

product is the *cis*-OH isomer derived from the simplest *ab* pathway (absolute stereochemistries were not assigned, but the asymmetry resulting from the 3-methyl substituent allowed assignment of the reaction pathways on the basis of the different regioisomeric photoproducts). The differing behaviours may be rationalized in terms of the interactions of the adamantyl groups with the environments in the crystals. In (1), rotation about the C(1)—C(11) bond is a relatively low-energy process, since the adamantyl group is close to spherical in shape. In the 3-methyl derivative, however, the bulky methyl substituent will tend to hinder rotation of the adamantyl group and thus favour the product resulting from minimum motion in the crystal.

Irradiation of (1) (plates) yields products similar to those from the needle crystals, but with a much reduced enantiomeric excess (12%). Since crystals of (1) (plates) contain both conformational enantiomorphs of the adamantylacetophenone anion, the 12% enantiomeric excess must result from a difference in the rate of reaction of the two enantiomers, due to their differing chiral surroundings.

Optical rotations (Jones *et al.*, 1992) indicate that the photoproduct in 12% excess is (2') [the enantiomer of (2)], which is most likely formed from the enantiomer of (1), which is opposite in chirality to that in the needle crystals, *i.e.* the lower numbered molecule of (1) in the plate crystals (Fig. 1 and Table 2). Inspection of non-bonded contact distances reveals no readily apparent rationalization for this phenomenon.

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### Crystal Studies of Musk Compounds. VIII.\* Structures of Five Homologues of Musk Phantolid†

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#### Abstract

The crystal structures of 6-acetyl-2-ethyl-1,1,3,3,5-pentamethylindan (3), 6-formyl-1,1,2,3,3,5-hexamethylindan (4), 5-acetyl-1,1,2,3,3-pentamethylindan (5), 5-acetyl-1,1,2,3,6-pentamethylindan (6) and 5-acetyl-1,1,3,3,6-pentamethylindan (7) have been established by X-ray diffraction. (4) is a strong musk, whilst (6) and (7) have only a weak musk odour. The quality of musks (3) and (5) is not available. (4) and (7) have two and three molecules in the asymmetric unit,

respectively; in both cases, no extra crystallographic symmetry could be detected. Some of the structures described show disorder in the cyclopentene ring and/or in the acyl group. This manifests itself in relatively high displacement parameters and in anomalous bond distances and angles. In two cases [(3) and (6)], a quasiplanar cyclopentene ring is observed. The data are discussed in the light of the necessity of coplanarity of the active group with a phenyl ring for the occurrence of a musk odour. With respect to recent studies dealing with the structure–activity relationships of musk compounds, the most striking observations are that the acetyl group is invariably facing the methyl group at C6 and that the alkyl group at C2 is invariably in the equatorial position.

#### Introduction

In part III of this series (De Ridder & Schenk, 1991), we reported the crystal structures of Musk Phantolid (1)

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

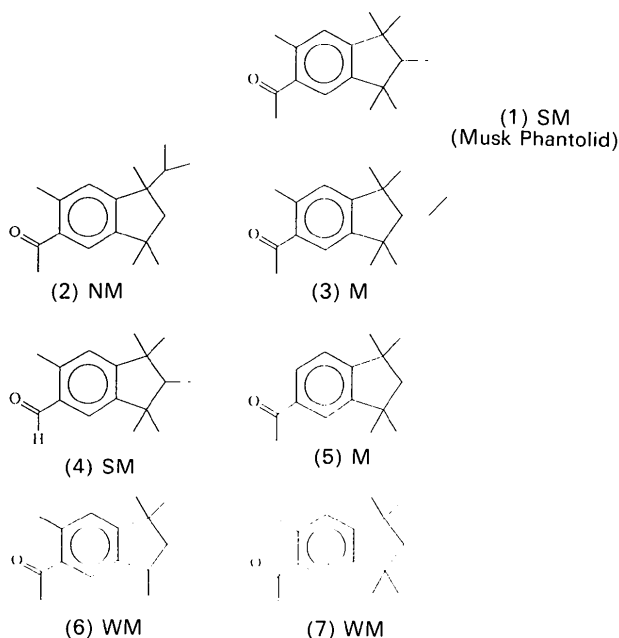
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and one of its (odourless) higher homologues (2). In the present paper, the crystal structures of five homologues of Musk Phantolid are described. All the compounds, which belong to the indan musk class, are presented in the scheme below.



Key: SM = strong musk; WM = weak musk; NM = no musk; M = musk for which the quality is not available.

Musk Phantolid (1) was discovered in the early 1950's by Kurt Fuchs (Wood, 1968). This compound has a strong musk odour. At the time of the patent application, the structure of this product was uncertain. The correct structure was deduced by Weber, Spoelstra & Polak (1955). (2) (Lenslink, 1988) and (3) are higher homologues of Musk Phantolid (1), but only (3) has a musk odour. No indication is available of its quality compared with (1) (Weber, Stofberg, Spoelstra & Kleipool, 1956).

(4) is the formyl homologue of Musk Phantolid; its musk odour is slightly stronger. Spoelstra, Weber & Kleipool (1957) observed that the musk odour decreased on going from formyl (H) to acetyl (CH<sub>3</sub>) and predicted that a propionyl group (C<sub>2</sub>H<sub>5</sub>) would further decrease the odoriferous properties, which was confirmed after its synthesis.

(5), (6) and (7) are lower homologues of Musk Phantolid (1). (5) is a musk, but no indication of its quality is available (Spoelstra, Weber & Kleipool, 1963). (6) has a weak musk odour; (7) has a musky and woody odour, weaker than Phantolid (Weber, Spoelstra & Polak, 1955).

(6) has only one quaternary C atom centre, in contrast to the other compounds. Beets (1977) and Theimer & Davies (1967) indicated that two quaternary centres (or at least one quaternary and one tertiary centre),

Table 1. *Crystal data*

	(3)	(4)	(5)	(6)	(7)
Formula	C <sub>18</sub> H <sub>26</sub> O	C <sub>18</sub> H <sub>26</sub> O	C <sub>18</sub> H <sub>26</sub> O	C <sub>18</sub> H <sub>26</sub> O	C <sub>18</sub> H <sub>26</sub> O
<i>M<sub>r</sub></i>	258.40	230.35	230.35	230.35	230.35
Crystal system	Orthorhombic	Triclinic	Monoclinic	Orthorhombic	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> <i>ab</i>	<i>P</i> <i>T</i>	<i>P</i> 2 <sub>1</sub> / <i>a</i>	<i>P</i> 2 <sub>1</sub> / <i>cn</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>
<i>a</i> (Å)	7.057 (1)	8.232 (4)	8.232 (2)	7.476 (8)	11.674 (1)
<i>b</i> (Å)	14.317 (1)	9.641 (1)	11.277 (1)	13.093 (2)	11.298 (1)
<i>c</i> (Å)	16.047 (2)	18.141 (3)	15.448 (3)	14.492 (2)	32.890 (5)
$\alpha$ (°)		78.29 (1)			
$\beta$ (°)		82.93 (2)	105.15 (2)		94.91 (2)
$\gamma$ (°)		89.70 (3)			
<i>V</i> (Å <sup>3</sup> )	1621.3 (3)	1398.8 (9)	1384.2 (5)	1419 (2)	4322 (1)
<i>Z</i>	4	4	4	4	12
<i>D<sub>c</sub></i> (g cm <sup>-3</sup> )	1.06	1.09	1.11	1.08	1.06
$\mu$ (Cu <i>K</i> $\alpha$ ) (cm <sup>-1</sup> )	4.50	4.73	4.78	4.66	4.59
<i>F</i> (000)	568	504	504	504	1512

attached at the *ortho* or *meta* position relative to the aromatic system, is one of the most important structural requirements for musk odour in the class of nitro-free aromatic musks. The presence of only one quaternary C atom centre in (6) results in a musk with only a weak odour. The fact that (2) has no odour indicates that the presence of two quaternary C centres is a necessary but not the only condition for muskiness.

### Experimental

The compounds were synthesized (by PFW-Amersfoort) by the literature methods mentioned in the preceding paragraph. The intensities of all the crystal structures described in this paper were collected with an Enraf-Nonius CAD-4 automatic diffractometer employing graphite-monochromated Cu *K* $\alpha$  radiation ( $\lambda = 1.5418$  Å) and  $\theta$ - $2\theta$  scans. Because of high volatility, some of the crystals were measured at reduced temperature (see Table 2). 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 [*SIMPEL* (Schenk & Hall, 1990)]. After isotropic refinement, an empirical absorption correction was applied [*DIFABS* (Walker & Stuart, 1983)]. The H-atom positions were introduced at their calculated positions 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  $w^{-1} = a + F_{\text{obs}} + b(F_{\text{obs}})^2$  was used (the values for *a* and *b* are given in Table 2). There are a few deviations from the above procedure which are indicated in the relevant sections. The crystal data are summarized in Table 1 and details of data collection and refinement are given in Table 2.

Table 2. Details of data collection and refinement

	(3)	(4)	(5)	(6)	(7)
Data collection					
Crystal size (mm)	0.3 × 0.3 × 0.05	1.5 × 0.3 × 0.25	0.75 × 0.6 × 0.5	0.8 × 0.75 × 0.4	0.8 × 0.8 × 0.5
Temperature (K)	250	243	188	298	253
Cell parameter determination					
No.	23	21	23	20	23
$\theta$ range of reflections ( $^{\circ}$ )	28.8–39.7	27.2–38.4	25.2–40.0	39.1–44.7	40.1–42.5
$\theta_{\min}$ , $\theta_{\max}$ ( $^{\circ}$ )	2.5, 75	2.5, 65	2.5, 55	2.5, 65	2.5, 65
$h$	0 → 8	–9 → 9	–8 → 0	–8 → 0	0 → 13
$k$	0 → 17	0 → 11	0 → 11	–15 → 0	0 → 13
$l$	0 → 20	–21 → 21	–16 → 16	0 → 17	–38 → 38
Intensity control reflections					
variation	002; 020	022; 121	117; 333	032; 013	006; 120
No. of intensity measurements	Not significant	Not significant	Not significant	3.5% decrease	3.0% decrease
No. of unique reflections	1993	4839	1889	1762	7918
No. of observed reflections [ $I > 2.5\sigma(I)$ ]	1803	4737	1734	1576	7313
No. of observed reflections [ $I > 2.5\sigma(I)$ ]	796	3603	1506	1124	5275
Max./min. absorption	1.23/0.58	1.20/0.67	1.42/0.74	1.39/0.29	1.17/0.75
Refinement					
$R$	0.085	0.090	0.056	0.071	0.083
$wR$	0.118	0.113	0.072	0.089	0.109
$S$	0.35	0.25	0.20	0.20	0.34
Weighting scheme					
(a)	3.96	6.02	6.96	2.62	6.44
(b)	0.0083	0.0043	0.0057	0.0019	0.0040
$(\Delta/\sigma)_{\max}$ in final cycle	0.18	0.78	0.33	0.91	0.82
No. of parameters refined	171	493	242	239	714
No. of restraints	26	45	22	44	66
Min.; max. heights in final $\Delta F$ map ( $e \text{ \AA}^{-3}$ )	–0.3; 0.3	–0.4; 0.9	–0.2; 0.4	–0.2; 0.2	–0.4; 0.6
Extinction parameter $g$	Negligible	$2(1) \times 10^{-6}$	Negligible	$4(1) \times 10^{-6}$	$16(3) \times 10^{-5}$

(1) 6-Acetyl-1,1,2,3,3,5-hexamethylindan (*Musk Phantolid*)

For the experimental details of this compound we refer to part III (De Ridder & Schenk, 1991) of this series. (CSD refcode: JILXIL; see also supplementary data publication no. SUP 53573.)

## (2) 6-Acetyl-3-isopropyl-1,1,3,5-tetramethylindan

The experimental details of this compound can also be found in part III (De Ridder & Schenk, 1991) of this series. (CSD refcode: JILXOR; see also supplementary data publication no. SUP 53573.) The numbering system in (2) has been changed in order to be consistent within the family of indan compounds.

## (3) 6-Acetyl-2-ethyl-1,1,3,3,5-pentamethylindan

A sample of crystals was recrystallized by slow evaporation from ethanol/methanol (*ca* 1:1). The crystals are orthorhombic, absent reflections  $h0l$ ,  $h = 2n + 1$ , and  $hk0$ ,  $k = 2n + 1$ , indicating space groups  $P2_1ab$  or  $Pmab$  (non-standard setting). Considering the molecular symmetry and the statistics of the  $E$  values, the structure was refined in  $P2_1ab$ . The displacement parameters of all the H atoms were kept fixed at  $0.08 \text{ \AA}^2$ .\*

## (4) 6-Formyl-1,1,2,3,3,5-hexamethylindan

A sample of crystals was recrystallized by slow evaporation from ethanol/methanol (*ca* 1:1). The crystals are triclinic. Considering the value of  $Z$  and the statistics of the  $E$  values, the structure was refined in  $P\bar{1}$ . There are two independent molecules in the asymmetric unit. One of the molecules (denoted *B*) showed disorder in the formyl group; two positions for the O atom were introduced and their population parameter refined; the O atom nearest the aromatic methyl group refined to a population parameter of 0.46. The displacement parameters of the H atoms attached to C2 (for both molecules) and those attached to C15 (for molecule *B*) were kept fixed at  $0.08 \text{ \AA}^2$ .\*

## (5) 5-Acetyl-1,1,2,3,3-pentamethylindan

The crystals are monoclinic.

## (6) 5-Acetyl-1,1,2,3,6-pentamethylindan

A sample of crystals was recrystallized by slow evaporation from ethanol/methanol (*ca* 1:1). The crystals are orthorhombic. Absent reflections  $h0l$ ,  $l = 2n + 1$ , and  $hk0$ ,  $h + k = 2n + 1$ , indicated the space groups  $P2_1cn$  or  $Pm\bar{c}n$  (non-standard setting). In view of the molecular symmetry and the statistics of the  $E$  values, the structure was refined in  $P2_1cn$ . The temperature parameter of the H atoms attached to C2 and C3 was kept fixed at  $0.08 \text{ \AA}^2$ .

\* Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: SH0044). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

\* See deposition footnote.

## (7) 5-Acetyl-1,1,3,3,6-pentamethylindan

A sample of crystals was recrystallized by slow evaporation from ethanol/methanol (*ca* 1:1). The crystals are monoclinic. There are three independent molecules in the asymmetric unit. The displacement parameters of the H atoms attached to C2 were kept fixed at  $0.08 \text{ \AA}^2$ .\*

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

*Compounds with more than one molecule in the asymmetric unit*

(4) and (7) have two and three molecules in the asymmetric unit, respectively. In both cases, the program *MISSYM* [*NRCVAX* package (Le Page, 1987)] could not detect any extra crystallographic symmetry with a search on all non-H atoms.

Molecules of (4*B*) show disorder in the formyl substituent. Matching of the common non-H atoms of (4*B*) with the highest population parameter for the formyl group *versus* (4*A*) resulted in a r.m.s. value of  $0.04 \text{ \AA}$ , indicating identical conformations.

(7) has three molecules in the asymmetric unit. Matching of the common non-H atoms of the different molecules to each other resulted in r.m.s. values  $\leq 0.10 \text{ \AA}$ .

*Compounds crystallizing in non-centrosymmetric space groups*

The non-centrosymmetric structures (3) and (6) show hypersymmetry. In both cases, *MISSYM* finds a centre of symmetry [at  $0.529, 1/2, 1/2$  in (3) and  $0.384, 1/2, 1/2$  in (6)], since the atoms of the indan moiety and the atoms directly attached to it tend to have the same *x* coordinates. During full-matrix least-squares refinement on *F*, no correlations between the refined parameters were found, nor did the  $U_{ij}$  matrices become not positive definite. From this it has been concluded that the assumed symmetry is correct.

**Results and discussion**

The final coordinates and equivalent displacement parameters of the non-H atoms are listed in Table 3 for (3)–(7). The bond distances and angles for all compounds are given in Table 4. *PEANUT* (Hummel, Hauser & Bürgi, 1990) drawings of the molecules, showing the geometry and the numbering system, are given in Figs. 1–7. In these diagrams, the H atoms are drawn as arbitrary spheres, but not labelled. Stereoscopic *PEANUT* diagrams illustrating the packing in the crystal lattice are given in Figs. 8–14. Because of disorder (*vide infra*), the accuracy of the results is not always optimal. Some aspects of the structures will be discussed.

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{eq}$
(3)				
C1	0.279 (4)	0.4362 (6)	0.2420 (5)	0.062 (6)
C2	0.280 (3)	0.4656 (6)	0.3333 (5)	0.075 (7)
C3	0.281 (4)	0.5731 (6)	0.3403 (5)	0.059 (6)
C4	0.291 (4)	0.6929 (6)	0.2145 (5)	0.054 (5)
C5	0.294 (3)	0.7030 (7)	0.1262 (5)	0.050 (5)
C6	0.295 (4)	0.6269 (8)	0.0737 (6)	0.067 (6)
C7	0.277 (4)	0.5395 (6)	0.1108 (5)	0.058 (6)
C8	0.292†	0.5269 (6)	0.1966 (5)	0.052 (5)
C9	0.295 (3)	0.6020 (5)	0.2496 (5)	0.047 (5)
C10	0.150 (3)	0.371 (1)	0.211 (1)	0.15 (2)
C11	0.499 (3)	0.391 (1)	0.232 (1)	0.13 (2)
C12	0.274 (3)	0.4069 (8)	0.4027 (6)	0.11 (1)
C13	0.147 (3)	0.617 (1)	0.394 (1)	0.13 (2)
C14	0.497 (3)	0.599 (1)	0.3754 (9)	0.12 (1)
C15	0.300 (4)	0.8038 (7)	0.0942 (6)	0.064 (7)
C16	0.302 (3)	0.8824 (6)	0.1558 (6)	0.067 (7)
C17	0.299 (3)	0.6373 (7)	−0.0208 (5)	0.090 (8)
C12†	0.266 (3)	0.316 (1)	0.4161 (8)	0.18 (2)
O	0.287 (4)	0.8167 (5)	0.0190 (4)	0.090 (6)
(4)				
C1 <i>A</i>	0.5437 (4)	0.3202 (4)	0.3755 (2)	0.055 (2)
C2 <i>A</i>	0.4197 (6)	0.3148 (7)	0.4475 (3)	0.087 (3)
C3 <i>A</i>	0.2487 (4)	0.2744 (4)	0.4289 (2)	0.050 (2)
C4 <i>A</i>	0.1509 (4)	0.3402 (4)	0.2947 (2)	0.048 (2)
C5 <i>A</i>	0.1939 (5)	0.3826 (4)	0.2166 (2)	0.050 (2)
C6 <i>A</i>	0.3597 (5)	0.4089 (4)	0.1862 (2)	0.052 (2)
C7 <i>A</i>	0.4774 (4)	0.3903 (4)	0.2361 (2)	0.053 (2)
C8 <i>A</i>	0.4326 (4)	0.3480 (4)	0.3139 (2)	0.046 (2)
C9 <i>A</i>	0.2698 (4)	0.3220 (4)	0.3435 (2)	0.044 (2)
C10 <i>A</i>	0.6604 (7)	0.4464 (6)	0.3691 (4)	0.089 (4)
C11 <i>A</i>	0.6480 (7)	0.1921 (5)	0.3680 (3)	0.077 (3)
C12 <i>A</i>	0.4700 (7)	0.2327 (6)	0.5217 (3)	0.075 (3)
C13 <i>A</i>	0.1229 (9)	0.3602 (7)	0.4672 (3)	0.091 (4)
C14 <i>A</i>	0.199 (1)	0.1188 (6)	0.4511 (3)	0.097 (4)
C15 <i>A</i>	0.0649 (6)	0.4014 (5)	0.1671 (3)	0.067 (3)
C17 <i>A</i>	0.4151 (7)	0.4532 (5)	0.1022 (3)	0.074 (3)
O1 <i>A</i>	−0.0787 (5)	0.3866 (5)	0.1891 (2)	0.111 (3)
C1 <i>B</i>	0.3247 (5)	−0.0821 (4)	0.1892 (2)	0.059 (2)
C2 <i>B</i>	0.2094 (7)	−0.1923 (7)	0.2436 (4)	0.101 (4)
C3 <i>B</i>	0.0325 (5)	−0.1333 (4)	0.2461 (2)	0.057 (2)
C4 <i>B</i>	−0.0774 (5)	0.0391 (4)	0.1338 (3)	0.064 (3)
C5 <i>B</i>	−0.0398 (5)	0.1370 (4)	0.0652 (2)	0.064 (3)
C6 <i>B</i>	0.1227 (5)	0.1686 (4)	0.0349 (2)	0.060 (2)
C7 <i>B</i>	0.2450 (5)	0.0984 (4)	0.0727 (2)	0.059 (2)
C8 <i>B</i>	0.2073 (4)	0.0010 (4)	0.1403 (2)	0.048 (2)
C9 <i>B</i>	0.0461 (4)	−0.0293 (4)	0.1709 (2)	0.049 (2)
C10 <i>B</i>	0.4224 (7)	0.0165 (6)	0.2241 (4)	0.084 (4)
C11 <i>B</i>	0.4486 (9)	−0.1600 (7)	0.1425 (4)	0.107 (5)
C12 <i>B</i>	0.2637 (9)	−0.2615 (7)	0.3188 (4)	0.096 (4)
C13 <i>B</i>	−0.016 (1)	−0.0541 (8)	0.3097 (4)	0.120 (6)
C14 <i>B</i>	−0.085 (1)	−0.2551 (7)	0.2499 (4)	0.108 (5)
C15 <i>B</i>	−0.1745 (8)	0.2058 (7)	0.0273 (5)	0.112 (5)
C17 <i>B</i>	0.1717 (9)	0.2774 (6)	−0.0378 (3)	0.094 (4)
O1 <i>B</i> ‡	−0.314 (1)	0.183 (1)	0.0441 (6)	0.137 (8)
O1 <i>B</i> §	−0.173 (2)	0.300 (1)	−0.0229 (8)	0.19 (1)
(5)				
C1	0.7866 (3)	0.4173 (2)	0.6630 (2)	0.031 (2)
C2	0.9156 (4)	0.4983 (3)	0.6338 (2)	0.036 (2)
C3	1.0311 (3)	0.5534 (2)	0.7200 (2)	0.027 (1)
C4	1.1138 (3)	0.4548 (2)	0.8784 (2)	0.028 (2)
C5	1.0834 (3)	0.3622 (3)	0.9324 (2)	0.032 (2)
C6	0.9540 (4)	0.2817 (3)	0.8971 (2)	0.039 (2)
C7	0.8523 (4)	0.2936 (6)	0.8114 (2)	0.037 (2)
C8	0.8837 (3)	0.3855 (2)	0.7574 (2)	0.027 (1)
C9	1.0157 (3)	0.4639 (2)	0.7905 (2)	0.024 (1)
C10	0.7444 (5)	0.3086 (3)	0.6011 (2)	0.050 (2)
C11	0.6208 (4)	0.4775 (3)	0.6654 (2)	0.049 (2)

\* See deposition footnote.

Table 3 (*cont.*)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>
C12	0.8406 (5)	0.5863 (3)	0.5586 (2)	0.051 (2)
C13	1.2140 (4)	0.5597 (3)	0.7119 (2)	0.044 (2)
C14	0.9809 (5)	0.6776 (3)	0.7448 (2)	0.043 (2)
C15	1.1869 (4)	0.3438 (3)	1.0265 (2)	0.044 (2)
C16	1.3100 (5)	0.4372 (4)	1.0708 (2)	0.053 (2)
O	1.1720 (3)	0.2522 (3)	1.0662 (2)	0.067 (2)

(6)				
C1	0.634 (2)	0.4907 (4)	0.3150 (3)	0.089 (3)
C2	0.623 (4)	0.3778 (5)	0.2985 (4)	0.157 (7)
C3	0.644 (3)	0.3509 (4)	0.2035 (4)	0.113 (4)
C4	0.627 (2)	0.4734 (4)	0.0606 (3)	0.088 (3)
C5	0.632 (2)	0.5725 (3)	0.0284 (3)	0.074 (2)
C6	0.635 (2)	0.6547 (3)	0.0919 (3)	0.078 (3)
C7	0.633 (2)	0.6312 (4)	0.1863 (3)	0.084 (3)
C8	0.628†	0.5324 (3)	0.2160 (3)	0.072 (2)
C9	0.635 (2)	0.4530 (3)	0.1547 (3)	0.082 (3)
C10	0.787 (2)	0.532 (1)	0.369 (1)	0.14 (1)
C11	0.460 (2)	0.523 (2)	0.365 (1)	0.15 (1)
C12	0.630 (2)	0.3034 (6)	0.3763 (5)	0.130 (6)
C13	0.622 (4)	0.2597 (5)	0.1558 (5)	0.152 (7)
C15	0.627 (2)	0.5899 (4)	-0.0741 (3)	0.093 (3)
C16	0.628 (2)	0.5019 (7)	-0.1364 (4)	0.114 (5)
C17	0.626 (2)	0.7650 (4)	0.0651 (5)	0.107 (4)
O	0.631 (2)	0.6746 (4)	-0.1073 (3)	0.145 (4)

(7)				
C1A	0.1623 (3)	0.3714 (3)	0.4304 (1)	0.061 (2)
C2A	0.0755 (4)	0.4168 (4)	0.3965 (1)	0.084 (3)
C3A	0.0247 (3)	0.5371 (3)	0.4103 (1)	0.062 (2)
C4A	0.1249 (3)	0.6803 (3)	0.4641 (1)	0.051 (2)
C5A	0.2111 (3)	0.6983 (3)	0.4959 (1)	0.049 (2)
C6A	0.2920 (3)	0.6072 (3)	0.5058 (1)	0.051 (2)
C7A	0.2794 (3)	0.5004 (3)	0.4850 (1)	0.053 (2)
C8A	0.1908 (3)	0.4827 (3)	0.4549 (1)	0.050 (2)
C9A	0.1142 (3)	0.5729 (3)	0.4441 (1)	0.048 (2)
C10A	0.2696 (4)	0.3191 (4)	0.4121 (2)	0.090 (3)
C11A	0.1141 (4)	0.2756 (4)	0.4571 (1)	0.081 (3)
C13A	0.0172 (4)	0.6247 (4)	0.3752 (1)	0.089 (3)
C14A	-0.0924 (4)	0.5231 (5)	0.4273 (2)	0.102 (4)
C15A	0.2140 (3)	0.8127 (3)	0.5186 (1)	0.060 (2)
C16A	0.1382 (4)	0.9125 (3)	0.5036 (1)	0.074 (3)
C17A	0.3914 (3)	0.6195 (4)	0.5382 (1)	0.072 (2)
O1A	0.2744 (3)	0.8259 (3)	0.5502 (1)	0.102 (2)

C1B	0.1415 (4)	0.3038 (4)	0.2571 (1)	0.079 (3)
C2B	0.0299 (6)	0.3467 (6)	0.2369 (2)	0.159 (6)
C3B	-0.0714 (4)	0.3088 (4)	0.2625 (1)	0.081 (3)
C4B	-0.0592 (3)	0.1496 (3)	0.3205 (1)	0.058 (2)
C5B	0.0096 (3)	0.0724 (3)	0.3458 (1)	0.048 (2)
C6B	0.1281 (3)	0.0659 (3)	0.3410 (1)	0.051 (2)
C7B	0.1735 (3)	0.1379 (3)	0.3124 (1)	0.059 (2)
C8B	0.1050 (3)	0.2157 (3)	0.2885 (1)	0.061 (2)
C9B	-0.0117 (3)	0.2212 (3)	0.2922 (1)	0.062 (2)
C10B	0.2165 (5)	0.3989 (4)	0.2775 (1)	0.091 (3)
C11B	0.2170 (6)	0.2414 (6)	0.2250 (2)	0.129 (5)
C13B	-0.1232 (7)	0.4078 (5)	0.2842 (2)	0.153 (6)
C14B	-0.1631 (4)	0.2503 (4)	0.2341 (1)	0.092 (3)
C15B	-0.0449 (3)	-0.0008 (3)	0.3763 (1)	0.062 (2)
C16B	-0.1722 (4)	-0.0199 (5)	0.3724 (1)	0.091 (3)
C17B	0.2085 (3)	-0.0181 (4)	0.3652 (1)	0.070 (2)
O1B	0.0101 (3)	-0.0459 (3)	0.4054 (1)	0.102 (2)
C1C	0.4838 (4)	0.6874 (4)	0.3726 (1)	0.079 (3)
C2C	0.4825 (5)	0.7102 (4)	0.4179 (1)	0.105 (4)
C3C	0.5199 (3)	0.8379 (4)	0.4286 (1)	0.065 (2)
C4C	0.5342 (3)	1.0095 (3)	0.3754 (1)	0.066 (2)
C5C	0.5246 (3)	1.0403 (4)	0.3329 (1)	0.069 (2)
C6C	0.4992 (3)	0.9570 (4)	0.3028 (1)	0.066 (2)
C7C	0.4864 (4)	0.8436 (4)	0.3148 (1)	0.071 (2)
C8C	0.4959 (3)	0.8102 (3)	0.3558 (1)	0.061 (2)
C9C	0.5182 (3)	0.8921 (3)	0.3862 (1)	0.056 (2)
C10C	0.3772 (7)	0.6268 (6)	0.3527 (2)	0.145 (6)
C11C	0.5891 (7)	0.6128 (5)	0.3619 (2)	0.139 (5)
C13C	0.4315 (5)	0.8977 (5)	0.4535 (1)	0.098 (4)

Table 3 (*cont.*)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>
C14C	0.6371 (4)	0.8474 (6)	0.4520 (2)	0.115 (4)
C15C	0.5453 (5)	1.1667 (4)	0.3235 (2)	0.098 (4)
C16C	0.5550 (7)	1.2510 (5)	0.2532 (2)	0.124 (5)
C17C	0.4816 (5)	0.9841 (4)	0.2561 (1)	0.093 (3)
O1C	0.5570 (9)	1.1896 (6)	0.2858 (2)	0.273 (8)

† Fixed to determine origin.

‡ Population parameter = 0.54.

§ Population parameter = 0.46.

Table 4. Bond distances (Å) and angles (°) of the non-H atoms with standard deviations in parentheses

	(1)*	(2)*	(3)	(4A)	(4B)
C1—C2	1.549 (5)	1.551 (3)	1.52 (1)	1.548 (6)	1.535 (7)
C1—C8	1.519 (4)	1.516 (2)	1.49 (1)	1.511 (5)	1.509 (5)
C1—C10	1.539 (5)	1.542 (3)	1.39 (3)	1.532 (7)	1.526 (8)
C1—C11	1.523 (5)	1.551 (3)	1.69 (4)	1.519 (7)	1.536 (9)
C2—C3	1.548 (5)	1.544 (3)	1.54 (1)	1.556 (7)	1.559 (7)
C2—C12	1.515 (6)	—	1.40 (1)	1.521 (7)	1.511 (9)
C3—C9	1.513 (4)	1.517 (2)	1.52 (1)	1.513 (5)	1.513 (5)
C3—C13	1.531 (6)	1.528 (3)	1.43 (3)	1.512 (7)	1.522 (9)
C3—C14	1.539 (5)	1.545 (3)	1.67 (3)	1.516 (7)	1.511 (8)
C4—C5	1.401 (4)	1.402 (2)	1.42 (1)	1.394 (5)	1.402 (6)
C4—C9	1.385 (4)	1.384 (2)	1.42 (1)	1.386 (5)	1.379 (6)
C5—C6	1.410 (4)	1.413 (2)	1.38 (1)	1.411 (5)	1.393 (6)
C5—C15	1.498 (4)	1.492 (2)	1.53 (1)	1.461 (6)	1.463 (9)
C6—C7	1.394 (4)	1.393 (3)	1.39 (1)	1.393 (6)	1.384 (6)
C6—C17	1.515 (4)	1.513 (3)	1.52 (1)	1.509 (6)	1.521 (6)
C7—C8	1.380 (4)	1.384 (2)	1.39 (1)	1.390 (5)	1.387 (5)
C8—C9	1.379 (4)	1.386 (2)	1.37 (1)	1.385 (4)	1.382 (5)
C11—C111	—	1.525 (3)	—	—	—
C11—C112	—	1.524 (3)	—	—	—
C12—C121	—	—	1.32 (2)	—	—
C15—C16	1.488 (5)	1.483 (3)	1.50 (1)	—	—
C15—O	1.208 (4)	1.207 (2)	1.23 (1)	1.200 (6)	1.16 (1)†
					1.15 (1)‡

	(1)	(2)	(3)	(4A)	(4B)
C2—C1—C8	100.9 (2)	101.9 (1)	103.3 (7)	101.4 (3)	101.7 (3)
C2—C1—C10	109.2 (3)	111.4 (2)	122 (2)	107.4 (4)	117.4 (4)
C2—C1—C11	117.0 (3)	113.3 (2)	101 (2)	119.4 (4)	108.6 (4)
C8—C1—C10	111.5 (3)	108.3 (2)	117 (2)	111.0 (4)	110.6 (4)
C8—C1—C11	110.7 (3)	111.6 (1)	104 (2)	110.0 (4)	111.3 (4)
C10—C1—C11	107.4 (3)	110.0 (2)	108 (1)	107.4 (4)	107.2 (4)
C1—C2—C3	108.4 (3)	108.7 (1)	110.2 (7)	107.8 (4)	108.3 (4)
C1—C2—C12	116.5 (3)	—	127.0 (8)	116.6 (4)	118.3 (5)
C3—C2—C12	117.6 (3)	—	122.8 (8)	115.7 (4)	116.6 (5)
C2—C3—C9	100.7 (2)	101.9 (1)	101.7 (6)	101.0 (3)	100.6 (3)
C2—C3—C13	110.2 (3)	112.2 (2)	119 (2)	107.5 (4)	114.7 (6)
C2—C3—C14	115.3 (3)	112.1 (2)	104 (2)	116.5 (4)	108.1 (4)
C9—C3—C13	111.7 (3)	112.6 (2)	120 (2)	112.1 (3)	109.0 (4)
C9—C3—C14	109.0 (3)	109.2 (1)	102 (2)	110.1 (4)	112.7 (4)
C13—C3—C14	109.7 (3)	108.8 (2)	108 (1)	109.5 (4)	111.3 (5)
C5—C4—C9	120.8 (2)	120.7 (2)	119.1 (8)	120.7 (3)	120.3 (4)
C4—C5—C6	119.4 (3)	119.3 (2)	121.9 (9)	120.3 (3)	120.3 (4)
C4—C5—C15	118.0 (2)	118.4 (2)	115.4 (8)	119.0 (3)	118.5 (4)
C6—C5—C15	122.6 (2)	122.3 (2)	122.7 (8)	120.7 (3)	121.2 (4)
C5—C6—C7	118.4 (2)	118.7 (2)	116.7 (9)	118.3 (3)	118.6 (3)
C5—C6—C17	123.5 (3)	123.4 (2)	122.1 (9)	123.1 (4)	122.9 (4)
C7—C6—C17	118.0 (3)	117.9 (2)	121.1 (9)	118.7 (4)	118.6 (4)
C6—C7—C8	121.4 (2)	121.4 (2)	122.2 (9)	120.8 (3)	120.9 (4)
C1—C8—C7	128.2 (2)	128.1 (2)	126.3 (8)	127.7 (3)	127.7 (3)
C1—C8—C9	111.4 (2)	112.0 (1)	112.4 (7)	111.6 (3)	111.8 (3)
C7—C8—C9	120.3 (3)	119.8 (2)	120.8 (8)	120.7 (3)	120.5 (3)
C3—C9—C4	127.9 (2)	128.3 (2)	129.1 (7)	128.7 (3)	128.7 (3)
C3—C9—C8	112.5 (2)	111.7 (1)	112.3 (7)	112.0 (3)	111.9 (3)
C4—C9—C8	119.6 (2)	120.0 (2)	118.3 (7)	119.3 (3)	119.4 (3)
C1—C11—C111	—	113.4 (2)	—	—	—
C1—C11—C112	—	113.0 (2)	—	—	—
C111—C11—C112	—	110.1 (2)	—	—	—
C2—C12—C121	—	—	136 (1)	—	—

Table 4 (cont.)

	(1)	(2)	(3)	(4A)	(4B)
C5—C15—C16	118.9 (3)	120.2 (2)	119.1 (8)	—	—
C5—C15—O	121.7 (3)	121.7 (2)	118.0 (9)	124.3 (4)	127.9 (8)† 130.1 (9)‡
C16—C15—O	119.4 (3)	118.1 (2)	122.5 (9)	—	—
	(5)	(6)	(7A)	(7B)	(7C)
C1—C2	1.554 (4)	1.499 (9)	1.529 (6)	1.492 (8)	1.515 (7)
C1—C8	1.512 (4)	1.537 (6)	1.515 (5)	1.522 (6)	1.504 (6)
C1—C10	1.537 (4)	1.49 (2)	1.551 (6)	1.506 (6)	1.519 (9)
C1—C11	1.534 (5)	1.55 (2)	1.532 (6)	1.596 (8)	1.555 (9)
C2—C3	1.550 (4)	1.430 (9)	1.565 (6)	1.569 (9)	1.539 (6)
C2—C12	1.530 (4)	1.49 (1)	—	—	—
C3—C9	1.514 (4)	1.514 (7)	1.516 (5)	1.516 (6)	1.522 (5)
C3—C13	1.545 (5)	1.39 (1)	1.518 (6)	1.483 (8)	1.530 (7)
C3—C14	1.537 (4)	—	1.529 (6)	1.513 (6)	1.516 (6)
C4—C5	1.400 (4)	1.379 (6)	1.402 (4)	1.407 (5)	1.435 (6)
C4—C9	1.391 (3)	1.392 (6)	1.381 (5)	1.385 (5)	1.389 (5)
C5—C6	1.397 (4)	1.418 (6)	1.416 (5)	1.407 (5)	1.380 (6)
C5—C15	1.494 (4)	1.503 (7)	1.492 (5)	1.486 (5)	1.486 (6)
C6—C7	1.376 (4)	1.402 (6)	1.389 (5)	1.383 (5)	1.352 (6)
C6—C17	—	1.496 (7)	1.512 (5)	1.513 (5)	1.564 (6)
C7—C8	1.397 (4)	1.364 (6)	1.384 (4)	1.385 (5)	1.394 (5)
C8—C9	1.390 (3)	1.368 (6)	1.382 (5)	1.380 (5)	1.371 (5)
C15—C16	1.498 (5)	1.464 (9)	1.490 (5)	1.496 (6)	1.363 (7)
C15—O	1.224 (4)	1.209 (7)	1.215 (5)	1.218 (5)	1.285 (8)
	(5)	(6)	(7A)	(7B)	(7C)
C2—C1—C8	101.0 (2)	101.5 (4)	102.1 (3)	103.4 (4)	102.4 (3)
C2—C1—C10	110.4 (3)	119 (1)	110.7 (3)	114.8 (4)	115.1 (5)
C2—C1—C11	115.3 (3)	107 (1)	113.7 (3)	111.1 (5)	112.9 (4)
C8—C1—C10	112.8 (2)	113 (1)	112.0 (3)	110.5 (3)	110.8 (4)
C8—C1—C11	109.3 (3)	108 (1)	110.8 (3)	111.2 (4)	108.4 (4)
C10—C1—C11	108.1 (2)	107.4 (9)	107.6 (3)	106.0 (4)	107.0 (4)
C1—C2—C3	107.4 (2)	113.0 (6)	109.0 (3)	109.9 (5)	110.8 (4)
C1—C2—C12	115.5 (3)	121.5 (6)	—	—	—
C3—C2—C12	115.3 (2)	124.2 (7)	—	—	—
C2—C3—C9	101.7 (2)	103.1 (5)	100.9 (3)	101.5 (4)	100.9 (3)
C2—C3—C13	109.9 (3)	132.7 (8)	110.2 (3)	114.1 (5)	110.1 (4)
C2—C3—C14	115.8 (2)	—	112.9 (4)	108.2 (4)	114.1 (4)
C9—C3—C13	110.8 (2)	121.4 (6)	112.1 (3)	111.5 (4)	110.9 (3)
C9—C3—C14	110.5 (3)	—	109.9 (3)	112.0 (3)	112.3 (3)
C13—C3—C14	108.1 (2)	—	110.6 (4)	109.3 (5)	108.4 (4)
C5—C4—C9	119.2 (2)	120.7 (4)	120.8 (3)	121.2 (3)	118.5 (4)
C4—C5—C6	119.3 (2)	119.7 (4)	119.2 (3)	118.9 (3)	121.8 (4)
C4—C5—C15	122.5 (3)	118.5 (4)	118.9 (3)	119.2 (3)	115.9 (4)
C6—C5—C15	118.2 (3)	121.8 (4)	121.9 (3)	121.9 (3)	122.3 (4)
C5—C6—C7	121.5 (3)	117.8 (4)	118.5 (3)	118.9 (3)	117.3 (4)
C5—C6—C17	—	124.3 (5)	123.5 (3)	123.0 (3)	125.0 (4)
C7—C6—C17	—	117.7 (5)	118.0 (3)	118.1 (3)	117.6 (4)
C6—C7—C8	119.1 (3)	121.1 (4)	121.3 (3)	121.5 (3)	122.5 (4)
C1—C8—C7	128.2 (2)	129.1 (4)	128.1 (3)	128.2 (4)	127.1 (4)
C1—C8—C9	111.7 (2)	109.5 (4)	111.6 (3)	111.4 (3)	111.8 (3)
C7—C8—C9	120.1 (2)	121.0 (4)	120.3 (3)	120.4 (3)	121.0 (4)
C3—C9—C4	127.9 (2)	129.0 (4)	127.8 (3)	128.8 (4)	128.8 (3)
C3—C9—C8	111.3 (2)	111.7 (4)	112.5 (3)	112.1 (3)	112.5 (3)
C4—C9—C8	120.7 (2)	119.2 (4)	119.7 (3)	119.2 (3)	118.7 (3)
C5—C15—C16	119.5 (3)	119.3 (5)	120.2 (3)	120.2 (3)	121.7 (5)
C5—C15—O	119.9 (3)	122.1 (5)	121.4 (3)	122.4 (3)	115.3 (5)
C16—C15—O	120.6 (3)	118.5 (5)	118.4 (3)	117.4 (4)	122.9 (5)

\* De Ridder &amp; Schenk (1991).

† For O1BA.

‡ For O1BB.

### Planarity

The aromatic ring in the molecules is essentially planar. In (1), (4A), (4B), (7B) and (7C), the maximum deviation of an atom from the six-atom plane is of the order 0.01 Å. For molecules (2), (5) and (7A), the maximum deviation is of the order 0.02 Å. The structures having the lowest accuracy show the highest deviations

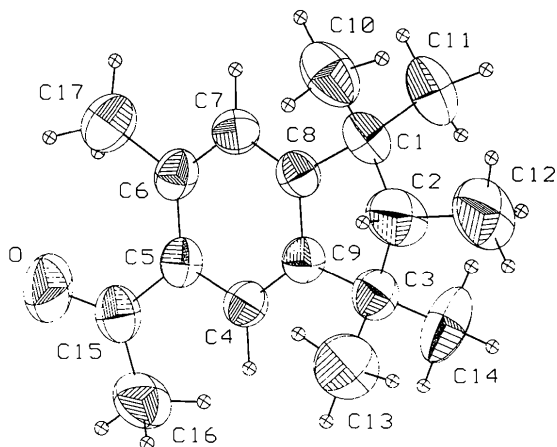


Fig. 1. Molecular structure of (1) (Musk Phantolid). Thermal ellipsoids are shown at 50% probability levels; H atoms as arbitrary spheres.

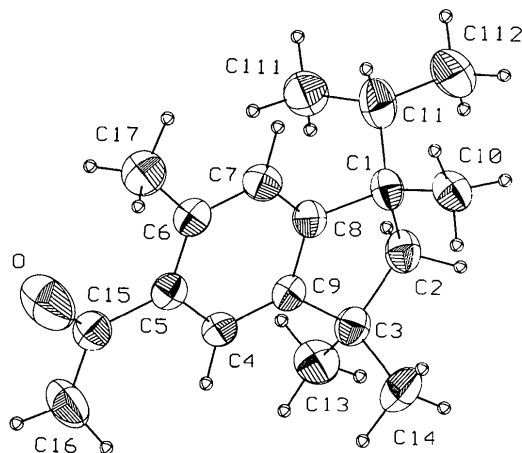


Fig. 2. Molecular structure of (2). Thermal ellipsoids are shown at 50% probability levels; H atoms as arbitrary spheres.

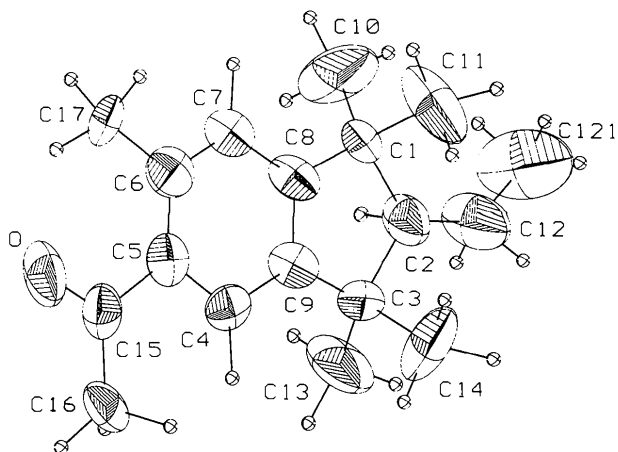


Fig. 3. Molecular structure of (3). Thermal ellipsoids are shown at 50% probability levels; H atoms as arbitrary spheres.

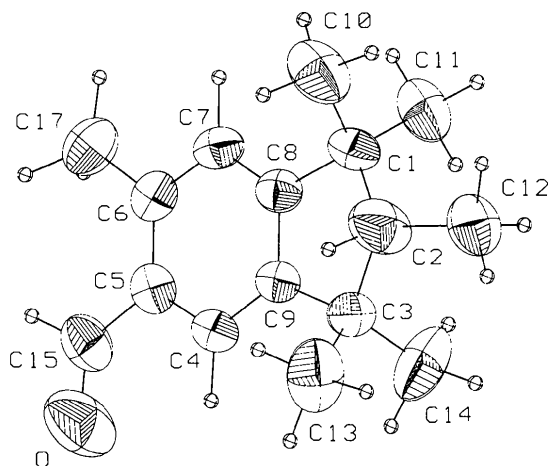


Fig. 4. Molecular structure of (4A). Thermal ellipsoids are shown at 50% probability levels; H atoms as arbitrary spheres.

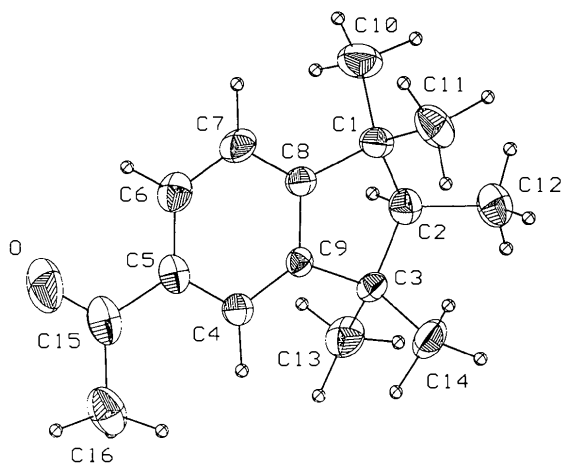


Fig. 5. Molecular structure of (5). Thermal ellipsoids are shown at 50% probability levels; H atoms as arbitrary spheres.

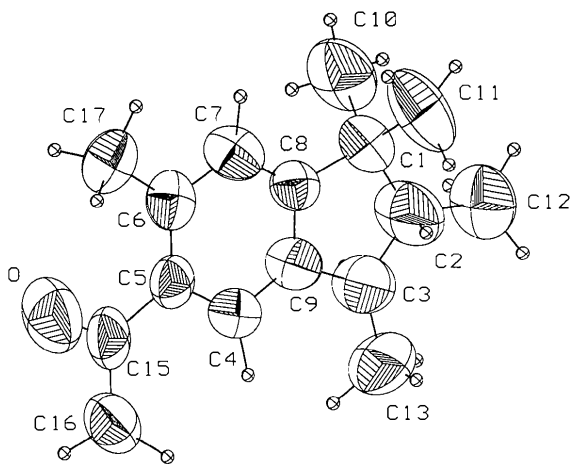


Fig. 6. Molecular structure of (6). Thermal ellipsoids are shown at 50% probability levels; H atoms as arbitrary spheres.

from planarity: 0.06 (3) and 0.04 (2) Å, respectively, for (3) and (6). A table showing deviations from planarity for the ring member atoms and the attached atoms has been deposited as supplementary material.\*

#### Conformation

Because the atoms C1, C8, C9 and C3 of the cyclopentene ring are constrained to lie in or near the plane of the benzene ring, the cyclopentene ring adopts an envelope conformation with C2 at the tip of the envelope. In structures (1), (3), (4), (5) and (6), where a methyl or ethyl group is attached to C2, this group is invariably in the equatorial position.

#### Disorder

*The cyclopentene ring.* Molecules of the compounds discussed in this paper are asymmetric, which involves the existence of two enantiomers in equal amounts, which are mirror images of each other. The cyclopentene ring is flexible and flipping over of C2 to the other

\* See deposition footnote.

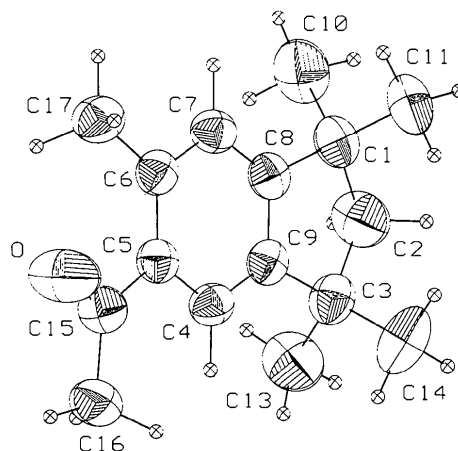


Fig. 7. Molecular structure of (7). Thermal ellipsoids are shown at 50% probability levels; H atoms as arbitrary spheres.

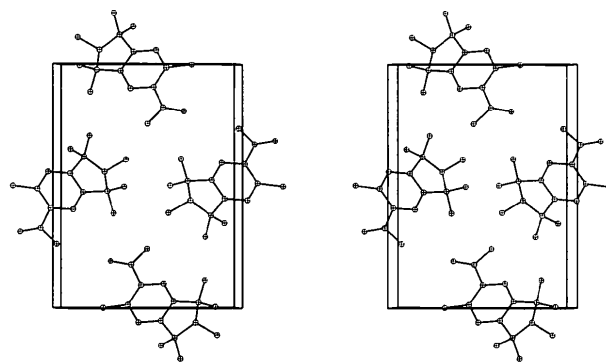


Fig. 8. Stereoscopic packing diagram of the unit cell of (1) (Musk Phantolid) viewed along the *a* axis (*c* axis horizontal).

site of the central plane is possible; the axial conformer having a somewhat higher energy than the equatorial. In solution there will be an equilibrium between the two conformers of each enantiomer. On crystallization, the enantiomers will pack in a specific way and with a specific conformation. However, as the greater part of the molecule is approximately planar, the two enantiomers will not be so different geometrically.

When the central parts of two enantiomeric molecules are superimposed, nine or ten atoms coincide; C2 and the groups attached to the cyclopentene ring are outside the

central plane. Fig. 15 shows the possible conformations for the two enantiomers of a molecule such as (1). In the crystal, the alkyl group at C2 is equatorial, which implies the occurrence of conformers 15.1*b* (i.e. C2'—C12') and 15.2*a* (i.e. C2—C12) in Fig. 15. In these conformers, the C2 atom and the alkyl group at C2 are not far from the central plane, nor are the methyl groups at C10, C11, C13 and C14 in 15.1*b* far from their counterparts in 15.2*a*. Therefore, if the packing allows

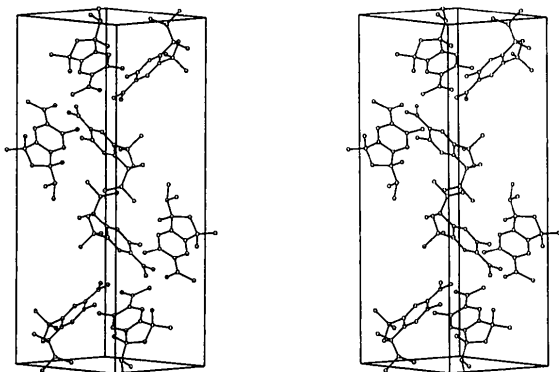


Fig. 9. Stereoscopic packing diagram of the unit cell of (2) viewed along  $[1\bar{1}0]$ .

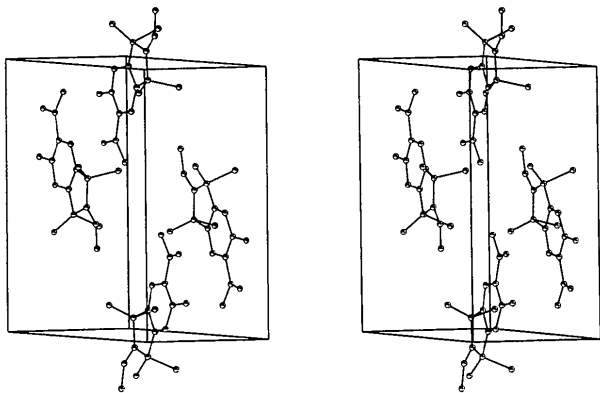


Fig. 10. Stereoscopic packing diagram of the unit cell of (3) viewed along  $[10\bar{1}]$ .

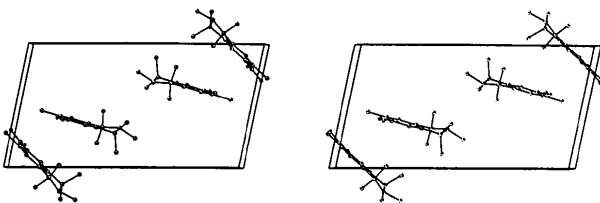


Fig. 11. Stereoscopic packing diagram of the unit cell of (4) viewed along the  $a$  axis ( $c$  axis horizontal).

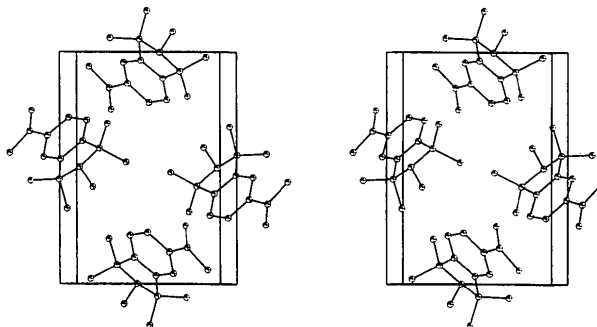


Fig. 12. Stereoscopic packing diagram of the unit cell of (5) viewed along the  $c$  axis ( $a$  axis horizontal).

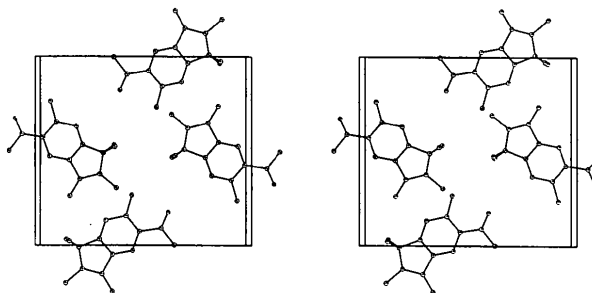


Fig. 13. Stereoscopic packing diagram of the unit cell of (6) viewed along the  $a$  axis ( $c$  axis horizontal).

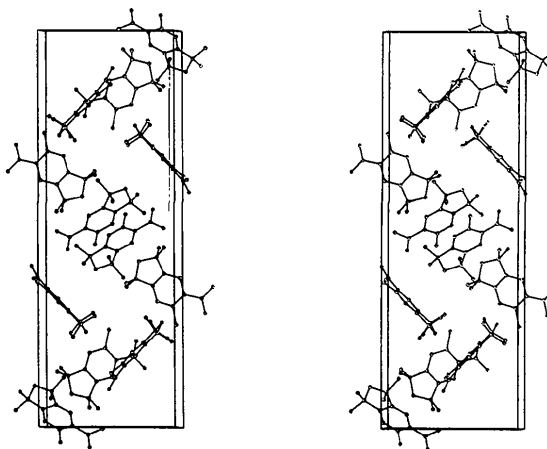


Fig. 14. Stereoscopic packing diagram of the unit cell of (7) viewed along the  $a$  axis ( $b$  axis horizontal).



space, it is imaginable that a molecule can be replaced by its enantiomer without seriously affecting interactions with neighbouring molecules, thus leading to disorder. If necessary, the acyl group can easily adopt itself to the new situation. If C2 carried two H atoms, the four conformers of Fig. 15 would be reduced to two.

The type of disorder suggested above is encountered in the structures of (3), (6) and (7B). Since the positions of the methyl(ene) groups in the 'correct' and 'wrong' molecules are less than *ca* 0.7 Å apart, the electron-density distributions of pairs of corresponding atoms are not resolved and a composite electron density will be observed. As a result, the disorder manifests itself in relatively high displacement parameters for C2 and the substituent atoms on the cyclopentene ring, and in deviating and sometimes anomalous values for the bond distances and angles involving these atoms. In two cases [(3) and (6)], a near 50/50 disorder is observed, giving rise to a quasiplanar cyclopentene ring. 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 5).

Structure (6) is a case apart. The molecules have two asymmetric C atoms (C2 and C3), implying the possible existence of four diastereomers. Apparently, in the crystal structure of (6), with one molecule in the asymmetric unit, only two enantiomers are represented; the other

Table 5. *Structural data of the cyclopentene ring*

	A*	B†	C‡
(1)§	0.385 (5)	25.2 (3)	342.5
(2)§	0.302 (3)	19.6 (2)	—
(3)	0.06 (4)	4 (2)	360.0
(4A)	0.391 (8)	25.3 (5)	340.1
(4B)	0.374 (8)	24.3 (5)	343.2
(5)	0.410 (4)	26.5 (3)	338.2
(6)	0.16 (3)	11 (2)	358.7
(7A)	0.312 (7)	20.2 (4)	—
(7B)	0.201 (7)	13.3 (6)	—
(7C)	0.185 (8)	12.5 (5)	—

\* Distance (Å) of C2 from the plane through C1—C8—C9—C3.

† Dihedral angle between the planes through C1—C8—C9—C3 and C1—C2—C3.

‡ Sum of the angles (°) around C2.

§ De Ridder & Schenk (1991).

Table 6. *Angle (°) of the substituent group with the aromatic plane; A = acetyl, F = formyl*

(1)*	A	-22.4 (3)
(2)*	A	-7.3 (3)
(3)	A	5 (2)
(4A)	F	-174 (2)
(4B) (O1BA)	F	172 (5)
(4B) (O1BB)	F	-10 (6)
(5)	A	10.6 (1)
(6)	A	2 (1)
(7A)	A	-11.8 (2)
(7B)	A	18.9 (2)
(7C)	A	-11.0 (5)

\* De Ridder & Schenk (1991).

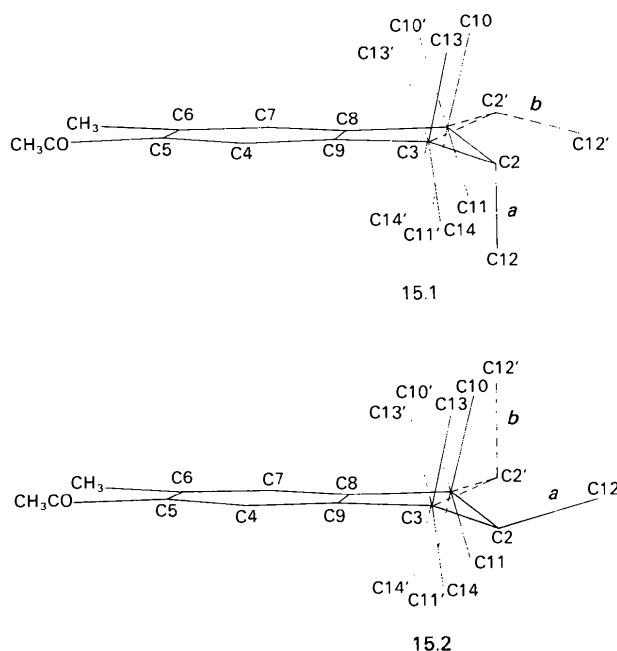


Fig. 15. Possible conformations for the two enantiomers of (1). The axial conformer 15.1a (full lines) is the mirror image of 15.1b (dashed lines). Analogous are the equatorial conformers 15.1b (C2'—C12') and 15.2a (C2—C12) mirror images.

two are probably energetically more unfavourable. There is disorder in which C2, C10, C11, C12 and C13 are involved, the cyclopentene ring being quasiplanar with C12 and C13 practically in the plane of the cyclopentene ring.

*The acyl group.* Another type of disorder originates in the acyl group not having a fixed orientation. Again this manifests itself in the displacement parameters and in the bond distances and angles involved. Clear examples of disorder of this kind are (3), (4B), (6) and (7C). An extreme case is demonstrated by (4B), where two separate partial O atoms are observed for the formyl group.

In general, crystals of this type of compound are of poor quality. Often, several recrystallization attempts were necessary in order to obtain crystals suitable for single-crystal X-ray diffraction experiments. In combination with the high disorder manifested, the refinement of structure factors led to *R* values >0.07 (Table 2).

#### *Orientation of the acyl group with respect to the benzene ring*

The angles the acyl group makes with the benzene ring are listed in Table 6. In the acyl groups attached to C5, the zero position of the O atom is in the plane of the

the phenyl ring facing C6. The acetyl groups at C5 in (1), (2), (3), (6) and (7) all have a similar environment with a methyl group (C17) at C6 and no substituent at C4. Nevertheless, there is a rather wide range for the angle between the acetyl group and the benzene ring (2–22.4°), which must be ascribed to differences in packing; the O atom is invariably facing the methyl group at C6. The acetyl group in (5) is unhindered by neighbouring groups, but the angle with the benzene ring is still 10.6(1)°, which again must be a question of packing; the O atom is facing C6.

The behaviour of the formyl group is interesting. Two orientations have been found in the structure of (4B), one in which the O atom is facing C4, as in (4A), and one in which the O atom is facing the methyl group at C6, as in (1), (2), (3), (6) and (7).

### Concluding remarks

Compounds (2) and (3) are structural isomers. The observation that (2) has no musk odour and (3) has a musk odour indicates the important influence of the molecular shape in the structure–activity relationships. The same applies to the structural isomers (4), (5), (6) and (7), where only the first has a strong musk odour.

A point that is supposed to be essential for the occurrence of musk odour is the coplanarity of the active group with a phenyl ring (or another conjugated system) [e.g. Bersuker, Dimoglo, Gorbachov, Vlad & Pesaro (1991)]. The crystal structures dealt with in this paper show that the orientation of the active group (acetyl, formyl) is not fixed at all: in many cases relatively unhindered groups show a variation of 25° or more. This demonstrates that the interaction with the surrounding molecules can easily compensate for the loss in conjugation energy with the phenyl group.

In a number of recent studies dealing with the correlation of molecular properties and muskiness (Narvaez, Lavine & Jurs, 1986; Bersuker, Dimoglo, Gorbachov, Vlad & Pesaro, 1991), geometric details play an important role. These details are taken from geometries obtained by means of molecular modelling. In none of these studies is it clear whether the alkyl group (mostly a CH<sub>3</sub> group) attached to C2 is equatorial (as found in the crystal structures and as expected since it has the lowest steric intramolecular hindrance) or axial. Furthermore, the acetyl group is invariably facing the methyl group at C6, whereas in several of the molecules discussed by Bersuker, Dimoglo, Gorbachov, Vlad & Pesaro (1991), the orientation seems to be varied at will.

At this point it should be noted that the C2 atom is asymmetric in the musk compounds (1), (3), (4), (5) and (6). The latter even has a second asymmetric C

atom in the cyclopentene ring (C3). The natural musk compounds, which are macrocyclic ketones or lactones, have no asymmetric C atom(s), but most of the synthetic bicyclic (and tricyclic) compounds have this feature. According to Ohloff, Winter & Fehr (1990), only the *S*-stereoisomer of Musk Tonalid has a 'strongly musky odour with a good fixation property', whereas the *R*-stereoisomer has only a 'light and sweet aromatic odour'. As a consequence, this would mean that only half of the molecules in centrosymmetric structures might have a musk odour.

The discussion of some structure–activity relationship studies in the light of the geometrical results of our crystal studies will be reported in a separate contribution (De Ridder & Schenk, 1994)

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