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Structure of 1-(4-Methylphenylamino)-2-phenyl-1,2-ethandione-1-oxime

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The crystal structure of 1-(4-methylphenylamino)-2-phenyl-1,2-ethandione-1-oxime ($C_{15}H_{14}N_2O_2$) has been determined by X-ray analysis. It crystallizes in the orthorhombic space group $Pna2_1$, with unit cell parameters: a = 23.516(3), b = 5.364(3), c = 21.872(3)Å, V = 2758.7(17)Å^3, D_c = 1.224 g/cm^3, and Z = 8. The crystal structure was solved by direct methods and refined by full-matrix least squares to a final R-value of 0.041 for 2204 observed reflections. There are two independent molecules, A and B. These molecules are linked by intermolecular O–H···N hydrogen bonds.

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In general, oximes and their derivations are very important compounds in the chemical industry and medicine due to their biological activity. Oximes have various insecticidal, miticidal and nematocidal activities and are employed as antidotes against organophosphorus poisons.[1] Carbonyl-oximes are employed in the separation and spectrophotometric determination of Ni, Pd, Co, Fe and Cu metals.[2,3] Oxime groups posses stronger hydrogen-bonding capabilities than alcohols, phenols and carboxylic acids.[4]

In this paper we report on the crystal structure of the title compound, shown in Fig. 1. The spectrum of H-NMR was recorded with a spectrometer 60-MHz VARIAN (EM-360). W-chloroisonitrosoacetophenone (2.75 g, 0.015 mol) was solved in 40 ml of dichloromethane; then a solution of (4.86 g, 0.03 mol) 4-methylaniline in 20 ml dichloromethane was added dropwise into this mixture. The precipitated product was filtered off. The filtered mixture was kept under room-temperature conditions for 3 days. Finally, the formed single crystals was filtered off and washed with ethanol.

Reflection data were collected on a Rigaku AFC7S diffractometer using Mo K_α monochromated with graphite at 20.0˚C, as summarized in Table 1, and corrected for Lorentz and polarization effects. The structure was solved by a direct method (SIR 92),[5] and refined by full-matrix least-squares with anisotropic thermal parameters for the non-hydrogen atoms. In a later stage of the refinement, reflection data were corrected for absorption and extinction. The oxime H atoms were located from a difference map and refined isotropically; the positions of the remaining H atoms were calculated geometrically. All of the calculations were performed using the program system teXsan crystallographic software package of Molecular Structure Corporation. The final results of the refinement and the atomic coordinates are shown in Tables 1 and 2, respectively. The bond distances and angles are listed in Table 3. The structure of the molecule is shown in Fig. 2. There are two molecules (A and B) in the crystal structure of the title compound. These two molecules are linked by H bonds, the geometric details of which are given in Table 4. As can be seen

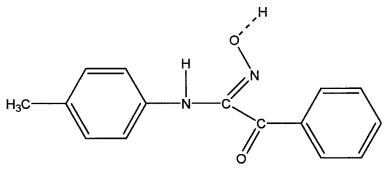

Fig. 1 Chemical structure.

Table 1 Crystal and experimental data

Formula: $C_{15}H_{14}N_2O_2$	
Formula weight = 254.28	
Crystal System: orthorhombic	
Space Group: $Pna2_1$	Z = 8
a = 23.516(3)Å	
b = 5.364(3)Å	
c = 21.872(3)Å	
V = 2758.7(17)Å^3	
D_c = 1.224 g/cm^3	
μ(Mo K_α) = 1.82 cm^{-1}	
λ(Mo K_α) = 0.71069 Å	
Crystal dimensions: 0.40 × 0.35 × 0.35 mm	
F(0 0 0) = 1072	
Scan Type: $\omega - 2\theta$	
$2\theta_{max}$ = 60.0˚	
R = 0.041	
Rw = 0.128	
No. of reflections measured = 4128	
No. of reflections used = 2204	($I > 2\sigma(I)$)
Goodness-of-fit = 1.06	
$(\Delta/\sigma)_{max}$ = 0.041	
$(\Delta/\rho)_{max}$ = 0.206 eÅ^{-3}	
$(\Delta/\rho)_{min}$ = –0.198 eÅ^{-3}	

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Table 2 Final atomic coordinates and equivalent isotropic thermal parameters for non-hydrogen atoms

Atom	*x*	*y*	*z*	U_{eq}
O1	0.56201(13)	-0.0232(8)	0.15092(15)	0.0818(12)
O2	0.50733(12)	0.0098(6)	0.34315(13)	0.0603(7)
O3	0.19397(13)	0.5545(8)	0.20609(13)	0.0777(10)
O4	0.25055(11)	0.5564(6)	0.01283(12)	0.0592(7)
N1	0.47571(13)	-0.1125(8)	0.21945(16)	0.0587(9)
N2	0.57461(13)	-0.0659(7)	0.21313(15)	0.0599(9)
N3	0.27948(13)	0.4394(7)	0.13684(16)	0.0511(7)
N4	0.18075(12)	0.5129(7)	0.14344(15)	0.0567(8)
C1	0.43308(17)	-0.4363(7)	0.28210(19)	0.0556(9)
C2	0.3863(2)	-0.5344(8)	0.3109(2)	0.0665(11)
C3	0.33297(19)	-0.4223(9)	0.3064(2)	0.0689(11)
C4	0.32818(17)	-0.2143(9)	0.2703(2)	0.0638(11)
C5	0.37508(15)	-0.1122(8)	0.24145(19)	0.0540(9)
C6	0.42786(13)	-0.2205(7)	0.24837(16)	0.0460(8)
C7	0.2828(3)	-0.5272(14)	0.3416(3)	0.111(2)
C8	0.52884(14)	-0.1097(7)	0.24253(16)	0.0480(8)
C9	0.53751(13)	-0.1204(7)	0.31181(15)	0.0446(7)
C10	0.58322(15)	-0.2791(7)	0.33679(15)	0.0453(7)
C11	0.60155(17)	-0.2383(8)	0.39641(17)	0.0601(10)
C12	0.64256(19)	-0.3848(9)	0.4219(2)	0.0711(12)
C13	0.6660(2)	-0.5776(9)	0.3902(2)	0.0733(12)
C14	0.6473(2)	-0.6241(10)	0.3314(2)	0.0740(13)
C15	0.60634(16)	-0.4774(8)	0.30472(19)	0.0563(9)
C16	0.38025(14)	0.3795(7)	0.11828(17)	0.0462(8)
C17	0.42380(13)	0.2419(7)	0.09408(18)	0.0484(8)
C18	0.41475(15)	0.0289(7)	0.06052(17)	0.0491(8)
C19	0.35813(16)	-0.0477(7)	0.05268(19)	0.0514(8)
C20	0.31410(15)	0.0837(6)	0.07842(18)	0.0479(8)
C21	0.32428(13)	0.3004(6)	0.11052(15)	0.0416(7)
C22	0.46256(18)	-0.1215(9)	0.0330(2)	0.0674(11)
C23	0.22621(13)	0.4562(7)	0.11378(15)	0.0435(7)
C24	0.21688(13)	0.4511(6)	0.04509(15)	0.0414(7)
C25	0.16478(14)	0.3293(6)	0.02095(15)	0.0437(7)
C26	0.14249(18)	0.4162(9)	-0.0337(2)	0.0611(10)
C27	0.0945(2)	0.3040(11)	-0.0578(2)	0.0823(15)
C28	0.0694(2)	0.1057(12)	-0.0281(3)	0.0904(17)
C29	0.0923(2)	0.0171(10)	0.0251(3)	0.0822(15)
C30	0.13919(17)	0.1279(8)	0.0501(2)	0.0592(9)

$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* (\boldsymbol{a}_i \cdot \boldsymbol{a}_j)$.

Table 3 Bond distance (Å) and angles (˚)

(molecule A)			(molecule B)		
atom	atom	distance	atom	atom	distance
O2	C9	1.209(4)	O4	C24	1.202(4)
C10	C9	1.476(5)	C24	C25	1.485(5)
C9	C8	1.530(5)	C24	C23	1.519(5)
C6	N1	1.415(4)	N3	C21	1.413(4)
N1	C8	1.348(5)	N3	C23	1.353(4)
O1	N2	1.411(5)	N4	O3	1.423(4)
N2	C8	1.276(4)	N4	C23	1.287(4)
C3	C7	1.517(6)	C18	C22	1.509(5)

(molecule A)				(molecule B)			
atom	atom	atom	angle	atom	atom	atom	angle
O2	C9	C10	123.4(3)	O4	C24	C25	122.8(3)
O2	C9	C8	117.5(3)	O4	C24	C23	118.5(3)
C1	C6	N1	120.8(3)	C16	C21	N3	119.6(3)
C8	N1	C6	125.1(3)	C23	N3	C21	125.0(3)
C8	N2	O1	109.8(3)	C23	N4	O3	109.9(3)
N2	C8	N1	126.6(3)	N4	C23	N3	126.6(3)
N2	C8	C9	113.2(3)	N4	C23	C24	112.5(3)
N1	C8	C9	119.6(3)	N3	C23	C24	120.1(3)

Table 4 Hydrogen bond geometry

D-H···A	D···A	D-H	H···A	<D-H···A
O1-H1A*...N4	2.798(10)	0.770(50)	2.122(10)	148.14(5)
O3-H1B*...N2	2.812(20)	0.940(50)	1.997(20)	142.22(4)

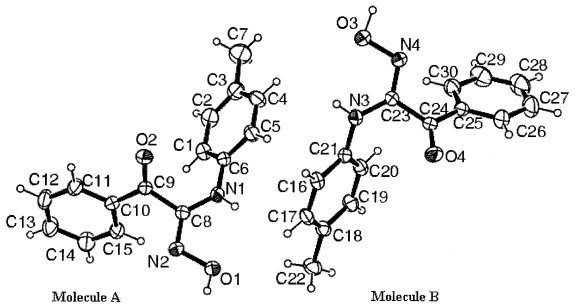

Fig. 2 ORTEP drawing of the title compound with the atom labeling scheme and 50% probability level displacement ellipsoids.

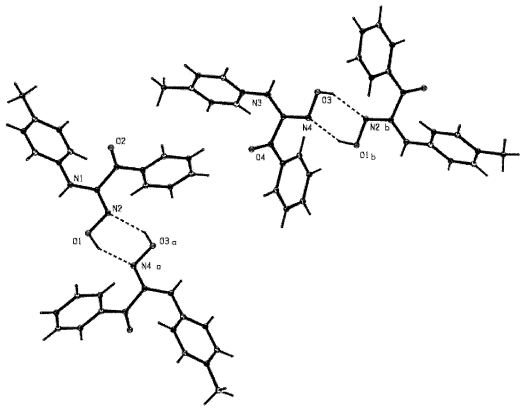

Fig. 3 ORTEP drawing of the intermoleculer hydrogen bonds between molecules (A and B) with the atom labeling scheme and 20% probability level displacement ellipsoids.

from Fig. 3, there are two kinds of intermolecular hydrogen bonds between molecule A and molecule B′, which is the repetition molecule of molecule B according to the symmetry in this unit cell. The first one is between the hydroxyl H atom of molecule A and the oxime N atom of molecule B′. The other intermolecular hydrogen bond is between the oxime N atom of molecule A and the hydroxyl H atom of molecule B′. Thus, the crystal structure is stabilized by the intermolecular hydrogen bonds.

In molecules A and B, the carbonyl-oxime groups are not planar, while the methylphenilamino rings are nearly planar with maximum deviations for C7 [0.0618(44)Å] in molecule A and C20 [0.0135(27)Å] in molecule B. The dihedral angle between the planes of the carbonyl-oxime group and methylphenilamino ring in molecules A and B are 45.75(34) and 50.46(23)˚, respectively.

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