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MOLECULAR INTERACTIONS IN 2-AMINOPYRIDINIUM MALONATE

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A new complex of 2-aminopyridine and malonic acid in a 1:1 stoichiometric ratio is obtained. The complex crystallizes in a centrosymmetric $P2_1/c$ space group with $a = 3.8522(2)$ Å, $b = 17.5226(8)$ Å, $c = 13.7317(7)$ Å and $\beta = 94.418(3)^\circ$. This complex is held by network of hydrogen bonds between the protonated 2-aminopyridinium cation and the malonate anion. There is no phase transition observed in this complex, which is verified using DSC and single crystal X-ray measurement studies. Unlike 2-aminopyridinium maleate, this complex crystallizes in the centrosymmetric space group and hence, this complex will not exhibit any non-linear optical property.

Keywords: 2-aminopyridinium, malonate, single crystal X-ray diffraction, Raman scattering, DSC, IR.

INTRODUCTION

Supramolecular interactions, which include hydrogen bonding, play a vital role in the design of supramolecular synthon [1, 2]. There are two categories: supramolecular homosynthon [3] and supramolecular heterosynthon [4]. The heterocyclic 2-aminopyridine molecule with two nitrogen atoms has often been used as a ligand in metal complexes [5] and with nitrophenols to generate a non-centrosymmetric lattice [6] that exhibits second harmonic generation. The complexes of 2-aminopyridine with carboxylic acids generally result in heterosynthon [7] as there are more than one hydrogen bonding groups present. Complexes of 2-aminopyridine with maleic acid resulted in complexes with varying stoichiometric ratios, i.e. 2-aminopyridinium maleate [8], bis(2-aminopyridinium) maleate [9], and the anomalous salt 2-aminopyridinium maleate maleic acid [10]. Out of the three complexes of 2-aminopyridine with maleic acid, the 1:1 and 2:1 complexes crystallized in a non-centrosymmetric space group with the crystal having a non-linear optical property. This prompted us to crystallize 2-aminopyridine with malonic acid (another dicarboxylic acid) in a 1:1 stoichiometric ratio. Unlike 2-aminopyridinium maleate, this complex crystallizes in a centrosymmetric space group. The 2-aminopyridine molecule exists in the protonated state and malonic acid exists in the monoionized state. We report here the structural study of a 1:1 complex of 2-aminopyridine and malonic acid.

CRYSTALLIZATION

Colorless single crystals of the title complex were grown as three-dimensional crystals by slow evaporation from an aqueous solution containing 2-aminopyridine and malonic acid in a 1:1 stoichiometric ratio.

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Table 1

Crystal data and structure refinement details for 2-aminopyridinium malonate at 300 K and 100 K

CCDC No.	781829	781828
Empirical formula	C ₈ H ₁₀ N ₂ O ₄	C ₈ H ₁₀ N ₂ O ₄
Formula weight	198.18	198.18
Temperature, K	300	100
Wavelength, Å	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> , <i>b</i> , <i>c</i> , Å; β, deg.	3.8522(2), 17.5226(8), 13.7317(7); 94.418(3)	3.7415(15), 17.5106(8) 13.6586(17); 95.990(9)
Volume, Å ³	924.14 (8)	890.0 (4)
<i>Z</i>	4	4
Calculated density, Mg·m ⁻³	1.424	1.479
Crystal size, mm ³	0.50×0.21×0.10	0.50×0.21×0.10
θ range for data collection, deg.	1.89—36.35	1.9—31.13
Limiting indices	−6 ≤ <i>h</i> ≤ 6, −29 ≤ <i>k</i> ≤ 28, −22 ≤ <i>l</i> ≤ 21	−5 ≤ <i>h</i> ≤ 5, −25 ≤ <i>k</i> ≤ 24, −19 ≤ <i>l</i> ≤ 19
Reflections collected / unique	16200 / 4450 [<i>R</i> (int) = 0.0296]	16559 / 2876 [<i>R</i> (int) = 0.038]
Data / restraints / parameters	4450/0/167	2876/0/167
Goodness-of-fit on <i>F</i> ²	1.00	1.05
Final <i>R</i> indices [<i>R</i> (<i>F</i> ² > 2σ(<i>F</i> ²))]	<i>R</i> 1 = 0.052, <i>wR</i> (<i>F</i> ²) = 0.1365	<i>R</i> 1 = 0.033, <i>wR</i> (<i>F</i> ²) = 0.094
<i>R</i> indices (all data)	<i>R</i> 1 = 0.1083, <i>wR</i> (<i>F</i> ²) = 0.1662	<i>R</i> 1 = 0.040, <i>wR</i> (<i>F</i> ²) = 0.0979

EXPERIMENTAL

For Raman measurements, Horiba Jobin Yvon HR 800 Micro Laser Raman instrument with a laser wavelength of 633 nm and a CCD-based detector with a spectral resolution of 1 cm⁻¹ was used. Spectral line positions were determined by fitting a Lorentzian to the measured spectra. Room temperature FT—IR spectra of polycrystalline sample were measured by a BOMEM MB series FTIR spectrometer. A Ge-coated KBr beamsplitter and a MCT detector were used to record the spectrum in the range of 200—3500 cm⁻¹ with a spectral resolution of 4 cm⁻¹.

The room and low temperature (100 K) data were collected on a Bruker-SMART Apex II 4K CCD diffractometer using MoK_α graphite-monochromated radiation (λ = 0.71073 Å).

The structure was determined using direct methods as implemented in SHELXS [11]. The atomic parameters so obtained were subjected to a series of isotropic and anisotropic full matrix least squares refinements using SHELXL97 [11]. All the reflections were used for the refinement. In the initial stages of the refinement, the reflection weight (*w*) was taken to be 1/σ(*F*₀²), which was derived using counting statistics. All the non-hydrogen thermal parameters were refined anisotropically and all the hydrogen atoms were located from the difference Fourier map, and their thermal parameters were refined isotropically. Crystallographic and refinement details for 300 K and 100 K are summarized in Table 1 respectively.

RESULTS AND DISCUSSION

A strong peak in the difference Fourier at a distance of 0.92 Å from N1 was observed, suggesting that the N1 atom is protonated in the present structure. The increased internal angles (C4—N1—C8 = 122.7(1)°) and the lengthening of bond lengths around (N1—C4 = 1.348(1) Å, N1—C8 = 1.355(2) Å) are also consistent with the protonation at N1. The bond distances in the C1O2O1 group (C1—O2 = 1.238(1) Å and C1—O1 = 1.260(1) Å) and in the C3O3O4 group (C3—O3 = 1.298(2) Å and C3—O4 = 1.210(2) Å) indicate that the former group appears as carboxylate —COO⁻ and the later

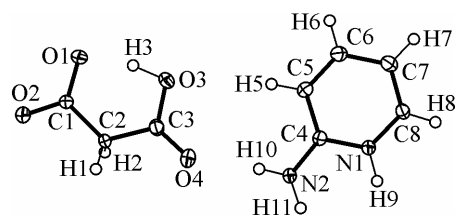


Fig. 1. ORTEP [12] picture of the asymmetric unit of 2-aminopyridinium malonate with a 50 % ellipsoidal probability

Table 2

Bond parameters of 2-aminopyridinium malonate at 300 K and 100 K

Atoms	Bond distance, Å		Atoms	Bond angle, deg.	
	300 K	100 K		300 K	100 K
2-aminopyridine					
N2—C4	1.330(2)	1.335(1)	N2—C4—N1	118.5(1)	118.67(7)
C4—N1	1.348(1)	1.352(1)	N2—C4—C5	123.5(1)	123.11(7)
C4—C5	1.410(2)	1.418(1)	N1—C4—C5	118.0(1)	118.22(7)
C5—C6	1.357(2)	1.369(1)	C6—C5—C4	119.3(1)	119.23(8)
C6—C7	1.403(2)	1.414(1)	N2—C4—N1	118.5(1)	118.67(7)
C7—C8	1.354(2)	1.364(1)	C5—C6—C7	121.3(1)	121.02(8)
C8—N1	1.355(2)	1.364(1)	C8—C7—C6	118.0(1)	118.15(8)
C6—H6	0.99(2)	0.98(1)	C4—N1—C8	122.7(1)	122.76(7)
C8—H8	0.97(2)	0.95(1)	C7—C8—N1	120.8(1)	120.61(7)
Malonate ion					
O1—C1	1.260(1)	1.271(1)	O1—C1—C2	118.5(1)	118.52(7)
O2—C1	1.238(1)	1.248(1)	C3—C2—C1	118.6(1)	118.25(7)
C1—C2	1.512(2)	1.523(1)	O2—C1—C2	116.8(1)	116.50(7)
C2—C3	1.502(2)	1.510(1)	O2—C1—O1	124.7(1)	124.97(7)
C3—O4	1.210(2)	1.221(1)	O4—C3—O3	121.9(1)	122.19(8)
C3—O3	1.298(2)	1.314(1)	O3—C3—C2	117.3(1)	117.22(7)
			O4—C3—C2	120.8(1)	120.56(7)

as carboxyl —COOH. Hence, malonic acid is in the monoionized state. Malonic acid transfers one of its protons to aminopyridine, thus the asymmetric unit consists of a 2-aminopyridine molecule in the protonated form and malonic acid in the monoionized state (Fig. 1). A comparison of the bond parameters at these two temperatures is listed in Table 2.

MOLECULAR INTERACTIONS

The interaction between 2-aminopyridine and malonic acid results in heteromolecular synthon arranged in layers. Fig. 2 shows the packing diagram of the complex as viewed down the *a* axis. The geometrical arrangement in the crystal structure was analysed using the RPLUTO program [13] to generate the graph set as shown in Table 3. The 2-aminopyridinium ion interacts through N—H...O hydrogen bonds to the neighboring malonate ions. The 1:1 supramolecular adduct is almost planar, with an angle between the planes being 13.77(0.04)° and 12.52(0.04)° for 300 K and 100 K respectively. Anti-oriented N—H of amine of the 2-aminopyridinium cation is involved in an additional N—H...O hydrogen bond with the neighboring malonate ion generating a 1D chain of supramolecular heterosynthons along the *b* axis, with an angle between these two being 83.70(0.06)° and 79.70(1)° at 300 K and 100 K respectively. The 1-dimensional chains within one layer are interconnected with each other through the C—H...O bonds. It is also seen that at 100 K an additional C—H...O hydrogen bond (Table 4b) is developed. The hydrogen bond parameters at 300 K and 100 K are listed in Table 4.

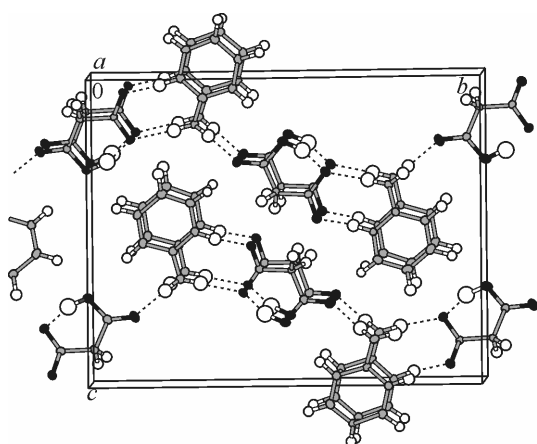
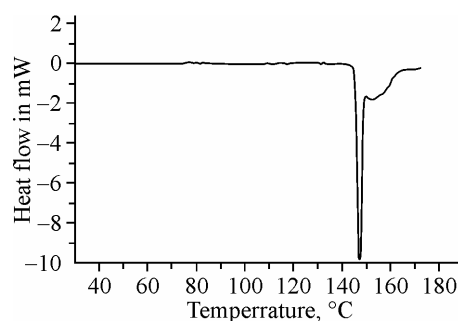
Fig. 2. Packing viewed down the *a* axis

Fig. 3. DSC curve of 2-aminopyridinium malonate

Another interesting aspect is the presence of the π — π interaction between the 2-aminopyridinium molecules that are related by $1+x, y, z$ (face-to-face interaction). Although the malonate anion is not aromatic, because of the intramolecular hydrogen bond there is a polarized multiple bond in the present structure. This results in face-to-face π — π interactions between the malonate molecules related by $1+x, y, z$. Various parameters associated with the π — π interactions are listed in Table 5.

The DSC curve of the present complex is shown in Fig. 3. There is a no phase transition observed in this range. The melting point of this complex occurs at 145.57 °C.

A comparison between 2-aminopyridinium malonate and 2-aminopyridinium maleate shows that in both complexes, the 2-aminopyridine molecule is in the protonated state with the positive charge

Table 3

Graph set				
Atoms	O3H3O1	N2H11O1	N2H10O4	N1H9O2
O3H3O1	S(6)			
N2H11O1		<i>D</i>		
N2H10O4		$C_2^2(8)$	<i>D</i>	
N1H9O2		$R_2^2(8)$	$C_2^2(10)$	<i>D</i>

Table 4

Hydrogen bond parameters (Å, deg.) of 2-Aminopyridinium malonate

Atoms	D—H		H...A		D...A		D—H...A	
	300K	100K	300K	100K	300K	100K	300K	100K
O3—H3...O1	1.02(2)	1.01(2)	1.49(2)	1.50(2)	2.474(2)	2.479(9)	160(2)	163(2)
N2—H11...O1 ⁱ	0.95(2)	0.95(2)	1.99(2)	1.99(2)	2.943(2)	2.936(1)	178(1)	176(1)
N2—H10...O4	0.91(2)	0.86(1)	1.96(2)	2.00(1)	2.854(2)	2.852(1)	169(2)	171(1)
N1—H9...O2 ⁱ	0.93(2)	0.95(1)	1.74(2)	1.71(1)	2.657(1)	2.660(2)	174(2)	173(1)
C2—H2...O2 ⁱⁱ	0.99(1)	0.99(1)	2.45(2)	2.40(1)	3.374(2)	3.312(1)	155(1)	154(1)
C8—H8...O4 ⁱⁱⁱ	0.97(2)	0.95(1)	2.58(2)	2.55(1)	3.495(2)	3.451(1)	158(1)	159(1)
C2—H1...O2 ^{iv}		0.99(1)		2.59(1)		3.377(1)		136(1)

Symmetry codes: (i) $-x, 1/2+y, 3/2-z$; (ii) $-x, 1-y, 1-z$; (iii) $-1+x, 3/2-y, 1/2+z$; (iv) $1-x, 1-y, 1-z$.

Table 5

 π — π interactions in 2-Aminopyridinium malonate at 300 K and 100 K

Temperature	Plane distance, Å		Plane angle, deg.		Centroid distance, Å	
	300 K	100 K	300 K	100 K	300 K	100 K
2-aminopyridine-2 aminopyridine	3.471	3.370	0.0	0.0	3.852	3.742
Malonate—malonate	3.485	3.330	0.0	0.0	3.852	3.742

Table 6

Assignment of internal modes (cm^{-1}) of Raman and IR Spectra of 2-aminopyridinium malonate by comparing with malonic acid and 2-aminopyridine

Mode	2-Aminopyridine		Malonic acid		2-Aminopyridinium malonate	
	Raman	IR	Raman	IR	Raman	IR
ν_{27} or C-NH ₂ in-plane bending	421				419	426
Asymmetrical twisting or bending (γ CCO)			432	451	433	459
C—N—C out-of-plane bend or ν_{10}	545	564			553	552
NH ₂ out-of-plane bend or ν_{19} mode	621	628			623	621
δ (COOH) and OCO wagging			765	770	745	757
CNC in-plane bend (γ CH, ν_{24})	767	766			778	773
Out-of-plane CH bending vibration or ν_8	840	845			847	855
π (OH)				918	898	896
ν_{sym} (C—C) stretch			961	960	944	940
Ring breathing mode ν_9	997	986			981	983
δ_{ring} or ν_7 mode	1048	1038			1034	1032
CH out-of-plane bending or δ (CH), ν_{18}	1131	1141			1141	
ν_{antisym} (C—C)			1180	1174	1172	1169
CH in-plane bend δ (CH), ν_{16}	1263	1278			1260	1273
ν (C—NH ₂), ν_3	1325	1314			1330	1338
δ CH ₂			1418	1435	1429	1434
ν_{ring} , ν_{14} , 19b	1445	1442				1452
C=N stretch or ν_5	1486	1491			1485	1494
C—C stretching in the ring	1545	1560			1547	
C—C stretching in the ring	1584	1599			1587	
H—N ⁺ —H scissoring	1627	1629			1627	1635
ν_{str} C=O			1686	1737		1682
ν_s (C—H)			2941		2912	2928
ν_{as} (C—H)			2980	2980	2961	2975
ν (C—H)	3028	3024			3046	3050
ν (C—H)	3053	3054			3073	3080
ν (C—H)	3070	3061			3094	3103
N—H stretch	3300	3309			3130	3149
N—H stretch	3442	3447			3241	
N—H stretch					3311	3335

The assignments for 2-amiopyridine has been taken from [14, 15, and 16] and for malonic acid from [17, 18, 19, and 25].

residing on the N1 ring nitrogen. It is observed that the melting point of 2-aminopyridinium malonate is not very different from that of 2-aminopyridinium maleate (144.69 °C) [8]. A comparison of hydrogen bonding parameters shows that in both complexes, 2-aminopyridinium molecules have similar hydrogen bonding parameters with shorter D...A distances and larger $\angle DH...A$ in the case of malonate. The O—H...O intramolecular hydrogen bond of malonate has a shorter O...O distance and a shorter O—H...O angle compared to that of maleate, which has a longer O...O distance and a larger O—H...O angle; furthermore, the intramolecular hydrogen bond is more symmetric in maleate compared to that in malonate.

The assignment of the internal modes (Table 6) of the Raman and IR spectra of 2-aminopyridinium malonate was achieved by comparing the Raman and IR frequencies of the title compound with those observed in the parent molecules, i.e 2-aminopyridine [14—16], malonic acid [17—19], and their complexes [8, 10, 20—25], as one expects close correspondence between the internal frequencies of these molecules.

CONCLUSIONS

2-Aminopyridinium malonate crystallizes in the centrosymmetric $P21/c$ space group with the protonated 2-aminopyridinium cation and the malonate anion. Both the 2-aminopyridinium ion and malonate ion are planar. The planarity of the malonate ion is stabilized by the intramolecular O—H...O hydrogen bond. The 2-aminopyridinium ion interacts through N—H...O and C—H...O hydrogen bonds to the neighboring malonate ions. The temperature reduction from 300 K to 100 K leaves the structure unchanged. In the case of 2-aminopyridinium maleate, the intramolecular hydrogen bond is more symmetric compared to that of 2-aminopyridinium malonate. Since 2-aminopyridinium malonate crystallizes in the centrosymmetric space group, unlike 2-aminopyridinium malonate, this crystal does not possess any non-linear optical property.

REFERENCES

1. Desiraju G.R. // *Angew // Chem. Int. Ed. Eng.* – 1995. – **34**, N 21. – P. 2311 – 2327.
2. Nangia A., Desiraju G.R. // *Top Curr // Chem.* – 1998. – **198**. – P. 57 – 95.
3. Walsh R.D.B., Bradner M., Fleischman S. et al. // *Chem. Commun.* – 2003. – **2**. – P. 86 – 187.
4. Vishweshwar P. *Hetersynthons in Crystal Engineering*, Ph.D. Thesis, University of Mumbai, India, 2003.
5. Qin J., Su N., Dai C. et al. // *Polyhedron.* – 1999. – **18**, N 26. – P. 3461 – 3464.
6. Jaya Prakash M., Radhakrishnan T.P. // *Cryst. Growth Design.* – 2005. – **5**, N 2. – P. 721 – 725.
7. Joanna B., Zaworotko M.J. // *Cryst. Growth Design.* – 2005. – **5**, N 3. – P. 1169 – 1179.
8. Chitra R., Roussel P., Capet F. et al. // *J. Mol. Struct.* – 2008. – **891**, N 1 – 3. – P. 103 – 109.
9. Büyükgüngör O., Odabaşoğlu M. // *Acta Cryst.* – 2003. – **C59**, N 3. – P. O105 – O106.
10. Chitra R., Roussel P., Capet F. et al. // *J. Mol. Struct.* – 2009. – **923**, N 1 – 3. – P. 45 – 52.
11. Sheldrick G.M. *SHELXS97: Program for the Crystal Structure Solution and Refinement*. University of Göttingen, Germany, 1997.
12. Farrugia L.J. // *J. Appl. Cryst.* – 1997. – **30**, N 5. – P. 565.
13. Motherwell W.D., Shields P.G., Allen F.H. // *Acta Cryst.* – 2000. – **B56**, N 3. – P. 466 – 473.
14. Carmona P., Molina M. // *Spectrochim. Acta. Part A.* – 1993. – **49**, N 1. – P. 1 – 9.
15. Jose S.P., Mohan S. // *Spectrochim. Acta. Part A.* – 2006. – **64**, N 1. – P. 240 – 245.
16. Büyükmurat Y., Akalin E., Özel A.E., Akyüz S. // *J. Mol. Struct.* – 1999. – **482 – 483**. – P. 579 – 584.
17. Bougeard D., Villepan J.De., Novak A. // *Spectrochim. Acta. Part A.* – 1988. – **44**, N 12. – P. 1281 – 1286.
18. Ganguly S., Fernandes J.R., Desiraju G.R., Rao C.N.R. // *Chem. Phys. Lett.* – 1980. – **69**, N 12. – P. 227 – 229.
19. Villepan J.De., Limage M.H., Novak A. et al. // *J. Raman Spectroscopy.* – 1984. – **15**, N 1. – P. 41 – 46.
20. Spinner E. // *J. Chem. Soc.* – 1962. – P. 3119 – 3126.
21. Odabaşoğlu M., Büyükgüngör O., Turgut G. et al. // *J. Mol. Struct.* – 2003. – **648**, N 1 – 2. – P. 133 – 138.
22. Ristova M., Petrusevski G., Raskovska A., Soptrajanov B. // *J. Mol. Struct.* – 2009. – **924 – 926**. – P. 93 – 99.
23. Brusau E.V., Narda G.E., Pedregosa J.C. et al. // *J. of Solid State Chemistry.* – 1999. – **143**, N 2. – P. 174 – 181.
24. Brusau E.V., Pedregosa J.C., Narda G.E. et al. // *The Journal of the Argentine Chemical Society.* – 2004. – **92**, N 1 – 3. – P. 43 – 52.
25. Schmelz M.J., Nakagawa I., Mizushima S.I. et al. // *J. Amer. Chem. Soc.* – 1959. – **81**, N 2. – P. 287 – 290.