Synthesis of 3-Amino-6a-thiathiophthens and the *X*-Ray Crystal Structure of the 2-Methylthio-5-phenyl Derivative

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Summary The synthesis, some chemical and spectroscopic properties of two substituted 3-amino-6a-thiathiophthens and the *X*-ray crystal structure of the 2-methylthio-5-phenyl derivative are described.

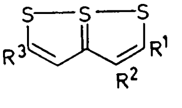
Although some 2-amino-6a-thiathiophthens (I; $R^1 = NH_2$) have been described,[1,3] 3-amino derivatives (I; $R^2 = NH_2$) have not hitherto been reported. We find that the nitro-group in (I; R^1 = MeS, $R^2 = NO_2$, R^3 = Ph) may be reduced by conventional methods (*e.g.* $SnCl_2$–HCl–EtOH) without disruption of the S–S bonds of the thiathiophthen nucleus. The resulting amine (I; R^1 = MeS, $R^2 = NH_2$, R^3 = Ph) forms black crystals [λ_{max} (EtOH) 252, 301, 560 nm (ϵ 54,800, 20,000, and 11,500)]. Unlike the 2-amino-6a-thiathiophthens, the 3-amino compound is basic [λ_{max} (0·1N HCl–EtOH) 255, 315, 502 nm (ϵ 51,500, 17,800, 11,200)]; it forms a red hydrochloride and a normal *N*-acetyl derivative, which is also obtained directly from the nitro-compound by reductive acetylation.

Compound (I; $R^1 = R^3$ = Ph, $R^2 = NO_2$), prepared by condensation of 3-methylthio-5-phenyl-1,2-dithiolium methosulphate with benzoylnitromethane and subsequent sulphurisation of the condensation product (II; R = NO_2) with phosphorus pentasulphide, is also reduced by $SnCl_2$–HCl, giving (I; $R^1 = R^3$ = Ph, $R^2 = NH_2$) [λ_{max} (EtOH) 253, 285, 550 nm (ϵ 45,500, 30,400, 9,800); λ_{max} (0·1N-HCl–EtOH) 253, 285, 502 nm (ϵ 48,500, 23,600, 9,500)]. Similar reduction of the nitro-group in the dithiolylidene ketone (II; R = NO_2) yields the corresponding amine (II; R = NH_2) [λ_{max} (EtOH) 307, 503 nm (ϵ 11,100, 16,100); λ_{max} (0·1N-HCl–EtOH) 301, 449 nm (ϵ 15,050, 28,350)].

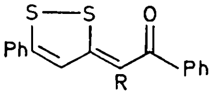
The anomalous properties of 2-amino-6a-thiathiophthen which are acidic rather than basic,[2] reflect the electrondeficient character of the 2-position in the nucleus. The 3-position, at which attack by electrophiles occurs,[4] is relatively electron-rich; attachment of the amino-group at this position should give rise to basic properties, in agreement with our results.

An X-ray structural analysis of (I; R^1 = MeS, R^2 = NH_2, R^3 = Ph) was undertaken.

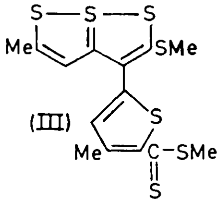
Crystal Data: $C_{12}H_{11}NS_4$, $M = 297{\cdot}4$, monoclinic, $a = 14{\cdot}103(3)$, $b = 8{\cdot}313(4)$, $c = 11{\cdot}353(7)$ Å, and $\beta = 102{\cdot}17(3)°$, $U = 1301{\cdot}7 \times 10^{-24}$ cm^3, $D_m = 1{\cdot}52$, $Z = 4$, $D_c = 1{\cdot}52$; space group $P2_1/c$. A total of 1696 reflections with intensities significantly above zero was collected on a Picker FACS-1 diffractometer (Cu-K_α). The structure has been refined to an R-factor of 0·084, incorporating anisotropic thermal parameters for the non-hydrogen atoms and including hydrogen atoms at fixed positions. A view of the structure showing the bond lengths and angles is given in the Figure.



(I)



(II)



(III)

The S–S bond lengths are significantly unequal [2·266(4) and 2·375(4) Å] with the longer bond in the ring containing the amino substituent. It is of interest to compare this structure with that of (I; R^1 = MeS, R^2 = PhCO, R^3 = p-C_6H_4Br),[5] where the "short" S–S bond lengths (on the side of the p-bromophenyl substituent) were 2·163(8) and 2·168(8) Å and the "long" S–S bond lengths were 2·454(8) and 2·561(8) Å; there were two crystallographically-independent molecules in the latter crystal. In the molecule now under study, the electron-releasing properties of the amino group have clearly caused the S–S bond lengths to become more nearly equal, although the long bond is still on the side of the methylthio group. By comparison of the dimensions obtained for 2,4-diphenyl- and 2-p-dimethylanilino-4-phenyl-6a-thiathiophthen, Hordvik and Saethre[6] have shown that an electron-releasing group in the 2-position also causes a shortening of the S–S bond in the ring to which it is attached. S–S Bond lengths of 2·197(7) and 2·546(7) Å have been found in (III) with the long bond being on the side of the molecule with the methylthio substituent.[7] There appears, therefore, to be a tendency for a methylthio substituent in the 2-position to influence the S–S bond lengths by causing some elongation of the S(1)–S(6a) bond.

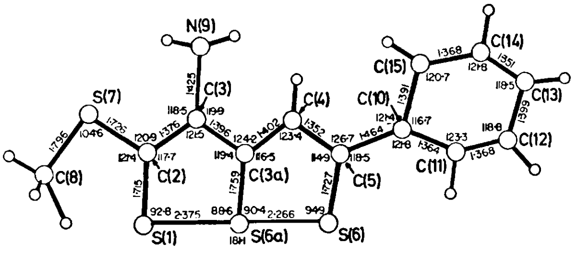


FIGURE. *Bond lengths* (Å) *and angles* (°) *in* 3-*amino*-2-*methylthio*-5-*phenyl*-6a-*thiathiophthen. Typical e.s.d.'s of the S–S, C–S, and C–C bonds are* 0·004, 0·008, and 0·013 Å, *respectively.*

As in other 6a-thiathiophthens,[8] the central C–S bond is significantly longer than the two "external" ones. The atoms of the nucleus, the amino nitrogen atom, and the two non-hydrogen atoms of the methylthio group are close to being coplanar (deviations −0·036 to 0·026 Å) with the 5-phenyl substituent both slightly bent and twisted out of this plane. There are no intermolecular contacts sufficiently short as to affect the bonding in the individual molecule.

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