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Molecular Structure and Disorder in Crystals of Octaphenyluranocene, $U[C_8H_4(C_6H_5)_4]_2$[1]

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Bis[π-(1,3,5,7-tetraphenylcyclooctatetraene)]uranium crystallizes with a novel disorder of the molecular packing which is described as frequent twinning of a monoclinic structure, of space group *P2/c*, with $a = 24.86$ (2) Å, $b = 7.587$ (6) Å, $c = 27.78$ (3) Å, $\beta = 116.58°$, $Z = 4$, and $d_x = 1.495$ g cm^{-3} at 23.0 (5) °C. The completely disordered structure has orthorhombic symmetry, of space group *Pccn*, with $a = 24.84$ (3) Å, $b = 12.43$ (1) Å, $c = 7.587$ (6) Å, and $Z = 2$. Refinement by least squares of x-ray diffractometer data reduced the weighted *R* to 0.033 for 723 reflections. The molecule is a sandwich compound with the C_8 rings in a nearly eclipsed configuration and with phenyl rings, tilted an average of 42° from the plane of the C_8 ring, in a staggered configuration. The C–C–C angles in the C_8 ring alternate between average values of 140° at carbon bonded to hydrogen and 130° at carbon bonded to phenyl. A similar alternation between 138 and 132° occurs in the analogous methyl-substituted compound. The phenyl compound in crystalline form is stable in air, with no significant change in x-ray diffraction intensities in 3 months.

Introduction

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 bis[π-(1,3,5,7-tetraphenylcyclooctatetraene)]uranium when it was synthesized by Streitwieser and Walker.[2] The immediate objective was a description of the molecular geometry and in particular the positions and orientations of the phenyl rings. In view of the discovery of two different rotomeric configurations in crystals of the analogous methyl-substituted compound,[3] there was some doubt what to expect. The x-ray diffraction data soon showed the existence of an unexpected and novel disorder problem concerning the molecular packing which made the analysis of the structure more involved than is ordinarily the case.

Experimental Section

Bis[π-(1,3,5,7-tetraphenylcyclooctatetraene)]uranium, $U[C_8H_4(C_6H_5)_4]_2$, was prepared by the reaction of UCl_4 with the dianion of 1,3,5,7-tetraphenylcyclooctatetraene.[2] The polycrystalline product, in a drybox, was loaded into a Pyrex tube fitted with a stopcock. The tube was pumped to about 10^{-6} Torr; then one end was plunged into a hot salt bath. Clusters of small dark brown single crystals condensed 1 or 2 cm above the bath. Various conditions were tried, and the best crystals were obtained with the bath at 400 °C. No solvent has been found good enough to permit crystal growth from solution.

When the x-ray work was started, it was believed that the compound decomposed significantly in a few days on exposure to air. The crystals were very thin needles, and we anticipated correctly that the diffraction intensities would be weak. In order to avoid the higher background associated with capillaries we glued crystals with epoxy to Pyrex glass fibers for x-ray diffraction work. As it turned out, the crystals were stable indefinitely.

The diffraction patterns consist of sharp reflections and diffuse streaks. We describe them by reference to a primitive orthorhombic lattice which corresponds to the sharp reflections. An oscillation pattern (*c*-axis rotation) showed the odd layers as continuous streaks superimposed on a few sharp reflections, while the even layers appeared as normal sharp reflections. Weissenberg photographs taken with long exposure times (up to 72 h) indicated orthorhombic symmetry and showed streaks which were continuous in the a^* direction at l odd and k half-integral.

Diffractometer measurements were made first considering only the sharp reflections, using a crystal with dimensions approximately 0.030 × 0.056 × 0.174 mm. Unit cell dimensions were determined from six hand-centered reflections with a Picker FACS-I automatic diffractometer equipped with a graphite monochromator and molybdenum radiation (λ 0.7107 Å for Kα). The same instrument was used to collect the intensity data. The integrated intensity of each reflection was measured using a θ–2θ scan technique with a scanning rate of 1°/min from 0.5° below the 2θ angle at which Kα_1 was diffracted to 0.5° above the 2θ angle at which Kα_2 was diffracted. Two 20-s background counts were taken with the apparatus stationary and offset 0.5° from each end of the scan. Three reflections ($00\bar{2}$, 510, 220) were remeasured at intervals of 200 reflections to check for crystal decomposition and/or instrument malfunction. The data show an average decay of about 4% from beginning to end, but this change is almost obscured by random variations. Since the decay rate is small and poorly established and since averaging of measurements made early and late tends to compensate for this effect, no correction was applied for decay. Measurements were made of most of the reflections in the hemisphere $\pm h,+k,\pm l$, $2\theta < 45°$. Absorption corrections calculated by an analytical integration[4] ranged from 1.098 to 1.215. Their validity was justified by multiple measurements of three reflections at various azimuthal angles. Equivalent reflections among the 4860 measured were averaged to give 1617 which are unique. For 800 of them $F^2 > s(F^2)$, where s is the standard deviation based on counting statistics. For derivation of weights in least-squares calculations, the variance of F^2 was taken as $\sigma^2(F^2) = s^2(F^2) + (pF^2)^2 + q^2$, where p and q were chosen by trial and error to give a flat distribution of $\langle w(\Delta F)^2\rangle$ as a function of magnitude of F. Zero weight was assigned when $F^2 < \sigma(F^2)$.

The same crystal was used to take a data set on the streaks. The same θ–2θ scan technique was employed as for the sharp features. Measurements were made at both integral and half-integral values of h, with k half-integral and l odd. These reflections were measured in the hemisphere $\pm h,\pm k,-l$ up to 2θ of 25°. Of the 1196 reflections measured, 599 were unique according to monoclinic symmetry, and for 508, $F^2 > \sigma(F^2)$. There was no decay for the three standards within the experimental accuracy of the experiment.

Crystal Data

For the ideal ordered structure described below, the symmetry is monoclinic, space group *P2/c*; at 23.0 ± 0.5 °C, $a = 24.86$ (2) Å, $b = 7.587$ (6) Å, $c = 27.78$ (3) Å, $\beta = 116.58°$, $Z = 4$, mol wt 1055.12, $d_x = 1.496$ g cm^{-3}, $V = 4684$ Å^3, and μ(Mo Kα) = 33.3 cm^{-1}. For the completely disordered structure the symmetry is orthorhombic, space group *Pccn*, with $a = 24.84$ (3) Å, $b = 12.43$ (1) Å, $c = 7.587$ (6) Å, and $Z = 2$.

Structure Determination

The data were analyzed in two stages. Consideration of reflections corresponding to the orthorhombic lattice (the sharp reflections), without any attention to the streaks, gave a result which represents the average of the structure over all of the orthorhombic unit cells. It was determined and refined by conventional methods. Subsequent analysis of the streaks revealed a monoclinic and orderly pattern of repetition which, with frequent twinning, is our model for the actual structure. The data are not sufficient for independent determination of all of the atomic parameters in the monoclinic symmetry, and the molecular dimensions which are reported below came from the refinement of the sharp reflections alone.

The sharp reflections exhibit orthorhombic Laue symmetry. A Patterson function calculated from these data shows four heavy-atom sites which each must be half-occupied, since the volume corresponds to only two molecules of $UC_{64}H_{48}$. The Patterson function also showed resolved U–C peaks among which one could recognize all of the carbon atoms of the molecular structure. Considerations of packing lead

Table I. Atomic Parameters and Esd's[a] (Orthorhombic Coordinate System)

Atom	x	y	z	B, Å^2
U	$^1/_4$	$^1/_4$	0.0100 (4)	*b*
C(1)	0.2826 (7)	0.387 (2)	0.258 (3)	2.9 (5)
C(2)	0.3184 (6)	0.297 (1)	0.260 (3)	2.9 (4)
C(3)	0.3050 (4)	0.4985 (8)	0.260 (3)	2.9 (2)
C(4)	0.3501 (5)	0.5217 (9)	0.362 (2)	3.0 (3)
C(5)	0.3747 (5)	0.622 (1)	0.349 (2)	4.9 (3)
C(6)	0.3565 (5)	0.6994 (9)	0.235 (3)	4.5 (3)
C(7)	0.3113 (5)	0.678 (1)	0.133 (2)	4.6 (3)
C(8)	0.2866 (5)	0.579 (1)	0.144 (2)	3.3 (3)
C(9)	0.3187 (6)	0.185 (1)	0.260 (3)	2.0 (4)
C(10)	0.2752 (6)	0.111 (1)	0.256 (3)	2.2 (4)
C(11)	0.3751 (3)	0.1415 (7)	0.249 (3)	2.5 (2)
C(12)	0.4146 (5)	0.1863 (9)	0.150 (2)	3.6 (3)
C(13)	0.4667 (5)	0.141 (1)	0.142 (2)	5.0 (3)
C(14)	0.4782 (5)	0.050 (1)	0.231 (3)	4.7 (3)
C(15)	0.4395 (5)	0.004 (1)	0.343 (2)	4.7 (3)
C(16)	0.3885 (5)	0.051 (1)	0.353 (2)	3.8 (3)
H(1)	0.3638	0.4691	0.4412	2.8 (10)
H(2)	0.4050	0.6364	0.4218	7.4 (18)
H(3)	0.3750	0.7661	0.2237	13.0 (42)
H(4)	0.2971	0.7318	0.0569	7.4
H(5)	0.2561	0.5643	0.0710	2.8
H(6)	0.3546	0.3224	0.2604	2.9
H(7)	0.4073	0.2504	0.0842	2.8
H(8)	0.4938	0.1743	0.0735	7.4
H(9)	0.5126	0.0173	0.2201	13.0
H(10)	0.4476	−0.0584	0.4097	7.4
H(11)	0.3626	0.0231	0.4319	2.8
H(12)	0.2881	0.0394	0.2564	2.2

[a] Estimated standard deviation of the last digit is in parentheses; if none is given, the parameter is subject to a constraint. [b] For U, $B_{11} = 2.20$ (5), $B_{22} = 3.52$ (6), $B_{33} = 1.88$ (5), $B_{12} = 1.7$ (2), $B_{13} = B_{23} = 0$.

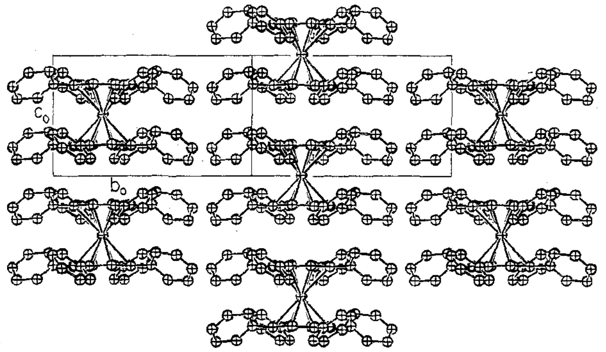

Figure 1. Structure of molecules whose centers are at $x = ^1/_4$. Two unit cells of the orthorhombic lattice which describes the periodicity of the hydrocarbon structure are outlined. The monoclinic cell, with $a_M = 2b_0$ and $b_M = c_0$, is required to describe the uranium structure, which is ordered within each layer.

uniquely to one pattern of relative molecular orientations. Up to this point no particular assumption was necessary about the space group. The structure which was found corresponded to space group *Pccn*, for which reflections are absent for the following classes: $0kl$, $l \neq 2n$; $h0l$, $l \neq 2n$; $hk0$, $h + k \neq 2n$. All such reflections were either weak or absent, but for 17 of them (out of 239) the structure factor was measured to be greater than its standard deviation. We ignored these reflections and chose *Pccn* as the space group for refinement of the disordered structure.

This model includes 16 independent carbon atoms in the asymmetric unit, along with one fractional uranium atom. After four cycles of least-squares refinement of these 17 atoms with isotropic thermal parameters and by using $p = 0.05$ and $q = 0$, $R = \sum|\Delta F|/\sum|F_o| = 0.13$ for 800 reflections with $F^2 > \sigma(F^2)$. Four more cycles, using anisotropic thermal parameters for the uranium atom but isotropic temperature factors for the carbon atoms, reduced R to 0.107 and $R_w = (\sum w(\Delta F)^2/\sum wF_o^2)^{1/2}$, the quantity minimized, to 0.068. Using anisotropic thermal parameters also for the carbon atoms gave several carbon atom thermal tensors that were not positive definite. Therefore, the data do not warrant making the carbon atoms anisotropic. Further refinements were made with $q = 8$. This reduced the number of reflections with $F^2 > \sigma(F^2)$ to 740, and deleting the reflections forbidden by space group *Pccn* reduced that number to 723. Refinement of the 17 atoms in the asymmetric unit, using anisotropic parameters only for uranium resulted in $R = 0.088$ for 723 reflections and $R_w = 0.058$. Hydrogen atom positions were calculated assuming planar-trigonal geometry at carbon atoms and a C–H bond length of 0.95 Å. The hydrogen contributions to the structure factors were calculated with the phenyl hydrogen atoms fixed in their calculated positions. The isotropic thermal parameters were constrained to be equal, respectively, for ortho, meta, and para hydrogen atoms. For hydrogen atoms on the cyclooctatetraene (COT) ring, each thermal parameter was constrained to be equal to that of the carbon atom bonded to it, and each C–H bond was held constant in length and direction. With all of these constraints, only three more independent parameters were added. When further refinement shifted the carbon atoms, the hydrogen atom positions were calculated a second time. With $p = 0.015$ and $q = 8$, the final $R = 0.081$ and $R_w = 0.033$ for 723 reflections. The standard deviation of observation of unit weight was 0.981. The scattering factors used were those of Doyle and Turner[5] for the neutral uranium and carbon atoms, those of Stewart, Davidson, and Simpson[6] for spherical hydrogen, and the dispersion corrections from Cromer and Liberman.[7] In the last cycle no parameter changed more than 0.004σ. Final parameters are listed in Table I.

The data from the streaks were used to calculate a Patterson function, without including the sharp reflections. This was done separately because the continuous nature of the streaks causes a problem about scaling which we did not attempt to solve. This function, if scaled properly, should be added to the previous Patterson function to give the function for the entire data set. Thus it can be examined to determine corrections to be made in the disordered structure determined before.

This correction function was calculated using monoclinic symmetry because deviations from orthorhombic symmetry were observed in the intensity measurements. It has periodicity according to the monoclinic lattice with *C*-centering and with the c axis doubled, because of the manner of sampling of the streaks. However, its main features repeat with periodicity c rather than $2c$. It is antisymmetric in relation to planes at $y = ^1/_4$ because of the absence of k-even terms (l-even in the orthorhombic description). By far the most prominent features are the origin peak and the peaks related to it by the above symmetries. These vectors and the absence of diffuse scattering except in the direction of c^* (orthorhombic a^*) show that the uranium structure must be ordered in any layer parallel with a and b (orthorhombic b and c) according to the pattern shown in Figure 1. Furthermore, this structure must repeat with considerable probability at a displacement equal to c. A considerably smaller peak at 0, 0, $^1/_2$ and equivalent points shows that the relation to a layer with displacement $c/2$ is nearly random between two choices of the uranium positions. These facts are explained by a model with space group *P*2/*c* and uranium in special positions 2(e), $\pm(0, y, ^1/_4)$, $y \approx 0$, and 2(f), $\pm(^1/_2, y, ^1/_4)$, $y \approx ^1/_2$. This structure is highly twinned with two distinct orientations of the monoclinic c axis as seen in Figure 2. This twinning constitutes simply a change in the stacking of adjacent layers. The deviations from orthorhombic symmetry in the streaks show that the specimen studied contains unequal amounts of the two orientations.

A remarkable feature of this structure is that the carbon and hydrogen atom positions need not change much regardless of the uranium positions. The space between adjacent molecules in a stack in the direction of b (orthorhombic c) is nearly the same as the space occupied within the molecule by the uranium atom, and the parallel COT rings with their attached phenyl rings have the same geometrical relation (to a good approximation) with either site (see Figure 1). A description of the structure in space group *P*2/*c* requires 64 carbon atoms in the asymmetric unit. The available data are quite insufficient to determine so many parameters, even without the formidable problems connected with the twinning and the large amount of pseudosymmetry. We made no attempts to refine the structure in the monoclinic symmetry.

Discussion

The method of refinement makes no distinction between the site occupied by uranium and the similar site between two

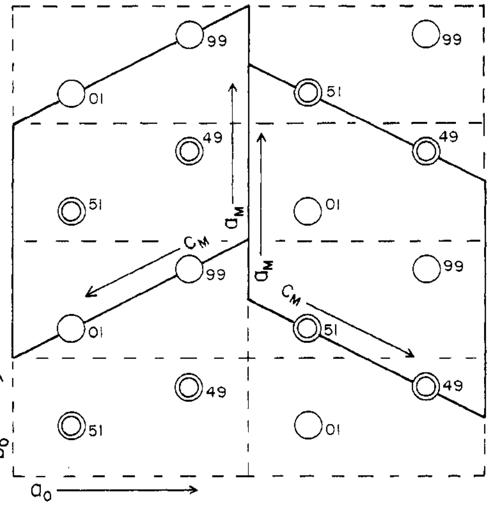

Figure 2. Twinning and relation of the monoclinic cell (solid lines) to the orthorhombic lattice (broken lines). The numbers indicate *z* coordinates (×100) of uranium atoms (orthorhombic). The uranium atoms just right of center are at the twin boundary and have coordinates appropriate to either orientation.

Table II. Bond Distances (Å)

C(1)–C(3)	1.49 (2)	C(9)–C(11)	1.51 (2)
	COT Ring		
C(1)–C(2)	1.43 (2)	C(10)–C(1′)	1.44 (1)
C(2)–C(9)	1.40 (1)	Mean C–C	1.42 (2)
C(9)–C(10)	1.42 (2)		
	Phenyl Bonded Carbons		
U–C(1)	2.66 (2)	U–C(9′)	2.67 (2)
U–C(9)	2.68 (2)	Mean U–C	2.68 (1)
U–C(1′)	2.69 (2)		
	Hydrogen Bonded Carbons		
U–C(2)	2.62 (2)	U–C(10′)	2.66 (2)
U–C(10)	2.62 (2)	Mean U–C	2.63 (2)
U–C(2′)	2.61 (2)		
	Phenyl Rings		
C(3)–C(4)	1.39 (2)	C(11)–C(12)	1.36 (2)
C(4)–C(5)	1.39 (2)	C(12)–C(13)	1.41 (2)
C(5)–C(6)	1.38 (2)	C(13)–C(14)	1.34 (2)
C(6)–C(7)	1.39 (2)	C(14)–C(15)	1.41 (2)
C(7)–C(8)	1.37 (2)	C(15)–C(16)	1.40 (2)
C(8)–C(3)	1.41 (2)	C(16)–C(11)	1.41 (2)
Mean C–C	1.39 (1)	Mean C–C	1.39 (3)

molecules. The plane-to-plane distance between COT rings, averaged for these two sites, is 3.793 (3) Å. The ring-to-ring distance is 3.847 (10) Å in the unsubstituted uranocene molecule[8] and 3.836 (9) Å in the octamethyl derivative.[3] A similar value could occur in the octaphenyl compound if carbon atoms are shifted less than 0.03 Å from the average positions reported here. Such shifts are small in comparison to the root-mean-square amplitudes of thermal motion estimated for carbon atoms, which average about 0.21 Å, and therefore are quite consistent with our diffraction data. Because of this disorder, the U–C distances listed in Table II are subject to a systematic error. If the ring-to-ring distance in the molecule is 3.84 Å, each U–C distance in Table II should be increased about 0.02 Å. The disorder is not expected to have any significant effect on the C–C distances and C–C–C angles (Tables II and III).

The molecule, Figures 1 and 3, is a sandwich compound with the COT rings rotated 6° from the eclipsed configuration found in unsubstituted uranocene.[8] The phenyl rings, attached to alternate carbon atoms, are staggered. They are also tilted, the four on one C_8 ring like a right-handed propeller and the four on the other ring in a left-handed manner. The dihedral angles between the planes of the C_8 ring and the phenyl rings are 43.8° (atoms C(3)–C(8)) and 40.3° (atoms C(11)–C(16)). The differences from the average value of 42° are not significant.

Table III. Bond Angles (deg)

C(8)–C(3)–C(4)	117 (1)	C(14)–C(15)–C(16)	118 (1)
C(3)–C(4)–C(5)	120 (1)	C(15)–C(16)–C(11)	121 (1)
C(4)–C(5)–C(6)	122 (1)	C(10′)–C(1)–C(3)	111 (2)
C(5)–C(6)–C(7)	119 (1)	C(2)–C(1)–C(3)	119 (1)
C(6)–C(7)–C(8)	120 (1)	C(8)–C(3)–C(1)	122 (2)
C(7)–C(8)–C(3)	122 (1)	C(1)–C(3)–C(4)	120 (2)
C(16)–C(11)–C(12)	118 (1)	C(2)–C(9)–C(11)	111 (2)
C(11)–C(12)–C(13)	121 (1)	C(10)–C(9)–C(11)	119 (1)
C(12)–C(13)–C(14)	121 (1)	C(9)–C(11)–C(12)	124 (1)
C(13)–C(14)–C(15)	120 (1)	C(9)–C(11)–C(16)	118 (2)

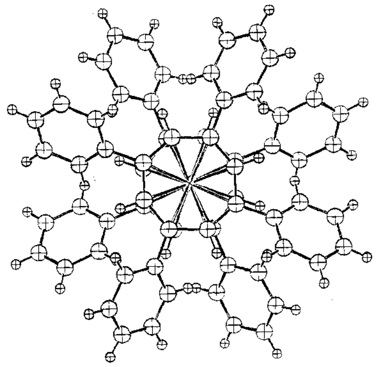

Figure 3. The $U(C_8H_4(C_6H_5)_4)_2$ molecule viewed down the orthorhombic *c* axis. Note that the COT rings are not quite eclipsed.

The C–C bond lengths (Table II) average 1.42 (2) Å in the COT ring and 1.39 (2) Å in the phenyl rings. This value for phenyl rings is well accepted. The COT-ring value is in agreement with the average 1.41 Å found in $U[C_8H_4(CH_3)_4]_2$[3] and with 1.407 (6) Å in a potassium salt of $C_8H_4(CH_3)_4$ dianion.[9] For these crystals the substituents on the rings prevent excessive torsional motion. Values near 1.39 Å are reported for several complexes of unsubstituted C_8H_8 dianion,[8,10] but in each of these cases the effects of thermal motion are appreciable and explain the lower result. For example, a correction calculated according to a rigid-body torsional model with the data for either uranocene or thorocene[8] gives a corrected average C–C = 1.42 Å. For this model, which probably is a good approximation here, the corrected distance is $d_{cor} = [d^2 + 4u^2 \sin^2 (\pi/n)]^{1/2}$, where d is the uncorrected distance, u is the root-mean-square amplitude of motion tangential to the ring, and n is the number of atoms equally spaced in the ring (8 in this case).

The inclusion of hydrogen atoms in the calculations was crucial for the good agreement of these C–C distances and also it made the bond angles more consistent with each other. Without the hydrogen atoms, the C–C distances averaged 1.44 (6) Å in the COT ring and 1.42 (2) Å in the phenyl rings.

The C–C–C angles in the COT ring show an interesting alternation (Figure 4) from about 140°, for angles at carbon atoms bonded to hydrogen, to 130° at those bonded to phenyl. A similar alternation, between 138 and 132°, occurs in tetramethylcyclooctatetraene dianion in the uranium complex[3] and the potassium salt.[9] For some of the angles the observed differences are less than the estimated errors, but with a total of 36 different angle determinations in the two structures the trend is unmistakable.[11] We are unsure whether this angle alternation is simply a steric effect (the sign is right to allow the bulky substituent groups to be more distant from the center of the molecule) or whether there is a deeper electronic explanation.

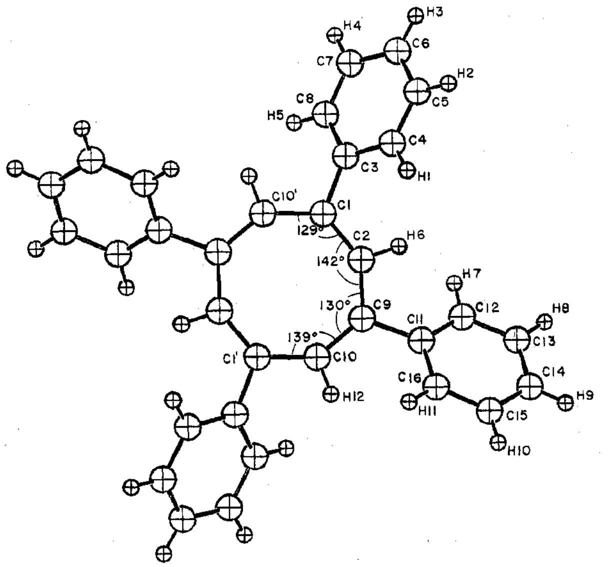

Figure 4. One ligand showing the angles in the COT ring and the numbering of the atoms. For each of these angles, $\sigma = 2°$.

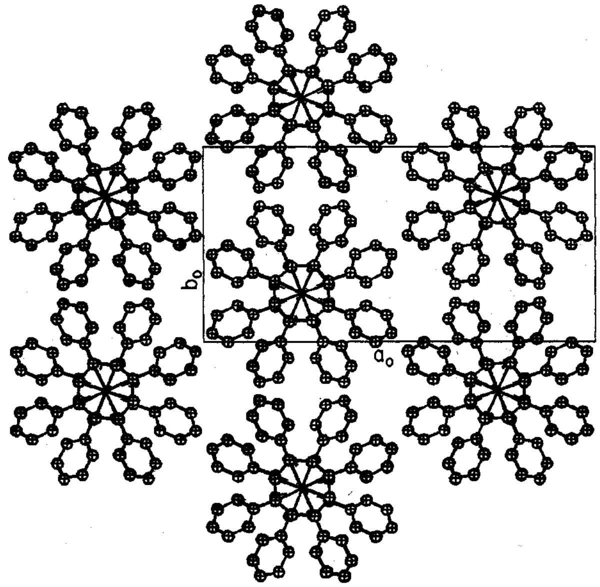

Figure 5. Molecular packing viewed down the orthorhombic *c* axis.

As shown in Figure 1, the molecules stack in columns. These columns, viewed end-on in Figure 5, pack in a triangular fashion. The intermolecular contacts involve the phenyl rings approaching each other in the nearly perpendicular fashion which is so widespread in crystal packing of aromatic compounds. The same kind of phenyl–phenyl proximity occurs within the molecule (Figure 3). The 6° rotation from the eclipsed configuration is attributed to an effect of this packing; the rotation relieves the crowding of phenyl groups in molecules adjacent in the orthorhombic *b* direction (Figure 5) without having much effect on other intermolecular contacts. We expect that isolated molecules in the gas phase would have ideal $\bar{8}$ symmetry.

In contrast to other known uranocene-type compounds, which are sensitive to the atmosphere, the octaphenyl compound in crystalline form is remarkably stable. There was no significant decrease in the diffraction intensities for the crystal when it was reexamined 3 months after the original measurements, and during all of this time it was exposed to the air. The dense packing of the phenyl rings around the molecule and the efficient manner in which molecules are packed together may both contribute to this lack of reactivity.

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Registry No. $U[C_8H_4(C_6H_5)_4]_2$, 58512-04-2.

Supplementary Material Available: Listing of structure factor amplitudes (7 pages). Ordering information is given on any current masthead page.

References and Notes

(1) This work was done in part with support from the U.S. Energy Research and Development Administration.
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(11) The angle alternation, which escaped notice at the time, was partially obscured by inconsistent designation of atoms in the lists of distances and angles for the fourth ring.[3]