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

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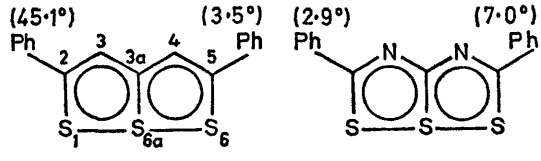
Summary The 2- and 5-phenyl groups in 2,5-diphenyl-3,4-diaza-1,6,6a-trithiapentalene are twisted 2·9 and 7·0° about the respective connection bonds, and the sulphur–sulphur bond lengths in the molecule are S(1)–S(6a) = 2·319(3) Å and S(6a)–S(6) = 2·328(3) Å.

A RECENT structure study of 2,5-diphenyl-6a-thiathiophthen (I) showed that the sulphur–sulphur bonds are 2·362(3) and 2·304(3) Å, although the 6a-thiathiophthen system is symmetrically substituted.[1]

It was suggested that the difference in S–S bond lengths in (I) might be partly due to the different twists of the phenyl groups, which are 45·1 and 3·5° respectively, and to a close contact of 3·25 Å which occurs in crystals of (I) between S(6) of the reference molecule and the 6a-thiathiophthen system in a symmetry related molecule.[1]



The results from CNDO/2 calculations on 2-phenyl-6a-thiathiophthen indicate that the phenyl substituent may cause a lengthening of the S(1)–S(6a) bond. The lengthening effect varies with the twist angle of the phenyl group, being negligible at twist angle 0° and most pronounced at 90°.[2] Thus, with respect to compound (I), S(1)–S(6a) should be a longer bond than S(6a)–S(6) in agreement with the experimental results.

A structure study of 2,5-diphenyl-3,4-diaza-1,6,6a-trithiapentalene (II) has been carried out in order to obtain further experimental evidence for the effect of phenyl substituents on the sulphur–sulphur bonding in 6a-thiathiophthens. The preliminary results from this study are given.

The phenyl groups in (II) are twisted 2·9 and 7·0° respectively, and the sulphur–sulphur bonds in the molecule are equal within three standard deviations; S(1)–S(6a) = 2·319(3) Å and S(6a)–S(6) = 2·328(3) Å. This agrees with the results from the CNDO/2 calculations.

Other bond lengths in the 6a-thiathiophthen system of (II) are: S(1)–C(2) = 1·692(9) Å, S(6a)–C(3a) = 1·786(8) Å, S(6)–C(5) = 1·698(8) Å, C(2)–N(3) = 1·325(10) Å, N(3)–C(3a) = 1·330(9) Å, C(3a)–N(4) = 1·344(10) Å, and N(4)–C(5) = 1·336(10) Å.

In crystals of (I) there are no intermolecular close contacts between sulphur and neighbouring atoms or groups.

A sample of (II) was generously supplied by Behringer.[3] The crystals are orange-red and belong to the orthorhombic space group $Pc2_1n$ with unit cell dimensions a = 12·494(12), b = 4·007(5), and c = 28·185(15) Å. There are four molecules per unit cell; D_c 1·480 g cm^{-3}, D_m 1·49 g cm^{-3}.

The structure was solved by the heavy atom (S) method from 1039 reflections (Equi-inclination Weissenberg) and refined by full-matrix least-squares. With anisotropic temperature factor coefficients for all atoms except hydrogen the final R is 0·065.

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