Cocrystallization of tetramethylurea (TMU) with one equivalent of either di(4-fluorobenzenesulfonyl)amine (FAH), di(4-chlorobenzenesulfonyl)amine (CAH), di(4-bromobenzenesulfonyl)amine (BAH), di(4-iodobenzenesulfonyl)amine (IAH), di(4-methylbenzenesulfonyl)amine (MAH), or di(4-nitrobenzenesulfonyl)amine (NAH), using dichloromethane/petroleum ether as the solvent, afforded the molecular complexes (FAH)$_2$·TMU (1, monoclinic, $P2_1/c$, $Z' = 1$, structure previously reported), CAH·TMU, BAH·TMU and IAH·TMU (2–4, isomorphic series, triclinic, $P\overline{1}$, $Z' = 1$), MAH·TMU (5, monoclinic, $P2_1$, $Z' = 1$), and the uronium salt TMUH$^+$NA$^-$ (6, monoclinic, $P2_1/c$, $Z' = 2$). The structural results obtained by X-ray crystallography at low temperatures indicate that the varying $p$-substituents of the di(arenesulfonyl)amines exert a decisive influence on (i) the stoichiometry of the cocrystallization reaction (2 : 1 for 1 vs. 1:1 for 2–4), (ii) the degree of proton transfer between the strongly acidic $(SO_2)_2NH$ moieties and the basic carbonyl function of TMU (molecular complexes assembled via N–H···O=C hydrogen bonds in 1–5 vs. two independent ion pairs based upon charge-assisted C–O–H$^+$···N$^-$ interactions in 6), and (iii) the conformation of the disulfonylamidine/amide units as defined by rotations about the S–N bonds (extended forms displaying anticalin C–S···S$'$–C$'$ torsions for the two molecules in 1 and the two anions in 6 vs. folded forms featuring synperiplanar C–S···S$'$–C$'$ torsions for the molecules in 2–5). The packing modes of 1–4 underline the well-known correlation between the atomic number of halogen atoms and their propensity to form halogen bonds. Thus, the structure of 1 is devoid of short F···O contacts, whereas the isomorphic cocrystals 2–4 consist of lamellar layers in which the inner lamellae include the TMU molecules and the peripheral regions are built up from CAH, BAH or IAH molecules associated into catemers via C–Hal···O=S bonds. The lamellar layers of the non-isomorphic methyl congener 5, although topologically similar to those of 2–4, are stacked according to a herringbone pattern that does not arise in the structures of 2–4. The most prominent packing feature of the uronium salt 6 are intimate dimers of two independent NA$^-$ ions, stabilized by dipolar nitro-nitro interactions and C–H···O=S contacts and further connected into monolayers through C–H···O$_{nitro}$ contacts. The uronium ions are inserted between these layers and bonded to the anion dimers by the strong hydrogen bonds mentioned above and numerous C–H···O$_{nitro}$ contacts. The presence of two independent formula units appears to arise from frustration between several competing interactions, e. g. dipolar nitro attractions, weak hydrogen bonding to sulfonyl and nitro acceptors and $\pi/\pi$ stacking of aromatic rings.

Key words: Cocrystals, Hydrogen Bonding, Halogen Bonding, Dipolar Nitro-Nitro Interactions, Sulfonamides, Tetramethyluronium Ion