

The X-Ray Structure Analysis of Anhydrous Heptamethyl Dicyanocobyrinate (Cobester)

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The X-ray structure analysis of the anhydrous form of heptamethyl dicyanocobyrinate (cobester) was carried out as part of a collaborative investigation with Battersby and co-workers and compared with that of the hydrated form.

The anhydrous form crystallises in the orthorhombic space group $P2_12_12_1$ with cell dimensions $a = 18.931(6)$, $b = 18.960(5)$, $c = 15.643(6)$ Å and one molecule in the asymmetric unit. The structure was solved by a combination of Patterson and direct methods and refined to $R = 0.132$. Several of the side-chains were disordered. The paper describes the structural details and gives a comparison with other relevant structures retrieved from the Structural Database. The best mean values for the corrin nucleus are given and a summary table of the conformations taken up by the pyrrole rings in various cobalt-corrin systems is presented.

HEPTAMETHYL DICYANOCOBYRINATE (cobester) (1) is the standard corrin for biosynthetic studies on vitamin B₁₂. The preceding paper describes the detailed study of its ¹H and ¹³C n.m.r. spectra.¹ The X-ray analysis of a hydrated form of cobester was reported by Fischli and Daly,² but we thought it would be of interest to examine crystals of the high melting point form provided originally by Professor R. B. Woodward. Cell-dimensions indicated that this was a different form of cobester and a complete structure analysis was carried out. This paper describes the results of the analysis. It also presents a detailed comparison of the geometry of the various structures containing the corrin-cobalt system reported in the literature (Figure 1). The Cambridge Structural Database and associated programs,³ particularly GEOM-78, were used to derive the tables presented in this paper. They give an overview of the current state of knowledge of the solid-state structure of these compounds.

EXPERIMENTAL

Crystal Data.—C₃₄H₇₃CoN₆O₁₄, $M = 1\ 089.3$, orthorhombic, $a = 18.931(6)$, $b = 18.960(5)$, $c = 15.643(6)$ Å, $U = 5\ 615(3)$ Å³, $D_x = 1.29$ g cm⁻³, $Z = 4$. Space group $P2_12_12_1$ from absences. Mo- K_α radiation $\lambda = 0.7107$ Å, $\mu(\text{Mo-}K_\alpha) = 3.32$ cm⁻¹. Dark red prisms were obtained from methyl acetate-hexane.

Cell dimensions were determined by least-squares fit of 15 reflexions located on a Syntex P2₁ diffractometer. The intensities of 4 128 independent reflexions were measured in the θ — 2θ scan mode. They were corrected for Lorentz and polarisation factors but not for absorption. A total of 2 253 structure factors having $F > 3\sigma(F)$ were used for the analysis and these are deposited as a Supplementary Publication (SUP. No. 23359 14 pages).[‡]

The position of the Co atom was readily located from a Patterson map at 0.43, 0.50, 0.00. Since this was a special position the Co atom was moved to 0.431, 0.495, 0.014 from which input phases calculated for the tangent expansion method.⁴ Two of the five-membered rings were recognised in the first E map and after four cycles all non-hydrogen atoms of the corrin rings, the methyl groups directly at-

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‡ For details of the Supplementary publications scheme, see Notice to Authors No. 7, *J. Chem. Soc., Perkin Trans. 1*, 1981, Index issue.

tached to the ring, two nitrile groups and two each of the CH₂CO₂Me and CH₂CH₂CO₂Me groups were located. The three CH₂CH₂CO₂Me groups at positions 3, 8, and 13 were suspected to be disordered. The R factor was 0.36.

The atomic positions for the disordered groups were located by alternative least squares and difference electron density syntheses. Site occupation factors were added as additional variables in the least-squares calculations. Hydrogen atoms in the ordered parts of the molecule were included at calculated positions and the C-H geometry was constrained in subsequent refinement with C-C(sp³)-H = 120° H-C(sp³)-H = 109.5° and C-H = 1.08 Å. The temperature factors for the H atoms were constrained to those of the attached carbon atoms. Refinement of atomic positions, anisotropic temperature factors of the Co atom, and isotropic temperature factors of the remaining atoms converged to a final $R = 0.132$. Final atomic co-ordinates are given in Tables 1, 2, and 3. Disordered sites are marked by suffixes A and B. The derived interatomic distances and angles are listed in Tables 4 and 5.

RESULTS AND DISCUSSION

Figure 2 is a stereoview of the molecule showing the substituents at C(3), C(8), C(13), and C(17) at the most highly occupied sites. At C(3) freedom of rotation about the C(28)—C(29) bond results in two sites being occupied: the torsion angle C(27)—C(28)—C(29)—O(3) is 31.7° in position A(65%) and 81.4° in B(35%). The substituent at C(8) is equally distributed about two sites with the main difference around the C(37)—C(38) bond where the C(36)—C(37)—C(38)—O(7) angles are 121.4° and -10° respectively. The disorder of the substituent at C(13) is of similar occupancy as that at C(3) with the main difference in the rotation about the C(13)—C(42) bond.

Details of the molecular conformation will be discussed in comparison with the hydrated form of cobester, reported by Fischli and Daly² and other cobalt-containing corrin derivatives, whose structures were determined by X-ray analysis. Atomic co-ordinates for 10 such compounds were retrieved from the 1982 version of the Cambridge Crystallographic Database. Corrole (triphenylphosphine)cobalt(III)⁵ was excluded from the comparison since it has no substituents on the corrole ring. Vitamin B₁₂⁶ and vitamin B₁₂ hexacarboxylic

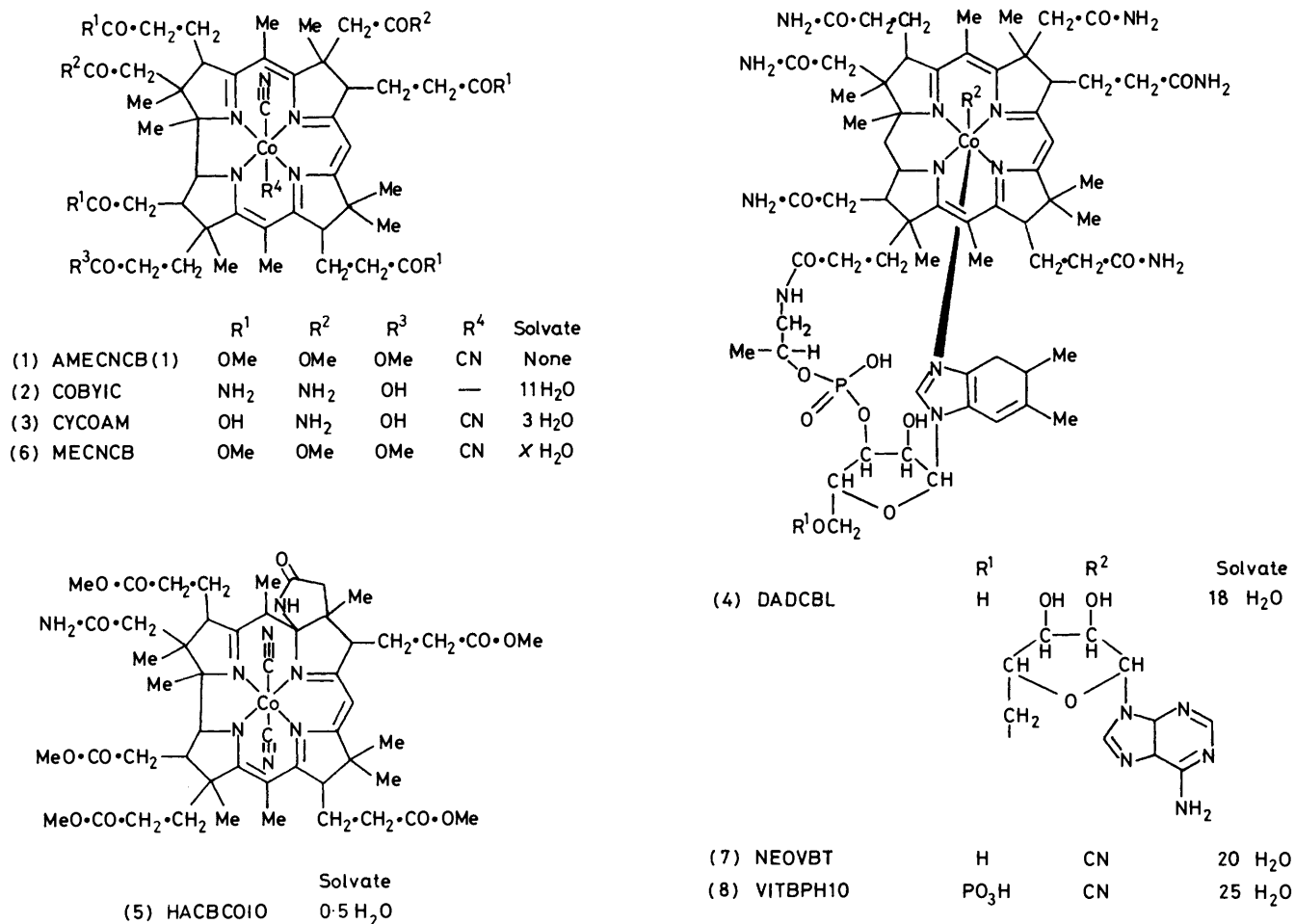


FIGURE 1 Chemical formulae of compounds discussed

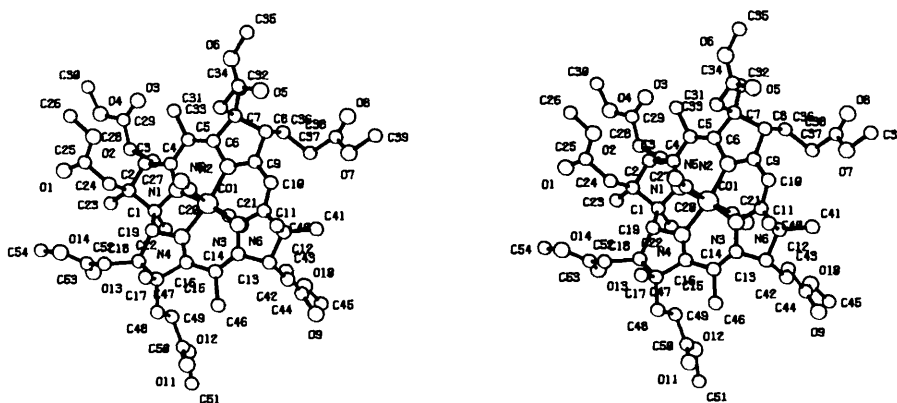


FIGURE 2 Stereoview of cobester drawn with program PLUTO (W. D. S. Motherwell, Cambridge University)

TABLE 1

Atom co-ordinates ($\times 10^4$) and isotropic temperature factors ($\text{\AA}^2 \times 10^3$)

| | x/a | y/b | z/c | U |
|--------|-----------|------------|-----------|---------|
| Co(1) | 4 290(2) | -56(2) | 4 864(2) | |
| O(1) | 6 985(15) | 1 908(15) | 3 027(18) | 103(10) |
| O(2) | 7 234(15) | 897(15) | 3 777(19) | 108(10) |
| O(3A) | 7 009(25) | -800(25) | 1 665(31) | 140(15) |
| O(3B) | 6 636(50) | -912(52) | 1 061(66) | 146(35) |
| O(4A) | 7 294(29) | 35(37) | 794(36) | 140(21) |
| O(4B) | 7 332(46) | 43(53) | 1 223(55) | 66(28) |
| O(5) | 5 818(15) | -2 430(15) | 7 006(18) | 106(9) |
| O(6) | 6 751(19) | -2 521(18) | 6 162(23) | 133(13) |
| O(7A) | 3 213(41) | -3 237(38) | 6 289(47) | 131(26) |
| O(7B) | 3 830(30) | -3 423(30) | 5 971(37) | 95(18) |
| O(8A) | 3 786(31) | -3 941(32) | 5 439(39) | 125(20) |
| O(8B) | 2 779(30) | -2 989(31) | 5 491(37) | 149(19) |
| O(9A) | 566(52) | -324(43) | 5 108(74) | 168(43) |
| O(9B) | 518(84) | -592(76) | 5 190(*) | 90(57) |
| O(10A) | 1 056(21) | -706(21) | 3 977(26) | 89(13) |
| O(10B) | 384(52) | 492(53) | 4 298(65) | 219(37) |
| O(11) | 1 596(15) | 2 809(15) | 4 634(18) | 98(9) |
| O(12) | 1 578(16) | 2 461(16) | 3 271(19) | 107(10) |
| O(13) | 4 566(11) | 2 935(12) | 2 800(14) | 64(7) |
| O(14) | 5 541(11) | 3 299(11) | 3 411(13) | 56(6) |
| N(1) | 4 916(10) | 191(10) | 3 979(12) | 24(5) |
| N(2) | 4 667(10) | -997(11) | 4 925(14) | 34(5) |
| N(3) | 3 563(11) | -177(12) | 5 700(14) | 38(6) |
| N(4) | 4 072(11) | 932(11) | 4 780(14) | 33(6) |
| N(5) | 5 308(15) | 284(14) | 6 339(18) | 64(9) |
| N(6) | 3 188(14) | -517(14) | 3 572(18) | 54(8) |
| C(1) | 4 826(15) | 888(15) | 3 562(18) | 33(8) |
| C(2) | 5 577(13) | 1 008(13) | 3 160(16) | 25(7) |
| C(3) | 5 815(13) | 255(12) | 2 970(15) | 23(6) |
| C(4) | 5 473(13) | -145(15) | 3 665(17) | 40(7) |
| C(5) | 5 688(15) | -817(13) | 3 984(16) | 31(6) |
| C(6) | 5 326(13) | -1 189(13) | 4 547(15) | 23(6) |
| C(7) | 5 512(15) | -1 922(16) | 4 965(21) | 65(9) |
| C(8) | 4 771(14) | -2 196(14) | 5 283(18) | 33(7) |
| C(9) | 4 394(14) | -1 500(14) | 5 413(16) | 32(7) |
| C(10) | 3 846(15) | -1 392(17) | 5 972(19) | 50(8) |
| C(11) | 3 456(13) | -802(13) | 6 117(16) | 22(6) |
| C(12) | 2 867(14) | -749(14) | 6 763(17) | 29(7) |
| C(13) | 2 489(17) | -73(22) | 6 443(21) | 59(9) |
| C(14) | 3 040(13) | 294(13) | 5 902(16) | 25(7) |
| C(15) | 3 044(12) | 951(13) | 5 659(15) | 21(6) |
| C(16) | 3 584(13) | 1 285(13) | 5 126(17) | 29(6) |
| C(17) | 3 725(12) | 2 072(12) | 5 012(17) | 26(6) |
| C(18) | 4 239(14) | 2 056(13) | 4 279(17) | 36(7) |
| C(19) | 4 606(13) | 1 335(13) | 4 380(15) | 21(6) |
| C(20) | 4 955(15) | 178(16) | 5 765(19) | 50(9) |
| C(21) | 3 615(14) | -374(14) | 4 056(16) | 25(7) |
| C(22) | 4 222(14) | 902(14) | 2 940(16) | 35(7) |
| C(23) | 5 546(15) | 1 475(16) | 2 382(18) | 56(9) |
| C(24) | 6 086(15) | 1 341(16) | 3 772(19) | 46(8) |
| C(25) | 6 852(20) | 1 427(21) | 3 432(26) | 67(12) |
| C(26) | 7 954(21) | 962(24) | 3 375(28) | 175(16) |
| C(27) | 5 639(17) | -65(19) | 2 126(17) | 63(8) |
| C(28) | 6 161(18) | 95(21) | 1 320(23) | 79(11) |
| C(29) | 6 844(19) | -251(19) | 1 361(24) | 66(11) |
| C(30A) | 8 016(41) | -169(44) | 707(49) | 109(27) |
| C(30B) | 7 993(76) | -390(78) | 1 103(96) | 85(49) |
| C(31) | 6 425(13) | -1 050(14) | 3 675(17) | 35(7) |
| C(32) | 5 887(17) | -2 517(17) | 4 453(21) | 62(10) |
| C(33) | 5 976(17) | -1 656(18) | 5 716(21) | 54(10) |
| C(34) | 6 153(19) | -2 213(20) | 6 313(24) | 71(11) |
| C(35) | 7 038(22) | -3 107(22) | 6 727(26) | 128(15) |
| C(36) | 4 390(15) | -2 632(16) | 4 594(18) | 48(8) |
| C(37) | 3 594(19) | -2 783(19) | 4 761(25) | 75(11) |
| C(38A) | 3 586(36) | -3 393(37) | 5 465(43) | 53(19) |
| C(38B) | 3 393(57) | -3 114(57) | 5 449(72) | 94(42) |
| C(39A) | 3 222(47) | -3 866(47) | 6 935(60) | 132(30) |
| C(39B) | 3 414(51) | -4 194(53) | 6 162(67) | 136(35) |
| C(40) | 3 227(19) | -589(21) | 7 628(23) | 81(12) |
| C(41) | 2 423(17) | -1 379(17) | 6 827(21) | 81(10) |
| C(42) | 1 808(25) | -215(24) | 5 963(30) | 109(16) |
| C(43A) | 1 829(23) | -443(23) | 5 073(30) | 45(12) |
| C(43B) | 1 413(66) | 207(65) | 5 305(82) | 102(43) |
| C(44A) | 1 080(33) | -449(34) | 4 613(42) | 84(20) |

TABLE 1 (continued)

| | x/a | y/b | z/c | U |
|--------|-----------|-----------|-----------|---------|
| C(44B) | 773(56) | 26(61) | 4 753(63) | 55(25) |
| C(45A) | 382(38) | -808(39) | 3 593(49) | 110(26) |
| C(45B) | -425(33) | 783(34) | 4 457(41) | 1(16) |
| C(46) | 2 449(15) | 1 463(16) | 6 063(19) | 54(9) |
| C(47) | 4 056(14) | 2 336(15) | 5 843(17) | 40(7) |
| C(48) | 3 074(15) | 2 550(16) | 4 816(21) | 50(9) |
| C(49) | 2 639(14) | 2 274(15) | 4 045(18) | 38(8) |
| C(50) | 1 893(15) | 2 552(15) | 4 007(19) | 40(8) |
| C(51A) | 896(25) | 2 890(28) | 3 173(31) | 27(13) |
| C(51B) | 718(34) | 2 474(32) | 3 365(37) | 45(15) |
| C(52) | 4 733(15) | 2 735(15) | 4 287(18) | 36(8) |
| C(53) | 4 912(14) | 2 976(15) | 3 414(18) | 35(7) |
| C(54) | 5 795(17) | 3 565(17) | 2 581(19) | 66(9) |

acid degradation product⁷ although of great historic importance were also omitted from the numerical tables in view of the limited accuracy which could be attained at the time these structures were analysed. The remaining seven compounds which have been used in this comparative study are listed, together with their 'reference codes' in Table 6. They will be referred to by these codes and the present structure by the acronym AMECNCB. Table 6 also gives R factors and space groups for these compounds. Formulae are given in Figure 2.

TABLE 2

Anisotropic temperature factors ($\text{\AA}^2 \times 10^3$)

| | U_{11} | U_{22} | U_{33} | U_{23} | U_{13} | U_{12} |
|-------|----------|----------|----------|----------|----------|----------|
| Co(1) | 24(1) | 26(2) | 25(2) | -2(2) | -5(2) | -3(2) |

The temperature factor exponent takes the form: $-2\pi^2 U_{11}h^2a^{*2} + \dots + 2U_{12}hka^*b^*$

Co-ordination around the Co Atom.—The co-ordination around the central Co atom is a distorted octahedron with approximate local symmetry $mm2$. The two-fold axis passes through C(10) and Co. Table 7 compares the various geometric parameters found in the present study with three compounds having the same co-ordination groups. One of these HACBCO10 has two molecules in the asymmetric unit for which individual values are given. The corresponding bond lengths in all these compounds are equal within experimental error. In MECNCB one of the $C\equiv N$ groups forms a hydrogen bond with a water molecule but is not affected significantly. The N-Co-N bond angles are also consistent within standard deviation. The angle opposite the direct pyrrole junction N(1)-Co-N(4) is significantly smaller (82.3° av.) and the angle N(2)-Co-N(3) is larger (96.7° av.) than 90° . The remaining two angles are equal within experimental error.

We have attempted to analyse the linearity of the $N\equiv C-Co-C\equiv N$ group separately. For the compounds listed in Table 7, an orthogonal molecular co-ordinate system was constructed with the X axis passing through the Co atom and C(10) and the Y axis perpendicular to this vector and in the plane of C(5), Co, C(10). Co-ordinates of C(20), N(5), C(21), and N(6) were calculated with reference to this axial system. As can be seen from Table 7b in all compounds one of the $N\equiv C-Co$ linkage is consistently bent away from the bond linking two pyrrole groups directly, while the other linkage can take

up a variety of orientations. The Co atom is displaced by 0.1 Å from the mid-point of the four pyrrole N atoms.

The deviation of the N atoms from the least-squares plane through N(1), N(2), N(3) and N(4), shows that the

TABLE 3

Hydrogen atom co-ordinates ($\times 10^4$) and isotropic temperature factors ($\text{Å}^2 \times 10^3$)

| | <i>x/a</i> | <i>y/b</i> | <i>z/c</i> | <i>U</i> |
|--------|------------|------------|------------|----------|
| H(3) | 6 385(13) | 242(12) | 2 931(15) | 47(6) |
| H(8) | 4 782(14) | -2 534(14) | 5 840(18) | 48(7) |
| H(10) | 3 701(15) | -1 848(17) | 6 351(19) | 55(8) |
| H(131) | 2 299(17) | 246(22) | 6 969(21) | 46(9) |
| H(18) | 3 994(14) | 2 089(13) | 3 657(17) | 52(7) |
| H(19) | 5 100(13) | 1 441(13) | 4 701(15) | 50(6) |
| H(221) | 4 187(14) | 1 424(14) | 2 660(16) | 49(7) |
| H(222) | 4 315(14) | 516(14) | 2 443(16) | 49(7) |
| H(223) | 3 733(14) | 780(14) | 3 265(16) | 49(7) |
| H(231) | 5 185(15) | 1 235(16) | 1 933(18) | 58(9) |
| H(232) | 5 355(15) | 1 995(16) | 2 555(18) | 58(9) |
| H(233) | 6 062(15) | 1 522(16) | 2 093(18) | 58(9) |
| H(241) | 6 102(15) | 1 011(16) | 4 335(19) | 52(8) |
| H(242) | 5 889(15) | 1 860(16) | 3 940(19) | 52(8) |
| H(261) | 8 294(21) | 551(24) | 3 621(28) | 115(16) |
| H(262) | 7 899(21) | 902(24) | 2 692(28) | 115(16) |
| H(263) | 8 180(21) | 1 475(24) | 3 515(28) | 115(16) |
| H(271) | 5 107(17) | 99(19) | 1 972(17) | 54(8) |
| H(272) | 5 655(17) | -634(19) | 2 200(17) | 54(8) |
| H(281) | 5 895(18) | -44(21) | 732(23) | 54(11) |
| H(282) | 6 269(18) | 657(21) | 1 324(23) | 54(11) |
| H(311) | 6 545(13) | -1 564(14) | 3 943(17) | 51(7) |
| H(312) | 6 420(13) | -1 086(14) | 2 986(17) | 51(7) |
| H(313) | 6 821(13) | -672(14) | 3 874(17) | 51(7) |
| H(321) | 6 390(17) | -2 319(17) | 4 232(21) | 52(10) |
| H(322) | 5 972(17) | -2 973(17) | 4 857(21) | 52(10) |
| H(323) | 5 568(17) | -2 667(17) | 3 910(21) | 52(10) |
| H(331) | 6 460(17) | -1 437(18) | 5 461(21) | 46(10) |
| H(332) | 5 692(17) | -1 249(18) | 6 058(21) | 46(10) |
| H(351) | 7 547(22) | -3 269(22) | 6 486(26) | 77(15) |
| H(352) | 7 094(22) | -2 917(22) | 7 374(26) | 77(15) |
| H(353) | 6 681(22) | -3 554(22) | 6 718(26) | 77(15) |
| H(361) | 4 660(15) | -3 134(16) | 4 532(18) | 54(8) |
| H(362) | 4 440(15) | -2 337(16) | 4 006(18) | 54(8) |
| H(401) | 2 830(19) | -537(21) | 8 120(23) | 51(12) |
| H(402) | 3 589(19) | -1 009(21) | 7 798(23) | 51(12) |
| H(403) | 3 513(19) | -97(21) | 7 566(23) | 51(12) |
| H(411) | 2 011(17) | -1 306(17) | 7 297(21) | 68(10) |
| H(412) | 2 188(17) | -1 489(17) | 6 212(21) | 68(10) |
| H(413) | 2 755(17) | -1 818(17) | 7 014(21) | 68(10) |
| H(461) | 2 501(15) | 1 990(16) | 5 802(19) | 53(9) |
| H(462) | 1 929(15) | 1 259(16) | 5 922(19) | 53(9) |
| H(463) | 2 524(15) | 1 481(16) | 6 747(19) | 53(9) |
| H(471) | 4 169(14) | 2 895(15) | 5 792(17) | 52(7) |
| H(472) | 3 698(14) | 2 247(15) | 6 370(17) | 52(7) |
| H(473) | 4 540(14) | 2 048(15) | 5 954(17) | 52(7) |
| H(481) | 2 734(15) | 2 566(16) | 5 370(21) | 46(9) |
| H(482) | 3 253(15) | 3 079(16) | 4 668(21) | 46(9) |
| H(491) | 2 909(14) | 2 419(15) | 3 463(18) | 49(8) |
| H(492) | 2 616(14) | 1 704(15) | 4 096(18) | 49(8) |
| H(521) | 4 474(15) | 3 162(15) | 4 623(18) | 45(8) |
| H(522) | 5 213(15) | 2 593(15) | 4 618(18) | 45(8) |
| H(541) | 6 304(17) | 3 812(17) | 2 670(19) | 59(9) |
| H(542) | 5 844(17) | 3 132(17) | 2 133(19) | 59(9) |
| H(543) | 5 425(17) | 3 950(17) | 2 336(19) | 59(9) |

co-ordination around the Co atom is markedly non-planar (Table 7a) with N(2) and N(4) above and N(1) and N(3) below the mean plane.

The consistency of these observations in the four compounds compared in Table 7 suggests that the Co-corrin system is not affected significantly by differences in the substituent groups, crystal-packing effects, or hydrogen-bonding schemes.

The Corrin Ring System.—A comparison of the geo-

metry of the corrin ring system for compounds which are expected to have the same conjugation from C(4) through C(16) is given in Table 8. This lists the bond lengths and the deviations of atoms from the mean plane of the whole system.

Two compounds NEOVBT and VITBPH10 have bond lengths which deviate significantly from normally expected values. They are both highly hydrated and it is

TABLE 4

Bond lengths (Å)

| | | | |
|---------------|-----------|---------------|-----------|
| N(1)-Co(1) | 1.883(21) | N(2)-Co(1) | 1.916(22) |
| N(3)-Co(1) | 1.924(23) | N(4)-Co(1) | 1.913(23) |
| C(20)-Co(1) | 1.940(32) | C(21)-Co(1) | 1.895(28) |
| C(25)-O(1) | 1.135(50) | C(25)-O(2) | 1.346(50) |
| C(26)-O(2) | 1.505(52) | C(29)-O(3A) | 1.182(61) |
| C(29)-O(3B) | 1.389(*) | C(29)-O(4A) | 1.344(70) |
| C(30A)-O(4A) | 1.426(97) | C(29)-O(4B) | 1.101(98) |
| C(30B)-O(4B) | 1.506(*) | C(34)-O(5) | 1.321(48) |
| C(34)-O(6) | 1.294(52) | C(35)-O(6) | 1.515(55) |
| C(38A)-O(7A) | 1.499(*) | C(39A)-O(7A) | 1.559(*) |
| C(38B)-O(7B) | 1.300(*) | C(39B)-O(7B) | 1.680(*) |
| C(38A)-O(8A) | 1.101(93) | C(38B)-O(8B) | 1.188(*) |
| C(44A)-O(9A) | 1.266(*) | C(44B)-O(9B) | 1.436(*) |
| C(44A)-O(10A) | 1.107(78) | C(45A)-O(10A) | 1.423(84) |
| C(44B)-O(10B) | 1.350(*) | C(45B)-O(10B) | 1.646(*) |
| C(50)-O(11) | 1.231(41) | C(50)-O(12) | 1.307(43) |
| C(51A)-O(12) | 1.532(59) | C(51B)-O(12) | 1.635(72) |
| C(53)-O(13) | 1.164(36) | C(53)-O(14) | 1.339(35) |
| C(54)-O(14) | 1.471(38) | C(1)-N(1) | 1.476(35) |
| C(4)-N(1) | 1.324(33) | C(6)-N(2) | 1.429(32) |
| C(9)-N(2) | 1.322(34) | C(11)-N(3) | 1.361(34) |
| C(14)-N(3) | 1.354(34) | C(16)-N(4) | 1.261(33) |
| C(19)-N(4) | 1.410(33) | C(20)-N(5) | 1.138(41) |
| C(21)-N(6) | 1.140(38) | C(2)-C(1) | 1.571(39) |
| C(19)-C(1) | 1.588(39) | C(22)-C(1) | 1.502(41) |
| C(3)-C(2) | 1.519(35) | C(23)-C(2) | 1.503(40) |
| C(24)-C(2) | 1.497(39) | C(27)-C(3) | 1.490(38) |
| C(5)-C(4) | 1.422(38) | C(6)-C(5) | 1.318(36) |
| C(31)-C(5) | 1.540(40) | C(7)-C(6) | 1.568(41) |
| C(8)-C(7) | 1.574(41) | C(32)-C(7) | 1.551(46) |
| C(33)-C(7) | 1.551(47) | C(36)-C(8) | 1.537(41) |
| C(10)-C(9) | 1.372(40) | C(12)-C(11) | 1.508(38) |
| C(13)-C(12) | 1.545(49) | C(40)-C(12) | 1.545(46) |
| C(41)-C(12) | 1.458(43) | C(42)-C(13) | 1.516(59) |
| C(15)-C(14) | 1.296(35) | C(16)-C(15) | 1.462(35) |
| C(46)-C(15) | 1.612(40) | C(17)-C(16) | 1.519(35) |
| C(18)-C(17) | 1.504(38) | C(47)-C(17) | 1.527(39) |
| C(48)-C(17) | 1.557(39) | C(52)-C(18) | 1.586(40) |
| C(29)-C(28) | 1.450(51) | C(34)-C(33) | 1.444(51) |
| C(38A)-C(37) | 1.593(80) | C(38B)-C(37) | 1.300(*) |
| C(43A)-C(42) | 1.457(68) | C(43B)-C(42) | 1.501(*) |
| C(44A)-C(43A) | 1.591(79) | C(44B)-C(43B) | 1.526(*) |
| C(49)-C(48) | 1.550(43) | C(50)-C(49) | 1.507(41) |
| C(53)-C(52) | 1.479(40) | | |

possible that solvent disorder affected the accuracy of these analyses.

Figure 3 gives the best average bond lengths (with values for NEOVBT and VITBPH10 omitted) currently available for the corrin system. As can be seen, two conjugated partial double bonds, C(4)-N(1) and C(16)-N(4), are shorter than average and the two adjacent C-C single bonds, C(4)-C(5) and C(15)-C(16), longer than other corresponding bonds.

Deviations of most of the atoms from the least-square planes of the conjugated corrin ring systems are relatively large and no systematic trend is apparent (Table 8).

Conformation of the Pyrrole Rings.—A careful analysis of the torsion angles and the deviation of atoms from the mean planes calculated for these rings in each of the

TABLE 5
 Bond angles (°)

| | | | |
|----------------------|-----------|----------------------|-----------|
| N(3)-Co(1)-N(1) | 170.3(9) | N(3)-Co(1)-N(2) | 97.2(10) |
| N(4)-Co(1)-N(1) | 81.0(10) | N(4)-Co(1)-N(2) | 170.5(9) |
| N(4)-Co(1)-N(3) | 90.4(10) | C(20)-Co(1)-N(1) | 94.0(12) |
| C(20)-Co(1)-N(2) | 86.1(12) | C(20)-Co(1)-N(3) | 90.2(12) |
| C(20)-Co(1)-N(4) | 88.2(12) | C(21)-Co(1)-N(1) | 90.7(11) |
| C(21)-Co(1)-N(2) | 89.5(11) | C(21)-Co(1)-N(3) | 85.8(11) |
| C(21)-Co(1)-N(4) | 96.8(11) | C(21)-Co(1)-C(20) | 173.7(12) |
| C(26)-O(2)-C(25) | 104.9(31) | C(30A)-O(4A)-C(29) | 124.2(60) |
| C(30B)-O(4B)-C(29) | 116.6(98) | C(35)-O(6)-C(34) | 122.3(35) |
| C(39A)-O(7A)-C(38A) | 113.7(64) | C(39B)-O(7B)-C(38B) | 101.6(69) |
| C(45A)-O(10A)-C(44A) | 118.4(55) | C(45B)-O(10B)-C(44B) | 130.2(86) |
| C(51A)-O(12)-C(50) | 113.8(31) | C(51B)-O(12)-C(50) | 111.9(32) |
| C(54)-O(14)-C(53) | 116.7(23) | C(1)-N(1)-Co(1) | 118.2(17) |
| C(4)-N(1)-Co(1) | 131.0(17) | C(4)-N(1)-C(1) | 110.8(22) |
| C(6)-N(2)-Co(1) | 122.7(17) | C(9)-N(2)-Co(1) | 123.2(18) |
| C(9)-N(2)-C(6) | 113.5(21) | C(11)-N(3)-Co(1) | 121.8(18) |
| C(14)-N(3)-Co(1) | 126.9(18) | C(14)-N(3)-C(11) | 111.0(22) |
| C(16)-N(4)-Co(1) | 129.9(19) | C(19)-N(4)-Co(1) | 113.7(17) |
| C(19)-N(4)-C(16) | 115.5(22) | C(2)-C(1)-N(1) | 101.6(21) |
| C(19)-C(1)-N(1) | 98.5(21) | C(19)-C(1)-C(2) | 119.0(22) |
| C(22)-C(1)-N(1) | 112.9(23) | C(22)-C(1)-C(2) | 115.3(24) |
| C(22)-C(1)-C(19) | 108.2(22) | C(3)-C(2)-C(1) | 102.2(21) |
| C(23)-C(2)-C(1) | 111.9(23) | C(23)-C(2)-C(3) | 113.7(22) |
| C(24)-C(2)-C(1) | 112.7(22) | C(24)-C(2)-C(3) | 109.0(22) |
| C(24)-C(2)-C(23) | 107.3(23) | C(3)-C(4)-N(1) | 112.2(24) |
| C(5)-C(4)-N(1) | 121.7(24) | C(5)-C(4)-C(3) | 126.1(24) |
| C(6)-C(5)-C(4) | 124.1(26) | C(31)-C(5)-C(4) | 113.8(23) |
| C(31)-C(5)-C(6) | 121.9(24) | C(5)-C(6)-N(2) | 126.5(24) |
| C(7)-C(6)-N(2) | 104.3(21) | C(7)-C(6)-C(5) | 129.2(25) |
| C(8)-C(7)-C(6) | 102.8(22) | C(32)-C(7)-C(6) | 121.6(27) |
| C(32)-C(7)-C(8) | 109.6(25) | C(33)-C(7)-C(6) | 99.0(23) |
| C(33)-C(7)-C(8) | 111.8(26) | C(33)-C(7)-C(32) | 111.4(26) |
| C(8)-C(9)-N(2) | 111.2(23) | C(10)-C(9)-N(2) | 123.8(26) |
| C(10)-C(9)-C(8) | 125.0(25) | C(12)-C(11)-N(3) | 111.4(22) |
| C(12)-C(11)-C(10) | 124.7(25) | C(13)-C(12)-C(11) | 100.4(23) |
| C(40)-C(12)-C(11) | 105.9(24) | C(40)-C(12)-C(13) | 109.1(26) |
| C(41)-C(12)-C(11) | 114.7(25) | C(41)-C(12)-C(13) | 115.3(26) |
| C(41)-C(12)-C(40) | 110.7(26) | C(13)-C(14)-N(3) | 109.0(24) |
| C(15)-C(14)-N(3) | 123.7(25) | C(15)-C(14)-C(13) | 127.3(27) |
| C(16)-C(15)-C(14) | 125.6(24) | C(46)-C(15)-C(14) | 117.0(23) |
| C(46)-C(15)-C(16) | 117.0(22) | C(15)-C(16)-N(4) | 122.1(23) |
| C(17)-C(16)-N(4) | 109.7(22) | C(17)-C(16)-C(15) | 127.7(22) |
| C(18)-C(17)-C(16) | 100.6(20) | C(47)-C(17)-C(16) | 106.8(22) |
| C(47)-C(17)-C(18) | 113.0(21) | C(48)-C(17)-C(16) | 116.7(21) |
| C(48)-C(17)-C(18) | 112.0(23) | C(48)-C(17)-C(47) | 107.6(22) |
| C(1)-C(19)-N(4) | 105.0(21) | C(18)-C(19)-N(4) | 101.5(20) |
| C(18)-C(19)-C(1) | 120.4(22) | N(6)-C(21)-Co(1) | 175.0(25) |
| O(2)-C(25)-O(1) | 134.3(38) | C(24)-C(25)-O(1) | 118.8(35) |
| C(24)-C(25)-O(2) | 106.7(31) | O(4A)-C(29)-O(3A) | 116.7(46) |
| O(4B)-C(29)-O(3B) | 128.6(72) | C(28)-C(29)-O(3A) | 130.5(40) |
| C(28)-C(29)-O(3B) | 97.9(49) | C(28)-C(29)-O(4A) | 110.8(40) |
| C(28)-C(29)-O(4B) | 120.9(61) | O(4B)-C(30A)-O(4A) | 25.4(41) |
| O(6)-C(34)-O(5) | 115.5(35) | C(33)-C(34)-O(5) | 130.1(33) |
| C(33)-C(34)-O(6) | 114.3(34) | C(38A)-C(37)-C(36) | 104.9(35) |
| C(38B)-C(37)-C(36) | 120.7(57) | O(8A)-C(38A)-O(7A) | 112.3(68) |
| C(37)-C(38A)-O(7A) | 117.2(54) | C(37)-C(38A)-O(8A) | 130.4(65) |
| O(8B)-C(38B)-O(7B) | 132.6(*) | C(37)-C(38B)-O(7B) | 123.2(91) |
| C(37)-C(38B)-O(8B) | 103.7(87) | C(43A)-C(42)-C(13) | 120.2(39) |
| C(43B)-C(42)-C(13) | 132.0(59) | C(44A)-C(43A)-C(42) | 114.2(42) |
| C(44B)-C(43B)-C(42) | 131.7(97) | O(10A)-C(44A)-O(9A) | 126.8(76) |
| C(43A)-C(44A)-O(9A) | 114.0(69) | C(43A)-C(44A)-O(10A) | 116.5(55) |
| O(10B)-C(44B)-O(9B) | 126.6(*) | C(43B)-C(44B)-O(9B) | 100.3(*) |
| C(43B)-C(44B)-O(10B) | 125.9(*) | O(12)-C(50)-O(11) | 123.0(30) |
| C(49)-C(50)-O(11) | 122.2(28) | C(49)-C(50)-O(12) | 114.6(27) |
| O(14)-C(53)-O(13) | 121.8(27) | C(52)-C(53)-O(13) | 127.8(27) |
| C(52)-C(53)-O(14) | 110.3(24) | | |

TABLE 6

Bibliographic and crystallographic data for compounds used in geometric comparisons

| | |
|--------------|---|
| (1) AMECNCB | Heptamethyl(dicyano)cobyrinate, $R = 0.132$; space group $P212121$; present study |
| (2) COBYIC | Cobyric acid undecahydrate $R = 0.120$; space group $P21$; K. Venkatesan, D. Dale, D. C. Hodgkin, C. E. Nockolds, F. H. Moore, and B. H. O'Connor, <i>Proc. R. Soc. London, Ser. A</i> , 1971, 323, 455 |
| (3) CYCOAM | Dicyanocobyrinic-a,c-diamide trihydrate, $R = 0.065$; space group $P212121$; B. Dresow, G. Schlingmann, W. S. Sheldrick, and V. B. Koppenhagen, <i>Angew. Chem., Int. Ed. Engl.</i> , 1980, 19, 321 |
| (4) DADCBL | 5'-Deoxyadenosylcobalamin, $R = 0.132$; space group $P212121$; P. G. Lenhert, <i>Proc. R. Soc. London, Ser. A</i> , 1968, 303, 45 |
| (5) HACBCO10 | 6-Amino(dicyano)-5,6-dihydrocobyrinic-pentamethyl ester-a-amide-c-lactam hemihydrate, $R = 0.115$; space group $P1$; G. Schlingmann, B. Dresow, V. B. Koppenhagen, W. Becker and W. S. Sheldrick, <i>Angew. Chem., Int. Ed. Engl.</i> , 1980, 19, 321 |
| (6) MECNCB | Heptamethyl(dicyano)cobyrinate(III) hydrate, $R = 0.106$; space group $P21$; A. Fischli and J. J. Daly, <i>Helv. Chim. Acta</i> , 1980, 63, 1628 |
| (7) NEOVBT | neo-Vitamin B(12) hydrate, $R = 0.159$; space group $P212121$; H. Stoeckli-Evans, E. Edmond, D. C. Hodgkin, <i>J. Chem. Soc., Perkin Trans. 2</i> , 1972, 605 |
| (8) VITBPH10 | Vitamin B(12)-5'-phosphate hydrate $R = 0.162$; space group $P212121$; S. W. Hawkinson, C. L. Coulter, and M. L. Greaves, <i>Proc. R. Soc. London, Ser. A</i> , 1970, 318, 143 |

compounds included in the survey have led to the conclusions shown in Table 9. In all compounds rings A and D are in the envelope form and appear unaffected by the nature of the side-chains or intermolecular packing

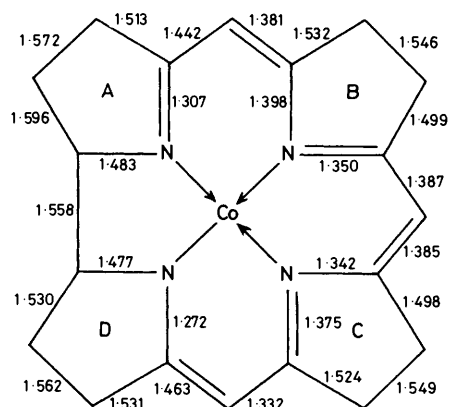


FIGURE 3 Mean bond lengths of corrin system derived from compounds listed in Table 8

forces. The other two rings are much more variable and can assume either an envelope or a half-chair conformation. For ring B the half-chair is formed about the two fold axis defined by N(2) and the mid-point of bond

C(7)-C(8) and for C by the axis through N(3) and the mid-point of bond C(12)-C(13).

Conformation of the Side-chains.—All compounds in this survey have relatively flexible side-chains, which seem to take up those conformations which lead to the

TABLE 7(a)

Parameters representing cobalt co-ordination

| Bond lengths (Å) | Co-N(1) Co-N(2) Co-N(3) Co-N(4) | | | |
|---|---|-------|-------|-------|
| | AMECNCB | 1.883 | 1.916 | 1.924 |
| CYCOAM | 1.899 | 1.915 | 1.915 | 1.877 |
| HACBCO10 | 1.909 | 1.930 | 1.899 | 1.933 |
| MECNCB | 1.859 | 1.925 | 1.922 | 1.952 |
| MECNCB | 1.898 | 1.932 | 1.912 | 1.897 |
| Mean | 1.890 | 1.924 | 1.914 | 1.914 |
| Std. devn. | 0.019 | 0.008 | 0.010 | 0.029 |
| Minimum | 1.859 | 1.915 | 1.899 | 1.877 |
| Maximum | 1.909 | 1.932 | 1.924 | 1.952 |
| Bond angles (°) | Co-C(20) Co-C(21) C(20)-N(5) C(21)-N(6) | | | |
| | AMECNCB | 1.940 | 1.895 | 1.138 |
| CYCOAM | 1.923 | 1.933 | 1.140 | 1.137 |
| HACBCO10 | 1.947 | 1.891 | 1.155 | 1.175 |
| MECNCB | 1.951 | 1.926 | 1.120 | 1.139 |
| MECNCB | 1.922 | 1.926 | 1.144 | 1.156 |
| Mean | 1.937 | 1.914 | 1.139 | 1.149 |
| Std. devn. | 0.013 | 0.020 | 0.013 | 0.016 |
| Minimum | 1.922 | 1.891 | 1.120 | 1.137 |
| Maximum | 1.951 | 1.933 | 1.144 | 1.156 |
| N-Co-N | | | | |
| N(1), N(2) N(2), N(3) N(3), N(4) N(4), N(1) | | | | |
| AMECNCB | 91.8 | 97.2 | 90.4 | 81.0 |
| CYCOAM | 90.6 | 96.6 | 90.3 | 82.9 |
| HACBCO10 | 92.0 | 97.3 | 88.3 | 82.8 |
| MECNCB | 93.0 | 95.6 | 90.1 | 81.6 |
| MECNCB | 90.8 | 96.7 | 89.6 | 83.1 |
| Mean | 91.6 | 96.7 | 89.7 | 82.3 |
| Std. devn. | 1.0 | 0.7 | 0.9 | 0.9 |
| Minimum | 90.6 | 95.6 | 88.3 | 81.0 |
| Maximum | 93.0 | 97.3 | 90.4 | 83.1 |

Deviations of atoms from least-squares plane of N(1), N(2), N(3), N(4) (Å × 10³)

| | Co | N(1) | N(2) | N(3) | N(4) |
|------------|-----|------|------|------|------|
| AMECNCB | -16 | -89 | 76 | -76 | 89 |
| CYCOAM | -5 | -81 | 71 | -72 | 82 |
| HACBCO10 | -8 | -71 | 63 | -65 | 73 |
| MECNCB | -5 | -68 | 60 | -59 | 68 |
| MECNCB | -14 | -52 | 45 | -46 | 53 |
| Mean | -10 | -72 | 63 | -64 | 73 |
| Std. devn. | 5 | 14 | 12 | 12 | 14 |
| Minimum | -16 | -89 | 45 | -76 | 53 |
| Maximum | -5 | -52 | 76 | -46 | 89 |

most favourable packing arrangements in the crystal structure. In three of the compounds AMECNCB, HACBCO10, and MECNCB the molecules are mainly held by van der Waals contacts, whereas the remaining compounds form a large number of hydrogen bonds in the crystal structure. In spite of the variability some patterns emerge: the side-chains attached to rings A have very similar conformation as far as the second exocyclic carbon atom (Table 10). In ring B this holds for only the first exocyclic carbon. In ring C there is full conformational freedom. In ring D the side-chain attached to C(17) assumes almost the same conformation in all

TABLE 7(b)
Co-ordinates of atoms with reference to orthogonal molecular axes

| | C(10) | | | C(15) | | | C(20) | | | N(5) | | | C(21) | | | N(6) | | |
|----------|-------|-------|------|-------|-------|-------|-------|-------|------|-------|-------|------|-------|-------|-------|------|-------|-------|
| | x | y | z | x | y | z | x | y | z | x | y | z | x | y | z | x | y | z |
| AMECNB | 3.17 | -0.31 | 3.30 | -0.20 | -3.26 | 0.21 | 0.09 | 0.24 | 1.92 | 0.24 | 0.33 | 3.05 | 0.12 | -0.22 | -1.88 | 0.14 | -0.44 | -3.00 |
| CYCOAM | 3.22 | -0.25 | 3.33 | -0.24 | -3.35 | 0.13 | -0.12 | 0.21 | 1.91 | -0.23 | 0.36 | 3.03 | 0.24 | -0.16 | -1.91 | 0.54 | -0.26 | -3.00 |
| HACBCO10 | 3.27 | -0.31 | 3.38 | -0.23 | -3.35 | -0.37 | -0.07 | -0.09 | 1.94 | -0.14 | -0.05 | 3.10 | 0.08 | 0.16 | -1.88 | 0.21 | 0.32 | -3.03 |
| | 3.26 | -0.30 | 3.39 | -0.21 | -3.37 | -0.39 | -0.14 | -0.08 | 1.94 | -0.19 | -0.09 | 3.06 | 0.14 | 0.12 | -1.92 | 0.44 | 0.21 | -3.01 |
| MECNB | 3.25 | -0.24 | 3.36 | -0.23 | -3.33 | 0.16 | 0.09 | 0.27 | 1.90 | 0.12 | 0.39 | 3.04 | 0.07 | -0.25 | -1.91 | 0.21 | -0.41 | -3.04 |

TABLE 8
Parameters defining the conformation of the corrin ring

Bond lengths (Å)

| C-N | | C(1)-N(1) | C(19)-N(4) | C(4)-N(1) | C(6)-N(2) | C(9)-N(2) | C(11)-N(3) | C(14)-N(3) | C(16)-N(4) |
|------------|--|-----------|------------|-----------|-----------|-----------|------------|------------|------------|
| AMECNCB | | 1.476 | 1.410 | 1.324 | 1.429 | 1.322 | 1.361 | 1.354 | 1.261 |
| COBYIC | | 1.502 | 1.487 | 1.329 | 1.374 | 1.330 | 1.327 | 1.407 | 1.288 |
| CYCOAM | | 1.481 | 1.494 | 1.277 | 1.397 | 1.336 | 1.345 | 1.382 | 1.317 |
| DADCBL | | 1.459 | 1.494 | 1.317 | 1.388 | 1.415 | 1.311 | 1.374 | 1.212 |
| MECNB | | 1.496 | 1.502 | 1.290 | 1.403 | 1.348 | 1.367 | 1.357 | 1.284 |
| NEOVBT | | 1.423 | 1.505 | 1.273 | 1.405 | 1.322 | 1.317 | 1.353 | 1.368 |
| VITBPH10 | | 1.561 | 1.578 | 1.452 | 1.463 | 1.480 | 1.305 | 1.429 | 1.261 |
| Mean | | 1.485 | 1.496 | 1.323 | 1.408 | 1.365 | 1.333 | 1.379 | 1.284 |
| Std. devn. | | 0.042 | 0.049 | 0.061 | 0.029 | 0.060 | 0.025 | 0.029 | 0.049 |
| Minimum | | 1.423 | 1.410 | 1.273 | 1.374 | 1.322 | 1.305 | 1.353 | 1.212 |
| Maximum | | 1.561 | 1.578 | 1.452 | 1.463 | 1.480 | 1.367 | 1.429 | 1.368 |

C-C

| | C(1)-C(2) | C(2)-C(3) | C(3)-C(4) | C(6)-C(7) | C(7)-C(8) | C(8)-C(9) | C(11)-C(12) | C(12)-C(13) | C(13)-C(14) | C(16)-C(17) |
|------------|-----------|-----------|-----------|-----------|-----------|-----------|-------------|-------------|-------------|-------------|
| AMECNCB | 1.571 | 1.519 | 1.474 | 1.568 | 1.574 | 1.507 | 1.508 | 1.545 | 1.512 | 1.519 |
| COBYIC | 1.618 | 1.580 | 1.524 | 1.569 | 1.524 | 1.526 | 1.504 | 1.549 | 1.509 | 1.522 |
| CYCOAM | 1.596 | 1.578 | 1.537 | 1.529 | 1.544 | 1.500 | 1.532 | 1.530 | 1.514 | 1.532 |
| DADCBL | 1.632 | 1.616 | 1.547 | 1.451 | 1.478 | 1.477 | 1.448 | 1.569 | 1.570 | 1.553 |
| MECNB | 1.565 | 1.565 | 1.482 | 1.541 | 1.608 | 1.483 | 1.497 | 1.554 | 1.514 | 1.529 |
| NEOVBT | 1.602 | 1.720 | 1.500 | 1.505 | 1.564 | 1.493 | 1.413 | 1.511 | 1.517 | 1.595 |
| VITBPH10 | 1.709 | 1.745 | 1.403 | 1.494 | 1.382 | 1.644 | 1.514 | 1.736 | 1.454 | 1.505 |
| Mean | 1.613 | 1.618 | 1.495 | 1.522 | 1.525 | 1.519 | 1.488 | 1.571 | 1.513 | 1.536 |
| Std. devn. | 0.048 | 0.084 | 0.049 | 0.043 | 0.075 | 0.058 | 0.042 | 0.075 | 0.034 | 0.030 |
| Minimum | 1.565 | 1.519 | 1.403 | 1.451 | 1.382 | 1.477 | 1.413 | 1.511 | 1.454 | 1.505 |
| Maximum | 1.709 | 1.745 | 1.547 | 1.569 | 1.608 | 1.644 | 1.532 | 1.736 | 1.570 | 1.595 |

C-C

| | C(17)-C(18) | C(18)-C(19) | C(19)-C(1) | C(4)-C(5) | C(5)-C(6) | C(9)-C(10) | C(10)-C(11) | C(14)-C(15) | C(15)-C(16) |
|------------|-------------|-------------|------------|-----------|-----------|------------|-------------|-------------|-------------|
| AMECNCB | 1.504 | 1.534 | 1.588 | 1.422 | 1.318 | 1.372 | 1.354 | 1.296 | 1.462 |
| COBYIC | 1.562 | 1.549 | 1.530 | 1.463 | 1.373 | 1.386 | 1.394 | 1.336 | 1.455 |
| CYCOAM | 1.581 | 1.539 | 1.558 | 1.437 | 1.376 | 1.391 | 1.368 | 1.355 | 1.458 |
| DADCBL | 1.583 | 1.478 | 1.589 | 1.391 | 1.494 | 1.406 | 1.412 | 1.315 | 1.489 |
| MECNB | 1.579 | 1.549 | 1.525 | 1.496 | 1.346 | 1.381 | 1.395 | 1.360 | 1.452 |
| NEOVBT | 1.487 | 1.577 | 1.455 | 1.540 | 1.279 | 1.345 | 1.448 | 1.367 | 1.367 |
| VITBPH10 | 1.604 | 1.640 | 1.442 | 1.378 | 1.155 | 1.286 | 1.338 | 1.679 | 1.476 |
| Mean | 1.557 | 1.552 | 1.527 | 1.447 | 1.334 | 1.367 | 1.387 | 1.387 | 1.451 |
| Std. devn. | 0.044 | 0.049 | 0.059 | 0.058 | 0.104 | 0.040 | 0.037 | 0.131 | 0.039 |
| Minimum | 1.487 | 1.478 | 1.442 | 1.378 | 1.155 | 1.286 | 1.338 | 1.296 | 1.367 |
| Maximum | 1.604 | 1.640 | 1.589 | 1.540 | 1.494 | 1.406 | 1.448 | 1.679 | 1.489 |

Deviations of atoms from the least-squares planes (Å × 10³)

| Atoms used for calculations of the planes | | | | | | | | | | | | | |
|---|------|------|------|------|-------|-------|-------|-------|-------|------|------|------|------|
| | C(4) | C(5) | C(6) | C(9) | C(10) | C(11) | C(14) | C(15) | C(16) | N(1) | N(2) | N(3) | N(4) |
| AMECNCB | -127 | 133 | 169 | -69 | 5 | 37 | -107 | -35 | 150 | -227 | -51 | -1 | 123 |
| COBYIC | -169 | 67 | -17 | -104 | 60 | 99 | -99 | -89 | 31 | -77 | -36 | 52 | 129 |
| CYCOAM | -145 | 112 | 173 | -43 | -58 | -24 | -63 | -10 | 118 | -205 | 26 | 32 | 88 |
| DADCBL | -127 | 293 | 235 | -134 | -81 | 37 | 5 | 110 | 89 | -287 | -114 | -3 | -23 |
| MECNB | -69 | 113 | 86 | -47 | 18 | 40 | -87 | -44 | 103 | -164 | -71 | 21 | 100 |
| NEOVBT | -147 | 394 | 271 | -194 | -120 | -20 | 155 | 169 | 47 | -312 | -103 | -6 | -136 |
| VITBPH10 | 5 | 192 | 160 | -87 | -196 | 191 | 133 | 35 | -8 | -228 | -97 | -85 | -15 |
| Mean | -111 | 186 | 154 | -97 | -53 | 51 | -9 | 19 | 76 | -214 | -64 | 1 | 38 |
| Std. devn. | 60 | 117 | 96 | 53 | 88 | 74 | 111 | 92 | 55 | 78 | 49 | 44 | 99 |
| Minimum | -169 | 67 | -17 | -194 | -196 | -24 | -107 | -89 | -8 | -312 | -114 | -85 | -136 |
| Maximum | 5 | 394 | 271 | -43 | 60 | 191 | 155 | 169 | 150 | -77 | 24 | 52 | 129 |

Other atoms

| | C(1) | C(2) | C(3) | C(7) | C(8) | C(12) | C(13) | C(17) | C(18) | C(19) | Co |
|------------|------|------|------|------|------|-------|-------|-------|-------|-------|------|
| AMECNCB | -441 | 22 | -324 | 477 | -153 | 135 | -311 | 599 | 334 | 490 | -55 |
| COBYIC | -221 | 495 | 22 | 133 | -312 | 283 | -386 | 217 | 52 | 467 | -22 |
| CYCOAM | -470 | -19 | -311 | 550 | -103 | -54 | -414 | 291 | 58 | 389 | -18 |
| DADCBL | -755 | -159 | -297 | 571 | -156 | 417 | -114 | 203 | -404 | 59 | -96 |
| MECNB | -340 | 142 | -142 | 327 | -207 | 122 | -370 | 384 | 185 | 465 | -42 |
| NEOVBT | -612 | -147 | -370 | 541 | -195 | -23 | 455 | 220 | -303 | 104 | -153 |
| VITBPH10 | -596 | 216 | -260 | 441 | -240 | 329 | -39 | 94 | -231 | 197 | -138 |
| Mean | -489 | 78 | -240 | 434 | -195 | 172 | -168 | 287 | -44 | 310 | -75 |
| Std. devn. | 182 | 230 | 136 | 157 | 67 | 178 | 310 | 164 | 273 | 185 | 55 |
| Minimum | -755 | -159 | -370 | 133 | -312 | -54 | -414 | 94 | -404 | 59 | -153 |
| Maximum | -211 | 495 | 22 | 571 | -103 | 417 | 455 | 599 | 334 | 490 | -18 |

TABLE 9
Conformation of the five-membered rings

| | A | B | C | D |
|---------------------|--------------------|-------------------------------|-----------------------------------|-------------------|
| AMECNCB | Envelope C(2) * | Envelope C(8) | Half-chair N(3), C(12)-C(13) † | Envelope C(18) |
| COBYIC | Envelope C(2) | Half-chair N(2), C(7)-C(8) | Half-chair N(3), C(12)-C(13) | Envelope C(18) |
| CYCOAM | Envelope C(2) | Envelope C(7) | Half-chair N(3), C(12)-C(13) | Envelope C(18) |
| DADCBL | Envelope C(2) | Envelope C(8) | Envelope C(12) | Envelope C(18) |
| HACBCO10 | Envelope C(2) | Envelope C(7) | Half-chair N(3), C(12)-C(13) | Envelope C(18) |
| MECNCB | Envelope C(2) | Envelope C(8) | Half-chair N(3), C(12)-C(13) | Envelope C(18) |
| NEOVBT | Envelope C(2) | Envelope C(8) | Half-chair N(3), C(12)-C(13) | Envelope C(18) |
| VITAMB ⁶ | Envelope C(2) | Envelope C(8) | Envelope C(12) | Envelope C(18) |
| VITBPH10 | Envelope C(2) | Envelope C(8) | Envelope C(14) | Envelope C(18) |
| VITCAC ⁷ | Envelope C(2) | Half-chair N(2), C(7)-C(8) | Envelope C(12) | Envelope C(18) |

* Atom lying out-of-plane: C(2) lying out-of-plane. † Position of two-fold axis: two-fold axis passes through N(3) and the centre of C(12)-C(13)

TABLE 10
Torsional angles in the side-chains

| | A | | | B | | | | |
|------------|------------------------|-------------------------|------------------------|-------------------------|--------------------------|------------------------|-------------------------|------------------------|
| | N(1)C(1)- C(2)C(24) | C(1)C(2)- C(24)C(25) | N(1)C(4)- C(3)C(27) | C(4)C(3)- C(27)C(28) | C(3)C(27)- C(28)C(29) | N(2)C(6)- C(7)C(33) | C(6)C(7)- C(33)C(34) | N(2)C(9)- C(8)C(36) |
| AMECNCB | -86.2 | 176.0 | -104.2 | -158.4 | 71.2 | -93.7 | -188.5 | -92.7 |
| COBYIC | -81.1 | 160.8 | -109.4 | -149.7 | 168.2 | -96.7 | 58.8 | -107.5 |
| CYCOAM | -82.7 | 169.1 | -107.0 | -149.1 | 192.5 | -81.4 | -66.7 | -95.4 |
| DADCBL | -80.3 | 172.1 | -105.2 | -163.1 | 60.0 | -90.8 | -168.4 | -95.3 |
| HACBCO10 | -84.1 | 178.8 | -112.2 | -165.8 | 149.1 | — | — | — |
| HACBCO10 | -81.7 | 178.9 | -109.3 | -163.9 | 146.3 | — | — | — |
| MECNCB | -85.9 | 173.0 | -110.9 | -154.1 | 163.5 | -95.4 | -190.0 | -98.9 |
| NEOVBT | -83.9 | 168.6 | -101.8 | -164.4 | 178.4 | -89.3 | -51.6 | -90.5 |
| VITBPH10 | -77.3 | 178.5 | -98.0 | -149.6 | 172.3 | -80.3 | -58.2 | -98.0 |
| Mean | -82.6 | 172.9 | -106.4 | -157.6 | 144.6 | -89.6 | -94.9 | -96.9 |
| Std. devn. | 2.8 | 6.1 | 4.6 | 7.0 | 47.0 | 6.5 | 92.1 | 5.5 |
| Minimum | -86.2 | 160.8 | -112.2 | -165.8 | 60.0 | -96.6 | -190.0 | -107.5 |
| Maximum | -77.3 | 178.9 | -98.0 | -149.1 | 192.5 | -80.3 | 58.8 | -90.5 |

| | B | | C | | D | | | | |
|------------|-------------------------|--------------------------|--------------------------|---------------------------|--------------------------|---------------------------|---------------------------|--------------------------|---------------------------|
| | C(9)C(8)- C(36)C(37) | C(8)C(36)- C(37)C(38) | N(3)C(14)- C(13)C(42) | C(14)C(13)- C(42)C(43) | N(4)C(16)- C(17)C(48) | C(16)C(17)- C(48)C(49) | C(17)C(48)- C(49)C(50) | N(4)C(19)- C(18)C(52) | C(19)C(18)- C(52)C(53) |
| AMECNCB | -56.3 | -76.3 | -106.7 | 39.4 | 140.6 | -52.8 | 160.4 | 150.8 | 96.6 |
| COBYIC | 45.0 | -188.4 | -93.9 | -163.8 | 132.5 | -40.3 | 174.2 | 156.8 | 154.3 |
| CYCOAM | -55.9 | -56.3 | -103.3 | -165.2 | 127.1 | -39.0 | 185.4 | 150.8 | 168.8 |
| DADCBL | -53.1 | -169.2 | -97.5 | -166.1 | 133.5 | -43.7 | 166.6 | 159.9 | 150.2 |
| HACBCO10 | — | — | -102.2 | 45.4 | 135.2 | -47.5 | 176.9 | 157.8 | 164.4 |
| HACBCO10 | — | — | -86.6 | -60.3 | 135.4 | -47.0 | 177.0 | 155.9 | 166.7 |
| MECNCB | 46.0 | -169.3 | -100.6 | -154.9 | 132.8 | -49.4 | 157.9 | 153.8 | 154.5 |
| NEOVBT | -55.1 | -180.7 | -259.4 | -45.6 | 135.2 | -54.4 | 163.8 | 152.7 | 164.3 |
| VITBPH10 | -37.0 | -179.2 | -88.3 | -170.3 | 139.9 | -47.6 | 162.2 | 172.6 | 296.9 |
| Mean | -23.8 | -145.6 | -115.4 | -93.5 | 134.7 | -46.9 | 169.4 | 156.8 | 168.5 |
| Std. devn. | 47.8 | 54.9 | 54.4 | 90.4 | 4.0 | 5.2 | 9.4 | 6.7 | 52.9 |
| Minimum | -56.3 | -188.4 | -259.4 | -170.3 | 127.1 | -54.4 | 157.9 | 150.8 | 96.6 |
| Maximum | 46.0 | -56.3 | -86.6 | 45.5 | 140.6 | -39.0 | 185.4 | 172.6 | 296.9 |

compounds and that attached to C(18) as far as the first exocyclic carbon atoms. The direct link between rings A and D, C(1)-C(19), seems to influence the conformation of the side-chains to a considerable extent.

Comparison with Spectroscopic Measurements.—The preceding paper¹ discusses the detailed analysis of the ¹H and ¹³C n.m.r. spectra of coberster. Of particular

interest in an interpretation of these spectroscopic experiments are the distances between the proton H(10) and those of the C(12) methyl groups. These are 2.77, 3.84, and 4.06 Å for the pseudo-equatorial C(41) (12 α) and 2.07, 2.95 and 3.67 Å for the pseudo-axial C(40) (12 β). The average values are in good agreement with the spectroscopic results.¹

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