Ring *D* is a distorted envelope with a phase angle of pseudorotation $\Delta = 27{\cdot}3\,(4)^\circ$ and maximum angle of torsion $\varphi = 41{\cdot}2\,(3)^\circ$ (Altona, Geise & Romers, 1968). The asymmetry parameter $\Delta C_s[\mathrm{C}(14)] = 4{\cdot}0\,(5)^\circ$, which represents the distortion from ideal mirror symmetry bisecting the C(16)—C(17) bond. Ring *E*, which contains the lone N atom in the structure, has an ideal C(20) envelope configuration $\{\Delta C_s[\mathrm{C}(20)] = 0{\cdot}4\,(2)^\circ$, $\Delta = 35{\cdot}5\,(3)^\circ$ and $\varphi = 40{\cdot}4\,(5)^\circ\}$.

Fig. 2 gives Newman projections along the bonds involved in ring fusion and shows that atoms H(8) and H(9) as well as C(18) and H(14) have antiperiplanar configurations. Table 2 gives observed torsional angles for the rings, together with values calculated for appropriately substituted cyclohexane and cyclopentane rings (Geise, Altona & Romers, 1967; Altona, Geise & Romers, 1968). The differences between observed and calculated values for ring *B* are probably the result of ring *A* being planar here, rather than puckered as in the above calculations. Torsional deviations of ring *C* from the expected values reflect the strain induced by ring *E* in the present compound.

In the crystal structure the lone water molecule forms three hydrogen bonds. One of these is with the phenolic O(3) atom $[\mathrm{O}(3)\text{—}\mathrm{H}(3)\cdots\mathrm{O}W(1) = 2{\cdot}735\ \text{Å}]$, the remaining two are with the keto O(1) atom $[\mathrm{O}W(1)\text{—}\mathrm{H}(\mathrm{O}W)\cdots\mathrm{O}(1) = 2{\cdot}809\ \text{Å}]$ and the N(1) atom $[\mathrm{O}W(1)\text{—}\mathrm{H}(\mathrm{O}W)\cdots\mathrm{N}(1) = 2{\cdot}865\ \text{Å}]$. The hydrogen bonds from the water molecule link the steroid molecules which are symmetrically related by $1-x, -\frac{1}{2}+y, \frac{3}{2}-z$; $1-x, \frac{1}{2}+y, \frac{3}{3}-x$ and $\frac{1}{2}+x, \frac{5}{2}-y, 1-z$.

The overall shape of the molecule is convex towards the α side, causing the vector C(10)—C(19) and ring *E* to diverge. The torsional angle C(1)—C(10)—C(13)—C(18) which gives the twist of the steroid molecule about the line joining C(10) and C(13) is 110·2 (3)°.

We thank the Departments of Science and Technology and Biotechnology, Government of India, for financial support.

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*Acta Cryst.* (1988). C**44**, 521–525

# Conformation and Structure of *N*-Benzyloxycarbonyl-L-arginine Hemihydrate

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(*Received* 8 *June* 1987; *accepted* 27 *October* 1987)

**Abstract.** $\mathrm{C_{14}H_{21}N_4O_4.\frac{1}{2}H_2O}$, $M_r = 318{\cdot}36$, monoclinic, $P2_1$, $a = 8{\cdot}671\,(3)$, $b = 21{\cdot}454\,(36)$, $c = 8{\cdot}733\,(2)$ Å, $\beta = 95{\cdot}86\,(2)^\circ$, $V = 1616\,(2)$ Å$^3$, $Z = 4$, $D_x = 1{\cdot}308$, $D_m$(flotation in $\mathrm{CHCl_3/CH_2Cl_2}$) = $1{\cdot}311\,(3)$ Mg m$^{-3}$, Mo $K\alpha$ ($\lambda K\alpha_1 = 0{\cdot}70926$, $\lambda K\alpha_2 = 0{\cdot}71354$ Å), $\mu = 1{\cdot}07$ cm$^{-1}$, $F(000) = 676$, $T = 295$ K, $R = 0{\cdot}060$, $wR = 0{\cdot}062$ for 1803 observations. There are two independent Z-Arg molecules in the cell, but the two independent molecules have very similar structures. The side-chain conformations observed in these two molecules are unusual, but are similar to that observed in one previous study.

**Introduction.** The interaction between the guanidyl groups of arginine residues and the dicarboxylate functionalities of γ-carboxyglutamic acid (Gla) residues in a variety of proteins including bovine prothrombin is believed to be of considerable importance

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0108-2701/88/030521-05$03.00

both in stabilizing the dicarboxylate groups and in contributing to the conformation of the active protein (Craig, Koehler & Hiskey, 1983; Gray, Hoke, Deerfield & Hiskey, 1985). We and others have, therefore, been conducting structural investigations aimed at elucidating the nature of the interactions between the arginyl side chain and carboxyl groups in small peptides and in amino acids (Eggleston & Hodgson, 1985; Suresh, Ramaswamy & Vijayan, 1986; Bray, Slattery & Russell, 1984; Suresh & Vijayan, 1983). Such studies continue to be of importance because although both low- and high-resolution crystal structures of fragment 1 of prothrombin, which contains ten Gla residues, have been published, the extensive disorder in the metal-binding region of the protein leaves the Gla residues unresolved (Olsson, Andersen, Lindqvist, Sjolin, Magnusson, Petersen & Sottrup-Jensen, 1982; Park & Tulinsky, 1986). The present study of *N*-benzyloxycarbonyl-L-Arg (hereinafter Z-Arg) was itself undertaken in order to obtain definitive information concerning the interactions available to this species in a small molecule in which the amino group is blocked.

Table 1. *Positional and equivalent isotropic thermal parameters*

$U_{eq} = (U_{11}U_{22}U_{33})^{1/3}$.

| | $x$ | $y$ | $z$ | $U_{eq}$(Å$^2$) |
|---|---|---|---|---|
| O(1*A*) | −0·7819 (5) | −0·2987 (2) | −0·7497 (5) | 0·057 (3) |
| O(2*A*) | −0·8662 (6) | −0·3885 (2) | −0·8547 (6) | 0·061 (3) |
| O(3*A*) | −1·1673 (5) | −0·2742 (2) | −0·7434 (5) | 0·060 (3) |
| O(4*A*) | −1·1455 (5) | −0·1688 (2) | −0·7799 (5) | 0·058 (3) |
| O(1*B*) | −0·1050 (6) | −0·6332 (2) | 0·0948 (5) | 0·062 (3) |
| O(2*B*) | −0·1839 (5) | −0·5408 (2) | 0·1779 (5) | 0·054 (3) |
| O(3*B*) | −0·2362 (6) | −0·5116 (2) | −0·2215 (5) | 0·057 (3) |
| O(4*B*) | −0·1965 (5) | −0·4070 (2) | −0·1711 (5) | 0·049 (3) |
| O*W* | −0·6124 (7) | −0·1239 (3) | −0·8702 (6) | 0·087 (4) |
| N(1*A*) | −0·7334 (7) | −0·0948 (0) | −1·4525 (6) | 0·057 (4) |
| N(2*A*) | −0·7507 (7) | −0·1807 (3) | −1·6170 (6) | 0·070 (4) |
| N(3*A*) | −0·8287 (6) | −0·1894 (3) | −1·3731 (6) | 0·051 (3) |
| N(4*A*) | −1·0196 (6) | −0·2334 (2) | −0·9218 (6) | 0·042 (3) |
| N(1*B*) | 0·5282 (7) | −0·3452 (3) | 0·2825 (7) | 0·069 (4) |
| N(2*B*) | 0·7019 (7) | −0·4191 (3) | 0·2204 (7) | 0·068 (4) |
| N(3*B*) | 0·4390 (6) | −0·4386 (3) | 0·1761 (6) | 0·047 (3) |
| N(4*B*) | −0·0397 (6) | −0·4792 (2) | −0·0472 (6) | 0·040 (3) |
| C(1*A*) | −0·7712 (7) | −0·1559 (3) | −1·4828 (7) | 0·049 (4) |
| C(2*A*) | −0·8785 (9) | −0·2545 (4) | −1·3912 (8) | 0·058 (5) |
| C(3*A*) | −0·9693 (8) | −0·2748 (3) | −1·2604 (8) | 0·054 (4) |
| C(4*A*) | −0·8734 (8) | −0·2866 (3) | −1·1085 (7) | 0·044 (4) |
| C(5*A*) | −0·9673 (7) | −0·2946 (3) | −0·9721 (7) | 0·039 (4) |
| C(6*A*) | −0·8672 (8) | −0·3280 (3) | −0·8460 (7) | 0·046 (4) |
| C(7*A*) | −1·1155 (7) | −0·2309 (3) | −0·8138 (7) | 0·044 (4) |
| C(8*A*) | −1·2383 (9) | −0·1582 (4) | −0·6529 (9) | 0·081 (5) |
| C(9*A*) | −1·2356 (8) | −0·0908 (4) | −0·6138 (7) | 0·058 (5) |
| C(10*A*) | −1·0992 (9) | −0·0555 (4) | −0·6005 (9) | 0·071 (5) |
| C(11*A*) | −1·0969 (11) | 0·0077 (5) | −0·5582 (11) | 0·106 (7) |
| C(12*A*) | −1·2287 (12) | 0·0345 (4) | −0·5190 (9) | 0·084 (6) |
| C(13*A*) | −1·3649 (11) | 0·0015 (4) | −0·5323 (11) | 0·092 (6) |
| C(14*A*) | −1·3662 (9) | −0·0602 (4) | −0·5775 (9) | 0·074 (5) |
| C(1*B*) | 0·5580 (8) | −0·4030 (3) | 0·2257 (8) | 0·054 (5) |
| C(2*B*) | 0·4498 (8) | −0·5000 (3) | 0·0991 (8) | 0·059 (5) |
| C(3*B*) | 0·3012 (8) | −0·5174 (4) | 0·0052 (8) | 0·057 (5) |
| C(4*B*) | 0·1688 (8) | −0·5370 (3) | 0·0969 (8) | 0·046 (4) |
| C(5*B*) | 0·0122 (8) | −0·5415 (3) | 0·0011 (8) | 0·045 (4) |
| C(6*B*) | −0·1017 (7) | −0·5721 (3) | 0·0984 (7) | 0·044 (4) |
| C(7*B*) | −0·1610 (8) | −0·4703 (4) | −0·1498 (8) | 0·054 (4) |
| C(8*B*) | −0·3313 (10) | −0·3919 (4) | −0·2735 (10) | 0·081 (6) |
| C(9*B*) | −0·3772 (8) | −0·3238 (3) | −0·2391 (8) | 0·052 (4) |
| C(10*B*) | −0·3701 (10) | −0·2765 (4) | −0·3461 (8) | 0·075 (5) |
| C(11*B*) | −0·4099 (11) | −0·2159 (4) | −0·3125 (9) | 0·089 (5) |
| C(12*B*) | −0·4498 (8) | −0·2013 (4) | −0·1739 (9) | 0·069 (5) |
| C(13*B*) | −0·4552 (10) | −0·2467 (4) | −0·0645 (9) | 0·081 (6) |
| C(14*B*) | −0·4170 (11) | −0·3066 (4) | −0·0989 (9) | 0·087 (6) |

**Experimental.** Colorless rods by slow evaporation of a methanol/DMF solution at room temperature. Crystal 1·4 × 0·3 × 0·2 mm. Enraf–Nonius CAD-4 diffractometer. Systematic absences $0k0$ for $k$ odd. Cell constants by least squares using 25 reflections with $21 \leq 2\theta(\mathrm{Mo}) \leq 29°$ measured on the diffractometer. Intensity data collected in an $\omega$–$2\theta$ scan mode, as suggested by peak-shape analysis. 3595 independent reflections, 1803 with $I > 3\sigma(I)$ considered observed, $2\theta \leq 54°$, $-11 \leq h \leq 11$, $0 \leq k \leq 27$, $0 \leq l \leq 11$. Lorentz–polarization correction, no absorption correction. No systematic fluctuations in $4\bar{3}\bar{3}$, $5\bar{7}0$, or $4\bar{3}3$ monitored at the beginning and after every 3 h of exposure time (20 times). Programs in the CAD-4 *Structure Determination Package* (Enraf–Nonius, 1979); atomic scattering factors from *International Tables for X-ray Crystallography* (1974).

Structure determined using *MULTAN*80 (Main *et al.*, 1980). *E* map revealed a ten-atom fragment, a nine-atom fragment, and two four-atom fragments of the molecules. The remainder of the non-H atoms were located from a difference Fourier synthesis after three cycles of least-squares refinement on the initial fragments. Two independent but substantially similar molecules in the asymmetric unit were revealed. Anisotropic full-matrix least-squares refinement (on $F$) of all 45 non-H atoms led to $wR = 0·080$; weights $4F_o^2/\sigma^2(I)$. Subsequent difference Fourier maps revealed positions for 39 of the 42 H atoms in the Z-Arg units; however, because of the paucity of data all H atoms were fixed at calculated positions (with C—H = 0·95 Å and N—H = 0·87 Å) with fixed isotropic temperature factors ($B = 5·0$ Å$^2$). Final cycle of full-matrix least squares [with the weighting scheme above and $\sigma(I)$ defined by Corfield, Doedens & Ibers (1967) with $p = 0·02$] gave $R = 0·060$, $wR = 0·062$, $S = 1·22$ using 1803 observations with $I \geq 3\sigma$ and 405 variables. $(\Delta/\sigma)_{\max} = 0·01$. Final difference Fourier map contained no peak higher than 0·23 e Å$^{-3}$.

**Discussion.** There are two crystallographically independent Z-L-Arg molecules and one water molecule in the asymmetric unit. The positional parameters, along with their standard deviations as estimated from the inverse matrix, are listed in Table 1.* The structure of a single molecule *A* is shown in Fig. 1, while a single molecule *B* is shown in Fig. 2. Principal bond lengths and angles are available as supplementary material (see deposition footnote).

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* Lists of bond lengths and bond angles, structure amplitudes, H-atom positional parameters and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44491 (26 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The bond lengths within the benzyloxycarbonyl group are very similar to the average values reported for these groups in recent compilations (Benedetti, Diblasio, Pavone, Pedone, Germain & Goodman, 1979; Eggleston & Hodgson, 1984; Blessing & Smith, 1982; Antolini, Menabue, Saladini, Sola, Battaglia & Bonamartini Corradi, 1984; Yokomori, Deerfield, Hiskey & Hodgson, 1987). The Z-group assumes the fully extended form in both molecules, with approximately linear torsion angles around C(7)—N(4) [O(4*A*)—C(7*A*)—N(4*A*)—C(5*A*) = −178·1; O(4*B*)—C(7*B*)—N(4*B*)—C(5*B*) = −175·8°], O(4)—C(7) [C(8*A*)—O(4*A*)—C(7*A*)—N(4*A*) = 174·5; C(8*B*)—O(4*B*)—C(7*B*)—N(4*B*) = 176·8°] and around C(8)—O(4) [C(9*A*)—C(8*A*)—O(4*A*)—C(7*A*) = −170·4; C(9*B*)—C(8*B*)—O(4*B*)—C(7*B*) = −162·2°]. This extended structure has been observed elsewhere (Coiro, Mazza & Mignucci, 1974; Blessing & Smith, 1982, Antolini *et al.*, 1984), and is more common than the partially extended form observed in Z-Gla(O$^t$Bu)$_2$-OMe (Yokomori, Deerfield *et al.*, 1987) and elsewhere (de Kock & Romers, 1981) in which two of these angles approximate 180° but the third approximates 60°. The two guanidyl groups are virtually planar, with no atom deviating by more than 0·009 (9) Å from the four-membered plane through C(1)—N(2)—N(3)—N(1).

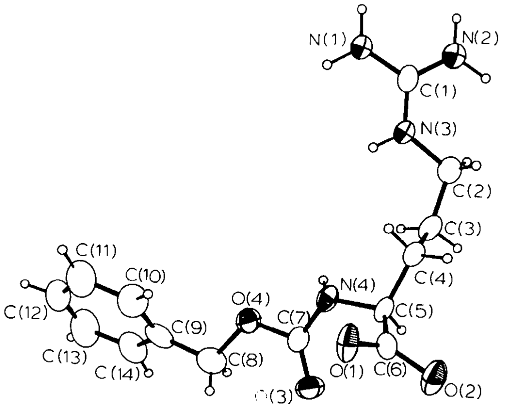

Fig. 1. View of a single molecule *A* of Z-L-Arg showing the atomic numbering scheme. In this and subsequent figures thermal ellipsoids are drawn at the 40% probability level, but H atoms are shown as spheres of arbitrary size.

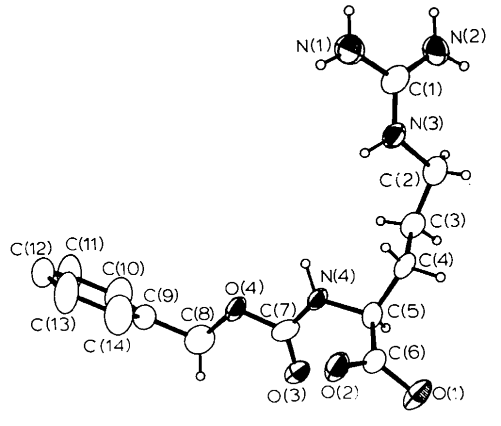

Fig. 2. View of a molecule *B* of Z-L-Arg. H atoms on the phenyl ring have been omitted for clarity.

Significant torsion angles are compared with those in other recent reports of arginyl group structures in Table 2. The long, flexible Arg side chain can, in principle, exhibit a very large array of different conformations. These conformations are described by the torsion angles $\chi_1$, $\chi_2$, $\chi_3$, $\chi_4$, where $\chi_1$ defines the orientation of the side chain relative to the backbone and the remaining angles define the conformation of the side chain itself. According to a recent survey, at least fifteen different conformations have been observed (Suresh, Ramaswamy & Vijayan, 1986); this value should presumably be amended to sixteen, since the authors were unaware of the unique *cis-cis-trans-trans* conformation exhibited in the dipeptide L-Arg-L-Asp.H$_2$O (Eggleston & Hodgson, 1985). The side-chain torsion angles in the two independent molecules in the present structure are very similar (−77·5, 168·8, −74·8, −167·7° in molecule *A*; −68·8, 168·3, −73·2, −158·4° in *B*) and approximate to the idealized alternating −60, 180, −60, 180° side-chain conformation seen previously in [L-ArgH$^+$][D-Asp$^-$] (Suresh, Ramaswamy & Vijayan, 1986).

The bond lengths within the two arginine groups are very similar to those reported elsewhere, with the possible exception of the C(6*A*)—O(2*A*) and C(6*B*)—O(1*B*) distances of 1·300 (6) and 1·311 (6) Å, respec-

Table 2. *Side-chain conformational angles* (°) *in arginine residues reported since* 1978

| Molecule | $\chi_1$ | $\chi_2$ | $\chi_3$ | $\chi_4$ | $\chi_5^1$ | $\chi_5^2$ | Idealized $\chi_1$, $\chi_2$, $\chi_3$, $\chi_4$ | Ref. |
|---|---|---|---|---|---|---|---|---|
| Z-Arg (*A*) | −77·5 | 168·8 | −74·8 | −167·7 | 178·0 | −2·2 | −60, 180, −60, 180 | (*a*) |
| Z-Arg (*B*) | −68·8 | 168·3 | −73·2 | −158·4 | 174·5 | −3·8 | −60, 180, −60, 180 | (*a*) |
| ArgH$^+$ D-Asp$^-$ (I) | −69·9 | −168·2 | −65·0 | 160·7 | −0·5 | 177·6 | −60, 180, −60, 180 | (*b*) |
| ArgH$^+$ D-Asp (II) | 178·5 | 167·8 | 63·7 | −175·5 | 1·3 | −178·4 | 180, 180, 60, 180 | (*b*) |
| Arg-Asp | −65·7 | −71·1 | 170·9 | 161·3 | 175·4 | −5·6 | −60, −60, 180, 180 | (*c*) |
| Arg-Glu | 76·3 | −178·2 | −174·6 | −173·7 | 177·3 | −2·2 | 60, 180, 180, 180 | (*c*) |
| ArgH$^+$ OAc | −67·9 | 172·3 | 53·0 | 100·9 | −9·9 | 170·1 | −60, 180, 60, 90 | (*d*) |
| ArgH$^+$ L-Asp | 59·1 | 168·7 | −69·9 | −104·0 | 7·2 | −175·6 | 60, 180, −60, −90 | (*e*) |
| ArgH$^+$ Asc | 69 | −176 | 177 | −94 | 12 | −166 | 60, 180, 180, −90 | (*f*) |

References: (*a*) present study, (*b*) Suresh, Ramaswamy & Vijayan (1986), (*c*) Eggleston & Hodgson (1985), (*d*) Suresh & Yijayan (1983), (*e*) Salunke & Vijayan (1982), (*f*) Sudhakar & Vijayan (1980).

tively, which are very long for a deprotonated carboxyl group and are longer than the C(6*A*)—O(1*A*) and C(6*B*)—O(2*B*) distances of 1·234 (5) and 1·242 (6) Å, respectively. It is, however, apparent from the packing (see below) and the geometry of the guanidyl moiety that the structure consists of Z-Arg molecules which are zwitterionic with the guanidyl group protonated and the carboxyl group deprotonated. Thus, the six C—N bonds in the two guanidyl moieties are all equivalent, falling in the range 1·316–1·370 Å with an average value of 1·335 (6) Å.

The intermolecular interactions are illustrated in Figs. 3 and 4. There are ten hydrogen bonds, whose metrical parameters are listed in Table 3. Most notably, in each molecule there are two intermolecular interactions of type *B* (Salunke & Vijayan, 1981) between the guanidyl and the carboxylate groups; interactions of this type involve parallel pairs of hydrogen bonds with both N(3)—H and N(1)—H [or N(2)—H] acting as donors to the two O atoms O(1) and O(2) of the same carboxylate group. In the present case, N(1*A*) and N(3*A*) form a pair of hydrogen bonds to O(2*B*) and O(1*B*), respectively, while N(1*B*) and N(3*B*) form a similar pair with O(1*A*) and O(2*A*), respectively. To the best of our knowledge, type-*B* interactions have only been documented in four other structures (Bhat & Vijayan, 1977; Bray, Slattery & Russell, 1984; Eggleston & Hodgson, 1985; Yokomori & Hodgson, 1987), although theoretical calculations (Sapse & Russell, 1984) suggest that these are more favorable than type-*A* interactions.

Table 3. *Probable hydrogen bonds in Z-Arg*

| *A*—H···*B* | *A*···*B* (Å) | *A*—H···*B* (°) | Symmetry operation |
|---|---|---|---|
| N(1*A*)—H(1*A*)···O(2*B*) | 2·821 (6) | 168 | $-1-x, \frac{1}{2}+y, -1-z$ |
| N(2*A*)—H(3*A*)···O(1*A*) | 2·786 (6) | 154 | $x, y, z-1$ |
| N(2*A*)—H(4*A*)···O*W* | 2·890 (6) | 166 | $x, y, z-1$ |
| N(3*A*)—H(5*A*)···O(1*B*) | 2·824 (5) | 174 | $-1-x, \frac{1}{2}+y, -1-z$ |
| N(1*B*)—H(1*B*)···O(1*A*) | 2·855 (6) | 166 | $1+x, y, 1+z$ |
| N(2*B*)—H(3*B*)···O(2*B*) | 2·830 (6) | 162 | $1+x, y, z$ |
| N(3*B*)—H(5*B*)···O(2*A*) | 2·844 (5) | 165 | $1+x, y, 1+z$ |
| N(4*B*)—H(13*B*)···O(2*A*) | 2·891 (5) | 162 | $1+x, y, 1+z$ |
| O*W*—H(*W*1)···O(1*B*) | 2·985 (6) | 146 | $-1-x, \frac{1}{2}+y, -1-z$ |
| O*W*—H(*W*2)···O(3*B*) | 2·896 (5) | 155 | $-1-x, \frac{1}{2}+y, -1-z$ |

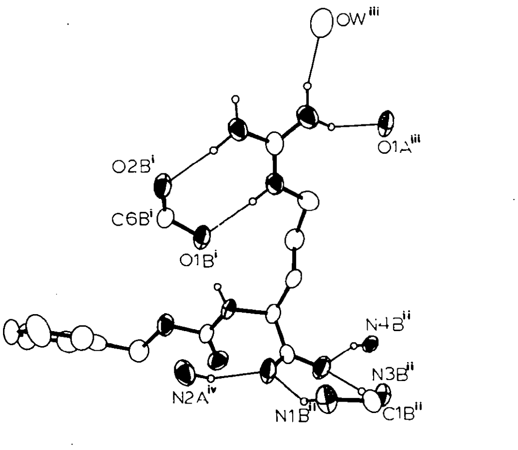

Fig. 3. The hydrogen bonding experienced by a single moelcule *A*. Symmetry operations are: (i) $-1-x, \frac{1}{2}+y, -1-z$; (ii) $x-1, y, z-1$; (iii) $x, y, z-1$; (iv) $x, y, z+1$.

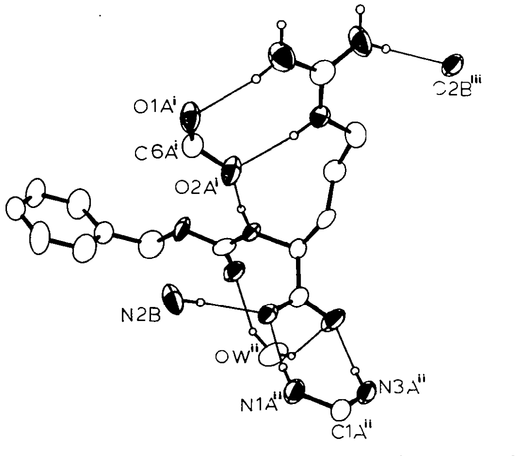

Fig. 4. The hydrogen bonding experienced by a single molecule *B*. Symmetry operations are: (i) $1+x, y, 1+z$; (ii) $-1-x, -\frac{1}{2}+y, -1-z$; (iii) $1+x, y, z$.

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# N—$CF_3$ Bonds in a Carbamate and a Triazene

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(*Received* 17 *September* 1987; *accepted* 2 *November* 1987)

**Abstract.** *tert*-Butyl *N*-trifluoromethylcarbamate, $C_6H_{10}F_3NO_2$, $M_r = 185{\cdot}146$, *Pbca*, $a = 11{\cdot}801$ (2), $b = 17{\cdot}030$ (4), $c = 9{\cdot}262$ (1) Å, $V = 1861{\cdot}3$ (6) Å$^3$, $Z = 8$, $D_x = 1{\cdot}321$ Mg m$^{-3}$, $\lambda$(Mo $K\alpha$) = 0·71073 Å, $\mu = 0{\cdot}13$ mm$^{-1}$, $F(000) = 768$, 296 K, $R = 0{\cdot}059$, 878 observed reflections. The carbamate possesses an unusually short N—$CF_3$ bond, 1·361 (6) Å, and a somewhat lengthened N—$C(O_2)$ bond, 1·369 (5) Å. The CNC(=O)OC section of the molecule is planar with the $CC_3$ and $CF_3$ groups staggered with respect to the C—O bond. Hydrogen bonding links the molecules into infinite chains. 3-Phenyl-1-trifluoromethyltriazene, $C_7H_6F_3N_3$, $M_r = 189{\cdot}143$, $P2_1/n$, $a = 9{\cdot}792$ (2), $b = 5{\cdot}240$ (1), $c = 16{\cdot}328$ (5) Å, $\beta = 95{\cdot}44$ (2)°, $V = 834{\cdot}0$ (6) Å$^3$, $Z = 4$, $D_x = 1{\cdot}506$ Mg m$^{-3}$, $\lambda$(Mo $K\alpha$) = 0·71073 Å, $\mu = 0{\cdot}13$ mm$^{-1}$, $F(000) = 384$, 295 K, $R = 0{\cdot}052$, 1172 observed reflections. A short N—$CF_3$ bond, 1·409 (3) Å, is found in the triazene, which exists as centrosymmetric dimers held together by weak hydrogen bonds. The CNNNC part of the molecule is planar and forms an angle of 160° with the plane of the phenyl ring. The $CF_3$ group is disordered.

**Introduction.** The N—$CF_3$ bond lengths in $N(CF_3)_{3-n}F_n$ ($n = 0,1,2$) compounds are known to increase as $n$ increases (Oberhammer, Günther, Bürger, Heyder & Pawelke, 1982). This substitution effect has been attributed to a polar interaction between the net charges on the C and N atoms (Oberhammer, 1983). Since the N atom should be more negatively charged in $CF_3NHCO_2C(CH_3)_3$ (1) than in $N(CF_3)_3$ (2), we have studied the structure of (1) to see if its N—$CF_3$ bond is indeed shorter than that of (2).

The structure of $CF_3NNNH(C_6H_5)$ (3), which was previously formulated as $CF_3NHNNC_6H_5$ (Makarov, Yakubovich, Filatov, Englin & Nikiforova, 1968), is also reported. Comparison of the N—$CF_3$ bond in (3) with that of *trans*-$CF_3NNCF_3$ (4) (Bürger, Pawelke & Oberhammer, 1982) offers an additional test of the polar interaction model.

**Experimental.** Crystals, which were sealed in glass capillaries, were grown by sublimation from material prepared according to Lutz & Sundermeyer (1979) for (1) and Makarov *et al.* (1968) for (3). Crystal sizes are 0·30 × 0·35 × 0·61 mm for (1) and 0·24 × 0·28 × 0·78 mm for (3). Siemens AED 1 diffractometer employing Zr-filtered Mo $K\alpha$ radiation. The widths in $\omega$ of the $\omega$–$2\theta$ step scans were $\Delta + 0{\cdot}34°\ \tan\theta$, with $\Delta = 1{\cdot}30°$ for (1) and 0·90° for (3), and 0·61 s per 0·02° step in $\omega$. Peak intensity from middle two-thirds of scan range with one remeasurement if $2\sigma(I) < I < 25\sigma(I)$. Cell constants from 52 reflections, $6{\cdot}3 < \theta < 12{\cdot}3°$, for (1) and 39 reflections, $8{\cdot}2 < \theta < 13{\cdot}7°$, for (3). Numerical absorption corrections vary from 1·051 to 1·070 for (1) and 1·022 to 1·044 for (3). Max. $(\sin\theta)/\lambda = 0{\cdot}594$ Å$^{-1}$. One octant for (1) with $0 \le h \le 14$, $0 \le k \le 20$, $0 \le l \le 11$; four octants for (3) with $-12 \le h \le 12$, $0 \le k \le 6$, $-19 \le l \le 19$. Standards remeasured hourly and their fluctuations are $00\overline{6}$ (±2·4%), 220 (±8·1%), $\overline{2}20$ (±4·7%) for (1) and $00\overline{8}$ (±3·8%), 600 (±1·7%), 230 (±3·1%) for (3). 1889 reflections measured for (1), 3446 for (3). 1624 unique for (1) and 1462 for (3) ($R_{\rm int} = 0{\cdot}03$). Unobserved $[F_o < 4\sigma(F_o)]$ were 746 and 290 for (1) and (3) respectively. Structures were solved by multisolution direct methods and refined on $F$. Disorder of F atoms in (3) treated with F($i$) anisotropic (occupancy $\alpha$) and F($iA$) isotropic (occupancy $1-\alpha$), $\alpha = 0{\cdot}855$ (5). All H atoms located in $\Delta F$ syntheses – 0·25 to 0·33 e Å$^{-3}$ for (1) and 0·40 to 0·50 e Å$^{-3}$ for (3). H(N) and H(N3) were refined isotropically. Phenyl and methyl H atoms

0108-2701/88/030525-04$03.00