

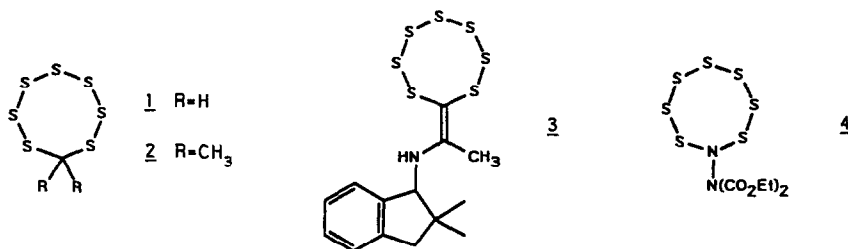
THE STRUCTURE OF A NOVEL HEPTATHIOCANE DERIVATIVE

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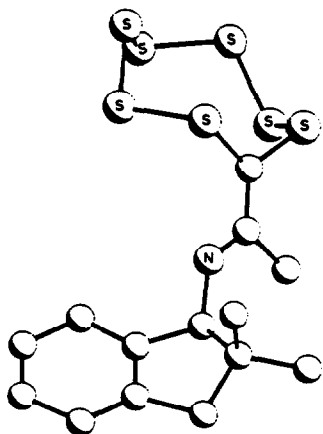
Summary: A novel heptathiocane derivative, formed in the reaction of 2,2-dimethyl-1-indanylamine with chloroacetone, CS₂ and sodium ethylate in ethanol in the presence of air, was characterized by spectroscopy and X-ray crystal structure analysis.

Heptathiocanes are rare: Only two substances have been reported in the chemical literature, namely the parent compound itself (1), prepared from S₅Cl₂ and CH₂(SH)₂ [1], and the dimethyl derivative 2, obtained



by the reaction of titanocene isopropyl tetrasulfide with S_nCl₂ (n = 1-30) as a component in a mixture ranging from six- to 35-membered rings [2]. No X-ray crystal structure analysis of heptathiocanes are available. We report here the structure of 3, which formed in the reaction of 2,2-dimethyl-1-indanylamine with chloroacetone, CS₂ and sodium ethylate in ethanol in the presence of air [3]. The structure of 3, deduced from its proton coupled ¹³C-NMR and its mass spectrum [4] as well as its elemental composition

was ascertained by X-ray crystal structure analysis [5]. A perspective view of the molecule is shown in the figure. Bond lengths and angles agree well with expected values. The eight membered ring adopts a crown conformation very similar to that observed in 4 [6]. The structure of 3 in CDCl₃ solution differs from that of the solid state by the presence of an amide type hindered rotation around the N-C= single bond due to the electron withdrawing effect of the heptathiocane ring. This effect is probably caused by electron backdonation from the ring C-atom to the adjacent S-atoms similar to the situation in the azaanalogue 4 [6].



PLUTO-Plot of 3

A possible explanation of the formation of **3** is the generation of S^{2-} from CS_2 and $NaOEt/EtOH$ [7] and its air oxidation to polysulfides [8], which react with the intermediary condensation product of the 2,2-dimethyl-indanylamine and chloroacetone. The imine formed rearranges to the corresponding enamine. Nucleophilic attack by the enamine on the seventh sulfur of the polysulfide chain would then lead to **3**. Similar reactions leading to S_8 are well known [9]. Attempts to isolate other cyclic polysulfides were unsuccessful so far, indicating that eight might be the optimal ring size for this system.

References and Notes

- [1] F. Fehér, W. Becher, *Z. Naturforschg.* **20b**, 1125 (1965)
- [2] R. Steudel, R. Strauss, D. Jensen, *Chemiker Ztg.* **109**, 349 (1985)
- [3] Preparation: To a solution of 2.3g (0.1 mole) Na in 90ml EtOH 16.1g (0.1 mole) 2,2-dimethyl-1-indanylamine was added at r.t. To the slightly cloudy solution 7.6g (0.1 mole) CS_2 was added maintaining the temperature below 30° . After 3h, 9.2g (0.1 mole) chloroacetone was added within 30 min. and the cloudy reaction mixture stirred at r.t. for 14 days. The reaction mixture was dissolved in EtOAc, washed with water and brine. The dried EtOAc phase was evaporated. From the resulting resin, **3** (1g) was isolated by MPLC (hexane/EtOAc 20/1), bright yellow crystals, mp. $142-143^\circ$.
- [4] ^{13}C -NMR ($CDCl_3$): Allyl moiety 167.1, 167.0, 70.32, 70.28, 17.6, 17.3 (the double bond carbons couple with the CH_3 protons, the CH_3 carbons with the NH protons); indanyl moiety: 141.6, 141.3, 141.2 (C(3a)), C(7a)); 123.8-128.6 (C(4)-C(7)); 68.6, 68.5 (C(1)); 46.8, 46.4 (C(2)); 45.7, 45.6 (C(3)); 27.0, 22.3, 22.2 (CH_3). FD-MS: 423; EI-MS: 423(M); 391(M-S); 359(M- S_2); 327(M- S_3); 295(M- S_4); 263(M- S_5), 231(M- S_6); 145(100%).
- [5] Crystal Data: $C_{14}H_{17}NS_7$, triclinic, space group P1, $a=8.667(2)$ Å, $b=9.696(1)$ Å, $c=12.220(1)$ Å, $\alpha=77.28(1)^\circ$, $\beta=104.86(1)^\circ$, $\gamma=108.22(1)^\circ$, $Z=2$. An ENTRAF-NONIUS CAD4 automatic diffractometer was used for data collection with $CuK\alpha$ radiation and graphite monochromator. The intensities of 4021 independent reflections with $\Theta < 75^\circ$ were measured, of which 3658 were classified as observed with $I > 2\sigma(I)$. The structure was solved by direct methods and refined by fullmatrix least squares calculations with anisotropic (Isotropic for hydrogen atoms) thermal parameters to a final R value of 0.092.
- [6] K.-H. Linke, D. Skupin, J. Lex, B. Engelen, *Angew. Chem.* **85**, 143 (1973)
- [7] M. Wroński, *Z. Phys. Chem. (Leipzig)* **211**, 113 (1959)
- [8] H. Remy, *Lehrbuch der Anorganischen Chemie Vol. I*, 891, Akad. Verlagsges. Geest & Portig, Leipzig 1965. Compound **3** is not formed in the absence of air.
- [9] R. Huisgen, *Phosphorus, Sulfur, and Silicon* **43**, 63 (1989) and lit cit.