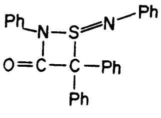
# The Molecular Structure of the Reaction Product from Sulfurdiimide and Diphenylketene

Noritake Yasuoka, Nobutami Kasai, Toru Minami, Yoshiki Ohshiro,
Toshio Agawa and Masao Kakudo

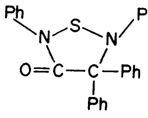
*Department of Applied Chemistry, Osaka University, Yamadakami, Suita, Osaka*

(Received March 7, 1970)

In a series of studies of the reaction of heterocumulenes with ketene, the reaction of sulfurdiimide with diphenylketene has been reported on by some of the present authors.[1] The structure of the reaction product was assumed to be 1-phenylimino-2,4,4-triphenyl-1,2-thiazetidine-3-one (I) on the basis of the IR, the mass spectra, and some chemical properties.



(I)



(II)

An X-ray structure investigation has, however, shown that the structure is an unexpected structure, 2,3,3,5-tetraphenyl-1,2,5-thiadiazolidine-4-one (II), instead of (I). After we completed our X-ray structure determination, Hoerhold and Eibisch have proposed a structure on the basis of some organochemical methods.[2] Their result agrees with ours.

The three-dimensional X-ray diffraction data were collected on a Rigaku on-line controlled single-crystal diffractometer with zirconium-filtered Mo*Kα* radiation. Crystal data: $C_{26}H_{20}ON_2S$, mp=167°C, F. W.=408.5, monoclinic, $P2_1/n$, $a=10.975$ (5), $b=15.315(6)$, $c=12.616(6)$ Å, $\beta=98.28(2)$°, $V=2098$ Å$^3$, $Z=4$, $D_c=1.29$ g·cm$^{-3}$.

The structure was established by the heavy-atom method. The refinement was carried out by the block-diagonal least-squares procedure ($R=0.089$ for 1483 non-zero reflections).

Table 1.* Selected bond lengths and angles

| | | | |
|---|---|---|---|
| S-N(1) | 1.726 (0.011) Å | N(1)-S-N(2) | 92.4 (0.5)° |
| S-N(2) | 1.701 (0.009) | S-N(1)-C(1) | 112.1 (0.8) |
| C(1)-N(1) | 1.360 (0.016) | S-N(2)-C(2) | 104.6 (0.6) |
| C(2)-N(2) | 1.509 (0.014) | N (1)-C(1)-C(2) | 109.7 (1.0) |
| C(1)-C(2) | 1.564 (0.016) | N (2)-C(2)-C(1) | 104.6 (0.8) |
| C(1)-O | 1.211 (0.015) | S-N(1)-C(31) | 120.9 (0.8) |
| C(2)-C(11) | 1.523 (0.015) | C(1)-N(1)-C(31) | 127.0 (1.0) |
| C(2)-C(21) | 1.522 (0.015) | S-N(2)-C(41) | 114.4 (0.7) |
| N(1)-C(31) | 1.410 (0.015) | C(2)-N(2)-C(41) | 117.6 (0.8) |
| N(2)-C(41) | 1.473 (0.014) | | |

* In Table 1, C(31) and C(41) are atoms of benzene rings attached to N(1) and N(2) respectively. Similarly, C(11) and C(21) are those bonded to C(2).

The molecular is shown in the Fig. 1.

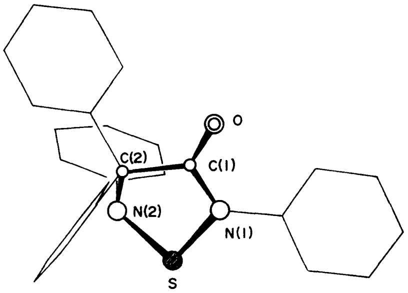


Fig. 1. The molecular structure.

Two S–N bond distances, S-N(1) and S–N(2), (Table 1) are comparable to, or somewhat shorter than, the sum of the covalent radii (1.74 Å) and are assumed to be normal single bonds. From this fact and from the N(1)–S–N(2) bond angle, the S atom seems to be bonded to nitrogen atoms using two mutually orthogonal 3*p* orbitals. This compound is probably the first one in which such a bonding scheme has been observed.

It is interesting to note that the C(1)–N(1) bond is significantly shorter than the C(2)–N(2) bond. The C–N bond distance in the =N–C=O group is usually shorter than the normal single bond distance: for example, the value of 1.326 Å has been reported in acetanilide.[3] The N(1) atom lies almost on the plane defined by C(1), S, and C(31). In contrast to this, the N(2) lies 0.4 Å above the plane defined by C(2), S, and C(41). These differences in the bonding states of N(1) and N(2) are interesting in connection with the reactivity of this compound.

---

[1] T. Minami, O. Aoki, H. Miki, Y. Ohshiro and T. Agawa, *Tetrahedron Lett.*, **1969**, 447.

[2] H. H. Hoerhold and H. Eibisch, *Tetrahedron*, **25**, 4277 (1969).

[3] C. J. Brown and D. E. C. Corbridge, *Acta Crystallogr.*, **7**, 711 (1954).