

2,4,5-Trimethoxy-1-nitrobenzene: a structure in the rare space group $P4_2$ Christophe M. L. Vande Velde,
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Key indicators

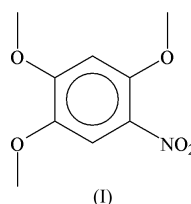
Single-crystal X-ray study
 $T = 293\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.003\text{ \AA}$
 R factor = 0.040
 wR factor = 0.118
Data-to-parameter ratio = 11.2For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

The achiral title compound, $\text{C}_9\text{H}_{11}\text{NO}_5$, crystallizes as a chiral structure in space group $P4_2$. Short contacts between the nitro group and two methoxy groups on neighbouring molecules can be seen, as can methoxy–methoxy contacts between the other methoxy groups not involved in this interaction.

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Comment

2,4,5-Trimethoxy-1-nitrobenzene, (I) (Fig. 1), was synthesized as an intermediate in the route to highly substituted PPV oligomers. It is achiral in solution, but crystallizes as a chiral structure (Flack, 2003) in the tetragonal space group $P4_2$ with four symmetry-equivalent molecules in the unit cell. There is one molecule in the asymmetric unit.



The solid-state structure of (I) is quite remarkable since only 30 compounds in the Cambridge Structural Database (CSD, Version 1.6 with April 2004 update; Allen, 2002) crystallize in space group $P4_2$ and, of those, only two are non-organometallic compounds without chiral centres, namely refcodes HYDTML (Liminga & Sørensen, 1967) and OKAHUD (Eaton *et al.*, 2003).

The distances and angles in this molecule conform to the expected values within experimental error. Note that the lengthening of the C4–C5 bond and the associated shortening of C3–C4 and C5–C6 are due to the lone-pair repulsion of the methoxy O atoms. Indeed, all the methoxy groups lie within 5° of the mean plane of the molecule (see Table 1). The

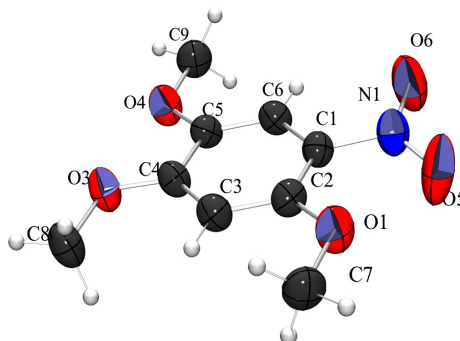


Figure 1

The molecular structure of (I), showing 50% probability displacement ellipsoids and the atom-numbering scheme.

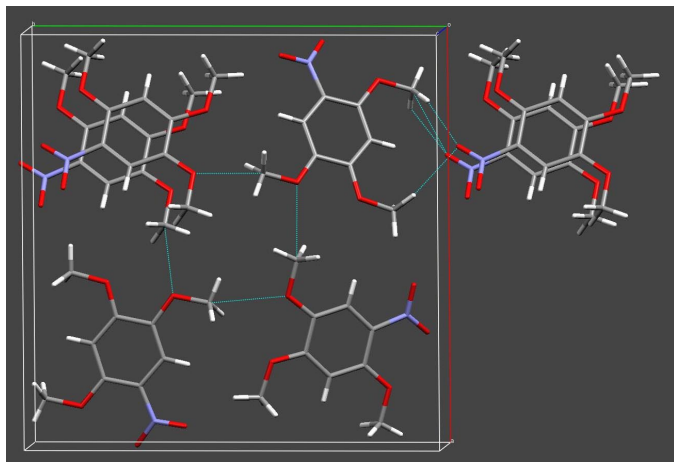


Figure 2

A view of the cell of (I), showing the methoxy double helix around the 4_2 axis and the contacts between atom O5 and the other methoxy groups.

angle between the least-squares planes of the nitro group and the benzene ring is $12.9(2)^\circ$. These out-of-plane torsions of the substituents introduce the chirality in the molecule. The reason for the existence of this torsion and the particular packing can be found in the interactions that exist in the crystal structure. The majority of the contacts shorter than the sum of the van der Waals radii are between nitro and methoxy groups. A nitro group, and in particular atom O5, contacts the 2- and 4-methoxy groups of neighbouring molecules (see Table 2, and Fig. 2 for a view of the structure and these interactions). Atom O6 also contacts a number of methoxy groups, but the distances for these contacts are longer than the van der Waals cut-off criterion. In the CSD, we found only 97 structures which display these kinds of phenyl-methoxy...nitro-phenyl contacts with a distance shorter than the sum of the van der Waals radii, and an N—O...H angle between 180 and 90° .

Even though these appear to be relatively rare features, in the present case it is clear that they are very important in the construction of the crystal structure, as hardly any other interactions are available to determine the stacking. The exception to this is the methoxy-methoxy contact between the 5-methoxy group designated by $C9 \cdots O4(y, 1-x, z-\frac{1}{2}) = 3.204(3) \text{ \AA}$ and $O-C9 \cdots O4(y, 1-x, z-\frac{1}{2}) = 161.95(18)^\circ$, which results in a double helix of interacting 5-methoxy groups around the fourfold screw axis; this can be seen clearly in Fig. 2. Another possible factor stabilizing the stacks of rings in the crystal structure is the parallel-displaced π - π interaction evident between the benzene rings, with a centroid-to-centroid distance equal to the length of the c axis [$3.900(2) \text{ \AA}$] and a perpendicular centroid-to-plane distance of $3.65(6) \text{ \AA}$. Thus we have stacks of benzene rings around the screw tetrad, which are stabilized *via* a double helix of methoxy interactions on one side and *via* weak hydrogen bonds between methoxy and nitro groups on the other. These last two types of interactions appear to force the structure into the unusual space group in which it crystallizes.

Experimental

Compound (I) was synthesized by slowly adding fuming nitric acid (6 g, 0.036 mol) to 1,2,4-trimethoxybenzene (2.3 g, 0.036 mol) in CH_2Cl_2 solution (50 ml) at 273 K and, after warming to room temperature, distilling off the solvent under vacuum and recrystallizing the brown compound from ethanol; the yield was 77% (5.9 g, 0.028 mol) of yellow-green crystals of (I). Crystals suitable for X-ray diffraction were grown by slow evaporation of a saturated solution in 1:1 hexane- CH_2Cl_2 . ^1H NMR (in p.p.m., 400 MHz, CDCl_3): 7.58 (s, 1H, H6), 7.26 (s, 1H, H3), 3.98 (s, 3H, 4-OCH₃), 3.98 (s, 3H, 5-OCH₃), 3.90 (s, 3H, 2-OCH₃). ^{13}C NMR (in p.p.m., 400 MHz, CDCl_3) 154.85 (C4), 150.36 (C2), 142.56 (C5), 131.15 (C1), 109.20 (C6), 97.96 (C3), 57.32, 56.61, 56.48 (OCH₃).

Crystal data

$\text{C}_9\text{H}_{11}\text{NO}_5$	Mo $K\alpha$ radiation
$M_r = 213.19$	Cell parameters from 25 reflections
Tetragonal, $P4_2$	$\theta = 5.8$ – 16.5°
$a = 15.749(9) \text{ \AA}$	$\mu = 0.12 \text{ mm}^{-1}$
$c = 3.900(2) \text{ \AA}$	$T = 293(2) \text{ K}$
$V = 967.3(9) \text{ \AA}^3$	Prism, yellow-green
$Z = 4$	$0.3 \times 0.3 \times 0.2 \text{ mm}$
$D_x = 1.464 \text{ Mg m}^{-3}$	

Data collection

Enraf-Nonius MACH3 diffractometer	$\theta_{\text{max}} = 32.0^\circ$
$\omega/2\theta$ scans	$h = -23 \rightarrow 19$
Absorption correction: none	$k = -23 \rightarrow 19$
5058 measured reflections	$l = -5 \rightarrow 0$
1895 independent reflections	3 standard reflections
1070 reflections with $I > 2\sigma(I)$	frequency: 60 min
$R_{\text{int}} = 0.029$	intensity decay: 1%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0635P)^2 + 0.0428P]$
$R[F^2 > 2\sigma(F^2)] = 0.040$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.118$	$(\Delta/\sigma)_{\text{max}} = 0.041$
$S = 1.00$	$\Delta\rho_{\text{max}} = 0.16 \text{ e \AA}^{-3}$
1895 reflections	$\Delta\rho_{\text{min}} = -0.17 \text{ e \AA}^{-3}$
169 parameters	
Only coordinates of H atoms refined	

Table 1

Selected torsion angles ($^\circ$).

C7—O1—C2—C1	$-176.6(3)$	C8—O3—C4—C5	$175.3(3)$
C9—O4—C5—C4	$176.2(3)$		

Table 2

Intermolecular nitro-methoxy contacts ($\text{\AA},^\circ$) in (I).

Atom 1	Atom 2 (B)	Distance	Symmetry code	N—O...B
O5	C7	$3.209(4)$	$-y, x, z - \frac{1}{2}$	$114.2(3)$
O5	H7C	$2.45(3)$	$-y, x, z - \frac{1}{2}$	$125.8(11)$
O5	H7A	$2.64(4)$	$-y, x, z + \frac{1}{2}$	$157.6(7)$
O5	H8C	$2.52(3)$	$-y, x, z + \frac{1}{2}$	$102.6(8)$

H atoms were located in a difference map and their coordinates were refined [$\text{C—H} = 0.94(3)$ – $1.05(4) \text{ \AA}$]. The $U_{\text{iso}}(\text{H})$ values were fixed at $1.2U_{\text{eq}}(\text{C}_{\text{aromatic}})$ and $1.5U_{\text{eq}}(\text{C}_{\text{methyl}})$. In the absence of significant anomalous scattering, Friedel pairs were merged.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms, 1996); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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