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NOTE

Synthesis and Structural Reports of $C_{12}H_{20}N_2O_4$

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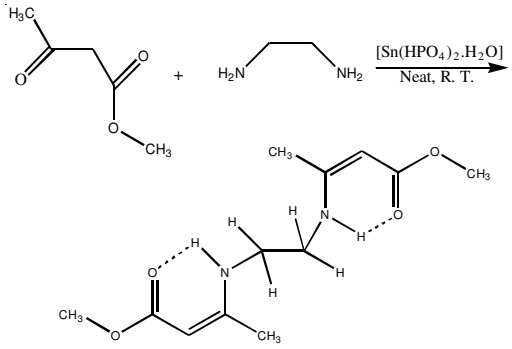
Present compound $C_{12}H_{20}N_2O_4$, a condensation product, is derived from ethylene diamine and methyl acetoacetate using Sn-nanodisks ($Sn(HPO_4)_2{\cdot}H_2O$) as catalyst. The crystalline form of these spring-like superstructure solids exhibits a plane layered structure, which is made up of $[M(PO_4)_2]_n^{2n}$ macro anions, potential active anode materials for the lithium-ion battery. The reported compound dimethyl (Z,Z)-3,3'-(ethane-1,2-diyldiimino)dibut-2-enoate, $C_{12}H_{20}N_2O_4$ crystallizes in monoclinic C2/c space group with unit cell parameters: a = 19.467(9) Å, b = 5.505(2) Å, c = 13.139(6) Å, β = 111.397(6)º, V = 1311.0(10) Å^3, Z = 4.

Key Words: Single crystal X-ray study, Sn-Nanodisks, Lithium ion battery.

The crystalline form of spring-like superstructure solids has got its potential application as active anode materials for lithium-ion battery. Extensive investigations have been made on condensation product of spring-like superstructure solids[1]. The reported compound, $C_{12}H_{20}N_2O_4$, is derived from ethylene diamine and methyl acetoacetate using Sn-nanodisks [$Sn(HPO_4)_2{\cdot}H_2O$] as catalyst.

Sample preparation: The condensation product of the compound $C_{12}H_{20}N_2O_4$, is synthesized from ethylene diamine and methyl acetoacetate using Sn-nanodisks ($Sn(HPO_4)_2{\cdot}H_2O$) as catalyst. The Sn-nanodisks were prepared by following the published procedure[1,2]. H_3PO_4 (85 %) (0.3 mL) was added to a solution of 0.35 g of $SnCl_4{\cdot}H_2O$ (AR) in anhydrous ethanol (12 mL). The resulting reaction mixture was transferred to a 22 mL teflon-sealed autoclave and stored at 180 ºC for 24 h, then air-cooled to room temperature. The product was washed ten times with anhydrous ethanol and finally dried at 60 ºC in a vacuum oven. The catalyst was characterized by SEM, XRD and FT-IR analysis[1].

In a 50 mL round-bottom flask, ethylenediamine (1 m mol) and methyl acetoacetate (2 m mol with molar ratio 2:1) were stirred in presence of Sn-nanodisks (10 mL %) under solvent free condition at room temperature for 1 h. The progress of the reaction was monitored by TLC. After completion of the reaction, methanol was added to dissolve the solid formed and the catalyst was filtered off. The filtrate was concentrated in vacuum and recrystallized from ethanol to afford the pure product (**Scheme-I**).



Scheme-I: Reaction scheme for preparation of dimethyl (Z,Z)-3,3'-(ethane-1,2-diyldiimino)dibut-2-enoate

X-Ray diffraction: The measurements were made on Rigaku Saturn-724 CCD area detector with graphite monochromator MoK_α ($\lambda = 0.71075$ Å) radiation. The routine crystallographic data and refinement parameters are listed in Tables 1 and 2, respectively. No. of reflections measured were 2414 out of which 1585 are unique ($R_{int} = 0.018$). The data were corrected for Lorentz and polarization effects. The data collection and processing with: Crystal Clear Software Package[3]; Direct method[4] with expanded Fourier Techniques[5]; least-square refinement with unweighted and weighted agreement factors: $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.0456$ and $R_w = [\Sigma w(|F_o|-|F_c|)^2/\Sigma wF_o^2]^{1/2} = 0.0426$, neutral atom scattering factor[6]; anomalous dispersion effects inclusion[7]; mass attenuation coefficients[8] were performed using Crystal Structure Software Package[9].

TABLE-1
CRYSTAL DATA

Empirical formula	$C_{12}H_{20}N_2O_4$
Formula weight	256.30
Temperature	293 K
Crystal dimensions	0.20 mm × 0.20 mm × 0.20 mm
Crystal system	Monoclinic
Lattice type	C-centered
Detector position	49.98 mm
Pixel size	0.034 mm
Lattice parameters	a = 19.467(9) Å
	b = 5.505(2) Å
	c = 13.139(6) Å
	β = 111.397(6)º
	V = 1311.0(10) Å^3
Space group	$C_{2/c}$ (#15)
Z value	4
Calculated density	1.298 g/cm^3
F_{000}	552.00
μ (MoK$_\alpha$)	0.974 cm^{-1}

TABLE-2
STRUCTURE SOLUTION AND REFINEMENT

Structure solution	Direct methods (SIR92)
Refinement	Full-matrix least-squares on F
Function minimized	$\Sigma w(\|F_o\| - \|F_c\|)^2$
Least squares weight	1
2θmax cutoff	58.9º
Anomalous Dispersion	All non-hydrogen atoms
No. observations (I > 2.00σ(I))	2309
No. variables	172
Reflection/parameter ratio	13.42
Residuals: R (I > 2.00σ(I)	0.0456
Residuals: Rw (I > 2.00σ(I)	0.0426
Goodness of fit indicator	7.483
Max shift/error in final cycle	0.122
Maximum peak in final diff. map	0.34 e$^-$/Å^3
Minimum peak in final diff. map	-0.88 e$^-$/Å^3

The molecular structure of dimethyl (Z.Z)-3,3'-(ethane-1,2-diyldiimino)dibut-2-enoate in ORTEP form is shown in Fig. 1. Table-1 shows the crystal data and Table-2 shows the structure solution and refinement. It is reported that the compound is being a solid crystalline product though it is aliphatic with two methyl ester groups and, in general, it should be liquid in nature. However, the formation of the solid crystalline product could be explained by intermolecular N-H···O hydrogen bonds leaving the molecule into a two-dimensional network. Table-3 shows the interatomic distances and bond angles. The C4=C8 bond value in butane group is 1.3699(17) Å which is longer than that of standard 1.34 Å with hybridization sp^2-sp^2 type. The N3-C4 bond length of 1.3386(14) Å is shorter than that of the standard N-C experimental bond length of 1.469 Å[10]. As a result of this difference π-π conjugation between the N atom and C=C bond occurred. On the other hand, the O1=C6 bond length of 1.2254(13) Å is longer than that of other derivative compounds, *e.g.*, 1.199(3) Å[11]. Another characteristics of the compound is its Z, Z configuration bonds N-H···O=C for which the compound is in solid form.

The bond values 1.2254(13) for O1=C6 and 1.4337(19) Å for O2-C9 are in agreement with Csp^2 = Osp^2 (1.22 Å) and Csp^3-Osp^3 (1.42 Å), respectively while, the bond value 1.5005 (17) Å for C(4)-C(7) is in agreement with Csp^3-Csp^2 (1.50 Å)[12].

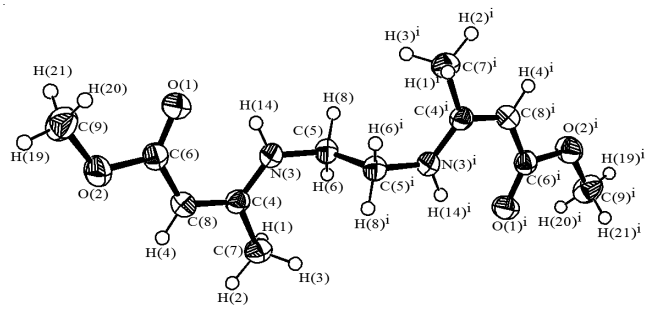


Fig. 1. ORTEP drawing of dimethyl (Z.Z)-3,3'-(ethane-1,2-diyldiimino) dibut-2-enoate

TABLE-3
SELECTED INTERATOMIC DISTANCE (Å)
AND VALENCE ANGLE (º)

Selected bond distances		Bond angles	
O(1)-C(6)	1.2254(13)	C(6)-O(2)-C(9)	117.06(11)
O(2)-C(9)	1.4337(19)	N(3)-C(4)-C(7)	117.63(11)
N(3)-C(5)	1.4578(18)	C(7)-C(4)-C(8)	119.04(10)
C(4)-C(8)	1.3699(17)	O(1)-C(6)-O(2)	121.22(10)
C(6)-C(8)	1.4267(16)	O(2)-C(6)-C(8)	111.66(9)
O(2)-C(6)	1.3598(15)	C(4)-N(3)-C(5)	125.98(10)
N(3)-C(4)	1.3386(14)	N(3)-C(4)-C(8)	123.31(10)
C(4)-C(7)	1.5005(17)	N(3)-C(5)-C(5)	111.55(10)
C(5)-C(5)^1	1.530(2)	O(1)-C(6)-C(8)	127.12(11)
–	–	C(4)-C(8)-C(6)	123.82(10)

Supplementary material: Supplementary data and figures for this paper are available from the Cambridge Crystallographic Data Centre electronic archives (Deposition number CCDC 770789).

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