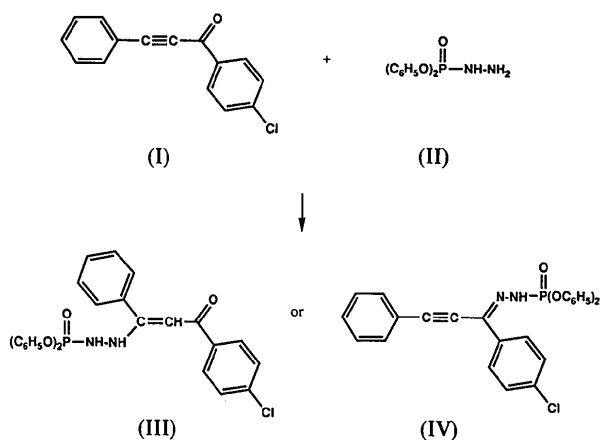


and goodness-of-fit = 0.042, 0.031, 1.82; maximum  $\Delta/\sigma = 0.51$ ; maximum and minimum values in final difference map of 0.23 and  $-0.23 \text{ e } \text{Å}^{-3}$ . The preliminary crystallographic calculations were performed on a UNISYS 1100/92 computer with the XRAY76 system (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976); final calculations were carried out with the TEXSAN program system (TEXSAN, 1989) on a Digital Equipment Corp. MicroVAX II computer. Atomic coordinates and isotropic temperature factors are listed in Table 1; bond lengths and angles are given in Table 2.\* An ORTEP drawing (Johnson, 1965) is shown in Fig. 1; the PLOTMD program (Luo, Ammon & Gilliland, 1989) was used to label the drawing and prepare a file which was printed on a Hewlett-Packard Laserjet II printer.

**Related literature.** Phosphino-hydrazine (II) could react with acetylenic ketone (I) via a Michael addition to yield enone (III) or to form hydrazone (IV) (El-Sayed, Refatt, Ammon, Vlasi, Fouli & Heiba, 1988). This determination has confirmed the product as hydrazone (IV). A search of the Cambridge Structural Database current to December 1989 revealed no other examples of a molecule containing the  $(R-O)_2P(=O)N-$  moiety.

\* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53202 (19 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.



### References

- DEBAERDEMAEKER, T., GERMAIN, G., MAIN, P., TATE, C. & WOOLFSON, M. M. (1987). *MULTAN87. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
- EL-SAYED, K., REFATT, L. S., AMMON, H. L., VLASSI, M., FOULI, M. A. & HEIBA, Z. K. (1988). *Z. Kristallogr.* **185**, 207.
- JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830, USA.
- LUO, J., AMMON, H. L. & GILLILAND, G. J. (1989). *J. Appl. Cryst.* **22**, 186.
- STEWART, J. M., MACHIN, P. A., DICKINSON, C. W., AMMON, H. L., HECK, H. & FLACK, H. (1976). *The XRAY76 System*. Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland 20742, USA.
- TEXSAN (1989). *TEXRAY* structure analysis system, version 5.0. Molecular Structure Corp., 3200A Research Forest Drive, The Woodlands, Texas 77381, USA.
- ZACHARIASEN, W. H. (1968). *Acta Cryst.* **A39**, 158–166.

*Acta Cryst.* (1991). **C47**, 196–198

## Structures of 8-Chloro-1,2,3,4-tetrahydrocinnolin-4-one and its 2-Chloroacetyl Derivative

BY MAREK L. GŁÓWKA AND IWONA IWANICKA

*Institute of General Chemistry, Technical University of Łódź, Zwirki 36, 90–924 Łódź, Poland*

(Received 15 December 1989; accepted 23 May 1990)

**Abstract.** (1) C<sub>8</sub>H<sub>7</sub>ClN<sub>2</sub>O, m.p. 397–398 K,  $M_r = 182.6$ , orthorhombic, *Pbca*,  $a = 4.873$  (1),  $b = 13.438$  (2),  $c = 25.526$  (3) Å,  $V = 1671.5$  Å<sup>3</sup>,  $Z = 8$ ,  $D_x = 1.451 \text{ Mg m}^{-3}$ ,  $\lambda(\text{Cu } K\alpha) = 1.54178$  Å,  $\mu = 3.7 \text{ mm}^{-1}$ ,  $F(000) = 752$ ,  $T = 293 \text{ K}$ , final  $R = 0.045$  for 1479 observed reflections. (2) C<sub>10</sub>H<sub>8</sub>Cl<sub>2</sub>N<sub>2</sub>O<sub>2</sub>· $\frac{1}{2}$ H<sub>2</sub>O,  $M_r = 268.1$ , orthorhombic, *Pbcn*,  $a = 18.740$  (3),  $b = 8.839$  (2),  $c = 14.124$  (2) Å,  $V = 2339.5$  Å<sup>3</sup>,  $Z = 8$ ,  $D_x = 1.522 \text{ Mg m}^{-3}$ ,  $\lambda(\text{Cu } K\alpha) =$

$1.54178$  Å,  $\mu = 5.05 \text{ mm}^{-1}$ ,  $F(000) = 1096$ ,  $T = 293 \text{ K}$ , final  $R = 0.051$  for 1941 observed reflections. The structures were solved by direct methods. Enhanced conjugation of N(1) lone-pair electrons with the benzene  $\pi$  system in (1) is evidenced by shortening of the C(benzene)—N(1) bond to 1.370 (2) compared with 1.400 (3) Å in (2). The hybridization state of the N(2) atom in (2) is  $sp^2$  [the sum of appropriate bond angles at N(2) is  $359.2^\circ$ ]

Table 1. Atomic coordinates and equivalent isotropic thermal parameters for non-H atoms for (1)

$$B_{eq} = (8\pi^2/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	$B_{eq}(\text{\AA}^2)$
Cl	0.1606 (2)	0.3709 (1)	0.1771 (1)	5.92 (2)
N(1)	0.2947 (4)	0.2518 (1)	0.0815 (1)	4.23 (4)
N(2)	0.3019 (3)	0.2147 (2)	0.0296 (1)	3.72 (3)
C(3)	0.3577 (4)	0.1086 (2)	0.0304 (1)	4.08 (5)
C(4)	0.1561 (4)	0.0512 (1)	0.0642 (1)	3.99 (5)
O(4)	0.1105 (4)	-0.0365 (1)	0.0562 (1)	5.44 (5)
C(5)	-0.1423 (4)	0.0612 (2)	0.1431 (1)	5.09 (6)
C(6)	-0.2343 (6)	0.1106 (2)	0.1868 (1)	6.01 (7)
C(7)	-0.1387 (5)	0.2066 (2)	0.1968 (1)	5.52 (7)
C(8)	0.0382 (4)	0.2529 (2)	0.1629 (1)	4.40 (5)
C(9)	0.1233 (3)	0.2059 (1)	0.1165 (1)	3.62 (4)
C(10)	0.0362 (4)	0.1074 (1)	0.1079 (1)	3.88 (4)

Table 2. Atomic coordinates and equivalent isotropic thermal parameters for non-H atoms for (2)

$$B_{eq} = (8\pi^2/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	$B_{eq}(\text{\AA}^2)$
Cl(8)	0.3928 (1)	0.1795 (1)	0.8167 (1)	7.46 (3)
Cl(12)	0.5030 (1)	0.1550 (1)	0.4008 (1)	6.72 (3)
N(1)	0.3890 (1)	0.3617 (3)	0.6434 (1)	4.76 (5)
O(1)	0.5000 (1)	0.5051 (4)	0.7500 (1)	5.09 (8)
N(2)	0.3872 (1)	0.4347 (3)	0.5551 (1)	4.56 (5)
O(4)	0.2149 (1)	0.5839 (4)	0.5340 (2)	7.86 (8)
C(3)	0.3406 (2)	0.5647 (4)	0.5439 (3)	5.65 (8)
C(4)	0.2664 (2)	0.5232 (4)	0.5714 (2)	5.40 (8)
C(5)	0.1949 (2)	0.3862 (4)	0.6920 (3)	6.57 (10)
C(6)	0.1897 (2)	0.2991 (6)	0.7704 (3)	7.66 (12)
C(7)	0.2503 (3)	0.2363 (5)	0.8107 (3)	7.54 (12)
C(8)	0.3170 (2)	0.2599 (4)	0.7695 (2)	5.60 (8)
C(9)	0.3223 (1)	0.3467 (3)	0.6869 (2)	4.56 (6)
C(10)	0.2604 (1)	0.4130 (4)	0.6492 (2)	4.97 (7)
C(11)	0.4197 (1)	0.3689 (3)	0.4805 (2)	4.40 (6)
O(11)	0.4179 (1)	0.4266 (3)	0.4023 (1)	6.25 (6)
C(12)	0.4573 (2)	0.2219 (4)	0.5023 (2)	5.44 (8)

owing to conjugation with the adjacent carbonyl group of the chloroacetyl substituent. Hydrogen-bonding networks in the structures consist of two intermolecular contacts, N(1)⋯O(4) and N(2)⋯N(2) in (1), and N(1)⋯O(water) and O(water)⋯O(acetyl) in (2).

**Experimental.** The compounds were synthesized by Dr A. Stańczak of the Pharmaceutical Chemistry and Drugs Analysis Department of the Medical Academy in Łódź and recrystallized from chloroform-methanol (1/1) [(2) from ethanol] solution. Data collection: crystal size 0.35 × 0.14 × 0.12 mm for (1) and 0.22 × 0.18 × 0.09 mm for (2), CAD-4, Cu K $\alpha$ , cell parameters from 25 reflections (21 ≤  $\theta$  ≤ 28°); 1712 (1) and 2405 (2) unique reflections measured [ $h_{\max} = 6$ ,  $k_{\max} = 16$ ,  $l_{\max} = 31$  for (1) and 11, 17, 23 for (2), respectively] in  $\omega/2\theta$  scan mode,  $\theta_{\max} = 75^\circ$ ; three standard reflections monitored every hour, less than 5% change in intensity during data collection; 1479 observed reflections [1941 for (2)] with  $F_o > 2\sigma(F_o)$ , Lp correction,

Table 3. Selected bond lengths (Å), bond angles (°) and torsion angles (°) with their e.s.d.'s in parentheses

	(1)	(2)*
N(1)—N(2)	1.415 (2)	1.405 (3)
N(1)—C(9)	1.370 (2)	1.400 (3)
N(2)—C(3)	1.452 (2)	1.451 (4)
C(3)—C(4)	1.519 (3)	1.491 (5)
C(4)—O(4)	1.217 (3)	1.225 (4)
C(4)—C(10)	1.467 (3)	1.472 (5)
C(8)—C(9)	1.404 (3)	1.400 (4)
C(8)—Cl(8)	1.732 (2)	1.723 (4)
C(9)—C(10)	1.407 (2)	1.404 (4)
N(2)—C(11)	—	1.349 (3)
N(2)—N(1)—C(9)	117.8 (2)	114.3 (2)
N(1)—N(2)—C(3)	109.8 (2)	118.4 (2)
N(1)—N(2)—C(11)	—	119.0 (2)
C(3)—N(2)—C(11)	—	121.8 (2)
N(2)—C(3)—C(4)	112.7 (2)	109.7 (3)
C(3)—C(4)—C(10)	115.3 (2)	115.4 (3)
C(3)—C(4)—O(4)	121.0 (2)	121.0 (3)
O(4)—C(4)—C(10)	123.7 (2)	123.5 (3)
C(4)—C(10)—C(9)	118.9 (2)	119.8 (2)
N(1)—C(9)—C(10)	120.3 (2)	122.1 (2)
C(9)—C(8)—Cl(8)	119.1 (2)	119.3 (2)
C(9)—N(1)—N(2)—C(3)	-53.5 (3)	-40.5 (3)
N(1)—N(2)—C(3)—C(4)	54.9 (2)	54.4 (4)
N(2)—C(3)—C(4)—C(10)	-28.3 (3)	-34.1 (4)
C(3)—C(4)—C(10)—C(9)	-2.8 (3)	4.7 (4)
C(4)—C(10)—C(9)—N(1)	6.8 (3)	10.9 (4)
C(10)—C(9)—N(1)—N(2)	22.3 (3)	6.1 (3)
N(1)—C(9)—C(8)—Cl(8)	-1.7 (3)	-1.9 (4)
H(1)—N(1)—C(9)—C(8)	-20 (2)	52 (2)
H(1)—N(1)—N(2)—H(2)	-77 (2)	—
H(1)—N(1)—N(2)—C(11)	—	-93 (2)
N(1)—N(2)—C(11)—O(11)	—	178.2 (2)

\* Signs of torsion angles for (2) calculated from parameters listed in Table 2 have been reversed for easier comparison.

absorption neglected; direct methods (Sheldrick, 1986), anisotropic refinement on  $F$  (Sheldrick, 1976), all H atoms from  $\Delta F$  isotropic, final cycle for (1) had 138 parameters,  $(\Delta/\sigma)_{\max} = 0.1$ ,  $R = 0.045$ ,  $wR = 0.059$ ,  $S = 0.58$ ,  $w^{-1} = \sigma^2(F_o) + 0.0032F_o^2$ , isotropic extinction parameter (Larson, 1967)  $g = 0.011$  (2),  $\Delta\rho_{\max} = 0.14 \text{ e \AA}^{-3}$  near C(3) and  $\Delta\rho_{\min} = -0.17 \text{ e \AA}^{-3}$ . Final cycle for (2) had 187 parameters,  $(\Delta/\sigma)_{\max} = 0.02$ ,  $R = 0.051$ ,  $wR = 0.062$ ,  $S = 0.94$ ,  $w^{-1} = \sigma^2(F_o) + 0.0008(F_o^2)$ , isotropic extinction  $g = 0.009$  (2),  $\Delta\rho_{\max} = 0.14 \text{ e \AA}^{-3}$  near C(10) and  $\Delta\rho_{\min} = -0.18 \text{ e \AA}^{-3}$ . Atomic scattering factors used were those in *SHELX76*. All calculations were performed on an Amstrad 1512 PC microcomputer.

Final atomic parameters are given in Tables 1 and 2.\* Bond lengths and angles are given in Table 3. Fig. 1 shows the two structures with their atom labelling.

\* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53162 (20 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

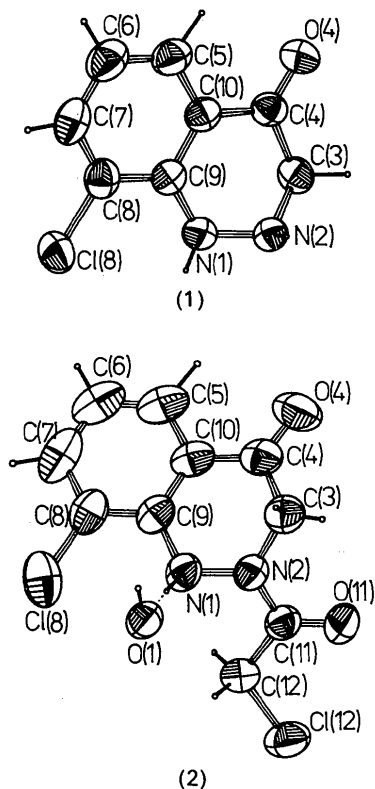


Fig. 1. Overall views and atomic labelling schemes for (1) and (2) (Johnson, 1976).

**Related literature.** Some cinnoline derivatives show interesting biological activity and they are used as anti-inflammatory (cinnopentazon, cinnofuradion), analgesic (difalton) and antibacterial (cinoxacin) agents. Cinnoline-type structures have also been used in the search for new non-narcotic analgesic drugs (Stańczak, 1987), which resulted in the preparation of a series of 6,7- or 8-substituted 1,2,3,4-tetrahydrocinnolin-4-ones (Groszkowski & Stańczak, 1989) and their 1,2-dichloroacetyl derivatives (Kwapiszewski, Stańczak & Groszkowski, 1990).

The authors wish to thank Dr A. Stańczak for the compounds and the Ministry of National Education for financial support under project RP.II.10.

#### References

- GROSKOWSKI, S. & STAŃCZAK, A. (1989). *Acta Pol. Pharm.* **46**, 320–326.
- JOHNSON, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- KWAPISZEWSKI, W., STAŃCZAK, A. & GROSKOWSKI, S. (1990). *Acta Pol. Pharm.* In the press.
- LARSON, A. C. (1967). *Acta Cryst.* **23**, 664–665.
- SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
- SHELDRIK, G. M. (1986). *SHELXS86*. Program for the solution of crystal structures. Univ. of Göttingen, Federal Republic of Germany.
- STAŃCZAK, A. (1987). PhD Thesis. Medical Academy, Łódź, Poland.

*Acta Cryst.* (1991). **C47**, 198–200

## Structure of a Synthetic Tricyclic Dione\* with an Ingenol-Like Ring System

BY MARY JANE HEEG,† TERRY L. MOORE AND JAMES H. RIGBY

*Department of Chemistry, Wayne State University, Detroit, Michigan 48202, USA*

(Received 11 July 1989; accepted 15 June 1990)

**Abstract.** C<sub>15</sub>H<sub>16</sub>O<sub>2</sub>, *M<sub>r</sub>* = 228.29, orthorhombic, *Pbca*, *a* = 7.8945 (5), *b* = 12.652 (2), *c* = 24.118 (5) Å, *V* = 2408.9 (5) Å<sup>3</sup>, *Z* = 8, *D<sub>x</sub>* = 1.259 g cm<sup>-3</sup>, λ(Cu Kα) = 1.5418 Å, μ = 6.17 cm<sup>-1</sup>, *F*(000) = 976, *T* = 298 (2) K, *R* = 0.046 and *wR* = 0.022 for 940 unique observed reflections. This structure consists of a tricyclic molecule with two exocyclic carbonyl groups and an exocyclic methyl substituent. The two seven-membered rings have three C atoms in

common creating a bicyclo ring system. The unsaturated cycloheptenone ring is in a diplanar conformation with the atoms C7–C10 planar to within 0.003 Å and the remaining three ring atoms (C6, C4, C11) defining a plane at 32.4 (3)°. The cycloheptanone ring is in a distorted twist-chair conformation; the asymmetry parameter for a twofold axis passing through C10 and the midpoint of C3–C15 is ΔC<sub>2</sub> = 4.2°. At the C3–C4 juncture a cyclopentenone ring is fused in an envelope conformation with the C2–C3 double bond at the base of the envelope and C5 on the flap. The dihedral angle between the body and the flap is 11.8°. The exocyclic O1 atom lies

\* IUPAC name: 8,9,10,11-tetrahydro-10-methyl-(3α,8α,10α)-3a,8-methano-3aH-cyclopentacyclodecene-2,12(3H)-dione.

† To whom correspondence should be addressed.