H_3P^+ could exist over only a very limited pH range. This conclusion has since been verified for protoporphyrin[62] in aqueous hydrochloric acid solutions, where it was found that, within the experimental error of the method of continuous variations, the two protons added simultaneously. Aronoff[63] later found, however, that upon titration of several porphyrins with perchloric acid in nitrobenzene, a distinct spectrum assumed to be that of the monocation was found for some porphyrins, while such a spectrum was totally absent for others. He also listed a third class of porphyrins, including tetraphenylporphine, for which an intermediate spectrum was indicated by small shifts in isosbestic points. Even in the cases where an intermediate spectrum was detected, however, K_2 was calculated to be at least three times greater than K_1. It should be mentioned that while the monosalts have never been isolated, there is now sufficient spectral evidence supporting their existence in anionic detergents,[2] which evidently stabilize the singly charged species with respect to the free base. There has been no conclusive proof that the monocations exist in detectable concentrations in aqueous solutions, although Neuberger and Scott[55] have presented spectra of what they claim to be the monoacids of a number of porphyrins in buffered, aqueous solutions. However, their results have been questioned because of their use of buffer solutions containing alkali ions and because the porphyrins they used contained carboxylic and sulfonic acid groups, whose pK's are in the pH range at which the supposed monocations appeared.

A careful study of porphyrin free base–diacid equilibria was undertaken on the water-soluble H_2TPyP^{24}

system. Excellent isosbestic points were obtained upon changing the pH of an aqueous hydrochloric acid solution from 2.30, at which point 98% of the porphyrin is in the free base form, to 0.00, where essentially all of the porphyrin is in the diacid form. In addition, the observed change in optical density was quantitatively consistent with the single equilibrium

$$H_4TPyP^{2+} \rightleftharpoons H_2TPyP + 2H^+ \qquad K = K_1K_2$$
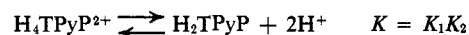
A value of 5.4×10^{-3} (moles/l.)^2 was reported for K.

Thus, the bulk of the experimental evidence indicates that the second proton is added (or abstracted) much more easily than the first. This, of course, is contrary to what is found for most dibasic acids, in which successive proton transfers occur with increasing difficulty as a result of the accumulating charge. The relative instability of the monoacid had previously been explained solely in terms of the loss of symmetry, which decreased the resonance stabilization. Undoubtedly, this factor is important, and perhaps, even predominant in reducing the relative stability of the monoacid. However, the nonplanar configuration found in the diacids affords a second explanation. The energy barrier for the addition of the first proton may be greater than that for the addition of the second, because the first proton attacks a relatively planar molecule, with lone-pair electrons on the unprotonated nitrogens directed toward the center of the ring, a sterically unfavorable location. Upon incorporation of the first proton to form the monoacid, the pyrrole rings are probably tilted up and down as in the diacid, so that the opposite nitrogen's nonbonding electron pair is quite accessible to attack by a second proton.[64]

(62) R. I. Walter, *J. Am. Chem. Soc.*, **75**, 3860 (1953).
(63) S. Aronoff, *J. Phys. Chem.*, **62**, 428 (1958).

The Crystal and Molecular Structure of Octahydroxycyclobutane

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Abstract: Octahydroxycyclobutane crystallizes in the monoclinic system P2$_1$/n, $a_0 = 7.525$ Å, $b_0 = 5.472$ Å, $c_0 = 7.491$ Å (all ±0.005 Å), $\beta = 90.00 \pm 0.05°$. The structure was solved by the symbolic addition method. The two molecules in the unit cell lie on centers of symmetry and thus require the cyclobutane ring to be planar. The average carbon–oxygen bond length is 1.385 Å and the carbon–carbon bond length is 1.562 Å. The average O–C–O bond angle is 111.8°. The structure is held together by a loose three-dimensional network of hydrogen bonds involving all of the hydroxyls in the system.

The synthesis of the novel compound octahydroxycyclobutane was first reported by West, Niu, and Ito[1] in 1963. The original workers on the compound predicted a planar structure for the cyclobutane ring on the basis of infrared data; however, the possibility of slight torsional deformation was not ruled out.

The variability of conformation in cyclobutane rings has been reviewed by Lambert and Roberts,[2] and from their work it would seem that there is no *a priori* way of predicting the conformation of the ring skeleton after substitution. The purpose of this study is to establish exactly the conformation of this molecular structure.

(1) R. West, H. Y. Niu, and M. Ito, *J. Am. Chem. Soc.*, **85**, 2584 (1963).

(2) J. B. Lambert and J. D. Roberts, *ibid.*, **87**, 3884 (1965).

Table I. Statistical Data for the Distribution of Normalized Structure Factors

Observed	Theoretical for centrosymmetric	Noncentro-symmetric
$\lvert E\rvert^2 = 1.02$	1.00	1.00
$\lvert E\rvert = 0.735$	0.798	0.886
$\lvert E\rvert^2 - 1 = 1.06$	0.968	0.736

Table II. Starting Set of Vectors for the Symbolic Addition Phase Determination

hkl	E	S
325	3.16	$+$
715	3.27	$+$
$\bar{3}34$	2.66	$+$
218	3.01	A
$\bar{8}02$	2.87	B
433	2.68	C

$$SE_{\vec{h}}^+ \sim S\sum_{\vec{k}} E_{\vec{k}}^+ E_{\vec{h}-\vec{k}}^+$$

where S means "sign of ."

From an initial σ_2 listing, 16 additional signs were developed relying on the probability relationship[6]

$$P + (E_h) = \frac{1}{2} + \frac{1}{2}\tanh\frac{\sigma_3 |E_{\vec{h}}| \sum_{\vec{k}} |E_{\vec{k}} E_{\vec{h}-\vec{k}}|}{\sigma^{3/2}}$$

where $\sigma_n = \Sigma_{j=1}^N Z_j{}^n$, Z_j being the atomic number of the jth atom in the unit cell containing N atoms.

Only those signs were accepted whose probability of a correct determination equalled or exceeded 99%. From the original set and the additional 16 signs, 52 additional signs were developed. In the course of the phase development, the tendency for C to be negative became overwhelming. Also, several indications developed that "A" was positive. From the σ_1 relationship,[4,7] the sign of $\bar{8}02$ was determined to be positive with an 89% confidence. Accordingly, a three-dimensional Fourier was computed for which the signs of A and B were positive and that for C was negative. The outline

Table III. Final Atom Positions and Thermal Parameters[a]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
O-1	$-0.4653\,(3)$	$0.2787\,(6)$	$0.2085\,(3)$	$0.0088\,(5)$	$0.0263\,(11)$	$0.0136\,(5)$	$-0.0012\,(5)$	$-0.0017\,(3)$	$-0.0044\,(5)$
O-2	$-0.4451\,(3)$	$-0.1267\,(6)$	$0.2752\,(2)$	$0.0081\,(5)$	$0.0369\,(12)$	$0.0102\,(5)$	$0.0000\,(5)$	$-0.0011\,(3)$	$0.0050\,(5)$
O-3	$-0.2713\,(4)$	$0.2253\,(7)$	$-0.0776\,(3)$	$0.0146\,(6)$	$0.0519\,(16)$	$0.0066\,(4)$	$-0.0167\,(8)$	$0.0009\,(3)$	$-0.0013\,(5)$
O-4	$-0.2402\,(4)$	$-0.1861\,(7)$	$-0.0175\,(3)$	$0.0095\,(6)$	$0.0599\,(18)$	$0.0076\,(5)$	$0.0133\,(7)$	$-0.0012\,(3)$	$-0.0058\,(6)$
C-1	$-0.4768\,(4)$	$0.0442\,(6)$	$0.1418\,(3)$	$0.0057\,(5)$	$0.0256\,(13)$	$0.0071\,(5)$	$-0.0003\,(6)$	$0.0000\,(3)$	$-0.0014\,(5)$
C-2	$-0.3551\,(4)$	$0.0084\,(8)$	$-0.0251\,(3)$	$0.0065\,(6)$	$0.0326\,(14)$	$0.0066\,(5)$	$-0.0006\,(7)$	$0.0000\,(4)$	$-0.0015\,(6)$

[a] Thermal parameters are of the form $T_{\text{exptl}}\{-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)\}$.

Experimental Section

Diketocyclobutenediol, "squaric acid," was synthesized by Dr. Wayne C. Solomon according to the method of Cohen, Lacher, and Park.[3] The conversion of squaric acid to octahydroxycyclobutane was accomplished after the method described by West, Niu, and Ito.[1] Attempts at recrystallization at ambient conditions from aqueous solutions yielded only several poor crystals from a frothy mass of decomposed material. The crystals used in this study were cut from clear, colorless, diamond-shaped crystals grown by slow evaporation from an aqueous solution in a refrigerator. Space group data were obtained from Weissenberg camera photographs.

Intensity data were gathered using a General Electric XRD-5 single crystal orienter equipped with a scintillation counter and a pulse height analyzer. Nickel-filtered copper radiation (λ 1.54178) was used for both lattice parameter measurements and the taking of the intensity record. Lattice parameters reported here were taken at a 1° take-off angle on high θ inflections showing α_1-α_2 splitting. The intensity record was taken at a take-off angle of 3° using an open counter and the θ-2θ scan technique. The crystal used was an approximately square prism $0.2 \times 0.2 \times 0.5$ mm.

Crystal Data. Octahydroxycyclobutane crystallizes in the monoclinic space group P2$_1$/n. Crystal data are $a_0 = 7.525 \pm 0.005$, $b_0 = 5.472 \pm 0.005$, $c_0 = 7.491 \pm 0.005$ Å; $\beta = 90.00 \pm 0.05°$; $\rho_{\text{obsd}} = 2.00$, $\rho_{\text{calcd}} = 1.98$; two molecules [C$_4(OH)_8$] in the unit cell. With two molecules per cell, the molecules are required to lie on centers of symmetry, and therefore the cyclobutane ring must be planar.

Solution of the Structure. After initial Lorentz and polarization correction, the intensity data were converted to normalized structure factors.[4] Statistical data derived from the distribution of E's are presented in Table I. The symbolic addition method of Karle and Karle[5] was used to determine phase relationships.

The starting set of origin-fixing vectors is listed in Table II. Also listed in Table II are the vectors for which symbolic signs were used in the σ_2 relationship. The σ_2[5] method consists of the application of the relationship

of the molecule was easily recognized from the Fourier, and atom positions were entered directly into a least-squares refinement[8] allowing atom x, y, z positions, one over-all temperature, and one over-all scale factor as variables. The conventional R factor for nonzero observed data rapidly fell to 20%, whereupon the atoms were allowed to assume individual isotropic thermal motion. The refinement of the structure rapidly converged to the rather high discrepancy index of $R = 19.0\%$ for nonzero observed data. The reason for the high discrepancy index at this point is interpreted as a manifestation of the highly anisotropic thermal motion of the oxygen atoms.

Introduction of a weighting scheme[9] of the form

$$w = 1/(a + \lvert F_o\rvert + c\lvert F_o\rvert^2)$$

where $a = 2/F_{o,\text{min}}$ and $c = 2/F_{o,\text{max}}$ and anisotropic thermal motion rapidly brought the R factor for nonzero observed data to 10.1%. R for all data is 14%. At this point, a difference Fourier was calculated; however, no features could be unequivocally identified as the missing hydrogen atoms and the refinement was therefore terminated. The failure of the difference Fourier to locate the hydrogen atoms may be because of the magnitude of thermal motion of the oxygen atoms coupled with the usual random error in the observed intensity data.[10] Low angle reflections which are apparently affected by extinction were weighted as zero in the final refinement. Omission of these reflections from the usual discrepancy index, R, yields 7.2% for nonzero observed data and 11.5% for all data. Final atom positions and thermal parameters are listed in Table III.

(3) S. Cohen, J. R. Lacher, and J. D. Park, *J. Am. Chem. Soc.*, **81**, 3480 (1959).

(4) H. Hauptman and J. Karle, "Solution of the Phase Problem I, the Centrosymmetric Crystal," American Crystallographic Association, Monograph No. 3, Polycrystal Book Service, Pittsburgh, Pa., 1953.

(5) I. L. Karle and J. Karle, *Acta Cryst.*, **16**, 969 (1963).

(6) M. M. Woolfson, *ibid.*, **7**, 61 (1954).

(7) I. L. Karle, K. Britts, and S. Brenner, *ibid.*, **17**, 1506 (1964).

(8) W. R. Busing, K. O. Martin, and H. A. Levy, "ORFLS," Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962.

(9) D. W. J. Cruickshank, "Computing Methods in Crystallography," J. S. Rollett, Ed., Pergamon Press, New York, N. Y., 1965, p 114.

(10) Observed and calculated structure factors have been deposited as Document No. 9651 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington, D. C. A copy may be secured by citing the document number and by remitting $1.50 for photoprints, or $1.25 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.
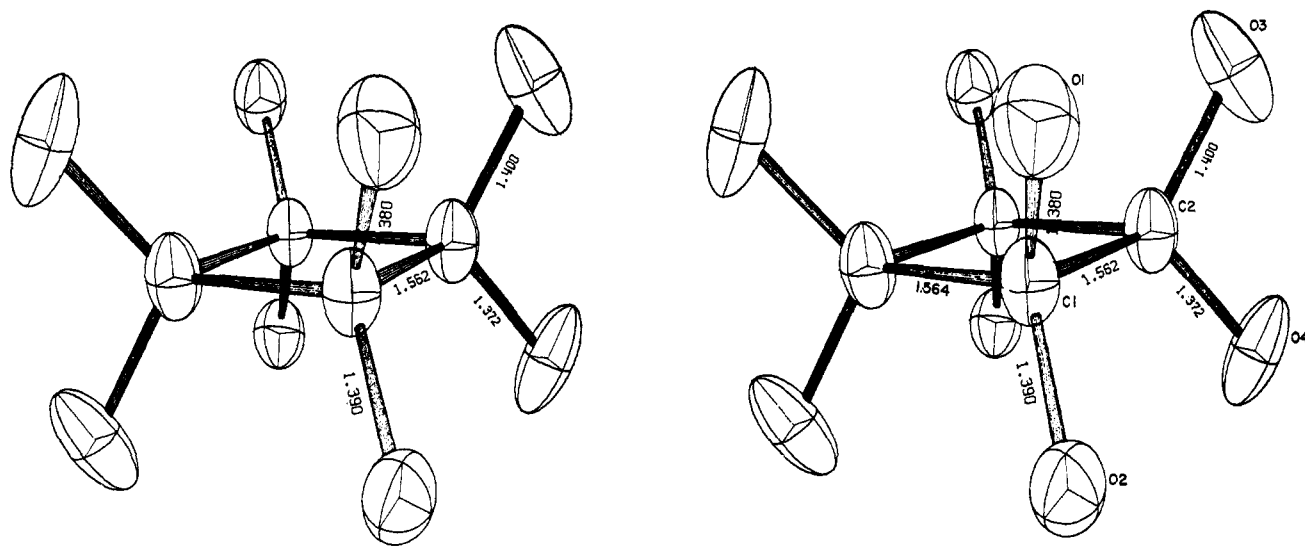
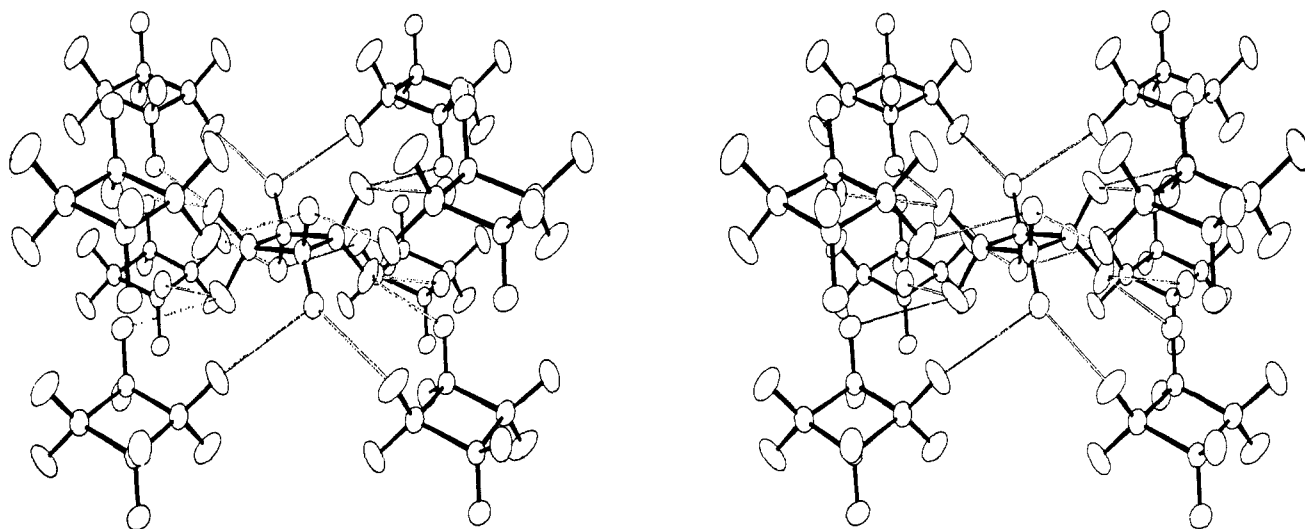Figure 1. Stereodiagram of the molecular structure of octahydroxycyclobutane.

Figure 2. Stereodiagram of the molecular packing of octahydroxycyclobutane. Hydrogen bonds to the central molecule are represented as open stick bonds.

Discussion

The configuration of the molecular structure and its packing arrangement are shown in the stereodiagrams in Figures 1 and 2. These diagrams were drawn with the aid of the computer program ORTEP.[11] Important interatomic distances and angles and their estimated standard errors were calculated with the program ORFEE[12] and are listed in Table IV. As expected, difference calculations among the carbon–oxygen bond lengths showed that the bonds are all equivalent within the error of the experiment. In this respect, the author prefers to use the philosophy of Hamilton[13] in that estimates of precision should be doubled before statistical inferences are made from the data.

The average C–O bond of 1.385 Å is considerably shorter than the normal paraffinic bond of 1.43 Å.[14]

(11) C. K. Johnson, "ORTEP," Oak Ridge National Laboratory Report 3794, Oak Ridge, Tenn., 1965.

(12) W. R. Busing, K. O. Martin, and H. A. Levy, "ORFEE," Oak Ridge National Laboratory Report 306, Oak Ridge, Tenn., 1964.

(13) W. C. Hamilton, "Transactions of the American Crystallographic Association," Vol. 1, S. C. Abrahms, Ed., Polycrystal Book Service, Pittsburgh, Pa., 1965.

Owen and Hoard[15] observed a similar shortening of the C–Cl bond in octachlorocyclobutane over the normal C–Cl single bond, and a similar shortening of a C–O bond to 1.39 Å was observed by Brown and Levy[16] in chloral hydrate wherein two hydroxyls are also bonded to a single carbon atom.

The difference between the angles O_1–C_1–O_2 and O_2–C_2–O_4 is apparently significant; however, this apparent difference may be due to inaccuracies in error estimation of the lack of consideration of the effect of thermal motion on bond angles and distances.

The observed carbon–carbon bond lengths of 1.562 and 1.564 Å are in excellent agreement with the 1.56-Å distance measured in cyclobutane by electron diffraction,[17] but it is shorter than the 1.59-Å distance observed in octachlorocyclobutane.[15] The planarity of the ring for the hydroxyl compound may be because of the

(14) "International Tables for X-Ray Crystallography," Vol. III, K. Lonsdale, Ed., The Kynoch Press, Birmingham, England, 1962, p 202.

(15) T. B. Owens and J. L. Hoard, Acta Cryst., 4, 172 (1964).

(16) G. M. Brown and H. A. Levy, J. Phys. Radium, 25, 469 (1964).

(17) J. D. Dunitz and V. Shoemaker, J. Chem. Phys., 20, 1703 (1952).

Table IV. Bond Distances and Angles for Octahydroxycyclobutane[a]

Atoms	Bond distance, Å	Bond angle, deg	H bond, Å
C_1–C_2	1.564 ± 0.004		
C_1–C_2	1.562 ± 0.004		
C_1–O_1	1.380 ± 0.005		
C_1–O_2	1.390 ± 0.004		
C_2–O_3	1.400 ± 0.005		
C_2–O_4	1.372 ± 0.005		
Mean C–O	1.385		
$O_1(I)$–$C_1(I)$–$O_2(I)$		110.8 ± 0.3	
$O_3(I)$–$C_2(I)$–$O_4(I)$		112.7 ± 0.3	
$C_1(I)$–$C_2(I)$–$C_1(II)$		89.8 ± 0.2	
$C_2(I)$–$C_1(I)$–$C_2(II)$		90.2 ± 0.2	
O_1–$O_4(III)$			2.790 ± 0.004
O_2–$O_3(IV)$			2.806 ± 0.004
O_2–$O_4(IV)$			2.897 ± 0.004
O_2–$O_3(V)$			2.905 ± 0.004
O_3–$O_1(VI)$			2.806 ± 0.004
O_3–$O_2(III)$			2.905 ± 0.004
O_4–$O_1(V)$			2.790 ± 0.004
O_4–$O_2(VII)$			2.897 ± 0.004
Mean O···O			2.850

Asymmetric unit I at	x	y	z
II	$-x - 1$	$-y$	$-z$
III	$1/2 + x$	$-1/2 - y$	$-1/2 + z$
IV	$1/2 + x$	$-1/2 + y$	$-1/2 - z$
V	$1/2 + x$	$1/2 - y$	$-1/2 + z$
VI	$-1/2 - x$	$-1/2 + y$	$1/2 - z$
VII	$-1/2 - x$	$1/2 + y$	$1/2 - z$

[a] All distances less than 4 Å were computed, but only significant approaches are listed.

hydrogen-bonding scheme. The fact that octafluoro-cyclobutane has a nonplanar ring[18] and that the oxygen and fluorine radii at 0.64 and 0.66 Å,[19] respectively, are essentially the same size would seem to rule out crowding as a cause of ring warping.

One referee pointed out that it is possible that a statistically nonplanar ring could satisfy these data. To test the hypothesis that a statistically disordered nonplanar ring could better explain the observed data, a split atom refinement was attempted. Atoms of half-weight were offset along b_0 ± 0.2 Å from their positions as listed in Table IV. After three full cycles of anisotropic least-squares full-matrix refinement varying three positional parameters and six thermal parameters per atom for alternate half-atoms, the residual for nonzero observed F data converged on a minimum of 0.097. According to Hamilton,[20] for the split atom refinement to have been significantly better than the ordered model at the 95% confidence level, the residual would have had to have been 0.092 or smaller. The hypothesis that a disordered warped ring can better explain the diffraction data is, therefore, rejected.

However, it should also be noted that the disordered model refinement does not rule out the possibility that statistically disordered skewed rings are present in the structure. Perhaps a structure determination at lower temperatures would resolve the problem; however, such an investigation is not currently within the capability of this laboratory.

The crystal structure is loosely held together by a three-dimensional network of hydrogen bonds involving all the hydroxyls in the structure. According to Pimentel and McClellan,[21] the average hydrogen bond length of 2.85 Å compares well with the average 2.74 ± 0.11 Å of alcohols.

(18) H. P. Lemoire and R. L. Livingston, *J. Am. Chem. Soc.*, 74, 5732 (1952).

(19) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1962, p 93.

(20) W. C. Hamilton, "Statistics in Physical Science," The Ronald Press Co., New York, N. Y., 1964, p 157.

(21) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Co., San Francisco, Calif., 1960, p 284.