

# The Crystal and Molecular Structure of BENTAZONE, $C_{10}H_{12}N_2O_3S$

Keun Il Park and Sung Il Cho

Department of Chemical Engineering, The University of Seoul, Seoul, 130-143, Korea

## BENTAZONE, $C_{10}H_{12}N_2O_3S$ 의 결정 및 분자구조

박권일 · 조성일

서울시립대학교 화학공학과

### Abstract

The molecular and crystal 3-dimensional structure of bentazone,  $C_{10}H_{12}N_2O_3S$ , has been determined from single crystal x-ray diffraction study. Crystal system is monoclinic:  $a=8.7817(9)$  Å,  $b=9.6059(9)$  Å,  $c=13.5747(9)$  Å,  $\beta=97.269(1)^\circ$ ,  $V=1136.1(6)$  Å<sup>3</sup>, space group:  $P2_1/c$ ,  $z=4$ . The molecular structure model was solved by direct method and refined by full matrix least squares. The final reliable factor, R, is 0.045 for 1396 independent reflections ( $F_o^2 > 4\sigma F_o^2$ ). A molecule has a staggered conformation with thiocarbazin ring and isopropyl functional group and the molecules linked by hydrogen bonds are cross stacked along the c-axis.

### 요 약

단결정 X-ray 회절법을 이용하여 Bentazone,  $C_{10}H_{12}N_2O_3S$ 의 결정 및 분자구조를 규명하였다. 공간군은  $P2_1/c$ 이며,  $a=9.7817(9)$  Å,  $b=9.6095(9)$  Å,  $c=13.5737(9)$  Å,  $\beta=97.269(1)^\circ$ ,  $Z=4$ ,  $V=1136.1(6)$  Å<sup>3</sup>. 직접법으로 개략적인 분자모델을 설정하고,  $1396(F_o^2 > 4\sigma F_o^2)$ 개의 독립 회절반점에 완전행렬 최소자승법으로 정밀화하여 최종신뢰도값,  $R=0.045$ 인 최종적인 분자모형을 구하였다. 분자내의 Thiocarbazin ring과 Isopropyl 작용기는 staggered conformation을 이루고 있으며, 수소결합에 의하여 결합된 분자들은 c-축 방향으로 교차 하면서 packing 되어 있다.

### 1. Introduction

Titled compound is bentazone,  $C_{10}H_{12}N_2O_3S$ , 3-isopropyl-1H-1,2,3-benzothiadiazin-4(3H)-one 2,2-dioxide that was synthesized by Zeidler *et al.*,<sup>1)</sup> and selective contact herbicide which is absorbed mainly by foliage, with very little translocation, but also absorbed by the roots, with translocation acropetally in the xylem. It is a contact herbicide controlling *Anthemis*, *Chamomilla* and *Matricaria spp.*, *Chrysanthemum segetum*, *Galium aparine*, *Lapsana Communis* and *Stellaria media* in winter and spring cereals. Other crops include peanuts, maize, peas, rice and

soybeans.<sup>2)</sup>

The characteristic structure of this compound shown in this paper, which is the first report to our certain knowledge, might offer an important information to elucidate the relationship between the crystal structure and biological activity.

### 2. Experimental

Single crystal of this compound was grown from saturated benzene-acetone solution. A transparent crystal of dimension  $0.20 \text{ mm} \times 0.25 \text{ mm} \times 0.40 \text{ mm}$  was mounted at the tip of a glass fiber. The accurate cell parameters were obtained

by least-squares refinement from 25 reflections in the ranges  $9^\circ < \theta < 14^\circ$  measured with graphite-monochromated Mo K $\alpha$  radiation on Enraf-Nonius CAD4 Diffractometer at  $293 \pm 3$ K.<sup>3)</sup>

X-ray intensity data were collected by  $\omega$ - $2\theta$  scan method ( $\omega$ -scan width =  $0.8 + 0.35 \tan \theta^\circ$ ) with  $2\theta = 49.94^\circ$  for the ranges  $-10 \leq h \leq 10$ ,  $0 \leq k \leq$

11,  $0 \leq l \leq 16$ . Three standard reflections monitored every 100 reflections showed maximum 3% deviation of intensity during the course of data collection. All reflections were corrected for L-p effect<sup>6)</sup> but not for absorption effect because of the small linear absorption coefficient (0.28/mm). Crystallographic details and data collection parameters are given in Table 1. The structure was solved by the application of direct methods using SHELXS-86<sup>4)</sup> and refined by full-matrix least-squares on  $F_o^2$  using SHELXL-93<sup>5)</sup> with anisotropic displacement factors for all 16 non-H atoms. The H atoms were located by geometrical

**Table 1. Crystal and crystal structure data of Bentazone, C<sub>10</sub>H<sub>12</sub>N<sub>2</sub>O<sub>3</sub>S**

- \* Molecular formula: C<sub>10</sub>H<sub>12</sub>N<sub>2</sub>O<sub>3</sub>S.
- \* Molecular weight: 240.3 g/mol.
- \* Density (calculated): 1.405 g/cm<sup>3</sup>.
- \* Crystal system: Monoclinic.
- \* Cell parameter: a = 8.7817(9) Å, b = 9.6059(9) Å, c = 13.5737(9) Å,  $\beta = 97.269(1)^\circ$ .
- \* Space group: P2<sub>1</sub>/c.
- \* Volume: 1136.1(6) Å<sup>3</sup>.
- \* Z: 4.
- \* Absorption coefficient: 0.28/mm.
- \* F(000): 504.0
- \* Crystal size.: 0.20 mm × 0.25 mm × 0.40 mm.
- \* Lattice parameter determination.: 25 reflections of  $9^\circ < \theta < 14^\circ$ .
- \* Diffractometer used: Enraf-Nonius CAD4 Diffractometer.
- \* Radiation: Graphite mono-chromated, Mo K $\alpha$  ( $\lambda = 0.7107$  Å).
- \* Data collection temperature.: 293 ± 3 K.
- \* Index range.:  $-10 \leq h \leq 10$ ,  $0 \leq k \leq 11$ ,  $0 \leq l \leq 16$ . (Maximum  $2\theta = 49.94^\circ$ ).
- \* Scan method:  $\omega$ - $2\theta$  ( $\omega$ -scan width =  $0.8 + 0.35 \tan \theta^\circ$ ).
- \* Data.: 1995 unique reflections are collected.
- \* Data conversion.: Correction of L-p effect is applied to intensity data.
- \* R (int): 0.018.
- \* R (sigma): 0.027.
- \* Structure: Direct method (SHELXS-86 program).
- \* Refine on  $F_o^2$ : Full-matrix least square method (SHELXL-93 program).
- \* Hydrogen atoms: Ideal geometric calculation.
- \* Final R factor: 0.045 for  $F_o^2 > 4\sigma F_o^2$  data (1396). 0.066 for  $F_o^2$  all data (1995).
- \* wR factor: 0.146 for  $F_o^2$  all data.  $(W = 1/[\sigma^2(F_o^2) + (0.0813P)^2 + 0.39P])$  Where  $P = [\text{Max}(F_o^2, 0) + 2F_c^2]/3$ .
- \* Total number of l.s. parameter.: 193.
- \*  $\Delta\rho_{\text{max}}$ : 0.45 e/zÅ<sup>3</sup>.
- \*  $\Delta\theta_{\text{min}}$ : -0.33 e/Å<sup>3</sup>.
- \* Atomic scattering factors from SHELXL93 (Sheldrick, 1993).

**Table 2. Fractional atomic coordinates(x104) and e-equivalent isotropic thermal parameters for non-hydrogen atoms of Bentazone,  $U_{\text{eq}} = 1/3 \sum_j \sum_k U_{jk} a_j^* a_k^* a_j a_k$  ( $\times 10^3$ ) Å<sup>2</sup>. The e.s.d.'s are in parentheses. Fractional atomic coordinates ( $\times 10^3$ ) and isotropic thermal parameters for hydrogen atoms of Bentazone**

atom	x	y	z	$U_{\text{eq}}$
1) S	2042 (1)	1273 (1)	4167 (1)	.0515 (3)
2) O1	1089 (3)	60 (3)	4019 (2)	.0749 (8)
3) O2	3499 (3)	1194 (3)	3851 (2)	.0850 (9)
4) O3	1105 (2)	2494 (2)	6658 (1)	.0526 (6)
5) N1	1185 (3)	2636 (3)	3694 (2)	.0524 (7)
6) N2	2209 (3)	1703 (3)	5364 (2)	.0415 (6)
7) C1	1043 (3)	2375 (3)	5763 (2)	.0368 (6)
8) C2	-216 (3)	2990 (3)	5079 (2)	.0381 (6)
9) C3	-1485 (4)	3529 (4)	5457 (3)	.0547 (8)
10) C4	-2640 (4)	4165 (4)	4844 (3)	.069 (1)
11) C5	-2530 (4)	4294 (4)	3840 (3)	.0656 (9)
12) C6	-1282 (4)	3777 (3)	3448 (2)	.0532 (8)
13) C7	-132 (3)	3120 (3)	4067 (2)	.0410 (6)
14) C8	3516 (4)	991 (3)	6002 (2)	.0501 (8)
15) C9	2970 (4)	-122 (4)	6648 (3)	.075 (1)
16) C10	4564 (4)	2052 (4)	6541 (3)	.075 (1)
atom	x	y	z	U
17) H1	127 (4)	269 (3)	317 (3)	.05 (9)
18) H3	-156 (4)	342 (3)	612 (3)	.05 (9)
19) H4	-347 (5)	452 (4)	510 (3)	.09 (1)
20) H5	-333 (4)	474 (4)	340 (3)	.08 (1)
21) H6	-116 (4)	388 (4)	280 (3)	.06 (9)
22) H8	405 (4)	56 (4)	553 (3)	.07 (1)
23) H9A	384 (4)	-59 (2)	700 (2)	.05 (1)
24) H9B	235 (3)	-78 (2)	624 (3)	.05 (1)
25) H9C	237 (3)	29 (5)	711 (1)	.05 (1)
26) H10A	547 (2)	160 (6)	686 (2)	.05 (1)
27) H10B	405 (1)	251 (2)	704 (1)	.05 (1)
28) H10C	484 (3)	273 (2)	608 (4)	.05 (1)

**Table 3. Bond distances (Å), Bond angles (°), Selected torsion angles (°) and Least squares plane and Shift (Å) from the plane of Bentazone. The e.s.d.'s are in parentheses**

Bond distances (Å)											
S	-O1	1.434	(3)	C2	-C7	1.391	(4)				
S	-O2	1.402	(3)	C2	-C3	1.385	(4)				
S	-N1	1.604	(3)	C3	-C4	1.372	(5)				
S	-N2	1.665	(3)	C4	-C5	1.384	(6)				
N1	-C7	1.400	(4)	C5	-C6	1.371	(5)				
N2	-C1	1.378	(4)	C6	-C7	1.382	(4)				
N2	-C8	1.511	(4)	C8	-C9	1.499	(5)				
C1	-O3	1.215	(3)	C8	-C10	1.500	(5)				
C1	-C2	1.474	(4)								
Bond angles (°)											
O2	-S	-O1	116.9	(2)	C5	-C4	-C3	119.9	(3)		
N1	-S	-O1	111.8	(2)	C6	-C5	-C4	120.6	(3)		
N1	-S	-O2	108.8	(2)	C6	-C7	-N1	120.4	(3)		
N2	-S	-O1	108.5	(2)	C6	-C7	-C2	121.0	(3)		
N2	-S	-O2	109.9	(2)	C7	-N1	-S	119.6	(2)		
N2	-S	-N1	99.6	(1)	C7	-C2	-C1	121.9	(2)		
N2	-C1	-O3	119.7	(2)	C7	-C2	-C3	118.6	(3)		
C1	-N2	-S	121.5	(2)	C7	-C6	-C5	119.2	(3)		
C2	-C1	-O3	121.8	(2)	C8	-N2	-S	114.4	(2)		
C2	-C1	-N2	118.4	(2)	C8	-N2	-C1	122.3	(2)		
C2	-C7	-N1	118.5	(2)	C9	-C8	-N2	112.5	(3)		
C3	-C2	-C1	119.4	(3)	C10	-C8	-N2	110.3	(3)		
C4	-C3	-C2	120.7	(4)	C10	-C8	-C9	114.9	(3)		
Torsion angles (°)											
O1	-S	-N1	-C7	63.8	(3)	C1	-N2	-C8	-C9	58.4	(3)
O2	-S	-N1	-C7	-165.7	(3)	C1	-N2	-C8	-C10	-71.2	(3)
N2	-S	-N1	-C7	-50.7	(2)	O3	-C1	-C2	-C3	-10.3	(3)
O1	-S	-N2	-C1	-77.2	(3)	O3	-C1	-C2	-C7	165.9	(4)
O1	-S	-N2	-C8	88.0	(2)	N2	-C1	-C2	-C3	172.7	(4)
O2	-S	-N2	-C1	153.9	(3)	N2	-C1	-C2	-C7	-11.1	(3)
O2	-S	-N2	-C8	-41.0	(2)	C1	-C2	-C3	-C4	177.0	(5)
N1	-S	-N2	-C1	39.7	(2)	C7	-C2	-C3	-C4	.6	(3)
N1	-S	-N2	-C8	-155.1	(2)	C1	-C2	-C7	-N1	.7	(3)
S	-N1	-C7	-C2	35.3	(2)	C1	-C2	-C7	-C6	-176.0	(4)
S	-N1	-C7	-C6	-148.1	(4)	C3	-C2	-C7	-N1	176.9	(4)
S	-N2	-C1	-O3	169.3	(4)	C3	-C2	-C7	-C6	(4)	
S	-N2	-C1	-C2	-13.5	(2)	C2	-C3	-C4	-C5	-1.1	(3)
C8	-N2	-C1	-O3	5.3	(3)	C3	-C4	-C5	-C6	.7	(4)
C8	-N2	-C1	-C2	-177.5	(4)	C4	-C5	-C6	-C7	.2	(3)
S	-N2	-C8	-C9	-106.6	(3)	C5	-C6	-C7	-N1	-177.2	(4)
S	-N2	-C8	-C10	123.7	(3)	C5	-C6	-C7	-C2	-.7	(3)
Least squares plane											
0.403 x+0.903 y+0.152 z=3.205											
C1	0.001	(3)									
C2	-0.003	(3)									
C7	0.003	(3)									
N1	-0.001	(3)									
out of plane											
S	-0.817	(1)									
N2	-0.223	(3)									

calculations and refined isotropically. The final R value was 0.045 with 1396 ( $F_o^2 > 4\sigma(F_o^2)$ ) observed reflections and 193 variables. The final positions and equivalent isotropic thermal parameters for non-hydrogen atoms and isotropic for hydrogen atoms are listed in Table 2. In The Table 3, crystal geometric properties are listed.

### 3. Result and discussion

The ORTEX drawing<sup>7)</sup> of the title compound with atomic numbering is shown in Fig. 1. Fig. 2 and 3 are crystal packing viewed to b and c-axis, respectively.

As shown in Table 3, S-N1 and S-N2 bond lengths of thiocarbazine ring (see Fig. 1) are each 1.604(3), 1.665(3) Å with bond length difference 0.061 Å, which may be due to the electron repulsion in isopropyl functional group. S-O1 and S-O2 bond distances are similar to those of other compound (3-Methyl-4h-pyridol[2,3-e]-1,2,4-thiadiazin 1,1-dioxide,  $C_7H_7N_3O_2S$ ).<sup>8)</sup> The bond lengths and bond angles of other benzene ring and isopropyl group are normal.

Thiocarbazine ring has a distorted planar conformation (N2:-0.223(3), S:-0.817(1) Å shift from C1, C2, C7, N1 least square plane) which may be attributed to the lone pair effects of N1

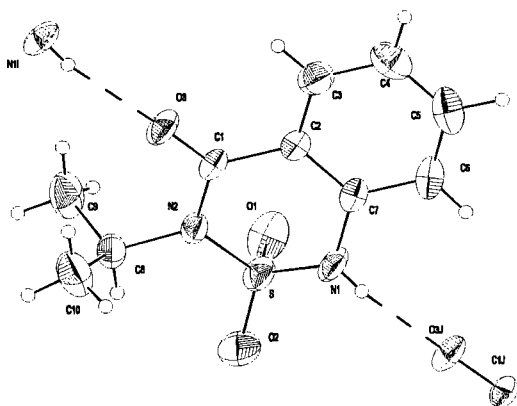


Fig. 1. ORTEX view of title compound with numbering scheme and displacement ellipsoids drawn at the 50% probability level. H atoms are drawn as small circles of arbitrary radii.

and N2, and N1-S-N2 bonding strain. This conformation is specified by torsion angles (C2-C7-N1-S:-35.3(2)°, C2-C1-N2-S:13.5(2)°, C7-C2-C1-N2:11.1(3)°). The torsion angles C1-N2-C8-C10:58.4(3)° and C1-N2-C8-C9:-71.2(3)° between thiocarbazine ring and isopropyl functional group indicate a staggered conformation of the molecule.

The unit cell packing diagrams of molecules (Fig. 2 and 3) show that the molecules linked by hydrogen bonds are cross stacked by hy-

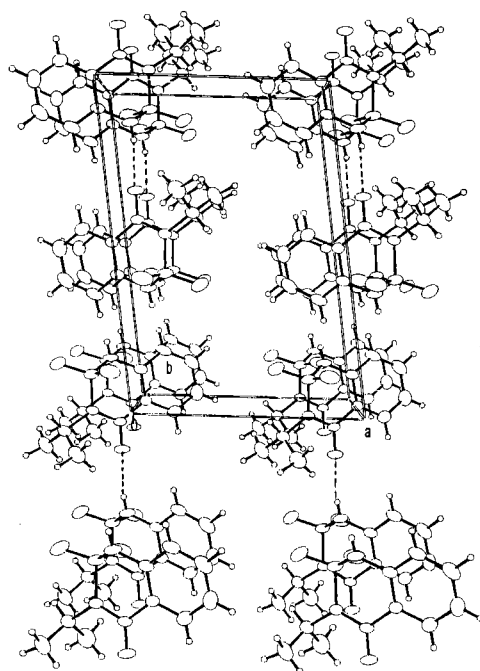


Fig. 2. Unit cell packing of bentazone, viewing along to the b axis, displacement ellipsoid with 30% (The dotted line is hydrogen bonding).

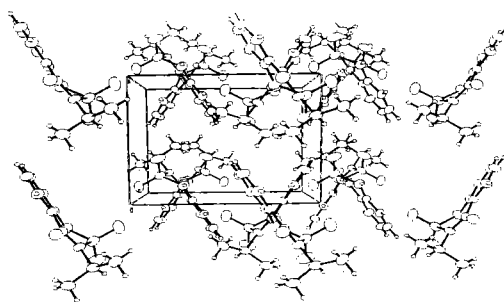


Fig. 3. Unit cell packing of this compound viewed to c-axis with 30% probability.

drogen bond along to the c-axis( $O3 \cdots H1^i: 2.046(3)$  Å,  $H1^i-N1^i: 0.727(4)$  Å,  $O3 \cdots N1^i: 2.759(3)$  Å,  $\angle O3 \cdots H1^i-N1^i: 166.5(5)^\circ$ , symmetry code  $i: X, 0.5-Y, 0.5+Z$ ).

### References

- 1) Zeidler, *et al.*, *U.S. pat.* 3,708,277 (1973).
- 2) Fisher, A., *Proc. Br. Weed Control Conf.*, 9th, 2,1042, (1968).
- 3) Enraf-Nonius, *CAD4 software, version 5.0. Enraf Nonius, Delft, The Netherlands* (1989).
- 4) Sheldrick, G. M., *SHELXS-86. Program for the Solution of Crystal Structures from dif-*  
*fraction Data*, Univ. of Göttingen, Germany (1986).
- 5) Sheldrick, G. M., *SHELXL-93. Program for the Refinement of Crystal Structure*, Univ. of Göttingen, Germany (1993).
- 6) Hall, S. R., Flack, H. D. and Stewart, J. M., *Xtal 3.2, Reference Manual*. Univs of Western Australia, Australia and Maryland, USA. (1992).
- 7) McArdle, P., *ORTEX, Ver 4.0*, UCG Crystallography Centre, Chemistry Department, University College Galloway, Ireland (1997).
- 8) Dupont, L., Pirotte, B., *et al.*, *Acta. Cryst.(C 51)*, 2064-2066. (1995).