

Molecular Structures of the Reduced 1,2,4-Triazine Derivative and Its Reaction Product with Electron-deficient Acetylene

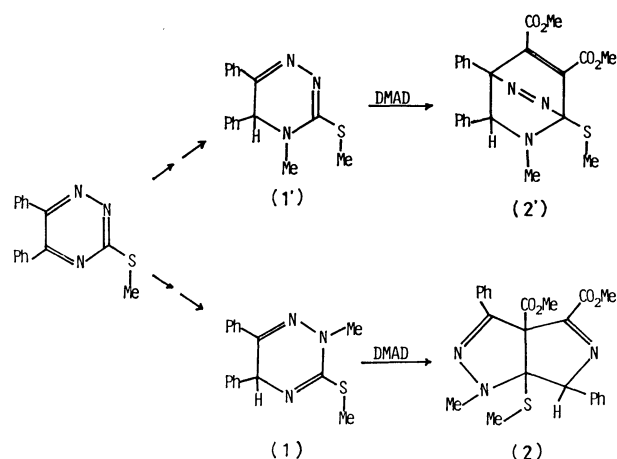
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The molecular structures of 3-methylthio-2-methyl-5,6-diphenyl-2,5-dihydro-1,2,4-triazine (**1**) and its reaction product with dimethyl acetylenedicarboxylate, 5,6-bis(methoxycarbonyl)-2-methyl-1-methylthio-4,8-diphenyl-2,3,7-triazabicyclo[3.3.0]octa-3,6-diene (**2**), were determined by the X-ray method. The former belongs to the triclinic system $P\bar{1}$, with $Z=2$, $a=10.776(2)$, $b=10.203(2)$, $c=8.556(1)$ Å, $\alpha=105.44(2)$, $\beta=104.94(2)$, and $\gamma=60.31(2)^\circ$; the latter belongs to the orthorhombic system $Pca2_1$, with $Z=4$, $a=18.166(2)$, $b=7.444(2)$, and $c=16.080(2)$ Å. Both structures were solved by the direct method. The final R -factors are 0.075 for **1** and 0.048 for **2**. In Compound **1** the dihydrotriazine ring is in the boat form, while in Compound **2** both of the *cis*-fused five-membered rings are in the envelope form.

Unlike the well-studied oxidation reaction of 1,2,4-triazines, the reduction chemistry here is still not completely established. Paudler has suggested that 1,2,4-triazines undergo covalent hydration across the N(4)–C(5) bond,¹⁾ and Neuenhoffer has shown that they can act as dienes in the Diels-Alder reaction.²⁾ Therefore, the reduced compound of 3-methylthio-5,6-diphenyl-1,2,4-triazine with NaBH₄ would be methylated by methyl iodide to give **1'**, and the reaction of **1'** with dimethyl acetylenedicarboxylate (DMAD) would produce **2'**.³⁾



The present X-ray study was attempted in order to confirm the structures of those reaction products; it showed that they were **1** and **2** instead of **1'** and **2'**. The detailed descriptions of their structures will be given in this paper.

Experimental

Compound 1. The intensity data were collected on a Rigaku automated four-circle diffractometer at the Ultra High Intensity X-Ray Diffraction Laboratory of this university, using graphite-monochromatized Mo $K\alpha$ radiation. The ω - 2θ scan method with the scan speed of $8^\circ/\text{min}$ (2θ) was applied. A total of 2749 independent reflections up to 50° (2θ) were collected. The crystal used for the experiment had the dimensions of $0.3 \times 0.3 \times 0.2$ mm³.

Crystal Data: C₁₇H₁₇N₃S, $P\bar{1}$, $a=10.776(2)$, $b=10.203(2)$, $c=8.556(1)$ Å, $\alpha=105.44(2)$, $\beta=104.94(2)$, $\gamma=60.31(2)^\circ$, $V=778.76$ Å³, $Z=2$, $d_{\text{obsd}}=1.25$, $d_{\text{caled}}=1.260$ g cm⁻³,

$\mu(\text{Mo } K\alpha)=2.042$ cm⁻¹.

Compound 2. The intensity data were collected on a Hilger & Watts four-circle diffractometer at the Faculty of Science, Nagoya University, using Ni-filtered Cu $K\alpha$ radiation. The ω -scan method for $2\theta \leq 80^\circ$ and the ω - 2θ scan for $80^\circ \leq 2\theta \leq 114^\circ$ were applied, and 1528 independent reflections were obtained. The crystal dimensions were $0.4 \times 0.2 \times 0.4$ mm³.

Crystal Data: C₂₃H₂₃N₃O₄S, $Pca2_1$, $a=18.166(2)$, $b=7.444(2)$, $c=16.080(2)$ Å, $V=2174.46$ Å³, $Z=4$, $d_{\text{obsd}}=1.33$, $d_{\text{caled}}=1.336$ g cm⁻³, $\mu(\text{Cu } K\alpha)=15.71$ cm⁻¹.

Structure Determination and Refinement

The intensity data of both compounds were corrected for Lorentz and polarization effects, but not for absorption. Both structures were solved by the *MULTAN* program⁴⁾ and refined by the block-diagonal least-squares procedure with the *HBLS V* program.⁵⁾ All the hydrogen atoms were located on the difference Fourier map. In the refinement, the function minimized was $\sum w(|F_o| - |F_c|)^2$, with $w = (\sigma^2(F) + a|F_o| + b|F_o|^2)^{-1}$ for $|F_o| > 0$ and $w = c$ for $|F_o| = 0$, where $\sigma(F)$ is the standard deviation based on the counting statistics. The thermal parameters of three hydrogen atoms in the *S*-methyl group of **1** were fixed at 8.0 Å² throughout the refinement, but all the others were subjected to the refinement. The final R -factors were 0.075 for **1** and 0.048 for **2**. The atomic scattering factors were taken from the International Tables for X-Ray Crystallography.⁶⁾ All the calculations were carried out on a FACOM 230-75 computer at Nagoya University. The final atomic parameters are given in Tables 1 and 2.⁷⁾

Results and Discussion

Compound 1. The bond lengths and angles are shown in Fig. 1, together with the atom-numbering system. The estimated standard deviations are 0.003–0.005 Å for the bond lengths and 0.2–0.4° for the angles. The equations of the best planes are listed in Table 3. A stereoscopic view of the molecule, as drawn by the *ORTEP II* program,⁸⁾ is shown in Fig. 2.

The dihydrotriazine ring is folded at N(2) and C(2) to take a boat form, with the dihedral angle between Plane (I) (N(2), N(1), C(3), C(2), and C(12)) and Plane (II) (N(2), C(1), N(3), C(2), and S) of 146.5° . The phenyl ring bonded to C(2) is in an

The N(1)–C(3) and C(1)–N(3) double-bond lengths are 1.286 Å and 1.269 Å respectively. The N(3)–C(2) bond length is compatible with the single-bond distance, while the N(2)–C(1) bond length of 1.383 Å is significantly shorter and the N(1)–N(2) of 1.394 Å is shorter than the single-bond distance of 1.44 Å.⁹⁾ These shortenings and the coplanarity of the C(3)-phenyl group and Plane (I) are due to the delocalization of the π -electrons and lone-pair electrons of N(2). The sp^2 character of the N(2) atom is further evidenced by the planar arrangement of the bonded atoms, as is indicated by the sum of the bond angles, 351.6°. The C(1)–S bond, 1.769 Å, is shorter than the normal

TABLE 2. ATOMIC PARAMETERS AND ESTIMATED STANDARD DEVIATIONS OF (2)

(a) Non-hydrogen atoms ($\times 10^4$ for the positional parameters and $\times 10^2$ for the thermal parameters).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$B_{eq}/\text{\AA}^2$	Atom	<i>x</i>	<i>y</i>	<i>z</i>	$B_{eq}/\text{\AA}^2$
S	3460(1)	6042(1)	4590(1)	374	C(9)	2932(2)	1909(7)	1833(3)	399
O(1)	3913(1)	2685(4)	3520(2)	401	C(10)	2633(3)	401(7)	1450(4)	453
O(2)	4654(1)	3852(4)	2544(3)	405	C(11)	1896(3)	265(9)	1303(4)	552
O(3)	3573(2)	5346(9)	901(3)	778	C(12)	1440(3)	1686(10)	1545(4)	520
O(4)	4649(2)	6727(5)	993(2)	468	C(13)	1724(2)	3171(8)	1939(4)	431
N(1)	2299(2)	6055(5)	2839(3)	382	C(14)	2233(3)	8586(9)	3767(5)	593
N(2)	2668(2)	7376(5)	3257(3)	401	C(15)	2709(3)	4449(8)	4669(4)	531
N(3)	4113(2)	8199(5)	2446(2)	339	C(16)	4669(2)	8306(6)	3838(3)	337
C(1)	3554(2)	5392(6)	2798(3)	272	C(17)	4691(3)	9115(7)	4620(4)	435
C(2)	2752(2)	4885(6)	2554(3)	279	C(18)	5334(3)	9098(7)	5081(4)	482
C(3)	3403(2)	6762(6)	3508(3)	309	C(19)	5973(3)	8308(8)	4762(3)	492
C(4)	3959(2)	8315(6)	3339(3)	304	C(20)	5957(2)	7576(9)	3983(5)	520
C(5)	3916(2)	6661(6)	2178(3)	279	C(21)	5308(2)	7547(7)	3509(3)	384
C(6)	4045(2)	3812(5)	3014(3)	274	C(22)	4028(2)	6170(6)	1278(3)	333
C(7)	5181(2)	2400(8)	2676(5)	528	C(23)	4801(3)	6222(8)	123(4)	603
C(8)	2484(3)	3300(6)	2089(3)	331					

(b) Hydrogen atoms ($\times 10^3$ for positional parameters and $\times 10$ for thermal ones).

Atom	Bonded to	<i>x</i>	<i>y</i>	<i>z</i>	$B/\text{\AA}^2$	Atom	Bonded to	<i>x</i>	<i>y</i>	<i>z</i>	$B/\text{\AA}^2$
H(1)	C(4)	368(2)	940(6)	348(4)	15(10)	H(13)	C(15)	268(4)	395(8)	530(5)	48(18)
H(2)	C(7)	564(4)	260(11)	233(6)	61(20)	H(14)	C(15)	279(3)	337(10)	425(5)	46(17)
H(3)	C(7)	495(3)	112(11)	253(6)	58(21)	H(15)	C(15)	221(3)	516(7)	453(5)	34(14)
H(4)	C(7)	531(3)	233(11)	329(7)	60(21)	H(16)	C(17)	418(3)	980(7)	487(4)	34(14)
H(5)	C(9)	349(2)	179(8)	196(4)	24(12)	H(17)	C(18)	529(3)	969(7)	566(4)	30(13)
H(6)	C(10)	300(3)	-77(8)	129(5)	36(15)	H(18)	C(19)	646(2)	838(7)	513(4)	25(12)
H(7)	C(11)	165(3)	-86(9)	104(5)	44(16)	H(19)	C(20)	641(2)	704(9)	371(4)	32(15)
H(8)	C(12)	86(3)	155(8)	142(4)	32(14)	H(20)	C(21)	531(2)	690(9)	290(4)	33(14)
H(9)	C(13)	137(3)	427(8)	210(5)	37(15)	H(21)	C(23)	533(2)	673(8)	8(5)	32(13)
H(10)	C(14)	175(3)	885(8)	347(4)	36(15)	H(22)	C(23)	439(3)	677(10)	-21(5)	50(17)
H(11)	C(14)	253(5)	955(7)	388(6)	57(19)	H(23)	C(23)	477(3)	478(7)	8(4)	33(14)
H(12)	C(14)	209(3)	802(10)	439(5)	46(17)						

TABLE 3. BEST PLANES OF (1)

(a) Equations ($X = ax + 0.4953by - 0.2578cz$, $Y = 0.8687by - 0.1595cz$, $Z = 0.9529cz$)

Plane (I): N(1), N(2), C(2), C(3), C(12)

0.5504X + 0.5556Y + 0.6232Z - 7.8915 = 0

Plane (II): S, N(2), N(3), C(1), C(2)

0.0230X + 0.7858Y + 0.6180Z - 3.6336 = 0

Plane (III): C(2), C(6), C(7), C(8), C(9), C(10), C(11)

0.7898X + 0.1161Y - 0.6023Z - 7.0700 = 0

Plane (IV): C(3), C(12), C(13), C(14), C(15), C(16), C(17)

0.5904X + 0.2788Y + 0.7574Z - 7.9449 = 0

(b) Dihedral angles ($\phi/^\circ$) between the planes

(I)-(II) 146.5 (I)-(IV) 162.2 (II)-(III) 105.2

(c) Displacements ($\delta/10^{-3}\text{\AA}$) of atoms from the planes

	(I)		(II)		(III)		(IV)
N(1)	-32	S	-28	C(2)	12	C(3)	14
N(2)	26	N(2)	11	C(6)	-10	C(12)	-9
C(2)	-6	N(3)	62	C(7)	-10	C(13)	-9
C(3)	-5	C(1)	8	C(8)	6	C(14)	1
C(12)	18	C(2)	-52	C(9)	5	C(15)	11
C(4) ^a	42	C(4) ^a	99	C(10)	1	C(16)	1
		C(5) ^a	-180	C(11)	-4	C(17)	-9

a) Atoms not included in the best-plane calculations.

C-S single-bond length of 1.81 Å, with a small amount of double-bond character. Consequently, the C(5) atom deviates from Plane (II) by only 0.18 Å, and a short contact, 2.893 Å, occurs between C(5) and N(3). Such a shortening is also observed in 2-(methylthio)benzothiazole,¹⁰ in which the C-S bond length is 1.77 Å.

Compound 2. The bond lengths and angles are shown in Fig. 3, together with the atom-numbering system. The estimated standard deviations are 0.006–0.012 Å for the bond lengths and 0.3–0.8° for the angles. The equations of the best planes are listed in Table 4. A stereoscopic view of the molecule is shown in Fig. 4.

The molecule consists of two central *cis*-fused five-membered rings and six peripheral side groups directly bonded to them. Each of the five-membered rings is in the envelope form. In one five-membered ring, C(1), C(2), N(1), and N(2) are coplanar (Plane (I)), including C(8) of the phenyl group, while in the other ring, C(1), C(5), N(3), and C(4) are coplanar (Plane (II)) with C(22) of the methoxycarbonyl group. These two planes form an angle of 107.7°. The C(3) atom is out of these planes by 0.47 Å and 0.39 Å respectively.

