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INTRAMOLECULAR SULPHUR(II)—OXYGEN INTERACTION IN SULPHIDES AND DISULPHIDES WITH 2-METHOXYCARBONYLPHENYL AND 2-NITROPHENYL GROUPS: AN X-RAY STUDY

Á. KÜCSMAN* and I. KAPOVITS

Institute of Organic Chemistry, L. Eötvös University, P.O.B. 325, H-1445 Budapest (Hungary)

L. PÁRKÁNYI, GY. ARGAY and A. KÁLMÁN*

Central Research Institute of Chemistry, Hungarian Academy of Sciences, P.O.B. 17, H-1525 Budapest (Hungary)

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ABSTRACT

The molecular structures of methyl 2-(methylthio)benzoate, dimethyl 2,2'-dithiodibenzoate, dimethyl 2,2'-thiodibenzoate, methyl 2-(2-nitrophenylthio)benzoate, 2,2'-dinitrodiphenyl sulphide and methyl 2-(2-nitrophenylthio)phenylacetate exhibiting S(II)···O(carbonyl) or S(II)···O—(nitro) close contact have been investigated by X-ray diffraction. Planar (ArSMe), equatorial (Ar_2S_2) and skew (Ar_2S) conformations are explained by steric and conjugative effects and sulphur(II)—oxygen interaction. Linear and nonlinear X—S···O close contacts resulting from favourable "bond direction" and unfavourable "lone-pair direction" approaches (2.619—2.722 and 2.900—3.402 Å, respectively) are discussed in detail. Possible aryl ring positions, the geometry of rings with S···O contact and the nature of counter-atom (X = C, S) are considered as decisive factors. The results are consistent with different neighbouring group effects found earlier for *o*-CO_2Me, *o*-CH_2CO_2Me and *o*-NO_2 groups. Data support the mutual dependence of S—S and S···O distances in compounds with a linear S—S···O arrangement. Other bond lengths, e.g. C=O, N=O and S(II)—C_{ar} are not affected significantly by sulphur—oxygen interaction

INTRODUCTION

Sulphur—oxygen nonbonded contacts with S···O distances longer than S——O hypervalent bonds (1.66—2.25 Å) but shorter than the sum of the van der Waals radii (3.25 Å) are rather common in organosulphur compounds [1]. Besides governing the conformation, intramolecular sulphur-oxygen interaction may have a decisive influence on spectroscopic (IR, ^{13}C NMR) and chemical behaviour, as well. Thus, the decreased reactivity of *o*-nitrobenzenesulphenyl chloride [2] and *o*-carboxyphenyl sulphilimines [3] in chlorine addition and acid-catalysed hydrolysis, respectively, have been attributed to this interaction shielding and stabilizing the initial state. In a similar

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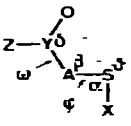
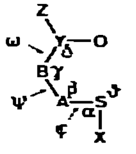
*To whom correspondence should be addressed.

way, the $CO_2Me \sim CO_2H \gg CH_2CO_2Me \sim CH_2CO_2H$ order of anchimeric assistance in the Cl^+-addition of sulphides has been explained on the one hand by the nearly equal activity of alkoxycarbonyl and carboxyl groups in stabilizing the sulphonium centre by Coulomb type sulphur—oxygen-(carbonyl) interaction, and by the lack of formation of a 6-membered ring with $S \cdots O$ contact [4], on the other.

In the case of sulphur—oxygen close contacts repulsive steric effects (interactions of doubly-filled orbitals) are presumably compensated by attractive effects (HOMO—LUMO and Coulomb interactions). This results in an optimum $S \cdots O$ distance characteristic for the interaction which is also controlled by both the constitution and geometry of the 4-, 5- or 6-membered "ring" closed by $S \cdots O$ contact (I—III)*. The formation of a planar 5-membered ring in a conjugated (X)—S—A=B—Y=O part with a nearly linear $X{-}S \cdots O$ arrangement (where X is an electronegative or polarizable "counter-atom"; cf. ref. 1b) seems to be favourable for an interaction between high-energy-HOMO n(O) and low-energy-LUMO $\sigma^*(S{-}X)$ and as well as for an attractive Coulomb interaction, too.



I



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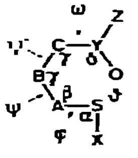

III

Since intramolecular sulphur—oxygen interactions play an important role in controlling the neighbouring group activity of *ortho* substituents, we initiated systematic X-ray investigations, being firmly convinced that solid state conformations reflect the initial stage of intramolecular and anchimerically assisted reactions (cf. ref. 5). Using o-CO_2Me, o-CH_2CO_2Me and o-NO_2 derivatives of aromatic sulphides and a disulphide, we started with studying how sulphur(II)—oxygen interaction, repulsive steric effects and conjugation contribute to bringing about the conformation observed in the crystalline state, how $X{-}\overset{|}{S} \cdots O{=}\overset{|}{Y}{-}$ nonbonded distances depend on the nature of the Y=O donor group and X counter-atom (Y = C or N, X = C or S), and how this interaction depends on the constitution and size of the ring closed by $S \cdots O$ contact (5- or 6-membered ring).

Model compounds

Methyl 2-(methylthio)benzoate (IV), dimethyl 2,2′-dithiodibenzoate (V), dimethyl 2,2′-thiodibenzoate (VI), methyl 2-(2-nitrophenylthio)benzoate

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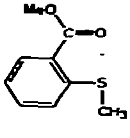
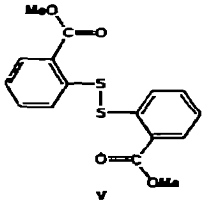
*In the generalized structures I—III the middle atom and middle axis are marked for bond angles (α, β, γ, δ and ϑ) and torsion angles (φ, ψ and ω), respectively.

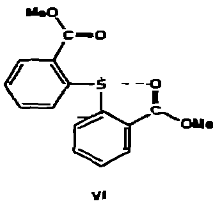
(VII), 2,2'-dinitrodiphenyl sulphide (VIII) and methyl 2-(2-nitrophenylthio)-phenylacetate (IX) were prepared and investigated by X-ray diffraction [6]:



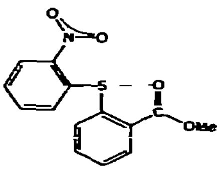
IV



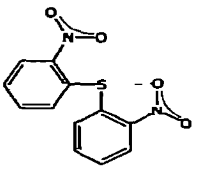
V



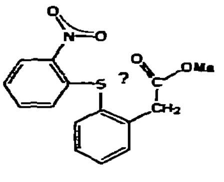
VI



VII



VIII



IX

These compounds seem to be suitable models for the following reasons (see empirical rules about sulphur—oxygen interactions and FMO interpretations in ref. 1a): (a) the $:\mathrm{S(II){-}C_{ar}\overset{--}{-}C_{ar}{-}Y}(sp^2)\mathrm{{=}O}$ part with Y = C or N is conjugated, (b) the *cis* configuration is established by the aromatic ring, (c) the *s-cis* conformation around the $\mathrm{C_{ar}{-}Y}$ bond allows the nonbonded sulphur and oxygen atoms to be close, (d) rotations about the $\mathrm{C_{ar}{-}Y}$ and $\mathrm{S{-}C_{ar}}$ bonds may result in a favourable 5-membered "ring" and a linear X—S···O arrangement with X = C or S "counter-atom" (e) in the diaryl sulphides VI—IX a double sulphur(II)—oxygen contact may occur involving one acceptor sulphur(II) atom and two identical or different Y=O donor groups, and (f) the chance of the formation of a 6-membered ring can be examined in the case of IX.

The dependence of sulphur—oxygen close contact on the valence state of the sulphur atom was also investigated by using sulphoxide and sulphilimine derivatives of the compounds IV and VI—IX, as will be shown in a subsequent paper [7].

EXPERIMENTAL

Materials

The compounds IV—VIII were prepared by known procedures and their purity was checked by m.p. determination, elemental analysis and spectroscopic methods (m.p. 66—67, 130—131, 84, 92 and 121—122°C, respectively).

Methyl 2-(2-nitrophenylthio)phenylacetate (IX)

The mixture of 2-(2-nitrophenylthio)benzoic acid (13.8 g, 50 mM) and thionyl chloride (30 ml) with some drops of pyridine was heated at 100° C for 3 h, then evaporated in vacuo, the residue extracted with boiling dry benzene (50 ml) and immediately filtered. After evaporation the oily residue was triturated with petroleum ether, filtered off, washed, then dried to yield crude 2-(2-nitrophenylthio)benzoyl chloride* (13.0 g, 88%, m.p. 81—83° C). IR (potassium bromide): 1785 vs (C=O), 1510 vs, 1334 vs (NO_2) cm^{-1}.

The crude acyl chloride (5.9 g, 20 mM) was dissolved in the mixture of dry ether (25 ml) and dry benzene (25 ml) and filtered. The filtrate was dropped into ether (70 ml) containing triethyl amine (2.8 ml) and diazomethane (generated from 5 g of *N*-nitroso-*N*-methylurea) under stirring and external cooling (salt—ice). The mixture was allowed to stand overnight (0° C). The precipitate (TEA·HCl) was filtered off and the filtrate was evaporated in vacuo. To the residue were added abs. methanol (75 ml), triethylamine (0.3 ml) and silver benzoate (0.3 g), and the mixture was heated to 60° C. After the vigorous evolution of nitrogen had subsided, the solution was refluxed for 30 min then charcoal (ca. 0.5 g) was added. The mixture was filtered and evaporated. The residue was triturated with ether (ca. 10 ml). The yellow crystals were filtered off, dried (3.1 g, 51%, m.p. 95—97° C) and recrystallized from 90% methanol to give the pure product, m.p. 99° C. IR (potassium bromide): 1733 vs (C=O), 1508 vs, 1333 vs (NO_2), 1206 vs (C—O—C) cm^{-1}. Elemental analysis: calculated for $C_{15}H_{13}NO_4S$, C = 59.4, H = 4.3, N = 4.6, O = 21.1, S = 10.6; found, C = 59.5, H = 4.4, N = 4.7, O = 20.8, S = 10.8(%).

Crystal structure determinations

Symmetry independent reflexions for compounds IV—IX were collected on an Enraf-Nonius CAD-4 computer controlled diffractometer with graphite monochromated MoK_α radiation (λ = 0.71073 Å) using an ω — 2Θ scan in the range $1.5 < \Theta < 25.0°$. In each case the lattice parameters and their standard deviations (Table 1) were determined by least-squares from the setting angles of 25 reflexions. After data corrections for Lorentz and polarization effects, the reflexions with $|F|^2 > 1.0\ \sigma(F^2)$ were taken as observed (for IV the $|F^2| > 2.0\ \sigma(F^2)$ criterion was applied). No absorption correction was performed in either case. The phase problems for each structures were solved by the MULTAN program [8], and subsequent structure factor and Fourier calculations. Full-matrix least-squares refinement of the positional and anisotropic vibrational parameters of nonhydrogen atoms resulted in the final conventional *R* values given in Table 1.

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*The crude product can be converted into VII by methanolysis (78%).

TABLE 1

Crystal and relevant X-ray data for compounds IV—IX

	IV	V	VI	VII	VIII	IX
Formula	$C_9H_{10}O_2S$	$C_{16}H_{14}O_4S_2$	$C_{16}H_{14}O_4S$	$C_{14}H_{11}NO_4S$	$C_{12}H_8N_2O_4S$	$C_{15}H_{13}NO_4S$
M.w.	182.24	334.42	302.35	289.31	276 27	303.34
Cryst sym.	orthorhombic	monoclinic	monoclinic	monoclinic	triclinic	monoclinic
Space group	$P2_12_12_1$	$P2_1/n$	Cc	$P2_1/n$	$P\bar{1}$	$P2_1/c$
a (Å)	5.445(2)	13.564(2)	10.531(3)	12.035(1)	7.677(2)	13.227(2)
b (Å)	11.701(3)	7.693(1)	14 381(2)	7.337(1)	7.840(1)	13 546(2)
c (Å)	14.144(4)	15.128(4)	9.650(6)	15.551(2)	11.679(2)	7.910(2)
α (deg)	90	90	90	90	102.78(1)	90
β (deg)	90	97.35(2)	99.00(2)	112.02(1)	88.95(2)	96.11(2)
γ (deg)	90	90	90	90	118.94(3)	90
U ($Å^3$)	901.1(8)	1566 3(9)	1443.4(9)	1359 7(6)	596 7(5)	1409.2(8)
D_c (Mg m^{-3})	1.343	1.418	1 391	1.413	1 538	1 430
Z	4	4	4	4	2	4
μ (mm^{-1})	0.309	0.349	0.237	0.238	0.270	0.233
$F(000)$	384	696	632	600	284	632
$N(F_{uni})$	1350	2745	1326	1956	2595	1926
$N(F_{obs})$	888	2395	1232	1629	2033	1744
R_{obs}	0.056	0.057	0.033	0.042	0.045	0.038
R_w	0.070	0.049	0.035	0.046	0 047	0 042

The fractional coordinates of hydrogen atoms were generated from geometries assumed for the IV and VII—IX structures These hydrogen atom positions were included in the structure factor calculations with individual isotropic temperature factors. The hydrogen positions for V and VI were located in difference Fourier map and were only included with a mean isotropic temperature factor (4.0 Å) in the final structure factor calculations. Atomic scattering factors were taken from ref. 9. All calculations were performed on a PDP 11/34 minicomputer (64 k) with the Enraf-Nonius SDP program package and local programs.

Fractional atomic coordinates determined for the hydrogen atoms in IV—IX and lists of structure factors and anisotropic temperature parameters are available from the authors on request.

RESULTS AND DISCUSSION

The solid-state conformations established for compounds IV—IX by X-ray analysis are given in Fig.1 by perspective representations IVa—IXa. Fractional atomic coordinates and mean temperature factors with e.s.d.s's in parentheses (in the units of the last significant digit) for nonhydrogen atoms are listed in Table 2. Selected bond lengths, bond angles and torsion angles including S···O nonbonded distances and X—S···O angles (with e.s d.s's in parentheses) related to sulphur(II)—oxygen interactions in compounds IV—IX are shown in Tables 3 and 4.

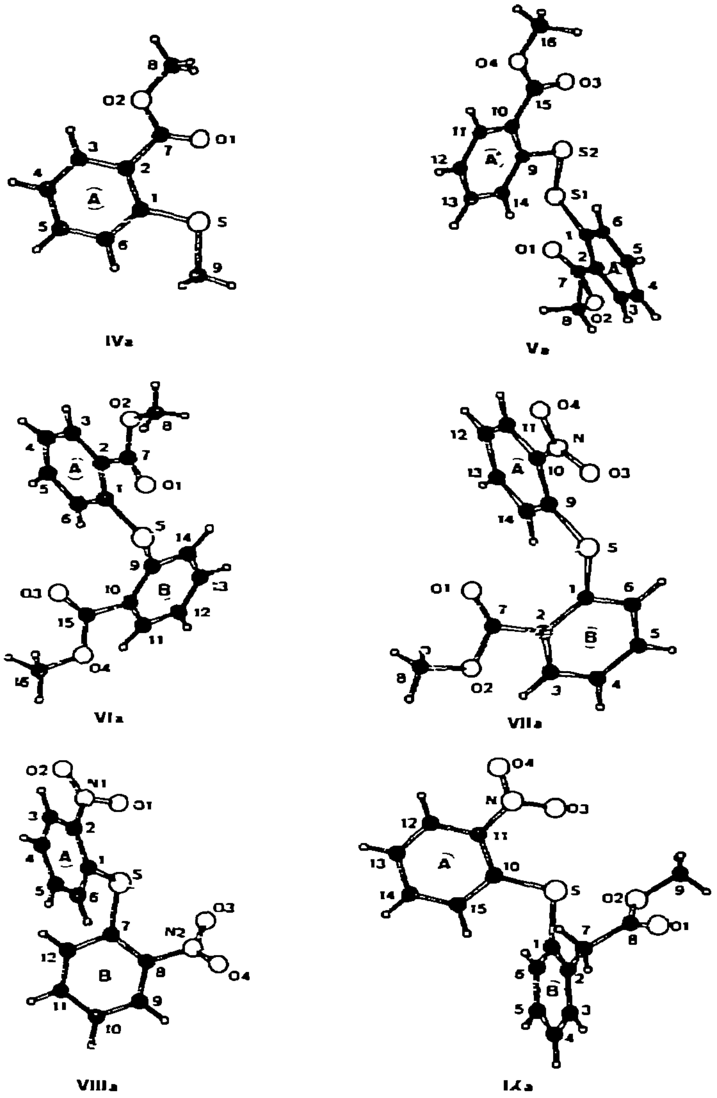
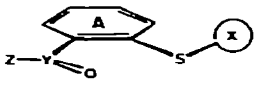


Fig. 1. Solid state conformations (IVa—IXa) for compounds IV—IX as obtained by X-ray analysis. Numbered atoms are carbon unless indicated otherwise; hydrogen atoms are also shown but not labelled. Rings are marked with symbols A (coplanar with C_{ar}—S—C/S plane), B perpendicular to C_{ar}—S—C/S plane and C (intermediate ring position as referred to C_{ar}—S—C/S plane).

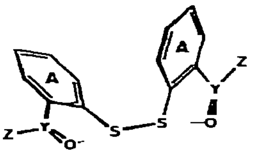
Conformations

Figure 1 reveals that the conformations of the sulphur(II) compounds IV—IX follow the general trends observed in case of alkyl aryl sulphides [10], diaryl disulphides [11] or diaryl sulphides [12]. Consequently, the possible formation of single or double sulphur—oxygen close contacts seems to have no decisive influence on the relative position of aromatic rings in these compounds.

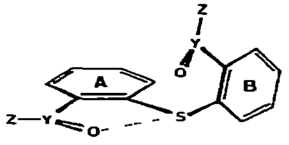
The monoaryl sulphide-ester IV is planar (see X, ZYO = CO_2Me, X = Me) like o-$NO_2C_6H_4SX$ sulphides with small X = R, OMe and Cl groups [13]. The ring position A is obviously required by the conjugative interaction between the aryl ring and the electron-releasing X-thio group



X



XI



XII

The disulphide-diester V exhibits equatorial conformation in which both aryl rings are coplanar with the C_{ar}—S—S plane (see XI, ZYO = Co_2Me) just like diphenyl disulphide and its $(QC_6H_4S)_2$ derivatives carrying an electron-withdrawing group in the *ortho* or even *para* position (Q = o-CO_2H, o-NO_2, p-NO_2) [14].

The symmetric diaryl sulphides VI and VIII assume the *skew* conformation (see XII, ZYO = CO_2Me/CO_2Me and NO_2/NO_2) in a similar way to most of the other $(QC_6H_4)_2S$ sulphides with Q = o-Me, p-NH_2 or m/p-OMe [15]. In these compounds only one ring (A) remains coplanar with the C_{ar}—S—C_{ar} plane ($\varphi \sim 180°$ can be observed for the torsion angle C_{ar}—S—C_{ar}—C^{o}_{ar} with C^{o}_{ar} *distal-ortho* ring atom), while the other ring (B) avoiding the perturbation of *proximal-ortho* groups becomes perpendicular ($\varphi \sim 90°$) to the C_{ar}—S—C_{ar} plane.

The unsymmetrical diaryl sulphides VII and IX preserve the *skew* conformation (see XII, ZYO = NO_2/CO_2Me and NO_2/CH_2CO_2Me). As in other sulphides with different aryl groups, the phenyl ring substituted with a stronger electron-withdrawing group, e.g. with o-NO_2 or p-NO_2, tends to occupy the planar ring position A [16]. This is probably due to the conjugative interaction between the electron-releasing X-thio group and the strongly electron-accepting nitro group through the aromatic ring which is coplanar with the interacting substituents.

In each of the compounds IV—IX the planar ring position A with a coplanar *distal-ortho* donor group allows the formation of both a planar 5-membered "ring" and a linear X—S···O arrangement with sulphur(II)—oxygen close contact (see X—XII, ZYO = CO_2Me or NO_2). This is favourable for an attracting HOMO—LUMO interaction, since the oxygen atom of the donor group as a "nucleophile" approaches the acceptor sulphur(II) atom in the direction of an S—X bond (cf. ref. 5).

In the disulfide V with two A-rings the *distal-ortho* position of the two donor groups results in a linear O···S—S···O arrangement of four atoms (see

TABLE 2

Fractional atomic coordinates (× 10^4 for four-digit data and × 10^5 for five-digit data of sulphur atoms) and mean temperature factors $B_{eq} = 4(B_{11}B_{22}B_{33}/a^{*2}b^{*2}c^{*2})^{1/3}$ (Å^2) for nonhydrogen atoms in molecules IV—IX

	x/a	y/b	z/c	B_{eq}		x/a	y/b	z/c	B_{eq}
IV					VII				
S	0006(2)	0532(1)	07114(7)	4,24(4)	S	13014(6)	02944(9)	39833(4)	3,51(1)
O(1)	−3801(7)	−0763(3)	0075(2)	5,3(1)	O(1)	3714(2)	1793(3)	4135(1)	5,97(7)
O(2)	−4454(7)	−1249(3)	−1410(2)	5,6(1)	O(2)	4202(1)	1159(3)	2931(1)	5,53(7)
C(1)	0193(9)	0711(3)	−0522(2)	3,5(1)	O(3)	1486(2)	−0808(2)	5621(1)	4,73(6)
C(2)	−1438(9)	0133(3)	−1127(3)	3,6(1)	O(4)	2059(2)	0516(3)	6913(1)	5,74(7)
C(3)	−1270(10)	0292(4)	−2108(3)	4,4(2)	N	1717(2)	0503(3)	6066(1)	3,62(6)
C(4)	0460(10)	1016(4)	−2490(3)	5,0(2)	C(1)	1180(2)	1075(3)	2875(1)	3,27(7)
C(5)	2020(10)	1576(4)	−1902(3)	5,2(2)	C(2)	2164(2)	1461(4)	2638(1)	3,27(7)
C(6)	1921(9)	1435(4)	−0936(3)	4,5(2)	C(3)	1960(2)	1856(4)	1721(2)	3,95(9)
C(7)	−3325(9)	−0652(3)	−0745(3)	3,8(1)	C(4)	0823(3)	1888(4)	1056(2)	5,3(1)
C(8)	−6270(10)	−2074(5)	−1087(4)	6,4(2)	C(5)	−0136(3)	1401(5)	1286(2)	5,8(1)
C(9)	2490(10)	1392(4)	1145(3)	5,1(2)	C(6)	0048(2)	1099(4)	2197(2)	4,65(9)
					C(7)	3418(2)	1496(4)	3329(2)	3.84(8)
V					C(8)	5446(3)	1245(6)	3523(2)	7,1(1)
S(1)	15295(5)	20869(9)	42612(5)	3,76(2)	C(9)	1421(2)	2162(3)	4637(1)	2,81(6)
S(2)	28110(5)	2158(1)	51318(4)	3,95(2)	C(10)	1605(2)	2128(3)	5589(1)	2,86(6)
O(1)	−0278(1)	1716(2)	3340(1)	4,65(8)	C(11)	1711(2)	3576(4)	6105(2)	3,53(7)
O(2)	−1482(1)	3703(2)	3166(1)	5,30(8)	C(12)	1628(2)	5151(4)	5708(2)	3,88(8)
O(3)	4496(1)	1624(2)	6236(1)	5,27(9)	C(13)	1439(2)	5230(4)	4773(2)	3,82(8)
O(4)	6038(1)	1709(3)	5880(1)	5,48(9)	C(14)	1348(2)	3796(4)	4258(1)	3,43(7)
C(1)	1074(1)	4272(3)	4207(1)	3,35(9)					
C(2)	0097(1)	4611(3)	3799(1)	3,21(9)	VIII				
C(3)	−0244(2)	6329(3)	3773(1)	4,1(1)	S	64705(9)	41301(7)	22283(5)	3,653(7)
C(4)	0347(2)	7678(3)	4123(2)	4,6(1)	O(1)	9018(3)	8020(2)	3059(2)	6,56(2)
C(5)	1304(2)	7312(3)	4512(2)	4,6(1)	O(2)	1,1360(2)[a]	9159(2)	4469(2)	6,40(3)
C(6)	1656(2)	5647(4)	4552(1)	4,1(1)	O(3)	3016(2)	3065(2)	0608(1)	3,70(2)
C(7)	−0546(1)	3177(4)	3420(1)	3,8(1)	O(4)	0360(2)	1024(2)	1324(2)	3,67(2)
C(8)	−2157(2)	2388(5)	2776(2)	7,0(1)	N(1)	9709(3)	7010(2)	3958(2)	4.22(2)
C(9)	3754(1)	2817(3)	4471(1)	3,5(1)	N(2)	2076(2)	1612(2)	1081(1)	2,73(2)
C(10)	4758(1)	2614(3)	4798(1)	3,6(1)	C(1)	6912(2)	4448(2)	3761(2)	2.40(2)

C(11)	5478(1)	3127(4)	4263(2)	4.5(1)
C(12)	5216(2)	3836(4)	3438(2)	4.8(1)
C(13)	4233(2)	4050(4)	3124(1)	4.6(1)
C(14)	3805(2)	3849(4)	3628(1)	4.2(1)
C(15)	5053(1)	1028(3)	5707(1)	4.1(1)
C(16)	6402(2)	1169(5)	6771(2)	5.6(1)
VI				
S	0000(0)	11838(5)	2559(0)	3.31(2)
O(1)	2058(2)	0752(1)	4533(2)	4.19(8)
O(2)	4087(2)	0751(1)	1120(2)	4.71(9)
O(3)	−1297(2)	3105(1)	2450(2)	4.27(8)
O(4)	−3438(2)	2838(1)	2096(2)	3.63(7)
C(1)	1290(2)	1783(2)	1959(3)	3.9(1)
C(2)	2674(3)	1629(2)	2609(3)	3.2(1)
C(3)	3068(3)	2100(2)	2111(3)	3.9(1)
C(4)	3323(3)	2717(2)	1011(3)	4.2(1)
C(5)	2062(3)	2890(2)	0387(3)	4.1(1)
C(6)	1058(3)	2416(2)	0870(3)	3.7(1)
C(7)	2848(3)	1007(2)	3843(3)	3.5(1)
C(8)	4410(3)	0159(3)	6323(4)	5.5(1)
C(9)	−1233(2)	1247(2)	1063(3)	3.0(1)
C(10)	−2261(2)	1878(2)	0963(3)	3.68(9)
C(11)	−3273(2)	1782(2)	−0130(3)	3.4(1)
C(12)	−3264(3)	1106(2)	−1138(3)	3.7(1)
C(13)	−2242(3)	0005(2)	−1051(3)	4.1(1)
C(14)	−1237(3)	0087(2)	0054(3)	3.7(1)
C(15)	−2240(2)	2093(2)	1924(3)	3.1(1)
C(16)	−3048(3)	3321(2)	2785(4)	4.3(1)
C(2)	8446(3)	6222(2)	4474(2)	2.75(2)
C(3)	8825(3)	6401(3)	5665(2)	3.36(3)
C(4)	7651(3)	4986(3)	6197(2)	3.07(3)
C(5)	6088(3)	3224(3)	5525(2)	3.02(3)
C(6)	5732(3)	2959(3)	4340(2)	2.88(2)
C(7)	5035(3)	1470(3)	1756(2)	2.43(2)
C(8)	3055(3)	0479(2)	1277(2)	2.11(2)
C(9)	1933(3)	−1581(3)	0044(2)	3.24(3)
C(10)	2792(3)	−2713(3)	1064(2)	3.47(3)
C(11)	4765(3)	−1783(3)	1518(2)	2.53(3)
C(12)	5856(3)	C272(3)	1864(2)	2.79(3)
IX				
S	31307(5)	61744(5)	82118(7)	4.01(2)
O(1)	1582(1)	5216(1)	4908(2)	5.59(7)
O(2)	2096(1)	3704(1)	5678(2)	4.77(6)
O(3)	5063(1)	6209(1)	7669(2)	4.92(7)
O(4)	6383(1)	6535(2)	9377(2)	5.60(7)
N	5481(1)	6343(1)	9100(2)	3.64(7)
C(1)	1854(2)	6378(2)	8667(3)	3.55(8)
C(2)	1120(2)	5665(2)	8296(3)	3 49(8)
C(3)	0121(2)	5891(2)	8486(3)	4.25(9)
C(4)	−0145(2)	6807(2)	9078(3)	4.6(1)
C(5)	0592(2)	7509(2)	9477(3)	4.5(1)
C(6)	1587(2)	7302(2)	9246(3)	4.20(9)
C(7)	1388(2)	4630(2)	7724(3)	4.20(9)
C(8)	1688(2)	4579(2)	5948(3)	3 75(8)
C(9)	2427(2)	3539(2)	4026(3)	5.7(1)
C(10)	3813(2)	6161(2)	1.0259(3)[a]	3.05(7)
C(11)	4873(2)	6259(2)	1.0523(3)[a]	3.04(7)
C(12)	5401(2)	6276(2)	1.2128(3)[a]	3.91(9)
C(13)	4883(2)	6166(2)	1.3528(3)[a]	4.44(9)
C(14)	3849(2)	6040(2)	1.3321(3)[a]	4.20(9)
C(15)	3318(2)	6045(2)	1.1722(3)[a]	3.82(9)

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[a] Total value for fractional atomic coordinate.

TABLE 3

Selected bond lengths (Å) for compounds IV—IX

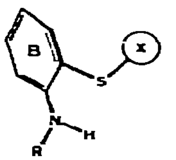
Compd[a]	Ring[a]	S···O[b]	X—S[c]	S—A[c]	A—B[d]	B—Y[e]	Y—O[f]	Y—Z[g]
IV	A	2.721(4)	1.793(6)[h]	1.760(4)	1.407(7)	1.480(7)	1.196(6)	1.323(6)
V	A	2.680(2)	2.047(1)*	1.789(3)	1.414(3)	1.478(4)	1.192(4)	1.342(3)
	A′	2.689(2)	2.047(1)*	1.792(2)	1.398(4)	1.481(3)	1.190(3)	1.340(3)
VI	A	2.722(2)	1.786(3)	1.785(3)	1.411(4)	1.481(4)	1.204(4)	1.341(4)
	B	3.077(3)	1.785(3)	1.786(3)	1.404(4)	1.492(4)	1.200(4)	1.344(4)
VII	A	2.619(1)*	1.782(2)	1.757(2)	1.413(1)	1.454(3)*	1.211(3)*	1.224(1)*
	B	3.058(2)	1.757(2)	1.782(2)	1.399(3)	1.489(3)	1.191(2)	1.335(3)
VIII	A	2.656(1)*	1.777(2)	1.768(2)	1.398(2)	1.464(2)*	1.223(3)*	1.220(2)*
	B	2.900(2)*	1.768(2)	1.777(2)	1.387(3)	1.466(1)*	1.219(1)*	1.219(2)*
IX	A	2.637(1)*	1.785(3)	1.768(2)	1.402(4)	1.456(3)*	1.219(2)*	1.218(2)*
	B[i]	3.402(2) 4.062(2)[k]	1.768(2)	1.785(3)	1.388(4)	1.514(4)[j] 1.501(3)[l]	1.189(3)	1.329(3)

[a] See II and IVa—IXa in Fig. 1. [b] S···O(carbonyl) or S···O(nitro)*. [c] C_{ar}—S or S—S*. [d] C_{ar}—C_{ar}. [e] C_{ar}—Csp^2 or C_{ar}—Nsp^2 *. [f] C=O or N=O*. [g] Csp^2—O or N=O*. [h] Csp^3—S [i] See III. [j] B—C = C_{ar}—Csp^3. [k] S···O(alkoxy). [l] C—Y = Csp^3—Csp^2.

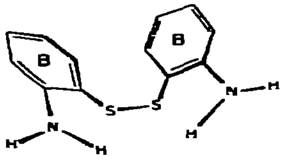
XI, ZYO = CO_2Me). Such a configuration has been observed for 1,2-dithiole derivatives having two acylamino, acylimino or acylmethylene groups in 3 and 5 positions [17].

In the *o,o′*-disubstituted diaryl sulphides VI—IX the second donor *ortho* group, belonging to the perpendicular ring B, can near the acceptor sulphur(II) atom only in a lone-pair direction. In this case there is no X counter-atom for a linear X—S···O contact, which is unfavourable. For such donor groups the observed S···O distances are rather long, and $\vartheta(C_{ar}$—S···O) angles as well as ω(A—B—Y—O) or ω(B—C—Y—O) torsion angles are far from being 180° or 0°, respectively.

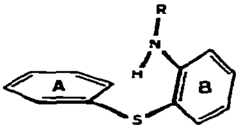
Although the ring position B perpendicular to the X—S—C_{ar} plane is unfavourable for intramolecular sulphur—oxygen interaction, this conformation involving intramolecular hydrogen bond seems to be preferred by 2-(R-amino)phenyl sulphides, 2,2′-diaminodiphenyl disulphide and 2-(R-amino)-diphenyl sulphides (XIII—XV, see refs. in Table 5).



XIII



XIV



XV

Indeed, the "electrophilic" amino-hydrogen approaches the "donor" sulphur(II) atom in a lone-pair direction (cf. ref. 5) resulting in a favourable N—H···S close contact as is shown in Table 5 by numerical values calculated by us from coordinates given in the original papers. The S···H distances are

TABLE 4

Selected bond angles (deg) and torsion angles (deg) for compounds IV—IX

Compd[a]	Ring[a]	X—S—O ϑ^{b}	X—S—A α^{c}	S—A—B β^{d}	A—B—Y γ^{e}	B—Y—O δ^{f}	X—S—A—B φ^{g}	S—A—B—Y ψ^{h}	A—B—Y—O ω^{i}
IV	A	179.2(4)	103.2(4)	120.6(6)	121.0(7)	124.9(8)	178.2(9)	−0.9(6)	8.5(9)
V	A	170.4(1)*	105.4(2)*	119.5(3)	120.5(4)	124.8(4)	−167.6(4)*	0.0(3)	−8.3(4)
	A′	169.6(1)*	104.9(2)*	120.1(3)	120.5(4)	125.0(4)	−165.1(4)*	−2.6(3)	−5.7(5)
VI	A	167.2(2)	102.1(2)	120.3(4)	120.3(5)	124.3(5)	−158.3(3)	−3.2(4)	−15.6(5)
	B	85.0(2)	102 1(2)	122.9(4)	121.9(4)	125.6(5)	−102.2(5)	15.4(4)	30.2(5)
VII	A	179.2(1)	103.5(2)	122.5(3)	119.9(3)*	119.6(3)*	−176.3(4)	0.7(2)*	−10.3(3)*
	B	76.5(1)	103.5(2)	123.9(3)	122.9(3)	125.8(4)	86.3(2)	−9.0(3)	−27.4(4)
VIII	A	171.7(1)	100.8(1)	122.1(2)	119.8(3)*	117.9(3)*	161.1(2)	1.8(2)*	24.6(3)*
	B	134.3(1)	100.8(1)	122.7(2)	120.6(2)*	118.0(2)*	115.3(3)	3.2(2)*	42.7(3)*
IX	A	169.8(2)	102.6(2)	122.7(3)	121.2(4)*	118.2(3)*	−164.2(5)	−2.3(2)*	−8.6(4)*
	B[j]	155.0(2)	102.6(2)	120.2(3)	122.0(4)[k] 114.5(4)[o]	126.2(4)[l]	−114.8(3)	8.3(3)[m] −72.0(4)[p]	−12.4(4)[n]

[a] See II and IVa—IXa in Fig. 1. [b] C_{ar}—S···O or S—S···O* angle. [c] C_{ar}—S—C_{ar} or S—S—C_{ar}* bond angle. [d] S—C_{ar}—C_{ar} bond angle. [e] C_{ar}—C_{ar}—Csp^2 or C_{ar}—C_{ar}—Nsp^2* bond angle. [f] C_{ar}—Csp^2—O or C_{ar}—Nsp^2—O* bond angle. [g] C_{ar}—S—C_{ar}—C^{o}_{ar} or S—S—C_{ar}—C^{o}_{ar}* torsion angle with substituted C^{o}_{ar} *distal-ortho* ring atom. [h] S—C_{ar}—C^{o}_{ar}—Csp^2 or S—C_{ar}—C^{o}_{ar}—Nsp^2* torsion angle. [i] C_{ar}—C^{o}_{ar}—Csp^2—O or C_{ar}—C^{o}_{ar}—Nsp^2—O* torsion angle. [j] See III. [k] A—B—C = C_{ar}—C_{ar}—Csp^3 bond angle. [l] C—Y—O = Csp^3—Csp^2—O bond angle. [m] S—A—B—C = S—C_{ar}—C^{o}_{ar}—Csp^3 torsion angle. [n] B—C—Y—O = C^{o}_{ar}—Csp^3—Csp^2—O torsion angle. [o] B—C—Y = C_{ar}—Csp^3—Csp^2 bond angle. [p] A—B—C—Y = C_{ar}—C^{o}_{ar}—Csp^3—Csp^2 torsion angle.

TABLE 5

N–H···S close contacts in *ortho*-amino derivatives of alkyl aryl sulphides, diaryl sulphides and diaryl disulphides

o-NHR–C$_6$H$_3$Q–S–X			Ref.	S···H (Å)	X–S···H (°)	C$_{ar}$–S···H (°)	N–H···S (°)	X–S–C$_{ar}$–C$_{ar}$(N) φ (°)
R	Q	X						
Ac	*m*-C$_6$H$_4$NHAc	Me	18a	2.68	71	79	110	109.4
H	H	CHZZ′	18b	3.07	71	126	78	124.8
H	H	SC$_6$H$_4$NH$_2$ *o*	18c	2.48	100	68	113	99.0
				2.64	89	71	110	97.4
Me$_2$N(CH$_2$)$_3$	*p* Cl	Ph	18d	2.63	74	70	110	116.9
Me$_2$N(CH$_2$)$_3$		C$_6$H$_4$Cl-*o*	18e	2.24	75	73	112	107.6
Me$_2$N(CH$_2$)$_4$	*p*-Cl	C$_6$H$_4$Cl-*o*	18f	2.62	82	68	117	107.2
Et$_2$N(CH$_2$)$_3$	*p*-Cl	Ph	18g	2.68	72	73	107	114.2

significantly shorter than the sum of van der Waals radii (2.85 Å, as given in ref. 5b).

All this reveals that a competition of sulphur—oxygen interaction with intra- or inter-molecular hydrogen bonding should also be taken into account when discussing the actual conformation of given organosulphur compounds (see for example the zig-zag structure of thiodipropionic acid in ref. 19)

S(II)···O distances in rings A

Although there are favourable conditions for sulphur(II)—oxygen interaction in ring A of the sulphide-esters IV and VI (conjugated, nearly planar 5-membered "ring", ϑ = 179.2 and 167.2°), the S···O distances, 2.721 and 2.722 Å are rather long. This may be ascribed (i) to the moderate electronegativity of the counter-atom X = C, (ii) to the common geometry (bond lengths and bond angles) of the aromatic ring and CO_2Me group, and (iii) to the slight deviation from planarity observed for the 5-membered ring with S···O close contact (ω = 8.5° and 15.6°). Even longer S···O distances have been found, however, in other esters with constitution and geometry less favourable for sulphur—oxygen interaction. Such compounds are nonconjugated esters of β-(X-thio)propionate type with nonplanar "SABYO" ring (2.768 and 2.857 Å), conjugated (planar) but nonaromatic esters of β-(X-thio)acrylate type with large β(S—A—B) angle (2.780, 2.887, 2.893 and 3.043 Å), and esters exhibiting 1,4 sulphur—oxygen close contact (2.826 and 2.997 Å) [20].

If the counter-atom X = C in the linear triatomic system X—S···O= (carbonyl) is replaced by an S atom, the S···O distance becomes markedly shorter as was observed for the disulphide-diester V (2.680 and 2.689 Å; cf. the 2.522 Å value found for a cyclic sulphenate-ester with an O—S···O part in ref. 21).

The comparison of the *o*-(methoxycarbonyl)phenyl disulphide V with *o*-carboxyphenyl disulphides (S···O 2.688 and 2.741 Å, ref. 22) shows that there is no significant difference in S(II)···O(carbonyl) close contacts for esters and carboxylic acids both exhibiting rather large δ(B—Y—O) angles. This is in accordance with the nearly identical anchimeric assistance of *o*-CO_2Me and *o*-CO_2H groups detected in some reactions of sulphides [4]. Since even S···O(carboxyl) and S···O—(carboxylate) distances do not differ markedly (as can be seen from S···O 2.628 and 2.771 Å data obtained for 2,2'-dithiodibenzoate salts in ref. 23), the enhanced neighbouring group activity of the nucleophilic carboxylate group [4] may be mainly attributed to the negative charge of the carboxylate oxygen atom.

Since the geometry of the nitro group is more favourable for sulphur—oxygen close contact than that of the alkoxycarbonyl group (A—B and B—Y distances are shorter, the B—Y—O angle is smaller in structure II), the S(II)···O distances obtained for the nitro-sulphides VII—IX (2.619, 2.656 and 2.637 Å) are markedly shorter than those in sulphide-esters. The former values agree well with the corresponding data of other compounds of (2-nitrophenyl) sulphide type having an X = C counter-atom (S···O 2.619, 2.639, 2.643 and 2.677 Å; see refs. 13a, 12, 16a and 24).

As expected, S···O(nitro) distances are shorter in aromatic disulphides, sulphenates and sulphenyl chlorides with X = S, O and Cl respectively (S···O 2.589, 2.44 and 2.414 Å; see refs. 14c, 13b, 13c) than in sulphides investigated by us where the counter-atom (X = C) is less electronegative. Note that S···O(nitro) distances are also strikingly short in compounds of β-(X-thio)-nitroethylene type with X = C or S (2.581 and 2.373 Å; ref. 25).

S(II)···O distances in rings B

The donor oxygen of the second ortho group in ring B lies rather far from the acceptor sulphur(II) atom in the *o,o'*-disubstituted diaryl sulphides VI—IX. The observed S···O distances, 3.077 and 3.058 (for *o*-CO_2Me in VI and VII), 2.900 (for *o*-NO_2 in VIII) and 3.402 Å (for *o*-CH_2CO_2Me in IX), may be accounted for by the lack of an X counter-atom joined linearly to the S···O part (see ϑ angles in Table 4) and by the turning out of the donor group from the plane common with the aromatic ring (ω = 30.2, 27.4, 42.7 and 12.4°; ψ' = 72° in IX). It is remarkable that *o*-CH_2CO_2Me group with a saturated carbon atom undoubtedly avoids forming a 6-membered ring with S···O close contact. This is in accordance with the lack of an anchimeric assistance by *o*-CH_2CO_2Me group in some reactions of sulphides [4].

Bond lengths

When discussing the geometry of compounds IV—IX it seems worth examining whether close contacts of X—S(II)···O=Y—Z type (see II) have any detectable effect on X—S, Y—O and Y—Z bond lengths in cases of CYZ = CO_2Me or NO_2, and X = C_{ar} or S(II).

The C_{ar}^A—S(II) and C_{ar}^B—S(II) bond lengths are somewhat different in VI and VIII of symmetric constitution (Δr = 0.001 and 0.009 Å), but conjugation may be more responsible for C_{ar}^A—S(II) bond shortening than sulphur—oxygen interaction for C_{ar}^B—S(II) bond lengthening. The above conclusion also seems to be supported by an inequality of C_{ar}—S(II) bonds (Δr = 0.002—0.015 Å) observed in symmetric diaryl sulphides without S···O close contact [16].

Unequal S——O hypervalent bond lengths in sulphuranes with unsymmetrical O^1——S——O^2 group are known to determine each other mutually [26]. Similarly, in case of X—S···O close contacts it is the S—S···O triatomic system with S(II)—S(II) bond where the mutual interaction of X—S and S···O linkages can be undoubtedly detected. The experimental distribution of S—S and S—S···O distances registered in the literature [27] indicates that short S···O distances go with a marked lengthening of S—S bonds. The hyperboloid curve in Fig. 2 constructed by plotting S—S···O distances vs. S—S

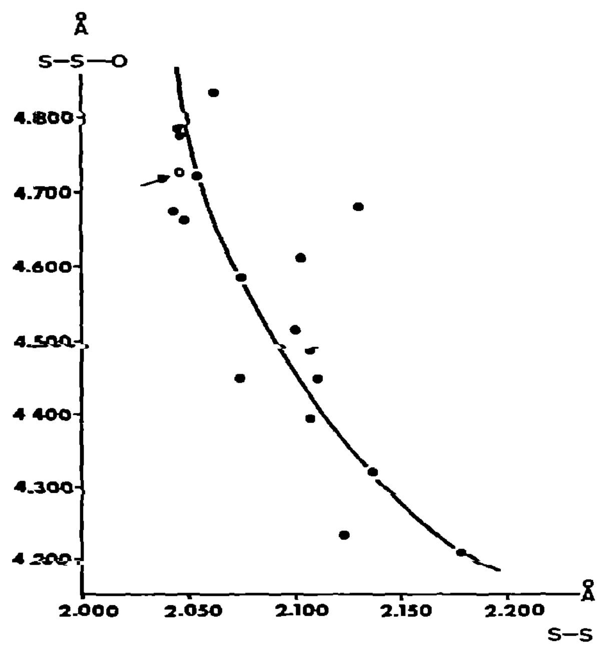


Fig. 2. Variation of the S–S bond length with the S · O distance in approximately linear S–S·· O triatomic systems [27].

bond lengths is similar to those shown earlier [5c] for the triatomic systems I–I···I (triiodide ions), S–S···S (thiathiophthenes) and H–O···H (hydrogen bonds).

For S–S distances the covalent S–S bond length of 2.023 Å in unsubstituted diphenyl disulphide [14a] exhibiting equatorial conformation and no S···O interaction, and the hypervalent S– –S– –S bond lengths of 2.538 Å in 2,5-dimethylthiathiophthene [28] can be regarded as extreme values (cf. the dependence of S–S bond length on substituents and conformations in ref. 11). Following the above trend, the slight but observable increase of S–S bond length (2.047 Å) in compound V may be attributed to a sulphur–oxygen contact with rather long S·· O distance (see point ○ in Fig. 2).

"Y–O" bond length data in the literature [27] indicate that a significant elongation of carbonyl C=O and nitro N=O bonds usually occurs only in S–S···O=Y–Z systems with extremely short S···O distances. Thus it is not surprising that in compounds IV–IX sulphur(II)–oxygen interactions involving relatively long S···O distances do not cause any remarkable alteration in the geometry of CO_2Me and NO_2 groups. The inequality of N=O bonds in compounds VII–IX (see Table 3) is not significant, because similar differences have also been observed for *para*-nitro derivatives exhibiting no S···O close contact [27].

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