Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

4,5,6,9-Tetramethoxy-11-phenyl-10-oxa-11-azatricyclo[7.2.2.0^{2,7}]trideca-2(7),3,5,12-tetraen-8-one

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Received 3 April 2001
Accepted 11 April 2001
Online 26 April 2001

The crystal structure of the adduct, $C_{21}H_{21}NO_2$, of tetramethylpurpurogallin with nitrosobenzene is reported. The compound exhibits a [3.2.2] bicyclic system corresponding to two seven-membered rings and one six-membered ring in distorted chair, boat and twist–boat conformations, respectively. One intramolecular and two intermolecular hydrogen bonds direct the packing and stabilize the molecule.

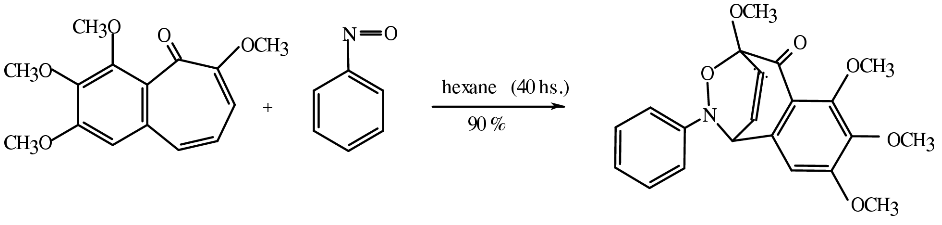
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
R factor = 0.043
wR factor = 0.145
Data-to-parameter ratio = 16.6

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

Continuing our studies on Diels–Alder reactions using NO compounds as dienophiles as the key reaction directed towards the total synthesis of naturally occurring alkaloids (Russi *et al.*, 2000), we report in this work the structure of the adduct, (I), between tetramethylpurpurogallin, a synthetic benzotropolone, and nitrosobenzene. The regiochemistry of the cycloaddition reaction is strongly dependent on stereoelectronic factors and can be analysed by spectroscopic methods and X-ray diffraction. However, crystal structure determination is the only technique that provides conclusive results on the conformation of the molecule. The NO bridge has the same orientation towards the carbonyl group as in the case of the eucarvone adduct. The O atom of the dienophile adds to C9, α to the carbonyl, and the N atom adds to the benzylic C1 atom exclusively, yielding only the *exo* adduct.



(I)

The adduct (Fig. 1) shows the characteristic [3.2.2] bicyclic system present in other similar compounds (Tinant & Declercq, 1991*a*,*b*; Russi *et al.*, 2000). Selected bond distances, endocyclic angles and torsion angles are given in Table 1. The six-membered ring exhibits a distorted twist–boat conformation. The puckering parameters (Cremer & Pople, 1975) for this ring are q_2 = 0.617 Å, q_3 = 0.125 Å, φ_2 = 100.41°, θ = 78.6 ° and Q_T = 0.630 Å. The seven-membered ring with the C12═C13 double bond has a distorted chair conformation (q_2 = 0.932 Å, q_3 = 0.354 Å, φ_2 = 322.65°, φ_3 = 58.71° and Q_T = 0.997 Å), and the one containing the N—O is a distorted boat

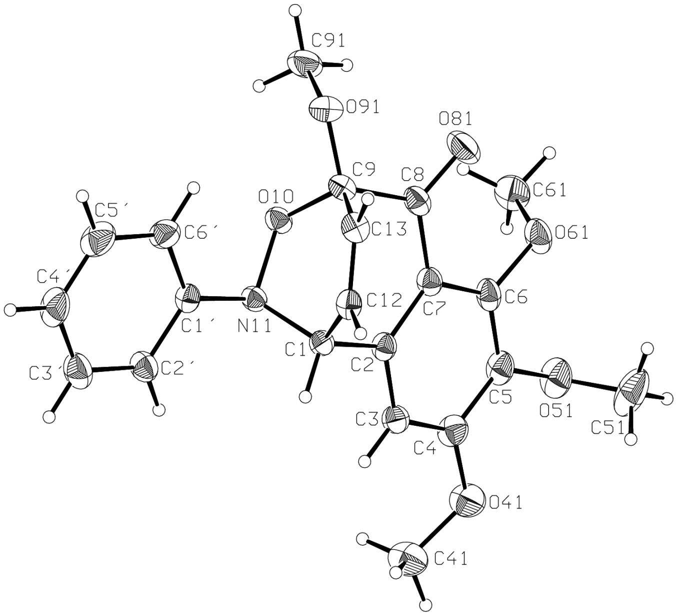


Figure 1
ZORTEP drawing (Zsolnai & Pritzkow, 1995) of the molecular structure of (I) showing 30% probability displacement ellipsoids.

($q_2 = 1.003$ Å, $q_3 = 0.313$ Å, $\varphi_2 = 322.77°$, $\varphi_3 = 290.06°$ and $Q_T = 1.051$ Å).

As in the eucarvone adduct (Russi *et al.*, 2000), there is no conjugation between the phenyl group and the NO. The N atom is pyramidal and is located 0.444 (2) Å from the C1/O10/C1′ plane. The N—O bond length is 1.434 (2) Å and the distance between O10 and the phenyl-group plane is 0.506 (1) Å (longer than in the eucarvone adduct).

The ring bonded to the [3.2.2] bicyclic system is planar and the maximum deviation from this plane is 0.012 (1) Å for C4. Steric factors place two of the C atoms belonging to the methoxy groups (C41 and C61) above the ring plane, while the other one (C51) is placed below. The dihedral angles are −161.8 (2)° for C5—C4—O41—C41, −91.7 (2)° for C7—C6—O61—C61 and 85.5 (3)° for C6—C5—O51—C51.

The combination of electronic and steric factors directs the cycloaddition to give a compound whose structure explains the spectral data (^{1}H and ^{13}C NMR), as the deshielding of H1 and H12 by an anisotropic effect due to the orientation of the phenyl group.

Experimental

Tetra-*O*-methyl purpurogallin (Barltrop & Nichols, 1948) (1.11 g, 4.02 mmol) and nitrosobenzene (0.52 g, 4.86 mmol) were dissolved in hexane (50 ml). The solution was left standing at room temperature, in the absence of light, for 40 h. The white crystals obtained were filtered and recrystallized from methanol to yield the tetra–*O*-methylpurpurogallin–nitrosobenzene adduct (1.39 g, 90%; m.p. 387–388 K). The filtrate was concentrated under vacuum and the crystals obtained were recrystallized from methanol (160 mg, 10%).

Crystal data

$C_{21}H_{21}NO_6$
$M_r = 383.39$
Monoclinic, $P2_1/n$
$a = 13.495$ (2) Å
$b = 10.2178$ (18) Å
$c = 15.154$ (3) Å
$\beta = 115.956$ (14)°
$V = 1878.8$ (6) Å^3
$Z = 4$
$D_x = 1.355$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 22.8$–$34.0°$
$\mu = 0.10$ mm^{-1}
$T = 293$ (2) K
Prismatic, colourless
0.15 × 0.12 × 0.10 mm

Data collection

Rigaku AFC-7*S* diffractometer
$\theta/2\theta$ scans
5381 measured reflections
4300 independent reflections
2466 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.047$
$\theta_{\rm max} = 27.5°$
$h = -1 \rightarrow 17$
$k = -1 \rightarrow 13$
$l = -19 \rightarrow 18$
3 standard reflections every 150 reflections intensity decay: 8.9%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.145$
$S = 1.01$
4300 reflections
259 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0624P)^2 + 0.3861P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.22$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.21$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0102 (15)

Table 1
Selected geometric parameters (Å, °).

C7—C2	1.409 (3)	C12—C13	1.311 (3)
C7—C8	1.499 (3)	C13—C9	1.495 (3)
C2—C1	1.524 (2)	C9—O10	1.460 (2)
C1—N11	1.490 (2)	C9—C8	1.548 (3)
C1—C12	1.502 (3)	O10—N11	1.4345 (18)
C2—C7—C8	122.61 (17)	O10—C9—C13	114.29 (14)
C7—C2—C1	123.23 (16)	O10—C9—C8	106.83 (15)
N11—C1—C12	109.18 (14)	C13—C9—C8	105.52 (16)
N11—C1—C2	108.51 (14)	N11—O10—C9	117.48 (12)
C12—C1—C2	113.40 (15)	O10—N11—C1	108.37 (13)
C13—C12—C1	116.62 (17)	C7—C8—C9	117.04 (16)
C12—C13—C9	117.08 (17)		
C8—C7—C2—C1	−4.5 (3)	C13—C9—O10—N11	−20.2 (2)
C7—C2—C1—N11	73.5 (2)	C8—C9—O10—N11	96.12 (16)
C7—C2—C1—C12	−48.0 (2)	C9—O10—N11—C1	−28.98 (18)
N11—C1—C12—C13	−45.9 (2)	C12—C1—N11—O10	62.14 (17)
C2—C1—C12—C13	75.2 (2)	C2—C1—N11—O10	−61.90 (17)
C1—C12—C13—C9	−5.4 (3)	C2—C7—C8—C9	−11.4 (3)
C12—C13—C9—O10	39.8 (2)	O10—C9—C8—C7	−47.3 (2)
C12—C13—C9—C8	−77.3 (2)	C13—C9—C8—C7	74.7 (2)

H atoms were located at geometrically suitable positions and refined with fixed isotropic displacement parameters $U_{\rm iso} = 1.2U_{\rm eq}$ of the parent atom.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *MSC/AFC Diffractometer Control Software*; program(s) used to solve structure:

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*SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ZORTEP* (Zsolnai & Pritzkow, 1995); software used to prepare material for publication: *PLATON* (Spek, 1990) and *CSD* (Allen & Kennard, 1993).

This research was supported by CONICYT (Consejo Nacional de Investigación Científica y Tecnológica, Uruguay) and CSIC (Comisión Sectorial de Investigación Científica, Universidad de la República), Project 195. We thank the Spanish Research Council (CSIC) for providing us with a free-of-charge license to the CSD system.

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