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3-(4-Nitroanilino)-2-cyclopenten-1-one

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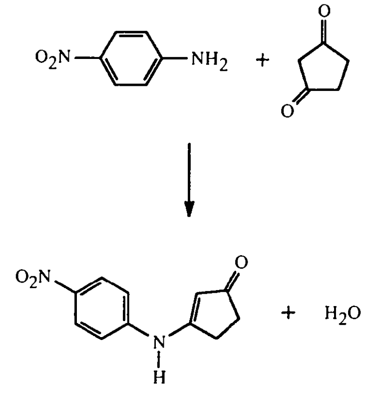
Abstract

The title compound, $C_{11}H_{10}N_2O_3$, is composed of a nitroanilino moiety and a cyclic α,β-unsaturated ketone moiety. The cyclic α,β-unsaturated ketone moiety forms a planar conformation, whereas the nitro group in the nitroanilino moiety is slightly out from the phenyl ring least-squares plane. The least-squares planes of the phenyl ring and the α,β-unsaturated ketone group are almost coplanar with respect to one another. The shortened C7—N1 and C8—C9 bond lengths suggest that the amino group is conjugated with the α,β-unsaturated ketone group. Intermolecular hydrogen bonds between the carbonyl O atom and the amino group link the molecules into infinite chains [N—H 0.87 (2), H···O^i 1.95 (2), N···O^i 2.812 (4) Å and N—H···O^i 169 (2)°; symmetry code: (i) $1-x, \frac{1}{2}+y, \frac{1}{2}-z$].

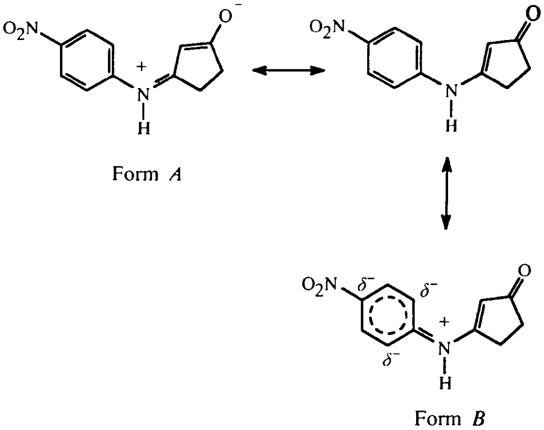
Comment

Nitroanilines and nitroaniline derivatives have long been of interest in non-linear optical (NLO) materials because of their inherently large molecular polarizability (β) (Williams, 1984). Hydrogen-bonding interactions have been found to be important in the non-centrosymmetric crystal packing of nitroanilines (Panunto, Urbanczyk-Lipkowska, Johnson & Etter, 1987) and other organic compounds (Zyss, Nicoud & Coquillay, 1984). In our continuing research on designing NLO materials using hydrogen-bonding interactions (Etter & Frankenbach, 1989; Etter & Huang, 1992), the title compound, (I), was synthesized from the reaction of *p*-nitroaniline with 1,3-cyclopentanedione.



(I)

X-ray analysis shows that the title compound is composed of a nitroanilino moiety and a cyclic α,β-unsaturated ketone moiety. The cyclic ketone moiety forms a planar conformation. The nitro group of the nitroanilino moiety is at an angle of 9.8 (4)° to the phenyl ring least-squares planes. The least-squares planes of the phenyl ring and the α,β-unsaturated ketone group are almost coplanar with respect to one another, with a dihedral angle of 3.2 (4)° between them. The C7—N1 bond distance of 1.358 (2) Å is slightly shorter than that of C1—N1 [1.389 (2) Å], suggesting that the lone pair of electrons in the amino group is more likely delocalized into the cyclic α,β-unsaturated ketone group than into the nitrophenyl group; thus, the resonance form *A* is more favorable than the resonance form *B*, shown below.



Form *A*

Form *B*

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Because of the resonance effect, the C8—C9 bond distance of 1.432 (3) Å is much shorter than a normal sp^2-sp^2 C—C single bond (1.48 Å; Allen *et al.*, 1987), C9—C10 [1.504 (3) Å], C7—C11 [1.503 (2) Å] or C10—C11 [1.518 (3) Å]. The resonance effect is also reflected by the longer C—N bond distance of both C1—N1 [1.389 (2) Å] and C4—N2 [1.468 (3) Å] in the title compound than the corresponding C—N bond distances [1.371 Å and 1.460 Å, respectively] in *p*-nitroaniline (Trueblood, Goldish & Donohue, 1961). The molecules form infinite chains *via* intermolecular hydrogen bonds between the carbonyl O atom and the amino group [N—H 0.87 (2), H···O^i 1.95 (2), N···O^i 2.812 (4) Å and N—H···O^i 169 (2)°; symmetry code: (i) $1-x, \frac{1}{2}+y, \frac{1}{2}-z$]. This type of hydrogen-bond pattern is designated $C^1_1(6)$ [or C(6)] according to Etter notation (Etter, MacDonald & Bernstein, 1990; Bernstein, Davis, Shimoni & Chang, 1995). [This notation indicates the chain nature (*C*) of the hydrogen-bonded aggregates, the one proton donor and one proton acceptor (as subscript and superscript) involved in the bonding and the chain length (in parentheses)].

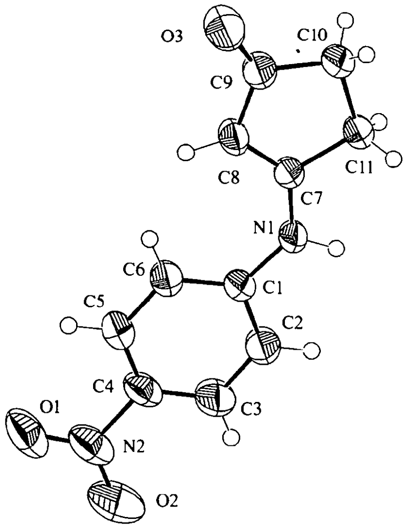

Fig. 1. The molecular structure of the title compound showing displacement ellipsoids at 50% probability.

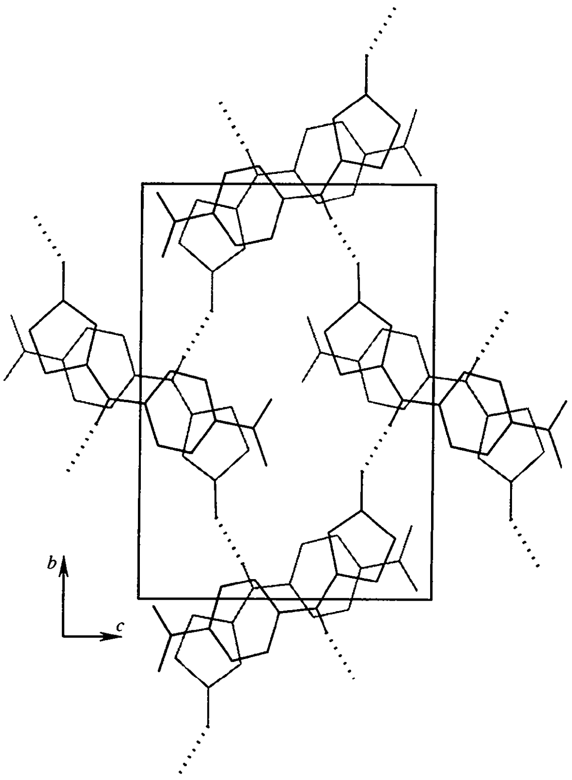

Fig. 2. A packing diagram of the title compound viewed down the *a* axis. Hydrogen bonds are indicated by dashed lines.

Experimental

The title compound was prepared directly in the solid state by heating *p*-nitroaniline and 1,3-cyclopentanedione in a 1:1 molar ratio at 383 K (Huang, Britton, Etter & Byrn, 1996). Single crystals were obtained from methanol using slow evaporation methods.

Crystal data

$C_{11}H_{10}N_2O_3$
$M_r = 218.21$
Monoclinic
$P2_1/c$
$a = 8.2725\ (7)$ Å
$b = 13.273\ (1)$ Å
$c = 9.5548\ (7)$ Å
$\beta = 97.510\ (6)°$
$V = 1040.1\ (3)$ Å^3
$Z = 4$
$D_x = 1.393$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.54184$ Å
Cell parameters from 25 reflections
$\theta = 40$–$53°$
$\mu = 0.824$ mm^{-1}
$T = 295$ K
Needle
0.25 × 0.17 × 0.13 mm
Yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
Profile data from ω–2θ scans
Absorption correction: none
2269 measured reflections
2123 independent reflections
1434 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.026$
$\theta_{\rm max} = 74.33°$
$h = -10 \rightarrow 0$
$k = -16 \rightarrow 0$
$l = -11 \rightarrow 11$
3 standard reflections frequency: 83 min intensity decay: <1%

Refinement

Refinement on F^2
$R(F) = 0.045$
$wR(F^2) = 0.117$
$S = 1.068$
2123 reflections
150 parameters
H-atom parameters not refined, except H1

$(\Delta/\sigma)_{\rm max} = 0.01$
$\Delta\rho_{\rm max} = 0.19$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.16$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0055 (7)

$w = 1/[\sigma^2(F_o^2) + (0.0612P)^2 + 0.2648P]$ where $P = (F_o^2 + 2F_c^2)/3$

Scattering factors from *International Tables for Crystallography* (Vol. C)

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

O1—N2	1.215 (3)	C3—C4	1.366 (3)
O2—N2	1.222 (3)	C4—C5	1.365 (3)
O3—C9	1.225 (2)	C5—C6	1.382 (3)
N1—C7	1.358 (2)	C7—C8	1.347 (3)
N1—C1	1.389 (2)	C7—C11	1.503 (2)
N2—C4	1.468 (3)	C8—C9	1.432 (3)
C1—C6	1.384 (3)	C9—C10	1.504 (3)
C1—C2	1.394 (3)	C10—C11	1.518 (3)
C2—C3	1.372 (3)	N1—H1	0.87 (2)
C7—N1—C1	131.6 (2)	C8—C7—N1	132.2 (2)
O1—N2—O2	123.7 (2)	C7—C8—C9	109.6 (2)
C6—C1—N1	125.4 (2)	O3—C9—C8	126.5 (2)
N1—C1—C2	116.3 (2)		

The structure was solved using the structure solution program *SHELXS*86 (Sheldrick, 1985). The remaining atoms were located in succeeding difference Fourier syntheses. All H atoms except H1, for which parameters were refined isotropically, were included in the refinement.

Data collection: *CAD*-4 *Operations Manual* (Enraf–Nonius, 1977). Cell refinement: *CAD*-4 *Operations Manual.* Data reduction: *MolEN* (Fair, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976) and/or *PLUTON* (Spek, 1991). Software used to prepare material for publication: *ORTEP*II and/or *PLUTON.*

We would like to thank Phillip Fanwick for his assistance with the refinement of this structure. We acknowledge financial support from the Byrn/Zografi joint project for study of the effect of water on the molecular mobility of pharmaceutical solids. In addition, we would like to appreciate Dr Isaac Ghebre-Sellasie (Pharmaceutical Research, Warner–Lambert Company) for his assistance in preparing this paper.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1319). Services for accessing these data are described at the back of the journal.

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4,4′-Dinitro-2,2′-bipyridine

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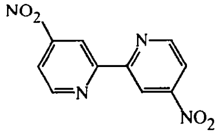
Abstract

The title compound, $C_{10}H_6N_4O_4$, has crystallographic C_i symmetry and is almost planar. Analysis of its crystal packing reveals molecular tapes formed by C—H···O hydrogen bonds.

Comment

The structure determination of the title compound, (I), has been undertaken to check the outcome of the chemical synthesis (Maerker & Case, 1958).



(I)

The title molecule sits on a centre of symmetry. It is almost planar. The NO_2 group is slightly displaced from the best plane through N1—C2—C3—C4—C5—C6 [N2 0.062 (2), O1 0.107 (2) and O2 0.059 (2) Å]. The planes of the two aromatic rings are slightly offset, as indicated by the torsion angle C3—C2—C2′—N1′ of 1.1 (3)°. The small angle C2—N1—C6 of 117.8 (1)° may be explained by the fact that a lone pair at an N atom needs more space than an N—C bonding electron pair (Gillespie & Hargittai, 1991). The C2—C2′ distance is about 0.1 Å longer than the C—C bonds in the ring and has strong single-bond character (Watson, Brammer, Orpen & Taylor, 1992).

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