organic compounds

7-Chloro-3,6-dimethyl-1*H*-indene-2-carbaldehyde

Marcella Pani,[a] Angelo Mugnoli[a]* and Enzo Sottofattori[b]

[a]Dipartimento di Chimica e Chimica Industriale, Università degli Studi di Genova, Via Dodecaneso 31, I-16146 Genova, Italy, and [b]Dipartimento di Scienze Farmaceutiche, Università degli Studi di Genova, 3 Viale Benedetto XV, I-16132 Genova, Italy

Correspondence e-mail: mugnoli@unige.it

In the crystal structure of $C_{12}H_{11}ClO$, the (planar) molecules give rise to a parallel packing. A model crystal obtained by semi-empirical and packing-energy calculations is consistent with the observed structure.

Comment

The Vilsmeier reaction has proven to be a versatile tool in achieving different synthetic transformations, ranging from the normal introduction of a formyl group into an activated aromatic nucleus to the access of different ring systems (Marson & Giles, 1994). The reaction between carvone, (I), and the Vilsmeier reagent (*N,N*-dimethylformamide and POCl₃, denoted VR in the reaction scheme) gave the expected product (II) along with a product (III), whose structure, initially not clarified by spectroscopic methods, has been determined by X-ray diffraction (this work).
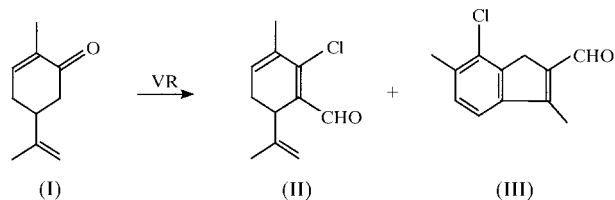
The *ORTEP* diagram (Johnson, 1976) of compound (III) is shown in Fig. 1. Bond lengths and bond angles are in the normal range and even in good agreement with those of compounds having the same frame of fused rings, as retrieved from the Cambridge Structural Database (Version 5.18; Allen & Kennard, 1993). The C2═C3 and C2—C10 bond lengths are, respectively, somewhat longer and shorter than the reported reference values (Allen *et al.*, 1987), indicating a tendency to π-delocalization. The orientation of the C12 methyl group is probably conditioned by two H···Cl intra-molecular contacts (C12—H 0.96, H12*B*···Cl 2.94, H12*C*···Cl
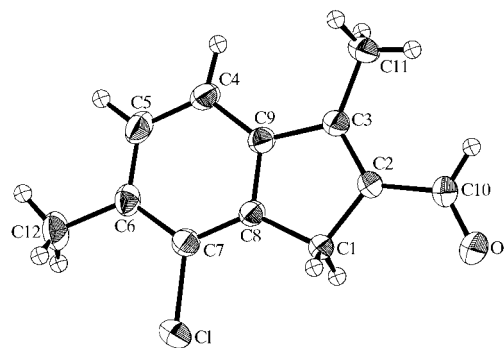

Figure 1
Compound (III) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 40% level of probability. H atoms are spheres of arbitrary size.

2.99 Å), both slightly shorter than the sum of van der Waals radii (Pauling, 1960).[1]

Considering the non-H atoms, the molecule adopts a planar conformation with a maximum deviation of 0.047 (2) Å (atom O1) from the mean plane. In the crystal, the molecules are in a parallel arrangement, in planes approximately normal to the *x* axis.

The geometry of the isolated molecule of the title compound has been investigated by simple semi-empirical molecular-orbital calculations. A starting model (with *m* symmetry) was generated using a graphical interface (*SPARTAN*; Wavefunction, 1998) and its geometry fully optimized at the *AM*1 level (Dewar *et al.*, 1985). The calculated C2═C3 and C2—C10 bond lengths (1.368 and 1.455 Å, respectively) do confirm the corresponding observed trend. The atomic charges were calculated with the method of the best-fit to the electrostatic potential. This subject has been reviewed by Williams (1991); the validity of its extension to semi-empirical wave functions has been assessed by Ferenczy *et al.* (1990). Some of the resulting net charges are reported here: Cl −0.02, C12 −0.26, C11 −0.22, C2 −0.23, C10 0.53, O1 −0.46, H10 0.00, the values for other H atoms ranging between 0.09 and 0.12 a.u. The molecular dipole moment (4.02 D) is oriented parallel to the C═O vector.

In order to study the most favoured molecular arrangement in a crystal structure and to calculate its packing energy, the program *PROMET* (Gavezzotti, 1991, 1998) was used, starting from the Cartesian coordinates and the atomic charges of the *AM*1-optimized molecule. The search was performed for molecular orientations and translations within the (standard) space group *Cc*, giving rise to a total of 6624 optimized structures. The solution of lowest energy corresponded to a parallel stacking of the molecules, with a packing energy of −113.2 kJ mol⁻¹ and a packing coefficient $C_K = 0.78$ (Kitaigorodski, 1961)[2]. The unit-cell parameters of the model crystal, referred back to the *Ia* space group, resulted in *a* = 7.086, *b* = 19.541, *c* = 7.387 Å, β = 105.21°, *V* = 987.10 Å³. The

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[1] We are grateful to a referee for calling our attention to this point.
[2] As a comparison, in the actual crystal the value of C_K is 0.76, having re-normalized the C—H bond lengths to 1.10 Å.

corresponding crystal coordinates of the oriented and displaced molecule were used for a short least-squares refinement. After four isotropic cycles (*SHELXL*97; Sheldrick, 1997), the $R1$ factor was 0.1212 for all 2289 data.

In the crystal, no remarkably short intermolecular contacts have been found. Considering the couples of molecules facing each other [(i) and (ii), (iii) and (iv); see Fig. 2], the phenyl rings lie on planes $a/2$ away, with an in-plane shift of 1.70 Å along the y axis. This parallel-displaced geometry is similar to that calculated for a low-energy arrangement of the benzene dimer, stabilized by 'π–π' interactions (Hobza *et al.*, 1994; distance between molecular planes, $R = 3.5$ Å; parallel shift $R2 = 1.6$ Å).
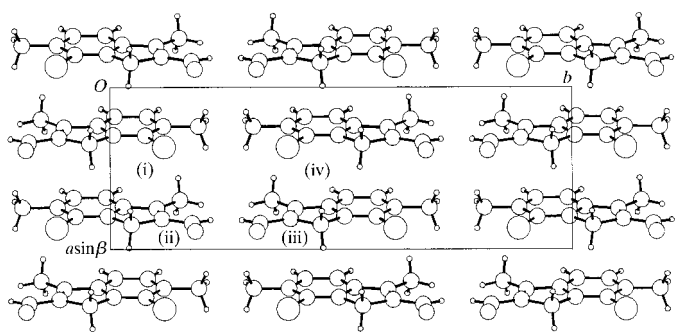

Figure 2
The crystal packing viewed along the z axis (*PLUTO*; Motherwell & Clegg, 1978). Equivalent positions: (i) x, y, z; (ii) $x + \frac{1}{2}, -y, z$; (iii) $x + \frac{1}{2}, y + \frac{1}{2}, z + \frac{1}{2}$; (iv) $x, -y + \frac{1}{2}, z + \frac{1}{2}$.

Experimental

Compound (III) was crystallized from cyclohexane.

Crystal data

$C_{12}H_{11}ClO$	Mo $K\alpha$ radiation
$M_r = 206.7$	Cell parameters from 25
Monoclinic, Ia	reflections
$a = 7.146$ (2) Å	$\theta = 17.3$–$20.7°$
$b = 19.751$ (4) Å	$\mu = 0.341$ mm^{-1}
$c = 7.408$ (1) Å	$T = 294$ (2) K
$\beta = 106.12$ (2)$°$	Trapezoidal irregular prism, light
$V = 1004.5$ (4) Å^3	yellow
$Z = 4.00$	$0.52 \times 0.44 \times 0.28$ mm
$D_x = 1.367$ Mg m^{-3}	

Data collection

Enraf–Nonius CAD-4 diffract-ometer	$R_{int} = 0.004$
	$\theta_{max} = 27.45°$
ω–2θ scans	$h = 0 \rightarrow 9$
Absorption correction: ψ scan	$k = 0 \rightarrow 25$
(North *et al.*, 1968)	$l = -9 \rightarrow 9$
$T_{min} = 0.698$, $T_{max} = 0.909$	2 standard reflections
2300 measured reflections	frequency: 150 min
2289 independent reflections	intensity decay: none
2140 reflections with $F_o > 4\sigma(F_o)$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0723P)^2]$
$R(F) = 0.038$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.095$	$(\Delta/\sigma)_{max} = 0.002$
$S = 1.071$	$\Delta\rho_{max} = 0.38$ e Å^{-3}
2289 reflections	$\Delta\rho_{min} = -0.30$ e Å^{-3}
151 parameters	Absolute structure: Flack (1983)
H atoms treated by a mixture of independent and constrained refinement	Flack parameter = -0.03 (5)

Within the θ range explored, a whole set of $h,k,\pm l$ reflections was measured, along with all their Friedel opposites. The absorption effects were corrected, according to the recommendations by Jones (1984). The final value and s.u. obtained for the Flack (1983) parameter assure that a polar dispersion error (Ueki *et al.*, 1966; Cruickshank & McDonald, 1967) has been avoided. The methyl H atoms were located by means of circular difference syntheses and refined as idealized rigid groups; for each methyl group, a general U_{iso} was also refined. All other H atoms were determined from difference syntheses and refined isotropically without constraints. The bond distance C12—H comes from the *AFIX*137 instruction of *SHELXL*97 (Sheldrick, 1997) for idealised methyl groups.

Data collection and cell refinement: *CAD*-4 *Software* (Enraf–Nonius, 1989); data reduction: *CADABS* (local software); program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976) and *PLUTO* (Motherwell & Clegg, 1978); software used to prepare material for publication: *PARST* (Nardelli, 1983, 1995) and *PARSTCIF* (Nardelli, 1991).

Table 1
Selected geometric parameters (Å, °).

Cl—C7	1.738 (2)	C2—C3	1.354 (2)
O1—C10	1.214 (2)	C2—C10	1.454 (3)
C1—C2—C10	122.5 (1)	C7—C6—C12	122.1 (2)
C3—C2—C10	125.9 (2)	Cl—C7—C6	119.8 (1)
C2—C3—C11	129.3 (2)	O1—C10—C2	123.2 (2)
C1—C2—C10—O1	2.4 (3)		

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