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3-(3-Nitroanilino)cyclohex-2-en-1-one: an Unexpected Product from the Co-Crystallization of *m*-Nitroaniline with 1,3-Cyclohexanedione

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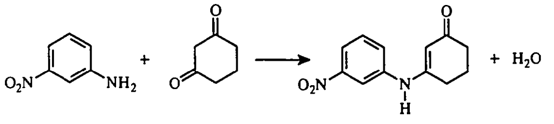
Abstract

The title compound, $C_{12}H_{12}N_2O_3$, is composed of a nitroanilino moiety and a cyclic α,β-unsaturated ketone moiety. The nitro group is oriented *anti* to the carbonyl group and the cyclic ketone ring is in a puckered conformation with C9 as the out-of-plane atom. The shortened C11—N2 and C7—C12 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 0.88 (3), H$\cdots$O$^{\rm i}$ 1.98 (3), N$\cdots$O$^{\rm i}$ 2.858 (3) Å, N—H$\cdots$O$^{\rm i}$ 175 (1)°; symmetry code: (i) $1+x$, y, z].

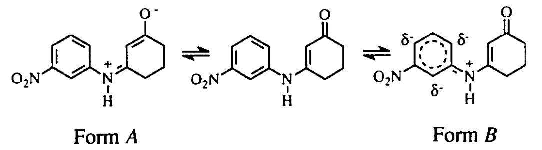
Comment

Hydrogen-bond directed co-crystallization has been demonstrated as a useful way to study the molecular recognition and hydrogen-bond properties of a class of related host molecules (Etter & Baures, 1988; Etter, Urbanczyk-Lipkowska, Zia-Ebrahimi & Panunto, 1990; Etter & Reutzel, 1991). As part of a comprehensive study of the hydrogen-bond properties of nitroanilines (Panunto, Urbanczyk-Lipkowska, Johnson & Etter, 1987; Etter & Huang, 1992), the title compound, (I), was obtained unexpectedly during an attempt to prepare an *m*-nitroaniline/1,3-cyclohexanedione co-crystal. The reaction is believed to proceed by a standard enamine formation in which nucleophilic addition to the carbonyl group of 1,3-cyclohexanedione by the amino group of *m*-nitroaniline is followed by dehydration, as shown in the scheme below.



(I)

The title compound is composed of a nitroanilino moiety and a cyclic α,β-unsaturated ketone moiety. The cyclic ketone ring is in a puckered conformation where C9 is out of the plane of the remaining atoms, a common conformation for cyclohexyl rings containing three adjacent sp^2-hybridized C atoms and three adjacent sp^3-hybridized C atoms (Katrusiak, 1990). The anilino group and the α,β-unsaturated ketone group are not coplanar. The nitro group is oriented *anti* to the carbonyl group and is at an angle of 28.3° to the phenyl ring least-squares plane, and the phenyl ring least-squares plane is at an angle of 32.8° to the α,β-unsaturated ketone least-squares plane to reduce the H atom–H atom repulsion between C5 and C12. The C11—N2 bond distance of 1.366 (3) Å is considerably shorter than that of C4—N2 [1.400 (3) Å], suggesting that the lone pair of electrons in the amino group is more easily 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.



(II)

This is understandable since the nitro group in the *meta* position cannot interact directly with the charge in the ring. Because of the resonance effect, the C7—C12 bond distance of 1.423 (3) Å is much shorter than a normal sp^2–sp^2 C—C single bond [1.48 Å] (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987), C7—C8 [1.503 (4) Å] or C10—C11 [1.499 (3) Å]. The molecules form infinite chains *via* intermolecular hydrogen bonds between the carbonyl O atom and the amino group [N—H 0.88 (3), H$\cdots$O$^{\rm i}$ 1.98 (3), N$\cdots$O$^{\rm i}$ 2.858 (3) Å, N—H$\cdots$O$^{\rm i}$ 175 (1)°; symmetry code: (i) $1+x$, y, z]. This type of hydrogen-bond pattern is designated $C_1^1(6)$ according to Etter notation (Etter, MacDonald & Bernstein, 1990). [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).]

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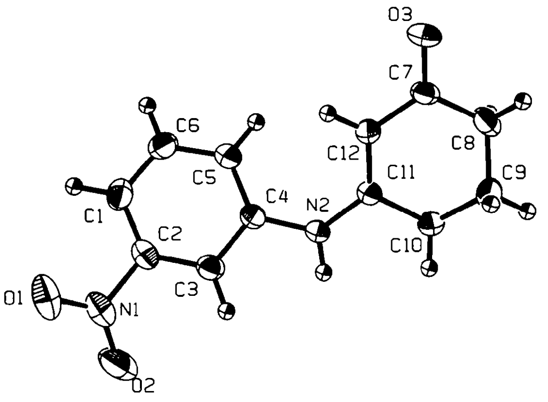

Fig. 1. The molecular structure of the title compound showing displacement ellipsoids at the 50% probability level.

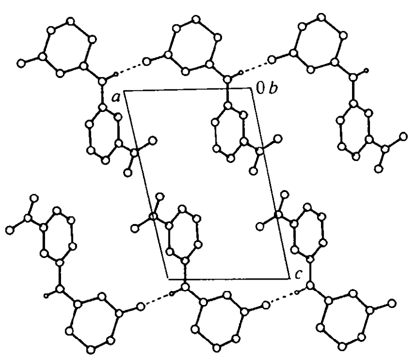

Fig. 2. A packing diagram of the title compound viewed down the *b* axis. Hydrogen bonds are indicated by dashed lines.

Experimental

The title compound was prepared by dissolving *m*-nitroaniline and 1,3-cyclohexanedione in a 1:1 molar ratio in acetonitrile at 323 K for 5 min and allowing the resulting solution to cool gradually to room temperature. Recrystallization was from methanol.

Crystal data

$C_{12}H_{12}N_2O_3$
$M_r = 232.24$
Triclinic
$P\overline{1}$
$a = 7.312$ (3) Å
$b = 8.349$ (4) Å
$c = 10.358$ (2) Å
$\alpha = 98.82$ (3)°
$\beta = 96.98$ (3)°
$\gamma = 114.70$ (4)°
$V = 555$ (1) Å^3
$Z = 2$
$D_x = 1.388$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 23 reflections
$\theta = 10.18–22.95°$
$\mu = 0.095$ mm^{-1}
$T = 297$ K
Prism
0.60 × 0.35 × 0.25 mm
Yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: none
5342 measured reflections
2671 independent reflections
1825 observed reflections [$I > 3\sigma(I)$]

$R_{\text{int}} = 0.025$
$\theta_{\max} = 28°$
$h = 0 \rightarrow 6$
$k = -7 \rightarrow 7$
$l = -9 \rightarrow 9$
3 standard reflections
frequency: 50 min
intensity decay: none

Refinement

Refinement on F
$R = 0.062$
$wR = 0.079$
$S = 2.15$
1825 reflections
158 parameters
$w = 4F^2/\sigma^2(F^2)$

$\Delta\rho_{\max} = 0.37$ e Å^{-3}
$\Delta\rho_{\min} = -0.55$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2A)

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

$$B_{\text{eq}} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
O1	0.8954 (4)	0.3478 (3)	0.5624 (2)	4.91 (8)
O2	1.1504 (3)	0.4954 (3)	0.7307 (2)	5.44 (9)
O3	0.2450 (3)	0.7949 (3)	1.1479 (2)	3.88 (7)
N1	0.9824 (4)	0.4627 (3)	0.6677 (2)	3.68 (8)
N2	0.8581 (3)	0.7853 (3)	1.0473 (2)	2.79 (6)
C1	0.7396 (4)	0.5914 (3)	0.6313 (2)	3.10 (7)
C2	0.8752 (3)	0.5648 (3)	0.7197 (2)	2.76 (7)
C3	0.9171 (3)	0.6283 (3)	0.8565 (2)	2.63 (7)
C4	0.8121 (3)	0.7221 (3)	0.9085 (2)	2.40 (7)
C5	0.6781 (3)	0.7550 (3)	0.8209 (2)	2.82 (7)
C6	0.6431 (4)	0.6902 (4)	0.6847 (2)	3.18 (8)
C7	0.4291 (3)	0.8302 (3)	1.1821 (2)	2.67 (7)
C8	0.5451 (4)	0.9352 (4)	1.3211 (3)	3.82 (9)
C9	0.7158 (4)	0.8884 (4)	1.3678 (2)	3.50 (8)
C10	0.8561 (3)	0.9140 (3)	1.2697 (2)	2.67 (7)
C11	0.7398 (3)	0.8197 (3)	1.1293 (2)	2.30 (6)
C12	0.5359 (3)	0.7759 (3)	1.0922 (2)	2.71 (7)

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

C7—O3	1.243 (3)	C11—C12	1.366 (3)
C4—N2	1.400 (3)	C7—C8	1.503 (4)
C11—N2	1.366 (3)	C8—C9	1.505 (4)
C2—N1	1.467 (3)	C9—C10	1.506 (3)
C7—C12	1.423 (3)	C10—C11	1.499 (3)
O3—C7—C12	121.8 (2)	C7—C12—C11	121.5 (2)
C4—N2—C11	129.5 (2)	N2—C11—C10	113.3 (2)
O1—N1—O2	123.9 (2)	N2—C11—C12	125.5 (2)

All H atoms except H2, for which all parameters were refined, were included in the structure-factor calculations placed in idealized positions (C—H 0.95 Å) with $B_{\text{iso}} = 1.2B_{\text{eq}}$ of the atoms to which they are bonded. The rather large value of R may be a result of the poor quality of the crystal.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1985). Program(s) used to solve structure: *MITHRIL* (Gilmore, 1984) and *DIRDIF* (Beurskens, 1984). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BK1107). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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2,3,5,6-Tetrakis(trifluoromethyl)-terephthaloyl Difluoride

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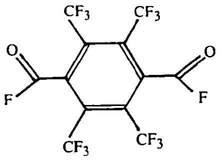
Abstract

2,3,5,6-Tetrakis(trifluoromethyl)terephthaloyl difluoride, $C_{12}F_{14}O_2$, crystallizes in space group *Fddd*, which requires the molecule to have 222 symmetry. This is achieved by disordering the F, O and C atoms of the acyl halide group. The bulky CF_3 groups cause a slight distortion from planarity of the six-membered ring and they are forced out of coplanarity with the ring. The plane of the —(C=O)—F group is rotated 62° from the plane of the phenyl ring.

Comment

The title compound, (I), was obtained while carrying out the exploratory oxidative coupling of *cis*–$F_2C{=}CFC(CF_3){=}C(CF_3)Cu$. The title compound exhibits two peaks in the ^{19}F NMR spectrum ($CFCl_3$, acetone-d_6) at +55.4 p.p.m. (*s*) [—C(=O)—F] and −54.0 p.p.m. (*s*) (CF_3) in a ratio of 1:6. The acyl halide group appears at 1858 cm^{-1} in the IR spectrum and HRMS analysis shows a molecular ion at 441.9687 corresponding to $C_{12}F_{14}O_2$.



(I)

The bond distances and angles in the title molecule have values close to those expected for this type of compound. The observed deviations from idealized bond

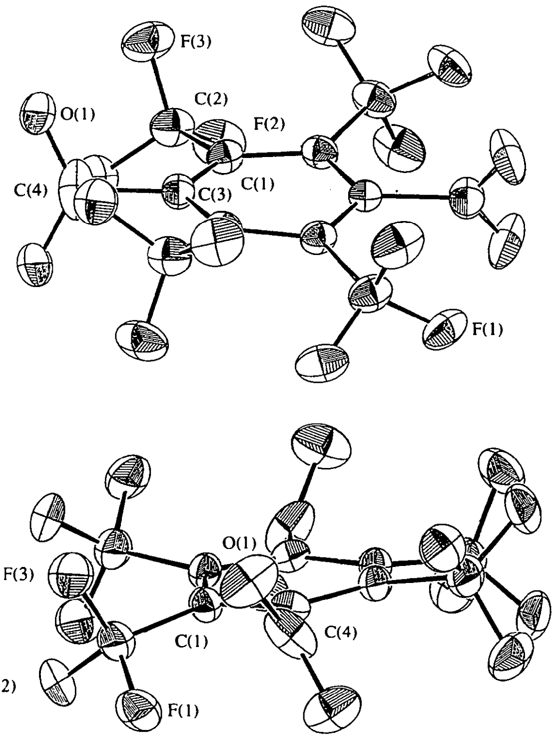


Fig. 1. Two views of the title compound. The upper view shows the —C—C(=O)—F plane lying horizontal, while the lower view is almost end-on along the —C—C(=O)—F plane showing the orientation of these groups relative to the plane of the phenyl ring. Displacement ellipsoids are plotted at the 25% probability level.

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