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(Benzoylmethyl)(3-hydroxypropyl)-dimethylammonium Bromide

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Abstract

The title compound is found in the open tautomeric form rather than the seven-membered cyclic form. The hydroxy group forms a C—C—C—O torsion angle with a magnitude of 59.2 (2)°, and the phenyl group is nearly coplanar with the carbonyl group, forming a C—C—C—O torsion angle with a magnitude of 4.6 (3)°.

Comment

Dynamic ring–chain tautomerism in aryl derivatives of hemiketal morpholinium salts was demonstrated over 40 years ago (Cromwell & Tsou, 1949; Lutz & Jordan, 1949). Our recent kinetic studies (Sorensen, McClelland & Gandour, 1991) have quantified this tautomerism. A report of the analogous seven-membered ring (Anderson, Casey, Force, Jensen, Matz & Rivard, 1966) led us to re-examine this chemistry. We have recently reported (Garcia, Fronczek & Gandour, 1992) that we found no evidence of the closed tautomeric form for a variety of *p*-substituted aryls. That study included the crystal structure determination of the 4-phenylphenyl derivative. Herein we report the structure of the unsubstituted phenyl compound, which also exists in the open tautomeric form.

In addition to the conformational features described in the *Abstract*, two subunits control the shape of the cation. The propyl group has an *anti* central torsion angle (C1—C2—C3—N1) and the ammonium N atom is *syn* to the carbonyl O atom. The phenyl group is planar with a maximum deviation from planarity of 0.007 (3) Å for C10. The carbonyl O2 atom lies 0.144 (2) Å out of this plane, while N1 lies only 0.005 (2) Å from it. The hydroxy group is oriented toward the anion, forming a contact with an O···Br distance of 3.277 (2) Å, and an angle about the H atom of 164 (2)°.

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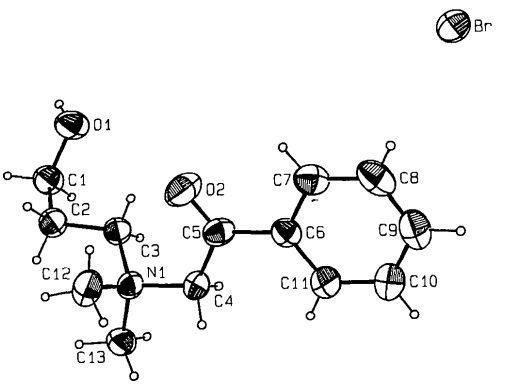

Fig. 1. *ORTEP*II (Johnson, 1976) drawing of the title compound with thermal ellipsoids drawn at the 40% probability level.

Experimental

Crystal data

$C_{13}H_{20}BrNO_2$
M_r = 302.2
Triclinic
$P\bar{1}$
a = 7.2471 (4) Å
b = 7.2644 (4) Å
c = 14.2762 (9) Å
α = 85.504 (5)°
β = 81.588 (5)°
γ = 75.323 (4)°
V = 718.57 (7) Å^3
Z = 2
D_x = 1.397 Mg m^{-3}
Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 12–14°
μ = 2.82 mm^{-1}
T = 294 K
Irregular fragment
0.55 × 0.45 × 0.30 mm
Colourless
Crystal source: slow cooling of 2-propanol–tetrahydrofuran (1:1)

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical
T_{min} = 0.9150, T_{max} = 0.9997
4177 measured reflections
4177 independent reflections
2764 observed reflections [$I > 3\sigma(I)$]
θ_{max} = 30°
h = 0 → 10
k = −10 → 10
l = −20 → 20
3 standard reflections
frequency: 167 min
intensity variation: −9.4% (linear correction)

Refinement

Refinement on F
Final R = 0.030
wR = 0.031
S = 1.665
2764 reflections
235 parameters
All H-atom parameters refined
$w = 4F^2[\sigma^2(I) + (0.02F^2)^2]^{-1}$
$(\Delta/\sigma)_{max}$ = 0.01
$\Delta\rho_{max}$ = 0.38 e Å^{-3}
$\Delta\rho_{min}$ = −0.09 e Å^{-3}
Extinction correction: $(I + gI_c)^{-1}$ applied to F_c
Extinction coefficient: 3.4 (10) × 10^{-7}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

$B_{eq} = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	B_{eq}
Br	0.21430 (3)	0.15853 (3)	0.14066 (1)	4.439 (4)
O1	0.5295 (2)	0.5852 (2)	0.7836 (1)	5.57 (4)
O2	0.2713 (2)	0.1949 (3)	0.6261 (1)	5.92 (4)
N1	0.1151 (2)	0.2386 (2)	0.8197 (1)	3.68 (3)
C1	0.4452 (3)	0.5437 (3)	0.8756 (2)	5.11 (5)
C2	0.3749 (3)	0.3656 (3)	0.8764 (2)	4.65 (5)
C3	0.2287 (3)	0.3905 (3)	0.8082 (1)	3.86 (4)
C4	−0.0077 (3)	0.2602 (3)	0.7412 (1)	3.86 (4)
C5	0.0970 (3)	0.2322 (3)	0.6416 (1)	4.09 (4)
C6	−0.0242 (3)	0.2502 (3)	0.5646 (1)	3.84 (4)
C7	0.0660 (3)	0.2366 (3)	0.4718 (2)	4.71 (5)
C8	−0.0401 (4)	0.2493 (3)	0.3985 (2)	5.65 (6)
C9	−0.2343 (4)	0.2734 (3)	0.4153 (2)	5.58 (6)
C10	−0.3262 (4)	0.2851 (4)	0.5066 (2)	5.71 (6)
C11	−0.2209 (3)	0.2753 (4)	0.5807 (2)	5.04 (5)
C12	0.2446 (3)	0.0412 (3)	0.8240 (2)	5.22 (5)
C13	−0.0219 (3)	0.2672 (3)	0.9106 (2)	4.87 (5)

Table 2. *Geometric parameters* (Å, °)

O1—C1	1.410 (3)	C1—C2	1.505 (4)
O2—C5	1.213 (3)	C2—C3	1.511 (3)
N1—C3	1.521 (3)	C4—C5	1.514 (3)
N1—C4	1.505 (3)	C5—C6	1.484 (3)
C3—N1—C4	110.6 (1)	N1—C4—C5	116.7 (2)
O1—C1—C2	109.9 (2)	O2—C5—C4	121.5 (2)
C1—C2—C3	110.3 (2)	O2—C5—C6	122.0 (2)
N1—C3—C2	114.4 (2)	C4—C5—C6	116.6 (2)
H10H—O1—C1—C2	−160 (2)	C1—C2—C3—N1	−166.6 (2)
C4—N1—C3—C2	−172.7 (2)	N1—C4—C5—O2	−0.2 (3)
C3—N1—C4—C5	63.5 (2)	O2—C5—C6—C7	−4.6 (3)
O1—C1—C2—C3	−59.2 (2)		

The crystal was sealed in a capillary. The space group was determined by successful refinement of a centrosymmetric model. Programs used include *MolEN* (Fair, 1990) and *ORTEP*II (Johnson, 1976).

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates complete geometry and least-squares-planes data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71247 (31 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: ST1053]

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Structure of 6-Fluoro-1,2,3,4,7,12-hexahydro-7-methyl-12-methylene-benz[*a*]anthracene

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Abstract

The X-ray analysis confirms the structure of the 12-methylene tautomer formed by the acid catalysis of 6-fluoro-1,2,3,4-tetrahydro-7,12-dimethylbenz-[*a*]anthracene. The central *C* ring is in a boat conformation, with the result that the molecule is bent about a line through atoms C(7) and C(12) with a dihedral angle of 32.5°. The cyclohexene *A* ring is in a half-chair conformation.

Comment

The study of the title compound (1) is part of an investigation of the carcinogenic activity of 1,2,3,4-tetrahydro-7,12-dimethylbenz[*a*]anthracene (THDMBA) (2) and its six aryl fluoro regioisomers (Witiak & Nair, 1990; Kumari, Milo & Witiak, 1990; Nair, Walker, Sharma, Witiak & DiGiovanni, 1992; Rinderle, Black, Sharma & Witiak, 1992). 6F-THDMBA (3) displays more mutagenic activity in human neonatal fibroblast (HNF) cells and more skin tumor initiating activity in mice than the parent compound (THDMBA) and its other aryl fluoro analogues. Acid-catalyzed isomerization of 6F-THDMBA results in formation of the 12- and 7-methylene tautomers, (1) and (4), respectively (Witiak, Abood, Goswami & Milo, 1986). Further work with the 12-methylene tautomer (1) indicated that it does not show any mouse skin tumor initiating activity (Nair, Walker, Sharma, Witiak & DiGiovanni, 1992). Although this tautomer was not studied in HNF cell transformation assays, a similar THDMBA analogue not having the planar anth-

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