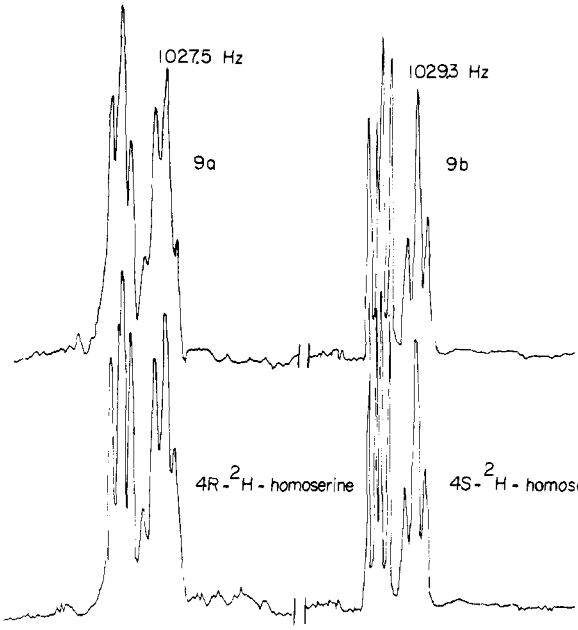
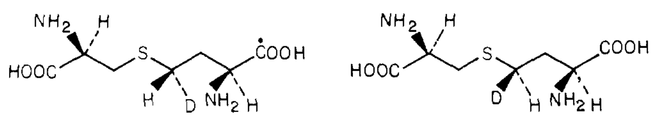


Figure 2. 270-MHz spectra of **9a** and **9b** together with that of authentic (R)-L-[4-^{2}H]homoserine and (S)-L-[4-^{2}H]homoserine.

and obtained as crystalline samples (5.5 mg of **9a** and 3.2 mg of **9b**, respectively). The 270-MHz spectra are shown in Figure 2 along with that of authentic (R)-L-[4-^{2}H]homoserine and (S)-L-[4-^{2}H]homoserine (we have recently determined the absolute chirality of such homoserine samples for just this purpose).[14] Clearly **9a** is (R)-L-[4-^{2}H]homoserine as shown and the product cystathionine **3a** must be S-4-^{2}H as is the methionine sample **7a**. Homoserine **9b** is in turn a S-4-^{2}H species and the cystathionine sample **3b** is a R-4-^{2}H isomer.

The stereochemical outcome in the first half-reaction could then be determined by chemical succinylation[15] of **9a** → **1a** and **9b** → **1b**, followed by cystathionine γ-synthetase mediated conversion to monodeuteriocystathionines upon incubation with L-cysteine. After purification, cystathionine from **1a** had its γ-H at 696.5 Hz (t, J = 7.0 Hz) and that from **1b** at 687.9 Hz by 270-MHz NMR, confirming that **1a** gives **3b**, (R)-L-[4-^{2}H]cystathionine,



3a 3b

given the absolute stereochemistry for monodeuteriocystathionines deduced via Scheme I. **1b** yields the opposite, S-4-^{2}H isomer **3a**.

Thus the overall γ-replacement process occurs with *retention of stereochemistry at the γ carbon (C4)* undergoing substitution. Fuganti and co-workers[16] reported in a preliminary way that the H_R proton at the β carbon of O-succinylhomoserine is removed; if this result is validated, then the β-H_R,γ-O-succinyl elimination would be a syn elimination to a cisoid form of conjugated intermediate **2**, given the sequences observed here: (R)-[4-^{2}H]-succinylhomoserine → (E)-[4-^{2}H]vinylglycine-PLP α-anion → (R)-[4-^{2}H]cystathionine and (S)-[4-^{2}H]succinylhomoserine → Z-4-^{2}H adduct → (S)-[4-^{2}H]cystathionine.

Acknowledgment. We thank Professor J. S. Hong for the generous gift of homogeneous β-cystathionase and Professor A. Redfield for the assistance and the use of his 270-MHz NMR spectrometer.

Michael N. T. Chang, Christopher Walsh*
Departments of Chemistry and Biology
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139
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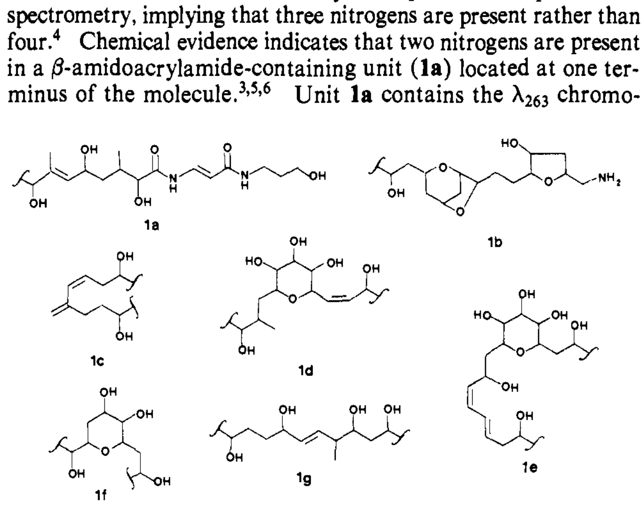
(13) Whatman, No. 1 Paper, 1-butanol–acetic acid–water (12:3:5), R_f = 0.2, located by ninhydrin spray and workup by extraction with hot water.
(14) Chang, M. N.; Walsh, C. *J. Am. Chem. Soc.* **1980**, *102*, 2499.
(15) Flavin, M.; Delavier-Klutchko, C.; Slaughter, C. *Science (Washington, DC)* **1964**, *143*, 50.
(16) Coggiola, D.; Fuganti, C. *Experientia* **1977**, 33 (7), 847.

Periodate Oxidation of *N*-(*p*-Bromobenzoyl)palytoxin

Sir:

The structure elucidation of palytoxin, an exceedingly poisonous substance from marine soft corals of the genus *Palythoa*,[1,2] presents a formidable challenge to the organic chemist because of its high molecular weight and lack of familiar repeating structural units such as those found in peptides and polysaccharides. Our work on palytoxin from Hawaiian *Palythoa toxica* and a Tahitian *Palythoa* sp. has suggested that the molecular weight is 3300 and that four nitrogens exist in the molecule.[3] Recently the molecular weight of palytoxin from Okinawan *P. tuberculosa* has been determined to be 2681.1 ± 0.35 by ^{252}Cf-plasma desorption mass spectrometry, implying that three nitrogens are present rather than four.[4] Chemical evidence indicates that two nitrogens are present in a β-amidoacrylamide-containing unit (**1a**) located at one terminus of the molecule.[3,5,6] Unit **1a** contains the λ_{263} chromophore.[2]



We report here that a third nitrogen, which accounts for the basicity of palytoxin, is present as a primary amino group in a unit (**1b**) situated at the other end of the molecule.

Treatment of palytoxin from Hawaiian or Tahitian *Palythoa* with *p*-bromobenzoic ethylcarbonic anhydride[7] in aqueous acetone at 0 °C leads to *N*-(*p*-bromobenzoyl)palytoxin. Oxidation of the derivatized toxin (25 mg) with $NaIO_4$ (50 mg) in H_2O at 0 °C for 9 min followed by $NaBH_4$ reduction of the resulting aldehydes and subsequent acetylation (Ac_2O/pyridine/N_2) of the alcohols gives a mixture of acetates which are separable by LC (silica gel, EtOAc to 5% EtOH–EtOAc). The degradation product possessing the *N*-*p*-bromobenzoyl group is a crystalline diacetate, mp

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(2) Moore, R. E.; Dietrich, R. F.; Hatton, B.; Higa, T.; Scheuer, P. J. *J. Org. Chem.* **1975**, *40*, 540.
(3) Moore, R. E.; Woolard, F. X.; Sheikh, M. Y.; Scheuer, P. J. *J. Am. Chem. Soc.* **1978**, *100*, 7758.
(4) Macfarlane, R. D.; Uemura, D.; Ueda, K.; Hirata, Y. *J. Am. Chem. Soc.* **1980**, *102*, 875.
(5) Hirata, Y.; Uemura, D.; Ueda, K.; Takano, S. *Pure Appl. Chem.* **1979**, *51*, 1875.
(6) The trisubstituted double bond is *E* since the ^{13}C NMR of palytoxin (Me_2SO-d_6) shows a signal at δ 12.70 for the olefinic methyl carbon.
(7) The mixed anhydride was prepared from triethylammonium *p*-bromobenzoate and ethyl chloroformate in wet acetone at 0 °C.

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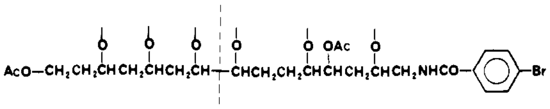
Table I. 600-MHz ^{1}H NMR Data for **2** in $CDCl_3$

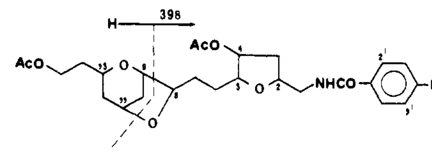
ppm[a]	no. of protons	assignment	multiplicity, J, Hz
7.628	2	2′,6′	d, $J_{2',3'} = J_{6',5'} = 8.5$
7.561	2	3′,5′	d, $J_{3',2'} = J_{5',6'} = 8.5$
6.457	1	NH	br t
5.320	1	4	br t
4.488	1	11[c]	br t, $J_{11,10A} = J_{11,12A} = 5.3, J_{11,12B} \sim 1$
4.335	1	2	m
4.191	1	8	dd, $J_{8,7A} = 5.6, J_{8,7B} = 8.4$
4.133	1	15A	dt, $J_{15A,15B} = -11.0, J_{15A,14A} = J_{15A,14B} = 6.3$
4.107	1	15B	dt, $J_{15B,15A} = -11.0, J_{15B,14A} = J_{15B,14B} = 6.3$
4.115	1	9[c]	br d, $J_{9,10A} \sim 2, J_{9,10B} \sim 1$
4.003	1	13[d]	ddt, $J_{13,12B} \sim 11, J_{13,14A}$ and $J_{13,14B} \sim 8$ and 4, $J_{13,12A} \sim 4$
3.991	1	5	ddd, $J_{5,6A} = 8.2, J_{5,6B} = 5.1, J_{5,4} = 3.4$
3.776	1	1A	ddd, $J_{1A,1B} = -13.9, J_{1A,NH} = 6.8, J_{1A,2} = 3.1$
3.301	1	1B	ddd, $J_{1B,1A} = -13.9, J_{1B,NH} = 4.8, J_{1B,2} = 7.9$
2.132	1	3A	br dd, $J_{3A,3B} = -14.4, J_{3A,2} = 6.8, J_{3A,4} \sim 1$
2.071	3	OAc	s
2.022	3	OAc	s
1.927	1	3B	ddd, $J_{3B,3A} = -14.4, J_{3B,2} = 9.0, J_{3B,4} = 5.0$
1.77[b]	1	6A	m
1.77[b]	1	10A[c]	m
1.77[b]	1	12A[c]	m
1.77[b]	2	14A,14B	m
1.709	1	10B[d]	br d, $J_{10B,10A} = -11.3, J_{10B,9} \sim 1$
1.536	1	6B	m, $J_{6B,6A} = -13.6,^e J_{6B,7A} = 10.8,^e J_{6B,7B} = 5.5,^e J_{6B,5} = 5.1$
1.448	1	7B	m, $J_{7B,7A} = -13.8,^e J_{7B,6A} = 10.4,^e J_{7B,6B} = 5.5,^e J_{7B,8} = 8.4$
1.362	1	7A	m, $J_{7A,7B} = -13.8,^e J_{7A,6A} = 5.3,^e J_{7A,6B} = 10.8,^e J_{7A,8} = 5.6$
1.315	1	12B[d]	br dd, $J_{12B,12A} = -13, J_{12B,13} = 10.9, J_{12B,11} \sim 1$

[a] Relative to Me_4Si ($\delta = 0$) or benzene ($\delta = 7.350$) as internal standard. [b] These signals separate in $CDCl_3$–C_6D_6 mixtures. [c] Equatorial. [d] Axial. [e] Values assessed by simulation of spectrum in 20% $C_6D_6/CDCl_3$.

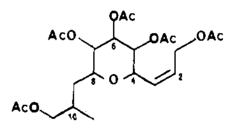
114–115.5 °C, which has the molecular formula $C_{26}H_{34}O_8NBr$ from mass spectral data.[8] Extensive ^{1}H NMR studies in $CDCl_3$ and $CDCl_3$–C_6D_6 mixtures at 360 and 600 MHz have established its structure. Spin–spin decoupling experiments generated sequences **2a** and **2b** which have to be connected via a C–C bond since the compound is not an acetal. Three ether rings are therefore present. Of the 15 possible gross structures, **2** fits the NMR (Table I) and MS[8] data best. The coupling constants for the protons on C-9, C-10, C-11, C-12, C-13 indicate that carbons 9–13 are in a tetrahydropyran ring in the chair conformation where the C-9 and C-11 protons are equatorial and the C-13 proton is axial. When C-11 and C-8 are joined in an ether ring and C-7 is exo on the resulting 2,6-dioxabicyclo[3.2.1]octane system, the dihedral angle between the C-8 and C-9 protons, which show no coupling to each other, is 90°. In addition, the dihedral angles between the C-10 axial and C-11 protons and between the C-12 axial and C-11 protons, which show 0 and 1 Hz couplings, are



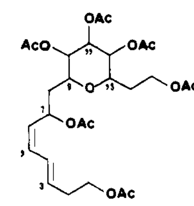
2a **2b**



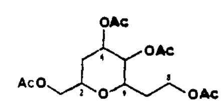
2



3



4



5

about 90° and 75°, respectively. The third ether ring therefore bridges C-2 and C-5. On this tetrahydrofuran ring C-1 is trans to both C-6 and the acetoxyl group on C-4, since the chemical shifts and coupling constants for the ring protons are very close to those reported for ring D of monensin.[9] The relative stereochemistry of **2** is therefore either $2S^*,4R^*,5R^*,8S^*,9R^*,11S^*,13S^*$ or $2R^*,4S^*,5S^*,8S^*,9R^*,11S^*,13S^*$.

We conclude from these data and from the fact that the precursor of **2** is a hydroxy aldehyde that palytoxin possesses partial structure **1b**. Units **1a** and **1b** appear to be present in all palytoxins. Between **1a** and **1b** are several units such as **1c**[3,10] and the three tetrahydropyran-containing units **1d**, **1e**, and **1f**.[10] Also found in the mixture of acetates mentioned above are **3**,[11,12] **4**,[13] and **5**.[12,14] All of the ring protons in **4** and all but one of the ring

(8) Field desorption MS (FDMS), m/e 568, 570 (M + 1) and 567, 569; high resolution electron ionization MS (EIMS) (relative intensity, composition), m/e 570.158 (0.3, $C_{26}H_{35}O_8N^{81}Br$), $C_{26}H_{35}O_8N^{81}Br$), (0.17, $C_{26}H_{34}O_8N^{81}Br$), 567.144 (0.11, $C_{26}H_{34}O_8N^{79}Br$), 453.092 (2.2, $C_{21}H_{26}O_5N^{81}Br$), 451.096 (2.5, $C_{21}H_{26}O_5N^{79}Br$), 400.057 (20, $C_{17}H_{21}O_5N^{81}Br$), 398.056 (20, $C_{17}H_{21}O_5N^{79}Br$), 340.037 (8, $C_{15}H_{17}O_3N^{81}Br$), 338.040 (7, $C_{15}H_{17}O_3N^{79}Br$), 308.164 (10, $C_{17}H_{24}O_5$), 295.154 (29, $C_{16}H_{23}O_5$), 248.140 (5, $C_{15}H_{20}O_3$), 239.127 (7, $C_{13}H_{19}O_4$), 235.132 (11, $C_{14}H_{19}O_3$), 141.093 (25, $C_8H_{13}O_2$), 137.061 (35, $C_8H_9O_2$), 125.059 (18, $C_7H_9O_2$), 123.044 (21, $C_7H_7O_2$), 109.065 (25, C_7H_9O), 95.049 (31, C_6H_7O), 81.034 (100, C_5H_5O).

(9) Anteunis, M. J. O. *Bull. Soc. Chim. Belg.* **1977**, *86*, 367.

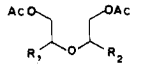
(10) The diene systems in **1c** and **1e** account for the two λ_{233} chromophores in the palytoxins.

(11) Compound **3**: FDMS, m/e 473 (M + 1); EIMS m/e (relative intensity), 472 (0.3, M$^+$), 412 (0.5), 370 (2), 352 (7), 310 (5), 301 (6), 294 (5), 292 (17), 250 (16), 237 (7), 199 (25), 195 (12), 139 (11), 43 (100); high-resolution EIMS m/e 352.152 ($C_{18}H_{24}O_7$), 292.131 ($C_{16}H_{20}O_5$), 310.140 ($C_{16}H_{22}O_6$), 250.121 ($C_{14}H_{18}O_4$), 237.077 ($C_{12}H_{13}O_5$); ^{1}H NMR ($CDCl_3$) δ 5.77 (dt, J = 11 and 5.5 Hz, C-2 H), 5.58 (dd, J = 11 and 7.5 Hz, C-3 H), 5.32 (t, J = 8.5 Hz, C-6 H), 5.07 (dd, J = 8.5 and 5.5 Hz, C-7 H), 4.86 (t, J = 8.5 Hz, C-5 H), 4.69 (dd, J = −12.5 and 5.5 Hz, C-1 H), 4.61 (dd, J = −12.5 and 5.5 Hz, C-1 H), 4.46 (dd, J = 8.5 and 7.5 Hz, C-4 H), 4.28 (ddd, J = 9, 5.5, and 3.5 Hz, C-8 H), 3.96 (d, J = 6 Hz, C-11 2H), 2.09 (s, OAc), 2.07 (s, OAc), 2.06 (s, OAc), OAc), (s, OAc), 2.02 (s, OAc), 2.05 (m, C-9 H and C-10 H), 1.25 (m, C-9 H), 0.93 (d, 6.5 Hz, Me on C-10).

(12) The structures of **3** and **5** are also supported by chemical evidence described by F. X. Woolard and R. E. Moore at the 177th National Meeting of the American Chemical Society, Honolulu, Hawaii, April 1979; American Chemical Society: Washington, DC, 1979; Abstract ORGN 564.

(13) Compound **4**: FDMS, m/e 570 (M$^+$); EIMS m/e (relative intensity) 528 (22, M − CH_2CO), 486 (8), 468 (77, M − CH_2CO − HOAc), 408 (20, M − CH_2CO − 2HOAc), 348 (12, M − CH_2CO − 3HOAc), 330 (18, M − 4HOAc), 288 (31, M − CH_2CO − 4HOAc), 270 (9, M − 5HOAc), 228 (24, M − CH_2CO − 5HOAc), 210 (16, M − 6HOAc), 123 (100), 107 (84); high resolution EIMS m/e 528.218 ($C_{25}H_{36}O_{12}$), 468.203 ($C_{23}H_{32}O_{10}$), 270.128 ($C_{17}H_{18}O_3$), 123.044 ($C_7H_7O_2$); ^{1}H NMR (30% $CDCl_3/C_6D_6$) δ 6.655 (br dd, J = 15.5 11 Hz, C-4 H), 6.113 (td, J = 9.5 and 3 Hz, C-7 H), 5.990 (t, J = 11 Hz, C-5 H), 5.58 (dt, J = 15.5 and 7 Hz, C-3 H), 5.267 (t, J = 9.5 Hz, C-11 H), 5.230 (br t, J = 11 Hz, C-6 H), 4.942 (t, J = 9.5 Hz, C-10 or C-12 H), 4.939 (t, J = 9.5 Hz, C-10 or C-12 H), 4.28 (m, C-15 H), 4.24 (m, C-15 H), 4.016 (t, J = 6.7 Hz, 2H on C-1), 3.381 (td, J = 9.5 and 2.5 Hz, C-9 H), 3.369 (td, J = 9.5 and 2.5 Hz, C-13 H), 2.340 (br quartet, J = 7 Hz, 2H on C-2), 1.92 (ddd, J = −13, 9.5, and 2.5 Hz, C-8 H), 1.867 (s, OAc), 1.862 (s, OAc), 1.845 (s, OAc), 1.800 (s, OAc), 1.765 (s, OAc), 1.753 (s, OAc), 1.64 (ddd, J = −13, 9.5, and 3 Hz, C-8 H), 1.6–1.9 (m, 2H on C-14).

protons in **3** and **5** are axial since the coupling constants are 7.2–9.5 Hz; the C-8 H in **3** and C-2 H in **5**, however, are equatorial as $J_{8,7}$ in **3** and $J_{2,3ax}$ and $J_{2,3eq}$ in **5** are 5–5.5 Hz. Since palytoxin possesses only one $-CH_2O-$ carbon, which is found in unit **1a**, the acetoxyl-bearing CH_2 carbons of **3**, **4**, and **5** are aldehydic carbons in the oxidation products and hydroxyl-bearing methine carbons in palytoxin. All of the –CHOAc– groups correspond to –CHOH– groups in palytoxin since compounds **6**, **7**,[15] and *meso*-**8** are formed instead of **3**, **4**, and **5** if the oxidation period is longer.



6 R_1 = $AcOCH_2CHCH_3CH_2$; R_2 = $CH\overset{c}{=}CHCH_2OAc$

7 R_1 = $AcOCH_2CH\overset{t}{=}CHCH\overset{t}{=}CHCHOAcCH_2$; R_2 = CH_2CH_2OAc

8 R_1 = R_2 = CH_2CH_2OAc

Unit **1g** may exist in palytoxin from Okinawan *P. tuberculosa*, but it is not present in the palytoxins from *P. toxica* and the Tahitian *Palythoa* sp. since we have been unable to convert them to the tetraacetate described by Hirata et al.[5] High-frequency ^{1}H NMR studies[16] indicate the presence of the *trans*-ĊH—CH=CH—ĊH(CH_3)- portion of **1g**, however, suggesting that our palytoxins have structural differences in **1g**. Moreover, the NMR signals for the olefinic protons and the methyl group are doubled, signifying that our palytoxins are two-component mixtures and that the components differ in structure **1g**.

Units **1a–1f** account for $C_{75}H_{125}O_{31}N_3$ of the palytoxins. If one also considers unit **1g** and the compositions of two other cyclic ether-containing units which we will describe shortly,[16] then at least an additional $C_{48}H_{90}O_{16}$ is accounted for. At this time we do not have enough information to determine the molecular formula of any of the palytoxins; however, there is little doubt that all previously suggested formulas[3-5] are incorrect.

Acknowledgment. This research was supported by Grant No. CA12623-07, awarded by the National Cancer Institute, Department of Health, Education, and Welfare. NMR studies at 360 MHz were carried at the Stanford Magnetic Resonance Laboratory under the auspices of NSF Grant No. GP-23633 and NIH Grant No. RR00711. The 600-MHz NMR studies at Carnegie–Mellon University were supported by NIH Grant No. RR00292. We thank Mr. K. Lee and Professors A. A. Bothner-By and J. Datok for their assistance. We also thank Dr. K. Straub at the University of California Bio-organic, Biomedical Mass Spectrometry Resource (A. L. Burlingame, Director), supported by NIH Grant No. RR00719, for determining the field desorption and high resolution electron ionization mass spectra.

(14) Compound **5**: FDMS, *m/e* 360 (M^+); ^{1}H NMR (C_6D_6) δ 5.330 (ddd, J = 9.0, 7.2, and 5.0 Hz, C-4 H), 5.061 (t, J = 7.2 Hz, C-5 H), 4.524 (dd, J = −11.9 and 8.7 Hz, C-1 H), 4.40 (m, C-8 H), 4.35 (m, C-8 H), 4.07 (m, C-6 H), 4.037 (br sextet, J = 8.7, 5, 5, and 3.8 Hz, C-2 H), 2.07 (m, C-7 H), 2.02 (m, C-7 H), 1.954 (s, OAc), 1.918 (s, OAc), 1.84 (m, equatorial C-3 H), 1.825 (s, OAc), 1.814 (s, OAc), 1.69 (ddd, J = −14, 9.0, and 5 Hz, axial C-3 H).

(15) The Δ^5-cis double bond in **1e** isomerizes to trans during long-term oxidation.

(16) In collaboration with J. Ford and A. A. Bothner-By, Carnegie-Mellon University, and K. Straub and A. L. Burlingame, University of California.

Richard E. Moore,* Frank X. Woolard, Giovanni Bartolini
Department of Chemistry, University of Hawaii
Honolulu, Hawaii 96822

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Structural and Spectroscopic Evidence That Cobalt to Carbon Bond Lengths Are Influenced by Conformational Effects in Cobaloximes. The Longest Co–C Bond in a Vitamin B_{12} Model: *trans*-Bis(dimethylglyoximato)(isopropyl)(triphenylphosphine)cobalt(III)

Sir:

Cobalt–carbon bond cleavage is widely believed to be an essential feature of the mechanism of action of coenzyme B_{12}–enzyme complexes.[1-3] Two fundamental questions which arise are the following: (1) What factors induce or "trigger" the cleavage reaction? (2) What is the nature of the intermediate formed? In secondary alkyl organocobalt compounds of this general type, the organic products of the cleavage reaction are olefins,[4,5] possibly produced either by a concerted β-hydride abstraction (leading to $Co^{III}H$ which eventually gives Co(II) and $^1/_2H_2$) or by a homolytic cleavage, yielding Co(II) and R· with subsequent H abstraction. The specific nature of this important reaction is under active investigation in several laboratories.[4,5]

Conformational changes induced in the coenzyme by the enzymes may be the responsible trigger mechanism. The instability of sterically crowded alkylcobalamins[4] may result either from conformational changes in the corrin ring brought about by the bulky alkyl group or from weakening (lengthening) of the Co–C bond induced by steric crowding or from a combination of both effects. However, even in unstrained environments, the corrin ring system in cobalamins and related compounds deviates quite appreciably from planarity,[6] and an assessment of further distortions may prove difficult.

Cobaloximes (the trivial name for complexes with the bis(dimethylglyoximato)cobalt unit, $Co(DH)_2$) have a relatively planar $Co(DH)_2$ unit in both $pyCo(DH)_2CH_3$ and $pyCo(DH)_2$-*i*-C_3H_7.[7] The Co–C bond length in the latter compound is ~0.1 Å longer than in the former. In this report, we investigate the influence of conformational distortion of the $Co(DH)_2$ unit on Co–C bond lengths and provide evidence that such a distortion does lead to increased Co–C bond lengths and that the basis of the effect is steric and not electronic. The compound *trans*-bis(dimethylglyoximato)(isopropyl)(triphenylphosphine)cobalt(III) (**1**) has by far the longest Co–C bond length discovered to date. Spectroscopic data (^{1}H NMR) are presented for this and related compounds which we interpret as suggesting that even longer Co–C bond lengths probably exist. However, these latter compounds have so far proved to be too unstable to obtain satisfactory crystals.

1, prepared by standard procedures,[7] crystallizes from acetone/H_2O (in the dark) in the monoclinic space group $P2_1$ with a = 10.536 (8), b = 15.918 (9), c = 8.906 (7) Å, β = 100.6 (1)° (Mo Kα), and Z = 2 formula units of $CoPO_4N_4C_{29}H_{36}$; observed and calculated densities are 1.34 and 1.35 g cm^{-3}, respectively. Three-dimensional X-ray diffraction data were collected on an automated SIEMENS-AED diffractometer by using Mo Kα radiation and a θ–2θ scan technique. The structure was solved by Patterson and Fourier methods and refined by the least-squares method with anisotropic temperature factors for Co, P, N, and O atoms to a final conventional R value of 0.058. The hydrogen atoms of the dioxime bridges were refined isotropically, while those belonging to the DH units and $(C_6H_5)_3P$ ligand were included with constant contribution (B = 5.0 Å^2). No attempt to locate the isopropyl hydrogen atoms was made owing to the high thermal motion of the ligand.[8] A total of 1147 independent reflections having $\theta_{max} \leq 25°$ and $I > 3\sigma(I)$ was used in the final calculations, since all crystals examined exhibited a significant falling off of intensities with increasing Bragg angle. No absorption correction was applied (μ(Mo Kα) = 9 cm^{-1}, 0.01 < r < 0.02 cm).

The crystals consist of discrete $(C_6H_5)_3PCo(DH)_2$(*i*-C_3H_7) units (Figure 1). The Co–C bond length of 2.22 (2) Å is even longer

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(8) The strong thermal motion of *i*-C_3H_7, especially its methyl groups, affects the accuracy of the Co(*i*-C_3H_7) fragment. However, the C–Me bond lengths of 1.49 (3) and 1.58 (5) Å and the bond angles Co–C–Me of 112 (2)° and 118 (2)° as well as the Me-C-Me angle of 113 (2)° are in agreement within experimental error with the values reported for $pyCo(DH)_2$-*i*-C_3H_7.[7]

