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## Crystal Studies of Musk Compounds. XII.\* Molecular Structures of Three Nitrotetralin-Related Compounds

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### Abstract

The crystal structures of 1,1,2,4,4,7-hexamethyl-6-nitrotetralin (1), 1,1,2,4,4,7-hexamethyl-6,8-dinitrotetralin (2) and 1,1,2,4,4,7-hexamethyl-5,6-dinitrotetralin (3) have been determined by X-ray diffraction. (2) is a strong musk and (1) is a musk for which the quality is not available, whereas the odour type of (3) is unknown. (2) has two molecules in the asymmetric unit; no extra crystallographic symmetry could be detected. The molecules of this compound show disorder in the cyclohexene ring, which is manifested in relatively high displacement parameters and in deviating bond distances and angles. In (2B) an almost planar cyclohexene ring is observed, which results from an average of two distinctly non-planar conformations. The endocyclic angles of the cyclohexene ring, at the fusion with the phenyl ring, are significantly larger than reported in a study of the geometry of small rings [Allen (1981). *Acta Cryst.*

**B37**, 900–906]. The position of the nitro groups at the aromatic ring is compared with acylated tetralin musk compounds, indicating that the nitro group in the  $\beta$ -position fulfils the osmophoric function. The possible muskiness of (3), which has been found in the same batch as (2), is discussed.

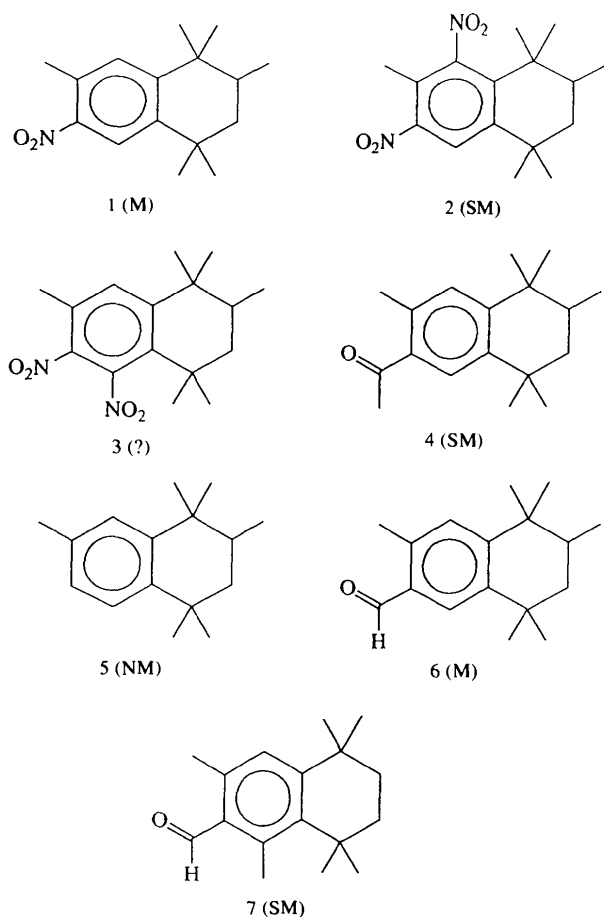
### Introduction

In parts VIII (De Ridder, Čapková, Hatjisymeon, Fraanje & Schenk, 1994) and XI (De Ridder & Schenk, 1994) of this series, the crystal structures of ten indan-related compounds are reported. These compounds have an aromatic six-membered ring fused with a non-aromatic five-membered ring in common. In this paper, the crystal structures of three nitrated tetralin compounds, in which an aromatic six-membered ring is fused with a non-aromatic six-membered ring, are described. The compounds are presented in the following scheme.

(1) and (2) are the tetralin counterparts of compounds (2) and (3) of De Ridder & Schenk (1994); (2) is a strong

\* This work forms part of a thesis by De Ridder (1992).

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Key: SM = strong musk; NM = no musk, ? = odour type unknown  
M = musk for which quality is not available

musk and (1) is reported as a musk of medium strength (Lenselink, 1988). (3) is an isomer of (2) and was found in a batch of crystals supposed to be (2). The odour of (3) is unknown. Because of its close relationship with the previous compounds, the crystal structure is reported and its possible muskiness is discussed (*cf.* also De Ridder & Schenk, 1995a).

Some of the compounds of this type of musks are excellent pre-emergence herbicides (Wood, 1968).

Note that (1) is the nitro-equivalent of musk tonalid (4), the crystal structure of which was reported in part II of this series [CSD Refcode: *KIBFUW*; De Ridder, Goubitz & Schenk (1990b)].

### Experimental

The intensities of all the crystal structures described in this paper were collected with an Enraf-Nonius CAD-4 diffractometer, employing graphite-monochromated Cu  $K\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) and  $\theta$ - $2\theta$  scans. Because of high volatility, one of the crystals was measured at reduced temperature (see Table 1). Two intensity control reflections were monitored every 3600 s. Three

Table 1. Crystal data, data collection and refinement parameters

	(1)	(2)	(3)
<b>Crystal data</b>			
Chemical formula	$C_{16}H_{23}NO_2$	$C_{16}H_{22}N_2O_4$	$C_{16}H_{22}N_2O_4$
Molecular weight	261.36	306.36	306.36
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
$a$ (Å)	8.695 (1)	8.2352 (14)	8.7422 (3)
$b$ (Å)	10.448 (1)	13.0225 (7)	10.2027 (5)
$c$ (Å)	16.310 (2)	15.4669 (13)	10.4811 (9)
$\alpha$ (°)		99.856 (8)	94.637 (5)
$\beta$ (°)	90.09 (1)	94.886 (10)	110.063 (5)
$\gamma$ (°)		97.018 (9)	110.765 (4)
$V$ (Å <sup>3</sup> )	1481.7 (3)	1612.4 (4)	799.0 (1)
$Z$	4	4	2
$D_x$ (g cm <sup>-3</sup> )	1.17	1.26	1.27
Radiation type	Cu $K\alpha$	Cu $K\alpha$	Cu $K\alpha$
Wavelength (Å)	1.5418	1.5418	1.5418
$\mu$ (cm <sup>-1</sup> )	5.71	7.11	7.17
$F(000)$	568	656	328
<b>Data collection</b>			
Crystal size (mm)	0.38 × 0.25 × 0.1	0.4 × 0.4 × 0.2	1.0 × 0.38 × 0.13
Temperature (K)	298	234	298
Cell parameter determination no.	23	23	23
$\theta$ range (°)	39.9–42.5	40.0–41.9	39.9–42.4
$\theta_{\min}, \theta_{\max}$ (°)	2.5–75	2.5–65	2.5–65
$h, k, l$	0 → $h$ → 10 0 → $k$ → 13 -20 → $l$ → 20	0 → $h$ → 9 -15 → $k$ → 15 -18 → $l$ → 18	-10 → $h$ → 10 -11 → $k$ → 11 0 → $l$ → 12
Intensity control reflections (variation)	(not significant)	(not significant)	(not significant)
No. of intensity measurements	3265	5602	2751
No. of unique reflections	3219	5467	2711
No. of observed reflections	2087	4195	2454
Observation criterion	$[I > 2.5\sigma(I)]$	$[I > 2.5\sigma(I)]$	$[I > 2.5\sigma(I)]$
Max./min. absorption	1.28/0.76	1.26/0.74	1.36/0.84
Direct methods program	<i>SIMPEL88</i> <sup>a</sup>	<i>SAP</i> <sup>b</sup>	<i>SIMPEL</i> <sup>c</sup>
<b>Refinement</b>			
$R$	0.069	0.078	0.047
$wR$	0.086	0.099	0.057
$S$	0.23	0.26	0.11
Weighting scheme			
$a$	6.2	6.7	7.9
$b$	0.0039	0.0050	0.0020
$(\Delta/\sigma)_{\max}$ in final cycle	0.88	0.51	0.27
No. of parameters refined	265	550	288
No. of restraints	23	44	0
Min./max. heights in final $\Delta F$ -map (e Å <sup>-3</sup> )	-0.3; 0.5	-0.6; 0.7	-0.2; 0.2
Extinction parameter $g$	$20(9) \times 10^{-6}$	$1(2) \times 10^{-6}$	$2(4) \times 10^{-8}$

References: (a) Peschar (1990); (b) Yao *et al.* (1985); (c) Schenk & Hall (1990).

orientation control reflections were checked every 250 reflections. The data were corrected for Lorentz and polarization effects. All structures were determined by direct methods; the program used is given in Table 1. After isotropic refinement, an empirical absorption

correction was applied [*DIFABS*; Walker & Stuart (1983)]. The H-atom positions were introduced at their calculated positions and kept fixed at 1.09 Å with respect to their carrier atoms. Refinement was performed using a full-matrix least squares algorithm on  $F$ , anisotropic for the non-H atoms and isotropic for the H atoms. The weighting scheme  $w^{-1} = a + F_{\text{obs}} + bF_{\text{obs}}^2$  was used (the values for  $a$  and  $b$  are given in Table 1).

There are a few deviations from the above procedure which are indicated in the relevant sections.

The crystal data and details of the data collection and refinement are summarized in Table 1.

(1) 1,1,2,4,4,7-Hexamethyl-6-nitrotetralin. Preliminary Weissenberg photographs indicated the crystals to be monoclinic. The H atoms were derived from a  $\Delta F$  synthesis.

(2) 1,1,2,4,4,7-Hexamethyl-6,8-dinitrotetralin. A sample of the crystals was recrystallized by sublimation. The crystals are triclinic. The unit cell contains two independent molecules in the asymmetric unit. Considering the value of  $Z$  and the statistics of the  $E$ -values, the structure was refined in  $P\bar{1}$ . The coordinates of the H atoms attached to C2 and C3 (of both molecules) were not refined and the displacement parameters of these H atoms were kept fixed at 0.08 Å<sup>2</sup>.

The program *MISSYM* [NRCVAX package; Le Page (1987)], with a search on all non-H atoms, could not detect any extra crystallographic symmetry. Matching of the common non-H atoms resulted in a r.m.s. value of 0.17 Å. The largest differences occur at the C2 and C3 atoms and at the methyl groups attached to C1 and C2, which suffer from disorder (*vide infra*) of the cyclohexene ring.

(3) 1,1,2,4,4,7-Hexamethyl-5,6-dinitrotetralin. Preliminary Weissenberg photographs indicated the crystals to be triclinic. Considering the value of  $Z$  and the statistics of the  $E$ -values, the structure was refined in  $P\bar{1}$ . No restraints have been applied for the H atoms in the structure-factor calculations.

The calculations were performed with *Xtal3.0* (Hall & Stewart, 1990). The scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV).

In preceding papers it has already been mentioned that difficulties were encountered upon (re)crystallizing this type of compound. In the present work, all attempts to recrystallize (2) with different solvents failed and the sublimation experiment only yielded a few small crystals.

In this series of papers, Cruickshank's weighting scheme has always been applied, in which the values of the parameters  $a$  and  $b$  have been taken according to Cruickshank's proposed values ( $a = 2F_{\text{obs, min}}$  and  $b = 2/F_{\text{obs, max}}$ ). During the structure-factor calculations, it has been observed that this leads to  $S$ -values significantly smaller than 1 (see Table 1).

## Results and discussion

The final coordinates and equivalent displacement parameters of the non-H atoms are collected in Table 2. The bond distances and angles are given in Table 3. A *PEANUT* (Hummel, Hauser & Bürgi, 1990) drawing of the molecules, showing the geometry and the numbering system, is given in Figs. 1–3, where the H atoms are shown as arbitrary spheres, but not labelled.

Due to disorder (*vide infra*), the accuracy of the results is not always optimal.

### Conformation

In the tetralin compounds, four atoms (C1, C9, C10 and C4) of the cyclohexene ring are constrained to lie in or near the plane of the phenyl ring (a table with the deviations of the ring member atoms and the attached atoms from the best plane through the six aromatic C atoms has been deposited as supplementary

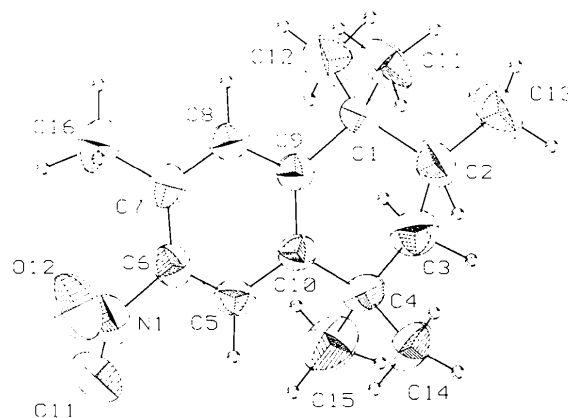


Fig. 1. Molecular structure of (1). Thermal ellipsoids are shown at 50% probability levels, H atoms as arbitrary spheres.

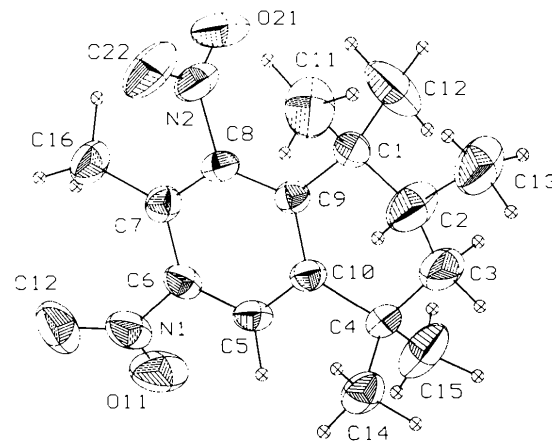


Fig. 2. Molecular structure of (2A). Thermal ellipsoids are shown at 50% probability levels, H atoms as arbitrary spheres. The numbering of (2B) is identical.

Table 2. Fractional coordinates of the non-H atoms and equivalent isotropic displacement parameters ( $\text{\AA}^2$ )
$$U_{eq} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	$U_{eq}$
(1)				
C1	0.5134 (3)	0.6987 (3)	0.2041 (2)	0.048 (2)
C2	0.4173 (5)	0.5733 (4)	0.2099 (2)	0.075 (2)
C3	0.3469 (5)	0.5351 (4)	0.1304 (3)	0.074 (2)
C4	0.2360 (3)	0.6305 (3)	0.0943 (2)	0.051 (2)
C5	0.2332 (3)	0.8628 (3)	0.0561 (2)	0.049 (2)
C6	0.2866 (3)	0.9868 (3)	0.0589 (2)	0.049 (2)
C7	0.4141 (4)	1.0220 (3)	0.1058 (2)	0.050 (2)
C8	0.4816 (3)	0.9236 (3)	0.1503 (2)	0.048 (2)
C9	0.4285 (3)	0.7965 (3)	0.1509 (2)	0.041 (1)
C10	0.3018 (3)	0.7656 (3)	0.1014 (2)	0.041 (1)
C11	0.5295 (6)	0.7502 (4)	0.2918 (2)	0.077 (3)
C12	0.6736 (5)	0.6769 (5)	0.1681 (3)	0.080 (3)
C13	0.5048 (7)	0.4609 (4)	0.2501 (3)	0.093 (3)
C14	0.0756 (4)	0.6267 (4)	0.1334 (3)	0.071 (2)
C15	0.2172 (6)	0.5928 (5)	0.0032 (3)	0.089 (3)
C16	0.4834 (5)	1.1546 (4)	0.1089 (3)	0.072 (2)
N1	0.2033 (4)	1.0810 (3)	0.0090 (2)	0.066 (2)
O11	0.1457 (4)	1.0457 (3)	-0.0553 (2)	0.090 (2)
O12	0.1935 (4)	1.1907 (3)	0.0335 (2)	0.101 (2)
(2) – molecule A				
C1	0.3772 (4)	0.8753 (3)	0.7104 (2)	0.044 (2)
C2	0.4189 (7)	0.9829 (4)	0.7709 (3)	0.085 (3)
C3	0.4799 (7)	1.0700 (4)	0.7353 (4)	0.100 (4)
C4	0.6244 (4)	1.0621 (3)	0.6817 (2)	0.044 (2)
C5	0.7435 (4)	0.9328 (3)	0.5781 (2)	0.040 (2)
C6	0.7561 (4)	0.8350 (3)	0.5322 (2)	0.040 (2)
C7	0.6482 (4)	0.7459 (3)	0.5371 (2)	0.040 (2)
C8	0.5313 (4)	0.7654 (2)	0.5951 (2)	0.038 (2)
C9	0.5121 (4)	0.8622 (2)	0.6467 (2)	0.035 (2)
C10	0.6239 (4)	0.9489 (2)	0.6353 (2)	0.037 (2)
C11	0.3728 (9)	0.7922 (5)	0.7691 (4)	0.088 (4)
C12	0.2109 (6)	0.8669 (7)	0.6554 (4)	0.096 (4)
C13	0.2850 (10)	1.0092 (5)	0.8338 (5)	0.101 (5)
C14	0.7881 (5)	1.1016 (3)	0.7392 (3)	0.054 (2)
C15	0.6090 (8)	1.1337 (4)	0.6127 (4)	0.082 (3)
C16	0.6489 (6)	0.6389 (3)	0.4799 (3)	0.056 (2)
N1	0.8875 (4)	0.8281 (3)	0.4737 (2)	0.058 (2)
N2	0.4188 (5)	0.6677 (2)	0.5972 (2)	0.055 (2)
O11	0.9114 (4)	0.8982 (3)	0.4306 (2)	0.080 (2)
O12	0.9670 (4)	0.7540 (3)	0.4723 (2)	0.081 (2)
O21	0.2913 (4)	0.6497 (3)	0.5482 (2)	0.081 (2)
O22	0.4668 (5)	0.6077 (2)	0.6234 (2)	0.086 (2)
(2) – molecule B				
C1	0.2278 (4)	0.4875 (3)	0.8719 (2)	0.043 (2)
C2	0.1629 (11)	0.4018 (5)	0.7935 (5)	0.173 (7)
C3	0.0425 (7)	0.3980 (4)	0.7378 (4)	0.100 (4)
C4	-0.0560 (4)	0.4874 (3)	0.7281 (2)	0.043 (2)
C5	-0.0913 (4)	0.6637 (3)	0.8105 (2)	0.044 (2)
C6	-0.0564 (4)	0.7484 (3)	0.8784 (2)	0.044 (2)
C7	0.0707 (4)	0.7580 (3)	0.9448 (2)	0.042 (2)
C8	0.1591 (4)	0.6725 (3)	0.9375 (2)	0.038 (2)
C9	0.1277 (4)	0.5806 (2)	0.8713 (2)	0.035 (2)
C10	-0.0037 (4)	0.5786 (3)	0.8065 (2)	0.035 (2)
C11	0.2073 (8)	0.4405 (5)	0.9540 (4)	0.084 (4)
C12	0.4101 (7)	0.5231 (5)	0.8676 (6)	0.104 (5)
C13	0.2601 (13)	0.3060 (6)	0.7807 (5)	0.128 (6)
C14	-0.2384 (5)	0.4456 (4)	0.7263 (3)	0.064 (3)
C15	-0.0292 (8)	0.5252 (5)	0.6429 (3)	0.081 (3)
C16	0.1137 (7)	0.8534 (3)	1.0184 (3)	0.063 (3)
N1	-0.1591 (5)	0.8333 (3)	0.8766 (3)	0.067 (2)
N2	0.2972 (4)	0.6882 (3)	1.0084 (2)	0.054 (2)
O11	-0.1859 (5)	0.8610 (3)	0.8056 (3)	0.105 (3)
O12	-0.2122 (5)	0.8701 (3)	0.9442 (3)	0.105 (3)
O21	0.4284 (4)	0.7321 (4)	0.9952 (2)	0.100 (3)
O22	0.2705 (5)	0.6636 (3)	1.0780 (2)	0.084 (2)
(3)				
C1	0.6830 (2)	0.2147 (2)	0.2734 (2)	0.046 (1)
C2	0.7470 (3)	0.0919 (2)	0.2874 (2)	0.052 (1)

Table 2 (cont.)

	x	y	z	$U_{eq}$
C3	0.9460 (3)	0.1517 (2)	0.3680 (2)	0.054 (1)
C4	1.0548 (2)	0.2447 (2)	0.2954 (2)	0.046 (1)
C5	1.0834 (2)	0.4874 (2)	0.2258 (2)	0.040 (1)
C6	1.0273 (3)	0.5975 (2)	0.2018 (2)	0.045 (1)
C7	0.8630 (3)	0.5862 (2)	0.1998 (2)	0.048 (1)
C8	0.7625 (3)	0.4579 (2)	0.2211 (2)	0.048 (1)
C9	0.8155 (2)	0.3467 (2)	0.2486 (2)	0.039 (1)
C10	0.9852 (2)	0.3598 (2)	0.2549 (2)	0.038 (1)
C11	0.6632 (4)	0.2649 (3)	0.4073 (3)	0.071 (2)
C12	0.5024 (3)	0.1581 (3)	0.1487 (3)	0.071 (2)
C13	0.6530 (4)	-0.0237 (3)	0.3524 (4)	0.078 (2)
C14	1.2494 (3)	0.3095 (3)	0.4040 (3)	0.073 (2)
C15	1.0363 (4)	0.1469 (3)	0.1658 (3)	0.067 (2)
C16	0.7916 (4)	0.7001 (3)	0.1740 (3)	0.068 (2)
N1	1.1413 (2)	0.7284 (2)	0.1751 (2)	0.058 (1)
N2	1.2611 (2)	0.5155 (2)	0.2258 (2)	0.051 (1)
O11	1.1996 (2)	0.7140 (2)	0.0867 (2)	0.076 (1)
O12	1.1706 (3)	0.8445 (2)	0.2426 (2)	0.085 (1)
O21	1.3897 (2)	0.6138 (2)	0.3171 (2)	0.070 (1)
O22	1.2688 (2)	0.4406 (2)	0.1324 (2)	0.068 (1)

material\*). This imposes the half-chair conformation on the cyclohexene ring with C2 and C3 at opposite sides of the plane through the atoms C1, C9, C10 and C4. The methyl group attached to C2 in the three structures is invariably in the equatorial position [cf. the indan compounds in De Ridder, Čapková, Hatjisymeon, Fraanje & Schenk (1994); De Ridder & Schenk (1994) or musk tonalid (4) and its precursor (5), CSD Refcode = KIBGAF; De Ridder, Goubitz & Schenk (1990b)].

#### Endocyclic angles

**Aromatic ring.** The endocyclic angle of the aromatic C atom which carries a nitro group [i.e. C6 (1, 2 and 3) and C8 (2) or C5 (3)] is significantly larger than the

\* Lists of anisotropic displacement parameters and structure factors have been deposited with the IUCr (Reference: SH0046). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

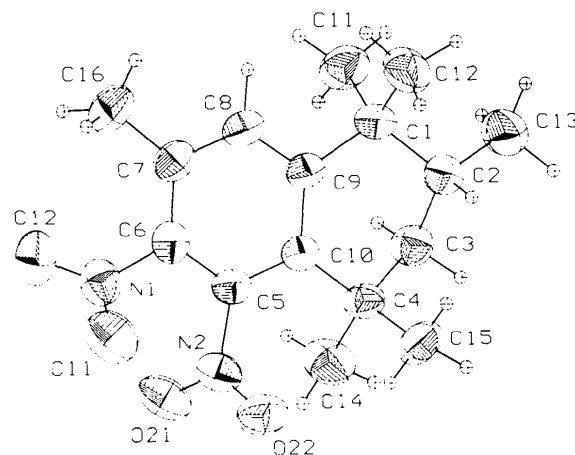


Fig. 3. Molecular structure of (3). Thermal ellipsoids are shown at 50% probability levels, H atoms as arbitrary spheres.

Table 3. Bond distances (Å) and angles (°) of the non-H atoms with standard deviations in parentheses

	(1)	(2A)	(2B)	(3)
C1—C2	1.557 (5)	1.527 (5)	1.511 (7)	1.541 (4)
C1—C9	1.530 (4)	1.553 (5)	1.547 (5)	1.543 (3)
C1—C11	1.533 (5)	1.526 (8)	1.514 (8)	1.541 (4)
C1—C12	1.529 (5)	1.530 (6)	1.527 (7)	1.533 (3)
C2—C3	1.488 (6)	1.401 (8)	1.247 (10)	1.507 (3)
C2—C13	1.545 (6)	1.563 (10)	1.557 (12)	1.536 (5)
C3—C4	1.506 (5)	1.511 (7)	1.519 (7)	1.535 (3)
C4—C10	1.527 (4)	1.524 (4)	1.535 (4)	1.530 (3)
C4—C14	1.535 (5)	1.531 (5)	1.530 (5)	1.542 (3)
C4—C15	1.545 (6)	1.539 (7)	1.507 (6)	1.543 (4)
C5—C6	1.377 (4)	1.369 (5)	1.370 (5)	1.384 (3)
C5—C10	1.390 (4)	1.390 (5)	1.390 (5)	1.406 (3)
C5—N2	—	—	—	1.477 (3)
C6—C7	1.395 (4)	1.390 (5)	1.381 (5)	1.392 (4)
C6—N1	1.468 (4)	1.470 (5)	1.474 (6)	1.471 (3)
C7—C8	1.388 (4)	1.387 (5)	1.397 (5)	1.379 (3)
C7—C16	1.511 (5)	1.519 (5)	1.518 (5)	1.505 (5)
C8—C9	1.406 (4)	1.406 (4)	1.416 (4)	1.386 (3)
C8—N2	—	1.487 (4)	1.481 (4)	—
C9—C10	1.402 (4)	1.412 (4)	1.406 (4)	1.419 (3)
N1—O11	1.218 (4)	1.225 (6)	1.223 (7)	1.222 (3)
N1—O12	1.217 (4)	1.229 (6)	1.214 (6)	1.222 (3)
N2—O21	—	1.215 (5)	1.210 (5)	1.222 (2)
N2—O22	—	1.222 (5)	1.204 (5)	1.228 (3)
C2—C1—C9	109.7 (3)	108.6 (3)	109.3 (4)	111.7 (2)
C2—C1—C11	106.6 (3)	107.4 (4)	107.2 (4)	110.6 (2)
C2—C1—C12	112.8 (3)	110.7 (4)	109.4 (5)	108.1 (2)
C9—C1—C11	109.8 (3)	111.0 (4)	110.6 (4)	107.6 (2)
C9—C1—C12	108.7 (3)	108.6 (3)	110.8 (4)	108.9 (2)
C11—C1—C12	109.2 (3)	110.6 (5)	109.5 (5)	109.9 (2)
C1—C2—C3	113.1 (3)	119.1 (5)	128.6 (7)	110.5 (2)
C1—C2—C13	113.7 (4)	113.6 (4)	115.4 (6)	114.5 (3)
C3—C2—C13	111.6 (3)	111.9 (5)	116.0 (6)	110.0 (2)
C2—C3—C4	115.2 (3)	118.8 (5)	125.9 (5)	114.3 (2)
C3—C4—C10	110.0 (3)	110.5 (3)	109.7 (3)	108.7 (2)
C3—C4—C14	113.7 (3)	111.5 (4)	108.0 (4)	104.9 (2)
C3—C4—C15	105.9 (3)	107.9 (4)	110.3 (4)	108.9 (2)
C10—C4—C14	109.4 (3)	109.7 (3)	110.1 (3)	112.6 (2)
C10—C4—C15	110.4 (3)	109.8 (3)	109.8 (3)	111.3 (2)
C14—C4—C15	107.3 (3)	107.3 (3)	108.8 (4)	110.2 (2)
C6—C5—C10	121.7 (3)	121.8 (3)	121.3 (3)	123.7 (2)
C6—C5—N2	—	—	—	115.2 (2)
C10—C5—N2	—	—	—	121.1 (2)
C5—C6—C7	122.3 (3)	122.7 (3)	123.3 (3)	121.4 (2)
C5—C6—N1	116.5 (3)	116.7 (3)	116.6 (3)	119.7 (2)
C7—C6—N1	121.2 (3)	120.5 (3)	120.1 (3)	118.9 (2)
C6—C7—C8	115.2 (3)	113.5 (3)	113.9 (3)	114.9 (2)
C6—C7—C16	125.2 (3)	123.6 (3)	123.5 (4)	124.8 (2)
C8—C7—C16	119.5 (3)	122.7 (3)	122.6 (3)	120.2 (3)
C7—C8—C9	124.4 (3)	127.6 (3)	126.4 (3)	125.4 (3)
C7—C8—N2	—	111.2 (3)	111.8 (3)	—
C9—C8—N2	—	121.2 (3)	121.8 (3)	—
C1—C9—C8	118.4 (2)	123.5 (3)	122.3 (3)	116.4 (2)
C1—C9—C10	123.4 (2)	121.6 (3)	122.3 (3)	123.9 (2)
C8—C9—C10	118.1 (2)	114.9 (3)	115.3 (3)	119.7 (2)
C4—C10—C5	118.3 (2)	116.0 (3)	116.6 (3)	123.7 (2)
C4—C10—C9	123.4 (2)	124.7 (3)	123.6 (3)	121.5 (2)
C5—C10—C9	118.3 (3)	119.3 (3)	119.7 (3)	114.7 (2)
C6—N1—O11	118.4 (3)	117.2 (4)	116.9 (4)	118.0 (2)
C6—N1—O12	118.9 (3)	118.1 (4)	118.6 (4)	117.5 (3)
O11—N1—O12	122.6 (3)	124.7 (4)	124.5 (4)	124.4 (2)
C5—N2—O21	—	—	—	117.6 (2)
C5—N2—O22	—	—	—	117.8 (2)
C8—N2—O21	—	117.5 (3)	117.7 (3)	—
C8—N2—O22	—	117.5 (3)	118.6 (3)	—
O21—N2—O22	—	124.7 (4)	123.5 (4)	124.7 (2)

other endocyclic angles, whereas the endocyclic angle at C7 (aromatic C atom which carries the methyl group) is significantly smaller, in agreement with the findings of Domenicano, Vacigo & Coulson (1975a,b).

*Cyclohexene ring.* The value of the endocyclic angles at the fusion with the aromatic ring (C1—C9—C10 and C4—C10—C9) lies in the range 121.5 (2)–124.7 (3)°. This range compares very well with musk tonalid (4) or its precursor (5) (De Ridder, Goubitz & Schenk, 1990b) or two formylated tetralin musk compounds [(6) and (7); De Ridder, Fraanje, Goubitz & Schenk (1994)]. In a study of the geometry of small rings, Allen (1981) found a value of 117.2 (9)° for 84 benzocyclohexene compounds (value of  $\epsilon$  in column 6, Table 2 of Allen's paper). In his contribution, the author allowed the C2 and C3 atoms to be C, N or O and benzoquinones were not included. A search (De Ridder, 1993) in the October 1993 release of the Cambridge Structural Database [Allen *et al.* (1991): Version 5.06, 114 924 entries] using a similar query resulted in 388 fragments with an average value of 117.0 (2)°. In the distribution of the averaged endocyclic angle, three distinct curves could be detected. The lowest curve with angles in the range 104–107° contains compounds in which C1 and C4 are connected by a C, N or O bridging atom, whereas the medium part of the distribution (110–116°) includes compounds in which C1 and C4 are in general connected by an ethylene bridge. The highest curve (from 116 to 124°) contains compounds in which there is no supplementary ring fusion between C1 and C4, as in the musk compounds of the tetralin group.

#### Disorder

Here the same type of disorder is possible as with the indan musks (De Ridder, Čapková, Hatjisyneon, Fraanje & Schenk, 1994), due to partial substitution of molecules by their enantiomers. This disorder affects C2 and C3 and the methyl groups attached to the cyclohexene ring. This type of disorder is encountered in (2A) and (2B). Again it manifests itself in relatively high displacement parameters and deviating bond distances and angles for the atoms involved. It is also apparent from the distances of C2 and C3 from the plane through the C1, C9, C10 and C4 atoms listed in Table 4. For comparison, the corresponding values of musk tonalid (4) and its precursor (5) (De Ridder, Goubitz & Schenk, 1990b) are also reported in Table 4.

The manifestly high disorder is also reflected in the high *R*-value of (2) in Table 1.

The C2—C3 bond lengths of 1.488 (6) and 1.507 (3) Å for (1) and (3), respectively, are significantly shortened and indicate that these compounds may also contain a small amount of the enantiomorphic molecule.

#### Orientation of the nitro groups with respect to the aromatic ring

The angles between the nitro groups and the phenyl ring are listed in Table 5.

The nitro groups behave as in the nitroindan and nitrobenzene musks [see, respectively, De Ridder &

Table 4. Distance (Å) from the plane through C1, C9, C10, C4

Structure	C2	C3
(1) <sup>a</sup>	0.340 (6)	-0.344 (6)
(2A) <sup>a</sup>	0.386 (8)	-0.134 (9)
(2B) <sup>a</sup>	0.022 (11)	0.096 (8)
(3) <sup>a</sup>	-0.242 (4)	0.500 (4)
(4) <sup>b</sup>	-0.400 (3)	0.301 (3)
(5) <sup>b</sup>	0.292 (4)	-0.408 (4)

(a) This work; (b) De Ridder, Goubitz & Schenk (1990b).

Table 5. Angles (°) of the nitro groups with the aromatic plane

Structure	C5	C6	C7	C8
(1)	—	33 (1)	—	—
(2A)	—	42.2 (2)	—	83.6 (2)
(2B)	—	46.4 (2)	—	88.6 (2)
(3)	66.2 (1)	51.3 (1)	—	—

Schenk (1994), De Ridder, Goubitz & Schenk (1990a), or De Ridder, Fraanje & Schenk (1994)]. Nitro groups with the two adjacent sites occupied by a methyl and a pseudo-*tert*-butyl group, as in (2), are nearly perpendicular to the phenyl ring. The nitro groups with only one neighbouring site occupied make an angle of *ca* 40° with the ring. The nitro groups in (3) are in an intermediate position. With both neighbouring sites occupied, the perpendicular position can be avoided by concerted rotation of the two nitro groups. This behaviour is in accordance with the results discussed in De Ridder & Schenk (1995b).

### Concluding remarks

The first crystal-structure determination of a crystal of the batch supposed to contain the compound with structure (2) yielded structure (3). No other crystals suitable for X-ray diffraction were found in this batch. Attempts to recrystallize samples of this batch by slow evaporation using different solvents (*e.g.* methanol, ethanol or 1:1 methanol/ethanol) at room temperature failed. A few crystals having structure (2) were obtained only after recrystallization of a sample by sublimation. Further nitration of the mononitro compound (1) will give a small amount of the *ortho*-dinitrotetralin (3) with a large yield of the *meta*-dinitrotetralin (2), but no satisfactory explanation can be given at this moment why the former compound forms single crystals more easily. The NMR spectrum obtained from the batch containing the mononitrotetralin corroborates with the crystal structure of (1), whereas the NMR spectrum obtained from the batch containing the dinitrotetralin corroborates with the crystal structure of (2) and no indication for (3) is found (De Ridder, Schenk & Genevasen, 1993).

The powder diffraction diagram calculated from the single-crystal data of (2) corresponds qualitatively with the experimental powder diffraction diagram obtained from the batch containing the dinitrotetralin, whereas the calculated powder diagram for (3) is significantly different (De Ridder, Driessen, Goubitz, & Schenk, 1991).

Analogous to the indan musk compounds [nitrated (see De Ridder & Schenk, 1994) as well as acylated (see De Ridder, Čapková, Hatjisymeon, Fraanje & Schenk, 1994)], the methyl group attached to C2 is found in an equatorial position. This feature is also observed in musk tonalid (4) and its precursor (5) (De Ridder, Goubitz & Schenk, 1990b) or in the formyl equivalent (6) of (1) and musk tonalid (De Ridder, Fraanje, Goubitz & Schenk, 1994). This feature becomes even more important if one takes into account that the sterical intramolecular hindrance between the methyl group attached to C2 and the other methyl groups substituted at the non-aromatic ring will be somewhat smaller for tetralin than for indan musk compounds. Therefore, recent structure-activity relationship studies on muskiness [Narvaez, Lavine & Jurs (1986); Bersuker, Dimoglo, Gorbachov, Vlad & Pesaro (1991)], in which geometric details play an important role, have to be considered with the necessary precautions. In both studies, these details are taken from geometries obtained by means of molecular modelling, but in none of the papers is it clear whether the alkyl group (mostly a methyl group) attached to C2 has been taken to be equatorial (as found in the crystal structure) or axial. It should also be noted that C2 is an asymmetric C atom. Although the natural musk compounds have no asymmetric C atom(s), some of the synthetic bicyclic compounds show this feature. According to Ohloff, Winter & Fehr (1990), only one of the stereoisomers shows muskiness analogous to androstenol (steroid musk): the  $\alpha$ -OH compound has a musk odour, whereas the  $\beta$ -OH compound is odourless.

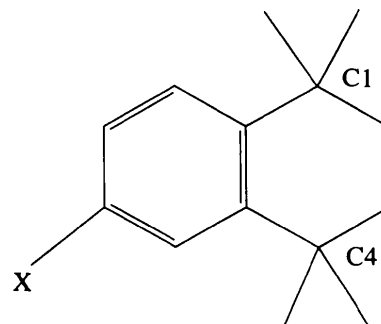


Fig. 4. Scheme of the 'osmophoric triangle' formed by the two quaternary C1 and C4 atoms and X, in which the latter is the N atom of a nitro group or the  $sp^2$ -C atom of an acyl group. In this scheme, the X atom is attached to a  $\beta$ -position.

Table 6. Dimensions of the triangle (Å, for definition see text)

Structure	Functional group	A	B	C
(1) <sup>a</sup>	$\beta$ -Nitro	3.086 (4)	5.773 (4)	4.916 (4)
(2A) <sup>a</sup>	$\alpha$ -Nitro (C8)	3.094 (5)	5.114 (4)	3.034 (5)
	$\beta$ -Nitro	3.094 (5)	5.825 (5)	4.876 (5)
(2B) <sup>a</sup>	$\alpha$ -Nitro (C8)	3.085 (5)	5.119 (4)	3.026 (4)
	$\beta$ -Nitro	3.085 (5)	5.819 (6)	4.899 (5)
(3) <sup>a</sup>	$\alpha$ -Nitro (C5)	3.080 (3)	5.118 (3)	3.019 (3)
	$\beta$ -Nitro	3.080 (3)	5.780 (3)	5.053 (3)
(4) <sup>b</sup>	Acetyl	3.0477 (8)	5.845 (1)	5.011 (1)
(5) <sup>b</sup>	—	3.0820 (2)	—	—
(6) <sup>c</sup>	Formyl	3.078 (5)	5.802 (7)	4.948 (7)
(7) <sup>c</sup>	Formyl	3.057 (5)	5.789 (6)	5.115 (6)

(A) Distance between quaternary C-atoms; (B) and (C) distance between quaternary C-atom and N or the  $sp^2$ -C atom.

(a) This work; (b) De Ridder, Goubitz & Schenk (1990b); (c) De Ridder, Fraanje, Goubitz & Schenk (1994).

Following the line of thought of the preceding paper (De Ridder & Schenk, 1994), there is again reason to assume that the nitro group in the  $\beta$ -position has the osmophoric function. Indeed, the angle between the  $\beta$ -nitro group in (1), (2A) and (2B) and the aromatic plane lies within the range found for the nitroindan musk compounds, whereas the more sterically hindered  $\alpha$ -nitro group in (2) is almost perpendicular to this plane and thus may function as a detail of the molecular profile according to Beets (1957, 1977).

As with the indan musks, it is possible to compare the dimensions of a triangle (see Fig. 4) defined by the two quaternary C atoms (C1 and C4) and the N atom of the nitro group(s) or the  $sp^2$ -C atom (C16) of the acyl group of the compounds described in De Ridder, Goubitz & Schenk (1990b) and De Ridder, Fraanje, Goubitz & Schenk (1994). From Table 6 it is seen that the dimensions for the  $\beta$ -nitro groups compare very well with the acetyl- or formyl-type compounds, whereas the C<sub>tert</sub>—N distances for the  $\alpha$ -nitro groups in (2) are significantly smaller.

The possible muskiness of (3) is an interesting question to be addressed. Although the dimensions of the triangle for the  $\beta$ -nitro group of (3) are comparable with the values found in (1) and (2), this does not mean that (3) will have a musk odour. From Table 5 it is seen that the angle between the  $\beta$ -nitro group and the aromatic ring in (3) is not much larger than in (2). If one takes into consideration that in the family of the nitrobenzene musk compounds the angle the nitro group makes is probably not a decisive factor for muskiness [49° in musk ambrette (De Ridder, Goubitz & Schenk, 1990a) compared with 84° in musk tibetene (De Ridder, 1992) or 79° in the odourless isomer of the latter (De Ridder, Fraanje & Schenk, 1994)], the  $\beta$ -nitro group in (3) may well fulfil the osmophoric function. Nevertheless, the intramolecular forces acting between the two *ortho*-nitro groups may well be too strong to

be overruled by the weaker intermolecular forces acting between the osmophoric group and the receptor site. A decisive answer to this question can only be given if (3) could be produced in a sufficient yield so that it could be subjected to odour panels.

Some structure–activity relationship studies will be discussed in the light of the geometrical results of our crystal studies in a separate contribution (De Ridder & Schenk, 1995a).

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## The Charge-Density Distribution in Hexamethylenetetramine at 120 K

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### Abstract

The charge-density distribution has been determined from 333 independent X-ray reflections with  $\sin\theta/\lambda < 1.47 \text{ \AA}^{-1}$ , which were collected with Ag  $K\alpha$  radiation. As found in a recent refinement using room-temperature data, full-matrix least squares refinement with a multipole model gives rise to an almost complete correlation between certain octapole deformation terms. This is the worst case example of a problem which will always arise to some degree when applying the multipole model in a noncentrosymmetric space group. In this example, the correlation arises between terms which are predominant for describing the bonding density between atoms of the molecule, thereby causing the deformation charge density to have little meaning. However, the total molecular electrostatic potential and the molecular octapole moment are reliably obtained.

### Introduction

The crystal structure of urotropin or hexamethylenetetramine (HMT,  $\text{C}_6\text{H}_{12}\text{N}_4$ ; see Fig. 1) is well known (Dickinson & Raymond, 1923) and has been intensively studied. This highly symmetric molecule crystallizes in a noncentrosymmetric space group with all three atoms in the asymmetric unit (C, N and H) lying in special positions. It is of special interest that the molecular symmetry ( $\bar{4}3m$ ) is fully expressed in the space group  $I\bar{4}3m$ .

We have measured new low-temperature (120 K) X-ray diffraction data for HMT in order to study the charge-density distribution. New neutron diffraction

data have also been measured at six temperatures (15, 50, 80, 120, 160 and 200 K) in a parallel study of neutron extinction and the nuclear thermal vibrations in HMT (Kampermann, Sabine, Craven & McMullan, 1994).

Terpstra, Craven & Stewart (1993) carried out multipole least-squares refinements for HMT using the pseudoatom model of Stewart (1976) and the room-temperature X-ray data of Stevens & Hope (1975). They found that the octapole deformation terms  $o_4$  for C and N atoms are almost completely correlated in the least-squares refinement. The effect is crucial for a detailed study of the deformation charge density, because the  $o_4$  term largely describes

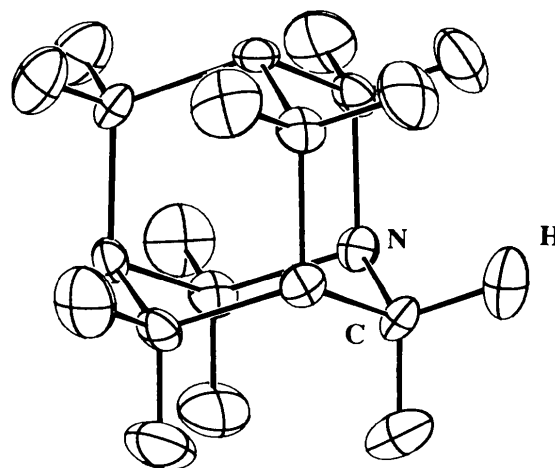


Fig. 1. Molecular structure for HMT (120 K) with harmonic m.s. displacements represented as thermal ellipsoids at the 50% probability level (Johnson, 1976).

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