

Tetracyclo[8.4.3.0.0<sup>2,9</sup>]heptadec-5-en-15-one

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**Abstract.** C<sub>17</sub>H<sub>24</sub>O, F.W. 244.38, monoclinic, space group  $P2_1/c$ ,  $a = 10.056$  (1),  $b = 12.476$  (1),  $c = 11.771$  (1) Å,  $\beta = 106.68$  (1)°,  $D_m = 1.15$  (by flotation),  $D_x = 1.147$  g cm<sup>-3</sup>,  $Z = 4$ ,  $R = 0.046$  for 1777 non-zero reflexions. The ring junction between the four- and eight-membered rings is *trans*. The molecule has the *cis-anti-trans* structure to minimize steric repulsions between adjacent H atoms.

**Introduction.** Photoreaction between bicyclo[4.3.0]non-1(6)-en-7-one and 1,5-cyclooctadiene gave a single cycloaddition product (yield 80%; Kunai, 1975), although four types of isomers were expected

to be formed (Fig. 1). In order to determine the stereochemistry of the cycloadduct, an X-ray analysis has been carried out. For the data collection, a crystal, 0.3 × 0.3 × 0.35 mm, was coated with collodion to

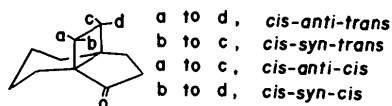


Fig. 1. Four isomers expected to be formed from the photoreaction between bicyclo[4.3.0]non-1(6)-en-7-one and 1,5-cyclooctadiene.

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>	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
O	1056 (2)	1284 (2)	5631 (1)	237 (3)	153 (2)	104 (1)	-74 (4)	152 (3)	-33 (3)
C(1)	1520 (2)	1516 (1)	3735 (2)	110 (2)	68 (1)	80 (2)	5 (3)	59 (3)	-4 (2)
C(2)	2875 (2)	2204 (2)	3864 (2)	125 (2)	63 (1)	87 (2)	-9 (3)	56 (3)	-8 (2)
C(3)	2799 (2)	3422 (2)	3942 (2)	196 (3)	71 (2)	144 (2)	-26 (4)	133 (5)	-48 (3)
C(4)	3881 (3)	4002 (2)	3485 (2)	201 (3)	68 (2)	156 (3)	-49 (4)	106 (5)	-15 (3)
C(5)	5319 (3)	3627 (2)	4021 (2)	183 (3)	101 (2)	142 (2)	-102 (4)	39 (5)	-7 (4)
C(6)	5948 (2)	2896 (2)	3557 (2)	132 (3)	121 (2)	180 (3)	-54 (4)	60 (5)	33 (4)
C(7)	5316 (2)	2318 (2)	2421 (2)	148 (3)	135 (2)	176 (3)	-29 (4)	174 (5)	-20 (4)
C(8)	4430 (2)	1358 (2)	2572 (2)	134 (3)	98 (2)	142 (2)	17 (4)	115 (4)	-27 (3)
C(9)	3030 (2)	1636 (2)	2743 (2)	110 (2)	66 (1)	88 (2)	12 (3)	59 (3)	-7 (2)
C(10)	2097 (2)	724 (1)	2980 (2)	125 (2)	57 (1)	91 (2)	2 (3)	54 (3)	-14 (2)
C(11)	1062 (2)	191 (2)	1928 (2)	183 (3)	97 (2)	119 (2)	-66 (4)	92 (4)	-65 (3)
C(12)	-169 (2)	875 (2)	1351 (2)	164 (3)	146 (3)	94 (2)	-75 (5)	17 (4)	-19 (4)
C(13)	-831 (2)	1308 (2)	2253 (2)	110 (2)	146 (3)	136 (2)	-7 (4)	39 (4)	16 (4)
C(14)	158 (2)	2058 (2)	3109 (2)	132 (3)	98 (2)	126 (2)	44 (4)	81 (4)	4 (3)
C(15)	1517 (2)	938 (2)	4858 (2)	129 (2)	99 (2)	93 (2)	-44 (3)	54 (3)	-6 (3)
C(16)	2162 (3)	-135 (2)	4866 (2)	199 (4)	112 (2)	140 (3)	23 (5)	93 (5)	88 (4)
C(17)	2889 (2)	-115 (2)	3908 (2)	179 (3)	73 (2)	158 (3)	44 (4)	91 (5)	35 (3)

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

	<i>x</i>	<i>y</i>	<i>z</i>	$B$ (Å <sup>2</sup> )		<i>x</i>	<i>y</i>	<i>z</i>	$B$ (Å <sup>2</sup> )
H(2)	364 (2)	194 (1)	456 (2)	4.7 (4)	H(11A)	73 (2)	-50 (2)	226 (2)	7.2 (5)
H(3A)	288 (2)	361 (2)	476 (2)	8.2 (6)	H(11B)	157 (2)	-4 (2)	134 (2)	8.4 (6)
H(3B)	186 (2)	367 (2)	346 (2)	8.4 (6)	H(12A)	-85 (2)	46 (2)	77 (2)	8.5 (6)
H(4A)	380 (2)	475 (2)	362 (2)	7.7 (6)	H(12B)	12 (2)	151 (2)	93 (2)	6.2 (5)
H(4B)	365 (2)	389 (2)	262 (2)	6.1 (5)	H(13A)	-111 (2)	72 (2)	268 (2)	7.4 (5)
H(5)	584 (2)	390 (2)	479 (2)	8.0 (6)	H(13B)	-172 (2)	179 (2)	185 (2)	8.7 (6)
H(6)	691 (3)	266 (2)	398 (2)	9.2 (7)	H(14A)	-28 (2)	232 (2)	369 (2)	5.6 (4)
H(7A)	603 (3)	204 (2)	213 (2)	9.3 (7)	H(14B)	31 (2)	265 (2)	262 (2)	7.0 (5)
H(7B)	468 (2)	286 (2)	186 (2)	7.6 (6)	H(16A)	139 (3)	-71 (2)	460 (3)	11.1 (8)
H(8A)	495 (2)	93 (2)	327 (2)	6.7 (5)	H(16B)	270 (3)	-34 (2)	565 (2)	10.1 (7)
H(8B)	426 (2)	90 (2)	187 (2)	6.9 (5)	H(17A)	392 (2)	11 (2)	431 (2)	8.2 (6)
H(9)	249 (2)	206 (1)	202 (1)	4.4 (4)	H(17B)	293 (2)	-76 (2)	352 (2)	8.3 (6)

prevent sublimation. A Rigaku four-circle diffractometer with Ni-filtered Cu  $K\alpha$  radiation was used for the measurement of lattice parameters and intensities. Systematic absences ( $h0l$  for  $l$  odd and  $0k0$  for  $k$  odd) indicated the space group  $P2_1/c$ . Intensities were measured by the  $\theta$ - $2\theta$  scan method at a  $2\theta$  rate of  $2^\circ \text{ min}^{-1}$ . Backgrounds were counted for 10 s before and after the scan of each peak. 2102 unique data collected up to  $2\theta = 120^\circ$  were corrected for the Lp effect but not for absorption [ $\mu(\text{Cu } K\alpha) = 5.3 \text{ cm}^{-1}$ ]. The structure was solved by the direct method with *MULTAN* (Germain, Main & Woolfson, 1971). All the non-hydrogen atoms appeared clearly in the  $E$  map based on the set of signs with the highest figure of merit. All the H atoms were located by difference syntheses. The refinement was carried out by block-diagonal least squares (*HBL5-5*; Ashida, 1973) with anisotropic temperature factors for non-hydrogen atoms. The final  $R$  values were 0.046 for the non-zero reflexions and 0.060 for all the reflexions. Atomic scattering factors for C and O were taken from Hanson, Herman, Lea & Skillman (1964), and for H from Stewart, Davidson & Simpson (1965). The final atomic parameters are listed in Table 1.\*

**Discussion.** The molecular structure viewed along C(1)–C(10) is shown in Fig. 2, which indicates that the ring junction between the four- and eight-membered rings is *trans* and the cycloadduct has the *cis-anti-trans* structure. This structure is similar to

\* A table of observed and calculated structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31990 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

that of tetracyclo[6.4.3.0.0<sup>2,7</sup>]pentadecan-13-one (Harada, Kai, Yasuoka & Kasai, 1976). Bond lengths and angles are given in Fig. 3. The conformation of the eight-membered ring is close to that of one of the stable forms of cyclooctene. Bond angles C(3)–C(2)–C(9),  $121.8(2)$ , and C(2)–C(9)–C(8),  $122.8(2)^\circ$ , are larger than the usual tetrahedral value. The four-membered ring has a puckered form, the dihedral angle between the planes C(1)C(2)C(10) and C(2)C(9)C(10) being  $30.1^\circ$ . The C(1)–C(2) bond length,  $1.581(3) \text{ \AA}$ , is much longer than the normal C–C single bond. The

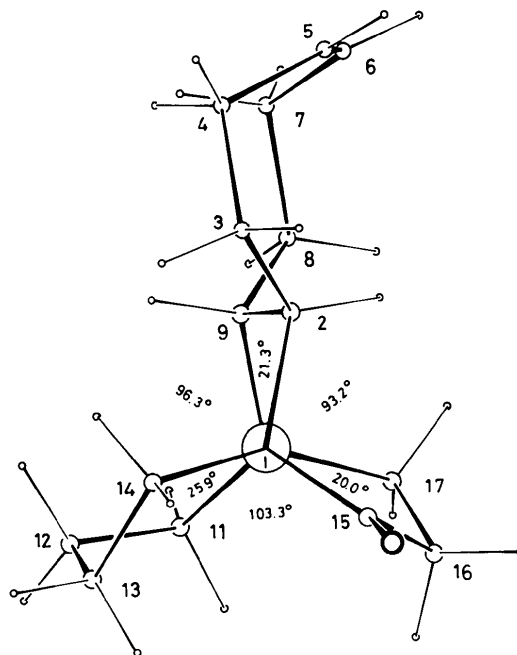


Fig. 2. A view of the molecule projected along C(1)–C(10).

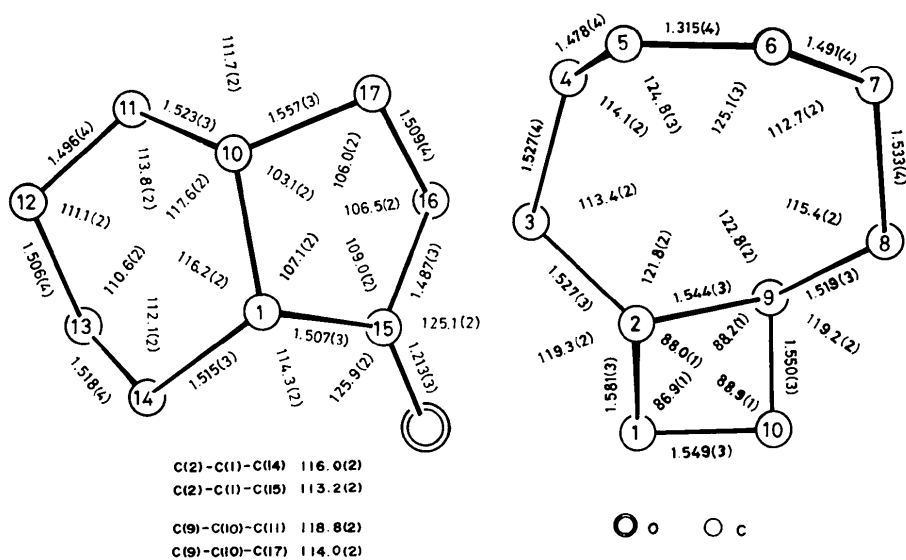


Fig. 3. Bond lengths ( $\text{\AA}$ ) and bond angles ( $^\circ$ ) involving the non-hydrogen atoms.

six-membered ring is in a chair form. The bond lengths other than C(1)—C(10) are shorter [especially C(11)—C(12), 1.496 (4), and C(12)—C(13), 1.506 (4) Å] than the standard value. The five-membered ring is in a half-chair form, C(1), C(15), C(16) and O being approximately in a plane. It can be concluded that the deformation of these rings has resulted from the minimization of steric repulsions between adjacent H atoms in the same ring and those between adjacent H atoms in different rings. This is clearly seen in Fig. 2.

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## References

- ASHIDA, T. (1973). *The Universal Crystallographic Computing System - Osaka*, pp. 55–61. The Computation Center, Osaka Univ.
- GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* **A27**, 368–376.
- HANSON, H. P., HERMAN, F., LEA, J. D. & SKILLMAN, S. (1964). *Acta Cryst.* **17**, 1040–1044.
- HARADA, M., KAI, Y., YASUOKA, N. & KASAI, N. (1976). *Acta Cryst.* **B32**, 625–627.
- KUNAI, A. (1975). Thesis, Osaka Univ.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

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## Dibromo(*N*-tetrakis-4-pyridinecarbaldehyde)cobalt(II)

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**Abstract.**  $\text{CoBr}_2(\text{OHC}_5\text{H}_4\text{N})_4$ , tetragonal,  $P4nc$ ,  $a = b = 11.713$  (4),  $c = 9.277$  (5) Å,  $U = 1272.8$  Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.69$  g cm<sup>-3</sup>. The structure was solved by Patterson methods and refined to an  $R$  of 0.049 for 328 unique diffractometer data. The Co and Br atoms lie on the fourfold molecular symmetry axis; the ligands are coordinated through their N atoms which complete the octahedral coordination of Co.

**Introduction.** The enzyme alcohol dehydrogenase catalyses the reduction of acetaldehyde by the cofactor nicotinamide adenine dinucleotide (NADH) and *in vitro* will catalyse the reduction of pyridinecarbaldehydes to the carbinols. Hughes & Prince (1977) have performed a kinetic study of this reaction and of the metal-catalysed reduction of pyridinecarbaldehydes by *N*-benzylidihydronicotinamide, an analogue of NADH. The mode of coordination of metals by pyridinecarbaldehydes is important in the interpretation of these experiments (Hughes, Prince & Wyeth, 1977).

The sample was obtained as red tetragonal parallelepipeds from the reaction between solutions of cobalt(II) bromide (0.05 *M*) and 4-pyridinecarbaldehyde (1.0 *M*) in anhydrous acetonitrile. 1890 reflexions were measured with a Syntex  $P2_1$  four-circle diffractometer,  $\text{Mo } K\alpha$  radiation, a graphite mono-

chromator and a crystal  $0.23 \times 0.24 \times 0.34$  mm. After application of  $L_p$  and numerical absorption corrections [ $\mu(\text{Mo } K\alpha) = 37.44$  cm<sup>-1</sup>], equivalent reflexions were averaged to give 328 unique reflexions with  $|F| > 4\sigma(F)$  based on counting statistics.

The Co and Br atoms, which lie on special positions (0, 0,  $z$ ), were located by Patterson methods, and the remaining atoms (except H) located by difference syntheses. The structure was refined by blocked cascade least squares with H atoms constrained to lie 1.08 Å from C on the external bisectors of the angles at C. An overall H-atom isotropic temperature factor was employed, with individual anisotropic factors for the remaining atoms. Complex neutral-atom scattering factors were used, and the weighting scheme was  $w = 1/\sigma^2(F)$ . The refinement converged to  $R' = \sum w^{1/2} \Delta / \sum w^{1/2} |F_o| = 0.0297$ ,  $R = 0.0488$ . The enantiomorphous structure refined to 0.0310 and 0.0502 respectively, and so was rejected. Final atomic coordinates and thermal parameters are given in Tables 1–3 and the resulting bond lengths and angles in Tables 4–5.\*

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31992 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.