# p-Dimethylaminobenzaldehyde 4-(p-Ethoxyphenyl) Thiosemicarbazone 構造의 精密化

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# Refinement of the Structure of p-Dimethylaminobenzaldehyde 4-(p-Ethoxyphenyl) Thiosemicarbazone

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## 요 약

p-dimethylaminobenzaldehyde 4−(p-ethoxyphen-yl)−thiosemicarbazone, $C_{18}H_{22}N_4OS$의, 단위포상수는 단사정계로 a=11.802(2), b=31.962(2), c=9.829(2)Å, $\beta$=100.12(1)°, V=3649.8Å³이며 F(000)=1472, $M_r$=342.47. 공간군은 $P2_1 / c$, Z=8, $D_x$=1.246 Mg $\bar{m}^3$, $D_m$=1.17 Mg $\bar{m}^3$ $\mu$=0.15mm⁻¹이다. T=294 K에서 Mo $K\alpha$($\lambda$=0.71073 Å)을 사용하여 측정한 3718개의 회절강도[$F_o$>3$\sigma$($F_o$)]에 대한 최종 R 값은 0.0856이다.

비대칭단위내의 두개 분자간의 구조상의 큰 차이는 C(1)−N(1)−C(6)−C(7)의 비틀림각이 각각 58.8(8)°와 1(1)° 인것으로, 각 분자는 길이가 각각 2.613(7)과 2.566(7) Å인 N(1)−H(10)⋯N(3) 분자내 수소결합을 하고 있으며 각 분자는 N(2) 원자를 정점으로 하여 V-모양을 하고있다.

독립적인 두 분자는 두개의 분자간 수소결합 N(2)−H(11)⋯S'=3.367(5) Å과 N(2')−H(11')⋯S=3.421(4) Å으로 연결되어 이중체(dimer)를 형성하고 있으며 그 이중체들은 van der Waals력으로 결합되어 있다.

## Abstract

$C_{18}H_{22}N_4OS$, Mr=342.47, monoclinic, $P2_1/c$, a=11.802(2), b=31.962(2), c=9.829(2) Å, $\beta$=100.12(1)°, V=3649.8 Å³, F(000)=1472, Z=8, $D_x$=1.246 Mg m⁻³, $D_m$=1.17 Mg m⁻³, $\lambda$=0.71073 Å, $\mu$=0.150 mm⁻¹, T=294 K, final R=0.0856 for 3718 observed reflections [$F_o$>3$\sigma$$F_c$)] There are two molecules in an asymmetric unit and a major difference between these molecules is in the C(9)–N(1)–C(6)–C(7) torsion angles [58.8(8)° and 1(1)°]. Both molecules have intramolecular N(1)–H(10)⋯N(3) hydrogen bonds [2.613(7) and 2.566(7) Å] and assume V-shaped conformation with N(2) atoms at the vertices. The two independent molecules are linked by the two N(2)–H(11)⋯S' hydrogen bonds [3.367(5) Å and 3.421(4) Å] and the dimers are held together by van der Waals forces.

## INTRODUCTION

Many derivatives of thiosemicarbazones have anti-bacterial and antitumor activities depending on the p-

arent aldehyde or ketone[1-3], and crystallographic st-
udies on the structures of the compounds have provided
valuable information which led to a better unders-
tanding of the properties of the compounds[4]. In this
work, the crystal structure of p-dimethylaminobezal-
dehyde 4-(p-ethoxyphenyl)-thiosemicarbazone, prev-
iously determined from photographic data with limit-
ed accuracy[5], has been redetermined using intensity
data collected using of a CAD4 diffractometer in or-
der to obtain a more accurate structure.

## EXPERIMENT

Yellow prism-shaped single crystals grown by slow
evaporation from an acetone solution in a refrigerat-
or ; crystal size : $0.3 \times 0.4 \times 0.5$mm. $D_m$ by floatation
method in benzene / carbon tetrachloride. The quick
adjustment methods for crystal orientation[6-7] for pr-
eliminary X-ray work. Data collection on an Enra-
f-Nonius CAD4 diffractometer using graphite mono-
chromatized Mo $K\alpha$ radiation. 25 reflections ($10° <
\theta < 15°$) for refining unit-cell dimensions. $\omega$-$2\theta$ sca-
ns, $\omega$ scan angle ($0.8 + 0.34 \tan \theta$). 5465 reflections
collected, $2 < \theta < 50°$,$h$. $k$. $\pm l$, $h_{max} = 13$, $k_{max} = 33$,
$l_{max} = 10$. Three orientations (5 14 0, 2 16 -3 and 0
21 3) and one intensity (6 8 0) control reflections, in-
tensity variation within 1.2 and -1.6 %. LP correctio-
ns, no absorption correction. Structure solved by dir-
ect methods[8]. H atoms located by difference-Fourier
syntheses. Anisotropic full-matrix least-squares refin-
ements (on $F_o$), isotropic for H atoms. Final refinem-
ent cycles with 3718 data [$F_o > 3 \sigma (F_o)$]. Final R=
0.0856 ($\omega$R=0.0806) for 609 variables and weight
$\omega$=4.374/ [$\sigma^2(F_o) + 0.001320 F_o^2$]. Max. $\triangle / \sigma =$
0.476 for the z coordinate of H(22) and average
$\triangle / \sigma = 0.033$, $\triangle \rho_{max}./\triangle \rho_{min}.$=0.356/-0.379 e
$Å^{-3}$. The final atomic parameters in Table 1[*]. SHE-
LX76 system[9] used for all calculations. Computer u-
sed : MV-10000.

**Table 1.** Atomic coordinates($\times 10^4$) and equivalent isotropic tempe-
rature factors($\times 10^4$ $Å^2$) for non-H atoms with their
e.s.d.'s in parentheses.

| Atom | X | Y | Z | *$U_{eq}$ |
|------|------|------|------|------|
| S | 6919(1) | 1901(0) | 5387(2) | 569 |
| O | 3600(3) | 3490(1) | 5825(4) | 650 |
| N(1) | 7036(4) | 2594(1) | 3874(5) | 516 |
| N(2) | 8408(4) | 2108(1) | 3806(5) | 542 |
| N(3) | 8947(4) | 2383(1) | 3054(5) | 489 |
| N(4) | 12694(5) | 3229(2) | -135(6) | 833 |
| C(1) | 2111(7) | 3974(2) | 5805(8) | 919 |
| C(2) | 2677(6) | 3697(2) | 4920(7) | 728 |
| C(3) | 4389(5) | 3263(2) | 5261(6) | 514 |
| C(4) | 4295(5) | 3162(2) | 3885(6) | 618 |
| C(5) | 5159(5) | 2933(2) | 3435(6) | 575 |
| C(6) | 6110(5) | 2810(2) | 4349(6) | 443 |
| C(7) | 6203(5) | 2916(2) | 5727(6) | 534 |
| C(8) | 5348(6) | 3132(2) | 6178(6) | 582 |
| C(9) | 7468(5) | 2228(2) | 4315(5) | 450 |
| C(10) | 9831(5) | 2235(2) | 2630(6) | 558 |
| C(11) | 10550(5) | 2498(2) | 1899(5) | 456 |
| C(12) | 11458(6) | 2330(2) | 1381(7) | 710 |
| C(13) | 12167(6) | 2557(2) | 710(7) | 782 |
| C(14) | 12007(5) | 2985(2) | 534(6) | 557 |
| C(15) | 11082(5) | 3157(2) | 1050(6) | 593 |
| C(16) | 10381(5) | 2924(2) | 1716(6) | 529 |
| C(17) | 12619(7) | 3680(3) | -128(9) | 1043 |
| C(18) | 13659(7) | 3039(3) | -638(9) | 1115 |
| S' | 9324(2) | 1124(1) | 3429(2) | 699 |
| O' | 11088(4) | -781(1) | 1362(5) | 793 |
| N(1') | 8612(4) | 355(2) | 3989(5) | 572 |
| N(2') | 7753(4) | 898(1) | 4854(5) | 603 |
| N(3') | 7103(4) | 604(1) | 5396(5) | 549 |
| N(4') | 3656(5) | -375(2) | 8645(6) | 752 |
| C(1') | 11594(8) | -1436(2) | 603(8) | 1070 |
| C(2') | 10888(6) | -1217(2) | 1478(7) | 733 |
| C(3') | 10461(6) | -509(2) | 2039(6) | 630 |
| C(4') | 9664(6) | -642(2) | 2803(6) | 616 |
| C(5') | 9065(5) | -333(2) | 3423(6) | 600 |
| C(6') | 9283(5) | 75(2) | 3323(6) | 484 |
| C(7') | 10123(6) | 203(2) | 2583(8) | 769 |
| C(8') | 10687(6) | -94(2) | 1944(8) | 790 |
| C(9') | 8543(5) | 765(2) | 4103(6) | 504 |
| C(10') | 6378(5) | 738(2) | 6122(6) | 562 |
| C(11') | 5669(5) | 443(2) | 6740(6) | 577 |
| C(12') | 4867(5) | 600(2) | 7505(6) | 628 |
| C(13') | 4209(5) | 329(2) | 8151(7) | 643 |
| C(14') | 4305(5) | -97(2) | 8034(6) | 601 |
| C(15') | 5108(6) | -257(2) | 7239(6) | 659 |
| C(16') | 5761(5) | 18(2) | 6617(6) | 609 |
| C(17') | 3889(7) | -819(3) | 8672(8) | 947 |
| C(18') | 2901(6) | -214(2) | 9572(7) | 826 |

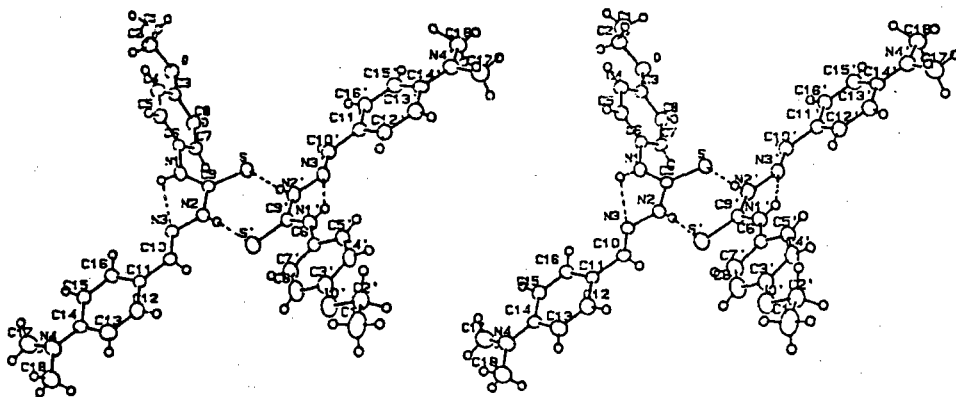*$U_{eq}$=(1/3)$[U_{22}+(1/\sin^2 \beta)(U_{11}+U_{33}+2U_{13}\cos \beta)]$.

**Fig. 1.** A steroview of the molecule with numbering scheme. Broken lines denote hydrogen bonds.

## DISCUSSION

An ORTEP[10] steroview of an asymmetric unit with the numbering scheme is shown in Figure 1. As s-

hown in Table 2, the bond lengths and angles of the unprimed (A) and primed (B) molecules are in good agreement with each other and they are comparable with other derivatives of thiosemicarbazone[4,11]. The

**Table 2.** Bond lengths(Å) and angles (°) for non–H atoms with e.s.d.'s in parentheses.

| | A | B | | A | B |
|---|---|---|---|---|---|
| S—C(9) | 1.692(6) | 1.678(6) | O—C(2) | 1.440(7) | 1.423(8) |
| O—C(3) | 1.372(8) | 1.386(8) | N(1)—C(6) | 1.438(7) | 1.428(8) |
| N(1)—C(9) | 1.318(7) | 1.320(8) | N(2)—N(3) | 1.374(7) | 1.378(7) |
| N(2)—C(9) | 1.350(7) | 1.355(8) | N(3)—C(10) | 1.281(8) | 1.280(8) |
| N(4)—C(14) | 1.373(9) | 1.380(9) | N(4)—C(17) | 1.44(1) | 1.44(1) |
| N(4)—C(18) | 1.45(1) | 1.48(1) | C(1)—C(2) | 1.48(1) | 1.48(1) |
| C(3)—C(4) | 1.376(9) | 1.37(1) | C(3)—C(8) | 1.382(8) | 1.357(9) |
| C(4)—C(5) | 1.390(9) | 1.413(9) | C(5)—C(6) | 1.366(8) | 1.336(8) |
| C(6)—C(7) | 1.383(8) | 1.39(9) | C(7)—C(8) | 1.360(9) | 1.37(1) |
| C(10)—C(11) | 1.469(8) | 1.461(9) | C(11)—C(12) | 1.374(9) | 1.400(9) |
| C(11)—C(16) | 1.385(8) | 1.370(9) | C(12)—C(13) | 1.36(1) | 1.39(1) |
| C(13)—C(14) | 1.39(1) | 1.37(1) | C(14)—C(15) | 1.396(9) | 1.425(9) |
| C(15)—C(16) | 1.361(9) | 1.382(9) | | | |
| | | | | | |
| S—C(9)—N(1) | 125.7(5) | 126.8(5) | S—C(9)—N(2) | 119.0(4) | 118.7(4) |
| O—C(2)—C(1) | 106.4(5) | 107.4(6) | O—C(3)—C(4) | 125.3(5) | 122.9(6) |
| O—C(3)—C(8) | 115.6(5) | 116.9(6) | N(1)—C(6)—C(5) | 120.6(5) | 116.6(5) |
| N(1)—C(6)—C(7) | 120.1(5) | 124.0(5) | N(1)—C(9)—N(2) | 115.2(5) | 114.6(5) |
| N(2)—N(3)—C(10) | 114.7(5) | 117.4(5) | N(3)—N(2)—C(9) | 120.4(4) | 118.7(5) |
| N(3)—C(10)—C(11) | 121.3(5) | 120.3(6) | N(4)—C(14)—C(13) | 122.8(6) | 122.9(6) |
| N(4)—C(14)—C(15) | 121.0(6) | 118.7(6) | C(2)—O—C(3) | 119.2(5) | 117.9(5) |
| C(3)—C(4)—C(5) | 119.9(5) | 117.6(6) | C(3)—C(8)—C(7) | 120.7(5) | 121.8(7) |
| C(4)—C(3)—C(8) | 119.1(6) | 120.2(6) | C(4)—C(5)—C(6) | 120.4(5) | 122.2(6) |
| C(5)—C(6)—C(7) | 119.2(5) | 119.3(6) | C(6)—N(1)—C(9) | 126.2(5) | 135.1(5) |
| C(6)—C(7)—C(8) | 120.6(5) | 118.9(6) | C(10)—C(11)—C(12) | 120.8(5) | 118.9(6) |
| C(10)—C(11)—C(16) | 123.0(5) | 122.8(6) | C(11)—C(12)—C(13) | 123.8(6) | 120.6(6) |
| C(11)—C(16)—C(15) | 120.9(6) | 122.2(6) | C(12)—C(11)—C(16) | 116.1(5) | 118.2(6) |
| C(12)—C(13)—C(14) | 120.3(6) | 121.2(6) | C(13)—C(14)—C(15) | 116.2(6) | 118.4(6) |
| C(14)—N(4)—C(17) | 121.5(6) | 121.5(6) | C(14)—N(4)—C(18) | 119.3(6) | 119.0(6) |
| C(14)—C(15)—C(16) | 122.6(6) | 119.3(6) | C(17)—N(4)—C(18) | 118.1(7) | 117.8(6) |

S–C(9) bond length of 1.692(6) Å in (A) and 1.678(6) Å in (B) are similar to 1.69 Å in salicyaldehyde–4–morpholinothiosemicarbazone[12] and 1.7 Å in p–amionobenzaldehyde cyclohexythiosemicarbazone[13]. The N(3)–C(10) bond lengths of 1.281(8) Å in (A) and 1.280(8) Å in (B) show clearly double bond character. Except these double bonds and benzene rings all the other bonds are normal single bonds.

Most interesting shape these molecules have is that the thiosemicarbazone groups are bent toward opposite directions with the similar torsion angles N(3)–N(2)–C(9)–N(1)=9.2(7)° in (A) and –0.9(7)° in (B), and N(3)–N(2)–C(9)–S=–173.0(4)° in (A) and 179.3(4)° in (B). Thus each molecule has an intramolecular N(1)·· N(3) hydrogen bond with the distances 2.613(7) and 2.566(7) Å (Table 3), and has V–like shape with N(2) atom at the vertex as shown in Fig. 1, where the distance of N(2)–N(2') is 4.110(5) Å.

All of the four benzene rings have good planarity with maximum deviation 0.016(5) Å. Two molecules in an asymmetric unit have different conformation. The C(9)–N(1)–C(6)–C(7) torsion angles showing the orientation of the p–ethoxyphenyl group with respect to the thiosemicarbazone plane are 58.8(8)° and 1(1)° in molecules (A) and (B), and the N(3)–C(10)–C(11)–C(16) torsion angles showing the orientation of the p–dimethylaminophenyl groups are 5.2(9)° in (A) and 2.0(9)° in (B) respectively. The whole molecule (B) is nearly planar with maximum deviation of 0.223(9) Å. The dihedral angle between two benzene rings in (B) is 2.7(2)° while it is 103.4(2)° in (A).

Two independent molecules are held together by two intermolecular hydrogen bonds, N(2)–H(11)···S' [3.367(5) Å] and N(2')–H(11')···S [3.421(4) Å]. These N···S hydrogen bond distances are similar to those of 3.48(2) Å and 3.49(2) Å in morpholinothiosemicarbzide[14].

Molecular packing is shown in Figure 2. There are no close contacts less than 3.35 Å as shown in Table 3 and the hydrogen–bonded molecular dimers are held together by normal van der Waals interactions.
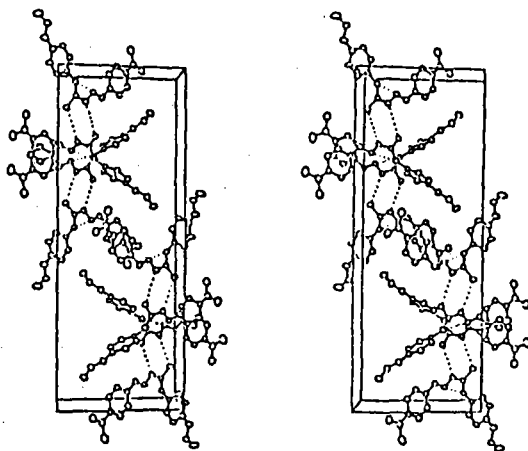


**Fig. 2.** A steroview of a unit cell packing. Origin, lower left ; a–axis, horizontal ; b–axis, vertical.

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**Table 3.** Dimensions of hydrogen bonds, and intermolecular contacts less than 3.4 (Å).

| D–H···A | D–H(Å) | H···A(Å) | D···A(Å) | ∠ D–A(°) |
|---|---|---|---|---|
| N(1)—H(10)···N(3) | 0.87(5) | 2.31(5) | 2.613(7) | 101(3) |
| N(1')—H(10')···N(3') | 0.81(5) | 2.08(5) | 2.566(7) | 118(4) |
| N(2')—H(11)···S' | 0.71(5) | 2.70(5) | 3.367(5) | 158(5) |
| N(2')—H(11')···S | 0.81(5) | 2.63(5) | 3.421(4) | 166(4) |
| | | | | |
| N(2)········N(16)ª | | | 3.358(7) | |
| N(1')········N(4')ᵇ | | | 3.382(7) | |
| N(1')········C(5')ᶜ | | | 3.397(7) | |
| N(16')········C(16')ᵈ | | | 3.367(8) | |

Symmetry code:ªx, 0.5—y, 0.5+z ᵇ1—x, —y, 1—z ᶜz—x, —y, 1—z ᵈ1—x, —y, 1—z

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