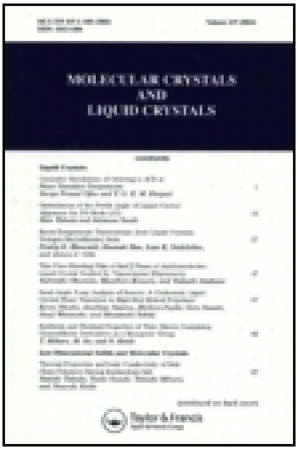

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Crystal and Molecular Structure of 1,4-Dihydropyridine with Different Substituents

H. C. Devarajegowda [a], J. Shashidhara Prasad [a], M. A. Sridhar [a], Harsukh C. Gevaria [b] & Anamik Shah [b]

[a] Department of Studies in Physics, University of Mysore, Manasagangotri, Mysore, 570 006, India

[b] Department of Chemistry, Saurashtra University, Rajkot, 360 005, India

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Crystal and Molecular Structure of 1,4-Dihydropyridine with Different Substituents

H.C. DEVARAJEGOWDA[a], J. SHASHIDHARA PRASAD[a], M.A. SRIDHAR[a]*, HARSUKH C. GEVARIA[b] and ANAMIK SHAH[b]

[a]Department of Studies in Physics, University of Mysore, Manasagangotri, Mysore 570 006, India and [b]Department of Chemistry, Saurashtra University, Rajkot 360 005, India

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The crystal and molecular structures of (A) 3,5-Diacetyl-2,6-dimethyl-4-(3′-nitrophenyl)-1,4-dihydropyridine, (B) 3,5-Dibenzoyl-2,6-dimethyl-4-(3′-nitrophenyl)-1,4-di hydropyridine and (C) 3,5-Dicarbomethoxy-2,6-dimethyl-4-(4′-methylthiophenyl)-1,4-dihydropyridine derivatives were determined by X-ray diffraction methods.

The compound (A), $C_{17}H_{18}N_2O_4$, crystallises in the monoclinic space group $P2_1/n$ with $a = 7.537(3)$ Å, $b = 16.273(3)$ Å, $c = 12.474(4)$ Å, $\beta = 92.60(3)°$, $V = 1528.4(8)$ Å^3, $Z = 4$, $D_{calc} = 1.3661$ Mg/m^3, $\mu = 0.812$ mm^{-1}, $F_{000} = 664$, Cu$K\alpha = 1.5406$ Å and $R = 0.0956$.

The compound (B), $C_{27}H_{22}N_2O_4$, crystallises in the monoclinic space group $P2_1/c$ with $a = 7.3113(7)$ Å, $b = 23.3925(7)$ Å, $c = 13.0737(7)$ Å, $\beta = 91.31(7)°$, $V = 2235(3)$ Å^3, $Z = 4$, $D_{calc} = 1.303$ Mg/m^3, $\mu = 0.176$ mm^{-1}, $F_{000} = 920$, Cu$K\alpha = 1.5406$ Å and $R = 0.0768$.

The compound (C), $C_{18}H_{21}NO_4S$, crystallises in the orthorhombic space group $Pnca$ with $a = 13.205(3)$ Å, $b = 26.558(3)$ Å, $c = 10.244(3)$ Å, $\alpha = 90°$, $\beta = 90°$, $\gamma = 90°$, $V = 3592.6(12)$ Å^3, $Z = 8$, $D_{calc} = 1.521$ Mg/m^3, $\mu = 2.050$ mm^{-1}, $F_{000} = 1728$, Cu$K\alpha = 1.5406$ Å and $R = 0.0535$.

Keywords: Crystal structure; 1,4-dihydropyridine

INTRODUCTION

The nitrogroup on the phenyl ring of dihydropyridine(DHP) at the 4-position, if properly substituted can yield many drug molecules [1–8]. It is noteworthy that the crystallographic studies of both 1,4-dihydropyridine antagonist and agonist show several common conformational features [9]. Structure-activity relationship studies on these class of molecules have discussed the effect of the size and

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* Corresponding author

the electronic character of the substituents [10], their position in the aryl ring [11] and the role of C3 and C5 substitution [12, 13]. It has been observed that the conformation of the substitution at C3 and C5 and the resultant hydrogen bonding pattern plays a major role and has been correlated with the calcium antagonist effect [9, 14–16]. In view of the importance of the DHP derivatives we have taken up for study, compounds with acetyl, methylcarbonyl, carboxymethyl or carboxyethyl groups substituted at 3 and 5 positions. In order to appreciate the biological activities it is useful to make a comparative study of the crystal and molecular structures of these compounds. Triggle and coworkers [17] have earlier studied the crystal structure of 3,5 dicarbomethoxy 2,6-dimethyl-4-(3′-nitrophenyl)-1,4-dihydropyridine.

EXPERIMENTAL

(A). Synthesis of 3,5-diacetyl-2,6-dimethyl-4-(3′-nitrophenyl)-1,4-dihydropyridine

A solution of *m*-nitrobenzaldehyde (1.51 g, 0.01 m), acetylacetone (2.0 g, 0.02 M) and ammonia (1.6 gm, 0.01 M) (2 ml) was heated under reflux with stirring for 10 hours. Upon cooling and pouring over ice cold water a sticky semisolid mass was obtained which was filtered, washed with water and recrystallized from methanol. The yield was 2.5 gm (78%) with M.P. 214°C. The purity of the compound was checked by TLC (Acetone, Benzene 3:7).

(B). Synthesis of 3,5-dibenzoyl-2,6-dimethyl-4-(3′-nitrophenyl)-1,4-dihydropyridine

A solution of *m*-nitrobenzaldehyde (1.51 gm, 0.01 M), 1,3-diketone-benzoylacetone (1.62 gm, 0.01 M) and ammonia (1.6 gm, 0.01 M) (2 ml) was heated under reflux with stirring for 10 hours. Upon cooling and pouring over ice cold water a sticky semisolid mass was obtained which was filtered, washed with water and recrystallized from methanol. The yield was 46% with M.P. 205°C. The purity of the compound was checked by TLC (Acetone, Benzene 3:7).

(C). Synthesis of 3,5-dicarbomethoxy-2,6-dimethyl-4-(4′-methylthiophenyl)-1,4-dihydropyridine

A solution of *p*-methylbenzaldehyde (1.5 gm, 0.01 M), methylacetoacetate (2.32 gm, 0.02 M) and ammonia (1.7 gm, 0.01 M) (2 ml) was heated under reflux with stirring for 8–9 hours. Upon cooling and pouring over ice cold water a sticky semisolid mass was obtained which was filtered, washed with water and recrystallized from methanol. The yield was 2 gm (56%) with M.P. 180°C. The purity of the compound was checked by TLC (Acetone, Benzene 4:6).

CRYSTAL DATA, X-RAY DATA COLLECTION AND SOLUTION AND REFINEMENT OF STRUCTURE

(A). Crystal structure of 3,5-diacetyl-2,6-dimethyl-4-(3′-nitrophenyl)-1,4-dihydropyridine

A pale yellow green rectangular crystal of dimension 0.2 × 0.2 × 0.3 mm was selected for X-ray data collection. All measurements were made on a Rigaku AFC7S diffractometer with graphite monochromated (Cu$K\alpha$) radiation. The data were collected at 293 K using the ω-2θ scan technique. Least squares refinement of 16 reflections in the range $28.84° \le 2\theta \le 37.38°$ yielded a primitive monoclinic cell. The data were corrected for Lorentz and polarization effects. An empirical absorption correction [18] based on the azimuthal scans of three reflections was applied which resulted in the transmission factors ranging from 0.931 to 1.00. A total of 2866 intensities were collected in the range of $0 \le 2\theta \le 139.86°$ of which 2659 were unique ($R_{\mathrm{int}} = 0.0308$). The structure was solved by direct methods (SHELXS-97 [19]). The structure was refined by full matrix least-squares using SHELXL-97 [20]. The function minimized throughout refinement was $\Sigma w(|F_o| - |F_c|)^2$ with $w{=}1/\sigma^2(F_o)$. Final refinement was carried out with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were placed at calculated positions and were not refined. The final cycle of full-matrix refinement based on 2288 observed reflections ($I \ge 2\sigma(I)$) and 228 parameters converged to R =0.0956 with goodness of fit = 1.640. The largest peak and deepest hole in the final difference map were 0.442 and –0.449 e.Å^{-3} respectively.

Results and Discussion

The final positional coordinates of all the atoms with equivalent isotropic thermal parameters, bond distances and bond angles angles for non-hydrogen atoms are given in tables I–III. Figure 1 represents the ORTEP [21] of the molecule at 50% probability. Figure 2 shows packing of the molecules in the unit cell down *a* axis. There are four molecules in the unit cell. Packing of the molecules shows stacking when viewed along *a*. The dihedral angle between least-squares planes (phenyl ring and pyridine ring) is 89.3(2)°. Intermolecular hydrogen bond of the type NH···O is observed in the structure (see Table XI).

TABLE I Atomic coordinates and equivalent isotropic displacement parameters in Å^2 for compound (A)

Atom	*x*	*y*	*z*	U_{eq}
O(1)	0.2061(4)	0.63539(19)	0.0675(2)	0.0818(9)
O(2)	0.2626(3)	0.6452(2)	−0.0995(2)	0.0865(10)
O(3)	−0.4973(3)	0.68773(18)	−0.4581(2)	0.0795(9)
O(4)	0.0076(3)	0.41050(15)	−0.30190(19)	0.0669(8)
N(1)	−0.6059(4)	0.45770(19)	−0.3141(2)	0.0593(8)
N(2)	0.1625(4)	0.62977(18)	−0.0279(2)	0.0657(9)
C(2)	−0.4700(4)	0.40170(19)	−0.2969(2)	0.0556(8)
C(3)	−0.2997(4)	0.42795(19)	−0.3028(2)	0.0525(8)
C(4)	−0.2640(4)	0.51995(18)	−0.3069(2)	0.0521(8)
C(5)	−0.4165(4)	0.56478(19)	−0.3658(2)	0.0543(8)
C(6)	−0.5818(4)	0.5339(2)	−0.3610(2)	0.0561(8)
C(7)	−0.7503(4)	0.5727(3)	−0.4044(3)	0.0666(10)
C(8)	−0.5367(5)	0.3175(2)	−0.2726(3)	0.0675(9)
C(9)	−0.1396(4)	0.3766(2)	−0.3031(2)	0.0573(8)
C(10)	−0.1453(5)	0.2857(2)	−0.3116(3)	0.0762(10)
C(11)	−0.3805(4)	0.6409(2)	−0.4250(2)	0.0577(8)
C(12)	−0.1911(5)	0.6597(2)	−0.4477(3)	0.0702(10)
C(13)	−0.2252(4)	0.55431(18)	−0.1938(2)	0.0530(8)
C(14)	−0.0541(4)	0.5772(2)	−0.1620(2)	0.0564(8)
C(15)	−0.0203(4)	0.6052(2)	−0.0588(2)	0.0591(9)
C(16)	−0.1488(5)	0.6112(2)	0.0162(2)	0.0671(10)
C(17)	−0.3196(5)	0.5899(3)	−0.0168(3)	0.0719(10)
C(18)	−0.3567(5)	0.5621(2)	−0.1204(3)	0.0639(9)

where $U_{eq} = 1/3\pi^2 \sum_i \sum_j a_i a_j \; a_i^* \cdot a_j^*$

TABLE II Bond Lengths in (Å) for compound (A)

Atoms	*Length*	*Atoms*	*Length*
O1-N2	1.223(3)	O2-N2	1.222(4)
O3-C11	1.222(4)	O4-C9	1.238(4)
N1-C2	1.381(4)	N1-C6	1.386(4)
N2-C15	1.469(4)	C2-C3	1.358(4)
C2-C8	1.495(5)	C3-C9	1.468(4)

Atoms	*Length*	*Atoms*	*Length*
C3-C4	1.522(4)	C4-C5	1.522(4)
C4-C13	1.534(4)	C5-C6	1.347(4)
C5-C11	1.473(4)	C6-C7	1.497(4)
C9-C10	1.484(5)	C11-C12	1.500(5)
C13-C14	1.383(4)	C13-C18	1.385(5)
C14-C15	1.378(4)	C15-C16	1.380(5)
C16-C17	1.378(5)	C17-C18	1.386(5)

TABLE III Bond Angles in (°) for compound (A)

Atoms	*Angle*	*Atoms*	*Angle*
C2-N1-C6	123.0(3)	O1-N2-O2	123.2(3)
O1-N2-C15	118.9(3)	02-N2-C15	117.8(3)
N1-C2-C3	118.7(3)	N1-C2-C8	112.5(3)
C3-C2-C8	128.8(3)	C2-C3-C9	126.9(3)
C2-C3-C4	118.7(3)	C9-C3-C4	114.4(3)
C3-C4-C5	110.9(2)	C3-C4-C13	110.7(2)
C5-C4-C13	112.2(2)	C6-C5-C11	121.9(3)
C6-C5-C4	118.6(3)	C11-C5-C4	119.5(3)
C5-C6-N1	119.5(3)	C5-C6-C7	126.6(3)
N1-C6-C7	113.9(3)	04-C9-C3	118.8(3)
04-C9-C10	117.9(3)	C3-C9-C10	123.1(3)
03-C11-C5	123.2(3)	03-C11-C12	119.0(3)
C5-C11-C12	117.8(3)	C14-C13-C18	118.2(3)
C14-C13-C4	119.9(3)	C18-C13-C4	121.9(3)
C13-C14-C15	119.1(3)	C14-C15-C16	123.5(3)
C14-C15-N2	117.8(3)	C16-C15-N2	118.7(3)
C17-C16-C15	117.0(3)	C16-C17-C18	120.5(3)
C17-C18-C13	121.7(3)		

TABLE IV Atomic coordinates and equivalent isotiopic displacement parameters in Å^2 for compound (B)

Atom	*x*	*y*	*z*	U_{eq}
O(1)	0.0928(3)	0.57267(9)	0.26667(17)	0.0556(6)
O(2A)	−0.125(3)	0.4162(8)	0.4700(15)	0.065(5)
O(2B)	−0.087(2)	0.4084(8)	0.441(2)	0.102(5)

Atom	*x*	*y*	*z*	U_{eq}
O(3)	0.2203(4)	0.38245(15)	−0.0497(2)	0.0972(10)
O(4)	0.3272(4)	0.39824(18)	0.1002(3)	0.1062(12)
N(1)	−0.5277(3)	0.53532(10)	0.31599(18)	0.0470(6)
N(2)	0.2049(4)	0.40078(13)	0.0360(2)	0.0675(8)
C(2)	−0.3943(3)	0.57480(11)	0.29503(19)	0.0423(6)
C(3)	−0.2161(3)	0.55801(10)	0.29739(18)	0.0417(6)
C(4)	−0.1724(3)	0.49472(11)	0.30009(19)	0.0432(6)
C(5)	−0.3187(4)	0.46178(10)	0.35581(19)	0.0432(6)
C(6)	−0.4918(4)	0.48213(11)	0.35879(19)	0.0448(6)
C(7)	−0.6527(4)	0.45519(13)	0.4099(2)	0.0528(7)
C(8)	−0.4707(4)	0.63215(12)	0.2661(2)	0.0554(7)
C(9)	−0.0572(3)	0.59470(11)	0.28686(19)	0.0439(6)
C(10)	−0.0560(4)	0.65796(12)	0.3038(2)	0.0500(7)
C(11)	0.0344(5)	0.69220(14)	0.2331(3)	0.0637(8)
C(12)	0.0557(6)	0.74975(17)	0.2501(4)	0.0866(12)
C(13)	−0.0069(6)	0.77406(17)	0.3381(5)	0.0914(14)
C(14)	−0.0947(6)	0.74010(17)	0.4093(4)	0.0838(12)
C(15)	−0.1206(4)	0.68248(14)	0.3916(3)	0.0630(8)
C(16)	−0.2525(4)	0.41005(13)	0.4107(3)	0.0568(8)
C(17)	−0.3566(4)	0.35563(12)	0.4094(2)	0.0523(7)
C(18)	−0.4677(5)	0.33964(15)	0.3270(3)	0.0662(8)
C(19)	−0.5532(6)	0.28677(19)	0.3270(4)	0.0849(12)
C(20)	−0.5299(7)	0.25058(17)	0.4096(4)	0.0882(13)
C(21)	−0.4211(6)	0.26579(15)	0.4902(4)	0.0812(11)
C(22)	−0.3313(5)	0.31783(14)	0.4900(3)	0.0631(8)
C(23)	−0.2948(5)	0.47112(15)	0.1221(2)	0.0613(8)
C(24)	−0.2763(5)	0.44990(18)	0.0241(3)	0.0699(9)
C(25)	−0.1103(5)	0.42739(14)	−0.0059(2)	0.0615(8)
C(26)	0.0307(4)	0.42617(11)	0.0656(2)	0.0529(7)
C(27)	0.0161(4)	0.44775(12)	0.1635(2)	0.0496(7)
C(28)	−0.1496(4)	0.47087(10)	0.1929(2)	0.0460(6)

where $U_{eq} = 1/3\pi^2 \sum_i \sum_j a_i a_j \, \mathrm{a}_i^* \cdot \mathrm{a}_j^*$

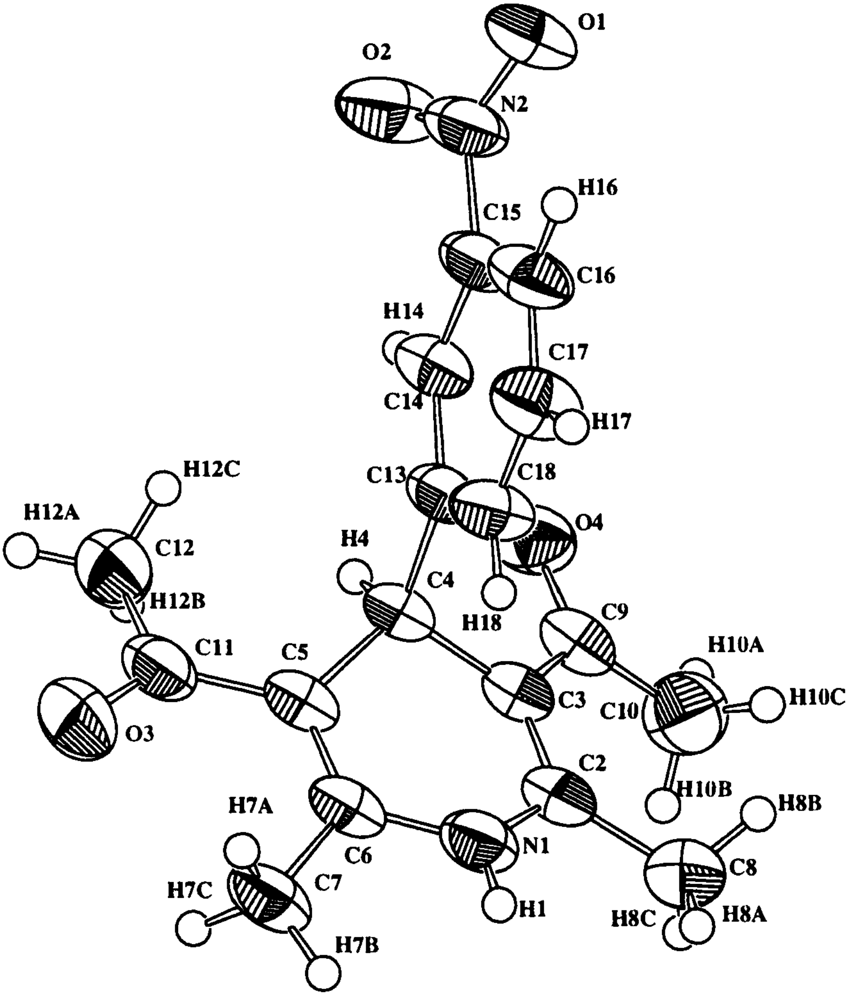

FIGURE 1 ORTEP of the molecule of compound (A)

(B). Crystal and molecular structure of 3,5-Dibenzoyl-2,6-dimethyl-4-(3′-nitrophenyl)-1,4-dihydropyridine

A yellow rectangular crystal of dimension 0.1 × 0.2 × 0.3 mm was selected for X-ray data collection. All measurements were made on a Rigaku AFC7S diffractometer with graphite monochromated (Cu$K\alpha$) radiation. The data were collected at 293 K using the ω-2θ scan technique. Least-squares refinement of 14 reflections in the range $28.79° \leq 2\theta \leq 40.46°$ yielded a primitive monoclinic cell.

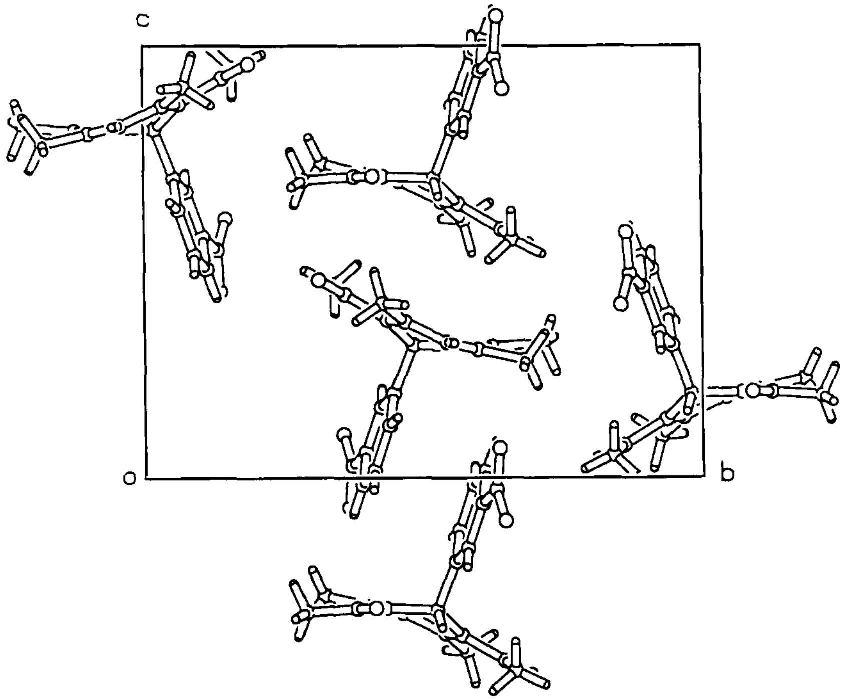

FIGURE 2 Packing of the molecules down *a* of compound (A)

The data were corrected for Lorentz and polarization effects. An absorption correction [18] was applied resulting in transmission factors ranging from 0.9390–1.0000. A total of 4120 data were collected in the range of $0 \leq 2\theta \leq 139.74°$ of which 3813 were unique ($R_{int} = 0.0337$). The structure was solved by direct methods (SHELXS-97 [19]). The structure was refined by full matrix least-squares using SHELXL-97 [20]. The function minimized through out refinement was $\Sigma w(|F_o| - |F_c|)^2$with $w = 1/\sigma^2(F_o)$. Final refinement was carried out with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were placed at the calculated positions and were not refined. The final cycle of full-matrix refinement based on 3073 observed reflections ($I \geq 2\sigma(I)$) and 356 parameters converged to $R = 0.0786$ with goodness of fit = 1.266. The largest peak and deepest hole in the final difference map were 0.358 and –0.369 e.Å^{-3} respectively.

Results and Discussion

The final positional coordinates of all the atoms with equivalent isotropic thermal parameters, bond distances and bond angles for non-hydrogen atoms are given in tables IV–VI. Figure 3 represents the ORTEP [21] of the molecule at 50% probability. Packing of the molecules do not show stacking along *a*, *b* and *c*. The disordered positions of O2 are represented as O2A and O2B. The dihedral angle between the least-squares planes of the dihydropyridine and the phenyl ring at 4 position is 89.3(1). The phenyl rings at 3 and 5 positions are perpendicular to the phenyl ring at 4 position (Dihedral angles are 86.6° and 89.8° respectively). Intermolecular hydrogen bond of the type NH···O is observed in the structure (see Table XI).

TABLE V Bond Lengths in (Å) for compound (B)

Atoms	*Length*	*Atoms*	*Length*
O1-C9	1.246(3)	O2A-C16	1.206(12)
O2B-C16	1.266(12)	O3-N2	1.208(4)
O4-N2	1.214(4)	N1-C2	1.375(3)
N1-C6	1.387(3)	N2-C26	1.465(4)
C2-C3	1.361(4)	C2-C8	1.498(4)
C3-C9	1.453(4)	C3-C4	1.515(3)
C4-C28	1.522(4)	C4-C5	1.518(4)
C5-C6	1.353(4)	C5-C16	1.482(4)
C6-C7	1.505(4)	C9-C10	1.496(4)
C10-C15	1.377(4)	C10-C11	1.400(4)
C11-C12	1.373(5)	C12-C13	1.371(7)
C13-C14	1.392(7)	C14-C15	1.380(5)
C16-C17	1.483(4)	C17-C18	1.386(5)
C17-C22	1.385(4)	C18-C19	1.386(5)
C19-C20	1.380(7)	C20-C21	1.353(7)
C21-C22	1.383(5)	C23-C24	1.383(5)
C23-C28	1.392(4)	C24-C25	1.388(5)
C25-C26	1.376(5)	C26-C27	1.383(4)
C27-C28	1.389(4)		

TABLE VI Bond Angles in (°) for compound (B)

Atoms	*Angle*	*Atoms*	*Angle*
C2-N1-C6	123.7(2)	O3-N2-O4	122.8(3)
O3-N2-C26	119.3(3)	O4-N2-C26	117.9(3)
C3-C2-N1	119.0(2)	C3-C2-C8	128.0(2)

Atoms	*Angle*	*Atoms*	*Angle*
N1-C2-C8	113.0(2)	C2-C3-C9	126.5(2)
C2-C3-C4	118.9(2)	C9-C3-C4	114.3(2)
C3-C4-C28	111.4(2)	C3-C4-C5	110.9(2)
C28-C4-C5	110.4(2)	C6-C5-C16	124.6(3)
C6-C5-C4	120.3(2)	C16-C5-C4	114.9(2)
C5-C6-N1	118.2(2)	C5-C6-C7	127.3(3)
N1-C6-C7	114.3(2)	O1-C9-C3	119.0(2)
O1-C9-C10	116.0(2)	C3-C9-C10	124.9(2)
C15-C10-C11	119.2(3)	C15-C10-C9	122.3(3)
C11-C10-C9	118.0(3)	C12-C11-C10	120.5(4)
C13-C12-C11	120.2(4)	C12-C13-C14	119.5(4)
C15-C14-C13	120.6(4)	C14-C15-C10	119.9(4)
O2B-C16-O2A	23.6(12)	O2B-C16-C5	118.4(6)
O2A-C16-C5	116.9(8)	O2B-C16-C17	117.7(7)
O2A-C16-C17	119.8(8)	C5-C16-C17	122.3(3)
C18-C17-C22	119.0(3)	C18-C17-C16	122.1(3)
C22-C17-C16	118.7(3)	C17-C18-C19	119.8(4)
C20-C19-C18	120.0(4)	C21-C20-C19	120.5(4)
C20-C21-C22	120.0(4)	C21-C22-C17	120.5(4)
C24-C23-C28	121.7(3)	C23-C24-C25	120.2(3)
C26-C25-C24	117.6(3)	C25-C26-C27	123.3(3)
C25-C26-N2	118.2(3)	C27-C26-N2	118.6(3)
C26-C27-C28	119.0(3)	C27-C28-C23	118.4(3)
C27-C28-C4	120.8(2)	C23-C28-C4	120.9(3)

(C). Crystal and molecular structure of 3,5-Dibenzoyl-2,6-dimethyl-4-(4′-methylthiophenyl)-1,4-dihydropyridine

A colourless rectangular crystal of approximate dimension 0.1 × 0.2 × 0.15 mm was selected for data collection. All measurements were made on a Rigaku AFC7S diffractometer with graphite monochromated (Cu*K*α) radiation. The data were collected at 293 K using the ω-2θ scan technique. Least-squares refinement of 25 reflections in the range $28.84° \leq 2\theta \leq 42.53°$ yielded a primitive orthorhombic cell. An empirical absorption correction [18] based on azimuthal scans of three reflections was applied which resulted in the transmission factors ranging from 0.9166–1.0000. The data were corrected for Lorentz and polarization effects. A total of 3393 data were collected in the range of $0 \leq 2\theta \leq 140°$, of

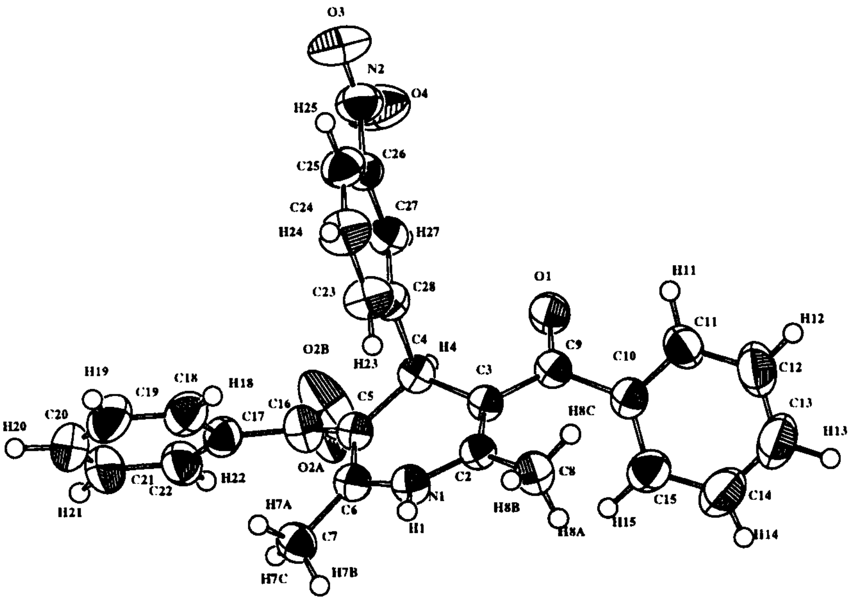

FIGURE 3 ORTEP of the molecule of compound (**B**)

which 3390 were unique ($R_{int} = 0.0150$). The structure was solved by direct methods (SIR-92 [22]). The structure was refined by full matrix least-squares using SHELXL-97[20]. Final refinement was carried out with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were included at chemically acceptable positions but not refined. Final full matrix least-squares cycle for 2288 reflections ($I \geq 2\sigma$ (I)) and 247 parameters converged to $R = 0.0535$ with goodness of fit = 1.067. The largest peak and deepest hole in the final difference map were 0.658 and −0.441 e.Å^{-3} respectively.

Results and Discussion

The final positional coordinates of all the atoms with equivalent isotropic thermal parameters, bond distances and bond angles for non hydrogen atoms are given in tables VII–IX. ORTEP [21] of the molecule is shown in figure 4. The disordered position of O3 is represented as O3A and O3B respectively. Packing of the molecules shows no stacking when viewed along *a*, *b* and *c*. There are eight molecules in the unit cell. The dihedral angle between least-squares planes of dihydropyridine ring and methylthiophenyl ring is 84.8(2)°. Intermolecular hydrogen bond of the type NH···O is observed in the structure (see Table XI).

TABLE VII Atomic coordinates and equivalent isotropic displacement parameters in Å^2 for compound (C)

Atom	*x*	*y*	*z*	U_{eq}
S(1)	0.67271(8)	0.42658(5)	0.0136(1)	0.0846(4)
N(1)	1.12545(18)	0.38278(11)	0.4086(3)	0.0516(7)
O(1)	0.83583(15)	0.41179(11)	0.6623(2)	0.0677(7)
O(2)	0.97153(16)	0.45764(10)	0.7084(2)	0.0672(7)
O(3A)	1.036(2)	0.2314(7)	0.389(6)	0.115(7)
O(3B)	1.029(3)	0 2284(9)	0.359(5)	0.131(12)
O(4)	0.89091(18)	0.25371(10)	0.4678(3)	0.0730(8)
C(2)	1.07719(19)	0.41174(11)	0.4993(3)	0.0439(6)
C(3)	0.98390(19)	0.39732(11)	0.5385(3)	0.0416(6)
C(4)	0.93017(19)	0.35437(11)	0.4713(3)	0.0428(7)
C(5)	1.0077(2)	0.31673(12)	0.4218(3)	0.0470(7)
C(6)	1.0994(2)	0.33347(12)	0.3834(3)	0.0511(8)
C(7)	1.1367(2)	0.45725(12)	0.5408(4)	0.0545(8)
C(8)	1.1802(2)	0.30359(16)	0.3146(4)	0.0737(11)
C(9)	0.9234(2)	0.42235(12)	0.6397(3)	0.0469(7)
C(10)	0.9136(3)	0.48267(18)	0.8086(4)	0.0817(13)
C(11)	0.9812(3)	0.4161(4)	0.4161(4)	0.0655(10)
C(12)	0.8587(4)	0.20229(17)	0.4759(6)	0.0989(16)
C(13)	0.86224(18)	0.37284(11)	0.3586(3)	0.0397(6)
C(14)	0.8859(2)	0.41509(12)	0.2870(3)	0.0465(7)
C(15)	0.8267(2)	0.43043(14)	0.1829(3)	0.0536(8)
C(16)	0.7405(2)	0.40349(13)	0.1498(3)	0.0516(8)
C(17)	0.7146(2)	0.36202(13)	0.2216(3)	0.0519(8)
C(18)	0.7750(2)	0.34619(12)	0.3257(3)	0.0478(7)
C(19)	0.5723(4)	0.3837(2)	−0.0030(6)	0.1083(19)

where $U_{eq} = 1/3\pi^2 \sum_i \sum_j a_i a_j \; a_i^* \cdot a_j^*$

TABLE VIII Bond Lengths in (Å) for compound (C)

Atoms	*Length*	*Atoms*	*Length*
S1-C19	1.756(5)	S1-C16	1.768(3)
N1-C2	1.364(4)	N1-C6	1.378(4)
O1-C9	1.212(3)	O2-C9	1.333(4)

Atoms	*Length*	*Atoms*	*Length*
O2-C10	1.442(4)	O3A-C11	1.16(2)
O3B-C11	1.27(3)	O4-C11	1.332(4)
O4-C12	1.433(5)	C2-C3	1.351(4)
C2-C7	1.503(4)	C3-C9	1.468(4)
C3-C4	1.510(4)	C4-C5	1.518(4)
C4-C13	1.541(4)	C5-C6	1.350(4)
C5-C11	1.452(5)	C6-C8	1.504(4)
C13-C14	1.377(4)	C13-C18	1.393(4)
C14-C15	1.384(4)	C15-C16	1.386(4)
C16-C17	1.368(5)	C17-C18	1.397(4)

TABLE IX Bond Angles in (°) for compound (C)

Atoms	*Angle*	*Atoms*	*Angle*
C19-S1-C16	103.5(2)	C2-N1-C6	123.2(3)
C9-O2-C10	116.6(3)	C11-O4-C12	118.7(3)
C3-C2-N1	117.9(3)	C3-C2-C7	128.4(3)
N1-C2-C7	113.7(2)	C2-C3-C9	125.3(3)
C2-C3-C4	120.5(3)	C9-C3-C4	114.1(2)
C3-C4-C5	109.5(2)	C3-C4-C13	112.0(2)
C5-C4-C13	110.6(2)	C6-C5-C11	121.6(3)
C6-C5-C4	119.1(3)	C11-C5-C4	119.4(3)
C5-C6-N1	118.8(3)	C5-C6-C8	126.8(3)
N1-C6-C8	114.4(3)	O1-C9-O2	121.1(3)
O1-C9-C3	123.3(3)	O2-C9-C3	115.6(2)
O3A-C11-O3B	15(3)	O3A-C11-O4	120.7(8)
O3B-C11-O4	118.5(14)	O3A-C11-C5	125.2(12)
O3B-C11-C5	128.0(13)	O4-C11-C5	113.1(3)
C14-C13-C18	118.2(3)	C14-C13-C4	121.7(2)
C18-C13-C4	120.0(3)	C13-C14-C15	121.5(3)
C14-C15-C16	120.1(3)	C17-C16-C15	119.3(3)
C17-C16-S1	125.2(2)	C15-C16-S1	115.5(3)
C16-C17-C18	120.7(3)	C13-C18-C17	120.3(3)

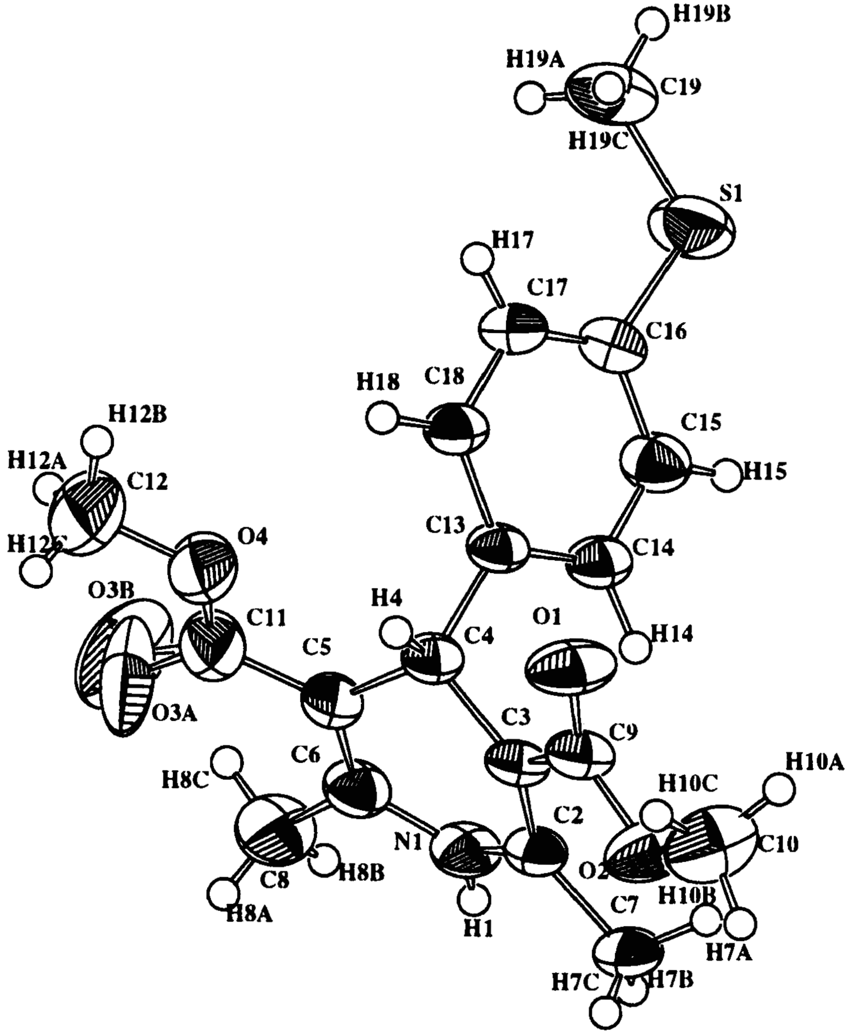

FIGURE 4 ORTEP of the molecule of compound (**C**)

CONCLUSION

It is observed that in all the three compounds the dihydropyridine ring is perpendicular to the phenyl ring while in the compound (C) the deviation from perpendicularity is due to the additional substitution at *p*-position.

TABLE X Torsion angle in deg

Compounds	*Atoms*	*Torsion angle in deg*
Compound (A)	C6-C5-C4-C3	30.7(4)
	C2-C3-C4-C5	−32.6(3)
	C6-N1-C2-C3	15.5(4)
	C2-N1-C6-C5	−17.6(4)
Compound (B)	C3-C4-C5-C6	26.8(3)
	C5-C4-C3-C2	−31.1(3)
	C5-C6-N1-C2	−17.6(4)
	C3-C2-N1-C6	13.1(4)
Compound (C)	C6-C5-C4-C3	−31.9(4)
	C2-C3-C4-C5	31.0(4)]
	C6-N1-C2-C3	−19.6(5)
	C2-N1-C6-C5	18.4(5)

TABLE XI Hydrogen bonds

Compound	*Atoms*	*Angle in (°)*	*Angle in (°)*	*Symmetry Code*
(A)	N1-H1···O4	3.023(4)	179(4)	$-1 + x, y, z$
(B)	N1-H1···O1	2.966(5)	172(4)	$-1 + x, y, z$
	C25-H25···O1	3.415(4)	147(4)	$-x, 1 - y, -z$
(C)	N1-H1···O1	2.9723(4)	178.51	$-1 + x, y, z$

The bond lengths and bond angles are comparable with those reported for the structures of 2,6-dimethyl-3,5-dicarbomethoxy-4-(unsubstituted, 3-methyl-, 4-methyl-, 3-nitro-, 4-nitro-, and 2,4-dinitrophenyl)-1,4-dihydropyridine [17]. The conformation of the dihydropyridine ring is best described in terms of the torsion angles about the intra-ring bonds. The degrees of the ring distortion at N1 and C4 are directly reflected in the magnitude of the torsion angles about the ring bonds emanating from these two atoms. The torsion angles about the C4 ring bonds are greater than those for the N1 bonds, indicating that the puckering is greater at C4. This is evident from the values of torsion angles given in Table X. The packing of the molecules of all the three compounds is stabilised by hydrogen bonds and Van der Waal's forces.

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