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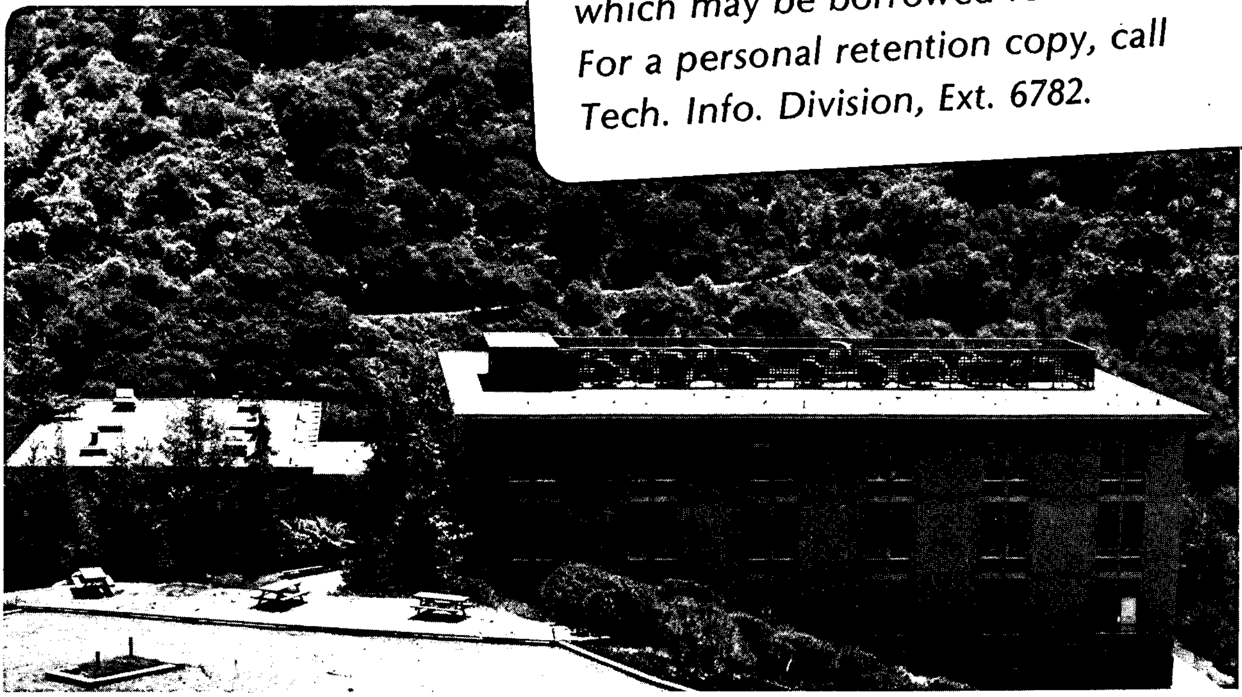

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THE DISORDERED STRUCTURE OF DIBENZOURANOCENE, $[C_8H_6(C_4H_4)]_2U$.

by Allan Zalkin*, David H. Templeton, Robert Kluttz, Andrew Streitwieser Jr.

ABSTRACT

Crystals of $[C_8H_6(C_4H_4)]_2U$, are monoclinic, space group $P2_1/c$, with $a = 9.524$ Å, $b = 8.558$ Å, $c = 11.758$ Å, $\beta = 113.52°$, and $Z = 2$, ($d_x = 2.065$ g/cm^3) at 23°C. For 944 data, $I > 3\sigma$, $R = 0.052$, and $R_w = 0.063$. The benzo-[8]annulene ligand is planar and consists of a six membered phenyl ring fused to an octagonal [8]annulene ring. The uranium atom is sandwiched by two of these ligands and is centered between the two 8-membered rings. The [8]-annulene rings in the sandwich are about 6° away from an eclipsed configuration. The molecules pack in a disordered manner with the uranium atom sometimes on one side of the center of symmetry and sometimes on the other. The results provide structural evidence for ring-metal covalency in uranocenes.

INTRODUCTION

The structure of a number of derivatives of uranocene, di-[8]annulene uranium(IV), have now been established.[1-5] Some of the examples are not centrosymmetric, some contain strained rings, but all show the uranium atom accurately centered between planar 8-membered rings. Bis-(benzo [8]annulene)uranium(IV),[6] 1, provides the further feature of extensive delocalization to the benzene ring. In benzocyclooctatetraene radical anion, for example, a substantial fraction of the odd electron spin density is on the benzene ring.[7] In the corresponding dianion, a substantial amount of charge is delocalized to the benzene ring.[8] Using HMO π- charge populations as a model the electrostatic minimum is located 0.4 Å away from the center of the [8]annulene ring towards the benzene ring. Accordingly, for a wholly ionic structure we would expect the uranium atom in 1 not to be located between the centered of the 8-membered rings. For this compound, a structure determination thus provides a unique contribution to the nature of the ring-metal bonding in these organoactinide compounds.

EXPERIMENTAL

Bis-(benzo[8]annulene)uranium(IV) (dibenzouranocene) 1. The preparation of this compound has been described.[6] The low solubility make the compound difficult to crystallize under normal conditions. An inverted U-tube equipped with a single joint and with 100 mg of solid crude 1 in one arm was filled with 1:2 benzene:hexane. This arm was maintained at 40° and the other at 25°C for a period of 2 mo without stirring. About 10 mg of crystalline product was obtained from the cooler arm. The solid is an intense olive green but the liquid phase was only faintly tinted. Attempted crystallization at a faster rate gave poorly formed disordered crystals.

X-RAY DIFFRACTION

Dark opaque crystals of the compound, because of their extreme sensitivity to the atmosphere, were sealed inside thin walled quartz capillaries. A crystal approximately 0.2 x 0.2 x 0.05 mm in size was examined with a Picker FACS-I automatic diffractometer equipped with a graphite monochromator and a Mo x-ray tube ($\lambda(K\alpha_1)0.70930$ Å). Omega scans of several low angle reflections showed peaks with half-widths of 0.13 to 0.16°. The space group is $P2_1/c$. The setting angles of twelve manually centered reflections ($43^\circ < 2\theta < 49^\circ$) were used to determine by least-squares the following cell parameters: $\underline{a}$ = 9.524(4) Å, $\underline{b}$ = 8.558(4) Å, $\underline{c}$ = 11.758(6) Å, V = 878.7 Å^3 and a molecular weight of 546.49, the calculated density is 2.065 g cm^{-3}.

Intensity data of all the reflections indices ±h, +k, ±l were collected using the θ-2θ scan technique with a scan speed of 2°/min in the range of $4^\circ < 2\theta < 45^\circ$. Each reflection was scanned 0.9° before the $K\alpha_1$ peak, to 0.9° after the $K\alpha_2$ peak, and backgrounds were counted for 4 sec at each end of the scan. The temperature during data collection was 23 ± 1°C. Three standard reflections were measured after every 250th scan to monitor for crystal decay, instrumental stablity and crystal alignment. A decay of 3 percent was observed in the intensities of the standards and the data were adjusted accordingly. A total of 4668 scans (including standards) were performed, resulting in 1727 unique data of which 944 had $I > 3\sigma(I)$. Correction for absorption (μ = 88 cm^{-1}) was made by an analytical integration method,[9] and the factors ranged from 1.47 to 3.84.

The uranium atom position was deduced from a three dimensional Patterson function, and was found to be in the general position of the space group. The short U-U vector of length 2.5 Å suggested disorder problems. The electron density map using the observed structure factors with the phases derived from the uranium positions, showed a collection of peaks in a plane about 2 Å from uranium. The pattern of peaks in the electron density map suggested a disorder of the type found in the structure of azulene,[10] a planar molecule consisting of a 5- and 7-membered ring fused to each other, in which successive azulene molecules are subject to random reversals.

From a scale model on paper of the $C_8H_8C_4H_4$ ligand, a reasonable accounting of the peaks in the electron density map was obtained. Figure 1 shows the electron density map through the plane of the ligand, with the final structure superimposed on it.

As the peaks are not well resolved, restraints on the interatomic distances[11] in the ligand were applied in the least-squares refinement of the structure. Interatomic distances between selected atoms are introduced into the least-squares calculations and treated as observations: estimated standard deviations of these distances are also introduced and used to calculate weights. Except that the derivatives of these distances with respect to the positional parameters are calculated by a special patch and that these "observations" are not included in the R values reported here, these terms are included in the least-squares calculations in the same manner as observed structure factors. This procedure allows the structure to adjust itself to the electron density with a flexibility governed by the weighting. The following C-C distance restraints were imposed: bonded carbons 1.40 ± 0.01 Å, 2nd neighbors in the phenyl ring, 2.43 ± 0.06 Å; 2nd neighbors in the COT ring, 2.60 ± 0.03 Å; 3rd neighbors in the phenyl ring, 2.80 ± 0.05 Å; 3rd neighbors in the COT ring, 3.38 ± 0.05 Å; 4th neighbors in the COT ring, 3.66 ± 0.05 Å. The planarity of the rings is restrained by imposing restraining distances to 2nd, 3rd and 4th neighbors within the ring.

Only the uranium atom was assigned anisotropic thermal parameters in the full matrix least squares refinement.[12] Atomic scattering factors from Doyle and Turner[13] were used and anomalous dispersion corrections were applied.[14] The discrepancy indices, with 106 parameters varied, 84 distance restraints, and 944 data, with ($F^2 > 3\sigma(F^2)$) are:

$$R = \Sigma||F_o|-|F_c||/\Sigma|F_o| = 0.052$$

$$R_w = \Sigma[\underline{w}(|F_o|-|F_c|)^2/\Sigma\underline{w}|F_o|^2]^{1/2} = 0.062$$

R for all 1811 data is 0.107. The error in an observation of unit weight is 2.37. In the last cycle of refinement all parameters changed less than 0.06σ.

RESULTS AND DISCUSSION

Atomic coordinates are given in Table I with the numbering scheme indicated in Fig. 2. Selected distances and angles are given in Table II. Because of the disorder a quantitatively precise description could not be made, however, the results are adequate to give a good description of the overall geometry.

The uranium atom is sandwiched in the center of two cyclooctatraene ([8]annulene) (COT) rings at an average distance of 1.91 Å from the least squares planes of the COT rings. This is within 0.01 Å of comparable distances found in uranocene,[1] octamethyluranocene,[2] octaphenyluranocene,[3], dicyclobutenouranocene,[4] and dicyclopentenouranocene.[5] The 8-membered rings of the ligands in the sandwich are about 6° from an eclipsed conformation, see Fig. 3.

All of the carbons in each 8-membered ring are within 0.03 Å of a common plane and the uranium atom is centered between these rings. Thus, the present determination provides structural evidence[15] for ring-metal covalency in uranocenes.

In some substituted uranocenes the substituents were found to be bent in towards the metal by several degrees.[2,4,5] Because of the disorder problem, the present structure determination is not sufficiently precise to establish this point with respect to the benzene rings. The benzene rings are clearly not bent in severely; we can only state that they are within several degrees (~5°) of coplanarity with the [8]annulene rings.

ACKNOWLEDGMENT

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract Number DE-AC03-76SF00098.

SUPPLEMENTARY MATERIALS AVAILABLE

Listing of observed and calculated structure factors (7 pages). Ordering information is given on any current masthead.

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Table I. Positional and Thermal Parameters in $[C_8H_6(C_4H_4)]_2U$.

Atom	x	y	z	B(Å^2)
U	.14113(13)	.00689(17)	.02844(8)	(a)
C(1)	.1206(24)	.032(3)	.2440(24)	3.4(6)
C(2)	.2788(28)	.040(3)	.2696(26)	2.1(6)
C(3)	.3682(29)	.128(40	.2202(29)	2.7(6)
C(4)	.325(3)	.239(4)	.122(3)	3.2(7)
C(5)	.1864(28)	.310(4)	.047(3)	2.9(7)
C(6)	.0328(29)	.298(40	.023(3)	3.8(8)
C(7)	-.0612(27)	.215(3)	.0686(26)	3.9(7)
C(8)	-.223(3)	.242(5)	-.806(4)	5.1(10)
C(9)	-.332(4)	.162(4)	.026(3)	4.6(9)
C(10)	-.303(3)	.051(4)	.127(3)	4.3(8)
C(11)	-.1461(29)	.037(4)	.185(3)	2.8(8)
C(12)	-.0207(24)	.101(3)	.1624(23)	2.7(5)
C(13)	.024(3)	-.029(6)	-.205(4)	10.4(16)
C(14)	.183(3)	-.016(5)	-.179(3)	4.2(9)
C(15)	.3051(29)	-.097(3)	-.0943(25)	2.4(6)
C(16)	.3270(26)	-.209(3)	.0012(23)	1.7(5)
C(17)	.2232(28)	-.285(4)	.042(3)	2.7(7)
C(18)	.0639(27)	-.292(3)	.0102(24)	2.3(6)
C(19)	-.0718(24)	-.222(3)	-.0824(23)	2.7(5)
C(20)	-.214(3)	-.269(5)	-.082(4)	4.3(9)
C(21)	-.357(4)	-.209(5)	-.163(4)	4.7(9)
C(22)	-.368(4)	-.092(6)	-.249(4)	6.3(12)
C(23)	-.235(3)	-.044(5)	-.260(3)	4.2(10)
C(24)	-.0888(26)	-.1081(29)	-.1773(22)	2.5(5)

(a) Anisotropic thermal parameters (Å^2) for U are: B_{11} = 3.07(4), B_{22} = 1.98(3), B_{33} = 2.03(3), B_{12} = -0.15(9), B_{13} = 1.08(3), B_{23} = -0.41(8). The form of the temperature factors are given in Ref. 10.

Table II. Selected Interatomic Distance (Å).[a]

U-C(1)	2.63(3)	U-C(13)	2.53(5)
-C(2)	2.62(3)	-C(14)	2.63(4)
-C(3)	2.64(3)	-C(15)	2.67(3)
-C(4)	2.58(3)	-C(16)	2.67(3)
-C(5)	2.62(3)	-C(17)	2.60(3)
-C(6)	2.69(4)	-C(18)	2.65(3)
-C(7)	2.80(3)	-C(19)	2.75(3)
-C(12)	2.73(3)	-C(24)	2.72(3)

C(1)-C(2)	1.42(2)	C(13)-C(14)	1.43(2)
C(2)-C(3)	1.43(2)	C(14)-C(15)	1.38(2)
C(3)-C(4)	1.42(2)	C(15)-C(16)	1.43(2)
C(4)-C(5)	1.40(2)	C(16)-C(17)	1.42(2)
C(5)-C(6)	1.38(2)	C(17)-C(18)	1.41(2)
C(6)-C(7)	1.40(20	C(18)-C(19)	1.45(2)
C(7)-C(12)	1.41(2)	C(19)-C(24)	1.44(2)
C(7)-C(8)	1.46(2)	C(19)-C(20)	1.41(2)
C(8)-C(9)	1.41(2)	C(20)-C(21)	1.41(2)
C(9)-C(10)	1.46(2)	C(21)-C(22)	1.39(2)
C(10)-C(11)	1.38(2)	C(22)-C(23)	1.39(2)
C(11)-C(12)	1.43(2)	C(23)-C(24)	1.45(2)

[a] The C-C bond lengths are calculated from the positional parameters calculated in a least-squares refinement procedure where the distances were restrained to 1.40 ± 0.01 Å as described on the text.

Table III. Selected Angles (deg).

C(12)-C(1) -C(2)	140(3)
C(1) -C(2) -C(3)	134(3)
C(2) -C(3) -C(4)	131(3)
C(3) -C(4) -C(5)	135(3)
C(4) -C(5) -C(6)	138(3)
C(5) -C(6) -C(7)	138(3)
C(6) -C(7) -C(12)	129(3)
C(7) -C(12)-C(1)	134(2)
C(12)-C(7) -C(8)	118(3)
C(7) -C(8) -C(9)	119(3)
C(8) -C(9) -C(10)	128(3)
C(9) -C(10)-C(11)	106(3)
C(10)-C(11)-C(12)	134(3)
C(11)-C(12)-C(7)	115(2)

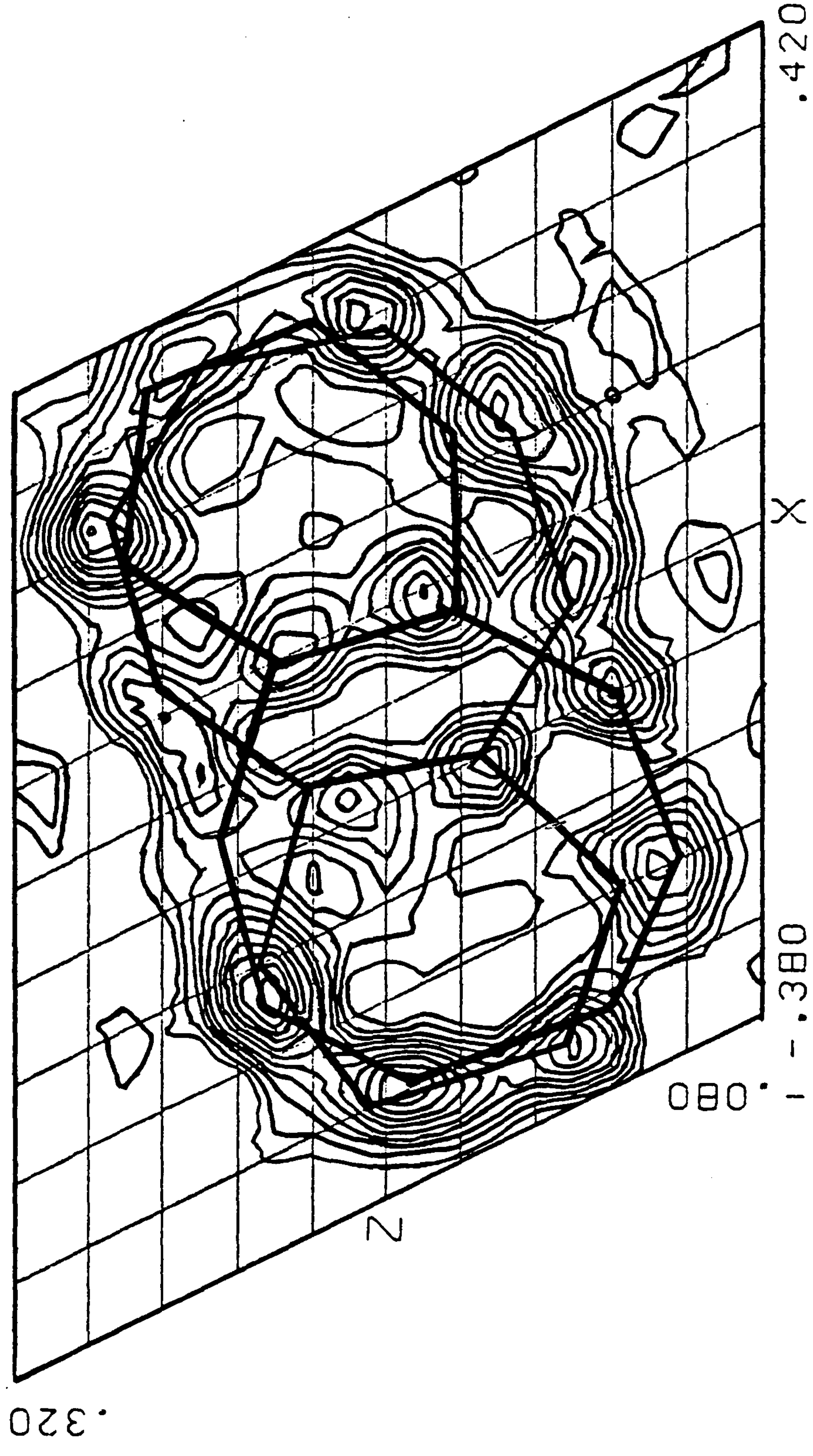
C(24)-C(13)-C(14)	146(4)
C(13)-C(14)-C(15)	129(3)
C(14)-C(15)-C(16)	136(3)
C(15)-C(16)-C(17)	132(2)
C(16)-C(17)-C(18)	139(2)
C(17)-C(18)-C(19)	136(3)
C(18)-C(19)-C(24)	131(2)
C(19)-C(24)-C(13)	130(3)
C(24)-C(19)-C(20)	112(3)
C(19)-C(20)-C(21)	125(3)
C(20)-C(21)-C(22)	121(4)
C(21)-C(22)-C(23)	118(3)
C(22)-C(23)-C(24)	120(3)
C(23)-C(24)-C(19)	124(2)

FIGURE CAPTIONS

Fig. 1. Electron density map through the plane of the ligand with the backbone of the disordered ligands superimposed.

Fig. 2. ORTEP[16] view of molecule showing the numbering scheme.

Fig. 3. ORTEP view perpendicular to the planes of the ligands.



XBL 817-10794

Fig. 1

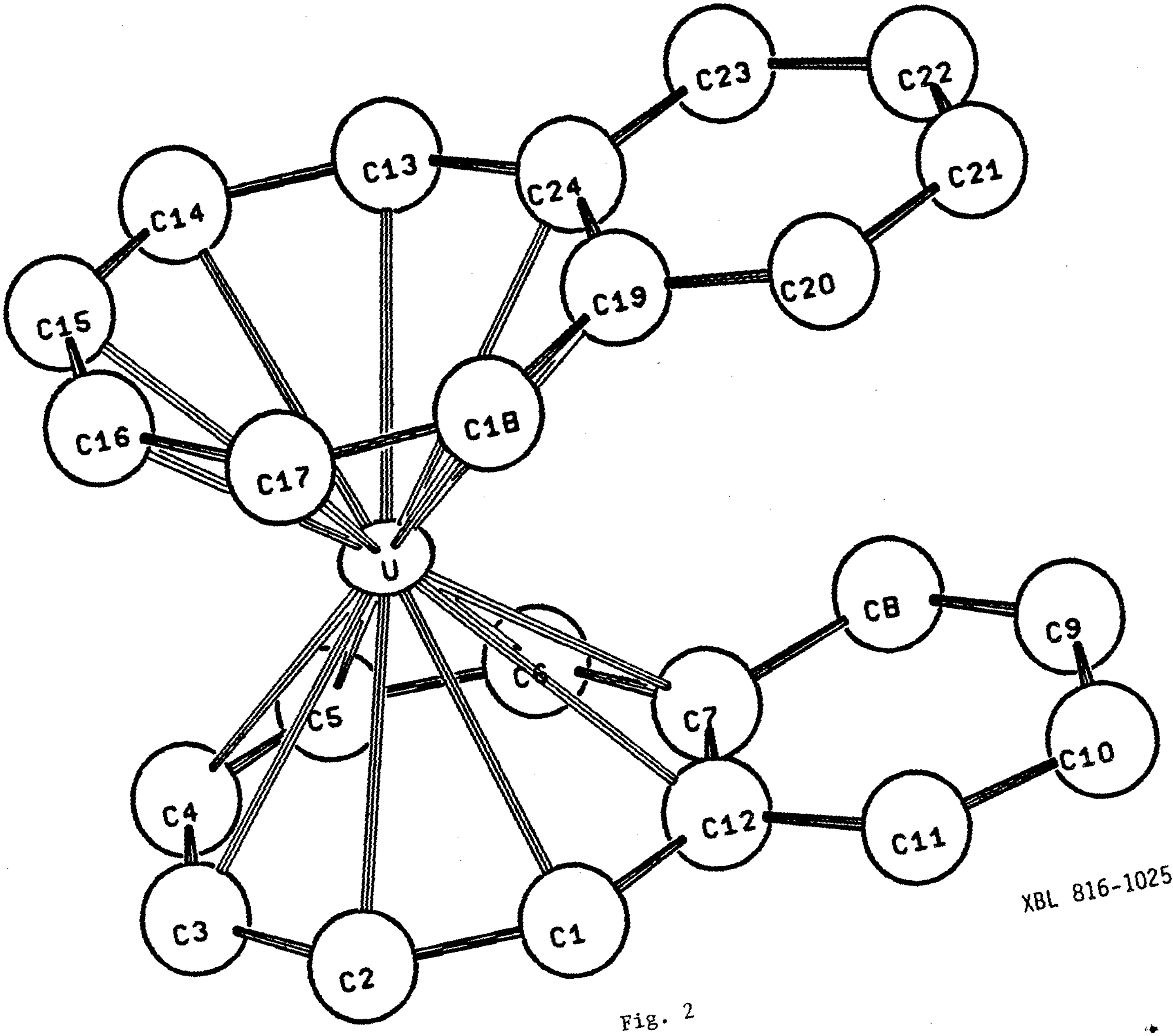


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Fig. 2

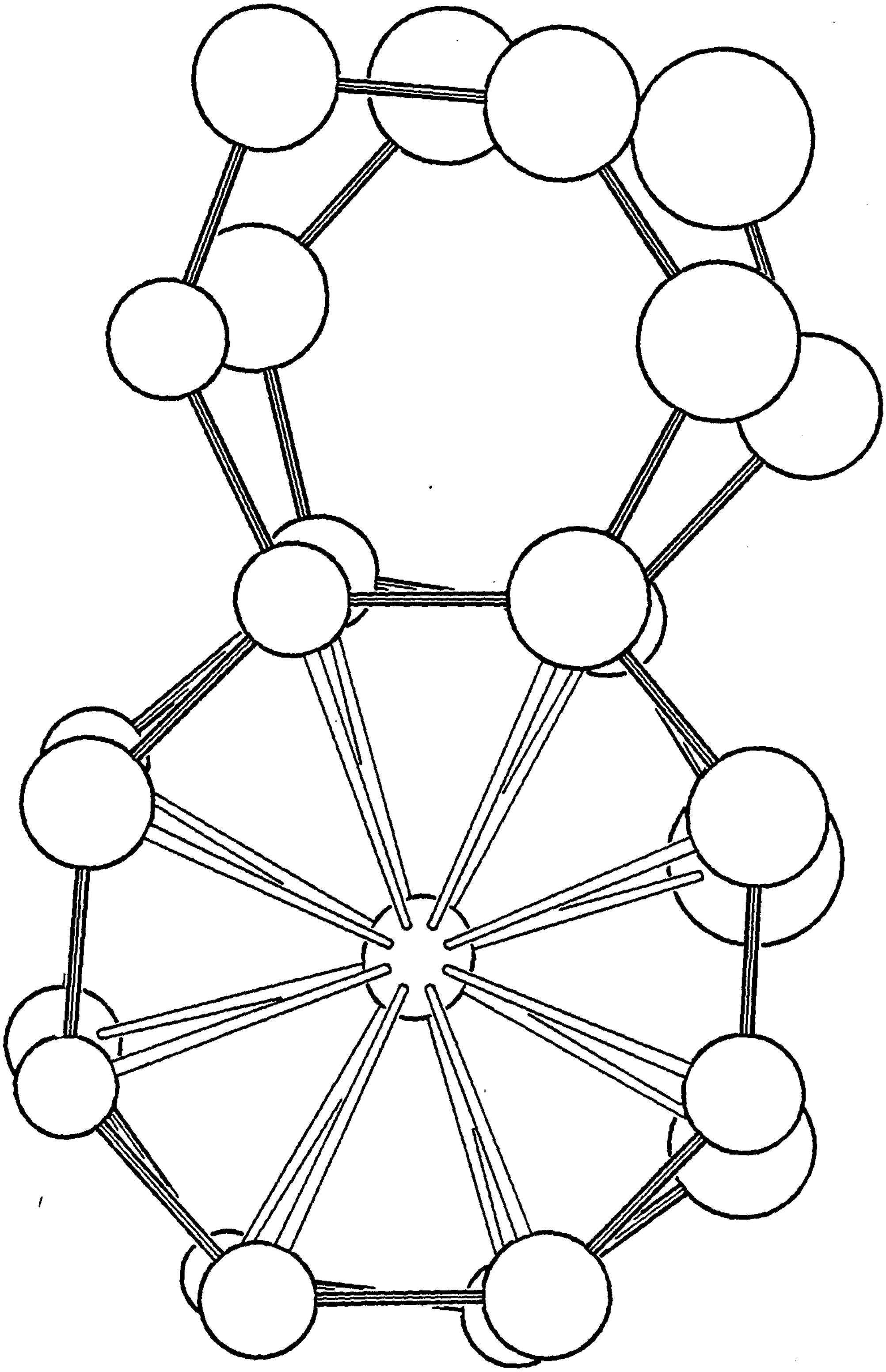

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Fig. 3

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