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Two Nitro-α-methoxy-*trans*-chalcones

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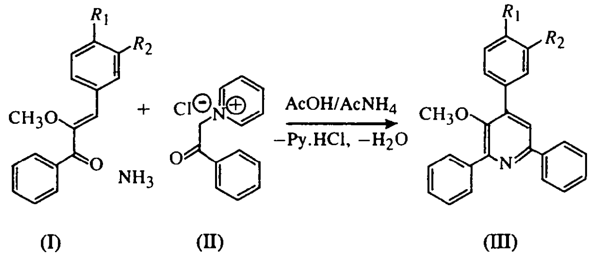
Abstract

The crystal structures of 2-methoxy-3-(3-nitrophenyl)-1-phenylprop-2-en-1-one, $C_{16}H_{13}NO_4$, (Ia), and 2-methoxy-3-(2-nitrophenyl)-1-phenylprop-2-en-1-one, $C_{16}H_{13}NO_4$, (Ib), are reported. These two molecules are constitutional isomers differing in the position of the nitro group attached to one of the phenyl rings. The central double bond has a *trans* configuration in both structures. The conformations of the two molecules are very similar, except that in compound (Ia), the phenyl ring with the nitro substituent is nearly coplanar with the nitro group and the double bond, while in (Ib), there are significant deviations from coplanarity of these moieties.

Comment

The title compounds display different reactivities towards arylpyridines in the ring-closure reaction according to the method of Kröhnke & Zecher (1962), with α-methoxychalcones as educts (Teuber, Schütz & Bader, 1977); while compound (Ia) is reactive, compound (Ib) is rather inert. Constitutional isomeric α-methoxychalcones incorporating other functional groups (except methyl) display the same effect.



(I) (II) (III)

	R_1	R_2
(Ia)/(IIIa)	NO_2	H
(Ib)/(IIIb)	H	NO_2

The present X-ray structure analyses constitute part of our investigation into the reasons for this behaviour. The hypothesis that the configuration of the double bond might be responsible for the different reactivities can now be excluded, since the double bonds in both molecules have a *trans* configuration. While the double bond in compound (Ia) (Fig. 1) is coplanar with the *p*-nitrophenyl ring [C2—C1—C11—C12 0.4 (4)°], a torsion angle of 18.6 (3)° is found in compound (Ib) (Fig. 2). In (Ia), the nitro group is coplanar with the adjacent phenyl ring [O14′—N14—C14—C13 −4.3 (4) and O14″—N14—C14—C15 −5.1 (4)°], but in compound (Ib), dihedral angles of 25.5 (2) and 26.1 (3)° are found for O13′—N13—C13—C14 and O13″—N13—C13—C12, respectively. This different conformational behaviour might be due to crystal-packing effects seeking to minimize repulsive interactions between the nitro groups of different molecules; a rather short intermolecular distance is found in (Ib) [O13′···O13′($2-x$, $-y$, $-z$) 2.803 (3) Å], while in (Ia), the shortest intermolecular contacts of both nitro O atoms to non-H atoms are O14′···C34($x-1$, y, z) 3.454 (5) and

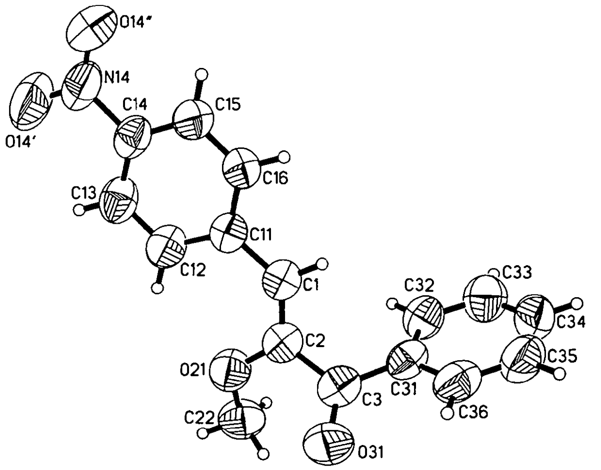


Fig. 1. Perspective view of compound (Ia) with the atom-numbering scheme and displacement ellipsoids at the 50% probability level.

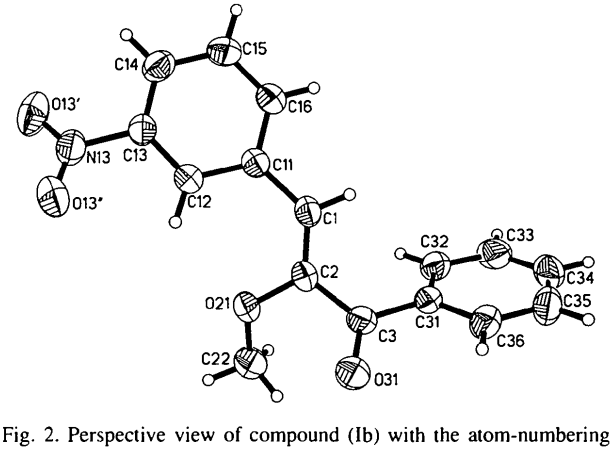


Fig. 2. Perspective view of compound (Ib) with the atom-numbering scheme and displacement ellipsoids at the 50% probability level.

O14″···C14($-x$, $-\frac{1}{2}+y$, $\frac{3}{2}-z$) 3.421 (5) Å. For the carbonyl O atoms, short intermolecular contacts can be found in both structures; O31···H36($1-x$, $-y$, $1-z$) 2.681 (4) Å in (Ia), and O31···H15(x, $y+1$, z) 2.711 (2) and O31···H16(x, $y+1$, z) 2.961 (2) Å in (Ib). Due to the different substitution pattern of the nitrophenyl ring, a short O···O intramolecular interaction arises in (Ib) [O13″···O21 4.457 (2) Å], while a comparable distance is missing in (Ia).

A least-squares fit (Fig. 3) of atoms C1–C3, O21, C22, O31 and C31–C36 (r.m.s. deviation 0.067 Å) shows the structural similarities of both molecules and the different conformations of the nitrophenyl rings.

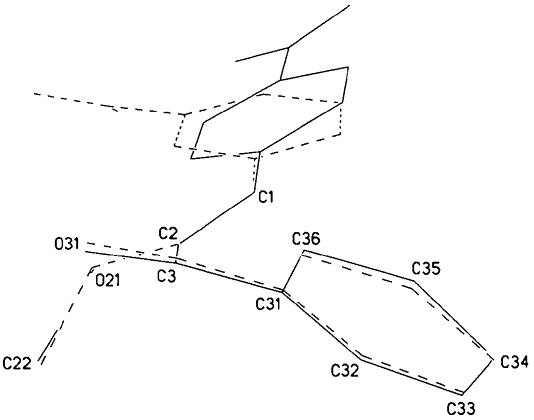


Fig. 3. A least-squares fit of the two title compounds. Fitted atoms are labelled.

Experimental

The title compounds (Ia) and (Ib) were prepared by the acyloin condensation of 3-nitrobenzaldehyde and 2-nitrobenzaldehyde, respectively, and ω-methoxyacetophenone with sodium methylate in methanol at room temperature (Teuber, Schütz & Bader, 1977; Malkin & Robinson, 1925). Single crystals were obtained from methanol solution in both cases.

Compound (Ia)

Crystal data

$C_{16}H_{13}NO_4$
$M_r = 283.27$
Orthorhombic
Pbca
$a = 14.140\,(5)$ Å
$b = 8.028\,(2)$ Å
$c = 25.133\,(4)$ Å
$V = 2853.0\,(13)$ Å^3
$Z = 8$
$D_x = 1.319$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 25 reflections
$\theta = 30$–$35°$
$\mu = 0.795$ mm^{-1}
$T = 291$ K
Cylinder
0.60 × 0.20 × 0.10 mm
Transparent yellow

Data collection

Enraf–Nonius CAD-4 four-circle diffractometer
ω scans
Absorption correction: none
3517 measured reflections
2115 independent reflections
1513 observed reflections [$I > 2\sigma(I)$]

$R_{int} = 0.0631$
$\theta_{max} = 60.06°$
$h = -15 \rightarrow 8$
$k = 0 \rightarrow 8$
$l = 0 \rightarrow 28$
3 standard reflections
frequency: 92 min
intensity decay: 0.80%

Refinement

Refinement on F^2
$R(F) = 0.0575$
$wR(F^2) = 0.1760$
$S = 1.063$
2115 reflections
191 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0946P)^2 + 0.3819P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.256$ e Å^{-3}
$\Delta\rho_{min} = -0.228$ e Å^{-3}
Extinction correction: *SHELXL*96
Extinction coefficient: 0.0087 (8)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

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

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

	x	y	z	U_{eq}
C1	0.31538 (17)	0.2612 (3)	0.61596 (11)	0.0644 (7)
C2	0.34203 (17)	0.3262 (3)	0.56947 (11)	0.0655 (7)
C3	0.43554 (18)	0.2764 (3)	0.54627 (12)	0.0716 (8)
C11	0.22293 (16)	0.2594 (3)	0.64149 (10)	0.0610 (7)
C12	0.14159 (18)	0.3290 (3)	0.62005 (12)	0.0746 (8)
C13	0.05616 (18)	0.3216 (3)	0.64645 (13)	0.0787 (8)
C14	0.05257 (16)	0.2414 (3)	0.69501 (12)	0.0704 (8)
N14	−0.03777 (17)	0.2319 (4)	0.72313 (13)	0.0931 (8)
O14′	−0.10574 (17)	0.3031 (4)	0.70451 (12)	0.1278 (10)
O14″	−0.04179 (17)	0.1470 (5)	0.76369 (12)	0.1369 (11)
C15	0.13039 (19)	0.1671 (4)	0.71681 (12)	0.0784 (8)
C16	0.21538 (18)	0.1783 (3)	0.69023 (11)	0.0714 (7)
O21	0.28065 (12)	0.4115 (2)	0.53837 (8)	0.0818 (6)
C22	0.3191 (2)	0.5372 (4)	0.50407 (12)	0.0884 (9)
O31	0.44021 (15)	0.2432 (3)	0.49897 (10)	0.0992 (8)
C31	0.51935 (17)	0.2604 (3)	0.58123 (11)	0.0683 (7)
C32	0.5357 (2)	0.3673 (4)	0.62295 (12)	0.0792 (8)
C33	0.6169 (2)	0.3566 (4)	0.65237 (15)	0.0986 (10)
C34	0.6806 (2)	0.2347 (6)	0.64154 (16)	0.1087 (13)
C35	0.6646 (2)	0.1239 (5)	0.60093 (17)	0.1082 (12)
C36	0.5848 (2)	0.1372 (4)	0.57038 (13)	0.0852 (9)

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

C1—C2	1.334 (4)	C14—N14	1.462 (4)
C1—C11	1.456 (3)	N14—O14′	1.212 (4)
C2—O21	1.354 (3)	N14—O14″	1.228 (4)
C2—C3	1.499 (4)	C15—C16	1.378 (4)
C3—O31	1.220 (4)	O21—C22	1.434 (3)
C3—C31	1.481 (4)	C31—C32	1.374 (4)
C11—C12	1.388 (4)	C31—C36	1.382 (4)
C11—C16	1.391 (4)	C32—C33	1.368 (4)
C12—C13	1.380 (4)	C33—C34	1.358 (5)
C13—C14	1.381 (4)	C34—C35	1.372 (5)
C14—C15	1.366 (4)	C35—C36	1.370 (5)
C2—C1—C11	130.1 (2)	O14′—N14—O14″	123.1 (3)
C1—C2—O21	121.5 (2)	O14′—N14—C14	118.8 (3)
C1—C2—C3	119.1 (2)	O14″—N14—C14	118.1 (3)
O21—C2—C3	118.4 (2)	C14—C15—C16	118.7 (3)
O31—C3—C31	121.1 (2)	C15—C16—C11	121.6 (3)
O31—C3—C2	119.0 (3)	C2—O21—C22	117.4 (2)
C31—C3—C2	119.9 (3)	C32—C31—C36	119.0 (3)
C12—C11—C16	117.8 (2)	C32—C31—C3	122.2 (2)
C12—C11—C1	124.7 (2)	C36—C31—C3	118.7 (3)

C16—C11—C1	117.5 (2)	C31—C32—C33	120.9 (3)
C13—C12—C11	121.4 (3)	C34—C33—C32	119.6 (3)
C12—C13—C14	118.5 (3)	C33—C34—C35	120.4 (3)
C15—C14—C13	121.9 (2)	C36—C35—C34	120.2 (3)
C15—C14—N14	119.1 (3)	C35—C36—C31	119.8 (3)
C13—C14—N14	118.9 (3)		

Compound (Ib)

Crystal data

$C_{16}H_{13}NO_4$
$M_r = 283.27$
Triclinic
$P\bar{1}$
$a = 8.384$ (1) Å
$b = 8.783$ (1) Å
$c = 9.492$ (1) Å
$\alpha = 95.01$ (1)°
$\beta = 97.17$ (1)°
$\gamma = 101.50$ (1)°
$V = 675.03$ (13) Å^3
$Z = 2$
$D_x = 1.394$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 25 reflections
$\theta = 30$–35°
$\mu = 0.840$ mm^{-1}
$T = 293$ K
Block
0.50 × 0.30 × 0.30 mm
Transparent yellow

Data collection

Enraf–Nonius CAD-4 four-circle diffractometer
ω scans
Absorption correction: none
3743 measured reflections
2000 independent reflections
1929 observed reflections [$I > 2\sigma(I)$]

$R_{\rm int} = 0.0592$
$\theta_{\rm max} = 59.96°$
$h = -9 \rightarrow 9$
$k = -9 \rightarrow 7$
$l = -10 \rightarrow 10$
3 standard reflections
frequency: 92 min
intensity decay: 1.20%

Refinement

Refinement on F^2
$R(F) = 0.0429$
$wR(F^2) = 0.1132$
$S = 1.129$
2000 reflections
191 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0369P)^2 + 0.1912P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$

$\Delta\rho_{\rm max} = 0.234$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.196$ e Å^{-3}
Extinction correction: *SHELXL*96
Extinction coefficient: 0.091 (4)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (Ib)*

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

	x	y	z	$U_{\rm eq}$
C1	0.4236 (2)	0.20512 (19)	0.31967 (17)	0.0390 (4)
C2	0.3812 (2)	0.33431 (19)	0.27837 (17)	0.0382 (4)
C3	0.3154 (2)	0.44049 (18)	0.37789 (17)	0.0390 (4)
C11	0.5213 (2)	0.10563 (18)	0.25410 (16)	0.0366 (4)
C12	0.6259 (2)	0.15689 (19)	0.15575 (17)	0.0389 (4)
C13	0.7172 (2)	0.0576 (2)	0.10234 (17)	0.0397 (4)
N13	0.82440 (19)	0.1135 (2)	−0.00276 (16)	0.0502 (4)
O13′	0.85805 (19)	0.01580 (19)	−0.08743 (15)	0.0675 (5)
O13″	0.8742 (2)	0.25451 (18)	0.00002 (18)	0.0767 (5)
C14	0.7132 (2)	−0.0904 (2)	0.14048 (19)	0.0485 (5)
C15	0.6112 (2)	−0.1408 (2)	0.2387 (2)	0.0510 (5)
C16	0.5172 (2)	−0.0441 (2)	0.29363 (18)	0.0432 (5)
O21	0.42545 (16)	0.39107 (15)	0.15617 (13)	0.0508 (4)
C22	0.3121 (3)	0.4679 (2)	0.0800 (2)	0.0570 (5)
O31	0.36778 (16)	0.58080 (13)	0.38610 (14)	0.0528 (4)
C31	0.1914 (2)	0.37273 (18)	0.46759 (17)	0.0378 (4)
C32	0.0757 (2)	0.2354 (2)	0.4205 (2)	0.0461 (5)
C33	−0.0435 (3)	0.1824 (2)	0.5040 (2)	0.0573 (6)
C34	−0.0447 (3)	0.2639 (2)	0.6345 (2)	0.0597 (6)
C35	0.0698 (3)	0.4003 (3)	0.6816 (2)	0.0574 (6)
C36	0.1864 (2)	0.4563 (2)	0.59722 (19)	0.0468 (5)

Table 4. *Selected geometric parameters (Å, °) for (Ib)*

C1—C2	1.331 (3)	N13—O13′	1.223 (2)
C1—C11	1.463 (2)	N13—O13″	1.222 (2)
C2—O21	1.366 (2)	C14—C15	1.384 (3)
C2—C3	1.499 (2)	C15—C16	1.381 (3)
C3—O31	1.215 (2)	O21—C22	1.432 (2)
C3—C31	1.491 (2)	C31—C36	1.386 (2)
C11—C16	1.394 (2)	C31—C32	1.388 (2)
C11—C12	1.401 (2)	C32—C33	1.386 (3)
C12—C13	1.374 (2)	C33—C34	1.377 (3)
C13—C14	1.375 (3)	C34—C35	1.378 (3)
C13—N13	1.476 (2)	C35—C36	1.383 (3)
C2—C1—C11	129.6 (1)	O13′—N13—C13	117.9 (2)
C1—C2—O21	121.1 (2)	O13″—N13—C13	118.1 (2)
C1—C2—C3	121.0 (1)	C13—C14—C15	117.6 (2)
O21—C2—C3	116.7 (1)	C14—C15—C16	120.1 (2)
O31—C3—C31	121.3 (2)	C15—C16—C11	122.1 (2)
O31—C3—C2	118.9 (1)	C2—O21—C22	116.2 (1)
C31—C3—C2	119.8 (1)	C36—C31—C32	119.9 (2)
C16—C11—C12	117.7 (2)	C36—C31—C3	118.1 (1)
C16—C11—C1	119.8 (1)	C32—C31—C3	121.9 (2)
C12—C11—C1	122.5 (2)	C33—C32—C31	119.7 (2)
C13—C12—C11	118.9 (2)	C34—C33—C32	120.1 (2)
C12—C13—C14	123.7 (2)	C35—C34—C33	120.4 (2)
C12—C13—N13	117.8 (2)	C34—C35—C36	119.9 (2)
C14—C13—N13	118.5 (2)	C35—C36—C31	120.0 (2)
O13′—N13—O13″	124.0 (2)		

The data were corrected for Lorentz and polarization effects. The structures were solved by direct methods using *SHELXS*86 (Sheldrick, 1990) and refined with *SHELXL*96 (Sheldrick, 1996) by full-matrix least-squares methods. All H atoms were located by a difference Fourier synthesis and refined with fixed individual displacement parameters [$U({\rm H}) = 1.5U_{\rm eq}({\rm C_{methyl}})$ or $U({\rm H}) = 1.2U_{\rm eq}({\rm C})$] using a riding model, with sp^2 C—H = 0.93 and methyl C—H = 0.96 Å. Molecular graphics were prepared using *SHELXTL-Plus* (Sheldrick, 1991).

For both compounds, data collection: *SDP* (Enraf–Nonius, 1985); cell refinement: *SDP*; data reduction: *SDP*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KA1206). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Enraf–Nonius (1985). *Structure Determination Package*. Enraf–Nonius, Delft, The Netherlands.
Kröhnke, F. & Zecher, W. (1962). *Angew. Chem.* **74**, 811–817.
Malkin, T. & Robinson, R. (1925). *J. Chem. Soc.* **127**, 369–377.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1991). *SHELXTL-Plus*. Release 4.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1996). *SHELXL96. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
Teuber, H. J., Schütz, G. & Bader, H. J. (1977). *Liebigs Ann. Chem.* pp. 1321–1334.