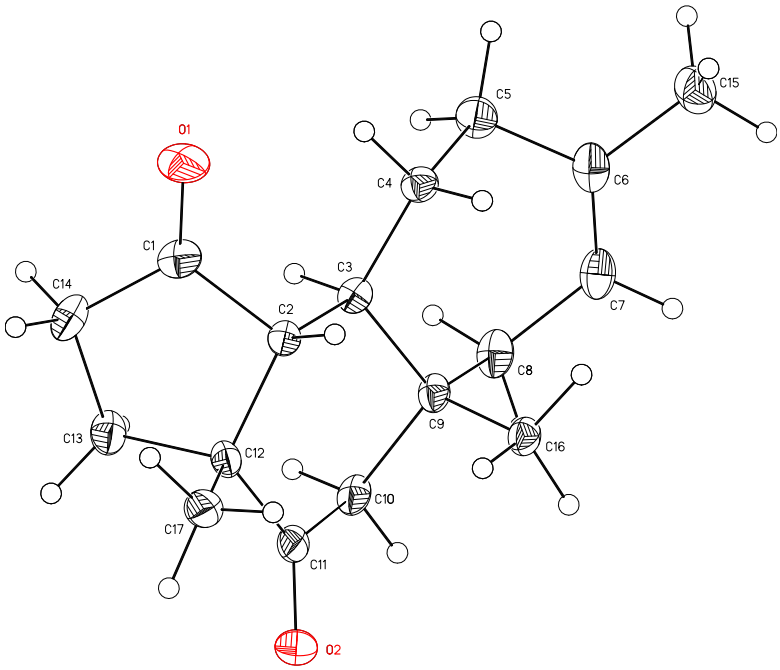
APPENDIX 3

X-ray Crystallography Reports Relevant to Chapter 2

A3.1 CRYSTAL STRUCTURE ANALYSIS OF DIKETONE *214*

*Figure A3.1 ORTEP drawing of tricyclic diketone **214** (shown with 50% probability ellipsoids).*



Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number 664430.

*Table A3.1 Crystal data and structure refinement for tricyclic diketone **214** (CCDC 664430).*

Empirical formula	$C_{17}H_{24}O_2$
Formula weight	260.36
Crystallization Solvent	Water/acetonitrile
Crystal Habit	Fragment
Crystal size	0.39 x 0.28 x 0.09 mm^3
Crystal color	Colorless

Data Collection

Type of diffractometer	Bruker SMART 1000
Wavelength	1.54178 Å CuKα
Data Collection Temperature	100(2) K
θ range for 5024 reflections used in lattice determination	4.12 to 65.79°
Unit cell dimensions	a = 7.4937(2) Å b = 9.0345(2) Å c = 21.4487(5) Å
Volume	1452.12(6) $Å^3$
Z	4
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Density (calculated)	1.191 Mg/m^3
F(000)	568
Data collection program	Bruker SMART v5.630
θ range for data collection	4.12 to 65.79°
Completeness to θ = 65.79°	96.1 %
Index ranges	$-7 \leq h \leq 8$, $-10 \leq k \leq 8$, $-21 \leq l \leq 24$
Data collection scan type	ω scans at 7 ϕ settings
Data reduction program	Bruker SAINT v6.45A
Reflections collected	7914
Independent reflections	2344 [R_{int}= 0.0753]
Absorption coefficient	0.593 mm^{-1}
Absorption correction	None
Max. and min. transmission	0.9486 and 0.8017

Table A3.1 (cont.)

Structure solution and Refinement

Structure solution program	SHELXS-97 (Sheldrick, 1990)
Primary solution method	Direct methods
Secondary solution method	Difference Fourier map
Hydrogen placement	Difference Fourier map
Structure refinement program	SHELXL-97 (Sheldrick, 1997)
Refinement method	Full matrix least-squares on F^2
Data / restraints / parameters	2344 / 0 / 268
Treatment of hydrogen atoms	Unrestrained
Goodness-of-fit on F^2	1.394
Final R indices [I>2σ(I), 2083 reflections]	R1 = 0.0335, *w*R2 = 0.0669
R indices (all data)	R1 = 0.0391, *w*R2 = 0.0686
Type of weighting scheme used	Sigma
Weighting scheme used	$w=1/\sigma^2(Fo^2)$
Max shift/error	0.000
Average shift/error	0.000
Absolute structure determination	Anomalous differences
Absolute structure parameter	0.2(2)
Largest diff. peak and hole	0.142 and -0.155 e.Å^{-3}

Special Refinement Details

Refinement of F^2 against ALL reflections. The weighted R-factor (*w*R) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

*Figure A3.2 Tricyclic diketone **214** (CCDC 664430)*

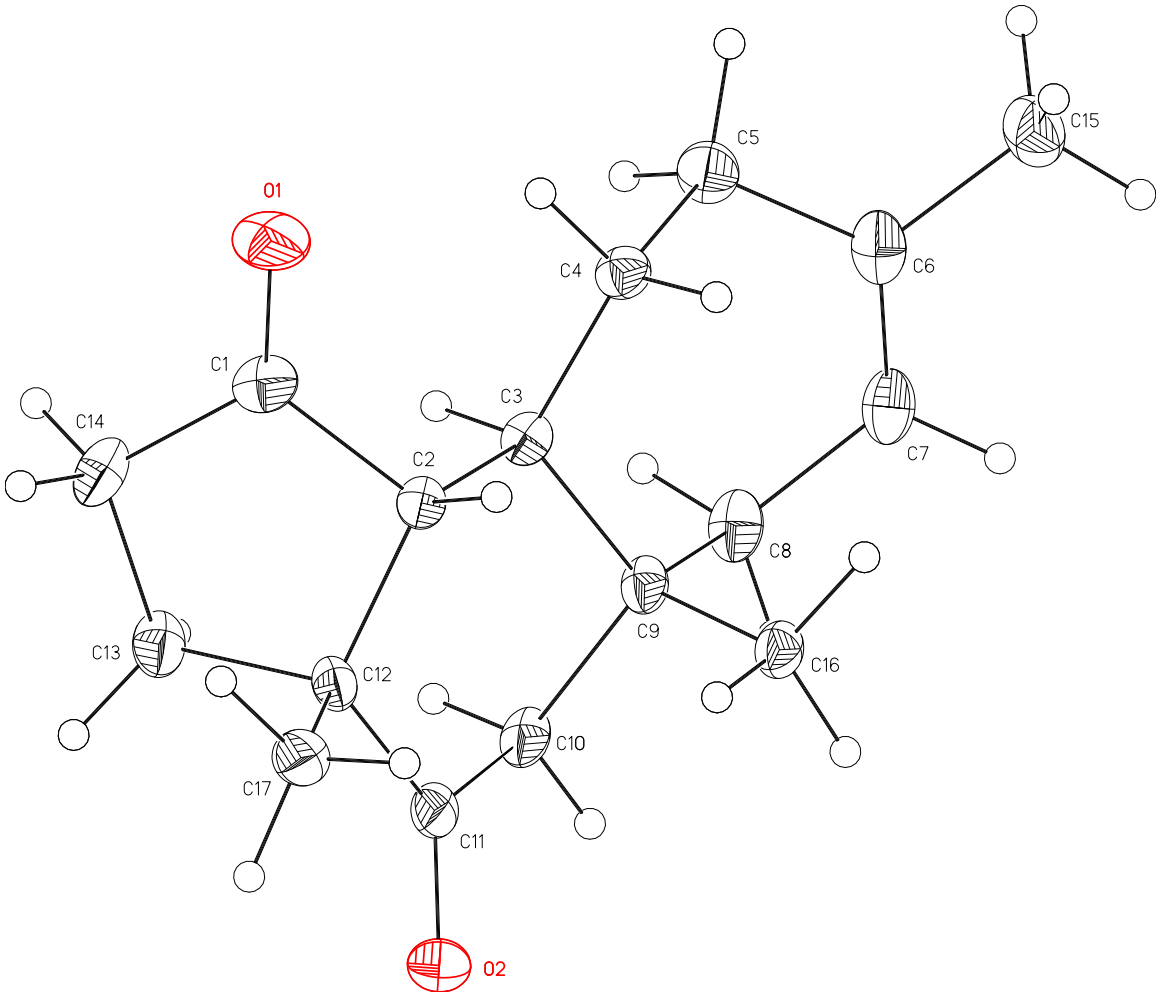


Table A3.2 Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for diketone ***214*** *(CCDC 664430). U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.*

	x	y	z	U_{eq}
O(1)	8369(2)	2053(2)	7466(1)	32(1)
O(2)	13478(2)	3487(2)	5446(1)	29(1)
C(1)	9211(2)	2001(2)	6981(1)	21(1)
C(2)	10059(2)	3336(2)	6653(1)	15(1)
C(3)	8595(2)	4237(2)	6306(1)	15(1)
C(4)	7465(3)	5062(2)	6791(1)	18(1)
C(5)	5740(3)	5787(2)	6542(1)	25(1)
C(6)	6041(2)	7246(2)	6214(1)	23(1)
C(7)	7053(3)	7331(2)	5712(1)	24(1)
C(8)	7949(3)	6025(2)	5407(1)	22(1)
C(9)	9420(3)	5246(2)	5792(1)	17(1)
C(10)	10444(3)	4224(2)	5340(1)	20(1)
C(11)	11962(2)	3449(2)	5658(1)	20(1)
C(12)	11518(2)	2593(2)	6244(1)	17(1)
C(13)	10651(3)	1092(2)	6049(1)	22(1)
C(14)	9615(3)	599(2)	6620(1)	24(1)
C(15)	5143(3)	8573(3)	6497(1)	30(1)
C(16)	10728(3)	6397(2)	6053(1)	19(1)
C(17)	13190(3)	2308(2)	6637(1)	23(1)

*Table A3.3. Bond lengths [Å] and angles [°] for diketone **214** (CCDC 664430)*

O(1)-C(1)	1.219(2)	C(1)-C(2)-C(3)	109.78(14)
O(2)-C(11)	1.224(2)	C(12)-C(2)-C(3)	116.84(14)
C(1)-C(14)	1.514(3)	C(1)-C(2)-H(2)	108.8(9)
C(1)-C(2)	1.533(2)	C(12)-C(2)-H(2)	111.2(9)
C(2)-C(12)	1.554(2)	C(3)-C(2)-H(2)	107.8(9)
C(2)-C(3)	1.556(2)	C(4)-C(3)-C(2)	108.61(14)
C(2)-H(2)	0.972(16)	C(4)-C(3)-C(9)	114.51(15)
C(3)-C(4)	1.534(3)	C(2)-C(3)-C(9)	111.44(14)
C(3)-C(9)	1.559(2)	C(4)-C(3)-H(3)	107.6(9)
C(3)-H(3)	1.050(16)	C(2)-C(3)-H(3)	106.6(9)
C(4)-C(5)	1.544(3)	C(9)-C(3)-H(3)	107.7(8)
C(4)-H(4A)	1.008(19)	C(3)-C(4)-C(5)	115.75(16)
C(4)-H(4B)	0.995(18)	C(3)-C(4)-H(4A)	111.3(11)
C(5)-C(6)	1.511(3)	C(5)-C(4)-H(4A)	107.4(11)
C(5)-H(5A)	0.994(19)	C(3)-C(4)-H(4B)	108.6(10)
C(5)-H(5B)	1.06(2)	C(5)-C(4)-H(4B)	107.8(10)
C(6)-C(7)	1.320(3)	H(4A)-C(4)-H(4B)	105.5(14)
C(6)-C(15)	1.503(3)	C(6)-C(5)-C(4)	113.95(17)
C(7)-C(8)	1.507(3)	C(6)-C(5)-H(5A)	109.1(11)
C(7)-H(7)	0.99(2)	C(4)-C(5)-H(5A)	106.3(11)
C(8)-C(9)	1.547(3)	C(6)-C(5)-H(5B)	108.4(12)
C(8)-H(8A)	1.046(19)	C(4)-C(5)-H(5B)	107.8(11)
C(8)-H(8B)	1.013(19)	H(5A)-C(5)-H(5B)	111.3(15)
C(9)-C(16)	1.535(2)	C(7)-C(6)-C(15)	122.73(18)
C(9)-C(10)	1.543(2)	C(7)-C(6)-C(5)	121.05(18)
C(10)-C(11)	1.500(3)	C(15)-C(6)-C(5)	116.21(18)
C(10)-H(10A)	1.008(19)	C(6)-C(7)-C(8)	124.41(19)
C(10)-H(10B)	0.94(2)	C(6)-C(7)-H(7)	121.8(11)
C(11)-C(12)	1.514(2)	C(8)-C(7)-H(7)	113.8(11)
C(12)-C(17)	1.532(3)	C(7)-C(8)-C(9)	116.25(16)
C(12)-C(13)	1.561(3)	C(7)-C(8)-H(8A)	109.8(11)
C(13)-C(14)	1.518(3)	C(9)-C(8)-H(8A)	108.7(11)
C(13)-H(13A)	0.966(18)	C(7)-C(8)-H(8B)	110.5(10)
C(13)-H(13B)	0.973(19)	C(9)-C(8)-H(8B)	105.5(10)
C(14)-H(14A)	0.99(2)	H(8A)-C(8)-H(8B)	105.5(15)
C(14)-H(14B)	1.00(2)	C(16)-C(9)-C(10)	108.47(16)
C(15)-H(15A)	1.00(2)	C(16)-C(9)-C(8)	109.99(15)
C(15)-H(15B)	1.01(2)	C(10)-C(9)-C(8)	106.98(15)
C(15)-H(15C)	0.96(2)	C(16)-C(9)-C(3)	112.96(14)
C(16)-H(16A)	1.03(2)	C(10)-C(9)-C(3)	106.99(14)
C(16)-H(16B)	1.000(19)	C(8)-C(9)-C(3)	111.19(15)
C(16)-H(16C)	1.036(19)	C(11)-C(10)-C(9)	111.79(15)
C(17)-H(17A)	1.00(2)	C(11)-C(10)-H(10A)	107.4(10)
C(17)-H(17B)	1.01(2)	C(9)-C(10)-H(10A)	110.6(10)
C(17)-H(17C)	0.95(2)	C(11)-C(10)-H(10B)	110.2(12)
		C(9)-C(10)-H(10B)	109.6(12)
O(1)-C(1)-C(14)	124.84(18)	H(10A)-C(10)-H(10B)	107.0(15)
O(1)-C(1)-C(2)	125.15(17)	O(2)-C(11)-C(10)	121.45(17)
C(14)-C(1)-C(2)	109.99(15)	O(2)-C(11)-C(12)	121.84(17)
C(1)-C(2)-C(12)	102.14(14)	C(10)-C(11)-C(12)	116.70(15)

C(11)-C(12)-C(17)	111.27(16)	C(6)-C(15)-H(15B)	110.4(12)
C(11)-C(12)-C(2)	113.80(14)	H(15A)-C(15)-H(15B)	106.7(18)
C(17)-C(12)-C(2)	109.74(15)	C(6)-C(15)-H(15C)	114.4(14)
C(11)-C(12)-C(13)	108.17(14)	H(15A)-C(15)-H(15C)	112.7(19)
C(17)-C(12)-C(13)	110.00(16)	H(15B)-C(15)-H(15C)	102.7(17)
C(2)-C(12)-C(13)	103.55(15)	C(9)-C(16)-H(16A)	109.4(11)
C(14)-C(13)-C(12)	104.54(15)	C(9)-C(16)-H(16B)	111.8(11)
C(14)-C(13)-H(13A)	110.1(10)	H(16A)-C(16)-H(16B)	111.5(15)
C(12)-C(13)-H(13A)	110.7(11)	C(9)-C(16)-H(16C)	107.7(10)
C(14)-C(13)-H(13B)	111.8(11)	H(16A)-C(16)-H(16C)	107.4(15)
C(12)-C(13)-H(13B)	112.1(12)	H(16B)-C(16)-H(16C)	108.8(14)
H(13A)-C(13)-H(13B)	107.6(15)	C(12)-C(17)-H(17A)	110.3(11)
C(1)-C(14)-C(13)	105.56(16)	C(12)-C(17)-H(17B)	112.1(12)
C(1)-C(14)-H(14A)	113.1(12)	H(17A)-C(17)-H(17B)	108.9(16)
C(13)-C(14)-H(14A)	111.2(12)	C(12)-C(17)-H(17C)	111.9(11)
C(1)-C(14)-H(14B)	109.3(12)	H(17A)-C(17)-H(17C)	109.2(16)
C(13)-C(14)-H(14B)	112.8(12)	H(17B)-C(17)-H(17C)	104.2(15)
H(14A)-C(14)-H(14B)	105.1(17)		
C(6)-C(15)-H(15A)	109.6(13)		

*Table A3.4 Anisotropic displacement parameters ($Å^2 x\ 10^4$) for diketone **214** (CCDC 664430). 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}
O(1)	372(9)	382(9)	203(8)	136(6)	113(6)	108(7)
O(2)	332(8)	252(8)	275(8)	-7(6)	149(6)	2(7)
C(1)	202(11)	268(11)	149(10)	90(8)	-25(8)	30(8)
C(2)	203(10)	152(10)	94(10)	-6(7)	-6(7)	-11(7)
C(3)	175(10)	170(10)	115(10)	12(7)	-25(7)	-14(8)
C(4)	183(11)	195(11)	170(11)	27(9)	1(8)	1(8)
C(5)	173(11)	242(12)	320(13)	9(9)	-27(10)	14(9)
C(6)	199(12)	187(10)	317(12)	2(9)	-117(9)	9(8)
C(7)	306(12)	175(11)	231(12)	53(8)	-85(9)	15(9)
C(8)	312(11)	188(11)	165(11)	37(8)	-69(9)	3(9)
C(9)	252(11)	141(10)	124(10)	15(7)	-2(8)	-2(8)
C(10)	332(12)	160(11)	98(10)	17(8)	33(8)	-30(9)
C(11)	296(12)	142(11)	163(11)	-59(7)	66(8)	-34(8)
C(12)	211(11)	130(10)	157(10)	1(7)	5(7)	26(7)
C(13)	340(12)	174(11)	160(11)	-5(8)	4(9)	-7(9)
C(14)	308(13)	197(11)	213(12)	38(8)	-22(9)	-82(9)
C(15)	233(12)	241(12)	421(15)	3(11)	-34(10)	51(9)
C(16)	244(11)	150(10)	178(11)	-20(8)	16(8)	-29(9)
C(17)	212(12)	212(12)	262(12)	30(9)	28(9)	30(9)

*Table A3.5 Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^{-3}) for diketone **214** (CCDC 664430)*

	x	y	z	U_{iso}
H(2)	10590(20)	3978(18)	6967(7)	5(4)
H(3)	7760(20)	3463(18)	6085(7)	7(4)
H(7)	7290(20)	8280(20)	5503(9)	29(5)
H(4A)	8180(20)	5860(20)	7005(8)	21(5)
H(5A)	5210(20)	5070(20)	6242(9)	24(5)
H(8A)	8490(30)	6340(20)	4977(9)	33(5)
H(10A)	9630(20)	3440(20)	5166(8)	22(5)
H(13A)	9850(20)	1230(20)	5701(9)	19(5)
H(14A)	8530(30)	40(20)	6501(9)	33(6)
H(15A)	5460(30)	9480(30)	6252(10)	46(7)
H(16A)	11750(30)	5860(20)	6279(9)	31(6)
H(17A)	14160(30)	1860(20)	6372(9)	30(5)
H(4B)	7120(20)	4350(20)	7125(8)	16(5)
H(5B)	4880(30)	5970(20)	6926(10)	41(6)
H(8B)	7040(20)	5230(20)	5307(8)	17(5)
H(10B)	10870(20)	4780(20)	5001(9)	26(5)
H(13B)	11540(30)	360(20)	5925(9)	24(6)
H(14B)	10310(30)	-90(20)	6890(10)	36(6)
H(15B)	5590(30)	8740(20)	6937(9)	34(6)
H(16B)	10120(20)	7120(20)	6333(8)	26(5)
H(17B)	12940(30)	1620(20)	7000(9)	37(6)
H(15C)	3890(30)	8470(30)	6556(10)	43(6)
H(16C)	11280(20)	6960(20)	5679(9)	22(5)
H(17C)	13620(20)	3190(20)	6827(8)	17(5)