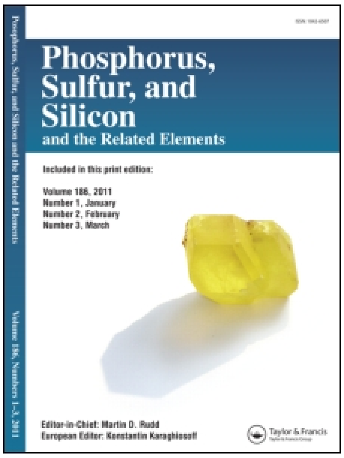

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Investigations on the Interaction Between sp 2 -Sulfur Atoms and Iodine Molecules Using the Cambridge Structural Database

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INVESTIGATIONS ON THE INTERACTION BETWEEN sp^2-SULFUR ATOMS AND IODINE MOLECULES USING THE CAMBRIDGE STRUCTURAL DATABASE

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The interaction between sp^2-sulfur and iodine was investigated using the Cambridge structural database (CSD). A CSD search for fragments containing at least two iodine atoms bonded to each other and exhibiting an S···I distance less than 5.0 Å to sp^2-sulfur atoms yields 136 fragments. The distribution of the number of fragments over the S···I distances shows that there are two different groups. The first group contains only fragments with S···I distances between 2.4 and 3.1 Å and the second group between 3.5 and 5.0 Å. The analysis of the orientation of the iodine atoms and the sulfur atoms shows that in the structures of the first group the iodine atoms are oriented predominantly in the direction of the lone-pairs of the sulfur atoms, whereas for S···I distances larger than 3.5 Å a random distribution is found. This preferred orientation can be regarded as a donor acceptor interaction which also is shown by the distribution of the S···I-I angles. For the group with S···I distances between 2.4 and 3.1 Å S···I-I angles of about 180° are found, whereas for S···I distances larger than 3.5 Å a random distribution of these angles occurs. In agreement with these results a correlation between the intermolecular S···I and the intramolecular I-I distances is found in the group of structures with shorter S···I bond lengths. These results are discussed as a model for the hypothetical reaction between thioketones and iodine under formation of a cationic species.

Keywords: CSD-search; S···I-interactions; sulfur-iodine adducts

INTRODUCTION

In the last years the development of methods or strategies for the well-defined construction of crystal structures has become of increasing

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interest. Because the crystal packing is determined predominantly by intermolecular interactions between atoms or molecules, understanding of these forces is very important in chemical sciences today.[1] This project uses the term "crystal engineering," which is defined as the understanding of intermolecular interactions in the context of crystal packing and the utilization of such understanding in the design of new solids with desired physical and chemical properties.[1] There are several methods for the investigation of intermolecular interactions, for example, theoretical calculations. Another powerful tool is the qualitative analysis of several crystal structures using crystallographic databases in order to find preferred orientations or correlations between bonding parameters.[2] Therefore, several articles on the investigation of intermolecular interactions like hydrogen bonding or interactions between heteroatoms using database searches have been published.[2–5] Even structures that are based on intermolecular interactions between electrophilic or nucleophilic atoms to sp^3-sulfur atoms were analyzed in this way.[6] Furthermore, based on the ideas of Bürgi and Dunitz such correlations can be used for investigating the reactivity of molecules.[2]

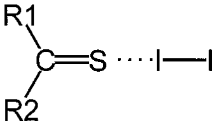
In our own investigations we have structurally characterized several compounds in which sp^3-sulfur atoms exhibit short intermolecular contacts to bromine or iodine atoms that can be regarded as donor acceptor interactions.[7,8] There also are several structures in which iodine atoms are connected to sp^2-sulfur atoms with a geometry completely different from that found for the halide contacts to sp^3-sulfur atoms.[9–28] One example for this is the crystal structure of N, N′-bis(morpholino)-dithiooxadiamide-bis(diiodine)[15] in which a relatively short S···I distance of 2.789 Å occurs, whereas the I-I distance of 2.805 Å is elongated compared to that of 2.715 found in elemental iodine Å[29,30] (Figure 1).

Regarding such structures, we were interested if there are any interactions between the sulfur and the iodine, how far these interactions reach, and what the nature of these interactions is. We have investigated these questions by analyzing structures retrieved from the Cambridge Crystallographic Database.[31]

RESULTS AND DISCUSSION

The CSD search for fragments containing at least two iodine atoms bonded to each other and exhibiting an S···I distances of less than 5.0 Å to sp^2-sulfur atoms yields 136 fragments (Scheme 1 and experimental).

The distribution of the number of fragments over the S···I distances shows that there are two different groups. The first one contains 35 fragments with short S···I distances between 2.4 and 3.1 Å (Table I)



SCHEME 1

and the second one fragments with larger S···I distances between 3.5 and 5.0 Å (Figure 2).

First of all we investigated if there is any preferred orientation between the iodine and the sp^2-sulfur atoms as a function of the S···I distance or if this orientation is random. The relative orientation of the iodine atoms with respect to the sp^2-sulfur atoms is described by the following parameters: phi (Φ)—the angle of rotation of the S···I vector about the normal to the lone pair plane and projected onto that plane; theta (θ)—the angle between the S···I vector and the R1R2CS plane (i.e., the plane of the sp^2 lone pairs) (Figure 3). If there is a preferred orientation of the iodine atoms with respect to the lone-pairs of the sulfur atoms, phi should be about 110° and theta about 0°.

The analysis of the orientation of the iodine molecules relative to the sp^2-sulfur atoms shows that in the structures of the first group containing fragments with S···I distances between 2.4 and 3.1 Å only a few orientations are found, whereas for structures with S···I distances larger than 3.5 Å a random distribution occurs. For most of the structures in the first group phi is about 110° and theta close to 0° which

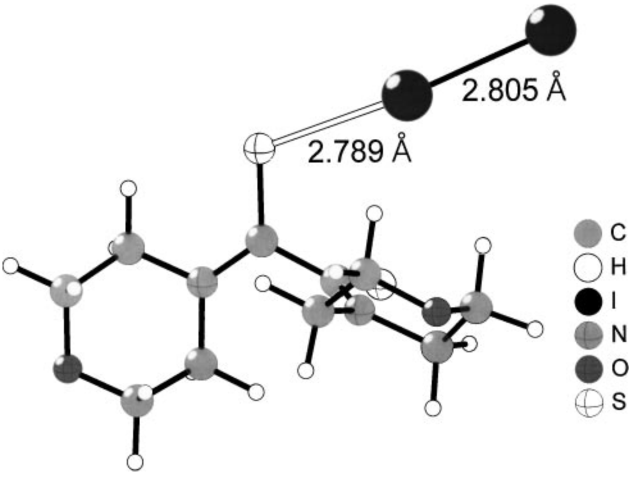


FIGURE 1 Part of the crystal structure of N,N′-bis(morpholino)-dithiooxadiamide-bis(diiodine)[15] with selected distances in Å.

TABLE I Refcodes, Literature Citations, and Geometrical Data for the Fragments with S···I Distances Up to 3.1 Å

Refcode	Theta/°	Phi/°	S···I/Å	S···I-I/Å	I-I/Å	Lit.
BIMMEP	2.03	101.93	2.716	177.45	2.808	(10)
BZHTIC10	77.20	115.83	2.663	178.49	2.917	(11)
BZHTID20	71.00	122.89	2.502	179.05	3.213	(11)
CEWMIA	3.87	102.71	2.487	177.90	3.148	(11)
CEWMOG	3.61	102.73	2.580	177.57	2.984	(11)
CEWNAT	0.03	101.21	2.588	178.23	2.986	(11)
DAYBOU	4.41	110.89	2.755	175.41	2.812	(12)
DAYCIP	1.05	102.74	2.805	175.44	2.812	(12)
GEGNUB01	79.96	165.23	2.607	177.11	2.984	(13)
GIDYOH	81.75	178.42	2.874	179.60	2.811	(14)
GIGLOX	4.76	107.74	2.920	175.53	2.751	(15)
GIGLOX	28.98	115.85	2.892	173.89	2.738	(15)
GIGLOX	7.55	108.78	2.789	174.73	2.805	(15)
GIGLOX	6.86	109.73	2.801	176.50	2.787	(15)
KUWDEL	4.26	103.68	2.748	176.88	2.817	(16)
KUWDIP	11.69	100.46	2.738	177.93	2.849	(16)
KUWDIP	20.92	106.78	2.843	173.74	2.767	(16)
KUWDOV	1.27	104.48	2.773	176.14	2.802	(16)
LOPQEM	6.97	104.85	2.503	176.04	3.054	(17)
LOPQIQ	0.28	104.25	2.466	176.08	3.145	(17)
LOPQIQ	4.20	105.91	2.437	171.59	3.168	(17)
LOPQIQ	0.06	104.91	2.507	173.69	3.056	(17)
MSNROD	77.06	137.78	3.099	178.46	2.751	(18)
PEJKIY	1.58	103.69	2.715	176.47	2.823	(19)
PIGXUY	2.27	102.01	2.715	176.71	2.843	(20)
TCAPLI	0.87	109.99	2.687	176.23	2.879	(21)
TOTWUU	81.22	140.76	2.683	175.71	2.897	(22)
TOTXAB	75.70	125.30	2.642	177.05	2.903	(22)
TURMEY	82.55	173.51	2.824	177.48	2.815	(23)
TURMIC	89.19	102.67	2.849	178.78	2.790	(23)
VARCIA	2.25	99.51	2.711	176.63	2.832	(24)
VEBCEK	75.13	110.94	2.774	174.82	2.822	(25)
YESHAF	4.64	104.91	2.583	175.11	2.964	(26)
ZARDOL	72.39	132.42	2.783	175.30	2.840	(27)
ZEBQOM	65.78	147.37	3.298	169.79	2.729	(28)

means that the iodine atoms are oriented in the direction of the lone-pairs of the sulfur atoms (Figure 4 and Table I). However, the preferred orientation in phi is much more pronounced than in theta. There are some structures with theta values of about 90° and phi values of about 180°, which means that the S···I vector in these structures is oriented perpendicular to the C=S bond and in the direction of the C=S vector (Figure 4 and Table I). Most of these structures are very similar metal complexes and contain large substitutents vicinal to the sulfur

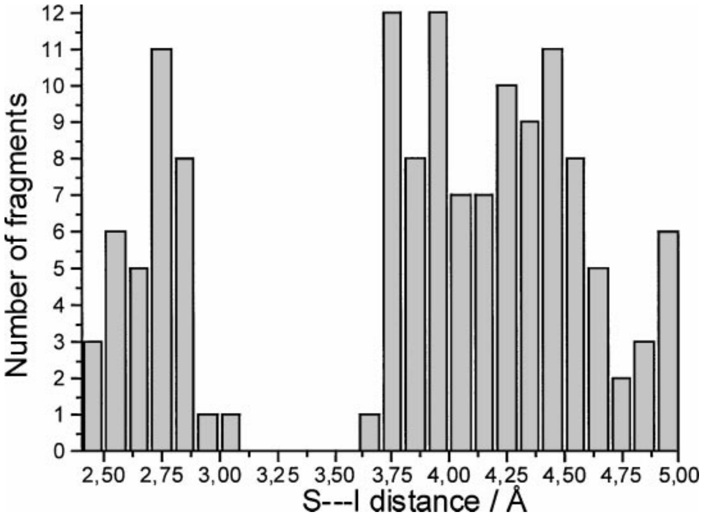


FIGURE 2 Number of fragments found as a function of S$\cdots$I distance.

atom which prevent an orientation of the iodine atoms in the direction of the sulfur lone-pair like in bis(1,3-Di-isopropylimidazolidine-2,4,5-trithionato)-nickel(ii) di-iodine[23] (Figure 5). In addition, in such metal complexes negative charge is transferred to the sulfur atom connected to iodine, which changes the electronic situation in a way that the sp^2-character of the sulfur atom is weakened. Therefore, strictly speaking, such compounds should not be considered.

These results show that at short S$\cdots$I distances preferred orientations for the sulfur atoms and the iodine molecules exist indicating some directional interaction between these atoms. This interaction could be explained for example on the basis of donor acceptor interactions in which the sulfur atom acts as the donor whereas the iodine atom acts as the acceptor. Donor acceptor interactions in which iodine atoms are involved are used, for example, for the interpretation of the

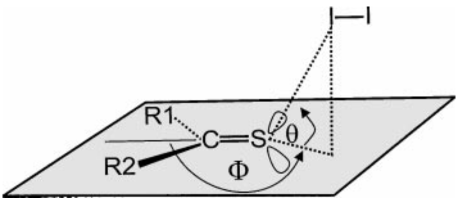


FIGURE 3 Definition of the parameters describing the relative orientation of the iodine atoms with respect to the sp^2-sulfur atoms.

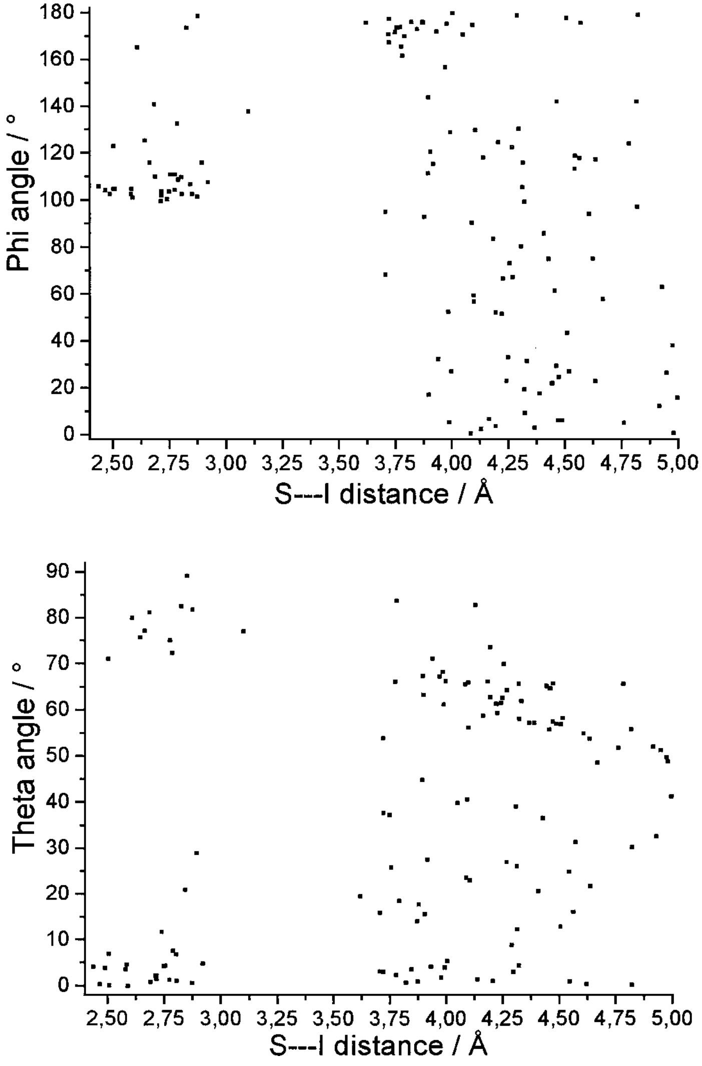


FIGURE 4 The angles phi (top) and theta (bottom) as a function of the S···I distance.

crystal structure of elemental iodine.[1] In the direction of the I-I vector, that is, in the direction of the σ^*-orbital the iodine molecules act as acceptors, whereas perpendicular to this vector the iodine molecules act as donors.[2] If the orientation of the iodine and the sulfur atoms in the structures discussed here can be regarded as such interactions the S···I-I angles should be about 180°. As is obvious from Figure 6, for

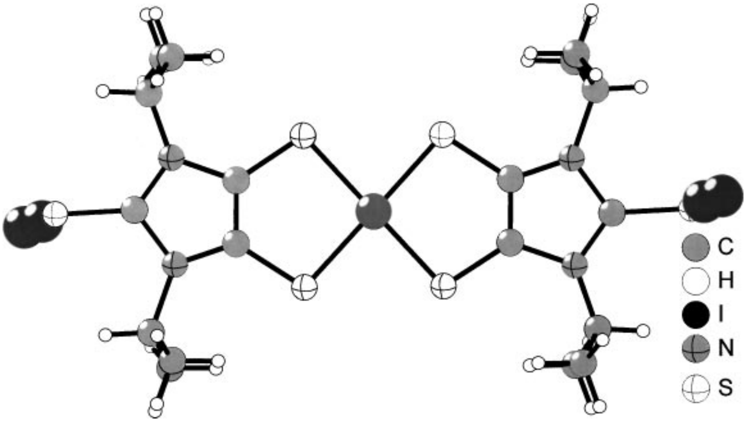


FIGURE 5 Part of the crystal structure of bis(1,3-Di-isopropylimidazolidine-2,4,5-trithionato)-nickel(ii) di-iodine.[23]

the group with S· · ·I distances between 2.4 and 3.1 Å all S· · ·I-I angles are about 180° whereas for S· · ·I distances larger than 3.4 Å a random distribution for this angle is found (Figure 6).

If this interaction can be explained on the basis of donor acceptor interactions involving iodine molecules the S· · ·I distance should be correlated with the I-I distance, too. In fact, such a correlation is found in the structures of the first group with S· · ·I bond lengths between

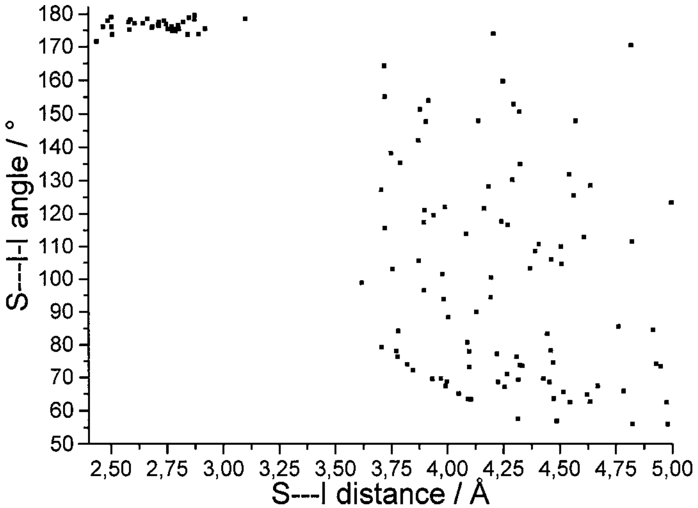


FIGURE 6 The S· · ·I-I angle as a function of the S· · ·I distance.

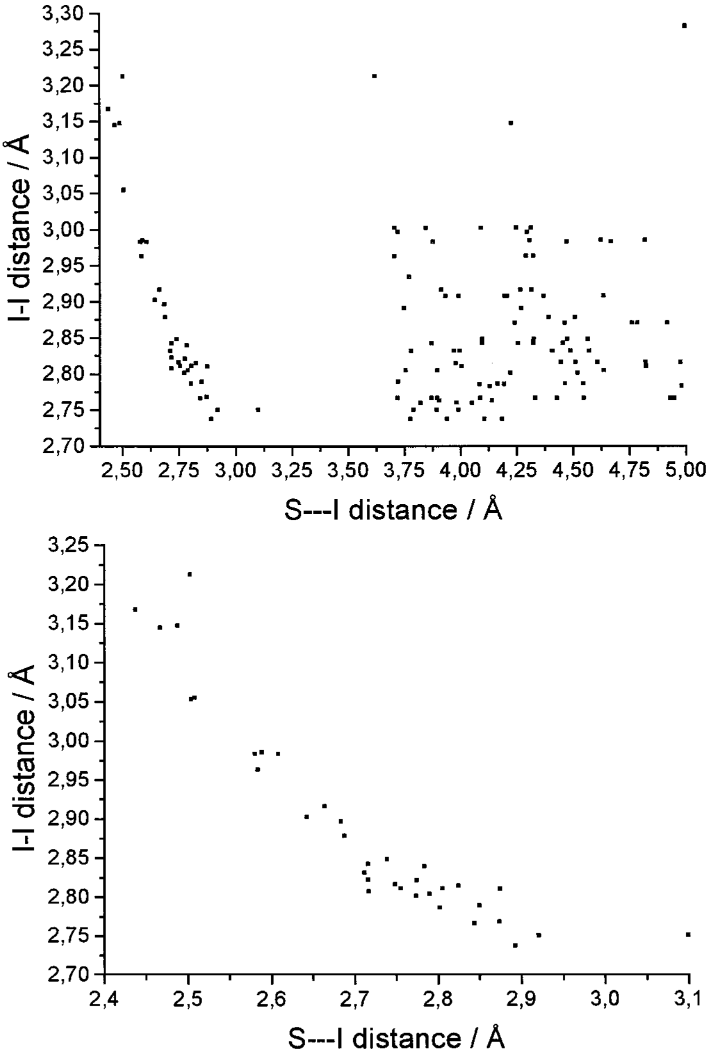


FIGURE 7 The I-I distance as a function of the S···I distance for S···I distances up to 5 Å (top) and between 2.4 and 3.1 Å (bottom).

2.4 and 3.1 Å (Figure 7). At shorter S···I distances the I-I distance is elongated to values of more than 3.2 Å because electron density is transferred to the σ^*-orbital of the iodine molecule which leads to very weak I-I interactions (Figure 7) like in 2-Imidazolidinethione bis(di-iodine)[11] (Figure 8). At longer S···I distances above 3.1 Å the I-I distance is close to the I-I distance found in elemental iodine of 2.715 Å.[29,30] As expected

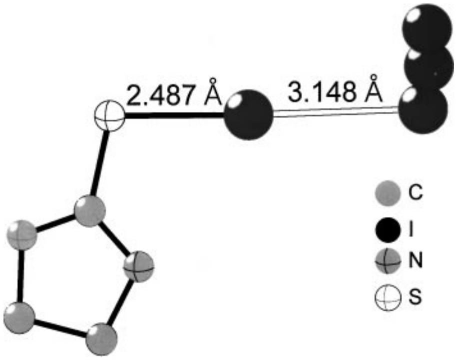


FIGURE 8 Crystal structure of 2-Imidazolidine-thione-bis(di-iodine).[11]

in the second group with S···I distances above 3.5 Å a random distribution is found which means that there should be no pronounced donor acceptor interactions.

If the principles of structure–structure and structure–reactivity correlation by Bürgi and Dunitz were utilized,[2] the data presented here could be used qualitatively as a model for a hypothetical reaction, in this case the addition of iodine to thioketones under formation of a formal cationic species and iodide anions. The geometrical data of each structure represent one point on the reaction pathway.

When the iodine molecule approaches the sulfur atom the I—I bond length increases whereas the S···I bond length decreases. At the end of the reaction the S—I bond length is close to a value for a S—I single bond, whereas the I—I distance is elongated to a value indicating that practically no covalent bond between the two I atoms exists. This situation is realized roughly in the crystal structure of 2-Imidazolidin-thione-bis(diiodine) (Figure 8).[11] In this case during the formation of the cationic species an additional iodine molecule acts as an acceptor of the iodide anion under formation of a triiodide anion (Figure 8).

In this article we have shown that in structures in which iodine molecules are connected to sp^2-sulfur atoms a preferred orientation can be found up to S···I distances of about 3.1 Å, whereas at longer S···I distances a random distribution of the I atoms around the S atom is found. This distance is about 0.6 Å shorter than the sum of the Van der Waals radii ($r_{VdW}(I + S) = 1.98 + 1.74 = 3.72$ Å) given by Bondi.[32,33] Assuming spheroidal atoms and therefore anisotropic van der Waals radii as calculated by Nyburg et al., this distance agrees roughly with the sum of the minimal van der Waals radii for sulfur and iodine ($r_{VdW}(I) = 1.76$–2.13 Å; $r_{VdW}(S) = 1.60$–2.03 Å).[34] Within these distances the iodine molecules are oriented predominantly in the direction of the sulfur lone-pairs. This geometry can be interpreted being due to donor-acceptor interactions in which the sulfur atom acts as a donor and the iodine molecule acts as an acceptor. According to the ideas of Bürgi and Dunitz the geometrical data extracted from this study can be discussed as a model for the reaction of iodine molecules with thioketones under formation of the cationic species and iodide anions. These results show that the analysis of structural data using database searches is a powerful tool for the investigation and interpretation of the structural properties of crystalline solids. Starting from the results obtained for sulfur, similar results can be expected for the heavier elements selenium and tellurium. Unfortunately, only a few of such compounds have been structurally characterized. This small number of structures is insufficient for a statistical analysis. However, first results show that even for these elements a similar behavior is found.

EXPERIMENTAL

The search in the CSD was performed using Conquest (Version 1.2, 2001). For this work two different searches were performed. In both cases the search fragment consisted of a three coordinated C atom bonded to two arbitrary atoms and one S atom. The bond type of all bonds was set to any type. In one of these searches the sulfur atom was defined to be two coordinated and bonded to an additional diiodine molecule, whereas in the second search the sulfur atom was defined to be only one coordinated. In this search only contact distances to diiodine molecules were considered. Symmetry equivalent crystal fragments were rejected and overlap of crystal fragments was permitted. The restriction of the coordination number of the sulfur atom was necessary to exclude thioethers and fragments in which the sulfur atom is coordinated to other atoms like metal cations which certainly influence the geometry of the S···I interaction. Because of this procedure some fragments in which the sulfur atom exhibits contacts to two different iodine atoms get lost. Unfortunately, there are some structures in the literature of which no coordinates have been deposited with in the CSD or for which no atomic coordinates are available. These structures are not considered in this work. However, by specifying the number of substituents 138 fragments were located. Two of the structures were redetermined and therefore not considered in the data analysis (Refcode: GEHNUB and VARCIA10). For the angles phi and theta only the absolute values were used.

REFCODES of the structures used for the data analysis (any structure in the CSD is defined clearly by the Refcode, which were assigned by the CSD; the literature citations for the structures with short S···I distances are found in Table I): BIMMEP, BZHTIC10, BZHTID20, CEWMIA, CEWMOG, CEWNAT, DAYBOU, DAYCIP, GEGNUB01, GIDYOH, GIGLOX, KUWDEL, KUWDIP, KUWDOV, LOPQEM, LOPQIQ, MSNROD, MSNROD, PEJKIY, PIGXUY, QIPYUX, TCAPLI, TOTWUU, TOTXAB, TURMEY, TURMIC, VARCIA, VEBCEK, YESHAF, YESHEJ, ZARDOL, ZEBQOM.

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