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Three Polychloromononitrobenzenes: C₆H₃Cl₂NO₂, C₆H₂Cl₃NO₂ and C₆HCl₄NO₂

Article in *Acta Crystallographica Section C Crystal Structure Communications* · February 1995

DOI: 10.1107/S0108270194002957

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Table 2. Selected geometric parameters (Å, °)

Mandelic acid moieties	Acid A	Acid B	Anion C
O(1)—C(1)	1.213 (3)	1.219 (2)	1.248 (2)
O(2)—C(1)	1.328 (2)	1.305 (2)	1.268 (3)
C(1)—C(2)	1.514 (3)	1.533 (3)	1.534 (3)
C(2)—O(3)	1.432 (2)	1.412 (2)	1.421 (2)
O(1)—C(1)—O(2)	124.2 (2)	123.8 (2)	125.2 (2)
O(1)—C(1)—C(2)	123.6 (2)	123.6 (2)	117.8 (2)
O(2)—C(1)—C(2)	112.1 (2)	112.6 (2)	117.0 (2)
O(3)—C(2)—C(1)	105.1 (2)	110.8 (2)	110.0 (2)
O(3)—C(2)—C(3)	113.2 (2)	109.8 (2)	111.4 (2)
C(1)—C(2)—C(3)	109.5 (2)	106.2 (2)	109.4 (2)
O(1)—C(1)—C(2)—O(3)	-12.6 (3)	-10.9 (3)	-12.2 (2)
O(3)—C(2)—C(3)—C(4)	-108.6 (2)	-137.4 (2)	-160.6 (2)
1-Phenylethylammonium ion			
N—C(10)		1.507 (3)	
C(9)—C(10)		1.523 (3)	
C(10)—C(11)		1.510 (3)	
N—C(10)—C(11)		110.3 (2)	
N—C(10)—C(9)		109.2 (2)	
C(11)—C(10)—C(9)		113.2 (2)	
N—C(10)—C(11)—C(12)		116.7 (2)	
C(9)—C(10)—C(11)—C(12)		-120.6 (3)	

Table 3. Hydrogen-bonding geometry (Å, °)

D—H...A	H...A	D...A	D—H...A
N—H(N1)...O(1C ⁱ)	1.90 (3)	2.812 (2)	180 (3)
N—H(N2)...O(3C)	1.92 (3)	2.834 (2)	165 (3)
N—H(N3)...O(3A)	1.91 (3)	2.818 (2)	149 (2)
N—H(N3)...O(1A)	2.22 (3)	2.991 (2)	133 (2)
O(2A)—H(O2A)...O(1B)	1.71 (3)	2.645 (2)	169 (3)
O(3A)—H(O3A)...O(2C ⁱⁱ)	1.85 (3)	2.616 (2)	173 (3)
O(2B)—H(O2B)...O(2C)	1.68 (4)	2.531 (2)	171 (3)
O(3B)—H(O3B)...O(3A ⁱⁱⁱ)	2.06 (3)	2.857 (2)	174 (3)
O(3C)—H(O3C)...O(1C)	2.03 (3)	2.626 (2)	123 (3)
O(3C)—H(O3C)...O(3B ^{iv})	2.17 (3)	2.875 (2)	135 (3)

Symmetry codes: (i) $x - \frac{1}{2}, -\frac{1}{2} - y, -z$; (ii) $x - 1, y, z$; (iii) $\frac{1}{2} + x, \frac{1}{2} - y, -z$; (iv) $x, y - 1, z$.

The data reduction was performed using the *DREADD* programs (Blessing, 1987). The structure was solved by direct methods using *SHELXS86* (Sheldrick, 1990) and refined by least-squares methods using *SHELXL93* (Sheldrick, 1993). All H atoms were shown in a difference electron density map. H atoms bonded to tertiary and aromatic C atoms were fixed in ideal positions, the H atoms in the methyl group were refined with the restraint of a fixed angle and distance to the C atom and the remaining H atoms were located from a difference Fourier map. The absolute configuration was chosen to be in agreement with the known absolute configuration for (*S*)-mandelic acid and the choice was supported by a Flack (1983) χ parameter of -0.06 (16).

I am grateful to Mr Flemming Hansen for help with the experimental crystallographic work and Dr Sine Larsen for valuable discussions. Support from The Carlsberg Foundation is gratefully acknowledged.

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: AS1116). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Blessing, R. H. (1987). *Crystallogr. Rev.* **1**, 3–58.
 Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
 Johnson, C. K. (1971). *ORTEP*. Report ORNL-3794, revised. Oak Ridge National Laboratory, Tennessee, USA.
 Larsen, S., Kozma, D. & Acs, M. (1994). *Acta Chem. Scand.* **48**, 32–36.
 Larsen, S. & Lopez de Diego, H. (1993a). *Acta Cryst.* **B49**, 303–309.
 Larsen, S. & Lopez de Diego, H. (1993b). *J. Chem. Soc. Perkin Trans.* **2**, pp. 469–473.
 Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
 Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. Univ. of Göttingen, Germany.

Acta Cryst. (1995). **C51**, 256–260

Three Polychloromononitrobenzenes: C₆H₃Cl₂NO₂, C₆H₂Cl₃NO₂ and C₆HCl₄NO₂

ABDENBI BHAR AND JEAN PIERRE AUNE

*URA-CNRS 1410 Activation et Catalyse, ENSSPICAM
Campus de Saint-Jerôme, 13397 Marseille CEDEX 20,
France*

NOURREDINE BENALI-CHERIF, LEILA BENMENNI
AND MICHEL GIORGI

*Laboratoire de bio-inorganique structurale C12,
Faculté des Sciences et Techniques de Saint-Jerôme,
13397 Marseille CEDEX 20, France*

(Received 1 June 1993; accepted 16 March 1994)

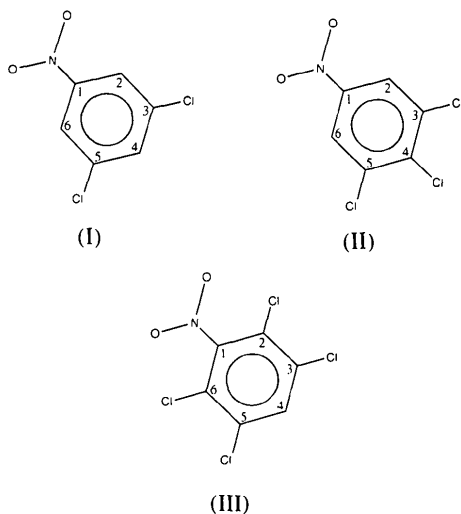
Abstract

3,5-Dichloronitrobenzene (I), 3,4,5-trichloronitrobenzene (II) and 2,3,5,6-tetrachloronitrobenzene (III) are frequently used as intermediates in the manufacture of dyes as well as phyto-sanitary and drug products. In both compounds (I) and (II), the NO₂ plane and the benzene ring plane are coplanar, but in (III) these planes have a mean dihedral angle of 88°.

Comment

In the field of substituted chloro derivatives of nitrobenzene, important synthetic problems often occur because some of these compounds can only be obtained using an indirect route. One method, of great potential interest, is the selective hydrodechlorination of 'overchlorinated' compounds (Tassara, Metzger & Aune, 1975). We are interested in this hydrodechlorination reaction in connection with polychloronitrobenzenes and we have undertaken the X-ray analysis of a

series of these compounds in order to investigate the relationship between their structures, and in particular, the Cl-NO₂ interactions.



Compound (I) crystallizes in the space group $P2_1/m$, compounds (II) and (III) in $P\bar{1}$. The structure of (I) has three atoms [C(1), C(4) and N] that are located on a special position, the mirror m , while compounds (II) and (III) crystallize with two independent molecules in the asymmetric unit.

The C—Cl distances in all three compounds vary between 1.703 (4) and 1.734 (7) Å, which is in agreement with the C—Cl distances found in other benzene derivatives (Sakurai, 1962; Holden & Dickinson, 1967; Silverman, Soltberg, Yannoni & Krukoni, 1971; Tanaka, Iwasaki & Aihara, 1974; Sharma, Paulus, Weiden & Weiss, 1985).

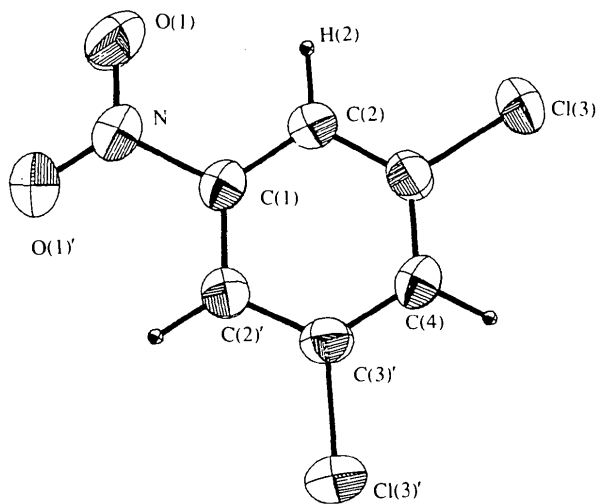


Fig. 1. ORTEPII (Johnson, 1976) view of compound (I). Displacement ellipsoids are shown at the 50% probability level.

Compounds (I) and (II) are nearly planar, but compound (III) has a large dihedral angle between the NO₂ group and the benzene ring in both molecules of the asymmetric unit [84.8 (1) and 90.8 (1)°]. This is due, in particular, to the steric repulsion between the electronegative O atoms and the Cl atoms in the *ortho* positions.

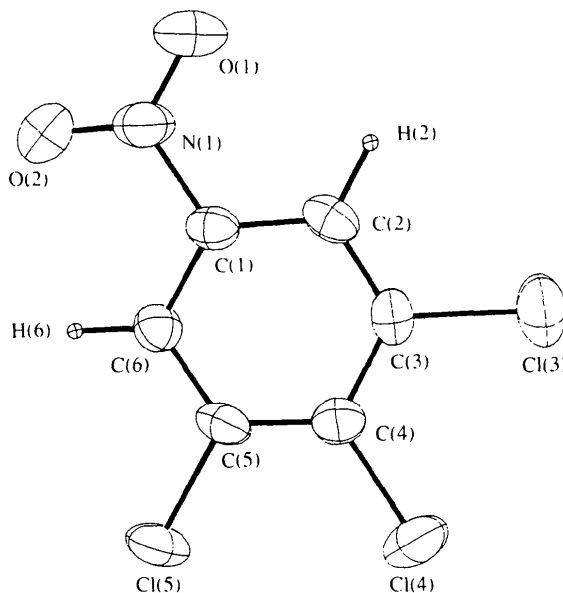


Fig. 2. ORTEPII view of one independent molecule of compound (II). Displacement ellipsoids are shown at the 50% probability level.

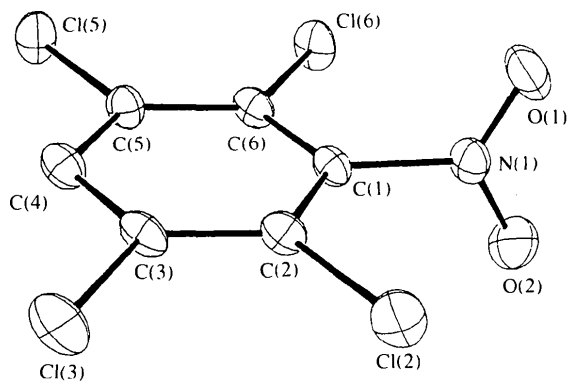


Fig. 3. ORTEPII view of one independent molecule of compound (III). Displacement ellipsoids are shown at the 50% probability level.

Experimental

Crystals suitable for X-ray work were obtained by slow evaporation of a saturated acetonitrile solution for compounds (I) and (II), and of a saturated hexane solution for (III), all at room temperature.

Compound (I)

Crystal data

C₆H₃Cl₂NO₂
M_r = 192

Mo K α radiation
 λ = 0.71069 Å

Monoclinic
 $P2_1/m$
 $a = 3.873 (2) \text{ \AA}$
 $b = 13.687 (2) \text{ \AA}$
 $c = 7.013 (3) \text{ \AA}$
 $\beta = 92.94 (6)^\circ$
 $V = 371.3 (1) \text{ \AA}^3$
 $Z = 2$
 $D_x = 1.716 \text{ Mg m}^{-3}$

Cell parameters from 25 reflections
 $\theta = 10\text{--}16^\circ$
 $\mu = 0.826 \text{ mm}^{-1}$
 $T = 293 \text{ K}$
 Rectangular
 $0.3 \times 0.2 \times 0.2 \text{ mm}$
 Yellow

Triclinic
 $P\bar{1}$
 $a = 7.842 (2) \text{ \AA}$
 $b = 14.450 (5) \text{ \AA}$
 $c = 7.548 (2) \text{ \AA}$
 $\alpha = 101.08 (2)^\circ$
 $\beta = 98.10 (2)^\circ$
 $\gamma = 84.38 (3)^\circ$
 $V = 828.9 (4) \text{ \AA}^3$
 $Z = 4$
 $D_x = 1.814 \text{ Mg m}^{-3}$

Cell parameters from 25 reflections
 $\theta = 11\text{--}17^\circ$
 $\mu = 1.062 \text{ mm}^{-1}$
 $T = 293 \text{ K}$
 Rectangular
 $0.5 \times 0.3 \times 0.3 \text{ mm}$
 Yellow

Data collection

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

$R_{\text{int}} = 0.102$
 $\theta_{\text{max}} = 24^\circ$
 $h = -4 \rightarrow 4$
 $k = 0 \rightarrow 15$
 $l = 0 \rightarrow 8$
 2 standard reflections
 frequency: 60 min
 intensity decay: 39.3%

Data collection

Enraf–Nonius CAD-4 diffractometer
 θ – 2θ scans
 Absorption correction: none
 1587 measured reflections
 1571 independent reflections
 1384 observed reflections
 $[I > 3\sigma(I)]$

$\theta_{\text{max}} = 24^\circ$
 $h = -8 \rightarrow 8$
 $k = -16 \rightarrow 16$
 $l = 0 \rightarrow 8$
 2 standard reflections
 frequency: 60 min
 intensity decay: 34.7%

Refinement

Refinement on F
 $R = 0.046$
 $wR = 0.059$
 $S = 2.024$
 460 reflections
 55 parameters
 H-atom parameters not refined

$w = 1/[\sigma^2(I_o) + (0.04I_o)^2]$
 $(\Delta/\sigma)_{\text{max}} = 0.03$
 $\Delta\rho_{\text{max}} = 0.37 (4) \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.36 (4) \text{ e \AA}^{-3}$
 Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Refinement

Refinement on F
 $R = 0.06$
 $wR = 0.08$
 $S = 3.086$
 1293 reflections
 217 parameters
 H-atom parameters not refined

$w = 1/[\sigma^2(I_o) + (0.04I_o)^2]$
 $(\Delta/\sigma)_{\text{max}} = 0.08$
 $\Delta\rho_{\text{max}} = 0.80 (2) \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.69 (2) \text{ e \AA}^{-3}$
 Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2) for (I)

	$B_{\text{eq}} = (4/3)\sum_i \sum_j \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j$			
	x	y	z	B_{eq}
Cl(3)	0.8704 (3)	0.44558 (7)	0.2327 (1)	5.40 (2)
O(1)	0.3460 (8)	0.3268 (2)	0.8587 (4)	6.99 (8)
N	0.4100 (1)	1/4	0.7874 (6)	4.4 (1)
C(1)	0.5670 (1)	1/4	0.5998 (6)	3.4 (1)
C(2)	0.6365 (9)	0.3387 (2)	0.5188 (5)	3.49 (7)
C(3)	0.7812 (8)	0.3366 (2)	0.3426 (5)	3.57 (7)
C(4)	0.8540 (1)	1/4	0.2539 (6)	3.6 (1)

Table 2. Selected geometric parameters (\AA , $^\circ$) for (I)

Cl(3)—C(3)	1.722 (3)	C(1)—C(2)	1.372 (4)
N—O(1)	1.196 (3)	C(2)—C(3)	1.382 (5)
N—C(1)	1.478 (6)	C(3)—C(4)	1.375 (4)
C(1)—N—O(1)	118.4 (2)	Cl(3)—C(3)—C(2)	118.9 (3)
N—C(1)—C(2)	117.8 (2)	Cl(3)—C(3)—C(4)	119.6 (3)
C(1)—C(2)—C(3)	116.7 (3)	C(2)—C(3)—C(4)	121.6 (3)

Compound (II)

Crystal data

C₆H₂Cl₃NO₂
 $M_r = 226.45$

Mo $K\alpha$ radiation
 $\lambda = 0.71069 \text{ \AA}$

Table 3. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2) for (II)

	$B_{\text{eq}} = (4/3)\sum_i \sum_j \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j$			
	x	y	z	B_{eq}
Cl(3)	0.8492 (2)	0.3602 (1)	0.4305 (3)	4.04 (4)
Cl(4)	0.4752 (3)	0.2984 (1)	0.3036 (3)	4.42 (4)
Cl(5)	0.1909 (2)	0.4417 (2)	0.1544 (3)	4.46 (5)
Cl(9)	0.7766 (3)	0.0878 (1)	1.3222 (3)	4.91 (5)
Cl(10)	0.6209 (2)	0.0835 (1)	0.9153 (3)	4.23 (4)
Cl(11)	0.7077 (3)	−0.0945 (1)	0.6217 (3)	4.93 (5)
O(1)	0.5460 (7)	0.7279 (3)	0.1707 (9)	6.6 (1)
O(2)	0.7993 (7)	0.7007 (3)	0.3050 (8)	5.6 (1)
O(3)	1.1517 (7)	−0.2271 (3)	1.2822 (7)	4.2 (1)
O(4)	1.1042 (8)	−0.3073 (4)	1.0117 (9)	5.1 (1)
N(1)	0.6551 (8)	0.6783 (3)	0.2451 (8)	3.6 (1)
N(2)	1.0824 (7)	−0.2372 (3)	1.1279 (8)	3.4 (1)
C(1)	0.6082 (8)	0.5840 (4)	0.2571 (9)	2.4 (1)
C(2)	0.7370 (8)	0.5239 (4)	0.3271 (9)	2.5 (1)
C(3)	0.6911 (8)	0.4348 (4)	0.3388 (9)	2.7 (1)
C(4)	0.5262 (8)	0.4084 (4)	0.2868 (9)	2.7 (1)
C(5)	0.4000 (8)	0.4733 (5)	0.2211 (9)	2.7 (1)
C(6)	0.4393 (9)	0.5622 (4)	0.2075 (9)	2.8 (1)
C(7)	0.9633 (8)	−0.1597 (4)	1.0742 (9)	2.3 (1)
C(8)	0.9297 (8)	−0.0853 (4)	1.2041 (9)	3.2 (1)
C(9)	0.8189 (8)	−0.0076 (4)	1.157 (1)	2.7 (1)
C(10)	0.7502 (8)	−0.0101 (4)	0.9754 (9)	2.6 (1)
C(11)	0.7897 (8)	−0.0876 (4)	0.8491 (9)	3.3 (1)
C(12)	0.8969 (8)	−0.1657 (4)	0.8944 (9)	2.6 (1)

Table 4. Selected geometric parameters (\AA , $^\circ$) for (II)

Cl(3)—C(3)	1.721 (6)	C(1)—C(2)	1.381 (8)
Cl(4)—C(4)	1.709 (7)	C(1)—C(6)	1.375 (9)
Cl(5)—C(5)	1.725 (6)	C(2)—C(3)	1.392 (9)
Cl(9)—C(9)	1.711 (6)	C(3)—C(4)	1.366 (9)
Cl(10)—C(10)	1.704 (6)	C(4)—C(5)	1.401 (9)
Cl(11)—C(11)	1.734 (7)	C(5)—C(6)	1.38 (1)
O(1)—N(1)	1.210 (8)	C(7)—C(8)	1.342 (8)
O(2)—N(1)	1.212 (8)	C(7)—C(12)	1.373 (9)
O(3)—N(2)	1.202 (7)	C(8)—C(9)	1.420 (9)
O(4)—N(2)	1.221 (7)	C(9)—C(10)	1.40 (1)
N(1)—C(1)	1.468 (8)	C(10)—C(11)	1.366 (8)
N(2)—C(7)	1.468 (8)	C(11)—C(12)	1.406 (9)
O(1)—N(1)—O(2)	124.6 (6)	C(5)—C(5)—C(6)	118.9 (5)
O(1)—N(1)—C(1)	116.5 (5)	C(4)—C(5)—C(6)	121.3 (6)
O(2)—N(1)—C(1)	118.8 (5)	C(1)—C(6)—C(5)	117.3 (6)
O(3)—N(2)—O(4)	124.8 (6)	N(2)—C(7)—C(8)	117.6 (6)
O(3)—N(2)—C(7)	117.9 (5)	N(2)—C(7)—C(12)	118.7 (5)
O(4)—N(2)—C(7)	117.3 (5)	C(8)—C(7)—C(12)	123.7 (6)
N(1)—C(1)—C(2)	117.7 (5)	C(7)—C(8)—C(9)	119.4 (6)
N(1)—C(1)—C(6)	118.9 (5)	Cl(9)—C(9)—C(8)	119.6 (5)
C(2)—C(1)—C(6)	123.9 (6)	Cl(9)—C(9)—C(10)	121.6 (5)
C(1)—C(2)—C(3)	116.7 (6)	C(8)—C(9)—C(10)	118.5 (5)
Cl(3)—C(3)—C(2)	117.1 (5)	Cl(10)—C(10)—C(9)	119.6 (4)
Cl(3)—C(3)—C(4)	121.0 (5)	Cl(10)—C(10)—C(11)	121.4 (5)
C(2)—C(3)—C(4)	121.8 (6)	C(9)—C(10)—C(11)	119.0 (5)
Cl(4)—C(4)—C(3)	120.4 (5)	Cl(11)—C(11)—C(10)	120.9 (5)
Cl(4)—C(4)—C(5)	120.7 (5)	Cl(11)—C(11)—C(12)	116.4 (5)
C(3)—C(4)—C(5)	118.9 (6)	C(10)—C(11)—C(12)	122.7 (6)
Cl(5)—C(5)—C(4)	119.8 (5)	C(7)—C(12)—C(11)	116.3 (5)

Compound (III)*Crystal data*C₆HCl₄NO₂ $M_r = 260.89$

Triclinic

P1

 $a = 10.920 (3) \text{\AA}$ $b = 10.944 (2) \text{\AA}$ $c = 8.740 (1) \text{\AA}$ $\alpha = 103.17 (1)^\circ$ $\beta = 112.68 (2)^\circ$ $\gamma = 78.25 (2)^\circ$ $V = 930.7 (4) \text{\AA}^3$ $Z = 4$ $D_x = 1.862 \text{ Mg m}^{-3}$ *Data collection*Enraf–Nonius CAD-4
diffractometer ω - 2θ scansAbsorption correction:
none3130 measured reflections
2910 independent reflections
2910 observed reflections*Refinement*Refinement on F^2 $R = 0.039$ $wR = 0.056$ $S = 2.194$

2408 reflections

235 parameters

H-atom parameters not
refinedMo $K\alpha$ radiation $\lambda = 0.71069 \text{\AA}$ Cell parameters from 25
reflections $\theta = 10\text{--}16^\circ$ $\mu = 1.24 \text{ mm}^{-1}$ $T = 293 \text{ K}$

Cubic

 $0.4 \times 0.4 \times 0.4 \text{ mm}$

Transparent

 $\theta_{\text{max}} = 24^\circ$ $h = -12 \rightarrow 12$ $k = -12 \rightarrow 12$ $l = 0 \rightarrow 10$

2 standard reflections

frequency: 60 min

intensity decay: 2.3%

 $w = 1/[\sigma^2(I_o) + (0.04I_o)^2]$ $(\Delta/\sigma)_{\text{max}} = 0.002$ $\Delta\rho_{\text{max}} = 0.25 (1) \text{ e \AA}^{-3}$ $\Delta\rho_{\text{min}} = -0.40 (1) \text{ e \AA}^{-3}$ Atomic scattering factors
from *International Tables*
for *X-ray Crystallography*
(1974, Vol. IV)Table 5. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2) for (III)

	$B_{\text{eq}} = (4/3)\sum_i \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j$			B_{eq}
	x	y	z	
Cl(2)	0.45863 (8)	0.15662 (9)	0.8604 (1)	6.15 (2)
Cl(3)	0.31551 (8)	0.24535 (8)	0.5065 (1)	5.96 (2)
Cl(5)	0.76650 (9)	0.0950 (1)	0.3764 (1)	7.23 (2)
Cl(6)	0.91023 (7)	0.00425 (8)	0.7299 (1)	6.00 (2)
Cl(8)	0.79164 (8)	0.42742 (8)	-0.41950 (9)	5.79 (2)
Cl(9)	1.07961 (7)	0.28088 (8)	-0.24892 (9)	5.92 (2)
Cl(11)	0.97747 (8)	0.33376 (8)	0.31483 (9)	5.60 (2)
Cl(12)	0.69019 (7)	0.47222 (8)	0.14247 (9)	5.31 (2)
O(1)	0.7227 (3)	-0.0660 (2)	0.9310 (3)	7.18 (7)
O(2)	0.8035 (2)	0.1098 (3)	1.0472 (3)	6.98 (7)
O(3)	0.6296 (2)	0.6281 (2)	-0.1799 (3)	6.67 (7)
O(4)	0.5378 (2)	0.4575 (2)	-0.2796 (3)	6.70 (7)
N(1)	0.7388 (2)	0.0391 (2)	0.9293 (3)	4.87 (6)
N(2)	0.6328 (2)	0.5146 (2)	-0.2023 (3)	4.53 (6)
C(1)	0.6732 (2)	0.0857 (2)	0.7675 (3)	3.72 (6)
C(2)	0.5411 (2)	0.1388 (2)	0.7244 (3)	3.76 (6)
C(3)	0.4798 (3)	0.1783 (2)	0.5690 (3)	4.07 (7)
C(4)	0.5504 (3)	0.1647 (3)	0.4641 (4)	4.74 (7)
C(5)	0.6823 (3)	0.1119 (3)	0.5105 (3)	4.46 (7)
C(6)	0.7467 (3)	0.0709 (2)	0.6652 (3)	4.10 (7)
C(7)	0.7635 (2)	0.4419 (2)	-0.1260 (3)	3.69 (6)
C(8)	0.8462 (2)	0.3997 (2)	-0.2181 (3)	4.01 (6)
C(9)	0.9716 (2)	0.3356 (3)	-0.1401 (3)	4.17 (6)
C(10)	1.0111 (3)	0.3171 (3)	0.0226 (3)	4.31 (7)
C(11)	0.9267 (3)	0.3587 (3)	0.1115 (3)	4.04 (6)
C(12)	0.8000 (2)	0.4218 (3)	0.0370 (3)	3.71 (6)

Table 6. Selected geometric parameters (\AA , $^\circ$) for (III)

Cl(2)—C(2)	1.707 (3)	N(2)—C(7)	1.470 (3)
Cl(3)—C(3)	1.717 (3)	C(1)—C(2)	1.378 (3)
Cl(5)—C(5)	1.703 (4)	C(1)—C(6)	1.381 (5)
Cl(6)—C(6)	1.709 (3)	C(2)—C(3)	1.388 (4)
Cl(8)—C(8)	1.705 (3)	C(3)—C(4)	1.376 (5)
Cl(9)—C(9)	1.725 (3)	C(4)—C(5)	1.380 (4)
Cl(11)—C(11)	1.714 (3)	C(5)—C(6)	1.392 (4)
Cl(12)—C(12)	1.716 (3)	C(7)—C(8)	1.378 (4)
O(1)—N(1)	1.202 (4)	C(7)—C(12)	1.380 (4)
O(2)—N(1)	1.207 (3)	C(8)—C(9)	1.392 (3)
O(3)—N(2)	1.208 (3)	C(9)—C(10)	1.368 (4)
O(4)—N(2)	1.206 (3)	C(10)—C(11)	1.372 (4)
N(1)—C(1)	1.474 (4)	C(11)—C(12)	1.392 (3)
O(1)—N(1)—O(2)	126.3 (3)	Cl(6)—C(6)—C(1)	120.0 (2)
O(1)—N(1)—C(1)	116.7 (2)	Cl(6)—C(6)—C(5)	122.3 (3)
O(2)—N(1)—C(1)	117.0 (3)	C(1)—C(6)—C(5)	117.7 (2)
O(3)—N(2)—O(4)	125.3 (3)	N(2)—C(7)—C(8)	118.7 (2)
O(3)—N(2)—C(7)	116.5 (2)	N(2)—C(7)—C(12)	118.6 (3)
O(4)—N(2)—C(7)	118.2 (3)	C(8)—C(7)—C(12)	122.6 (2)
N(1)—C(1)—C(2)	118.5 (3)	Cl(8)—C(8)—C(7)	119.3 (2)
N(1)—C(1)—C(6)	118.0 (2)	Cl(8)—C(8)—C(9)	123.3 (2)
C(2)—C(1)—C(6)	123.4 (2)	C(7)—C(8)—C(9)	117.4 (3)
Cl(2)—C(2)—C(1)	120.4 (2)	Cl(9)—C(9)—C(8)	119.5 (2)
Cl(2)—C(2)—C(3)	122.0 (2)	Cl(9)—C(9)—C(10)	119.5 (2)
C(1)—C(2)—C(3)	117.6 (3)	C(8)—C(9)—C(10)	120.9 (3)
Cl(3)—C(3)—C(2)	120.3 (3)	C(9)—C(10)—C(11)	120.7 (2)
Cl(3)—C(3)—C(4)	119.4 (2)	Cl(11)—C(11)—C(10)	120.1 (2)
C(2)—C(3)—C(4)	120.3 (2)	Cl(11)—C(11)—C(12)	120.0 (2)
C(3)—C(4)—C(5)	121.0 (3)	C(10)—C(11)—C(12)	119.9 (3)
Cl(5)—C(5)—C(4)	119.7 (2)	Cl(12)—C(12)—C(7)	120.3 (2)
Cl(5)—C(5)—C(6)	120.4 (2)	Cl(12)—C(12)—C(11)	121.4 (2)
C(4)—C(5)—C(6)	119.9 (3)	C(7)—C(12)—C(11)	118.3 (3)

During X-ray exposure measurements compounds (I) and (II) showed a significant loss in intensity (39 and 34%, respectively). However, a linear plot of standard intensity versus time allowed us to apply a decay correction on all reflections. The crystals are very stable outside the X-ray beam.

Program used for data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Programs used for data reduction and structure resolution: *SDP software* (Frenz, 1978) via direct methods *MULTAN* (Main *et al.*, 1980), completed by difference Fourier synthesis.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and least-squares-planes data have been deposited with the IUCr (Reference: PA1066). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Enraf–Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
- Frenz, B. A. (1978). *The Enraf–Nonius CAD-4 SDP – a Real-Time System for Concurrent X-ray Data Collection and Crystal Structure Solution*. *Computing in Crystallography*, edited by H. Schenk, R. Olthof-Hazekamp, H. van Koningsveld & G. C. Bassi, pp. 64–71. Delft Univ. Press.
- Holden, J. R. & Dickinson, C. (1967). *J. Phys. Chem.* **71**, 1129–1204.
- Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
- Sakurai, T. (1962). *Acta Cryst.* **15**, 1164–1173.
- Sharma, S., Paulus, H., Weiden, N. & Weiss, A. (1985). *Z. Kristallogr.* **171**, 101–112.
- Silverman, J., Soltberg, L. J., Yannoni, N. F. & Krukoni, A. P. (1971). *J. Phys. Chem.* **75**, 1246–1250.
- Tanaka, I., Iwasaki, F. & Aihara, A. (1974). *Acta Cryst.* **B30**, 1546–1549.
- Tassara, J. P., Metzger, J. & Aune, J. P. (1975). French Patent 2 259 810.

Acta Cryst. (1995). **C51**, 260–261

1,5-Di-*tert*-butyl-2,4-dinitrobenzene, C₁₄H₂₀N₂O₄

MILCO NUMAN AND HENK SCHENK

Laboratory for Crystallography, AIMS,
University of Amsterdam, Nieuwe Achtergracht 166,
1018 WV Amsterdam, The Netherlands

DIETRICH DÖPP

Fachgebiet Organische Chemie, Universität Duisburg,
Lotharstrasse 1-21, 47048 Duisburg, Germany

(Received 17 December 1993; accepted 15 July 1994)

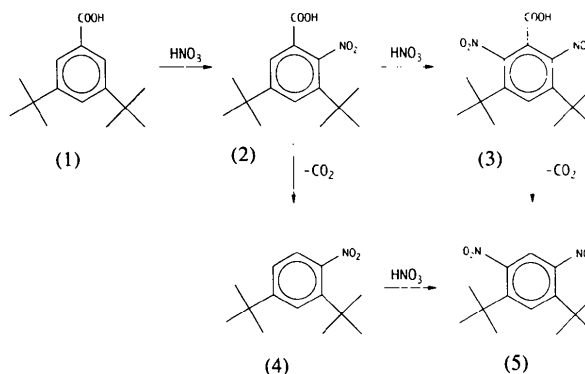
Abstract

The present crystal study was undertaken to gain a better insight into the geometry of the nitro group. The nitro groups in 1,5-di-*tert*-butyl-2,4-dinitrobenzene are

rotated by approximately 65° out of the plane of the aromatic ring.

Comment

Crystals suitable for X-ray diffraction were grown *in vacuo* at 473 K by sublimation of a crude sample of 3,5-di-*tert*-butyl-2-nitrobenzoic acid (2) prepared according to Franck & Leser (1970); this crude sample probably also contained compound (3). The m.p. of the title compound (5) was 432–433 K (*cf.* 436.5–437 K; Knoester, De Konig, Verkade & Wepster, 1967). The crystals were of poor quality.



The maximum distance of a ring atom from the best plane through the benzene ring is 0.019 (5) Å. The nitro groups are tilted by 63.0 (2) and 68.0 (2)° out of the plane of the aromatic ring, whereas an average of 35 (2)° is reported for a set of nitrobenzenes with only one *ortho* substituent (De Ridder, 1992). In the title compound, the endocyclic angles are increased at the substituent sites carrying the nitro groups and decreased at the sites carrying the alkyl groups, in accordance with the observations of Domenicano & Murray-Rust (1979).

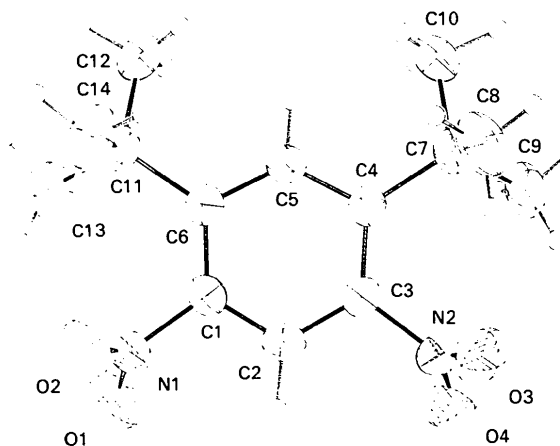


Fig. 1. PLATON (Spek, 1990) drawing showing the numbering system for the title compound. Displacement ellipsoids are drawn at the 50% probability level. The H atoms are shown but not labelled.