A novel 4-(4,5-dimethoxy-2-nitrophenyl)-2,6-dimethyl-3,5-dicarbethoxy-1,4-dihydropyridine (C₂₁H₂₆N₂O₈): Microwave irradiated Hantzsch ester synthesis, characterization and molecular crystal

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Abstract

The novel 4-(4,5-dimethoxy-2-nitrophenyl)-2,6-dimethyl-3,5-dicarbethoxy-1,4-dihydropyridine was synthesized through multi-component one pot Hantzsch ester synthesis using 4,5-dimethoxy-2-nitrobenzaldehyde, ethyl 3-oxobutanoate and ammonium carbonate under microwave irradiation and subsequently characterized by several spectroscopic techniques i.e. ESI mass, IR, ¹H and ¹³C NMR along with single crystal X-ray diffraction method. The single crystal of 4-(4,5-dimethoxy-2-nitrophenyl)-2,6-dimethyl-3,5-dicarbethoxy-1,4-dihydropyridine (C₂₁H₂₆N₂O₈) was developed in 0.35 × 0.30 × 0.25 mm dimension in methanol. The crystal structure parades only intermolecular hydrogen bonding of the N(2)-H(2A)...O(2) type and the boat conformation of the dihydropyridine ring.

Supplementary data of the article: Figure 3 to 8.

Figure 3. Mass spectrum of title compound ($C_{21}H_{26}N_2O_8$)

Figure 4. IR spectrum of title compound ($C_{21}H_{26}N_2O_8$)

Figure 5a. ^1H NMR spectrum of title compound ($\text{C}_{21}\text{H}_{26}\text{N}_2\text{O}_8$)

Figure 5b. ¹H NMR spectrum of title compound (C₂₁H₂₆N₂O₈)

Figure 5c. ¹H NMR spectrum of title compound (C₂₁H₂₆N₂O₈)

Figure 5d. ¹H NMR spectrum of title compound (C₂₁H₂₆N₂O₈)

Figure 6a. ¹³C NMR spectrum of title compound (C₂₁H₂₆N₂O₈)

Figure 6b. ¹³C NMR spectrum of title compound (C₂₁H₂₆N₂O₈)

Figure 6c. ¹³C NMR spectrum of title compound (C₂₁H₂₆N₂O₈)

Figure 7a. ^1H NMR- D_2O exchange spectrum of title compound ($\text{C}_{21}\text{H}_{26}\text{N}_2\text{O}_8$)

Figure 7b. ^1H NMR- D_2O exchange spectrum of title compound ($\text{C}_{21}\text{H}_{26}\text{N}_2\text{O}_8$)

Figure 7c. ^1H NMR- D_2O exchange spectrum of title compound ($\text{C}_{21}\text{H}_{26}\text{N}_2\text{O}_8$)

Figure 7d. ^1H NMR- D_2O exchange spectrum of title compound ($\text{C}_{21}\text{H}_{26}\text{N}_2\text{O}_8$)

Figure 8. PXRD of 4-(4,5-dimethoxy-2-nitrophenyl)-2,6-dimethyl-3,5-dicarbethoxy-1,4-dihydropyridine, the title compound ($C_{21}H_{26}N_2O_8$)

Figure 8. PXRD of previously reported compound 4-(4,5-dimethoxy-2-nitrophenyl)-2,6-dimethyl-3,5-dicarbmethoxy-1,4-dihydropyridine [25]

Table S1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $C_{21}H_{26}N_2O_8$

No.	Atom	x	y	z	U(eq)
1	C(1)	8205(2)	1933(1)	5557(1)	56(1)
2	C(2)	7829(2)	1735(1)	6420(1)	53(1)
3	C(3)	9101(2)	1761(1)	7198(1)	47(1)
4	C(4)	10400(2)	2312(1)	6977(1)	44(1)
5	C(5)	10746(2)	2461(1)	6092(1)	49(1)

6	C(6)	11180(2)	2661(1)	7768(1)	55(1)
7	C(9)	6208(2)	1478(1)	6636(2)	72(1)
8	C(12)	7115(3)	1936(1)	4709(1)	81(1)
9	C(13)	12123(3)	2894(1)	5740(1)	74(1)
10	N(1)	9722(2)	2197(1)	5404(1)	56(1)
11	C(14)	9848(2)	1008(1)	7369(1)	46(1)
12	O(5)	8157(13)	1340(8)	9021(9)	105(4)
13	O(6)	10178(6)	872(2)	9738(2)	84(2)
14	O(7)	12470(30)	-301(12)	6069(12)	72(4)
15	O(8)	12200(30)	-1024(12)	7466(16)	77(4)
16	N(2)	9373(11)	991(5)	9036(6)	60(2)
17	C(15)	9950(50)	637(13)	8198(10)	50(4)
18	C(16)	10800(30)	-15(9)	8240(9)	47(3)
19	C(17)	11360(40)	-363(10)	7471(13)	52(3)
20	C(18)	11490(30)	42(10)	6661(11)	51(4)
21	C(19)	10680(20)	703(9)	6650(8)	57(5)
22	C(20)	12530(20)	142(10)	5264(13)	68(4)
23	C(21)	12641(15)	-1267(5)	8430(9)	51(3)
24	O(5')	8770(9)	1383(3)	9215(5)	92(2)
25	O(6')	8261(4)	272(2)	9396(2)	109(1)
26	O(7')	12080(17)	-291(6)	6001(7)	75(3)
27	O(8')	12367(16)	-964(7)	7638(9)	72(2)
28	N(2')	8903(7)	761(3)	8981(4)	66(2)
29	C(15')	9820(30)	581(8)	8157(6)	56(3)
30	C(16')	10552(16)	-94(6)	8281(7)	63(3)
31	C(17')	11500(20)	-342(6)	7597(8)	54(2)
32	C(18')	11388(19)	15(5)	6746(7)	57(2)
33	C(19')	10622(12)	680(4)	6641(5)	51(3)
34	C(20')	12429(13)	84(5)	5171(8)	74(3)
35	C(21')	12709(15)	-1302(5)	8480(8)	124(4)
36	O(1)	12035(8)	3252(3)	7594(6)	58(1)
37	O(2)	10897(17)	2433(6)	8526(4)	73(2)
38	C(7)	12674(12)	3643(4)	8399(6)	77(2)
39	C(8)	13690(20)	4205(8)	7960(12)	113(6)
40	O(1')	12536(13)	3031(7)	7568(6)	98(3)
41	O(2')	10805(17)	2653(8)	8563(5)	89(4)
42	C(7')	13416(18)	3468(6)	8244(7)	107(4)
43	C(8')	13460(20)	4265(8)	8052(12)	102(4)
44	C(10)	4358(19)	1117(9)	7750(10)	118(3)
45	C(11)	4265(18)	1247(11)	8719(10)	156(5)
46	O(3)	5931(17)	1415(6)	7530(4)	99(3)
47	O(4)	5233(11)	1293(6)	6031(7)	113(3)
48	C(10')	4660(20)	1126(17)	7928(11)	104(5)
49	C(11')	4720(20)	1016(14)	8900(11)	137(6)
50	O(3')	6200(20)	1340(9)	7546(5)	76(3)
51	O(4')	4951(18)	1450(12)	6192(13)	112(5)

U(eq) = 1/3 of the trace of the orthogonalized Uij tensor

Table S2. Selected bond lengths [Å] and angles [°] for C₂₁H₂₆N₂O₈

No.	Atoms	Lengths [Å]	No.	Atoms	Angles [°]
1	C(6)-O(2')	1.206(6)	38	C(2)-C(1)-N(1)	119.10(15)
2	C(6)-O(2)	1.209(5)	39	C(2)-C(1)-C(12)	127.53(19)
3	C(6)-O(1)	1.323(5)	40	N(1)-C(1)-C(12)	113.30(17)
4	C(6)-O(1')	1.354(6)	41	C(1)-C(2)-C(9)	121.75(18)
5	C(9)-O(4')	1.208(7)	42	C(1)-C(2)-C(3)	120.31(16)
6	C(9)-O(4)	1.221(5)	43	C(9)-C(2)-C(3)	117.93(17)
7	C(9)-O(3)	1.333(5)	44	C(4)-C(3)-C(2)	110.04(13)
8	C(9)-O(3')	1.347(7)	45	C(4)-C(3)-C(14)	110.37(13)
9	C(12)-H(12A)	0.9600	46	C(2)-C(3)-C(14)	111.10(13)
10	C(12)-H(12B)	0.9600	47	O(4')-C(9)-O(3)	110.0(11)
11	C(12)-H(12C)	0.9600	48	O(4)-C(9)-O(3)	123.1(7)
12	C(13)-H(13A)	0.9600	49	O(4')-C(9)-O(3')	118.9(11)
13	C(13)-H(13B)	0.9600	50	O(4)-C(9)-O(3')	129.0(7)
14	C(13)-H(13C)	0.9600	51	O(3)-C(9)-O(3')	11.2(14)
15	N(1)-H(1)	0.896(14)	52	O(4')-C(9)-C(2)	132.8(9)
16	C(14)-C(15)	1.383(7)	53	O(4)-C(9)-C(2)	121.6(6)
17	C(14)-C(15')	1.388(5)	54	O(3)-C(9)-C(2)	115.2(5)
18	C(14)-C(19)	1.389(7)	55	O(3')-C(9)-C(2)	107.7(7)
19	C(14)-C(19')	1.394(4)	56	C(5)-C(13)-H(13C)	109.5
22	O(7)-C(18)	1.362(8)	57	C(1)-N(1)-C(5)	123.56(14)
23	O(7)-C(20)	1.426(7)	58	C(1)-N(1)-H(1)	119.2(12)
24	O(8)-C(17)	1.40(2)	59	C(5)-N(1)-H(1)	115.9(12)
25	O(8)-C(21)	1.50(2)	60	C(15)-C(14)-C(15')	7(3)
26	N(2)-C(15)	1.474(9)	61	C(15)-C(14)-C(19)	116.0(8)
27	C(15)-C(16)	1.390(7)	62	C(15')-C(14)-C(19)	114.6(7)
28	C(16)-C(17)	1.379(7)	63	C(15)-C(14)-C(19')	115.6(6)
29	C(16)-H(16)	0.9300	64	C(15')-C(14)-C(19')	113.9(5)
30	C(17)-C(18)	1.399(7)	65	C(19)-C(14)-C(19')	2.6(13)
31	C(18)-C(19)	1.384(7)	66	C(15)-C(14)-C(3)	126.7(5)
32	C(19)-H(19)	0.9300	67	C(15')-C(14)-C(3)	128.6(3)
33	C(21)-H(21A)	0.9600	68	C(17)-O(8)-C(21)	111.0(17)
34	C(21)-H(21B)	0.9600	69	O(5)-N(2)-O(6)	123.3(9)
35	C(21)-H(21C)	0.9600	70	O(5)-N(2)-C(15)	121.3(14)
36	O(8')-C(21')	1.393(16)	71	C(17)-C(16)-H(16)	118.5
37	N(2')-C(15')	1.476(6)	72	N(1)-C(5)-C(13)	113.50(14)

Symmetry transformations used to generate equivalent atoms:

Table S3. Anisotropic displacement parameters (Å² × 10³) for C₂₁H₂₆N₂O₈

No.	Atoms	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
1	C(1)	67(1)	45(1)	55(1)	-11(1)	-19(1)	7(1)
2	C(2)	51(1)	47(1)	59(1)	-11(1)	-8(1)	4(1)
3	C(3)	51(1)	54(1)	37(1)	-5(1)	3(1)	-3(1)
4	C(4)	51(1)	49(1)	33(1)	-3(1)	-1(1)	-2(1)
5	C(5)	60(1)	52(1)	34(1)	-2(1)	-1(1)	0(1)

6	C(6)	67(1)	61(1)	36(1)	0(1)	-4(1)	-9(1)
7	C(9)	51(1)	57(1)	106(2)	-16(1)	-8(1)	2(1)
8	C(12)	101(2)	65(1)	74(1)	-9(1)	-46(1)	8(1)
9	C(13)	87(2)	92(2)	42(1)	4(1)	11(1)	-21(1)
10	N(1)	76(1)	62(1)	30(1)	-3(1)	-6(1)	0(1)
11	C(14)	47(1)	52(1)	40(1)	-2(1)	-2(1)	-8(1)
12	O(5)	95(6)	152(9)	69(7)	12(5)	37(4)	37(6)
13	O(6)	120(4)	94(3)	37(2)	-2(2)	-6(2)	7(3)
14	O(7)	85(7)	79(5)	54(4)	11(3)	14(4)	30(4)
15	O(8)	129(7)	43(4)	59(8)	9(4)	-13(4)	14(4)
16	N(2)	83(5)	51(5)	47(4)	9(3)	14(3)	-5(4)
17	C(15)	60(8)	51(6)	40(6)	-3(5)	-7(4)	-5(5)
18	C(16)	52(6)	58(5)	30(4)	19(3)	-4(4)	-5(4)
19	C(17)	70(7)	40(5)	46(5)	-1(4)	-11(5)	-3(4)
20	C(18)	60(7)	60(7)	33(5)	13(5)	0(4)	3(5)
21	C(19)	53(9)	75(9)	44(10)	13(7)	-4(7)	20(7)
22	C(20)	76(7)	92(9)	37(4)	-10(4)	16(5)	46(7)
23	C(21)	74(6)	23(4)	56(6)	10(4)	17(5)	7(4)
24	O(5')	150(6)	74(3)	54(3)	-10(2)	31(3)	-7(3)
25	O(6')	131(3)	98(2)	104(2)	30(2)	64(2)	5(2)
26	O(7')	114(7)	57(3)	53(3)	3(2)	20(3)	30(3)
27	O(8')	101(4)	64(4)	51(4)	7(3)	7(4)	15(3)
28	N(2')	79(3)	73(3)	46(2)	11(2)	14(2)	-3(2)
29	C(15')	53(4)	76(6)	37(3)	4(4)	5(4)	-3(4)
30	C(16')	66(5)	67(4)	57(3)	16(3)	12(3)	-6(3)
31	C(17')	64(4)	53(4)	46(3)	9(3)	-2(4)	-3(3)
32	C(18')	78(5)	47(4)	48(4)	-8(3)	14(3)	-3(3)
33	C(19')	78(6)	38(4)	36(5)	-1(3)	9(4)	-10(3)
34	C(20')	112(6)	64(4)	48(4)	2(3)	13(3)	-18(4)
35	C(21')	148(8)	113(7)	111(6)	63(5)	-10(6)	20(6)
36	O(1)	74(3)	54(2)	46(2)	-11(2)	-1(2)	-19(2)
37	O(2)	121(4)	73(5)	23(2)	-5(2)	-6(2)	-34(3)
38	C(7)	84(5)	84(4)	64(4)	-28(3)	-3(3)	-34(3)
39	C(8)	103(7)	115(8)	123(10)	-52(6)	18(6)	-67(7)
40	O(1')	121(5)	124(6)	47(2)	4(4)	-18(3)	-70(5)
41	O(2')	118(4)	112(9)	39(3)	-24(3)	10(2)	-47(5)
42	C(7')	125(7)	140(7)	54(4)	-5(4)	-27(5)	-66(6)
43	C(8')	127(9)	111(6)	70(5)	-26(5)	22(6)	-10(6)
44	C(10)	50(5)	129(6)	178(8)	-45(6)	22(5)	-25(5)
45	C(11)	63(6)	230(11)	178(9)	-84(9)	37(6)	-27(6)
46	O(3)	49(3)	134(5)	114(4)	-48(4)	11(2)	-8(3)
47	O(4)	54(3)	140(4)	144(5)	-49(4)	-17(3)	-23(3)
48	C(10')	35(7)	161(10)	119(8)	-28(7)	21(5)	-48(6)
49	C(11')	54(8)	235(15)	125(7)	36(10)	41(6)	-35(8)
50	O(3')	42(5)	93(5)	96(6)	7(4)	25(3)	-28(4)
51	O(4')	49(4)	168(10)	117(7)	30(8)	-19(5)	2(5)

The anisotropic displacement factor exponent takes the form: $-2 \pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

Table S4. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{C}_{21}\text{H}_{26}\text{N}_2\text{O}_8$

No.	Atom	x	y	z	U(eq)
1	H(3)	8582	1917	7761	57
2	H(12A)	6249	1597	4787	122
3	H(12B)	7718	1797	4185	122
4	H(12C)	6681	2416	4615	122
5	H(13A)	11905	3405	5809	110
6	H(13B)	12255	2785	5101	110
7	H(13C)	13093	2771	6084	110
8	H(16)	11005	-228	8814	56
9	H(19)	10692	969	6106	69
10	H(20A)	11462	192	4995	102
11	H(20B)	13216	-83	4827	102
12	H(20C)	12948	614	5427	102
13	H(21A)	13162	-874	8759	76
14	H(21B)	13361	-1676	8408	76
15	H(21C)	11684	-1406	8738	76
16	H(16')	10402	-368	8810	76
17	H(19')	10624	913	6072	61
18	H(20D)	11439	237	4868	112
19	H(20E)	13000	-235	4772	112
20	H(20F)	13081	504	5314	112
21	H(21D)	13347	-982	8867	186
22	H(21E)	13297	-1745	8381	186
23	H(21F)	11720	-1414	8774	186
24	H(7A)	13314	3327	8803	93
25	H(7B)	11820	3864	8744	93
26	H(8A)	14607	3975	7699	170
27	H(8B)	14049	4554	8414	170
28	H(8C)	13068	4448	7483	170
29	H(7'1)	14517	3290	8293	128
30	H(7'2)	12940	3395	8838	128
31	H(8'1)	13873	4346	7451	153
32	H(8'2)	14145	4502	8506	153
33	H(8'3)	12389	4462	8075	153
34	H(10A)	3497	1366	7409	142
35	H(10B)	4301	599	7614	142
36	H(11A)	5144	1005	9039	234
37	H(11B)	3262	1062	8931	234
38	H(11C)	4327	1762	8835	234
39	H(10C)	3871	1500	7779	125
40	H(10D)	4303	678	7632	125
41	H(11D)	5389	603	9049	205
42	H(11E)	3648	928	9105	205
43	H(11F)	5154	1442	9200	205
44	H(1)	10000(20)	2297(10)	4826(11)	65(5)

Table S5. Selected torsion angles [°] for C₂₁H₂₆N₂O₈

No.	Atom	Angle [°]	No.	Atom	Angle [°]
1	N(1)-C(1)-C(2)-C(9)	177.41(16)	43	C(20)-O(7)-C(18)-C(19)	-4(4)
2	C(12)-C(1)-C(2)-C(9)	0.7(3)	44	C(20)-O(7)-C(18)-C(17)	180(2)
3	N(1)-C(1)-C(2)-C(3)	-3.8(2)	45	C(16)-C(17)-C(18)-O(7)	162(3)
4	C(12)-C(1)-C(2)-C(3)	179.48(16)	46	O(8)-C(17)-C(18)-O(7)	-3(4)
5	C(1)-C(2)-C(3)-C(4)	25.0(2)	47	C(16)-C(17)-C(18)-C(19)	-15(4)
6	C(9)-C(2)-C(3)-C(4)	-156.14(15)	48	O(8)-C(17)-C(18)-C(19)	-179(3)
7	C(1)-C(2)-C(3)-C(14)	-97.52(18)	49	O(7)-C(18)-C(19)-C(14)	-172(3)
17	C(5)-C(4)-C(6)-O(2')	167.5(11)	50	C(15)-C(14)-C(15')-N(2')	81(8)
18	C(3)-C(4)-C(6)-O(2')	-11.2(11)	51	C(19)-C(14)-C(15')-N(2')	-174.8(18)
19	C(5)-C(4)-C(6)-O(2)	-172.5(9)	52	C(19')-C(14)-C(15')-N(2')	-172.1(16)
20	C(3)-C(4)-C(6)-O(2)	8.8(9)	53	C(3)-C(14)-C(15')-N(2')	5(3)
21	C(5)-C(4)-C(6)-O(1)	13.5(4)	54	O(5')-N(2')-C(15')-C(14)	-35(3)
22	C(3)-C(4)-C(6)-O(1)	-165.2(3)	55	O(6')-N(2')-C(15')-C(14)	142.6(17)
23	C(5)-C(4)-C(6)-O(1')	-14.1(8)	56	O(5')-N(2')-C(15')-C(16')	147.9(14)
24	C(3)-C(4)-C(6)-O(1')	167.2(7)	57	O(6')-N(2')-C(15')-C(16')	-34(2)
25	C(1)-C(2)-C(9)-O(4')	-7.6(17)	58	C(14)-C(15')-C(16')-C(17')	6(3)
26	C(3)-C(2)-C(9)-O(4')	173.6(17)	59	N(2')-C(15')-C(16')-C(17')	-177.8(16)
27	C(1)-C(2)-C(9)-O(4)	14.8(7)	60	C(21')-O(8')-C(17')-C(16')	-18(3)
28	C(3)-C(2)-C(9)-O(4)	-164.0(7)	61	C(21')-O(8')-C(17')-C(18')	171.9(15)
29	C(1)-C(2)-C(9)-O(3)	-169.6(7)	62	C(15')-C(16')-C(17')-O(8')	176(2)
30	C(3)-C(2)-C(9)-O(3)	11.6(7)	63	C(15')-C(16')-C(17')-C(18')	-14(3)
31	C(1)-C(2)-C(9)-O(3')	-178.7(8)	64	C(20')-O(7')-C(18')-C(19')	16(2)
32	C(3)-C(2)-C(9)-O(3')	2.5(9)	65	C(20')-O(7')-C(18')-C(17')	-162.7(16)
33	C(2)-C(1)-N(1)-C(5)	-18.4(3)	66	O(8')-C(17')-C(18')-O(7')	3(2)
34	O(6)-N(2)-C(15)-C(14)	-142(3)	67	O(4)-C(9)-O(3)-C(10)	-0.8(15)
35	O(5)-N(2)-C(15)-C(16)	-148(3)	68	O(3')-C(9)-O(3)-C(10)	-126(5)
36	O(6)-N(2)-C(15)-C(16)	29(4)	69	C(2)-C(9)-O(3)-C(10)	-176.3(9)
37	C(14)-C(15)-C(16)-C(17)	-9(5)	70	C(11)-C(10)-O(3)-C(9)	-168.8(11)
38	N(2)-C(15)-C(16)-C(17)	180(3)	71	O(4')-C(9)-O(3')-C(10')	3(2)
39	C(15)-C(16)-C(17)-O(8)	-179(3)	72	O(4)-C(9)-O(3')-C(10')	-19(2)
40	C(15)-C(16)-C(17)-C(18)	19(5)	73	O(3)-C(9)-O(3')-C(10')	43(4)
41	C(21)-O(8)-C(17)-C(16)	-8(4)	74	C(2)-C(9)-O(3')-C(10')	175.7(18)
42	C(21)-O(8)-C(17)-C(18)	155(2)	75	C(11')-C(10')-O(3')-C(9)	-177.6(19)

Symmetry transformations used to generate equivalent atoms: