



Synthesis and Crystal Structure of Fumaropimaric Acid Triacid Amide

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The compound fumaropimaric acid triacid amide was synthesized by acyl chlorination and ammonolysis reaction between fumaropimaric acid and SOCl_2 and aqueous ammonia. It was characterized by single crystal X-ray diffraction. The colourless crystals crystallized in the orthorhombic system, space group $P2_{12121}$ with cell dimensions: $a = 7.2910(15) \text{ \AA}$, $b = 15.221(3) \text{ \AA}$, $c = 21.822(4) \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$, $V = 2421.7(8) \text{ \AA}^3$ and $R_1 = 0.0645$, $wR_2 = 0.1404$. The two fused and unbridged cyclohexane rings have chair conformations. The other rings are twist-boat forms. The molecular structure includes two molecules (fumaropimaric acid triacid amide and methanol). The molecules are linked by hydrogen bonds and van der Waals forces. The crystal structure has been deposited at the Cambridge crystallographic data centre and allocated the deposition number CCDC 790373.

Key Words: Fumaropimaric acid triacid amide, Synthesis, Crystal structure.

INTRODUCTION

Rosin, a versatile and abundant natural resin, possesses a rare combination of many useful properties and has consequently found numerous industrial uses in a modified form or in conjunction with other natural or synthetic resins¹. In addition, it has been discovered that rosin and its derivatives possess a pronounced anticarcinogenic effect, which makes them worthy of study as a cancer chemopreventive agent². Rosin amide, as an example, was found inhibition to hepatoma carcinoma cell SMMC7721³. In addition, rosin amide can be used as epoxy curing agents⁴ and rust preventives and corrosion inhibitors⁵. Considering the extensive application of rosin amide, it deserves further study.

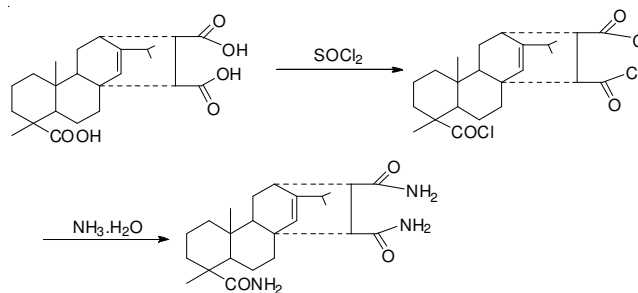
Fumaropimaric acid triacid amide had once been synthesized by Halbrook *et al.*⁶ with very long reaction time and the crystal structure was not reported. In this paper, fumaropimaric acid triacid amide was synthesized with shorter time under mild reaction conditions and its structure was determined using single-crystal X-ray methods.

EXPERIMENTAL

SOCl_2 (freshly-distilled), CH_2Cl_2 (anhydrous), ammonia water (AR), fumaropimaric acid was synthesized according to reference⁷.

IR spectrum was obtained on a FTIR-650 Fourier transform infrared spectrometer, ^{13}C NMR spectrum was recorded on a Bruker AM-300 spectrometer (75 MHz, CDCl_3).

The synthetic scheme of fumaropimaric acid triacid amide was shown in **Scheme-I**.



Scheme-I: Synthetic scheme of fumaropimaric acid triacid amide

Synthesis of fumaropimaric acid triacyl chloride:

Freshly-distilled SOCl_2 (15 mL) was added dropwise into fumaropimaric acid (3.00 g) at room temperature. The stirred reaction mixture was kept at room temperature for 2 h. The excessive SOCl_2 was removed under vacuum.

Synthesis of fumaropimaric acid triacid amide:

Fumaropimaric acid triacyl chloride was dissolved in anhydrous CH_2Cl_2 and was added dropwise into stirred ammonia water (30 mL) at 273 K. The reaction mixture was kept at 273 K for 2 h. The white precipitate was filtered and washed with water. Colourless single crystals were grown by recrystallization, with petroleum ether and methanol as solvent. Yield: 86.3 %. IR: (KBr, ν_{max} , cm^{-1}), 3449, 3325, 2929, 2867, 1647, 1601, 1459, 1430, 1385, 1355. ^{13}C NMR: (CDCl_3 , δ/ppm , 75 MHz), 15.9,

16.9, 19.5, 21.1, 22.6, 32.3, 34.4, 36.9, 37.6, 40.3, 49.8, 54.8, 55.3, 124.5, 147.8, 176.9, 177.9, 183.5.

X-Ray crystallography: The crystal structure of fumaropimaric acid triacid amide was determined by X-ray single crystal diffraction. A single crystal with suitable size was placed on a Bruker-AXS CCD area detector with MoK α ($\lambda = 0.71073 \text{ \AA}$) as radiation at 293 K. The structure of fumaropimaric acid triacid amide was solved by direct methods and refined by full-matrix least squares on F². All the non-hydrogen atoms were refined with anisotropic temperature factors, with R₁ = 0.0645, wR₂ = 0.1404. SHELXS97 were used to solve the structure and SHELTL were used to refine the structure⁸⁻¹⁰.

RESULTS AND DISCUSSION

Crystal structure descriptions: The molecular structure contains a fumaropimaric acid triacid amide molecule and a methanol molecule. The crystallographic details are summarized in Table-1. The selected bond lengths and angles are listed in Tables 2 and 3, respectively. The torsion angles are shown in Table-4. Fig. 1 presents the molecular structure of the fumaropimaric acid triacid amide, which contains two fused and unbridged cyclohexane rings adopt approximate chair conformations while other six-membered rings have boat conformations. Crystal methanol and fumaropimaric acid triacid amide were stabilized through hydrogen bonds and van der Waals forces. Fig. 2 shows the packing of the fumaropimaric acid triacid amide, the nitrogen atoms of amino groups form hydrogen bonds with oxygen atoms of carbonyl groups of different molecules, the oxygen of methanol connects with oxygen atom of one carbonyl group by hydrogen bond. The hydrogen bond lengths and angles are exhibited in Table-5.

TABLE-1
CRYSTAL DATA AND STRUCTURE
REFINEMENT FOR THE TITLE COMPOUND

Empirical formula	C ₂₅ H ₄₁ N ₃ O ₄
Formula weight	447.61
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system, space group	ortho-Rhombic, P2 ₁ 2 ₁ 2 ₁
Unit cell dimensions (Å, °)	
a	7.2910 (15)
b	15.221 (3)
c	21.822 (4)
α	90
β	90
γ	90
Volume (Å ³)	2421.7 (8)
Z, calculated density (mg m ⁻³)	4, 1.228
Absorption coefficient (mm ⁻¹)	0.083
F(000)	976
Crystal size (mm ³)	0.30 × 0.20 × 0.10
θ range for data collection (°)	1.63-25.28
Limiting indices	0 < h < 8, 0 < k < 18, -18 < l < 26
Reflections collected/unique	4617/4186 [R(int) = 0.0424]
Goodness-of-fit on F ²	1.004
Final R indices [I > 2 σ (I)]	R ₁ = 0.0645, wR ₂ = 0.1404
R indices (all data)	R ₁ = 0.1106, wR ₂ = 0.1852
Large diff. peak and hole (e Å ⁻³)	0.209 and -0.249

TABLE-2
BOND LENGTHS (Å) FOR THE TITLE COMPOUND

N1-C20	1.328 (6)	C7-C8	1.519(6)
O1-C20	1.216(5)	C8-C9	1.526(6)
C1-C23	1.525(7)	C9-C15	1.512(6)
C1-C24	1.535(8)	C9-C10	1.567(6)
C1-C6	1.558(6)	C9-C14	1.573(6)
C1-C2	1.563(7)	C10-C11	1.554(6)
O2-C21	1.239(5)	C11-C12	1.533(7)
C2-C3	1.535(8)	C12-C16	1.519(7)
N3-C24	1.324(7)	C12-C13	1.545(6)
O3-C24	1.234(6)	C13-C20	1.533(6)
N2-C21	1.330(6)	C13-C14	1.546(6)
C3-C4	1.523(7)	C14-C21	1.517(6)
C4-C5	1.543(6)	C15-C16	1.319(7)
C5-C22	1.542(7)	C16-C17	1.509(7)
C5-C6	1.557(6)	C17-C19	1.521(9)
C5-C10	1.559(6)	C17-C18	1.525(9)
C6-C7	1.541(6)	C25-O4	1.379(8)

TABLE-3
ANGLES (°) FOR THE TITLE COMPOUND

C23-C1-C24	107.4(4)	O1-C20-N1	121.7(4)
C24-C1-C6	110.8(4)	O1-C20-C13	123.7(4)
C3-C2-C1	113.0(4)	N1-C20-C13	114.6(4)
C3-C4-C5	114.5(4)	O2-C21-N2	121.1(4)
C22-C5-C6	114.0(4)	O2-C21-C14	122.0(4)
C7-C6-C5	110.4(4)	N2-C21-C14	117.0(4)
C8-C7-C6	109.5(4)	O3-C24-N3	120.2(5)
C15-C9-C14	107.3(3)	O3-C24-C1	121.1(5)
C16-C12-C11	109.6(4)	N3-C24-C1	118.7(5)
C20-C13-C12	110.5(4)		

TABLE-4
TORSION ANGLES (°) FOR THE TITLE COMPOUND

C23-C1-C2-C3	-72.9(6)	C14-C13-C20-N1	167.6(4)
C6-C1-C2-C3	52.8(6)	C13-C14-C21-O2	-37.3(6)
C4-C5-C6-C7	-175.6(4)	C9-C14-C21-O2	85.9(5)
C10-C5-C6-C1	167.5(4)	C13-C14-C21-N2	142.7(4)
C24-C1-C6-C5	-167.9(4)	C9-C14-C21-N2	-94.1(5)
C7-C8-C9-C10	49.5(5)	C23-C1-C24-O3	-14.7(7)
C15-C9-C10-C11	-53.6(5)	C6-C1-C24-O3	-140.0(5)
C16-C12-C13-C14	174.4(4)	C2-C1-C24-O3	103.1(5)
C20-C13-C14-C21	-105.5(4)	C23-C1-C24-N3	167.2(5)
C12-C13-C20-O1	108.4(5)	C6-C1-C24-N3	41.9(6)
C14-C13-C20-O1	-14.3(7)	C2-C1-C24-N3	-75.0(6)
C12-C13-C20-N1	-69.7(5)		

TABLE-5
HYDROGEN BONDS FOR THE TITLE COMPOUND (Å AND °)

D-H...A	D-H	H...A	D...A	D-H...A
N1-H1A...O2 ⁱ	0.86	2.11	2.939(5)	163
N1-H1B...O3 ⁱⁱ	0.86	2.17	3.027(6)	175
N2-H2C...O4 ⁱⁱⁱ	0.86	2.54	3.167(6)	131
N2-H2D...O1 ⁱⁱⁱ	0.86	2.09	2.892(5)	155
N3-H3B...O4	0.86	2.15	2.946(7)	153
O4-H4C...O2 ^{iv}	0.82	1.97	2.755(6)	160
C2-H2A...O2 ^v	0.97	2.54	3.429(6)	152
C6-H6A...N3	0.98	2.50	2.895(6)	104
C13-H13A...O2	0.98	2.34	2.846(5)	111
C14-H14A...O1	0.98	2.37	2.870(6)	111

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

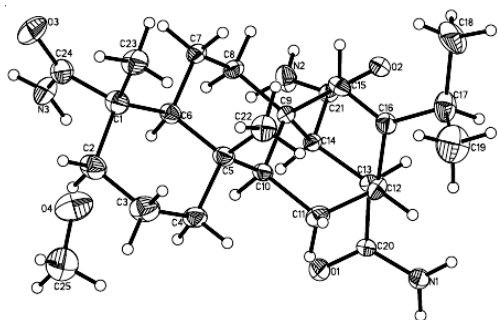


Fig. 1. A view of the molecular structure of the title compound, showing displacement ellipsoids at the 50 % probability level

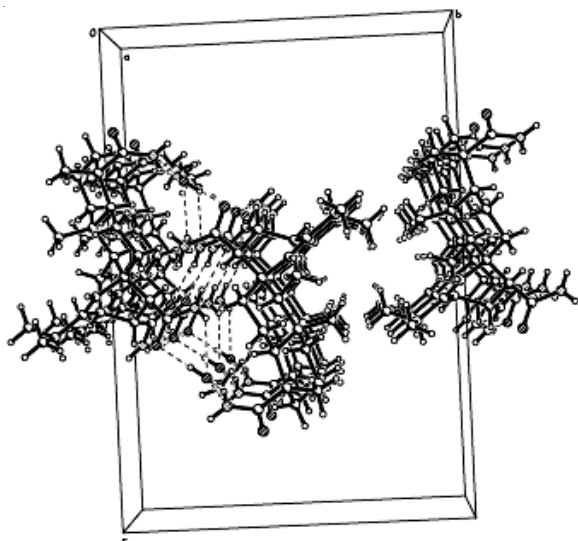


Fig. 2. Packing of the fumaropimaric acid triacid amide

Conclusion

Fumaropimaric acid triacid amide was synthesized successfully under mild reaction conditions. Colourless single crystals were grown by recrystallization, with petroleum ether and methanol as solvent. The two fused and unbridged cyclohexane rings have chair conformations while the other rings are twist-boat forms. Crystal methanol exists in the molecular and stabilizes the structure through hydrogen bonds and van der Waals forces.

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