CHEMISTRY LETTERS, pp. 723-726, 1976. Published by the Chemical Society of Japan

THE STRUCTURE OF THE 1:1 ADDUCT OF "HECTOR'S BASE" WITH ARYLCYANAMIDES BOND SWITCH ON HYPERVALENT SULFUR[1)]

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The structure of the 1:1 adduct of "Hector's base" with arylcyanamides was determined by X-ray analysis of tris-p-bromophenyl derivative (1a). The molecule is almost planar and the strong interaction was exemplified between the sulfur and the nitrogen atoms.

The chemistry of hypervalent heterocyclic systems related to 6a-thiathiophthene and non-classical aromatics containing sulfur has been of considerable interest and is still in active discussion.[2)] This paper describes the unique role of hypervalent sulfur both in processing the reaction and in stabilizing the final product.

Now the structure of the 1:1 adduct of 4-aryl-3-arylimino-5-imino-1,2,4-thiadiazolidines (2: Hector's base[3)]) with arylcyanamides has been determined to be 1 by X-ray crystal structure analysis of tris-p-bromophenyl derivative (1a: $Ar^1 = Ar^2 = p\text{-}BrC_6H_4$), showing the presence of bond switch on the hypervalent sulfur, hence the previously proposed structure should be revised.[4)]

Three dimensional X-ray data of the single crystal of 1a containing one mole of THF ($C_{21}H_{15}N_6SBr_3 \cdot C_4H_4O$) were collected on a Philips automated, four-circle diffractometer, PW 1100, using the θ-2θ scan technique with Ni-filtered Cu·Kα radiation. The structure was solved by the standard heavy-atom techniques.

Least-squares refinement by block-matrix with anisotropic temperature factors for all non-hydrogen atoms resulted in R=0.114 for 3974 non-zero independent reflections.

The crystal is monoclinic, a=11.44$_0$, b=19.25$_9$, c=13.34$_1$ Å, β=109.2$_2$°, U=2775.$_3$ Å, Dm=1.66 g·cm^{-3} (by floatation), Z=4, Dc=1.65 g·cm^{-3}, space group $P2_1/n$, and perspective view of the molecule is shown in Fig. 1.

S-N(1)=2.538(9), N(1)-C(1)=1.28(1), C(1)-N(3)=1.39(1), N(3)-C(2)=1.36(1), C(2)-N(4)=1.30(1), N(4)-C(3)=1.39(1), C(3)-N(6)=1.29(1), N(6)-S=1.670(9), and S-C(2)=1.741(10) Å; ∠C(2)SN(1)=74.4(4), ∠SN(1)C(1)=103.1(7), ∠N(1)C(1)N(3)=116.2(9), ∠C(1)N(3)C(2)=121.5(8), ∠N(3)C(2)S=124.5(7), ∠SC(2)N(4)=112.7(7), ∠C(2)N(4)C(3)=107.4(8), ∠N(4)C(3)N(6)=120.8(9), ∠C(3)N(6)S=107.7(7), and ∠N(6)SC(2)=91.3(4)°. The dihedral angle between the best plane [S, C(2), N(4), C(3), N(6)] and the best plane [S, C(2), N(3), C(1), N(1)] is 4.4°.

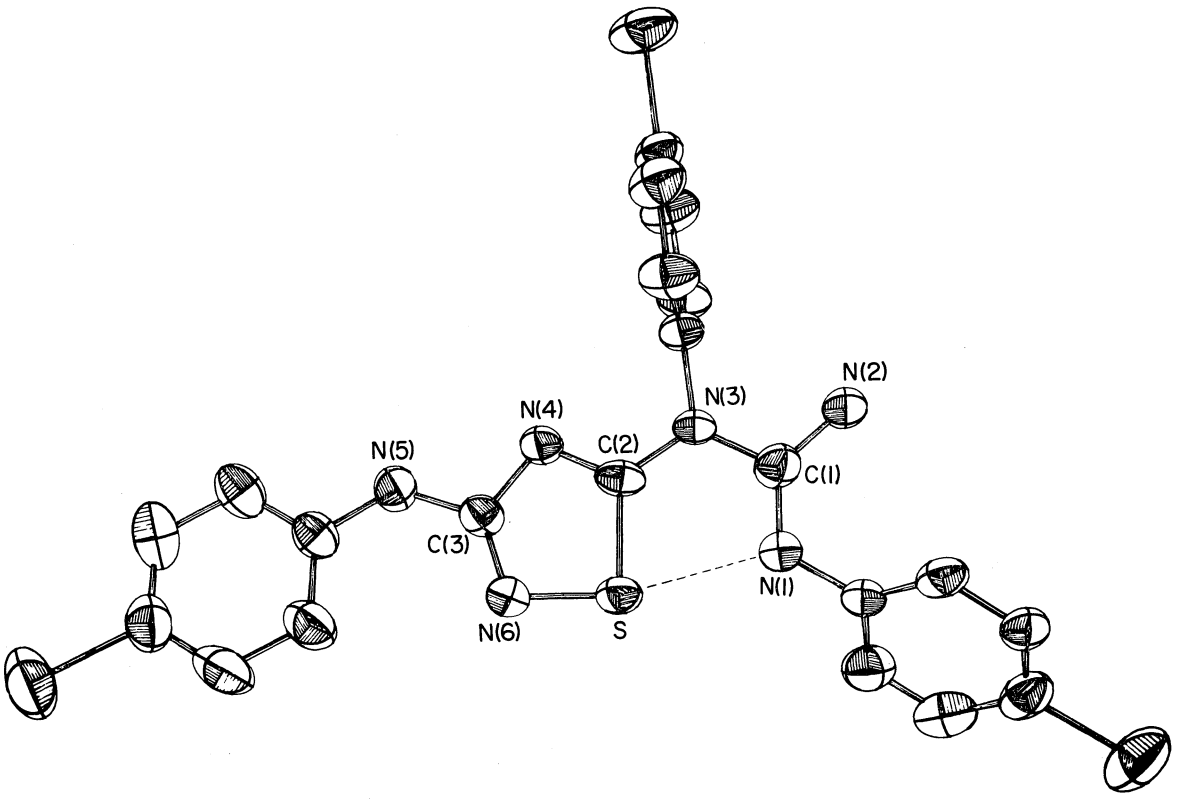
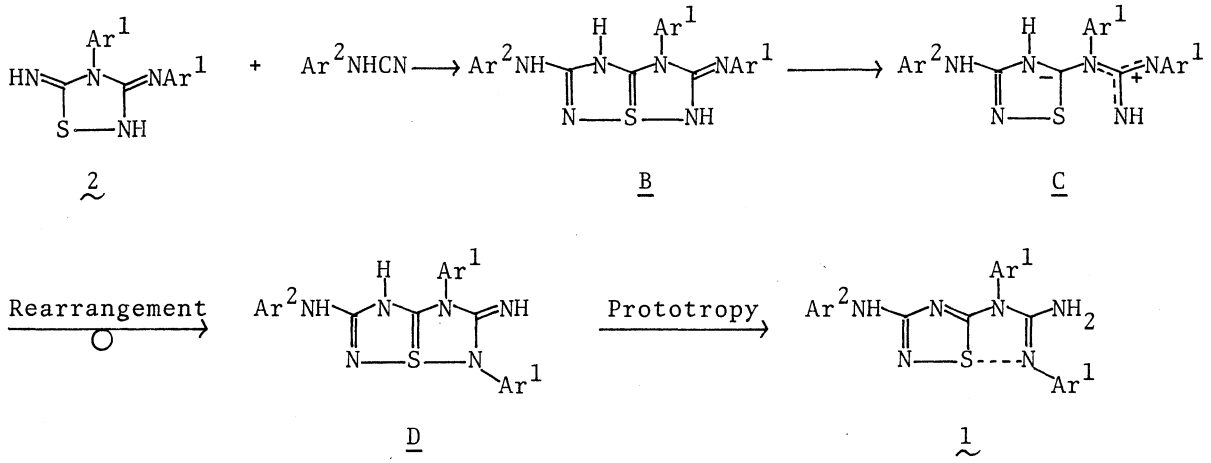


Fig. 1 Perspective View of 1a

The approximate planarity of the molecule, three p-bromophenyl groups being excluded, and the S-N(1) distance of 2.538(9) Å suggest that there is some significant interaction between the S and N(1) atoms, compared with the sum of the van der Waals radii of 3.35 Å.

From this result, formation of 1 can be rationalized by 1,3-dipolar cycloaddition of 2 with an arylcyanamide followed by rearrangement as shown below.



It is not yet clear whether B is directly formed by 1,3-dipolar cycloaddition or by stepwise nucleophilic substitution: in any case, it is evident that hypervalency of the sulfur plays an important role in the reaction and in the stability of the final structure of the adduct (1).

References and Notes

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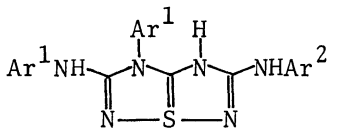
3) D. S. Hector, Ber., 22, 1179 (1889); F. Kurzer, J. Chem. Soc., 1956, 2345. For the structure determination of Hector's base, see: F. Kurzer, "Advances in Heterocyclic Chemistry", Vol. 5, Academic Press, N. Y., 1965, p. 119; C. Christophersen, T. Ottersen, K. Seff, and S. Treppendahl, J. Amer. Chem. Soc., 97, 5237 (1975).

4) K. Akiba, T. Tsuchiya, M. Ochiumi, and N. Inamoto, Tetrahedron Lett., 1975, 455. A tentative structure (A) was suggested for 1. Summary of MS and UV of 1 and related compounds are shown in this paper. These data are compatible with the revised structure (1).



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(Received April 19, 1976)