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Crystal and Molecular Structure of Bis[π-(cyclobutenocyclooctatetraene)]uranium(IV), $U[C_8H_6(CH_2)_2]_2$[1]

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Crystals of bis[π-(bicyclo[6.2.0]deca-1,3,5,7-tetraene)]uranium(IV), $U[C_8H_6(CH_2)_2]_2$, are monoclinic: space group $P2_1/n$, $a = 9.906$ (8) Å, $b = 11.039$ (9) Å, $c = 7.221$ (6) Å, $\beta = 98.89$ (5)°, $V = 780.15$ Å^3, $Z = 2$, and $D_x = 2.122$ g cm^{-3} at 22 °C. X-ray diffraction data were measured with counter methods and Mo Kα radiation. With anisotropic temperature factors for the uranium and carbon atoms and isotropic temperature factors for the hydrogen atoms, $R = 0.020$ for 1315 independent reflections ($I > 3\sigma$). The molecule is a sandwich compound with the C_8 rings in an eclipsed configuration about the uranium atom which is on a center of symmetry. The average U–C distance is 2.64 ± 0.02 Å, and the average C–C distance in the C_8 ring is 1.39 ± 0.01 Å (uncorrected for thermal motion). The cyclobuteno ring is planar and at an angle of 6.8° to the plane of the C_8 ring. The C–C bond length is 1.47 (2) Å in the $-CH_2-CH_2-$ moiety, and it is 1.55 (2) Å where this group is fused to the C_8 ring.

Introduction

Following the initial characterization of bis(cyclooctatetraene)uranium(IV), "uranocene", by Streitwieser and Müller-Westerhoff,[2] its crystal and molecular structure was determined.[3] Subsequently the preparation[4] and structure[5] of bis(cyclooctatetraene)thorium(IV), "thoracene", were reported as well as the preparations and structures of octamethyluranocene,[6,7] $U(C_8H_4(CH_3)_4)_2$, and octaphenyluranocene,[8,9] $U(C_8H_4(C_6H_5)_4)_2$.

As part of a program to extend knowledge of the chemical and structural properties of compounds of actinide elements, we undertook a study of the structure of butenouranocene synthesized by Berryhill and Streitwieser.[10] The immediate objective was a description of the molecular geometry for use in the interpretation of the NMR spectra.[10]

Experimental Section

Crystals grown from a hexane solution were dark green. As the material is extremely air sensitive they were manipulated and kept in an argon-filled drybox until they could be inserted into 0.2-mm quartz capillaries and sealed. Weissenberg photographs were taken of the crystals from which the space group and rough cell dimensions were obtained. Some of the crystals exhibited twinning and were rejected for data collection. A wedge-shaped crystal fragment was placed on a Picker FACS-I automated diffractometer equipped with graphite-monochromated Mo Kα radiation (λ 0.709 30 Å) for study. Cell dimensions were obtained from carefully centered settings on the Kα_1 peaks of 12 reflections where 35° < 2θ < 38°. The cell dimensions, crystal description, and other details of the experiment are given in Table I. The width of ω scans at half-height were typically 0.1°. Intensity data were collected by using the θ–2θ scan method for the hemisphere $\pm h$, $+k$, $\pm l$. Three standards were measured after each 200th scan, and the maximum variation of these measurements from their mean value was about 2%. The data were corrected for absorption.[11] Several azimuthal scans in diverse regions of reciprocal space were performed to test the validity of the absorption correction and to make minor adjustments on the crystal dimensions. After the absorption correction the equivalent data were averaged and given estimated standard deviations by using formulas presented in the supplementary material. The factor $p = 0.04$ was used in the calculation of $\sigma(F^2)$.

The position of the uranium atom at the origin was evident from the strong pseudo body centering exhibited by the data. A Patterson function and subsequent Fourier maps after least-squares refinement of part of the structure revealed the positions of all the carbon atoms. The structure was refined by full-matrix least squares where the function $\sum w||F_o| - |F_c||^2/\sum wF_o^2$ was minimized. The two reflections below $(\sin\theta)/\lambda$ of 0.08 were zero weighted because of excessively large discrepancies. Because the observed values of the larger intensities were consistently below the calculated values, an empirical extinction correction was applied; the largest correction to F due to extinction was 1.2. The uranium and carbon atom parameters were refined by using anisotropic temperature factors. The hydrogen atom positions were estimated from the carbon atom geometry and were refined with isotropic temperature factors. All of the hydrogen atoms with the exception of H(1) refined to acceptable positions; H(1) shifted to a position about 0.5 Å from C(1), and it was then restrained to a distance of 0.95 ± 0.05 Å from the carbon atom in the least-squares refinement in the manner suggested by Waser[12] and described in one of our previous papers.[13] Scattering factors for U, C, and H were taken from

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Table I. Summary of Crystal Data and Intensity Collection

compd	$U(C_{10}H_{10})_2$
fw	498.41
a	9.906 (8) Å
b	11.309 (9) Å
c	7.221 (6) Å
β	98.89 (5)°
V	780.15 Å^3
density (calcd)	2.12 g/cm^3
space group[a]	$P2_1/n$ (alternate setting of $P2_1/c$)
cryst shape and size	wedge-shaped fragment approximately described by the 5 faces 110, $\bar{1}10$, $1\bar{1}0$, $\bar{5}28$, $\bar{1}\bar{1}5$; dimens = 0.2 mm long × 0.2 mm wide × 0.1 mm deep
cryst vol	0.0047 mm^3
temp	21 ± 1 °C
radiation	Mo Kα (λ 0.709 30 and 0.713 57 Å), monochromated from (002) face of mosaic graphite

μ	99 cm^{-1}
transmission factor	0.16-0.45
data collectn method	θ-2θ scan (2°/min along 2θ)
scan range	0.6° below Kα_1 to 0.6° above Kα_2
bkgd counts	8 s; bkgd offset from scan limits by 0.5°
2θ limits	3-60°
no. of scans	4872 (including stds)
no. of unique data	2296
unique data used ($F_o^2 > 3\sigma(F_o^2)$; $0.706 > (\sin\theta)/\lambda > 0.08$)	1315
final no. of variables	135
extinction factor, k ($F_{cor} = F_o(1 + kI)$)	1.8 × 10^{-6}
R_w[b]	0.027
R[c] (1315 data used in R_w)	0.020
R (all 2296 data)	0.061
goodness of fit	1.06

[a] The general positions are $\pm(x, y, z; \frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z)$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$. [c] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

Table II. Positional and Thermal Parameters[a]

atom	x	y	z	atom	x	y	z
U		0		H(1)	0.051 (9)	0.07 (1)	0.43 (1)
C(1)	0.0848 (9)	0.1002 (8)	0.335 (1)	H(2)	−0.096 (8)	0.186 (8)	0.33 (1)
C(2)	−0.0244 (9)	0.1694 (8)	0.254 (1)	H(3)	−0.146 (9)	0.260 (9)	0.04 (2)
C(3)	−0.0605 (9)	0.2235 (7)	0.077 (2)	H(4)	−0.064 (6)	0.274 (5)	−0.177 (9)
C(4)	−0.005 (1)	0.2313 (7)	−0.089 (2)	H(5)	0.114 (8)	0.199 (7)	−0.27 (1)
C(5)	0.112 (1)	0.1843 (7)	−0.152 (1)	H(6)	0.287 (7)	0.104 (7)	−0.13 (1)
C(6)	0.2240 (8)	0.1138 (7)	−0.074 (1)	H(7)	0.302 (8)	−0.134 (9)	0.39 (1)
C(7)	0.2569 (6)	0.0648 (6)	0.103 (1)	H(8)	0.38 (1)	0.006 (8)	0.47 (2)
C(8)	0.1993 (8)	0.0598 (6)	0.268 (1)	H(9)	0.46 (1)	−0.006 (7)	0.20 (2)
C(9)	0.308 (1)	−0.0316 (9)	0.356 (2)	H(10)	0.370 (6)	−0.113 (6)	0.09 (1)
C(10)	0.370 (1)	−0.0269 (9)	0.183 (2)				

atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
U	1.920 (9)	1.692 (9)	2.26 (1)	0	−0.062 (6)	0
C(1)	6.0 (4)	4.0 (3)	2.1 (2)	−1.9 (3)	1.0 (2)	−0.9 (2)
C(2)	4.2 (3)	4.0 (3)	5.0 (4)	−0.8 (3)	1.9 (3)	−2.4 (3)
C(3)	2.3 (3)	2.1 (3)	9.0 (7)	0.1 (2)	0.0 (4)	−1.3 (4)
C(4)	4.3 (4)	2.1 (2)	5.9 (4)	0.6 (3)	−2.2 (3)	0.5 (3)
C(5)	6.6 (5)	2.9 (3)	2.6 (3)	−1.1 (3)	0.3 (3)	0.0 (2)
C(6)	4.3 (3)	3.4 (3)	4.7 (4)	−1.2 (3)	2.4 (3)	−0.9 (3)
C(7)	2.0 (2)	2.3 (2)	5.6 (4)	−0.3 (2)	−0.3 (2)	−0.2 (2)
C(8)	4.0 (3)	2.5 (3)	3.5 (3)	−0.9 (2)	−1.7 (2)	0.3 (2)
C(9)	6.4 (6)	3.8 (4)	9.0 (8)	−0.8 (3)	−5.0 (6)	1.6 (4)
C(10)	3.2 (3)	4.9 (6)	10.3 (9)	1.0 (3)	−1.9 (4)	−1.5 (5)

atom	B, Å^2	atom	B, Å^2	atom	B, Å^2
H(1)	6.6 (26)	H(5)	3.4 (18)	H(8)	7.2 (32)
H(2)	4.1 (18)	H(6)	3.2 (17)	H(9)	5.6 (23)
H(3)	6.7 (28)	H(7)	5.7 (22)	H(10)	2.3 (14)
H(4)	1.3 (11)				

[a] The anisotropic temperature factor has the form $\exp(-0.25(B_{11}h^2a^{*2} + 2B_{12}hka^*b^* + \ldots))$.

Table III. Interatomic Distances (Å)

U-2C(1)	2.675 (7)	C(8)-C(1)	1.38 (2)
-2C(2)	2.654 (7)	C(8)-C(9)	1.54 (2)
-2C(3)	2.618 (7)	C(9)-C(10)	1.47 (2)
-2C(4)	2.631 (8)	C(10)-C(7)	1.55 (2)
-2C(5)	2.637 (8)	C(1)-H(1)	0.87 (5)
-2C(6)	2.674 (7)	C(2)-H(2)	0.96 (8)
-2C(7)	2.637 (6)	C(3)-H(3)	0.94 (9)
-2C(8)	2.626 (6)	C(4)-H(4)	0.93 (6)
C(1)-C(2)	1.38 (2)	C(5)-H(5)	0.87 (9)
C(2)-C(3)	1.41 (2)	C(6)-H(6)	0.79 (8)
C(3)-C(4)	1.39 (2)	C(9)-H(7)	1.16 (9)
C(4)-C(5)	1.41 (2)	-H(8)	1.06 (14)
C(5)-C(6)	1.40 (2)	C(10)-H(9)	0.92 (11)
C(6)-C(7)	1.38 (2)	-H(10)	1.15 (8)
C(7)-C(8)	1.40 (2)		

ref 14, 15, and 16, respectively; dispersion corrections used were from ref 17.

The R indices are given in Table I and the parameters in Table II. In the last cycle the largest shift was 0.26σ. The largest peak

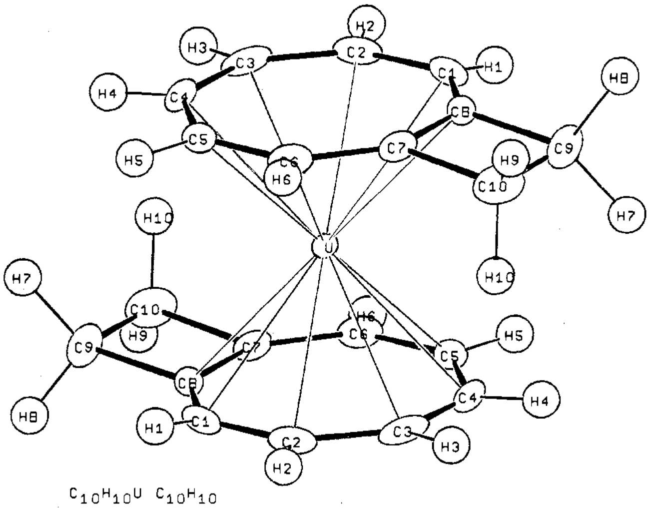

Figure 1. ORTEP drawing of the molecule.

Table IV. Selected Angles (deg)

C(8)-C(1)-C(2)	131.7 (8)	C(8)-C(7)-C(10)	91.3 (9)
C(1)-C(2)-C(3)	134.0 (8)	C(7)-C(8)-C(9)	91.4 (10)
C(2)-C(3)-C(4)	136.7 (8)	C(8)-C(9)-C(10)	89.0 (9)
C(3)-C(4)-C(5)	135.0 (9)	C(7)-C(10)-C(9)	88.4 (8)
C(4)-C(5)-C(6)	135.7 (8)	C(8)-C(9)-H(7)	132 (4)
C(5)-C(6)-C(7)	130.6 (7)	C(8)-C(9)-H(8)	112 (6)
C(6)-C(7)-C(8)	137.2 (7)	H(7)-C(9)-H(8)	106 (6)
C(7)-C(8)-C(1)	139.0 (7)	C(7)-C(10)-H(9)	121 (5)
C(6)-C(7)-C(10)	131.0 (9)	C(7)-C(10)-H(10)	113 (4)
C(1)-C(8)-C(9)	129.2 (11)	H(9)-C(10)-H(10)	102 (6)

in the final difference map was 1.1 e/Å^3. A list of distances and angles is given in Tables III and IV, with atoms numbered as in Figure 1.

Discussion

The title compound exists as discrete molecules in the solid state. With the uranium at the origin of the unit cell, the molecule has a center of symmetry imposed on it by the space group, and the C_8 rings are exactly eclipsed. The molecular symmetry is close to C_{2h}. The uranium atom is sandwiched by the two cyclobutenocyclooctatetraene moieties, and it is accurately centered on the cyclooctatetraene (C_8) rings; i.e., the U atom is very nearly equidistant from all of the atoms in the C_8 ring; see Figure 1 and Table III. The cyclobuteno (C_4) ring is planar, and the plane of ring is bent about 6.8° from the plane of the C_8 ring toward the center of the molecule (i.e., the two most distant carbon atoms are both 0.18 Å below the least-squares plane through the C_8 ring); none of the atoms in the C_8 ring is more than 0.016 Å from its least-squares plane. The U–C(9) and U–C(10) nonbonded distances are 3.69 (1) and 3.71 (1) Å, respectively.

Bond angles and distances are comparable to those found in other uranocenes. The mean U–C value in this compound is 2.64 ± 0.02 Å: this compares with a value of 2.65 Å in uranocene,[5] 2.66 Å in U$(C_8H_4(CH_3)_4)_2$,[7] and 2.65 ± 0.03 Å in octaphenyluranocene.[9] Variations in the U–C bond length in the title compound are statistically significant. They result from a slight distortion of the C_8 ring caused by the cyclobuteno adduct; i.e., where C(9) and C(10) are attached to the COT ring the angles inside the ring are 2 or 3° more than the ideal value of 135°, while the other angles around the ring compensate to maintain planarity. The mean C–C bond length, uncorrected for thermal motion, is 1.39 ± 0.02 Å. It is evident from the ORTEP drawing in Figure 1 that there is considerable torsional motion in the plane of the ring. We estimate an increase to 1.41 Å for the average C–C bond length due to this motion.[9] This compares to 1.42 Å in octaphenyluranocene,[9] 1.41 Å in U$[C_8H_4(CH_3)_4]_2$,[7] 1.41 Å in a potassium salt of the $C_8H_4(CH_3)_4$ dianion,[18] and 1.42 Å (after correction for torsional motion) in thoracene and uranocene.[5] The bond lengths of C(8)–C(9), C(7)–C(10), and C(9)–C(10) are aliphatic in nature with the first two being close to the accepted C–C bond length. The C(9)–C(10) bond length is 1.47 (2) Å, which would increase to 1.49 Å with a correction for torsional motion, and is still somewhat short of the expected value of 1.54 Å.

Although the four-membered cyclobuteno ring is very nearly planar, the hydrogen atoms of the CH_2 groups, H(7) through H(10) in Figure 1, are not symmetrically disposed across the plane. The H(7)–C(9)–H(8) and H(9)–C(10)–H(10) groups are twisted in such a way as to move H(7) away from the uranium atom and H(10) toward it. This distortion, which results in a staggered configuration of the hydrogen atoms of the two methylene groups, is presumably a consequence of hydrogen–hydrogen repulsion, but crystal packing forces must be invoked to explain why this configuration occurs rather than the reverse one with H(7) closer to the uranium atom.

If the molecules are regarded as spheres, their packing corresponds approximately to the tetragonal protactinium metal structure[19] with ten nearest neighbors at the following distances, measured between uranium atoms: two at 7.22 Å, four at 7.91 Å, and four at 8.58 Å. Other nearby molecules are two at 9.91 Å, two at 11.04 Å, and two at 11.32 Å. Inspection of intermolecular hydrogen–hydrogen distances shows that each molecule is in van der Waals contact with its ten nearest neighbors and also, through the hydrogen atoms on the C_4 rings, with the neighbors at 9.91 and 11.32 Å.

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Registry No. U$[C_8H_6(CH_2)_2]_2$, 70377-87-6.

Supplementary Material Available: Data processing formulas, a calculated powder pattern, and a listing of observed structure factors (12 pages). Ordering information is given on any current masthead page.

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