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2,3,4,5-TETRAHYDRO-1,6-DIETHYL-3,4-PROPANO-6a-THIA(S^{IV})-1,3,4,6-TETRA-AZAPENTALENE-2,5-DITHIONE

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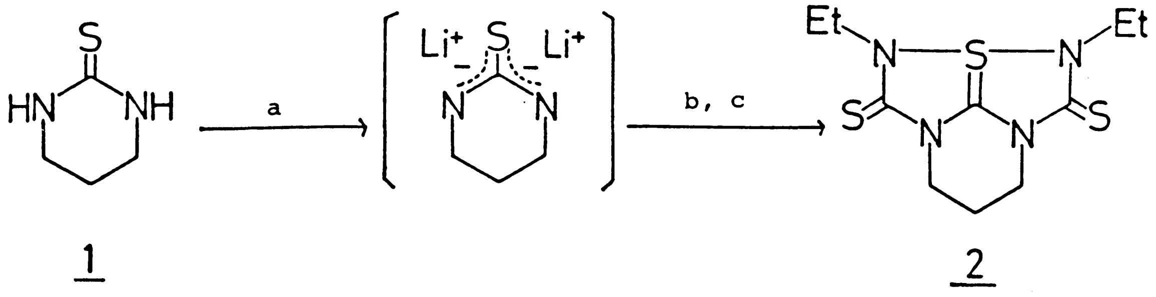
A new heteropentalene, 2,3,4,5-tetrahydro-1,6-diethyl-3,4-propano-6a-thia(S^{IV})-1,3,4,6-tetra-azapentalene-2,5-dithione, was synthesized by a convenient one pot reaction, and its structure was determined by a single crystal X-ray diffraction.

The synthesis of the first 2,3,4,5-tetrahydro-1,6-diphenyl-3,4-propano-6a-thia(S^{IV})-1,3,4,6-tetra-azapentalene-2,5-dithione was reported in 1973 by Beer and co-workers.1) Compounds of this type are of considerable interest with respect to the structure and stability in comparison with those of the other 6a-thia(S^{IV})-pentalene analogs containing S-S^{IV}-S,2) O-S^{IV}-O,3) or N-S^{IV}-N4) bond. However, the structure of this type has not been established yet unambiguously by a single crystal X-ray structure analysis.

We report here the first example of the X-ray crystallographic structure of a new heteropentalene, 2,3,4,5-tetrahydro-1,6-diethyl-3,4-propano-6a-thia(S^{IV})-1,3,4,6-tetra-azapentalene-2,5-dithione (2). Scheme 1 shows a reaction pathway for the preparation of 2.



Scheme 1. a: Bu^nLi, THF, 0 °C, 1 h; b: $PhCOCH_2Cl$, reflux, 1 h; c: CH_3CH_2NCS, room temp, 20 h.

A typical procedure for the preparation of 2 is as follows: To a cooled THF solution (0 °C) of 3,4,5,6-tetrahydro-2-pyrimidinethiol (1; 2.0 mmol) was added a hexane solution of Bu^nLi (4.4 mmol) with stirring at 0 °C under argon, and the mixture was stirred for 1 h under the same conditions. To the resulting dianion of 1 was added dropwise a THF solution of phenacyl chloride (2.0 mmol). The solution immediately became wine red, and the reaction mixture was refluxed for 1 h under argon. After cooling to room temperature, a solution of ethyl isothiocyanate (6.0 mmol) in THF was added, and the reaction mixture was stirred at room temperature for 20 h under argon. After THF was evaporated, the residue was poured into an aqueous ammonium chloride. The solution was extracted with chloroform, and the extract was washed with water, dried over anhydrous Na_2SO_4, and condensed under reduced pressure. The residue was chromatographed on a silica gel column or preparative TLC to give heteropentalene 2 in 63% yield. Compound 2 was recrystallized from hexane-chloroform to give 2 as colorless needles. [2, mp 217-220 °C (dec.); IR (KBr) 2960, 2910, 1570, 1530, 1490, 1420, 1310, 1230, 1180, 1120, 1050, 970, 910, and 830 cm^{-1}; m/e 201 ($M^+-C_2H_5NCS$), 186, 173, 168, 140, 116, 109, 100, 87, 83, 72, and 59; ^1H NMR ($CDCl_3$) δ 1.33(t, 6H, J=7.0 Hz, 2 x $CH_2C\underline{H}_3$), 2.36(m, 2H, $NCH_2C\underline{H}_2CH_2N$), 3.78(q, 4H, J=7.0 Hz, 2 x $C\underline{H}_2CH_3$), and 4.41(t, 4H, J=6.0 Hz, 2 x $NC\underline{H}_2$); ^{13}C NMR ($CDCl_3$) δ 13.82, 20.01, 39.93, 44.61, 156.11, and 168.65; Found: C, 41.52; H, 5.56; N, 19.55%. Calcd for $C_{10}H_{16}N_4S_3$: C, 41.64; H, 5.59; N, 19.42%.]

The structure of 2 was determined by the X-ray diffraction. Colorless crystals were grown from hexane-chloroform solution. The crystal shape was a hexagonal prism. A single crystal of dimensions 0.52 x 0.24 x 0.17 mm was selected for X-ray investigations. Crystal data for 2: $C_{10}H_{16}N_4S_3$, M = 288.433, monoclinic, space group $P2_1$, a = 13.060(5), b = 9.988(3), c = 5.211(2) Å, β = 98.31(3)°, U = 672.6(4) $Å^3$, Z = 2, Dc = 1.42 gcm^{-3}, F(000) = 304, μ(Mo-Kα) = 5.19 cm^{-1}. Data were collected on a Rigaku AFC-5 diffractometer using Mo-Kα radiation. The structure was solved by the direct method with MULTAN 78 and refined by block-diagonal least-squares to final R value of 0.043 for 1315 absorption corrected independent reflection [$|F_0| > 3\sigma(F_0)$].5)

Figure 1 shows the molecular structure of **2**. The X-ray crystallographic analysis provides the following structural characteristics: (i) the S(1)-N(1) [1.927(4) Å] and S(1)-N(2) [1.891(4) Å] bond lengths differ from each other, and it means that **2** has a unsymmetrical structure; (ii) the S-N bond length [1.91 Å, average] is 9% longer than the normal S-N single bond length [1.74 Å],6) and the external C=S bond length [1.68 Å, average] is 4% longer than the normal C=S double bond length [1.61 Å];6) and (iii) the heteropentalene framework can be regarded as planar, because the maximum distance between the framework atoms and plane is only 0.013(5) Å (see Fig. 1b).

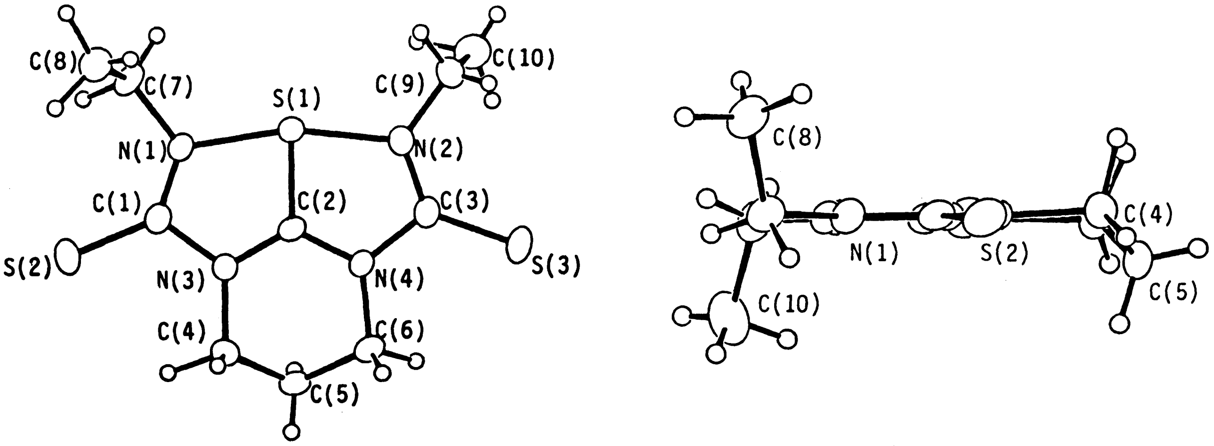


Fig. 1a.

Fig. 1b.

Fig. 1. Molecular structure of **2**. Selected bond lengths (Å) and angles (°) : S(1)-N(1) 1.927(4), S(1)-N(2) 1.891(4), S(1)-C(2) 1.705(4), S(2)-C(1) 1.683(5), S(3)-C(3) 1.674(5), N(1)-C(1) 1.289(6), N(2)-C(3) 1.311(6), N(3)-C(1) 1.428(6), N(3)-C(2) 1.327(6), N(4)-C(2) 1.339(6), N(4)-C(3) 1.417(6); N(1)-S(1)-N(2) 165.5(2), N(1)-S(1)-C(2) 82.0(2), N(2)-S(1)-C(2) 83.5(2), S(1)-N(1)-C(1) 116.0(3), S(1)-N(2)-C(3) 115.7(3), C(1)-N(3)-C(2) 114.3(4), C(2)-N(4)-C(3) 115.0(4), N(1)-C(1)-N(3) 108.7(4), S(1)-C(2)-N(3) 119.0(3), S(1)-C(2)-N(4) 117.3(3), N(3)-C(2)-N(4) 123.8(4), N(2)-C(3)-N(4) 108.5(4).

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5) A list of atomic coordinates and thermal parameters can be obtained from the author (N. M.) on request.

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