The Crystal Structure of 2,5-Dianilino-3,4-diaza-1,6,6a-trithiapentalene

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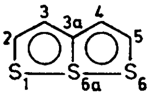
Summary The sulphur–sulphur bond lengths in 2,5-dianilino-3,4-diaza-1,6,6a-trithiapentalene are 2·475(3) and 2·225(3) Å, and the difference in sulphur–sulphur bond lengths may be partly due to intermolecular N–H···N bonding and to the different geometries of the anilino-groups.

The sulphur–sulphur bonds in 6a-thiathiophthen (I) are weaker than the other bonds in the molecule and therefore more susceptible to changes in bond lengths when the bonding system in the molecule is perturbed to some extent. It has been suggested that intermolecular environment (donating or accepting groups) as well as intramolecular environment (substituents) may cause such perturbation.[1]

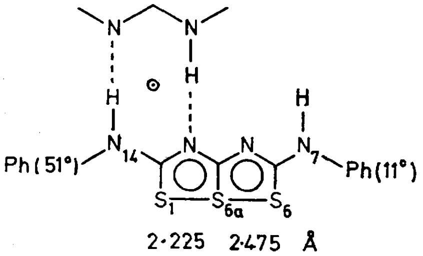
Structural studies on 6a-thiathiophthens show that different substituents perturb the S–S bonding to different degrees.[2] The observed effect which phenyl and methyl substituents have on the S–S bonding is consistent with the results from CNDO/2 calculations.[3]

The degree to which interaction between molecules perturbs the S–S bonding is much less known, and a structural study of 2,5-dianilino-3,4-diaza-1,6,6a-trithiapentalene (II), where intermolecular N–H···N bonding might be expected to occur, has been carried out in order to obtain experimental evidence for such effects.

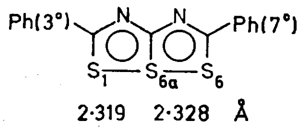
(II) was prepared according to the method of Behringer and Weber.[4] Crystals from pyridine are light yellow and belong to the monoclinic space group $P2_1/c$ with unit cell dimensions $a = 17{\cdot}915(3)$, $b = 4{\cdot}004(1)$, and $c = 20{\cdot}958(3)$ Å, and $\beta = 98{\cdot}25(2)°$. There are four molecules per unit cell; $D_c = 1{\cdot}537$ g cm^{-3}, $D_m = 1{\cdot}533$ g cm^{-3}.



(I)



(II)



(III)

The structure was solved by the heavy-atom (S) method from 2207 reflections (equi-inclination Weissenberg) and refined by full-matrix least-squares. With anisotropic temperature factors for all atoms except hydrogen, the final R is 0·09.

In the crystals of (II) the molecules are arranged in pairs over centres of symmetry by means of N–H···N hydrogen bonding, N···N = 3·03(1) Å. The S–S bonds in (II) are unequal, S(1)–S(6a) = 2·225(3) Å and S(6a)–S(6) = 2·475(3) Å, as compared with the S–S bonds in 2,5-diphenyl-3,4-diaza-1,6,6a-trithiapentalene (III), which are almost equal, S(1)–S(6a) = 2·319(3) Å and S(6a)–S(6) = 2·328(3) Å.[5]

The amino-groups in (II) are nearly coplanar with the central ring system, but the phenyl groups are twisted differently about the respective C–N bonds. Thus a somewhat stronger π bond may be formed between N(14) and C(2) than between N(7) and C(5).

It seems likely that the difference in S–S bond lengths in (II) is partly due to the hydrogen bonding and to the different twists of the phenyl groups.

Other bond lengths in (II) are S(1)–C(2) = 1·728(8), S(6a)–C(3a) = 1·790(8), S(6)–C(5) = 1·693(9), C(2)–N(3) = 1·34(1), N(3)–C(3a) = 1·33(1), C(3a)–N(4) = 1·33(1), N(4)–C(5) = 1·35(1), C(2)–N(14) = 1·34(1), N(14)–C(15) = 1·42(1), C(5)–N(7) = 1·35(1), and N(7)–C(8) = 1·40(1) Å.

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