since the Fe^{IV}=O moiety is unlikely to be a strong base. A possible location for this added proton is suggested by recent resonance Raman results,[61] which indicate the presence of an ionizable group (probably imidazole) within hydrogen-bonding distance of the oxo ligand. A proton in this location would then be available when HRP-II is converted, with the uptake of an electron and a second proton, to ferric HRP and water (Figure 6).[62a] The fact that HRP-I and HRP-II have similar iron-site structures may facilitate rapid reduction of HRP-I during the catalytic cycle, since there would be only a small reorganizational energy barrier to this reaction. The apparently pervasive nature of short Fe=O bonds in high-valent Fe porphyrins (HRP-I, HRP-II, **1**, and **2**),[62b] together with the similar reactivity of HRP and P-450 on treatment with peroxide, suggests that a similar ferryl (Fe=O) complex may be the active oxygen species in P-450.

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Registry No. 1, 95724-73-5; **2**, 73133-16-1; **3**, 93862-19-2; **4**, 80584-26-5; **5**, 84192-46-1; **6**, 96482-28-9; Fe, 7439-89-6; Cr, 7440-47-3; O_2, 7782-44-7; N_2, 7727-37-9; peroxidase, 9003-99-0; heme, 14875-96-8.

Supplementary Material Available: A listing of X-ray absorption vs. energy for the spectra reported herein (34 pages). Ordering information is given on any current masthead page.

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[62] **Notes Added in Proof.** (a) A similar compound II reduction mechanism has recently been proposed by Makino et al. (Makino, R.; Uno, T.; Nishimura, Y.; Iizuka, T.; Tsuboi, M.; Ishimura, Y. *J. Biol. Chem.* **1986**, *261*, 8376-8382) on the basis of variable pH resonance Raman measurements. (b) Additional examples of short Fe-O bonds have recently been reported by M. Chance et al. for ferryl myoglobin (Chance, M.; Powers, L.; Kumar, C.; Chance, B. *Biochemistry*, **1986**, *25*, 1259-1266) and cytochrome *c* peroxidase compound ES (Chance, M.; Powers, L.; Poulos, T.; Chance, B. *Biochemistry*, **1986**, *25*, 1266-1270). This new evidence provides further support for our finding that the Fe=O moiety is a common structural feature of high-valent iron porphyrins.

Single Crystal Neutron Diffraction Refinement of Bullvalene at 110 K

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Abstract: A low-temperature neutron diffraction refinement of the crystal structure of bullvalene, $C_{10}H_{10}$, tricyclo-[3.3.2.0^{2,8}]deca-2,5,8-triene, shows that the molecule is distorted only very slightly from the C_{3v} symmetry expected for the isolated molecule, although the crystal structure symmetry is monoclinic. There is a small but significant difference between the shortest and longest of the C-C bonds in the cyclopropane ring, which are 1.536 (1), 1.533 (1), and 1.530 (1) Å. The three ethylenic wings of the molecule are virtually identical, except for small differences in planarity and C-C-H angles. One wing is exactly planar within 0.002 (3) Å. In the other two, one of the hydrogen atoms in each is significantly displaced from the plane by 0.027 (3) and 0.023 (3) Å. The mean bond lengths in the ethylenic wings are C_{ring}—C, 1.4727 (7) Å; C=C, 1.3423 (7) Å; =C—C, 1.5163 (7)Å. The C-H bond lengths range from 1.086 (2) to 1.092 (2) Å. The thermal motion analysis gives an unusually good fit to the rigid-body model. Corrections for harmonic thermal motion lengthened all C—C and C=C bonds uniformly by 0.003 Å. For the C-H bonds, the harmonic riding motion and anharmonicity corrections almost cancel, so that the thermally corrected bond lengths differ from those measured by ±0.001 Å.

Bullvalene attracted much interest when first synthesized[1] 23 years ago because of the interesting chemistry involved.[2] This prompted X-ray structure analyses of first some bullvalene $AgBF_4$ complexes[3] and then of bullvalene itself.[4,5] The solid-state ^{1}H NMR shows an unusual decrease in line width with increase of temperature at about 20 °C, which was attributed either to valence bond isomerism or molecular reorientation.[6] The room temperature X-ray analysis provided no evidence in support of the valence isomerism hypothesis, and the NMR results were interpreted as due to the onset of molecular motion leading to the

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Table I. Crystal Data and Neutron Diffraction Refinement Data for Bullvalene at 110 ± 1 K[a]

$C_{10}H_{10}$, tricyclo[3.3.2.$0^{2,8}$]deca-2,5,8-triene
space group $B2_1/c$, $Z = 8$
cell dimensns, based on 32 reflectns with $50° < 2\theta < 56°$, $a = 6.466$ (2), $b = 20.559$ (4), $c = 10.360$ (2) Å, $\beta = 90.19$ (2)°
approximate crystal dimensns: 4 mm × 2 mm × 0.5 mm
neutron wave length 1.0504 (2) Å, calibrated by KBr crystal (a_0 = 6.6000 Å at 298 K)
3077 reflectns were measured of which 2742 were unique
scan widths $\Delta 2\theta = 2.8°$ for $2\theta < 55°$, $\Delta 2\theta = (1.080 + 3.120 \tan \theta)$ for $55° < 2\theta < 110°$
absorptn correctns[7] were applied by using μ_ρ for hydrogen[8] = 24.88 $cm^2 g^{-1}$. Linear absorption coeff $\mu = 2.417\ cm^{-1}$. Min value 1.189, max value 1.438
functn minimized, $\Sigma\omega(|F_o|^2 - k|F_c|^2)$ where $\omega = \sigma(F_o^2)^{-2}$, by using LINEX, a locally modified versn of ORFLS[9]
An isotropic extinctn param, g, was included and refined to a value corresponding to an rms mosaic spread of 0.226×10^{-4} rad
final agreement factors $R(F^2) = 0.066$, $wR(F^2) = 0.065$, $S = 0.955$, based on 2742 observatns

[a] The analysis was carried out by using a transformed B-centered unit cell to avoid the obtuse β angle ($a_p = 6.097$ Å, $\beta_p = 147.98°$). The transformation from primitive cell (space group $P2_1/c$) is $\vec{a}_B$ 2 0 1 $\vec{a}_p$, $\vec{b}_B$ 0 $\bar{1}$ 0 $\vec{b}_p$, $\vec{c}_B$ 0 0 $\bar{1}$ $\vec{c}_p$.

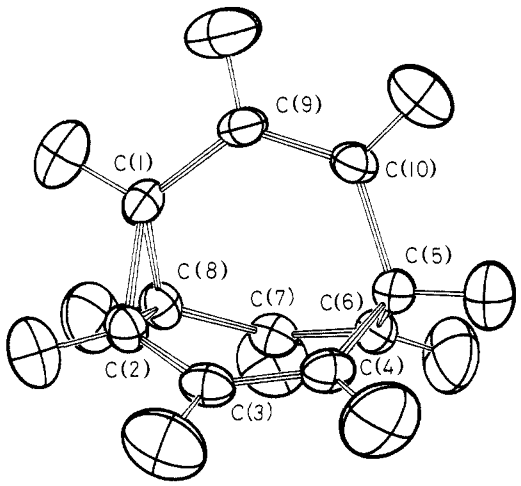

Figure 1. Perspective view of molecule with thermal ellipsoids[10] at 75% probability surfaces. Hydrogen atoms are denoted in Table II with same numbers as carbon atoms to which they are bonded.

Table II. Atomic Positional Parameters and Equivalent Isotropic Temperature Factors[a]

atom	x/a	y/b	z/c	U_{eq}[b]
C(1)	19683 (14)	−15708 (4)	−37155 (9)	158 (4)
C(2)	2934 (15)	−19443 (4)	−44596 (8)	157 (4)
C(3)	−13499 (14)	−16109 (5)	−51929 (8)	159 (4)
C(4)	−23288 (14)	−10626 (4)	−48485 (8)	159 (4)
C(5)	−18536 (14)	−6886 (4)	−36214 (9)	150 (4)
C(6)	−22520 (14)	−10998 (4)	−24329 (8)	154 (4)
C(7)	−12480 (14)	−16573 (4)	−21768 (8)	152 (4)
C(8)	3377 (15)	−19679 (4)	−29837 (8)	153 (4)
C(9)	20130 (14)	−8547 (4)	−36609 (8)	154 (4)
C(10)	3722 (14)	−4557 (4)	−36154 (8)	149 (3)
H(1)	3488 (3)	−1796 (1)	−3747 (2)	35 (1)
H(2)	851 (4)	−2390 (1)	−4904 (2)	33 (1)
H(3)	−1772 (4)	−1836 (1)	−6108 (2)	38 (1)
H(4)	−3518 (4)	−870 (1)	−5490 (2)	38 (1)
H(5)	−2864 (3)	−261 (1)	−3591 (2)	32 (1)
H(6)	−3385 (4)	−928 (1)	−1732 (2)	37 (1)
H(7)	−1606 (4)	−1907 (1)	−1281 (2)	36 (1)
H(8)	921 (4)	−2429 (1)	−2607 (2)	33 (1)
H(8)	3544 (3)	−635 (1)	−3652 (3)	37 (1)
H(10)	640 (4)	65 (1)	−3574 (3)	36 (1)

[a] Positional parameters for non-hydrogen atoms are $\times 10^5$, for hydrogen atoms $\times 10^4$. The equivalent isotropic temperature factors are $\times 10^4$ for non-hydrogen atoms, $\times 10^3$ for hydrogen atoms. esd's given in parentheses refer to the least significant digit. [b] $U_{eq} = 1/3\Sigma_i\Sigma_j U_{ij}(a_i^*)(a_j^*)(\vec{a}_i)\cdot(\vec{a}_j)$.

Table III. Rigid Body Motion of the Carbon Framework with Respect to the Inertial Axes[11]

	I_1, deg	I_2, deg	I_3, deg
T, Å			
0.111	17.4	102.1	102.3
0.106	74.5	23.4	72.9
0.100	82.3	109.7	21.3
ω, deg			
3.04	71.8	75.0	156.1
2.61	90.0	15.9	74.1
2.18	18.2	94.9	72.6

formation of a plastic crystalline phase prior to melting.[5] Both X-ray analyses suggested that the molecular symmetry departed significantly from the expected C_{3v} symmetry, particularly with respect to the cyclopropane ring, where a difference of 0.036 Å in the C–C bond lengths was reported. Since the crystal structure is monoclinic, some departures from the ideal molecular symmetry must result from the crystal field forces. This study was undertaken to determine the magnitude of these distortions.

Experimental Section

Single crystals suitable for neutron diffraction were grown from ethanol at −8 °C from a sample provided by Prof. G. Schröder of the University of Karlsruhe. Under normal conditions crystals of bullvalene sublime rapidly. The neutron diffraction data were collected at the Brookhaven high flux beam reactor. The relevant experimental data are given in Table I. The refinement calculations were started from the atomic coordinates of the X-ray analysis transformed to the B lattice used in this analysis. The final atomic parameters are given in Table II, with the atomic notation shown in Figure 1.

A rigid body thermal motion analysis was carried out for the carbon framework only.[11] The fit was exceptionally good giving rms ΔU_{ij} = 0.00032. The principal values of the libration, translation, and screw-coupling tensors are given in Table III.

The thermal motion corrections to the bond lengths were uniformly +0.003 Å for the C—C and C═C bonds. The C–H bond lengths were corrected both for harmonic riding motion[12] and anharmonicity.[13] These two corrections were similar in magnitude, 0.015 −0.020 Å, but opposite in sign, so that the thermally corrected C–H bond lengths were within ±0.001 Å of the observed values.

Discussion

The primary interest of this study is in the precise molecular dimensions and distortions from C_{3v} symmetry caused by crystal field effects. For the idealized configuration, the cyclopropane ring must be an equilateral triangle, and the three HC—CH═CH—C *wings* of the molecule must be identical and planar, with the planes intersecting on the molecular three-fold axis with angles of 120°.

In Table IV, we test these symmetry requirements against the observed structure. In the C—CH═CH—C wings, bond lengths and angles that are equivalent by C_{3v} symmetry are equal within 2σ, except for the C–C–H angles which differ as much as 1.0° (6σ). Wing B is exactly planar with the standard deviation from the least-squares plane of 0.003 Å. In wing A, only H(7) is significantly out of the plane, by 0.027 (3) Å. In wing C, only H(3) is out of the plane by 0.023 (3) Å.

The wings are significantly bent away from the ideal 120° relative orientations. The angles between the A and C wings are

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Table IV. The Dimensions and Distortions from C_{3v} Symmetry in the Crystal Structure of Bullvalene[a] .

	wing A C(8)H.C(7)H:C(6)H.C(5)	wing B C(1)H.C(9)H:C(10)H.C(5)	wing C C(2)H.C(3)H:C(4)H.C(5)
		Torsion Angles (i.e., planarity) of Wings	
C_r—C=C—C	-1.22	-0.39	+0.81
C_r—C=C—H	-179.48	179.79	179.95
H—C=C—C(5)	177.80	179.99	-178.22
H—C=C—H	0.46	0.16	0.93
		Bond Lenghts in Wings	
C_r—C=	1.471	1.474	1.473
C=C	1.343	1.342	1.342
=C—C(5)	1.516	1.517	1.516
C_r—H	1.092	1.087	1.088
>C—H	1.086	1.088	1.089
>C—H	1.091	1.086	1.089
C(5)—H	1.096		
		Bond Angles	
C_r—C=C	126.6	126.6	126.4
C=C—C	123.6	123.9	123.7
H—C_r—C=	114.5	114.2	114.4
H—C=C	117.9	117.8	118.1
	118.0	118.6	118.4
=C—C—H	109.6	110.7	108.1
		Cyclopropane Ring	
	C(1)-C(8), 1.536 (1) Å	C(1)-C(2), 1.533 (1) Å	C(2)-C(8), 1.530 (1) Å
		Interwing Angles	
	A:B = 118.4 (5)°	A:C = 121.8 (5)°	B:C = 119.8 (5)°
		Selected Bond Angles	
	C(8)-C(1)-C(2), 59.8 (1)°	C(1)-C(2)-C(8), 60.2 (1)°	C(1)-C(8)-C(2), 60.0 (1)°

[a] Bond lengths in Å, angles in deg. The standard deviations on bond lengths are 0.001 Å for C-C bonds, 0.003 Å for C-H bonds, 0.08° for C-C-C angles, 0.15° for C-C-H angles, and 0.25° for torsion angles. Differences greater than 3σ are considered significant.

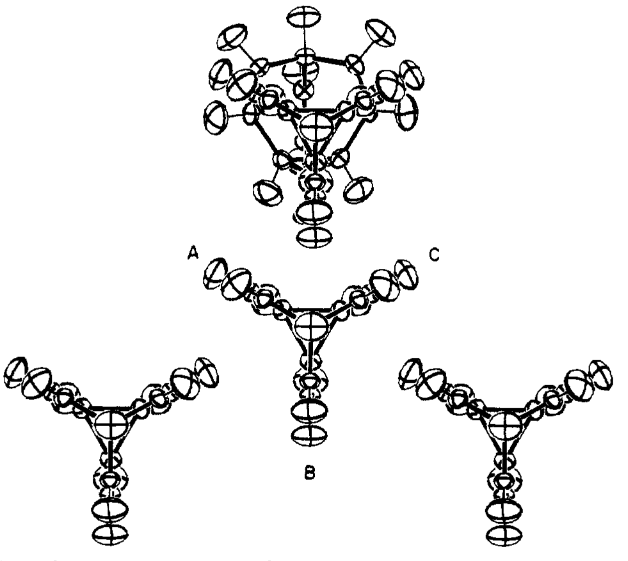

Figure 2. Local environment of a molecule viewed down the molecular three-fold axis.

greater than 120° at the expense of those between A and B, B and C. The reason for this asymmetry is shown in Figure 2, which displays the local environment of a molecule in the crystal. Where this is local mirror symmetry, about wing B, the vinyl group is planar within the experimental limits.

The molecular packing is as described from the X-ray analysis. In the cyclopropane ring, the C(2)–C(8) bond, which subtends the 121.8° interwing angle, is 0.006 Å shorter than the C(1)–C(8) bond, which subtends the 118.4° angle. This difference, of 4σ, is possibly significant, since it is associated with the small torsional difference. These bond lengths (1.536 (1), 1.533 (1), 1.530 (1) Å) are all significantly longer than the 1.5096 (15) Å reported for unsubstituted cyclopropane by electron diffraction,[14] 1.514 (2) Å by Raman spectroscopy,[15] and 1.488 (4) Å for the vinyl substituted ring from the statistical survey of substitution effects in cyclopropane derivatives.[16]

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Registry No. Bullvalene, 1005-51-2.

Supplementary Material Available: Tables of anisotropic temperature parameters (2 pages); observed and calculated structure factors (15 pages). Ordering information is given on any current masthead page.

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