2$ π MO (7, 9, and 23%, respectively, from each atom), in which a contribution of the 3p AO of sulfur is absent. The 3p AO of sulfur (20%) and the 2p AO of nitrogen (18% from each atom) participate simultaneously only in the lowest-lying $1b_1$ π MO. Thus, despite the participation of the p AO of nitrogen and sulfur in the formation of the united π system of the molecule, a π bond between them is virtually absent. In other words, the order of the NS bonds is only slightly greater than unity.

This is in agreement with the data on the geometry of the III molecule [12], viz., the NS distance (1.63 Å) significantly exceeds the standard length of the sulfur–nitrogen double bond (1.52 Å). It follows from a comparison of the results of the MNDO calculations with the data in [12] that it is incorrect to use the greater length of the NS bond as an argument in favor of a quinoid structure for III.

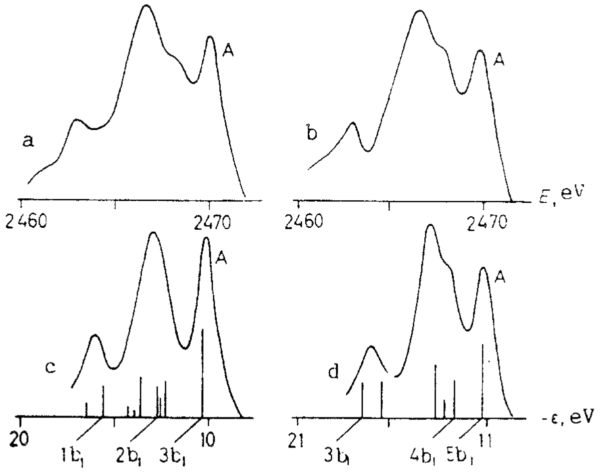


Fig. 1. Experimental (a, b) and theoretical (c, d) SK_β spectra of III (a, c) and V (b, d). The theoretical spectra on the scale of the MO energies were synthesized with a computer from the results of MNDO calculations by the method in [28]. The position of the π MO with b_1 symmetry is indicated. The transitions from the π MO with a_2 symmetry of the two compounds, as well as from the π MO of V with $2b_1$ and $1b_1$ symmetries, which do not contain contributions of the 3p AO of sulfur, do not appear in the spectra. The individual transitions were approximated by Lorentzian lines with a width of 1 eV at half the height; their relative intensities, which are proportional to the contributions of the 3p AO of sulfur to the corresponding MO, are represented by the vertical segments. The experimental spectra on the scale of the transition energies were taken from [10]. The spectra were superimposed with respect to the position of maximum A.

TABLE 1. Localization of the π MO of III, V, and VII in the Molecular Fragments according to the Results of MNDO Calculations

Compound	π-MO	$-\varepsilon$,* eV	Localization	
			atoms i**	$\sum_i c_i^2 \cdot 100$
III	$2a_2$***	9,74	C_4—C_7	80
	$3b_1$	10,08	S_2	48
	$1a_2$	12,29	N_1, N_3, C_{3a}, C_{7a}	84
	$2b_1$	12,46	C_4—C_7	76
	$1b_1$	15,62	N_1, S_2, N_3, C_{3a}, C_{7a}	90
V	$4a_2$***	10,51	C_4—C_7, F_4—F_7	86
	$5b_1$	11,08	S_2	40
	$4b_1$	12,69	Delocalized	—
	$3a_2$	13,21	N_1, N_2, C_{3a}, C_{7a}	88
	$3b_1$	16,35	N_1, S_2, N_3, C_{3a}, C_{7a}	80
	$2a_2$	16,99	F_4—F_7	94
	$2b_1$	17,28	F_4—F_7	78
	$1a_2$	17,84	F_4—F_7	78
	$1b_1$	18,68	C_4—C_7, C_{3a}, C_{7a}, F_4—F_7	100
VII	$3a_2$***	7,03	N_1, N_3, C_4, C_6, C_7, C_9	92
	$4b_1$	10,09	C_4, C_5, C_{6a}, C_8, C_9, C_{9b}	96
	$3b_1$	10,18	S_2, C_{3a}, C_6, C_{6a}, C_7, C_{9a}, C_{9b}	89
	$2a_2$	10,89	N_1, N_3, C_4—C_9	100
	$2b_1$	12,92	Delocalized	—
	$1a_2$	13,39	N_1, N_3, C_{3a}, C_4, C_9, C_{9a}	94
	$1b_1$	15,58	N_1, S_2, N_3, C_{3a}, C_{9a}, C_{9b}	91

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*The energy of the MO with the opposite sign.

**The index of the F atom coincides with the index of the C atom to which it is bonded.

***The highest occupied molecular orbital (HOMO).

TABLE 2. Frequencies of the Vibrations (ν, cm^{-1}) of III-VI and Their Changes ($\Delta\nu$, cm^{-1}) when the ^{15}N and ^{77}Se Isotopes are Introduced into the Compositions of the Molecules*

Compound	IR spectrum		Raman spectrum		ν calc	$\Delta\nu$ calc 15	Contribution to the potential energy,** %
	ν exp	$\Delta\nu$ ^{15}N ($\Delta\nu$ ^{77}Se)	ν exp	$\Delta\nu$ ^{15}N			
1	2	3	4	5	6	7	8
III					1601	1	61Q, 18α, 13CN
	1528 s	1	1532 m	2	1589	1	73Q, 9γ
	1521 s	1			1530	2	41Q, 33β, 23CN
	1479 s	1	1485 w	2			
	1434 w		1438 s	1	1431	1	59β, 30Q
			1410 vw				
	1363 w	1	1365 s	1	1357	2	37 β, 34Q, 26CN
	1332 m	3	1319 vw		1344	4	34CN, 33β, 15Q, 13α
	1274 m	4	1275 w	4	1266	1	64β, 14Q, 10γ
	1231 w	1	1233 vw		1227	1	86Q, 10γ, 9β
	1140 m	1	1142 m		1150		69β, 29Q
	1132 s	1	1137 m		1105	1	44Q, 34β, 11γ
			1070 vw				
	988 w		992 m	2	1003		82Q, 10β
	951 w		957 vw				
	919 m	5	923 vw	6	926	8	78NS$_{as}$, 12β
			898 vw				
	850 vs	5	857 m	8	872	4	54α, 23NS$_{as}$, 16β
	836 m	2	848 vw	4			
	814 s	10	819 vs	11	850	13	81NS$_{s}$, 10γ
	782 w						
	762 s				762	4	57Q, 23CN, 10α
	747 vs						
	657 w		656 m	1			
	588 w	1	590 m	3	595	2	57α, 20Q, 14β
	529 m	5			529	4	43α, 30γ, 11CN, 9Q
	500 vw		504 s				
	426 w						
	417 s						
	391 m	1			365		51γ, 16Q, 14CN, 12NS
					351		57γ, 13Q, 12α, 11NS
IV	1612 w				1609	1	59Q, 16CN, 10α
					1581		77Q
	1508 s	1			1505	2	39Q, 38β, 20CN
	1494 sh						
	1476 m	4					
	1439 w				1430		59β, 32Q
	1356 w	4			1340	3	32β, 32Q, 33CN
	1351 w				1329	4	39β, 28CN, 17Q, 11α
	1292 s	4			1254	1	63β, 15Q
	1221 m	2			1226		88Q
	1143 m				1149		69β, 30Q
	1134 s	1			1095	2	47Q, 31β, 10α, 10γ
					1005		79Q, 10β
	974 w						
	950 w						
	900 w				875	3	49α, 20CN, 14β, 10NSe
	854 vw	3					
	800 w	6			858	9	58NSe$_{as}$, 29Q, 9γ
	758 vs						
	750 vs	4			738	5	34Q, 21NSe, 18CN ,15α
	744 vs						
	711 m	12 (1,6)			732	10	71NSe$_{s}$, 15γ
	597 m	2			563	3	52α, 14γ, 13β, 10CN
	556 w	2			523	4	46α, 29γ, 12CN
	489 w	2					
	390 m	1					
	386 vs	3					
	351 m	(1)					
					328		49γ, 24NSe
					221		82γ

TABLE 2 (continued)

1	2	3	4	5	6	7	8
V	1677 m	1			1682	1	72Q, 11β
	1653 m				1646		74Q, 9β
	1613 w						
	1588 w		1597 m				
	1530 vs	2	1538 m		1519	1	47Q, 29q, 9CN
	1508 m	3			1506		48Q, 26q, 10CN, 9β
	1490 vs				1488	3	38Q, 30q, 30CN
	1469 m	5					
	1437 vw						
	1368 vs	4	1359 s				
	1353 s				1337		94Q
	1310	3	1316 w		1327	3	39q, 24CN, 19α, 11β
	1199 w	2			1147	3	58q, 22CN
	1082 w				1124	2	67q, 15CN
	1052 w		1050 w				
	1032 vs	3					
	1016 vs	3			976	4	30q, 21CN, 17β, 15Q
	970 vw						
	942 w				956	2	47q, 16β, 14Q, 11γ
	881 m	6			910	8	62NS$_{as}$, 17β, 15γ
	838 m	12	842 s		824	10	78NS$_{s}$
	781 m		748 vw		741	1	55β, 21NS, 14γ
	728 w	4					
			644 vw				
	611 vw						
			571 vw		586	2	34α, 23β, 20q, 13CN
	510 m	4	507 s		547	4	51Q, 24q, 12γ
	447 w		456 m		430	1	40α, 31β, 17γ
	401 vw		412 m		410	2	45α, 28β, 18γ
	367 w				342		47β, 20Q, 12γ
					307		76β, 15Q
					290		94β
					265	1	58γ, 16β, 12Q
					198	1	56γ, 16Q, 13β
VI	1677 s				1678		72Q, 11β
	1642 m				1641		74Q, 12β
	1593 s						
	1522 vs	4			1511		45Q, 38q, 11β
	1478 vs				1502	1	48Q, 27q, 10CN, 10β
	1461 s	2			1444	3	42Q, 36CN
	1401 w						
	1378 vs						
	1352 vs				1328		94Q
	1329 s	7			1325		38q, 25CN, 19α, 13β
	1204 w	3					
	1134 vw				1145	2	58q, 23CN
	1104 vw				1128	2	67q, 16CN
	1072 w	2					
	1035 vs	2			973	3	32q, 26CN, 21β, 15Q
	1016 vs	1			956	2	50q, 20β, 15Q
	829 w	3 (0,4)			852	6	42NSe$_{as}$, 38β, 20γ
	757 s	11 (0,4)			786	12	82NSe$_{s}$, 9γ
	689 vs	6 (0,8)			707	5	44NSe$_{as}$, 39β
	668 w						
	637 m	4					
	588 w	6 (2)			586	2	36α, 25β, 26Q
	463 m	2			453	3	53Q, 26q, 10CN, 10γ
	442 m	1			427		43α, 35β, 11γ
	356 vw				409	2	55β, 30Q, 15γ
	347 s	1			338		54β, 34Q
	262 w				306		77β, 15Q
					290		95β
					205	1	59γ, 15β, 10NSe, 9Q
					175		34β, 23γ, 15Q, 10NSe

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*The experimental data are presented for the IR and Raman spectra.

**Symbols: Q, q, the CC and CH (CF) stretching vibrations; α, β, the $\widehat{CCC}$ and $\widehat{CCH}$ ($\widehat{CCF}$) deformation vibrations; CN, stretching vibrations of the CN bonds; NS (NSe), stretching vibrations of the NS (NSe) bonds; s, the symmetrical, as are the asymmetrical, and γ, the deformation in-plane vibrations of the five-membered ring.

TABLE 3. Stretching Force Constants of the Bonds in III-VI ($\cdot 10^6$, cm^{-2})

Compound	$K_{C_5C_6}$	$K_{C_6C_7}$	$K_{C_{7a}C_7}$	$K_{C_{7a}C_{3a}}$	K_{CN}	$K_{NS(NSe)}$
III	10,11	11,97	10,50	10,50	9,02	6,45
IV	10,11	11,97	10,50	10,50	8,37	6,37
V	11,08	11,28	11,09	11,03	8,20	6,10
VI	11,08	11,28	11,09	11,03	8,19	6,04

An important peculiarity of the π MO of III, V, and VII is the tendency for localization in the individual molecular fragments (Table 1); a consequence of this should be weakening of the aromatic character and, within the limit, conversion of the molecules to nonaromatic (but not antiaromatic) molecules. In III, of the five occupied π MO, not one is delocalized over all of the centers possible for it (taking symmetry into account); in V and VII, of the nine and seven occupied π MO, respectively, only one is delocalized over the entire molecule (Table 1). In each compound there are π MO that are almost completely localized in the ring that includes an NSN fragment: $1b_1$ in III and VII, and $3b_1$ in V. The $2a_2$, $2b_1$, and $1a_2$ π MO of V are made up primarily from the 2p AO of fluorine.

In III, the NSN group is a π acceptor, and its effective charge q(NSN) = –0.10 e [q(S) = 0.48 e, q(N) = –0.29 e], including the π charge q_π(NSN) = –0.06 e. The transition from the benzene carbocycle to the naphthalene carbocycle is accompanied by an important change in the distribution of the π-electron density, and in VII the NSN group becomes a π donor while remaining a σ acceptor with q(NSN) = –0.04 e [q(S) = 0.66 e, q(N) = –0.35 e] and q_π(NSN) = 0.10 e. In V, the NSN group is also a π donor with q(NSN) = 0.04 e [q(S) = 0.54 e, q(N) = –0.25 e] and q_π(NSN) = 0.12 e. The large effective charges of the nitrogen and sulfur atoms in conjunction with the low order of the bond between them make it possible to conclude that the chemical bond within the limits of the azathiene fragment of III, V, and VII is best described in the $(-\overset{-}{N}-\overset{+}{S}=N-)\leftrightarrow(-N=\overset{+}{S}-\overset{-}{N}-)$ form.

Calculations by the MNDO method are not possible for IV and VI because of the lack of parameters for selenium. In this connection, the intramolecular interaction of the NSeN group with the carbocycle in these compounds was studied from the changes in the force constants of the CC bonds (K_{CC}) as compared with model arenes, viz., benzene for IV and 1,2,3,4-tetrafluorobenzene for VI. An analysis of the force constants of the CN (K_{CN}) and NSe (K_{NSe}) bonds makes it possible to draw some conclusions regarding the π-electron structure of the five-membered ring of these compounds. To establish a correlation with the MNDO data we also examined the force constants of II and V.

The experimental frequencies of vibrations of III-VI in the IR and Raman spectra and their changes when the ^{15}N (III-VI, the 1 position) and ^{77}Se (IV and VI) isotopes were introduced into the compositions of the molecules were studied in conjunction with the results of calculations of the frequencies and forms of the in-plane normal vibrations within the stretching-force field approximation (the spectra of III and IV were previously known [13]) (see Table 2), as well as the stretching force constants of these compounds (see Table 3). It follows from Table 2 that the correlation between the calculated and experimental values is good and makes it possible to give a complete interpretation of the vibrational spectra of III-VI. The small deviations below 1000 cm^{-1} are evidently associated with neglecting the out-of-plane vibrations that appear in this spectral region in the calculations. The shifts of the bands by the ^{15}N isotope are sufficiently large for a reliable experimental assignment of the vibrations with the participation of nitrogen. In contrast to this, the shifts of the bands by the ^{77}Se isotope are small and cannot always be used for diagnostic purposes.

A comparison of the K_{CC} force constants of III (Table 3) and benzene (11.10·10^6 cm^{-2} [14]) indicates their increase for the C_4C_5 and C_6C_7 bonds and decrease for the C_5C_6, C_7C_{7a}, and $C_{3a}C_{7a}$ bonds. The K_{CN} value provides evidence for the multiple character of the CN bonds. The K_{NS} force constant is relatively small (Table 3). For example, in the acyclic compound 1,3-bis(trimethylsilyl)-1,3-diaza-2-thiaallene, which contains an –N=S=N– group, the K_{NS} value is greater by a factor of more than two (13.76·10^6 cm^{-2}) [15]. If it is postulated that the order of the NS bond in the latter is approximately two, in III the order of the NS bond, starting from these data, can be evaluated as being close to unity, which corresponds to the results of the MNDO calculations.

In the case of V, the K_{CC} values are less changed as compared with the K_{CC} values of 1,2,3,4-tetrafluorobenzene ((11.14, 11.14, 11.11, 11.01)·10^6 cm^{-2} for the C_1C_2, C_2C_3, C_4C_5, and C_5C_6 bonds, respectively [16]) than the K_{CC} values for III as compared with the K_{CC} values of benzene. The K_{CN} and K_{NS} force constants decrease somewhat on passing from III to V (Table 3).

The K_{CC} values of IV do not differ from those for III. The K_{CN} force constant of IV is appreciably smaller than the K_{CN} value of III, while the K_{NSe} value is extremely close to the K_{NS} value of the thia analog (Table 3).

The K_{CC} and K_{CN} force constants of VI do not differ from the force constants of V; however, the K_{NSe} value is somewhat smaller than the K_{NS} value (Table 3).

The ν(NX) (X = S, Se) vibrational frequencies decrease substantially on passing from III to IV and from V to VI (Table 2).

Thus, if one judges from the K_{CC} values, replacement of the sulfur atoms by selenium atoms does not affect the intramolecular interaction of the NXN groups with the carbocycle in III-VI. In the III-IV and V-VI pairs the transition from the thia derivatives to the Se analogs gives rise to only a small decrease in the K_{NX} force constants. The complete replacement of the hydrogen atoms in III and IV by fluorine atoms is accompanied by a much greater decrease in the K_{NS} and K_{NSe} force constants.

The results obtained make it possible to assume that the structure of the nitrogen–chalcogen bond does not change substantially on passing from III to IV and from V to VI and that the observed decrease in the ν(NX) frequencies is similar to the isotopic shift, i.e., it is associated primarily with an increase in the mass of X.* The latter is possible only under the condition that the π overlapping of the 2p AO of nitrogen with the 3p AO of sulfur in the III and V molecules is so small that the transition to the 4p AO of selenium (very unfavorable from the point of view of the effectiveness of overlapping) has virtually no effect on it. Precisely this circumstance was noted above as a peculiarity of the π-electron structure of the azathiene fragment of III and V according to the results of the MNDO calculations. Thus, the results of vibrational spectroscopy and the quantum-chemical calculations are mutually confirmed in this respect. All of the information set forth above makes it possible to conclude that the results (for example, MNDO calculations) obtained for thia analogs III and V, respectively, can be used for the description (qualitative, in any case) of the electron structures of IV and VI.

A comparison of the data on the interaction of the NXN groups with the benzene and naphthalene carbocycles and the structures of the nitrogen–chalcogen bonds obtained for I and II in [7, 8] and III-VII in the present research shows that there are no fundamental differences between them. In all I-VII, the group NXN π orbitals interact effectively with the group π orbitals of the carbocycles; the π overlapping of the p AO of nitrogen with the p AO of the chalcogen is small, while the π overlapping with the p AO of carbon is great; replacement of sulfur by selenium does not give rise to substantial changes in the π-electron structures of the molecules. Consequently, it may be assumed that, like III-VII, I and II are not quinoid structures but rather aromatic structures (with weakened aromatic character) and that their π systems have the same peculiarity as the π systems of III-VII, viz., the p AO of nitrogen and the chalcogen participate in different π MO.

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EXPERIMENTAL

The IR absorption spectra of KBr pellets of the compounds (4:800 for III, IV, and VI and 2:800 for V) were recorded with Specord M-80 and Perkin–Elmer 325 spectrometers. The Raman spectra were obtained with a Coderg PH-1 spectrometer with a helium–neon laser (λ_{exc} 6328 Å). The UV spectra were obtained with a Beckman DU-8 spectrophotometer. The ^{19}F NMR spectra were obtained with a Varian A56/60A spectrometer (56.4 MHz, C_6F_6 as the internal standard). The ^{15}N and ^{77}Se NMR spectra were obtained with a Bruker CXP-300 pulse spectrometer [30.40 and 57.23 MHz, respectively, NH_3 and $Se(CH_3)_2$ as the external standards]; a relaxant, viz., chromium acetylacetonate, was added to the solutions. The mass spectra were obtained with a Finnigan MAT MS-8200 spectrometer (70 eV). The x-ray electron (XRE) spectra were obtained with a Vacuum Generators ESCA-3 spectrometer (Al Kα 1486.6 eV) with calibration with respect to the C_{1s} line of carbon black (285.0 eV); the samples were applied to a nickel support.

The calculations of the frequencies and forms of the normal vibrations within the stretching-force field approximation were made from the programs in [19]. The force fields of benzene [14] (for III and IV) and 1,2,3,4-tetrafluorobenzene [16] (for V and VI) were taken as a zero approximation. The force constants were refined by solution of the inverse spectral problems.

The calculations by the MNDO method were carried out by means of the MNDO-86 program, which is a further development of the MNDO-85 program [20], with the standard parameters for C, H, N, and F and improved parameters [21] for S. The geometry of III was taken from [12], the geometries of C_6H_6, $C_{10}H_8$, and 1,2,3,4-$C_6F_4H_2$ were taken from [22, 23], and the geometries of V, VII, and XI were optimized.

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*This is in agreement with the principal idea of the "selenization" method (i.e., replacement of sulfur by selenium) proposed in [17, 18] for the interpretation of the vibrational spectra of organosulfur compounds. It is interesting to note that the K_{NSe} value for IV virtually coincides with the K_{CSe} value determined in [18] for bis(benzoxazole-, benzoimidazole-, benzothiazole-2-selenol)methanes.

The percentages of the ^{15}N and ^{77}Se isotopes in the isotopically enriched samples were determined by mass spectrometry. The ^{15}N-labeled (in the 1 position) starting o-phenylenediamine and 3,4,5,6-tetrafluoro-1,2-phenylenediamine were synthesized by the methods in [24, 25] using ^{15}N-ammonia.

The synthesis of III and V was previously described in [10]. Samples of III and V containing 86 and 89%, respectively, of the ^{15}N isotope in the 1 position were synthesized similarly.

Naphtho[1,8-c,d][1.2.6]thiadiazine (VII). A triturated (until it was homogeneous) mixture of 1.58 g (10 mmoles) of 1,8-naphthalenediamine and 5.0 g of freshly calcined NaF was placed in a steel autoclave, into which 1.08 g (10 mmoles) of SF_4 was condensed with cooling to –60°C. Cooling was discontinued, and the autoclave was opened after 2 h. The reaction mass was extracted with hot hexane, the extract was evaporated to dryness at reduced pressure, and the residue was sublimed in vacuo. This procedure gave 1.49 g (80%) of VII in the form of shiny dark-blue crystals with mp 141-142°C (mp 142-143°C [26]) and M^+ 186.

4,5,6,7-Tetrafluorobenzo-2,1,3-selenadiazole (VI, $C_6F_4N_2Se$). A solution of 1.10 g (5 mmoles) of selenium tetrachloride in 10 ml of monoglyme was added dropwise at 0°C in an argon atmosphere to a stirred solution of 0.90 g (5 mmoles) of 3,4,5,6-tetrafluoro-1,2-phenylenediamine and 1.58 g (20 mmoles) of pyridine in 10 ml of monoglyme. After stirring for 1 h at room temperature, the solution was filtered, the solvent was removed by distillation at reduced pressure, and the residue was recrystallized from ethanol and sublimed in vacuo. This procedure gave 1.17 g (91%) of light-yellow crystals of VI with mp 202-203°C (sealed capillary). ^{19}F NMR spectrum (dioxane): 13.7 (2F), 6.7 ppm (2F). ^{15}N NMR spectrum (DMSO): 370.8 ppm. ^{77}Se NMR spectrum (DMSO): 1123 ppm. X-ray electron spectrum, E_{bond}: 689.3 (F_{1s}), 401.3 (N_{1s}), 289.8 (C_{1s}), 59.6 eV (Se_{3d}). UV spectrum (ethanol): 327 (4.13), 237 nm (3.65). Found: M^+ 256 (^{80}Se). Calculated: M 256 (^{80}Se).

Benzo-2,1,3-selenadiazole (IV). This compound was similarly synthesized. It was recrystallized from hexane and sublimed in vacuo to give colorless crystals (in 88% yield) with mp 76-77°C (mp 76°C) [27]) and M^+ 184 (^{80}Se). ^{77}Se NMR spectrum (DMSO): 1192 ppm.

Samples of VI (with 84% of the ^{15}N isotope in the 1 position), VI (with 82% of the ^{77}Se isotope), IV (with 91% of the ^{15}N isotope in the 1 position), and IV (with 80% of the ^{77}Se isotope) were similarly synthesized.

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