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The Structure and Electron-donor Properties of Organic Compounds of Selenium(II)

E.N.Gur'yanova

The results of studies of the structure and complex-forming power of organic compounds of selenium have been summarised. The principal characteristics of the geometry of the molecules and their orbital state and electron-donor properties have been discussed. Quantitative estimates of the complex-forming power of selenium compounds have been given. The questions of the generation of selenium-centred free radicals and their stabilisation by complex formation have been examined. The bibliography contains 225 references.

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I. INTRODUCTION

The organic chemistry of selenium has developed intensively in recent years, and is acquiring increasing importance in various branches of science and technology. One factor responsible for this was the discovery of the part played by selenium in living organisms.[1-3] The biochemical role of this element was understood when it was shown that selenium-containing proteins are components of various enzymes.[3] Another important factor in the development of the organic chemistry of selenium was the discovery of "organic metals", that is organic superconductors obtained from charge-transfer complexes and radical-ion salts using selenium compounds.[4,5] Research is being carried out to find new promising selenium-containing compounds for these purposes, and their structures are being studied.[6-9] Organic selenium compounds are used to obtain films of semiconducting materials.[10] In addition, a number of organoselenium compounds are highly reactive towards free radicals, and this opens up the possibility of their use as antioxidants.[3] There are indications that selenium compounds are more effective antioxidants than the corresponding sulphur compounds.

Various aspects of the chemistry of selenium have been dealt with in a monograph,[1] collected papers,[2,3] and reviews,[11-13] but a number of problems which have developed in recent years have not yet been summarised. This applies, in particular, to studies of the electronic structure and orbital state of organoselenium compounds, and their complex-forming power.

An extremely important aspect of the electronic structure of molecules is the nature of the occupied and unoccupied molecular orbitals: their energy, symmetry, and degree of delocalisation. Of particular interest are the boundary orbitals—the highest occupied (HOMO) and the lowest unoccupied (LUMO) molecular orbitals, since the nature of these orbitals is the main factor determining such important properties of molecules as the ionisation potential, electron affinity, spectral properties, and reactivity, including complex-forming power. Published summaries of the coordination properties of selenium compounds deal chiefly with inorganic compounds[11] and complexes with transition metal ions.[12,13]

In the present review, an attempt has been made to summarise the results, obtained chiefly in recent years, of studies of the geometry and molecular-orbital state of organic compounds of divalent selenium, and their coordination properties with respect to acceptors of different types (σ, ν, π). Particular attention has been paid to the quantitative estimation of the electron-donor power of organoselenium compounds. The questions of the generation of selenium-containing free radicals and their stabilisation by complex formation have been examined.

II. SELENIDES

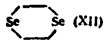
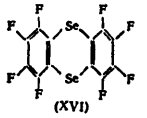
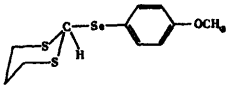
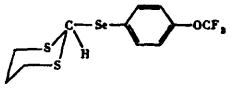
1. The Geometry and Molecular-Orbital State of Selenides

The selenium atom in organic selenides R_2Se, as in compounds of the type $RSe-SeR$ or $R_nE=Se$ (E = C, P) in accordance with the state of the valence electrons $4s^2p_z^2p_xp_y$, has two bonded (p_x, p_y and four non-bonded (s^2, p_z^2) electrons. The extent of the participation of the atomic orbitals of selenium in the formation of the molecular orbitals of a given compound to a large extent determines the geometry of the molecules and their properties.

The structural parameters of a number of selenides, found by X-ray diffraction (XRD) in the crystalline state, by microwave spectroscopy (MWS) and by electron diffraction (ED) in the vapour are given in Table 1. For a complete picture, Table 1, in addition to data obtained in recent years, also includes data given earlier.[2,3] Judging from the values of the valence angle CSeC (92-96°) for the aliphatic selenides (I)-(V), the participation of the valence 4*s* orbital in the formation of the Se-C σ-bond in these compounds is slight. In the aromatic compounds (VI)-(VIII), the CSeC angle is larger, 100-106°. The Se-C bond lengths depend to a marked extent on the state of hybridisation of the carbon atom, and have the following values: for the aliphatic compounds ($Se-C_{sp^3}$) 1.94-1.98 Å (I)-(V), (XVII), (XVIII), for the aromatic compounds ($Se-C_{sp^2}$) 1.90-1.92 Å (VI)-(X), (XVII), (XVIII), and for $Se-C_{sp}$ (selenocyanate group) 1.84-1.85 Å (IV), (IX). The differences in the Se-C bond lengths for aliphatic and aromatic compounds can be seen particularly clearly by comparing the data for the cyclic compounds(XII), (XIII), and (XIV)-(XVI). The observed changes in the bond length in the order $Se-C_{sp^3} > Se-C_{sp^2} > Se-C_{sp}$ are fairly large, and apparently cannot be attributed entirely to the differences in the state of hybridisation and hence in the dimensions of the corresponding carbon atoms. Thus the difference in the C-H bond lengths for different valence states of the carbon atom does not exceed 0.03 Å: $C_{sp^3}-H$ (1.09), $C_{sp^2}-H$ (1.07), $C_{sp}-H$ (1.06 Å), whereas in the CC multiple bond series, these differences

are ten times greater: $C_{sp^3}-C_{sp^3}$ (1.54), $C_{sp^2}-C_{sp^2}$ (1.39), $C_{sp}-C_{sp}$ (1.20 Å). Comparison of these data makes it possible to regard the decrease in the length of the Se–C bond in the above series as evidence of additional Se–C bonding as a result of the interaction of the lone pair of electrons (LPE) of the selenium atom with the π-system of the electrons of the aromatic (unsaturated) fragment ($p\pi$-conjugation).

Table 1. Structural parameters of selenides.

Selenide	Bond length, Å		Angle CSeC, °	Method	Refs.
	$Se-C_{sp^3}$	$Se-C_{sp^2}$			
CH_3SeH (I)	1.959	—	95.5	MWS	[14]
CH_3SeCH_3 (II)	1.943	—	96.2	MWS	[15]
CF_3SeCF_3 (III)	1.978	—	95.5	ED	[16]
CF_3SeCN (IV)	1.984	*	92.2	ED	[17]
$(C_6H_5COCH_2)_2Se$ (V)	1.951	—	96.3	XRD	[18]
$C_6H_5SeCH_3$ (VI)	1.957	1.912	99.6±2.5	ED	[19]
C_6H_5SeBr (VII)	—	1.899	99.8±1.2	ED	[20]
$(4\text{-}CH_3C_6H_4)_2Se$ (VIII)	—	1.925	106.2	XRD	[21]
$1,4\text{-}C_6H_4(SeCN)_2$ (IX)	**	1.916	94.4±0.9	XRD	[22]
$2\text{-}NO_2C_6H_4SeBr$ (X)	—	1.917	98.5	ED	[23]
$2\text{-}CHOC_6H_4SeBr$ (XI)	—	1.876	98.0	XRD	[24]
 (XII)	1.99; 2.04	—	98±3.5	XRD	[25]
 (XIII)	1.945; 1.947; 1.967	—	96.8±1.0; 100.3±1.0	XRD	[26]
 (XIV)	—	1.899	86.6±0.2	XRD	[27]
 (XV)	—	1.87	86.0±1.0	XRD	[28]
 (XVI)	—	1.87—1.90	96.2—97	XRD	[29]
	1.966	1.915	100.8	XRD	[30]
	1.963	1.920	100.6	XRD	[30]

*Se–CN bond length 1.854 Å, **1.837 Å.

A similar sequence is observed in the change in the dipole moments of the Se–C bonds. The dipole moments of the Se–C bonds,[31] calculated from the experimental dipole moments of the corresponding compounds by the vector additivity method, are:

$$\overleftarrow{Se}-C_{sp^3}\ 0.70 > \overleftarrow{Se}-C_{sp^3\,(unsaturated)}$$

$$0.53 > \overleftarrow{Se}-C_{sp^3\,(aromatic)}\ 0.30 > \overleftarrow{Se}-C_{sp}\ -0.75\ (Д).$$

The decrease in the dipole moment of the Se–C bond for different valence states of the carbon atom, and the change in its direction (for $Se-C_{sp}$) may be due to a number of factors. In Ref.31, the observed changes in the dipole moments were attributed to differences in the electronegativity of the carbon atom in different valence states:

$$C_{sp^3}\text{—}2.6,\ C_{sp^3\,(unsaturated)}\ \text{—}2.7,\ C_{sp^2}\ \text{—}2.8,\ C_{sp}\ \text{—}3.2,$$

electronegativity of the selenium atom –2.4.[32] The sequence indicated, however, may be determined not only by this factor but also by the changes in the lengths of the corresponding bonds, and also by the possibility of charge transfer from the selenium atom to the aromatic (unsaturated) p-electron system ($p\pi$-conjugation).

The idea of possible $p\pi$-conjugation in aromatic and unsaturated selenium compounds is often used to explain the properties of the corresponding compounds, as described below. The most reliable information on the orbital state of molecules is given by photoelectron spectroscopy (PES). When combined with quantum-chemical calculations in the approximation of Koopman's theory, according to which the ionisation potential is equal to the energy of the corresponding orbital with the sign reversed ($IP_i = -\varepsilon i$), this method makes possible the quantitative characterisation of the orbital state of molecules.

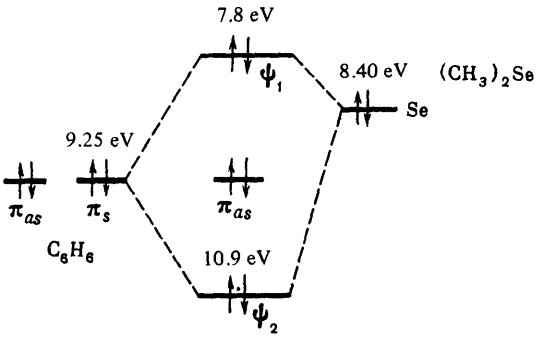


Figure 1. Formation of the HOMO of selenoanisole.[35]

According to quantum-chemical calculations, the first ionisation potential of aliphatic selenides corresponds to an HOMO which is a 4p orbital populated chiefly by an LPE of the selenium atom.[33] An interesting feature is that this orbital is the HOMO not only in dialkyl selenides but also in the series of compounds $(H_3M)_2Se$, where M = Si, Ge.[34] The HOMO of the aromatic selenides includes not only a 4p orbital of the selenium atom but also a contribution from the π_s orbital of the aromatic fragment. The formation of the molecular orbitals of selenoanisole is represented in Fig.1.[35] The mixing of the π_s orbital of the aromatic fragment with the p orbital of the LPE of the heteroatom raises the HOMO relative to the levels of the orbitals of the interacting fragments. Estimation of the contribution of the LPE of the selenium atom to the HOMO of selenoanisole by the HMO method with the parametrisation of the PES calculation[36–38] gave the value 0.834,[39] which is appreciably greater than that for the anisole molecule (0.446) and close to the contribution for the thioanisole molecule (0.738). According to Ref.40, the contribution of the LPE of the heteroatom to the HOMO of the compounds $C_6H_5ECH_3$ of the oxygen sub-group increases in the order: O (0.54) < S (0.77) < Se (0.84) < Te (0.89). The opposite order was obtained in an estimation of the contribution of the π-component of the aromatic fragment.[41] Similar results were obtained by calculating the resonance integrals $\beta(C_{sp^2}-E)$,

where E = O, S, Se, for compounds $C_6H_5ECH_3$. The participation of the LPE of the selenium atom in the general $p\pi$-conjugation system is indicated by the results of the determination of the dipole moments of the interaction ($\Delta\mu_{int}$) for substituted selenoanisoles[42] and phenylselenoacetylenes.[43]

The state of the HOMO is extremely sensitive to the steric and electronic effects of the substituents. For *p*-substituted selenoanisoles, a linear relationship has been established between the first ionisation potential (IP_1), characterising the energy of the HOMO, and the σ^+-constants of the substituents.[39] A similar relationship between IP_1 and σ_m was established for disubstituted selenophenes.[44] For the aromatic compounds C_6H_5SeR, the conformation of the selenide molecules, like that of the corresponding compounds of oxygen and sulphur, is determined to a large extent by the competition between two effects: $p\pi$-conjugation (which is a maximum for a planar molecule, when the angle φ between the plane of the phenyl ring and the CSeC plane is 0°) and steric effects (the tendence for the SeR group to be displaced from the plane of the ring as a result of the mutual repulsion of the substituent R and the *ortho*-hydrogen atoms of the phenyl ring). Depending on the contributions of these effects, which determine the barrier to the rotation of the SeR group relative to the aromatic fragment, an affective conformation of the molecule with a definite angle φ, or an equilibrium between planar (φ = 0°) and orthogonal (φ = 90°) conformers can apparently be produced.

From the doublet character of the first PES band of selenoanisole, it was concluded that the gas phase contains two rotamers;[3] the first component of the band (8.0 eV) was assigned to the HOMO of a planar conformer, and the second (8.3 eV) to a rotamer with minimum overlap of the $4p-\pi$-orbitals. Judging from the intensity of these bands, the ratio of the rotamers is ~1 : 1. At the same time, PES did not detect the presence of rotamers for the corresponding compounds C_6H_5SeR (R = C_2H_5 or iso-C_3H_7) where the 8.3 eV band was assigned to an orthogonal conformer.[45] The differences in the energies of the rotamers are small, even for the corresponding oxygen and sulphur compounds. Thus the difference between the energies of the planar and orthogonal conformers does not exceed 1.3 kcal mole^{-1} for anisole ,[46] and 0.8 kcal mole^{-1} for thioanisole.[47,48] For the selenium compounds, the difference between the energies of the planar and orthogonal conformations should be even smaller. This is apparently one of the reasons why they cannot be distinguished by some methods. Studies of the dipole moments and Kerr constants of selenoanisole and diphenyl selenide in inert solvents indicated that these compounds are conformationally homogeneous, with an angle φ = 32° for the first compound[49] and φ = 48° for the second.[50] According to electron diffraction data, the angle φ in the selenoanisole molecule in the gas phase is 40 ± 13°.[19] The introduction of electron-acceptor substituents in position 4 of the phenyl ring of selenoanisole leads to flattening of the molecules: for the 4-Cl- and 4-Br-derivatives, $\varphi < 20°$, and for the 4-NO_2-derivative, $\varphi \simeq 0°$.[49] At the same time, the ^1H and ^2H NMR spectra of 4-chloroselenoanisole in a liquid-crystal solvent[51] indicated that the angle of rotation of the phenyl ring relative to the CSeC plane is ~40°. The planar *s-trans*-structure with a maximum conjugation is characteristic of aryl vinyl selenides.[52] According to the dipole moments and the Kerr constants, the C_6H_5SeCN molecule, unlike selenoanisole, has a planar conformation.[53] The infrared (IR) spectra of crystalline specimens in polarised light[54] also detected no signs of conformational nonhomogeneity in aryl selenocyanates. Electron-donor substituents (OCH_3, $N(CH_3)_2$ in position 4 of the phenyl ring do not break down the planar conformation of phenyl selenocyanates, but electron-acceptor substituents (Cl, Br, NO_2) lead to slight breakdown of the coplanarity of the C_6H_4SeCN fragment.[53] Birefringence established an increase in the non-coplanarity of 1,4-disubstituted compounds of selenium of the type $RSeC_6H_4SeR$ (R = CN or CH_3), compared with the monosubstituted compounds.[55] In a study of the conformation of the molecules of aliphatic selenides R_2Se (R = CH_3, C_2H_5), proton magnetic resonance data, in agreement with IR and Raman spectroscopic data, showed that in these compounds there is free rotation of R about the C–Se bond.[56] The IR and Raman spectra of diethyl selenide in argon and nitrogen matrices, however, indicate the existence of conformational isomerism in the solid state.[57] NMR is extremely promising for the study of the electronic and geometric structure of organic selenides. Various nuclei are studied, including the ^{77}Se isotope, whose natural concentration is 7.6%.

The differences between the chemical shifts δ of ^{77}Se in different compounds are fairly large (in a number of cases reaching 10^2-10^3 p.p.m.[58,59]) and are not sensitive to the solvent,[59,60] and this makes possible a fairly reliable determination of the electronic state of the molecules.

The number of published papers on the study of organic selenides by ^{77}Se NMR has increased considerably in recent years, Since the chemical shift reflects the charge state of an atom, the values of δ for ^{77}Se are sidely used in studies of intramolecular electronic interactions. For a large group of compounds of the type XC_6H_4SeR, a linear relationship has been established between δ for ^{77}Se and the Hammett constant σ (X).[59] A more detailed ^{13}C and ^{77}Se NMR study of compounds of the type XC_6H_4SeR indicated that δ $^{13}C(1)$ are linearly correlated with σ_I and σ_R of the substituents.[61] The values of δ ^1H, δ ^{13}C, and δ ^{77}Se have been used in studies of the conformation and intramolecular electronic interactions in a number of compounds: $PhSeCH=CH_2$,[62] $CH_3SeC\equiv CR$,[63] mono-, di-, and triseleno-substituted ethylenes,[64] and condensed five-membered heterocyclic compounds based on selenophene.[65] Data on the temperature dependence of δ ^{77}Se for phenylselenylcyclohexane derivatives have been used to estimate the barrier to inversion of the cyclohexyl fragment.[66] ^{77}Se NMR has been used to study the structure of molecules containing selenium–sulphur bonds, of the type XC_6H_4Se-SR, which provide models of biological systems.[67] Measurements of the ^{77}Se and ^{125}Te chemical shifts for analogous organic selenides and tellurides indicated that there is a linear relationship between these quantities: δ Te = 1.60 δ Se.[68,69] The relationship between δ ^1H, δ ^{13}C, and δ ^{77}Se for cyclic compounds of selenium has been studied.[70,71] ^{77}Se NMR gives extensive information on the composition of the compounds formed in the binary sulphur–selenium system.[72]

In addition to the chemical shift of the selenium atom, another parameter extremely sensitive to change in the electronic structure of molecules is the spin–spin coupling constant $^1J(^{77}Se-^{13}C)$. In a series of selenides RSeR', this constant increases with increase in the *s*-character of the hybridised orbital or the carbon atom forming the bond with the selenium atom.[73,74] In a series of selenoanisoles, $^1J(^{77}Se-^{13}C)$ increases when acceptor substituents (4-NO_2-) are introduced into the aromatic ring, and decreases when donor substituents (4-NH_2-) are introduced, due to the change in the intensity of the $p\pi$-conjugation and the Se–C bond order.[73] In Ref.75, the stereochemistry of aromatic compounds of selenium was studied using the spin–spin coupling constant of atoms at a greater distance from one another, namely $^2J[^{77}Se-^{13}C(2, 6)]$. The nature of the dependence of $^2J[^{77}Se-^{13}C(1)]$ on the number and nature of the *ortho*-substituents in various aromatic compounds of selenium has been established. The influence of the $^{13}C:^{12}C$ isotope effect on the shielding of ^{77}Se in compounds RSeR' has been determined,[76] and a correlation between Δ ^{77}Se and the length of the Se–C bonds established. The measured spin–spin coupling constants of the selenium nuclei for a number of dialkyl polyselenides $R-(Se)_n-R$ (n = 2–5) indicated that the polyselenide chain has a linear structure.[77]

Valuable information on the electronic and spatial structure of aromatic and unsaturated compounds of selenium is provided by ^{13}C NMR. For selenides C_6H_5SeR, the values of δ for ^{13}C in position 4 of the phenyl ring (relative to TMS) are as follows:[78]

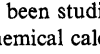
R	CH_3	C_2H_5	C_3H_7	*iso*-C_3H_7	$C(CH_3)_3$
$\delta^{13}C$ (4)	125.55	126.24	126.16	126.84	128.10 .

The differences in the inductive constants of these R are comparatively small, so that they should have practically no influence on the charge state and hence on the magnitude of δ for the C(4) atom. The observed nature of the change in δ $^{13}C(4)$ with increase in the size of R reflects the influence of steric effects on $p\pi$-conjugation in aromatic selenides; this is indicated by the fairly good correlation between $\delta^{13}C(4)$ and the steric constants E_s^0 of the substituents.[78] ^{13}C NMR has been used to determine the dependence of the degree of $p\pi$-conjugation and the conformational state on the nature of the substituents in substituted selenoanisoles.[79–81] Acceptor substituents lead to an improvement, and donor substituents to a deterioration, in the conditions for $p\pi$-conjugation and hence for coplanarity of the molecules. The relationship between the values of σ for ^{13}C and the constants σ_I and σ_R of the substituents has been established for phenyl vinyl selenides[82] and divinyl selenides.[83] δ ^{13}C data have been used to determine the previously unknown values of σ_R^0 for the selenium-containing substituents C_2H_5Se (–0.12) and $CH_2=CHSe$ (–0.09),[83] and ^{19}F NMR data for the *para*-fluorine atom in the aromatic fragment have been used to determine σ_p for the substituents CF_3Se (0.44) and $(CF_3)_3CSe$ (0.54).[84] The interaction of the LPE of the selenium atom with the π-electron system of the aromatic (unsaturated) fragment has been studied by ultraviolet spectroscopy combined with quantum-chemical calculations. The nature of the electron transitions has been studied in derivatives of selenoanisole and their isologues[85] and in substituted aryl allyl selenides,[86] alkyl vinyl selenides, and divinyl selenide.[87] Quantum-chemical calculations of the electron transitions in the PPP approximation have shown that the resonance integrals and hence the degree of $p\pi$-conjugation in a series of analogous compounds of the group VI elements decrease in the order: $\beta(C-O) \gg \beta(C-S) > \beta(C-Se) > \beta(C-Te)$.[85,87] Possible $p\pi$-bonding in the compounds $CH_2=CH-C\equiv CSeCH_3$ and $C_2H_5C\equiv C-C\equiv CSeCH_3$ is indicated by the results of quantum-chemical calculations (CNDO/2).[88] At the same time, studies of the IR spectra of selenoanisole, phenyl selenocyanate, and their derivatives[89,90] showed that the spectra of these compounds represent the sum of the practically non-perturbed spectra of the phenyl ring and the $SeCH_3(SeCN)$ group), from which it was concluded that there is very little intramolecular interaction. As the authors themselves point out, however, this conclusion was reached without carrying out a normal-coordinate analysis, so that it is not sufficiently well-founded.

2. The Electron-Donor Properties of Selenides

The properties of selenides as electron donors is determined to a large extent by the state of the HOMO, and primarily by its energy and symmetry. According to quantum-chemical calculations (CNDO/2) for dimethyl selenide, the contribution of the LPE of the selenium atom to the HOMO is 0.88, so that the charge on the selenium atom is 0.77.[88] Evidence that the HOMO of aliphatic selenides consists chiefly of the $4p^2$-LPE of the selenium atom is provided by the results of structural studies of the complexes formed by selenides. Table 2 gives the published structural parameters of complexes of selenides with σ-acceptors (A = I_2, ICl) and ν-acceptors (A = $PdCl_2$, $PtBr_2$). The angle (<C–Se–A) formed by the coordinate bond Se–A with the Se–C bond is 100–107°, that is the donor–acceptor bond Se–A, in accordance with the orientation of the orbital of the $4p^2$-LPE, is almost perpendicular to the plane of the C–Se–C bonds of the selenide molecule. The lengths of the intermolecular bonds (r_{DA}) of the complexes vary over a fairly wide range; this can be clearly seen by comparing the values of $\Delta r = e_{DA}^{expt} - (r_D + r_A)_{cov}$, where r_{DA}^{expt} is the experimental length of the intermolecular bond, and r_D and r_A the covalent radii of the atoms of the molecules of the donor and the acceptor involved in the formation of the donor–acceptor bond (the covalent radii of the atoms given by Pauling[98] were used in the calculations). For the comparatively weak complexes formed by selenides with halogens, the values of Δr are large, whereas for the complexes with compounds of Pd and Pt, the length of the intermolecular bond is practically equal to the sum of the covalent radii of the corresponding atoms.

Table 2. Structure of selenide complexes.

Complex	D–A bond	r_{DA}, Å	Δr *, Å	C–Se–A angle, °	Refs.
	Se–I	2.762	0.26	100.5	[91]
	Se–I	2.829	0.33	100.5	[92]
	Se–I	2.755	0.25	107.0; 102.0	[93, 94]
	Se–I	2.630	0.13	104.1; 99.0	[93]
$PdCl_2 \cdot 2(C_4H_9)_2Se$	Se–Pd	2.424	0	100.8; 109.5	[95]
$PdCl_2 \cdot [CH_3SeCH(CH_3)_2]_2$	Se–Pd	2.40 2.36	–0.07	105.5; 103.7; 107.4; 104.2	[96]
$PtBr_2 \cdot 2$	Se–Pt	2.43	0	110.5; 107.2	[97]

*$\Delta r = r_{DA}^{expt} - (r_D + r_A)_{cov}$.

From the previously established relationship between $-\Delta H$ and Δr,[99] covering a wide range of molecular complexes of the $n\nu$ and $n\sigma$ types, including the complexes of selenides with a number of acceptors, the energy of formation of the Pd–Se and Pt–Se bonds in these complexes should be greater than 15 kcal mole^{-1}.

Complex formation by organic selenides with iodine has been studied in most detail by electronic spectroscopy.[100–134] The spectra of the complexes contain new bands, charge-transfer bands (CTB), not present in the spectra of the starting materials. The positions (ν_{CTB}) and energies ($h\nu_{CTB}$) of the charge-transfer bands in the spectra of the complexes have been established, and the stability constants determined. The temperature dependence of the equilibrium constants has been used to determine the thermodynamic parameters of complex formation by iodine with alicyclic[101] and cyclic selenides,[102,103] and with aromatic selenides of the substituted selenoanisole[104–109] and diphenyl selenide[100,110,111] types. In Ref.112, complex formation by selenides of different kinds with iodine was studied not only by electronic spectroscopy but also by calorimetric titration. The compositions and enthalpies of formation of the complexes were determined, and their electronic spectra studied. The values of $-\Delta H$ for the complexes of a number of selenides with iodine are given in Table 3. For aliphatic selenides, equations were obtained, relating the values of $-\Delta H$ to $h\nu_{CTB}$ and $-\Delta H$ to $\Sigma\sigma^+$ (the sum of the inductive constants of the substituents). Aromatic selenides, like the aliphatic compounds, behave as

n-donors towards I_2, and the coordination centre is the selenium atom. A noteworthy feature is that the absolute values of $-\Delta H$ for the complexes of I_2 with aromatic selenides are smaller than those for aliphatic selenides (Table 3); this is apparently related not only to the differences in the influence of the inductive effects but also to the expenditure of energy to break down the $p\pi$-conjugation in the aromatic selenides. According to Raman spectroscopic data, the wavenumber of the I—I vibrations decreases from 215 cm^{-1} in the original I_2 molecule to 165 cm^{-1} in the complex $(CH_3)_2Se.I_2$ and 160 cm^{-1} in the complex $(C_2H_5)_2Se.I_2$.[113] The stretching wavenumber of the intermolecular Se—I bond in the complex $(C_2H_5)_2Se.I_2$ was found to be 100 cm^{-1}.[114] This value is much lower than the vibrational wavenumber of the intermolecular Se—B bond (256 cm^{-1}) in the complex $(CH_3)_2.Se.BF_3$.[115] These differences are apparently due to the difference in the strengths of the intermolecular bonds in these complexes. Systematic spectral studies of complexes of iodine with substituted selenoanisoles[104–109] revealed a number of general regularities of complex formation. A linear relationship was established between the values of $-\Delta H$ and the constants $\sigma_{m,p}$ of the substituents in the phenyl ring, and also between $-\Delta H$ and the displacement of the iodine band in the electronic spectrum on complex formation $\Delta\nu_{I_2}$, and between the changes in the enthalpy ΔH and the entropy ΔS in complex formation.[104–106] The solvatochromism of the charge transfer bands was used to study the influence of solvents of different character on the thermodynamics of the formation of complexes of selenoanisoles with iodine.[108,109] Analysis of the experimental data showed that the observed differences in the values of $-\Delta H$ for a given complex in different solvents are due chiefly to the contribution of the specific solvation of the iodine molecule. For the molecules of the donor and the complex in the series of solvents studied, specific solvation takes place for the most part.

Table 3. Enthalpies of formation of the complexes (kcal $mole^{-1}$).

Selenide	I_2 (Ref.112) 1:1	$AlBr_3$ (Ref.129) 1:1	$SnCl_4$ (Ref.128) 1:1	$SnCl_4$ (Ref.128) 1:2
$(C_2H_5)_2Se$	9.9	—	—	—
$(C_3H_7)_2Se$	9.7	29.9	14.3	27.7
$(C_4H_9)_2Se$	10.2	—	14.6	28.4
$(C_8H_{17})_2Se$	9.8	30.1	13.9	27.8
$(C_6H_5CH_2)_2Se$	9.2	27.4	—	—
$C_6H_5SeCH_3$	7.6	24.9	—	—
$C_6H_5SeC_3H_7$	8.4	26.2	—	—
$C_6H_5SeCH_2CH{=}CH_2$	8.0	26.1	—	—
$(C_6H_5)_2Se$	3.6	22.6	—	—
$(4\text{-}CH_3C_6H_4)_2Se$	—	23.8	—	—

Organic selenides form complexes with π-acceptors; the complexes of aromatic selenides and derivatives of selenophene with tetracyanoethylene (TCE) have been studied in most detail by electronic spectroscopy. The observed charge-transfer bands in the spectra of these complexes are due to electron transitions from the HOMO of the selenide to the LUMO of the TCE molecule. In most cases, the spectra of the complexes of aromatic selenides, like the spectra of the complexes of other π-donors with TCE, contain not one but two charge-transfer bonds, corresponding to electron transitions from the highest orbitals [π_s, $\nu_{max}(CTB_1)$ and π_{as}, $\nu_{max}(CTB_2)$, see Fig.1] of the selenide molecule to the LUMO of the acceptor molecule. The position of the maximum of the first CTB [$\nu_{max}(CTB_1)$] and its energy [$h\nu_{max}(CTB_1)$] are directly related to the energy of the HOMO and to the first ionisation potential (IP_1) of the corresponding selenide. A linear correlation between $\nu_{max}(CTB_1)$ and IP_1 was established for the complexes of TCE with selenophene and its substituted derivatives.[116,117] The complexes formed by heterocyclic compounds of selenium with TCE are more stable than those formed by the corresponding heterocyclic compounds containing sulphur.[118] For selenophenes containing different substituents in position 2, a correlation was established between the first ionisation potential and the σ_m-constants of the substituents.[119] Spectral studies of the complexes of TCE with substituted selenoanisoles, together with photoelectron spectroscopic data and quantum-chemical calculations,[39,107,120–123] established the principal regular features of the formation of the intermolecular bonds and the properties of the complexes. The nature of the electron transitions and the two observed CTB in the spectra of the complexes was examined, the regular features of the influence of electronic and steric effects on the position and intensity of the CTB were established, and the relationship between the spectral parameters and the orbital characteristics of the molecules determined. A large amount of experimental material on the complexes of TCE with substituted selenoanisoles and phenyl selenocyanates[124] established a linear relationship between the energy of the first CTB and the electrophilic σ^+-constants of the substituents.

A study of the electrochemical oxidation of substituted selenoanisoles[125] also established a linear relationship between the potential $E_{1/2}$ and the electrophilic constants of the substituents σ^+. The value of the electrochemical reaction constant ($\rho = -0.28$) was found to be practically equal to the constant found from a spectrophotometric study of the complexes of selenoanisoles with TCE ($\rho = -0.25 \pm 0.03$). This appears quite logical, since both of these methods characterise the state of the HOMO of the compounds being studied. The second charge-transfer band of the complexes of TCE with substituted selenoanisoles, unlike the first band, is little influenced by substituents,[123] and its position and energy are close to those of the CTB of the complex of TCE with benzene.

The linear relationship between $\nu_{max}(CTB_1)$ and IP_1 for TCE complexes covers a wide range of varied electron donors containing different heteroatoms, and has the form:[126]

$$IP_1\,(eV) = 5.86(\pm 0.06) + (1.31 \pm 0.03) \times 10^{-4}\,\nu_{max}(CTB_1)\,(cm^{-1}). \quad (1)$$

This equation is widely used to determine the ionisation potentials of complex heteroaromatic compounds, including selenium-containing compounds (such as arylselenoacetylenes,[127] selenides containing a carbonyl group,[107] etc.) from the measured CTB in the spectra of the complexes with TCE. Thus the electron-donor properties of selenides towards iodine (σ-acceptor) and TCE (π-acceptor) have now been fairly fully studied by electronic spectroscopy. There are extremely few published data, however, on the structural and thermodynamic parameters of complexes of selenides with other acceptors, including *v*-acceptors. Calorimetric titration has been used to determine the enthalpies of formation of the complexes of a number of selenides with tine tetrachloride (with the 1:1 and 2:1 compositions),[128] aluminium tribromide,[129] and boron tribromide.[130] The enthalpy of formation of the complex $(CH_3)_2Se.Ga(CH_3)_3$ has been determined by the gas dissociation method.[131] The values of $-\Delta H$ (kcal $mole^{-6}$) for a number of complexes of selenides with aluminium tribromide and tin tetrachloride are given in Table 3. The selenides form fairly stable complexes with these acceptors. Studies of the complex-forming power of bis-selenides of the type $RSe(CH_2)_nSeR$ towards PT and Pd salts by ^1H, ^{77}Se, and ^{195}Pt NMR, ultraviolet, and IR spectroscopy made it possible to solve various problems of the stereochemistry of the complexes formed and to determine the relationship between the parameters found.[132] ^1H NMR and IR spectroscopy established the formation of H-complexes of a number of selenides with phenol.[133-135]

Analysis of the results of an IR Fourier spectroscopic study of the complex $H_2Se.HF$ in an argon matrix led to the conclusion that it has a pyramidal structure,[136] which is consistent with the view that the $4p^2$-LPE of the selenium atom takes part in the formation of an intermolecular H-bond. Non-empirical quantum-chemical calculations for the complex $H_2Se.HCN$ [137] also indicate that it has a pyramidal structure.

A detailed study of the IR and Raman spectra of the complex $(C_2H_5)_2Se.HCl$ in argon and nitrogen matrices revealed fine effects due to conformational isomerism. The different rotational isomers of diethyl selenide react with HCl to give complexes with different stability.[57] In addition to the 1 : 1 complexes, 1 : 2 complexes with branched H-bonds were detected. The formation of complexes with the same composition was also established in the reaction of diethyl selenide with HCl in CCl_4.[138] It was concluded that the H-bond in the complex in the argon matrix is stronger than that in an inert solvent.

The high sensitivity of the chemical shift in the ^{77}Se NMR spectra has been used successfully to study complex formation by phenyl selenylacetate with the enzyme α-chymotrypsin. The composition of the complex (1 : 1) was established, and its dissociation constant determined.[139] Thus organic compounds of selenium, like the corresponding compounds of the other elements of the oxygen subgroup of group VI form fairly stable complexes with various acceptors. To estimate the degree of similarity and difference in the electron-donor properties of these compounds, various parameters of the complexes which they form can be compared. The most reliable characteristic of the complex-forming power of a given donor towards a given acceptor is the enthalpy of formation of the complex. The enthalpies of formation $-\Delta H$ (kcal mole^{-1}) of a number of 1 : 1 complexes are given below.[129,130,135,140] There are practically no published quantitative data on the complex-forming power of tellurium(II) compounds.

Donor	Acceptor				
	I_2	BBr_3	$AlBr_3$	$SnCl_4$	C_6H_5OH
$(C_2H_5)_2O$	4.3	18.8	36.5	5.8	5.9
$(C_3H_7)_2S$	8.1	22.8	31.1	12.6	4.2
$(C_3H_7)_2Se$	9.7	22.8	29.9	14.6	3.7

Thus the order of change in the values of $-\Delta H$ in the series ethers – sulphides – selenides is different for the reactions with different acceptors.

As noted above, the electron-donor properties of molecules are determined to a large extent by the energy state of the HOMO, given by the first ionisation potential. For the compounds RER^1 of the elements of the oxygen sub-group, the values of IP_1 (eV) are as follows:

R	R^1	O	S	Se	Te
—	—	13.6	10.4	9.75	9.01
CH_3	CH_3	10.0	8.65	8.40	7.89
C_6H_5	CH_3	9.29	8.07	7.99	7.60
C_6H_5	C_6H_5	8.09	7.80	7.79	—

The values of IP_1 decrease with increase in the principal quantum number of the element, in the order O > S > Se > Te. A large change is observed on going from the oxygen compounds to the sulphur compounds, and the differences in the IP_1 values for the sulphur and selenium compounds are much smaller. Judging from the IP_1 values, the donor properties of the compounds of the elements of group VI should increase in the following order: O < S < Se < Te. This order is not always observed, however, This can be clearly seen by comparing the order of change in the values of $-\Delta H$ for the complexes of ethers, sulphides, and selenides with iodine (Se > S > O) and with phenol (O > S > Se). Of considerable importance in the formation of the intermolecular bond are the conditions of overlap of the interacting orbitals—the HOMO of the donor molecule and the LUMO of the acceptor molecule.

The overlap integrals of the corresponding orbitals (indicated in brackets) for a number of model donor – acceptor bonds are given below:[130,140]

Acceptor	Donor			
	R_2O ($2sp^2$)	R_2S ($3p$)	R_2Se ($4p$)	$R_3P{=}Se$ ($4p$)
I ($5p$)	0.27	0.34	0.41	0.47
B ($2sp^2$)	0.34	0.46	0.41	0.50
Al ($3sp^2$)	0.40	0.38	0.43	—
Sn ($5sp^2d$)	0.76	0.60	0.63	—
OH ($1s$)	0.43	0.36	—	—

The order of change in the overlap integrals for the complexes of the oxygen, sulphur, and selenium compounds with iodine agrees with the order of change in IP_1, so that the enthalpy of formation of the complexes of I_2 with the selenides should be greater than for the sulphides and ethers, as observed experimentally. For the complexes with compounds of boron, aluminium, and tin, the order is slightly different, and this is reflected in their enthalpies of formation. An important part in the formation of intermolecular bonds is played by steric effects. These decrease with increase in the size of the central atom of the donors indicated (O > S > Se), and for the above acceptors they are most clearly revealed in the complexes $D.BBr_3$ and $D.SnCl_4$. Thus the order of change in the electron-donor properties of a given series of compounds is determined by a number of factors, and may be different for the reactions with different acceptors.

III. THE STRUCTURE AND COORDINATION PROPERTIES OF COMPOUNDS OF THE TYPE $R_nE{=}Se$

The intensive development of the chemistry of selenium in recent years has drawn the attention of research workers to the selenium analogues of ketones, phosphine oxides, and carboxylic acid amides, that is compounds containing E = Se bonds. Of these, the compounds containing $\geqslant P{=}Se$ and $\geqslant C{=}Se$ bonds have been most fully studied. Structural studies have shown that the phosphorus atom in selenophosphoryl compounds (Table 4) is at the centre of a slightly distorted tetrahedron; the average values of the SePC and CPC valence angles are 11 – 114° and 103 – 106° respectively. The rings of the aromatic fragments of the compounds studied are rotated relative to one another; the angles made by the plane of the ring with the C – P – Se plane are different compounds, and also vary over a wide range for different rings in the same compound, for example from 13° to 56° in compound (XVII). An exception is the fairly symmetrical (C_3) structure of the molecule of tris(2-furyl)-phosphine selenide (XX); the angles made by all three furyl groups with the C – P – Se plane in this compound are almost identical, and the torsional angles O – C – P – Se are 48.2, 46.3, and 46.7°. A noteworthy feature is the relatively large difference in the lengths of the C – P and P = Se bonds for different phosphine selenides. The observed differences have been attributed to the influence of steric effects [for example for compounds (XVII) and (XVIII)], the inductive effect of the substituents [for compounds (XVIII) and (XIX)], and the ability to form $C_{(2p)\pi}-P_{(3d)\pi}$ bonds. Thus according to Ref.145, the fact that the C – P bond in the molecule of tris-(2-furyl)phosphine selenide (XX) is shorter than that in other triarylphosphine selenides is due to the increase in the extent of the $C_{(2p)\pi}-P_{(3d)\pi}$ interaction resulting from the stronger σ-electron-acceptor properties of the 2-furyl group compared with the phenyl group. The fact that the P = Se bond in compounds (XIX) and (XX) is shorter than in compounds (XVI) – (XVIII) has also been attributed to the σ-electron-acceptor properties of the trifluoromethylphenyl or furyl groups and the consequent increase in the *s*-character of the orbital of the P atom in the bond with Se.[145,149]

The vibrations of the $\geqslant P{=}Se$ bond are not characteristic, and vary over a wide range, depending on the composition and structure of the substituents on the phosphorus atom. Thus for compounds

of the type $R_3P=Se$, the vibrational wavenumbers assigned to the P=Se bond are:[150]

R_3	$(CH_3)_3$	$(C_2H_5)_3$	(cyclo-C_6H_{11})$_3$	$(C_6H_5)_3$
$\nu_{P=Se}$ (cm^{-1})	441	422	543	560

According to Raman spectroscopic data, the values of $\nu_{P=Se}$ for the compounds $(C_6H_5)_2P(Se)CH_2-P(X)(C_6H_5)_2$ vary in the range 525–535 cm^{-1} for X = O, S, Se, or the LPE of the P atom.[151]

Table 4. Structural parameters of compounds containing $\geqslant P=Se$ and $\geqslant C=Se$ bonds.

Compound	Bond length, Å C–P, P = Se, or C = Se	Angle C–P–Se, °	Refs.
$(C_6H_5)_3P=Se$ (XVI)	1.826; 2.106	—	[141]
$(2\text{-}CH_3C_6H_4)_3P=Se$ (XVII)	1.834; 2.116	112.7	[142]
$(3\text{-}CH_3C_6H_4)_3P=Se$ (XVIII)	1.820; 2.109	—	[143]
$(3\text{-}CF_3C_6H_4)_3P=Se$ (XIX)	1.815; 2.094	113	[144]
$(2\text{-}C_4H_3O)_3P=Se$ (XX)	1.778; 2.094	114.9	[145]
4-$(CH_3)_2NC_6H_4P(=Se)(CH_3)_2$ (XXI)	1.82; 2.105	113.3	[146]
$CH_2=C=Se$ (XXII)	— 1.706	—	[147]
O=C=Se (XXIII)	— 1.7098	—	[147]
S=C=Se (XXIV)	— 1.695	—	[147]
HN=C=Se (XXV)	— 1.717	—	[147]
$CH_3N=C=Se$ (XXVI)	— 1.708	—	[147]
$C_2H_5N=C=Se$ (XXVII)	— 1.709	—	[148]

For compounds with different substituents on the phosphorus atom, such as $(C_2H_5)_2ClP=Se$ [152] or $(RO)_nR_{3-n}P=Se$ (n = 1–3; R = CH_3, C_2H_5),[153,154] the spectra show splitting of the $\nu_{P=Se}$ bands, attributed to the presence of rotational isomers. The ratio of the intensities of the corresponding bands can be used to determine the relative concentration of the isomers in the mixture and the thermodynamic parameters of the equilibrium.[154]

A study of the electronic spectra of compounds R′R″R‴P=Se [155] showed that the selenophosphoryl group, like the thiophosphoryl group, has chromophoric properties. The relationship between the position of the long-wave band (230–280 nm), assigned to a $n-\pi^*$ transition, and the nature of the substituents on the phosphorus atom has been studied.

Extremely important characteristics of a chemical bond are its polarity, polarisability, and the anisotropy of the polarisability. The P=Se bond is fairly polar; the magnitude of its dipole moment depends on the nature of the substituents, and for compounds of the type $R_3P=Se$ has the following values:[156]

R_3	$(C_6H_5)_3$	$[(CH_3)_2N]_3$	CH_3Cl_2
$\mu_{P=Se}$ (D)	3.73	3.88	2.89

A linear correlation is observed between the dipole moments of the P=Se bond and the inductive constants of the substituents.[156] Measurements of the dipole moments and the Kerr effect have been used to determine the polarisability and the anisotropy of the polarisability of the P=Se bond in the cyclic selenophosphate $CH_3-C(CH_2O)_3P=Se$.[157]

Vaulable information on the nature of the P=Se bond has been obtained by ^1H, ^{31}P, and more particularly ^{77}Se NMR.[145,149,151,158,159] The values of the chemical shifts δ ^{77}Se and the spin–spin coupling constants $^1J(^{31}P-^{77}Se)$ depend to a significant extent on the nature and stereochemistry of the substituents on the phosphorus atom. Electron-acceptor substituents in compounds of the type $R_3P=Se$ lead to an increase in $^1J(^{31}P-^{77}Se)$, whereas electron-donor and bulky substituents decrease it.[159] For a number of compounds $(XC_6H_4)_3P=Se$, a linear relationship has been established between $^1J(^{31}P-^{77}Se)$ and the constants of the substituents.[158]

The spin–spin coupling constant between directly bonded atoms is increased chiefly by the Fermi-contact interaction of the moment of the nucleus and the spin of the electron of the *s*-orbital. This made it possible to examine the observed changes in the values of $^1J(^{31}P-^{77}Se)$ in a series of analogous compounds in relation to the influence of the substituents on the population of the 3*s*-orbital of the phosphorus atom.[145,159] The $^1J(^{31}P-^{77}Se)$ values for compounds of the type $Ar_3P=Se$ indicate that the 2-thienyl and 2-furyl groups in the corresponding phosphine selenides are electron-accepting.[145,159]

Stable compounds containing C=Se bonds were obtained comparatively recently,[160–162], and have been less extensively studied. Structural studies have shown that the C=Se bonds, like the P=Se bonds (see Table 4) have similar lengths in different compounds; the differences do not exceed ±0.01 Å.

The NMR spectra of organoselenium compounds containing C=Se bonds have shown that the ^{77}Se chemical shift has an unusually high sensitivity to the electronic state of the selenium atom.[161–163] The values of δ ^{77}Se for a number of compounds of this type are much greater, sometimes by ~2000 p.p.m., than δ ^{77}Se for dimethyl selenide, and are extremely sensitive to the structural and electronic characteristics of the molecules.[161] The ^{13}C and ^{77}Se NMR spectra of a number of heterocyclic compounds containing C=Se bonds show that δ (C=^{77}Se) is much more sensitive (by a factor of more than 70) to the influence of structural and electronic effects than δ (^{13}C=Se).[163] Thus ^{77}Se NMR opens up extensive possibilities for studying the structure of organoselenium compounds of this type. Published data on the coordination properties of compounds of the type $R_nE=Se$ relate chiefly to compounds containing $\geqslant P=Se$ bonds. The $\nu_{P=Se}$ band in the IR spectrum is displaced to lower wavenumbers on complex formation. The magnitude of the displacement depends on the composition and structure of the phosphine selenide molecules, and also on the properties of the acceptor. Thus for the complexes of triphenylphosphine selenide with tantalum pentafluoride[164] and iodophenylacetylene,[165] $\Delta\nu_{P=Se}$ had the values 20 cm^{-1} and 21 cm^{-1} respectively. A displacement of the $\nu_{P=Se}$ band by 13–14 cm^{-1} has been observed in the spectra of the complexes of various bidentate phosphine selenides with mercury thiocyanate.[166] Ultraviolet (UV) spectroscopy and calorimetry have been used to determine the thermodynamic parameters of complex formation by phosphine selenides with I_2 [167,168] and $SnCl_4$.[167,169] The enthalpies of formation ($-\Delta H$, kcal $mole^{-1}$) of the 1:1 complexes studied are given below; the values of $-\Delta H$ for the corresponding complexes with $R_3P=O(S)$ are given for comparison:

Donor	Acceptor I_2	Acceptor $SnCl_4$	Donor	Acceptor I_2
$(C_4H_9)_3P=O$	6.4	25.8	$[(CH_3)_2N]_3P=O$	7.3
$(C_4H_9)_3P=S$	9.0	15.6	$[(CH_3)_2N]_3P=S$	8.1
$(C_4H_9)_3P=Se$	13.0	15.4	$[(CH_3)_2N]_3P=Se$	12.5

Thus phosphine selenides form fairly stable complexes with I_2 and $SnCl_4$. The donor properties of the selenium atom in the compounds $R_3P=Se$ are slightly stronger than in the corresponding compounds R_2Se. The relative complex-forming power of the series of compounds $R_3P=X$, where X = O, S, Se, judging from the $-\Delta H$ values for the complexes with I_2, is given by the sequence Se > S > O. The same order was found by UV spectroscopy for the complexes with I_2, ICl, and IBr.[170] The opposite order is observed for the complexes with tin tetrachloride: O > S ⩾ Se. The values of $\Delta\nu_{OH}$ and $\Delta\nu_{NH}$ in the IR spectra of a number of proton donors (naphthol, phenol, pyrole, halogenated alcohols) in their reaction with the compounds $(C_6H_5)_3P=O(S)(Se)$ showed that

their ability to form H-complexes also decreases in the order O > S > Se.[171] Since the differences in the influence of steric factors in complex formation involving these compounds are apparently small, the reversal of the order of their donor properties in the H-complexes and the complexes with $SnCl_4$, compared with I_2, is apparently related chiefly to the conditions of overlap of the interacting orbitals of the molecules of the donor and acceptor, as noted above. The complexes of phosphine selenides of the series $(C_6H_5)_n.(C_4H_9)_{3-n}P{=}Se$ (n = 1–3) with HgX_2 and CdX_2 (X = Cl, Br) have been studied by ^{31}P NMR.[172] The spin–spin coupling constant $^1J(^{31}P-^{77}Se)$ decreases on complex formation, in agreement with IR spectroscopic data ($\Delta\nu_{P=Se}$).

There are almost no published data on the electron-donor properties of compounds containing P=Se bonds. UV spectroscopy has been used to study complex formation by a number of cyclic selenoamides with iodine.[173] The temperature dependence of the equilibrium constants was used to determine the enthalpies of formation of the complexes, which vary over a fairly wide range (6.0–12.0 kcal mole^{-1}), depending on the substituents.

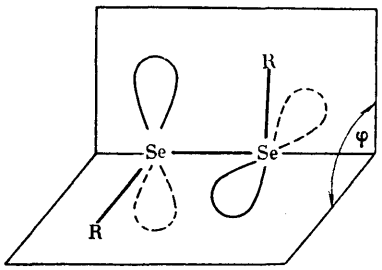


Figure 2. Spatial structure of organic diselenides.[177]

Table 5. Structural parameters of diselenides.

Diselenide	r, Å C–Se, Se–Se		Angle C–Se–C, °	θ, °	Method	Refs.
$(CH_3Se)_2$ (XXVIII)	1.954	2.326	98.9	87.5	ED	[174]
$(CF_3Se)_2$ (XXIX)	2.018	2.292	98.0	—	ED	[175]
$[(C_6H_5)_2CHSe]_2$ (XXX)	1.97	2.285	100.1	82	XRD	[176]
$(C_6H_5Se)_2$ (XXXI)	1.93	2.29	106±2	82	XRD	[177]
$(C_6F_5Se)_2$ (XXXII)	1.910	2.319	98.7	75.3	XRD	[178]
$(4\text{-}CH_3C_6H_4Se)_2$ (XXXIII)	1.915	2.328	101.6	80.3	XRD	[179]
$(4\text{-}ClC_6H_4Se)_2$ (XXXIV)	1.93	2.333	101.1	74.5	XRD	[180]
(XXXV)	1.910	2.364	—	—	XRD	[181]

IV. THE STRUCTURE AND ELECTRON-PROPERTIES OF DISELENIDES

Diselenides R–Se–Se–R, like other compounds of the oxygen sub-group with dielement bonds, have a skewed conformation (Fig.2). Structural data (Table 5) show that the interplanar angle C–Se–Se/Se–Se–C (θ) is 75–90°, depending on the composition and structure of R. The Se–C_{sp^3} bond lengths (1.95–2.02 Å) in the molecules of aliphatic diselenides are longer than the Se–C_{sp^2} bond lengths (1.91–1.93 Å) in aromatic diselenides (Table 5). The reason for the observed differences is apparently analogous to that examined above in the analysis of the bond lengths in monoselenides. The Se–Se bond lengths depend on the composition and structure of the groups R, vary over a fairly wide range from 2.28 Å to 2.33 Å for the diselenides indicated in Table 5, and differ from the value 2.34 Å for the length of the ordinary Se–Se bond in elemental selenium.[182]

The main factors responsible for the skewed conformation of diselenides (Fig.2) are: a) the mutual repulsion of the $4p^2$ lone pairs of electrons of the selenium atoms; b) the possibility of additional $p_\pi-d_\pi$ Se–Se bonding; and c) the mutual repulsion of the groups R. Quantum-chemical calculations of the barrier to rotation relative to the diselenide bond in dimethyl diselenide, carried out by the CNDO/2 method with optimisation of the geometry[183] and by the expanded Hückel method,[184] and also non-empirical calculations using different basis sets,[185] showed that they are fairly high. Thus according to these data, the energy of the conversion of the skewed conformation (θ ≃ 90°) into the *cis*-form (θ = 0°) has the values 6,[184] 11.19,[185] or 18.09 [2185] kcal mole^{-1}, and the energy of the conversion into the *trans*-form (θ = 180°) has the values 3,[184] 4.86,[185] or 11.51 [185] kcal mole^{-1}. Analogous calculations of the barrier to rotation relative to the diselenide bond in the $CF_3Se-SeCF_3$ molecule gave the values 45 kcal mole^{-1} for the *cis*-form and 15 kcal mole^{-1} for the *trans*-form.[184] The determination of the barriers to rotation (kcal mole^{-1}) from the temperature dependence of the ^1H NMR spectra of a number of aromatic diselenides gave the following results:

$C_6H_5CH_2Se-SeC_6H_5$	6.3	[186]
$(C_6H_5CH_2)_2Se_2$	<5.6	[186]
$[2,4,6\text{-}(t\text{-}C_4H_9)_3C_6H_2]_2Se_2$	12.5	[187]

The barrier to rotation in the diselenides is ~20% lower than that in the corresponding disulphides.[186] The greater length of the Se–Se bond, compared with that of the S–S bond, apparently decreases the interaction in the diselenide bond, compared with the disulphide. This can explain the lower stability of polyselenides (for example triselenides) compared with polysulphides. It has been suggested[188] that bulky groups such as $[(CH_3)_3Si]_3C$ can stabilise polyselenide bridges. The structure of the triselenide $[(CH_3)_3Si]_3C-Se-Se-Se-C[Si(CH_3)_3]_3$ has been determined.

The measured dipole moments of aromatic diselenides[189–193] indicated that in inert solvents, as in the crystalline state, the diselenides have a coiled conformation; the dihedral angle is 72–85°. The temperature dependence of the dipole moments of diphenyl diselenide and its symmetrically disubstituted derivatives (CH_3, F, Br) confirmed the skewed conformation of the molecules in solution (benzene, 298°) and slight oscillation or rotation of the ArSe groups about the Se–Se bond with increase in temperature.[191] The dipole moments and Kerr constants of disubstituted diphenyl diselenides were used to estimate not only the dihedral angles θ but also the angles of rotation of the phenyl rings (Φ) relative to the C–Se–Se plane in the diselenides studied.[190,192] When electron-donor substituents ($N(CH_3)_2$, OCH_3, CH_3) are introduced into the 4 and 4′ positions of the phenyl rings, the angle Φ increases in proportion to the electron-donor strength of the substituent. On the other hand, strong electron-acceptor substituents (for example NO_2) lead to flattening of the $4\text{-}NO_2C_6H_4Se$ fragment (angle Φ ≃ 0). A linear relationship was established between $\cos^2\Phi$ and σ^+ for the substituent. The dependence of the observed increase in the polarisability of diaryl diselenides on the nature of the substituent has been interpreted in terms of possible conjugation of the two aromatic fragments through the dislenide bridge.[189,192] The possible interaction of the π-electron system of the phenyl rings with the diselenide bridge is indicated by the results of quantum-chemical calculations (Del Re, SSP-PPP), the dipole moments, and the magnitude of the π-charges on the atoms of diphenyl diselenide and a number of

its 4,4′-disubstituted derivatives.[194] Evidence of intramolecular π-electron interaction involving the diselenide bridge of diaryl diselenides is provided by the dependence of the observed changes in the integral intensity of the absorption bands of the Se–Se bond in the Raman spectra on the nature and position (*ortho*, *meta*, *para*) of the substituents.[195] Electron-donor substituents, which increase the electron density of the diselenide bond and hence its polarisability, lead to an increase in the intensity of the corresponding band in the Raman spectrum. For the substituents CH_3, OCH_3, and $N(CH_3)_2$, its value was greatest for 4,4′-dimethylaminodiphenyl diselenide. The decrease in intensity on going from the *para*- to the *ortho*- or *meta*-substituted diphenyl diselenides indicates a decrease in the degree of interaction of the $p\pi$-conjugation type between the diselenide bridge and the substituents in the isomer order indicated.[195] Evidence of $p\pi$-electron interaction between the diselenide bridge and the aromatic fragments of diaryl diselenides is also provided by the observed linear dependence of the intensity of the Raman bands assigned to the Se–Se bond on the angle of rotation of the phenyl ring. The vibrational wavenumbers of the Se–Se bond for different dislenides lie in the range 270–300 cm^{-1}.[195–200]

The UV spectra of aliphatic diselenides contain one absorption band at about 310 nm.[201] The appearance of this band is usually attributed to an electron transition from the HOMO, formed by a n^--combination of the atomic orbitals of the LPE of the selenium atoms, into the antibonding σ*-orbital of the diselenide bridge. The UV spectra of aromatic diselenides contain three absorption bands at ~250, 270, and 330 nm.[202] The spectral characteristics of the long-wave band are apparently analogous to those of the band observed in the spectra of aliphatic diselenides. The electron transitions at shorter wavelengths are analogous to the absorption bands of selenoanisole, and are probably due to the transfer of electron density from the diselenide bridge to the aromatic fragments.

The formation of the molecular orbitals and the nature of the electron transitions in aromatic diselenides and their isologues were examined in Ref.202.

Valuable information on the nature of the intramoelcular electronic interactions in diselenides has been obtained by ^{77}Se NMR,[203,204] and more particularly by combined ^{13}C and ^{77}Se NMR studies.[205] Comparison of the value of δ $^{13}C(4)$ and δ $^{13}C(3, 5)$ of diphenyl diselenide with δ ^{13}C for benzene showed that the C_6H_5. .SeSe group behaves as both a π-donor and a δ-acceptor towards the phenyl ring, increasing the shielding of C(4) and decreasing the shielding of C(3, 5). The specific features of the influence of substituents in the phenyl rings on the shielding of the selenium atoms of diselenides have been established.[205]

There are extremely few published data on the complex-forming power of diselenides. Spectrophotometry has been used to study complex formation by a number of 4,4′-disubstituted diphenyl diselenides with iodine in heptane.[206,207] Irrespective of the component ratio in the solution, the diaryl diselenides react with I_2 to form 1 : 1 complexes. In contrast to this, in the dimethyl diselenide–I_2 system, 1 : 2 complexes are formed in addition to the 1 : 1 compounds.[206] The difference in the behaviour of the dialkyl and diaryl diselenides in their reactions with I_2 to some extent reflects the difference in their electronic states. Calculations of the electron density distribution by the Del Re and HMO methods showed that the effective (σ + π) electronic charge on each selenium atom of the diphenyl diselenide molecule is much lower than the σ-charge on the selenium atom in the dimethyl diselenide molecule.[206] The results of this calculation indicate that the localisation of electron density on the selenium atoms is greater in dimethyl diselenide than in diphenyl diselenide. This on the one hand confirms the $p\pi$-conjugation in aromatic compounds of selenium and on the other hand explains the differences in the donor properties of aromatic and aliphatic diselenides.

Spectrophotometry has been used to study complexes of diphenyl diselenide and its disubstituted derivatives with tetracyanoethylene.[207,208] 1 : 1 complexes are formed in the systems studied. The spectra of the complexes, like the spectra of the complexes of TCE with diaryl monoselenides, contain two CTB. The position of CTB_1 depends on the nature of the substituents in the aromatic fragments. A linear relationship was established between $h\nu_{max}(CTB_1)$ and $\Sigma\sigma^+$. The position of CTB_2 is approximately the same in the spectra of all the complexes (380–390 nm). The spectral characteristics of the complexes of TCE with diaryl diselenides were used, in accordance with Eqn.(1), to estimate the ionisation potentials of the latter. The ionisation potentials were obtained for a large group of *p*-disubstituted diphenyl dislenides. The ionisation potential of diphenyl diselenide, found from the correlation equation (1) (8.2 eV),[208], shows good agreement with the value of IP_1, 8.3 eV, determined by PES.[193] PES has been used to determine the ionisation potentials of a number of compounds with dielement bonds, of the type $(CH_3)_2XYCH_3$, where X = P, As; Y + S, Se. The experimental IP_1 values have been compared with the calculated (CNDO/2) energies of the HOMO. The first two PES bands are due to the removal of electrons from orbitals which are linear combinations of orbitals occupied by the LPE of the corresponding heteroatoms.[209]

The heat of formation of the complex of diphenyl diselenide with phenol has been estimated by IR spectroscopy. The donor properties of the selenium atom in the diselenide are much weaker than in the monoselenide: 1.9 kcal $mole^{-1}$ and 3.3 kcal $mole^{-1}$ respectively.[135]

Table 6. Ionisation potentials of diselenides (eV) and the dipole moments (μ_c, D) and enthalpies of formation ($-\Delta H_c^0$, kJ $mole^{-1}$) of their complexes with $GaCl_3$ (benzene, 298 K).[210]

Complex	IP_1 diselenide (Ref.207)	μ_c	$-\Delta H_c^0$
$(4\text{-}CH_3C_6H_4)_2Se_2\cdot GaCl_3$	8.07	8.6	87
$(C_6H_5)_2Se_2\cdot GaCl_3$	8.21	7.5	82
$(4\text{-}FC_6H_4)_2Se_2\cdot GaCl_3$	8.28	—	80
$(4\text{-}ClC_6H_4)_2Se_2\cdot GaCl_3$	8.28	6.2	79
$(4\text{-}BrC_6H_4)_2Se_2\cdot GaCl_3$	—	6.5	77

Cryometric, calorimetric, and dielectric constant measurements have been used to study complex formation by a number of diaryl diselenides with gallium trichloride. Irrespective of the reagent ratio in these systems, the 1 : 1 complexes are formed. Only one of the selenium atoms of the diselenide bridge forms a donor–acceptor bond with the gallium halide. The high values of the dipole moments and the heats of formation of the complexes (Table 6) indicate that they are *nv*-complexes, like the complexes formed by monselenides with aluminium tribromide.[129] Table 6 shows that the donor properties of the selenium atom in diaryl diselenides, characterised by the $-\Delta H_c^0$ values, depend on the nature of the substituents in the ring. Electron-donor substituents (CH_3) increase the strength of the intermolecular Se → Ga bond, and halogen atoms (F, Cl, Br) decrease it. Although the data are limited, the relationship between the $-\Delta H_c^0$ values and the constants σ of the substituents can be followed.[210] A correlation is also observed between the $-\Delta H_c^0$ values and the ionisation potentials the diselenides, obtained from spectrophotometric data for the charge-transfer complexes (CTC) with TCE.[207] An attempt to determine the thermodynamic parameters of complex formation by diaryl diselenides with the stronger

acceptor aluminium tribromide led to the discovery of a new method for generating and stabilising selenium-containing radicals (see below).

Thus published data on the coordination properties of organic diselenides indicate that only the first steps have been taken in this field.

Table 7. *g*-Values and line widths (G) in the EPR spectra of diaryl diselenide – aluminium tribromide – benzene systems at 298 K.[210]

Diselenide	Signal No. in the EPR spectrum		
	I	II	III
$(C_6H_5)_2Se_2$	2.0761 (23.75)	2.0300 (9.60)	2.0021 (1.67)
$(4\text{-}FC_6H_4)_2Se_2$	2.0694 (17.50)	2.0332 (5.83)	2.0025 (6.25)
$(4\text{-}ClC_6H_4)_2Se_2$	2.0730 (23.30)	2.0380 (11.70)	2.0027 (5.42)
$(4\text{-}BrC_6H_4)_2Se_2$	2.0744 (24.17)	2.0319 (12.50)	2.0026 (4.58)

V. SELENIUM-CONTAINING FREE RADICALS

Free radicals containing an unpaired electron on a selenium atom have been little studied. Until recently, the possible participation of selenium-centred radicals in chemical reactions was doubted. Thus in a published review[2] it was noted that there is very little published information on the preparation and chemistry of organoselenium radicals, and from its analysis it was concluded that there is no convincing proof that organoselenium radicals take part in the processes examined. A similar conclusion that the existence of organoselenium radicals has not been proved was reached in Ref.211. At the same time, photochemical reactions involving organoselenium compounds are acquiring increasing importance in present-day organic synthesis, and the mechanism of these reactions is discussed in terms of the formation of selenium-centred radicals.[212] Selenium-centred radicals have been detected by EPR in the low-temperature photolysis of a number of organic selenides and diselenides;[213–215] determination of the *g*-values showed that they are greater for radicals containing selenium (2.095 – 2.099) than for sulphur-containing radicals (2.06).[214] The EPR spectrum of the photolysis products of organoselenium compounds in a number of cases are much more complex than the corresponding spectra of the sulphur compounds. It has been shown that, in contrast to sulphur compounds, the photolysis and radiolysis of various selenium compounds, in particular diselenides, are accompanied by the rupture of not only the Se – Se bond but also the C – Se bond, to give the radicals R$^{\cdot}$, RSe$^{\cdot}$, and RSe – Se$^{\cdot}$.[213,215,216] This distinguishes the photochemistry of the diselenides from that of the disulphides, where only the S – S bond is broken, to give RS$^{\cdot}$ radicals. Interesting results were obtained in a study of the photolysis of a number of selenides and diselenides in the presence of nitrosodurene, used to trap radical species.[217] In a number of systems, EPR detected the selenylnitroxide radical. The mechanism of the process was found to depend on the composition and structure of the organoselenium compound. Thus dibenzyl diselenide and diphenyl diselenide react differently on ultraviolet irradiation in the presence of nitrosodurene; the C – Se bond is broken in the first compound, and the Se – Se bond in the second.[217] In addition, studies of the photochemical reactions of a number of diselenides with tertiary phosphines[218,219] showed that, irrespective of the nature of R in the R_2Se_2 molecule (CH_2, C_2H_5, $CH_2C_6H_5$, C_6H_5) and the composition of the phosphine [$CH_3(C_6H_5)_2P$, $(CH_3)_2C_6H_5P$, $(C_6H_5)_3P$], the reaction

$$R_2Se_2 + Ar_3P \xrightarrow{h\nu} R_2Se + Ar_3P{=}Se$$

takes place by a chain mechanism, and the first stage in all cases is the rupture of the diselenide bond. This reaction has been recommended as a method for synthesising the corresponding selenides, and phosphine selenides, since it gives almost quantitative yields of the products under mild conditions.

Thus organoselenium free radicals, like the sulphur-containing radicals, formed by photolysis and radiolysis, are unstable. They are detected only at low temperatures in solid matrices. The stability of free radicals is usually increased by increasing the delocalisation of the electron spin density, and also by steric shielding of the atoms carrying the unpaired electron.[211] Complex formation has been proposed[220–222] as a new effective method for generating and stabilising free radicals containing a heteroatom. Thus stable sulphur-containing radicals of the type $ArS^{\cdot}.MX_3$ were obtained for the first time by the reaction of diaryl disulphides with strong electron acceptors (aluminium and gallium halides). The formation of these radical complexes results from the decrease in the strength of the disulphide bond on complex formation, and the homolytic rupture of the bond when the interactions are sufficiently strong. Quantum chemistry has shown that the free electron of the radical complex is localised chiefly on the sulphur atom. The properties and reactivity of a number of radical complexes $RS^{\cdot}.MX_3$ have been studied.[223,224] Studies of similar reactions of diaryl diselenides with aluminium tribromide and gallium trichloride in benzene or cyclohexane[210,225] have shown that the first stage is the formation of 1 : 1 donor – acceptor complexes. This stage, like all complex-formation reactions, is very rapid. The second stage, leading to the rupture of the corresponding bonds with the addition of a second molecule of the halide to the 1 : 1 complex, is slower. Its rate depends on the nature of the acceptor and the aryl fragment of the diselenide. As noted above, the relatively low rate of the second stage of the reaction of diaryl diselenides with gallium trichloride made it possible to measure the heat of formation and dipole moments of the complexes $Ar_2Se_2.GaCl_3$, formed in the first stage.[210] Freshly prepared benzene solutions of the complexes of diaryl diselenides with gallium trichloride do not give signals in the EPR spectra. When solutions containing an excess of gallium trichloride are left to stand, a brightly coloured oil separates, and signals appear in the EPR spectra, indicating the presence of paramagnetic species. In the reaction of diaryl diselenides with a stronger electron acceptor (aluminium tribromide) in benzene or cyclohexane, the separation of paramagnetic products is observed when the components are mixed. The EPR spectra of $Ar_2Se_2 - AlBr_3$ – benzene systems contain three singlets. The high *g*-values of the singlets I ($\sim$2.070) and II ($\sim$2.030) differ considerably from the *g*-value of the free electron (2.0023); the large line width makes it possible to assign them to radicals containing a heavy atom, in this case selenium. In view of what has been said on the possible rupture of the C – Se and Se – Se bonds in the diaryl diselenide molecule, the observed singlet I ($g \simeq 2.07$) was assigned to the radical complex $ArSeSe^{\cdot}.AlBr_3$, and the singlet II ($g \simeq 2.03$) to the radical complex $ArSe^{\cdot}.AlBr_3$. This assignment was confirmed by the signal in the EPR spectrum of the $(C_6H_5)_2Se - AlBr_3$ – benzene system, where only the rupture of the C – Se bond is possible, to give the radical complex $C_6H_5Se^{\cdot}.AlBr_3$. The spectrum of this system contains a singlet with a *g*-value of 2.034, which was assigned to singlet II (the radical complex $C_6H_5Se^{\cdot}.AlBr_3$). The *g*-value and the form of the third singlet in the EPR spectra of $Ar_2Se_2 - AlBr_3$ – benzene systems differ from those of the singlets assigned to the selenium-centred radicals. The *g*-value, which is close to that of the free electron, indicates that this singlet is due to a stabilised hydrocarbon radical, formed by the homolytic rupture of the C – Se bond.

The proposed mechanism of the reaction of diaryl diselenides with aluminium tribromide was confirmed by gas–liquid chromatography (GLC). The displacement of the radicals from the complexes formed in the $(C_6H_5)_2Se_2-AlBr_3-$benzene system by a stronger donor (D = $(C_2H_5)_2O$, H_2O) gives the complexes D.$AlBr_3$ and the products of the reaction of the displaced free radicals. GLC showed that the reaction mixture contains diphenyl diselenide, diphenyl selenide, and diphenyl. Other products, including C_6H_5SeH and C_6H_5Br, were not detected. Like the thiyl radical complexes Ar$^{\cdot}$.MX_3, the selenium-containing radical complexes are highly stable; the EPR spectra of specimens in sealed ampoules (in the absence of moisture) remain unchanged for a long time (several months). By analogy with the radical complexes ArS$^{\cdot}$.MX_3,[223] the stability of the organoselenium radical complexes is apparently due to the following effects: a) a decrease in the electron density on the selenium atom on formation of a donor–acceptor bond involving a lone pair of electrons of the selenium atom and a vacant orbital of the metal atom, and a consequent lowering of the level of the orbital of the unpaired electron; b) the steric shielding, by the acceptor molecule MX_3, of the selenium atom carrying the free electron.

The formation of radical complexes by the reaction of diaryl diselenides with the halides of group III metals has been observed not only when the reaction is carried out in solution, but also when the components are fused together. The EPR spectra indicate that the nature of the radical complexes formed is the same for the reactions in the melt and in solution.[210]

Thus complex formation by diaryl selenides and diaryl diselenides with strong electron acceptors can provide a source of stable selenium-centred radicals.[210,225]

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Karpov Physicochemical
Scientific Research
Institute, Moscow