

# A QUANTUM TOPOLOGICAL STUDY OF THE ELECTRON DENSITY IN MONOMERS AND DIMERS OF ACYCLIC AZATHIENS WITH AROMATIC SUBSTITUENTS

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A theoretical study of electron density,  $\rho(\mathbf{r})$ , and the Laplacian (*ab initio*, DFT B3LYP/6-31G(*d, p*) basis set) has been carried out for nine molecules of azathiens with aryl substituents ( $\text{Ar-N=S=N-Ar}_1$ ) and for sixteen dimers corresponding to typical arrangements of neighboring molecules in the crystal structures of  $\text{Ar-N=S=N-Ar}_1$ . A dependence was established of the values of the electron density at (3, -1) critical points in the area of inter-stack and intra-stack atom-atom contacts on the internuclear distance.

**Keywords:** azathiens, polyfluoroarenes, supramolecular motifs, pincer-like structures, electron density.

The specific character of acyclic azathiens with aromatic substituents ( $\text{Ar-N=S=N-Ar}_1$ ) lies in their  $\pi$ -excessiveness: in these substances the number of  $\pi$ -electrons is greater than the number of atomic centers. Aromatic substituents prolong the conjugated chain, thereby causing these compounds to take on the character of polyconjugated  $\pi$ -excessive systems. In this connection they are of certain interest as possible molecular conductors [1].

Earlier we used X-ray diffraction analysis to study a number of crystal structures of aromatic azathiens (Table 1). In the absence of bulky substituents, the molecules of  $\text{Ar-N=S=N-Ar}_1$  in the crystal usually have the *Z,E* configuration that is ideally or almost ideally planar. Sterically hindered  $\text{Ar-N=S=N-Ar}_1$  compounds overcome steric hindrances in two ways:

**TABLE 1.** Crystalline Acyclic Azathiens with Aromatic Substituents Studied by X-ray Diffraction

Structure	Reference
$\text{C}_6\text{H}_5\text{-N=S=N-Si}(\text{CH}_3)_3\cdot\text{C}_{10}\text{H}_8$	[2]
$(4\text{-FC}_6\text{H}_4\text{-N})_2\text{S}$	[3]
$2,6\text{-(CH}_3)_2\text{C}_6\text{H}_3\text{-N=S=N-C}_{10}\text{F}_7\cdot 1/2\text{C}_{10}\text{H}_8$	[3]
$(\text{C}_6\text{H}_5\text{-N})_2\text{S}\cdot\text{C}_{10}\text{F}_6\text{N}_2\text{S}$	[3]
$(2,6\text{-F}_2\text{C}_6\text{H}_3\text{-N})_2\text{S}$	[4]
$(2,6\text{-Cl}_2\text{C}_6\text{H}_3\text{-N})_2\text{S}$	[4]
$(2\text{-NO}_2\text{C}_6\text{H}_4\text{-N})_2\text{S}$	[5]
$(\text{C}_6\text{F}_5\text{-N})_2\text{S}$	[6]
$2,6\text{-(CH}_3)_2\text{C}_6\text{H}_3\text{-N=S=N-C}_6\text{F}_5$	[6]
$2,6\text{-(CH}_3)_2\text{C}_6\text{H}_3\text{-N=S=N-2,4,6-Br}_3\text{C}_6\text{H}_2$	[7]
$(2,4,6\text{-Br}_3\text{C}_6\text{H}_2\text{-N})_2\text{S}$	[7]

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**TABLE 2.** Calculated Values of the Electron Density  $\rho(\mathbf{r})$ , au, at the (3, -1) Critical Points

Compound	Formula	Number of points	Minimal value	Maximal value
<b>1a</b>	(2,6-(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> -N) <sub>2</sub> S	3	0.006	0.009
<b>1b</b>	(2,6-Cl <sub>2</sub> C <sub>6</sub> H <sub>3</sub> -N) <sub>2</sub> S	5	0.006	0.007
<b>1c</b>	(2,6-F <sub>2</sub> C <sub>6</sub> H <sub>3</sub> -N) <sub>2</sub> S	3	0.007	0.008
<b>1d</b>	2,6-(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> -N=S=N-2,4,6-Br <sub>3</sub> C <sub>6</sub> H <sub>2</sub>	3	0.007	0.008
<b>1e</b>	(F <sub>5</sub> C <sub>6</sub> -N) <sub>2</sub> S	1	0.009	0.009
<b>1f</b>	2,6-(CH <sub>3</sub> ) <sub>2</sub> F <sub>3</sub> C <sub>6</sub> -N=S=N-C <sub>6</sub> F <sub>5</sub>	4	0.006	0.008
<b>2a</b>	(2,4,6-Br <sub>3</sub> C <sub>6</sub> H <sub>3</sub> -N) <sub>2</sub> S	2	0.003	0.005
<b>2b</b>	(C <sub>6</sub> H <sub>5</sub> -N) <sub>2</sub> S	1	0.014	0.014
<b>2c</b>	C <sub>6</sub> H <sub>5</sub> -N=S=N-Si(CH <sub>3</sub> ) <sub>3</sub>	1	0.012	0.012

1) by turning the rings in the *Z,E* configuration perpendicular to the plane and 2) by changing the configuration from *Z,E* to *Z,Z*. Substantially non-planar *Z,Z* isomers of Ar-N=S=N-Ar<sub>1</sub> resemble so-called molecular pincers. In the crystals of these isomers stacked packing of virtually parallel aromatic molecular fragments is usually observed. In most cases the molecules containing halogen atoms, it is possible to distinguish several supramolecular motifs: those resulting from non-bonded intra-stack interactions ( $\pi$ -stacking of aromatic fragments) and those determined by inter-stack interactions of halogen...halogen or halogen...hydrogen type.

The goal of the present study was to investigate the features of intermolecular interactions that determined the formation of stacked packing of aromatic and polyhalogenoaromatic fragments of azathiens in crystals and to examine the characteristics of non-bonded interactions within substantially nonplanar, pincer-like molecules. To achieve this goal we considered the distribution of the electron density  $\rho(\mathbf{r})$  (au) and the Laplacian in the area of intra-stack and inter-stack interactions of aromatic fragments.

For nine azathiens with aryl substituents (Table 2) we have performed *ab initio* quantum chemical calculations (DFT B3LYP/6-31G(*d, p*)) and a topological analysis of the electron density  $\rho(\mathbf{r})$  and of the Laplacian using the Bader algorithm [8] and the AIMPAC program package [9]. The geometry of six pincer-like molecules (**1a-1f**) is such that aromatic rings lie over each other at a certain angle to one another, and at the same time they are slightly shifted relative to each other. In such structures the (3, -1) critical points of the electron density are located in the cavity of the “pincer,” i.e. in the area between aromatic rings. Since phenyl groups are arranged at a rather large angle relative to each other in such molecules, the critical points occur only in the narrowest part of the pincer-like structure. Typically, such critical points are located between the atoms of aromatic rings that have substituents at positions 2 and 6. As a rule, they correspond to halogen...halogen, halogen...carbon or halogen...hydrogen contacts. In three structures (**2a-2c**) the molecules in crystals do not have a pincer-like form, but exhibit a *Z,E* configuration.

It should be noted that though the (3, -1) critical points of the electron density are located in the area of shortened atom-atom contacts, they do not always lie exactly on the straight line connecting centers of the nuclei of the atoms that form these contacts. In some cases it is rather difficult to assign a critical point to a particular contact, because it can lie between the centers of different possible bonds.

In the case of a considerable displacement of  $\pi$ -systems, like in the molecule **1e** (F<sub>5</sub>C<sub>6</sub>-N)<sub>2</sub>S, only one critical point of the electron density is observed, and its value is the highest for series **1** (0.009, Table 3). It is located between the carbon atoms that are linked to azathien fragments. For the molecule **1b** (2,6-Cl<sub>2</sub>C<sub>6</sub>H<sub>3</sub>-N)<sub>2</sub>S, in the case of which the displacement of aromatic rings of the molecule is minimal, but the angle between the planes of the rings is rather large, we have found five critical points, among which there are points with the values of 0.007, which correspond to intramolecular contacts Cl...Cl and Cl...C.

**TABLE 3.** Characteristics of Intermolecular Interactions in the Dimers ( $E_{\text{tot}}$  is the Energy of Formation;  $\rho(r)$  is the Mean Value of the Electron Density in Intermolecular Space;  $N$  is the Number of the (3, -1) Critical Points)

Compound	Type of interaction in the dimer	$E_{\text{tot}}$ , au	$\rho(r)$ , au	$N$
<b>1a</b> (2,6-(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> -N) <sub>2</sub> S	$\pi$ -stacking	-2253.3086	0.004	5
<b>1b</b> (2,6-Cl <sub>2</sub> C <sub>6</sub> H <sub>3</sub> -N) <sub>2</sub> S	—''—	-5616.9435	0.004	8
	Inter-stack	-5616.9463	0.004	5
<b>1c</b> (2,6-F <sub>2</sub> C <sub>6</sub> H <sub>3</sub> -N) <sub>2</sub> S	$\pi$ -stacking	-2734.3335	0.005	2
	Inter-stack	-2734.3390	0.003	5
	—''—	-2734.3361	0.005	2
<b>1d</b> 2,6-(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> -N=S=N-2,4,6-Br <sub>3</sub> C <sub>6</sub> H <sub>2</sub>	$\pi$ -stacking (Br)	-17523.9100	0.004	10
	$\pi$ -stacking (CH <sub>3</sub> )	-17523.9027	0.005	3
	Inter-stack	-17523.9054	0.010	1
	—''—	-17523.9062	0.004	3
<b>1e</b> (F <sub>5</sub> C <sub>6</sub> -N) <sub>2</sub> S	$\pi$ -stacking	-3924.8527	0.005	4
	Inter-stack	-3924.8453	0.0045	2
	F...F	-3924.8593	0.004	7
	F...F	-3924.8581	0.003	8
	C...N	-3924.8607	0.0045	2
	S...F	-3924.8604	0.003	3

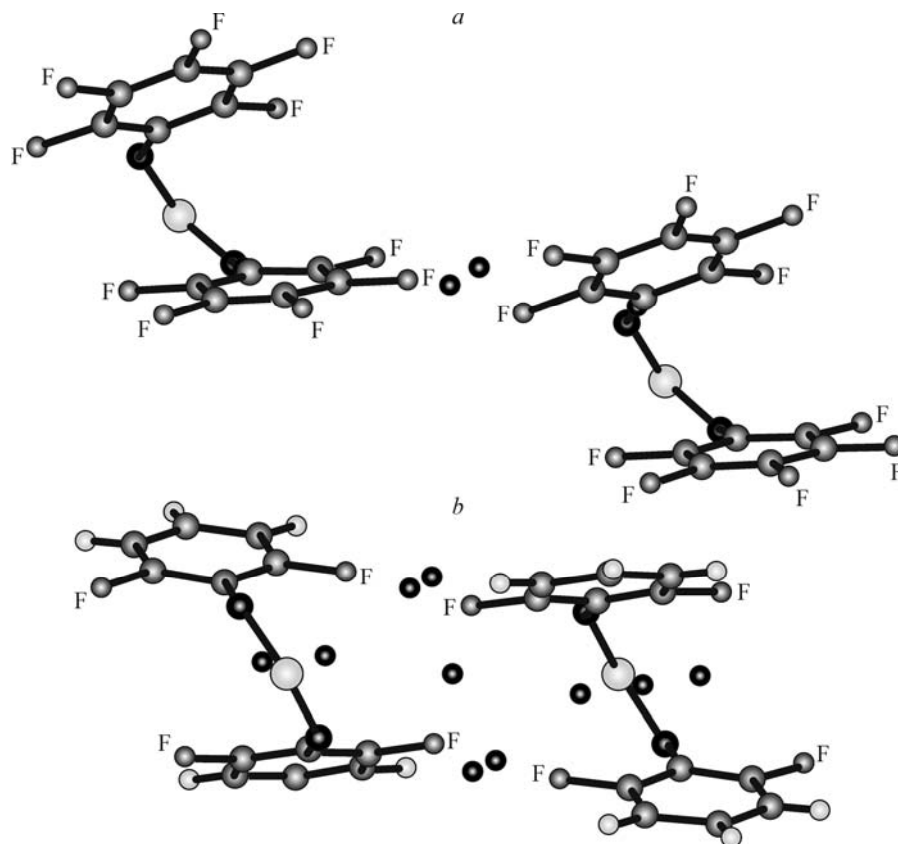
For the azathiens that do not have a pincer-like structure (**2a-2c**) the (3, -1) critical points are found either between the nitrogen atom of the azathien group and the nearest substitute in the aromatic ring or between two halogen atoms in *ortho* positions of neighboring rings. For the molecule **2b** (C<sub>6</sub>H<sub>5</sub>-N)<sub>2</sub>S the electron density in such a point reaches 0.014.

On the whole, when characterizing non-bonded intramolecular interactions in the molecules of azathiens with aromatic substituents, it can be noted that molecules with pincer-like structures typically have more critical points than molecules with linear structures. In the structures that are not pincer-like the interactions of aryl fragments with nitrogen atoms are characterized by high values of the electron density. At the same time intramolecular interactions Br...Br in the molecule **2a** correspond to low values of the electron density (see Table 2).

The (3, -1) critical points of the Laplacian in the molecules of azathiens have three typical localization zones. First, these are the layers of critical points located above the  $\pi$ -systems of aromatic rings. These are separated from the nuclei of the aromatic system on the average by 0.75 Å. The value of the Laplacian at the points of the layer above halogen substituted rings is about 0.110. Above methyl substituted rings these values are somewhat smaller: 0.105 on the average. The next localization zone of the critical points of the Laplacian is the area of the azathien group (N=S=N), both inside and outside the cavity of the pincer. In this area there occur several points with the values ranging from 0.152 to 0.210 at the distance of 0.65 Å from the sulfur atom.

With the aim of studying intermolecular interactions in the crystals of azathiens we have also performed quantum chemistry calculations of the energy of formation (*ab initio* DFT B3LYP/6-31G(*d*, *p*)) and a topological analysis of the electron density of the dimers that correspond to typical arrangements of neighboring molecules in the crystals.

Many different types of dimers can be distinguished in the considered azathiens with pincer-like structures. One of the frequently occurring is the stacked packing of aromatic rings with a slight (1.0-1.5 Å) relative displacement. While choosing particular dimers, we looked at all the pairs of neighboring molecules with  $\pi$ -stacking; we particularly considered the inter-stack contacts that could help to assess the corresponding specific interactions. As a rule, there existed a shortened atom-atom contact between the selected molecules, i.e. the interatomic distance was shorter than the sum of van der Waals radii. A special group of the dimers that can be distinguished in the crystals is comprised of those dimers in which there are contacts between the sulfur or nitrogen atoms of the azathien group and the atoms of the aromatic system of the neighboring molecule.



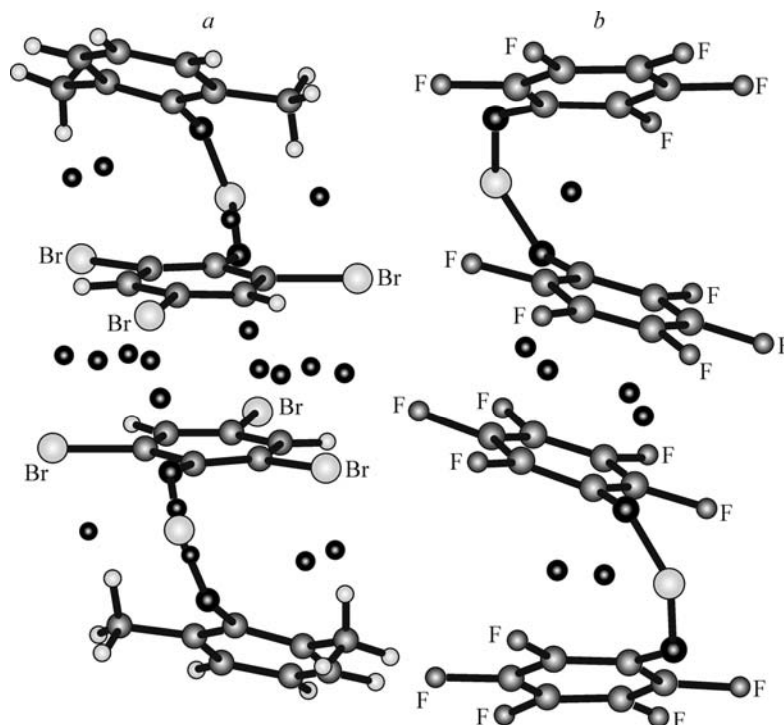
**Fig. 1.** The (3, -1) critical points of electron density in the area of inter-stack interactions of pentafluorophenyl systems of dimers **1e** ( $\text{F}_5\text{C}_6\text{-N}$ )<sub>2</sub>S — *a*, difluorophenyl rings of dimers **1c** ( $2,6\text{-F}_2\text{C}_6\text{H}_3\text{-N}$ )<sub>2</sub>S — *b*.

Let us first consider the results obtained for the dimers with shortened halogen...halogen inter-stack contacts. In this case the halogen substituted aryl molecular fragments that belong to different stacks are, as a rule, located virtually in the same plane or at a small angle to each other. The values of the electron density at the critical points that correspond to such contacts are relatively high.

The maximum value of the electron density which corresponds to inter-stack contacts is observed for dimer **1d**  $2,6\text{-(CH}_3)_2\text{C}_6\text{H}_3\text{-N=S=N-2,4,6-Br}_3\text{C}_6\text{H}_3$ . The only (3, -1) critical point of the electron density with the value of 0.010 was found in the area of the shortened Br...Br contact (internuclear distance is 3.43 Å). This contact is formed by the bromine atoms that are located at *para*-positions of tribromophenyl rings of neighboring molecules. These rings lie in almost parallel planes.

In the crystal structure of **1e** ( $\text{F}_5\text{C}_6\text{-N}$ )<sub>2</sub>S there are inter-stack F...F contacts formed between atoms of the pentafluorophenyl rings arranged at an angle of approximately 30° to each other (Fig. 1*a*). It is interesting to note that for the contact with internuclear F...F distance of 2.89 Å the value of the electron density at the critical point reaches 0.005, whereas in the case of the contact with internuclear F...F distance of 3.04 Å it is only 0.003. For the dimer **1c** ( $2,6\text{-F}_2\text{C}_6\text{H}_3\text{-N}$ )<sub>2</sub>S (see Fig. 1*b*), more (3, -1) critical points were found in the inter-stack space. Four of such points correspond to the contacts of F atoms at the *ortho*-position of the ring of one molecule with F (3.1 Å) and H (2.94 Å) atoms in the aromatic ring of the other molecule. One (3, -1) point with a relatively high value (0.006) of the electron density corresponds to the F...F contact (2.93 Å) between the atoms of aromatic rings that are located in different layers of neighboring stacks.

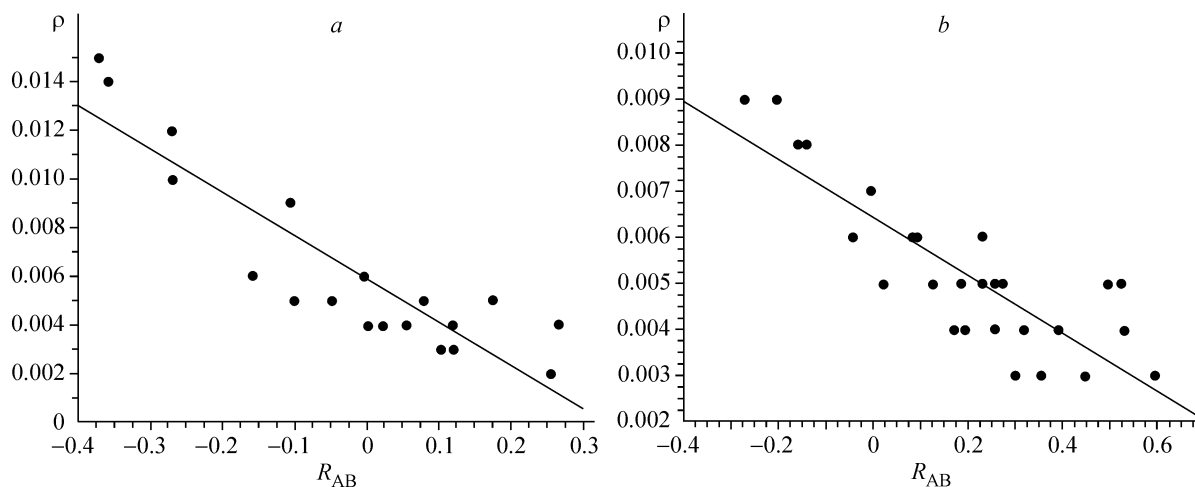
In the case of the  $\pi$ -stacking of aryl substituted fragments of neighboring molecules the number of critical points, their location and the values of the electron density depends both on the nature of the substitutes in aromatic rings and the relative positions of the benzene rings (see Table 3). For example, in the crystal structure of **1d**,  $2,6\text{-(CH}_3)_2\text{C}_6\text{H}_3\text{-N=S=N-2,4,6-Br}_3\text{C}_6\text{H}_3$ , the virtually parallel mutual arrangement of benzene rings of neighboring molecules is realized in two ways:



**Fig. 2.** The (3, -1) critical points of electron density in the area of  $\pi$ -stacking interactions of trifluoro substituted rings of compound (**1d**) 2,6- $\text{CH}_3\text{C}_6\text{H}_3\text{-N=S-N-2,4,6-Br}_3\text{C}_6\text{H}_3$  — *a*, in the area of  $\pi$ -stacking of trimethyl substituted rings of compound (**1e**)  $(\text{F}_5\text{C}_6\text{-N})_2\text{S}$  — *b*.

the  $\pi$ -stacking of bromine substituted rings and the  $\pi$ -stacking of methyl substituted rings. According to X-ray analysis, the interplanar distance between tribromoaryl systems is 3.55 Å; the distance between dimethylaryl rings of neighboring molecules is somewhat greater and reaches 3.60 Å. The relative displacement of the aromatic systems along the side of the bromine substituted ring is 0.89 Å; in the case of the  $\pi$ -stacking of dimethylaryl rings such relative displacement is greater and reaches 0.96 Å. In the area of intermolecular interactions of tribromine substituted rings, 10 critical points of the electron density are observed with the values between 0.004 and 0.005 (Fig 2*a*). They correspond to contacts  $\text{Br}\dots\text{Br}$ ,  $\text{Br}\dots\text{H}$ ,  $\text{C}\dots\text{C}$  and  $\text{Br}\dots\text{N}$ . In the area of interactions between methyl substituted aromatic systems there are only three critical points of electron density. One of these points, which has the value of 0.004, corresponds to the contact between carbon atoms at *ortho*-positions of neighboring rings. The hydrogen atoms of methyl groups form a shortened contact (2.86 Å) with the carbon atoms located at *para*-position of the rings. Two points with the value of 0.006 are observed in this area.

In the crystal structure of the pincer-like molecule **1e**  $(\text{F}_5\text{C}_6\text{-N})_2\text{S}$ , an atypical  $\pi$ -stacking between polyfluorinated rings is realized. Such an arrangement of the molecules is in contradiction with the electrostatic (quadrupole) model, and hence currently attracts particular interest. We have considered several dimers, including a pair with the  $\pi$ -stacking of pentafluoroaryl fragments (see Fig. 2*b*), for this crystal. In this stack, the interplanar distance is 3.44 Å, the dihedral angle between the rings of neighboring molecules is 2.2°, the relative displacement in the stack along the planes of pentafluoroaryl rings is 1.58 Å. Four (3, -1) critical points with the electron density 0.005 were found in the area of the  $\pi$ -stacking. These points are located at an equal distance from the planes of pentafluorophenyl rings and correspond to two different types of contacts. First, these are the contacts between the carbon atom of the aromatic ring at position 1 of one molecule and the carbon atom at position 2 of the other molecule; the length of this  $\text{C}\dots\text{C}$  contact is 3.42 Å. Second, there are critical points in the area of the  $\text{C}\dots\text{N}$  contact with internuclear distance 3.43 Å (the carbon at position 4 of one molecule and the nitrogen of the azathien group of the other molecule).



**Fig. 3.** Dependence of the electron densities  $\rho(r)$  at the (3, -1) critical points on the shortening of the contact  $R_{AB}$  for inter-stack contacts — *a*, for intra-stack  $\pi$ -stacking contacts — *b*.

The value of the electron density in the area of a particular contact depends on the internuclear distance between the atoms that form this contact. The analysis of the electron density  $\rho(r)$  at the critical points for pairs of neighboring molecules shows the relationship between this value and the shortening of the contact (Fig. 3). In this case, the shortening  $\Delta R_{AB}$  is the difference between the internuclear distance and the sum of van der Waals radii of the atoms according to Bondi [10], i.e.  $\Delta R_{AB} = R_{AB} - (r_A + r_B)$ , where  $r_A$  and  $r_B$  are the van der Waals radii of the corresponding atoms. According to our results, this relationship can be approximated by a linear function. The electron density increases with the shortening of the contact. For inter-stack contacts it increases somewhat faster than for intra-stack contacts (the slope ratio is -0.018 for inter-stack contacts and -0.006 for intra-stack contacts). It is interesting that the parameters of this relationship slightly differ in the contacts of different types. Halogen...halogen and halogen...hydrogen contacts prevail among inter-stack contacts, whereas halogen...hydrogen and carbon...carbon contacts between different aromatic fragments are typical among intra-stack contacts.

In general, for intra-stack contacts the values of the electron density at (3, -1) critical points are rather low. However, when the number of points is taken into account, the total value of the electron density is comparable with the values observed in typical specific contacts. For example, according to the data of [11], the value of the electron density at the (3, -1) critical point that corresponds to the hydrogen bond in urea is 0.019.

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