HETEROCYCLES, Vol 20, No 1, 1983

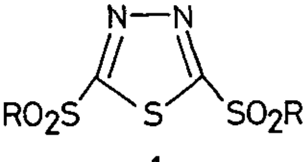
Molecular Structure of 2,5-Bis(ethylsulfonyl)-1,3,4-thiadiazole

Kazunobu Harano, Masami Yasuda, and Ken Kanematsu*

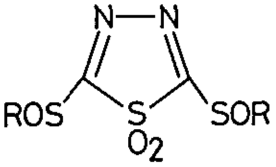
Faculty of Pharmaceutical Sciences, Kyushu University 62, Maidashi,
Higashi-ku, Fukuoka 812, Japan

Abstract —— An X-ray crystallographic analysis was carried out to elucidate the molecular structure of the oxidized compound of 2,5-bis(ethylthio)-1,3,4-thiadiazole.

Peroxide oxidation of 2,5-bis(alkylthio)-1,3,4-thiadiazoles has been reported to produce bis-sulfones (1)[1] instead of sulfoxides (2).[2] However, there still leaves some ambiguity on the assignment, since the mass spectrum of the oxidized compound (R = Et) of 2,5-bis(ethylthio)-1,3,4-thiadiazole shows ion at 206 ($M^+ - SO_2$), indicating the possibility of the alternative structure 2a. It was difficult to assign the structure on the basis of spectroscopic data only.



1



2

a: R = Et
b: R = Me
c: R = CH_2Ph

In view of the importance of the structure assignment, we tried an X-ray crystallographic study of the oxidized compound (R = Et). Single crystals of the compound were obtained from the ethanol-benzene solution by slow evaporation at room temperature. Crystals are *monoclinic*, space group $P2_1$, with a = 7.348 (2), b = 15.360 (4), c = 5.108 (1) Å; β = 102.32 (2)°; Z = 2; V = 563.2 (2) $Å^3$; D_m (KI + H_2O) = 1.579 and D_c = 1.594 g cm^{-3}. The intensity data were collected on a Syntex $P\bar{1}$ automated diffractometer with Mo-$K\alpha$ radiation (λ = 0.71069 Å) using θ-2θ scan technique up to a 2θ limit of 60°. Of 1541 independent reflections, 1235 were treated to be observed ($I > 2.3\sigma(I)$). The structure was solved by the direct method using the *MULTAN* series of programs.[3] The disordered structures[4] were refined by block-diagonal least-squares method using *UNICS II* program system.[5,6] The final R value was 0.066 for the observed reflections. Further refinement of the structure was not deemed justifiable in light of the relatively poor quality of the crystals and

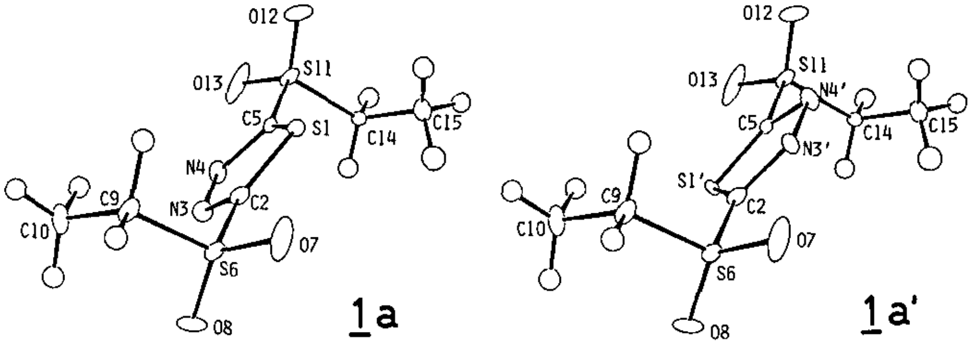
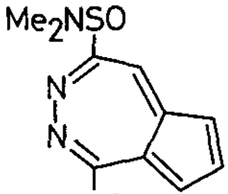


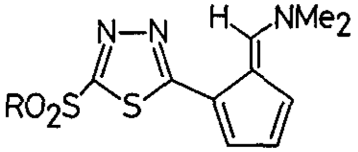
Figure 1. *ORTEP* drawing of 1a and 1a'.

owing to the objective of determination of the molecular structure had been achieved. The molecular structure drawn by the *ORTEP* program[7] is shown in Figure 1 with numbering sequences. As can be seen in Figure 1, the structure of the oxidized compound (R = Et) was fully confirmed as 2,5-bis(ethylsulfonyl)-1,3,4-thiadiazole (1a). The disorder is consistent with the molecule occurring in two statistical positions in the asymmetric unit, corresponding to the structures (1a and 1a') in Figure 1. The atoms where the effects of the disorder are particularly pronounced are S(1), N(3), and N(4).

The structure of the facile reaction products of the thiadiazoles (1) and 6-dimethylaminofulvene should therefore be revised to be the substitution products (4) as suggested by Boulton and Chong[1] instead of 5,6-diazaazulenes (3).[2]



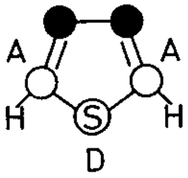
3



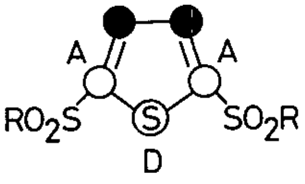
4

a: R = Et
b: R = Me
c: R = CH_2Ph

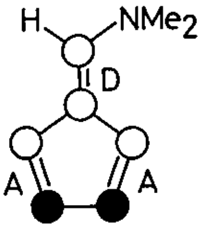
With these facts in mind, we attempt to interpret the oxidation and substitution reactions on the concept of cyclic conjugation,[8,9] which is very useful for prediction of aromaticity and reactivity of various molecules. In thiadiazole (5), electron-donating sulfur lone pair electrons and electron-accepting C=N bond are donor (D) and acceptors (A's), respectively. The cyclic conjugation is continuous



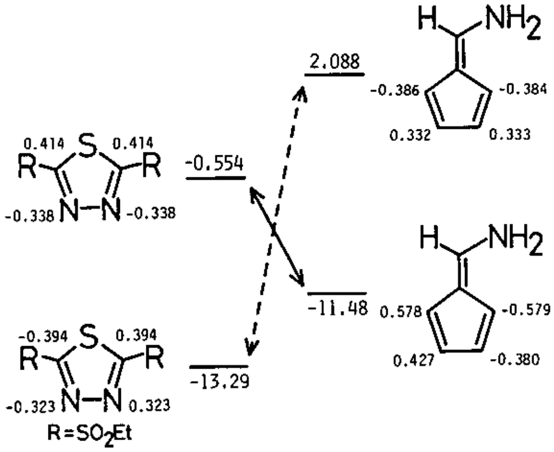
5



1



and the orbital phase continuity requirements[10] are satisfied responsible for aromatic electron system. In 2,5-bis(alkylsulfonyl)-1,3,4-thiadiazoles (1), electron delocalization is expected to be more extensive, in which replacement of the hydrogens of thiadiazole (5) by acceptors, $R-SO_2-$, makes effective donor-acceptor interaction possible. By contrast, in 2,5-bis(alkylsulfinyl)-1,3,4-thiadiazole 1,1-dioxides (2), donor-acceptor interaction does not occur effectively to result in the destabilization of the cyclic electron-system interaction. On the other hand, in 6-dimethylaminofulvene, the cyclic conjugation is continuous and the orbital phase continuity requirements are satisfied responsible for aromatic electron system similar to thiadiazole (5). Because bis-sulfones (1) and 6-dimethylaminofulvene have aromatic electron properties, the transition state of the cycloaddition may be energetically unfavorable. As the result, nucleophilic substitution occurs resulting in increasing of the resonance energy between two aromatic rings. Semiempirical SCF MO calculations on CNDO/2 approximation[11] suggest that the dominant interaction is



1a

Figure 2. FMO energy levels and coefficients of thiadiazole (1a) and 6-aminofulvene calculated by CNDO/2 MO method.

the low-lying LUMO of 1a and the HOMO of 6-aminofulvene and that the LUMO coefficient of 1a and the HOMO coefficient of the fulvene at C-2 (C-5) position are large enough to interact each other (Figure 2).

The absence of a noticeable solvent effect upon the rate constants (4.43×10^{-3} sec^{-1} in chloroform, 1.35×10^{-3} sec^{-1} in acetone, and 2.36×10^{-3} sec^{-1} in dimethylsulfoxide) does not seem consonant with an intermediate involving any significant degree of charge separation. The observed low sensitivity may be attributed to the non-ionic nature of the transition state controlled by frontier molecular orbitals (FMO's).

REFERENCES AND NOTES

1. Boulton, A. J.; Chong, A. K. A. *J. Chem. Soc. Chem. Comm.* 1981, 736-737.
2. Mori, M.; Kanematsu, K. *ibid.* 1980, 873-874.
3. Main, P.; Hull, S. E.; Lessinger, L.; Germain, G.; Declercq, J. P.; Woolfson, M. M. *"MULTAN 78, a System of Computer Program for Automatic Solution of Crystal Structures from X-ray Diffraction Data"*; University of York, England, 1978.
4. An *E* map calculated with 233 signed *E*'s ($|E| > 1.20$), which gave the combined figure of merit 2.6577, revealed the positions of 13 of non-hydrogen atoms and an additional atom due to disorder associated with S(1). The positions of the remaining two nitrogen atoms were located on a subsequent difference fourier map. The atomic multiplicities of S(1), N(3), and N(4) to give the lowest residual index were determined to be 0.5 by the structure factor calculations.
5. (a) Sakurai, T.; Iwasaki, J.; Watanabe, Y.; Kobayashi, K.; Bando, Y.; Nakamichi, Y. *Rikagaku Kenkyusho Hookoku* 1974, *50*, 75-91. (b) Kawano, S. *Koho, Computer Center of Kyushu University* 1980, *13*, 39-50.
6. All the calculations were performed on the FACOM M-200 computer in the Computer Center of Kyushu University.
7. Johnson, C. K. *ORTEP. Report ORNL-3794.* Oak Ridge National Laboratory, Tennessee, 1965.
8. Inagaki, S.; Hirabayashi, Y. *J. Am. Chem. Soc.* 1977, *99*, 7418-7423.
9. Kanematsu, K.; Harano, K.; Dantsuji, H. *Heterocycles* 1981, *16*, 1145-1150.
10. The orbital phase continuity requirements[8] are as follows: (a) the HOMO's of the neighboring systems should be out of phase; (b) the LUMO's of the neighboring systems should be in phase.
11. Pople, J. A.; Beveridge, D. L. *"Approximate Molecular Orbital Theory"*; McGraw-Hill: New York, 1970. The geometry of 6-aminofulvene was optimized by MINDO/3 MO method[12] with the Fletcher-Powell technique.
12. Dewar, M. J. S. *Q.C.P.E.* 1975, *11*, 279.

Received, 20th September, 1982