

Fig. 1. Structure of a single molecule with atomic numbering, projected on the five-membered ring.

distances in the cyclopropane part of the molecule are interesting: the C(3)–C(4) distance of 1.584 (6) Å is unusually long compared with the one found in the normal cyclopropane ring [1.52 Å (Dunitz, Feldmann & Schomaker, 1952)]. This may be caused by the repulsion between the phenyl rings at C(3) and C(4). C(4)–C(6), 1.537 (6) Å, is also somewhat longer than expected, whereas the C(3)–C(6) distance, 1.511 (6) Å, agrees with the expected value. At present the reason for these different distances is not clear. The distances obtained make it clear why the opening of the enlarged and consequently weakened bonds of the three-membered ring, C(4)–C(6) (Brune, Lach & Schmidtberg, 1985a,b), C(3)–C(4) (Brune, Lach & Schmidtberg, 1985c), form the primary step in the photo-isomerization. The C(5)–C(7) double bond, 1.348 (6) Å, corresponds, within experimental errors, to the value found for a bond at the end of a conjugated system, whereas the C(1)–C(2) double bond, 1.384 (7) Å, clearly shows the additional partial conjugation with the phenyl ring at C(2). The spatial

orientations of the phenyl rings at C(3) and C(4) do not allow conjugated interactions with the Walsh π orbitals of the cyclopropane ring.

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3-Benzylidene-4-chromanone

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Abstract. $C_{16}H_{12}O_2$, $M_r = 236.1$, triclinic, $P\bar{1}$, $a = 600.7$ (2) Å³, $Z = 2$, $D_x = 1.305$ (1) g cm⁻³, $\lambda(\text{Cu K}\alpha) = 1.54178$ Å, $\mu = 6.01$ cm⁻¹, $F(000) = 248$, $T = 95.64$ (1), $\beta = 107.64$ (1), $\gamma = 89.90$ (1)°, $V = 292$ K, $R = 0.0411$ for 1380 unique observed reflections.

tions. The two phenyl rings are linked by a non-planar *cisoid* 1,3-enone bridge. The inclination angle between the two phenyl rings is 59.1 (4)°. The pyrone ring adopts a distorted sofa conformation with the unsubstituted C atom deviating most from the ring plane.

Introduction. 3-Benzylidene-4-chromanone [hereinafter referred to as (I)] is an α,β -unsaturated aromatic ketone. The substances of this important class of organic compounds have high physiological activity and are often found to be the basic structures of the pigments of many plants – flavones and isoflavones (Dhar, 1981). The chemical and biological characteristics of these substances can be directly related to the conformation of their molecules. The present paper is a continuation of X-ray diffraction structural studies of α,β -unsaturated ketones (Kaluski, Skrzypczak-Jankun, Orlov & Borovoi, 1978; Hoser, Kaluski, Małuszyńska & Orlov, 1980; Carpy, Leger & Nuhlich, 1978; Rabinovich, 1970; Rabinovich & Schmidt, 1970; Rabinovich, Schmidt & Shaked, 1973).

Experimental. Crystals of (I) to be used in the X-ray diffraction study were grown from solution by the slow evaporation of ethanol solvent. The crystal selected for data collection was a colourless plate with dimensions 0.54 × 0.30 × 0.24 mm, and was mounted on a Syntex P2₁ diffractometer. Graphite-monochromated Cu K α radiation was used. The unit-cell parameters were determined by least-squares fit of setting angles of 15 automatically centred reflections (11 < 2 θ < 28°). The 2 θ - θ scan technique with a variable scan speed (2.0 to 19.3° min⁻¹) was used. Two control reflections were monitored every 50 measurements and showed no systematic variation of intensity. Up to 2 θ = 115.0° 1840 reflections were measured including the controls and equivalents, with h -9→9, k -9→9, l 0→8. The integrated intensity was calculated according to the profile-analysis method of Lehmann & Larsen (1974). Of 1583 unique reflections ($R_{int} = 0.020$) 1386 reflections had $I \geq 1.96\sigma(I)$ and were used in the structure refinement. Only Lp corrections were applied.

The structure was solved using MULTAN80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). After the non-H atoms were refined anisotropically, all H atoms were located from a ΔF map and included in the refinement with isotropic temperature factors. The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = 1/[\sigma^2(F_o) + 0.0001F_o^2]$. Six strong reflections with $(F_o - F_c)/\sigma > 6.0$ were excluded from the last cycles. The final cycles of the full-matrix least-squares refinement gave $R = 0.041$, $wR = 0.046$ and $S = 3.96$, $S = (n - m)^{-1/2} \sum (F_o^i - F_c^i)^2 / \sigma_i^2$, $n = 1380$, $m = 211$. For all the parameters the final shift/ σ was smaller than 0.3, the highest peak on the final ΔF map was 0.11 e Å⁻³, the minimum -0.18 e Å⁻³. The final atomic

Table 1. Fractional coordinates of the atoms, their temperature factors (U_{eq} for the non-H atoms and U_{iso} for the H atoms) and C-H distances

$$U_{eq} = (U_{11} \times U_{22} \times U_{33})^{1/3}.$$

	x	y	z	$U_{eq}(\text{Å}^2)$	
O(1)	0.0371 (2)	0.8255 (1)	0.5578 (2)	0.063	
C(2)	0.1873 (3)	0.8796 (2)	0.5401 (3)	0.058	
C(3)	0.2978 (2)	0.7586 (2)	0.5158 (3)	0.050	
C(4)	0.2173 (2)	0.6372 (2)	0.3813 (3)	0.052	
O(4)	0.2941 (2)	0.5516 (2)	0.3115 (2)	0.068	
C(5)	-0.0520 (3)	0.5153 (2)	0.2136 (3)	0.061	
C(6)	-0.2169 (3)	0.4980 (3)	0.1848 (3)	0.069	
C(7)	-0.2935 (3)	0.5885 (3)	0.2830 (3)	0.069	
C(8)	-0.2078 (3)	0.6960 (2)	0.4070 (3)	0.063	
C(9)	-0.0416 (2)	0.7161 (2)	0.4331 (3)	0.052	
C(10)	0.0387 (2)	0.6251 (2)	0.3384 (2)	0.051	
C(11)	0.4557 (2)	0.7505 (2)	0.6058 (3)	0.053	
C(12)	0.5627 (2)	0.8563 (2)	0.7401 (2)	0.053	
C(13)	0.6937 (3)	0.8052 (3)	0.8687 (3)	0.066	
C(14)	0.7985 (3)	0.8999 (3)	0.9962 (3)	0.078	
C(15)	0.7786 (3)	1.0480 (3)	0.9974 (3)	0.076	
C(16)	0.6513 (3)	1.1010 (3)	0.8693 (3)	0.070	
C(17)	0.5452 (3)	1.0069 (2)	0.7424 (3)	0.059	
H(21)	0.236 (3)	0.949 (2)	0.653 (3)	$U_{iso}(\text{Å}^2)$	$d_{C-H}(\text{Å})$
H(22)	0.162 (3)	0.940 (2)	0.433 (3)	0.061 (6)	1.02 (2)
H(5)	0.003 (3)	0.452 (3)	0.153 (3)	0.077 (7)	1.04 (2)
H(6)	-0.289 (3)	0.417 (3)	0.092 (3)	0.075 (7)	0.94 (2)
H(7)	-0.413 (3)	0.577 (3)	0.269 (3)	0.082 (7)	1.05 (2)
H(8)	-0.256 (3)	0.765 (3)	0.478 (3)	0.089 (7)	1.00 (3)
H(11)	0.503 (3)	0.666 (2)	0.584 (2)	0.077 (7)	0.98 (2)
H(13)	0.707 (3)	0.703 (2)	0.861 (3)	0.056 (6)	0.91 (2)
H(14)	0.894 (4)	0.865 (3)	1.081 (4)	0.072 (7)	0.94 (2)
H(15)	0.855 (3)	1.112 (3)	1.084 (3)	0.132 (11)	0.97 (3)
H(16)	0.632 (3)	1.202 (2)	0.867 (3)	0.094 (9)	0.95 (3)
H(17)	0.458 (3)	1.045 (2)	0.649 (3)	0.073 (7)	0.94 (2)
				0.072 (7)	0.98 (2)

parameters are listed in Table 1.* Most of the calculations were performed with SHELX76 (Sheldrick, 1976) and on a RIAD 32 computer, atomic scattering factors from *International Tables for X-ray Crystallography* (1974) were applied.

Discussion. Fig. 1 shows a perspective view of the molecule with the numbering of its atoms and with the torsion angles describing its conformation. The torsion angles indicate a deviation from planarity of both phenyl rings: the value of χ^2 for the least-squares plane fitted to phenyl ring C(5)-C(6)-C(7)-C(8)-C(9)-C(10) is 61.9 and for phenyl ring C(12)-C(13)-C(14)-C(15)-C(16)-C(17) -42.1. The conformation of the pyrone ring can be described as distorted sofa, with atom C(2) most off the plane of the ring. In 2-benzylidene-1-tetralone (2-benzylidene-1,2,3,4-tetrahydro-1-naphthalenone) (Kaluski *et al.*, 1978), a compound with the same structure as (I) but with atom O(1) being replaced by a C atom, this ring has a distorted half-chair conformation. The conformation of molecule (I) as a whole can be described conveniently by the angle between the planes fitted to its two phenyl

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43279 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

rings. This angle for (I) equals $59.1(4)^\circ$, this conformation being mainly due to the intramolecular interactions between the H atoms on atom C(2), H(21) and H(22), and atom H(17) bonded to C(17) (see Fig. 1). The intramolecular distance $H(21)\cdots H(17)$ is $2.13(3)$ Å and is commensurate with the sum of the van der Waals radii of H atoms (Bondi, 1964). A similar magnitude of the inclination angle of 52.9° between the phenyl rings was observed in 2-benzylidene-1-tetralone (Kałuski *et al.*, 1978), where analogous interactions between the H atoms are present, while in chalcone (Rabinovich, 1970), where the steric hindrances between the H atoms are absent, the phenyl rings are off-plane by only 11.4° . Similarly, the absence of strong intramolecular interactions between the H atoms in 2-benzylidene-1-indanone (Hoser *et al.*, 1980) allows an angle of 15.3° between the phenyl rings.

The bond lengths and valency angles are listed in Table 2. They agree with the values expected for the structure of the molecule and show no significant

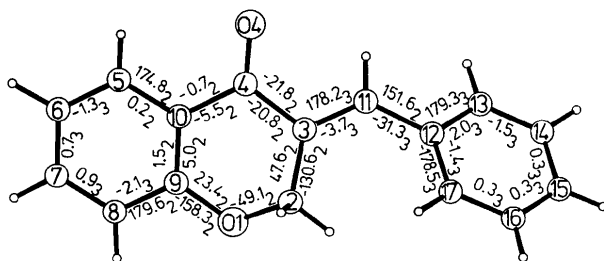


Fig. 1. A PLUTO drawing of the molecule of (I) viewed along the direction perpendicular to the best plane of the chromanone skeleton. The torsion angles ($^\circ$) refer to the bonds between the non-H atoms along the outline of the molecule on the drawing.

Table 2. Bond lengths (Å) and valency angles ($^\circ$) with their standard variations

O(1)—C(2)	1.439 (3)	C(8)—C(9)	1.394 (3)
O(1)—C(9)	1.365 (2)	C(9)—O(1)	1.365 (2)
C(2)—C(3)	1.501 (3)	C(9)—C(10)	1.394 (3)
C(3)—C(4)	1.483 (3)	C(11)—C(12)	1.466 (3)
C(3)—C(11)	1.339 (2)	C(12)—C(13)	1.393 (3)
C(4)—O(4)	1.227 (3)	C(12)—C(17)	1.394 (3)
C(4)—C(10)	1.474 (2)	C(13)—C(14)	1.373 (4)
C(5)—C(6)	1.376 (3)	C(14)—C(15)	1.374 (4)
C(5)—C(10)	1.400 (3)	C(15)—C(16)	1.380 (4)
C(6)—C(7)	1.389 (4)	C(16)—C(17)	1.372 (3)
C(7)—C(8)	1.368 (3)		
C(2)—O(1)—C(9)	115.54 (14)	C(8)—C(9)—C(10)	120.71 (16)
O(1)—C(2)—C(3)	112.14 (15)	C(4)—C(10)—C(5)	121.22 (15)
C(2)—C(3)—C(4)	114.50 (15)	C(4)—C(10)—C(9)	120.03 (14)
C(2)—C(3)—C(11)	126.23 (16)	C(5)—C(10)—C(9)	118.53 (15)
C(4)—C(3)—C(11)	119.24 (15)	C(3)—C(11)—C(12)	129.62 (15)
C(3)—C(4)—O(4)	122.35 (16)	C(11)—C(12)—C(13)	118.74 (16)
C(3)—C(4)—C(10)	115.51 (14)	C(11)—C(12)—C(17)	123.60 (15)
O(4)—C(4)—C(10)	122.14 (15)	C(13)—C(12)—C(17)	117.61 (18)
C(6)—C(5)—C(10)	120.66 (18)	C(12)—C(13)—C(14)	121.00 (20)
C(5)—C(6)—C(7)	119.68 (20)	C(13)—C(14)—C(15)	120.60 (22)
C(6)—C(7)—C(8)	120.99 (21)	C(14)—C(15)—C(16)	119.31 (21)
C(7)—C(8)—C(9)	119.39 (19)	C(15)—C(16)—C(17)	120.40 (21)
O(1)—C(9)—C(8)	116.71 (16)	C(12)—C(17)—C(16)	121.06 (18)
O(1)—C(9)—C(10)	122.55 (15)		

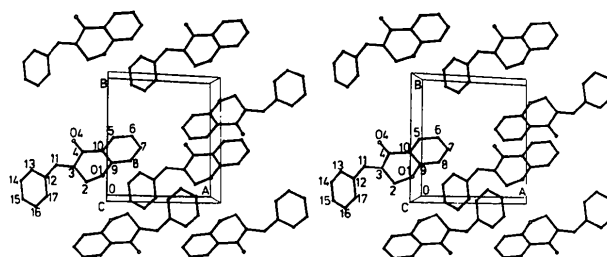


Fig. 2. A stereoscopic view along *c* of the arrangement of molecules in the crystal. H atoms are omitted for clarity.

differences when compared to the corresponding values of 2-benzylidene-1-tetralone (Kałuski *et al.*, 1978). According to the dependence of bond lengths on the total bond order estimated by Allmann (1977), there is no conjugation in the alternating π -electron bond system of the 1,3-enone.

A stereoscopic view of the unit-cell contents (Motherwell & Clegg, 1978) is presented in Fig. 2. The shortest intermolecular distances involving the O atoms are $O(1)\cdots C(2)$ 3.349 (2), $O(1)\cdots C(15)$ 3.501 (3), $O(4)\cdots C(13)$ 3.471 (3) and $O(4)\cdots C(11)$ 3.508 (3) Å. There are no intermolecular distances shorter than the sum of appropriate van der Waals radii.

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