

Crystal Studies of Musk Compounds. II. Structures of 6-Acetyl-1,1,2,4,4,7-hexamethyltetralin (Musk Tonalid) (I) and 1,1,2,4,4,7-Hexamethyltetralin (II)

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(Received 13 December 1989; accepted 14 February 1990)

Abstract. (I): $C_{18}H_{26}O$, $M_r = 258.40$, monoclinic, $P2_1/c$, $a = 8.590$ (3), $b = 19.415$ (4), $c = 10.079$ (3) Å, $\beta = 111.26$ (2)°, $V = 1567$ (1) Å³, $Z = 4$, $D_x = 1.10$ g cm⁻³, $\lambda(\text{Cu } K\alpha) = 1.5418$ Å, $\mu(\text{Cu } K\alpha) = 4.66$ cm⁻¹, $F(000) = 568$, room temperature, final $R = 0.073$ for 923 observed reflections. (II): $C_{16}H_{24}$, $M_r = 216.37$, monoclinic, $P2_1/n$, $a = 10.2213$ (9), $b = 15.593$ (2), $c = 8.6991$ (9) Å, $\beta = 97.183$ (8)°, $V = 1375.6$ (3) Å³, $Z = 4$, $D_x = 1.05$ g cm⁻³, $\lambda(\text{Cu } K\alpha) = 1.5418$ Å, $\mu(\text{Cu } K\alpha) = 3.96$ cm⁻¹, $F(000) = 480$, $T = 247$ K, final $R = 0.061$ for 1724 observed reflections. In musk tonalid the acetyl group is twisted 22° out of the plane of the aromatic ring. The geometry of musk tonalid (I) is compared with that of its precursor (II).

Introduction. This is the second paper in a series dealing with musk compounds [I: De Ridder, Goubitz & Schenk (1990)]. The musk compound of the first paper belongs to the nitrobenzene family, the one described in this paper is classified in the group of the non-nitro tetralins. Compound (I) is a synthetic product with a strong musk-like odour, used in cosmetic industries for the preparation of perfumes. Compound (II) is its precursor, which has no musk odour.

Experimental. The intensities were collected with an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Cu $K\alpha$ radiation and θ - 2θ scans. Preliminary Weissenberg photographs indicated both crystals to be monoclinic.

Structure (I): Crystal dimensions approximately $0.25 \times 0.15 \times 0.15$ mm. A total of 1612 unique reflections within the ranges $2.5 \leq \theta \leq 50^\circ$, $-10 \leq h \leq 10$, $0 \leq k \leq 19$, $0 \leq l \leq 8$ were measured, of which 923 were above the significance level of $2.5\sigma(I)$. Two standard reflections ($\bar{1}, \bar{1}\bar{5}, 0$, $\bar{1}\bar{4}\bar{1}$), measured hourly, suffered a 24.5% decrease during 19 h collecting time which was corrected for. Unit-cell parameters were refined by a least-squares algorithm using 18 reflections with $64 < 2\theta < 80^\circ$. Corrections were applied

for Lorentz and polarization effects, not for absorption. The structure was determined by direct methods using the program *SIMPEL83* (Schenk & Kiers, 1983). The H atoms were found in a ΔF synthesis. Block-diagonal least-squares refinement on F , anisotropic for the non-H atoms and isotropic for the H atoms, converged to $R = 0.073$, $wR = 0.110$. A weighting scheme $w^{-1} = 6.7 + F_{\text{obs}} + 0.013F_{\text{obs}}^2$ was used. The isotropic secondary-extinction coefficient refined to $3(1) \times 10^{-7}$ (Larson, 1967). In the final refinement cycle the largest Δ/σ was 0.78 (extinction coefficient). A final difference Fourier map revealed a residual electron density between -0.1 and 0.3 e \AA^{-3} .

Structure (II): A crystal (dimensions approximately $0.38 \times 0.33 \times 0.15$ mm) was mounted in a capillary. A total of 2596 unique reflections were measured at 247 K within the ranges $2.5 \leq \theta \leq 65^\circ$, $-12 \leq h \leq 12$, $0 \leq k \leq 18$, $0 \leq l \leq 10$. Of these 1724 were above the significance level of $2.5\sigma(I)$. Unit-cell parameters were refined by a least-squares fitting procedure using 23 reflections with $80 < 2\theta < 86^\circ$. The intensities of two standard reflections ($\bar{1}31$, 220), measured hourly, showed no significant decrease during 30 h collection time. Corrections for Lorentz and polarization effects were applied. The structure was determined by direct methods using the program *SIMPEL83* (Schenk & Kiers, 1983). The H atoms were derived from a ΔF synthesis. Block-diagonal least-squares refinement on F , anisotropic for the non-H atoms and isotropic for the H atoms, converged to $R = 0.061$, $wR = 0.078$. The maximum Δ/σ was 0.28. A weighting scheme $w^{-1} = 9.1 + F_{\text{obs}} + 0.0066F_{\text{obs}}^2$ was used. Extinction was negligible. After isotropic refinement an empirical absorption correction was applied, with corrections in the range 0.68 – 1.29 (*DIFABS*; Walker & Stuart, 1983). A final difference Fourier map revealed a residual electron density between -0.1 and 0.4 e \AA^{-3} .

All calculations were performed with *XRAY76* (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976) unless stated otherwise. The scattering factors were taken from Cromer & Mann (1968).

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

Compound (I)	x	y	z	U_{eq}
C(1)	0.1318 (10)	0.1651 (4)	0.4178 (8)	0.041 (5)
C(2)	0.262 (1)	0.1072 (4)	0.4535 (9)	0.050 (5)
C(3)	0.384 (1)	0.1137 (4)	0.6026 (10)	0.050 (5)
C(4)	0.4857 (9)	0.1783 (4)	0.6362 (8)	0.035 (5)
C(5)	0.4362 (9)	0.3061 (4)	0.6139 (7)	0.034 (4)
C(6)	0.3483 (9)	0.3667 (4)	0.5655 (8)	0.035 (5)
C(7)	0.1826 (9)	0.3604 (4)	0.4626 (8)	0.042 (5)
C(8)	0.1241 (9)	0.2950 (4)	0.4208 (8)	0.034 (5)
C(9)	0.2150 (9)	0.2349 (4)	0.4718 (8)	0.032 (5)
C(10)	0.3773 (9)	0.2413 (4)	0.5725 (7)	0.028 (4)
C(11)	0.041 (1)	0.1676 (4)	0.2535 (9)	0.054 (6)
C(12)	-0.001 (1)	0.1523 (5)	0.485 (1)	0.056 (6)
C(13)	0.188 (1)	0.0338 (5)	0.423 (1)	0.073 (7)
C(14)	0.6251 (10)	0.1751 (4)	0.5768 (9)	0.044 (5)
C(15)	0.566 (1)	0.1846 (5)	0.8003 (9)	0.061 (6)
C(16)	0.421 (1)	0.4350 (5)	0.6224 (9)	0.050 (6)
C(17)	0.604 (1)	0.4402 (5)	0.687 (1)	0.073 (7)
C(18)	0.067 (1)	0.4206 (4)	0.3963 (10)	0.056 (6)
O(1)	0.3322 (9)	0.4844 (3)	0.6178 (9)	0.095 (6)

Compound (II)	x	y	z	U_{eq}
C(1)	0.2756 (3)	0.2917 (2)	0.9697 (3)	0.041 (1)
C(2)	0.4181 (3)	0.3087 (2)	0.9307 (4)	0.058 (2)
C(3)	0.4210 (3)	0.3297 (2)	0.7648 (4)	0.058 (2)
C(4)	0.3475 (3)	0.4109 (2)	0.7102 (3)	0.040 (1)
C(5)	0.1165 (3)	0.4688 (2)	0.6999 (3)	0.046 (1)
C(6)	-0.0094 (3)	0.4722 (2)	0.7435 (3)	0.054 (2)
C(7)	-0.0445 (3)	0.4167 (2)	0.8572 (3)	0.049 (2)
C(8)	0.0502 (3)	0.3609 (2)	0.9236 (3)	0.044 (1)
C(9)	0.1789 (2)	0.3563 (2)	0.8837 (3)	0.034 (1)
C(10)	0.2115 (2)	0.4110 (2)	0.7656 (3)	0.035 (1)
C(11)	0.2804 (4)	0.3057 (2)	1.1452 (3)	0.066 (2)
C(12)	0.2284 (4)	0.2012 (2)	0.9293 (5)	0.070 (2)
C(13)	0.5147 (4)	0.2354 (2)	0.9818 (5)	0.076 (2)
C(14)	0.4232 (3)	0.4919 (2)	0.7677 (4)	0.060 (2)
C(15)	0.3355 (3)	0.4104 (3)	0.5326 (4)	0.073 (2)
C(18)	-0.1812 (3)	0.4196 (3)	0.9063 (5)	0.073 (2)

Discussion. Final positional parameters for the non-H atoms for both structures are listed in Table 1. Bond lengths and angles are given in Table 2 and have normal values.* A *PLUTO* (Motherwell & Clegg, 1978) drawing of molecule (I), showing the numbering system, is given in Fig. 1 [the numbering of (II) is similar, the acetyl group being replaced by an H atom].

In both molecules the aromatic ring is essentially planar within the limits of accuracy. Following the criteria defined by Foces-Foces, Cano & Garcia-Blanco (1976) the non-aromatic ring is classified as a half chair with the twofold axis running through the midpoints of the bonds C(2)—C(3) and C(9)—C(10). In molecule (I) the torsion angle C(7)—C(6)—C(16)—O(1) is 22° . The endocyclic angle at C(6) is significantly smaller than in molecule (II). This distortion can be explained in terms of the conjugation of the aromatic ring with the acetyl substituent

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, bond distances and angles involving H atoms, and least-squares-planes data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53062 (39 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Bond lengths (\AA) and bond angles ($^\circ$)

	Compound (I)	Compound (II)
C(1)—C(2)	1.53 (1)	1.559 (4)
C(1)—C(9)	1.54 (1)	1.538 (3)
C(1)—C(11)	1.55 (1)	1.537 (4)
C(1)—C(12)	1.54 (1)	1.518 (4)
C(2)—C(3)	1.49 (1)	1.484 (5)
C(2)—C(13)	1.55 (1)	1.539 (5)
C(3)—C(4)	1.50 (1)	1.518 (4)
C(4)—C(10)	1.53 (1)	1.527 (4)
C(4)—C(14)	1.52 (1)	1.532 (4)
C(4)—C(15)	1.55 (1)	1.534 (4)
C(5)—C(6)	1.39 (1)	1.387 (4)
C(5)—C(10)	1.36 (1)	1.394 (4)
C(6)—C(7)	1.430 (9)	1.395 (4)
C(6)—C(16)	1.49 (1)	—
C(7)—C(8)	1.37 (1)	1.374 (4)
C(7)—C(18)	1.52 (1)	1.512 (5)
C(8)—C(9)	1.39 (1)	1.404 (4)
C(9)—C(10)	1.401 (9)	1.407 (3)
C(16)—C(17)	1.47 (1)	—
C(16)—O(1)	1.22 (1)	—
C(2)—C(1)—C(9)	110.9 (6)	110.1 (2)
C(2)—C(1)—C(11)	108.3 (7)	106.1 (2)
C(2)—C(1)—C(12)	111.8 (7)	112.7 (3)
C(9)—C(1)—C(11)	109.8 (6)	109.2 (2)
C(9)—C(1)—C(12)	108.0 (7)	109.3 (2)
C(11)—C(1)—C(12)	107.9 (7)	109.4 (3)
C(1)—C(2)—C(3)	111.1 (7)	112.5 (2)
C(1)—C(2)—C(13)	114.6 (7)	113.2 (3)
C(3)—C(2)—C(13)	111.5 (7)	110.8 (3)
C(2)—C(3)—C(4)	116.0 (7)	114.8 (3)
C(3)—C(4)—C(10)	111.0 (6)	109.7 (2)
C(3)—C(4)—C(14)	110.8 (7)	112.1 (2)
C(3)—C(4)—C(15)	107.8 (7)	106.6 (3)
C(10)—C(4)—C(14)	108.3 (7)	109.8 (2)
C(10)—C(4)—C(15)	110.6 (7)	110.9 (2)
C(14)—C(4)—C(15)	108.3 (6)	107.8 (3)
C(6)—C(5)—C(10)	125.5 (6)	122.3 (3)
C(5)—C(6)—C(7)	117.0 (7)	120.0 (3)
C(5)—C(6)—C(16)	121.4 (6)	—
C(7)—C(6)—C(16)	121.6 (7)	—
C(6)—C(7)—C(8)	117.3 (7)	117.4 (3)
C(6)—C(7)—C(18)	124.9 (7)	120.7 (3)
C(8)—C(7)—C(18)	117.8 (6)	121.8 (3)
C(7)—C(8)—C(9)	124.5 (6)	124.1 (3)
C(1)—C(9)—C(8)	118.8 (6)	118.6 (2)
C(1)—C(9)—C(10)	123.2 (6)	123.8 (2)
C(8)—C(9)—C(10)	118.0 (6)	117.7 (2)
C(4)—C(10)—C(5)	120.5 (6)	119.1 (2)
C(4)—C(10)—C(9)	121.8 (6)	122.5 (2)
C(5)—C(10)—C(9)	117.7 (6)	118.4 (2)
C(6)—C(16)—C(17)	117.6 (8)	—
C(6)—C(16)—O(1)	121.2 (8)	—
C(17)—C(16)—O(1)	121.2 (8)	—

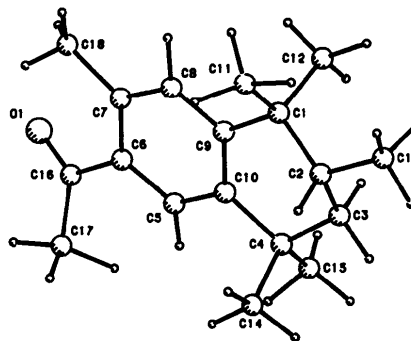


Fig. 1. The numbering system of musk tonalid [molecule (I)]. In molecule (II) the acetyl group is replaced by an H atom.

(Domenicano, Vaciago & Coulson, 1975). The intramolecular distances C(18)—O(1) and H(183)—O(1) are 2.83 (1) and 2.35 (9) \AA respectively.

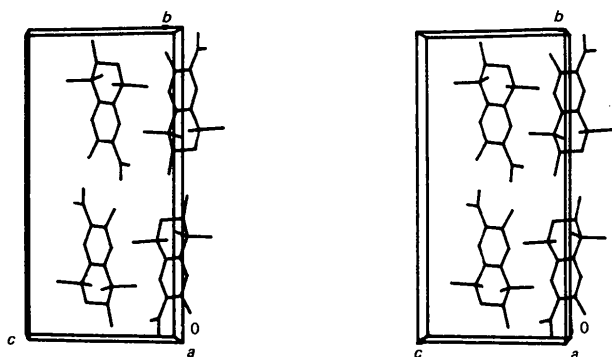


Fig. 2. A view of the unit-cell contents of structure (I) along [100].

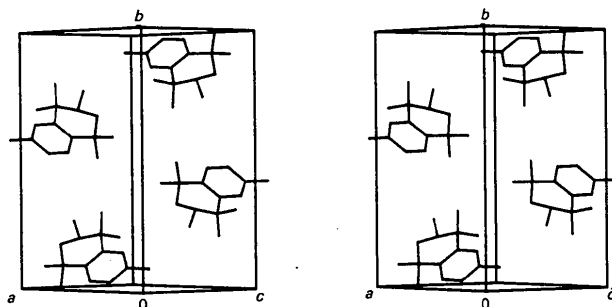


Fig. 3. A view of the unit-cell contents of structure (II) along [100].

The packing of the molecules is illustrated in Figs. 2 and 3 for musk tonalid and its precursor respectively. In both structures there are no intermolecular distances significantly shorter than the sum of the van der Waals radii.

The shortest intermolecular C—O distance in musk tonalid is 3.62 (2) Å [O(1)—C(17) through symmetry operation $1-x, 1-y, 1-z$].

Matching of the two molecules [leaving out the substituent on C(6) and the H atoms] resulted in an r.m.s. value of 0.09 Å, which means that the addition of the osmophoric group has little influence on the geometry of the molecule. The largest difference between the corresponding atoms occurs at C(11) and C(12).

The authors would like to express their thanks to Dr A. M. Cohen and Drs W. Lenselink of PFW-Nederland for providing the crystals and D. Heijdenrijk for technical assistance.

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Structure of Solanida-2,4,6-triene

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(Received 21 December 1989; accepted 8 February 1990)

Abstract. C₂₇H₃₉N, $M_r = 377.6$, orthorhombic, $P2_12_12_1$, $a = 16.066$ (2), $b = 13.575$ (2), $c = 10.332$ (2) Å, $V = 2253$ (1) Å³, $Z = 4$, $D_x =$

1.12 Mg m^{-3} , $\lambda(\text{Cu } K\alpha) = 1.54184 \text{ Å}$, $\mu = 0.44 \text{ mm}^{-1}$, $F(000) = 832$, $R = 0.042$ for 2253 unique observed reflections. The six-membered *A* ring has a half-chair conformation, the *B* ring exhibits a transitional form between sofa and half-chair conforma-

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