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Varieties in symmetry non-equivalent structural arrangements in solvates of 2-(3-methylene-1,3,7-trioxo-6-(2-carboxy-phenyl)-3,5,6,7-tetrahydro-1*H*-pyrrolo[3,4-*f*]isoindol-2-yl)benzoic acid

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ABSTRACT

The crystal structures of few solvates of 2-(3-methylene-1,3,7-trioxo-6-(2-carboxy-phenyl)-3,5,6,7-tetrahydro-1*H*-pyrrolo[3,4-*f*]isoindol-2-yl)benzoic acid (**A**) namely **A·4H$_2$O; A·2DMF; A·2Py; A·3Py** are determined (where Py = pyridine, DMF = dimethylformamide). The crystal structure of the hydrated form has $Z' = 0.5$, whereas other solvates with DMF and pyridine has $Z' = 1$. The neighboring host molecules in the crystal lattices of these solvates have different orientations; these orientations are related by translation or translation cum rotation of the orientation to the neighboring host molecules that has the most symmetric structure.

1. Introduction

The term Z' in crystallography refers to the number of formula units present in an asymmetric unit [1–5]. The Z' is decided by the number of formula units in a unit cell divided by independent general positions. Depending on Z' value, numbers of molecules that requires independent set of coordinate per unit cell varies [1–5]. A good amount of discussions on the symmetry non-equivalent molecules [6–15] are available in literature. Solvent molecules during crystallization play a major role in formation of lattice with high Z' value [16]. Systematic examples on solvates of same host showing high Z' value is difficult to obtain and it is a concern in understanding their mechanism of formation. Much attention is needed to identify systems that would have different Z' since different orientations in lattices would enhance Z'. The processes like self assembling, solvation and host–guest interactions may cause symmetry non-equivalence among host molecules and cause higher Z'. Symmetry non-equivalence may occur in cocrystals [6–15] as well as in unsolvated molecules [17]. Since the above mentioned processes involve assembly formation, the occurrence of high Z' may be related to metastable [18,19] states. It is a well known fact that crystallization of same compound under different conditions leads to polymorphs [20] and symmetry non-equivalent molecules [21]. Our interest has been to trap different solvated species to understand the role of solvents in making symmetry non-equivalent hosts and vice versa. With such an approach, we present the structural features of few solvates of 2-(3-methylene-1,3,7-trioxo-6-(2-carboxy-phenyl)-3,5,6,7-tetrahydro-1*H*-pyrrolo[3,4-*f*]isoindol-2-yl)benzoic acid (**A**).

2. Experimental

The X-ray single crystal diffraction data were collected at 296 K with MoK$_\alpha$ radiation ($\lambda = 0.71073$ Å) using a Bruker Nonius SMART CCD diffractometer equipped with a graphite monochromator. The SMART software was used for data collection and also for indexing the reflections and determining the unit cell parameters; the collected data were integrated using SAINT software. The structures were solved by direct methods and refined by full-matrix least-squares calculations using SHELXTL software. All the non-H atoms were refined in the anisotropic approximation against F^2 of all reflections. The H-atoms, except those attached to nitrogen and oxygen atoms were placed at their calculated positions and refined in the isotropic approximation; those attached to nitrogen and oxygen were located in the difference Fourier maps, and refined with isotropic displacement coefficients. Crystallographic data collection was done at room temperature and the data are tabulated in Table 1.

2.1. Synthesis of compound **A**

A solution of pyromellitic dianhydride (1.090 g, 5 mmol) and 2-aminobenzoic acid (1.31 g, 10 mmol) in acetic acid (25 ml) was

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Table 1
Crystallographic parameters of the solvates of **A.**

Compound name	**A.4H$_2$O**	**A.2DMF**	**A.2Py**	**A.3Py**
Formulae	$C_{24}H_{20}N_2O_{12}$	$C_{30}H_{26}N_4O_{10}$	$C_{34}H_{22}N_4O_8$	$C_{39}H_{27}N_5O_8$
Moiety formula	**0.5A.2H$_2$O**	**A.2DMF**	**A.2Py**	**A.3py**
CCDC No.	728168	728171	728169	728170
Mol. wt.	528.42	602.55	614.56	693.66
Crystal system	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	C2/c	P-1	P-1	P-1
a/Å	25.5700(8)	10.2817(4)	10.9902(8)	10.1284(5)
b/Å	7.8587(2)	13.0590(4)	12.4771(9)	13.6116(7)
c/Å	13.3821(4)	13.1451(4)	13.2683(10)	14.2771(7)
α/°	90.00	60.9530(10)	116.622(4)	92.706(3)
β/°	118.488(3)	78.2450(10)	90.239(5)	110.091(3)
γ/°	90.00	72.6000(10)	107.989(5)	108.302(3)
V/Å^3	2363.49(12)	1468.75(9)	1525.12(19)	1728.26(15)
Z	4	2	2	2
Density/Mgm^{-3}	1.485	1.362	1.338	1.333
Abs. Coeff. /mm^{-1}	0.121	0.104	0.097	0.095
Abs. correction	None	None	None	None
F(000)	1096	628	636	720
Total No. of reflections	10293	16464	15651	21127
Reflections, $I > 2\sigma(I)$	1947	3655	2957	3680
Max. θ/°	26.00	28.31	25.00	28.23
Ranges (h, k, l)	$-30 <= h <= 31$ $-9 <= k <= 9$ $-16 <= l <= 16$	$-13 <= h <= 13$ $-16 <= k <= 17$ $-15 <= l <= 17$	$-12 <= h <= 12$ $-14 <= k <= 14$ $-15 <= l <= 15$	$-13 <= h <= 13$ $-17 <= k <= 17$ $-18 <= l <= 18$
Complete to 2θ (%)	99.6	97.8	95.8	97.3
Data/restraints/parameters	2361/0/189	7167/0/403	5142/0/417	8294/0/472
Goof (F^2)	1.056	1.056	1.016	1.068
R indices [$I > 2\sigma(I)$]	$R_1 = 0.0406$ $wR_2 = 0.1083$	$R_1 = 0.0751$ $wR_2 = 0.2223$	$R_1 = 0.0556$ $wR_2 = 0.1354$	$R_1 = 0.0790$ $wR_2 = 0.2401$
R indices (all data)	$R_1 = 0.0506$ $wR_2 = 0.1163$	$R_1 = 0.1375$ $wR_2 = 0.2665$	$R_1 = 0.1043$ $wR_2 = 0.1658$	$R_1 = 0.1635$ $wR_2 = 0.2882$

refluxed for 3 h. The reaction mixture was cooled to room temperature; a brown colored precipitate of the product was obtained, filtered and washed several times with water to remove the acetic acid and dried in open air to give **A** in anhydrous form. Yield: 92%. IR(KBr, cm^{-1}): 3483 (bm), 2927 (w), 2620 (w), 1777 (s), 1724 (s), 1492 (m), 1455 (m), 1380 (s), 1253 (s), 1191(m), 1118 (s), 844 (w), 752 (m), 646 (w). ^{1}H NMR (400 MHz, DMSO-d_6): 8.33 (s, 2H), 8.14 (d, 2H, J = 8.0 Hz), 7.64 (t, 2H, J = 7.6 Hz), 7.52 (t, 2H, J = 7.6 Hz), 7.34 (d, 2H, J = 7.6 Hz). ^{13}C NMR (100 MHz; DMSO-d_6): 166.1, 165.6, 137.4, 133.4, 131.5, 131.2, 130.6, 129.4, 129.0, 118.6. ESI-MS: 457.098 (M+H)$^+$.

2.2. A·4H$_2$O

Anhydrous form of **A** upon crystallization from ordinary acetone resulted in tetrahydrate product **A·4H$_2$O**. IR(KBr, cm^{-1}): 3521 (m), 3429 (m), 2925 (w), 2629 (w), 1776 (s), 1716 (s), 1698 (s), 1643 (s), 1492 (m), 1453 (m), 1384 (s), 1281 (m), 1264 (m), 1121 (s), 1071 (w), 921 (w), 846 (w), 754 (m), 728 (w), 628 (w). ^{1}H NMR (400 MHz, DMSO-d_6): 8.49 (s, 2H), 8.10 (d, 2H, J = 8.0 Hz), 7.82 (t, 2H, J = 7.6 Hz), 7.68 (t, 2H, J = 7.6 Hz), 7.60 (bs, 2H), 2.08 (s, 8H).

2.3. A·2DMF

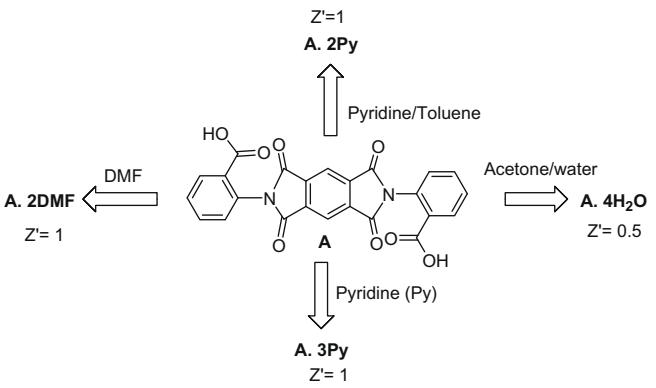
The solvate **A·2DMF** was obtained as crystals from a solution of A in *N*,*N*-dimethylformamide. It crystallized as colorless blocks after 7 days. IR(KBr, cm^{-1}): 3481 (m), 2925 (m), 2501 (w), 1776 (s), 1721 (s), 1630 (s), 1600 (m), 1491 (m), 1455 (m), 1383 (s), 1291 (m), 1256 (m), 1190 (w), 1121 (s), 845 (w), 757 (m), 728 (m), 670 (w), ^{1}H NMR (400 MHz, DMSO-d_6): 8.50 (s, 2H), 8.11 (d, 2H, J = 7.6 Hz), 7.95 (s, 2H), 7.83 (t, 2H, J = 7.6 Hz), 7.68 (t, 2H, J = 7.6 Hz), 7.59 (d, 2H, J = 7.2 Hz), 2.88 (s, 6H), 2.72 (s, 6H).

2.4. A·2Py

A solution of compound **A** in pyridine and toluene gave the solvate **A·2Py** as colourless blocks in quantitative yield. IR(KBr, cm^{-1}): 3446 (bm), 3077 (w), 2460 (w), 1778 (s), 1724 (s), 1601 (m), 1489 (m), 1453 (m), 1437 (m), 1381 (m), 1284 (m), 1189 (m), 1119 (m), 1063 (m), 1008 (w), 845 (w), 752 (m), 727 (w), 630 (w). ^{1}H NMR (400 MHz, DMSO-d_6): 8.57 (s, 4H), 8.50 (s, 2H), 8.11 (d, 2H, J = 7.6 Hz), 7.81 (m, 4H), 7.68 (t, 2H, J = 7.6 Hz), 7.60 (d, 2H, J = 7.6 Hz), 7.39 (t, 4H, J = 5.6 Hz).

2.5. A·3Py

The solvate **A·3Py** was obtained as colorless needles from the pyridine solution of compound **A**. IR(KBr, cm^{-1}): 3502 (bm), 2924 (w), 2623 (w), 1776 (s), 1720 (s), 1634 (s), 1492 (m), 1454 (m), 1384 (s), 1281 (m), 1264 (m), 1190 (m), 1121 (s), 845 (w), 754 (m), 728 (w). ^{1}H NMR (400 MHz, DMSO-d_6): 8.50 (s, 6H), 8.32



Scheme 1. Different solvated species of **A**.