

Related literature. Two similar tetraazabicyclononanes were reported by Flippen-Anderson, George & Gilardi (1990).

This work was supported in part by the Office of Naval Research, Mechanics Division.

Acta Cryst. (1992). **C48**, 1701–1703

2-Chloro-2'-methoxyacetophenone and 2-Chloro-4'-methoxyacetophenone

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(Received 24 October 1991; accepted 3 February 1992)

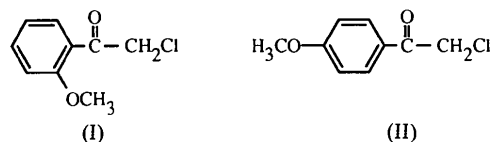
Abstract. 2-Chloro-2'-methoxyacetophenone (I), $C_9H_9ClO_2$, $M_r = 184.6$, monoclinic, $P2_1/c$, $a = 8.1261$ (11), $b = 14.4215$ (9), $c = 7.6839$ (6) Å, $\beta = 103.173$ (9)°, $V = 876.8$ (3) Å³, $Z = 4$, $D_x = 1.399$ g cm⁻³ at 296 K, $\lambda(Cu K\alpha) = 1.54184$ Å, $\mu = 35.5$ cm⁻¹, $F(000) = 384$, 1750 unique data measured, final $R = 0.035$ for 1297 reflections with $I > 3.0\sigma(I)$. 2-Chloro-4'-methoxyacetophenone (II), $C_9H_9ClO_2$, $M_r = 184.6$, monoclinic, $P2_1/c$, $a = 7.6079$ (7), $b = 12.296$ (2), $c = 9.9240$ (13) Å, $\beta = 111.097$ (9)°, $V = 866.1$ (2) Å³, $Z = 4$, $D_x = 1.416$ g cm⁻³ at 295 K, $\lambda(Cu K\alpha) = 1.54184$ Å, $\mu = 35.9$ cm⁻¹, $F(000) = 384$, 1782 unique data measured, final $R = 0.040$ for 1411 reflections with $I > 3.0\sigma(I)$. Maximum deviation from planarity of the aromatic ring is 0.005 (2) Å in (I) and 0.009 (2) Å in (II). In both (I) and (II) the methoxy substituent is nearly coplanar with the benzenoid ring with C—C—O—C torsion angles of -4.2 (2)° in (I) and -5.5 (3)° in (II). The C—Cl distance [1.779 (2) Å] in (I) is indistinguishable from that [1.772 (2) Å] in (II). The close $CH_3O \cdots CCl$ intramolecular contact [2.676 (2) Å] and the nearly linear angle [160.7 (1)°] for $CH_3O \cdots C—Cl$ in (I) suggest predisposition for an intramolecular nucleophilic substitution. The lack of dramatic change in the C—Cl distance in (I) discounts any strong interaction between the O atom and C—Cl bond.

Experimental. Data for both structures were obtained on an Enraf-Nonius CAD-4 diffractometer with a graphite monochromator using $Cu K\alpha$ radiation, from colorless crystals mounted in capillaries. The ω - 2θ scans were designed for $I = 50\sigma(I)$, subject to maximum scan time of 120 s. Data reduction included corrections for background, Lorentz and

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polarization effects. Standard reflections exhibited only random fluctuations in intensity: $\pm 1.3\%$ for (I) and $\pm 1.2\%$ for (II). Absorption corrections were based on ψ scans. The structure of (I) was solved by direct methods using *MULTAN*11/82 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982). Compound (II) is isomorphous with the bromo analog (Fronczek, Fouad & Gandour, 1991) and coordinates from that structure were used as a beginning refinement model. Refinements were carried out by full-matrix least squares based on F with weights $w = 4F_o^2[\sigma^2(I) + (0.02F_o^2)^2]^{-1}$ using Enraf-Nonius *SDP/VAX* (Frenz & Okaya, 1980), scattering factors of Cromer & Waber (1974) and anomalous coefficients of Cromer (1974). Non-H atoms were refined anisotropically; H atoms were located in difference maps and refined isotropically.



A colorless crystal of compound (I) was grown by evaporation of benzene from the crude reaction product of 2'-methoxyacetophenone with phosphorus pentachloride and phosphorus trichloride. Details of the data collection and structural refinement are given in Table 1. Coordinates† and

† Lists of H-atom positional parameters, bond distances and angles involving H atoms, torsion angles, least-squares planes, anisotropic thermal parameters, and structure-factor amplitudes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55126 (26 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: ST0566]

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Table 1. *Experimental details for (I) and (II)*

	(I)	(II)
Crystal dimensions (mm)	0.05 × 0.15 × 0.50	0.20 × 0.30 × 0.30
Unit-cell determination: No. of reflections; θ range (°)	25; 25 < θ < 30	25; 25 < θ < 30
Standard reflections	100, 080, 002	200, 060, 004
R_{int}	0.015	0.013
Minimum relative transmission (%)	70.35	84.01
Maximum relative transmission (%)	99.87	99.77
Scan rate (° min ⁻¹)	0.46–3.30	0.57–3.30
2 θ range (°)	2–75 (one quadrant)	2–75 (one quadrant)
Range of h	0 → 10	0 → 9
k	0 → 18	0 → 15
l	–9 → 9	–12 → 12
Total No. of reflections measured	1940	2004
No. of unique reflections	1750	1782
No. of observed reflections [$I > 3\sigma(I)$]	1297	1411
No. of parameters refined	146	146
R , wR , R_{int}	0.035, 0.043, 0.055	0.040, 0.052, 0.051
Goodness of fit, S	2.116	2.879
Maximum shift/e.s.d.	< 0.01	0.05
Maximum, minimum $\Delta\rho$ (e Å ⁻³)	0.21, –0.21	0.26, –0.23
Extinction coefficient	4.0 (4) × 10 ⁻⁶	4.2 (3) × 10 ⁻⁶

Table 2. *Coordinates and equivalent isotropic thermal parameters (Å²)*

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

	x	y	z	B_{eq}
(I)				
C1	0.92228 (7)	0.24475 (4)	0.99725 (8)	6.44 (1)
O1	0.5672 (2)	0.23250 (9)	1.0007 (2)	6.17 (4)
O2	0.6674 (2)	–0.01114 (8)	0.7702 (2)	5.19 (3)
C1	0.4724 (2)	0.0998 (1)	0.8283 (2)	4.29 (4)
C2	0.5032 (2)	0.0126 (1)	0.7587 (2)	4.31 (4)
C3	0.3696 (2)	–0.0455 (1)	0.6861 (3)	5.12 (4)
C4	0.2061 (3)	–0.0183 (2)	0.6791 (3)	5.95 (5)
C5	0.1730 (2)	0.0674 (2)	0.7452 (3)	6.01 (5)
C6	0.3049 (2)	0.1247 (1)	0.8179 (3)	5.20 (4)
C7	0.6042 (2)	0.1677 (1)	0.9158 (2)	4.61 (4)
C8	0.7824 (2)	0.1557 (1)	0.8934 (3)	5.10 (4)
C9	0.7035 (3)	–0.1027 (1)	0.7155 (3)	5.61 (5)
(II)				
C1	0.28539 (8)	0.16557 (5)	0.42518 (6)	6.11 (1)
O1	0.1355 (2)	0.3681 (2)	0.2867 (2)	6.64 (4)
O2	0.2922 (2)	0.8052 (1)	0.6492 (1)	5.52 (4)
C1	0.2340 (2)	0.4936 (2)	0.4793 (2)	3.99 (4)
C2	0.1426 (2)	0.5797 (2)	0.3931 (2)	4.58 (4)
C3	0.1568 (2)	0.6847 (2)	0.4445 (2)	4.64 (4)
C4	0.2656 (2)	0.7052 (2)	0.5878 (2)	4.38 (4)
C5	0.3558 (3)	0.6195 (2)	0.6771 (2)	4.96 (5)
C6	0.3410 (2)	0.5156 (2)	0.6246 (2)	4.62 (4)
C7	0.2176 (2)	0.3840 (2)	0.4147 (2)	4.46 (4)
C8	0.3115 (3)	0.2920 (2)	0.5159 (2)	4.79 (4)
C9	0.2170 (3)	0.8970 (2)	0.5589 (3)	6.05 (6)

equivalent isotropic thermal parameters are given in Table 2; bond distances and angles are given in Table 3. The molecule is illustrated in Fig. 1.

Compound (II) was prepared by acetylation of anisole with chloroacetyl chloride (Giordano, Castaldi, Casagrande & Belli, 1982). Crystals were grown in methanol. Details of the data collection and structural refinement are given in Table 1. Coordinates* and equivalent isotropic thermal parameters are given in Table 2; bond distances and

* See deposition footnote.

Table 3. *Bond distances (Å) and angles (°)*

	(I)	(II)
C11—C8	1.779 (2)	1.772 (2)
O1—C7	1.216 (2)	1.213 (2)
O2—C2	1.361 (2)	
O2—C4		1.355 (3)
O2—C9	1.437 (2)	1.427 (3)
C1—C2	1.412 (2)	1.381 (3)
C1—C6	1.392 (3)	1.404 (2)
C1—C7	1.493 (2)	1.478 (3)
C2—C3	1.384 (2)	1.378 (3)
C3—C4	1.374 (3)	1.387 (2)
C4—C5	1.385 (3)	1.389 (3)
C5—C6	1.367 (3)	1.369 (3)
C7—C8	1.506 (3)	1.510 (3)
C2—O2—C9	118.4 (1)	
C4—O2—C9		118.3 (1)
C2—C1—C6	117.6 (2)	117.7 (2)
C2—C1—C7	125.7 (2)	119.0 (1)
C6—C1—C7	116.7 (2)	123.2 (2)
C1—C2—C3	120.1 (2)	122.3 (1)
C2—C3—C4	120.4 (2)	119.2 (2)
O2—C2—C3	122.8 (2)	
O2—C4—C3		124.3 (2)
O2—C2—C1	117.1 (1)	
O2—C4—C5		116.2 (1)
C3—C4—C5	120.4 (2)	119.5 (2)
C4—C5—C6	119.3 (2)	120.7 (2)
C1—C6—C5	122.2 (2)	120.6 (2)
O1—C7—C1	120.3 (2)	122.2 (2)
O1—C7—C8	120.8 (2)	121.1 (2)
C1—C7—C8	118.9 (2)	116.7 (1)
C11—C8—C7	113.5 (1)	112.3 (1)

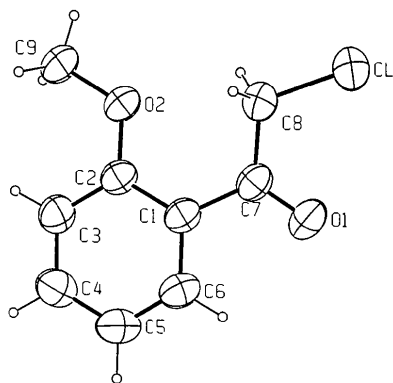


Fig. 1. ORTEP (Johnson, 1965) drawing of (I), with thermal ellipsoids drawn at the 40% probability level.

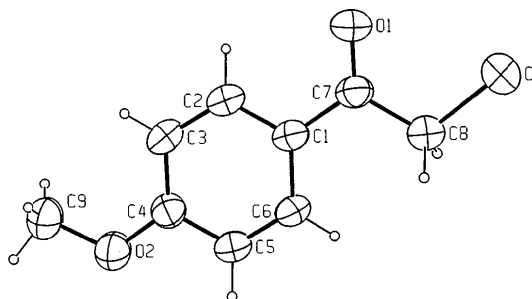


Fig. 2. ORTEP (Johnson, 1965) drawing of (II), with thermal ellipsoids drawn at the 40% probability level.

angles are given in Table 3. The molecule is illustrated in Fig. 2.

Related literature. Structure of 2-chloroacetophenone: Grossert, Dubey, Gill, Cameron & Gardner (1984); structure of 2-chloro-1-(2,4-dihydroxyphenyl)ethanone: van Rooyen & Breytenbach (1988). Activation of α -bromo ketones by complexation with hard and soft Lewis acids: Laube, Weidenhaupt & Hunziker (1991). Cyclization of 2-chloro-2'-hydroxyacetophenone to coumaran-3-one: Bell, Earls & Timimi (1974).

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Acta Cryst. (1992). **C48**, 1703–1705

Structure of a Tricyclic Subunit of Manzamine A

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(Received 31 October 1991; accepted 21 January 1992)

Abstract. ($4a\alpha, 7a\beta, 10a\beta$)-2-Benzyl-1,2,3,4,4a,7,7a,8,9,10-decahydro-8,8-dimethylpyrrolo[2,3-*h*]isoquinolinium iodide, $C_{20}H_{29}N_2^+ \cdot I^-$, $M_r = 424.37$, monoclinic, $P2_1/n$, $a = 9.441$ (4), $b = 10.378$ (4), $c = 20.023$ (9) Å, $\beta = 91.56$ (3)°, $V = 1961$ (1) Å³, $Z = 4$, $D_x = 1.44$ g cm⁻³ (188 K), $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu = 16.16$ cm⁻¹, $F(000) = 864$, $T = 188$ K, $R = 0.0288$ for 3070 reflections [$F_o \geq 4\sigma(F_o)$]. The crystal structure determination was undertaken in order to establish the configuration around C10a. The rings of the isoquinoline group are *trans*, with the pyrrole moiety *cis* fused. The *A* ring is in the chair conformation, while the cyclohexene ring, *B*, is in the boat conformation owing to the *cis* fusion of the five-membered pyrrole ring. The pyrrole ring, *C*, assumes the half-chair conformation. The C—N bonds of the quaternary N atom, N8, are longer than those of the tertiary N atom, N2 [1.517 (2) for N8 and 1.463 (2) Å for N2].

Experimental. Compound (1) was synthesized by an intramolecular Diels–Alder reaction of the corresponding substrate. Treatment of (1) with lithium aluminium hydride (LAH) yielded (2) which was

then treated with methyl iodide in methanol resulting in the formation of (3). Synthetic details are described elsewhere (Martin, Rein & Liao, 1991). Crystals of (3) were obtained by slow evaporation from methanol. The data crystal was a colorless

