

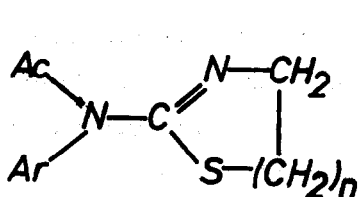
STRUCTURE INVESTIGATION OF THE 2-ARYLAMINO-2-THIAZOLINE AND THE ANALOGOUS THIAZINE AMIDES XIV: CRYSTAL STRUCTURE OF 2(2,6-DIMETHYL-PHENYL)-IMINO-3(2-CHLOROBENZOYL)-THIAZOLIDINE

Gy. Argay, A. Kálmán[§], G. Tóth^o and L. Toldy^o

Central Research Institute for Chemistry of the Hungarian Academy of Sciences Budapest, 114/17., and ^oResearch Institute for Pharmaceutical Chemistry, Budapest, Hungary.

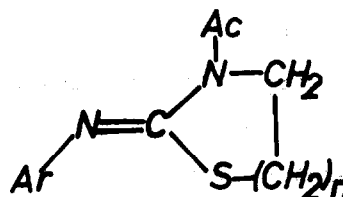
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Acylation of the 2-arylamino-2-thiazolines and the analogous thiazines resulted mostly in two types of isomers; I and II [1], which (e.g. mesylamides) can be distinguished by their NMR and mass spectra [2-5].



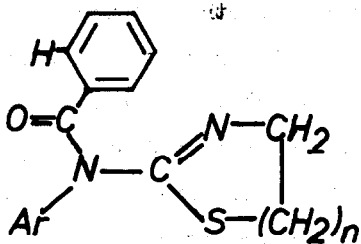
I

n=1 : thiazolines
n=2 : thiazines

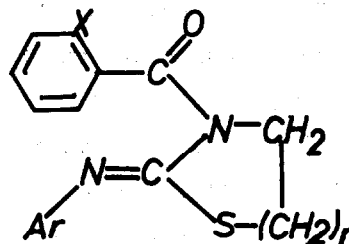


II

In the case of benzamide derivatives, however, analysis of the NMR spectra suggested that only one isomer (III) with structure of type I could exist.



III



IV

But this conclusion was queried when the NMR data of benzamides with an ortho-substituent ($X = \text{CH}_3, \text{Cl}, \text{etc.}$) on the benzoyl group, were compared with similar spectra of their salts [3,4]. These investigations suggested structures of type II for the ortho-substituted benzamides (IV). This idea was also supported by mass spectra [5].

The arguments for structure IV were, nevertheless, weakened by the possibilities that : (i) an altered solvation in the case of structure I (presumably caused by a greater steric hindrance on ortho-substitution) could also lead to the anomalous NMR spectra obtained; (ii) the steric effects discussed in [5] might also account for the phenomena in the mass spectra of the structures of type I. In order to answer these questions and to give a firm basis for further complex studies of these derivatives of thiazoline and thiazine, an X-ray study of the title compound has been performed.

The structure of $\text{C}_{18}\text{H}_{17}\text{ON}_2\text{SCl}$ ($a = 6.518, b = 13.547, c = 19.314 \text{ \AA}$, $Z = 4, d_c = 1.335, d_x = 1.323 \text{ g.cm}^{-3}$, $P2_12_12_1$) was solved by the direct method [6] using intensities measured on a two-circle Stoe-Güttinger diffractometer. Block-diagonal least-squares refinement [7] of the positional and vibrational parameters gave the present conventional R factor of 11.2 %.

The molecular structure (fig. 1) is consistent with the supposed model IV (i.e. type II) and thus confirms the interpretation of the NMR and mass spectra for the ortho-substituted benzamides. The benzene rings (A and B) are almost perpendicular (98.2° and 82.1° , respectively) to the plane P formed by the C(9),N(1),N(2) and S moiety. Plane P also involves some other atoms; C(1),C(12) and oxygen within experimental error. In agreement with this, the intermediate bond lengths; C(1)-N(1) = 1.44, C(9)-S = 1.77, C(9)-N(2) = 1.41 and N(2)-C(12) = 1.34 \AA , indicate that a mesomeric system is formed on the group of atoms mentioned with the participation of a rather localized double bond, N(1)-C(9) = 1.28 \AA . The thiazoline group itself, however, is not planar, the C(10) and C(11) carbon atoms deviate ($\Delta = 0.30$ and -0.23 \AA , respectively) from the plane P thus forming an envelope shape for ring C. The other bond lengths [except S-C(11) = 1.87 \AA] and bond angles agree, within experimental error,

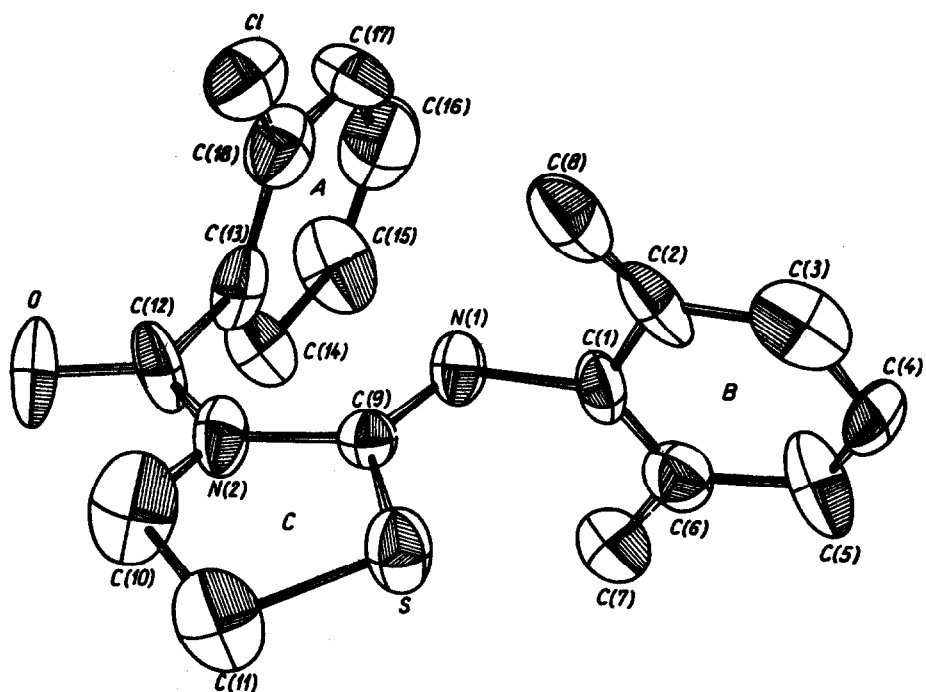


Fig. 1 : Molecular conformation observed in the crystal structure of the title compound, showing atomic and ring numbering used and the anisotropic vibrational ellipsoids.

with the corresponding data reported in the literature (e.g. [8]). The S-C(11) bond is considerably longer than the sum of Pauling's covalent radii corrected for the electronegativities (1.81 Å). A similarly long S(II)-C(sp³) bond is found in N,N-diglycyl-L-cystine dihydrate [9], however.

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LITERATURE

- [1] L.Toldy, P.Sohár, K.Faragó and L.Bartalits: Tetrahedron Letters, 2177, (1970).
- [2] L.Toldy, P.Sohár and K.Faragó: Tetrahedron Letters, 2183, (1970).
- [3] G.Tóth and L.Toldy: Tetrahedron, 27, 1967, (1971).
- [4] G.Tóth and L.Toldy: Tetrahedron, submitted for publication
- [5] The intensity of the (M-X)⁺ peak was considerably stronger when the substituent (X) was either CH₃ or Cl instead of a hydrogen atom; G.Tóth, J.Tamás and L.Toldy: Magyar Kémikusok Lapja [in Hungarian], 561, (1971).
- [6] G.Germain, P.Main and M.M.Woolfson: Acta Cryst., A27, 368, (1971).
- [7] V.Albano, A.Domenicano and A.Vaciago: Full and Block Diagonal Matrix Least-Squares Refinement Program for the IBM 7040 Computer (Centro di Studio per la Strutturistica Chimica del CNR, Roma) adapted for the CDC 3300 computer by K.Sasvári (Budapest).
- [8] J.P.Morton and Raveau: Acta Cryst., B27, 95, (1971).
- [9] H.L.Yakel and E.W.Hughes: Acta Cryst., 7, 291, (1954).

* To whom all the correspondence concerning this paper should be addressed.