Table 2. *Selected bond distances (Å) and angles (°) for the bromide ion and the succinimide molecules*

Br···N1	3.338 (11)	C5—O5	1.18 (2)
Br···N2	3.380 (10)	C5—C6	1.51 (2)
Br···H1	2.44	C6—C7	1.55 (2)
Br···H2	2.43	C7—C8	1.50 (2)
N1—C1	1.38 (3)	C8—O8	1.18 (2)
N1—C4	1.40 (2)	N3—C31	1.50 (2)
C1—O1	1.21 (2)	N3—C33	1.50 (2)
C1—C2	1.52 (2)	N3—C35	1.50 (2)
C2—C3	1.51 (2)	N3—C37	1.52 (2)
C3—C4	1.52 (2)	C31—C32	1.52 (2)
C4—O4	1.18 (2)	C33—C34	1.52 (2)
N2—C5	1.37 (2)	C35—C36	1.51 (2)
N2—C8	1.40 (2)	C37—C38	1.49 (2)
N1···Br···N2	102.8 (3)	N1—H1···Br	158
H1···Br···H2	96	N2—H2···Br	178

The structure was solved by direct methods (*MULTAN*87; Debaerdemaeker, Germain, Main, Tate & Woolfson, 1987). Some of the H atoms were found in $\Delta\rho$ maps, the others were placed in calculated positions (C—H and N—H distances 0.95 Å). All were assigned an isotropic displacement parameter of 4.0 Å^2, which is an approximate average of the displacement parameters of the corresponding C and N atoms. Br, N and O atoms were refined with anisotropic displacement parameters. The H atoms were not refined. The system of computer programs used for this study is described by Lundgren (1982).

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References

Chemistry Data Book (1982). Compiled by J. G. Stark & H. G. Wallace, 2nd ed. in SI. London: John Murray.

Dahan, F. & Lefébvre-Soubeyran, O. (1976). *Acta Cryst.* B32, 2863–2866.

Debaerdemaeker, T., Germain, G., Main, P., Tate, C. & Woolfson, M. M. (1987). *MULTAN87. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

Elding, M., Albertsson, J., Svensson, G. & Eberson, L. (1990). *Acta Chem. Scand.* 44, 135–138.

Elding, M., Larsson, A.-K., Svensson, G., Albertsson, J. & Eberson, L. (1992). *Acta Cryst.* C48, 2078–2080.

Hamilton, W. C. & Ibers, J. A. (1968). *Hydrogen Bond in Solids: Methods of Molecular Structure Determination.* Amsterdam: Benjamin.

Lundgren, J.-O. (1982). Report No. UUIC-B13-4-05. Univ. of Uppsala, Sweden.

Oskarsson, Å. (1973). *Acta Cryst.* B29, 1747–1751.

Stålhandske, C. (1972). *Acta Chem. Scand.* 26, 3029–3036.

Refinement of the Molecular Structure of Benzhydrylamine Hydrochloride

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Abstract

The molecular conformation of the title compound, α-phenylbenzylammonium chloride, is helical C_2 with ring twist angles of 57.8 (3) and 68.3 (2)°. Pairs of doubly hydrogen-bonded molecules, connected by hydrogen bonds, form infinite chains along **b**.

Comment

Benzhydrylamine inhibits smooth-muscle spasms (Bruno Blanch, 1990); some of its derivatives obtained by arylic and/or aminic mono- and di-substitution present greater biological activity than the parent compound. Comparison of the molecular structure of the title compound and its derivatives would help towards understanding the structure–activity relationship. Consequently, a study of the structure of benzhydrylamine hydrochloride (BH), a salt used in activity determination, was performed (Rivero, Punte, Rigotti, Goeta, Quinteros Rivero, Vega & Bruno Blanch, 1991) but all attempts to obtain an R factor smaller than 0.07 failed. A thorough analysis of the information was conducted; an instability of the equipment was found that mimics crystal decay. Therefore, to provide a more accurate starting model to analyze the influence of substituents on molecular geometry, a freshly grown single crystal was used to perform the present study.

Intramolecular bond distances and angles in BH do not deviate notably from the expected values. The aromatic rings are planar within experimental error. The bridge angle, Φ, is 113.7 (3)°, in agreement with that in diphenylmethane (DPM) [112.5 (6)° (Barnes, Paton, Damewood & Mislow, 1981)]. The dihedral angles subtended between the least-squares planes of the two rings and the central plane defined by C1*A*—C7—C1*B*, Φ_1 and Φ_2, are 57.8 (3) and 68.3 (2)°, respectively. The angle between the rings, Φ_{12}, is 97.7 (2)°. Barnes, Paton, Damewood & Mislow (1981) found, from data retrieved from the Cambridge Structural Database, that

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steric effects and/or hydrogen bonds produce changes in the molecular conformation when substituents at arylic H-atom positions are introduced in DPM. Comparison between the conformations of BH and DPM shows that the substitution of the ammonium group for a methane H atom decreases Φ_1 and Φ_2 [63.9 (6) and 71.1(6)°, respectively, in DPM] and increases Φ_{12} (80.9°) but does not alter the overall helical C_2 conformation (Barnes, Paton, Damewood & Mislow, 1981).

The atomic displacement parameters have been analyzed using the program *THMA*11 (Maverick & Trueblood, 1988). Orthogonalized U_{ij} values were calculated for each phenyl group separately and for the whole molecule (without H atoms), assuming a rigid-body model in each case: R_U = 0.055 and 0.063 for the phenyl groups and 0.13 for the whole molecule. As expected, the whole molecule is less rigid than each phenyl group. A non-rigid model allowing internal torsions gave R_U = 0.081.

Examination of the packing, exhibited in Fig. 2, shows that the NH_3^+ group is a donor in three hydrogen bonds involving chloride ions as acceptors. The average distance between the N atoms and the accepting chloride ions is 3.21 (3) Å, in agreement with the mean Cl—N distance of 3.19 (7) Å found by Fuller (1959). Pairs of doubly hydrogen-bonded molecules are related by the symmetry operation $0.5 - x, 0.5 - y, 1 - z$.
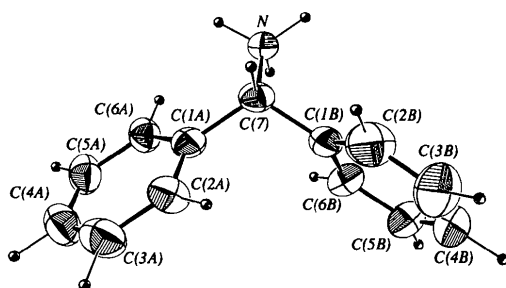

Fig. 1. *ORTEP* drawing of the molecule with non-H atom labels. The atoms are represented by their 50% probability ellipsoids for thermal motion. H atoms have been arbitrarily reduced.
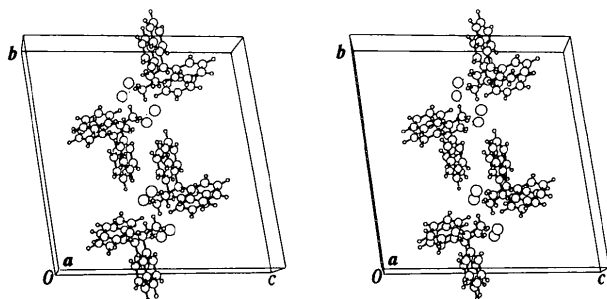

Fig. 2. Stereoscopic view of molecular packing.

Experimental

Crystal data

$C_{13}H_{14}N^+.Cl^-$
M_r = 219.72
Monoclinic
$C2/c$
a = 21.474 (4) Å
b = 5.523 (3) Å
c = 20.161 (2) Å
β = 98.24 (1)°
V = 2366 (1) Å^3
Z = 8
D_x = 1.233 Mg m^{-3}
Mo $K\alpha$ radiation
λ = 0.7093 Å

Cell parameters from 25 reflections
θ = 5–17°
μ = 0.288 mm^{-1}
T = 295 K
Prism
0.37 × 0.15 × 0.12 mm
Colorless
Crystal source: the compound was synthesized by Leuckart's method (Moore, 1949)

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
2391 measured reflections
1779 independent reflections
1115 observed reflections
[$I > 3.0\sigma(I)$]

R_{int} = 0.018
θ_{max} = 25°
h = 0 → 25
k = 0 → 6
l = −24 → 24
3 standard reflections frequency: every 60 min intensity variation: 3%

Refinement

Refinement on F
Final R = 0.044
wR = 0.045
S = 1.91
1115 reflections
140 parameters
Only H-atom U's refined
Calculated weights
$w=k/[\sigma^2(F)+0.000177F^2]$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.21 e Å^{-3}
$\Delta\rho_{min}$ = −0.20 e Å^{-3}

Extinction correction:
$F' = F(1 - CF^2/\sin\theta)$
(Sheldrick, 1976)
Extinction coefficient:
$C = 7 \times 10^{-7}$
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

The H atoms were refined riding on their bound atoms. Overall temperature factors were refined for H atoms of the phenyl, CH_3 and ammonium groups. Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELX*76 (Sheldrick, 1976). Software used to prepare material for publication: *ORTEP* (Johnson, 1965), *MolEN*.

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

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

	x	y	z	U_{eq}
Cl	0.3230	0.0280 (2)	0.4608 (1)	0.0448 (4)
N	0.1759 (1)	−0.0230 (6)	0.4573 (2)	0.042 (1)
C7	0.1378 (2)	−0.0150 (7)	0.3893 (2)	0.039 (1)
C1A	0.1573 (2)	−0.2116 (7)	0.3435 (2)	0.040 (1)
C2A	0.1292 (2)	−0.2119 (9)	0.2773 (2)	0.054 (3)
C3A	0.1465 (2)	−0.384 (1)	0.2327 (2)	0.064 (3)
C4A	0.1920 (2)	−0.5516 (9)	0.2538 (2)	0.060 (3)
C5A	0.2201 (2)	−0.5527 (8)	0.3188 (2)	0.054 (3)

C6A	0.2031 (2)	−0.3841 (8)	0.3638 (2)	0.044 (1)
C1B	0.0683 (2)	−0.0155 (8)	0.3947 (2)	0.044 (1)
C2B	0.0310 (2)	0.1722 (9)	0.3672 (3)	0.073 (3)
C3B	−0.0337 (3)	0.169 (1)	0.3709 (3)	0.098 (4)
C4B	−0.0589 (2)	−0.018 (1)	0.4019 (3)	0.086 (3)
C5B	−0.0224 (2)	−0.203 (1)	0.4297 (3)	0.068 (3)
C6B	0.0410 (2)	−0.2036 (9)	0.4255 (2)	0.053 (3)

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

N—C7	1.493 (5)	C6B—C5B	1.376 (6)
C7—C1A	1.522 (6)	C5B—C4B	1.359 (8)
C7—C1B	1.512 (6)	C4B—C3B	1.359 (9)
C1A—C2A	1.384 (5)	C3B—C2B	1.402 (8)
C1A—C6A	1.388 (6)	Cl···N	3.162 (2)
C2A—C3A	1.395 (7)	Cl···H1	2.2 (1)
C6A—C5A	1.385 (6)	Cl···N^i	3.192 (4)
C5A—C4A	1.362 (5)	Cl···N^ii	3.239 (4)
C4A—C3A	1.369 (7)	Cl···H2^i	2.3 (1)
C1B—C6B	1.383 (7)	Cl···H3^ii	2.3 (1)
C1B—C2B	1.377 (6)		
N—C7—C1A	111.9 (3)	C1A—C6A—C5A	120.7 (4)
N—C7—C1B	110.5 (3)	C6A—C5A—C4A	120.3 (4)
C1A—C7—C1B	113.7 (3)	C5A—C4A—C3A	120.0 (4)
C7—C1A—C2A	117.8 (4)	C2A—C3A—C4A	120.3 (4)
C6B—C5B—C4B	119.6 (5)	C7—C1B—C6B	121.3 (4)
C5B—C4B—C3B	121.1 (5)	C7—C1B—C2B	119.5 (4)
C4B—C3B—C2B	119.8 (5)	C6B—C1B—C2B	119.1 (4)
C1B—C2B—C3B	119.5 (5)	C1B—C6B—C5B	120.8 (5)
C7—C1A—C6A	123.7 (3)	Cl···H1—N	161.4 (4)
C2A—C1A—C6A	118.4 (4)	Cl···H2^i—N^i	161.1 (2)
C1A—C2A—C3A	120.2 (4)	Cl···H3^ii—N^ii	157.7 (3)

Symmetry codes: (i) ½ − x, ½ − y, 1 − z; (ii) ½ − x, −½ − y, 1 − z.

References

Barnes, J. C., Paton, J. D., Damewood, J. R. & Mislow, K. (1981). *J. Org. Chem.* **46**, 4975–4979.

Bruno Blanch, L. (1990). Doctoral thesis, Univ. Nacional de La Plata, Argentina.

Enraf-Nonius (1989). *CAD-4 Software.* Version 5.0. Enraf-Nonius, Delft, The Netherlands.

Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis.* Enraf-Nonius, Delft, The Netherlands.

Fuller, W. (1959). *J. Phys. Chem.* **63**, 1705–1717.

Johnson, C. K. (1965). *ORTEP.* Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.

Maverick, E. F. & Trueblood, K. N. (1988). *THMA11. A Program for Thermal Motion Analysis, Including Internal Torsion.* Univ. of California, Los Angeles, USA.

Moore, M. L. (1949). *The Leuckart Reactions.* In *Organic Reactions,* Vol. 5, edited by R. Adams, p. 301. New York: Wiley.

Rivero, B. E., Punte, G., Rigotti, G., Goeta, A. E., Quinteros Rivero, M. F., Vega, D. & Bruno Blanch, L. (1991). *Proc. Am. Crystallogr. Assoc. Meet.* p. 23, Abstract 19.

Sheldrick, G. M. (1976). *SHELX76. Program for Crystal Structure Determination.* Univ. of Cambridge, England.

Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures.* Univ. of Göttingen, Germany.

Conformation of 4,4′-Dichloro-N,N-diethylbenzhydrylamine

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Abstract

The molecular conformation of the title compound, 4-chloro-α-(4-chlorophenyl)-N,N-diethylbenzylamine hydrochloride ($C_{17}H_{20}Cl_2N^+ \cdot Cl^-$), is helical C_s with ring twist angles of −77.0 (3) and 62.9 (4)°. The C—H bridge group is involved in a short C—H···Cl contact [3.599 (5) Å].

Comment

Benzhydrylamine (I) as well as its derived compounds, obtained by aminic and/or arylic substitution, displays inhibitive activity of the smooth musculature spasms. Some correlation between activity and hydrophobic effects has been observed (Bruno Blanch, 1990). A relationship between charge density localized at the bridge, as obtained by molecular-orbital calculations, and biological activity has been established for monoaminic substituted derivatives (Stiu, Cachau, Castro & Bruno Blanch, 1990).

The present study has been performed as part of a systematic study of derivatives of (I) to investigate the parameters governing the structure-activity relationship, especially in the case of diaminic substitution. Towards this goal the crystal structure of 4,4′-dichloro-N,N-diethylbenzhydrylamine hydrochloride (II) (the salt used