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Crystal Studies of Musk Compounds. X.†‡ 1,1,2,3,3-Pentamethyl-2,3,4,5,6,7-hexahydroinden-4-one

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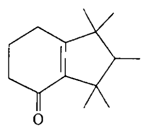
Abstract

The structure of the title compound, $C_{14}H_{22}O$, which is a strong musk, has been established by X-ray diffraction. The five- and six-membered rings adopt envelope and sofa conformations, respectively. The molecular dimensions are discussed with respect to the known structure-activity relationships of musk compounds.

Comment

The title compound (I) is the main component of the commercial product *Cashmeran* and has a strong musk odour (International Flavors & Fragrances Inc., 1973). It is one of the most intriguing musk compounds, since it is, as yet, the only known bicyclic musk compound without an aromatic ring and may be the first example of a new series of musk compounds. The crystal structures of a number of bicyclic compounds belonging to the indan family (*i.e.* an aromatic six-membered ring fused with a non-aromatic five-membered ring) have been discussed in part III (De Ridder & Schenk, 1991*a*) and part VIII (De Ridder, Čapková, Hatjisymeon, Fraanje & Schenk, 1994) of this series.



(I)

In this compound the methyl group attached to C2 is found to be in the equatorial position, analogous to the indan compounds described previously. The six-membered ring has two conjugated double bonds which constrain atoms C1, C3, C4, C5, C7, C8, C9 and O to be coplanar or nearly so [the maximum deviation from the least-squares plane through these atoms is 0.046 (5) Å]. As a result, the six-membered ring has to adopt a C6-sofa conformation and the five-membered ring a C2-envelope conformation; the ring-displacement asymmetry parameters (Duax, Weeks & Rohrer, 1976) are $\Delta_s^6 = 4.3°$ and $\Delta_s^2 = 0.7°$, respectively.

The cyclopentene ring shows the same type of disorder as discussed in part VIII (De Ridder, Čapková, Hatjisymeon, Fraanje & Schenk, 1994) of this series. The quantities defined in part VIII are as follows for the title compound: the dihedral angle between the least-squares planes through atoms C1, C8, C9, C3 and atoms C1, C2, C3 is 7.1 (8)°; the distance of atom C2 from the former plane is 0.11 (1) Å; the sum of the angles around atom C2 is 358.7°. For comparison, the average values for four compounds not having a disordered cyclopentene ring are 25.3°, 0.39 Å and 341°, respectively. This corroborates with the high displacement parameter observed for C2.

For a number of indans and tetralins (both acetyl and nitro compounds), the dimensions of a triangle defined by the two quaternary C atoms of the non-aromatic ring and the sp^2-C atom of the acetyl group (or the N atom of a nitro group in the same position) attached to the aromatic ring, have been compared (De Ridder & Schenk, 1991*b*). The distances between the quaternary atoms were 2.51–2.54 and 3.05–3.09 Å for the indans and tetralins, respectively, the former being comparable to the distance in the title compound [C1···C3 2.497 (6) Å]. However, the two other dimensions of the triangle, in the ranges 4.91–5.09

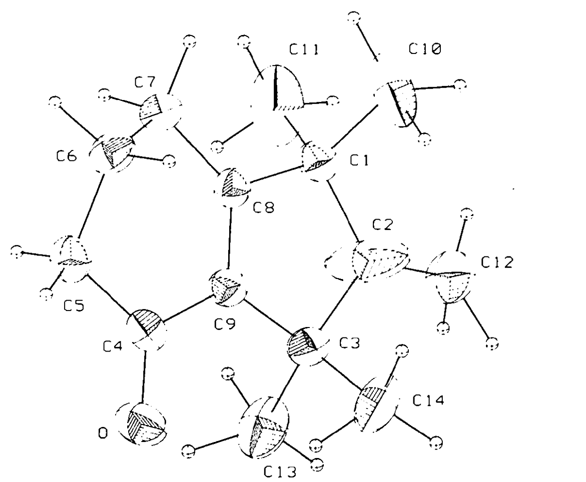


Fig. 1. *PEANUT* drawing (Hummel, Hauser & Bürgi, 1990) of the title compound. Displacement ellipsoids are shown at the 30% probability level; H atoms (not labelled) are drawn as spheres of arbitrary size.

† This work forms part of a thesis by De Ridder (1992).
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and 5.72-5.85 Å, respectively, are significantly larger than found in the title compound [C3···C4 2.651 (6) and C1···C4 3.760 (6) Å]. Narvaez, Lavine & Jurs (1986) proposed a slightly different descriptor to correlate the musk odour, namely the distance of the quaternary C centres to the O atom. Their average intermolecular distances (3.7, 5.8 and 6.3 Å) are significantly larger than in *Cashmeran*: C1···C3 2.497 (6), C3···O 3.004 (6) and C1···O 4.725 (6) Å. Based on the electron-topology approach to the quantitative structure–activity relationships (QSAR) problem, Bersuker *et al.* (1991) postulated that the necessary conditions for a compound to have a musk odour involve two independent molecular fragments: the first consists of a polar group (CO, NO, CN) whose electronegative atom is situated symmetrically and at a distance of 6.7 (5) Å with respect to two methyl (or methylene) groups, the distance between them being 2.5 (5) Å; the second fragment includes two other methyl (or methylene) groups situated at a distance of 5.5 (5) Å from each other. *Cashmeran* is an example of a strong musk not fulfilling the conditions for the first fragment. The best combination of atoms to get the first fragment is obtained by combining atoms C10 and C11 with the O atom at distances of 5.72 (1) (O···C10), 5.705 (9) (O···C11) and 2.46 (1) Å (C10···C11). The first two distances are significantly below the lower range proposed by Bersuker *et al.* (1991).

Experimental

Crystal data

$C_{14}H_{22}O$
M_r = 206.33
Monoclinic
$P2_1/c$
a = 13.327 (1) Å
b = 7.0693 (9) Å
c = 14.115 (1) Å
β = 104.588 (9)°
V = 1286.9 (2) Å^3
Z = 4
D_x = 1.065 Mg m^{-3}
Cu $K\alpha$ radiation
λ = 1.5418 Å
Cell parameters from 23 reflections
θ = 40.1-44.5°
μ = 0.462 mm^{-1}
T = 231 K
Block
0.6 × 0.3 × 0.1 mm
Colourless

Data collection

Enraf-Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: empirical (*DIFABS*; Walker & Stuart, 1983)
T_{min} = 0.50, T_{max} = 1.49
2458 measured reflections
2389 independent reflections
2190 observed reflections [$I_{net} > 2.5\sigma(I_{net})$]
θ_{max} = 64.83°
$h = -15 \rightarrow 15$
$k = -8 \rightarrow 0$
$l = 0 \rightarrow 16$
2 standard reflections frequency: 60 min intensity variation: none

Refinement

Refinement on F
R = 0.084
wR = 0.11
S = 0.268
1520 reflections
224 parameters
$w = 1/(4.20 + F_o + 0.0075F_o^2)$
$(\Delta/\sigma)_{max}$ = 0.59
$\Delta\rho_{max}$ = 0.454 e Å^{-3}
$\Delta\rho_{min}$ = −0.378 e Å^{-3}
Extinction correction: Zachariasen (1967)
Extinction coefficient: 5 (22) × 10^{-7}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
C1	0.2746 (3)	−0.0765 (6)	0.1949 (3)	0.053 (2)
C2	0.3428 (8)	−0.029 (2)	0.2935 (7)	0.20 (1)
C3	0.2931 (3)	0.1206 (7)	0.3450 (3)	0.057 (2)
C4	0.1209 (3)	0.3149 (6)	0.2714 (3)	0.052 (2)
C5	0.0299 (3)	0.3362 (6)	0.1855 (3)	0.058 (2)
C6	0.0539 (4)	0.2841 (6)	0.0883 (3)	0.059 (2)
C7	0.1022 (3)	0.0877 (6)	0.0941 (3)	0.052 (2)
C8	0.1881 (3)	0.0680 (5)	0.1837 (3)	0.046 (2)
C9	0.1987 (3)	0.1724 (6)	0.2652 (3)	0.048 (2)
C10	0.3366 (6)	−0.042 (1)	0.1189 (6)	0.110 (5)
C11	0.2296 (6)	−0.2747 (8)	0.1787 (8)	0.114 (5)
C12	0.4323 (5)	−0.139 (1)	0.3423 (5)	0.088 (4)
C13	0.2640 (5)	0.060 (1)	0.4395 (4)	0.089 (4)
C14	0.3676 (4)	0.287 (1)	0.3718 (4)	0.089 (4)
O	0.1294 (3)	0.4120 (5)	0.3463 (2)	0.074 (2)

Table 2. *Selected geometric parameters* (Å, °)

C1—C2	1.50 (1)	C3—C14	1.524 (8)
C1—C8	1.518 (6)	C4—C5	1.491 (5)
C1—C10	1.53 (1)	C4—C9	1.464 (6)
C1—C11	1.519 (7)	C4—O	1.241 (5)
C2—C3	1.53 (1)	C5—C6	1.530 (7)
C2—C12	1.45 (1)	C6—C7	1.524 (6)
C3—C9	1.507 (5)	C7—C8	1.484 (5)
C3—C13	1.541 (8)	C8—C9	1.344 (5)
C2—C1—C8	102.3 (5)	C13—C3—C14	107.0 (4)
C2—C1—C10	107.9 (6)	C5—C4—C9	117.7 (4)
C2—C1—C11	118.1 (6)	C5—C4—O	121.2 (4)
C8—C1—C10	110.5 (4)	C9—C4—O	121.2 (3)
C8—C1—C11	110.2 (4)	C4—C5—C6	113.2 (4)
C10—C1—C11	107.7 (6)	C5—C6—C7	110.6 (4)
C1—C2—C3	111.4 (7)	C6—C7—C8	110.9 (3)
C1—C2—C12	123.8 (8)	C1—C8—C7	123.6 (3)
C3—C2—C12	123.5 (7)	C1—C8—C9	111.6 (3)
C2—C3—C9	101.1 (4)	C7—C8—C9	124.8 (4)
C2—C3—C13	116.9 (6)	C3—C9—C4	126.3 (3)
C2—C3—C14	108.5 (6)	C3—C9—C8	113.2 (4)
C9—C3—C13	111.7 (4)	C4—C9—C8	120.4 (3)
C9—C3—C14	111.6 (4)		

The structure was solved by direct methods. The H atoms were introduced at calculated positions, 1.09 Å from their carrier atom, and included as riding atoms in the structure-factor calculations. The temperature factor of the H atom attached to C2 was kept fixed at 0.08 Å^2. Refinement was performed using a full-matrix least-squares algorithm on F, anisotropic for non-H atoms and isotropic for H atoms. Data collection: *CAD-4 Software* (Enraf-Nonius, 1989). Cell refinement: *CELCON* program, comparable to *Xtal LATCON* (Hall & Stewart, 1990). Data reduction: *Xtal ADDREF*, *SORTRF*. Program(s) used to solve structure: *Xtal SIMPEL*. Program(s) used to refine structure: *Xtal CRYLSQ*. Molecular graphics: *PEANUT* (Hummel, Hauser & Bürgi, 1990). Software used to prepare material for publication: *Xtal BONDLA*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71822 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: SH1085]

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X-ray Study of Static Disorder in *N*-Methylacetamide

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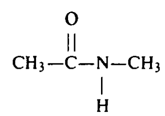
Abstract

N-Methylacetamide (NMA), C_3H_7NO, is the smallest molecule to contain a peptide bond and is considered to be the basic structural unit of peptide chains in proteins. An X-ray electron density study at 110 K showed the presence of static disorder. The present work describes this disorder and the configuration of this biologically important molecule.

Comment

NMA is a small planar molecule of fundamental importance which has been extensively investigated by IR and Raman spectroscopy (Mizushima & Shimanouchi, 1950). A preliminary report of the structure of NMA at 238 K has been published (Katz & Post, 1960) in which the authors describe the structure as ordered (space group *Pnma* with $R = 0.13$). The results of an accurate electronic density study of the molecule would be an important contribution to complete the work cited above in order to gain a better understanding of the peptide bond.



NMA

The refinement was initially carried out using the least-squares program *LINEX* (Coppens, 1974). An anisotropic refinement in which the coordinates of the H atoms were adjusted to result in tetrahedral bond angles and C—H bond lengths of 1.09 Å gave $R = 0.09$. A difference Fourier synthesis revealed a second position for the molecule (Fig. 1). An occupation factor of 0.9 was assigned to the first molecule (molecule *A*) and a factor of 0.1 was assigned to the second one (molecule *B*). The positions of the atoms of the second molecule were corrected to adjust its geometry to that of molecule *A*.

Further refinement was carried out using the least-squares program *ORION* (André, Fourme & Renaud, 1971), in which atoms may be constrained in groups. The thermal motion of the molecules was analysed initially in terms of rigid-body motion, but this resulted in a singularity in the least-squares normal matrix, giving the errors 'the atoms lie on a quadratic curve' (Schomaker & Trueblood, 1968). Therefore, the five non-H atoms of molecule *A* were allowed to refine freely with anisotropic displacement factors, while molecule *B* was treated as a rigid body with isotropic displacement factors *B* of 2.03 Å^2 for the non-H atoms; for H atoms an isotropic Debye–Waller factor refined to 1.81 Å^2. This second refinement procedure resulted in a decreased *R* value of 0.066. The structure of molecule *A* is shown in Fig. 2.

In order to determine the nature of this disorder a second X-ray study was carried out at 210 K. Using the same refinement procedure described above, a