We thank the Natural Sciences and Engineering Research Council of Canada for financial support.

Details of synthesis and photolysis, stereo molecular and packing diagrams, and lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71715 (47 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CD1057]

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N-[2-(2-Formylphenyl)ethyl]-2-nitroaniline

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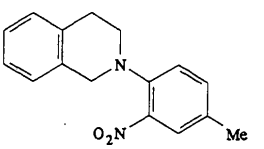
Abstract

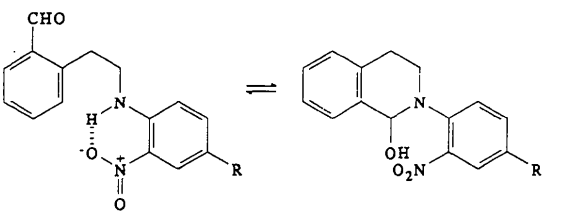
The structure of the molecule, $C_{15}H_{14}N_2O_3$, consists of essentially planar and parallel nitroaniline and benzaldehyde fragments [dihedral angle 2.7 (4)°], linked through an ethylene bridge between the aniline N atom and an *ortho* C atom of the benzaldehyde fragment. The aldehyde and nitro substituents are essentially coplanar with their respective rings. Intramolecular hydrogen bonding occurs between the amino and nitro groups; there are no significant intermolecular interactions.

Comment

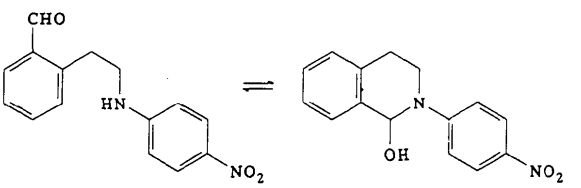
The reaction between *N*-(4-methyl-2-nitrophenyl)-1,2,3,4-tetrahydroisoquinoline (1) with oxygen yielded *N*-[2-(2-formylphenyl)ethyl]-4-methyl-2-nitroaniline (2) (Shawcross & Stanforth, 1990). In principle, this product aldehyde may exist as the hemi-aminal (3), but proton NMR spectroscopy firmly established the aldehyde structure (2). We anticipated that the aldehyde would be preferred to the hemi-aminal because of intramolecular hydrogen bonding between the amine group and the adjacent nitro group. Consequently, the title compound (4) has been prepared (Hedley & Stanforth, 1992) in order to establish by X-ray crystallography both the structural form and the presence of intramolecular hydrogen bonding. In a previous report (Streith & Fizet, 1977), NMR spectroscopy indicated that the aldehyde (4) and not the corresponding hemi-aminal (5) was present. It is noteworthy that (7), which has also been prepared, exists in the hemi-aminal and not in the aldehyde form (6), presumably because intramolecular hydrogen bonding is not possible in this case (Stanforth, 1993).



(1)



(2) R = Me (3) R = Me
(4) R = H (5) R = H



(6) (7)

The structure determination shows clearly that the aldehyde form is present and that intramolecular hydrogen bonding occurs between the amine and nitro groups. The O19···N11 distance is 2.578 (8), O19···H11 is 1.920 (9) Å and the O19···H11—N11 angle is 129.4 (3)°, giving a six-membered ring involving the hydrogen bond.

An ethylene bridge links the two ring systems of the molecule; the bridge connects an *ortho* C atom of the benzaldehyde fragment to the amino N atom of the nitroaniline fragment. The two rings are essentially planar (r.m.s. deviation 0.008 Å for both) and parallel [dihedral

angle 2.7 (4)°], the ethylene bridge forming a step between them. The substituents of each ring (nitro, amino NH and aldehyde) are essentially coplanar with their respective rings, so that all the atoms of the molecule, with the exception of the H atoms of the ethylene bridge, lie virtually in two parallel planes. There are no significant intermolecular interactions.

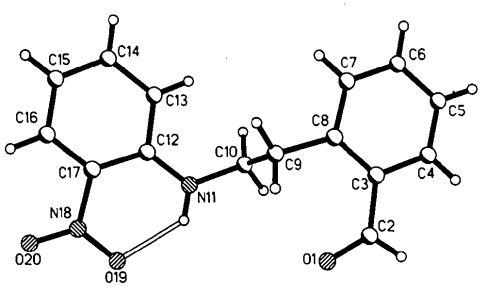


Fig. 1. A view of the molecule of (4) showing the intramolecular hydrogen bonding

Experimental

Crystal data

$C_{15}H_{14}N_2O_3$
M_r = 270.28
Monoclinic
$P2_1/n$
a = 7.413 (3) Å
b = 23.750 (10) Å
c = 7.933 (3) Å
β = 110.92 (4)°
V = 1304.6 (9) Å^3
Z = 4
D_x = 1.376 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 24 reflections
θ = 11.05–12.34°
μ = 0.097 mm^{-1}
T = 240.0 (10) K
0.48 × 0.24 × 0.12 mm
Colourless
Crystal source: cooling from an ethanol solution

Data collection

Stoe Siemens diffractometer
ω/θ scans with on-line profile fitting (Clegg, 1981)
Absorption correction: none
1703 measured reflections
1703 independent reflections
700 observed reflections [$I > 2\sigma(I)$]

θ_{max} = 22.52°
$h = -7 \rightarrow 7$
$k = 0 \rightarrow 25$
$l = 0 \rightarrow 8$
3 standard reflections
frequency: 60 min
intensity variation: none

Refinement

Refinement on F^2
$R(F)$ = 0.0637
$wR(F^2)$ = 0.2068
S = 1.0333
1703 reflections
181 parameters
Calculated weights $w = 1/[\sigma^2(F_o^2) + (0.0738P)^2 + 1.3224P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max}$ <0.0005
$\Delta\rho_{max}$ = 0.350 e Å^{-3}
$\Delta\rho_{min}$ = −0.221 e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8, 6.1.1.4)

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

$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
O1	0.0594 (8)	0.2856 (2)	1.0711 (7)	0.070 (4)
C2	0.1376 (11)	0.2780 (3)	0.9634 (10)	0.054 (6)
C3	0.0910 (8)	0.3050 (2)	0.7864 (8)	0.031 (4)
C4	0.1869 (9)	0.2844 (3)	0.6747 (9)	0.038 (4)
C5	0.1524 (10)	0.3052 (3)	0.5071 (10)	0.046 (5)
C6	0.0194 (10)	0.3475 (3)	0.4434 (9)	0.046 (5)
C7	−0.0735 (9)	0.3688 (3)	0.5493 (9)	0.042 (4)
C8	−0.0406 (8)	0.3492 (3)	0.7232 (8)	0.030 (4)
C9	−0.1484 (9)	0.3762 (3)	0.8323 (9)	0.043 (4)
C10	−0.3331 (10)	0.3437 (3)	0.8124 (11)	0.055 (5)
N11	−0.4325 (8)	0.3667 (2)	0.9305 (8)	0.054 (4)
C12	−0.5555 (8)	0.4105 (3)	0.8833 (8)	0.031 (4)
C13	−0.5972 (10)	0.4366 (3)	0.7130 (9)	0.053 (5)
C14	−0.7289 (10)	0.4832 (3)	0.6594 (10)	0.048 (5)
C15	−0.8165 (11)	0.5024 (3)	0.7732 (12)	0.060 (5)
C16	−0.7764 (11)	0.4792 (3)	0.9400 (13)	0.065 (5)
C17	−0.6493 (9)	0.4341 (3)	0.9910 (9)	0.045 (4)
N18	−0.6218 (10)	0.4107 (3)	1.1711 (9)	0.061 (5)
O19	−0.5103 (9)	0.3696 (3)	1.2222 (7)	0.083 (4)
O20	−0.7042 (10)	0.4322 (3)	1.2610 (8)	0.103 (6)

Table 2. *Selected geometric parameters* (Å, °)

O1—C2	1.205 (8)	N11—C12	1.344 (8)
C2—C3	1.467 (9)	C12—C17	1.398 (9)
C3—C8	1.399 (8)	C12—C13	1.417 (9)
C3—C4	1.407 (8)	C13—C14	1.436 (9)
C4—C5	1.354 (9)	C14—C15	1.365 (9)
C5—C6	1.372 (9)	C15—C16	1.364 (11)
C6—C7	1.360 (9)	C16—C17	1.387 (10)
C7—C8	1.392 (8)	C17—N18	1.477 (9)
C8—C9	1.514 (8)	N18—O20	1.205 (7)
C9—C10	1.530 (8)	N18—O19	1.250 (8)
C10—N11	1.487 (8)		
O1—C2—C3	127.3 (7)	N11—C12—C17	125.2 (7)
C8—C3—C4	118.6 (6)	N11—C12—C13	120.0 (6)
C8—C3—C2	124.5 (6)	C17—C12—C13	114.8 (6)
C4—C3—C2	116.9 (6)	C12—C13—C14	120.9 (7)
C5—C4—C3	122.1 (6)	C15—C14—C13	119.7 (7)
C4—C5—C6	119.2 (7)	C16—C15—C14	121.1 (8)
C7—C6—C5	120.0 (7)	C15—C16—C17	119.0 (8)
C6—C7—C8	122.7 (6)	C16—C17—C12	124.5 (7)
C7—C8—C3	117.3 (6)	C16—C17—N18	114.6 (7)
C7—C8—C9	118.9 (6)	C12—C17—N18	120.9 (7)
C3—C8—C9	123.7 (6)	O20—N18—O19	123.7 (8)
C8—C9—C10	111.3 (5)	O20—N18—C17	119.3 (8)
N11—C10—C9	112.1 (5)	O19—N18—C17	117.0 (6)
C12—N11—C10	123.2 (6)		

H atoms were inserted in idealized positions using *HFIX* from *SHELXL93* (Sheldrick, 1993). Refinement was on F^2 for all reflections except those flagged for possible systematic errors. Data collection: *DIF4* (Stoe & Cie, 1988). Cell refinement: *DIF4*. Data reduction: local programs. Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93*. Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXL93* and local programs.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71726 (8 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HU1068]

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6-Amino-5-[(*E*)-1,2-bis(methoxycarbonyl)-vinyl]-2-methoxy-3-methylpyrimidin-4(3*H*)-one

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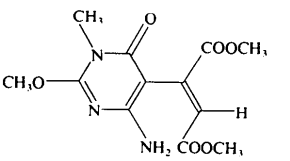
Abstract

The title compound, dimethyl 2-(6-amino-2-methoxy-3-methyl-4-oxo-3,4-dihydro-5-pyrimidyl)butenedioate, $C_{12}H_{15}N_3O_6$, contains a pyrimidine ring and a bis(methoxycarbonyl)vinyl moiety, the planes of which are inclined at an angle of 66.4 (1)°. The molecular dimensions are normal and show that the bonding in the pyrimidine ring is delocalized. The molecules are linked *via* intermolecular N—H···O=C hydrogen bonds [N···O 2.904 (3) and 3.219 (3) Å] to form a three-dimensional network.

Comment

5-Vinylpyrimidine derivatives have been studied because of interest in their pharmacologic activity (De Clerq & Walker, 1984). 6-Amino-5-[(*E*)-1,2-bis(methoxycarbonyl)vinyl]pyrimidine systems are intermediates in the synthesis of the pyrido[2,3-*d*]pyrimidine ring system, which is a part of many biologically active compounds including antitumour (Grivsky, Lee, Sigel, Duch & Nichol, 1980), antibacterial (Suzuki, 1980) and anticonvulsive (Kretzchmar, 1980) agents.

The 6-amino-5-[(*E*)-1,2-bis(methoxycarbonyl)vinyl]-2-methoxy-3-methylpyrimidin-4(3*H*)-one molecule (I) contains two main structural features: a pyrimidine ring and a bis(methoxycarbonyl)vinyl moiety (Fig. 1). A



(I)

search of the April 1993 release of the Cambridge Structural Database (Allen, Kennard & Taylor, 1983) revealed no similar molecules. A comparison with compounds containing pyrimidine, methoxycarbonyl and vinyl moieties showed that all the bond lengths and angles of the molecule lie within the expected ranges. The pyrimidine ring is planar to within two standard deviations and the bond lengths are consistent with substantial delocalization in the pyrimidine ring. In the bis(methoxycarbonyl)vinyl moiety, the C522, C51, C521 and C531 atoms are planar to within one standard deviation. The relative orientation of the pyrimidine ring

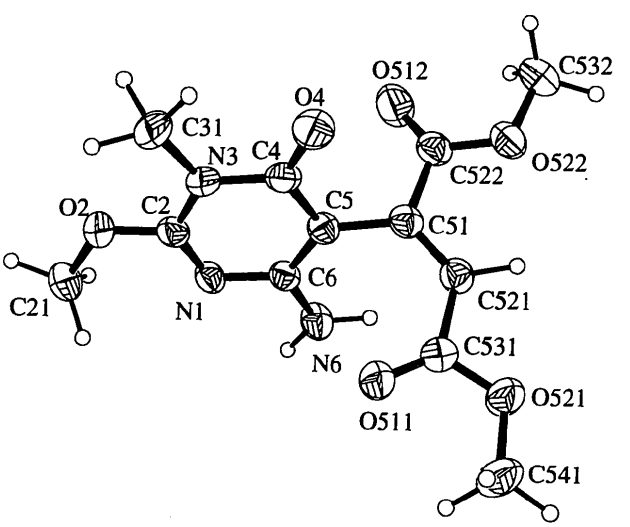


Fig. 1. An *ORTEPII* (Johnson, 1976) view of the molecule showing the numbering scheme. Non-H atoms are shown with displacement ellipsoids drawn at the 50% probability level. For clarity, the H atoms are drawn as small spheres of arbitrary size.