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DONOR-ACCEPTOR NATURE OF SPECIFIC NONBONDED INTERACTIONS OF SULFUR
AND HALOGEN ATOMS. INFLUENCE ON THE GEOMETRY AND PACKING
OF MOLECULES

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The nature of the specific nonbonded contacts of atoms X (S, Cl, Br, and I) with other atoms has been discussed on the basis of the current ideas regarding van der Waals interactions with the use of "natural bond orbitals" (NBO's) and "equivalent orbitals" (EO's). It has been shown that a decisive role in the formation of specific nonbonded contacts is played by the interaction of one of the NOB's with one of the EO's, and the change in the electronic structure of partners occurring as a result of the appearance of a specific nonbonded contact enhance the interaction. The conclusions drawn have been confirmed by x-ray structural data on the distribution of the electron density and by the stereochemical features of the environment of atoms of X in crystals. The proposed approach makes it possible to supplement the principle of the closest packing of molecules in a crystal with the principle of the maximal overlap of the orbitals cited, as well as to use widely accepted chemical conceptions to interpret specific nonbonded contacts and the special features of the packing molecules associated with them.

In many organic crystals the distances from an atom of X to another atom of any element A not covalently bonded to it may be significantly smaller than the sum of the van der Waals radii $R_X + R_A$ (or the quantity $2\sqrt{R_X R_A}$). This provides some basis to state that there are specific (enhanced) van der Waals interactions involving the atoms of X. In order to understand the nature of such specificity, we shall take advantage of some modern quantum-chemical theories [1]. The Hartree-Fock energy of an intermolecular interaction can be separated into two parts:

$$\Delta E = \Delta E_{oo} + \Delta E_{ou}. \quad (1)$$

The first term consists of the energy of the interaction of the occupied orbitals of one molecule with the occupied orbitals of another molecule, and the second term consists of the energy of the interaction of the occupied orbitals of one molecule with the unoccupied orbitals of another molecule. The first term supplemented by a correction for electron correlation, thus corresponds to the classical components of the energy of an intermolecular interaction (the orientational, polarization, dispersion, and exchange components). As we know, these components can be described with a good degree of accuracy in the framework of additive schemes, among which the systems of van der Waals radii [2] and atom-atom potentials [3] are most widely known.

The second term corresponds to the nonclassical decrease in the energy resulting from the mixing of occupied (donor) and unoccupied (acceptor) orbitals, which equals (in second-order perturbation theory)

$$\Delta E_{ou} = -k S_{ou}^2 / (\epsilon_u - \epsilon_o), \quad (2)$$

where ϵ_u and ϵ_o are the energies of the unoccupied and occupied orbitals, S_{ou} in their overlap integral, and k is a constant [1]. Such an interaction can similarly be described as a donor-acceptor (DA) chemical bond appearing between a nucleophile Nu (a Lewis base) and electrophile El (a Lewis acid). Therefore, it would be logical to call it donor-acceptor (or Lewis acid-base) on the basis of its mechanism of formation and "chemical" on the basis of its nature (in contrast to the classical components of an intermolecular interaction, which have a "physical" nature). A synonym for a DA interaction is a "charge-transfer inter-

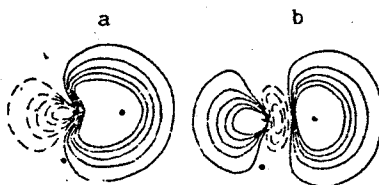


Fig. 1. Contour maps of the natural bond orbitals in the molecule of H_2O (data from [1]): a) $\sigma(\text{OH})$; b) $\sigma^*(\text{OH})$.

action." This should not be taken literally, since an interaction which is significant according to the value of its energy (~ 1 kcal/mole) may correspond to an insignificant amount of transferred charge (~ 0.001 e) [1].

The dependence of ΔE_{ou} on the form and the mutual orientation of the orbitals (the directedness of DA interactions) sometimes results in appreciable deviations of the structure and other properties of a substance from those predicted on the basis of atomically additive models. It was shown in [4] and confirmed in [5], for example, that the use of isotropic atom-atom potentials does not make it possible to obtain the experimentally observed crystal structure of Cl_2 .

It is easier, however, to detect deviations from the scheme of van der Waals radii: in the case of this scheme it is sufficient to demonstrate that the distance d_{AB} between not covalently bonded atoms A and B in a crystal $d_{\text{AB}} < R_{\text{A}} + R_{\text{B}} + \delta$ [2]. Such a pair of atoms is usually called a shortened (or specific) nonbonded contact. At the same time, this distance exceeds the usual length of an A-B covalent bond (i.e., the sum of the covalent radii r) or, stated differently, $d_{\text{AB}} > r_{\text{A}} + r_{\text{B}}$ (bond). It is convenient to characterize a diatomic fragment (A, B) by the "covalency ratio" [1]:

$$\chi_{\text{AB}} = \frac{R_{\text{A}} + R_{\text{B}} - d_{\text{AB}}}{R_{\text{A}} + R_{\text{B}} - r_{\text{A}} - r_{\text{B}}}$$

The value of χ_{AB} can vary from 1 (an ordinary bond) to 0 (a normal nonbonded contact) and even down to $-\infty$ (the absence of a contact).

The purpose of the present work was to discuss the orbital nature of an X...A specific nonbonded contact in detail with the use of literature data from x-ray structural investigations of organic crystals and quantum-chemical calculations. In Section 1 we shall substantiate the need to use natural antibonding orbitals and the hybrid orbitals of lone pairs to describe specific nonbonded contacts, and we shall propose using the principle of maximal overlap of these orbitals to interpret and predict the angular characteristics of a specific nonbonded contacts. It will also be shown that the specific nonbonded contacts of the atoms of X in crystals obey this principle in the statistical-mean sense. An analysis of theoretical maps of the fragment deformation density in the molecular complex $\text{HF} \dots \text{ClF}$ in section 2 shows that the polarization of the interaction molecules plays a decisive role in the redistribution of the electrons upon formation of the complex (although its energy effect is insignificant). As a result of polarization, the overlap of the orbitals cited becomes more effective. The reality of the hybrid orbitals of lone pairs and the conclusions of Section 2 will be confirmed in Section 3 by experimental data.

In Section 4 it will be shown in the case of p-substituted biphenyls that the principle of closest packing must be supplemented by the principle of maximal overlap in interpreting the structure of molecular crystals with specific contacts. Some other consequences of the orbital nature of specific nonbonded contacts will be examined in Section 5.

1. STEREOCHEMICAL FEATURES OF SHORTENED NONBONDED CONTACTS OF ATOMS OF X

When the charge-transfer energy E_{ou} is calculated, the unoccupied and occupied orbitals may be selected by different methods. It is more convenient to select them such that the main contribution to E_{ou} would be made by only one pair of interacting orbitals. In the case of π complexes of flat conjugated molecules, the interaction of the canonical frontier molecular orbitals (the highest occupied and the lowest unoccupied orbitals) predominates. How-

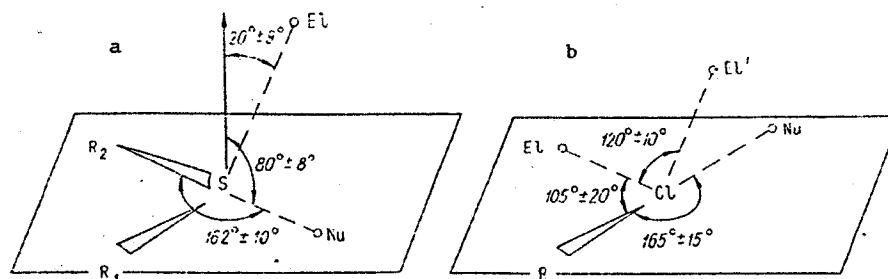


Fig. 2. Mean values and standard deviations of the angular characteristics of the contacts of S (a) and Cl (b) atoms obtained as a result of a statistical analysis of the Cambridge Structural Database [8, 9].

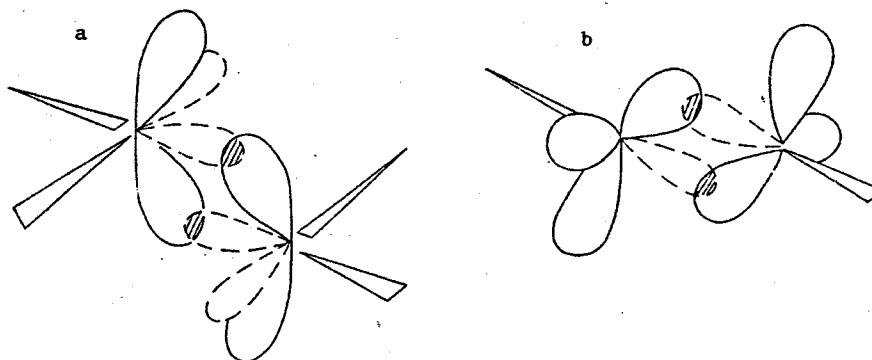


Fig. 3. Scheme of the overlap of antibonding orbitals (dashed lines) with hybrid orbitals of lone pairs (solid lines) in symmetric nonbonded S...S (a) and Cl...Cl (b) contacts. The regions of overlap are hatched.

an important role is frequently played (in $n-v$ and $n-\sigma$ complexes) by all the canonical orbitals in which the lone pairs of the donor atom appear [6]. The transition from canonical to natural bond orbitals, which can be obtained by block diagonalization of the density matrix [1], makes it possible to single out the dominant two-orbital interaction. After such a transition, the value of E_{ou} can be obtained with the aid of a nonempirical calculation or in an approximation with the use of Eq. (2). In that case it is sufficient to take into account only one of the occupied orbitals of the donor molecule [a bonding (σ or π) or a nonbonding (n) orbital] and one unoccupied orbital of the acceptor molecule [an antibonding (σ^* or π^*) bond].

Natural bond orbitals are in good agreement with the chemical conceptions of localized bonds. If an A-B σ bond is formed by hybrid orbitals (h) of atoms A and B and has the form

$$\sigma(AB) = C_A h(A_B) + C_B h(B_A), \quad (3)$$

the antibonding orbital orthogonal to it will be

$$\sigma^*(AB) = C_B h(A_B) - C_A h(B_A). \quad (4)$$

The orbital $\sigma(AB)$ is localized mainly in the internuclear region (Fig. 1a), and the $\sigma^*(AB)$ orbital is localized along the line of the bond beyond the atoms (Fig. 1b).

As quantum-chemical calculations of molecular complexes have shown, in the case of donor specific nonbonded contacts of sulfur and oxygen, the s -orbital character of the lone pair participating in a DA bond and that of the lone pair not participating in such a bond are equalized [6]. This points out the correctness of using equivalent (hybrid) orbitals of lone pairs (n) to describe intermolecular forces.

After the occupied and unoccupied orbitals whose overlap mainly determines the DA part of the interaction energy and, therefore, the specificity of a nonbonded contact have been identified in this manner, we can use the principle of maximal overlap to interpret and predict the special features of specific nonbonded contacts. For example, according to the data from microwave spectroscopy in [7], the geometric parameters for the complex HF...ClF

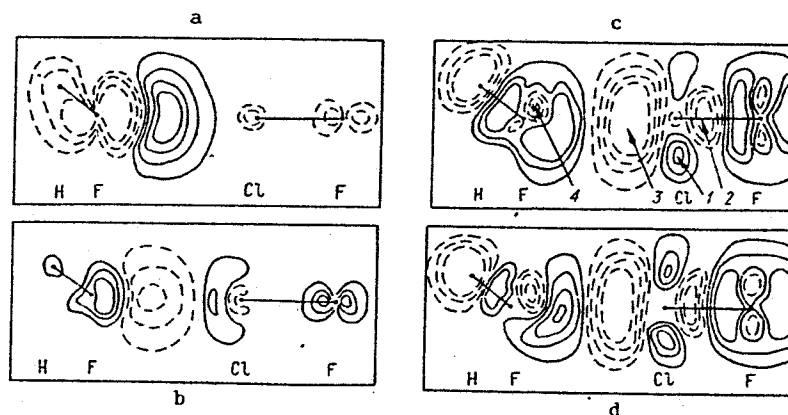


Fig. 4. Maps of the fragment deformation density corresponding to different components of the intermolecular interaction in the complex HF...ClF (according to the data from the quantum-chemical calculation in [11]): a) Donor-acceptor component; b) exchange contribution; c) polarization component; d) overall picture.

in the gaseous phase are: $d(\text{F} \cdots \text{Cl}) = 2.76 \text{ \AA}$; $\chi(\text{F} \cdots \text{Cl}) = 0.34$; $\angle \text{HFC1} = 115^\circ$; $\angle \text{FC1F} = 175^\circ$. On the basis of the values of the angular parameters, we may conclude that the acceptor Cl atom is positioned in the direction of the $n(\text{F})$ orbital and that the donor F atom is located along the $\sigma^*(\text{ClF}')$ orbital. Such a configuration ensures achievement of the maximum of S_{no}^* . In addition, angular parameters of the complex under consideration that are close to the experimental values can apparently be obtained by restricting the molecules to the external surface of the nonoverlapping van der Waals atomic spheres and attaining maximal overlap of $n(\text{F})$ and $\sigma^*(\text{ClF}')$ by altering the relative orientation of the molecules. The balance between E_{no}^* and the exchange-repulsion energy must be considered in order to obtain the linear characteristics. The pair of interacting orbitals must be selected on the basis of the orbital energies, but in many cases it can be selected on the basis of chemical conceptions of the DA capacity of the functional groups.

In a crystal the influence of the environment distorts the equilibrium geometry of specific nonbonded contacts. However, the laws noted are maintained on the average. For example, an analysis of the Cambridge Structural Database [8] revealed the existence of 54 shortened contacts of an S atom with an atom of an electrophile El (Na, H, C, Cu, Ni, and Pd) and 99 shortened contacts with an atom of a nucleophile Nu (N, O, and F); in the cases of Cl, Br, and I 39 and 332, 4 and 397, and 4 and 60 specific nonbonded contacts, respectively, were discovered with the same electrophiles and nucleophiles [9].

The mean values and the standard deviations of the angular characteristics obtained as a result of analysis are shown in Fig. 2. It is seen that the atom of El approaches the atom of X (in a donor-type specific nonbonded contact) in the direction of the lone pairs (type I) and that the atom of Nu approaches it (in an acceptor-type specific nonbonded contact) along the antibonding orbitals of the X-C bond (type II). Contacts of type I are bent, and contacts of type II are linear.

The analyses in [9, 10] also considered specific nonbonded contacts between atoms of the same element (150 S...S contacts [10], 176 Cl...Cl contacts, 173 Br...Br contacts, and 66 I...I contacts [19]). It was discovered that in most of the X...X' contacts assigned to types I and II in those investigations, the CXX' angle is close to a straight angle, while the C'X'X angle is close to a right angle. It was found that atom X approaches atom X' in the contact of type I, while atom X' approaches atom X in a contact of type II. This means that the $n_{\text{X}'} - \sigma^* \text{CX}$ interaction is the main interaction. However, 20% of the X...X' contacts turned out to be symmetric and nearly linear ($\angle \text{CXX} \approx \angle \text{C}'\text{X}'\text{X} \approx 160^\circ$).

Such contacts were assigned to type III in [9, 10]. Obviously, the overlap integrals and the energies of the $n_{\text{X}'} - \sigma^* \text{CX}$ and $n_{\text{X}} - \sigma^* \text{C}'\text{X}'$ interactions in such specific nonbonded contacts are close. Therefore, they may be interpreted as two-way contacts, i.e., both atoms of X act as donors and acceptors. The hypothesis that the specific nonbonded contacts of type III have a "dual" character is confirmed by the fact that they are shorter on the average than the contacts of types I and II [9, 10]. The scheme of the overlap of the orbitals in a specific nonbonded contact of type III is presented in Fig. 3.

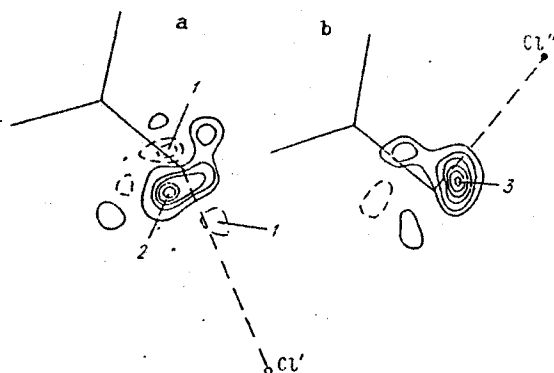


Fig. 5. Experimentally obtained [12] maps of the distribution of $\delta\rho$ near a Cl atom in a crystal of 2-amino-6-chloropyridine: a) Cross section drawn through the plane of the molecule (the acceptor contact is indicated by the dashed line); b) cross section drawn at a distance of 0.4 Å above the plane of the molecule (the donor contact is indicated by the dashed line). The Cl' atom is located 2.3 Å above the plane of the molecule, and the Cl'' atom is located 0.6 Å below the plane of the molecule.

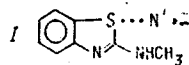
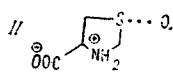
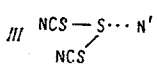
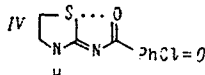
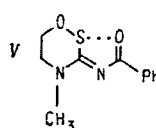
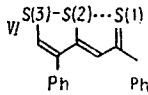
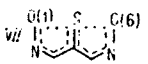
Thus, we see that the specific nonbonded contacts not only in nonbonded complexes, but also in crystals can be described satisfactorily as the result of the overlap of one or two pairs of isolated orbitals.

2. THEORETICAL ANALYSIS OF A NONBONDED Cl...F CONTACT

The redistribution of the electron density ρ upon the formation of a nonbonded contact makes it possible to obtain a picture of the function $\delta f\rho$ (the fragment deformation density), which can be obtained by subtracting ρ of the isolated molecules from ρ of the molecular complex. In [11] cross sections of $\delta f\rho$ and its components in the plane of the complex HF...ClF (Fig. 4) were obtained with the aid of a nonempirical calculation by the SCF method in the 4-31G** basis. Decomposition of the intermolecular interaction into components (according to the Kitaura-Morokuma method) made it possible to analyze its nature. The donor-acceptor component of the interaction (Fig. 4a) is manifested in the transfer of ρ from HF to the midpoint of the F...Cl segment. The small magnitude of the transferred charge renders this part of $\delta f\rho$ proportional to the overlap density of the $n(F)$ and $\sigma^*(ClF')$ orbitals. The exchange component (Fig. 4b), on the other hand, "expels" electrons from the intermolecular region, practically completely compensating for the charge-transfer effect. The energies of these two effects are also close in magnitude and opposite in sign. The energy of the polarization component of the interaction is an order of magnitude smaller, however, its contribution to the redistribution of ρ (Fig. 4c) determines the overall picture (Fig. 4d). Finally, the interaction of the donor-acceptor and polarization components (the polarization of the transferred charge) causes a negligibly small change in the energy, but it plays an appreciable role in the redistribution of ρ (it shifts the transferred charge in the direction of the F' atom) [11].

In our opinion, the changes in the electronic structure of the HF and ClF molecules as a result of polarization can be interpreted on the basis of the maps $\delta f\rho$ in the following manner. It is seen from Fig. 4c that the polarity of both molecules increases (this is consistent with the values of the Mulliken charges presented in [11]). According to Walsh's rule, when the polarity of an $A\delta^+-B\delta^-$ bond increases, the p character of the $h(A_B)$ orbital should increase, while that of the $h(B_A)$ orbital results in enhancement of the s character of the three $n(Cl)$ orbitals, which is manifested in the map of $\delta f\rho$ in the form of peak 1 (Fig. 4c). In fact, in the limiting case of a transition from the pyramidal configuration of the lone pairs (sp^3) to the planar triangular configuration (sp^2), the increase in the s character of the $n(Cl)$ orbitals should be accompanied by displacement of the π electrons of the Cl atom toward its covalent partner.

TABLE 1. Sulfur Compounds for Which the Distribution of $\delta\rho$ Has Been Studied Experimentally (d is the length; χ is the covalency ratio of the intra- or intermolecular acceptor contacts of the S atom)

	Structural formula	d	χ	Literature cited
I		3,80	-0,29	[13]
II		3,35	-0,27	[14]
III		3,08	0,17	[15]
IV		2,68	0,33	[16]
V		2,25	0,65	[16]
VI		S(1)-S(2) 2,48 S(2)-S(3) 2,12	0,75 0,91	[17]
VII		S-O(6) 1,836 S-O(1) 1,834	0,95 0,95	[18]

In addition, the increase in the polarity of ClF' is associated with a decrease in the contribution of the $h(\text{ClF}')$ orbital to the $\sigma(\text{ClF}')$ orbital. The population of the $h(\text{ClF}')$ orbital and its main component $p_\sigma(\text{Cl})$ undergoes a decrease in this case, which is manifested on the map of $\delta\rho$ in the form of minima 2 and 3 (Fig. 4c). According to Eqs. (3) and (4), a decrease in the contribution of the $h(\text{ClF}')$ orbital to $\sigma(\text{ClF}')$ signifies an increase in its contribution to $\sigma^*(\text{ClF}')$, which increases the overlap of $\sigma^*(\text{ClF}')$ with the nonbonding $n(\text{F})$.

For its part, the increase in the polarity of HF signifies an increase in the p character of the $n(\text{F})$ orbital, which is manifested in the form of withdrawal of the π electrons of the F atom away from the H atom (minimum 4 in Fig. 4c). As a result, the diffuseness of the $n(\text{F})$ orbital and the degree of its overlap with the $\sigma^*(\text{ClF}')$ orbital increases. When molecules are polarized, they are "prepared" for the appearance of a DA interaction.

Similar results were provided by the theoretical investigations of hydrogen bonds by the Kitaura-Morokuma method [11] and with the aid of natural bond orbitals [1]. Therefore, the conclusions which we have drawn apparently have a fairly general character. When a specific nonbonded contact is formed, the polarization of the partners makes a decisive contribution to the redistribution of the electrons (despite the comparatively small energy effect). The change in the electronic structure is confined to a decrease in the population of the acceptor orbital (and the acceptor atom as a whole), an increase in the s character of the lone pairs of the acceptor atom (if they are present), and a decrease in the s character of the lone pairs of the donor atom. The effectiveness of the DA interaction should increase as a result.

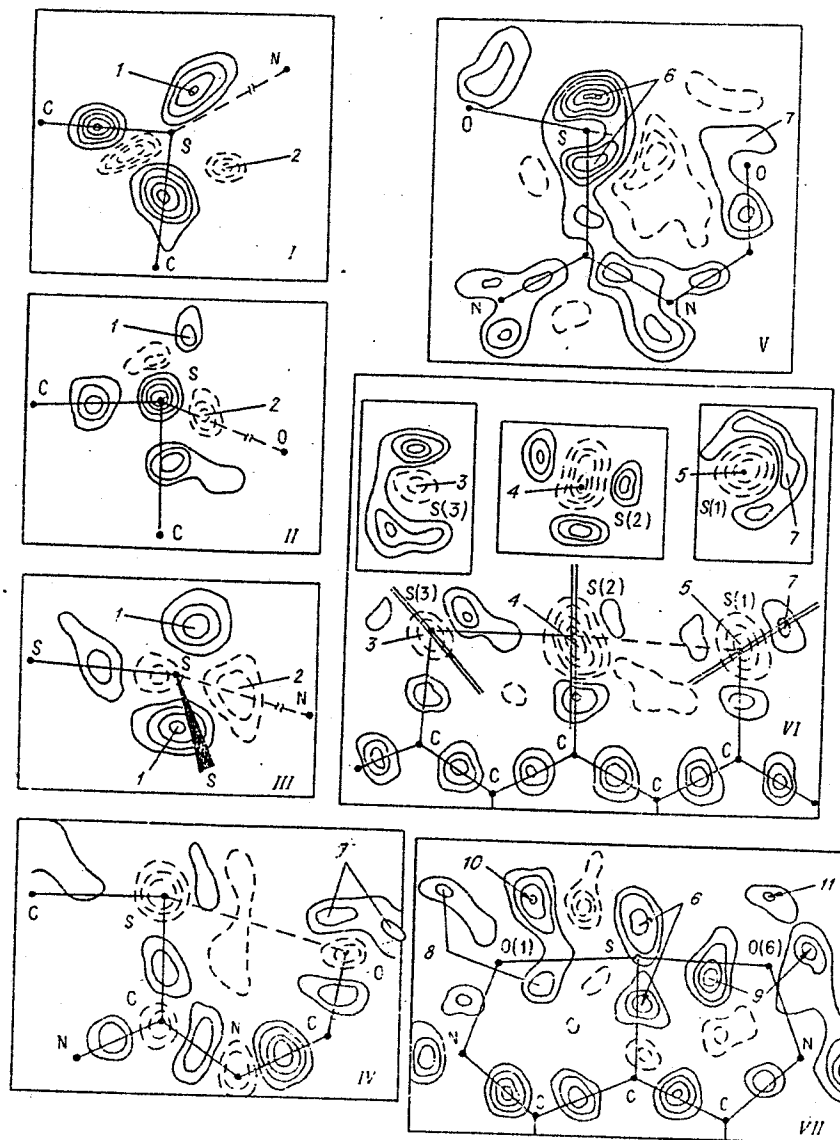


Fig. 6. Experimentally obtained maps of the distribution of $\delta\rho$ in the sulfur compounds listed in Table 1. All the cross sections except III are given in the plane of the molecule. In the case of compound VI, the figure is supplied with perpendicular cross sections, whole location is indicated by double lines.

3. ANALYSIS OF EXPERIMENTAL MAPS OF THE DEFORMATION DENSITY IN THE REGION OF SPECIFIC NONBONDED CONTACTS

Experimental data on the distribution of ρ can be obtained with the aid of precision x-ray diffraction analysis. Its results are most frequently presented in the form of maps of the deformation electron density $\delta\rho$, i.e., the difference between ρ of a molecule and the electron density of the set of free spherically symmetric atoms. In this case the changes caused by the nonbonded interactions are often masked by the stronger covalent effects. Nevertheless, important information can be extracted from maps of $\delta\rho$.

In a crystal of 2-amino-5-chloropyridine the Cl atoms form chains of nonbonded contacts with 2_1 crystallographic symmetry. In this case each Cl atom has one donor (type I) contact and one acceptor (type II) contact ($d = 3.70 \text{ \AA}$, $\chi = 0.06$). Two cross sections of $\delta\rho$ designated by the number 1 in Fig. 5a correspond to a decrease in the population of the p_σ orbital from 5/3 in the free atom to ~ 1 in the molecule. When there is no specific nonbonded contact, an approximately identical minimum and, in addition, a doughnut-shaped maximum, which is oriented in a plane perpendicular to the C-Cl bond and corresponds to its

TABLE 2. Type of Packing of Molecules and Specific Nonbonded Interactions in Crystals of Several Substituted Biphenyls

A-C ₆ H ₄ -C ₆ H ₄ -B	Structural class	Type of packing	Type of specific nonbonded contact	Literature cited
A = B = H	$P2_1/a$, $Z = 2(\bar{1})$	Layers	—	[19]
A = B = F	$P2_1/a$, $Z = 2(\bar{1})$	»	—	[20]
A = B = OH	$P2_1/a$, $Z = 2(\bar{1})$	»	OH ... OH ... OH	[21]
A = H, B = OH	$P2_1/a$, $Z = 4(1)$	»	»	[22]
A = H, B = OH	$P2_12_1$, $Z = 8(1^2)$	»	»	[22]
A = H, B = Br	$Pna2_1$, $Z = 8(1^2)$	»	I-II: —Br ... Br	[23]
A — B = SH	$P2_1/a$, $Z = 2(\bar{1})$	Layers and straight chains	III: HS ... SH	[24]
A = Br, B = CN	$P2_1/a$, $Z = 8(1^2)$	Straight chains	II: —Br ... NC—	[25]
A = B = Br	$P2_1/a$, $Z = 8(1^2)$	»	III: —Br ... Br—	[26]

lone pairs, are observed on the continuation of the C—Cl bond. In the case under consideration, on the other hand, the lone pairs are separated in space: one of them lies in the plane of the molecule (peak 2 in Fig. 5a), and another is directed toward the acceptor Cl atom (which lies 2.3 Å above the plane of the molecule), as is clearly seen in the other cross section (peak 3 in Fig. 5b). The third lone pair should be observed below the plane of the molecule (at the third vertex of the triangle formed by peaks 2 and 3 with its center at the nucleus of the Cl atom). Unfortunately, the information needed to test this hypothesis was not presented in [12].

Unlike the known examples of the doubling of the peak of $\delta\rho$ of a single lone pair under the influence of several electrophiles, in present case there is only one weak negatively polarized electrophile. Thus, the data on the distribution of $\delta\rho$ in crystals of 2-amino-5-chloropyridine provide a weighty argument in support of the correctness of the use of hybrid orbitals of lone pairs.

A considerably greater amount of experimental data has been obtained on the distribution of ρ in sulfur compounds [13-18]. Some of them are listed in Table 1. In the case of compounds I-III and VI, the distribution of $\delta\rho$ was obtained with the aid of an X—X synthesis, in the case of compounds IV and V it was obtained with the aid of an X—N synthesis, and in the case of compound VII, it was obtained from an X—(X + N) synthesis. The compounds are arranged in order of increasing degrees of covalency of the S...Nu contact. The increase in the value of χ from 0 to 1 as the internuclear distance decreases from the sum of the van der Waals radii to the sum of the covalent radii may be interpreted as motion of the system along the path of a nucleophile substitution reaction at the corner S atom from reactants with a nonbonded —S...Nu contact to an intermediate with a hypervalent —S⁺Nu.

A comparison of the maps of $\delta\rho$ arranged in the same order in Fig. 6 makes it possible to trace the evolution of the electron distribution as the donor-acceptor interaction is enhanced. In particular, diffuse maximum 1 (Fig. 6, I and II), which corresponds to two n(S) orbitals, is separated into two sharp peaks located above and below the plane of the molecule (Fig. 6, III and VI). This fact confirms our conclusion regarding the enhancement of the s character of the lone pairs of the acceptor atom (see Section 2).

As the nucleophile is approached, the minimum of $\delta\rho$ on the continuation of the A—S bond also becomes sharper (it is designated by the number 2 in Fig. 6, I, II, and III). This sharpening is caused by a decrease in the population of the $p_\sigma(S)$ orbital, which makes the main contribution to the acceptor antibonding $\sigma^*(AS)$ orbital. The use of the insufficiently exact thermal parameters obtained from a high-angle refinement can result in the appearance of near-nuclear minima of $\delta\rho$ (for example, minima, 3, 4, and 5 in Fig. 6, VI), which mask the decrease in the population of the $p_\sigma(S)$ orbital. However, the greater depth of minimum 4 in comparison to minima 3 and 5 reflects the smaller total population of the S(2) acceptor atom. The increase in the positive charge of the acceptor atom should result in contraction of its s orbitals, which is, in fact, manifested in the form of peak 6 (Fig. 6, V and VII). Such spherical changes in the electron density are detected only when the

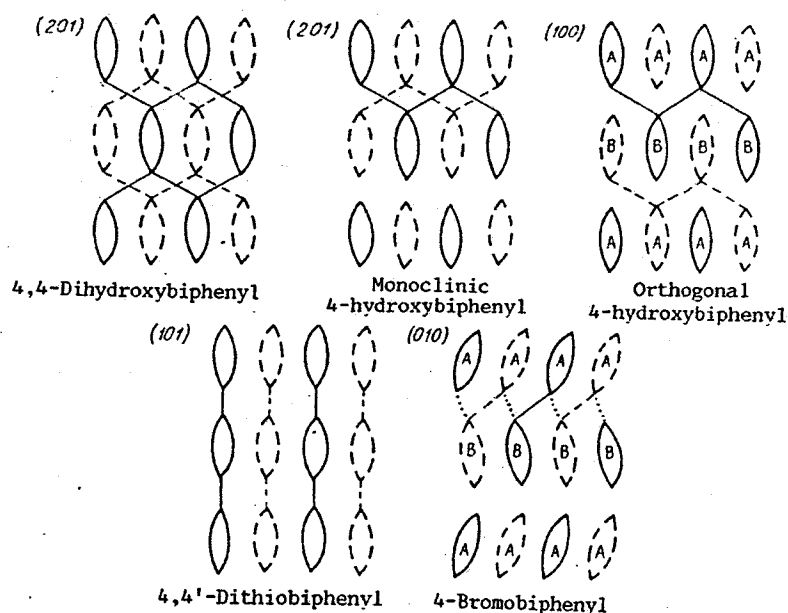


Fig. 7. Schematic representation of molecules in crystals of para-substituted biphenyls. Molecules whose centers lie in the plane of the drawing are indicated by solid contours, and molecules which are at a distance of $1/2$ (or $1/4$) of a translation from it are indicated by dashed contours. The solid connecting segments depict specific nonbonded contacts lying in the plane of the drawing, the dashed segments indicate specific nonbonded contacts which are parallel to that plane, and the dotted segments indicate inclined specific nonbonded contacts. The direction of the long axis of the contour of each molecule coincides with the direction of the projection of the long axis of the molecule. In the case of symmetrically inequivalent contacts, they are marked by the letters A and B. The crystallographic indices of the plane of each projection are given in parentheses.

neutron-diffraction thermal parameters are used. The slight aspherical character of peak 6 is caused by the decrease in the population of the acceptor $p_O(S)$ orbital discussed above. In accordance with the conclusions of Section 2 and despite the intuitive conceptions, the experimental data attest to a decrease in the population of the acceptor orbital and the S atom as a whole as a result of the DA interaction, rather than the transfer of electrons from the donor atom.

The lone pairs of the donor atom also undergo definite changes as χ is increased. In the case of weak specific nonbonded contacts, the lone pairs of the carbonyl group are manifested in the form of two separate peaks (which are designated by the number 7 in Fig. 6, IV). An increase in χ causes these peaks to merge and become diffuse (peaks 7 in Fig. 6, V and VI). Enhancement of the p-orbital character of the lone pairs (a process which is the reverse of the changes in the n orbitals or the acceptor atom) takes place. In the limiting case of a hypervalent bond, the lone pairs of the O atoms occupy practically pure p orbitals (peaks 8 and 9 in Fig. 6, VII). Peaks 10 and 11 in the same figure indicate the increased population of the $p_O(O)$ orbitals (in comparison to $4/3$ in the free atom). It may be caused by back donation from the S atom to the $\sigma^*(ON)$ orbital or an interaction of the $n(O) \rightarrow \sigma^*(ON)$ type.

It should be noted that the slight (within the range of error elongation of the S-O(6) bond in comparison to the S-O(1) bond results in significant changes in the electronic structure (inversion of the relative heights of peaks 9 and 11 and peaks 8 and 10).

Thus, it may be stated that the experimental facts confirm the ideas developed with respect to the nature of a DA interaction and make it possible to supplement them with new information.

4. NONBONDED INTERACTIONS AND PACKING OF MOLECULES IN CRYSTALS

In the absence of intermolecular interactions with a large DA component, the structure of molecular crystals can be described fairly well on the basis of the theory of closest packing [3]. The appearance of such interactions requires consideration of the principle of maximal overlap (see Section 1). Let us consider the structural consequences of the simultaneous action of these two factors in the example case of p-substituted biphenyls (Table 2).

Figure 7 presents schematic representations of the packing of molecules in these crystals. The plane of projection is selected such that the directions of the specific nonbonded contacts would coincide with it (this cannot be accomplished only in the case of 4-BrBP). Table 2 explains the symbols used to describe these planes and the direction of projection.

In a crystal of unsubstituted biphenyl (BP) the molecules are packed in layers built up according to a parquet motif in such a manner that the centers of the molecules lie in one plane and their lone axes are at a 73° angle to the plane of the layer. Figure 7 presents a projection of the structure of BP onto the (201) plane along the x axis. The molecular layers are oriented at an angle to this projection, intersecting it with the formation of horizontal series, which are seen in the figure. In addition, the H atoms occupying the para positions in the molecules form protuberances on the "surface" of the layer, and the H atoms located in meta positions occupy the bottom of the recesses between these protuberances. The layers are stacked according to the law of closest packing: the protuberances of one layer fit into the recesses of another layer.

Similar layers are present in the crystals of 4,4'-F₂BP and 4,4'-(OH)₂BP, which are isostructural to the crystals of biphenyl, as well as in the closely related structures of the two modifications of 4-(OH)BP and in the structure of 4,4'-(HS)₂BP. They are also found in crystals of 4-BrBP; however, in this case the layers are oriented not at an acute angle, but perpendicularly to the projection shown in Fig. 7 (owing to the inequivalence of the molecules with respect to their Fedorov groups, layers with somewhat different inclination of the molecular axes relative to the plane of the layer alternate here). Such layers are not found in crystals of 4'-Br-4-CNBP and 4,4'-Br₂BP. Nevertheless, specific nonbonded contacts having characteristic specific features are observed in all the derivatives of biphenyl considered, except 4,4'-F₂BP.

In the crystals of the two modifications of 4-(OH)BP and 4,4'-(OH)₂BP, systems of conjugated H bonds [27] of the type $\dots \text{OH} \dots \text{OH} \dots \text{OH} \dots$, which are extended along screw axes (parallel to the layers and perpendicularly to the direction of the molecules in a layer) appear between the molecules in neighboring layers. In the structure of orthogonal 4-(OH)BP the network of H bonds formed is, of course, only half as dense as the network in 4,4'-(OH)₂BP, and in monoclinic 4-(OH)BP the layers are jointed only in pairs. Similar chains of cooperative Br...Br specific nonbonded contacts are formed between the molecules in neighboring layers in the structure of 4-BrBP. However, these chains are extended along crystallographic mirror planes. In addition, the long axes of the molecules are not perpendicular to the chains of specific nonbonded contacts, and the symmetrically inequivalent molecules are inclined differently to the plane of the layer (77° and 71°). As a result of such inclination, the Br atoms forming Br...Br contacts approach one another.

A different type of packing of the layers is realized in crystals of 4,4'(SH)₂BP. The molecules of neighboring layers practically follow one another (i.e., they are arranged in a nonmeshing pattern) and are joined in straight chains by centrosymmetric S...S specific nonbonded contacts. Similar straight chains are also found in the structures of 4,4'-Br₂BP and 4'-Br-4-CNBP, where the molecules are joined by Br...Br and CN...Br specific nonbonded contacts, respectively. Each straight chain is surrounded by six neighbors, which are displaced differently relative to the central straight chain, in a crystal. The centers of the nearest molecules are not found in a single plane, and layers similar to the layers in the crystals of BP are not formed.

The special features of the structure of the substituted biphenyls described can be interpreted in the following manner. In the absence of atoms which are inclined to form strong specific nonbonded contacts, the crystal is built up in accordance with the principle

of closest packing. Such placement of the molecules does not prevent the formation of bent

$$\begin{array}{c} | \\ \text{O} - \text{H} \cdots \text{O} - \\ | \end{array}$$
 contacts, which are characteristic of hydroxyl groups. The contacts of Br atoms can be both bent (type I) and linear (type II). The formation of contacts of both types by each Br atom results in the appearance of chains of the $\text{Br} \cdots \text{Br} \cdots \text{Br}$ type. The

reversed inclination of the molecules in the neighboring layers of 4-BrBP does not prevent the formation of such layers. The Br atoms involved in a specific nonbonded contact tend to approach one another, and, in addition, each Br atom directs its own antibonding orbital to the donor partner. As a result the molecules are turned somewhat, deforming the layers. It may be postulated that the replacement of the H atom in the para position of 4-BrBP by a second Br atom would result in further deformation of the layers. The layers cease to be dense, and this type of packing of the molecules becomes unfavorable. In fact, crystals of 4,4'-Br₂BP have a different structure.

Unlike the halogens, the SH group can utilize not only the $\sigma^*(\text{S}-\text{C})$ orbital, but also the $\sigma^*(\text{S}-\text{H})$ orbitals, which are oriented perpendicularly to the C-S bond to form acceptor contacts. This is apparently due to the significant spread of angular characteristics revealed during the statistical investigation of S...S contacts [10]. This same feature allows SH groups to form centrosymmetric specific nonbonded contacts with a CSS' angle equal to 152° in the structure of 4,4'-(SH)₂BP. As a result, a protuberance of one layer (an S atom) "rests" on the edge of a recess in another layer (the S' atom), rather than at the bottom of that recess (the H atom in the meta position). A compromise between the layered structure of BP and the tendency of S...S specific nonbonded contacts of type III to achieve an equilibrium geometry is realized. A strictly linear equilibrium geometry for the $\text{Br} \cdots \text{NC}$ specific nonbonded contacts (of type II) might have resulted in stacking of the layers in a nonmeshing pattern. However, such minimally dense packing is not realized: a denser straight-chain type of packing turns out to be preferable for the molecules of 4'-Br-4-CNBP. The $\text{Br} \cdots \text{Br}$ contacts of type III, in accordance with their tendency to be linear, occupy an intermediate position between the $\text{Br} \cdots \text{NC}$ and $\begin{array}{c} \text{H} \\ | \\ \text{S} \cdots \text{S} \\ | \end{array}$ specific nonbonded contacts, but they also result in straight-chain packing in 4,4'-Br₂BP.

The strong association of the SH groups in crystals of 4,4'-(SH)₂BP cannot be attributed to weak S-H...S bonds. In our opinion, the short S...S contact ($d = 3.51 \text{ \AA}$, $\chi = 0.1$), which is assigned to type III, should be interpreted as was done in section 1. Such association may also occur in biological systems. In particular, the formation of disulfide bridges in native proteins may be preceded by the appearance of hydrophobic nonbonded contacts between the SH groups.

5. SOME CONSEQUENCES OF THE ORBITAL NATURE OF SPECIFIC NONBONDED INTERACTIONS

It is easy to see that the lengths of specific nonbonded contacts (unlike chemical bonds) vary over a broad range. It may be postulated that the reason for such flexibility is the weak dependence of the energy of a specific nonbonded contact on the internuclear distance. In fact, several examples of nonempirical calculations [1] have shown that the energy gain resulting from the approach of the donor and the acceptor is compensated to a considerable extent by the increase in the exchange repulsion.

The gently sloping form of the potential-energy curve causes the position of the minimum to be very sensitive to changes in the covalent partners of the donor and acceptor atoms and to changes in the crystal-chemical environment. According to Eq. (2), a decrease in the denominator as a result of an increase in the energy of the $n(\text{A})$ orbital and a decrease in the energy of the $\sigma^*(\text{XZ})$ orbital results in enhancement of the $\text{Z}-\text{X} \cdots \text{A}$ DA interaction [and, therefore, in an increase in $\chi(\text{X} \cdots \text{A})$]. Such changes in the orbital energies can be achieved, if the electronegativity of atoms X and A decreases, and the electronegativity of group Z increases.

In fact, significant (of the order of 1 Å) shortening of a Z-S...O=Y intermolecular contact as the electronegativity of group Z increases and the electronegativity of the donor group decreases was discovered in the x-ray structural investigations in [28] and is confirmed by the series of nonempirical calculations [29]. Additional support for this law may be provided by the isostructural crystals of halogenated cyanoacetylenes described in [30, 31]. Along the series from Cl to I the increasing strength of the DA interaction more than compensates for the increase in the size of the halogen atom so that the length of the linear CX...NC specific nonbonded contact decreases slightly (from 2.97 to 2.93 Å), and the covalency ratio increases considerably (from 0.26 to 0.43).

The approach of the donor and the acceptor, which is accompanied by an increase in the overlap of the orbitals will, in turn, alter the electronic structure of the interacting fragments. As a result of the increase in the population of the antibonding $\sigma^*(XZ)$ orbital and the polarization of the $\sigma(XZ)$ orbital, the X-Z bond should be weakened. One of the numerous examples of such weakening is the case of the three symmetrical independent linear

C-Br...N- in crystalline complexes of CBr₄ with quinuclidine [32]:

	$d(\text{Br} \cdots \text{N})$	$\chi(\text{Br} \cdots \text{N})$	$d(\text{C}-\text{Br})$	$\chi(\text{C}-\text{Br})$
1	2.88	0.37	2.04	0.93
2	2.76	0.45	2.12	0.88
3	2.53	0.59	2.24	0.81

The back donation of the lone pairs of the acceptor atom to the natural antibonding orbitals of the donor group and the polarization of this group should also weaken the bonds of the donor atom. In the case of Z-S...O=C, specific nonbonded contacts, for example, a decrease in the frequency of the stretching vibrations and elongation of the C=O bond were detected experimentally in [28].

The development of the conception of the DA nature of specific nonbonded contacts also predicts some consequences which have not yet been confirmed experimentally. First, the polarization occurring upon the formation of a specific nonbonded contact results in an increase in the electronic population of the donor atom and a decrease in that of the acceptor atom (see Section 2). Therefore, the formation of an acceptor specific nonbonded contact by an atom of X will weaken its donor activity, and vice versa. In other words, unlike hydrogen bonds [1], a negative cooperative effect will be displayed in X...X contacts.

Second, the increase in the contribution of the p orbitals of the substituents to the bond with an atom of X upon the formation of a donor specific contact weakens the p-orbital character of the remaining bonds, and this should result in increases in the angles between them. Conversely, when an acceptor specific nonbonded contact is formed, the bond angles in the substituent should increase. This, however, may be counteracted by the steric factors caused by the elongation of the bond between the acceptor atom and its substituent.

Thus, the use of natural bond orbitals and the equivalent orbitals of the lone pairs makes it possible not only to interpret the stereochemical features of the nonbonded contacts of atoms of X and the types of packing of the molecules containing such atoms on the basis of the principal of maximum overlap, but also to predict fine changes in the intermolecular structure upon the formation of these specific contacts.

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