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Changes in the Structure of the 1:2 Complex of *N*-Ethyl-*N*-methylmorpholinium and 7,7,8,8-Tetracyano-*p*-quinodimethane, MEM(TCNQ)$_2$, above Room Temperature. II. Determination of the Structure (above the Phase Transition) at 348 K

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Abstract

Crystals of MEM(TCNQ)$_2$ above the high-temperature phase transition at T_c = 340 K are triclinic, with (at 348 K) a = 7·666 (3), b = 15·684 (3), c = 6·585 (5) Å, α = 105·97 (1), β = 80·33 (3), γ = 110·86 (3)°, U = 709 Å^3. Intensities were collected at 348 K with Zr-filtered Mo radiation on a Nonius CAD-4F diffractometer. The structure was solved in space group $P\bar{1}$ under the assumption of random disorder for the MEM group over two centrosymmetrically related orientations. Anisotropic least-squares refinement with w = 1 gave R_F = 0·082 for 1233 reflections. The disorder of the MEM group is enhanced at the phase transition. The strongly dimerized TCNQ stacks below T_c become nearly regular above T_c with TCNQ distances of 3·29 (1) Å and overlap approaching the ring–external-bond type. The strong conductivity above T_c is tentatively explained by the regularity of the stack and the uniform charge distribution along the stack due to the MEM disorder, but work on further TCNQ compounds is required to make this explanation definite. The bending of the crystal observed macroscopically around T_c has been related to the microscopic structural changes during the phase transition.

Introduction

In the previous paper the increase in dynamical disorder of the MEM group observed by X-ray diffraction and NMR spectroscopy (van Bodegom, 1981; Nechtschein, Huizinga, Oostra, van Bodegom, Sawatzky & Kommandeur, 1981) has been correlated with the anomalous increase of the electrical conduc-

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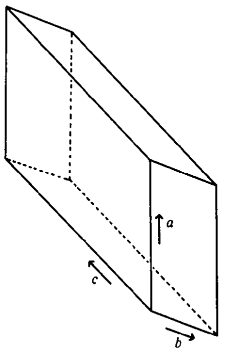

Fig. 1. Single crystal of MEM(TCNQ)$_2$. The axes chosen for the unit cell are given.

tivity along **c** between 290 and 320 K. To obtain a better insight into the strong increase in the conductivity along **c** (by three orders of magnitude) at the transition at 340 K, the structure determination described in the present paper was undertaken.

Macroscopic study of the crystals

Fig. 1 shows a drawing of a single crystal of MEM(TCNQ)$_2$ obtained by cooling a mixture of hot saturated solutions of *N*-ethyl-*N*-methylmorpholinium iodide and TCNQ in acetonitrile. As indicated in the figure, the base vectors chosen for the X-ray structure determinations lie along the edges of the triclinic crystal. The crystals can easily be cleaved along the (001) plane by a razor blade. In addition to single crystals the batch contained twins in which the individuals are related by a rotation of 180° around **c**. As in this case the (001) planes of the individuals do not coincide, easy cleaving is not achieved, which is one way to recognize the twins and to reject them from single-crystal experiments. In many cases, heating of a single crystal through the phase transition gives a large number of crystal slices with (001) as largest boundary planes. Even in the few cases where the crystal resists the strain and does not break, the internal structural changes become apparent by a bending of the crystal as a whole. By heating the crystal with an intense beam of light, such that there is a temperature gradient along the needle axis, the bending edge can be forced to move slowly forward and backwards along this axis.

Structure factors

A crystal with regular dimensions, 0·4–0·5 mm, was used for the intensity measurements. Intensities were collected on an automatic Nonius CAD-4F diffractometer, equipped with a heating device as used for the measurement at 323 K (van Bodegom, 1981). Reflections were measured for one half of reciprocal space up to $\theta = 22°$ by the θ–2θ method with Zr-filtered Mo radiation. 1714 reflections were measured, of which 1461 had a net intensity $I > 0$. Corrections were applied for Lorentz and polarization effects, and for intensity changes of the primary beam from two reference reflections measured twice after each 28 reflections. Corrections for absorption were not made [μ(Mo $K\bar{\alpha}$) = 0·09 mm^{-1}].

Reflections with a net negative intensity were given zero weight. For the remaining reflections the weight w_c was calculated from $w_c = [\sigma_c(F_o)]^{-2}$, $\sigma_c(F_o)$ being the e.s.d. in $|F_o|$ due to counting statistics and the error in the filter factor. During the measurement the centre of gravity of a reflection was determined after each 60 reflections. A deviation larger than 0·22° from its calculated position was followed by a check on the orientation of the crystal, a situation which was encountered seven times. Cell constants were determined 12 times during the measurement by least-squares adjustment of the θ, φ and χ values of five reflections. The average values for cell constants found from these determinations and the unbiased e.s.d.'s (in parentheses) are a = 7·666 (3), b = 15·684 (3), c = 6·585 (5) Å, α = 105·97 (1), β = 80·33 (3), γ = 110·86 (3)°, U = 709 Å^3. For each of the 12 independent determinations the observed values are equal to the corresponding average values within twice the e.s.d.

Determination of the structure

At 348 K the space group of the triclinic crystals is $P1$ or $P\bar{1}$, with one MEM(TCNQ)$_2$ unit per cell. As the previous structure determinations had shown an increasing disorder of the MEM group with increasing temperature and thus a decreasing deviation from symmetry $P\bar{1}$, the present structure was solved in $P\bar{1}$. For the MEM group random disorder over two centrosymmetrically related positions was assumed. Although this model has given reasonable values for the refinement indices (see below), the presence of additional MEM positions with low occupancy and slight deviations from centrosymmetry cannot be excluded. We have not been able to detect such deviations with certainty, however, because of the small intensities of the higher-order reflections ($\sin\theta/\lambda >$ 0·5 Å^{-1}) due to the disorder and the large thermal motion.

The TCNQ coordinates were found from a Patterson map.* Blocked-matrix isotropic refinement of the TCNQ groups with 1233 reflections with $|F_o| > 2\sigma_c(F_o)$ and unit weights decreased $R = \sum||F_o| - |F_c||/\sum|F_o|$ to 0·265. A subsequent difference map

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* Unless mentioned otherwise the calculations were performed with XRAY system (1976).

showed a highly smeared electron density in the region of the MEM molecule. The highest peak, 3·2 e Å^{-3}, was found at $(0,\frac{1}{2},0)$ where the N atoms of the two centrosymetrically related MEM molecules lie close together.

The next highest peak had to be attributed to a superposition of the density of C(40) (Fig. 6 of Bosch & van Bodegom, 1977) and C′(34) [*i.e.* C(34) $(-x, 1-y, -z)$] of the centrosymmetrically related molecule. The next six highest independent peaks ranging from 1·1–0·8 e Å^{-3} could be assigned to the remaining six heavy atoms of the MEM group. All further refinements were carried out in $P\bar{1}$ with $w = 1$. A difference map after isotropic and anisotropic refinement of the heavy atoms showed peaks of 0·5–0·4 e Å^{-3} at the positions expected for the H atoms of the TCNQ groups. Their positions were calculated on the basis of geometrical considerations and constrained at 1·08 Å from their respective C atoms; their isotropic temperature factors were refined. MEM H atoms were not taken into account.

Scattering curves according to Cromer & Mann (1968) for the non-hydrogen atoms and of Stewart, Davidson & Simpson (1965) for H were used. Refinement gave $R = 0{\cdot}082$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0{\cdot}080$ for 1233 reflections with $|F_o| > 2\sigma_c(F_o)$ and $w = 1$. The goodness-of-fit $G = [\sum w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2} = 1{\cdot}05$ with $N_o = 1233$ and N_v (number of variables) = 228. During the last cycle parameter shifts were all $<0{\cdot}06\sigma$. Final positional parameters are given in Table 1.*

Table 1. *Final parameters for MEM(TCNQ)$_2$ at* 348 K

Coordinates are multiplied by 10^4, and U_{eq} (Å^2) values by 10^3. Hydrogen atoms were constrained to their respective C atoms. For numbering of atoms see Figs. 5 and 6 of Bosch & van Bodegom (1977). $U_{eq} = \sum_l U_{ll}/3$ after diagonalization of the **U** tensor.

	x	y	z	U_{eq}
N(1)	3232 (12)	3924 (5)	4174 (15)	131 (4)
C(2)	3522 (11)	3228 (6)	3762 (13)	88 (3)
C(3)	3867 (10)	2354 (5)	3220 (11)	71 (3)
C(4)	5799 (12)	2414 (6)	3036 (14)	92 (4)
N(5)	7314 (11)	2459 (6)	2838 (16)	142 (5)
C(6)	2422 (9)	1505 (4)	2950 (10)	57 (3)
C(7)	2778 (9)	636 (4)	2425 (10)	59 (3)
C(8)	1358 (8)	−182 (4)	2175 (9)	52 (2)
C(9)	−564 (9)	−220 (4)	2452 (9)	50 (2)
C(10)	−890 (9)	668 (4)	3009 (9)	55 (2)
C(11)	533 (9)	1488 (4)	3245 (10)	58 (3)
N(12)	−5448 (9)	−1109 (5)	2751 (11)	94 (3)
C(13)	−3917 (10)	−1084 (4)	2505 (10)	61 (3)
C(14)	−2028 (8)	−1056 (4)	2215 (9)	52 (2)
C(15)	−1753 (9)	−1943 (5)	1662 (10)	62 (2)
N(16)	−1566 (10)	−2656 (4)	1261 (11)	97 (3)
H(C7)	4205	638	2230	
H(C8)	1663	−833	1743	
H(C10)	−2314	673	3243	
H(C11)	243	2142	3652	
N(33)	0	5000	0	106 (5)
C(34)	2232 (42)	4890 (16)	46 (62)	183 (16)
C(35)	2505 (90)	5706 (50)	2410 (133)	280 (41)
C(36)	1321 (58)	6418 (24)	1962 (69)	219 (23)
C(37)	690 (46)	5908 (16)	829 (85)	201 (22)
C(38)	−939 (89)	5266 (37)	1966 (65)	272 (31)
C(39)	−333 (39)	5534 (20)	−1755 (49)	144 (13)
C(40)	−3599 (48)	4208 (28)	−898 (75)	158 (17)
O	3241 (46)	6336 (24)	1399 (75)	245 (20)

Description of the structure

Packing

Projections of the structure along [001] and [100] are given in Figs. 2 and 3. The TCNQ molecules are located in sheets parallel to (010) separated by MEM molecules. The plane of the TCNQ units is almost perpendicular to **c**.

The TCNQ sheet

The normal projection of the TCNQ units along their longest molecular axes is shown in Fig. 4, and the types of overlap of neighbouring TCNQ molecules in Fig. 5. Table 2 gives short intermolecular distances between

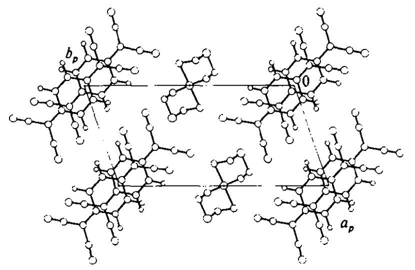

Fig. 2. Projection of the structure of MEM(TCNQ)$_2$ along [001] onto the plane perpendicular to [001]. The MEM group is disordered and indicated schematically. a_p, b_p, and c_p denote projections of axes.

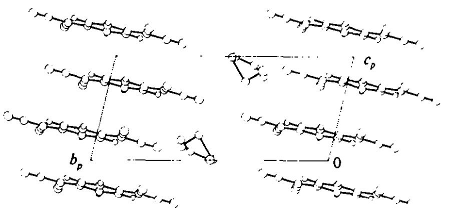

Fig. 3. Projection of the structure of MEM(TCNQ)$_2$ along [100] onto the plane perpendicular to [100]. The MEM group is disordered. Only the part within the unit cell is indicated.

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* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35697 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

TCNQ units, and Table 3 numerical values for the relative shifts of the TCNQ molecules parallel to the plane of the *p*-quinodimethane group, along and perpendicular to the longest molecular axis. Figs. 4 and 5, and Tables 2 and 3 show that the TCNQ molecules form columns along **c**, with an almost regular mode of mutual stacking. The distances between successive *p*-quinodimethane least-squares planes along the column (Table 3) are equal within the e.s.d.'s, the average value of 3·29 Å being equal to the average value for the distances $A\cdots B$ and $A\cdots B'$ found at 323 K.

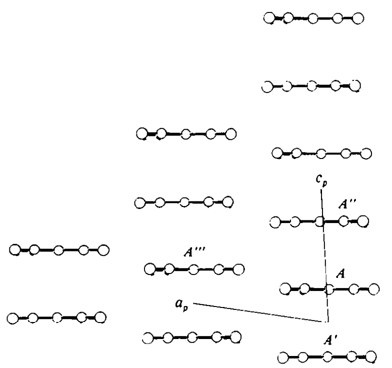
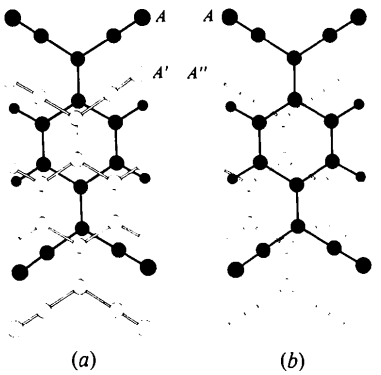


Fig. 4. Normal projection of the sheet of TCNQ molecules in MEM(TCNQ)$_2$ along the longest molecular axes.



(*a*) (*b*)

Fig. 5. Projection of two neighbouring TCNQ molecules in MEM(TCNQ)$_2$ along the normal to the *p*-quinodimethane least-squares plane. (*a*) Molecules A and A', (*b*) molecules A and A''.

Although the two overlap types found are not exactly equal, their difference is negligible compared with the large difference below the phase transition.

The TCNQ group

In Fig. 6 the molecular geometry of the TCNQ unit is shown. Within twice the e.s.d.'s the molecule satisfies *mmm* symmetry with respect to its bond lengths. The average values for corresponding bond lengths are in the range usually observed for this molecule in other TCNQ complexes. Numerical data for the *p*-quinodimethane least-squares plane are given in Table 4. The angle between the normal to this plane and **c** is 2·7°, which is much smaller than the 20·5 and 21·3° found at 113 K, and thus below the phase transition.

Table 3. *Shifts of TCNQ A' and A'' relative to TCNQ A as seen along the normal to the p-quinodimethane least-squares plane, and distances* (Å) *between these planes*

$S(\perp)$: shift perpendicular to the longest molecular axis; $S(\parallel)$ shift along this axis. E.s.d.'s are ≤ 1 in the last digit given.

	A–A'	A–A''	Distances between the planes	
$S(\parallel)$	−1·96 Å	−2·02 Å	$D(A$–$A')$	3·28
$S(\perp)$	0·10	0·40	$D(A$–$A'')$	3·30

Table 2. *Short intermolecular distances* (Å) *between TCNQ molecules in MEM(TCNQ)$_2$ at* 348 K

All distances shorter than the sum of the relevant van der Waals radii (Pauling, 1960) plus 0·2 Å are given. Van der Waals radii: $r_C = 1·7$, $r_N = 1·5$, $r_H = 1·2$ Å.

(*a*) TCNQ A to TCNQ A' distances							
C(6)–C(13)^{i}	3·54 (1)	C(7)–C(13)^{i}	3·42 (1)	C(8)–C(10)^{i}	3·34 (1)	C(11)–C(14)^{i}	3·54 (1)
C(6)–C(14)^{i}	3·32 (1)	C(7)–C(14)^{i}	3·47 (1)	C(9)–C(9)^{i}	3·39 (1)	C(11)–C(15)^{i}	3·41 (1)
C(6)–C(15)^{i}	3·45 (1)	C(8)–C(9)^{i}	3·46 (1)	C(9)–C(10)^{i}	3·53 (1)		
(*b*) TCNQ A to TCNQ A'' distances							
C(6)–C(14)^{ii}	3·39 (1)	C(7)–C(13)^{ii}	3·41 (1)	C(8)–C(9)^{ii}	3·41 (1)	C(9)–C(9)^{ii}	3·43 (1)
C(6)–C(15)^{ii}	3·41 (1)	C(7)–C(14)^{ii}	3·40 (1)	C(8)–C(10)^{ii}	3·39 (1)	C(11)–C(15)^{ii}	3·45 (1)
(*c*) TCNQ A to TCNQ A''' distances							
C(8)–N(12)^{iii}	3·38 (1)	H(C8)–N(12)^{iii}	2·62 (1)	N(5)–H(C11)^{iii}	2·63 (1)		

Symmetry code: (i) $-x, -y, -z$; (ii) $-x, -y, 1-z$; (iii) $1+x, y, z$.

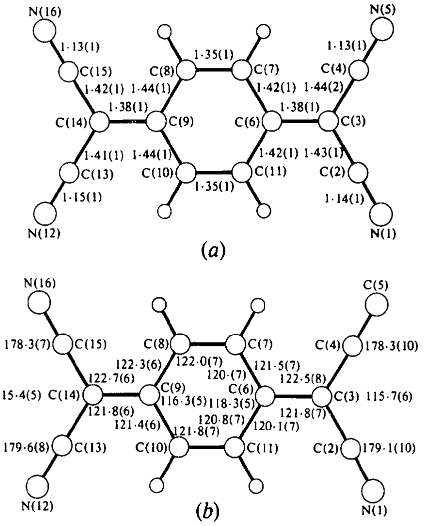


Fig. 6. Molecular geometry of the TCNQ unit in MEM(TCNQ)$_2$. Values for (*a*) bond lengths (Å) and (*b*) angles (°) are not corrected for libration effects.

Table 4. *Least-squares plane for the p-quinodimethane* (C_8) *group of the TCNQ unit in MEM(TCNQ)$_2$, at* 348 K, *and deviations of atoms from this plane*

x, y and z are relative coordinates in the axial system **a**, **b** and **c**. The atoms used to define the plane are equally weighted. Δ = Distance to the plane.

(*a*) Equation of the plane [C(3); C(6)–C(11); C(14)]

$$1{\cdot}021x - 3{\cdot}697y + 6{\cdot}577z = 1{\cdot}639$$
$$[(\textstyle\sum \Delta^2)/8]^{1/2} = 0{\cdot}004$$

(*b*) Deviations of all atoms from the plane (Å $\times 10^2$) (e.s.d.'s are ≤ 1 in the last digit shown).

N(1)	−1	N(5)	7	C(9)	0	C(13)	1
C(2)	0	C(6)	−1	C(10)	0	C(14)	0
C(3)	0	C(7)	0	C(11)	0	C(15)	−1
C(4)	6	C(8)	0	N(12)	2	N(16)	1

The MEM group

The large thermal motion of the MEM atoms ($\langle U_{ii} \rangle$ = 0·20 Å^2) in comparison with the TCNQ heavy atoms ($\langle U_{ii} \rangle$ = 0·08 Å^2) indicates that the description of the MEM disorder over only two centrosymmetrically related positions is certainly not completely correct.

The present results agree with the indication of a strong disorder of the MEM groups at 348 K from NMR experiments (Nechtschein, Oostra, Huizinga, van Bodegom, Sawatzky & Kommandeur, 1981). Because of the disorder no reliable molecular geometry could be obtained for the MEM molecule.

Discussion

Structural changes during the phase transition

The structural changes during the high-temperature phase transition at T_c can be deduced from a comparison of the structures below (Bosch & van Bodegom, 1977; van Bodegom, 1981) and above (present paper) the phase transition and from a study of the NMR spectra (Nechtschein, Oostra, Huizinga, van Bodegom, Sawatzky & Kommandeur, 1981). Both the structures and the NMR spectra as a function of temperature reveal that the disorder of the MEM group, which has already begun at about room temperature, is enhanced during the phase transition. The major structural change is observed, however, for the TCNQ stacks. Below T_c the stacks of TCNQ molecules are strongly dimerized. These stacks contain dimers with an intradimer distance of 3·22 Å and ring–external-bond-type overlap; successive dimers are separated by 3·36 Å and have hardly any interdimer overlap. Above T_c successive distances between the TCNQ units are all 3·29 (1) Å and all overlaps are strongly analogous and approach the ring–external-bond type. The change in overlap at T_c is mainly due to rotations of the TCNQ dimers around an axis **L** (parallel to the longest molecular axis) which is nearly perpendicular to **c** and in the plane ($\bar{1}20$) (Fig. 2). The sequence TCNQ···MEM···TCNQ *etc.* in the ($\bar{1}20$) planes (Fig. 2) hardly changes during the phase transition, apart of course from the increase in disorder of the MEM groups and the rotation of the TCNQ units around **L** discussed above. Successive ($\bar{1}20$) planes in the **a** direction are displaced by −0·7 Å along **c** relative to each other at T_c. The bending along **c** observed macroscopically is caused by the fact that, due to the temperature gradient in the crystal, the rotations around **L** (and the displacements along **c**) do not take place simultaneously for all successive TCNQ groups along **c**. The resulting strain in the crystal causes cleaving along (001).

Comparison with other TCNQ compounds; electrical conductivity

Changes in TCNQ stacks from a distorted to a more regular type have also been observed for three other complexes for which the structures have been determined above and below the phase transition: NaTCNQ (T_c = 348 K; Konno & Saito, 1974, 1975), KTCNQ (T_c = 395 K; Konno, Ishii & Saito, 1977), and methyltriphenylphosphonium–(TCNQ)$_2$, MTPP(TCNQ)$_2$ (T_c = 316 K; McPhail, Semeniuk & Chesnut, 1971; Konno & Saito, 1973). A difference from MEM(TCNQ)$_2$ is that in the above-mentioned compounds the stack distortions below T_c are much smaller. Moreover, although they show an anomaly in the electrical conductivity σ at T_c, a strong increase as observed for MEM(TCNQ)$_2$ does not occur.

It has been shown in the preceding paper that the increase in conductivity in MEM(TCNQ)$_2$ between 290 and 320 K might be attributed to the increase of the disorder of the MEM molecules in this temperature interval. At the phase transition a further sharp increase of the MEM disorder has been observed by NMR measurements (Nechtschein, Oostra, Huizinga, van Bodegom, Sawatzky & Kommandeur, 1981) in agreement with the present structural study. As it seems unlikely that the increase in disorder alone explains the drastic increase of the conductivity at T_c, we tentatively assume that the larger regularity of the stacks also plays a role. It is clear, however, that more structure determinations and careful physical measurements on analogous TCNQ compounds above and below their phase transitions are required to reach definite conclusions.

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Conformational Characteristics of Anhydrous Sulfaguanidine: Computer Retrieval and Analysis of *N*-Substituted Arylsulfonamides

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Abstract

$C_7H_{10}N_4O_2S$, $M_r = 214{\cdot}25$, monoclinic, $P2_1/c$, $a = 9{\cdot}912\,(1)$, $b = 7{\cdot}530\,(1)$, $c = 24{\cdot}496\,(2)$ Å, $\beta = 95{\cdot}32\,(1)°$, $V = 1820{\cdot}4\,(6)$ Å^3, $D_c = 1{\cdot}563$ Mg m^{-3}, $Z = 8$ (two molecules in the asymmetric unit), $F(000) = 896$. The final $R = 0{\cdot}045$ for 3331 intensities. In both symmetry-independent molecules (SG) and (SG*) the coplanar guanidine moiety is fixed to the sulfone group *via* an intramolecular NH···O(1) bond and assumes the tautomeric form [$H_2N{-}C_6H_4SO_2N{=}C(NH_2)_2$] as shown, for example, by the short $S^{VI}{-}N(sp^2)$ distances of 1·589 (2) and 1·594 (2) Å. As revealed by a search of the Cambridge Crystallographic Data File for (121) compounds containing (aryl)SO$_2$NX,X' (X,X' = H,C,N,S,P) fragments, the conformations of these groups in SG and SG* about the S^{VI}–N bond fall in the range determined by the majority of the molecular structures retrieved. The arylamino groups exhibit, however, significantly different rotations about S^{VI}–C(ring). One of them (SG*) resembles [N(1)–S^{VI}–C(1)–C(6) = 94·4°] the conformations found in SG.H_2O and Pd(SG)$_2$Cl$_2$ and in the majority of compounds possessing (aryl)SO$_2$NX,X' groups. The