

Fig. 2. Hydrogen-bonding scheme and packing viewed along *b*. H atoms from the organic ligands not involved in hydrogen bonding and those belonging to the water molecules have been omitted for clarity.

$2.683(6) < \text{N}-\text{H}\cdots\text{O} < 2.851(6) \text{ \AA}$ and $162 < \text{N}-\text{H}\cdots\text{O} < 176^\circ$. Two of them, $\text{N}(23)-\text{H}(23)\cdots\text{O}(2)(-x+1, -y+1, -z)$ and $\text{N}(33)-\text{H}(33)\cdots\text{O}(1)(-x+1, -y, -z)$, are very strong (especially the former) and nearly linear. Their $\text{N}\cdots\text{O}$ lengths, and angles at H being $2.638(6)$, $2.777(5) \text{ \AA}$ and 162 , 170° respectively. A similar short and nearly linear $\text{N}-\text{H}\cdots\text{O}(\text{P})$ hydrogen bond is observed in the crystal structure of imidazolium dihydrogen orthophosphate, where the corresponding values are $2.712(10) \text{ \AA}$ and 172° (Blessing & McGandy, 1972).

Of the atoms participating in hydrogen bonding only the water O atoms serve simultaneously as both acceptor and donor. There are four non-coordinated water molecules of crystallization, and all are involved in $\text{O}-\text{H}\cdots\text{O}(\text{water})$ and $\text{O}-\text{H}\cdots\text{O}(\text{P})$ hydrogen-bond formation. But while two of them, O(6) and O(8), are donors in two and acceptors in one such contact, water

molecule O(5) is a donor in two, and water molecule O(7) is a donor in only one hydrogen bond.

Fig. 2 shows the structure projected along *b* with the hydrogen-bonding scheme.

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References

- AKHTAR, F., GOODGAME, D. M. L., RAYNER-CANHAM, G. W. & SKAPSKI, A. C. (1968). *Chem. Commun.* pp. 1389–1390.
- BLESSING, R. H. & MCGANDY, E. L. (1972). *J. Am. Chem. Soc.* **94**, 4034–4035.
- EICHHORN, G. I. (1973). In *Inorganic Biochemistry*, Ch. 4. Amsterdam: Elsevier.
- FRANSSON, G. & LUNDBERG, B. K. S. (1972). *Acta Chem. Scand.* **26**, 3969–3976.
- FRANSSON, G. & LUNDBERG, B. K. S. (1978). *Acta Chem. Scand. Ser. A*, **28**, 578–588.
- FREEMAN, H. C. (1967). *Adv. Protein Chem.* **22**, 257.
- FREEMAN, H. F. & COLVER, C. W. (1938). *J. Am. Chem. Soc.* **60**, 750–752.
- HUQ, F. & SKAPSKI, A. C. (1971). *J. Chem. Soc. A*, pp. 1927–1931.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.
- JOHNSON, C. K. (1976). *ORTEP*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee.
- LUNDBERG, B. K. S. (1972a). *Acta Chem. Scand.* **26**, 3902–3912.
- LUNDBERG, B. K. S. (1972b). *Acta Chem. Scand.* **26**, 3977–3983.
- McFADDEN, D. L., MCPHAIL, A. T., GARNER, C. D. & MABBS, F. E. (1975). *J. Chem. Soc. Dalton Trans.* pp. 263–268.
- McFADDEN, D. L., MCPHAIL, A. T., GARNER, C. D. & MABBS, F. E. (1976). *J. Chem. Soc. Dalton Trans.* pp. 47–52.
- McMULLAN, R. K., EPSTEIN, J., RUBLE, J. R. & CRAVEN, B. M. (1979). *Acta Cryst.* **B35**, 688–689.
- MARTINEZ-CARRERA, S. (1966). *Acta Cryst.* **20**, 783–789.
- MOREHOUSE, S. M., POLYCHRONOPOULOU, A. & WILLIAMS, G. I. B. (1980). *Inorg. Chem.* **19**, 3558–3561.
- SJÖBERG, S. (1972). *Acta Chem. Scand.* **26**, 3400–3403.
- Syntax (1976). *XTL/XTLE Structure Determination System*. Syntax Analytical Instruments, Cupertino, California.

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Disordered Structure of Dibenzouranocene, $[\text{U}(\text{C}_{12}\text{H}_{10})_2]$

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Abstract. $M_r = 546.46$, monoclinic, $P2_1/c$, $a = 9.524(4)$, $b = 8.558(4)$, $c = 11.758(6) \text{ \AA}$, $\beta = 113.52(4)^\circ$, $V = 878.7 \text{ \AA}^3$, $Z = 2$, $D_x = 2.065 \text{ g cm}^{-3}$, $\lambda(\text{Mo K}\alpha) = 0.71073 \text{ \AA}$, $\mu = 88 \text{ cm}^{-1}$, $F(000) = 512$, $T = 296 \text{ K}$, $R = 0.052$ for 944 observed data. The uranium atom is sandwiched at the center (mean distance 1.91 \AA) of two planar and parallel [8]annulene

rings that are $\sim 6^\circ$ from an eclipsed conformation. The molecules pack in a disordered manner across a center of symmetry.

Introduction. The structures of a number of derivatives of uranocene, di[8]annuleneuranium(IV) ([8]annulene is cyclooctatetraene), have now been established

(Zalkin & Raymond, 1969; Avdeef, Raymond, Hodgson & Zalkin, 1972; Hodgson, Dempf & Raymond, 1971; Hodgson & Raymond, 1973; Templeton, Templeton & Walker, 1976; Zalkin, Templeton, Berryhill & Luke, 1979; Zalkin, Templeton, Luke & Streitwieser, 1982). Some of the examples are not centrosymmetric, some contain strained rings, but all show the uranium atom accurately centered between planar eight-membered rings. Bis(benzo[8]annulene)uranium(IV), (1), provides the further feature of delocalization of electron density to a peripheral benzene ring. Its structure, reported here, was studied to learn if this shift of charge results in any shift of the uranium atom from the center toward the benzene rings. Such a shift would be evidence for ionic character of the bonding. The analysis, even though hampered by disorder, rules out any such shift larger than about 0.05 Å.

Experimental. The preparation of (1) was described by Streitwieser, Klutz, Smith & Luke (1983). The low solubility makes 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 313 K and the other at 298 K for a period of two months 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.

A dark opaque crystal was sealed in a quartz capillary because of its reactivity in the atmosphere. No measured density is reported for the same reason. Crystal size 0.2 × 0.2 × 0.05 mm; Picker automatic diffractometer, graphite monochromator; cell dimensions from 12 manually centered reflections, $43 < 2\theta < 49^\circ$; θ - 2θ scan, 2° min^{-1} , $4 < 2\theta < 45^\circ$, h -11 to 10, k 0 to 9, l -14 to 13, 2θ scan width (1.8 + 0.693 × tan θ) $^\circ$; analytical absorption correction (Templeton & Templeton, 1973), range 1.47-3.84; three reference reflections, every 250 scans, 3% decrease; 4668 scans, 1727 unique, 944 with $F^2 > 3\sigma(F^2)$, $R_{\text{int}} = 0.052$; structure solved by Patterson and Fourier methods; refined on F ; local unpublished programs.

A short U-U vector of length 2.5 Å observed in the Patterson function indicated disorder problems with half a uranium atom in a general position of the space group. The electron density map, using phases derived from the uranium positions, showed a collection of peaks in a plane about 2 Å from uranium, with a pattern that suggested a disorder of the type found in the structure of azulene (Robertson, Shearer, Sim & Watson, 1962), in which successive azulene molecules are subject to random reversals. A scaled paper model of the $\text{C}_8\text{H}_6(\text{C}_4\text{H}_4)$ ligand was moved about the electron density map to obtain trial positions for the carbon atoms. As the peaks are not well resolved, distance

restraints (Waser, 1963) were imposed on the carbon atoms in the least-squares refinement, with $\sigma = 0.01$ to 0.06 Å, to maintain the shape and size (and to a lesser extent the planarity) of each ring.* Only the uranium atom was assigned anisotropic thermal parameters in the full-matrix least-squares refinement. Atomic scattering factors of Doyle & Turner (1968) were used and

* Lists of structure factors, anisotropic thermal parameters, distance restraints, additional figures and selected interatomic distances and angles have been deposited with the British Library Lending Division as Supplementary Publication No. 39831 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional and isotropic thermal parameters in [U{C₈H₆(C₄H₄)₂}]*

Because of restraints on C-C distances the coordinates of carbon atoms are strongly correlated and their standard deviations do not represent the accuracy with which they can be determined by the diffraction data alone.

| | <i>x</i> | <i>y</i> | <i>z</i> | <i>B</i> (Å ²) |
|-------|--------------|--------------|--------------|----------------------------|
| U | 0.14113 (13) | 0.00689 (17) | 0.02844 (8) | 2.34* |
| C(1) | 0.1206 (24) | 0.032 (3) | 0.2440 (24) | 3.4 (6) |
| C(2) | 0.2788 (28) | 0.040 (3) | 0.2696 (26) | 2.1 (6) |
| C(3) | 0.3682 (29) | 0.128 (4) | 0.2202 (29) | 2.7 (6) |
| C(4) | 0.325 (3) | 0.239 (4) | 0.122 (3) | 3.2 (7) |
| C(5) | 0.1864 (28) | 0.310 (4) | 0.047 (3) | 2.9 (7) |
| C(6) | 0.0328 (29) | 0.298 (4) | 0.023 (3) | 3.8 (8) |
| C(7) | -0.0612 (27) | 0.215 (3) | 0.0686 (26) | 3.9 (7) |
| C(8) | -0.223 (3) | 0.242 (5) | -0.006 (4) | 5.1 (10) |
| C(9) | -0.332 (4) | 0.162 (4) | 0.026 (3) | 4.6 (9) |
| C(10) | -0.303 (3) | 0.051 (4) | 0.127 (3) | 4.3 (8) |
| C(11) | -0.1461 (29) | 0.037 (4) | 0.185 (3) | 2.8 (8) |
| C(12) | -0.0207 (24) | 0.101 (3) | 0.1624 (23) | 2.7 (5) |
| C(13) | 0.024 (3) | -0.029 (6) | -0.205 (4) | 10.4 (16) |
| C(14) | 0.183 (3) | -0.016 (5) | -0.179 (3) | 4.2 (9) |
| C(15) | 0.3051 (29) | -0.097 (3) | -0.0943 (25) | 2.4 (6) |
| C(16) | 0.3270 (26) | -0.209 (3) | 0.0012 (23) | 1.7 (5) |
| C(17) | 0.2232 (28) | -0.285 (4) | 0.042 (3) | 2.7 (7) |
| C(18) | 0.0639 (27) | -0.292 (3) | 0.0102 (24) | 2.3 (6) |
| C(19) | -0.0718 (24) | -0.222 (3) | -0.0824 (23) | 2.7 (5) |
| C(20) | -0.214 (3) | -0.269 (5) | -0.082 (4) | 4.3 (9) |
| C(21) | -0.357 (4) | -0.209 (5) | -0.163 (4) | 4.7 (9) |
| C(22) | -0.368 (4) | -0.092 (6) | -0.249 (4) | 6.3 (12) |
| C(23) | -0.235 (3) | -0.044 (5) | -0.260 (3) | 4.2 (10) |
| C(24) | -0.0888 (26) | -0.1081 (29) | -0.1773 (22) | 2.5 (5) |

$$* B_{\text{eq}} = \frac{1}{3} \sum_i \sum_j a_i^* a_j^* a_i a_j B_{ij}$$

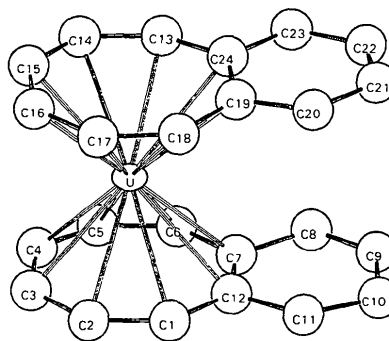


Fig. 1. ORTEP (Johnson, 1965) view of the molecule showing the numbering scheme.

anomalous-dispersion corrections were applied (Cromer & Liberman, 1970). With 106 parameters, 84 distance restraints and 944 observed data, $R = 0.052$, $R_w = 0.062$, $w = 1/\sigma^2(F)$, $S = 2.37$, and $(\Delta/\sigma)_{\max} = 0.06$. For all 1811 data, $R = 0.107$. Max. and min. height in final difference Fourier map 3.3 and $-4.8 e \text{ \AA}^{-3}$.

Discussion. Atomic coordinates are given in Table 1 with the numbering scheme indicated in Fig. 1.

While the disorder limits the accuracy, the results are adequate to describe the overall geometry. The uranium atom is at a mean distance of 1.91 Å from the centers of the two parallel [8]annulene rings, the same within 0.01 Å as comparable distances found in uranocene (Zalkin & Raymond, 1969; Avdeef *et al.*, 1972), octamethyluranocene (Hodgson *et al.*, 1971), octaphenyluranocene (Templeton *et al.*, 1976), dicyclobutenouranocene (Zalkin *et al.*, 1979), and dicyclopentenouranocene (Zalkin *et al.*, 1982). The eight-membered rings of the ligands in the sandwich are about 6° from an eclipsed conformation. The mean U—C bond length is 2.65 (7) Å.

According to HMO π -electron population calculations for the benzo[8]annulene dianion, charge delocalization into the benzene ring shifts the electrostatic minimum 0.4 Å from the center of the [8]annulene ring (Paquette, Ewing, Traynor & Gardik, 1977). For a wholly ionic model of the bonding we would expect some shift of the uranium atom in the same direction. In fact, the uranium atom is found 0.04 Å from the center of gravity of its 16 nearest carbon neighbors, but in a direction away from the benzene rings. Thus there is no evidence for a shift toward the displaced charge. The precision of this displacement is estimated as about 0.03 Å, but is somewhat uncertain because of the disorder.

In some of the substituted uranocenes mentioned above the substituents were found to be bent in towards the metal by several degrees. In the present structure the benzene rings are clearly not bent in severely, but the coplanarity with the [8]annulene rings is established only within a limit of about 5° because of the disorder.

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References

- AVDEEF, A., RAYMOND, K. N., HODGSON, K. O. & ZALKIN, A. (1972). *Inorg. Chem.* **11**, 1083–1088.
 CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.
 DOYLE, P. A. & TURNER, P. S. (1968). *Acta Cryst.* **A24**, 390–397.
 HODGSON, K. O., DEMPF, D. & RAYMOND, K. N. (1971). *Chem. Commun.* **24**, 1592–1593.
 HODGSON, K. O. & RAYMOND, K. N. (1973). *Inorg. Chem.* **12**, 458–466.
 JOHNSON, C. K. (1965). Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
 PAQUETTE, L. A., EWING, G. D., TRAYNOR, S. & GARDIK, J. M. (1977). *J. Am. Chem. Soc.* **99**, 6115–6117.
 ROBERTSON, J. M., SHEARER, H. M. M., SIM, G. A. & WATSON, D. G. (1962). *Acta Cryst.* **15**, 1–8.
 STREITWIESER, A. JR, KLUTTZ, R. Q., SMITH, K. A. & LUKE, W. D. (1983). *Organometallics*, **2**, 1873–1877.
 TEMPLETON, L. K. & TEMPLETON, D. H. (1973). Am. Crystallogr. Assoc. Summer Meet. Abstr. E10.
 TEMPLETON, L. K., TEMPLETON, D. H. & WALKER, R. (1976). *Inorg. Chem.* **15**, 3000–3003.
 WASER, J. (1963). *Acta Cryst.* **16**, 1091–1094.
 ZALKIN, A. & RAYMOND, K. N. (1969). *J. Am. Chem. Soc.* **91**, 5667–5668.
 ZALKIN, A., TEMPLETON, D. H., BERRYHILL, S. R. & LUKE, W. D. (1979). *Inorg. Chem.* **18**, 2287–2289.
 ZALKIN, A., TEMPLETON, D. H., LUKE, W. D. & STREITWIESER, A. JR (1982). *Organometallics*, **1**, 618–622.

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Tetraphenylphosphonium-octachlorodiarsenat, $(\text{PPh}_4)_2[\text{As}_2\text{Cl}_8]$

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Abstract. $M_r = 1112.26$, triclinic, $P\bar{1}$, $Z = 1$, $a = 10.575$ (8), $b = 10.803$ (6), $c = 12.38$ (2) Å, $\alpha = 102.15$ (8), $\beta = 113.24$ (8), $\gamma = 92.36$ (6)°, $V = 1258$ (4) Å³, $D_x = 1.47$ g cm⁻³, $\lambda(\text{Mo K}\alpha) = 0.7107$ Å, $\mu = 18.5$ cm⁻¹, $T = 293$ K, $F(000) = 560$, $R = 0.060$ for 1466 observed independent reflexions. Crystals were obtained from AsCl_3 and PPh_4Cl as well

as from $\text{As}_2\text{S}_5 + \text{PPh}_4\text{Cl} + \text{HCl}$ in H_2CCl_2 solution. The centrosymmetric $\text{As}_2\text{Cl}_8^{2-}$ ion consists of two square pyramids sharing a basal edge. The As—Cl bond lengths show a marked *trans* effect. The cations are grouped to form $(\text{PPh}_4^+)_2$ pairs, eight of which surround an anion. Infrared and Raman spectral data are reported.

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