Crystal Studies of Musk Compounds. I. 4-*tert*-Butyl-3-methoxy-2,6-dinitrotoluene (Musk Ambrette)

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Abstract. $C_{12}H_{16}N_2O_5$, $M_r = 268.27$, monoclinic, $P2_1/n$, $a = 9.875$ (5), $b = 9.865$ (1), $c = 14.326$ (5) Å, $\beta = 101.90$ (4)°, $V = 1366$ (1) Å^3, $Z = 4$, $D_x = 1.30$ Mg m^{-3}, $\lambda(\text{Cu } K\alpha) = 1.5418$ Å, $\mu = 0.66$ mm^{-1}, $F(000) = 568$, room temperature. Final $R = 0.048$ for 1455 observed reflections. The investigation was undertaken to determine the positions of the substituent groups. The ring geometry undergoes a considerable distortion with endocyclic angles larger than in other known nitrobenzenes. The methoxy and nitro groups are rotated out of the plane of the benzene ring.

Introduction. Despite the great interest and the consequent substantial activity in the field of olfaction, the mechanism of odour perception remains ambiguous. One of the most studied and most universally appreciated odour groups is the musk family as the compounds which comprise it can be considered to be pure olfactive stimulants which are uncomplicated by other stimuli-generating properties. Musk compounds belong to a large group of closely related chemical structures, including isomers and homologs, which exhibit wide variations in odour strength and quality, affording comparisons based upon subtle differences in molecular dimensions. Although the use of principal component analysis and discriminant analysis (Chastrette, Zakarya & Elmouaffek, 1986) or pattern recognition (Ham & Jurs, 1985; Narvaez, Lavine & Jurs, 1986) has given promising results, the greater importance of molecular shape and the lesser importance of functional groups, as stated by Beets (1957), may lead to the relation between the structure and its activity. In order to obtain quantitative information, an X-ray investigation of a series of musk compounds has been undertaken.

The title compound is a synthetic product used in cosmetic industries for the preparation of perfumes. It holds a dominant position among the synthetic nitro musks due to its fine persistent musk-like odour. Until now, three different structures have been proposed for the title compound (Barbier, 1928; Darzens & Lévy, 1931; Zeide & Dubinin, 1932).

Experimental. The intensities were collected with an Enraf–Nonius CAD-4 diffractometer using graphite-monochromated Cu $K\alpha$ radiation and ω–2θ scans. Crystal dimensions $0.25 \times 0.23 \times 0.10$ mm. A total of 2325 reflections within the ranges $2.5 \le \theta \le 65°$, $-11 \le h \le 11$, $0 \le k \le 11$, $0 \le l \le 16$ was measured, of which 1455 were above the significance level of $2.5 \times \sigma(I)$. One standard reflection (273), measured hourly, suffered a 5.5% decrease during 27 h collection time. Unit-cell parameters were refined by a least-squares algorithm using 15 reflections with $70 < 2\theta < 80°$. Corrections applied for Lorentz and polarization effects, not for absorption. Structure determined by direct methods using the program *SIMPEL*83 (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 $R = 0.048$, $wR = 0.067$. Maximum $\Delta/\sigma = 0.50$. A weighting scheme $w^{-1} = 4.86 + F_{ob}^2 + 0.0094\ F_{obs}^2$ was used. The isotropic secondary extinction coefficient refined to 9.7 (8) $\times 10^{-4}$ (Zachariasen, 1968). A final difference synthesis revealed residual electron density within the range ± 0.4 e Å^{-3}. All calculations were performed with *XRAY*76 (Stewart *et al.*, 1976), unless stated otherwise. The scattering factors were taken from Cromer & Mann (1968); *International Tables for X-ray Crystallography* (1974).

Discussion. Final atomic parameters for the non-H atoms are listed in Table 1.* A *PLUTO* (Motherwell & Clegg, 1978) drawing of the molecule showing the atomic numbering scheme is given in Fig. 1. Bond lengths and angles are given in Table 2.

This crystal-structure determination proves that in Musk Ambrette the methoxy group is not *para* relative to the *tert*-butyl group as stated by Darzens & Lévy (1931) and their adherents (Brockmann & Vol-

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52354 (12 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional parameters and equivalent iso-*
tropic thermal parameters of the non-H atoms with
e.s.d.'s in parentheses

$$U_{eq} = (1/6\pi^2)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
C(1)	0·7847 (3)	0·7158 (3)	0·0825 (2)	0·043 (2)
C(2)	0·7697 (3)	0·5944 (3)	0·1288 (2)	0·043 (2)
C(3)	0·6539 (3)	0·5553 (3)	0·1622 (2)	0·043 (2)
C(4)	0·5416 (3)	0·6447 (3)	0·1545 (2)	0·042 (2)
C(5)	0·5558 (3)	0·7689 (3)	0·1113 (2)	0·043 (2)
C(6)	0·6702 (3)	0·7994 (3)	0·0754 (2)	0·042 (2)
C(7)	0·9145 (4)	0·7514 (4)	0·0481 (3)	0·067 (2)
C(8)	0·6494 (3)	0·3111 (3)	0·1515 (3)	0·073 (2)
C(9)	0·4120 (3)	0·6121 (3)	0·1939 (2)	0·052 (2)
C(10)	0·3399 (4)	0·4850 (4)	0·1462 (3)	0·077 (3)
C(11)	0·3077 (4)	0·7284 (4)	0·1754 (4)	0·080 (3)
C(12)	0·4535 (4)	0·5915 (5)	0·3016 (3)	0·082 (3)
N(1)	0·8924 (3)	0·5045 (3)	0·1481 (2)	0·061 (2)
N(2)	0·6715 (3)	0·9317 (3)	0·0276 (2)	0·059 (2)
O(3)	0·6530 (3)	0·4331 (2)	0·2079 (1)	0·058 (1)
O(11)	0·9116 (4)	0·4302 (3)	0·0848 (2)	0·104 (2)
O(12)	0·9686 (3)	0·5127 (4)	0·2247 (2)	0·104 (2)
O(21)	0·6369 (3)	1·0309 (2)	0·0678 (2)	0·088 (2)
O(22)	0·6997 (4)	0·9363 (3)	−0·0493 (3)	0·121 (3)

Table 2. *Bond distances (Å) and angles (°) of the*
non-H atoms with e.s.d.'s in parentheses

C(1)—C(2)	1·392 (3)	C(6)—N(2)	1·475 (3)
C(1)—C(6)	1·386 (4)	C(8)—O(3)	1·446 (3)
C(1)—C(7)	1·507 (5)	C(9)—C(10)	1·531 (4)
C(2)—C(3)	1·382 (4)	C(9)—C(11)	1·528 (4)
C(2)—N(1)	1·481 (4)	C(9)—C(12)	1·526 (4)
C(3)—C(4)	1·403 (4)	N(1)—O(11)	1·211 (3)
C(3)—O(3)	1·373 (2)	N(1)—O(12)	1·198 (4)
C(4)—C(5)	1·393 (3)	N(2)—O(21)	1·220 (3)
C(4)—C(9)	1·536 (4)	N(2)—O(22)	1·192 (4)
C(5)—C(6)	1·368 (4)		
C(2)—C(1)—C(6)	112·4 (3)	C(5)—C(6)—N(2)	117·1 (3)
C(2)—C(1)—C(7)	122·5 (3)	C(4)—C(9)—C(10)	110·7 (3)
C(6)—C(1)—C(7)	125·0 (3)	C(4)—C(9)—C(11)	111·2 (3)
C(1)—C(2)—C(3)	125·6 (3)	C(4)—C(9)—C(12)	109·2 (3)
C(1)—C(2)—N(1)	116·2 (3)	C(10)—C(9)—C(11)	107·6 (3)
C(3)—C(2)—N(1)	118·1 (4)	C(10)—C(9)—C(12)	110·2 (3)
C(2)—C(3)—C(4)	119·6 (3)	C(11)—C(9)—C(12)	107·8 (3)
C(2)—C(3)—O(3)	119·8 (3)	C(2)—N(1)—O(11)	118·1 (3)
C(4)—C(3)—O(3)	120·4 (3)	C(2)—N(1)—O(12)	117·7 (3)
C(3)—C(4)—C(5)	115·9 (3)	O(11)—N(1)—O(12)	124·1 (3)
C(3)—C(4)—C(9)	123·0 (3)	C(6)—N(2)—O(21)	117·4 (2)
C(5)—C(4)—C(9)	121·0 (3)	C(6)—N(2)—O(22)	119·3 (3)
C(4)—C(5)—C(6)	121·8 (3)	O(21)—N(2)—O(22)	123·2 (3)
C(1)—C(6)—C(5)	124·5 (3)	C(3)—O(3)—C(8)	117·8 (2)
C(1)—C(6)—N(2)	118·4 (3)		

stituents, the ring geometry undergoes distortion (Domenicano, Vaciago & Coulson, 1975). The endo-cyclic angles of the ring at the C atoms carrying the nitro-group substituents are larger than both the sp^2 angle and those in other nitrobenzenes (Domenicano *et al.*, 1975), presumably because of the adjacent groups.

Due to sterical hindrance, the methoxy and nitro groups are rotated out of the plane of the benzene ring, as can be seen in the Newman projections in Fig. 2. This results in a specific molecular profile which will be investigated in further detail.

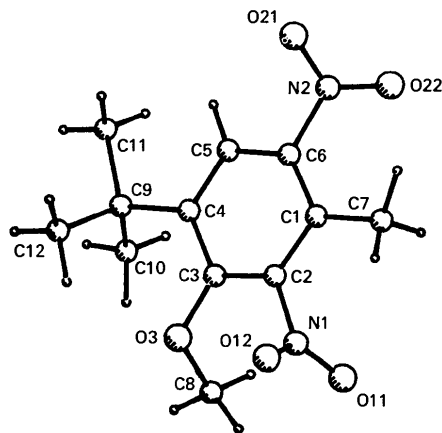There are no intermolecular interactions less than 3·0 Å.

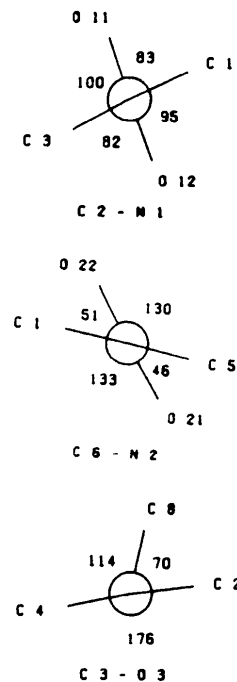Fig. 1. The numbering of the non-H atoms.

Fig. 2. Newman projections of selected bonds.

pers, 1947; Nightingale, 1947) and also that it does not have the structure originally proposed by Barbier (1928)   (2-*tert*-butyl-3-methoxy-4,6-dinitrotoluene). The conclusions made by de Capeller (1928) and Ruzicka (1928) and by Zeide & Dubinin (1932) are hereby confirmed.

The benzene ring is essentially planar, the maxi-mum deviation of a ring atom from the least-squares plane through the ring being 0·019 (3) Å. There is a considerable deformation of the benzene ring (Table 2) with significant deviations of the bond angles from the normally accepted values. It is known that when there are electron-donating or -accepting sub-

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Structure of Benzyl 2-Oxo-2,3-dihydro-1,3-benzothiazoleacetate

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Abstract. $C_{16}H_{13}NO_3S$, $M_r = 299\cdot3$, monoclinic, $P2_1$, $a = 4\cdot714$ (0·5), $b = 10\cdot914$ (1), $c = 14\cdot419$ (2) Å, $\beta = 94\cdot29$ (1)°, $V = 739\cdot7$ (1) Å^3, $Z = 2$, $D_m = 1\cdot33$, $D_x = 1\cdot34$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0\cdot23$ mm^{-1}, $F(000) = 312$, room temperature. The structure was refined by full-matrix least squares to a final $R = 0\cdot043$ for 786 observed reflections. Packing is essentially determined by the shortest CH···O = 2·28 and 2·48 Å intermolecular contacts. The atoms of the 2(3*H*)-benzothiazolone moiety are coplanar to within ±0·015 (7) Å.

Introduction. Derivatives of benzothiazole are a new group of compounds which exhibit biological growth activity in plants. Exceptionally, in higher concentrations they display growth retardation activity as well. Of these derivatives benzyl 2-oxo-2,3-dihydro-1,3-benzothiazoleacetate (I) has especially remarkable

biological properties (Varkonda, Hýblová, Sutoris, Konečný & Mikulášek, 1985). We now report the X-ray crystal structure determination of this compound.

(I)
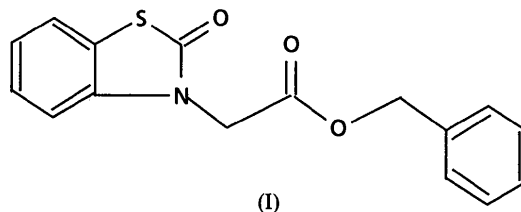
Experimental. (I) was prepared by dissolving equimolar quantities of benzothiazole-2-ol and chloromethyl benzeneacetate in anhydrous acetone and triethylamine (Sutoris, Mikulášek, Sekerka & Konečný, 1984). Recrystalization from ethanol gave