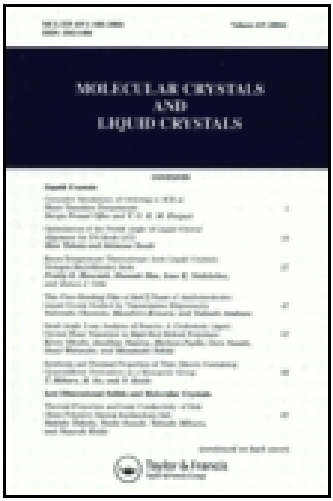

Molecular Crystals and Liquid Crystals

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Microwave-Assisted Synthesis and Crystal Structure of 1-(4-Chlorophenyl)-4,5-diphenyl-2-(3,4,5-trimethoxy-phenyl)-1H-imidazole

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Microwave-Assisted Synthesis and Crystal Structure of 1-(4-Chlorophenyl)-4,5-diphenyl-2-(3,4,5-trimethoxy-phenyl)-1H-imidazole

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The title compound, 1-(4-chlorophenyl)-4,5-diphenyl-2-(3,4,5-trimethoxy-phenyl)-1H-imidazole, was synthesized using a domestic microwave oven, and the structure of the product obtained was confirmed by X-ray diffraction (XRD) studies. The compound, $C_{30}H_{25}ClN_2O_3$, crystallizes in the triclinic crystal class in the space group $P\bar{1}$ with cell parameters $a = 10.635(15)$ Å, $b = 12.262(2)$ Å, $c = 11.656(3)$ Å, $\alpha = 69.817(15)^\circ$, $\beta = 64.630(6)^\circ$, $\gamma = 73.503(16)^\circ$, and $Z = 2$. The structure has been solved by direct methods and refined to $R_1 = 0.0764$ for 3078 unique reflections with $I > 2\sigma(I)$. The imidazole ring in the structure adopts a planar conformation. No classic hydrogen bonds were found in the structure.

Keywords: crystal structure; equatorial confirmation; imidazole ring; microwave oven

INTRODUCTION

Several biologically active synthetic compounds possess five-membered nitrogen containing heterocycles in their structure [1]. The imidazole core is a common moiety in a large number of natural products and pharmacologically active compounds [2]. Recently, there has been considerable amount of progress in imidazole structure in biological process. Of late in drug therapy, imidazole containing compounds such as etomidate, cimetidine, omeprazole, and lansoprazole find large applications [3]. On the other hand, microwave assisted solid phase organic synthesis is a relatively new technique that has

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shown significant improvement in the generation of combinatorial libraries of small molecules [4]. Various types of thermally conducted organic reactions have been accelerated by microwave irradiation [5]. Microwave irradiation has been demonstrated to dramatically accelerate many organic reactions and improves the yields and selectivity [6]. These advantage offer an opportunity for a convenient and rapid library synthesis of substituted imidazoles.

EXPERIMENTAL

All the chemicals and solvents used in this work were obtained from E-Merck, Ltd., Mumbai and S.D. Fine Chem., Ltd., Mumbai, and were used without further purification. Kenstar microwave system (OM 9925-E) was used, and the output of microwave power is mentioned as percent intensity (20%, 40%, 60%, 80%, 100%). The elemental analysis (CHNS analysis) was done on a CHNS rapid analyzer. Purity of the compounds was checked by thin layer chromatography (TLC).

Synthesis of 1-(4-Chlorophenyl)-4,5-diphenyl-2(3,4,5-trimethoxy-phenyl)-1H-imidazole

A mixture of 5 g silica gel, Benzil (631 mg, 3 m mol), 3,4,5-trimethoxybenzaldehyde (589 mg, 3 m mol), *p*-chloroaniline (391 mg, 3 m mol), and ammonium acetate (232 mg, 3 m mol) was ground in a mortar until a fine powder was formed. The reaction mixture was then transferred into an open beaker (250 ml) and irradiated with microwaves for 9 minutes at 70% power. The progress of the reaction was monitored by thin layer chromatography (TLC) using C_6H_{14}:EtOAc. (90:10) as the eluent. The mixture was extracted with CH_2Cl_2 ($3 \times 30\,cm^3$), filtered and washed with water. The organic phase was removed under reduced pressure. Further purification by column chromatography (eluent C_6H_{14}:EtOAc. (90:10)) on silica gel gave the desired product [7]. Schematic diagram of the molecule is as shown in the Fig. 1.

Crystal Structure Determination

A single crystal of the title compound with dimensions $0.3 \times 0.27 \times 0.25$ mm was chosen for X-ray diffraction (XRD) study. The data were collected on a DIPLabo Image Plate system equipped with a normal focus, 3 kW sealed X-ray source (graphite monochromated MoK_α). The crystal to detector distance is fixed at 120 mm with a detector area of $441 \times 240\,mm^2$. Thirty-six frames of data were collected at room temperature by the oscillation method. Each exposure of the image

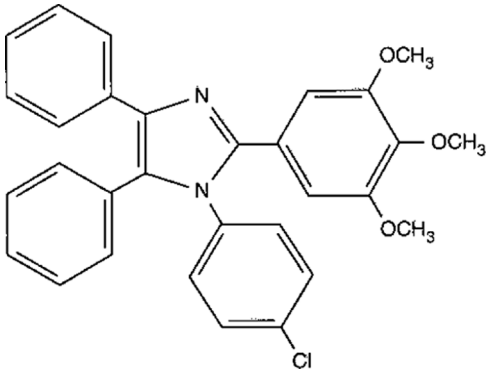

FIGURE 1 Schematic diagram of the molecule.

plate was set to a period of 400 s. Successive frames were scanned in steps of 5° per minute with an oscillation range of 5°. Image processing and data reduction were done using Denzo [8]. The reflections were merged with Scalepack [9]. All the frames could be indexed using primitive triclinic lattice. The structure was solved by direct methods using SHELXS-97. All of the non-hydrogen atoms were revealed in the first Fourier map itself. Full-matrix least squares refinement using SHELXL-97, with isotropic temperature factors for all the atoms converged the residuals to $R_1 = 0.1577$. Refinement of the non-hydrogen atoms with anisotropic thermal parameters was started at this stage. The hydrogen atoms were placed at chemically acceptable positions and were allowed to ride on the parent atoms; 329 parameters were refined with 3078 unique reflections which saturated the residuals to $R_1 = 0.0764$. The details of the crystal data and refinement are given in Table 1.[1]

Table 2 gives the list of atomic coordinates and equivalent thermal parameters. Tables 3 and 4 give the list of bond lengths and bond angles, respectively, which are in good agreement with the standard values. An ORTEP diagram of the molecule with thermal ellipsoids drawn at 50% probability is shown in Fig. 2.

The molecule consists of two phenyl rings, one chlorophenyl ring, and one trimethoxyphenyl ring. The imidazole ring is planar with a maximum deviation of −0.008(5) Å for the atom C5. The formal single

[1]CCDC 730169 consists the supplementary crystallographic data for this paper. These data can be obrained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB21EZ, UK; Fax: +45(0)1233-336033). E-mail: deposit@ccdc.cam.ac.uk

TABLE 1 Crystal Data and Structure Refinement Table

CCDC Deposition number	CCDC 730169
Empirical formula	$C_{30}H_{25}ClN_2O_3$
Formula weight	496.97
Temperature	293(2)K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	$P\bar{1}$
Cell dimensions	$a = 10.635(3)$ Å $b = 12.262(2)$ Å $c = 11.656(3)$ Å $\alpha = 69.817(15)^\circ$ $\beta = 64.630(6)^\circ$ $\gamma = 73.503(16)^\circ$
Volume	1272.4(5) Å^3
Z	2
Density (calculated)	1.297 Mg/m^3
Absorption coefficient	0.185 mm^{-1}
F_{000}	520
Crystal size	$0.3 \times 0.27 \times 0.25$ mm
Theta range for data collection	2.2° to 23.3°
Index ranges	$-11 \le h \le 11$ $-12 \le k \le 12$ $-12 \le l \le 12$
Independent reflections	3078 [R(int) = 0.056]
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data/parameters	3078/329
Goodness-of-fit on F^2	1.056
Final R indices	$R1 = 0.0764$
Largest diff. peak, and hole	0.88 and −0.32 e Å^{-3}

bonds C2–N3 (1.372(4) Å) and N3–C4 (1.394(5) Å) have a partial double bond character, and are significantly shorter than the Csp^2–N bond distance. The bond angle values of 117.3(4)° and 118.2(4)° about C25 and C31 are relatively smaller compared to the standard value, which can be attributed to the steric hindrance between the imidazole ring and the respective phenyl rings. The two phenyl rings are equatorial to each other as the dihedral angle between the two rings is 67.8(2)°. The rings C25–C30 and C31–C36 are twisted by the angles 15.2(3)° and 68.2(3)°, respectively, with respect to the imidazole ring, which are different from the values of 31.5(1)°, 41.7(1)° reported for 2-(2-methylphenyl)-4,5-diphenyl-1H-imidazole [10]. The dihedral angle between the imidazole ring and the chlrophenyl ring is 71.4(2)° which deviates from the value of 40.74(8)° reported earlier for 1-benzyl-2-(4-chlorophenyl)-4,5-diphenyl-1H-imidazole [11]. The torsion angles

TABLE 2 Atomic Coordinates and Equivalent Thermal Parameters of the Non-Hydrogen Atoms

Atom	*x*	*y*	*z*	U_{eq}
C2	0.4248(4)	0.8574(3)	−0.1056(3)	0.0543(1)
N1	0.3381(3)	0.9523(3)	−0.1360(3)	0.0584(9)
C5	0.2490(4)	0.9815(3)	−0.0206(4)	0.0571(1)
C4	0.2848(4)	0.9033(3)	0.0828(4)	0.0565(1)
N3	0.3979(3)	0.8229(3)	0.0268(3)	0.0550(9)
C6	0.4647(4)	0.7226(3)	0.1010(3)	0.0549(1)
C7	0.5495(5)	0.7394(4)	0.1525(4)	0.0668(1)
C8	0.6161(5)	0.6414(4)	0.2238(4)	0.0733(1)
C9	0.5970(5)	0.5304(4)	0.2394(4)	0.0671(1)
C10	0.5112(4)	0.5145(4)	0.1867(4)	0.0645(1)
C11	0.4459(4)	0.6106(4)	0.1171(4)	0.0611(1)
C112	0.6767(2)	0.4108(1)	0.3302(2)	0.0999(6)
C13	0.5389(4)	0.7966(3)	−0.2026(3)	0.0537(1)
C14	0.6611(4)	0.7301(3)	−0.1844(4)	0.0567(1)
C15	0.7633(4)	0.6767(3)	−0.2794(4)	0.0542(1)
C16	0.7469(4)	0.6911(3)	−0.3958(3)	0.0566(1)
C17	0.6263(4)	0.7608(3)	−0.4156(3)	0.0571(1)
C18	0.5218(4)	0.8121(3)	−0.3195(4)	0.0574(1)
O19	0.8858(3)	0.6079(3)	−0.2675(3)	0.0736(9)
C20	0.9173(5)	0.6032(5)	−0.1600(5)	0.0891(2)
O21	0.8514(3)	0.6394(3)	−0.4919(3)	0.0709(9)
C22	0.8236(6)	0.5329(5)	−0.4916(5)	0.0935(2)
O23	0.6198(3)	0.7711(3)	−0.5335(3)	0.0746(9)
C24	0.4992(5)	0.8452(4)	−0.5603(4)	0.0774(1)
C25	0.1345(4)	1.0824(3)	−0.0184(4)	0.0584(1)
C26	0.1334(5)	1.1648(4)	−0.1357(5)	0.0770(1)
C27	0.0260(6)	1.2602(5)	−0.1372(6)	0.0962(2)
C28	−0.0841(5)	1.2744(5)	−0.0206(7)	0.0948(2)
C29	−0.0848(5)	1.1934(5)	0.0937(6)	0.0851(2)
C30	0.0222(5)	1.0985(4)	0.0960(5)	0.0745(1)
C31	0.2314(4)	0.8967(3)	0.2244(4)	0.0578(1)
C32	0.2537(4)	0.9814(4)	0.2645(4)	0.0642(1)
C33	0.2049(5)	0.9778(5)	0.3949(5)	0.0779(1)
C34	0.1366(5)	0.8858(5)	0.4883(4)	0.0796(1)
C35	0.1167(5)	0.8003(4)	0.4512(4)	0.0795(1)
C36	0.1614(5)	0.8063(4)	0.3204(4)	0.0703(1)

about N1–C2–C13–C14 and N3–C2–C13–C18 are 153.0(4)° and 156.5(4)°, respectively, which determines the conformation of the junction between the imidazole and trimethoxyphenyl rings. The chlorophenyl and trimethoxyphenyl rings are in the *–synperiplanar* conformation as indicated by the torsion angle value of −3.2(7)° about the atoms C6–N3–C2–C13. No classic hydrogen bonds were found in the molecule.

TABLE 3 Bond Length (Å)

Atoms	Length	Atoms	Length
C2–N1	1.309(5)	C15–C16	1.385(5)
C2–N3	1.373(4)	C16–O21	1.384(4)
C2–C13	1.483(5)	C16–C17	1.386(5)
N1–C5	1.371(5)	C17–O23	1.367(5)
C5–C4	1.381(5)	C17–C18	1.381(5)
C5–C25	1.468(5)	O19–C20	1.408(5)
C4–N3	1.393(5)	O21–C22	1.417(6)
C4–C31	1.477(5)	O23–C24	1.433(5)
N3–C6	1.435(5)	C25–C30	1.387(6)
C6–C7	1.368(6)	C25–C26	1.394(6)
C6–C11	1.381(6)	C26–C27	1.385(7)
C7–C8	1.403(6)	C27–C28	1.390(8)
C8–C9	1.371(6)	C28–C29	1.358(8)
C9–C10	1.383(6)	C29–C30	1.380(6)
C9–C112	1.728(4)	C31–C32	1.386(6)
C10–C11	1.374(6)	C31–C36	1.391(6)
C13–C14	1.384(5)	C32–C33	1.369(6)
C13–C18	1.392(5)	C33–C34	1.387(7)
C14–C15	1.379(5)	C34–C35	1.360(7)
C15–O19	1.371(5)	C35–C36	1.371(6)

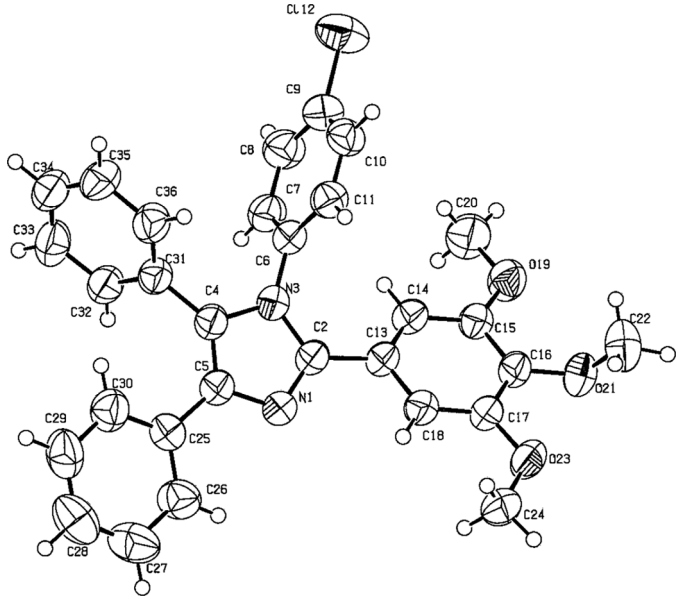

FIGURE 2 ORTEP of the molecule with thermal ellipsoids drawn at 50% probability.

TABLE 4 Bond Angles (°)

Atoms	Angle	Atoms	Angle
N1–C2–N3	111.3(3)	O19–C15–C16	115.7(3)
N1–C2–C13	124.2(3)	C14–C15–C16	120.6(4)
N3–C2–C13	124.5(3)	O21–C16–C15	120.3(4)
C2–N1–C5	106.7(3)	O21–C16–C17	120.8(3)
N1–C5–C4	110.0(3)	C15–C16–C17	119.0(3)
N1–C5–C25	121.1(3)	O23–C17–C18	124.2(4)
C4–C5–C25	128.8(4)	O23–C17–C16	114.9(3)
C5–C4–N3	105.1(3)	C18–C17–C16	120.8(3)
C5–C4–C31	133.1(4)	C17–C18–C13	119.8(4)
N3–C4–C31	121.7(3)	C15–O19–C20	118.1(3)
C2–N3–C4	106.8(3)	C16 O21–C22	113.6(3)
C2–N3–C6	129.3(3)	C17–O23–C24	117.0(3)
C4–N3–C6	123.8(3)	C30–C25–C26	117.3(4)
C7–C6–C11	120.7(4)	C30–C25–C5	123.0(4)
C7–C6–N3	119.2(4)	C26–C25–C5	119.7(4)
C11–C6–N3	120.2(4)	C27–C26–C25	121.2(5)
C6–C7–C8	119.2(4)	C26–C27–C28	120.0(5)
C9–C8–C7	119.8(4)	C29–C28–C27	119.1(5)
C8–C9–C10	120.5(4)	C28–C29–C30	121.1(5)
C8–C9–C112	119.3(4)	C29–C30–C25	121.3(5)
C10–C9–C112	120.2(4)	C32–C31–C36	118.2(4)
C11–C10–C9	119.6(4)	C32–C31–C4	119.6(3)
C10–C11–C6	120.2(4)	C36–C31–C4	122.1(4)
C14–C13–C18	119.4(3)	C33–C32–C31	120.9(4)
C14–C13–C2	123.5(3)	C32–C33–C34	119.5(5)
C18–C13–C2	117.0(3)	C35–C34–C33	120.6(4)
C15–C14–C13	120.3(4)	C34–C35–C36	119.8(4)
O19–C15–C14	123.7(3)	C35–C36–C31	120.9(5)

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