

son, we may give other calculations of the *R* factor. When we calculate the structure factors without the contribution of the cyclopentanone molecule in the threefold site, the value of *R* is 0.117 instead of 0.086; the structure-factor calculation without the contribution of the guest in the sixfold site gives an *R* value of 0.095 instead of 0.086.

In conclusion, the best match between the molecular shape and the neutron diffraction density in the threefold site corresponds to the chiral conformer (2), strongly supporting the idea of chiral discrimination. Better discrimination in the threefold site than in the sixfold site may be explained by the greater interaction between host and guest in relation with the shorter intermolecular distances as seen above.

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## Crystal Studies of Musk Compounds. XI.\* Molecular Structures of Musk Moskene and Two Homologues

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#### Abstract

The crystal structures of 1,1,3,3,5-pentamethyl-4,6-dinitroindan (1), 1,1,2,3,3,6-hexamethyl-5-nitroindan (2) and 1,1,2,3,3,5-hexamethyl-4,6-dinitroindan (3) have been established by X-ray crystallography. (1) and (3) are strong musks. Some of the structures described show disorder in the cyclopentene ring and/or in the nitro groups. This manifests itself in relatively high displacement parameters and in deviating bond distances and angles. The endocyclic angles of the cyclopentene ring, at the fusion with the aromatic ring,

are significantly larger than reported in a study of the geometry of small rings [Allen (1981). *Acta Cryst.* **B37**, 900–906]. The geometry and position on the aromatic ring of the nitro groups is compared with the acylated indan musk compounds and evidence is given that the nitro group in the  $\beta$ -position fulfils the osmophoric function.

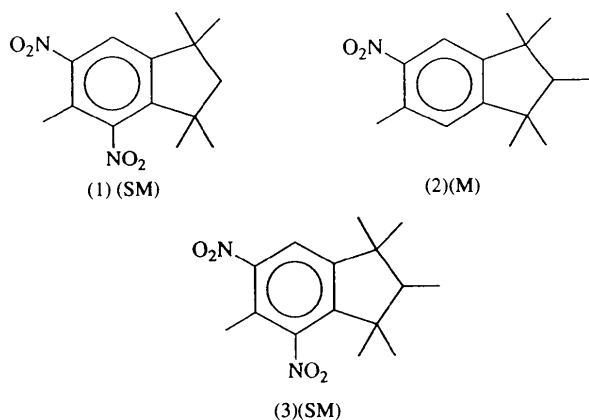
#### Introduction

In part VIII of this series (De Ridder, Čapková, Hatjisymeon, Fraanje & Schenk, 1994), the crystal structures of five homologues of musk phantolid are reported, which all carry an acyl group on the aromatic ring. In this paper, the crystal structures of indan compounds having one or more nitro groups attached

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

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to the aromatic ring are described. They are presented in the following scheme.



Key: SM = strong musk; M = musk

Compound (1), a strong musk, was first prepared by Henri Barbier (1932) by condensing *p*-cymene with *tert*-butylalcohol in the presence of sulfuric acid and nitrating the resulting product. He called it *moskene* and assigned it the structure 2,6-dinitro-3-*tert*-butyl-4-isopropyltoluene (C<sub>14</sub>H<sub>20</sub>N<sub>2</sub>O<sub>4</sub>). This structure remained unquestioned for more than 20 years until Carpenter & Easter's (1954) unsuccessful attempt to replace the isopropyl group by a nitro group under drastic conditions. The authors then questioned the correctness of Barbier's structure and subsequently identified *moskene* as 1,1,3,3,5-pentamethyl-4,6-dinitroindan (C<sub>14</sub>H<sub>18</sub>N<sub>2</sub>O<sub>4</sub>).

(2) and (3) are closely related to *moskene*: (3) has an additional CH<sub>3</sub> at position 2 and is a strong musk (Lenselink, 1989). (2) is an intermediate in the synthesis of (3), with only one NO<sub>2</sub> group, and also has a musk odour (Lenselink, 1989). (2) is the nitro equivalent of musk phantolid, of which the crystal structure has been reported earlier (De Ridder & Schenk, 1991a).

It is interesting to remark that, besides their odour qualities, some compounds of this type of musk are excellent pre-emergence herbicides, especially against grasses (Wood, 1968).

The research of nitro musks knew only a short popularity in the 1950's, after which the emphasis shifted towards research of the non-nitro aromatic musks. From about 1980 onwards, the use of nitro musks has been put into question on the suspicion that they might have phototoxic and photoallergic properties and might possibly even cause liver cancer.

### Experimental

The compounds were synthesized (by PFW-Amersfoort) by the literature methods mentioned in the Introduction. All crystals are colourless. The intensities of all the crystal structures described in this paper were

Table 1. Crystal data, data collection and refinement parameters

	(1)	(2)	(3)
<b>Crystal data</b>			
Chemical formula	C <sub>14</sub> H <sub>18</sub> N <sub>2</sub> O <sub>4</sub>	C <sub>15</sub> H <sub>21</sub> NO <sub>2</sub>	C <sub>15</sub> H <sub>20</sub> N <sub>2</sub> O <sub>4</sub>
Molecular weight	278.31	247.34	292.33
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>a</i> (Å)	9.6789 (9)	8.623 (1)	8.364 (2)
<i>b</i> (Å)	15.6129 (15)	10.600 (10)	11.668 (1)
<i>c</i> (Å)	9.5209 (12)	15.366 (2)	15.996 (2)
$\beta$ (°)		94.49 (1)	100.17 (2)
<i>V</i> (Å <sup>3</sup> )	1438.8 (2)	1400 (1)	1536.5 (5)
<i>Z</i>	4	4	4
<i>D<sub>x</sub></i> (g cm <sup>-3</sup> )	1.29	1.17	1.26
Radiation type	Cu <i>K</i> α	Cu <i>K</i> α	Cu <i>K</i> α
Wavelength (Å)	1.5418	1.5418	1.5418
$\mu$ (cm <sup>-1</sup> )	7.49	5.79	7.24
<i>F</i> (000)	592	536	624
<b>Data collection</b>			
Crystal size (mm)	0.4 × 0.3 × 0.15	0.3 × 0.3 × 0.05	0.5 × 0.4 × 0.25
Temperature (K)	198	236	259
Cell parameter determination no.			
$\theta$ range (°)	35.7–44.8	23.0–28.0	39.9–43.5
$\theta_{\min}$ , $\theta_{\max}$ (°)	2.5–70	2.5–70	2.5–70
<i>h</i> , <i>k</i> , <i>l</i>	0 → <i>h</i> → 11 0 → <i>k</i> → 19 0 → <i>l</i> → 11	-10 → <i>h</i> → 10 0 → <i>k</i> → 12 0 → <i>l</i> → 18	-10 → <i>h</i> → 10 0 → <i>k</i> → 14 0 → <i>l</i> → 19
Intensity control reflections (variation)	320; 013	101; 103	210; 002
No. of intensity measurements	(not significant)	(not significant)	(not significant)
No. of unique reflections	1628	2888	3128
No. of observed reflections	1576	2644	2902
No. of observed reflections	1401	997	1914
Observation criterion	[ <i>I</i> > 2.5σ( <i>I</i> )]	[ <i>I</i> > 2.5σ( <i>I</i> )]	[ <i>I</i> > 2.5σ( <i>I</i> )]
Max./min. absorption	1.64/0.63	1.11/0.65	1.30/0.71
Direct methods program	SAPP <sup>a</sup>	SIMPEL <sup>b</sup>	SIMPEL <sup>b</sup>
Crystallographic program package	Xtal2.6 <sup>c</sup>	Xtal3.0 <sup>d</sup>	Xtal3.0 <sup>d</sup>
<b>Refinement</b>			
<i>R</i>	0.064	0.071	0.081
<i>wR</i>	0.083	0.102	0.106
<i>S</i>	0.23	0.33	0.28
Weighting scheme			
<i>a</i>	6.6	6.0	5.2
<i>b</i>	0.0024	0.015	0.0070
(Δ/σ) <sub>max</sub> in final cycle	0.06	0.94	0.61
No. of parameters refined	254	247	270
No. of restraints	18	21	20
Min./max. heights in final Δ <i>F</i> -map (e Å <sup>-3</sup> )	-0.3/0.6	-0.3/0.4	-0.4/1.1
Extinction parameter <i>g</i>	3 (5) × 10 <sup>-7</sup>	4 (22) × 10 <sup>-7</sup>	2 (2) × 10 <sup>-6</sup>

(a) Yao *et al.* (1985); (b) Schenk & Hall (1990); (c) Hall & Stewart (1989); (d) Hall & Stewart (1990).

collected with an Enraf-Nonius CAD-4 diffractometer, employing graphite-monochromated Cu *K*α radiation ( $\lambda = 1.5418$  Å) and  $\theta$ -2 $\theta$  scans. Because of high volatility, the crystals were measured at reduced tem-

perature (see Table 1). Two intensity control reflections were monitored every 3600 s. Three 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 derived from a  $\Delta F$  synthesis and restrained in such a way that the distances to their carrier atoms were fixed at 1.09 Å. 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 data collection and refinement are summarized in Table 1.

(1) 1,1,3,3,5-Pentamethyl-4,6-dinitroindan (*musk moskene*). A crystal was mounted inside a thin-walled glass capillary. Preliminary Weissenberg photographs indicated the crystals to be orthorhombic.

(2) 1,1,2,3,3,6-Hexamethyl-5-nitroindan. A sample of the crystals was recrystallized by slow evaporation at low temperature from ethanol. The crystals are monoclinic. The H-atom positions were introduced at their calculated positions. The displacement parameter of H2 was kept fixed at 0.08 Å<sup>2</sup>.

(3) 1,1,2,3,3,5-Hexamethyl-4,6-dinitroindan. A sample of the crystals was recrystallized by slow evaporation from methanol. A crystal from the sample was then mounted inside a thin-walled glass capillary. Preliminary Weissenberg photographs indicated the crystals to be monoclinic.

The final residual electron density for (1) and, in particular, for (3) is significant and can presumably be attributed to an artefact of *DIFABS* (Walker & Stuart, 1983).

The calculations for structure (1) were performed with *Xtal2.6* (Hall & Stewart, 1989) and *Xtal3.0* (Hall & Stewart, 1990) for the remaining structures. The scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. 4).

A note should be made on the fact that this type of compound often needs several recrystallization attempts in order to obtain crystals suitable for single-crystal X-ray diffraction experiments. The Weissenberg photographs were taken at room temperature, during which the crystal evaporated most of the time. For this reason, (1) and (3) were mounted on a thin-walled glass capillary and measured at reduced temperature.

### Results and discussion

The final coordinates and equivalent displacement parameters of the non-H atoms are listed in Table 2.

Table 2. Fractional coordinates of the non-H atoms and equivalent isotropic displacement parameters

$$U_{\text{eq}} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

Structure (1)	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}$ (Å <sup>2</sup> )
C1	0.8751 (4)	0.0394 (3)	0.9940 (5)	0.034 (2)
C2	0.8319 (6)	0.1304 (3)	0.9493 (6)	0.045 (3)
C3	0.6770 (5)	0.1455 (3)	0.9888 (6)	0.036 (2)
C4	0.4930 (4)	0.0200 (3)	1.0022 (5)	0.032 (2)
C5	0.4612 (4)	-0.0670 (3)	1.0138 (5)	0.031 (2)
C6	0.5752 (5)	-0.1202 (3)	1.0194 (5)	0.035 (2)
C7	0.7117 (4)	-0.0920 (3)	1.0150 (5)	0.031 (2)
C8	0.7350 (4)	-0.0050 (3)	1.0043 (5)	0.028 (2)
C9	0.6258 (4)	0.0530 (3)	0.9972 (4)	0.029 (2)
C10	0.9513 (6)	0.0369 (4)	1.1357 (5)	0.049 (3)
C11	0.9645 (5)	-0.0018 (4)	0.8813 (6)	0.047 (3)
C13	0.6580 (7)	0.1920 (4)	1.1302 (7)	0.056 (3)
C14	0.6069 (7)	0.1974 (4)	0.8711 (6)	0.048 (3)
C15	0.3119 (5)	-0.0970 (4)	1.0215 (8)	0.053 (3)
N1	0.5547 (5)	-0.2136 (2)	1.0317 (5)	0.045 (2)
N2	0.3731 (4)	0.0791 (3)	0.9945 (6)	0.046 (2)
O11	0.6218 (5)	-0.2516 (3)	1.1225 (5)	0.067 (3)
O12	0.4736 (6)	-0.2485 (3)	0.9582 (7)	0.103 (4)
O21	0.3415 (5)	0.1172 (3)	1.0998 (6)	0.077 (3)
O22	0.3152 (4)	0.0853 (3)	0.8800 (5)	0.067 (3)
Structure (2)				
C1	0.7397 (8)	0.8552 (7)	0.3815 (5)	0.046 (4)
C2	0.623 (1)	0.893 (1)	0.302 (1)	0.110 (9)
C3	0.4915 (9)	0.7984 (8)	0.2932 (5)	0.054 (5)
C4	0.5010 (8)	0.5661 (7)	0.3477 (5)	0.045 (4)
C5	0.5769 (8)	0.4710 (7)	0.3975 (5)	0.046 (4)
C6	0.7130 (8)	0.5086 (7)	0.4457 (4)	0.041 (4)
C7	0.7736 (8)	0.6286 (8)	0.4462 (5)	0.047 (4)
C8	0.6962 (8)	0.7195 (7)	0.3935 (5)	0.042 (4)
C9	0.5582 (8)	0.6860 (7)	0.3448 (4)	0.044 (4)
C10	0.904 (1)	0.870 (1)	0.3554 (7)	0.074 (7)
C11	0.719 (2)	0.930 (1)	0.4624 (9)	0.11 (1)
C12	0.595 (1)	1.0270 (9)	0.2822 (7)	0.074 (7)
C13	0.458 (2)	0.762 (1)	0.1965 (6)	0.098 (9)
C14	0.337 (1)	0.838 (1)	0.3260 (7)	0.079 (7)
C15	0.508 (1)	0.3415 (8)	0.3979 (6)	0.055 (5)
N1	0.8013 (7)	0.4174 (7)	0.5027 (4)	0.050 (4)
O11	0.8645 (7)	0.4543 (6)	0.5708 (4)	0.071 (4)
O12	0.8088 (8)	0.3082 (5)	0.4772 (4)	0.075 (4)
Structure (3)				
C1	-0.0039 (5)	0.4616 (4)	0.2915 (3)	0.052 (2)
C2	0.1669 (7)	0.4715 (6)	0.3468 (3)	0.078 (3)
C3	0.2902 (5)	0.4978 (4)	0.2857 (3)	0.049 (2)
C4	0.2541 (5)	0.4150 (3)	0.1290 (3)	0.044 (2)
C5	0.1572 (5)	0.3695 (3)	0.0573 (2)	0.048 (2)
C6	-0.0048 (5)	0.3523 (3)	0.0663 (3)	0.048 (2)
C7	-0.0647 (5)	0.3779 (4)	0.1391 (3)	0.047 (2)
C8	0.0385 (4)	0.4257 (3)	0.2075 (2)	0.041 (2)
C9	0.2010 (4)	0.4442 (3)	0.2036 (2)	0.041 (2)
C10	-0.0953 (8)	0.3651 (7)	0.3300 (4)	0.080 (4)
C11	-0.1151 (7)	0.5660 (5)	0.2787 (4)	0.073 (4)
C12	0.1795 (8)	0.5515 (6)	0.4232 (3)	0.081 (4)
C13	0.4452 (8)	0.4345 (7)	0.3235 (4)	0.091 (4)
C14	0.324 (1)	0.6228 (6)	0.2728 (4)	0.107 (5)
C15	0.2262 (8)	0.3413 (5)	-0.0213 (3)	0.070 (3)
N1	-0.1202 (6)	0.3017 (4)	-0.0034 (3)	0.069 (3)
N2	0.4292 (5)	0.4307 (4)	0.1251 (3)	0.064 (3)
O11	-0.2149 (6)	0.2332 (5)	0.0140 (3)	0.124 (4)
O12	-0.1146 (6)	0.3314 (4)	-0.0764 (2)	0.097 (3)
O21	0.5191 (4)	0.3508 (4)	0.1429 (3)	0.100 (3)
O22	0.4727 (6)	0.5231 (4)	0.1049 (4)	0.119 (4)

The bond distances and angles are given in Table 3. A table showing the deviations of the atoms of the aromatic ring and the attached atoms from the least-squares plane through the ptenyl ring atoms has been deposited as

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

	(1)	(2)	(3)
C1—C2	1.541 (7)	1.57 (1)	1.545 (6)
C1—C8	1.525 (6)	1.50 (1)	1.510 (6)
C1—C10	1.538 (7)	1.51 (1)	1.548 (8)
C1—C11	1.521 (7)	1.50 (2)	1.524 (7)
C2—C3	1.564 (7)	1.51 (1)	1.571 (7)
C2—C12	—	1.47 (1)	1.527 (9)
C3—C9	1.529 (6)	1.52 (1)	1.525 (5)
C3—C13	1.541 (8)	1.54 (1)	1.521 (8)
C3—C14	1.541 (8)	1.52 (1)	1.507 (8)
C4—C5	1.397 (6)	1.40 (1)	1.388 (5)
C4—C9	1.386 (6)	1.37 (1)	1.386 (6)
C4—N2	1.484 (6)	—	1.489 (6)
C5—C6	1.381 (6)	1.40 (1)	1.402 (6)
C5—C15	1.521 (7)	1.50 (1)	1.509 (7)
C6—C7	1.394 (6)	1.38 (1)	1.379 (6)
C6—N1	1.477 (6)	1.48 (1)	1.465 (6)
C7—C8	1.380 (6)	1.39 (1)	1.385 (5)
C8—C9	1.394 (6)	1.401 (9)	1.388 (5)
N1—O11	1.234 (7)	1.206 (9)	1.193 (7)
N1—O12	1.184 (8)	1.226 (9)	1.226 (6)
N2—O21	1.205 (7)	—	1.200 (6)
N2—O22	1.230 (7)	—	1.200 (7)
C2—C1—C8	101.3 (4)	101.0 (6)	101.0 (4)
C2—C1—C10	113.3 (4)	108.8 (8)	107.4 (4)
C2—C1—C11	110.4 (4)	113.7 (9)	119.9 (4)
C8—C1—C10	111.0 (4)	112.4 (7)	111.2 (4)
C8—C1—C11	111.1 (4)	110.8 (8)	109.6 (4)
C10—C1—C11	109.6 (4)	109.8 (9)	107.6 (4)
C1—C2—C3	109.4 (4)	109.1 (9)	107.5 (4)
C1—C2—C12	—	119.5 (9)	115.4 (5)
C3—C2—C12	—	120.9 (9)	114.7 (5)
C2—C3—C9	100.4 (4)	102.9 (7)	100.4 (3)
C2—C3—C13	113.3 (5)	109.7 (9)	105.4 (4)
C2—C3—C14	109.1 (4)	117.2 (8)	115.7 (5)
C9—C3—C13	111.2 (4)	109.9 (8)	113.4 (4)
C9—C3—C14	113.1 (4)	110.4 (7)	110.7 (4)
C13—C3—C14	109.5 (5)	106.6 (8)	110.0 (5)
C5—C4—C9	124.6 (4)	122.3 (7)	125.2 (4)
C5—C4—N2	115.9 (4)	—	116.6 (4)
C9—C4—N2	119.5 (4)	—	118.2 (3)
C4—C5—C6	114.3 (4)	115.0 (7)	113.7 (4)
C4—C5—C15	120.8 (4)	119.7 (6)	121.3 (4)
C6—C5—C15	124.9 (4)	125.2 (7)	125.0 (4)
C5—C6—C7	124.5 (4)	124.8 (7)	123.9 (3)
C5—C6—N1	119.3 (4)	120.0 (7)	119.9 (4)
C7—C6—N1	116.2 (4)	115.2 (6)	116.2 (4)
C6—C7—C8	117.9 (4)	118.1 (6)	119.0 (4)
C1—C8—C7	126.7 (4)	128.4 (6)	127.1 (4)
C1—C8—C9	112.0 (4)	112.8 (6)	112.5 (3)
C7—C8—C9	121.3 (4)	118.9 (7)	120.4 (4)
C3—C9—C4	130.8 (4)	128.6 (6)	131.3 (3)
C3—C9—C8	111.8 (4)	110.6 (6)	111.0 (3)
C4—C9—C8	117.4 (4)	120.9 (7)	117.7 (3)
C6—N1—O11	117.4 (4)	118.6 (7)	117.9 (3)
C6—N1—O12	119.8 (5)	117.8 (6)	118.7 (4)
O11—N1—O12	122.8 (5)	123.5 (7)	123.4 (5)
C4—N2—O21	117.6 (5)	—	118.3 (4)
C4—N2—O22	116.6 (5)	—	118.0 (4)
O21—N2—O22	125.7 (5)	—	123.7 (5)

supplementary material.\* 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, but not labelled.

\* Lists of structure factors and anisotropic displacement parameters have been deposited with the IUCr (Reference: SH0045). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

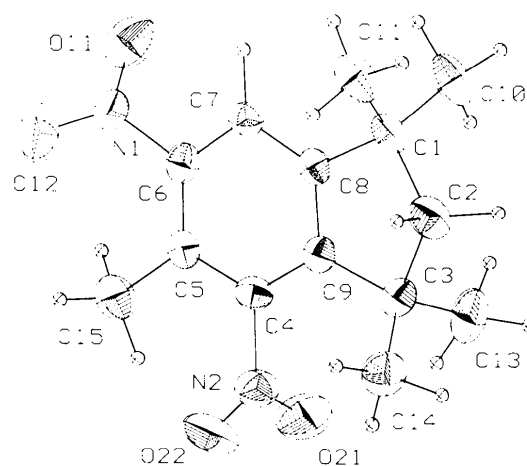


Fig. 1. Molecular structure of (1) (musk moskene). Thermal ellipsoids are shown at 50% probability levels, H atoms as arbitrary spheres.

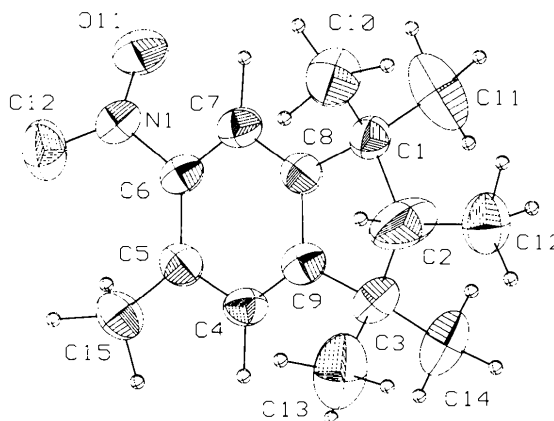


Fig. 2. Molecular structure of (2). Thermal ellipsoids are shown at 50% probability levels, H atoms as arbitrary spheres.

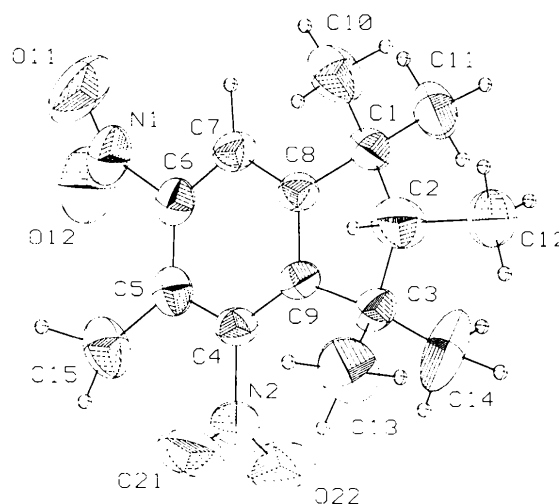


Fig. 3. Molecular structure of (3). Thermal ellipsoids are shown at 50% probability levels, H atoms as arbitrary spheres.

Because of disorder (*vide infra*) the accuracy of the results is not always optimal.

#### Conformation

Because the atoms C1, C8, C9 and C3 of the alicyclic ring are constrained to lie in or near the plane of the aromatic ring, the cyclopentene ring adopts an envelope conformation with C2 at the tip of the envelope. In (2) and (3), where a methyl group is attached to C2, this group is invariably in the equatorial position, analogous to the acylated indan compounds discussed in De Ridder & Schenk (1991a) and De Ridder, Čapková, Hatjisymeon, Fraanje & Schenk (1994).

#### Endocyclic angles

**Aromatic ring.** The endocyclic angle at C5 (aromatic C atom which carries the methyl group) is significantly smaller than the other endocyclic angles, whereas the endocyclic angle of the aromatic C atom, which carries a nitro group (*i.e.* C4 and C6), is significantly larger in accordance with the findings of Domenicano, Vaciago & Coulson (1975a,b).

**Cyclopentene ring.** The average value of the endocyclic angles C1—C8—C9 and C8—C9—C3 for the three structure determinations lies in the range 111.7(8)–111.9(6)°. This range compares very well with the acyl indan musk compounds (De Ridder & Schenk, 1991a; De Ridder, Čapková, Hatjisymeon, Fraanje & Schenk, 1994), if the apparently disordered structures 6-acetyl-2-ethyl-1,1,3,3,5-pentamethylindan and 5-acetyl-1,1,2,3,6-pentamethylindan are not taken into account (quasiplanar cyclopentene ring). In a study of the geometry of small rings, Allen (1981) found a value of 108.5(4)° for 80 benzocyclopentene compounds (value of  $\epsilon$  in column 5A, Table 2 of Allen's paper) and 108.0(5)° for 21 compounds in which C1 and C3 are  $sp^3$ -hybridized C atoms (column 5B). In his contribution, the author allowed C2 to be C, N or O (in Allen's paper, C1, C2 and C3 are labelled 7, 9 and 8, respectively). 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 392 fragments with an average value of 109.0° (109.3° for C1 and C3  $sp^3$ -hybridized, 148 fragments). In the distribution of the averaged endocyclic angle, two distinct curves could be detected, one with a maximum around 106–106.5° and the other around 108.5–109.0°. Closer inspection of the first curve revealed that this group contained compounds in which C1 and C3 are connected by an ethylene bridge, thus forming a cyclohexene ring in which the double bond and its two adjacent bonds are in common with the cyclopentene ring. In the case in which there is no CH<sub>2</sub>CH<sub>2</sub> bridge between C1 and C3 and both C1 and C3 are  $sp^3$ -hybridized C atoms, as in the musk compounds

Table 4. Structural data of the cyclopentene ring

Structure	A	B	C
(1)	0.348 (8)	22.9 (5)	—
(2)	0.30 (2)	20 (1)	349.5
(3)	0.433 (8)	28.0 (5)	337.6

(A) Distance (Å) of C2 from the plane through C1—C8—C9—C3; (B) dihedral angle (°) between the planes through C1—C8—C9—C3 and C1—C2—C3; (C) Sum of the angles (°) around C2.

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

Structure	C4	C6
(1)	79.0 (2)	47.5 (3)
(2)	—	36.3 (3)
(3)	85.5 (2)	40.3 (2)

of the indan family, values significantly higher (up to 113°) than the average value are observed.

#### Disorder

**The cyclopentene ring.** The type of disorder in the cyclopentene ring suggested in De Ridder, Čapková, Hatjisymeon, Fraanje & Schenk (1994) (replacement of a molecule by its mirror image-related enantiomer if packing allows) is encountered in the structure of (2). This disorder manifests itself in relatively high displacement parameters for C2 and the substituent atoms of the cyclopentene ring, and in deviating and sometimes anomalous values for the bond distances and angles involving these atoms. The disorder is also apparent from the distance of C2 to the plane through C1, C8, C9 and C3 and the sum of the angles around C2, which should be *ca* 0.35 Å and 340°, respectively (see Table 4).

**Nitro groups.** Another type of disorder originates from the nitro groups not having fixed orientations. Again this manifests itself in the displacement parameters and the bond distances and angles involved.

Disorder is always accompanied by a lowering of the local accuracy, but also the general accuracy usually suffers. In cases where different types of disorder are acting simultaneously, the accuracy can be rather poor. This manifestly high disorder combined with the generally poor quality of the crystals of this type of compounds is reflected in the high *R*-values (Table 1).

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

The angles between the nitro groups and the benzene ring are listed in Table 5. The nitro groups at C4 in (1) and (3), hemmed in between the methyl group at C5 and the pseudo-*tert*-butyl group at C9, are forced into a near perpendicular orientation. The nitro groups at C6 in (1), (2) and (3) have only one neighbouring group and have smaller angles of rotation. The behaviour of

the nitro groups is in agreement with the findings of the nitrobenzene compounds discussed in parts I (De Ridder, Goubitz & Schenk, 1990) and VII (De Ridder, Fraanje & Schenk, 1994) of this series (*cf.* also De Ridder & Schenk, 1994a).

O12—C15 distances range from 2.80 (1) in (2) to 2.899 (8) Å in (1) and indicate close contact between O and CH<sub>3</sub>.

### Concluding remarks

The structure for musk moskene (1) proposed by Carpenter & Easter (1954) is confirmed. The NMR spectra reported earlier (De Ridder, Schenk & Geenevasen, 1993) corroborate with the respective crystal structures.

Since (2) has a musk odour, there is reason to assume that the nitro group in the  $\beta$ -position has the osmophoric function. The angle the  $\beta$ -nitro group makes with the aromatic plane lies within the range 36.3 (3)–47.5 (3) $^\circ$ , which is again an indication that the coplanarity of the active group with a phenyl ring (or another conjugated system) is not an essential condition for the occurrence of musk odour, as proposed by Bersuker, Dimoglo, Gorbachov, Vlad & Pesaro (1991). The more sterically hindered  $\alpha$ -nitro group is almost perpendicular to this plane [79.0 (2)–85.5 (2) $^\circ$ ] and may function as a detail of the molecular profile according to Beets (1957, 1977).

The idea that the nitro group in the  $\beta$ -position fulfils the osmophoric function is strengthened by the comparison of the dimensions of a triangle defined by the two quaternary C-atoms (C1 and C3) and the N-atom of the nitro group(s) or the  $sp^2$ -C atom (C15) of the acyl group of the compounds described in De Ridder & Schenk (1991a) and De Ridder, Čapková, Hatjisyneon, Fraanje & Schenk (1994) [Fig. 4; this descriptor was first introduced in De Ridder & Schenk (1991b)]. From Table 6 it is seen that the dimensions for the  $\beta$ -nitro groups compare very well with acetyl- or formyl-type

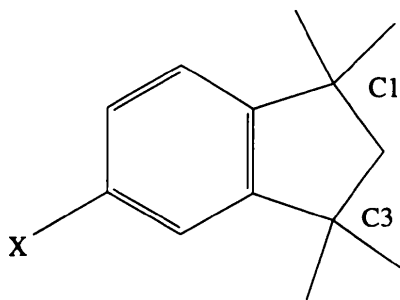


Fig. 4. Scheme of the 'osmophoric triangle' formed by the two quaternary C1 and C3 atoms and X, in which the latter is the N-atom of a nitro group or the  $sp^2$ -C atom of an acyl group. In this scheme the atom X is attached to a  $\beta$ -position.

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

Structure	Functional group	A	B	C
(1) <sup>a</sup>	$\alpha$ -Nitro	2.534 (6)	4.889 (6)	3.119 (6)
	$\beta$ -Nitro	2.534 (6)	5.744 (6)	5.034 (6)
(2) <sup>a</sup>	$\beta$ -Nitro	2.52 (1)	5.70 (1)	5.01 (1)
(3) <sup>a</sup>	$\alpha$ -Nitro	2.514 (6)	4.873 (7)	3.101 (6)
	$\beta$ -Nitro	2.514 (6)	5.727 (6)	5.007 (6)
(4) <sup>b</sup>	Acetyl	2.512 (4)	5.784 (4)	5.087 (5)
(5) <sup>b</sup>	Acetyl	2.515 (3)	5.785 (3)	5.098 (3)
(6) <sup>c</sup>	Acetyl	2.52 (1)	5.77 (1)	5.15 (1)
(7) <sup>c,d</sup>	Formyl	2.508 (7)	5.729 (11)	5.071 (10)
(8) <sup>c</sup>	Acetyl	2.502 (4)	5.780 (4)	5.145 (4)
(9) <sup>c</sup>	Acetyl	2.443 (7)	5.788 (7)	5.099 (8)
(10) <sup>c,e</sup>	Acetyl	2.513 (10)	5.756 (10)	5.102 (10)

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

(4) 6-Acetyl-1,1,2,3,3,5-hexamethylindan (*musk phantolid*); (5) 6-acetyl-3-isopropyl-1,1,3,5-tetramethylindan; (6) 6-acetyl-2-ethyl-1,1,3,3,5-pentamethylindan; (7) 6-formyl-1,1,2,3,3,5-hexamethylindan; (8) 5-acetyl-1,1,2,3,3-pentamethylindan; (9) 5-acetyl-1,1,2,3,6-pentamethylindan; (10) 5-acetyl-1,1,3,3,6-pentamethylindan.

(a) This work, (b) De Ridder & Schenk (1991a), (c) De Ridder, Čapková, Hatjisyneon, Fraanje & Schenk (1994), (d) average value of two molecules and (e) average value of three molecules.

compounds, whereas the C<sub>tert</sub>—N distances for the  $\alpha$ -nitro groups are significantly smaller. Therefore, it can be said that the  $\beta$ -nitro group is equivalent to the acetyl or formyl group that concerns its osmophoric function, whereas the  $\alpha$ -nitro group will presumably improve the overall profile with respect to the receptor site. It has to be remarked that the occurrence of a triangle with the specified dimensions may be a necessary condition for this type of musk compounds. Nevertheless it is not a sufficient condition since 6-acetyl-3-isopropyl-1,1,3,5-tetramethylindan (De Ridder & Schenk, 1991a) has no musk odour.

The discussion of some structure-activity relationship studies with respect to the geometrical results of our crystal studies will be contributed in a separate paper (De Ridder & Schenk, 1994b).

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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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