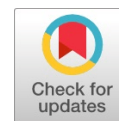


# Synthesis, Characterization and DFT Analysis of Benzimidazolylpyrazolylacrylonitrile

Ramar Sivaramakarthykeyan, Krishnaraj Padmavathy, Shunmugam Iniyaval,  
Chennan Ramalingan



**Abstract:** A novel heterocyclic molecule possessing two important scaffolds such as pyrazole and benzimidazole was synthesized and the structure of the same was corroborated based on analytical and spectroscopic techniques. The molecular structure of 6 was optimized; FMO energies associated properties were calculated. The hyperpolarizability ( $\beta_{tot}$ ) and electric dipole moment ( $\mu_{tot}$ ) of 6 were computed. When compared to urea, the  $\beta$  was 7.6 times superior, which validate the target 6 may serve as a candidate for NLO applications.

**Keywords:** HOMO-LUMO, Electrophilicity index, NLO.

## I. INTRODUCTION

In current decade, the organic materials have attained the interest of material chemists/scientists around the globe due to their outstanding approaches for the utilization of donor-acceptor (D-A) combinations in achieving specific targets. These materials display a wide spectrum of applications in the field of organic light emitting diodes (OLEDs) [1-3], lasers [4], various types of solar cells in particular organic / dye-sensitized solar cells (DSSCs) [5], field-effect transistors (FETs) [6,7] and sensors [8]. Particularly, organic materials display efficient nonlinear optical properties (NLO) and rapid responsiveness due to the presence of highly movable electrons. Pyrazole is one of the important five membered heterocyclic compounds with a couple of nitrogen's at adjacent positions (i.e., 1, 2 positions) in its aromatic structural motif. Pyrazole analogous exert a wide variety of not only biological properties [9-15], but also exert a diverse range of electronic properties. Some of the other specific applications of pyrazole includes

electroluminescence (EL) properties [16], semiconductors [17], liquid crystals [18], organic light emitting diodes (OLEDs) [19] and solar cells [20]. It has also been reported that ethoxy carbonyl substituted pyrazolyl benzoic acid as potential NLO materials [21].

On the other hand, benzimidazole is another nitrogen heterocyclic compound with two nitrogen atoms at alternate positions. Similar to that of pyrazole, benzimidazoles also possess an extensive range of bioactivities [22-27]. Also, from literature, benzimidazolium phthalate was found to show non-linear optical properties with second harmonic generation efficiency, 0.3 times greater than that of standard urea [28]. Thus, we propose to synthesize a scaffold with both pyrazole and benzimidazole moieties with extended conjugation with an idea of enhancing the NLO properties. The structure of the molecule was established using spectroscopic techniques. Further, the structural optimization, HOMO-LUMO analysis, NLO studies and associated quantum parameters were determined by subjecting into computational calculations.

## II. EXPERIMENTAL SECTION

### A. General

The reagent / solvents utilized in this piece of work were obtained through commercial sources and used as such / purified through standard procedure before their use. Progress and completion of the reactions were checked TLC (Merck). All melting points reported were measured in Sigma MP apparatus (open capillaries). IR spectra were recorded as KBr pellet using Shimadzu-IR Tracer 100 spectrophotometer.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on Bruker AVANCE III (400 and 100 MHz) NMR spectrometer at 25 °C. Chemical shift values are expressed in terms of ppm.

### B. Synthesis of carbaldehyde 4

Stirred a mixture of 4-methylacetophenone (0.01 mol) and phenyl hydrazine (0.01 mol) in glacial acetic acid (10 ml) and was heated for 30 minutes. The solid formed, after cooling, was filtered, washed with dil.HCl and recrystallized using ethanol to obtain the corresponding arylhydrazone. The arylhydrazone thus obtained by the above process was treated with the cold Vilsmeier-Haack reagent, prepared from  $\text{POCl}_3$  (1 ml, 0.28 mol) and DMF (10 ml). It was stirred at 70-80 °C for 6h. After completion, it was poured in to ice-cold water after brought into ambient temperature.

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\* Correspondence Author (s)

**Ramar Sivaramakarthykeyan**, Department of Chemistry, School of Advanced Sciences, Kalasalingam Academy of Research and Education (Deemed to be University), Krishnankoil, 626 126, Tamilnadu, India. Email: [sivaram.ramar@gmail.com](mailto:sivaram.ramar@gmail.com)

**Krishnaraj Padmavathy**, Department of Chemistry, School of Advanced Sciences, Kalasalingam Academy of Research and Education (Deemed to be University), Krishnankoil, 626 126, Tamilnadu, India. Email: [ovshada@gmail.com](mailto:ovshada@gmail.com)

**Shunmugam Iniyaval**, Department of Chemistry, School of Advanced Sciences, Kalasalingam Academy of Research and Education (Deemed to be University), Krishnankoil, 626 126, Tamilnadu, India. Email: [iniyaval.s@klu.ac.in](mailto:iniyaval.s@klu.ac.in)

\***Chennan Ramalingan**, Department of Chemistry, School of Advanced Sciences, Kalasalingam Academy of Research and Education (Deemed to be University), Krishnankoil, 626 126, Tamilnadu, India. Email: [ramalingan@gmail.com](mailto:ramalingan@gmail.com)

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# Synthesis, Characterization and DFT Analysis of Benzimidazolylpyrazolylacrylonitrile

It was then neutralized by using saturated solutions of sodium bicarbonate, filtered, washed with water and dried to afford pure **4** [29].

## C. Synthesis of novel acrylonitrile **6**

To a mixture of carbaldehyde **4** (0.5 g, 1.9 mmol) and benzimidazolyl acetonitrile **5** (0.3 g, 1.9 mmol) in methanol, piperidine (0.19 ml, 1.9 mmol) was added. It was heated at 60 °C for 6h. After completion of reaction, as indicated by TLC, it was poured into water (ice-cold) and neutralized using K<sub>2</sub>CO<sub>3</sub> (saturated solution). The precipitate formed was recrystallized from ethanol, after filtration followed by washed with water and dried, to give the target **6**. Yield, 89 %; MP: 315-316 °C; FT-IR (KBr, cm<sup>-1</sup>):  $\nu$  3295.4, 2190.5, 1705.6, 1600.7, 1531.3, 1418.1, 1368.5, 1355.3, 1244.5, 1111.2, 1052.7, 969.6, 856.5, 813.3, 757.0, 677.7, 663.5, 635.3, 497.6; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.75 (t, *J* = 4 Hz, 2H), 8.48 (s, 1H), 7.64-7.55 (m, 8H), 7.34-7.17 (m, 5H), 2.35 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  150.5, 143.3, 139.3, 129.9, 129.8, 129.5, 128.5, 123.4, 128.3, 127.1, 126.9, 125.3, 123.7, 119.1; EI-MS (*m/z*): 401 (M<sup>+</sup>).

## III. RESULTS AND DISCUSSION

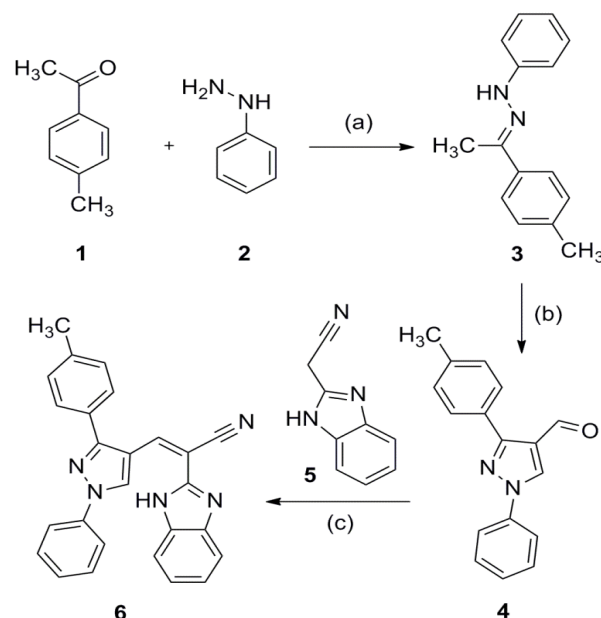
### Chemistry

#### A. Synthesis and characterization

In the first part, we have synthesized compound **4** from *p*-methyl acetophenone (**1**) through a two-step process. Condensation of hydrazine **2** with ketone **1** followed by cyclization and formylation using Vilsmeier Haack reagent yielded **4**. The carbaldehyde **4**, upon Knoevenagel condensation with the active methylene group of **5** in methanol using piperidine catalyst under reflux condition gave the target acrylonitrile **6** as shown in **Scheme 1**. The characteristic carbonyl vibrational frequency of aldehyde was absent in the IR spectra. Instead, a nitrile peak at 2190 cm<sup>-1</sup> is visualized. Methyl proton was observed as three protons singlet at  $\delta$  2.35 ppm. All aromatic protons inclusive of NH proton and newly formed CH proton appeared in the region  $\delta$  7.17-8.75 ppm in the <sup>1</sup>H NMR spectra. <sup>13</sup>C NMR spectra has approved well with the structure of target compound.

#### B. Geometry optimization

The structural optimization of compound **6** was made using computational DFT/B3LYP [6-311G (d,p)] method. The optimized structure (ground state) is depicted in **Fig. 1** and structural parameters (bond lengths, bond angles, and dihedral angles) are furnished in **Tables 1 & 2**. As exposed in **Fig. 1**, the molecular geometry of the parental pyrazole structural ornament has a typical butterfly form. The N25-H43, C17-C123, C19-C122, and C1-N4 bond lengths are 1.0071, 1.7533, 1.7533 and 1.1549 Å respectively agrees with the expected values 1.0 (N-H), 1.76 (C-Cl) and 1.16(CN). The bond angles between C8-C3-H33, C2-C3-C8, C3-C8-C9, and C3-C2-C24 are 114.233, 130.171, 130.124 and 127.719, respectively.



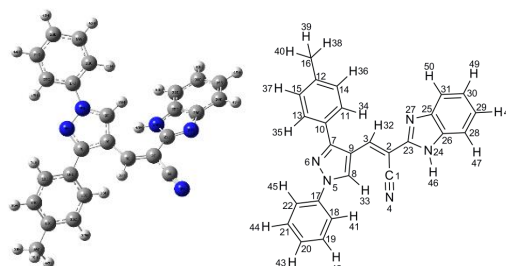
**Scheme 1. Synthesis of acrylonitrile **6**: Reagents and conditions: (a) Glacial acetic acid, reflux, 30 mins; (b) DMF-POCl<sub>3</sub>, 70-80 °C, 6h; (c) piperidine, methanol, 60 °C, 6h.**

#### C. Computational details

The computational calculations of the molecule **6** have been performed employing DFT-B3LYP; 6-311G (d,p) method [30]. Optimized molecular geometry, FMO energy levels, MEP, Mulliken atomic charge distributions and NLO properties of compound **6** were derived from the computational details.

#### D. Optimized geometry

The ground state optimized geometry of compound **6** has been computed using DFT/B3LYP [6-311G (d,p)]. The theoretically obtained optimized parameters such as bond lengths and bond angles are shown in **Tables 1 & 2**, respectively. The optimized structure is shown in **Fig 1**. The N24-H46 and C1-N4 bond lengths are 1.0073, and 1.1549 Å, respectively approves with the anticipated values 1.0 (N-H), and 1.16(CN). The bond angles between C2-C3-C8, C7-C10-C13, N5-C17-C22 and C2-C23-N27 are 129.7903, 121.7801, 119.3125 and 123.9935 degrees respectively, thus, the molecule is planar with slight deviation in bond angles are observed due to optimization in gas phase.



**Fig. 1. Optimized Structure of **6****

**Table 1: Computed Bond length of 6**

Bond	[Å]	Bond	[Å]
C1-C2	1.4339	C16-H40	1.0916
C1-N4	1.1549	C17-C18	1.3967
C2-C3	1.3608	C17-C22	1.3961
C2-C23	1.4669	C18-C19	1.3915
C3-C8	1.45	C18-H41	1.0827
C3-H32	1.0852	C19-C20	1.3927
N5-N6	1.3562	C19-H42	1.0837
N5-C9	1.356	C20-C21	1.3938
N5-C17	1.4234	C20-H43	1.0835
N6-C7	1.3285	C21-C22	1.3903
C7-C8	1.4384	C21-H44	1.0838
C7-C10	1.4706	C22-H45	1.0807
C8-C9	1.3887	C23-N24	1.3828
C9-H33	1.0761	C23-N27	1.3133
C10-C11	1.4038	N24-C25	1.3808
C10-C13	1.4003	N24-H46	1.0073
C11-C14	1.3868	C25-C26	1.4156
C11-H34	1.0828	C25-C31	1.3947
C12-C14	1.4015	C26-N27	1.3806
C12-C15	1.3961	C26-C28	1.3997
C12-C16	1.5086	C28-C29	1.3871
C13-C15	1.3924	C28-H47	1.083
C13-H35	1.0835	C29-C30	1.4086
C14-H36	1.0855	C29-H48	1.0838
C15-H37	1.0849	C30-C31	1.3898
C16-H38	1.0934	C30-H49	1.0839
C16-H39	1.0952	C31-H50	1.0839

**Table 2: Computed Bond angle of 6**

Bond Angles	[°]	Bond Angles	[°]
C1-C2-C3	117.3201	N5-C17-C18	120.2953
C1-C2-C23	115.0086	N5-C17-C22	119.3125
C3-C2-C23	127.6485	C18-C17-C22	120.3922
C2-C3-C8	129.7903	C17-C18-C19	119.5234
C2-C3-H32	115.7288	C17-C18-H41	120.7599
C8-C3-H32	114.4469	C19-C18-H41	119.7067
N6-N5-C9	111.9148	C18-C19-C20	120.4812
N6-N5-C17	120.2525	C18-C19-H42	119.2924
C9-N5-C17	127.8305	C20-C19-H42	120.2225
N5-N6-C7	105.9312	C19-C20-C21	119.5400
N6-C7-C8	110.8097	C19-C20-H43	120.1805
N6-C7-C10	120.4686	C21-C20-H43	120.2785
C8-C7-C10	128.7215	C20-C21-C22	120.6305
C3-C8-C7	126.6666	C20-C21-H44	120.093
C3-C8-C9	128.7019	C22-C21-H44	119.2758
C7-C8-C9	103.9337	C17-C22-C21	119.4241
N5-C9-C8	107.4072	C17-C22-H45	119.0822
N5-C9-H33	122.0895	C21-C22-H45	121.4928
C8-C9-H33	130.3081	C21-C22-H45	121.4928
C7-C10-C11	120.0454	C2-C23-N27	123.9935
C7-C10-C13	121.7801	N24-C23-N27	112.4828
C11-C10-C13	118.1685	C23-N24-C25	107.1505
C10-C11-C14	120.7057	C23-N24-H46	125.7644
C10-C11-H34	118.9792	C25-N24-H46	126.9815
C14-C11-H34	120.3143	N24-C25-C26	104.5593
C14-C12-C15	117.8466	N24-C25-C31	132.9512
C14-C12-C16	120.7943	C26-C25-C31	122.4895
C15-C12-C16	121.3557	C25-C26-N27	110.2892
C10-C13-C15	120.7272	C25-C26-C28	119.8254
C10-C13-H35	120.0992	N27-C26-C28	129.8849
C15-C13-H35	119.1514	C23-N27-C26	105.5155
C11-C14-C12	121.3077	C26-C28-C29	117.979
C11-C14-H36	119.2938	C26-C28-H47	120.0658
C12-C14-H36	119.3979	C29-C28-H47	121.9548
C12-C15-C13	121.2375	C28-C29-C30	121.4251

C12-C15-H37	119.5354	C28-C29-H48	119.5904
C13-C15-H37	119.225	C30-C29-H48	118.9843
C12-C16-H38	111.3336	C29-C30-C31	121.654
C12-C16-H39	110.9627	C29-C30-H49	119.1639
C12-C16-H40	111.4317	C31-C30-H49	119.1819
H38-C16-H39	107.2151	C25-C31-C30	116.6266
H38-C16-H40	108.0874	C25-C31-H50	122.0714
H39-C16-H40	107.6223	C30-C31-H50	121.3013

**E. Mulliken charge distribution**

The partial atomic charges can be predictable from Mulliken population analysis method. Also, it helps to determine the ability of an atom to be attacked by an electrophile or nucleophile. Thus, the optimized structure of compound **6** was computed and the atomic charges are shown in **Table 3**. **Fig. 2** indicates the distribution of clear atomic charge of **6**, symbolized by coloring. The charge distributions of the atoms imply the formation of acceptor and donor pairs relating the charge transfer in the molecule [31,32]. In **6**, the C7 and C23 atoms have more positive charges signifying that these regions are susceptible for nucleophilic attack or they are called as nucleophilic attack regions, whereas the nitrogen, N24, carbon, C8 have more negative charges compared to other atoms indicative of electrophilic attack prone site. The Mulliken population chart of charge distributions of compound **6** was shown in **Fig. 3**.

**Table 3: Mulliken Atomic Charges of Compound 6**

Atom	Charges	Atom	Charges
C1	0.075762	C26	-0.016674
C2	-0.041953	N27	-0.323222
C3	-0.014578	C28	-0.060469
N4	-0.223077	C29	-0.103199
N5	-0.334236	C30	-0.108966
N6	-0.252513	C31	-0.057913
C7	0.315071	H32	0.145064
C8	-0.411435	H33	0.139120
C9	0.227653	H34	0.100317
C10	-0.085572	H35	0.105021
C11	-0.029553	H36	0.088141
C12	-0.092947	H37	0.090875
C13	-0.072153	H38	0.120971
C14	-0.080195	H39	0.129966
C15	-0.074499	H40	0.110733
C16	-0.255472	H41	0.111074
C17	0.215705	H42	0.104112
C18	-0.112122	H43	0.102549
C19	-0.099161	H44	0.104683
C20	-0.079822	H45	0.129211
C21	-0.098339	H46	0.248706
C22	-0.063019	H47	0.103686
C23	0.316713	H48	0.096854
N24	-0.468007	H49	0.096947
C25	0.187097	H50	0.093066

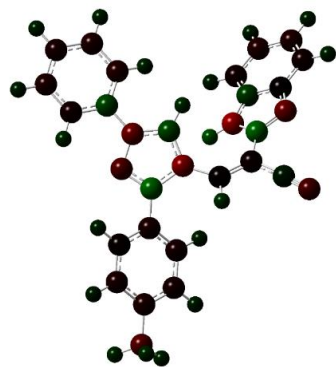


Fig. 2. Optimized Structure and Mulliken charge distribution of 6

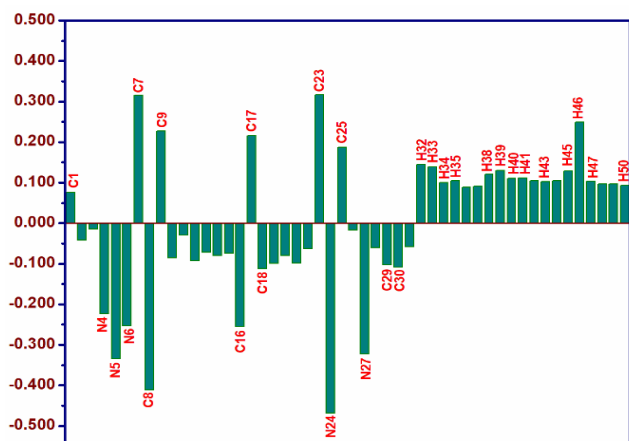


Fig. 3. Mulliken charge distribution Chart of 6

#### F. HOMO-LUMO Analysis

The electronic structure of target molecules and charge transport properties are conceived from HOMO-LUMO energy gap [33]. Huge variance in HOMO-LUMO values specifies that target compound is stable. The electron spreading on FMOs viz., HOMO-2-LUMO+2, HOMO-1-LUMO+1, and HOMO-LUMO energy levels of compound 6 is furnished in Fig. 4 (energy values are provided in Table 4). Fig 4 reveals the possibilities of inter-electron transfer within the molecule. In the HOMO, the orbitals spread over the entire molecule while in LUMO its concentration is large on the nitrile part. In the case of HOMO-1, the orbital localization over the entire molecule is larger while the same is true on the pyrazole part in LUMO+1. On the other hand, in the case of HOMO-2, the orbitals are precisely located on the benzimidazole scaffold while in LUMO+2, the same is precisely located on phenyl ring connected to pyrazole scaffold. All these characteristics support the electron transfer with the molecule.

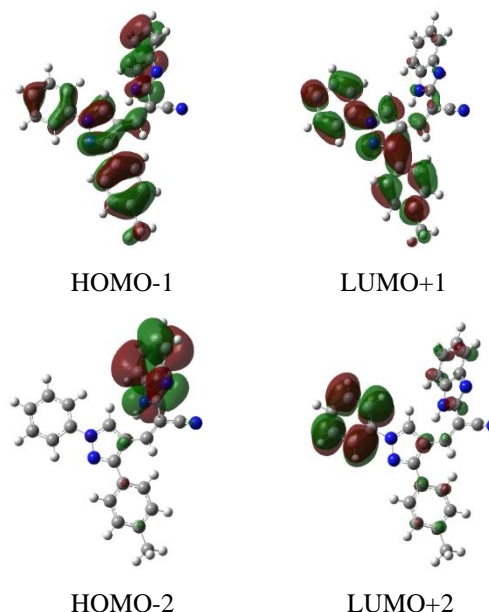
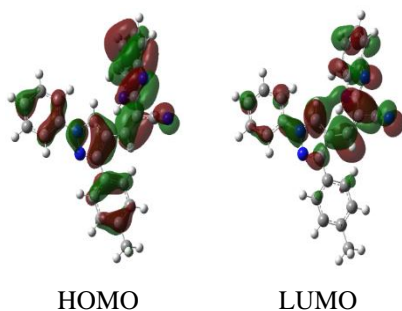


Fig. 4. 3D Plots of FMO of 6

Table 4. Calculated Molecular Orbital Energies of 6

Parameters	(eV)
HOMO	-6.1073
LUMO	-2.4082
$\Delta E$	3.6991
HOMO-1	-6.5857
LUMO+1	-1.5470
$\Delta E1$	5.0387
HOMO-2	-6.5990
LUMO+2	-0.9396
$\Delta E2$	5.6594

#### G. Non-linear optical characteristics

The dipole moment, polarizability and first order hyperpolarizabilities of 6 were determined through computational calculations and the results obtained were compared with the non-linear optical molecule urea, considered as a standard. Normally, the NLO molecules exhibit superior first order hyperpolarizability, molecular polarizability, and dipole moment values. The parameters of NLO of the target 6 are furnished in Table 5.

Table 5. NLO Parameters of 6

Parameters	Values
Dipole moment	
$\mu_x$	1.9401
$\mu_y$	6.7079
$\mu_z$	3.2874
$\mu(D)$	7.7179
Polarizability	
$\alpha_{xx}$	-156.8089
$\alpha_{yy}$	-188.1295
$\alpha_{zz}$	-187.7466
$\alpha_{total}$	$4.0515 \times 10^{-23}$

$\alpha_0$	-177.5617
Hyper-polarizability	
$\beta_{xxx}$	63.2960
$\beta_{xxv}$	-4.5856
$\beta_{xvv}$	54.3708
$\beta_{vvv}$	258.4406
$\beta_{xxz}$	30.6724
$\beta_{xvz}$	-7.1321
$\beta_{vvz}$	67.6870
$\beta_{xzz}$	-2.9004
$\beta_{vzz}$	25.6297
$\beta_{zzz}$	23.9072
$\beta_0$	$2.81583 \times 10^{-30}$

The calculated hyperpolarizability, polarizability and total dipole moment values of **6** are found to be and  $2.81583 \times 10^{-30}$  esu,  $4.0515 \times 10^{-23}$  Debye-Ang and 7.7179 Debye, respectively whereas the NLO molecule, urea was reported to have hyperpolarizability ( $0.37 \times 10^{-30}$  esu) and dipole moment ( $\mu = 1.3732$  D) [34]. Thus, compound **6** shows 5.6-fold increases in dipole moment and 7.6 time increase in hyperpolarizability value than the urea molecule. This indicates that the compound **6** could serve as an NLO material or could serve as a template to construct efficient NLO materials.

#### H. Molecular electrostatic potential analysis

The molecular electrostatic potential of a compound is associated to density of electrons, which connects molecule's reactivity the nature of the molecule's regulation [35]. The molecular electrostatic potential formed in space is a prime factor in understanding the approachable positions for nucleophile, electrophile and hydrogen bonding interactions [36]. The molecular electrostatic potential can easily be read (color map; red - lowest electrostatic potential; blue - highest electrostatic potential energy values). MEP map of **6** was gained from the optimized operational calculation.

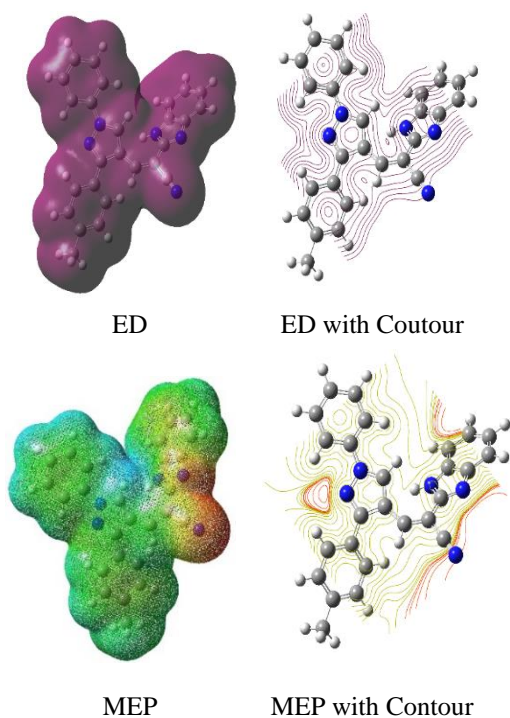


Fig. 5. MEP map of **6**

#### IV. CONCLUSION

To conclude, we have successfully synthesized and characterized a novel acrylonitrile **6**. The target molecule **6** was computed using DFT- B3LYP [6-311++ G(d,p)]. Further, structural optimization, Mulliken charges, MEP analysis, HOMO-LUMO analysis and related parameters were determined. Additionally, the NLO properties were also determined by computing polarizability and hyperpolarizability values and compared the respective values of urea molecule. Thus, the novel acrylonitrile **6** could either serve as potent NLO material or could serve as a building block to construct effective NLO material.

#### ACKNOWLEDGMENT

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## AUTHORS PROFILE



**Ramar Sivaramakarthekeyan** earned his BSc degree in Chemistry from VHNSN College, Virudhunagar, affiliated to Madurai Kamaraj University, Tamilnadu, India in 2013. He completed his MSc in Chemistry in 2015 from Kalasalingam Academy of Research and Education, Krishnankoil. Currently he is pursuing PhD at Kalasalingam Academy of Research and Education, Krishnankoil. He has been working in the area of biopertinent heterocycles.



**Krishnaraj Padmavathy** received her Bachelor of Science degree in Chemistry from Bharathidasan college for women, Pondicherry in 2004. She obtained her Master's degree from Kanchi Mamunivar Centre for Postgraduate Studies, Pondicherry in 2006. She is currently a PhD student at Kalasalingam Academy of Research and Education, Krishnankoil, India. Her focus of research is methodology development and heterocyclic construction for biological applications.



**Shunmugam Iniyaval** obtained her Bachelor of Science degree in Chemistry from Sri Parasakthi College for Women, Courtallam in 2013. She earned her Master's degree in Chemistry in 2015 from Sri Paramakalyani College, Alwarkuruchi. She is currently a PhD student at Kalasalingam Academy of Research and Education, Krishnankoil. She has been working in the area of heterocyclic synthesis and medicinal chemistry.



**Dr. Chennan Ramalingan** is serving as Professor of Chemistry at KARE. He received his PhD in Organic Chemistry from Annamalai University (2002). After he served as Research Professor at Kyungpook National University, South Korea followed by Assistant Professor at Osaka University, Japan (8 years), he joined at Kalasalingam Academy of Research and Education, Krishnankoil (2011). His research interests include organic synthesis, medicinal chemistry and material chemistry. He published more than 70 International research articles.