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Synthesis, Crystal Structure and Application of Maleopimaric Acid Mono-Ethyl Ester

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The compound maleopimaric acid mono-ethyl ester (MAMEE) was synthesized by Diles-Alder, acyl chlorination and esterification reaction between rosin and maleic anhydride, $SOCl_2$ and anhydrous enthanol. It was characterized by single crystal X-ray diffraction. The white crystals crystallized in the orthorhombic system, space group $P2_{12121}$ with cell dimensions: a = 7.3830 (15) Å, b = 17.877 (4) Å, c = 19.601 (4) Å, $\alpha = 90°$, $\beta = 90°$, $\gamma = 90°$, V = 2587.1 (9) $Å^3$ and $R_1 = 0.0568$, $wR_2 = 0.1407$. The two fused and unbridged cyclohexane rings adopt approximate chair conformations while other six-membered rings have boat conformations and the two methyl groups in axis positions. Crystal water existed in the molecular and stabilized the structure through intermolecular hydrogen bonds. The soldering flux prepared by using maleopimaric acid mono-ethyl ester achieves a high wetting ability and is excellent in spreading rate and storage stability.

Key Words: Maleopimaric acid mono-ethyl ester, Synthesis, Crystal structure, Soldering flux.

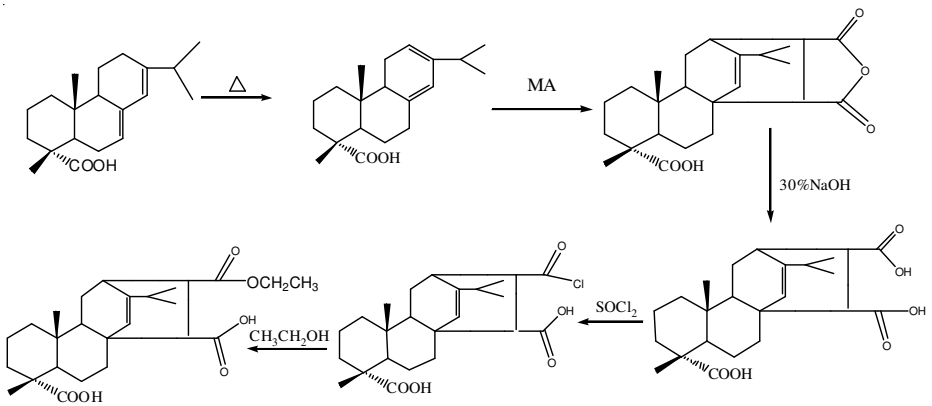
INTRODUCTION

Rosin is predominantly a mixture of resin acids belonging to one of four basic skeletal classes, abietane, pimarane, isopimarane and labdane, with the general chemical formula $C_{20}H_{30}O_2$. Most rosin used today is modified by reactions with different chemicals. One of the most common modifications is the Diels-Alder reaction of levopimaric acid, formed from abietic acid in rosin with maleic anhydride or fumaric acid[1]. This type of modified products are widely used in the field of article sizing, printing inks, vanishes, surface coating and it is widely studied as intermediate for design and synthesis of fine chemical products[2,3].

Conventionally, rosin may be used in soldering flux for its properties as a weak acidic activator but it is also added to protect the metals from oxidation for example as a protective coating[4]. At a high temperature, the active ingredient of rosin, *i.e.*, abietic acid removes the oxides in junction zone, increases the degree of spreading and viscosity of a flux composition against a base metal and helps block contacting with oxygen in the air. Examples of such rosin include hydrogenated rosin, dehydrogenated rosin or unmodified rosin. Usually, some organic compounds containing

halides is needed to add in rosin to enhance the flux activity, therefore, when it is used for the Pb-free solder, such as Sn-Ag or Sn-Ag-Bi based solder, a silver halide is mostly produced from Ag and the halide ion such as Cl.sup.- and Br.sup. The inventors found that production of the silver halide is a main cause of deterioration of material or defect in durability. Therefore, it is necessary to prepare the better activity rosin derivatives.

Herein, we report the synthesis and crystal structure of compound maleopimaric acid mono-ethyl ester (MAMEE) and test the properties of soldering flux prepared by using MAMEE (**Scheme-I**).



Scheme-I: Synthetic scheme of maleopimaric acid mono-ethyl ester (MAMEE)

EXPERIMENTAL

All chemicals purchased were of reagent grade and used as received. Melting point was determined by a XT5 m.p. apparatus. ^{1}H NMR spectrum was recorded on a DPX-400 Bruker AVANCE 400 spectrometer ($CDCl_3$ as solvent).

Synthesis and isolation of maleopimaric acid (MPA): 0.33 mol of maleic anhydride (MA) was added to 100 g rosin and heated until 200 ºC, the mixture was quickly stirred for 2 h at 200 ºC. After cooling to room temperature, the mixture was dissolved in 100 mL acetic acid, the crystal was filtrated and recrystallized from acetic acid. Subsequently, 30 % NaOH was droped into the crystal until the solution clear, at this time, the anhydride ring of MPA was opened to two carboxy group. Above solution was acidified by 10 % HCl, the sediment was filtrated and the water was distilled off under vaccum, then MPA was produced.

Synthesis of MPA chloride: Maleopimaric acid (0.25) was dissolved in 100 mL CH_2Cl_2 was gradually added to a solution of $SOCl_2$ (19 mL) in CH_2Cl_2 (20 mL). The reaction was performed for 3 h at 40-50 ºC, the solvent was distilled off under vacuum.

Synthesis of MAMEE: MPA chloride (0.1 mol) was slowly added to 50 mL anhydrous ethanol, the mixture was constantly stirred for 3 h at room temperature

and the solvent was distilled off under vaccum and recrystallized from ethanol and dried under vaccum. Yield: 73.2 %. m.p.: 144.5 ºC acid value: 227.3 mg/g. ^{1}H NMR: ($CDCl_3$. δ/ppm. 400 MHz), 7.26 (2H, -COOH); 5.40 (1H, -C=CH); 4.03-3.89 (2H, -COO-CH_2-); 2.81 (1H, -CH $(Me)_2$); 2.97-2.90 (2H, -CH-COO-); 2.77-2.66 (3H, >CH-); 1.94-1.45 (12H, -CH_2-); 1.26-0.90 (15H, -CH_3).

X-Ray crystallography: The crystal structure of the MAMEE was determined by X-ray single crystal diffraction. XRD data were collected on a Bruker-AXS CCD area detector equipped with diffractometer with Mo-Ka (λ = 0.07103) at 293 K. A single crystal suitable for determination was mounted inside a glass fiber capillary. The structure of the MAMEE was solved by direct methods and refined by full-matrix least squares on F^2. All the hydrogen atoms were added in their calculated positions and all the nonhydrogen atoms were refined with anisotropic temperature factors. SHELXS97 were used to solve the structure and SHELTL were used to refine the structure[5-9].

Preparation of soldering flux: A flux composition was prepared by uniformly mixing at about 35 % of activator (MAMEE), 45 % of solvent (1,3-butadiol), 17 % of viscosity modifier (PEG200) and 3 % of surface active agents (TX-10).

Soldering flux test of MAMEE: This test was carried out in accordance with China national standard GB/T 9491-2002 liquid soldering flux (rosin-based).

RESULTS AND DISCUSSION

Structure descriptions: White crystals of the MAMEE suitable for X-ray analysis were obtained after several days of being undisturbed at room temperature. The crystals contained one MAMEE and one H_2O molecule. The crystallographic details of MAMEE are summarized in Table-1. The selected bond lengths and angles are shown in Table-2, the torsion angles are listed in Table-3. As shown in Fig. 1, the structure of carbocyclic skeleton is as usual, the bond lengths and angles are close to average values, MAMEE contains two fused and unbridged cyclohexane rings adopt approximate chair conformations while other six-membered rings have boat conformations, the two methyl grounps in axis positions. Crystal water existed in the molecule and MAMEE were stabilized through hydrogen bonds formed with atoms of intermolecule. In the crystal packing of MAMEE (Fig. 2), the oxygen atom of ester form hydrogen bonds with oxygen of carboxyl of different molecule and two oxygen atoms of carboxyl of different molecule form hydrogen bond. The hydrogen bond lengths and angles are listed in Table-4.

Properties of soldering flux: The flux was prepared, the properties of the flux compared to typical flux which was purchased from market are shown in Table-5.

As shown in Table-5, the flux has better appearance and higher spreading rate than typical flux and that, it doesn't contain compound that contains the halide ion. Furthermore, the flux, unlike typical flux, which is employed for welding between iron plates or zinc-coated steel plates, not leave brown residues during a welding

TABLE-1
CRYSTAL DATA AND STRUCTURE REFINEMENT FOR MAMEE

Empirical formula	$C_{26}H_{40}O_7$
Formula weight	464.58
Temperature (K)	293 (2)
Wavelength (Å)	0.71073
Crystal system, space group	*ortho*-rhombic, $P2_{12121}$
Unit cell dimensions (Å,^{0})	
a	7.3830 (15)
b	17.877 (4)
c	19.601 (4)
α	90
β	90
γ	90
Volume (A^3)	2587.1 (9)
Z, calculated density (mgm^{-3})	4, 1.193
Absorption coefficient (mm^{-1})	0.085
F(000)	1008
Crystal size (mm^3)	0.30 × 0.20 × 0.10
θ range for data collection (^{0})	0.996-25.24
Limiting indices	$0 < h < 8$, $0 < k < 21$, $0 < l < 23$
Reflections collected/unique	2523/2523 [R(int) = 0.0000]
Completeness to θ = 25.24	99.9 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	1.001
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0568$, $wR_2 = 0.1407$
R indices (all data)	$R_1 = 0.08521$, $wR_2 = 0.1587$
Largest diff. peak and hole (e A^{-3})	0.226 and -0.228

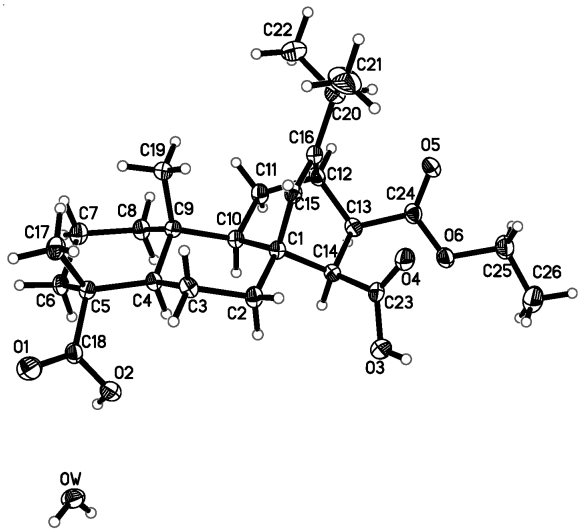


Fig. 1. MAMEE with H atoms represented by small spheres of arbitrary radius and displacementellipsoids at the 30 % probability level

TABLE-2
BOND LENGTHS (Å) AND ANGLES (º) FOR MAMEE

C1-C15	1.491 (6)
C1-C2	1.543 (6)
O1-C18	1.199 (6)
O3-C23	1.314 (6)
C4-C9	1.547 (6)
O5-C24	1.208 (6)
C5-C18	1.523 (7)
O6-C25	1.462 (6)
C25-C26	1.446 (9)
C15-C1-C2	114.5 (4)
C15-C16-C12	112.4 (4)
C12-C16-C20	119.8 (5)
C23-C14-C13	114.1 (4)
C24-C13-C14	115.7 (4)
C18-C5-C17	107.4 (4)
C24-O6-C25	116.2 (4)
C16-C20-C21	111.6 (6)
O1-C18-O2	121.2 (5)
C16-C20-C22	109.9 (5)
C21-C20-C22	112.3 (6)
O4-C23-O3	123.1 (5)
O5-C24-O6	122.5 (5)
O6-C24-C13	113.0 (4)
C26-C25-O6	108.7 (5)

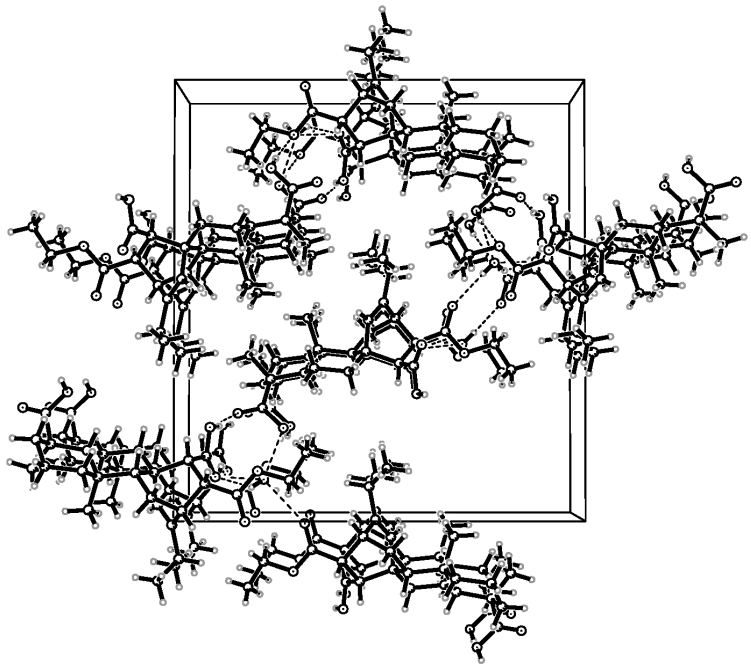


Fig. 2. Packing diagram for MAMEE

TABLE-3
TORSION ANGLES (º) FOR MAMEE

C15-C1-C2-C3	78.2 (5)
C10-C1-C2-C3	-46.9 (6)
C11-C12-C13-C24	167.0 (4)
C24-C13-C14-C23	7.7 (6)
C12-C13-C14-C23	-120.5 (4)
C15-C1-C14-C23	70.3 (5)
C10-C1-C14-C23	-173.6 (4)
C17-C5-C6-C7	75.8 (5)
C1-C15-C16-C20	-179.2 (5)
C17-C5-C18-O2	-158.6 (5)
C15-C1-C10-C11	49.7 (5)
C4-C5-C18-O2	-32.9 (6)
C14-C13-C24-O5	-127.1 (6)
C24-O6-C25-C26	173.8 (6)

TABLE-4
HYDROGEN BONDS FOR MAMEE (Å AND º)

D–H···A	D–H	H···A	D···A	D-H···A
OW-HWA...O5^{i}	0.85	2.23	2.7509	120
OW-HWB...O4	0.85	2.02	2.7413	142
O2-H2C...O6^{ii}	0.82	2.42	3.2303	173
O3-H3C...O1^{iii}	0.82	1.88	2.6819	165
C4-H4A...O2	0.98	2.30	2.7203	105

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

TABLE-5
PROPERTIES OF FLUX

Sample	Appearance	Storage stability	Content of halogen (%)	Spreading rate (%)	Wetting ability	Insulation resistance of flux residue (Ω)
The flux	white	Good	0	80	Good	3×10^9
Typiccal flux	yellow	Good	8	74	Good	2×10^9

operation. Soldering by using the flux composition generates no smokes, provides an excellent soldering quality even in the wet condition and complete adhesion of the soldered parts.

Conclusion

The compound maleopimaric acid mono-ethyl ester (MAMEE) was successfully synthesized by a Diles-Alder, acyl chlorination and esterification reaction and the single crystals were obtained after several days of undisturbed. The two fused and unbridged cyclohexane rings adopt approximate chair conformations while the other six-membered rings have boat conformations and the two methyl groups in axis positions. Crystal water existed in the molecular and stabilized the structure through intermolecular hydrogen bonds.

The flux prepared by using MAMEE has a number of desirable functions, such as, the appearance and spreading rate are better than typical flux and that, it is a free-halogen environmentally-friendly product.

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