Appendix II

The distribution of magnetic field intensity H for a sphere of radius r_0 in a uniform external field H_0 can be expressed as[20]

$$r \geqslant r_0$$

$$\psi = -H_0 r \cos\theta +$$

$$\{(\mu_s - \mu_m)/(\mu_s + 2\mu_m)\} \frac{r_0{}^3}{r^2} H_0 \cos\theta \quad (A5)$$

$$r \leqslant r_0$$

$$\psi = -3\mu_m H_0 r \cos\theta/(\mu_s + 2\mu_m) \quad (A6)$$

$$H = -\nabla\psi$$

ψ is a scalar potential, γ is the distance from the center of the sphere O to the point of interest P, θ is the angle between the vector OP and the direction of the uniform field H_0, and μ_s and μ_m are the magnetic permeabilities of the sphere and the medium, respectively. The field gradient exists three dimensionally. But for the purposes of approximation and mathematical simplicity, only the most important z component will be considered. The gradient of this component is considered as a major cause for the diffusion effect in spin–echo experiments. From eq A5 and A6

$$\frac{\partial H_z}{\partial Z} = G_z = (H_0 A/r_0{}^4)(9\cos\theta - 15\cos^3\theta)$$

$$r \geqslant r_0 \quad (A7)$$

where $A = (\mu_s - \mu_m)r_0{}^3/(\mu_s - 2\mu_m)$. Or, since $\mu = 1 + 4\pi\psi_v$

$$A = 4\pi r_0{}^3(\chi_{v,s} - \chi_{v,m})/\{3 + 4\pi(\chi_{v,s} - 2\chi_{v,m})\}$$

(20) D. Menzel, "Fundamental Formulas of Physics," Prentice-Hall, New York, N. Y., 1955, pp 315 and 325.

Here $\chi_{v,s}$ and $\chi_{v,m}$ are magnetic volume susceptibilities of the sphere and the medium, respectively. Coordinate transformation is necessary to obtain eq A7. The volume average field gradient from the surface ($r = r_0$) to a location r can be obtained by the following integration. Since the gradient is symmetric with respect to the plane of $\theta = \pi/2$, the integration has to be done over only half of the sphere.

$$\bar{G}_z = \frac{\int^{\pi/2} \int^{2\pi} \int^r G_z r^2 \sin\theta \, dr d\theta d\varphi}{\iiint r^2 \sin\theta \, dr d\theta d\varphi} =$$

$$(9/4)H_0 A\left(\frac{1}{r^2 + rr_0 + r_0{}^2}\right)\left(\frac{1}{rr_0}\right) \quad (A8)$$

Appendix III

The constant total sample volume detected by the receiver coil can be expressed as a function of bead radius r_i, filling factor ϵ, and total number of beads N_i. The filling factor was 0.62 for all sizes of beads.

$$V = 4\pi r_i{}^3 N_i/3\epsilon$$

The total surface area of all the beads in volume V is

$$A = 4\pi r_i{}^2 N_i$$

$$= 3V\epsilon/r_i$$

A is inversely proportional to the diameter of the bead. The average thickness of the water (or void space) can be approximated by dividing the total void volume by total surface area.

$$(\bar{r} - r_i) = V(1 - \epsilon)/A$$

$$= 3V\epsilon/r = 0.204r_i \quad (A9)$$

Crystal and Molecular Structure of C$_{14}$O$_7$NH$_{21}$, 1-Acetyl-*trans*-3,*trans*-4-isopropylidenedioxy-*cis*-4-acetoxymethyl-2-acetoxypyrrolidine

Yuan-yuan H. Chiu and William N. Lipscomb*

Contribution from the Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138. Received September 6, 1973

Abstract: The compound C$_{14}$H$_7$NH$_{21}$, a branched-chain sugar containing nitrogen as the heteroatom of the ring, shows an equilibrium between two conformers in which the 1-acetyl group bonded to N is cis, with the CH$_3$ near C$_2$ and O near C$_5$, or trans, with the CH$_3$ near C$_5$ and O near C$_2$. The structure of the more stable isomer, which is crystalline, is shown to have the cis conformation. The absolute configuration of the molecule was not established. There are four molecules in an orthorhombic unit cell having dimensions $a = 11.843$, $b = 16.393$, and $c = 8.246$ Å. The space group is $P2_12_12_1$, and the final value of $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ is 0.084 for the 1153 independent X-ray diffraction maxima.

A s part of an effort to synthesize *N*-acetylpyrrolidines and their nucleosides, Halford, Ball, and Long have prepared a branched-chain sugar having nitrogen as the heteroatom of the ring,[1,2] 1-acetyl-*trans*-3,*trans*-

4-isopropylidenedioxy-*cis*-4-acetoxymethyl-2-acetoxypyrrolidine (NAP). This molecule contains an N–C–O linkage characteristic of amides and polypeptides. Two isomers exist in solution, related by a high barrier

(1) M. H. Halford, D. H. Ball, and L. Long, *Chem. Commun.*, 255 (1969).

(2) D. H. Ball, F. A. Carey, I. L. Klundt, and L. Long, *Carbohyd. Res.*, 10, 121 (1969).
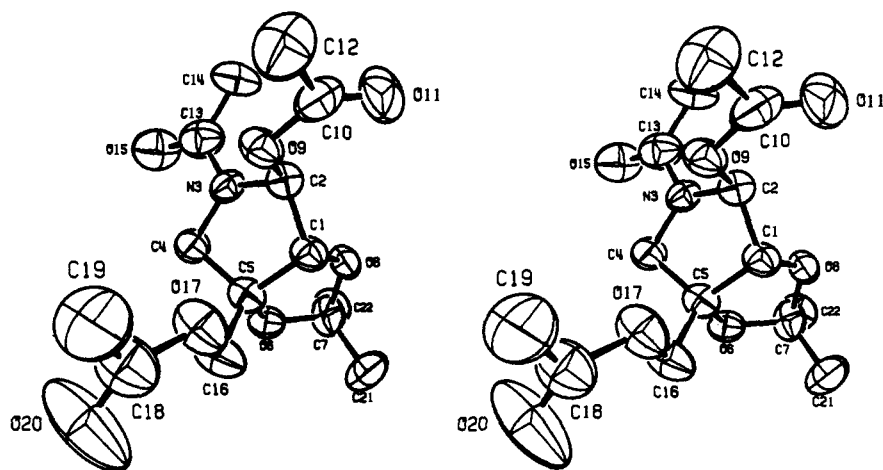
Figure 1. Stereoscopic showing of the molecule and numbering scheme for $C_{14}O_7NH_{21}$.

$(E_a = 19 \text{ kcal/mol})$ to rotation about this C–N bond.[3] The present X-ray diffraction study of crystalline conformer (I) was carried out to establish the configuration of the N-acetyl group about its C–N bond. We also confirm other aspects of the stereochemistry assigned in the chemical and nmr studies.[1-3]

Structure Determination

The colorless, plate-like crystals showed orthorhombic diffraction symmetry and have unit cell dimensions of $a = 11.843$ (3), $b = 16.393$ (2), and $c = 8.246$ (2) Å, where the error in the last digit is indicated in parentheses. These dimensions were determined from scattering angles measured on the Buerger automatic diffractometer with the use of Cu $K\alpha$ radiation. A least-squares procedure was used to minimize

$$\sum_{n=1}^{M} w_n(\sin \theta_{\text{obsd}} - \sin \theta_{\text{calcd}})^2$$

where w_n is $(\sin \theta_{\text{obsd}})^{-2}$, and M is the total of 54 reflections employed for unit cell calibration. Weissenberg films showed systematic absences only of $h00$ when h is odd, of $0k0$ when k is odd, and of $00l$ when l is odd, consistent with $P2_12_12_1$ as the most probable space group. Hence, there are $4m$ molecules in the unit cell, but only the case $m = 1$ yields a reasonable calculated density of 1.375 g cm^{-3}.

Integrated intensities were measured using Weissenberg geometry and ω scan on a Supper-Pace automatic Buerger diffractometer. A scintillation counter recorded the scattered Cu $K\alpha$ radiation which had been filtered through Ni foil. Two crystals were employed in the collection of 1359 nonzero independent X-ray diffraction maxima. Levels hkL for $0 \leqslant L \leqslant 7$ and Hkl for $0 \leqslant H \leqslant 4$ were recorded. Errors were assigned empirically as 0.02 times the uncorrected intensity plus the square root of the sum of peak and background counts. After correction for Lorentz and polarization factors, the data were correlated by least-squares procedures in which the function[4]

$$R = \sum_{hi,hj} W_{hij}(\ln S_i I_{hi} - \ln S_j I_{hj})^2$$

was minimized. Here, S_i is the scale factor for the ith set, I_{hi} is the intensity of reflection h in the ith set $W_{hij} = (\sigma_{hi}^2 + \sigma_{hj}^2)^{-1}$, and σ_{hi} is the statistical error in I_{hi}. The correlation factor

$$R_c = \frac{\sum_h |I_{hi} - I_{hj}|}{\sum_h |I_{hi} + I_{hj}|}$$

is 0.047 for these data. An initial estimate, by Wilson's method, of the scale factor was refined later by least-squares procedures.

Attempts to solve this structure by symbolic addition procedures[5] failed, possibly due to the relatively low E values of the centrosymmetric reflections, where

$$|E_H|^2 = |F_H|^2/[\epsilon \sum_{j=1}^{N} f_{jH}^2]$$

In this expression the structure factor $|F_H|$ for $H = hkl$ has been corrected for thermal motion, f_{jH} are the atomic scattering factors, N is the number of atoms per unit cell, and ϵ is 2 for $h00$, $0k0$, and $00l$ but 1 for all other hkl.

The structure was solved using the MULTAN program[6,7] using the starting set

hkl	E	ϕ
11.6.0	3.45	$\pi/2$
3.13.3	2.50	$\pi/4$
327	3.23	$\pm\pi/4, \pm3\pi/4$
622	2.08	$\pm\pi/4, \pm3\pi/4$
221	2.43	$\pm\pi/4, \pm3\pi/4$

where 11.6.0 is fixed by the choice of origin and 3.13.3 determines the enantiomorph. Some 120 reflections having $E \geqslant 1.50$ were phased by iterative use of the weighted tangent formula. The E map having the highest figure of merit revealed all 22 nonhydrogen atoms, two of which were weak but at chemically reasonable locations (12 and 22). Because the identity of CH_3 and O of the three acetyl groups is not clear at this stage, these six first-row atoms were given scattering factors of nitrogen (atoms 11, 12, 14, 15, 19, and 20 of Figure 1),[8] and, of course, hydrogen atoms were omitted

(3) C. H. Bushweller, J. W. O'Neil, M. H. Halford, and F. H. Bissett, *J. Amer. Chem. Soc.*, **93**, 1471 (1971).

(4) (a) P. G. Simpson, Ph.D. Thesis, Harvard University, 1963; (b) A. D. Rae, *Acta Crystallogr.*, **19**, 683 (1965); (c) A. D. Rae and A. B. Blake, *ibid.*, **20**, 586 (1966).

(5) J. Karle and I. L. Karle, *Acta Crystallogr.*, **21**, 849 (1966).

(6) G. Germain, P. Main, and M. M. Woolfson, *Acta Crystallogr., Sect. B*, **26**, 274 (1970).

(7) G. Germain, P. Main, and M. M. Woolfson, *Acta Crystallogr., Sect. A*, **27**, 368 (1971).

(8) The numbering system of Figure 1 is different from the chemical nomenclature in that C_5 (chemical) is C(4) in Figure 1.

Table I. Final Positional Parameters of the Molecule with Standard Deviations in Parentheses

Atoms	x	y	z
C(1)	0.6879 (7)	0.2741 (5)	0.5213 (10)
C(2)	0.6471 (7)	0.1858 (5)	0.5217 (10)
N(3)	0.5448 (6)	0.1884 (4)	0.6180 (8)
C(4)	0.4851 (7)	0.2654 (5)	0.5974 (11)
C(5)	0.5808 (7)	0.3261 (5)	0.5618 (9)
O(6)	0.6127 (5)	0.3683 (3)	0.7085 (7)
C(7)	0.7319 (7)	0.3617 (6)	0.7323 (11)
O(8)	0.7597 (5)	0.2853 (3)	0.6569 (7)
O(9)	0.6124 (5)	0.1624 (3)	0.3573 (7)
C(10)	0.6921 (7)	0.1235 (5)	0.2675 (11)
O(11)	0.7844 (5)	0.1110 (4)	0.3150 (8)
C(12)	0.6440 (8)	0.1041 (6)	0.1015 (10)
C(13)	0.4932 (9)	0.1211 (6)	0.6862 (12)
C(14)	0.5559 (10)	0.0416 (5)	0.6829 (13)
O(15)	0.4002 (6)	0.1306 (4)	0.7468 (8)
C(16)	0.5435 (9)	0.3905 (5)	0.4424 (10)
O(17)	0.5299 (5)	0.3474 (4)	0.2862 (7)
C(18)	0.4491 (9)	0.3747 (6)	0.1882 (11)
C(19)	0.4423 (10)	0.3270 (6)	0.0395 (12)
O(20)	0.3906 (8)	0.4310 (5)	0.2223 (9)
C(21)	0.7985 (9)	0.4302 (6)	0.6428 (15)
C(22)	0.7505 (9)	0.3580 (6)	0.9104 (11)

finements the nitrogen scattering factors were replaced by O and C, except for the pair of greatest interest (14 and 15) which were left as N until later. Three cycles of refinement with isotropic thermal parameters ($R = 0.16$), followed by refinement using anisotropic thermal parameters, reduced R to 0.11. A three-dimensional difference electron density map revealed six nonmethyl hydrogen atoms, and after further refinement, a difference map showed three hydrogen atoms bonded to atom 14 but none to atom 15. Assignment of scattering factors of carbon to 14 and oxygen to 15, followed by further least-squares refinement, yielded $R = 0.10$. Location of all hydrogens, some disordered, in a final difference electron density followed by further refinement and a correction of a few large reflections[9] for secondary extinction gave the final value of R as 0.084 (Table I). The value of $R_w = \Sigma w[|F_o|^2 - |F_c|^2]^2/\Sigma w \cdot |F_o|^4$ is 0.023.

Results and Discussion

Positional parameters are given for nonhydrogen atoms (Table I). We also give their thermal parameters

Table II. Final Thermal Parameters as $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$ with Standard Deviations in Parentheses

Atoms	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	0.0077 (13)	0.0033 (6)	0.0134 (24)	0.0010 (18)	−0.0007 (33)	−0.0032 (25)
C(2)	0.0073 (12)	0.0035 (6)	0.0112 (24)	−0.0002 (17)	0.0006 (34)	−0.0002 (23)
N(3)	0.0070 (9)	0.0032 (5)	0.0151 (21)	−0.0022 (13)	0.0022 (29)	−0.0001 (19)
C(4)	0.0065 (12)	0.0034 (6)	0.0178 (26)	0.0006 (16)	0.0043 (32)	−0.0042 (23)
C(5)	0.0081 (14)	0.0035 (6)	0.0099 (20)	0.0013 (17)	−0.0015 (33)	−0.0026 (24)
O(6)	0.0093 (9)	0.0034 (4)	0.0141 (17)	0.0004 (12)	−0.0003 (25)	−0.0014 (17)
C(7)	0.0074 (12)	0.0059 (8)	0.0157 (27)	−0.0002 (20)	−0.0075 (33)	−0.0048 (28)
O(8)	0.0058 (7)	0.0036 (4)	0.0172 (17)	0.0015 (10)	−0.0044 (24)	−0.0053 (16)
O(9)	0.0082 (9)	0.0036 (4)	0.0144 (17)	0.0019 (12)	0.0007 (23)	−0.0031 (16)
C(10)	0.0095 (14)	0.0041 (6)	0.0187 (27)	−0.0050 (19)	0.0099 (37)	−0.0062 (24)
O(11)	0.0086 (10)	0.0073 (6)	0.0212 (20)	0.0016 (14)	0.0070 (27)	−0.0103 (20)
C(12)	0.0106 (16)	0.0067 (9)	0.0102 (23)	−0.0034 (22)	0.0020 (35)	−0.0057 (27)
C(13)	0.0134 (18)	0.0049 (7)	0.0163 (29)	−0.0007 (22)	−0.0046 (43)	−0.0029 (28)
C(14)	0.0160 (21)	0.0033 (7)	0.0214 (35)	0.0021 (21)	0.0053 (54)	−0.0013 (29)
O(15)	0.0136 (12)	0.0057 (5)	0.0230 (23)	−0.0025 (16)	0.0143 (35)	0.0017 (23)
C(16)	0.0138 (17)	0.0043 (7)	0.0109 (22)	0.0045 (21)	−0.0124 (38)	−0.0029 (26)
O(17)	0.0113 (10)	0.0058 (5)	0.0118 (16)	0.0046 (13)	−0.0060 (25)	−0.0018 (19)
C(18)	0.0128 (17)	0.0063 (10)	0.0141 (27)	0.0025 (23)	−0.0050 (44)	0.0025 (30)
C(19)	0.0139 (20)	0.0059 (8)	0.0181 (30)	0.0008 (25)	−0.0064 (50)	−0.0053 (29)
O(20)	0.0300 (17)	0.0120 (8)	0.0236 (24)	0.0254 (18)	−0.0289 (49)	−0.0128 (50)
C(21)	0.0114 (18)	0.0051 (8)	0.0276 (42)	−0.0058 (20)	0.0009 (50)	0.0036 (33)
C(22)	0.0119 (15)	0.0060 (8)	0.0149 (26)	0.0013 (23)	−0.0129 (36)	−0.0027 (27)

until later. At this stage a value of $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.33$ was obtained, assuming a value of 5.0 Å^2 for isotropic thermal parameters of all atoms. All further calculations included only those 1153 reflections greater than 3σ. Three cycles of least-squares refinement of scale, positional, and isotropic thermal parameters reduced R to 0.18. The function which was minimized was $\Sigma w[|F_o|^2 - |F_c|^2]^2$, where $w = |F_o|^{-2}$ for all $|F_o| \geqslant 10.8$ (400 reflections), $w = (10.8)^{-1}|F_o|^{-1}$ for $10.8 \geqslant |F_o| \geqslant 2.7$ (728 reflections), and $w = (2.7)^{-2}$, i.e., constant, for all $|F_o| \leqslant 2.7$ (25 reflections).

The identities of CH$_3$ and O of all acetyl groups were then clear. Atom 11 ($B = 2.6$ Å^2, 1.12 Å from 10), atom 20 ($B = 5.9$ Å^2, 1.27 Å from 18), and atom 15 ($B = 2.7$ Å^2, 1.18 Å from 13) were all assigned as oxygen. Atoms 12 ($B = 5.1$ Å^2, 1.61 Å from 10), 19 ($B = 5.1$ Å^2, 1.77 Å from 18), and 14 ($B = 4.3$ Å^2, 1.69 Å from 13) were assigned as methyl groups. Hence, in further re-

(Table II) and hydrogen atom coordinates (Table III). Bond distances (Table IV) and angles (Table V) exclude the hydrogen atoms. The C–H distances vary from 1.00 to 1.06 Å but are comparatively unreliable and systematically short.[10] A stereoview of the molecular structure is shown in Figure 1, and a view of the crystal structure along the c axis is given in Figure 2.

The peptide-like C(13)–N(3) bond of 1.38 Å is the most interesting feature. Although it is longer than the characteristic or standard peptide bond distance of 1.32 Å,[11] it is actually in very good agreement with the value of 1.376 ± 0.010 Å found in formamide.[12] In

(9) See paragraph at end of paper regarding supplementary material.
(10) T. A. Halgren, R. J. Anderson, D. S. Jones, and W. N. Lipscomb, *Chem. Phys. Lett.*, **8**, 547 (1971).
(11) L. Pauling and R. B. Corey, *Proc. Nat. Acad. Sci. U. S.*, **37**, 235 (1951).
(12) C. C. Costain and J. M. Dowling, *J. Chem. Phys.*, **32**, 158 (1960).

Table III. Positional Parameters[a] of Hydrogens

H atoms	Bonded to	Pop.	x	y	z
H(23)	C(1)	1.0	0.723	0.293	0.415
H(24)	C(2)	1.0	0.701	0.146	0.587
H(25)	C(4)	1.0	0.432	0.259	0.500
H(26)	C(4)	1.0	0.428	0.281	0.687
H(27)	C(16)	1.0	0.469	0.408	0.500
H(28)	C(16)	1.0	0.616	0.422	0.407
H(29)	C(12)	0.5	0.690	0.135	0.016
H(29')	C(12)	0.5	0.706	0.083	0.029
H(30)	C(12)	0.5	0.653	0.044	0.078
H(30')	C(12)	0.5	0.579	0.062	0.115
H(31)	C(12)	0.5	0.560	0.119	0.101
H(31')	C(12)	0.5	0.616	0.157	0.049
H(32)	C(14)	1.0	0.638	0.048	0.741
H(33)	C(14)	1.0	0.575	0.026	0.566
H(34)	C(14)	1.0	0.516	−0.004	0.748
H(35)	C(19)	0.5	0.485	0.357	−0.058
H(35')	C(19)	0.5	0.523	0.328	−0.023
H(36)	C(19)	0.5	0.485	0.271	0.050
H(36')	C(19)	0.5	0.424	0.267	0.058
H(37)	C(19)	0.5	0.362	0.318	−0.013
H(37')	C(19)	0.5	0.384	0.352	−0.044
H(38)	C(21)	1.0	0.876	0.436	0.698
H(39)	C(21)	1.0	0.751	0.480	0.663
H(40)	C(21)	1.0	0.797	0.422	0.523
H(41)	C(22)	1.0	0.835	0.344	0.938
H(42)	C(22)	1.0	0.701	0.318	0.967
H(43)	C(22)	1.0	0.741	0.419	0.962

[a] Positional parameters of hydrogens were obtained from successive difference Fourier maps.

Table IV. Bond Distances (Å) in the Molecule with Standard Deviations[a] in Parentheses

Bonds	Distances	Bonds	Distances
C(1)—C(2)	1.53 (1)	C(7)—C(21)	1.56 (1)
C(1)—C(5)	1.56 (1)	C(7)—C(22)	1.49 (1)
C(1)—O(8)	1.42 (1)	O(9)—C(10)	1.36 (1)
C(2)—N(3)	1.45 (1)	C(10)=O(11)	1.18 (1)
C(2)—O(9)	1.47 (1)	C(10)—C(12)	1.52 (1)
N(3)—C(4)	1.46 (1)	C(13)—C(14)	1.50 (1)
N(3)—C(13)	1.38 (1)	C(13)=O(15)	1.22 (1)
C(4)—C(5)	1.54 (1)	C(16)—O(17)	1.48 (1)
C(5)—O(6)	1.44 (1)	O(17)—C(18)	1.33 (1)
C(5)—C(16)	1.51 (1)	C(18)—C(19)	1.46 (1)
O(6)—C(7)	1.43 (1)	C(18)=O(20)	1.19 (1)
C(7)—O(8)	1.44 (1)		

[a] Standard deviations were calculated from the errors of atomic coordinates.

terms of the analysis of Winkler and Dunitz,[13] the out-of-plane deformation parameters are, for formamide and our compound (NAP), respectively 19 and 18° for χ_N, the angle between C(2)N(3)C(13) and C(4)N(13)C-(13) in NAP; 0 and 1° for χ_C, the angle between C(14)C-(13)N(3) and O(15)C(13)N(3) in NAP; and τ 2.5 and 0.5°, the mean of the two torsion angles C(14)C(13)N-(3)C(2) of 10° and O(15)C(13)N(3)C(4) of −9° in NAP. These last two torsion angles in formamide are 12° for HCNH″ and −7° for OCNH′, yielding the average of 2.5° for τ, as noted. Perhaps the rather long C–N bonds in these two compounds are reflected in the large nonplanarity at the N atom on which the lone pair is probably somewhat more localized than it is in the usual peptides.

We have here regarded this isomer of NAP as a cis-like peptide linkage. In the very strained trans pep-

(13) F. K. Winkler and J. D. Dunitz, *J. Mol. Biol.*, **59**, 169 (1971).
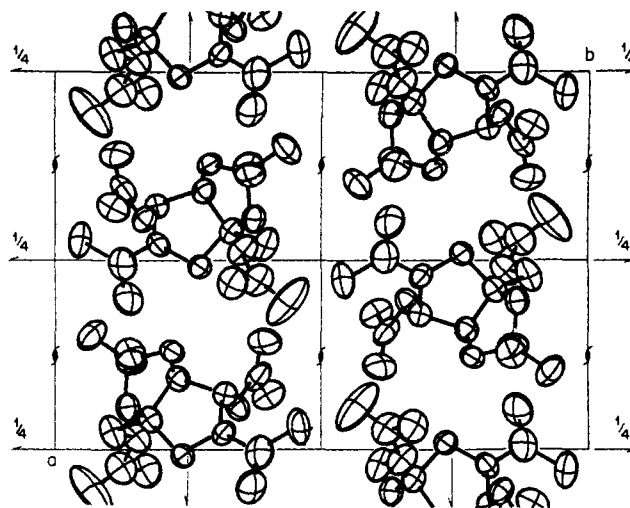
Figure 2. The packing of molecules in the unit cell, viewed along the c axis.

Table V. Bond Angles in the Molecule with Standard Deviations[a] in Parentheses

Angles	Degrees	Angles	Degrees
C(2)–C(1)–C(5)	105 (1)	O(6)–C(7)–C(21)	112 (1)
C(2)–C(1)–O(8)	108 (1)	O(6)–C(7)–C(22)	107 (1)
C(5)–C(1)–O(8)	104 (1)	O(8)–C(7)–C(21)	108 (1)
C(1)–C(2)–N(3)	104 (1)	O(8)–C(7)–C(22)	111 (1)
C(1)–C(2)–O(9)	110 (1)	C(21)–C(7)–C(22)	115 (1)
N(3)–C(2)–O(9)	106 (1)	C(1)–O(8)–C(7)	108 (1)
C(2)–N(3)–C(4)	112 (1)	C(2)–O(9)–C(10)	116 (1)
C(2)–N(3)–C(13)	125 (1)	O(9)–C(10)–O(11)	123 (1)
C(4)–N(3)–C(13)	122 (1)	O(9)–C(10)–C(12)	109 (1)
N(3)–C(4)–C(5)	103 (1)	O(11)–C(10)–C(12)	128 (1)
C(1)–C(5)–C(4)	107 (1)	N(3)–C(13)–C(14)	118 (1)
C(1)–C(5)–O(6)	103 (1)	N(3)–C(13)–O(15)	118 (1)
C(1)–C(5)–C(16)	119 (1)	C(14)–C(13)–O(15)	124 (1)
C(4)–C(5)–O(6)	110 (1)	C(5)–C(16)–O(17)	105 (1)
C(4)–C(5)–C(16)	111 (1)	C(16)–O(17)–C(18)	117 (1)
O(6)–C(5)–C(16)	107 (1)	O(17)–C(18)–C(19)	112 (1)
C(5)–O(6)–C(7)	110 (1)	O(17)–C(18)–O(20)	123 (1)
O(6)–C(7)–O(8)	103 (1)	C(19)–C(18)–O(20)	126 (1)

[a] Standard deviations were calculated from the errors of atomic coordinates.

tide bond of caprylolactam these out-of-plane deformation parameters are χ_N = 21.5°, χ_C = 5.5°, and τ 162°. This rather shorter bond, 1.336 Å in length, shows a large net torsion angle corresponding to a deviation of 18° from planarity, as well as a larger nonplanarity at N as compared with C.

Other aspects of the molecular structure appear to be quite normal in terms of previously known structures. For example, the bond angles N(3)C(13)C(14) = 118°, N-(3)C(13)O(15) = 118°, and C(14)C(13)O(15) = 124° are similar to the 117, 122, and 121° of the normal peptide linkage, respectively. We also note that the N(3)C(13)-C(14) angle of 118° in the peptide linkage is much larger than the angles O(9)C(10)C(12) of 109° and O(17)-C(18)C(19) of 112° of the other two acetyl groups. We note that in one oxygen linkage C(10)–O(9) = 1.36 Å is significantly shorter than C(2)–O(9) = 1.47 Å, and in the other oxygen linkage C(18)–O(17) = 1.33 Å is significantly shorter than C(16)–O(17) = 1.48 Å, perhaps due to delocalization of electrons by the carbonyls of the acetyl groups.

Details of the molecular packing, summarized in

Figure 2, show a shortest intermolecular C···C distance of 4.0 Å and a shortest intermolecular C···O contact of 3.3 Å. No abnormal van der Waals distances occur.

Crystal and Molecular Structure of the Radical Perchloratotetraphenylporphinatozinc(II)

Len D. Spaulding, P. G. Eller, J. A. Bertrand, and R. H. Felton*

Contribution from the School of Chemistry, Georgia Institute of Technology, Atlanta, Georgia 30332. Received October 9, 1973

Abstract: The X-ray crystal structure of the radical, perchloratotetraphenylporphinatozinc(II), has been determined by the heavy-atom method and refined to a final agreement factor, $R = 0.073$, for 2244 reflections greater than 3σ. The compound crystallizes in the space group $P2_1/c$, with $a = 13.638$ (4), $b = 13.017$ (5), $c = 20.452$ (8) Å, $\beta = 107.63$ (2)°, and $Z = 4$. The perchlorate group is covalently coordinated to the zinc with a Zn–O distance of 2.079 (8) Å, the shortest metal to oxygen (perchlorate) distance yet reported, and a Zn–O–Cl angle of 130.2 (5)°. Distances and angles within the porphyrin agree with those found for other metalloporphyrins. ESCA and ir data suggest that the molecule has an electronic distribution similar to that of neutral metalloporphyrins. Intermolecular interactions of the phenyl groups prevent the dimer formation observed in Zn or Mg octaethylporphyrin radicals. A model for these dimers is the recently proposed π-complex.

Zinc tetraphenylporphyrin (ZnTPP) is one of a number[1-4] of metalloporphyrins which possess the ability to undergo oxidation or reduction of the porphyrin moiety with apparently little or no change in the central metal substituent. Solution epr and optical investigations[5] of the singly oxidized species have affirmed the correctness of an assignment in which a single electron is removed from the highest filled molecular orbital (a_{2u}) of the porphyrin.

Notwithstanding the characterizations mentioned above, the X-ray determination of the ZnTPPClO₄ molecular structure was undertaken to answer the following questions. (1) The preference of zinc in the porphyrin complex to assume square-pyramidal five-coordinate geometry is satisfied in ZnTPP by neutral ligands such as water and pyridine.[6-8] Halides in solution with ZnTPP⁺· are known[9] to form 1:1 complexes and, in the absence of a stronger ligand, will perchlorate now assume the role of an axial ligand? (2) No evidence for dimer formation of ZnTPPClO₄ at low temperatures or in the solid state is found from epr or optical data, yet the analogous cation radicals of octaethylporphyrin Zn(II) or Mg(II) as the ClO₄⁻ or Br⁻ salts dimerize easily.[5,10] Can the phenyl rings sterically restrict dimer formation? (3) Does removal of a bonding electron affect significantly the molecular structure of the ring? (4) Are the physical properties of this model porphyrin radical, *i.e.*, crystalline order and stability to X-ray irradiation, well-behaved enough to attempt a similar study of the bacteriochlorophyll cation radical?

Experimental Section

ZnTPP was prepared by Adler's method.[11] The supporting electrolyte, tetra-*n*-propylammonium perchlorate, (Pr)₄N⁺ClO₄⁻, was synthesized using the procedure of House.[12] Dichloromethane was fractionally distilled from CaH₂ and stored over molecular sieves. Hexane was fractionally distilled and stored over molecular sieves.

The previously reported synthesis of ZnTPPClO₄ was modified slightly. A 0.1 M solution of (Pr)₄N⁺ClO₄⁻ in CH₂Cl₂ was swept with argon and preelectrolyzed at +1.20 V *vs.* sce (aq) to remove oxidizable impurities. When a base current was reached, approximately 30 mg of ZnTPP was added to the electrolysis cell and controlled potential oxidation proceeded at +0.80 V until the base cell current was reached. The potential was then raised to +0.85 V until the base current again was obtained. This sequence avoided demetalation of ZnTPP. The anolyte was transferred to a rotary evaporator and reduced to dryness. The residue was extracted with three 15-ml aliquots of benzene, and the combined solutions were filtered to remove supporting electrolyte. After taking the filtrate to

(1) D. Dolphin and R. H. Felton, *Accounts Chem. Res.*, **7**, 26 (1974).

(2) D. Dolphin, Z. Muljiani, K. Rousseau, D. C. Borg, J. Fajer, and R. H. Felton, *Ann. N. Y. Acad. Sci.*, **206**, 177 (1973).

(3) J.-H. Fuhrhop and D. Mauzerall, *J. Amer. Chem. Soc.*, **91**, 4174 (1969).

(4) A. Wolberg and J. Manassen, *J. Amer. Chem. Soc.*, **92**, 3982 (1970).

(5) J. Fajer, D. C. Borg, A. Forman, D. Dolphin, and R. H. Felton, *J. Amer. Chem. Soc.*, **92**, 3451 (1970).

(6) M. D. Glick, G. H. Cohen, and J. L. Hoard, *J. Amer. Chem. Soc.*, **89**, 1996 (1967).

(7) D. M. Collins and J. L. Hoard, *J. Amer. Chem. Soc.*, **92**, 3761 (1970).

(8) J. L. Hoard, *Science*, **174**, 1295 (1970).

(9) A. Forman, D. C. Borg, J. Fajer, and R. H. Felton, *J. Amer. Chem. Soc.*, **93**, 2790 (1971).

(10) J.-H. Fuhrhop, P. Wasser, D. Riesner, and D. Mauzerall, *J. Amer. Chem. Soc.*, **94**, 7796 (1972).

(11) A. Adler, F. Kampas, and J. Kim, *J. Inorg. Nucl. Chem.*, **32**, 3443 (1970).

(12) H. House, E. Feng, and N. Pert, *J. Org. Chem.*, **36**, 237 (1971).