Steric Effects in the Reversible Oxygenation of Cobalt–Schiff-base Complexes. Part III.[1] Crystal and Molecular Structure of the *meso*-Form of *NN'*-Cyclohexylenebis(salicylideneiminato)cobalt(II)

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The crystal structure of the title compound has been determined from three-dimensional *X*-ray data by Fourier methods and refined by the anisotropic least-squares method to a final *R* of 0·046 using 1979 independent reflections. Crystals are monoclinic, space group $P2_1/c$, with cell parameters *a* = 12·320(9), *b* = 24·200(10), *c* = 12·260(9) Å, and β = 108·07(9)°, *Z* = 8. The two crystallographically independent molecules are geometrically similar, the cobalt atom having a square-planar stereochemistry slightly tetrahedrally distorted.

PREVIOUS investigations [1-3] have shown the importance of steric effects in determining the oxygen-carrier properties of ethylene-bridge-substituted compounds of *NN'*-ethylenebis(salicylideneiminato)cobalt(II), hereinafter Co(salen). On the basis of structural results [1] we have suggested an interpretation of the influence of the conformation of the substituted bridge on the oxygenation reaction. In fact a pseudo-axial conformation of the bridge substituents appears much more stable than the pseudo-equatorial one, despite the steric hindrance of the apical ligand. This clearly differentiates the behaviour towards the oxygen molecule attack of the *meso*- with respect to the optically active forms. In the latter the bridge substituents

TABLE 1

Fractional co-ordinates (× 10^4) and anisotropic temperature factors * (× 10^4) of molecule (a), with estimated standard deviations in parentheses

(*a*) Non-hydrogen atoms

	x	*y*	*z*	B_{11}	B_{12}	B_{13}	B_{22}	B_{23}	B_{33}
Co	4309(2)	1895(1)	181(2)	66(1)	12(1)	34(2)	14	0(1)	44(1)
O(1)	3092(8)	2352(4)	163(7)	101(9)	42(8)	45(12)	27(2)	5(7)	43(6)
O(2)	4669(8)	1885(4)	1758(7)	93(8)	19(7)	36(12)	17(1)	3(7)	61(6)
N(1)	4109(9)	1980(4)	−1390(8)	69(9)	4(7)	41(13)	13(2)	2(7)	50(7)
N(2)	5375(9)	1348(5)	155(9)	59(9)	4(7)	57(14)	13(2)	5(7)	74(9)
C(1)	2413(12)	2621(6)	−708(11)	87(12)	8(10)	27(18)	15(2)	−6(9)	46(9)
C(2)	1524(13)	2943(7)	−527(13)	89(13)	45(11)	44(20)	28(3)	0(11)	73(11)
C(3)	740(14)	3219(7)	−1423(13)	94(14)	12(12)	44(21)	20(3)	−16(11)	84(11)
C(4)	837(13)	3215(6)	−2505(12)	70(13)	7(10)	17(20)	13(3)	4(9)	79(11)
C(5)	1709(12)	2933(6)	−2706(12)	69(12)	0(10)	22(20)	17(3)	6(9)	71(11)
C(6)	2495(11)	2621(5)	−1819(10)	57(10)	−16(8)	41(16)	12(2)	−3(8)	53(9)
C(7)	3366(12)	2300(6)	−2107(11)	85(12)	−28(10)	52(17)	15(2)	−7(9)	52(9)
C(8)	5023(12)	1692(6)	−1768(12)	76(12)	11(10)	80(17)	19(3)	2(10)	73(10)
C(9)	4697(14)	1545(8)	−3051(12)	100(14)	18(13)	72(19)	31(4)	−14(12)	64(10)
C(10)	3756(15)	1114(8)	−3404(13)	104(16)	25(14)	11(24)	32(4)	−43(12)	77(12)
C(11)	4083(14)	596(7)	−2674(13)	95(15)	10(12)	17(22)	19(3)	−30(10)	74(12)
C(12)	4337(13)	726(6)	−1403(13)	83(13)	−2(11)	54(21)	14(3)	−4(10)	93(13)
C(13)	5292(11)	1172(6)	−1019(11)	58(10)	9(9)	50(16)	16(2)	−10(3)	61(9)
C(14)	6133(12)	1121(6)	1018(11)	80(11)	7(11)	75(17)	16(2)	0(10)	73(10)
C(15)	6250(12)	1257(6)	2192(12)	63(12)	−14(10)	15(19)	15(2)	9(10)	73(11)
C(16)	7157(13)	983(7)	3074(13)	69(13)	6(11)	37(22)	19(3)	37(11)	105(13)
C(17)	7265(14)	1074(7)	4214(13)	80(14)	2(12)	−30(23)	22(3)	38(11)	78(13)
C(18)	6500(14)	1425(7)	4530(13)	99(15)	6(12)	34(24)	20(3)	24(11)	88(13)
C(19)	5661(13)	1702(6)	3720(11)	92(13)	6(10)	35(19)	14(2)	9(9)	53(10)
C(20)	5502(11)	1629(6)	2534(12)	53(11)	14(10)	40(18)	15(2)	16(10)	80(11)

(*b*) Hydrogen atom co-ordinates (×10^3); hydrogen atoms are numbered according to the atom to which they are bonded

	x	*y*	*z*		*x*	*y*	*z*
H(2)	147	298	36	1-H(11)	338	30	−295
H(3)	3	345	−127	2-H(11)	482	41	−283
H(4)	23	344	−321	1-H(12)	357	88	−124
H(5)	182	295	−355	2-H(12)	461	36	−88
H(7)	341	233	−299	H(13)	610	100	−103
H(8)	579	196	−153	H(14)	672	80	85
1-H(9)	440	193	−356	H(16)	773	70	282
2-H(9)	543	140	−326	H(17)	795	88	488
1-H(10)	299	129	−328	H(18)	662	148	545
2-H(10)	358	102	−430	H(19)	510	199	399

* In the form: $\exp -[(B_{11}h^2 + B_{12}hk + B_{13}hl + B_{22}k^2 + B_{23}kl + B_{33}l^2)]$.

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[1] Part II, N. Bresciani, M. Calligaris, G. Nardin, and L. Randaccio, *J.C.S. Dalton*, 1974, 498.

[2] C. Busetto, F. Cariati, A. Fusi, M. Gullotti, F. Morazzoni, A. Pasini, R. Ugo, and V. Valenti, *J.C.S. Dalton*, 1973, 754, and references therein.

[3] M. Calligaris, G. Nardin, and L. Randaccio, *J.C.S. Dalton*, 1973, 419.

are both axial whereas in the former only one is axial, the other being equatorial.

We report here the crystal and molecular structure of the *meso*-form of *NN'*-cyclohexylenebis(salicylideneiminato)cobalt(II),[4] [Co(*meso*-salschx)].

EXPERIMENTAL

Crystal Data.—$C_{20}H_{20}CoN_2O_2$, $M = 379{\cdot}3$, Monoclinic, $a = 12{\cdot}320(9)$, $b = 24{\cdot}200(10)$, $c = 12{\cdot}260(9)$ Å, $\beta = 108{\cdot}07(9)°$, $U = 3474{\cdot}9$ Å^3, D_m (by flotation) $= 1{\cdot}46$, $Z = 8$, $D_c = 1{\cdot}45$. Mo-K_α radiation, $\lambda = 0{\cdot}7107$ Å; μ(Mo-K_α) $= 10{\cdot}4$ cm^{-1}. Space group $P2_1/c$ (C^5_{2h}).

TABLE 2

Fractional co-ordinates ($\times 10^4$) and anisotropic temperature factors * ($\times 10^4$) of molecule (b), with estimated standard deviations in parentheses

(*a*) Non-hydrogen atoms

	x	y	z	B_{11}	B_{12}	B_{13}	B_{22}	B_{23}	B_{33}
Co	1556(2)	−246(1)	−28(2)	57(1)	−1(1)	24(2)	13(3)	0(1)	62(1)
O(1)	1484(9)	−991(4)	−390(8)	100(9)	−9(7)	37(14)	13(1)	−10(6)	79(8)
O(2)	1375(9)	−111(4)	−1569(8)	95(9)	4(8)	42(14)	21(2)	−26(7)	73(8)
N(1)	1643(9)	−365(5)	1513(9)	41(8)	−7(7)	40(14)	16(2)	−4(8)	77(9)
N(2)	1738(10)	509(5)	358(10)	62(9)	−10(8)	25(15)	14(2)	−5(8)	80(9)
C(1)	1618(12)	−1420(7)	322(13)	54(11)	0(10)	26(19)	20(3)	5(10)	80(12)
C(2)	1674(13)	−1960(6)	−127(13)	78(12)	7(11)	30(20)	17(3)	−15(11)	94(12)
C(3)	1831(15)	−2398(7)	578(17)	89(14)	7(12)	0(28)	14(3)	−1(13)	146(18)
C(4)	1909(15)	−2347(7)	1745(15)	107(16)	−10(13)	18(27)	19(3)	17(13)	118(17)
C(5)	1851(13)	−1843(6)	2202(14)	86(13)	5(11)	42(22)	11(2)	22(11)	112(13)
C(6)	1726(11)	−1368(6)	1498(13)	48(11)	−6(9)	10(20)	15(2)	1(10)	90(12)
C(7)	1686(12)	−842(7)	2022(13)	50(11)	−18(10)	43(19)	23(3)	3(11)	89(12)
C(8)	1591(13)	181(7)	2135(13)	71(12)	−5(11)	40(20)	20(3)	−21(11)	84(12)
C(9)	2070(13)	156(6)	3469(12)	72(12)	−3(10)	55(19)	17(3)	−21(10)	85(11)
C(10)	3365(14)	103(7)	3866(13)	96(14)	5(11)	7(22)	19(3)	−10(10)	65(12)
C(11)	3914(14)	552(7)	3330(15)	79(14)	−16(12)	27(24)	20(3)	−15(12)	109(15)
C(12)	3468(13)	545(7)	2021(14)	77(13)	−24(11)	33(22)	17(3)	−14(11)	106(13)
C(13)	2165(13)	603(6)	1593(13)	76(12)	−9(11)	43(20)	15(2)	−2(11)	90(12)
C(14)	1547(13)	926(6)	−323(12)	78(12)	4(10)	77(19)	16(3)	2(10)	91(12)
C(15)	1199(12)	859(6)	−1530(12)	71(12)	−10(10)	78(18)	14(2)	9(10)	91(11)
C(16)	852(13)	1359(7)	−2240(14)	90(13)	−9(11)	99(21)	19(3)	14(12)	119(13)
C(17)	506(14)	1330(7)	−3398(14)	96(14)	−5(12)	92(21)	23(3)	58(11)	123(13)
C(18)	500(14)	823(7)	−3957(14)	87(14)	−14(13)	45(22)	26(3)	22(12)	90(13)
C(19)	817(14)	353(7)	−3321(13)	104(14)	24(11)	79(21)	21(3)	26(10)	89(12)
C(20)	1147(13)	369(6)	−2114(12)	77(12)	1(10)	34(19)	15(3)	17(9)	73(11)

(*b*) Hydrogen atom co-ordinates ($\times 10^3$); hydrogen atoms are numbered according to the atom to which they are bonded

	x	y	z		x	y	z
H(2)	161	−202	−102	1-H(11)	374	95	364
H(3)	186	−281	22	2-H(11)	485	49	362
H(4)	204	−271	230	1-H(12)	386	88	167
H(5)	190	−181	311	2-H(12)	371	15	170
H(7)	172	−84	294	H(13)	192	102	177
H(8)	69	30	192	H(14)	168	133	7
1-H(9)	183	53	384	H(16)	87	176	−180
2-H(9)	169	−19	377	H(17)	23	171	−390
1-H(10)	368	13	480	H(18)	23	81	−491
2-H(10)	359	−30	361	H(19)	81	−5	−375

* See footnote to Table 1.

Cell parameters were determined from Weissenberg photographs taken with Co-K_α radiation and refined with an on-line automated Siemens diffractometer.

Intensity Measurements.—Three-dimensional intensity data were collected on a Siemens diffractometer by the θ—2θ scan technique with Mo-K_α radiation for a maximum 2θ angle of 60°. A crystal of mean dimensions 0·25 mm was used. All reflections having $I_0 < 3\sigma(I_0)$ were rejected, the remainder being corrected for Lorentz-polarization effects. A total of 1979 independent reflections was used in the subsequent calculations. No correction for absorption (μR *ca.* 0·13) or anomalous dispersion of the cobalt atom was applied.

Structure Determination and Refinement.—The structure was solved by conventional Patterson and Fourier methods. Least-squares isotropic refinement reduced R to 0·082. After anisotropic refinement, a three-dimensional difference Fourier synthesis was calculated to locate the hydrogen atoms. Calculated positions (C–H = 1·08 Å) of these all occurred in regions of positive electron density. The final anisotropic block-diagonal matrix least-squares refinement gave R 0·046. The co-ordinates and the temperature factors of the hydrogen atoms (set at B 5·0 Å^2) were not allowed to vary. The final weighting scheme was $w = 1/(A + B|F_o| + C|F_o|^2)$, where $A = 90{\cdot}0$, $B = 1{\cdot}0$, and $C = 0{\cdot}0012$ were chosen to maintain $w(|F_o| - |F_c|)^2$ essentially constant over all ranges of $|F_o|$ and $(\sin\theta/\lambda)$. Final atomic parameters are listed in Tables 1 and 2, together with their estimated standard deviations. The numbering scheme for the atoms is shown in Figure 1. Observed and calculated structure factors are listed in Supplementary

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[4] N. Bresciani, part of degree thesis, University of Trieste, Italy, 1973.

Publication No. SUP 21013 (5 pp., 1 microfiche).* Atomic scattering factors were calculated according to ref. 5.

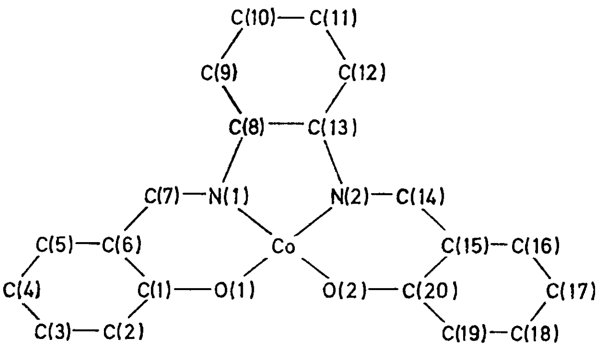

FIGURE 1 Numbering scheme of the atoms for both crystallographically independent molecules

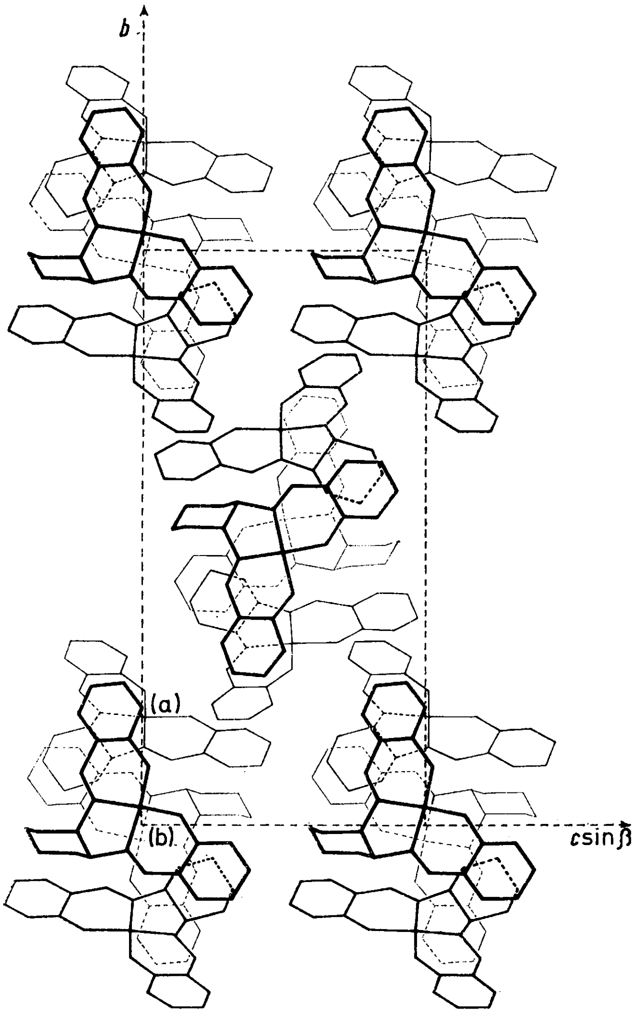

FIGURE 2 A projection of the structure viewed along the *a* axis

Calculations.—All calculations were carried out on a CDC 6200 computer with programs described in refs. 6 and 7 of Part II.[1]

RESULTS AND DISCUSSION

The crystal is built up of discrete molecules of Co(*meso*-salchx) held together by van der Waals forces (Figure 2). The intermolecular contacts are quite normal.

The two crystallographically independent molecules are very similar, the cobalt atom having a square-planar stereochemistry slightly tetrahedrally distorted. The distortion is more pronounced in molecule (a) than in molecule (b). Figure 3 shows a side-view of the two molecules, together with the deviations of individual atoms from the plane passing through the cobalt atom and the four ligand donors. Figure 3 compares analogous views of Co(+)-(salbn),† Co(*meso*-salbn),† and Co(salen). It is quite evident that the introduction of bulky groups in the ethylene bridge causes a slight but significant tetrahedral distortion of the co-ordination polyhedron.

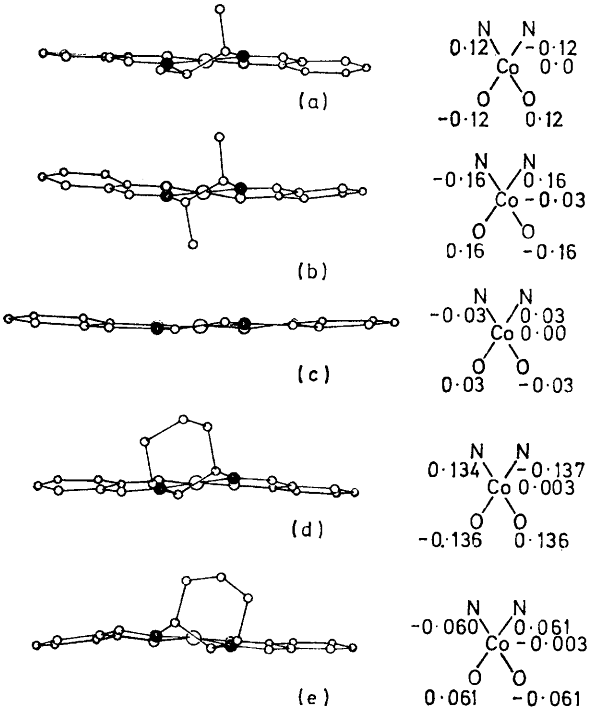

FIGURE 3 A side-view of Co(salen) and of its ethylene-bridge-substituted derivatives. Displacements of the Co, N, and O atoms from the best molecular plane of the donor atoms are shown on the right-hand side. (a) Co(*meso*-salbn), (b) Co(+)-(salbn), (c) Co(salen), (d) Co(*meso*-salchx), molecule (a), and (e) Co(*meso*-salchx), molecule (b)

The bond lengths and angles (Tables 3 and 4) are not different in the two crystallographically independent molecules and are in good agreement with those reported for analogous compounds[6] within the accuracy of the present determination.

Since we are dealing with the *meso*-form, one *N*-bonded

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1973, Index issue (items less than 10 pp. are sent as full-size copies).

† Co(salbn) = *NN'*-Butylenebis(salicylideneiminato)cobalt (II).

[5] F. H. Moore, *Acta Cryst.*, 1963, **16**, 1169.

[6] M. Calligaris, G. Nardin, and L. Randaccio, *Co-ordination Chem. Rev.*, 1972, **7**, 385.

CH_2-group of the cyclohexylene ring is pseudo-axial, the other being equatorial. In both molecules the angle N(1)–C(8)–C(9) corresponding to the equatorial CH_2 group is significantly larger than that corresponding to the axial CH_2 group. The values 116(1)° and 115(1)° for the two crystallographically independent molecules are similar to those found in the *meso*-form of Co(salbn) [115·4(4)°] and *ca.* 5° larger than those found for axial substituents or hydrogen atoms. This indicates that bulky equatorial groups cause distortion of the N–C–C bond angle to alleviate van der Waals repulsion with the adjacent CH group. However the bis-equatorial conformation, although less stable,[1] must be assumed in the optically active form of Co-(salchx) because of the closing of the cyclohexylene ring. This hypothesis is in agreement with the complete inversion of the Cotton effects in the region 18—30 kK for Co(−)-(salchx) with respect to those of Co(−)-(salbn).[2]

TABLE 3

Bond lengths (Å), with estimated standard deviations in parentheses, for the two molecules

	(a)	(b)
Co–O(1)	1·858(10)	1·852(10)
Co–O(2)	1·845(9)	1·861(10)
Co–N(1)	1·876(10)	1·881(12)
Co–N(2)	1·872(12)	1·883(12)
O(1)–C(1)	1·308(15)	1·333(17)
O(2)–C(20)	1·318(15)	1·326(17)
N(1)–C(7)	1·308(16)	1·305(21)
N(1)–C(8)	1·514(20)	1·537(21)
N(2)–C(13)	1·474(18)	1·458(18)
N(2)–C(14)	1·296(16)	1·284(18)
C(1)–C(2)	1·417(23)	1·428(21)
C(1)–C(6)	1·397(20)	1·412(22)
C(2)–C(3)	1·388(20)	1·343(23)
C(3)–C(4)	1·368(23)	1·409(28)
C(4)–C(5)	1·358(23)	1·353(23)
C(5)–C(6)	1·427(17)	1·417(21)
C(6)–C(7)	1·454(21)	1·434(23)
C(8)–C(9)	1·540(20)	1·558(19)
C(8)–C(13)	1·532(20)	1·509(24)
C(9)–C(10)	1·519(25)	1·522(22)
C(10)–C(11)	1·520(24)	1·532(25)
C(11)–C(12)	1·524(22)	1·527(22)
C(12)–C(13)	1·558(20)	1·533(21)
C(14)–C(15)	1·439(20)	1·416(20)
C(15)–C(16)	1·452(19)	1·474(22)
C(15)–C(20)	1·441(22)	1·376(21)
C(16)–C(17)	1·380(23)	1·352(23)
C(17)–C(18)	1·409(26)	1·404(24)
C(18)–C(19)	1·366(20)	1·366(23)
C(19)–C(20)	1·417(20)	1·408(21)

The two CH_2 groups are in a nearly gauche conformation in both molecules, the torsion angles being 51·0 and 51·1°. The nitrogen atoms are also in a nearly gauche conformation with torsion angles of 44·3 and 43·7°. The cyclohexylene ring conformation is the same in the two molecules (a) and (b) and very close to the most stable chair conformation of cyclohexane.

TABLE 4

Bond angles (°), with estimated standard deviations in parentheses, for the two molecules

	(a)	(b)
Co–O(1)–C(1)	128·0(10)	127·9(9)
Co–O(2)–C(20)	130·0(10)	127·2(9)
Co–N(1)–C(7)	126·6(10)	126·6(11)
Co–N(1)–C(8)	113·0(7)	111·6(9)
Co–N(2)–C(13)	112·6(8)	112·9(9)
Co–N(2)–C(14)	128·1(10)	128·0(9)
O(1)–Co–O(2)	87·2(4)	86·9(4)
O(1)–Co–N(1)	94·2(4)	94·3(5)
O(1)–Co–N(2)	171·4(5)	176·1(5)
O(1)–C(1)–C(2)	118·4(13)	118·1(13)
O(1)–C(1)–C(6)	125·1(14)	123·5(13)
O(2)–Co–N(1)	171·8(5)	176·3(5)
O(2)–Co–N(2)	93·8(5)	93·0(5)
O(2)–C(20)–C(15)	120·6(13)	121·6(13)
O(2)–C(20)–C(19)	120·7(13)	116·9(13)
N(1)–Co–N(2)	85·9(5)	86·0(5)
N(1)–C(7)–C(6)	124·6(13)	124·9(15)
N(1)–C(8)–C(9)	115·8(11)	115·3(12)
N(1)–C(8)–C(13)	103·7(12)	105·4(13)
N(2)–C(13)–C(8)	106·5(11)	106·5(11)
N(2)–C(13)–C(12)	108·2(12)	110·1(14)
N(2)–C(14)–C(15)	122·9(14)	121·6(13)
C(1)–C(2)–C(3)	121·5(15)	119·2(15)
C(1)–C(6)–C(5)	120·4(13)	120·5(14)
C(1)–C(6)–C(7)	121·2(11)	122·1(14)
C(2)–C(1)–C(6)	116·5(12)	118·3(13)
C(2)–C(3)–C(4)	121·0(16)	122·3(16)
C(3)–C(4)–C(5)	119·4(13)	120·2(16)
C(4)–C(5)–C(6)	121·0(14)	119·2(16)
C(5)–C(6)–C(7)	118·4(12)	117·4(14)
C(7)–N(1)–C(8)	119·9(11)	121·7(12)
C(8)–C(13)–C(12)	112·7(10)	111·8(12)
C(8)–C(9)–C(10)	112·6(14)	110·9(13)
C(9)–C(8)–C(13)	111·2(12)	114·3(12)
C(9)–C(10)–C(11)	111·0(12)	111·2(12)
C(10)–C(11)–C(12)	111·4(13)	112·3(12)
C(11)–C(12)–C(13)	110·4(14)	110·9(15)
C(13)–N(2)–C(14)	119·3(12)	119·1(12)
C(14)–C(15)–C(16)	117·1(14)	117·5(13)
C(14)–C(15)–C(20)	124·0(12)	126·3(13)
C(15)–C(16)–C(17)	119·4(15)	121·1(15)
C(15)–C(20)–C(19)	118·6(12)	121·5(14)
C(16)–C(15)–C(20)	118·9(13)	116·2(13)
C(16)–C(17)–C(18)	120·8(14)	120·7(15)
C(17)–C(18)–C(19)	121·0(15)	119·4(14)
C(18)–C(19)–C(20)	121·1(15)	121·0(15)

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