hydrogen bonding found in the tryptophan–oxalic acid adduct (Bakke & Mostad, 1980). The benzene rings of each acid in (1) are stacked in the *c* cell direction. The protonated amino group on 4-ABA forms possible hydrogen bonds to a water molecule $N(4B)\cdots Ow$ (2.74 Å, $x - 1 + y$, z) and both deprotonated carboxylic acid oxygens [$N(4B)\cdots O(11A)$ 2.71 Å, x, $-y$, $1 - z$; $N(4B)\cdots O(12A)$ 2.69 Å, $1 - x$, y, $1\frac{1}{2} - z$], while the water molecules hydrogen bond with each other [$Ow\cdots Ow'$ 2.68 Å, $1 - x$, y, $1\frac{1}{2} - z$], and with carboxylic oxygens [$Ow\cdots O(12B)$ 2.91 Å, x, $1 - y$, $\frac{1}{2} + z$].

Structure (2) is a 1:1 TNBA and 3-HP adduct, with the carboxylic acid proton of TNBA delocalized on the pyridine nitrogen of 3-HP. As for (1), the molecules are planar, except for the carboxylic acid group of the acid [comparative torsion angle −72.9 (3)°]. Hydrogen bonding exists between the carboxylic acid group and the pyridine nitrogen [$O(11A)\cdots N(1B)$ 2.68 Å, x, y, z]. No significant interactions exist between the hydroxy group and the acid. One set of *o*-nitro groups forms a dimerized pair across the centre of symmetry. The benzene rings of each compound are stacked in the *b* cell dimension. Extensive hydrogen bonding and zwitterion formation in both adducts may be the reason for the stability of the TNBA molecules towards decarboxylation.

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Structure of Methyl 4-Chloro-*N*-(2-tolyl)benzimidate

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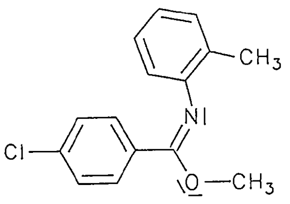
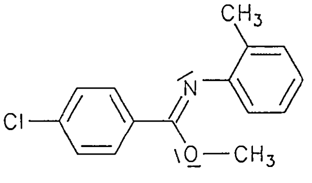
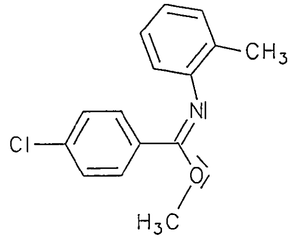
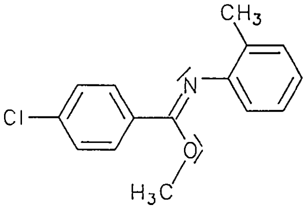
Abstract. $C_{15}H_{14}ClNO$, $M_r = 259.74$, monoclinic, $P2_1/c$, $a = 11.078$ (3), $b = 13.076$ (5), $c = 9.828$ (3) Å, $\beta = 111.71$ (1)°, $V = 1322.7$ (8) Å^3, $Z = 4$, $D_x = 1.304$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 2.73$ cm^{-1}, $F(000) = 544$, $T = 300$ K, final $R = 0.063$ for 1497 unique reflections with $F < 2\sigma(F)$. The conformation corresponds to that of the unsubstituted compound. The two phenyl rings make an angle of 73.3 (1)°.

Introduction. Four stereoisomers of *N*-substituted imidates may exist. They are characterized as *ZsZ*, *ZsE*, *EsZ* or *EsE*. Lumbroso & Bertin (1970) reported the structure *EsZ* based on dipole measurements for imidates without a substituent on the N atom.


a_1 (*EsZ*)


b_1 (*ZsZ*)


a_2 (*EsE*)


b_2 (*ZsE*)

We have synthesized methyl 4-chloro-*N*-(2-tolyl)benzimidate by the reaction of the substituted nitrogen imidate with the primary ammonium hydrochloride (Schmidt, 1914) in order to check if a substituent on the N atom will change the conformation.

Experimental. Prismatic yellow cystals were obtained by evaporation of diethyl ether solution. A small crystal with dimensions 0.15 × 0.15 × 0.25 mm was used for X-ray measurements. The final cell parameters were determined from 36 reflections in the range $25.2 < 2\theta < 36.8°$. A total of 2806 reflections up to 45° in 2θ were measured on a Stoe Stadi-4 four-circle diffractometer using graphite-monochromated Mo $K\alpha$ radiation (h $-11\rightarrow 11$, k $0\rightarrow 14$, l $-11\rightarrow 0$), $\sin\theta/\lambda = 0.54$ Å^{-1}, with $2\theta/\omega = 1/1$ learnt-profile scanning mode. 1738 unique reflections ($R_{\rm int} = 0.022$), 1497 with $F > 2\sigma(F)$ used for structure refinement. Three standard reflections (112, $\bar{2}21$, $02\bar{1}$) were measured every 3 h. We observed that the crystal vanished slowly during the experiment and a decrease of intensity of about 30% was noted at the end of the data collection. The intensities were corrected for Lorentz–polarization effects and an empirical absorption correction with $T_{\rm min} = 0.821$ and $T_{\rm max} = 0.994$ was also applied. At the end of the refinement an isotropic extinction correction with a coefficient $g = 1.37 \times 10^{-2}$ was applied. The structure was solved with *SHELXS*86 (Sheldrick, 1986) and refined by least squares on F with *SHELX*76 (Sheldrick, 1976). Final $R = 0.063$, $wR = 0.049$ and $S = 2.0$; 170 parameters were refined. The weighting scheme was $2.14/\sigma^2(F)$ and $(\Delta/\sigma)_{\rm max}$ was less than 0.8 in the last cycle of refinement. All H atoms were found in the Fourier map but they were located by geometrical calculations (C—H = 1.08 Å) with fixed isotropic thermal parameters (0.05 Å^2) for those belonging to the phenyl rings and 0.075 Å^2 for those of the methyl groups. In the final difference Fourier map $(\Delta\rho)_{\rm min}$ and $(\Delta\rho)_{\rm max}$ were between -0.25 and 0.27 e Å^{-3}. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). Calculations were performed on VAX 8530 and IBM 3090 computers.

Table 1. *Atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$U_{\rm eq} = \frac{1}{3}$ trace **U**.

	x	y	z	$U_{\rm eq}$
Cl(1)	−0.0083 (1)	−0.1398 (1)	0.1214 (1)	0.080 (1)
C(1)	0.0720 (4)	−0.1001 (4)	0.3023 (4)	0.057 (2)
C(2)	0.0916 (4)	0.0009 (3)	0.3336 (4)	0.057 (2)
C(3)	0.1540 (4)	0.0314 (3)	0.4777 (4)	0.051 (2)
C(4)	0.1954 (4)	−0.0413 (3)	0.5888 (4)	0.048 (2)
C(5)	0.1737 (4)	−0.1441 (3)	0.5540 (4)	0.055 (2)
C(6)	0.1128 (4)	−0.1744 (3)	0.4107 (4)	0.059 (2)
C(7)	0.2579 (4)	−0.0086 (3)	0.7446 (4)	0.051 (2)
O(1)	0.2159 (3)	−0.0686 (2)	0.8325 (3)	0.057 (1)
C(8)	0.2793 (5)	−0.0503 (4)	0.9883 (4)	0.070 (2)
N(1)	0.3375 (3)	0.0624 (3)	0.8008 (3)	0.053 (2)
C(9)	0.4005 (4)	0.1168 (3)	0.7210 (4)	0.048 (2)
C(10)	0.4896 (4)	0.0663 (3)	0.6760 (4)	0.056 (2)
C(11)	0.5639 (4)	0.1199 (4)	0.6144 (5)	0.066 (2)
C(12)	0.5497 (4)	0.2238 (4)	0.5966 (5)	0.075 (3)
C(13)	0.4602 (4)	0.2743 (4)	0.6384 (5)	0.066 (2)
C(14)	0.3837 (4)	0.2226 (3)	0.7016 (4)	0.053 (2)
C(15)	0.2847 (4)	0.2776 (4)	0.7463 (5)	0.073 (2)

Discussion. The atomic coordinates are listed in Table 1 and bond lengths and angles in Table 2.* A projection of the molecule and the packing of the molecules in the cell are shown in Figs. 1 and 2 respectively. The conformation of the molecule is that of the *EsZ* isomer. Owing to electrostatic repulsion between the lone pair and the N atom, the a_2 isomer is expected to be less stable than the a_1 isomer. On the other hand, steric repulsion between the methyl and the phenyl in b_1 and the two phenyls in a_1 should stabilize b_2 as compared with b_1 and a_1. We also noticed that the configuration a_1 or *EsZ* adopted by the molecule does not allow the phenyl rings to be coplanar. Our X-ray data indicate an angle of 73.3 (1)° between the planes. All these observations led to the conclusion that the title compound crystallizes in the a_1 or *EsZ* conformation. The *p*-chlorophenyl is almost in the plane of the imidate group C=N (the dihedral angle of the two planes is 141°) and is conjugated to the imidate function, as

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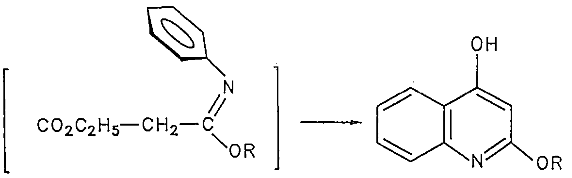
* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54505 (12 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond distances* (Å) *and bond angles* (°) *with e.s.d.'s in parentheses*

C(1)—C(1)	1.747 (4)	O(1)—C(8)	1.450 (4)
C(1)—C(2)	1.355 (6)	N(1)—C(9)	1.419 (5)
C(1)—C(6)	1.388 (6)	C(9)—C(10)	1.389 (5)
C(2)—C(3)	1.385 (5)	C(9)—C(14)	1.399 (5)
C(3)—C(4)	1.391 (5)	C(10)—C(11)	1.380 (5)
C(4)—C(7)	1.491 (5)	C(11)—C(12)	1.373 (6)
C(4)—C(5)	1.385 (5)	C(12)—C(13)	1.375 (6)
C(5)—C(6)	1.376 (5)	C(13)—C(14)	1.396 (5)
C(7)—O(1)	1.369 (4)	C(14)—C(15)	1.506 (5)
C(7)—N(1)	1.258 (5)		

Cl(1)—C(1)—C(2)	119.9 (3)	C(7)—O(1)—C(8)	115.3 (3)
Cl(1)—C(1)—C(6)	118.2 (3)	C(7)—N(1)—C(9)	122.4 (3)
C(2)—C(1)—C(6)	121.9 (4)	N(1)—C(9)—C(10)	119.3 (4)
C(1)—C(2)—C(3)	119.3 (4)	N(1)—C(9)—C(14)	120.3 (4)
C(2)—C(3)—C(4)	120.0 (4)	C(10)—C(9)—C(14)	120.1 (4)
C(3)—C(4)—C(5)	119.5 (4)	C(9)—C(10)—C(11)	120.5 (5)
C(3)—C(4)—C(7)	120.2 (4)	C(10)—C(11)—C(12)	120.0 (4)
C(5)—C(4)—C(7)	120.3 (4)	C(11)—C(12)—C(13)	119.9 (4)
C(4)—C(5)—C(6)	120.4 (4)	C(12)—C(13)—C(14)	121.6 (4)
C(1)—C(6)—C(5)	118.7 (4)	C(9)—C(14)—C(13)	117.9 (4)
C(4)—C(7)—O(1)	110.2 (4)	C(9)—C(14)—C(15)	120.4 (4)
C(4)—C(7)—N(1)	130.3 (4)	C(13)—C(14)—C(15)	121.7 (4)
O(1)—C(7)—N(1)	119.5 (4)		

suggested by the length of the C(4)—C(7) bond [1.491 (5) Å] which is closer to 1.47 Å, the typical length of a double bond, than to the 1.54 Å of a single bond. On the other hand, C(9)—N(1) [1.419 (5) Å] should have single-bond character and can be explained by the fact that the *o*-tolyl is not in the imidate-group plane. C(7)—O(1) [1.369 (4) Å] also has pronounced double-bond character and is close to 1.36 Å which is typical of the C—O bond in esters. This leads to a planar N(1)—C(7)—O(1)—C(8) sequence. The observation of the a_1 or *EsZ* structure (Fig. 2) for the title compound may explain the reactivity of the *N*-phenyl derivatives (Harris, 1976) which have C—*R* or CO_2R as reactive groups. These compounds are difficult to synthesize and immediately undergo cyclization.



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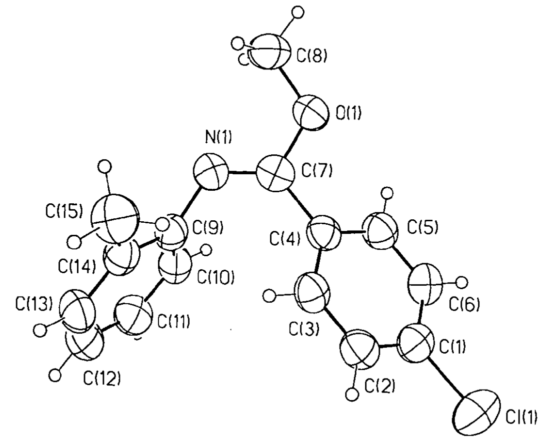

Fig. 1. General view (*SHELXTL-Plus* graphic; Sheldrick, 1987) of the molecule, showing the atom-numbering scheme. Anisotropic ellipsoids represent 50% probability boundaries. H atoms are represented as spheres of arbitrary radii.

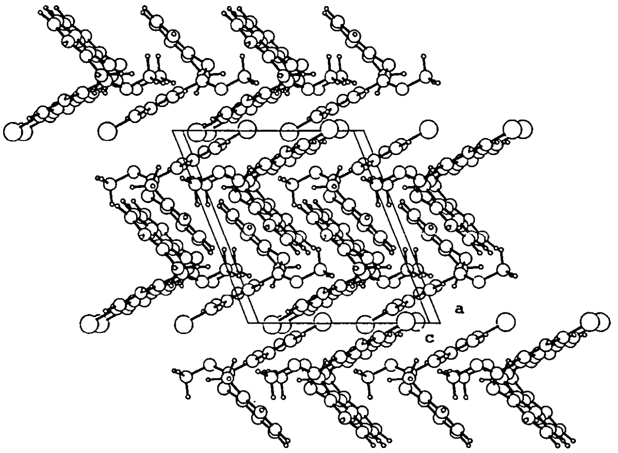

Fig. 2. Packing of the molecules in the unit cell.

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