

## Original Research Article

# Single Crystal XRD and NMR Analysis of (Z)-Methyl 3-(benzo[d][1,3]dioxol-5-yl)-2-((2-formyl-1 H-pyrrol-1-yl) methyl) acrylate

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## ABSTRACT

### Keywords

Benzodioxole,  
Pyrrole,  
Acrylate,  
NMR, X-ray  
Crystallo  
graphy

Crystal of the title compound (Z)-methyl 3-(benzo[d][1,3]dioxol-5-yl)-2-((2-formyl-1H-pyrrol-1-yl) methyl) acrylate (MBDPA) was grown by the recrystallization of the compound using ethyl acetate. The diffraction data were collected using X-ray diffractometer. The compound  $C_{14}H_{15}NO_3$  crystallizes in triclinic space group  $P\bar{1}$ . The benzodioxolo moiety assumes planar conformation and the attached pyrrol ring were also found to be planar. Both the benzodioxolo and pyrrol groups are oriented with an angle of  $80.55(5)^\circ$ . The structure was solved by Direct Methods and refined by  $F^2$  Full matrix least squares method. The R-factor was converged at 3.86%. The crystal packing is stabilized by C-H...O type of intra and inter molecular hydrogen bond interactions in addition to van der Waals forces.

## Introduction

Low dense, chemically stable benzodioxane moiety with a variety of liquid crystal building blocks makes it a promising candidate in the development of new liquid crystal materials (Wanwan *et al.*, 2013). The third-order nonlinear optical (NLO) materials have attracted considerable attention due to their potential applications including optical power limiting, optical switching and 3-D optical memory devices. Structural optimizations are widely carried out to adjust the best suitable nonlinear material for optical device applications (Seetharam Shettigar *et al.*, 2010). Interestingly, nitrogen incorporated systems such as benzoxazole moiety have been

lavishly utilized in the synthesis of new classes of antibacterial drugs (Ahmed *et al.*, 2014). Also benzodioxazole derivatives are found to be most important bioactive heterocyclic organic compounds in pharmaceutical chemistry.

The benzodioxane moiety has been widely used in the design of therapeutic agents with  $\alpha$ -adrenergic blocking, antigastric, spasmolytic, antipsychotic, anxiolytic and hepatoprotective properties (Krisztina *et al.*, 2008). The benzodioxane group of drugs would be expected to prevent the effects of circulating epinephrine produced by a pheochromocytoma and thus reduce blood

pressure (Victor, 1949). X-ray diffraction and NMR characterization of MBDPA has been undertaken to understand the structural and conformational features. Chemical structure of MBDPA is shown in figure 1.

## Materials and Methods

### Synthesis of MBDPA

A solution of pyrrole-2-carboxaldehyde (4 mmol) and potassium carbonate (8 mmol) in acetonitrile solvent was stirred for 15 minutes at room temperature. To this solution, methyl 2-(acetoxymethyl)acrylate (4.8 mmol) was added drop wise till the addition is complete. After the completion of reaction (checked with TLC), acetonitrile was evaporated. The crude mass was added to EtOAc (15 mL) and water (15 mL). Organic layer was extracted and washed with water ( $2 \times 10$  mL) and brine solution ( $2 \times 10$  mL). The organic layer was dried over anhydrous sodium sulphate. Removal of solvent led to the crude product which was purified through pad of silica gel (100-200 mesh) using ethylacetate and hexane (1:9) solvents (Scheme 1).

### X-Ray diffraction analysis

Pale yellow block crystal ( $0.3 \times 0.25 \times 0.20$  mm<sup>3</sup>) was used for data collection. Diffraction data set for the title compound were collected at room temperature ( $T = 293(2)$  K) using a Bruker Smart Apex II X-ray diffractometer with graphite monochromated MoK $\alpha$  radiation ( $\lambda = 0.71073$  Å) (Bruker, 2008). The structure was solved by the direct methods using SHELXS-97 (Sheldrick, 1997) and was refined by full matrix least squares based on  $F^2$  using SHELXL-97 (Sheldrick, 1997). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were positioned geometrically and refined using a

riding model with C–H = 0.93 and 0.97 Å, and with  $U_{iso}(H) = 1.2 U_{eq}(C)$ . The molecular graphics were drawn using ORTEP-3 (Farrugia, 1997) and PLATON programs (Spek, 2009).

### NMR and mass spectra analysis

The NMR spectra were recorded on a Bruker DRX 400 spectrometer (operating frequency 400 MHz for <sup>1</sup>H and 100 MHz for <sup>13</sup>C) for the crystals dissolved in deuterated chloroform (TMS as reference). Mass spectra are recorded on EIMS (Shimadzu) and ESI-esquire 300 Bruker Daltonics instrument (Table 1). The electro spray mass spectrometer (API-ES). This mass spectrometer scanned from 100 to 1000 m/z in 0.169 amu steps with a dwell time of 0.851 ms, which required 10 s for one complete scan. The crystals of MBDPA were used for the analysis.

## Results and Discussion

### NMR spectra assignment and mass spectra

Structure assignments have been made based on characteristic chemical shifts of functional groups and corresponding spin multiplicity from respective NMR spectra. Aromatic benzene and pyrrole protons were appeared in the ranges of 6.80 - 6.99 ppm and 6.22 – 6.71 ppm respectively. The methoxy protons are resonating in the region of 3.78 ppm and ethylene proton at 7.99 ppm. Aliphatic methylene protons show peak at 5.46 ppm and the methylene protons of dioxole ring appear at 5.98 ppm as singlet in the proton integrals. Aldehyde protons are evidenced from the peak appeared at 9.61 ppm in the compound analyzed as shown in figure 2.

The aliphatic methylene, methoxy carbons were evidenced by peaks at the region of

45.55 ppm and 52.61 ppm. The methylene carbon of dioxolo ring appears in the region of 101.81 ppm. The aromatic benzene carbons were evidenced by peaks at 108.94 ppm, 110.14 ppm, 124.54 ppm, and 125.20 ppm in the corresponding <sup>13</sup>C NMR analysis. The carbonyl carbon belongs to ester linkage and aldehyde group resonated at 167.83 ppm and 179.85 ppm respectively and are given in figure 3. Relevant detail of the chemical shift values are given in table 1. The molecular weight of the compound is determined as 313.1 (Fig. 4).

### Crystal structure analysis

The thermal ellipsoid plot of the molecule is shown in figure 5. Crystallographic data are given in table 2. Selected bond lengths and bond angles are given table 3. The title compound C<sub>14</sub>H<sub>15</sub>NO<sub>3</sub> crystallizes in triclinic space group P $\bar{1}$ , with the unit cell parameters of a = 7.5594(4) Å, b = 7.8717(5) Å; c = 13.7959(8) Å, α = 87.146(3) °, β = 77.582(3) ° and γ = 65.713(3) °.

**Table.1** 1H and 13C NMR chemical shift values and Mass value of MBDPA

Proton ( <sup>1</sup> H <sup>1</sup> ) chemical shift (δppm in CDCl <sub>3</sub> )	Carbon ( <sup>6</sup> C <sup>13</sup> ) chemical shift (δppm in CDCl <sub>3</sub> )
3.78 (S, 3H, -OCH <sub>3</sub> )	45.55 (S, N-CH <sub>2</sub> -C, METHYLENE)
5.46 (S, 2H, N-CH <sub>2</sub> -C, METHYLENE)	52.61 (S, O-CH <sub>3</sub> )
5.98 (S, 2H, O-CH <sub>2</sub> -O, DIOXOLE)	101.81 (S, O-CH <sub>2</sub> -O, DIOXOLE)
6.22 (S, 1H, C-CH-CH, PYRROLE)	108.94(S, C-CH-C, C <sub>6</sub> H <sub>6</sub> )
6.71 (S, 1H, CH-CH-N, PYRROLE)	109.22 (S, CH-CH-CH, PYRROLE)
6.80 (S, 2H, C-CH-C, C <sub>6</sub> H <sub>5</sub> )	110.14 (S, O-C-CH, C <sub>6</sub> H <sub>6</sub> )
6.95 (S, 1H, O-C-CH, C <sub>6</sub> H <sub>5</sub> )	124.54 (S, C-CH-CH, C <sub>6</sub> H <sub>6</sub> )
6.99 (S, 1H, C-CH-CH, PYRROLE)	125.16 (S, C-CH-CH, PYYROLE)
7.99 (S, 1H, C-CH-C, ETHYLENE)	125.20 (S, C-CH-C, C <sub>6</sub> H <sub>6</sub> )
9.61 (S, 1H, O=CH)	128.09 (S, C-CH <sub>2</sub> -C, ETHYLENE)
	129.16 (S, N-C-CH, PYRROLE)
	131.95 (S, N-CH-CH, PYRROLE)
	145.39 (S, C-CH-C, ETHYLENE)
	148.42 (S, O-C-CH, C <sub>6</sub> H <sub>6</sub> )
	149.36 (S, CH-C-O, C <sub>6</sub> H <sub>6</sub> )
	167.83 (S, C-C-O, CARBOXYL)
	179.85 (S, O=CH CARBONYL)
[M+1] <sup>+</sup> = 314.1, Molecular mass (C <sub>17</sub> H <sub>15</sub> NO <sub>5</sub> ) 313.1. Calculated (%): 65.17 (C), 4.83 (H), 4.47 (N), 25.53 (O).	

**Table.2** Crystal data of MBDPA

<b>Parameters</b>	<b>Values</b>
Empirical formula	C <sub>17</sub> H <sub>15</sub> N O <sub>5</sub>
Formula weight	313.1
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P $\bar{1}$
Unit cell dimensions	a = 7.5594(4) Å $\alpha$ = 87.146(3)° b = 7.8717(5) Å $\beta$ = 77.582(3)° c = 13.7959(8) Å $\gamma$ = 65.713(3)°
Volume	730.08(7) Å <sup>3</sup>
Z, Calculated density	2, 1.425 Mg/m <sup>3</sup>
Absorption coefficient	0.106 mm <sup>-1</sup>
F(000)	328
Crystal size	0.30 x 0.25 x 0.20 mm
Theta range for data collection	1.51 to 26.43°
Limiting indices	-9<=h<=9, -9<=k<=9, -17<=l<=17
Reflections collected / unique	10617 / 2999 [R(int) = 0.0291]
Completeness to theta = 26.43	99.40%
Max. and min. transmission	0.9791 and 0.9689
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	2999 / 0 / 209
Goodness-of-fit on F <sup>2</sup>	1.036
Final R indices [I>2sigma(I)]	R1 = 0.0386, wR2 = 0.1001
R indices (all data)	R1 = 0.0531, wR2 = 0.1122
Largest diff. peak and hole	0.218 and -0.183 e.Å <sup>-3</sup>

**Table.3** Selected bond lengths and bond angles of MBDPA

Atoms	Length	Atoms	Angle
C1-O2	1.423(2)	O2-C1-O1	108.56(13)
C1-O1	1.426(2)	H1A-C1-H1B	108.4
C2-C7	1.371(2)	C7-C2-O1	128.23(14)
C2-O1	1.3719(18)	C7-C2-C3	121.63(14)
C2-C3	1.379(2)	O1-C2-C3	110.09(13)
C3-C4	1.358(2)	C4-C3-O2	127.89(14)
C3-O2	1.3773(18)	C4-C3-C2	122.50(14)
C4-C5	1.414(2)	O2-C3-C2	109.60(13)
C5-C6	1.399(2)	C3-C4-C5	117.74(14)
C5-C8	1.461(2)	C6-C5-C4	118.86(14)
C6-C7	1.392(2)	C6-C5-C8	125.79(13)
C8-C9	1.340(2)	C4-C5-C8	115.34(13)
C9-C16	1.489(2)	C7-C6-C5	122.38(14)
C9-C10	1.508(2)	C2-C7-C6	116.78(14)
C10-N1	1.4658(19)	C9-C8-C5	131.99(14)
C11-N1	1.3638(19)	C8-C9-C16	115.59(14)
C11-C12	1.376(2)	C8-C9-C10	125.85(14)
C12-C13	1.378(2)	C16-C9-C10	118.55(13)
C13-C14	1.382(2)	N1-C10-C9	112.27(12)
C14-N1	1.3751(19)	H10A-C10-H10B	107.9
C14-C15	1.422(2)	N1-C11-C12	109.54(14)
C15-O5	1.214(2)	O3-C16-O4	122.22(15)
C16-O3	1.197(2)	O3-C16-C9	125.52(15)
C16-O4	1.3321(19)	O4-C16-C9	112.25(13)
C17-O4	1.440(2)	C11-N1-C14	107.48(12)

**Table.4** Hydrogen bond geometry

D-H...A	D-H	H...A	D...A	DHA
C1-H1B...O2(i)	0.97	2.49	3.190(3)	128
C4-H4...O3 (ii)	0.93	2.59	3.421(2)	149
C11-H11...O1(iii)	0.93	2.52	3.410(2)	159
C12-H12...O5 (iv)	0.93	2.38	3.279(2)	162

Symmetry Equivalent Positions:

- i. -x,1-y,1-z
- ii. 2-x,-y,1-z
- iii. 1+x,-1+y,z
- iv. x,-1+y,z

Scheme.1 Synthesis of MBDPA

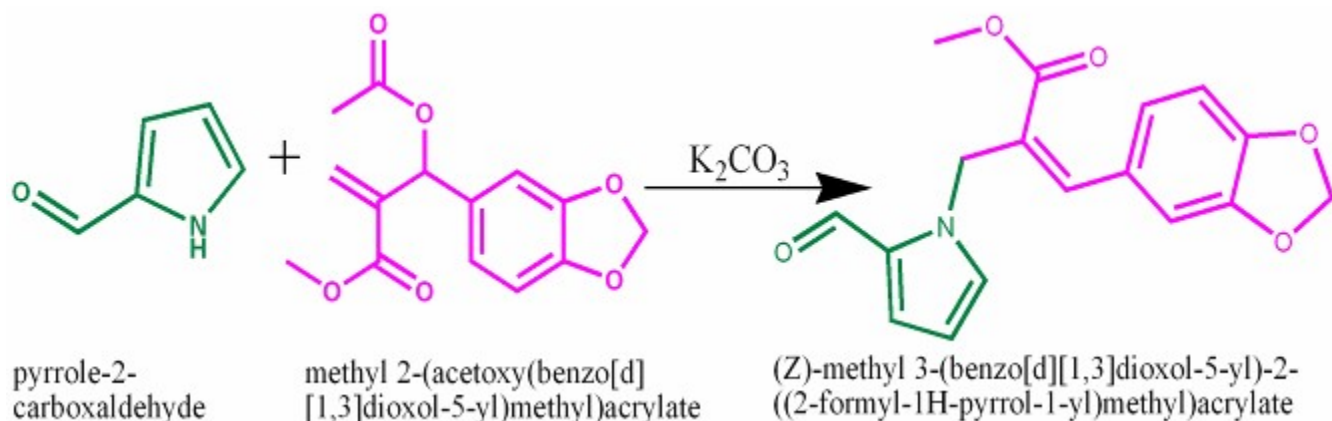


Fig.1 Chemical structure of MBDPA

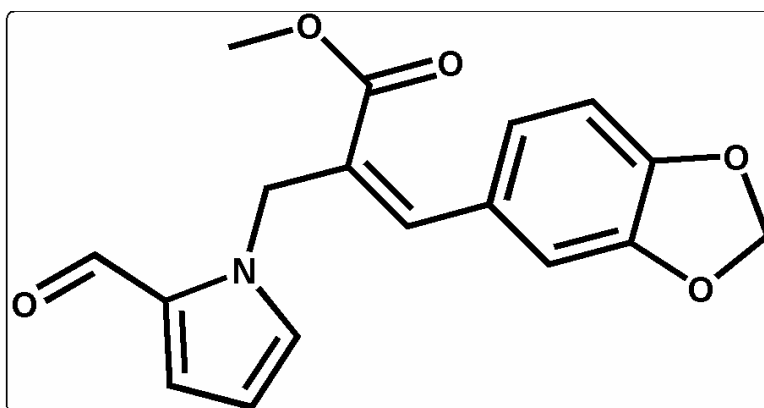
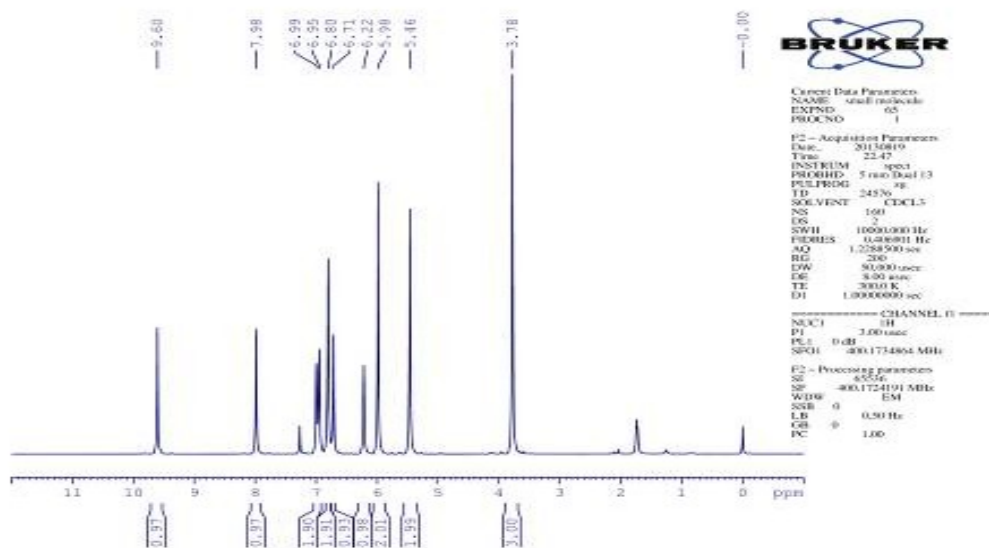
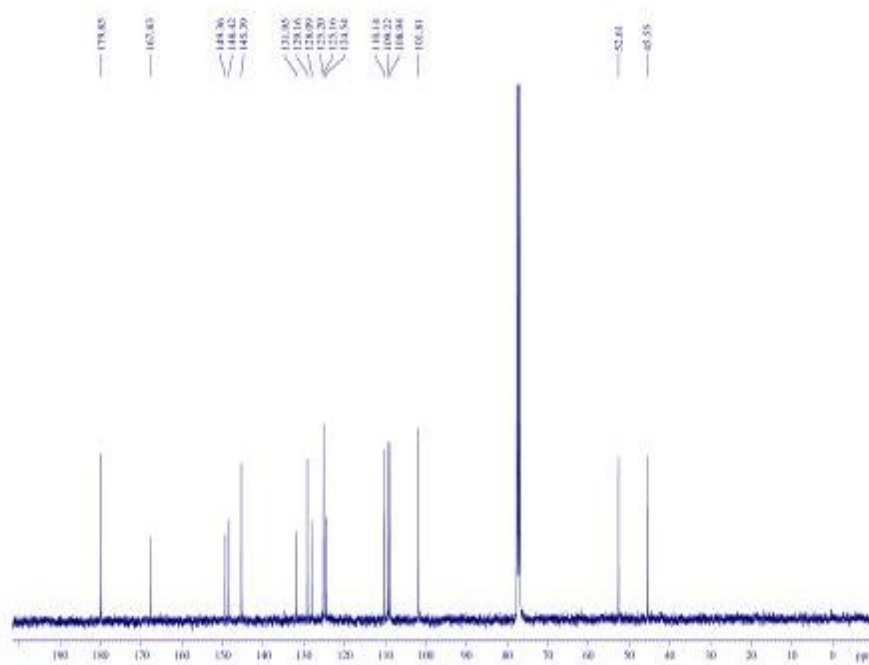


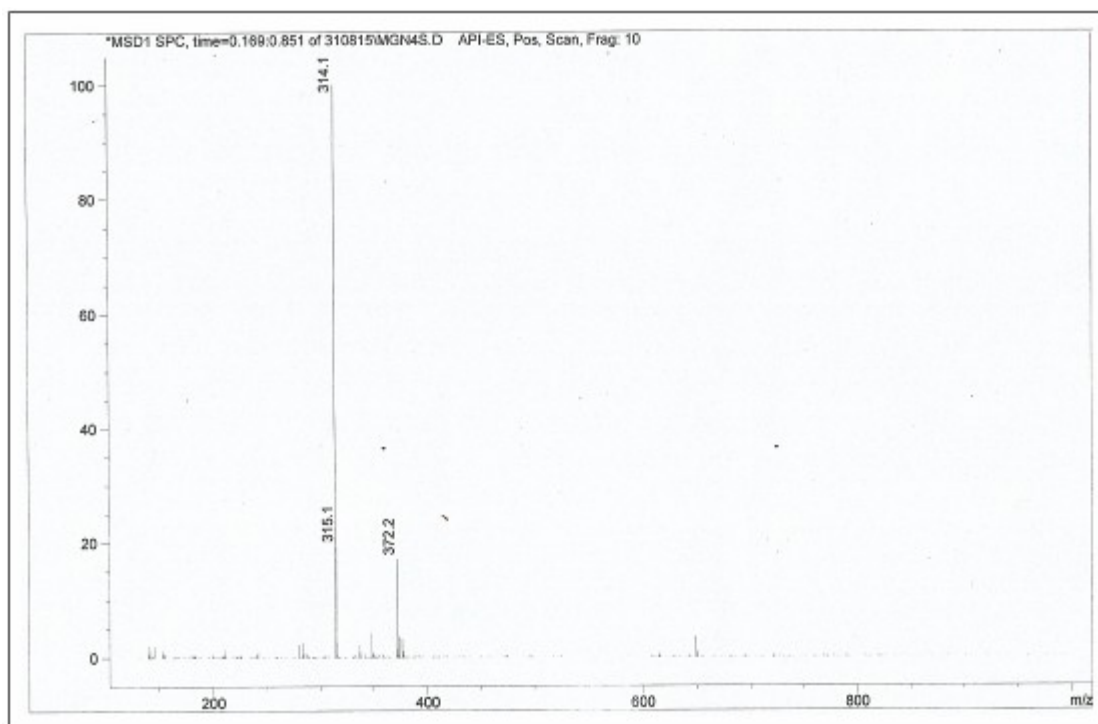
Fig.2 Proton NMR Spectrum of MBDPA



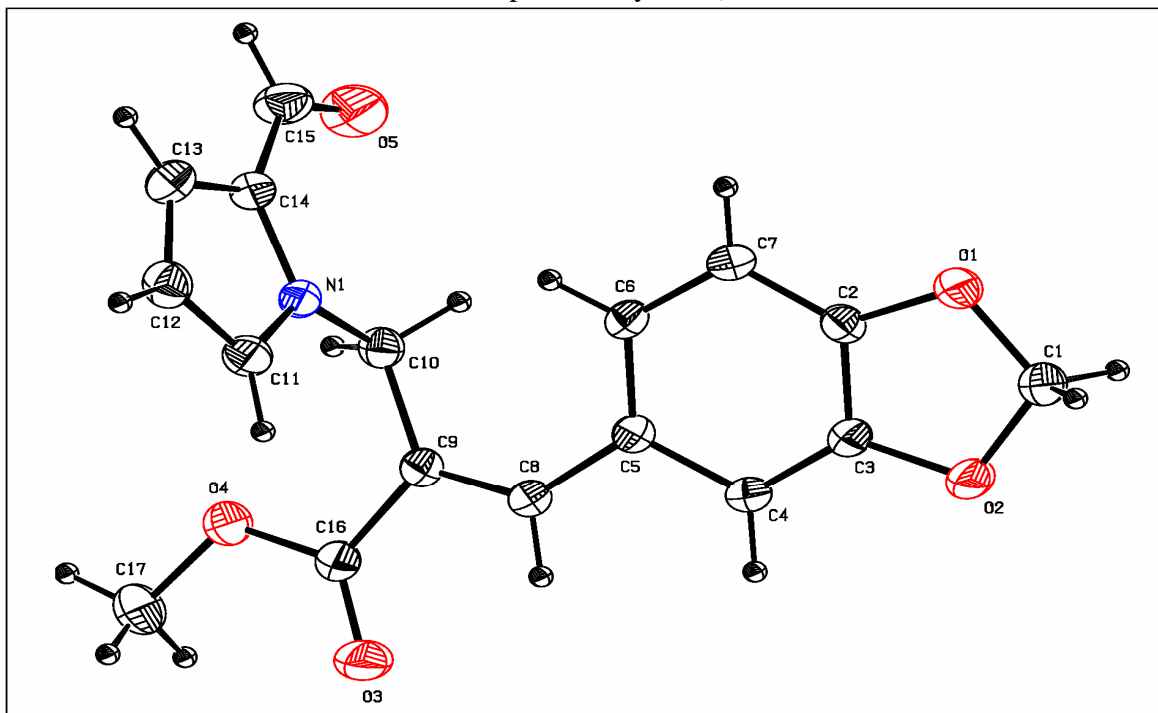
**Fig.3**  $^{13}\text{C}$  NMR Spectrum of MBDPA Mass Spectrometry



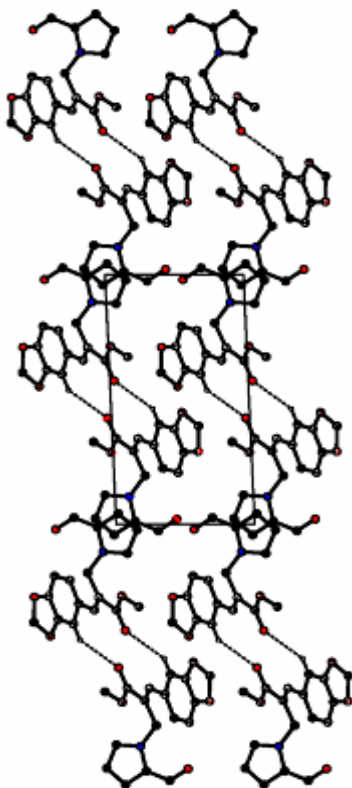
**Fig.4** Mass spectrum of MBDPA



**Fig.5** Perspective view of MBDPA with atom labeling (displacement ellipsoids are drawn at 30% probability level)

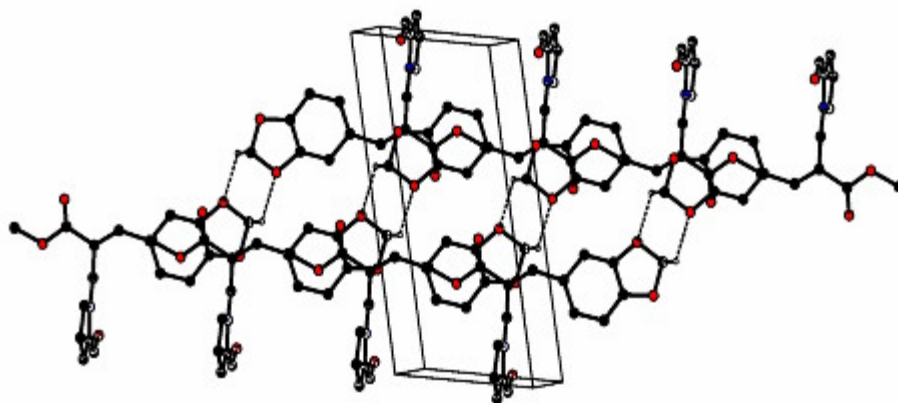


**Fig.6** Packing of the molecules  $R^2_2$  (14) ring motif (Dashed lines indicate the intra-molecular hydrogen bonds)





**Fig.7** Packing of the molecules  $R^2_2(6)$  ring motif (Dashed lines indicate the intra-molecular hydrogen bonds)



Both the benzodioxolo and pyrrol moieties were planar with the maximum deviations of 0.033(2) Å and -0.02(2) Å respectively. Three moieties, benzodioxo, pyrrol and acrylate occupy at corners of a regular triangle where atom C9 being at the centre. Because of bulkiness of the benzodioxo and pyrrole containing groups, the C8-C9-C10 angle is widened to 125.86(14)°. As a consequence of this, C8-C9-C16 angle is found to be shortened to 115.57(14)°. The corresponding values of the trigonal arrangement are [C8-C9-C16=] 115.57(14)°, [C8-C9-C10=] 125.86(14) ° and [C16-C9-C10=] 118.55(14)°. The benzodioxo and pyrrol groups are relatively oriented with a dihedral angle of 80.55(5)°. The acrylate group maintains co planarity with benzodioxo ring, as evidenced from torsion angles -178.94(15)° [C16-C9-C8-C5] and 175.62(14)° [O4-C16-C9-C8]. The aldehyde group [C15/H15/O5] lie in the same plane with pyrrole by a dihedral angle of 1.0(4)° [N1-C14-C15-O5].

### Packing features

The crystal packing is stabilized by C-H...O types of intra and inter molecular interactions along with van der Waals forces. Atom C4 with its hydrogen H4

interacts with atom O3 (2-x, -y, 1-z) to form  $R^2_2(14)$  dimers running along c-axis as shown in figure 6. Other dimer formation by C1 and O2 (-x, 1-y, 1-z) with  $R^2_2(6)$  arrangement (Fig. 7). The hydrogen bond C11-H11...O1 (1+x,-1+y,z) and C12-H12...O5 (x,-1+y,z) forms S(16) ring motifs. Relevant hydrogen bonding details are given in table 4.

In conclusion of this study, the structure of a new dioxol (MBDPA) synthesized is characterized by X-ray crystallography, NMR and Mass spectroscopy techniques. Dioxol compound is crystallized in triclinic space group wherein the dioxol ring take up planar conformations. In the compound, C-H...O hydrogen bonds lead to  $R^2_2(14)$  and  $R^2_2(6)$  dimer formations. The mass spectrum showed a molecular weight of 314.1 and the <sup>1</sup>H, <sup>13</sup>C NMR spectrum indicated the presence of benzene, pyrrole, one methoxy, an aliphatic methylene and a ring methylene groups. These spectroscopic and crystal structure results clearly explain the conformational features of the compound.

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### Additional Information

Crystallographic data (excluding structure factors) for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC-1420418 [www.ccdc.cam.ac.uk](http://www.ccdc.cam.ac.uk).

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