International Journal of Chemistry and Applications.
ISSN 0974-3111 Volume 6, Number 1 (2014), pp. 33-38

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Synthesis and X-ray Crystal Structure of (3, 4-dimethoxybenzylidene) propanedinitrile

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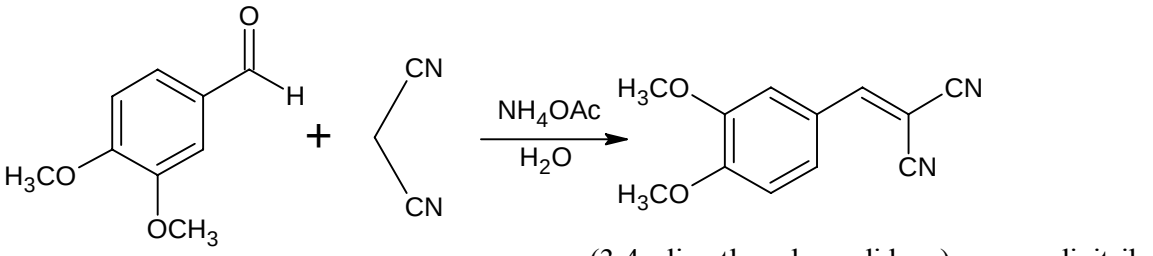
Abstract

The title compound (3, 4-dimethoxybenzylidene) propanedinitrile ($C_{12}H_{10}N_2O_2$) crystallizes in the triclinic space group P $\bar{1}$ with unit cell parameters: a = 7.5726 (4), b = 8.9178 (4), c = 9.2334 (5) Å, α = 93.832 (4)º, β = 104.641 (4)º, γ = 110.379 (5)º, Z = 2. The crystal structure was solved by direct methods and refined by full-matrix least-squares procedures to a final R-value of 0.0422 for 1627 observed reflections. The dihedral angle between phenyl ring and propanedinitrile fragment is 13.49 (7)°. The crystal structure is stabilized by intramolecular (C-H…N) and inter molecular (C-H…N and C-H…O) hydrogen bonds.

Introduction

The Knoevenagel condensation of aldehydes with active methylene groups is useful and widely employed in many industrial applications for fine chemical synthesis [1-3]. The condensation of malononitrile with cyclohexanone, benzophenone, etc. yields alkenes containing electron withdrawing nitrile groups and these alkenes are subsequently found useful in anionic polymerization reactions leading to plastics, synthetic fibers or the production of liquid crystals. The preparation of several anti-fouling agents, herbicides, insecticides, cosmetics, perfumes, polymers, antihypertensive, calcium antagonists and pharmaceuticals are carried out by using this condensation process [4-7]. In prolongation of our investigations of the synthesis and structure of the (3, 4 -dimethoxybenzylidene) propanedinitrile, we explain herein

the synthesis and structure of a compound (3, 4 -dimethoxybenzylidene) propanedinitrile (Scheme 1).



(3,4- dimethoxybenzylidene)propanedinitrile

Scheme 1 Synthesis of (3, 4-dimethoxybenzylidene) propanedinitrile

Materials and methods

Synthesis

All the chemicals were purchased from S D Fine Chem Limited, used as received without further purification. Melting point was determined on Labstar melting apparatus. The IR spectra was run on a Perkin-Elmer, FTIR-1600 spectrophotometer and expressed in cm^{-1} (KBr). ^1H NMR spectra was recorded on Bruker Avance (300 MHz) spectrometer in DMSO - d_6 using TMS as the internal standard. Elemental analysis was performed on a EURO-EA elemental analyzer.

A mixture of malononitrile (1mmole), 3, 4- dimehoxy benzaldehyde (1 mmole) and ammonium acetate (10 mol %) in 5 ml water was stirred at 70ºC for 15 min. The solid separated was filtered and re crystallized from ethanol. The product was characterized by IR, ^1H-NMR, Elemental and Single Crystal Analysis. M.P.: 150-151ºC, Yield: 83%. IR (KBr): 2917, 2215, 1613 cm^{-1}. ^1H-NMR (300MHz-DMSO-d_6): δ 3.80 (s, 3H, OCH_3); 3.89 (s, 3H, OCH_3); 7.22-7.24 (d, 1H, J= 6.6 Hz, Ar- H); 7.60-7.65 (m, 2H, Ar-H); 8.37 (s, 1H, CH). Analysis calculated for $C_{12}H_{10}N_2O_2$ (214.22): C, 67.28%; H, 4.71%; N, 13.08%; Found: C, 67.25%; H, 4.67%; N, 13.12%.

Crystal Structure Determination and Refinement

The X-ray intensity data for a well defined crystal (0.30 x 0.20 x 0.10 mm) were collected at room temperature (293K) by using a CCD area-detector diffractometer (*X'calibur system – Oxford diffraction, 2010*) which is equipped with graphite monochromated MoK□ radiation (□=0.71073 Å). The cell dimensions were determined by the least-squares fit of angular settings of 4919 reflections in the □range 3.56 to 28.75. Data were corrected for Lorentz, polarization and absorption factors.

The structure was solved by direct methods using SHELXS97 [8]. All non-hydrogen atoms of the molecule were located from the E-map. Full-matrix least-squares refinement was carried out by using SHELXL97 software [8]. The geometry of the molecule is determined by PLATON [9]. All the hydrogen atoms were geometrically fixed and allowed to ride on the corresponding non-H atoms with C-H

distances of 0.93-0.96 Å; and with *U*iso (H) = 1.2*U*eq (C), except for the methyl groups where *U*iso (H) = 1.5*U*eq (C). The final refinement cycles yielded an R- factor of 0.042 (wR (F^2) = 0.1078) for the observed data. Atomic scattering factors were taken from International Tables for X-ray Crystallography (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4). The crystallographic data are presented in Table 1. The structure carries CCDC number 958094 and it contains the requisite supplementary crystallographic data for this paper.

Table 1: Crystal data and other experimental details

CCDC Number	958094
Crystal description	white block
Crystal size (mm)	0.30 x 0.20 x 0.10
Empirical formula	$C_{12}\ H_{10}\ N_2\ O_2$
Formula weight	214.22
Radiation, Wavelength (Å)	Mo *K*α, 0.71073
Unit cell dimensions	a = 7.5726 (4), b = 8.9178 (4), c = 9.2334 (5) Å, α = 93.832 (4)º, β = 104.641 (4)º, γ = 110.379 (5)º
Crystal system, Space group	triclinic, P $\bar{1}$
Unit cell volume ($Å^3$)	557.23 (5)
No. of molecules per unit cell, Z	2
Absorption coefficient (mm^{-1})	0.089
F (000)	224
θ range for entire data collection (º)	3.57≤θ < 26.00
Reflections collected / unique	8432/2182
Reflections observed (I > 2□ (I))	1627
Limiting indices	h= -9 to 9, k= -10 to 10, l= -11 to 11
No. of parameters refined	147
Final R-factor	0.0422
wR (F^2)	0.1078
Goodness-of-fit	1.044
(□)$_{max}$	0.001
Final residual electron density ($eÅ^{-3}$)	-0.187 ≤□ □ < 0.140

Results and discussion

An ORTEP view of the title compound with atomic labeling is shown in Figure 1 [10]. Bond lengths and angles have normal values (Table 2) and are found in related structures [11-12]. The dihedral angle between phenyl ring and propanedinitrile fragment is 13.49 (7)°. There is a slight variation in O-C/ C-O bond distances and C-O-C bond angles. This could be due to the free rotation of the methyl groups. The bond lengths and bond angles of both the cyano groups [(C10-N10) 1.146 (2) Å, (C9-N9) 1.1358 (2) Å, (C8-C10-N10) 179.2 (2)° and (C8-C9-N9) 178.7 (2)°] indicates linearity, a feature quite commonly observed in carbonitrile compounds [12].

Packing of the molecules in the unit cell down the a-axis is shown in Figure 2. In the crystal structure, C-H…N and C-H…O hydrogen bonds (Table 3) link the molecules into infinite chains forming a *zig-zag* pattern. An intramolecular C-H…N hydrogen bond generates a pseudo ring of S (7) graph set motif [13].

Table 2 Selected bond lengths (Å) and bond angles (º) for non hydrogen atoms (e.s.d.'s are given in parentheses)

Bond Lengths		**Bond Angles**	
C3- O3	1.368 (2)	O3- C3- C4	114.55 (13)
O3- C11	1.418 (2)	C3- O3- C11	116.79 (13)
C4- O4	1.348 (2)	O4- C4- C5	125.50 (14)
O4- C12	1.430 (2)	O4- C4- C3	115.55 (13)
C9- N9	1.136 (2)	C4- O4 -C12	118.19 (13)
C10- N10	1.146 (2)	N9- C9- C8	178.73 (19)
		N10- C10- C8	179.19 (18)

Table 3 Geometry of intra- and inter molecular hydrogen bonds

D̃H…A	D̃H (Å)	H…A (Å)	D…A (Å)	□ [D̃H…A (º)]
C2-H2...N9	0.930 (2)	2.668 (2)	3.481 (3)	146 (1)
C7-H7...N10^{i}	0.930 (2)	2.584 (2)	3.495 (2)	166 (1)
C12-H12B...O4^{ii}	0.960 (3)	2.569 (1)	3.336 (3)	137 (1)

Symmetry code: ^{i}-x+2, -y+1, -z+1 ^{ii}-x, -y+1, -z+2

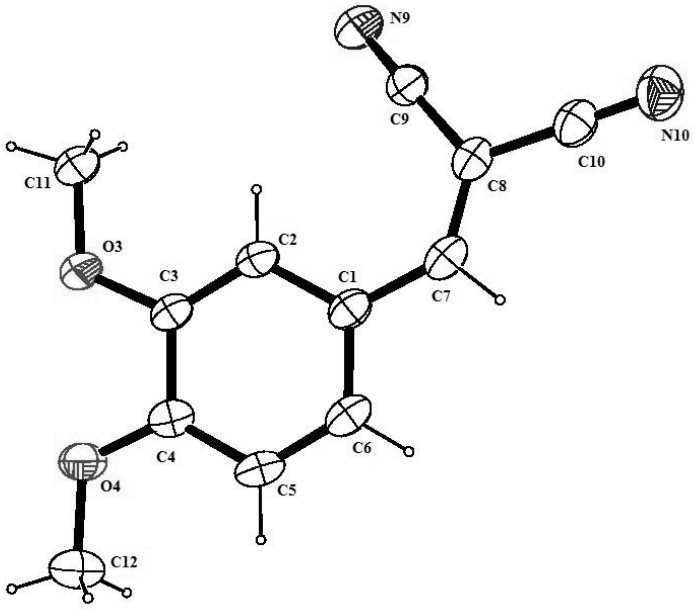


Figure 2 *ORTEP* view of the molecule with displacement ellipsoids drawn at 50% probability level. H atoms are shown as small spheres of arbitrary radii.

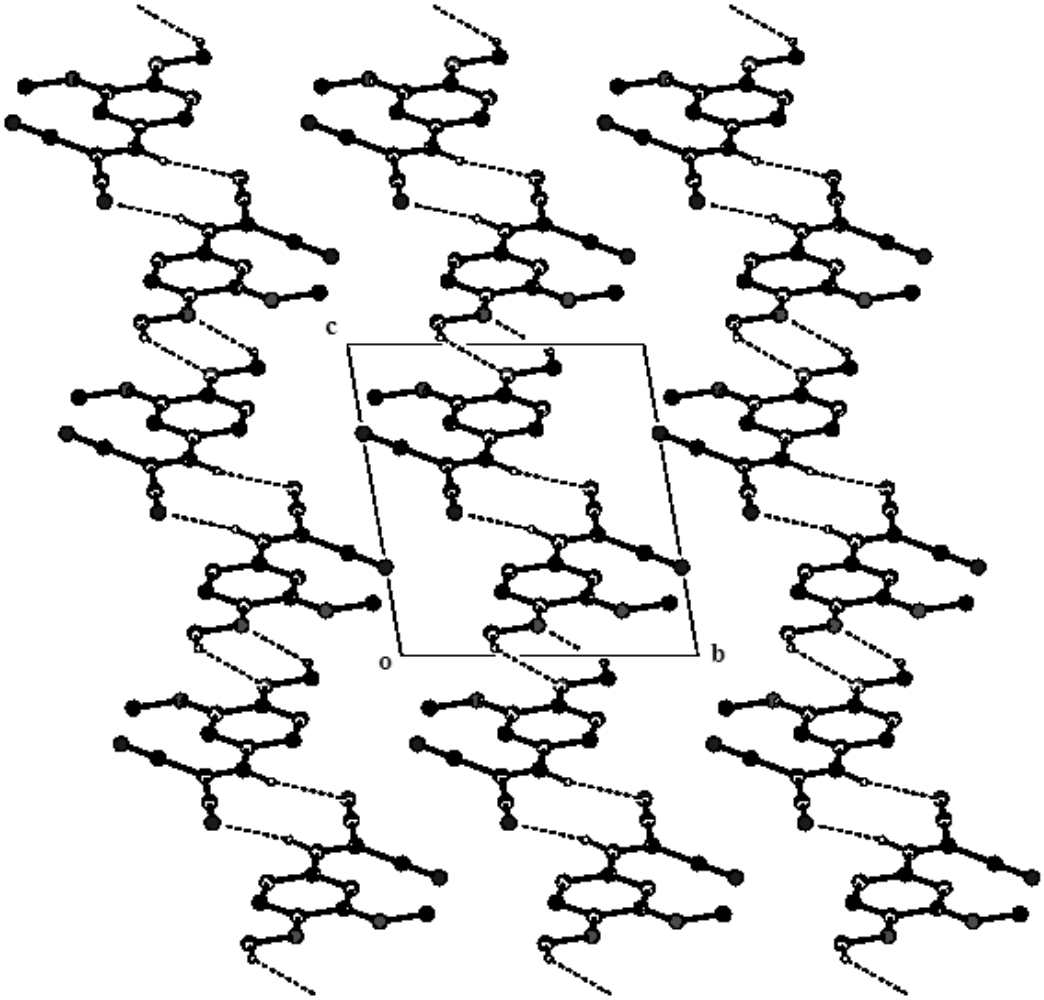


Figure 3 The packing arrangement of molecules viewed along the a-axis. The dashed lines show intermolecular C-H···N and C-H…O hydrogen bonds.

Conclusions

The compounds (1) was synthesized by adopting Knoevenagel condensation reaction and the corresponding molecular and crystal structure was determined by single-crystal X-ray diffraction with final R-factor of 0.0422. C-H…N, C-H…O intra and inter molecular hydrogen bonds stabilizes the crystal structure.

Acknowledgements

One of the authors (Rajni Kant) acknowledges the Department of Science & Technology for single crystal X-ray diffractometer as a National Facility under Project No. SR/S2/CMP-47/2003.

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