diffraction ripples and steep gradients could readily result in spurious peaks and significant displacement of main peaks.

It should be added finally that, for the purposes of computation, cosh (as) exp $(-\pi^2 s^2/p)$ is best expressed in the form

$$\tfrac{1}{2}[\exp(A-B)+\exp(-A-B)]\,, \tag{4}$$

where $A=as$ and $B=(\pi^2/p)s^2$.

The factor $\tfrac{1}{2}$ may be absorbed outside the loop over the indices leaving an increase in computation of only three additions and one exponential term over that required to modify a structure amplitude in the usual way.

The author wishes to record his appreciation of fruitful discussions with Drs B. Dawson and A. McL. Mathieson and Mr A. F. Moodie, the latter having also derived the expression for the two-dimensional transform.

References

ABRAHAMSSON, S. & MASLEN, E. N. (1963). *Z. Kristallogr.* **118**, 1.

DONOHUE, J. & TRUEBLOOD, K. N. (1952). *Acta Cryst.* **5**, 414.

HODGKIN, D. C. & MASLEN, E. N. (1961). *Biochem. J.* **79**, 393.

JACOBSON, R. A., WUNDERLICH, J. A. & LIPSCOMB, W. N. (1961). *Acta Cryst.* **14**, 598.

WASER, J. & SCHOMAKER, V. (1953). *Rev. Mod. Phys.* **25**, 671.

Acta Cryst. (1965). **19**, 202

The Crystal and Molecular Structure of Cyclopentadiene*

BY GERALD LIEBLING † AND RICHARD E. MARSH

Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, California, U.S.A.

(*Received* 16 *November* 1964)

The crystal structure of cyclopentadiene, C_5H_6, has been determined from X-ray diffraction photographs made at about −150 °C. The crystals are monoclinic, space group $P2_1/n$, with cell dimensions $a=7{\cdot}89$, $b=5{\cdot}65$, $c=10{\cdot}45$ Å, $\beta=114°\ 10'$. Intensities of 70 reflections recorded on four zero-level precession photographs were estimated visually and used in a least-squares refinement of the atomic coordinates. The final R index for these reflections is 0·10.

The five-membered ring of carbon atoms is planar; the values for the bond distances are in close agreement with those previously determined by electron diffraction techniques.

Introduction

Cyclopentadiene, C_5H_6, when irradiated with ultraviolet light at 77 °K, is damaged to form the very interesting cyclopentadienyl radical C_5H_5 (Liebling & Mc Connell, 1965). While trying to interpret electron paramagnetic resonance spectra of this radical we found that a knowledge of the crystal structure of the parent compound cyclopentadiene was necessary. Accordingly, the present investigation was undertaken.

Experimental

Cyclopentadiene (m.p. −80°C) was prepared by distilling dicyclopentadiene (Moffett, 1952). Single crystals were obtained by slowly lowering a sealed tube of cyclopentadiene from a dry-ice–acetone bath, at which temperature the compound is stable with respect to dimerization (Busler, Williams & Bonin, 1962), into a Dewar vessel of liquid nitrogen. The tube was then broken open under liquid nitrogen and clear monoclinic prisms, elongated along the **b** direction, were extracted from the frozen mass. All further operations on these crystals, including mounting and orientation, were carried out under liquid nitrogen.

A crystal about 2 × 1 × 1 mm in size was inserted into a 1 mm capillary which was then mounted on a goniometer head and transferred to a precession camera. During X-ray photography (Mo $K\alpha$ radiation) the capillary was kept in a steady stream of liquid nitrogen; although the nitrogen vaporized before reaching the crystal, it is estimated that the temperature of the crystal was about −150 °C.

A rather hasty (owing to the limited size of the liquid nitrogen reservoir) but systematic search of the reciprocal nets containing the b^* axis turned up four principal zones which were subsequently identified as $0kl$, $hk0$, $hk\bar{h}$, and $h,k,\bar{3}h$. Single photographs of the zero layer for each of these zones were prepared, the precession angle being 27°. Intensities were measured by visual comparison with a standard strip and were

---

* Contribution No. 3187 from the Gates and Crellin Laboratories of Chemistry. This work was supported in part by a grant (GP-930) from the National Science Foundation.

† Present address: General Electric Company, Valley Forge, Pennsylvania, U.S.A.

Table 1. *Atomic parameters and their standard deviations*

The last column, *D*, gives the deviation of each atom from the best plane of the carbon atoms.

	x (σ)	y (σ)	z (σ)	B (σ)	D
C(1)	0·565(5)	0·424(4)	0·226(3)	2·53(67)	−0·00 Å
C(2)	0·483(5)	0·604(4)	0·247(4)	2·37(53)	0·01
C(3)	0·294(6)	0·623(4)	0·145(4)	2·62(53)	−0·02
C(4)	0·259(4)	0·428(3)	0·059(4)	2·37(58)	0·02
C(5)	0·437(5)	0·287(4)	0·104(5)	2·47(60)	−0·01
H(1)	0·689(57)	0·383(38)	0·280(29)	1·0	0·00
H(2)	0·550(61)	0·740(48)	0·332(35)	1·0	0·00
H(3)	0·240(42)	0·792(31)	0·198(20)	1·0	0·16
H(4)	*0·140	0·393	−0·020	1·0	0·02
H(5)	0·414(43)	0·184(38)	0·185(43)	1·0	1·08
H(6)	0·435(44)	0·289(39)	0·011(35)	1·0	−0·78

* The least-squares refinement moved H(4) to a chemically unacceptable position. These are the coordinates of its 'proper' position.

corrected for Lorentz and polarization effects. Of a total of 133 reflections which could be recorded on these photographs, 70 were of measurable intensity.

The unit-cell dimensions determined from measurements of these photographs are:

$$a=7{\cdot}89\pm0{\cdot}02,\ b=5{\cdot}65\pm0{\cdot}02,\ c=10{\cdot}45\pm0{\cdot}03\ \text{Å},$$
$$\beta=114^\circ\ 10'\pm20'\ (\lambda\ \text{Mo}\ K\alpha=0{\cdot}7107\ \text{Å}).$$

The absence of reflections $0k0$ with k odd and $h0l$ with $(h+l)$ odd indicates that the space group is $P2_1/n$. A density of about 1·0 g.cm^{-3} was estimated by observing the volume contraction of the liquid as it was frozen; the density calculated on the basis of four molecules in the unit cell is 1·031 g.cm^{-3}.

Table 2. *Observed and calculated structure factors*

hkl	$10F_o$	$10F_c$	hkl	$10F_o$	$10F_c$	hkl	$10F_o$	$10F_c$	hkl	$10F_o$	$10F_c$
000	---	1440*	$71\bar{7}$	62	-66	230	174	-159	054	<36	-11*
002	249	-269*	$81\bar{8}$	45	50	$33\bar{3}$	<36	-3*	055	<36	44
004	<36	40	020	<36	30*	330	<36	-3*	056	<36	-15*
006	157	-158	021	38	-43	$43\bar{4}$	<36	9*	$15\bar{3}$	<36	13*
$10\bar{3}$	326	465*	022	<36	-52	430	104	-102	$15\bar{1}$	71	-101
$20\bar{6}$	<36	-51	023	87	96	$53\bar{5}$	<36	14*	150	51	-44
$20\bar{2}$	316	-545*	024	125	128	530	50	-35	$25\bar{6}$	<36	5*
200	109	106	025	114	111	$63\bar{6}$	52	-44	$25\bar{2}$	<36	-11*
$30\bar{3}$	<36	-26*	026	48	-41	630	99	-83	250	<36	12*
400	251	198*	$12\bar{3}$	65	55	040	94	-107	$35\bar{3}$	<36	11*
$50\bar{5}$	75	68	$12\bar{1}$	36	50	041	<36	-19*	350	<36	-6*
$60\bar{6}$	99	105	120	54	-64	042	104	93	$45\bar{4}$	<36	12*
600	93	-88	$22\bar{6}$	<36	4*	043	<36	-14*	450	<36	-32*
$70\bar{7}$	62	-72	$22\bar{2}$	58	-72	044	61	-48	$55\bar{5}$	<36	45
011	233	-339*	220	79	-82	045	71	54	550	63	-50
012	138	-141	$32\bar{3}$	81	-94	046	<36	6*	$65\bar{6}$	<36	-13*
013	69	76	320	70	-73	$14\bar{3}$	49	-46	650	40	23
014	115	-121	$42\bar{4}$	<36	30*	$14\bar{1}$	<36	-46	060	83	-90
015	<36	16*	420	<36	47	140	<36	14*	061	94	80
016	<36	-27*	$52\bar{5}$	49	51	$24\bar{6}$	<36	45	062	<36	25*
$11\bar{3}$	285	-282*	520	<35	-6*	$24\bar{2}$	69	64	063	<36	22*
$11\bar{1}$	106	-112	$62\bar{6}$	<36	-9*	240	<36	28*	064	<36	-41
110	271	388*	620	<36	-3*	$34\bar{3}$	78	78	065	<36	9*
$21\bar{6}$	86	-78	031	44	56	340	150	-134	066	39	47
$21\bar{2}$	304	305*	032	55	52	$44\bar{4}$	<36	-5*	$16\bar{3}$	45	-47
210	<36	19*	033	46	-50	440	71	-63	$16\bar{1}$	<36	6*
$31\bar{3}$	<36	-26*	034	<36	-33*	$54\bar{5}$	<36	-26*	160	74	60*
310	49	54	035	<36	-45	540	<36	-34*	$26\bar{6}$	<36	0*
$41\bar{4}$	95	-103	036	122	-122	$64\bar{6}$	<36	9*	$26\bar{2}$	65	59
410	98	96	$13\bar{3}$	36	-45	640	<36	-26*	260	<36	-12*
$51\bar{5}$	76	73	$13\bar{1}$	<36	12*	051	<36	13*	$36\bar{3}$	<36	-1*
510	103	83	130	94	-106	052	88	-75	360	<36	-1*
$61\bar{6}$	<36	-24*	$23\bar{6}$	<36	18*	053	<36	-16*	464	<36	-8*
610	<36	-20*	$23\bar{2}$	<36	28*						

*These reflections have been omitted from the least-squares refinement.

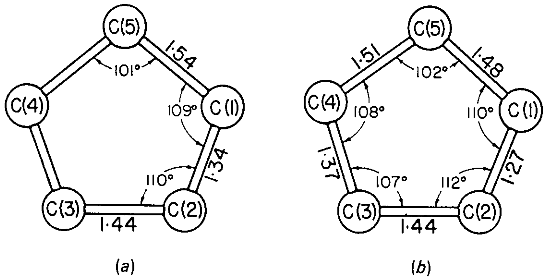

Fig. 1. (*a*) The assumed molecular geometry used in deriving the trial structure. (*b*) The bond distances and angles determined in this investigation.

Determination and refinement of the structure

A trial structure was generated by a search method similar to that of Kupfer & Tsoucaris (1963). A program was written for the IBM 7094 computer to calculate the *R* index for the $hk0$ reflections as a function of two coordinates defining the position of the center of the molecule and three Euler angles defining its orientation; the molecule was treated as a planar ring of carbon atoms (the hydrogen atoms were neglected) with dimensions as shown in Fig. 1(*a*). The resulting trial structure had an *R* index for the observed $hk0$ reflections of 0·25.

The structure was refined on the basis of all available data, with the monoclinic least-squares sub-program of the CRYRM crystallographic system for the IBM 7094 (Duchamp, 1964). The three coordinates of all 11 atoms and the isotropic temperature parameters of the five carbon atoms were included in about 20 cycles of full-matrix refinement; the quantity minimized was $\Sigma w(F_o^2-F_c^2)^2$ and the weights w were assigned according to the function suggested by Hughes (1941). Preliminary values for the scale and temperature factors were derived from a Wilson plot; the starting coordinates for the hydrogen atoms were based on C–H bond distances of 1·0 Å. Atomic scattering factors were taken from *International Tables for X-Ray Crystallography* (1962). Reflections too weak to be observed were included in the refinement only if F_c exceeded the threshold value of F_o. In the last few cycles eight strong reflections whose intensities were too great to be measured with confidence were assigned zero weight.

Refinement was concluded when the maximum shift in any parameter was less than 10% of its standard deviation. The final *R* index for 72 reflections of non-zero weight was 0·10. The final parameters and their estimated standard deviations are listed in Table 1 and the observed and calculated structure factors in Table 2. Bond distances and angles are shown in Fig. 1(*b*). Electron density projections along the *a* and *c* axes, calculated at the conclusion of the refinement, are shown in Fig. 2.

Discussion

The experimental difficulties encountered in preparing diffraction photographs of this very low-melting compound resulted in a reduction in both the quality and the quantity of the experimental data, and the resulting structure is not of high precision; the estimated standard deviation in the C–C bond distances is about 0·04 Å. These relatively large uncertainties notwithstanding, several features of the structure are evident.

The locations of the two double bonds and the expected shortening of the single bond between them (Pauling, Springall & Palmer, 1939) are quite evident [Fig. 1(*b*)]; indeed, the observed values of the bond distances and angles are in good agreement with those obtained by Schomaker & Pauling (1939) in an electron-diffraction investigation of cyclopentadiene. The five carbon atoms are closely coplanar, all five lying within 0·02 Å of the plane

$$0{\cdot}588X+0{\cdot}533Y-0{\cdot}609Z=2{\cdot}016\ \text{Å},$$

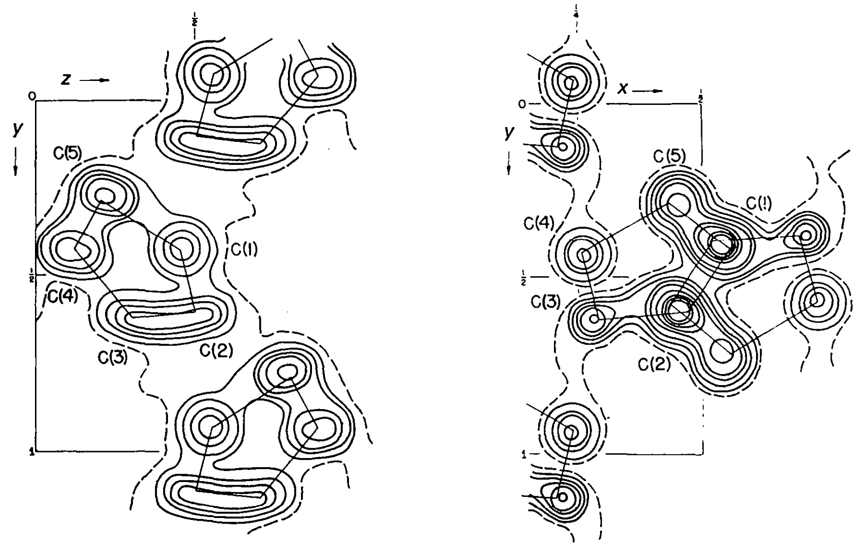

Fig. 2. The electron density projected along (*a*) the *a* axis, (*b*) the *c* axis. Contours are at intervals of 1 e.Å^{-3} beginning with (*a*) 2 e.Å^{-3} (dashed) and (*b*) 3 e.Å^{-3} (dashed).

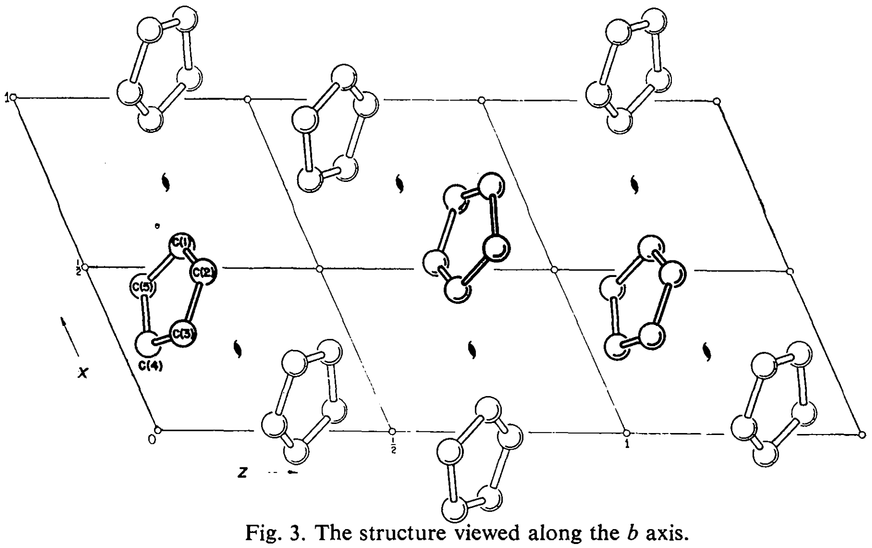

Fig. 3. The structure viewed along the *b* axis.

where the coefficients are direction cosines relative to *a*, *b*, and *c**.

The bond distances and angles involving the hydrogen atoms are listed in Table 3. The standard deviations in the coordinates of the hydrogen atoms are so large (about 0·4 Å) as to make these values of little significance. Indeed, the final least-squares position of H(4) was so ridiculous – somewhere near the center of the carbon ring – as to cause us to return it forcibly to its logical position and to remove it from the refinement.

Table 3. C–H *bond distances and angles*

C(1)–H(1)	0·94 Å	C(4)–H(4)	0·98 Å
C(2)–H(2)	1·12	C(5)–H(5)	1·10
C(3)–H(3)	1·26	C(5)–H(6)	0·97
C(5)–C(1)–H(1)	124°	C(5)–C(4)–H(4)	127°
C(2)–C(1)–H(1)	125	C(4)–C(5)–H(5)	96
C(1)–C(2)–H(2)	125	C(4)–C(5)–H(6)	93
C(3)–C(2)–H(2)	123	C(1)–C(5)–H(5)	83
C(2)–C(3)–H(3)	99	C(1)–C(5)–H(6)	126
C(4)–C(3)–H(3)	151	H(5)–C(5)–H(6)	147
C(3)–C(4)–H(4)	125		

A view of the structure looking down the *b* axis is shown in Fig. 3. The shortest intermolecular C · · · C contact is 3·65 Å between C(5) atoms related by a center of symmetry.

One of us (G. L.) is grateful to the National Science Foundation for financial support during the course of this investigation.

References

Busler, W. R., Williams, F. & Bonin, M. A. (1962). *J. Amer. Chem. Soc.* **84**, 4355.
Duchamp, D. J. (1964). ACA meeting, Bozeman, Montana. Paper B-14.
Hughes, E. W. (1941). *J. Amer. Chem. Soc.* **63**, 1737.
International Tables for X-Ray Crystallography (1962). Vol. II, pp. 202–203. Birmingham: Kynoch Press.
Kupfer, D. & Tsoucaris, G. (1963). *Bull. Soc. franç. Minér. Crist.* **86**, 389.
Liebling, G. & McConnell, H. M. (1965). *J. Chem. Phys.* To be published.
Moffett, R. B. (1952). *Organic Syntheses*, **32**, 41.
Pauling, L., Springall, H. D. & Palmer, K. J. (1939). *J. Amer. Chem. Soc.* **61**, 927.
Schomaker, V. & Pauling, L. (1939). *J. Amer. Chem. Soc.* **61**, 1769.

Acta Cryst. (1965). **19**, 205

The Crystal Structure of Rubidium Uranyl Nitrate: A Neutron-Diffraction Study

By G. A. Barclay
School of Chemistry, University of New South Wales, P.O. Box 1, Kensington, N.S.W., Australia
T. M. Sabine
Australian Atomic Energy Commission, Lucas Heights, N.S.W., Australia
and J. C. Taylor*
School of Chemistry, University of New South Wales, P.O. Box 1, Kensington, N.S.W., Australia

(*Received* 9 *November* 1964)

The crystal structure of rubidium uranyl nitrate, $RbUO_2(NO_3)_3$, has been determined from neutron-diffraction intensities for two zones of reflexions. The light-atom positions have been defined more accurately than was possible with X-ray data. The uranium atom is surrounded by eight oxygen atoms at the corners of a distorted hexagonal bipyramid (six nitrate oxygen atoms at 2·48 Å and two uranyl oxygen atoms at 1·78 Å). Each nitrate group acts as a bidentate chelate forming a four-membered ring system. The rubidium atom has twelve oxygen atoms as its near neighbours.

Introduction

In their X-ray study of rubidium uranyl nitrate, Hoard & Stroupe (1949) were able to locate the rubidium and uranium atoms in the unit cell but, because of the overwhelming scattering by the metal atoms, they were unable to determine directly the positions of the nitrate group atoms and the uranyl oxygen atoms. A neutron-diffraction study was undertaken by us to locate these nitrogen and oxygen atoms.

Few accurate studies of uranyl compounds have been made by X-ray diffraction; notable exceptions are the studies of Zachariasen, which are referred to in a paper on sodium uranyl acetate (Zachariasen & Plettinger, 1959). A review of the structural chemistry of uranyl compounds has been given by Evans (1963).

Crystal data

See Hoard & Stroupe (1949).

Rubidium uranyl nitrate, $RbUO_2(NO_3)_3$, crystallizes in the rhombohedral division of the trigonal system with

---

* Present address: Argonne National Laboratories, 9700 S. Cass Avenue, Argonne, Ill., U.S.A.