

All three conformations are of the $\text{H}_3\text{O}^+(\text{H}_2\text{O})_2$ type and not of the $\text{H}_5\text{O}_2^+(\text{H}_2\text{O})$ type since the two internal hydrogen bonds do not differ significantly in any of the conformations. The geometries agree well with the mean values given by Taesler (1981). It is not evident from the internal geometry why conformation (a) is the most favorable. However, both (b) and (c) give rise to non-bonded O—O distances which are less than 3.0 Å. These contacts which are close to van der Waals contacts, can give an energy difference favoring conformation (a).

When the water to proton ratio in a crystal is three or more the hydrated proton complex can appear either isolated or as part of an infinite water structure (Taesler, 1981). A high water to proton ratio together with a high overall water content favors the non-isolated situation. The present compound is the only one so far reported with four water molecules per proton which contains an isolated water-proton complex. The occurrence of the isolated H_7O_3^+ complex is probably due to the large anion with favorable hydrogen-bond-accepting properties.

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References

- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.
- LEHMANN, M. S. & LARSEN, F. K. (1974). *Acta Cryst.* **A30**, 580–584.
- LUNDGREN, J.-O. (1974). *Acta Univ. Ups.* No. 271.
- LUNDGREN, J.-O. (1979). *Acta Cryst.* **B35**, 780–783.
- LUNDGREN, J.-O. (1982). *Crystallographic Computer Programs*. Report UUIC-B13-4-04. Institute of Chemistry, Univ. of Uppsala, Sweden.
- LUNDGREN, J.-O. & OLOVSSON, I. (1976). *The Hydrogen Bond, Recent Developments in Theory and Experiments*, edited by P. SCHUSTER, G. ZUNDEL & C. SANDORFY, pp. 471–526. Amsterdam: North Holland.
- MCCANDLISH, L. E., STOUT, G. H. & ANDREWS, L. C. (1975). *Acta Cryst.* **A31**, 245–249.
- MO, F. & ADMAN, E. (1975). *Acta Cryst.* **B31**, 192–198.
- TAESLER, I. (1981). *Hydrated Proton Complexes in the Solid State*. *Acta Univ. Ups.* No. 591.
- TAKUSAGAWA, F., HIROTSU, K. & SHIMADA, A. (1971). *Bull. Chem. Soc. Jpn.* **44**, 1274–1278.
- VYAS, N. K., SAKORE, T. D. & BISWAS, A. B. (1978). *Acta Cryst.* **B34**, 3486–3488.

Acta Cryst. (1985). **C41**, 446–450

Structures of Five α -Cyclohexylacetophenones, $\text{XC}_6\text{H}_4\text{COCH}_2\text{C}_6\text{H}_{11}$ *

BY SARA ARIEL AND JAMES TROTTER

Department of Chemistry, University of British Columbia, Vancouver, BC, Canada V6T 1Y6

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Abstract. $T = 295$ K, Mo $K\alpha$, $\lambda = 0.71073$ Å. (1) $X = \text{CH}_3$, $\text{C}_{15}\text{H}_{20}\text{O}$, $M_r = 216.32$, monoclinic, $P2_1/c$, $a = 8.065$ (2), $b = 11.977$ (1), $c = 13.281$ (3) Å, $\beta = 92.84$ (1)°, $V = 1281.3$ (5) Å³, $Z = 4$, $D_x = 1.121$ g cm⁻³, $\mu = 0.68$ cm⁻¹, $F(000) = 472$, final $R = 0.085$ for 810 observed reflections. (2) $X = \text{Cl}$, $\text{C}_{14}\text{H}_{17}\text{ClO}$, $M_r = 236.73$, monoclinic, $P2_1/a$, $a = 7.944$ (1), $b = 10.789$ (1), $c = 14.898$ (2) Å, $\beta = 95.81$ (1)°, $V = 1270.3$ (3) Å³, $Z = 4$, $D_x = 1.238$ g cm⁻³, $\mu = 2.79$ cm⁻¹, $F(000) = 504$, final $R = 0.053$ for 1749 observed reflections. (3) $X = \text{CH}_3\text{O}$, $\text{C}_{15}\text{H}_{20}\text{O}_2$, $M_r = 232.31$, triclinic, $P\bar{1}$, $a = 6.377$ (2),

$b = 10.613$ (4), $c = 10.735$ (5) Å, $\alpha = 111.13$ (2), $\beta = 100.62$ (2), $\gamma = 97.02$ (2)°, $V = 651.8$ (5) Å³, $Z = 2$, $D_x = 1.184$ g cm⁻³, $\mu = 0.73$ cm⁻¹, $F(000) = 252$, final $R = 0.070$ for 959 observed reflections. (4) $X = \text{CO}_2\text{H}$, $\text{C}_{15}\text{H}_{18}\text{O}_3$, $M_r = 246.31$, monoclinic, $P2_1/n$, $a = 13.450$ (5), $b = 5.470$ (1), $c = 17.800$ (5) Å, $\beta = 93.42$ (1)°, $V = 1307.3$ (7) Å³, $Z = 4$, $D_x = 1.251$ g cm⁻³, $\mu = 0.80$ cm⁻¹, $F(000) = 528$, final $R = 0.053$ for 1351 observed reflections. (5) $X = \text{CN}$, $\text{C}_{15}\text{H}_{17}\text{NO}$, $M_r = 227.31$, triclinic, $P\bar{1}$, $a = 7.161$ (4), $b = 7.945$ (3), $c = 11.927$ (5) Å, $\alpha = 89.21$ (3), $\beta = 79.34$ (3), $\gamma = 80.77$ (3)°, $V = 658.1$ (5) Å³, $Z = 2$, $D_x = 1.147$ g cm⁻³, $\mu = 0.73$ cm⁻¹, $F(000) = 244$, final $R = 0.059$ for 1131 observed reflections. All five compounds crystallize in a common conformation in which the carbonyl-containing side chain is equatorial with respect to the chair-shaped cyclohexane ring. An equatorial γ -H atom is suitably oriented for abstraction

* (1) 2-Cyclohexyl-1-(*p*-tolyl)ethanone. (2) 1-(4-Chlorophenyl)-2-cyclohexylethanone. (3) 2-Cyclohexyl-1-(4-methoxyphenyl)ethanone. (4) 1-(4-Carboxyphenyl)-2-cyclohexylethanone (alternative name 4-cyclohexylmethylcarbonylbenzoic acid). (5) 1-(4-Cyanophenyl)-2-cyclohexylethanone (alternative name 4-cyclohexylmethylcarbonylbenzonitrile).

Table 1. Crystallographic and experimental details for (1)–(5)

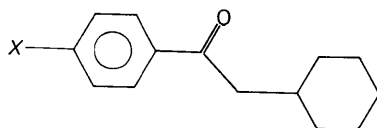
	(1)	(2)	(3)	(4)	(5)
Crystal shape	Prism	Prism	Prism	Needle	Prism
Crystal size (mm)	0.3 × 0.3 × 0.1	0.2 × 0.4 × 0.5	0.1 × 0.2 × 0.5	0.2 × 0.3 × 0.5	0.1 × 0.2 × 0.3
Scan mode	ω - 2θ	ω - $\dot{\theta}$	ω - $\dot{\theta}$	ω - 2θ	ω - $\dot{\theta}$
$\Delta\omega$ (°)	1.0	1.0	1.2	1.0	1.0
$\sin\theta(\text{max.})/\lambda$ (Å ⁻¹)	0.59	0.64	0.59	0.59	0.57
Range of: h	-9 to 9	-10 to 10	-7 to 7	-16 to 16	-8 to 8
k	0 to 14	0 to 13	-12 to 12	0 to 6	-9 to 9
l	0 to 15	0 to 19	0 to 12	0 to 21	0 to 13
Monitor reflections	302,045, 111	062,327, 004	222,201, 310	008,421, 400	223,304, 400
Fluctuations (%)	16*	<3	<3	<3	<1
Total No. of unique data	1624	2387	1754	1914	1664
R_{int}	0.030	0.020	0.026	0.028	0.029
R (all data)	0.140	0.089	0.147	0.087	0.092
R_w (all data)	0.060	0.054	0.067	0.055	0.058
Significant reflections [$F_o \geq 3\sigma(F_o)$]	810	1749†	959	1351	1131
No. of parameters	166	162	177	184	171
R (observed data)	0.085	0.053	0.070	0.053	0.059
R_w (observed data)	0.053	0.047	0.046	0.045	0.049
$(\Delta/\sigma)_{\text{max}}$	0.05	0.10	0.15	0.06	0.02
$(\Delta\rho)_{\text{max}}$ (e Å ⁻³)	0.30	0.23	0.23	0.18	0.15
Reflections used for measuring lattice parameters					
number	25	24	22	21	23
θ range (°)	13–19	20–24	16–22	17–21	17–21

* Isotropic decay correction applied during data reduction.

† Nine strong reflections were given zero weight during refinement.

in a solid-state Norrish type II photochemical reaction, through a boat-like six-atom geometry with abstraction distance 2.6 Å.

Introduction. The light-induced cleavage and/or cyclization of organic carbonyl compounds possessing favorably oriented γ -H atoms, termed the Norrish type II reaction, is one of the most widespread of all organic photorearrangements and remains the object of much current mechanistic and synthetic interest (Scaiano, 1982). Study of this type II reaction in the crystalline state, where the reactant geometry is fixed and determinable by X-ray diffraction methods, can provide information on the mechanism of the primary H-abstraction process itself (Ariel, Ramamurthy, Scheffer & Trotter, 1983). The present crystallographic work was undertaken to establish the geometric requirements for the Norrish type II reaction in the α -cyclohexylacetophenones (1)–(5).



- (1) X = CH₃ (4) X = COOH
 (2) X = Cl (5) X = CN
 (3) X = CH₃O

Experimental. Enraf–Nonius CAD-4F single-crystal X-ray diffractometer, graphite-monochromatized Mo $K\alpha$ radiation. Lattice parameters from setting of 21–25 reflections with $\theta = 13$ – 24° . Crystallographic data, details of intensity measurements and structure refinement are given in Table 1. ω -scan width

($\Delta\omega + 0.3\tan\theta$) $^\circ$, extended 25% on each side for background measurement. Horizontal aperture (1.0 + $\tan\theta$) mm, vertical aperture 4 mm. Lp corrections, no absorption correction. Three standard reflections, 16% decay for (1), no decay for (2)–(5). The structures were solved by direct methods using *SHELX76* (Sheldrick, 1976) and refined by full-matrix least squares minimizing $\sum w(|F_o| - |F_c|)^2$; $w = 1/\sigma^2(F)$, where $\sigma^2(I) = S + 2B + [0.04(S - B)]^2$, S = scan count, B = time-averaged background count. The carboxyl H atom of (4) was located in a difference Fourier synthesis, all other H-atom coordinates of (1)–(5) were calculated, their isotropic temperature factors refined. Atomic scattering factors from Cromer & Mann (1968) and Stewart, Davidson & Simpson (1965). All calculations were performed on a 16 Mbyte Amdahl 470 V/8 (MTS-G) computer. Pictures were drawn using *PLUTO* (Motherwell & Clegg, 1978).

Discussion. Final atomic coordinates are in Table 2, bond distances and bond angles in Table 3.* The C(sp^3)–C(sp^3) bond distances (Table 3) are in the range 1.508 (4)–1.538 (12) Å [mean 1.525 (5) Å], C(sp^2)–C(sp^3) are 1.495 (4)–1.512 (12) Å [mean 1.504 (5) Å], C–C(phenyl) are 1.371 (3)–1.409 (13) Å [mean 1.386 (7) Å], C(sp^2)–C(sp^2) are 1.481 (12)–1.501 (3) Å [mean 1.493 (8) Å], and C=O(carbonyl) lengths are 1.214 (5)–1.228 (9) Å [mean 1.219 (4) Å].

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, and bond distances and angles involving H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39844 (37 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The cyclohexane ring angles are 109.4 (9)–112.7 (2) $^\circ$ [mean 111.1 (6) $^\circ$], with the smallest angle at substituted C(9) in every case.

Table 2. Atom coordinates ($\times 10^4$) and equivalent isotropic temperature factors ($\text{\AA}^2 \times 10^3$)

$$U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

Compound (1)	x	y	z	U_{eq}
O(1)	9311 (5)	4695 (3)	2824 (3)	66
C(1)	8927 (7)	6812 (6)	3655 (4)	54
C(2)	8846 (7)	7845 (6)	4114 (5)	59
C(3)	8268 (7)	7936 (6)	5095 (5)	56
C(4)	7812 (6)	6965 (6)	5557 (4)	55
C(5)	7857 (7)	5925 (5)	5095 (5)	52
C(6)	8435 (6)	5845 (5)	4129 (5)	46
C(7)	8526 (7)	4765 (5)	3591 (4)	48
C(8)	7659 (7)	3758 (5)	4006 (4)	49
C(9)	7501 (7)	2762 (4)	3284 (4)	49
C(10)	6296 (8)	3012 (5)	2378 (4)	63
C(11)	6117 (8)	1996 (6)	1678 (4)	75
C(12)	5547 (8)	966 (5)	2241 (5)	69
C(13)	6721 (8)	705 (5)	3147 (5)	72
C(14)	6905 (8)	1729 (5)	3839 (4)	63
C(15)	8153 (8)	9066 (5)	5598 (5)	84
Compound (2)				
O(1)	4625 (2)	2663 (1)	3904 (1)	57
C(1)	4055 (3)	2823 (2)	5707 (1)	42
C(2)	3770 (3)	2933 (2)	6603 (1)	48
C(3)	2843 (3)	3934 (2)	6866 (1)	47
C(4)	2223 (3)	4822 (2)	6262 (1)	51
C(5)	2500 (3)	4698 (2)	5365 (1)	46
C(6)	3417 (3)	3693 (2)	5076 (1)	37
C(7)	3729 (3)	3516 (2)	4107 (1)	39
C(8)	2947 (3)	4422 (2)	3416 (1)	43
C(9)	3178 (3)	4132 (2)	2434 (1)	42
C(10)	2126 (3)	3024 (2)	2085 (1)	49
C(11)	2290 (3)	2751 (3)	1096 (2)	65
C(12)	1843 (4)	3889 (3)	515 (2)	77
C(13)	2885 (4)	4998 (3)	847 (2)	76
C(14)	2710 (3)	5263 (2)	1837 (1)	57
Cl(1)	2478 (1)	4074 (1)	7994 (<1)	76
Compound (3)				
O(1)	7083 (4)	6691 (3)	8319 (3)	72
C(1)	7538 (6)	4215 (4)	8636 (4)	58
C(2)	7727 (6)	3054 (4)	8920 (4)	62
C(3)	5847 (7)	2184 (4)	8810 (4)	57
C(4)	3816 (6)	2449 (4)	8421 (4)	64
C(5)	3681 (6)	3608 (4)	8131 (4)	56
C(6)	5545 (6)	4524 (4)	8238 (4)	50
C(7)	5449 (7)	5798 (4)	7972 (4)	53
C(8)	3272 (6)	5953 (4)	7280 (5)	60
C(9)	3232 (6)	7175 (4)	6854 (4)	49
C(10)	4344 (7)	7048 (4)	5678 (5)	61
C(11)	4220 (7)	8268 (4)	5251 (5)	69
C(12)	1896 (7)	8415 (6)	4842 (6)	83
C(13)	776 (7)	8545 (5)	6008 (6)	80
C(14)	889 (6)	7328 (4)	6434 (5)	64
C(15)	7832 (8)	598 (5)	9382 (6)	86
O(2)	5811 (4)	1010 (3)	9078 (3)	75
Compound (4)				
O(1)	3607 (2)	4259 (3)	4305 (1)	77
C(1)	3417 (2)	-312 (5)	2845 (1)	46
C(2)	3687 (2)	-680 (5)	2116 (1)	46
C(3)	4270 (2)	1017 (5)	1767 (1)	42
C(4)	4571 (2)	3117 (5)	2157 (1)	47
C(5)	4302 (2)	3487 (5)	2883 (1)	47
C(6)	3729 (2)	1783 (4)	3239 (1)	41
C(7)	3460 (2)	2249 (5)	4032 (1)	49
C(8)	2994 (2)	224 (5)	4458 (1)	51
C(9)	2869 (2)	677 (4)	5290 (1)	44
C(10)	3861 (2)	751 (5)	5747 (1)	53
C(11)	3716 (2)	1096 (5)	6585 (1)	57
C(12)	3050 (2)	-891 (5)	6879 (1)	58
C(13)	2057 (2)	-962 (6)	6434 (1)	61
C(14)	2193 (2)	-1281 (5)	5597 (1)	56
C(15)	4584 (2)	582 (6)	995 (1)	48
O(2)	4308 (1)	-1423 (4)	681 (1)	71
O(3)	5104 (1)	2131 (4)	688 (1)	69

Table 2 (cont.)

Compound (5)	x	y	z	U_{eq}
O(1)	2580 (3)	-764 (2)	561 (2)	96
C(1)	2257 (4)	2092 (3)	-765 (3)	90
C(2)	2192 (4)	3520 (3)	-1425 (3)	60
C(3)	2391 (4)	5072 (3)	-958 (3)	63
C(4)	2632 (4)	5186 (3)	153 (3)	54
C(5)	2705 (4)	3725 (3)	811 (2)	58
C(6)	2527 (4)	2166 (3)	349 (3)	59
C(7)	2660 (4)	564 (3)	1028 (2)	50
C(8)	2952 (4)	631 (3)	2234 (2)	56
C(9)	2994 (4)	-1064 (3)	2856 (2)	61
C(10)	1009 (5)	-1532 (4)	3199 (3)	60
C(11)	1072 (6)	-3227 (5)	3819 (4)	85
C(12)	2038 (6)	-3200 (5)	4853 (3)	109
C(13)	4022 (6)	-2716 (5)	4525 (3)	107
C(14)	3941 (5)	-1038 (4)	3892 (3)	102
C(15)	2361 (4)	6566 (4)	-1660 (3)	85
N(1)	2348 (4)	7747 (3)	-2218 (2)	70

Table 3. Bond lengths (\AA) and bond angles ($^\circ$)

	(1)	(2)	(3)	(4)	(5)
C(1)–C(2)	1.382 (13)	1.382 (3)	1.385 (7)	1.383 (5)	1.372 (4)
C(2)–C(3)	1.409 (13)	1.386 (3)	1.379 (6)	1.386 (5)	1.399 (4)
C(3)–C(4)	1.373 (12)	1.371 (3)	1.381 (6)	1.390 (6)	1.374 (4)
C(4)–C(5)	1.390 (12)	1.384 (3)	1.382 (7)	1.378 (6)	1.392 (4)
C(5)–C(6)	1.389 (12)	1.398 (3)	1.399 (6)	1.386 (6)	1.396 (4)
C(1)–C(6)	1.386 (11)	1.387 (3)	1.381 (6)	1.394 (6)	1.381 (4)
C(6)–C(7)	1.481 (12)	1.501 (3)	1.486 (7)	1.500 (6)	1.498 (4)
C(7)–O(1)	1.228 (9)	1.221 (3)	1.218 (5)	1.214 (5)	1.215 (3)
C(7)–C(8)	1.512 (12)	1.507 (3)	1.506 (6)	1.500 (6)	1.495 (4)
C(8)–C(9)	1.531 (11)	1.526 (3)	1.525 (7)	1.521 (6)	1.528 (4)
C(9)–C(10)	1.538 (12)	1.520 (3)	1.532 (7)	1.521 (6)	1.508 (4)
C(10)–C(11)	1.533 (12)	1.521 (3)	1.527 (8)	1.527 (6)	1.525 (4)
C(11)–C(12)	1.525 (12)	1.523 (4)	1.510 (6)	1.521 (6)	1.523 (5)
C(12)–C(13)	1.526 (13)	1.510 (4)	1.525 (9)	1.512 (6)	1.511 (5)
C(13)–C(14)	1.535 (12)	1.523 (4)	1.523 (8)	1.522 (6)	1.522 (4)
C(9)–C(14)	1.530 (11)	1.533 (3)	1.525 (6)	1.527 (6)	1.517 (4)
C(3)–Y*	1.515 (13)	1.742 (2)	1.375 (6)	1.480 (6)	1.443 (4)
Y–Z†			1.430 (6)	1.277 (5)	1.143 (3)
$\sigma = 0.2$ $\sigma = 0.4$					
C(3)–C(2)–C(1)	120.1 (12)	118.9	118.4	120.7 (4)	119.4 (3)
C(6)–C(1)–C(2)	121.8 (11)	120.9	122.5	120.2 (4)	120.9 (3)
C(4)–C(3)–C(2)	117.1 (11)	121.7	121.3	119.0 (4)	120.9 (3)
C(5)–C(4)–C(3)	123.2 (10)	118.9	118.9	120.3 (4)	119.1 (3)
C(6)–C(5)–C(4)	119.2 (11)	120.8	121.7	120.9 (4)	120.4 (3)
C(5)–C(6)–C(1)	118.6 (11)	118.8	117.1	118.8 (4)	119.3 (3)
C(7)–C(6)–C(1)	119.2 (11)	118.8	120.0	122.0 (4)	119.2 (3)
C(7)–C(6)–C(5)	122.2 (11)	122.5	122.8	119.2 (4)	121.5 (3)
C(6)–C(7)–O(1)	120.0 (11)	119.4	120.6	119.2 (4)	118.3 (3)
C(8)–C(7)–O(1)	120.9 (10)	122.0	121.5	122.0 (4)	122.1 (3)
C(8)–C(7)–C(6)	119.1 (9)	118.5	117.9	118.8 (4)	119.6 (3)
C(9)–C(8)–C(7)	114.8 (9)	116.1	117.5	116.5 (4)	115.1 (3)
C(10)–C(9)–C(8)	111.6 (8)	112.0	112.5	112.4 (4)	112.0 (3)
C(14)–C(9)–C(8)	110.3 (9)	110.3	110.2	109.7 (4)	111.2 (3)
C(14)–C(9)–C(10)	109.4 (9)	109.5	109.7	110.5 (3)	110.2 (3)
C(11)–C(10)–C(9)	110.9 (8)	112.7	111.1	111.5 (4)	111.4 (3)
C(12)–C(11)–C(10)	111.5 (9)	110.9	111.8	111.1 (4)	111.3 (3)
C(13)–C(12)–C(11)	111.2 (9)	111.3	110.4	111.0 (4)	111.3 (4)
C(14)–C(13)–C(12)	110.2 (9)	111.4	111.0	111.2 (4)	110.9 (4)
C(13)–C(14)–C(9)	112.4 (10)	111.9	111.9	112.2 (4)	112.6 (3)
C(2)–C(3)–Y	120.5 (12)	119.0	124.2	120.6 (4)	119.3 (3)
C(4)–C(3)–Y	122.4 (11)	119.2	114.5	120.3 (4)	119.8 (3)
C(3)–Y–Z			118.2	117.0 (4)	179.3 (3)
Z–Y–Z				119.8 (4)	123.2 (4)
*Y	C(15)	Cl(1)	O(2)	C(15)	C(15)
†Z			C(15)	O(2)	N(1)
			O(3)		

Table 4 summarizes selected torsion angles of (1)–(5). The cyclohexane-type ring has a chair conformation in all five compounds, with absolute values of torsion angles in the range 54.1 (5)–56.7 (7) $^\circ$ [mean

Table 4. *Torsion angles of (1)–(5) (°)*

	(1)	(2)	(3)	(4)	(5)
14–9–10–11*	–56.1 (6)	55.1 (2)	55.4 (5)	–54.7 (3)	–55.6 (4)
9–10–11–12	56.7 (7)	–55.5 (3)	–56.6 (5)	56.2 (3)	55.9 (4)
10–11–12–13	–56.1 (7)	54.7 (3)	56.1 (6)	–56.3 (3)	–54.9 (5)
11–12–13–14	55.0 (7)	–55.3 (3)	–55.7 (6)	55.6 (3)	54.1 (5)
12–13–14–9	–56.4 (7)	56.0 (3)	56.6 (5)	–55.1 (3)	–55.1 (4)
13–14–9–10	56.7 (6)	–54.9 (3)	–56.0 (5)	54.3 (3)	55.7 (4)
Mean	56.2	55.3	56.1	55.4	55.2
11–10–9–8	–178.5 (5)	177.8 (2)	178.4 (4)	–177.5 (2)	180.0 (3)
13–14–9–8	179.9 (5)	–178.7 (2)	179.7 (4)	178.7 (2)	–179.3 (5)
10–9–8–7	–68.6 (6)	71.3 (2)	68.3 (5)	–68.8 (3)	–75.3 (3)
14–9–8–7	169.6 (5)	–166.4 (2)	–169.0 (4)	167.8 (2)	160.9 (3)
9–8–7–O(1)	–13.5 (8)	6.5 (3)	7.9 (6)	–9.7 (4)	–4.3 (4)
9–8–7–6	167.2 (5)	–174.8 (2)	–172.8 (4)	171.8 (2)	177.9 (2)

* 14–9–10–11 refers to C(14)–C(9)–C(10)–C(11), etc.

Table 5. *Solid-state H-abstraction distances and angles (Å and deg)*

The angle τ is the degree by which the hydrogen in question lies outside the mean plane of the carbonyl group. The angle Δ is formed between the hydrogen in question and the C(7)–O(1) bond.

Ketone	O...H _e (Å)	τ_e (°)	Δ_e (°)	O...H _a (Å)	τ_a (°)	Δ_a (°)	O...H _{β} (Å)	τ_{β} (°)	Δ_{β} (°)
(1)	2.60	49.6	87.8	3.83	38.4	65.3	2.57	6.8	83.6
(2)	2.60	42.0	90.1	3.83	35.7	67.1	2.59	12.7	81.4
(3)	2.61	42.5	91.1	3.82	37.0	67.8	2.64	11.6	81.0
(4)	2.60	43.7	90.0	3.81	37.5	66.6	2.61	10.0	82.0
(5)	2.65	42.1	88.3	3.90	33.2	67.0	2.55	12.9	82.4

55.6 (5)°, similar to an ideal chair conformation with 111.5° valency angles (torsion angle 55°; Bucourt & Hainaut, 1965). The angle formed between the carbonyl group [plane of C(6), C(7), C(8) and O(1)] and the aromatic ring, in (1)–(5), is 13.3 (2), 4.2 (1), 12.9 (2), 11.2 (1), and 2.7 (1)°, respectively.

The five compounds crystallize in a common conformation in which the carbonyl-containing side chain is equatorial with respect to the chair-shaped cyclohexane ring. A Newman projection down the equatorial C–C bond [C(8)–C(9)] and a stereoview of ketone (1) (Fig. 1) clearly indicate that the equatorial hydrogen H_e [H(102)] is suitably oriented for abstraction in the solid state, through a boat-like six-atom geometry. This conclusion is borne out quantitatively by the abstraction distances and angles in Table 5. The carbonyl O is much closer to H_e (2.6 Å) than to H_a [H(101)] (3.8 Å). This H-abstraction distance of 2.6 Å is consistent with the suggested upper limit of 2.72 Å (van der Waals radii sum) for this type of process (Appel, Jiang, Scheffer & Walsh, 1983). The angle τ_e in Table 5, the degree to which the H being abstracted lies outside the mean plane of the carbonyl group, is 45°. Wagner (1976) has pointed out that coplanar ($\tau = 0^\circ$) H abstraction is not a strict requirement for the type II process, and has suggested a $\cos^2\tau$ dependence for abstraction, which, in our case, would reduce the relative reactivity of H_e by a factor of 2. The angle Δ_e (Table 5), formed between H_e and the C(7)–O(1) bond, is close to the ideal value of 90°.

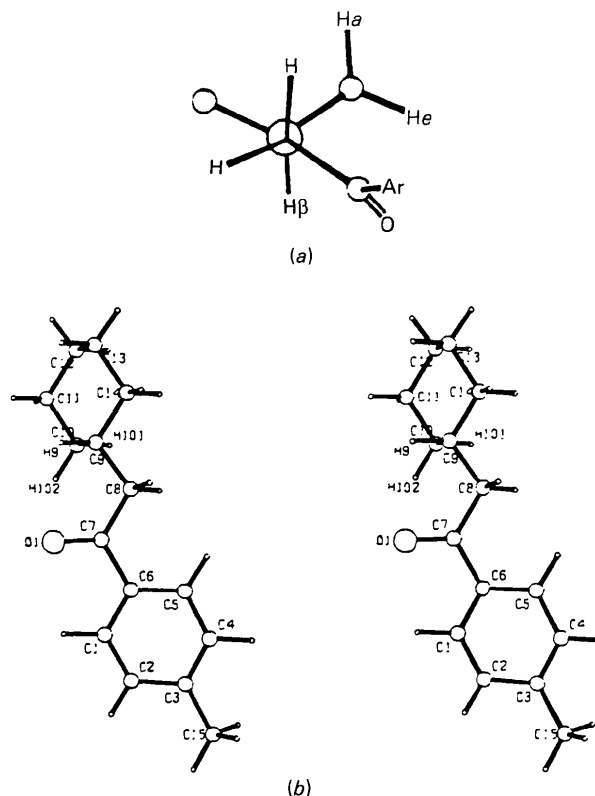


Fig. 1. (a) Newman projection down the equatorial C–C bond, C(8)–C(9), of (1). (b) Stereoview of (1) with crystallographic atomic labeling; H_e=H(102), H_a=H(101), H _{β} =H(9).

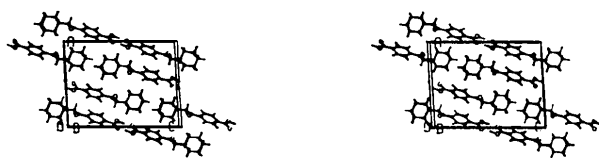


Fig. 2. Packing arrangement of (4).

Table 5 also indicates that H_β [H(9) in (1)–(5)] is in a position favorable for abstraction through a five-membered transition state and in fact is more nearly coplanar with the abstracting oxygen n orbital ($\tau = 7$ – 13°) than is H_e ; the tertiary nature of H_β should also facilitate its abstraction (Wagner, 1976). Nevertheless, no products corresponding to abstraction of H_β could be detected either in solution or in the solid state (Ariel, Ramamurthy, Scheffer & Trotter, 1983). Reversible β -H abstraction is a possibility.

Intermolecular distances in (1)–(3) and (5) correspond to van der Waals interactions. Crystals of (4) contain hydrogen-bonded centrosymmetric carboxylic acid dimers (Fig. 2) with an O(2)···O(3) distance of 2.634 (4) Å, and an O(2)–H(O)···O(3) angle of 172.9°. The C(15)–O(2) and C(15)–O(3) bond lengths are quite close, 1.277 (5) and 1.245 (5) Å, respectively [Table 3, column (4)], as are the corresponding bond angles C(3)–C(15)–O(2) [117.0 (4)°] and C(3)–C(15)–O(3) [119.8 (4)°]. Although the doubly bonded O(3) and the hydroxyl oxygen, O(2), are not very distinguishable, on the basis of their dimensions,

the difference Fourier map (with a cut-off of $\sin\theta/\lambda = 0.3 \text{ \AA}^{-1}$) revealed only one carboxyl hydrogen H(O) 1.3 Å away from O(2) [and 1.4 Å from O(3)]. The carboxyl group may be somewhat disordered, but the X-ray room-temperature data could not define this disorder more precisely. The angle between the carboxyl group and the aromatic ring is 2.3 (1)°.

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References

- APPEL, W. K., JIANG, Z. Q., SCHEFFER, J. R. & WALSH, L. (1983). *J. Am. Chem. Soc.* **105**, 5354–5364, and references therein.
 ARIEL, S., RAMAMURTHY, V., SCHEFFER, J. R. & TROTTER, J. (1983). *J. Am. Chem. Soc.* **105**, 6959–6960.
 BUCOURT, R. & HAINAUT, D. (1965). *Bull. Soc. Chim. Fr.* pp. 1366–1378.
 CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.
 MOTHERWELL, W. D. S. & CLEGG, W. (1978). *PLUTO*. A program for plotting molecular and crystal structures. Univ. of Cambridge, England.
 SCAIANO, J. C. (1982). *Acc. Chem. Res.* **15**, 252–258, and references therein.
 SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
 STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
 WAGNER, P. J. (1976). *Top. Curr. Chem.* **66**, 1–52.

Acta Cryst. (1985). **C41**, 450–453

Effect of Metal Ions in Organic Synthesis. XXVI. Structure of Methyl 1-(3-Chlorobenzoylamino)-4-diethylaminocarbonyl-2,5-dimethyl-1H-pyrrole-3-carboxylate, $C_{20}H_{24}ClN_3O_4$

BY GIUSEPPE GIUSEPPETTI AND CARLA TADINI

CNR Centro di Studio per la Cristallografia Strutturale, c/o Dipartimento di Scienze della Terra, Sezione Mineralogico-Petrografica, Università, Via A. Bassi 4, 27100 Pavia, Italy

AND ORAZIO ATTANASI, MARIO GROSSI AND FRANCO SERRA-ZANETTI

Cattedra di Chimica Organica della Facoltà di Scienze, Università, Piazza Rinascimento 6, 61029 Urbino, Italy

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Abstract. $M_r = 405.9$, monoclinic, $C2/c$, $a = 11.050$ (1), $b = 26.041$ (2), $c = 14.413$ (1) Å, $\beta = 90.84$ (1)°, $V = 4146.9$ (6) Å³, $Z = 8$, $D_x = 1.30 \text{ Mg m}^{-3}$, $\lambda(\text{Mo K}\alpha) = 0.7107$ Å, $\mu = 0.2104 \text{ mm}^{-1}$, $F(000) = 1712$, $T = 296 \text{ K}$, $R = 0.032$ for 1477 observed reflections. The X-ray crystal structure of the title compound clearly shows a pyrrole ring instead of the theoretically possible dihydro-

pyridazine ring. The crystal packing exhibits two bimolecular hydrogen bonds, providing the formation of an unusual fourteen-membered pseudo ring.

Introduction. In previous papers, some of us (Attanasi, Bonifazi, Foresti & Pradella, 1982; Attanasi, Bonifazi & Buiani, 1983; Attanasi & Santeusano, 1983; Attanasi, Filippone, Mei & Santeusano, 1984a,b;