
The structures of S-substituted 1-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) Pbcn, a=17.101, b=15.327, c=13.195 A, Z=8, R=0.078 (for 1973 reflections), (II) P2_1/n, a=11.701, b=10.593, c=18.960 A, Z=4, R=0.053 (3221), (III) Pbcn, a=18.702, b=16.352, c=17.70 A, Z=8, R=0.043 (2427), (IV) P2_1/c, a=8.515, b=9.444, c=16.33 A, Z=2, 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 A for (I), (II), (III) and (IV), respectively.

09.2–17 NON-STACKING \( m-n \) COMPLEXES OF SULPHONAMIDES WITH 1,3,5-TRINITROBENZENES. By Hazel A. Barnes, John G. Barnes, and Roy Koster, 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 DMSO solution, often with a suggestion of higher complexes in addition to those of 1:1 stoichiometry. Most \( m-n \) complexes involve donor (D) and acceptor (A) molecules which are both essentially flat, allowing crystallisation in stacks... 

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 S-N distance (1.63 A) suggests some double-bond character, also shown by the flattened arrangement of the bonds at S. 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 3.45, 3.45 Å (IV), typical of medium strength interactions. Projections suggest that the overlap integrals of the D and A 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-carboxymethanesulphonamide. Orthorhombic, Pbcn, a = 16.72, b = 13.44, c = 10.15 (1), R = 0.10, Z = 4, \( \mu \) (Cu Ka) = 24.2 cm\(^{-1}\).

Final R = 0.056 for 1447 observed reflections.

II N,N-Dimethyl-4-methylbenzenesulphonamide. Monoclinic, P2_1/a, a = 8.91, b = 12.93 (1), c = 12.15 (1), R = 0.056 for 1309 observed reflections.

III N,N-Dimethyl-4-methylbenzenesulphonamide-1,3,5-trinitrobenzene complex, 1,3,5-trinitrobenzene adduct (1:1:2).

Triclinic, P1, a = 12.71 (3), b = 15.91 (3), c = 14.148 (3), \( \alpha = 96.50, \beta = 109.50, \gamma = 112.47, Z = 4, \mu \) (Cu Ka) = 21.1 cm\(^{-1}\).

Final R = 0.075 for 3055 observed reflections.

IV N,N-Dimethyl-4-methylbenzenesulphonamide-1,3,5-trinitrobenzene complex, 1,3,5-trinitrobenzene adduct (2:1:1).

Monoclinic, P2_1/c, a = 12.77 (1), b = 26.099 (3), c = 14.146 (3), \( \beta = 92.54 (6), Z = 4, \mu \) (Cu Ka) = 1.7 cm\(^{-1}\).

Final R = 0.049 for 3895 observed reflections.

09.2–18 STRUCTURE OF A TCNQ CHARGE-TRANSFER COMPLEX WITH UNUSUAL STOICHIOMETRY. By Joan Halfpenny, Department of Applied Chemical College, Colinton Road, Edinburgh EH10 5HF, Scotland.

The structure of the complex ((C_6H_5)_2N(TCNQ)^+)(TCNQ^-)_{10}CH_3CN has been determined by diffractometer - measured data (2833 reflections, \( R_h = 0.056 \)). The stoichiometry of the complex is unusual. The structural unit contains one and a half TCNQ molecules, the half arising from the molecule TCNQ(A) 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 = tetracyanoquinodimethane)