Origins of selectivity for the [2+2] cycloaddition of α,β-unsaturated ketones within a porous self-assembled organic framework.

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X-Ray Structure Determination, $C_{12}H_{16}O_2$

X-ray diffraction intensity data from a colorless plate crystal were measured at 150(1) K using a Bruker SMART APEX diffractometer (Mo Kα radiation, λ = 0.71073 Å).[1] Raw area detector data frame integration was performed with SAINT+.[1] Final unit cell parameters were determined by least-squares refinement of 2964 strong reflections from the data set. Direct methods structure solution, difference Fourier calculations and full-matrix least-squares refinement against F^2 were performed with SHELXTL.[2]

The compound crystallizes in the space group $P2_1/n$ as determined uniquely by the pattern of systematic absences in the intensity data. The asymmetric unit consists of half of one molecule located on a crystallographic inversion center. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were located in difference maps

before being placed in geometrically idealized positions and included as riding atoms with refined isotropic displacement parameters.

(1) SMART Version 5.630 and SAINT+ Version 6.45. Bruker Analytical X-ray Systems, Inc., Madison, Wisconsin, USA, 2003.

(2) Sheldrick, G. M. SHELXTL Version 6.14; Bruker Analytical X-ray Systems, Inc., Madison, Wisconsin, USA, 2000.

Table 1. Crystal data and structure refinement for mecp2m.

Identification code	mecp2m	
Empirical formula	C12 H16 O2	
Formula weight	192.25	
Temperature	150(1) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 7.0223(7) Å	α= 90°.
	b = 6.4259(7) Å	β= 99.693(2)°.
	c = 10.9846(11) Å	γ = 90°.
Volume	488.60(9) $Å^3$	
Z	2	
Density (calculated)	1.307 Mg/m^3	
Absorption coefficient	0.087 mm^{-1}	
F(000)	208	
Crystal size	0.48 x 0.30 x 0.12 mm^3	
Theta range for data collection	3.22 to 25.00°.	
Index ranges	-8<=h<=8, -7<=k<=7, -13<=l<=13	
Reflections collected	4987	
Independent reflections	867 [R(int) = 0.0578]	
Completeness to theta = 25.00°	100.0 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	867 / 0 / 73	
Goodness-of-fit on F^2	1.062	
Final R indices [I>2sigma(I)]	R1 = 0.0400, wR2 = 0.1037	
R indices (all data)	R1 = 0.0431, wR2 = 0.1068	
Largest diff. peak and hole	0.307 and -0.181 e.$Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for mecp2m. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	3141(2)	711(2)	3208(1)	22(1)
C(2)	3716(2)	925(2)	4602(1)	21(1)
C(3)	5931(2)	1315(2)	4817(1)	21(1)
C(4)	6515(2)	1676(2)	3547(1)	25(1)
C(5)	4920(2)	676(2)	2609(1)	26(1)
C(6)	2398(2)	2416(2)	5136(1)	27(1)
O(1)	1491(1)	556(2)	2670(1)	28(1)

Table 3. Bond lengths [Å] and angles [°] for mecp2m.

C(1)-O(1)	1.2126(17)
C(1)-C(5)	1.507(2)
C(1)-C(2)	1.5223(19)
C(2)-C(6)	1.5169(19)
C(2)-C(3)	1.5538(19)
C(2)-C(3)#1	1.5774(18)
C(3)-C(4)	1.536(2)
C(3)-H(3)	1.0000
C(4)-C(5)	1.530(2)
C(4)-H(4A)	0.9900
C(4)-H(4B)	0.9900
C(5)-H(5A)	0.9900
C(5)-H(5B)	0.9900
C(6)-H(6A)	0.9800
C(6)-H(6B)	0.9800
C(6)-H(6C)	0.9800
O(1)-C(1)-C(5)	125.45(13)
O(1)-C(1)-C(2)	124.58(13)
C(5)-C(1)-C(2)	109.96(11)
C(6)-C(2)-C(1)	111.72(11)
C(6)-C(2)-C(3)	119.97(12)
C(1)-C(2)-C(3)	104.87(11)
C(6)-C(2)-C(3)#1	118.98(12)
C(1)-C(2)-C(3)#1	108.77(11)
C(3)-C(2)-C(3)#1	90.02(10)
C(4)-C(3)-C(2)	107.45(11)
C(4)-C(3)-C(2)#1	117.22(11)
C(2)-C(3)-C(2)#1	89.98(10)
C(4)-C(3)-H(3)	113.3
C(2)-C(3)-H(3)	113.3
C(2)#1-C(3)-H(3)	113.3
C(5)-C(4)-C(3)	105.70(11)
C(5)-C(4)-H(4A)	110.6

C(3)-C(4)-H(4A)	110.6
C(5)-C(4)-H(4B)	110.6
C(3)-C(4)-H(4B)	110.6
H(4A)-C(4)-H(4B)	108.7
C(1)-C(5)-C(4)	105.46(11)
C(1)-C(5)-H(5A)	110.6
C(4)-C(5)-H(5A)	110.6
C(1)-C(5)-H(5B)	110.6
C(4)-C(5)-H(5B)	110.6
H(5A)-C(5)-H(5B)	108.8
C(2)-C(6)-H(6A)	109.5
C(2)-C(6)-H(6B)	109.5
H(6A)-C(6)-H(6B)	109.5
C(2)-C(6)-H(6C)	109.5
H(6A)-C(6)-H(6C)	109.5
H(6B)-C(6)-H(6C)	109.5

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y,-z+1

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for mecp2m. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	25(1)	16(1)	25(1)	1(1)	3(1)	0(1)
C(2)	21(1)	20(1)	23(1)	0(1)	4(1)	-1(1)
C(3)	22(1)	19(1)	23(1)	0(1)	3(1)	-2(1)
C(4)	24(1)	25(1)	26(1)	4(1)	5(1)	-3(1)
C(5)	27(1)	28(1)	22(1)	1(1)	4(1)	0(1)
C(6)	28(1)	28(1)	27(1)	-1(1)	5(1)	4(1)
O(1)	24(1)	30(1)	28(1)	0(1)	-1(1)	-2(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for mecp2m.

	x	y	z	U(eq)
H(3)	6350	2461	5419	23(4)
H(4A)	6611	3183	3381	37(5)
H(4B)	7778	1018	3509	31(4)
H(5A)	4704	1477	1829	34(4)
H(5B)	5268	-771	2428	34(5)
H(6A)	2472	3796	4767	37(5)
H(6B)	2805	2508	6032	37(5)
H(6C)	1065	1906	4953	36(5)

Table 6. Torsion angles [°] for mecp2m.

O(1)-C(1)-C(2)-C(6)	-42.44(18)
C(5)-C(1)-C(2)-C(6)	138.77(12)
O(1)-C(1)-C(2)-C(3)	-173.90(13)
C(5)-C(1)-C(2)-C(3)	7.31(14)
O(1)-C(1)-C(2)-C(3)#1	90.90(15)
C(5)-C(1)-C(2)-C(3)#1	-87.89(13)
C(6)-C(2)-C(3)-C(4)	-117.34(14)
C(1)-C(2)-C(3)-C(4)	9.19(14)
C(3)#1-C(2)-C(3)-C(4)	118.64(13)
C(6)-C(2)-C(3)-C(2)#1	124.02(15)
C(1)-C(2)-C(3)-C(2)#1	-109.46(12)
C(3)#1-C(2)-C(3)-C(2)#1	0.0
C(2)-C(3)-C(4)-C(5)	-21.91(15)
C(2)#1-C(3)-C(4)-C(5)	77.37(14)
O(1)-C(1)-C(5)-C(4)	160.29(13)
C(2)-C(1)-C(5)-C(4)	-20.93(15)
C(3)-C(4)-C(5)-C(1)	26.01(14)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y,-z+1