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Supplementary Information

Growth, physicochemical and quantum chemical investigations on 2-amino 5-chloropyridinium 4-carboxybutanoate – An organic crystal for biological and optoelectronic device applications

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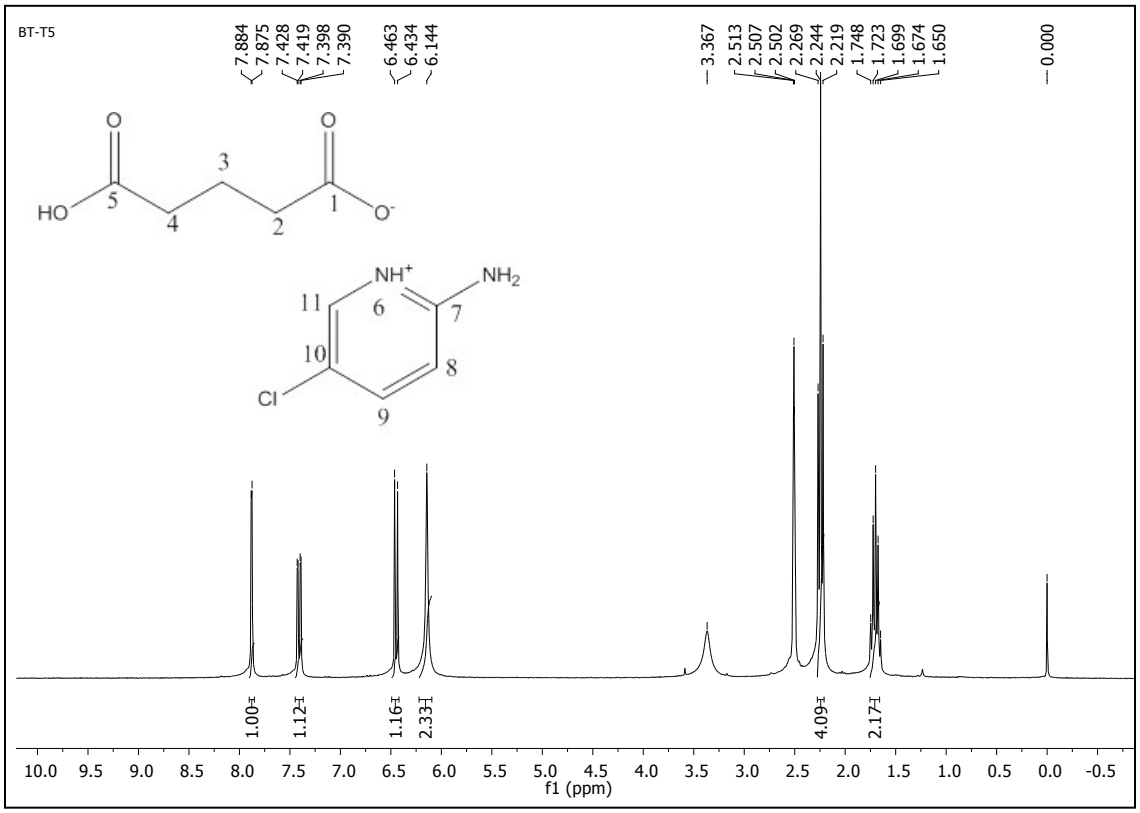

Fig. S1. ^{1}H NMR spectrum of 2A5C4C.

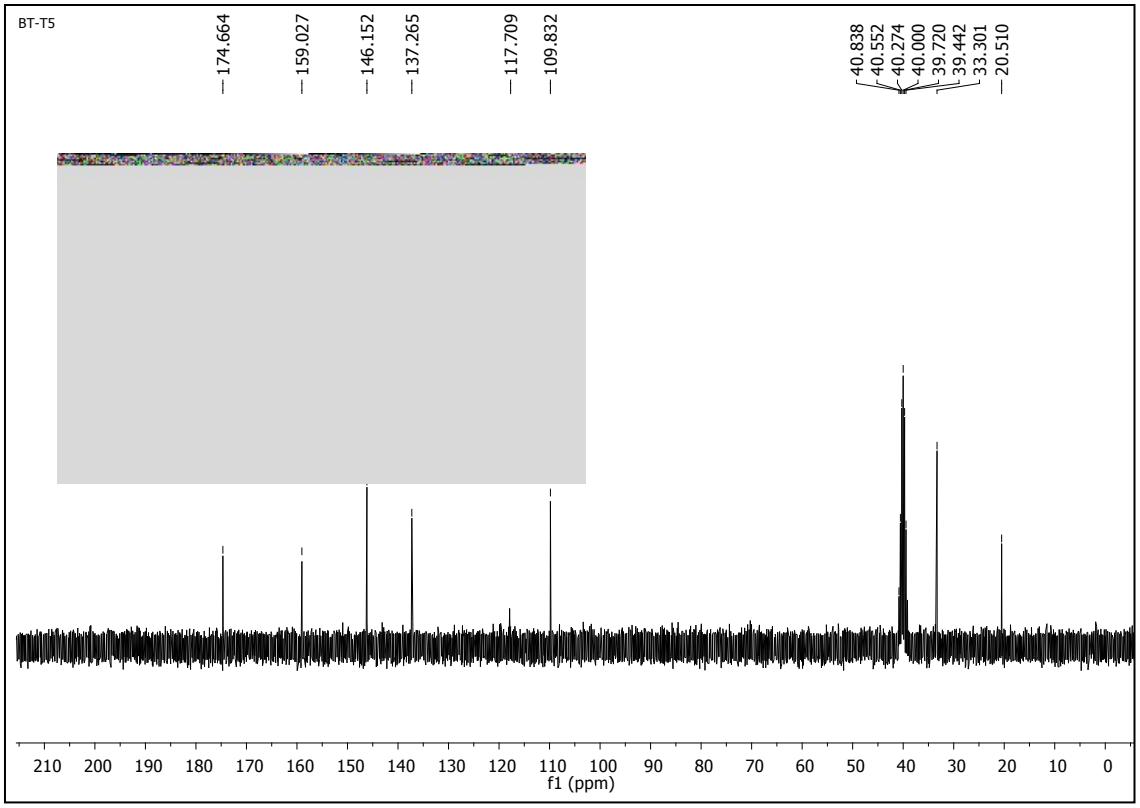

Fig. S2. ^{13}C NMR spectrum of 2A5C4C.

Table S1

^{1}H and ^{13}C NMR chemical shift values of 2A5C4C crystal.

Chemical shift value (ppm)	**Assignment**
The ^{1}H NMR spectral data	
7.88-7.87	Aliphatic carboxylic acid proton.
7.42-7.39	$C_{9,11}$ aromatic proton of the pyridinium moiety.
6.46-6.43	C_8 aromatic proton of the pyridinium moiety.
6.14	NH_2 proton signal.
2.26-2.21	C_2, C_5, aliphatic methylene protons.
1.74-1.65	C_3 aliphatic methylene protons.
^{13}C NMR spectral data	
174.6	Carboxyl carbon of the butanoic acid moiety.
159.0	C_7 carbon of the pyridinium moiety.
146.1	C_{10} carbon of the pyridinium moiety.
137.2	C_9 carbon of the pyridinium moiety.
117.7	C_{11} carbon of the pyridinium moiety.
109.8	C_8 carbon of the pyridinium moiety.
33.3	C_2, C_4 Methylene carbon of butanoic acid.
20.5	C_3 Methylene carbon of butanoic acid.

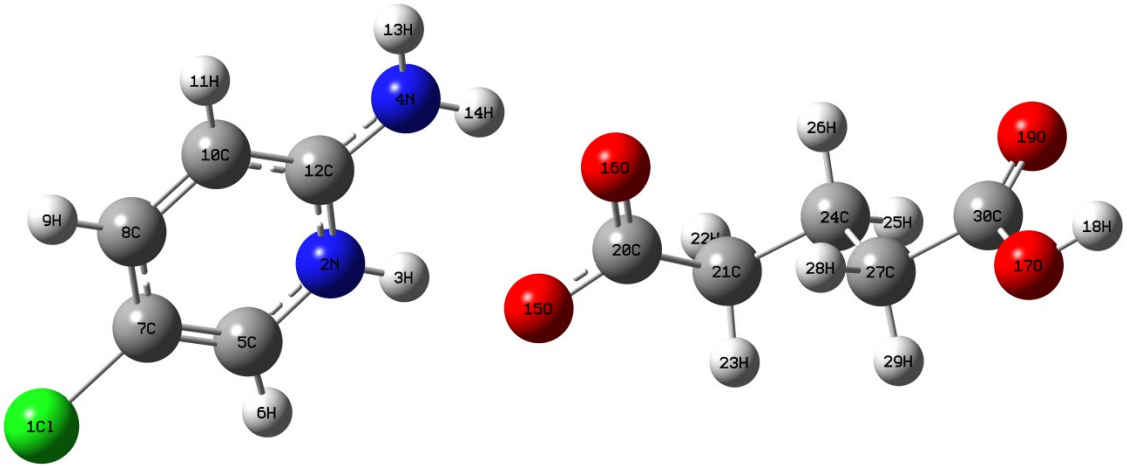

Fig. S3 Molecular structure of 2A5C4C along with numbering of atoms.

Table S2: Optimized geometric parameters of 2A5C4C at B3LYP/6-311++G(d,p) level of theory.

Bond lengths	B3LYP (Å)	XRD (Å)	Bond angles	B3LYP (°)	XRD (°)	Dihedral Angles	B3LYP (°)	XRD (°)
Cl_1-C_7	1.731	1.723	H_3-N_2-C_5	117.36	118.40	H_3-N_2-C_5-H_6	0.15	1.06
N_2-H_3	1.025	0.860	H_3-N_2-C_{12}	118.90	118.46	H_3-N_2-C_5-C_7	-179.82	-178.07
N_2-C_5	1.365	1.349	C_5-N_2-C_{12}	123.74	123.13	C_{12}-N_2-C_5-H_6	-179.99	-178.93
N_2-C_{12}	1.360	1.350	C_{12}-N_4-H_{13}	119.78	119.32	C_{12}-N_2-C_5-C_7	0.04	1.04
H_3-O_{15}	1.924	1.800	C_{12}-N_4-H_{14}	122.21	122.88	H_3-N_2-C_{12}-N_4	-0.15	-0.21
N_4-C_{12}	1.340	1.315	H_{13}-N_4-H_{14}	118.01	116.99	H_3-N_2-C_{12}-C_{10}	179.79	178.25
N_4-H_{13}	1.008	0.874	N_2-C_5-H_6	116.29	119.76	C_5-N_2-C_{12}-N_4	180.00	179.78
N_4-H_{14}	1.014	0.894	N_2-C_5-C_7	119.89	120.42	C_5-N_2-C_{12}-C_{10}	-0.07	-1.76
C_5-H_6	1.082	0.930	H_6-C_5-C_7	123.82	119.82	H_{13}-N_4-C_{12}-N_2	-179.95	-171.01
C_5-C_7	1.371	1.342	Cl_1-C_7-C_5	120.55	120.74	H_{13}-N_4-C_{12}-C_{10}	0.11	10.65
C_7-C_8	1.416	1.405	Cl_1-C_7-C_8	120.91	120.40	H_{14}-N_4-C_{12}-N_2	-0.75	-1.60
C_8-H_9	1.085	0.930	C_5-C_7-C_8	118.55	118.77	H_{14}-N_4-C_{12}-C_{10}	179.32	179.94
C_8-C_{10}	1.375	1.346	C_7-C_8-H_9	119.36	120.01	N_2-C_5-C_7-Cl_1	-179.99	-179.20
C_{10}-H_{11}	1.084	0.930	C_7-C_8-C_{10}	120.51	119.99	N_2-C_5-C_7-C_8	0.02	0.59
C_{10}-C_{12}	1.417	1.403	H_9-C_8-C_{10}	120.13	120.01	H_6-C_5-C_7-Cl_1	0.04	0.77
H_{14}-O_{16}	2.065	1.920	C_8-C_{10}-H_{11}	120.91	119.82	H_6-C_5-C_7-C_8	-179.95	-179.44
O_{15}-C_{20}	1.269	1.274	C_8-C_{10}-C_{12}	120.09	120.80	Cl_1-C_7-C_8-H_9	-0.01	-1.68
O_{16}-C_{20}	1.270	1.233	H_{11}-C_{10}-C_{12}	119.01	119.59	Cl_1-C_7-C_8-C_{10}	179.96	178.38
O_{17}-H_{18}	0.973	0.810	N_2-C_{12}-N_4	119.06	118.57	C_5-C_7-C_8-H_9	179.98	178.54
O_{17}-C_{30}	1.348	1.317	N_2-C_{12}-C_{10}	117.22	116.87	C_5-C_7-C_8-C_{10}	-0.05	-1.40
O_{19}-C_{30}	1.210	1.192	N_4-C_{12}-C_{10}	123.71	124.54	C_7-C_8-C_{10}-H_{11}	-179.97	-179.34
C_{20}-C_{21}	1.489	1.512	H_{18}-O_{17}-C_{30}	107.03	115.76	C_7-C_8-C_{10}-C_{12}	0.02	0.65
C_{21}-H_{22}	1.099	0.969	O_{15}-C_{20}-O_{16}	109.02	122.66	H_9-C_8-C_{10}-H_{11}	0.01	0.72
C_{21}-H_{23}	1.096	0.970	O_{15}-C_{20}-C_{21}	125.53	116.57	H_9-C_8-C_{10}-C_{12}	179.99	179.20
C_{21}-C_{24}	1.538	1.516	O_{16}-C_{20}-C_{21}	125.43	120.76	C_8-C_{10}-C_{12}-N_2	0.04	0.80
C_{24}-H_{25}	1.093	0.971	C_{20}-C_{21}-H_{22}	105.57	108.50	C_8-C_{10}-C_{12}-N_4	179.97	179.25
C_{24}-H_{26}	1.094	0.970	C_{20}-C_{21}-H_{23}	107.50	108.50	H_{11}-C_{10}-C_{12}-N_2	-179.97	-179.13
C_{24}-C_{27}	1.530	1.504	C_{20}-C_{21}-C_{24}	114.07	115.19	H_{11}-C_{10}-C_{12}-N_4	-0.04	-0.77
C_{27}-H_{28}	1.097	0.971	H_{22}-C_{21}-H_{23}	106.09	107.51	H_{18}-O_{17}-C_{30}-O_{19}	-0.68	-6.98
C_{27}-H_{29}	1.097	0.970	H_{22}-C_{21}-C_{24}	110.27	108.48	H_{18}-O_{17}-C_{30}-C_{27}	179.43	173.44
C_{27}-C_{30}	1.518	1.494	H_{23}-C_{21}-C_{24}	112.79	108.42	O_{15}-C_{20}-C_{21}-H_{22}	80.34	-52.02
			C_{21}-C_{24}-H_{25}	108.02	109.17	O_{15}-C_{20}-C_{21}-H_{23}	-32.58	64.40
			C_{21}-C_{24}-H_{26}	110.11	109.25	O_{15}-C_{20}-C_{21}-C_{24}	-158.43	-173.73

C_{21}-C_{24}-C_{27}	113.44	112.07	O_{16}-C_{20}-C_{21}-H_{22}	-97.96	-114.31
H_{25}-C_{24}-H_{26}	105.66	107.90	O_{16}-C_{20}-C_{21}-H_{23}	149.12	120.18
H_{25}-C_{24}-C_{27}	109.46	109.19	O_{16}-C_{20}-C_{21}-C_{24}	23.27	7.47
H_{26}-C_{24}-C_{27}	109.84	109.17	C_{20}-C_{21}-C_{24}-H_{25}	-167.79	-166.49
C_{24}-C_{27}-H_{28}	112.00	108.85	C_{20}-C_{21}-C_{24}-H_{26}	-52.88	-48.73
C_{24}-C_{27}-H_{29}	111.52	108.83	C_{20}-C_{21}-C_{24}-C_{27}	70.67	72.41
C_{24}-C_{27}-C_{30}	111.47	113.56	H_{22}-C_{21}-C_{24}-H_{25}	-49.21	-44.70
H_{28}-C_{27}-H_{29}	106.01	107.74	H_{22}-C_{21}-C_{24}-H_{26}	65.71	73.07
H_{28}-C_{27}-C_{30}	107.63	108.83	H_{22}-C_{21}-C_{24}-C_{27}	-170.74	-165.80
H_{29}-C_{27}-C_{30}	107.94	108.80	H_{23}-C_{21}-C_{24}-H_{25}	69.19	71.76
O_{17}-C_{30}-O_{19}	123.84	122.58	H_{23}-C_{21}-C_{24}-H_{26}	-175.89	-170.47
O_{17}-C_{30}-C_{27}	111.29	112.78	H_{23}-C_{21}-C_{24}-C_{27}	-52.34	-49.34
O_{19}-C_{30}-C_{27}	124.87	124.64	C_{21}-C_{24}-C_{27}-H_{28}	-59.81	-59.09
			C_{21}-C_{24}-C_{27}-H_{29}	58.82	58.07
			C_{21}-C_{24}-C_{27}-C_{30}	179.53	179.52
			H_{25}-C_{24}-C_{27}-H_{28}	179.47	179.82
			H_{25}-C_{24}-C_{27}-H_{29}	-61.91	-63.02
			H_{25}-C_{24}-C_{27}-C_{30}	58.81	58.43
			H_{26}-C_{24}-C_{27}-H_{28}	63.89	62.08
			H_{26}-C_{24}-C_{27}-H_{29}	-177.49	-179.25
			H_{26}-C_{24}-C_{27}-C_{30}	-56.77	-59.31
			C_{24}-C_{27}-C_{30}-O_{17}	-179.19	144.64
			C_{24}-C_{27}-C_{30}-O_{19}	0.92	-34.03
			H_{28}-C_{27}-C_{30}-O_{17}	57.63	23.24
			H_{28}-C_{27}-C_{30}-O_{19}	-122.26	-156.33
			H_{29}-C_{27}-C_{30}-O_{17}	-56.40	-93.94
			H_{29}-C_{27}-C_{30}-O_{19}	123.71	86.40

Table S3. Second order perturbation theory analysis of Fock matrix in NBO basis including the stabilization energies using DFT/B3LYP/6-311++G(d,p) method.

Donor (*i*)	ED(i) (e)	Acceptor (*j*)	ED(*j*) (e)	E(2)[a] (kJ/mol)	E(*j*)-E(*i*)[b] (kJ/mol)	F(*i*, *j*)[c] (kJ/mol)
$\sigma(N_4\text{-}H_{13})$	0.9934	$\sigma^*(N_2\text{-}C_{12})$	0.0155	13.31	4.73	0.32
$\sigma(N_4\text{-}H_{14})$	0.9939	$\sigma^*(C_{10}\text{-}C_{12})$	0.0108	10.26	4.94	0.28
$\sigma(C_5\text{-}H_{6)}$	0.9897	$\sigma^*(N_2\text{-}C_{12})$	0.0155	10.76	4.23	0.27
$\sigma(C_{10}\text{-}H_{11})$	0.9883	$\sigma^*(N_2\text{-}C_{12})$		10.72	4.14	0.27
n_2Cl_1	0.9812	$\sigma^*(C_5\text{-}C_7)$	0.0129	10.13	3.60	0.24
n_1C_7	0.5457	$\pi^*(N_2\text{-}C_5)$	0.3108	423.49	0.38	0.55
n_1C_7		$\pi^*(C_8\text{-}C_{10})$	0.1033	106.18	0.71	0.44
n_1O_{15}	0.9784	$\sigma^*(N_2\text{-}H_3)$	0.0255	20.98	4.90	0.41
n_1O_{16}	0.9829	$\sigma^*(N_4\text{-}H_{14})$	0.0137	13.06	5.11	0.33
$\sigma(O_{15}\text{-}O_{16})$	0.9473	$\sigma^*(O_{15}\text{-}C_{20})$	0.0145	17.92	3.31	0.31
$\sigma(O_{15}\text{-}O_{16})$		$\sigma^*(O_{16}\text{-}C_{20})$	0.0146	18.00	3.31	0.31
$\sigma(O_{15}\text{-}O_{16})$		$\sigma^*(C_{20}\text{-}C_{21})$	0.0313	42.62	2.97	0.46
$\sigma(O_{15}\text{-}C_{20})$	0.9817	$\sigma^*(O_{15}\text{-}O_{16})$	0.0448	25.37	3.52	0.38
$\sigma(O_{16}\text{-}C_{20})$	0.9792	$\sigma^*(O_{15}\text{-}O_{16})$		32.91	3.48	0.44
$\sigma(O_{17}\text{-}H_{18})$	0.9931	$\sigma^*(C_{27}\text{-}C_{30})$	0.0334	10.09	4.65	0.28
$\sigma(C_{21}\text{-}H_{23})$	0.9819	$\sigma^*(O_{16}\text{-}C_{20})$	0.0146	10.47	4.06	0.26
n_1O_{17}	0.9877	$\sigma^*(O_{19}\text{-}C_{30})$	0.0114	16.33	5.07	0.36
n_2O_{17}	0.9071	$\pi^*(O_{19}\text{-}C_{30})$	0.1079	103.92	1.42	0.49
n_2O_{19}	0.9194	$\sigma^*(O_{17}\text{-}C_{30})$	0.0491	69.88	2.60	0.54
n_2O_{19}		$\sigma^*(C_{27}\text{-}C_{30})$	0.0334	43.42	2.64	0.44

Table S4

Theoretical first hyperpolarizability values of 2A5C4C.

Dipole (Debye)		Polarazibility (a.u)		Hyperpolarazibility (a.u)	
μ_x	3.38427319	α_{xx}	235.190613	β_{xxx}	1905.92510
μ_y	-3.85133901	α_{yy}	-24.5448184	β_{yyy}	-1110.14756
μ_z	-0.393309184	α_{zz}	147.814191	β_{zzz}	673.793837
		α_{xy}	-21.5663200	β_{xyy}	-516.394448
		α_{xz}	-8.48561424	β_{xxy}	16.9186946
		α_{yz}	121.929851	β_{xxz}	-53.1985168
				β_{xzz}	26.9124082
				β_{yzz}	35.4530743
				β_{yyz}	-55.6048558
				β_{xyz}	23.3409203

Thermodynamical properties

On the basis of vibrational analysis at B3LYP/ 6-311++G (d,p) basis set the values of several thermodynamic parameters such as zero point vibrational energy (ZPVE), thermal energy, specific heat capacity ($C_{v)}$, rotational constants, entropy (S) of 2A5C4C is calculated and are presented in Table S5. The obtained value of ZPVE of 2A5C4C is 142.50220 kcl/mol at B3LYP/ 6-311++G (d,p). Dipole moment reflects the molecular charge distribution and is given as a vector in three dimensions. Therefore, it can be used as a descriptor to depict the charge movement across the molecule. The direction of the dipole moment vector in a molecule depends on the centers of positive and negative charges. Dipole moments are strictly determined for neutral molecules. For charged systems, its value depends on the choice of origin and molecular orientation. As a result of B3LYP/ 6-311++G (d,p) basis set calculations the dipole moment of 13.0698 was observed.

Table S5 Thermodynamical properties of 2A5C4C.

Basis Set	B3LYP/ 6-311++G(d,p)
Zero point energy (Kcal/Mol)	142.50220
Rotational constant	0.86930
Rotational temperature	0.04172
Energy (E)	
Translational	0.889
Rotational	0.889
Vibrational	147.625
Total	149.402
Specific heat (C_v)	
Translational	2.981
Rotational	2.981
Vibrational	40.359
Total	46.320
Entropy(S)	
Translational	42.567
Rotational	34.287
Vibrational	28.540
Total	105.394
Dipole moment	13.0698

Mulliken population analysis and natural population analysis

The calculation of atomic charges plays an important role in the application of quantum chemical calculation to a molecular system because of atomic charges effect dipole moment, molecular polarizability, electronic structure and more a lot of properties of molecular systems. The Mulliken and Natural Population analyses are very common and effective population analysis methods and the total atomic charge values are obtained by Mulliken population analysis, and natural charges are obtained by NBO (natural bond analysis), although, both methods predict the same tendencies. In the present study B3LYP/6-311++G (d,p) method was employed to study both the atomic charge population of 2A5C4C. In both the NPA and Mulliken analysis the charges of the N2 and N4 nitrogen atoms (-0.25976&-0.39174 (NPA) and -0.58473 & -0.64878 (Mulliken)) and O15, O16, O17 and O19 oxygen atoms (-0.47217, -0.48174, -0.35148, -0.29587 (NPA) and -0.37721, -0.35075, -0.47992, -0.44602 (Mulliken)) exhibits substantial negative values and act as a electron donors. All the hydrogen atoms exhibit a net positive charge. The presence of large negative charge on O atom and net positive charge on H atom may suggest the formation of intramolecular interaction in solid forms.[1]

Minor dissimilarities in the natural and Mulliken atomic charges are noted (Fig. S4 and Table S6). The variation error between the natural and Mulliken atomic charges has been expressed by root mean square deviation (RMSD) using the following equation[2]

$$RMSD = \sqrt{\frac{1}{n-1}\sum_{i}^{n}(\gamma_{i}^{Natural} - \gamma_{i}^{Mulliken})^2} \qquad (1)$$

Where n is the number of natural or Mulliken data. The RMSD value is found to be 0.00001% error for natural and Mulliken atomic charges.

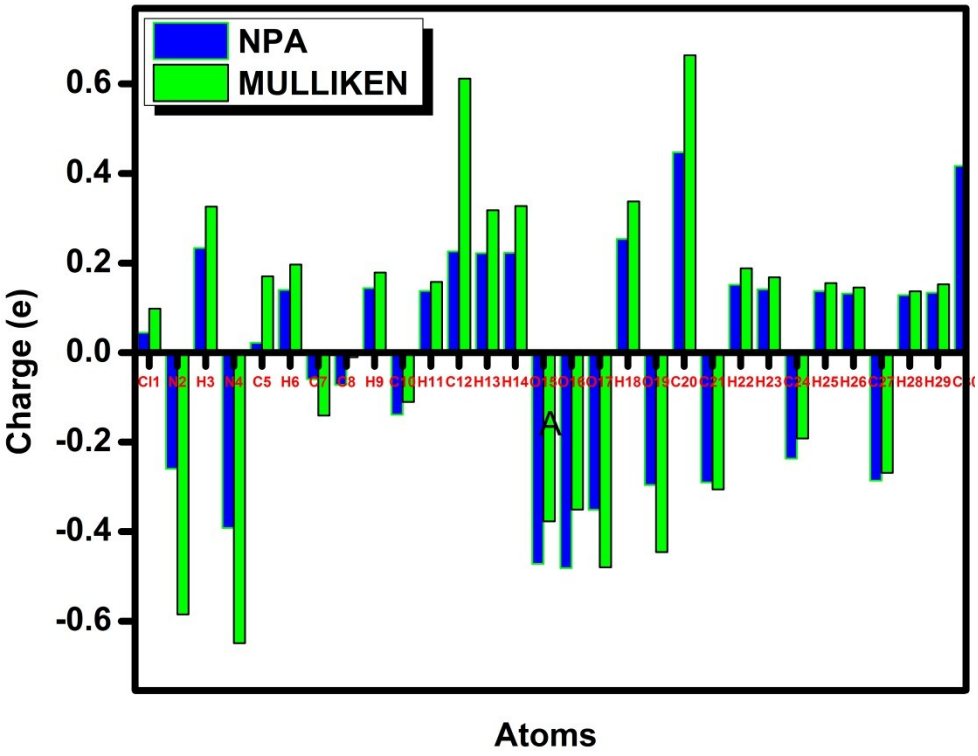

Fig. S4. Atomic charge population of 2A5C4C..

Table S6 Atomic charge population of 2A5C4C.

Atoms	Natural population	Mulliken population
Cl1	0.04447	0.097923
N2	-0.25976	-0.58473
H3	0.23367	0.326296
N4	-0.39174	-0.64878
C5	0.022	0.170512
H6	0.13983	0.196798
C7	-0.05926	-0.14074
C8	-0.0725	-0.01035
H9	0.14406	0.178909
C10	-0.13883	-0.11013
H11	0.13802	0.157856

C12	0.22628	0.611799
H13	0.2223	0.318144
H14	0.22293	0.327321
O15	-0.47217	-0.37721
O16	-0.48174	-0.35075
O17	-0.35148	-0.47992
H18	0.25397	0.337649
O19	-0.29587	-0.44602
C20	0.44753	0.663785
C21	-0.29021	-0.30563
H22	0.15176	0.188238
H23	0.14152	0.168087
C24	-0.23711	-0.19185
H25	0.13727	0.155062
H26	0.13181	0.145538
C27	-0.28604	-0.26864
H28	0.12858	0.136911

References

1. Rubarani P. Gangadharan, and S. Sampath Krishnan, *Acta Physica Polonica A* 2015, **127,** 748-752.
2. R. Agilandeswari, A. Aditya Prasad, S. Sivaraman, S. Kalainathan and SP. Meenakshisundaram, *Mol. Cryst. Liq. Cryst.,* 2016, **625,** 238-252.