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Synthesis and Structure of 3,4-(Methylenedioxy)benzaldehyde 2,4-Dinitrobenzalhydrazone

by J.-L. Wang[1] and Y.-J. Jia[1,2]

[1]*College of Chemistry and Life Science, Tianjin Normal University, Tianjin, 300074, P. R. China*
[2]*Tianjin High School, Tianjin, 300191, P. R. China*

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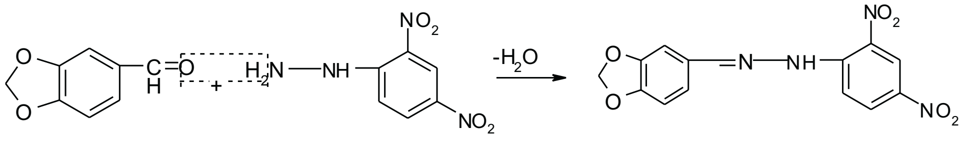
Various benzoylhydrazones, derived from arylaldehydes, phenylalkyl aldehydes and phenylalkyl ketones, as well as some related compounds, were evaluated for anticonvulsant activity [1]. Most of these compounds displayed anticonvulsant activity and regulate plant-growing activities [2].

Ethanol solution of 20 mL (0.01 mol) of 2,4-dinitrobenzalhydrazine was added dropwise into ethanol solution of 20 mL (0.01 mol) of 3,4-(methylenedioxy)benzaldehyde. At 70~80°C stirring the solution about 2 h, when 1 mL of hydrochloric acid solution was added into the mixture solution, the dark-yellow precipitation was separated out. Keeping the temperature at 70~80°C and stirring for about 3~4 h, the color of the solution changed to orange when 20 mL of water was added. Crude product was isolated when the solvents had been evaporated. The product – 3,4-(methylenedioxy)benzaldehyde 2,4-dinitrobenzalhydrazone ($C_{14}H_{10}N_4O_6$, M = 330.26) was filtered and washed using anhydrous ether solution for several times and dried in the vacuum desiccator over $CaCl_2$. Reaction equation is shown in Scheme 1.



Scheme 1. Reaction equation.

IR and UV data for the compounds are listed in Table 1. 3320 and 3420 cm^{-1} of the 2,4-dinitrobenzalhydrazine was changed to 3250 cm^{-1} (broad band) in the title compound, which indicates that N–H---O intra-hydrogen bond is formed in the title compound. 1670 cm^{-1} of $\nu_{C=O}$ for the 3,4-(methylenedioxy)benzaldehyde and 1645 cm^{-1} of the 2,4-dinitrobenzalhydrazine was changed to 1600 cm^{-1} in the title compound. Especially, new C=N absorption frequency at 1580 cm^{-1} in the title compound indicates the existence imine nitrogen. 269.0 nm of 3,4-(methylenedioxy)benzaldehyde and 230.5 nm of 2,4-dinitrobenzalhydrazine was red shifted to 275.0 nm for the title compound. 311.0 nm of 3,4-(methylenedioxy)benzaldehyde and 310.0 nm of 2,4-dinitrobenzalhydrazine was red shifted to 354.0 nm for the title compound, indicating a much more electron-conjugated system existing in the title compound.

Table 1. IR (cm^{-1}) and UV (nm) data of the compounds.

Compound	IR (cm^{-1})			UV (nm)	
	ν_{NH}	$\nu_{C=O}$	$\nu_{C=N}$	π–π*	n–π*
3,4-methylenedioxybenzaldehyde		1670		209.0, 269.0	311.0
2,4-dinitrobenzalhydrazine	3330, 3420	1645		209.5, 230.5	310.0
3,4-methylenedioxybenzaldehyde 2,4-dinitrobenzalhydrazone	3250 (broad)	1600	1580	209.5, 275.0	354.0

Bright orange single crystals suitable for X-ray analysis were obtained by slowly evaporated ethanol solution. A single crystal with dimensions of 0.18×0.22×0.24 mm^3 was mounted on a Smart-1000 CCD diffractometer with a graphite monochromated MoKα radiation (λ = 0.071073 nm). A total of 6364 independent reflections were collected in the range of $2.00 \leq \theta \leq 26.39°$ using ω-ϕ scan technique at 293 K, of which 2724 reflections with $I \geq 2\sigma(I)$ were used for refinements. The intensities were corrected for LP factor and no empirical absorption was corrected. The crystal data are as follows: a = 0.66064(18), b = 1.4354(3), c = 1.4549(4) nm, β = 95.247(5)°, monoclinic, space group P2$_1$/c, Z = 4, F(000) = 680, D$_c$ = 1.597 g · cm^{-3}, μ = 0.128 mm^{-1}. The structure was solved by direct method with the SHELXS program [3]. All the non-hydrogen atoms were refined anisotropically, and all H atoms were fixed geometrically at calculated distances. The final refinement converges to R = 0.0494 on F^2, the goodness of fit is 1.027. The highest and lowest electron densities on the final difference Fourier map were 197 and –189 e · nm^{-3}. All work was performed on a PC computer with the WINGX package [4].

An ORTEP view of the title compound is shown in Fig 1. Selected bond lengths (nm) and bond angles (°) are listed in Table 2. The molecule exhibits a planar structure approximately; with two nitro groups slightly inclined to the plane with angles of 2.09 and 11.52°, respectively. This value is bigger than 1.5(4), 2.8(4)° for compound of benzaldehyde 2,4-dinitrophenylhydrazone [5] and 1.4(3), 0.8(3)° for compound of acetophenone 2,4-dinitrophenylhydrazone [6]. In the 3,4-methylenedioxybenzene plane composed of C11, C12, C13, C14, C15, C16, O17, O18 and C20 atoms, the largest deviation from this plane is 0.0111(3) nm for C20 atom. In this moiety 0.1427(3) and 0.1435(3) nm of O10–C20 and O20–C20 bond lengths are longer than 0.1382(3) and 0.1379(3) nm of adjacent O10–C24 and O20–C25 bond lengths, which is according to the case for compound of 3,4-(methylenedioxy)benzaldehyde semicarbazone [7]. The dihedral angles between the 3,4-methylenedioxybenzene plane with zone group and 2,4-dinitrobenzene plane with zone group are 6.04(3)° and 6.84(3)°, respectively. 0.1279(3) nm of N2–C10 bond length is near the values of 0.1280(5) nm of imine bond length in the compound of p-dimethylenedioxybenzaldehyde 2,4-dinitrobenzalhydrazone [8], which is between the classical single and double bond lengths, indicating a part electron delocalization over this moiety.

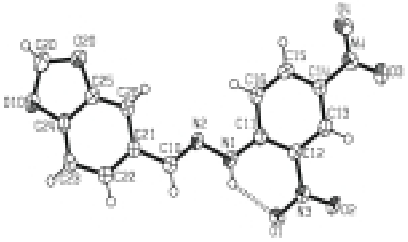


Figure 1. Perspective drawing of the molecule.

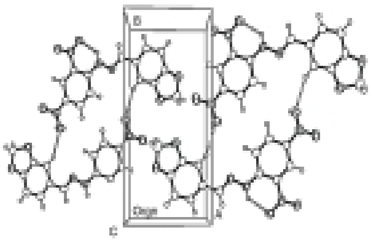


Figure 2. Crystal stack drawing along 001 plane.

0.3416(3) nm of the separation distance, between adjacent parallel phenyl rings, indicates an aromatic stacking interaction, according to the case of salicylaldehyde 4-nitrophenylhydrazone [9]. Stronger intra-molecular hydrogen bond of N1–H1---O1 0.2626(3) nm [128(2)°] is observed. In addition, weaker inter-molecular hydrogen bonds of N1–H1---O1_$1, C(26)–H(26)---O(4)_$2 and C(23)–H(23)---O(3)_$3 are 0.3370(3) nm [154(2)°], 0.3384(3) nm [157(2)°] and 0.3244(3) nm [133(2)°], respectively, hold together with adjacent molecules, forming 24-membered rings (see Fig. 2) [symmetry code: $1, $2 and $3 are 1-x, 1-y, 1-z; 1-x, -y, 1-z and x-2, 0.5-y, z-0.5, respectively]. These cases indicate the molecules stack in the crystal besides the van der Waals force and aromatic stacking interactions; the hydrogen forces are dependent on.

Table 2. Selected bond lengths (nm) and angles (°) for the title compound.

Bond	Length (nm)	Bond	Length (nm)	Bond	Length (nm)
O1–N3	0.1237(3)	N1–N2	0.1388(3)	C15–C16	0.1356(4)
O2–N3	0.1229(2)	N2–C10	0.1279(3)	C21–C22	0.1388(3)
O3–N4	0.1221(3)	N3–C12	0.1440(3)	C21–C26	0.1402(3)
O4–N4	0.1233(3)	N4–C14	0.1452(3)	C21–C10	0.1466(3)
O10–C24	0.1382(3)	C11–C16	0.1409(4)	C22–C23	0.1403(3)
O10–C20	0.1427(3)	C11–C12	0.1426(3)	C23–C24	0.1362(4)
O20–C25	0.1379(3)	C12–C13	0.1393(3)	C24–C25	0.1384(3)
O20–C20	0.1435(3)	C13–C14	0.1364(3)	C25–C26	0.1364(3)
N1–C11	0.1363(3)	C14–C15	0.1396(3)		

Table 2 (continuation)

Bond	Angle (°)	Bond	Angle (°)	Bond	Angle (°)
C24–O10–C20	105.56(19)	O3–N4–C14	119.4(2)	C13–C14–N4	119.8(2)
C25–O20–C20	105.9(2)	O4–N4–C14	117.4(2)	C15–C14–N4	119.0(2)
C11–N1–N2	119.1(2)	N1–C11–C16	119.0(2)	C23–C24–O10	128.2(2)
C10–N2–N1	115.8(2)	N1–C11–C12	124.1(2)	O10–C24–C25	110.0(2)
O2–N3–O1	122.4(2)	C16–C11–C12	116.9(2)	C26–C25–O20	127.8(2)
O2–N3–C12	119.0(2)	C13–C12–C11	121.6(2)	O20–C25–C24	109.1(2)
O1–N3–C12	118.6(2)	C13–C12–N3	116.3(2)	N2–C10–C21	120.7(2)
O3–N4–O4	123.1(2)	C11–C12–N3	122.1(2)	O10–C20–O20	107.5(2)

Supplementary material: Crystal data have been deposited at CCDC (No. 228639).

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