APPENDIX 8

X-Ray Crystallography Reports Relevant to Chapter 4

A8.1 CRYSTAL STRUCTURE ANALYSIS OF DIKETONE 193

Low-temperature diffraction data (ϕ-and ω-scans) were collected on a Bruker AXS D8 VENTURE KAPPA diffractometer coupled to a PHOTON 100 CMOS detector with Cu K_α radiation (λ = 1.54178 Å) from an IμS micro-source for the structure of compound P16423. The structure was solved by direct methods using SHELXS[1] and refined against F^2 on all data by full-matrix least squares with SHELXL-2014[2] using established refinement techniques.[3] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included into the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms they are linked to (1.5 times for methyl groups).

Tricyclic diketone **193** (P16423) crystallizes in the monoclinic space group $P2_1$ with one molecule in the asymmetric unit.

*Table A8.1 Crystal data and structure refinement for tricyclic diketone **193** (P16423).*

Identification code	P16423	
Empirical formula	$C_{17} H_{26} O_2$	
Formula weight	262.38	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = 9.4497(4) Å	a= 90°.
	b = 6.4699(3) Å	b= 99.507(2)°.
	c = 12.5564(6) Å	g = 90°.
Volume	757.14(6) $Å^3$	
Z	2	
Density (calculated)	1.151 Mg/m^3	
Absorption coefficient	0.569 mm^{-1}	
F(000)	288	
Crystal size	0.350 x 0.050 x 0.050 mm^3	
θ range for data collection	3.569 to 74.508°.	
Index ranges	$-11 \le h \le 11, -8 \le k \le 7, -14 \le l \le 15$	
Reflections collected	8282	
Independent reflections	3039 [$R_{int} = 0.0473$]	
Completeness to θ = 67.679°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7538 and 0.5623	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3039 / 1 / 175	
Goodness-of-fit on F^2	1.062	
Final R indices [$I>2\sigma(I)$]	R1 = 0.0380, *w*R2 = 0.0898	
R indices (all data)	R1 = 0.0422, *w*R2 = 0.0924	
Absolute structure parameter	-0.23(15)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.196 and -0.190 $e.Å^{-3}$	

Figure A8.1 ORTEP drawing of tricyclic diketone ***193*** *(P16423) (shown with 50% probability ellipsoids).*

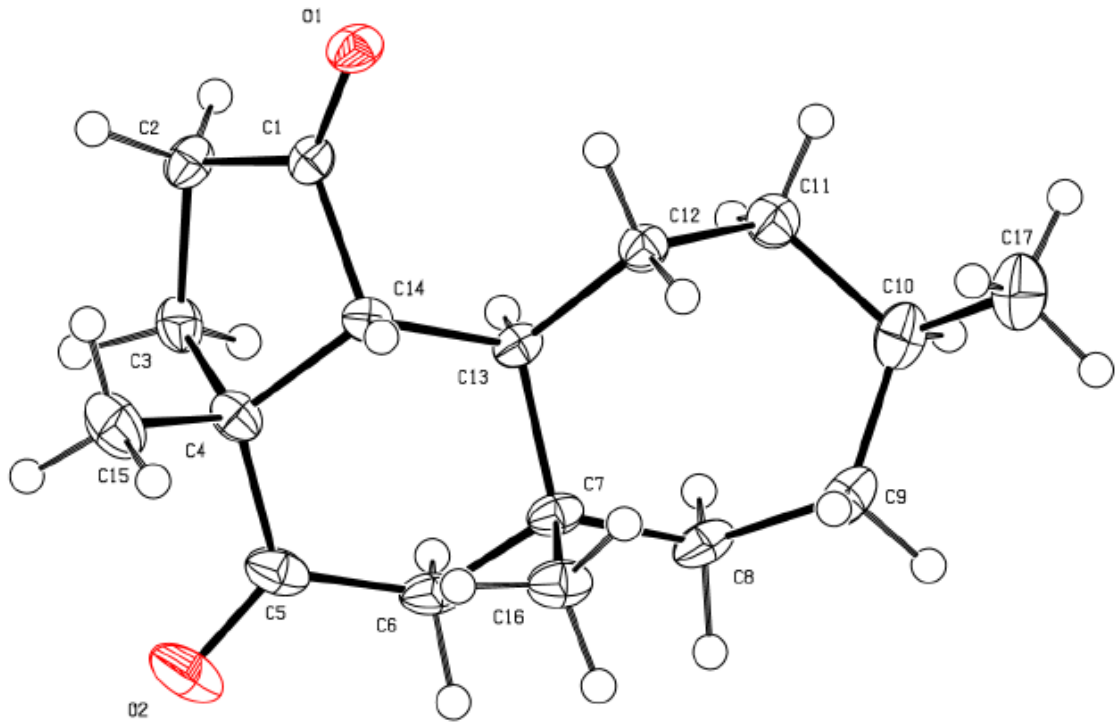

Table A8.2 Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for ***193*** *(P16423). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.*

	x	y	z	U(eq)
C(1)	6553(2)	6937(3)	4492(2)	17(1)
O(1)	6064(2)	8638(2)	4601(1)	23(1)
C(2)	7176(2)	5540(3)	5423(2)	21(1)
C(3)	7566(2)	3544(3)	4893(2)	22(1)
C(4)	7846(2)	4238(3)	3754(2)	21(1)
C(15)	9315(2)	5285(4)	3839(2)	33(1)
C(5)	7780(3)	2338(3)	3043(2)	26(1)
O(2)	8861(2)	1348(3)	2975(2)	46(1)
C(6)	6324(3)	1641(3)	2478(2)	24(1)

C(7)	5353(2)	3429(3)	1991(2)	20(1)
C(16)	6076(3)	4467(3)	1121(2)	25(1)
C(8)	3900(3)	2462(3)	1487(2)	24(1)
C(9)	2816(3)	3881(4)	797(2)	30(1)
C(10)	1790(3)	5062(4)	1403(2)	31(1)
C(17)	1056(3)	6798(5)	691(2)	44(1)
C(11)	2499(2)	5896(4)	2510(2)	25(1)
C(12)	4053(2)	6648(3)	2589(2)	19(1)
C(13)	5175(2)	4943(3)	2917(2)	17(1)
C(14)	6655(2)	5873(3)	3416(2)	17(1)

*Table A8.3 Bond lengths [Å] and angles [°] for **193** (P16423).*

C(1)-O(1)	1.210(3)
C(1)-C(2)	1.517(3)
C(1)-C(14)	1.534(3)
C(2)-C(3)	1.526(3)
C(2)-H(2A)	0.9900
C(2)-H(2B)	0.9900
C(3)-C(4)	1.562(3)
C(3)-H(3A)	0.9900
C(3)-H(3B)	0.9900
C(4)-C(5)	1.514(3)
C(4)-C(15)	1.533(3)
C(4)-C(14)	1.551(3)
C(15)-H(15A)	0.9800
C(15)-H(15B)	0.9800
C(15)-H(15C)	0.9800
C(5)-O(2)	1.221(3)
C(5)-C(6)	1.510(3)
C(6)-C(7)	1.539(3)
C(6)-H(6A)	0.9900
C(6)-H(6B)	0.9900
C(7)-C(16)	1.536(3)

C(7)-C(8)	1.546(3)
C(7)-C(13)	1.550(3)
C(16)-H(16A)	0.9800
C(16)-H(16B)	0.9800
C(16)-H(16C)	0.9800
C(8)-C(9)	1.532(3)
C(8)-H(8A)	0.9900
C(8)-H(8B)	0.9900
C(9)-C(10)	1.532(4)
C(9)-H(9A)	0.9900
C(9)-H(9B)	0.9900
C(10)-C(17)	1.529(4)
C(10)-C(11)	1.537(3)
C(10)-H(10)	1.0000
C(17)-H(17A)	0.9800
C(17)-H(17B)	0.9800
C(17)-H(17C)	0.9800
C(11)-C(12)	1.535(3)
C(11)-H(11A)	0.9900
C(11)-H(11B)	0.9900
C(12)-C(13)	1.538(3)
C(12)-H(12A)	0.9900
C(12)-H(12B)	0.9900
C(13)-C(14)	1.556(3)
C(13)-H(13)	1.0000
C(14)-H(14)	1.0000

O(1)-C(1)-C(2)	124.14(19)
O(1)-C(1)-C(14)	126.07(19)
C(2)-C(1)-C(14)	109.78(16)
C(1)-C(2)-C(3)	104.98(17)
C(1)-C(2)-H(2A)	110.7
C(3)-C(2)-H(2A)	110.7
C(1)-C(2)-H(2B)	110.7
C(3)-C(2)-H(2B)	110.7
H(2A)-C(2)-H(2B)	108.8

C(2)-C(3)-C(4)	104.26(17)
C(2)-C(3)-H(3A)	110.9
C(4)-C(3)-H(3A)	110.9
C(2)-C(3)-H(3B)	110.9
C(4)-C(3)-H(3B)	110.9
H(3A)-C(3)-H(3B)	108.9
C(5)-C(4)-C(15)	110.38(18)
C(5)-C(4)-C(14)	115.78(18)
C(15)-C(4)-C(14)	109.01(17)
C(5)-C(4)-C(3)	108.03(17)
C(15)-C(4)-C(3)	110.57(19)
C(14)-C(4)-C(3)	102.79(16)
C(4)-C(15)-H(15A)	109.5
C(4)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5
C(4)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5
O(2)-C(5)-C(6)	121.2(2)
O(2)-C(5)-C(4)	121.0(2)
C(6)-C(5)-C(4)	117.72(18)
C(5)-C(6)-C(7)	113.55(18)
C(5)-C(6)-H(6A)	108.9
C(7)-C(6)-H(6A)	108.9
C(5)-C(6)-H(6B)	108.9
C(7)-C(6)-H(6B)	108.9
H(6A)-C(6)-H(6B)	107.7
C(16)-C(7)-C(6)	107.78(17)
C(16)-C(7)-C(8)	110.77(18)
C(6)-C(7)-C(8)	106.84(17)
C(16)-C(7)-C(13)	111.89(16)
C(6)-C(7)-C(13)	107.98(16)
C(8)-C(7)-C(13)	111.35(17)
C(7)-C(16)-H(16A)	109.5
C(7)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5

C(7)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5
C(9)-C(8)-C(7)	117.05(18)
C(9)-C(8)-H(8A)	108.0
C(7)-C(8)-H(8A)	108.0
C(9)-C(8)-H(8B)	108.0
C(7)-C(8)-H(8B)	108.0
H(8A)-C(8)-H(8B)	107.3
C(10)-C(9)-C(8)	115.9(2)
C(10)-C(9)-H(9A)	108.3
C(8)-C(9)-H(9A)	108.3
C(10)-C(9)-H(9B)	108.3
C(8)-C(9)-H(9B)	108.3
H(9A)-C(9)-H(9B)	107.4
C(17)-C(10)-C(9)	109.8(2)
C(17)-C(10)-C(11)	111.0(2)
C(9)-C(10)-C(11)	114.03(19)
C(17)-C(10)-H(10)	107.2
C(9)-C(10)-H(10)	107.2
C(11)-C(10)-H(10)	107.2
C(10)-C(17)-H(17A)	109.5
C(10)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
C(10)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
C(12)-C(11)-C(10)	116.08(19)
C(12)-C(11)-H(11A)	108.3
C(10)-C(11)-H(11A)	108.3
C(12)-C(11)-H(11B)	108.3
C(10)-C(11)-H(11B)	108.3
H(11A)-C(11)-H(11B)	107.4
C(11)-C(12)-C(13)	113.59(17)
C(11)-C(12)-H(12A)	108.8
C(13)-C(12)-H(12A)	108.8

C(11)-C(12)-H(12B)	108.8
C(13)-C(12)-H(12B)	108.8
H(12A)-C(12)-H(12B)	107.7
C(12)-C(13)-C(7)	114.06(17)
C(12)-C(13)-C(14)	111.38(15)
C(7)-C(13)-C(14)	110.18(16)
C(12)-C(13)-H(13)	106.9
C(7)-C(13)-H(13)	106.9
C(14)-C(13)-H(13)	106.9
C(1)-C(14)-C(4)	102.32(16)
C(1)-C(14)-C(13)	110.22(15)
C(4)-C(14)-C(13)	114.19(16)
C(1)-C(14)-H(14)	110.0
C(4)-C(14)-H(14)	110.0
C(13)-C(14)-H(14)	110.0

Symmetry transformations used to generate equivalent atoms:

*Table A8.4 Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **193** (P16423). The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + \ldots + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$*

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	16(1)	15(1)	19(1)	-1(1)	3(1)	-6(1)
O(1)	30(1)	14(1)	23(1)	-2(1)	3(1)	-1(1)
C(2)	24(1)	19(1)	18(1)	0(1)	1(1)	-4(1)
C(3)	21(1)	19(1)	24(1)	4(1)	0(1)	2(1)
C(4)	18(1)	20(1)	26(1)	2(1)	6(1)	1(1)
C(15)	20(1)	33(1)	47(2)	2(1)	10(1)	-1(1)
C(5)	33(1)	21(1)	27(1)	4(1)	12(1)	8(1)
O(2)	37(1)	43(1)	60(1)	-8(1)	12(1)	19(1)
C(6)	38(1)	13(1)	21(1)	-1(1)	8(1)	4(1)
C(7)	31(1)	13(1)	15(1)	0(1)	6(1)	0(1)
C(16)	38(1)	21(1)	20(1)	2(1)	11(1)	2(1)
C(8)	36(1)	18(1)	18(1)	-4(1)	4(1)	-4(1)
C(9)	36(1)	32(1)	19(1)	-2(1)	-2(1)	-4(1)
C(10)	26(1)	35(1)	30(1)	-1(1)	-2(1)	-6(1)

C(17)	38(1)	52(2)	37(2)	2(1)	-8(1)	8(1)
C(11)	24(1)	28(1)	24(1)	-1(1)	4(1)	0(1)
C(12)	22(1)	17(1)	19(1)	0(1)	3(1)	-1(1)
C(13)	23(1)	13(1)	14(1)	0(1)	3(1)	-2(1)
C(14)	21(1)	11(1)	18(1)	2(1)	6(1)	0(1)

*Table A8.5 Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for **193** (P16423).*

	x	y	z	U(eq)
H(2A)	6460	5271	5900	25
H(2B)	8037	6175	5856	25
H(3A)	6769	2536	4829	26
H(3B)	8437	2911	5314	26
H(15A)	10069	4302	4132	49
H(15B)	9353	6485	4319	49
H(15C)	9464	5737	3121	49
H(6A)	5838	884	3000	28
H(6B)	6454	667	1894	28
H(16A)	7081	4766	1417	38
H(16B)	5576	5759	891	38
H(16C)	6032	3539	500	38
H(8A)	4097	1280	1033	29
H(8B)	3441	1901	2079	29
H(9A)	3354	4899	432	35
H(9B)	2237	3034	229	35
H(10)	1024	4071	1534	37
H(17A)	1759	7878	613	66
H(17B)	281	7386	1025	66
H(17C)	660	6243	-22	66
H(11A)	1911	7058	2706	30
H(11B)	2476	4793	3053	30
H(12A)	4221	7781	3125	23

H(12B)	4188	7219	1881	23
H(13)	4835	4109	3496	20
H(14)	6974	6887	2904	20

*Table A8.6 Torsion angles [°] for **193** (P16423).*

O(1)-C(1)-C(2)-C(3)	176.75(19)
C(14)-C(1)-C(2)-C(3)	-3.7(2)
C(1)-C(2)-C(3)-C(4)	26.6(2)
C(2)-C(3)-C(4)-C(5)	-162.43(17)
C(2)-C(3)-C(4)-C(15)	76.7(2)
C(2)-C(3)-C(4)-C(14)	-39.6(2)
C(15)-C(4)-C(5)-O(2)	29.3(3)
C(14)-C(4)-C(5)-O(2)	153.7(2)
C(3)-C(4)-C(5)-O(2)	-91.7(3)
C(15)-C(4)-C(5)-C(6)	-154.3(2)
C(14)-C(4)-C(5)-C(6)	-29.9(3)
C(3)-C(4)-C(5)-C(6)	84.7(2)
O(2)-C(5)-C(6)-C(7)	-141.1(2)
C(4)-C(5)-C(6)-C(7)	42.5(3)
C(5)-C(6)-C(7)-C(16)	63.0(2)
C(5)-C(6)-C(7)-C(8)	-177.92(18)
C(5)-C(6)-C(7)-C(13)	-58.0(2)
C(16)-C(7)-C(8)-C(9)	-53.9(3)
C(6)-C(7)-C(8)-C(9)	-171.00(19)
C(13)-C(7)-C(8)-C(9)	71.3(2)
C(7)-C(8)-C(9)-C(10)	-89.1(3)
C(8)-C(9)-C(10)-C(17)	165.3(2)
C(8)-C(9)-C(10)-C(11)	40.1(3)
C(17)-C(10)-C(11)-C(12)	-88.9(3)
C(9)-C(10)-C(11)-C(12)	35.7(3)
C(10)-C(11)-C(12)-C(13)	-89.5(2)
C(11)-C(12)-C(13)-C(7)	76.8(2)
C(11)-C(12)-C(13)-C(14)	-157.72(17)
C(16)-C(7)-C(13)-C(12)	70.1(2)

C(6)-C(7)-C(13)-C(12)	-171.45(17)
C(8)-C(7)-C(13)-C(12)	-54.5(2)
C(16)-C(7)-C(13)-C(14)	-56.0(2)
C(6)-C(7)-C(13)-C(14)	62.4(2)
C(8)-C(7)-C(13)-C(14)	179.42(16)
O(1)-C(1)-C(14)-C(4)	158.91(19)
C(2)-C(1)-C(14)-C(4)	-20.66(19)
O(1)-C(1)-C(14)-C(13)	-79.3(2)
C(2)-C(1)-C(14)-C(13)	101.17(18)
C(5)-C(4)-C(14)-C(1)	153.68(17)
C(15)-C(4)-C(14)-C(1)	-81.2(2)
C(3)-C(4)-C(14)-C(1)	36.16(18)
C(5)-C(4)-C(14)-C(13)	34.6(2)
C(15)-C(4)-C(14)-C(13)	159.74(18)
C(3)-C(4)-C(14)-C(13)	-82.9(2)
C(12)-C(13)-C(14)-C(1)	66.2(2)
C(7)-C(13)-C(14)-C(1)	-166.21(15)
C(12)-C(13)-C(14)-C(4)	-179.32(17)
C(7)-C(13)-C(14)-C(4)	-51.7(2)

A8.2 NOTES AND REFERENCES

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