Compound (3)

Crystal data

$C_{32}H_{46}O_6$
$M_r = 526.7$
Monoclinic
$P2_1/n$
$a = 9.241$ (2) Å
$b = 11.402$ (3) Å
$c = 14.877$ (2) Å
$\beta = 91.13°$
$V = 1567.2$ (5) Å^3
$Z = 2$
$D_x = 1.116$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 25 reflections
$\theta = 11-18°$
$\mu = 0.08$ mm^{-1}
$T = 293$ K
Plate
0.40 × 0.40 × 0.10 mm
Clear

Data collection

Siemens $R3m/V$ diffractometer
$\theta/2\theta$ scans
Absorption correction: none
2421 measured reflections
2061 independent reflections
1335 observed reflections [$F_o > 3\sigma(F_o)$]

$R_{\text{int}} = 0.019$
$\theta_{\text{max}} = 22.5°$
$h = 0 \rightarrow 9$
$k = 0 \rightarrow 12$
$l = -15 \rightarrow 16$
3 standard reflections monitored every 97 reflections intensity variation: 4.4%

Refinement

Refinement on F
$R = 0.064$
$wR = 0.065$
$S = 1.66$
1335 reflections
194 parameters
$w = 1/[\sigma^2(|F_o|) + 0.00023(F_o)^2]$
$\Delta\rho_{\text{max}} = 0.18$ e Å^{-3}
$\Delta\rho_{\text{min}} = -0.20$ e Å^{-3}

Extinction correction: $F^* = F[1 + (0.002\chi \times F^2/\sin 2\theta)]^{-1/4}$
Extinction coefficient: $\chi = 0.0029$ (5)
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Data were collected using a variable scan speed, with the ω-scan rate a function of count rate, and were corrected for Lorentz and polarization effects. The structure solution, by direct methods, and the full-matrix least-squares refinement used programs in *SHELXTL-Plus* (Sheldrick 1991). Atomic coordinates and anisotropic displacement parameters were refined for all non-H atoms. H atoms were included using a riding model (coordinate shifts of C applied to attached H atoms, C—H distance set to 0.96 Å, H angles idealized), and U_{iso}(H) were set to fixed values. The disordered *tert*-butyl groups in (3) were refined with bond distance and bond angle constraints, and the lower occupancy *tert*-butyl C atoms were refined isotropically. The occupancy ratio was 9:1.

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Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71758 (38 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HH1075]

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3-[5-(3-Nitrophenyl)furfurylidene]-2,4-pentanedione, $C_{16}H_{13}NO_5$

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Abstract

The crystal structure consists of monomeric non-centrosymmetric nearly planar molecules. The shortest intermolecular distance [C(15)···O(2)′

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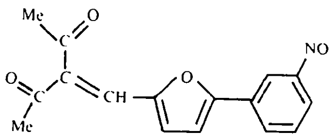
3.211 (6) Å] indicates the presence of a weak hydrogen bond between a phenyl ring and a ketone O atom, H(15)···O(2)′ (2.60 Å). The O(1), C(1), C(2), C(5) ketone fragment, the furfurylidene moiety and the attached nitrophenyl group are almost in the same plane; their conjugation explains the compounds yellow colour.

Comment

Some 2-substituted-5-phenylfuran derivatives obtained by condensation of substituted 5-phenyl-2-furaldehyde with various nitrogen bases have been reported to exhibit an antimicrobial, mainly tuberculostatic, activity. The condensation of 5-(3-nitrophenyl)-2-furaldehyde with the methylene group of 2,4-pentanedione afforded the conjugated title compound, (I). Single crystals were obtained by slow evaporation of solvent from ethyl acetate solution at room temperature. The molecular structure and the atom-numbering scheme are shown in Fig. 1.



(I)

The crystal structure of the title compound consists of discrete molecules. The pentanedione fragment O(1), C(1), C(2), C(5), the furan ring and the nitrophenyl group are almost in the same plane. The angle between the least-squares planes of the phenyl ring and the planar furan ring is 3.5 (2)°. The near coplanarity of these two groups and the short length of the C(10)—C(11) bond [1.421 (6) Å] suggests that the π conjugation extends between the groups. The phenyl ring is aproximately planar [maximum deviation from the least-squares plane is 0.013 (5) Å for C(14)] with an average C—C bond of 1.373 Å.

The O(1)=C(1) bond length of 1.222 (5) Å is elongated in comparison to the length of the C_{sp^2}=O bond of 1.207 (4) Å in the molecule of acetaldehyde in the vapour phase (Barrow, Long & Millen, 1974). The coplanar arrangement of the nitro substituent gives rise to the shorter non-bonded O(4)···C(12) and O(5)···C(14) distances of 2.665 (6) and 2.698 (6) Å, respectively [the sum of van der Waals radii being 3.22 Å (Bondi, 1966)].

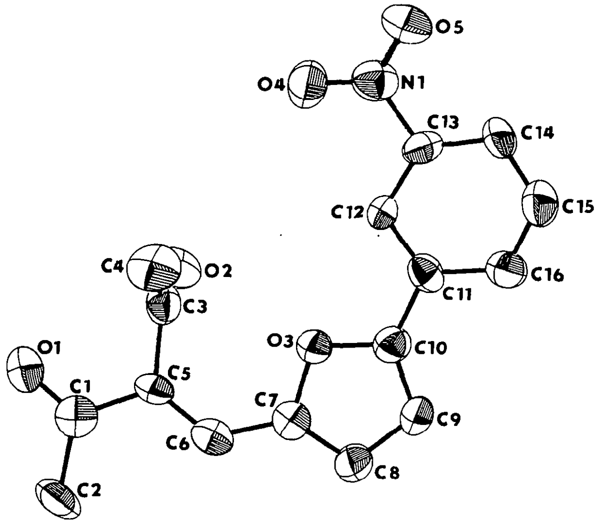


Fig. 1. Perspective view of the title molecule with atom-numbering scheme. Displacement ellipsoids are drawn at the 40% probability level.

Experimental

Crystal data

$C_{16}H_{13}NO_5$
M_r = 299.282
Monoclinic
$P2_1/c$
a = 8.023 (6) Å
b = 10.393 (4) Å
c = 19.092 (8) Å
β = 117.74 (8)°
V = 1409 (2) Å^3
Z = 4
D_x = 1.41 Mg m^{-3}
D_m = 1.39 (3) Mg m^{-3}
D_m measured by flotation in $ZnSO_4$ solution

Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 15 reflections
θ = 4–15°
μ = 0.0992 mm^{-1}
T = 293 K
Prisms
0.2 × 0.2 × 0.1 mm
Yellow
Crystal source: crystallization from CCl_4

Data collection

XP2₁ diffractometer
$\theta/2\theta$ scans
Absorption correction: empirical
T_{min} = 0.675, T_{max} = 0.988
3325 measured reflections
3172 independent reflections
701 observed reflections [$I > 1.96\sigma(I)$]

R_{int} = 0.035
θ_{max} = 27.5°
$h = 0 \rightarrow 10$
$k = 0 \rightarrow 13$
$l = -22 \rightarrow 21$
2 standard reflections frequency: 100 min intensity variation: <5%

Refinement

Refinement on F
R = 0.053
wR = 0.055
S = 0.89
701 reflections
199 parameters
H-atom parameters not refined
Unit weights applied

$(\Delta/\sigma)_{max}$ = 0.1
$\Delta\rho_{max}$ = 0.24 e Å^{-3}
$\Delta\rho_{min}$ = −0.23 e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

$B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	B_{eq}
O(1)	−0.5123 (4)	0.9937 (3)	0.1466 (2)	5.72 (6)
O(2)	−0.0815 (4)	0.8790 (3)	0.2028 (2)	5.54 (6)
O(3)	0.0725 (3)	0.7912 (3)	0.3732 (1)	3.38 (5)
O(4)	0.4914 (4)	1.0823 (3)	0.3432 (2)	6.72 (7)
O(5)	0.7827 (4)	1.0874 (3)	0.4244 (2)	6.54 (7)
N(1)	0.6270 (5)	1.0408 (3)	0.4004 (2)	4.78 (7)
C(1)	−0.4910 (6)	0.9116 (4)	0.1959 (2)	4.00 (8)
C(2)	−0.6560 (5)	0.8585 (5)	0.2011 (3)	5.48 (8)
C(3)	−0.1459 (5)	0.9355 (4)	0.2395 (2)	4.02 (7)
C(4)	−0.0878 (7)	1.0662 (4)	0.2701 (3)	5.65 (9)
C(5)	−0.2992 (5)	0.8727 (4)	0.2518 (2)	3.48 (6)
C(6)	−0.2668 (5)	0.7821 (4)	0.3058 (2)	3.54 (7)
C(7)	−0.0911 (5)	0.7322 (4)	0.3638 (2)	3.56 (7)
C(8)	−0.0446 (6)	0.6351 (4)	0.4157 (2)	4.21 (8)
C(9)	0.1510 (5)	0.6319 (4)	0.4590 (2)	4.42 (7)
C(10)	0.2222 (5)	0.7276 (4)	0.4325 (2)	3.77 (6)
C(11)	0.4037 (5)	0.7772 (4)	0.4518 (2)	3.53 (6)
C(12)	0.4235 (5)	0.8839 (4)	0.4147 (2)	3.17 (6)
C(13)	0.6059 (5)	0.9247 (4)	0.4410 (2)	3.59 (7)
C(14)	0.7644 (5)	0.8708 (5)	0.4984 (2)	4.56 (8)
C(15)	0.7332 (6)	0.7655 (5)	0.5349 (3)	5.04 (9)
C(16)	0.5602 (5)	0.7161 (5)	0.5133 (2)	4.69 (8)

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

O(1)—C(1)	1.222 (5)	N(1)—C(13)	1.486 (6)
O(2)—C(3)	1.199 (6)	C(1)—C(2)	1.480 (7)
O(3)—C(7)	1.383 (5)	C(1)—C(5)	1.463 (5)
O(3)—C(10)	1.376 (4)	C(3)—C(4)	1.468 (5)
O(4)—N(1)	1.207 (4)	C(3)—C(5)	1.504 (7)
O(5)—N(1)	1.213 (5)	C(10)—C(11)	1.421 (6)
C(7)—O(3)—C(10)	107.8 (4)	O(1)—C(1)—C(2)	120.2 (4)
O(4)—N(1)—O(5)	122.4 (4)	C(2)—C(1)—C(5)	121.2 (4)
O(5)—N(1)—C(13)	118.3 (4)	O(2)—C(3)—C(5)	119.0 (4)
O(4)—N(1)—C(13)	119.3 (4)	O(2)—C(3)—C(4)	122.9 (5)

Data reduction was performed with *XP*2_1 software (Pavelčík, 1987). The structure was solved by direct methods using *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). Refinement was by block-diagonal approximation. H atoms were located at calculated positions, their coordinates and displacement parameters were fixed. All remaining calculations were performed with a local version of the *NRC* program system (Ahmed, Hall, Pippy & Huber, 1973) and *PARST* (Nardelli, 1984).

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Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: VS1007). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Synthèses et Structures de Deux Acides 5,6-Dihydro-6-[aryl]-4-{2-[aryl]-éthényl}-2-oxo-2*H*-pyrane-3-carboxylique

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Abstract

The structures of two 5,6-dihydro-2-oxo-2*H*-pyran derivatives with links to an acid, an aryl and an arylethenyl group at C3, C6 and C4 of the heterocycle, respectively, are reported. The benzene rings in (I), 6-(2-methoxyphenyl)-4-[2-(2-methoxyphenyl)ethenyl]-2-oxo-5,6-dihydro-2*H*-pyran-3-carboxylic acid, $C_{22}H_{20}O_6$, and in (II), 6-(4-methoxyphenyl)-4-[2-(4-methoxyphenyl)ethenyl]-2-oxo-5,6-dihydro-2*H*-pyran-3-carboxylic acid, $C_{22}H_{20}O_6$, are substituted at the *ortho* and at the *para* positions, respectively. These compounds are typical of a series of analogues obtained as by-products in some Knoevenagel condensations of α,β ethylenic aldehydes with the dimethyl ester of isopropylidenemalonic acid.

Commentaire

Une synthèse développée par Rebuffat, Giraud & Molho (1978), a permis d'obtenir stéréospécifiquement des acides diéthyléniques de configuration *E,E*. Celle-ci se réalise en une étape par condensation d'un alkylidène malonate de méthyle avec des aldéhydes aromatiques. Dans le cas particulier où l'isopropylidène malonate de méthyle est employé comme malonate éthylénique, on observe, à côté de l'acide ester attendu, la formation

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