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Dithiocarbimates from Sulfonamides
Part 3*. The Crystal Structure of Bis(tetraphenylarsonium)-*N*-(*p*-chlorphenylsulfonyl)-dithiocarbimatodisulfide Hydrate and an *ab initio* MO Study on the Characteristic S–S Dihedral Angle in the Dinegative Model System $[HN{=}C(S)C{-}S(S)C{=}NH]^{2-}$

H.-U. HUMMEL, U. KORN
Institute of Inorganic Chemistry, University of Erlangen-Nürnberg, D-8520 Erlangen (F.R.G.)
and P. OTTO
Institute of Theoretical Chemistry, University of Erlangen-Nürnberg, D-8520 Erlangen (F.R.G.)

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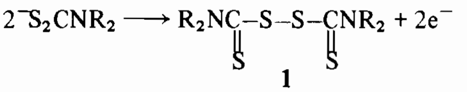
Abstract

The *N*-(*p*-chlorphenylsulfonyl)-dithiocarbimatodisulfide $[-S(S)C{=}N{-}S(O_2){-}C_6H_4{-}Cl]_2{}^{2-}$ has been prepared from the corresponding dithiocarbimate $[S_2C{=}N{-}S(O_2){-}C_6H_4{-}Cl]^{2-}$ by oxidation with I_2. A complete X-ray structure has been carried out on the bis(tetraphenylarsonium) salt. The bond length of the central disulfide group S–S is 2.047 Å, the dihedral angle C–S–S–C is 80.8°. The characteristics of the disulfide group concerning the S–S dihedral angle are investigated by *ab initio* SCF MO calculations using different basis-sets. A point-charge model has been introduced to simulate crystal field effects.

Introduction

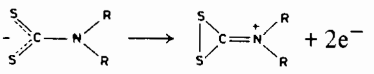
Dithiocarbamates and related chelating ligands $YCS_2{}^{n-}$ ($n = 1$, 2) frequently stabilize metallic centres in unusually high oxidation states and also have a propensity for stabilizing novel stereochemical configurations, unusual mixed oxidation states and intermediate spin states [2–6].

As covalency and charge distribution seem insufficient to explain the exceptional ability of the 1,1-dithiolate ligands to stabilize metal ions in formal high oxidation states, sulfur–sulfur interactions are discussed as formal electron-donating mechanisms [7, 8].



$$2\,{}^{-}S_2CNR_2 \longrightarrow R_2N\underset{\underset{S}{\|}}{C}{-}S{-}S{-}\underset{\underset{S}{\|}}{C}NR_2 + 2e^- \qquad (1)$$

1



(2)

2

A two-electron oxidized dithiocarbamate cation **2** has not been isolated but its existence was postulated [9]. On the other hand, thiuram disulfides **1** can easily be prepared from dithiocarbamates with iodine or bromine in ethanol and play an important role in industrial processes and biological systems [10–12]. Nevertheless there are relatively few reports on structural studies or metal complexes of thiuram disulfide ligands [13, 14].

Recently we reported on the electrochemical oxidative dimerization reactions [15, 16]

$$2\,[S_2C{=}C(CN)_2]^{2-} \longrightarrow [(NC)_2C{=}C(S)S{-}S(S)C{=}C(CN)_2]^{2-} + 2e^- \qquad (3)$$

3

$$2\,[S(O)C{=}C(CN)_2]^{2-} \longrightarrow [(NC)_2C{=}C(O)S{-}S(O)C{=}C(CN)_2]^{2-} + 2e^- \qquad (4)$$

4

X-ray structures of $(AsPh_4)_2$**3** and $(AsPh_4)_2$**4**$\cdot H_2O$ revealed anions consisting of two mutually perpendicular planes of the monomer fragments linked by a disulfide group [15, 16].

During our investigation on new dithiocarbimates based on sulfonamides [1, 17] we observed the one-electron oxidation (5) followed by the rather fast chemical radical-dimerization (6) (EC_{irr} mechanism) by use of cyclic voltammetry [18]. On continuation of the anodic scan an intramolecular cyclization occurs which involves sulfur formation (7). The products have been identified by mass spectroscopy after generation at a constant potential.

$$\underset{\mathbf{5}}{[S_2C{=}N{-}S(O_2){-}C_6H_4{-}X]^{2-}} \rightleftharpoons \underset{\mathbf{6}}{[S_2C{=}N{-}S(O_2){-}C_6H_4{-}X]^{\cdot-}} + e^- \qquad (5)$$

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*Part 2 is ref. 1.

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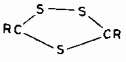
$$2[S_2C{=}N{-}S(O_2){-}C_6H_4{-}X]^{\dot{-}} \xrightarrow{K}$$
6

$$[{-}S(S)C{=}N{-}S(O_2){-}C_6H_4{-}X]_2^{2-} \qquad (6)$$
7

$$[{-}S(S)C{=}N{-}S(O_2){-}C_6H_4{-}X]_2^{2-} \longrightarrow$$



$$+ 2e^- + \frac{1}{8} S_8 \qquad (7)$$
8

R = $NS(O)_2C_6H_4X$

X = H: **5a**, **7a**; $E = +0.272$ V **8a**; $E = +1.042$ V
X = CH_3: **5b**, **7b**; $E = +0.302$ V **8b**; $E = +1.092$ V
X = Cl: **5c**, **7c**; $E = +0.402$ V **8c**; $E = +1.142$ V

Single crystals of $(AsPh_4)_2$**7c**$\cdot H_2O$ suitable for X-ray structure analysis have been obtained and the results are presented below.

In molecular compounds R–S–S–R as well as in the negatively charged species **3** and **4** dihedral angles are usually close to 90° [15, 16, 19–22]. In order to rule out the influences of negative charge and crystal packing on the molecular structures of **3** and **7** we investigated the nature of the S–S bond by using an *ab initio* molecular orbital method for the model system $[H{-}N{=}C(S)S{-}S(S)C{=}N{-}H]^{2-}$ (**9**) with (a) a minimal basis set, (b) double zeta plus polarization on S atoms, (c) minimal basis plus point-charge contribution and (d) minimal basis plus polarization for anionic sulfur atoms plus point-charge contribution, based on crystal structure analysis.

Experimental

Preparation of $(AsPh_4)_2[Cl{-}C_6H_4{-}S(O_2){-}N{=}C(S)S{-}]_2 \cdot H_2O$

The *N*-(*p*-chlorphenylsulfonyl)-dithiocarbimate was prepared according to the literature [1]. A mixture of 4.0 g K_2**5c**$\cdot H_2O$ and 1.34 g iodine in 100 ml ethylacetate was stirred at room temperature for 10 min. After filtration of precipitated KI the solution was slowly evaporated to give a yellow powder which was dissolved in 30 ml acetone. To this solution 4.0 g $AsPh_4Cl$ in 40 ml acetone were added slowly. On addition of 500 ml water, a solid white precipitate was yielded, which was recrystallized from acetone/H_2O.

The TG curve (Netzsch STA 426, N_2-atmosphere, reference: Al_2O_3) of the title compound shows one distinct peak due to the loss of one mole H_2O at 200 °C; decomposition is monitored at $T = 235$ °C.

The ESCA spectrum (Leybold-Heraeus photoelectron spectrometer, Al Kα radiation, C_{1s} internal standard, pressure: 10^{-7} torr) of $(AsPh_4)_2$**7c**$\cdot H_2O$ exhibits three different signals of the S_{2p} electrons according to three different oxidation states of sulfur in **7c** (BE_{S2p} = 169.6, 164.6 and 162.6 eV).

The CV measurements were performed using a PAR 361 Scanning Potentiostat with a three-electrode unit (Au working-electrode versus SCE). The solvent was CH_3CN with $TBAClO_4$ as conduction salt. Scan rates were 200–500 mV s^{-1}.

Crystal Data

$T = 295 \pm 1$ K. $C_{62}H_{50}N_2As_2Cl_2O_5S_6$._ Formula weight = 1315.13. Triclinic, space group $P\bar{1}$ (C_i^1, No. 2), $a = 24.101(2)$, $b = 12.189(1)$, $c = 11.079(1)$ Å, $\alpha = 108.31(2)$, $\beta = 78.47(1)$, $\gamma = 92.20(1)°$, $V = 3026.4$ Å^3. $D_c = 1.44$ g cm^{-3} for $Z = 2$.

Data Collection

Philips PW1100 diffractometer, graphite monochromated Ag Kα radiation, $\lambda = 0.5597$ Å, $\mu = 7.04$ cm^{-1}, $F(000) = 1324$, 16934 symmetry-dependent reflections measured with $2 \leqslant \theta \leqslant 18°$.

Structure Solution and Refinement

Data were corrected for Lorentz and polarization effects but not for absorption. Merging gave 8467 symmetry-independent reflections. A total of 3180 reflections with $I < 4\sigma(I)$ were omitted, 4083 reflections were used as observed. Structure solution was by direct methods using SHELXS-86 [23a]. Least-squares refinement was performed using SHELX-76 [23b]. Phenyl and O atoms isotropic, phenyl rings as rigid bodies with geometrically fixed H atoms with common isotropic temperature factor $U_{iso} = 0.099$ Å^2. Unit weights, final $R = 0.0599$.

Atomic scattering factors were taken from International Tables for X-ray Crystallography [24]. Calculations were performed on a Micro-Vax II workstation with VMS operating system. Final atomic parameters for selected atoms are given in Table 1, and details of the geometry of the disulfide in Tables 2 and 3.

Ab Initio Calculations

Ab initio calculations were performed on a CYBER 995 E with NOS-VE operating system and an IBM-MO-SCF program [25]. For all calculations the model system $[H{-}N{=}C(S)S{-}S(S)C{=}N{-}H]^{2-}$ (**9**) was introduced with available bond lengths and angles from the X-ray crystal structure of **7c** and H–N distances of 1.01 Å. Calculations on free **9** have been carried out using a rigid geometry at various dihedral S–S angles of 70, 90, 120, 150 and 180° and a minimal basis-set [26] as well as a double-zeta basis [(H; 6s), (N, C; 9s 3p), (S; 13s 10p) contracted to (H; 2s), (N, C; 4s 2p), (S; 6s 5p)] [26]. In order to simulate the crystal field 6 surrounding anions **9** with charge distribution obtained with a Mulliken popula-

TABLE 1. Atomic parameters for non-phenyl atoms of $AsPh_4$ with e.s.d. s in parentheses

Atom	*x*	*y*	*z*
As1	0.3650(1)	0.8592(1)	0.3527(1)
As2	0.0626(1)	0.0100(1)	0.2367(1)
S11	0.1534(1)	0.5605(3)	0.1497(3)
S21	0.1616(1)	0.5962(3)	0.9055(3)
C1	0.1760(4)	0.5002(8)	0.9771(9)
N1	0.2013(3)	0.3997(7)	0.9339(7)
S31	0.2312(1)	0.3468(2)	0.7831(3)
O11	0.1942(3)	0.3388(6)	0.6943(7)
O21	0.2583(3)	0.2392(6)	0.7712(7)
C11	0.2861(2)	0.4406(4)	0.7564(5)
C21	0.3160(2)	0.4937(4)	0.8540(5)
C31	0.3646(2)	0.5549(4)	0.8273(5)
C41	0.3832(2)	0.5629(4)	0.7029(5)
C51	0.3533(2)	0.5099(4)	0.6052(5)
C61	0.3047(2)	0.4487(4)	0.6320(5)
Cl1	0.4431(1)	0.6385(3)	0.6714(4)
S12	0.1567(1)	0.4322(3)	0.2311(3)
S22	0.2304(1)	0.3160(3)	0.3231(3)
C2	0.2287(5)	0.4123(9)	0.2451(9)
N2	0.2674(4)	0.4673(7)	0.1877(7)
S32	0.3334(1)	0.4530(2)	0.1935(3)
O12	0.3441(3)	0.4857(6)	0.3222(7)
O22	0.3640(3)	0.5143(6)	0.1095(7)
C12	0.3533(2)	0.3070(4)	0.1189(5)
C22	0.3861(2)	0.2526(4)	0.1749(5)
C32	0.4069(2)	0.1399(4)	0.1092(5)
C42	0.3948(2)	0.0816(4)	0.9875(5)
C52	0.3620(2)	0.1360(4)	0.9315(5)
C62	0.3412(2)	0.2487(4)	0.9972(5)
Cl2	0.4215(2)	0.9439(3)	0.9054(4)
OW	0.1333(4)	0.4724(8)	0.5857(9)

TABLE 2. Selected bond lengths (Å) and angles (°) for the monomer fragments 1 and 2 in 7c

	1	2	
S1–C	1.796(9)	1.81(1)	
S2–C	1.686(8)	1.668(9)	
C–N	1.29(1)	1.31(1)	
N–S3	1.614(8)	1.62(1)	
S3–O1	1.434(9)	1.428(8)	
S3–O2	1.445(6)	1.445(7)	
S3–C1	1.757(5)	1.750(4)	
Cl–C4	1.719(7)	1.717(5)	
C–S1–S12	108.4(3)		
C–S1–S11		109.3(3)	
S1–C–S2	109.3(5)	109.3(6)	
S1–C–N	117.1(6)	116.4(8)	
S2–C–N	133.5(8)	134(1)	
C–N–S3	120.7(6)	119.8(7)	
O1–S3–O2	115.2(4)	116.3(4)	
N–S3–C1	105.7(3)	107.7(3)	
S11–S12		2.047(4)	
OW–O11		2.89(1)	
C1–S11–S12–C2		80.8(7)	
As1–C111	1.892(5)	As2–C112	1.905(5)
As1–C121	1.906(4)	As2–C122	1.890(5)
As1–C131	1.885(5)	As2–C132	1.896(5)
As1–C141	1.878(5)	As2–C142	1.884(6)

TABLE 3. Mean deviations from least-square planes (Å)

Plane defined by atoms	d_{mean}
S11, S21, C1, N1, O21, S31	0.047
S12, S22, C2, N2, S32, O22	0.049
Cl2, -⌬-, S32, O12	0.038
Cl1, -⌬-, S31, O11	0.048

tion analysis on free **9** [27] and 14 point-charge contributions with charge of +1 based on crystallographic positions of the $AsPh_4$ centres in $(AsPh_4)_2$**7c**·H_2O have been included. Calculations based on a rigid geometry of **9** with S–S dihedral angles 70, 90, 120, 150 and 180° have been performed using a minimal basis and an extended basis-set including polarization functions for anionic sulfur atoms (p, d) [28].

Results and Discussion

Figure 1 shows a single anion to indicate the atomic labelling scheme and Fig. 2 illustrates the packing of anions and cations in the crystal.

In **7c** there are several alterations within the CS_2 fragments when compared to **5c**. The decreased bond angle S–C–S (109° in **7c** versus 120° in **5c**) is obviously caused by a less pronounced repulsion between S atoms in the CS_2 units induced by a decrease of negative charge located on the disulfide atoms S1 in **7c**. While in **5c** the C–S bond lengths are of the same magnitude (1.70; 1.74 Å) they are different in

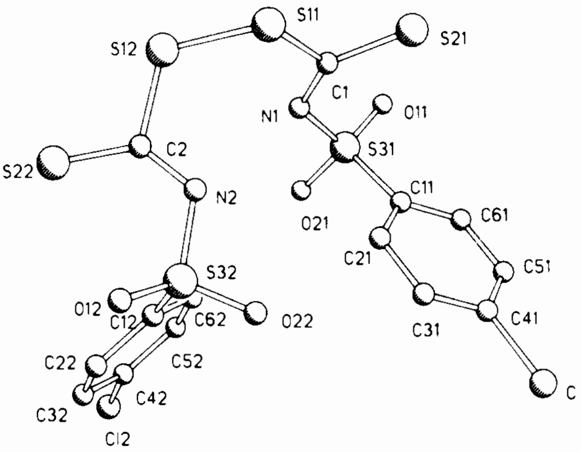


Fig. 1. Atom labelling of 7c.

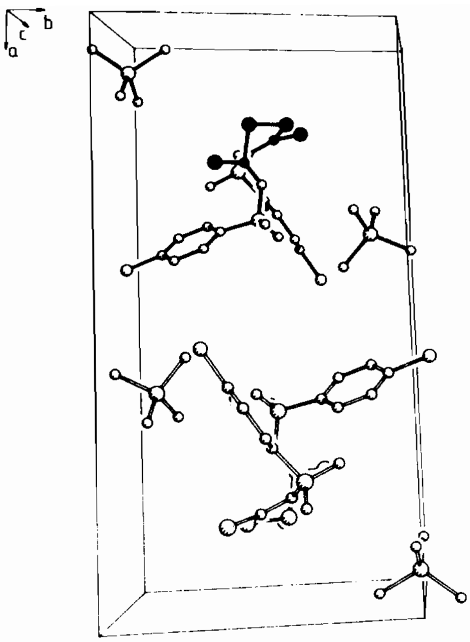


Fig. 2. Crystal packing of $(AsPh_4)_2$**7c**·H_2O. The tetraphenylarsonium cations are schematically depicted.

7c. The average value of 1.80 Å for S1–C corresponds to a C–S single bond while the C–S2 bond lengths are unusually short (av. 1.677 Å) [29].

The other features concerning the monomere units in **7c** are quite similar to **5c**. There are two distinct planar arrangements of atoms in each part of **7c** (Table 3). The two planes are oriented nearly perpendicular to each other and give rise to conjugation involving the SO_2 groups [1]. According to Koch and Moffitt such a conformation of compounds containing SO_2 groups can be described as 'case I of conjugation' referring to the π-system of the phenyl ring and the lone-pair located on $N_{sp}2$ while the orientation of the π-system of the S_2CN moiety with respect to SO_2 is of 'case II' [30]. The case I-type should favour strong conjugation with weakened oxy–sulfur bonds while case II conjugation is considered to be not very pronounced.

The bond angles C1–S11–S12 and C2–S12–S11 in **7c** indicate that the outer electrons on sulfur atoms S11 and S12 are roughly sp^3 hybridized. As reviewed by Abrahams the valency angles for two-bonded sulfur are normally tetrahedral or slightly less [31]. The observed S–S bond length corresponds to a Pauling value of 2.08 Å for a pure single bond between divalent sulfur atoms [32]. The torsion angle C1–S11–S12–C2 is 80.8°. Dihedral angles in molecules R–S–S–R are usually close to 90° [33, 34]. This is believed to be in accordance with the optimum π overlap of orbitals while an angle of 0° is associated with the maximum repulsion between nonbonding orbitals on sulfur atoms. Although in **7c** there is considerable repulsion between anionic sulfur atoms a *cis* configuration is realized.

The energies, charge densities on sulfur (disulfide atoms are denoted as S*) and overlap populations for the S–S bond of the investigated conformers of the free model system **9** are presented in Table 4 while the results of calculations on **9** including crystal field simulations are presented in Table 5. Figure 3 shows the relative energies for free **9** and **9** in the crystal field as function of the dihedral angle C–S–S–C.

The results for free **9** (F̲) depend significantly of the basis-set which is applied. Although with the minimal basis as well as the double-zeta basis the minimum in energy is observed at 180°, the curve obtained with the extended basis is very smooth in the region $90 \leqslant$ C–S–S–C $\leqslant 180°$ exhibiting a local minimum at 110°. Well pronounced energy minima at 100 and 110° are observed on application of the point-charge model (N̲). Here an extension of the basis (inclusion of polarization functions on S) effects the energy minimum to occur at C–S–S–C = 100°.

The overlap population for S–S is regarded as a rough indication for the bond strength between sulfur atoms in the disulfide group. The values as function of the S–S dihedral angle together with the charge densities on S and S* are depicted in Fig. 4.

From inspection of Figs. 3 and 4 it can be seen that the energy minimum for the point-charge model with polarization functions coincides roughly with

TABLE 4. Energy, Mulliken charge distribution for S atoms and overlap population for S–S for free $[H{-}N{=}C(S)S{-}]_2^{2-}$[a]

Angle (°)	$-E$ (Kcal mol^{-1})		Mulliken charge densities				Overlap population	
	Minimal	DZ	Minimal		DZ		Minimal S–S	DZ
			S*	S	S*	S		
70	111.684	2148.558	16.0217	16.4075	16.0282	16.5258	0.3992	0.2205
90	122.121	2158.962	16.0038	16.4270	15.9953	16.5485	0.4122	0.2649
110	123.758	2160.072	15.9949	16.4352	15.9722	16.5667	0.3998	0.2631
150	125.294	2160.086	15.9871	16.4431	15.9657	16.5776	0.3238	0.0688
180	126.174	2160.927	15.9851	16.4452	15.9721	16.5749	0.2915	0.0418

[a] Sulfur atoms in S–S are denoted by S*.

TABLE 5. Energy, Mulliken charge distribution for S atoms and overlap population for S–S in $[H-N=C(S)S-]_2^{2-}$ influenced by neighbours (see text)

Angle (°)	$-E$ (Kcal mol^{-1})		Mulliken charge densities				Overlap population	
	Minimal	M + P	Minimal		M + P		Minimal S–S	M + P
			S*	S	S*	S		
70	918.428	1030.657	16.0142	16.4293	16.0183	16.4759	0.4055	0.4511
90	932.614	1040.096	15.9957	16.4611	15.9923	16.5252	0.4193	0.4703
110	934.267	1040.876	15.9900	16.4759	15.9923	16.5252	0.4071	0.4628
150	921.721	1026.313	16.0001	16.4721	16.0035	16.5199	0.3312	0.3873
180	911.721	1014.209	16.0123	16.4580	16.0153	16.5027	0.3001	0.3552

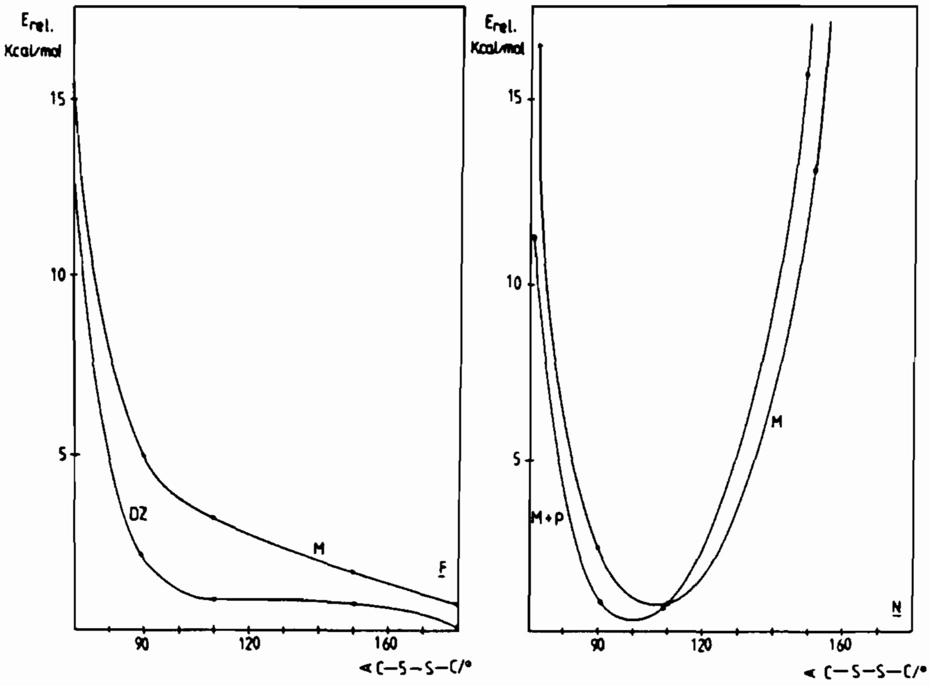


Fig. 3. The calculated energies as functions of the S–S dihedral angles.

the maximum in overlap population for S–S. Although the maximum in overlap population for S–S in free **9** occurs at C–S–S–C = 110°, the most stable conformation in this case should be the *trans* form. This indicates that the point-charge model with polarization functions is the most appropriate one to describe the geometry of the molecule.

The *cis* configuration is considered as the result of a careful balance between repulsion of negatively charged sulfur atoms and the overlap population in the S–S bond which could be attributed to hyperconjugation between C and S [35].

Supplementary Material

Additional crystal structure data have been deposited at the Fachinformationszentrum Energie, Physik, Mathematik GmbH, D-7514 Eggenstein-Leopoldshafen 2, F.R.G. Inquiries should be accompanied by the depository number CSD-53970, the names of the authors, and the literature citation.

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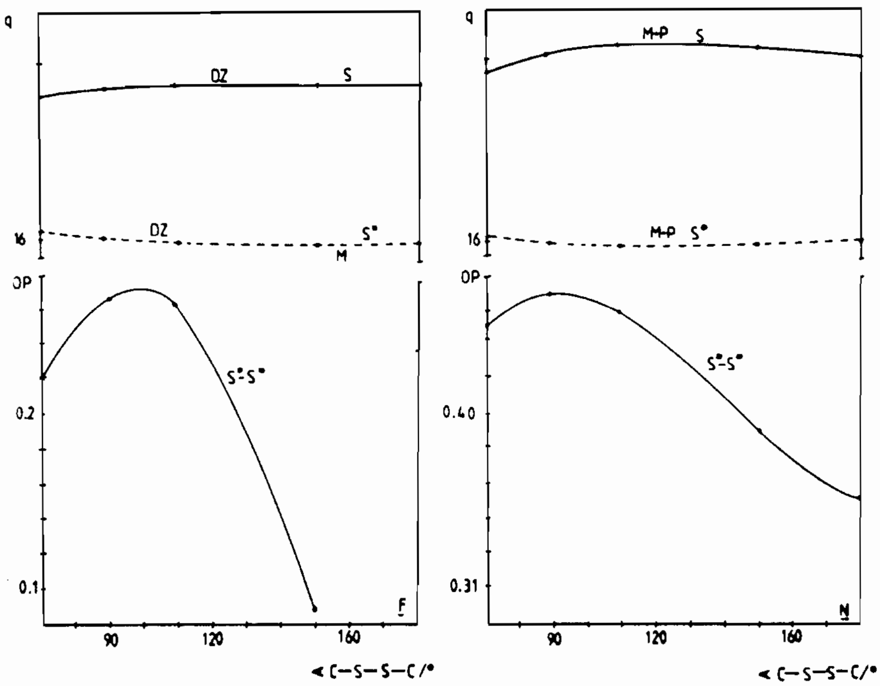

Fig. 4. The calculated overlap populations for S–S and charge densities at anionic sulfur and S* as functions of the S–S dihedral angles.

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