957 reflections
111 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0608P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = 0.01 (15)

Table 1. *Selected geometric parameters (Å, °)*

S1—C5	1.708 (5)	N3—C4	1.397 (5)
S1—C2	1.749 (4)	C4—C5	1.354 (5)
N3—C2	1.299 (5)	C4—C6	1.473 (5)
C5—S1—C2	88.7 (2)		

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N—H*B*···N3ⁱ	0.86	2.18	2.990 (5)	156.0

Symmetry code: (i) $y - 1, 1 - x, \frac{1}{4} + z$.

Since (I) crystallizes in a polar space group, polar-axis restraints were applied according to the method of Flack & Schwarzenbach (1988), and the absolute structure of the crystal was established according to Flack (1983).

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *PROFIT* (Strel'tsov & Zavodnik, 1989). Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997). Software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DA1045). Services for accessing these data are described at the back of the journal.

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A functionalized dimethyl maleate (maleic acid dimethyl ester)

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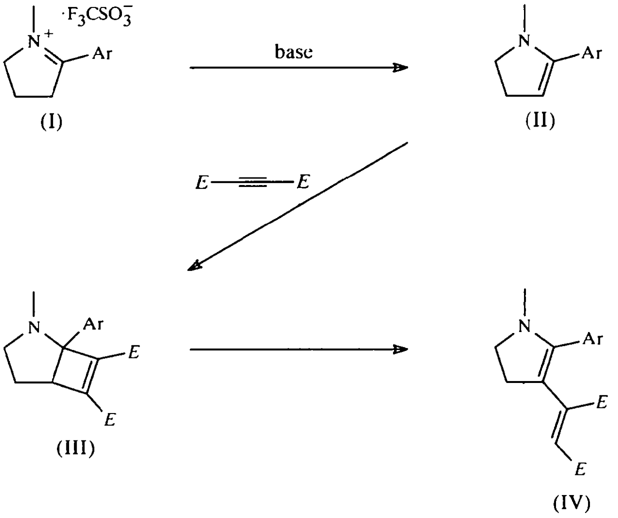
Abstract

In the title compound, dimethyl (*Z*)-2-[1-methyl-2-(*p*-tolyl)-4,5-dihydro-1*H*-pyrrol-3-yl]but-2-enedioate ($C_{18}H_{21}NO_4$), the central butadienyl segment is in a *trans* conformation. The terminal enone segment is in-plane with the butadienyl segment and participates in the conjugated system, whereas the lateral methoxycarbonyl group and the phenyl ring are orientated perpendicular to the butadienyl segment.

Comment

Specifically substituted 1-methyl-5-aryl-3,4-dihydro-2*H*-pyrrolium salts, (I), react with dimethyl acetylene dicarboxylate under basic conditions. The functionalization of the 4-position can be explained as a result of consecutive transformations. Deprotonation of (I) by ethyl diisopropylamine at the 4-position generates the reactive enamine, (II), followed by a [2+2] cycloaddition with dimethyl acetylene dicarboxylate. The resulting bicyclic intermediate, (III), isomerizes in a cycloreversion to the title compound, (IV). These consecutive reac-



Ar = 4-CH$_3$-C$_6$H$_4$
E = CO-OCH$_3$

tions are of general interest concerning the reactivity of cyclic 1-azaallyl systems and annellated cyclobutenyl ring systems (Livingstone, 1973; Zellmer *et al.*, 1997; Chinchilla *et al.*, 1994; Hickmott, 1994; Jung, 1991). Compounds (I), (III) and (IV) have been characterized by ^{1}H NMR, ^{13}C NMR and mass spectroscopy. Single crystal X-ray diffraction of the title compound, (IV), was carried out to confirm the spectroscopic results, to determine the configuration of the exocyclic C═C double bond and to characterize the conformation in the solid phase.

The C═C double bond connected with the methoxycarbonyl groups has the *Z* configuration. In the solid state, the C11—C12—C3—C4 butadienyl segment prefers a *trans* conformation and the terminal enone segment adopts a *syn* conformation with respect to the linking single bond (C4—C5).

The torsion angles [N1—C11—C12—C3 178.4 (3), C12—C3—C4—C5 178.3 (3) and C3—C4—C5—O3 2.8 (6)°], the shortened single bonds (N1—C11, C12—C3 and C4—C5) and the elongated double bonds (C11—C12 and C3—C4) are indications of the planarity and conjugation of the dienamine segment with the terminal methoxycarbonyl group. The lone pair at the donor atom, N1, is delocalized onto the conjugated system with the carbonyl-O atom as acceptor. The phenyl ring and the lateral methoxycarbonyl group are out-of-plane, with C22—C21—C11—C12 −89.6 (5) and O2—C2—C3—C4 91.1 (4)°, and cannot participate in conjugation. Therefore, the C2═O2 double bond is slightly shorter and the C2—C3 and C2—O1 single bonds longer than the corresponding bonds of the terminal methyl ester group (C5—O3, C4—C5 and C5—O4).

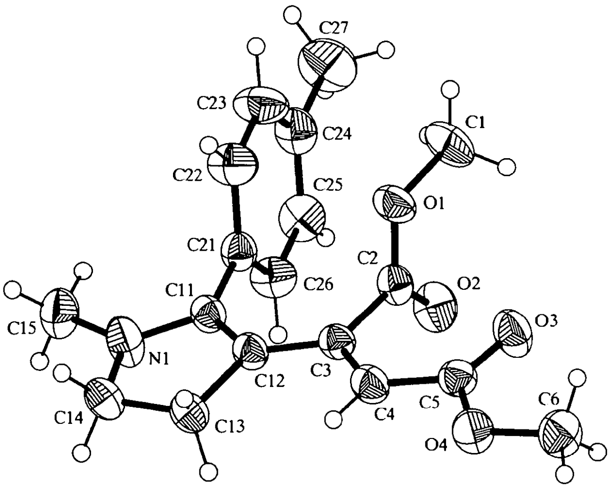


Fig. 1. *DIAMOND* (Brandenburg, 1998) plot of the title compound, showing the labelling of all non-H atoms. Displacement ellipsoids are drawn at the 40% probability level and H atoms are shown as spheres of arbitrary radii.

The five-membered heterocyclic ring is nearly planar (r.m.s. deviation 0.027 Å), because of the double bond character of N1—C11 and as a consequence of the planarity of the segment N1—C11—C12—C13.

Crystal cohesion is possibly due to C—H···O hydrogen bonds. The shortest intermolecular distances (O—H < 2.7, C···O < 3.5 Å) are C25—H25···O2, C6—H6*B*···O3, C14—H14*A*···O3 and C14—H14*A*···O4 (Table 2).

Experimental

2-Methyl-1-(4-methylphenyl)-2-azabicyclo[3.2.0]hept-6-ene-6,7-dicarboxylic acid dimethyl ester, (III), was prepared by the reaction of 1-methyl-5-(4-methylphenyl)-3,4-dihydro-2*H*-pyrrolium trifluoromethanesulfonate, (I), with dimethyl acetylene dicarboxylate in the presence of ethyl diisopropylamine in dry dichloromethane at room temperature (reaction time 5 min). The oily reaction product, (III), can be isolated from the organic phase and purified by column chromatography (silica gel/diethyl ether). After a reaction time of 3 d only the title compound, (IV), was present as a yellow solid (m.p. 452 K). The isomerization could be accelerated by addition of silica gel and cyclohexane to (III). Recrystallization from ethanol afforded single crystals suitable for X-ray diffraction data collection.

Crystal data

$C_{18}H_{21}NO_4$
$M_r = 315.36$
Triclinic
$P\bar{1}$
$a = 6.914\,(3)$ Å
$b = 9.480\,(7)$ Å
$c = 13.644\,(4)$ Å
$\alpha = 102.90\,(4)°$
$\beta = 90.30\,(3)°$
$\gamma = 106.85\,(5)°$
$V = 832.0\,(8)$ Å^3
$Z = 2$
$D_x = 1.259$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 12–17°$
$\mu = 0.089$ mm^{-1}
$T = 293\,(2)$ K
Needle
0.30 × 0.15 × 0.13 mm
Yellow

Data collection

Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
3050 measured reflections
2916 independent reflections
1409 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.034$
$\theta_{\rm max} = 24.97°$
$h = -8 \rightarrow 8$
$k = -11 \rightarrow 10$
$l = 0 \rightarrow 16$
3 standard reflections every 100 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.054$
$wR(F^2) = 0.142$

$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.191$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.185$ e Å^{-3}

$S = 1.090$
2916 reflections
213 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0522P)^2 + 0.3195P]$
where $P = (F_o^2 + 2F_c^2)/3$

Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.017 (4)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

C2—O2	1.193 (4)	C4—C5	1.438 (5)
C2—O1	1.332 (4)	C5—O3	1.203 (4)
C2—C3	1.502 (5)	C5—O4	1.349 (4)
C3—C4	1.352 (4)	C11—N1	1.357 (4)
C3—C12	1.424 (4)	C11—C12	1.365 (5)
O2—C2—C3—C4	91.1 (4)	N1—C11—C12—C3	178.4 (3)
C12—C3—C4—C5	178.3 (3)	C21—C11—C12—C13	−179.0 (3)
C3—C4—C5—O3	2.8 (6)	C12—C11—C21—C22	−89.6 (5)

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C25—H25···O2^{i}	0.930	2.528	3.404 (5)	157.1
C6—H6*B*···O3^{ii}	0.960	2.680	3.477 (5)	140.8
C14—H14*A*···O3^{iii}	0.970	2.589	3.468 (5)	150.8
C14—H14*A*···O4^{iv}	0.970	2.603	3.393 (4)	138.7

Symmetry codes: (i) $-x, -y, -z$; (ii) $-x, 1-y, 1-z$; (iii) $x, y-1, z$; (iv) $1-x, -y, 1-z$.

The structure was solved by direct methods (Sheldrick, 1985) and successive difference Fourier syntheses. Refinement applied full-matrix least-squares methods (Sheldrick, 1997). All H atoms were found in difference Fourier syntheses, but the final refinement was carried out using a riding model, with displacement parameters for the H atoms constrained to 1.5 times (CH_3 groups) or 1.2 times (secondary CH_2 groups and conjugated CH groups) the displacement parameters of the respective C atoms.

Data collection: *CAD*-4-*PC* (Enraf–Nonius 1994). Cell refinement: *CAD*-4-*PC*. Data reduction: *CAD*-4-*PC*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *DIAMOND* (Brandenburg, 1998).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1327). Services for accessing these data are described at the back of the journal.

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4-Chloro-*N*-(*p*-fluorobenzyl)-2-nitroaniline

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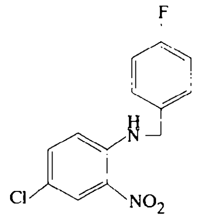
Abstract

The title molecule, $C_{13}H_{10}ClFN_2O_2$, is bent almost orthogonally at the methylene, with a dihedral angle of 91.60 (6)° between the two benzene rings. The *o*-nitro and amino groups are almost coplanar with the benzene ring due to intramolecular hydrogen bonds.

Comment

The nitro-aromatic amines crystallize as planar molecules joined by intermolecular hydrogen bonds between the amine group and the O atoms of the nitro group (Dhaneshwar *et al.*, 1978; Prasad *et al.*, 1982). However, in the absence of any specific electrostatic interaction, the *o*-nitro group is twisted out of the plane of the aryl ring (Punte *et al.*, 1989; Punte & Rivero, 1991; Low *et al.*, 1996). In order to investigate the effect of the *p*-fluorobenzyl group on the planarity of the *o*-nitro group and its attached aryl ring, the structure determination of the title compound, (I), was undertaken.



(I)

The present compound is a precursor which is used for the selective synthesis for *N*′-(*p*-fluorobenzyl)-5-chloro-1*H*-benzimidazole derivatives (Göker *et al.*, 1995). Its structure was also assigned by NMR.