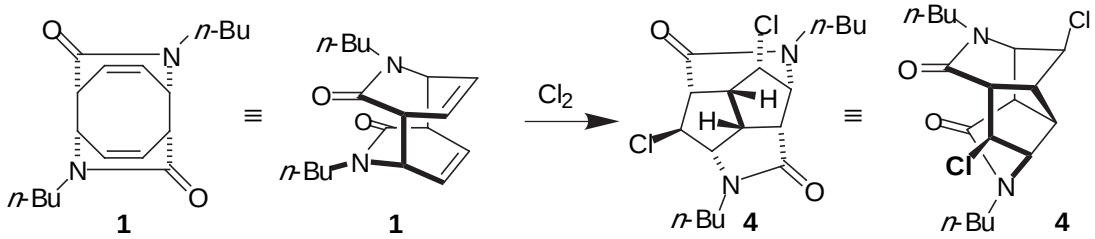


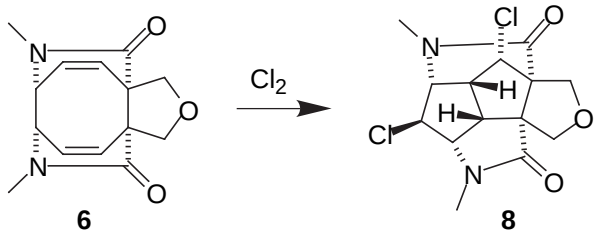
Compound 4. Prepared by the method described for compound **8** (below).

^{1}H ($CDCl_3$) δ = 4.36 (m, 1H), 4.17 (m, 1H), 4.08 (m, 1H), 3.95 (m, 1H), 3.47 (m, 1H), 3.4-3.1 (m, 5H), 2.96 (m, 1H), 2.62 (m, 1H), 1.45 (m, 4H), 1.35 (m, 4H), 0.90 (m, 6H).

^{13}C ($CDCl_3$) δ = 170.8, 167.3, 70.9, 63.9, 62.8, 56.7, 54.1, 52.3, 48.9, 48.2, 42.9, 42.0, 29.3, 29.0, 20.1, 13.8, 13.6.

MS (EI) m/z 372 (M^+, 72), 343 (71), 329 (100), 317 (30), 309 (27), 152 (33).

Exact Mass (EI) m/z Calcd for $C_{18}H_{26}N_2O_2Cl_2$: 372.1371, Found: 372.1355



6 **8**

Chlorination product 8.

Into a solution of *cis*-photoproduct **6** (29.8 mg, 0.115 mmol) in chloroform (10 mL) was bubbled in chlorine gas until no starting material was observed by TLC (5 min). The solution was then mixed with saturated sodium bicarbonate solution and the aqueous phase extracted with chloroform. The combined organic layers were dried over anhydrous sodium sulfate and the solvent was removed by rotary evaporator. The crude product was purified by flash chromatography (4:4:4:1 ethyl acetate: hexane:CH_2Cl_2:MeOH) to give **8** (16.9 mg, 45%) as a colorless solid.

R_f = 0.21 (ethyl acetate/hexane/CH_2Cl_2/MeOH 20:20:20:5).

mp = 264 - 265 °C.

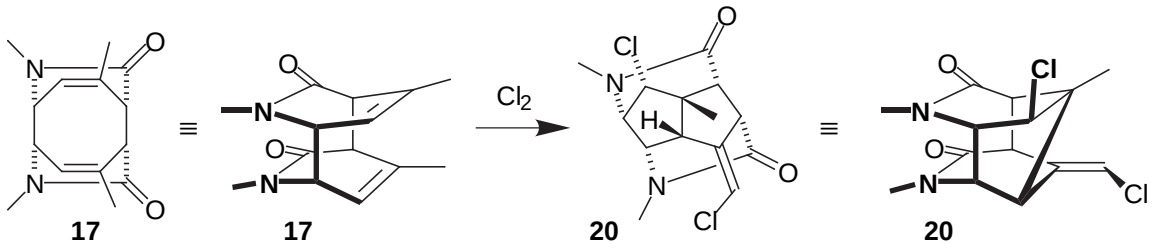
^{1}H NMR ($CDCl_3$): δ = 4.50 (d, *J* = 4.2 Hz, 1H), 4.37 (d, *J* = 9.3 Hz, 1H), 4.36 (s, 1H), 4.31 (d, *J* = 9.9 Hz, 1H), 4.16 (dd, *J* = 8.1, 1.5 Hz, 1H), 4.07 (d, *J* = 9.6 Hz, 1H), 4.00 (d, *J* = 6.0 Hz, 1H), 3.90 (d, *J* = 9.9 Hz, 1H), 3.69 (m, 1H), 3.31 (t, 1H), 2.95 (s, 3H), 2.89 (s, 3H).

^{13}C NMR ($CDCl_3$): δ = 171.9, 165.4, 75.2, 70.6, 68.9, 68.2, 64.1, 58.9, 57.2, 50.0, 48.8, 32.5, 29.7, 29.6.

IR (KBr): 3440, 2968, 2934, 2885, 1663, 1481, 1469, 1402, 1068 cm^{-1}.

MS *m/z* (%) : 331 (MH^+, 100), 314 (9), 297 (87), 263 (18).

Exact Mass Calcd for $C_{14}H_{16}Cl_2N_2O_2$: 331.0616, Found 331.0626.



***Cis* Head-to-head dimer 17**

An NMR tube was prepared containing 1,4-dimethyl-2-pyridone (50.7mg, 0.41mmol) in methanol-d_4 (0.82mL, 0.5M), sealed with a rubber septum and purged with nitrogen for 10-15 mim. This tube was taped to the side of a water-cooled quartz jacket surrounding a 450W medium-pressure mercury lamp fitted with a pyrex filter and lowered into an ice-bath. Irradiation was conducted for 20 h, following the photoreaction by ^{1}H NMR and TLC. The solvent was removed and the crude mixture was purified by flash chromatography (3:97 MeOH/methylene chloride) to afford the *trans* head-to-tail dimer, the *cis* head-to-tail dimer, the cis head-to-head dimer **17**, and the Dewar pyridone, in ratio of 4 : 2 : 1 : 0.7 and overall yield of 80%.

17: mp = 184 °C.

R_f = 0.20 (1:19 MeOH/CH_2Cl_2).

^{1}H NMR ($CDCl_3$): δ = 6.11 (s, 1H), 3.93 (m, *J* = 6.6 Hz, 1H), 3.39 (s, 1H), 2.89 (s, 3H), 1.72 (s, 3H).

^{13}C NMR ($CDCl_3$): δ = 173.5, 140.4, 127.9, 61.9, 54.4, 35.2, 21.1.

IR (KBr): 3055, 2961, 1667, 1645, 1482, 1461, 1405 cm^{-1}.

Chlorination of *cis* head-to-head dimer **17** to give **20.**

To a solution of cis head-to-head dimer **17** (100 mg, 0.40 mmol) in chloroform (40mL, 0.01M) was bubbled in chlorine gas for about 30s at 0 °C. The solution was then mixed with saturated sodium bicarbonate solution and the aqueous phase was extracted with chloroform. The combined organic layers were dried over anhydrous magnesium

sulfate and concentrated *in vacuo*. The product was purified by flash chromatography (2:98 MeOH/CH_2Cl_2) to give **20** (54.2 mg, 43%).

R_f : 0.5 (2:98 MeOH/CH_2Cl_2).

mp = 143 °C.

^{1}H NMR ($CDCl_3$): δ 6.15 (s, 1H), 4.18 (m, 2H), 3.98 (t, 1H), 3.65 (dd, *J* = 9Hz, 1H), 3.13 (d, *J* = 9, 1H). 2.95 (s, 3H), 2.82 (s, 3H), 1.16 (s, 3H).

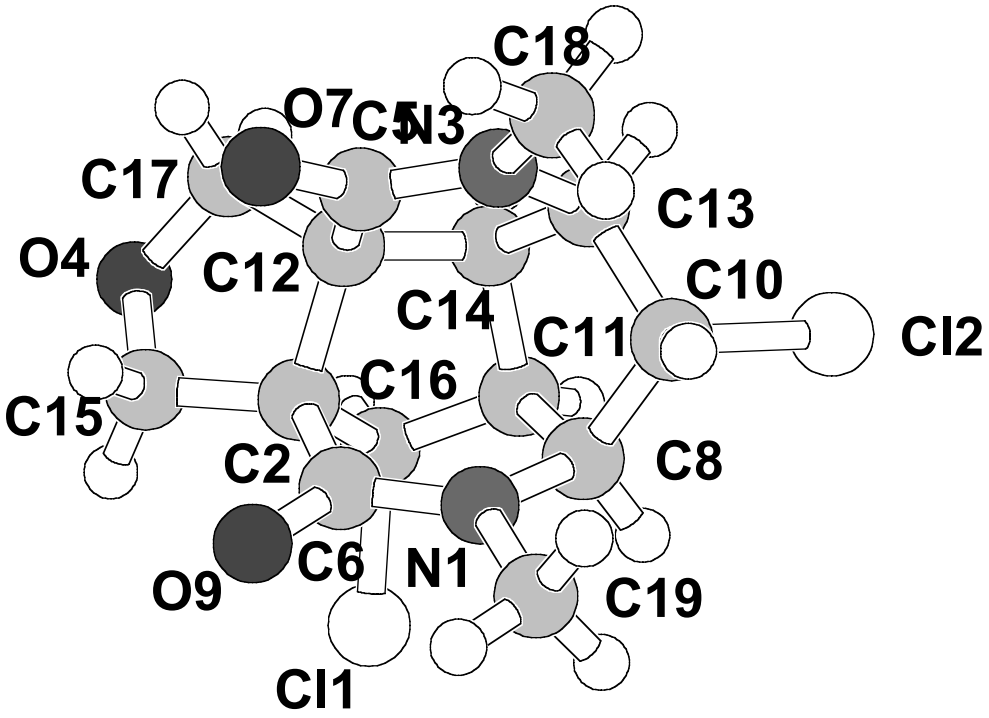
^{13}C NMR ($CDCl_3$): δ = 171.1, 169.5, 137.2, 111.7, 65.3, 64.6, 62.8, 54.1, 52.8, 51.1, 37.1, 33.6, 9.3.

IR (KBr): 3359, 3329, 3055, 2926, 1673, 1668, 1479 cm^{-1}.

MS (DCI/NH_3) m/z 315 (MH^+).

Exact Mass (DCI/NH_3) m/z Calcd for $C_{14}H_{17}Cl_2N_2O_2$: 315.0667, Found: 315.0665

Molecular Structure and Crystallographic Data for **8**



Empirical formula	$C_{14}\ H_{16}\ Cl_2\ N_2\ O_3$
Formula weight	331.19
Crystal system	Triclinic
Space group	P1
Lattice Parameters	a = 6.9014 (12) $\alpha = 65^o$
	b = 7.6944 (13) $\beta = 82^o$
	c = 8.3578 (14) $\gamma = 65^o$
Z value	1
Density (calculated)	1.502 Mg/m^3
Absorption coefficient	0.454 mm^{-1}
F(000)	172
Completeness to theta = 23.27	99.4 %
Data / restraints / parameters	1314 / 3 / 210
Goodness-of-fit Indicator	1.034
Final R indices [I>2sigma(I)]	R1 = 0.0437, wR2 = 0.1182
R indices (all data)	R1 = 0.0480, wR2 = 0.1234

Atomic Coordinates for **8**

Atom	x	y	z	U(eq)
Cl(1)	-2896(2)	9096(2)	2915(2)	67(1)
Cl(2)	-3995(3)	4308(3)	9899(2)	95(1)
N(1)	83(7)	6337(6)	6540(5)	42(1)
C(2)	393(8)	5168(8)	4189(6)	39(1)
N(3)	1632(7)	1310(7)	8324(6)	49(1)
O(4)	1030(9)	3620(8)	2220(5)	77(2)
C(5)	2455(9)	1646(8)	6717(7)	49(1)
C(6)	1168(8)	6105(8)	5114(7)	43(1)
O(7)	4374(7)	1083(8)	6399(6)	71(1)
C(8)	-1907(9)	6007(9)	7070(7)	48(1)
O(9)	2692(7)	6622(8)	4595(5)	65(1)
C(10)	-1507(9)	4091(9)	8825(7)	50(1)
C(11)	-2701(8)	5461(9)	5807(7)	49(1)
C(12)	657(9)	2856(8)	5323(6)	45(1)
C(13)	-678(10)	2181(9)	8334(7)	50(1)
C(14)	-1405(10)	3066(10)	6377(7)	49(1)
C(15)	1584(10)	5030(11)	2546(8)	58(2)
C(16)	-2024(8)	6301(9)	3943(7)	47(1)
C(17)	1021(13)	1991(11)	3880(8)	69(2)
C(18)	2992(11)	235(10)	9943(8)	68(2)
C(19)	661(14)	7286(12)	7497(9)	74(2)

Bond Lengths for **8**

Cl(1)-C(16)	1.802(6)	O(4)-C(15)	1.421(8)
Cl(2)-C(10)	1.800(6)	O(4)-C(17)	1.430(8)
N(1)-C(6)	1.353(7)	C(5)-O(7)	1.238(7)
N(1)-C(19)	1.467(7)	C(5)-C(12)	1.516(8)
N(1)-C(8)	1.474(8)	C(6)-O(9)	1.237(7)
C(2)-C(6)	1.519(7)	C(8)-C(11)	1.521(9)
C(2)-C(15)	1.519(7)	C(8)-C(10)	1.539(8)
C(2)-C(16)	1.523(7)	C(10)-C(13)	1.548(9)
C(2)-C(12)	1.570(8)	C(11)-C(16)	1.507(7)
N(3)-C(5)	1.347(7)	C(11)-C(14)	1.561(8)
N(3)-C(13)	1.449(8)	C(12)-C(14)	1.551(8)
N(3)-C(18)	1.472(7)	C(12)-C(17)	1.552(8)
		C(13)-C(14)	1.550(8)

Bond Angles for **8**

C(6)-N(1)-C(19)	120.0(5)	C(8)-C(10)-Cl(2)	109.0(4)
C(6)-N(1)-C(8)	124.2(4)	C(13)-C(10)-Cl(2)	109.2(4)
C(19)-N(1)-C(8)	115.1(5)	C(16)-C(11)-C(8)	113.9(5)
C(6)-C(2)-C(15)	114.0(4)	C(16)-C(11)-C(14)	101.5(4)
C(6)-C(2)-C(16)	107.7(4)	C(8)-C(11)-C(14)	104.8(4)
C(15)-C(2)-C(16)	115.7(4)	C(5)-C(12)-C(14)	104.8(4)
C(6)-C(2)-C(12)	114.6(4)	C(5)-C(12)-C(17)	113.5(5)
C(15)-C(2)-C(12)	102.8(4)	C(14)-C(12)-C(17)	119.2(5)
C(16)-C(2)-C(12)	101.5(4)	C(5)-C(12)-C(2)	113.6(5)
C(5)-N(3)-C(13)	115.3(4)	C(14)-C(12)-C(2)	104.2(4)
C(5)-N(3)-C(18)	122.0(5)	C(17)-C(12)-C(2)	101.5(4)
C(13)-N(3)-C(18)	122.6(5)	N(3)-C(13)-C(10)	110.7(5)
C(15)-O(4)-C(17)	107.9(4)	N(3)-C(13)-C(14)	104.4(4)
O(7)-C(5)-N(3)	126.1(5)	C(10)-C(13)-C(14)	105.5(5)
O(7)-C(5)-C(12)	124.5(5)	C(13)-C(14)-C(12)	105.7(5)
N(3)-C(5)-C(12)	109.4(5)	C(13)-C(14)-C(11)	106.5(4)
O(9)-C(6)-N(1)	122.3(5)	C(12)-C(14)-C(11)	105.1(4)
O(9)-C(6)-C(2)	122.0(5)	O(4)-C(15)-C(2)	103.3(5)
N(1)-C(6)-C(2)	115.6(5)	C(11)-C(16)-C(2)	101.3(4)
N(1)-C(8)-C(11)	113.4(4)	C(11)-C(16)-Cl(1)	114.9(4)
N(1)-C(8)-C(10)	109.8(4)	C(2)-C(16)-Cl(1)	112.8(4)
C(11)-C(8)-C(10)	103.6(5)	O(4)-C(17)-C(12)	107.7(5)
C(8)-C(10)-C(13)	106.0(5)		

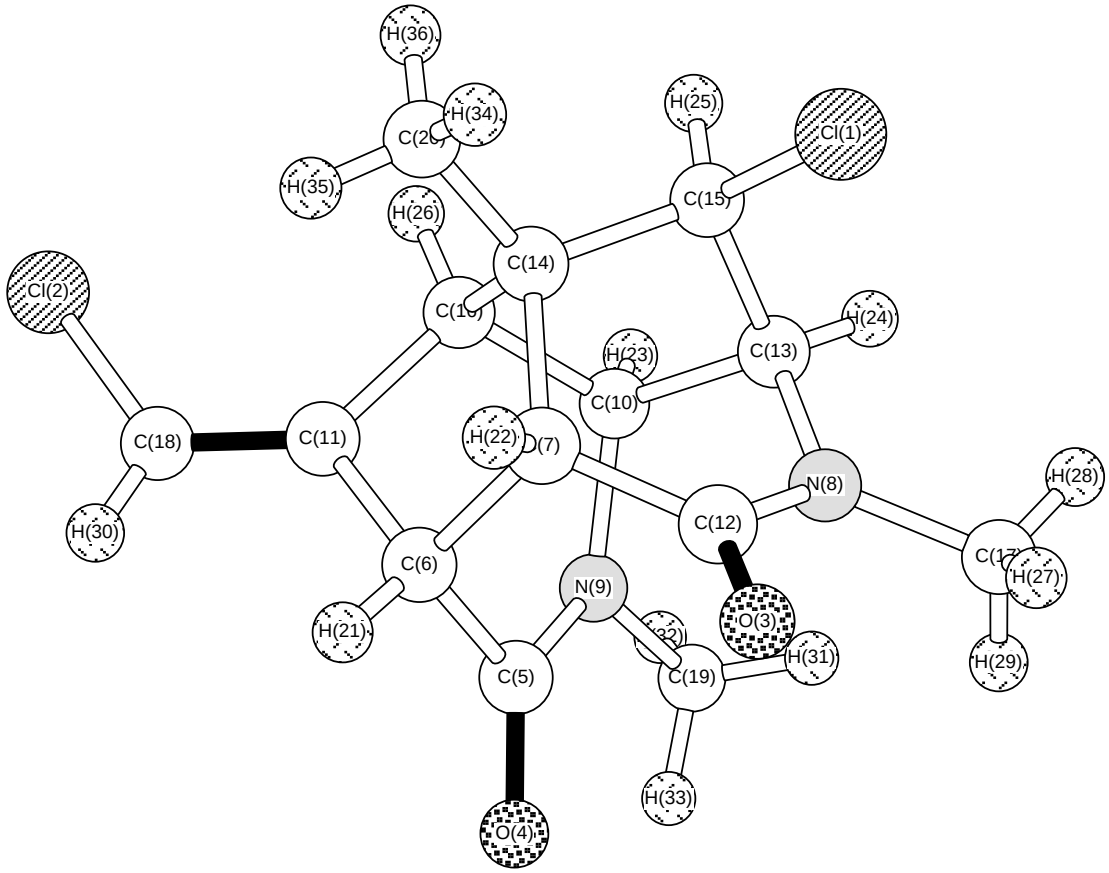
Anisotropic Displacement Parameters for **8**

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cl(1)	59(1)	59(1)	53(1)	-4(1)	-8(1)	-10(1)
Cl(2)	75(1)	84(1)	75(1)	-16(1)	46(1)	-16(1)
N(1)	48(3)	40(2)	35(2)	-16(2)	-1(2)	-14(2)
C(2)	37(3)	48(3)	29(2)	-13(2)	3(2)	-16(2)
N(3)	51(3)	43(2)	37(2)	-15(2)	-9(2)	-2(2)
O(4)	117(4)	82(3)	39(2)	-31(2)	1(2)	-38(3)
C(5)	51(4)	47(3)	45(3)	-27(3)	8(3)	-10(3)
C(6)	40(3)	46(3)	7(3)	-15(2)	1(2)	-14(2)
O(7)	43(3)	75(3)	65(3)	-26(2)	5(2)	1(2)
C(8)	41(3)	45(3)	38(3)	-14(3)	7(2)	-3(2)
O(9)	58(3)	99(4)	61(3)	-39(3)	14(2)	-50(3)
C(10)	44(3)	53(3)	34(3)	-12(3)	6(2)	-10(2)
C(11)	31(3)	59(3)	43(3)	-12(3)	6(2)	-14(2)
C(12)	56(3)	46(3)	34(3)	-17(2)	2(2)	-22(2)
C(13)	54(3)	50(3)	36(3)	-13(3)	7(2)	-16(3)
C(14)	50(3)	61(4)	46(3)	-23(3)	5(2)	-30(3)
C(15)	58(4)	73(4)	48(3)	-33(3)	15(3)	-25(3)
C(16)	41(3)	53(3)	39(3)	-11(3)	-8(2)	-16(2)
C(17)	101(6)	65(4)	49(4)	-32(3)	8(3)	-34(4)
C(18)	77(5)	57(4)	45(3)	-17(3)	-16(3)	-1(3)
C(19)	111(6)	78(5)	58(4)	-41(4)	5(4)	-47(4)

Hydrogen Coordinates and Isotropic Displacement Parameters for **8**

Atom	x	y	z	U(eq)
H(8)	-3020(110)	7250(100)	7200(80)	57
H(10)	-460(110)	3970(100)	9580(80)	60
H(11)	-4240(110)	5830(100)	5860(80)	59
H(13)	-1230(110)	1130(110)	9100(90)	60
H(14)	-2210(100)	2370(100)	6180(80)	59
H(15A)	1122	6383	1565	69
H(15B)	3111	4495	2755	69
H(16)	-2540(100)	5840(90)	3220(80)	56
H(17A)	2371	794	4112	83
H(17B)	-110	1559	3868	83
H(18A)	4459	-335	9664	102
H(18B)	2604	-871	10774	102
H(18C)	2799	1210	10446	102
H(19A)	1680	7841	6848	111
H(19B)	1273	6249	8639	111
H(19C)	-592	8390	7629	111

Molecular Structure and Crystallographic Data for **20**



Empirical formula	$C_{14} H_{16} Cl_2 N_2 O_2$	
Formula weight	315.19	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 9.025(2) Å	α= 90°.
	b = 12.062(3) Å	β= 105.219(4)°.
	c = 13.651(3) Å	γ = 90°.
Volume	1433.9(6) $Å^3$	
Z	4	
Density (calculated)	1.460 Mg/m^3	
Absorption coefficient	0.455 mm^{-1}	
F(000)	656	
Crystal size	.3 x .3 x .2 mm^3	
Theta range for data collection	2.29 to 28.54°.	
Index ranges	-7<=h<=11, -15<=k<=14, -18<=l<=17	
Reflections collected	8688	

Independent reflections	3292 [R(int) = 0.0621]
Completeness to theta = 28.54°	90.2 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3292 / 0 / 202
Goodness-of-fit on F^2	0.842
Final R indices [I>2sigma(I)]	R1 = 0.0515, wR2 = 0.1259
R indices (all data)	R1 = 0.1065, wR2 = 0.1422
Largest diff. peak and hole	0.497 and -0.192 e.$Å^{-3}$

Atomic Coordinates for **20**

Atom	x	y	z	U(eq)
Cl(1)	5843(1)	636(1)	1179(1)	63(1)
Cl(2)	12433(1)	3688(1)	3621(1)	79(1)
O(1)	7026(2)	-643(2)	3927(2)	57(1)
O(2)	8839(2)	1506(2)	5887(2)	63(1)
C(6)	8714(3)	1796(2)	5012(2)	49(1)
C(10)	9662(3)	1293(2)	4353(2)	45(1)
C(5)	8648(3)	662(2)	3381(2)	43(1)
N(1)	6011(2)	1037(2)	3367(2)	48(1)
N(2)	7801(2)	2646(2)	4557(2)	50(1)
C(7)	7515(3)	2824(2)	3470(2)	47(1)
C(9)	10293(3)	2256(2)	3901(2)	45(1)
C(1)	7157(3)	281(2)	3573(2)	46(1)
C(2)	6219(3)	2048(2)	2827(2)	48(1)
C(4)	8510(3)	1500(2)	2474(2)	45(1)
C(3)	6838(3)	1752(2)	1942(2)	49(1)
C(8)	8941(3)	2607(2)	3061(2)	47(1)
C(11)	4516(3)	760(3)	3541(3)	67(1)
C(14)	11722(3)	2592(2)	4182(2)	55(1)
C(13)	6819(4)	3200(3)	5090(3)	73(1)
C(12)	9523(4)	1204(3)	1797(2)	64(1)

Bond Lengths for **20**

Cl(1)-C(3)	1.792(3)	N(1)-C(11)	1.468(3)
Cl(2)-C(14)	1.734(3)	N(2)-C(13)	1.449(4)
O(1)-C(1)	1.233(3)	N(2)-C(7)	1.454(4)
O(2)-C(6)	1.220(3)	C(7)-C(8)	1.554(4)
C(6)-N(2)	1.359(3)	C(7)-C(2)	1.574(4)
C(6)-C(10)	1.521(4)	C(9)-C(14)	1.309(4)
C(10)-C(9)	1.496(4)	C(9)-C(8)	1.500(4)
C(10)-C(5)	1.593(4)	C(2)-C(3)	1.501(4)
C(5)-C(1)	1.509(4)	C(4)-C(12)	1.503(4)
C(5)-C(4)	1.578(4)	C(4)-C(3)	1.524(4)
N(1)-C(1)	1.352(3)	C(4)-C(8)	1.553(4)
N(1)-C(2)	1.462(4)		

Bond Lengths for **20**

O(2)-C(6)-N(2)	123.5(3)	C(10)-C(9)-C(8)	102.3(2)
O(2)-C(6)-C(10)	122.8(3)	O(1)-C(1)-N(1)	123.0(3)
N(2)-C(6)-C(10)	113.5(2)	O(1)-C(1)-C(5)	121.7(2)
C(9)-C(10)-C(6)	105.6(2)	N(1)-C(1)-C(5)	115.2(2)
C(9)-C(10)-C(5)	103.0(2)	N(1)-C(2)-C(3)	109.4(2)
C(6)-C(10)-C(5)	113.2(2)	N(1)-C(2)-C(7)	113.0(2)
C(1)-C(5)-C(4)	116.2(2)	C(3)-C(2)-C(7)	102.2(2)
C(1)-C(5)-C(10)	110.1(2)	C(12)-C(4)-C(3)	116.1(2)
C(4)-C(5)-C(10)	104.9(2)	C(12)-C(4)-C(8)	114.3(2)
C(1)-N(1)-C(2)	118.4(2)	C(3)-C(4)-C(8)	99.0(2)
C(1)-N(1)-C(11)	119.8(2)	C(12)-C(4)-C(5)	113.2(2)
C(2)-N(1)-C(11)	121.1(2)	C(3)-C(4)-C(5)	111.5(2)
C(6)-N(2)-C(13)	119.7(3)	C(8)-C(4)-C(5)	100.9(2)
C(6)-N(2)-C(7)	120.1(2)	C(2)-C(3)-C(4)	101.2(2)
C(13)-N(2)-C(7)	118.4(2)	C(2)-C(3)-Cl(1)	114.3(2)
N(2)-C(7)-C(8)	113.6(2)	C(4)-C(3)-Cl(1)	114.16(19)
N(2)-C(7)-C(2)	112.8(2)	C(9)-C(8)-C(4)	101.2(2)
C(8)-C(7)-C(2)	105.3(2)	C(9)-C(8)-C(7)	110.9(2)
C(14)-C(9)-C(10)	124.9(2)	C(4)-C(8)-C(7)	102.2(2)
C(14)-C(9)-C(8)	132.7(3)	C(9)-C(14)-Cl(2)	123.8(2)

Symmetry transformations used to generate equivalent atoms:

Anisotropic displacement parameters ($Å^3 \times 10^3$) for **20**

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cl(1)	65(1)	61(1)	52(1)	-6(1)	-6(1)	-1(1)
Cl(2)	59(1)	72(1)	105(1)	16(1)	17(1)	-8(1)
O(1)	58(1)	46(1)	60(1)	7(1)	3(1)	-2(1)
O(2)	64(1)	81(2)	43(1)	3(1)	11(1)	7(1)
C(6)	43(2)	50(2)	47(2)	-6(1)	2(1)	-5(1)
C(10)	39(2)	46(2)	44(2)	-1(1)	0(1)	6(1)
C(5)	43(2)	40(2)	42(1)	3(1)	5(1)	9(1)
N(1)	41(1)	48(1)	51(1)	2(1)	5(1)	3(1)
N(2)	45(1)	55(2)	47(1)	-6(1)	6(1)	8(1)
C(7)	48(2)	39(2)	49(2)	3(1)	4(1)	8(1)
C(9)	40(2)	45(2)	47(2)	-1(1)	5(1)	2(1)
C(1)	46(2)	48(2)	37(1)	-2(1)	-2(1)	-1(1)
C(2)	42(2)	41(2)	54(2)	4(1)	-1(1)	8(1)
C(4)	45(2)	49(2)	39(2)	1(1)	5(1)	4(1)
C(3)	55(2)	44(2)	41(2)	5(1)	1(1)	3(1)
C(8)	46(2)	42(2)	50(2)	8(1)	7(1)	2(1)
C(11)	47(2)	76(2)	79(2)	3(2)	18(2)	-1(2)
C(14)	51(2)	53(2)	59(2)	0(1)	10(2)	3(1)
C(13)	62(2)	88(2)	69(2)	-18(2)	17(2)	17(2)
C(12)	64(2)	76(2)	54(2)	-4(2)	16(2)	5(2)

Hydrogen coordinates ($x10^4$) and isotropic displacement parameters ($Å^3 \times 10^3$) for **20**

	x	y	z	U(eq)
H(10)	10480(30)	820(20)	4750(20)	54
H(5)	9220(30)	10(20)	3260(20)	51
H(7)	7190(30)	3600(20)	3320(20)	57
H(2)	5250(30)	2450(20)	2600(20)	58
H(3)	6790(30)	2410(20)	1510(20)	59
H(8)	9170(30)	3210(20)	2640(20)	57
H(11A)	4351	-26	3469	101
H(11B)	3718	1141	3053	101
H(11C)	4503	983	4213	101
H(14)	12394	2221	4714	66
H(13A)	5770	2992	4794	110
H(13B)	6925	3989	5037	110
H(13C)	7112	2988	5792	110
H(12A)	9181	518	1456	96
H(12B)	10563	1126	2200	96
H(12C)	9471	1780	1304	96