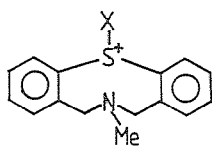
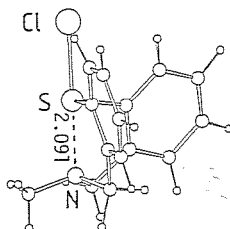


09.2-16 THE STRUCTURES OF σ -AMMONIOSULFURANES: THE TRANSANNULAR S-N INTERACTIONS. By F. Iwasaki, Dept. of Materials Science, The Univ. of Electro-Communications, Tokyo 182 and K. Akiba, Dept. of Chemistry, Univ. of Hiroshima, Hiroshima 730, Japan.



- (I) X=Cl (PF₆⁻)
 (II) X=OMe (SbCl₆⁻)
 (III) X=Me (PF₆⁻)
 (IV) X=O



The structures of S-substituted N-methyl-6,7-dihydro-5H-dibenzo[b,g][1,5]thiazocinium salts were determined by X-ray method in order to investigate the hypervalency of sulfur. Crystal data; (I) Pbc_a, a=17.101, b=15.327, c=13.195 Å, Z=8, R=0.078 (for 1973 reflections), (II) P2₁/c, a=11.791, b=10.593, c=18.860 Å, β =98.25°, Z=4, R=0.053 (3221), (III) Pbc_a, a=16.702, b=16.352, c=12.770 Å, Z=8, R=0.064 (2272), (IV) P $\bar{1}$, a=8.515, b=9.444, c=16.831 Å, α =99.23, β =99.12, γ =91.69°, Z=4, R=0.043 (4260).

The structure of (I) is shown in Figure. The molecular conformations of three other substances are essentially same as that of (I). In these molecules very strong transannular interactions are found between S and N. S-N distances are 2.091, 2.206, 2.446 and 2.609 Å for (I), (II), (III) and (IV), respectively. The sum of the van der Waals radii is 3.35 Å. X, S and N are collinear, and S-N bond is approximately perpendicular to the CSC plane. The configuration about S is distorted trigonal bipyramidal, with apical S-N and S-X bonds. Therefore, these structures are concluded to be of a new type of σ -ammoniosulfuran.

II and the same molecule in complex III is that the almost perfect mirror symmetry of II is broken by rotation of an ethyl group. The N-S distance (1.60 - 1.65 Å) suggests some double-bond character, also shown by the flattened arrangement of the bonds at N. The angles between the D and A ring planes are 2.65° (III) and 2.08, 4.75° (IV). The perpendicular distances between the D and A aromatic rings are 3.41 Å (III) and 3.43, 3.45 Å (IV), typical of medium strength interactions. Projection diagrams suggest that the overlap integrals of the D and A π systems are large.

Although I and the corresponding 1,4-sulphonamide complex with TNB in solution no solid complexes have been prepared.

I N,N-Dimethyl-3-carbomethoxybenzenesulphonamide. Orthorhombic, Pbc_a, a = 16.72 (2), b = 13.44 (1), c = 10.15 (1) Å, Z = 8, μ (Cu K α) = 24.2 cm⁻¹. Final R = 0.056 for 1447 observed reflexions.

II N,N-Diethyl-4-methylbenzenesulphonamide. Monoclinic, P2₁/c, a = 8.31 (1), b = 12.31 (1), c = 12.69 (2) Å, β = 110.52 (5)°, Z = 4, μ (Cu K α) = 21.1 cm⁻¹. Final R = 0.067 for 1309 observed reflexions.

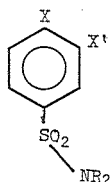
III N,N-Diethyl-4-methylbenzenesulphonamide-1,3,5-trinitrobenzene complex, 1,3,5-trinitrobenzene adduct (1:1:2). Triclinic, P $\bar{1}$, a = 12.71 (3), b = 15.91 (3), c = 10.07 (1) Å, α = 96.50 (3), β = 103.47 (3), γ = 72.54 (6)°, Z = 2, μ (Cu K α) = 15.08 cm⁻¹. Final R = 0.075 for 3055 observed reflexions.

IV N,N-Dimethyl-4-methylbenzenesulphonamide-1,3,5-trinitrobenzene complex, 1,3,5-trinitrobenzene adduct (2:1:1). Monoclinic, P2₁/c, a = 12.771 (1), b = 26.099 (3), c = 14.148 (3) Å, β = 125.53 (2)°, Z = 4, μ (Mo K α) = 1.7 cm⁻¹. Final R = 0.049 for 3295 observed reflexions.

09.2-17 NON-STACKING π - π^* COMPLEXES OF SULFONAMIDES WITH 1,3,5-TRINITROBENZENE. By Hazel A. Barnes, John C. Barnes, and Roy Foster, Department of Chemistry, The University, DUNDEE, DD1 4HN, Scotland.

NMR studies have shown that sulphonamides form relatively strong complexes with 1,3,5-trinitrobenzene (TNB) in CCl₄ solution, often with a suggestion of higher complexes in addition to those of 1:1 stoichiometry. Most π - π^* complexes involve donor (D) and acceptor (A) molecules which are both essentially flat, allowing crystallisation in stacks ...ADADAD... In sulphonamides, such as I and II, the C-S-N plane is perpendicular to the plane of the benzene ring so that the two faces of the ring are sterically very different, precluding the formation of stacks. In crystalline complexes of sulphonamides with TNB (III,IV), the acceptor occupies the face of the sulphonamide which is remote from the -NR₂ group.

It is not possible to deduce the structural units actually present in a crystalline complex from the bulk stoichiometry. III has the stoichiometry DA₃, made up of isolated DA pairs with two uncomplexed molecules of A in the lattice. IV has the stoichiometry D₂A₂ with isolated DAD complexes and one uncomplexed A molecule. The molecules of uncomplexed A lie approximately perpendicular to the complex in each case.



Bond lengths and angles in all the molecules have typical values. The only difference between the pure sulphonamide

	I	II	III	IV
X	H	Me	Me	Me
X'	COOMe	H	H	H
R	Me	Et	Et	Me

09.2-18 STRUCTURE of a TCNQ CHARGE-TRANSFER COMPLEX WITH UNUSUAL STOICHIOMETRY. By Joan Halfpenny, Department of Applied Chemical Sciences, Napier College, Colinton Road, Edinburgh EH10 5DT, Scotland.

The structure of the complex

$((C_6H_5)_3P)_2N^+(TCNQ)^-(TCNQ)_{0.5}CH_3CN$ has been determined from diffractometer - measured data (2833 reflections, $R_w = 0.056$). The stoichiometry of the complex is unusual. The structural unit contains one and a half TCNQ molecules, the half arising from the molecule TCNQ(B) sited on a centre of symmetry, TCNQ(A) being in a general position. The TCNQ's are stacked in groups of three, ABA, the distance between mean molecular planes being 3.30 Å. The cation is by far the largest and most complex in a TCNQ compound which has been studied by X-ray diffraction. Solvated methyl cyanide is included in the structure.

(TCNQ = tetracyanoquinonedimethane)