**Discussion.** Final positions and thermal parameters for the structure are given in Table 1,* selected bond distances and angles are listed in Table 2. A view of the molecule with the numbering scheme is presented in Fig. 1.

$Cu^{II}$ and Cl atoms are located on special positions: Cu on the twofold axis (site *g*) and Cl on site *d* of 2/*m* symmetry. The structure reveals a dimeric molecule with the two parts of the molecule linked by a bridging $\mu$-Cl atom.

Each $Cu^{II}$ ion is five-coordinated with ligation from pyridines and two primary amine donor groups. The pentacoordination of the Cu atoms is completed by the $\mu$-Cl atom. The geometry around the Cu atoms is described as square-based pyramidal with Cl occupying the axial position. The Cu—Cl bond distances [2.530 (1) Å] are in the range expected for this kind of $Cu^{II}$ complex {2.50 Å found in $[Cu_2(tet\text{-}b)_2](ClO_4)_3$, were tet-b is 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (Bauer, Robinson & Margerum, 1973)}. However, the coordination geometry around the $Cu^{II}$ atom is different to that previously found. In $[Cu_2(tet\text{-}b)_2Cl](ClO_4)_3$ it is trigonal bipyramidal with the $\mu$-Cl atom in equatorial position, while in complex (3) we have found a square-based pyramid with the Cl occupying the axial position. The linearity of the Cu—Cl—Cu bridge is imposed by the symmetry and, as far as we know, is the first example of such a $\mu$-chloro bridge of 180°. In $[Cu_2(tet\text{-}b)_2Cl](ClO_4)_3$ the deviation of the Cu—Cl—Cu bonds from linearity (174.2°) appears to be the result of the disposition of the perchlorate groups situated in special positions along the twofold axis. An O atom of one perchlorate group lies on the twofold axis and is hydrogen bonded to axial N atoms in the coordination polyhedra of both Cu ions.

* Lists of structure factors, anisotropic thermal parameters, bond distances and angles, and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55133 (14 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: PA0275]

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# 3,3,6,9,9-Pentamethyl-2,10-diazabicyclo[4.4.0]dec-1-ene Hydrogen Trifluoroacetate


BY D. PATEL, D. S. BROWN AND J. R. TRAYNOR

*Department of Chemistry, Loughborough University of Technology, Loughborough, Leicestershire LE*11 3*TU, England*


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**Abstract.** $C_{15}H_{25}F_3N_2O_2$, $M_r = 322.4$, orthorhombic, *Pmmn* (origin at centre of symmetry), $a = 10.21$ (1), $b = 13.99$ (1), $c = 5.91$ (1) Å, $V = 845.9$ Å$^3$, $Z = 2$, $D_x = 1.28$ g cm$^{-3}$, $\lambda$(Mo $K\alpha$) = 0.71069 Å, $\mu = 0.69$ cm$^{-1}$, $F(000) = 344$, $T = 293$ K, final $R = 0.0422$ for 807 observed reflections [$F/\sigma(F) > 5$]. The compound is the crystalline TFA salt of a bicyclic amidine formed following treatment of a peptide TFA salt, prepared by solid-phase synthetic methods, with a bicyclic amidine. The N···N distance in the amidine and the O···O distance in the carboxyl function of TFA are equivalent and explain the ease of salt formation.


**Introduction.** The bicyclic amidine 3,3,6,9,9-pentamethyl-2,10-diazabicyclo[4.4.0]dec-1-ene readily forms salts of carboxylic acids and related proton complexes of bidentate ligands (Heinzer, Soukup & Eschenmoser, 1978; Eschenmoser & Petrilka, 1970), and has been used as a non-nucleophilic base in

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Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters* ($Å^2 \times 10$)

$U_{eq}$ is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

| | $x$ | $y$ | $z$ | $U_{eq}$ |
|---|---|---|---|---|
| C(1) | 1251 (7) | 0 | 3699 (7) | 46 (4) |
| N(2) | 1750 (6) | 814 (2) | 4406 (5) | 51 (2) |
| C(3) | 1491 (5) | 1794 (2) | 3530 (5) | 51 (3) |
| C(4) | 234 (6) | 1801 (3) | 2146 (8) | 68 (4) |
| C(5) | 61 (7) | 901 (3) | 729 (7) | 70 (4) |
| C(6) | 40 | 0 | 2212 (8) | 54 (4) |
| C(11) | 1380 (7) | 2456 (3) | 5581 (7) | 71 (4) |
| C(12) | 2663 (7) | 2074 (4) | 2063 (1) | 80 (5) |
| C(13) | −1153 (8) | 0 | 3823 (1) | 81 (7) |
| C(16) | 9368 (6) | 5000 | 2203 (9) | 58 (5) |
| C(17) | 10564 (7) | 5000 | 637 (13) | 84 (7) |
| O(1) | 8969 (6) | 4205 (2) | 2751 (7 ) | 106 (4) |
| F(1) | 10886 (9) | 4167 (5) | −165 (17) | 136 (10) |
| F(2) | 11696 (11) | 5000 | 2050 (27) | 113 (19) |
| F(3) | 10007 (25) | 5000 | −1750 (27) | 117 (28) |
| F(4) | 11503 (16) | 4489 (9) | 1404 (41) | 133 (25) |
| F(5) | 10480 (22) | 4474 (7) | −1126 (29) | 133 (25) |

Table 2. *Bond lengths* (Å) *and angles* (°)

| | | | |
|---|---|---|---|
| N(2)—C(1) | 1.316 (3) | F(1)—C(17) | 1.301 (7) |
| C(6)—C(1) | 1.518 (6) | F(2)—C(17) | 1.427 (16) |
| C(3)—N(2) | 1.491 (4) | F(3)—C(17) | 1.523 (22) |
| C(4)—C(3) | 1.523 (5) | F(4)—C(17) | 1.279 (20) |
| C(11)—C(3) | 1.531 (5) | F(5)—C(17) | 1.280 (17) |
| C(12)—C(3) | 1.530 (5) | C(5)—C(4) | 1.524 (6) |
| C(6)—C(5) | 1.536 (4) | C(13)—C(6) | 1.547 (8) |
| C(17)—C(16) | 1.533 (7) | O(1)—C(16) | 1.229 (3) |

| | | | |
|---|---|---|---|
| C(6)—C(1)—N(2) | 120.0 (2) | F(5)—C(17)—F(1) | 37.3 (8) |
| C(3)—N(2)—C(1) | 128.1 (3) | F(5)—C(17)—F(2) | 122.1 (11) |
| N(2)—C(1)—N(2′) | 119.9 (4) | F(5)—C(17)—F(3) | 38.6 (9) |
| C(4)—C(3)—N(2) | 110.0 (3) | F(5)—C(17)—F(4) | 91.0 (11) |
| C(11)—C(3)—N(2) | 107.1 (3) | O(1)—C(16)—O(1′) | 129.8 (5) |
| C(11)—C(3)—C(4) | 111.1 (3) | C(6)—C(5)—C(4) | 111.5 (3) |
| C(12)—C(3)—N(2) | 107.1 (3) | C(5)—C(6)—C(5) | 110.3 (4) |
| C(12)—C(3)—C(4) | 110.7 (3) | C(5)—C(6)—C(1) | 108.6 (3) |
| C(12)—C(3)—C(11) | 110.7 (3) | C(13)—C(6)—C(1) | 106.6 (4) |
| C(5)—C(4)—C(3) | 112.8 (3) | C(13)—C(6)—C(5) | 111.3 (3) |
| O(1)—C(16)—C(17) | 115.1 (2) | F(1)—C(17)—C(16) | 115.0 (3) |
| F(2)—C(17)—C(16) | 107.0 (7) | F(2)—C(17)—F(1) | 90.5 (7) |
| F(3)—C(17)—C(16) | 105.2 (10) | F(4)—C(17)—C(16) | 112.6 (9) |
| F(4)—C(17)—F(2) | 35.4 (8) | F(4)—C(17)—F(1) | 55.8 (8) |
| F(4)—C(17)—F(3) | 127.5 (12) | F(5)—C(17)—F(5) | 70.2 (13) |
| F(5)—C(17)—C(16) | 116.0 (9) | | |

synthetic procedures (Denmark, 1981; Mohr, Tori, Grossen, Herold & Tamm, 1982). We have recently used this compound to obtain peptides following solid-phase synthetic strategies. This methodology inevitably involves release of the peptide chain from the solid resin support, and frequently involves the use of acidic reagents (Wang, 1973; Lu, Mojsov, Tamm & Merrifield, 1981), in particular $CF_3CO_2H$. Neutralization of the resultant solution with the bicyclic amidine affords the free peptide, which remains in aqueous solution, and crystallization of the bicyclic amidine–acid salt, which can be removed. Owing to the importance of the amidine, the crystal structure of the salt has been determined in order to confirm the basis behind its ready ability to interact with carboxylic acids.

**Experimental.** Preparation was by addition of the bicyclic amidine (1 mol equivalent) (Fluka Chemicals Ltd) to an acetonitrile water (1:1) solution of dynorphin(1-8).trifluroacetate salt (1 mol equivalent) under a nitrogen atmosphere. Crystals formed over a period of 48 h and were found to be stable in air. A colourless acicular crystal, 0.35 × 0.67 × 0.27 mm, was mounted about **c** on a Stoe Stadi-2 diffractometer. Lattice parameters were determined from optimum fit of axial row reflections ($15 < 2\theta < 40°$). Intensity data were collected from sequential scans in $\omega$; $(\sin\theta)/\lambda < 0.6$ Å$^{-1}$. 1192 unique reflections were measured of which 807 had $F/\sigma(F) > 5$ and were classed as observed; $0 \le h \le 7$, $0 \le k \le 12$, $0 \le l \le 16$. Standard reflections on each layer were measured every 50 reflections and showed no significant change. No corrections for absorption or extinction were applied. The structure was solved by direct methods using *SHELXS*86 (Sheldrick, 1986) and refined by full-matrix least squares based on $F$ to a final $R = 0.0422$, $wR = 0.0422$ (unit weights chosen on the basis of agreement analysis and successful refinement). 177 parameters were refined; all H atoms were found from a difference Fourier map and

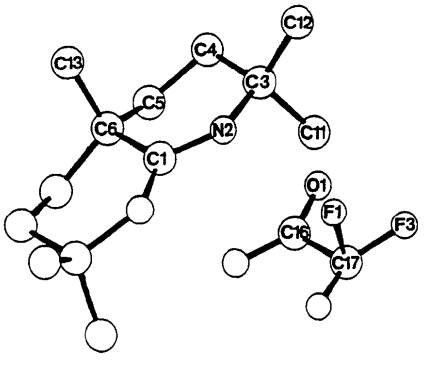


Fig. 1. *ORTEP* plot (Johnson, 1965) of the title compound, with atom labelling.

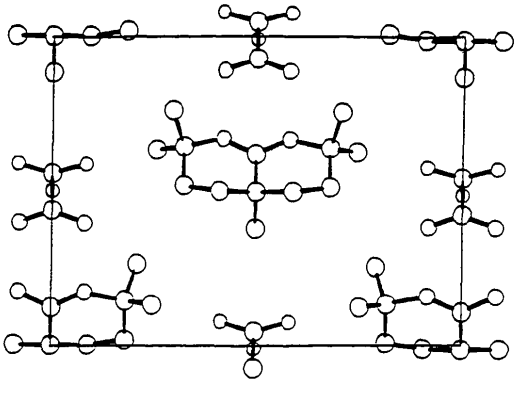

Fig. 2. Projection down the *c* axis of the cell contents.

refined isotropically, all non-H atoms anisotropic. Maximum $\Delta/\sigma = 0.016$; $\Delta\rho$ excursions = 0.17 to $-0.16$ e Å$^{-3}$. Scattering factors were obtained from *International Tables for X-ray Crystallography* (1974, Vol. IV) and structure refinement used *SHELX*76 (Sheldrick, 1976) as implemented at the University of Manchester Regional Computer Centre.

**Discussion.** The final atomic coordinates are listed in Table 1* and bond lengths and angles in Table 2. The molecular structure and atomic numbering are shown in Fig. 1; unit-cell contents projected down **c** are represented in Fig. 2.

The structure of the crystalline solid was confirmed to be that of the bicyclic amidine–trifluroacetate salt. The molecule possesses a twofold axis of symmetry with C(1), C(6), C(13), C(16), C(17), F(1), F(3) and H(12) occupying special positions. The $CF_3$ group appeared disordered; as a model, five F-atom positions were assigned, all having a variety of occupancy factors < 1. The C(1)—N(2) bond length of 1.316 (3) Å suggests a partial double-bond character [single C—N bond 1.47 Å, double C—N bond 1.27 Å (Stark & Wallace, 1982)] owing to $\pi$-electron delocalization about N(2)—C(1)—N(2′). Similarly the C(16)—O(1) bond length of 1.229 (3) Å [single C—O bond 1.48 Å, double C=O bond 1.21 Å (Stark & Wallace, 1982)] also suggests partial double-bond characteristics owing to delocalization of $\pi$ electrons about the carboxylate. The N(2)—H(1) distance of 0.81 (3) Å implies that covalent bonding exists between these atoms and not a disordered bond between N(2)—H(1)—O(1). The H(1)—O(1) distance of 2.02 (3) Å indicates the existence of a hydrogen bond, further exemplified by the N(2)—H(1)—O(1) bond angle of 175.5 (1)°. A further factor contributing to the stability of the product is the close agreement of several intramolecular distances, namely O(1)···O(1′) [2.22 (5) Å], H(1)···H(1′) [2.13 (4) Å] and N(2)···N(2′) [2.27 (6) Å]. The ability of the base to form a stable salt with carboxylic acids is a direct consequence of similarities between the intramolecular N···N distance in the bicyclic amidine and the O···O distance of the carboxyl moiety.

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# Structure of *N*,*N*-Di-*tert*-butyloxycarbonyl-glycine *N*′-Methoxy-*N*′-methylamide


BY J. ŁUBKOWSKI AND L. ŁANKIEWICZ

*Department of Chemistry, University of Gdańsk, Sobieskiego* 18, 80-952 *Gdańsk, Poland*

AND Z. KOSTURKIEWICZ*

*Department of Crystallography, A. Mickiewicz University, Grunwaldzka* 6, 60-780 *Poznań, Poland*


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**Abstract.** $C_{14}H_{26}N_2O_6$, $M_r = 318.37$, orthorhombic, *Pbca*, $a = 11.973$ (2), $b = 17.036$ (3), $c = 17.765$ (4) Å, $V = 3623$ (1) Å$^3$, $Z = 8$, $D_m = 1.17$, $D_x = 1.163$ Mg m$^{-3}$, $\lambda$(Cu $K\alpha$) = 1.54178 Å, $\mu = 0.725$ mm$^{-1}$, $F(000) = 1376$, room temperature, $R = 0.041$ for 1701 observed reflections. The bond lengths

* To whom correspondence should be addressed.

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