

Tetracyclo[6,4,3,0,2⁷]pentadecan-13-one

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(Received 20 September 1975; accepted 1 October 1975)

Abstract. C₁₅H₂₂O, F.W. 218.34, monoclinic, space group $P2_1/n$, $a=14.871$ (1), $b=7.014$ (1), $c=12.144$ (1) Å, $\beta=91.44$ (1)°, $D_m=1.14$ (by flotation), $D_x=1.145$ g cm⁻³, $Z=4$, $R=0.040$ for 1715 non-zero reflexions. Molecular geometry shows that the *A/B* ring junction is *trans* and that steric repulsions between adjacent H atoms are minimized by the deformation of each ring.

Introduction. Preliminary Weissenberg photographs showed systematic extinctions of $h0l$ for $h+l=2n+1$ and $0k0$ for $k=2n+1$ indicative of space group $P2_1/n$ (No. 14). For the data collection, a crystal with approximate dimensions of $0.21 \times 0.27 \times 0.27$ mm was coated

by collodion to prevent sublimation. Unit-cell dimensions and intensities were measured on a Rigaku automated four-circle diffractometer, using graphite monochromatized Cu $K\alpha$ radiation. The θ - 2θ scan method was employed at a rate of 2° min^{-1} in 2θ . Backgrounds were measured for 10 s before and after the scan of each peak. In total, 1881 independent reflexions were measured up to $2\theta=120^\circ$. Intensity data were corrected for Lorentz and polarization effects but not for absorption [$\mu(\text{Cu } K\alpha)=5.36 \text{ cm}^{-1}$].

The structure was solved by the symbolic addition method (Karle & Karle, 1966), and refined anisotropically by the block-diagonal least-squares method with

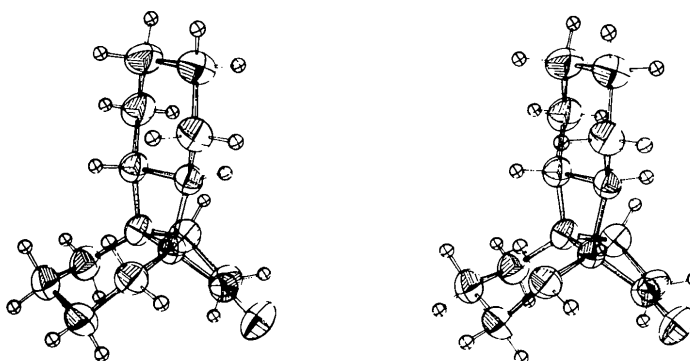


Fig. 1. Stereoscopic view of the molecule by ORTEP (Johnson, 1965). The thermal ellipsoids are drawn at 50% probability level; H atoms are given at an arbitrary temperature factor.

Table 1. Final atomic coordinates and thermal parameters with *e.s.d.*'s in parentheses

(a) O and C atoms ($\times 10^4$)

The anisotropic temperature factor is of the form: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

	<i>x</i>	<i>y</i>	<i>z</i>	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
O	4018 (1)	-877 (2)	9261 (1)	77 (1)	220 (3)	83 (1)	-54 (2)	30 (1)	71 (3)
C(1)	4511 (1)	1005 (2)	7718 (1)	36 (1)	128 (3)	56 (1)	1 (2)	10 (1)	9 (3)
C(2)	3766 (1)	1439 (2)	6813 (1)	36 (1)	155 (3)	62 (1)	18 (2)	11 (1)	10 (3)
C(3)	3447 (1)	270 (3)	5838 (1)	46 (1)	219 (4)	74 (1)	-2 (3)	-8 (2)	-10 (4)
C(4)	2882 (1)	1646 (3)	5114 (2)	50 (1)	317 (5)	81 (1)	20 (4)	-19 (2)	22 (5)
C(5)	3359 (1)	3520 (3)	4839 (2)	61 (1)	327 (5)	78 (1)	66 (4)	-8 (2)	99 (5)
C(6)	3748 (1)	4611 (3)	5843 (2)	65 (1)	198 (4)	91 (2)	43 (3)	15 (2)	88 (4)
C(7)	4314 (1)	3171 (2)	6480 (1)	44 (1)	148 (3)	66 (1)	13 (3)	14 (2)	32 (3)
C(8)	4748 (1)	3188 (2)	7656 (1)	47 (1)	132 (3)	65 (1)	-15 (3)	12 (2)	3 (3)
C(9)	5737 (1)	3697 (3)	7819 (2)	56 (1)	239 (4)	84 (1)	-74 (3)	2 (2)	10 (4)
C(10)	6369 (1)	2233 (3)	7339 (2)	37 (1)	384 (6)	85 (1)	-48 (4)	6 (2)	43 (5)
C(11)	6164 (1)	243 (3)	7767 (2)	41 (1)	326 (5)	82 (1)	57 (3)	5 (2)	32 (4)
C(12)	5234 (1)	-397 (2)	7378 (1)	46 (1)	181 (4)	71 (1)	41 (3)	11 (2)	11 (3)
C(13)	4149 (1)	666 (2)	8848 (1)	37 (1)	191 (4)	63 (1)	-8 (3)	4 (1)	22 (3)
C(14)	3998 (1)	2563 (3)	9403 (1)	66 (1)	235 (4)	63 (1)	42 (3)	24 (2)	-9 (4)
C(15)	4148 (1)	4100 (2)	8542 (1)	65 (1)	164 (4)	77 (1)	14 (3)	18 (2)	-43 (4)

Table 1 (cont.)

(b) H atoms (atomic coordinates $\times 10^3$)

	x	y	z	B (\AA^2)
H(2)	322 (1)	189 (2)	719 (1)	3.5 (3)
H(3A)	308 (1)	-83 (2)	606 (1)	4.5 (4)
H(3B)	399 (1)	-22 (2)	540 (1)	3.9 (3)
H(4A)	229 (1)	202 (3)	555 (1)	5.4 (4)
H(4B)	267 (1)	100 (3)	441 (2)	6.2 (5)
H(5A)	291 (1)	436 (3)	439 (2)	6.3 (5)
H(5B)	389 (1)	327 (3)	430 (2)	5.9 (4)
H(6A)	327 (1)	511 (3)	635 (1)	5.1 (4)
H(6B)	412 (1)	569 (3)	563 (2)	6.0 (4)
H(7)	481 (1)	272 (2)	597 (1)	3.3 (3)
H(9A)	586 (1)	381 (3)	866 (1)	5.5 (4)
H(9B)	582 (1)	499 (3)	750 (2)	6.2 (5)
H(10A)	700 (1)	259 (3)	754 (2)	6.2 (5)
H(10B)	632 (1)	221 (2)	650 (1)	5.1 (4)
H(11A)	621 (1)	31 (3)	862 (1)	5.1 (4)
H(11B)	661 (1)	-73 (3)	751 (1)	5.5 (4)
H(12A)	507 (1)	-168 (2)	767 (1)	4.8 (4)
H(12B)	523 (1)	-52 (2)	654 (1)	4.0 (3)
H(14A)	445 (1)	261 (3)	998 (2)	6.3 (5)
H(14B)	340 (1)	261 (3)	973 (2)	6.9 (5)
H(15A)	445 (1)	522 (3)	886 (2)	5.5 (4)
H(15B)	356 (1)	453 (3)	820 (1)	5.2 (4)

HBL5-5 (Ashida, 1973). After the *R* value converged to 0.117, all the 22 H atoms were located by difference syntheses. They were included in the subsequent refinement. Final *R* value was 0.046 for all (0.040 for 1715 non-zero) reflexions. Atomic scattering factors for C and O were taken from Hanson, Herman, Lea & Skillman (1964), and for H from Stewart, Davidson &

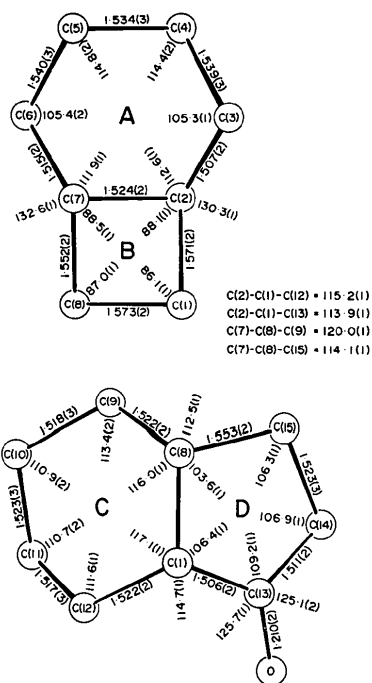


Fig. 2. Bond lengths (\AA) and bond angles ($^\circ$) involving the non-hydrogen atoms.

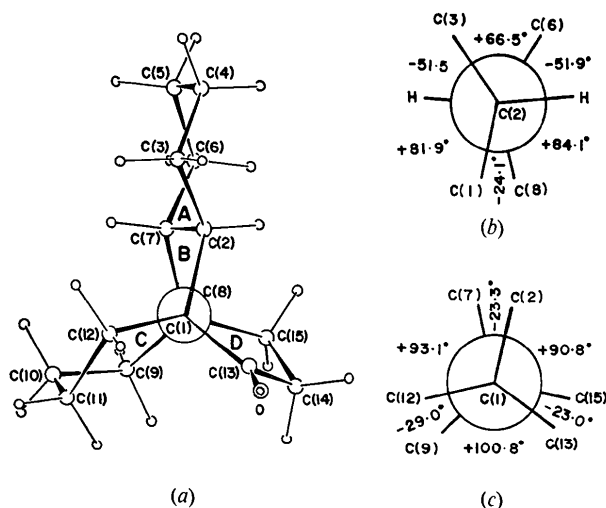


Fig. 3. (a) A view of the molecule projected along the C(1)-C(8) bond. (b) Newman projection along the C(2)-C(7) and (c) along the C(1)-C(8) bond.

Simpson (1965). The final atomic parameters are listed in Table 1.*

Discussion. A stereoscopic view of the molecule is shown in Fig. 1. Bond lengths and angles are given in Fig. 2. The geometry around the C(2)-C(7) bond shows that the *A/B* ring junction is *trans*. The conformation of the six-membered ring, *A* is a chair form. The bond lengths of C(2)-C(3) 1.507 (2) and C(6)-C(7) 1.515 (2) \AA are significantly shorter than the normal C-C single bond. The angles of C(2)-C(3)-C(4) 105.3 (1) and C(5)-C(6)-C(7) 105.4 (2) are smaller, whereas, those of C(3)-C(4)-C(5) 114.4 (2) and C(4)-C(5)-C(6) 114.8 (2) $^\circ$ are larger than the usual value of sp^3 C. These deviations from normal cyclohexane may be due to the strain introduced by the *trans* fusion to the cyclobutane ring. The cyclobutane ring *B* is puckered, the dihedral angle between the planes defined by C(1), C(2) and C(8) and C(2), C(7) and C(8) being 33.9 $^\circ$. A significant lengthening of C(1)-C(2) 1.571 (2) and C(1)-C(8) 1.573 (2) \AA (bridgehead-bridgehead bond) is clearly observed. Another cyclohexane ring, *C*, fused to the cyclobutane ring by the C(1)-C(8) bond is in a fairly distorted chair form, bond lengths except C(1)-C(8) ranging from 1.517 to 1.523 \AA . The five-membered ring, *D*, also fused to the cyclobutane ring is in a half-chair form C(1), C(13), C(14) and O atoms being approximately in a plane. Fig. 3(a), molecular structure projected down along the C(1)-C(8) bond, clearly shows that the deformations mentioned above occur in order to minimize the steric repulsions between adjacent H atoms attached to the ring C atoms.

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31431 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

We thank Professor Y. Odaira and co-workers for the crystals.

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The Oxidation Product of Bis(glyoximato)palladium(II) with Iodine

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(Received 6 October 1975; accepted 9 October 1975)

Abstract. Pd(C₂H₃N₂O₂)₂I, tetragonal, *P*4₂/*mcm*, *a* = 8.645 (1), *c* = 6.488 (1) Å, *Z* = 2, *D*_x = 3.50 g cm⁻³. The metal complex units form columnar stacks with a Pd-Pd distance of 3.244 (1) Å. Linear, probably disordered, iodine chains run parallel to the stacks of the complex molecules.

Introduction. The crystal used was from a preparation reported by Endres, Keller & Lehmann (1975).

The systematic absences *Ok**l* for *l* = 2*n* + 1 are consistent with the space groups *P*4̄*c*2, *P*4*cm*, *P*4₂/*mcm*. Accurate lattice constants were determined from the *θ* values of 23 reflexions by a least-squares procedure (Berdiesinski & Nuber, 1966). Intensities were measured with Mo *K*α radiation on an automatic diffractometer (Siemens) by a *θ*/*2θ* scan. 323 reflexions were observed in a *θ* range up to 30° for *l* = 2*n* and 15° for *l* = 2*n* + 1; reflexions with an intensity *I* < 2.58σ*I* were regarded as unobserved. The heavy-atom positions were taken from a Patterson map, which also showed the ligand to lie in the plane of the metal atom. As this condition can be allowed for in each of the possible space groups and the molecular symmetry is consistent with the symmetry operations of the relevant space groups, the calculations were based on the centrosymmetric space group *P*4₂/*mcm* (*D*_{2h}¹⁰). The positions of the light atoms were obtained by Fourier syntheses.

Least-squares refinement with *ORFLS* and *CRYLSQ* of the X-RAY System (Stewart, Kundell & Baldwin, 1970) led to an *R* of 12.8% with isotropic temperature factors. Refinement with anisotropic temperature factors converged at an *R* of 6.4% (average shift/error 0.02, maximum shift/error 0.08). Scattering factors were those of Hanson, Herman, Lea & Skillman (1964). Atomic parameters are listed in Table 1.*

Discussion. Fig. 1 shows the complex with bond distances and angles. The molecular symmetry is *D*_{2h}, the central Pd atom occupying a crystallographic *mmm* position.

The planar complexes are stacked in columns. Two adjacent molecules within the same stack are twisted by 90° with respect to one another. Parallel to the Pd chains run linear chains of I atoms (Figs. 2 and 3). The complexes stack perpendicular to their planes with a Pd-Pd distance of 3.244 Å, whereas in the unoxidized form the Pd-Pd distance of 3.558 Å is considerably longer and the stacking direction is not perpendicular to the planes of the complexes (Calleri, Ferraris &

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31443 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. Atomic parameters (× 10⁴)

The anisotropic temperature factor is exp [−2π²(*U*₁₁*h*²(*a*^{*})² + ⋯ + 2*U*₂₃*klb*^{*}*c*^{*})].

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
Pd	0	0	0	827 (13)	827 (17)	368 (10)	−99 (32)	0	0
I	5000	5000	2500	854 (13)	854 (17)	1183 (24)	0	0	0
N	2291 (22)	9785 (27)	0	816 (122)	627 (150)	455 (70)	−200 (118)	0	0
O	3216 (23)	985 (23)	0	1160 (176)	1100 (172)	632 (108)	−55 (123)	0	0
C	2822 (36)	1547 (34)	0	1265 (227)	930 (206)	407 (108)	−110 (182)	0	0