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(±)-Carbocamphenilone

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Abstract. $C_{10}H_{14}O_2$, $M_r = 166.22$, m.p. 59–60°, monoclinic, $P2_1/c$, $Z = 4$, $a = 7.785$ (2), $b = 10.239$ (3), $c = 13.510$ (4) Å, $\beta = 120.06$ (4)°, $D_x = 1.185$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu(\text{Mo } K\alpha) = 0.874$ cm⁻¹, $R = 0.051$ for 834 observed reflections. In the crystal the six-membered ring exists in the chair conformation and the dihedral angle between the two carbonyl groups is –34.0 (4)° in the (+)-enantiomer.

Introduction. (±)-Carbocamphenilone, m.p. 59–60°, was prepared from (±)-camphene by the method of Hüchel (1947) and crystallized from ligroin. X-ray photographs of the chunky, yellow crystals indicated monoclinic symmetry and systematic absences consistent with the space group $P2_1/c$ ($h0l$ reflections absent when l odd and $0k0$ reflections absent when k odd). Because the substance is volatile and sensitive to moisture, the crystal (0.3–0.4 mm to a side) selected for the data collection was attached to the inside wall of

a sealed, thin-walled glass capillary. Three-dimensional data were collected using a Syntex $P\bar{1}$ diffractometer, graphite-monochromated Mo $K\alpha$ radiation and a θ - 2θ scan procedure, the details of which have been reported (Seccombe, Lee & Henry, 1975). Intensities were measured in shells of 2θ 0–20, 20–30, 30–35, 35–40, 40–43, and 43–47°. The data collection was terminated in the middle of the last shell because the intensities of the decay-monitoring reflections fell below 90% of the original values and because most of the intensities in this shell were undetectably low. There were 1064 reflections with $2\theta \leq 43^\circ$, of which 834 reflections had $I > 3\sigma(I)$. These intensity data were corrected for the decay and reduced to the structure factors by the application of Lorentz and polarization corrections. No absorption or extinction correction was applied.

The structure was determined with *MULTAN* (Germain, Main & Woolfson, 1971) and refined by least-squares procedures, in which all non-hydrogen atoms were assigned anisotropic temperature factors. H

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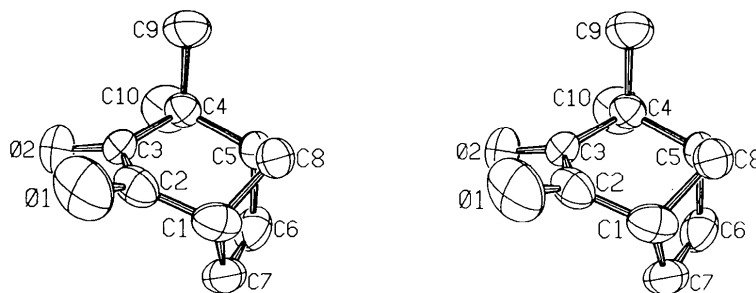


Fig. 1. Stereoview of the molecule (+)-carbocamphenilone.

atoms were included at fixed calculated positions and with fixed isotropic temperature factors. All 1064 reflections were used with weights derived from the counting statistics (Seccombe, Lee & Henry, 1975). Refinement was terminated when shifts in the parameters were all less than 0.05 of the estimated standard deviations. Final $R = \sum |F_o| - |F_c| / \sum |F_o|$ and $R' = [\sum (|F_o| - |F_c|)^2 / \sum |F_o|^2]^{1/2}$ were 0.065 and 0.069, respectively, for the 1064 reflections used. For the 834 observed reflections ($I \geq 3\sigma$), R and R' were 0.051 and 0.067 respectively.

The structure of the molecule and the atom-numbering scheme are shown in Fig. 1. The final atomic coordinates are given in Table 1, and bond lengths and angles in Tables 2 and 3.*

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32614 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. Fractional positional parameters ($\times 10^4$) and their estimated standard deviations

| | x | y | z |
|-------|-----------|----------|----------|
| O(1) | 1910 (3) | 3497 (3) | 5687 (2) |
| O(2) | -373 (3) | 1455 (2) | 5716 (2) |
| C(1) | 449 (4) | 3125 (3) | 3676 (3) |
| C(2) | 654 (4) | 2980 (2) | 4820 (3) |
| C(3) | -877 (3) | 2097 (2) | 4867 (2) |
| C(4) | -2929 (3) | 2083 (2) | 3850 (2) |
| C(5) | -2820 (3) | 2326 (2) | 2756 (2) |
| C(6) | -1583 (5) | 1293 (3) | 2568 (3) |
| C(7) | 533 (5) | 1770 (3) | 3212 (3) |
| C(8) | -1679 (4) | 3561 (3) | 2854 (2) |
| C(9) | -4074 (4) | 3195 (3) | 4025 (3) |
| C(10) | -3961 (5) | 789 (3) | 3788 (3) |

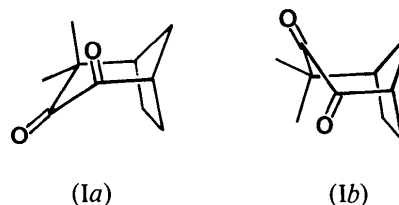
Table 2. Bond lengths (Å)

| | | | |
|------------|-----------|-----------|-----------|
| C(2)—O(1) | 1.209 (3) | C(1)—C(2) | 1.479 (4) |
| C(3)—O(2) | 1.205 (3) | C(2)—C(3) | 1.523 (3) |
| C(4)—C(9) | 1.536 (4) | C(3)—C(4) | 1.497 (4) |
| C(4)—C(10) | 1.530 (4) | C(4)—C(5) | 1.542 (3) |
| C(8)—C(1) | 1.527 (4) | C(5)—C(6) | 1.536 (4) |
| C(8)—C(5) | 1.513 (4) | C(6)—C(7) | 1.507 (4) |
| | | C(7)—C(1) | 1.537 (4) |

Table 3. Bond angles (°)

| | | | |
|-----------------|-----------|----------------|-----------|
| C(8)—C(1)—C(2) | 107.4 (2) | C(8)—C(5)—C(6) | 101.6 (2) |
| C(1)—C(2)—C(3) | 115.2 (2) | C(5)—C(6)—C(7) | 106.0 (2) |
| C(2)—C(3)—C(4) | 117.7 (2) | C(6)—C(7)—C(1) | 105.7 (2) |
| C(3)—C(4)—C(5) | 109.4 (2) | C(7)—C(1)—C(8) | 102.7 (2) |
| C(4)—C(5)—C(8) | 111.3 (2) | | |
| C(5)—C(8)—C(1) | 101.2 (2) | C(2)—C(1)—C(7) | 109.3 (2) |
| | | C(4)—C(5)—C(6) | 112.8 (2) |
| C(9)—C(4)—C(3) | 106.6 (2) | O(1)—C(2)—C(1) | 125.5 (3) |
| C(9)—C(4)—C(5) | 110.0 (2) | O(1)—C(2)—C(3) | 119.3 (3) |
| C(9)—C(4)—C(10) | 108.7 (2) | O(2)—C(3)—C(2) | 118.4 (2) |
| C(10)—C(4)—C(3) | 110.4 (2) | O(2)—C(3)—C(4) | 123.9 (2) |
| C(10)—C(4)—C(5) | 111.5 (2) | | |

Discussion. Optically active carbocamphenilone is of some importance in the study of the chiroptical properties of nonplanar α -diketones (Hug & Wagnière, 1971; Burgstahler & Naik, 1971; Hug & Wagnière, 1972). The absolute configuration is not in question, but interest centers on whether the cyclohexane moiety, for example of the (+)-enantiomer, has a chair (1a) or a boat (1b) conformation.



These two possibilities give rise to opposite chiralities for the dione chromophore. The crystal structure (Fig. 1) shows that the preferred conformation is of the chair (1a) type in which the dihedral angle O(1)—C(2)—C(3)—O(2) is $-34.0(4)^\circ$ in the (+)-enantiomer. A preliminary summary of these results together with further data on the conformational-chiroptical aspects of (–)-carbocamphenilone has been presented (Lee, Seymour & Burgstahler, 1974).

The structure of the molecule is essentially that expected from molecular models. In particular, the groups attached to C(4) and C(5) are in a staggered arrangement as can be seen from the following dihedral angles: C(8)—C(5)—C(4)—C(9), $63.1(3)^\circ$; C(8)—C(5)—C(4)—C(3), $-53.8(2)^\circ$; C(6)—C(5)—C(4)—C(3), $59.6(3)^\circ$; C(6)—C(5)—C(4)—C(10), $-62.8(3)^\circ$. [These signs are for the (+)-enantiomer (1a).]

In addition the following features are noteworthy: (a) The C(2)—C(3) bond between the two carbonyl groups is significantly longer than the adjoining C(1)—C(2) or C(3)—C(4) bond. This finding is interesting because the structure does not permit conjugation or enolization as a mechanism for shortening these peripheral bonds. (b) The five-membered ring is constrained to the half-chair form in which the four atoms C(1), C(7), C(6), and C(5) lie within 0.03 Å of being coplanar, whereas the fifth atom, C(8), lies 0.70 Å off the plane defined by these four atoms. The ring is therefore strongly folded along a line joining C(1) and C(5). Consistent with this large deviation of the five-membered ring from planarity is the significant reduction in the bond angles of the ring (Dunitz, 1972), especially the angles C(7)—C(1)—C(8), C(6)—C(5)—C(8), and C(1)—C(8)—C(5), the latter being the bond angle at the one-atom bridge.

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5'-tert-Butoxycarbonyl-4'-methoxycarbonylethyl-3',4-dimethyl-3-ethyl-2,2'-methylenedipyrrol-5(2H)-one

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Abstract. C₂₂H₃₂N₂O₅, monoclinic, *P*2₁/*c*, *a* = 13.369 (3), *b* = 14.502 (8), *c* = 11.751 (4) Å, β = 95.02 (3)°, *M_r* = 404.5, *Z* = 4, *D_x* = 1.26 g cm⁻³. The interplanar angle between the ring systems is 99.6°. The molecules are linked together through two intermolecular N–H···O hydrogen bonds of length 2.86 and 2.85 Å.

Introduction. Cell dimensions were obtained from a least-squares fit to the settings for 15 reflexions (*±hkl*) on a Syntex *P*2₁ diffractometer (Cu *K*, λ = 1.54178 Å). Intensity measurements were carried out in the θ–2θ mode (3.5 ≤ 2θ ≤ 135.0°) with graphite-monochromated Mo *K*α radiation, at scan speeds varying linearly between 2.93° min⁻¹ (150 counts s⁻¹ and below) and 29.30° min⁻¹ (5000 counts s⁻¹ and above). Scan and background times were equal. Lorentz and polarization but no absorption [*μ*(Cu *K*α) = 6.03 cm⁻¹] corrections were applied. After application of the acceptance criterion *I* > 1.5σ(*I*), 3590 unique reflexions were retained for use in the refinement. The structure was solved by direct methods (*SHELX* 76, G. M. Sheldrick) and refined by blocked full-matrix least squares with anisotropic temperature factors for all the non-hydrogen atoms. The H positional parameters were freely refined with individual isotropic temperature factors and a joint factor for the ethyl and *tert*-butyl groups. The terminal value of

R_G [= (Σ *w*Δ²/Σ *wF_o*²)^{1/2}] was 0.049, with *R_w* (= Σ *w*^{1/2}Δ/Σ *w*^{1/2}|*F_o*|) 0.049 and *R* 0.051. The weights adopted were those from the counting statistics. Complex neutral-atom scattering factors were employed (Cromer & Waber, 1965; Cromer & Liberman, 1970). Tables 1 and 2 list the final atomic parameters.* The atom-numbering scheme is given in Fig. 1.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32619 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

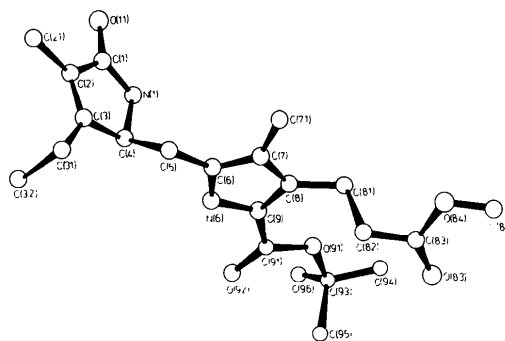


Fig. 1. The molecule of (I) in perspective view with the numbering system.