

by the alternance of the torsion angles given in Table 2(c). The shortest contact distance C(2)···O(20) is 3.115 (3) Å and governs the packing by dimer associations of molecules shown in Fig. 3.

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Structure of Methyl 4-Methoxy-2,6-dimethylbenzoate

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Abstract. C₁₁H₁₄O₃, $M_r = 194.23$, m.p. 329–330 K, monoclinic, $P2_1/c$, $a = 13.455$ (5), $b = 11.692$ (2), $c = 6.851$ (3) Å, $\beta = 102.48$ (3)°, $V = 1052.3$ (6) Å³, $Z = 4$, $D_x = 1.226$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu = 0.083$ mm⁻¹, $F(000) = 416$, $T = 293$ K, final $R = 0.050$ for 1407 independent reflections with $F > 2\sigma(F)$. The methoxycarbonyl group is rotated by 64° with respect to the benzene-ring plane, a finding which is relevant to a recent ¹³C NMR study [Dell'Erba, Sancassan, Novi, Petrillo, Mugnoli, Spinelli, Consiglio & Gatti (1988). *J. Org. Chem.* 53, 3564–3568]. Even with this rotation, the O atoms of the methoxycarbonyl group have close contacts with the *ortho*-C atoms.

Introduction. A recent ¹³C NMR study (Dell'Erba *et al.*, 1988) has shown that the effect of 4-*X* substituents on the carbonyl-C-atom chemical shift in methyl 4-*X*-benzoates and in methyl 2,6-dimethyl-4-*X*-benzoates is very similar, in spite of an expected steric inhibition to conjugation between the COOMe group and the aromatic ring in the latter series of compounds. To rationalize the observed spectroscopic behaviour, definite structural information on the relevant benzoates seemed necessary; as a first step, the crystal structure of the title compound has been determined.

Experimental. The compound (Kuhn & Corwin, 1948) was crystallized by slow evaporation from a diethyl ether solution. A crystal ground to a sphere ($r = 0.18$ mm) was sealed in a thin glass capillary and used to collect data on a Nonius CAD-4 diffractometer with graphite-monochromated Mo $K\alpha$ radiation, ω/θ scan mode, scan width 1.5°, scan speed 1–10° min⁻¹, θ range 2.5–27.5°; unit cell from 25 reflections, $16 < \theta < 19^\circ$, least-squares refinement; max. $(\sin\theta)/\lambda = 0.65$ Å⁻¹; 2415 unique reflections collected with $h = 17$ to 17, $k = 0$ to 15, $l = 0$ to 8; two check reflections monitored every one hour to test the crystal stability, and three to test the crystal orientation; no absorption correction applied ($\mu r = 0.015$); $P2_1/c$ from systematic absences; 1407 reflections with $F > 2\sigma(F)$ considered observed. Crystal-structure solution and refinement with *SHELX76* (Sheldrick, 1976); E map calculated with 405 largest E values ($E \geq 1.2$); full-matrix anisotropic least squares on F for 14 non-H atoms; H atoms located on difference maps and included in structure-factor calculations with an isotropic temperature factor equal to U_{eq} of the bonded C atom; 127 parameters refined minimizing $\sum w(\Delta F)^2$ with weights $w = [\sigma^2(F) + 0.009F^2]^{-1}$; $R = 0.050$, $wR = 0.068$ for 1407 observed reflections, $S = 0.882$, $(\Delta/\sigma)_{\text{max}} = 0.003$,

Table 1. Heavy-atom positional parameters ($\times 10^4$) and equivalent isotropic thermal parameters ($\text{\AA}^2 \times 10^4$)
$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	U_{eq}
C(1)	2688 (2)	5252 (2)	278 (4)	428 (8)
C(2)	2287 (2)	4825 (2)	-1653 (4)	451 (8)
C(3)	1322 (2)	5149 (2)	-2610 (4)	475 (8)
C(4)	743 (2)	5872 (2)	-1678 (4)	456 (8)
C(5)	1138 (2)	6281 (2)	229 (4)	462 (8)
C(6)	2123 (2)	5985 (2)	1211 (4)	457 (8)
C(7)	3749 (2)	4939 (2)	1347 (4)	472 (8)
C(8)	2536 (2)	6484 (3)	3238 (5)	697 (12)
C(9)	2893 (2)	4046 (3)	-2690 (5)	616 (11)
C(10)	-859 (2)	6798 (3)	-1858 (5)	617 (11)
C(11)	4839 (3)	3444 (3)	2763 (6)	753 (12)
O(1)	4437 (1)	5595 (2)	1821 (4)	698 (9)
O(2)	3834 (1)	3825 (2)	1761 (3)	642 (8)
O(3)	-198 (1)	6141 (2)	-2782 (3)	578 (7)

Table 2. Selected bond distances (\AA) and angles ($^\circ$)

C(1)–C(7)	1.502 (3)	C(2)–C(9)	1.499 (4)
C(7)–O(1)	1.192 (3)	C(6)–C(8)	1.499 (4)
C(7)–O(2)	1.333 (3)	C(4)–O(3)	1.363 (3)
O(2)–C(11)	1.448 (4)	O(3)–C(10)	1.423 (4)
C(2)–C(1)–C(7)	120.2 (2)	C(3)–C(2)–C(9)	119.7 (2)
C(6)–C(1)–C(7)	118.9 (2)	C(1)–C(6)–C(8)	122.4 (2)
C(1)–C(7)–O(1)	125.2 (2)	C(5)–C(6)–C(8)	118.3 (2)
C(1)–C(7)–O(2)	111.8 (2)	C(3)–C(4)–O(3)	115.4 (2)
O(1)–C(7)–O(2)	123.0 (3)	C(5)–C(4)–O(3)	124.4 (2)
C(7)–O(2)–C(11)	115.5 (2)	C(4)–O(3)–C(10)	118.2 (2)
C(1)–C(2)–C(9)	121.6 (2)		

$\Delta\rho_{\max}$ 0.20, $\Delta\rho_{\min}$ -0.23 e \AA^{-3} . The final atomic coordinates are given in Table 1 and selected bond distances and angles in Table 2. Most of the geometry calculations were performed with the program *PARST* (Nardelli, 1983). Scattering factors were taken from *SHELX76*. The atom-numbering scheme is shown in Fig. 1; the drawing was made using *ORTEP* (Johnson, 1965).*

Discussion. The geometry of the substituents is quite normal. Bond lengths and bond angles in the methoxy-carbonyl moiety are in very good agreement with the typical geometry rationalized by Borthwick (1980) for carboxylic groups. In particular, the bond angle opposite to the double bond is remarkably smaller than 120° . For the benzene ring and the ester group the distance of the least-squares plane from the plane-defining atoms is within 0.009 (3) \AA and 0.016 (4) \AA , respectively. With reference to the plane of the benzene ring, the dihedral angle for the methoxy-group plane and for the ester-group least-squares plane is 6.0 (2)

* Lists of structure factors, H-atom coordinates, anisotropic thermal parameters, bond lengths, bond angles and least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51163 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

and 64.2 (1) $^\circ$, respectively. This last figure deserves some comment, being one of the highest values found so far for the rotation angle of an alkoxy-carbonyl group in a benzoate derivative: the steric hindrance exerted by the two methyl groups in the *ortho* positions causes a striking rotation of the methoxycarbonyl group to a synclinal (Klyne & Prelog, 1960) conformation. To compare this result with the geometry of other alkyl benzoates, a literature search was run with the Cambridge Structural Database (Allen, Bellard, Brice, Cartwright, Doubleday, Higgs, Hummelink, Hummelink-Peters, Kennard, Motherwell, Rodgers & Watson, 1979), accessed through Servizio Italiano di Diffusione Dati Cristallografici del CNR. The 41 values found for the rotation angle of the COOR group in 26 structures of 2,6-unsubstituted alkylbenzoates range from 0.3 to 21.0° , with an average value of 5.3 (7) $^\circ$.* The six values found in four 2-chlorobenzoates range from 16.6 to 36.0° , with an average value of 28 (3) $^\circ$; for ethyl 2,4-dichloro-5-hydroxy-6-methylbenzoate (Gillespie, Murray-Rust, Murray-Rust & Porter, 1981), a rotation angle as high as 83.6 (1) $^\circ$ has been found. (Two 2-methyl-6-hydroxy derivatives have not been considered in this screening because of the presence of intramolecular hydrogen bonds.)

In the present compound the internal strain is relieved both by the rotation of the COOMe group and by a (slight) deformation of the C(1)–C(2)–C(9) and C(1)–C(6)–C(8) bond angles, with respect to the nominal value of 120° . Nevertheless, the 1...5 intramolecular distances C(8)...O(1) and C(9)...O(2) [3.105 (4) and 3.050 (4) \AA , respectively] do correspond to rather short contacts, if compared with the pertinent sum of van der Waals radii, 3.40 \AA (Pauling, 1960). This residual hindering suggests that the COOMe rotation angle should exhibit quite a large value also in the isolated molecule and in weakly

* The figure in parentheses for these average values refers to the e.s.d. of a weighted mean, $\{[\sum w_i(x_i - \bar{x})^2]/(n-1)\sum w_i\}^{1/2}$, with $w_i = 1/\sigma_i^2$.

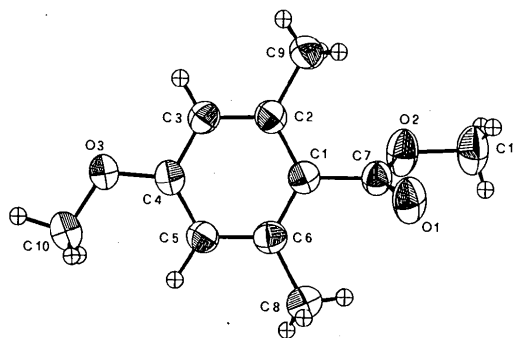


Fig. 1. Thermal ellipsoids of $C_{11}H_{14}O_3$, at the 0.40 probability level. H atoms, treated as isotropic, are on an arbitrary scale.

interacting solvents.* Accordingly, the similar NMR behaviour of the carbonyl-C-atom chemical shifts of methyl 4-*X*- or 2,6-dimethyl-4-*X*-benzoates must be given a rationale which leaves only a minor conjugation effect between the COOMe group and the aromatic ring even in the 2,6-unsubstituted compounds Dell'Erba *et al.*, 1988).

The internal strain seems scarcely to affect the C(1)–C(7) bond distance, whose length [1.502 (3) Å] can be compared with the 41 corresponding bond distances for the 26 aforementioned 2,6-unsubstituted alkylbenzoates [average 1.487 (2) Å], with the six values reported for the four 2-chloro derivatives [average 1.496 (1) Å], and finally with the value found in the 2-chloro-6-methyl derivative [1.506 (3) Å] (Gillespie *et al.*, 1981). The increase in the hindrance and in the rotation angle of the methoxycarbonyl group seems thus to be accompanied by a small increase in the C(aromatic)–C(ester) bond length; the title compound is sited correctly in this sequence.

Intermolecular distances are in the normal range. There are only few contacts appreciably shorter than the sum of the van der Waals radii (Pauling, 1960):

* This finding could be compared with results obtained through molecular-mechanics calculations (MM2), indicating a torsion angle of 54° for methyl 2,6-dimethylbenzoate (Baumstark, Balakrishnan, Dotrong, McCloskey, Oakley & Boykin, 1987).

C(9)··C(10) ($-x, -\frac{1}{2}+y, -\frac{1}{2}-z$) 3.759 (4) Å;
C(10)··C(10) ($x, \frac{3}{2}-y, -\frac{1}{2}+z$) 3.799 (5) Å.

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The Structure of an Alkaloid, Picrinine, from *Alstonia scholaris*

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Abstract. 2,5-Epoxy-1,2-dihydroakuammilan-17-oic acid, methyl ester, C₂₀H₂₂N₂O₃, orthorhombic, *P*2₁2₁2₁, *a* = 7.065 (2), *b* = 8.117 (1), *c* = 28.834 (3) Å, *V* = 1653.53 Å³, *Z* = 4, *D_m* = 1.37, *D_x* = 1.36 g cm⁻³, *M_r* = 338.40, *μ* = 7.037 cm⁻¹, *F*(000) = 720, λ(Cu Kα) = 1.54184 Å. The structure was solved by direct methods and refined by least squares to *R* = 0.045 for 1555 independent reflections. Picrinine is a naturally

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