

The Conformation of a Fifteen-Membered Ring: Crystal and Molecular Structure of Cyclopentadecanone Phenylsemicarbazone at 183 K

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Abstract

$C_{22}H_{35}N_3O$ is triclinic, space group $P\bar{1}$, with $a = 5.808$ (2), $b = 11.675$ (2), $c = 15.537$ (3) Å, $\alpha = 95.84$ (2), $\beta = 95.18$ (2), $\gamma = 102.40$ (2)°, $Z = 2$. The structure was refined to an R of 0.048 with 2094 diffractometer data collected at 183 K, and consists of hydrogen-bonded dimers. The C_{15} ring is in a quadrangular conformation.

Introduction

Cycloalkane conformations have been the subject of theoretical studies for a long time. Conformational energies have been analysed by Wiberg (1965), Bixon & Lifson (1967), Hendrickson (1969) and Dale (1973). Comparison with experimental evidence for high odd-membered rings is hampered by the lack of structural data. For that reason crystal structure determinations on cycloalkanones were undertaken by Groth (see e.g., Groth, 1976). In large cycloalkanones, structure determination fails because of disorder; the 11-membered ring is the largest example determined by X-ray analysis (Groth, 1974).

In the 15-membered-ring compound cyclopentadecanone (exaltone) we avoided the problem of disorder by synthesizing its phenylsemicarbazone.

This paper reports the X-ray analysis of the structure of exaltone phenylsemicarbazone at 183 K.

Experimental

The title compound was prepared from cyclopentadecanone, kindly provided by Firminich S.A., Geneva.

It crystallized from ethanol as clear colourless needles. Cell dimensions and intensities were measured on an automatic Nonius CAD-4 diffractometer equipped with a graphite monochromator. The crystal was cooled in a stream of cold nitrogen to 183 K. No phase transition was observed between room temperature and 183 K. The data were collected by the moving-crystal–moving-counter technique with a variable scan angle $(1.2 + 0.35 \tan \theta)^\circ$. They were not corrected for

absorption or extinction. Reflexions with $I \geq 2.5\sigma(I)$ were considered as observed and only these were used in the subsequent analysis. Space group $P\bar{1}$ rather than $P1$ was indicated by intensity statistics and confirmed by the refinement. The crystal data are summarized in Table 1. Most of the calculations were carried out with the XRAY 76 system (Stewart, 1976) complemented and extended by local versions.

Structure determination and refinement

The structure was solved with *MULTAN 77* (Main, Lessinger, Woolfson, Germain & Declercq, 1977). The phase set with the highest COMB FOM (2.8115) gave an electron-density map from which all non-hydrogen atoms could be identified. The structure was refined by block-diagonal least squares, first isotropically ($R = 0.134$) then anisotropically ($R = 0.118$). The 35 H atoms located from a difference synthesis were added; their coordinates were included in the refinement, but their isotropic thermal parameters were set equal to those of the carrier atoms and were kept constant. Refinement was continued to convergence: $R = 0.048$ for 2094 observed reflexions. The maximum shift in the last cycle was 0.59σ . The maximum absolute peak height in the final difference map was $0.24 e \text{ \AA}^{-3}$. Standard tabulations of scattering factors were used for C, O and N (Cromer & Mann, 1968) and H (Stewart, Davidson & Simpson, 1965). Final positional parameters are listed in Table 2.†

† Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34437 (27 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Crystal data*

| | | | |
|-------------------|--------------------|--|-------------------|
| Formula | $C_{22}H_{35}N_3O$ | V (Å ³) | 1017 |
| Formula weight | 357.54 | Z | 2 |
| Melting point (K) | 425 | D_c (Mg m ⁻³) | 1.168 |
| Space group | $P\bar{1}$ | λ (Mo K α) (Å) | 0.7107 |
| $F(000)$ | 392 | μ (Mo K α) (mm ⁻¹) | 0.078 |
| a (Å) | 5.808 (2) | Crystal dimensions (mm) | 0.05 × 0.15 × 0.4 |
| b (Å) | 11.675 (2) | Minimum θ angle (°) | 0.1 |
| c (Å) | 15.537 (3) | Maximum θ angle (°) | 27.5 |
| α (°) | 95.84 (2) | Number of unique reflexions | 4667 |
| β (°) | 95.18 (2) | Number of unobserved reflexions | 2573 |
| γ (°) | 102.40 (2) | | |

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Discussion

The atom numbering is given in Fig. 1; Fig. 2 shows the *a*-axis projection of the crystal structure. Bond lengths and angles are listed in Table 3. Table 4 gives the torsion angles. The actual conformation of the cycloalkanone derivative does not match one of the conformations suggested by Dale (1973) for a cyclopentadecane. It can best be compared with his [13434],* which can be obtained through ring expansion of cyclotetradecane. However, in the theoretical model the

* This shorthand notation represents the number of bonds in sequential all-*anti* chains.

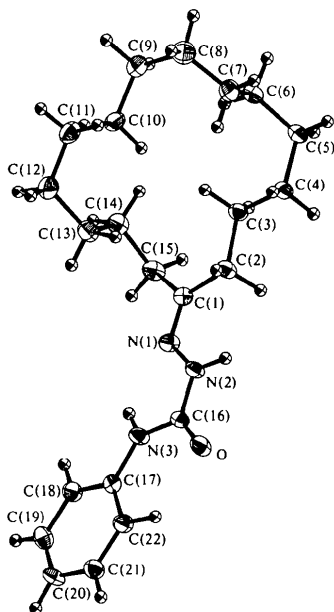


Fig. 1. ORTEP plot (Johnson, 1965) of exaltone phenylsemicarbazone showing the crystallographic numbering of the non-hydrogen atoms. Boundary surfaces for C, N and O are drawn at the 50% probability level and arbitrarily for H, which are numbered to correspond to their carrier atoms.

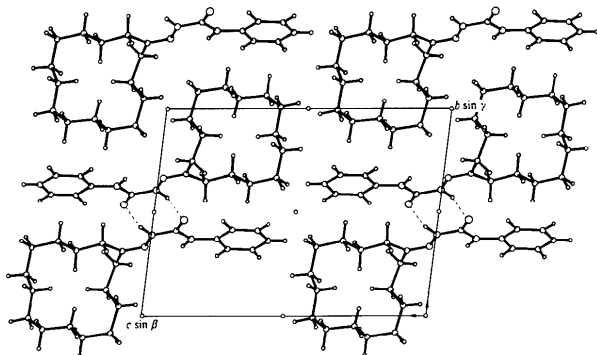


Fig. 2. Projection of the structure down *a* showing intermolecular hydrogen bonding as dashed lines.

ring is widened in the least-squares plane of the molecule, whereas in our case the chain ends, C(1) and C(14), are shifted up and down respectively perpendi-

Table 2. Atomic coordinates ($\times 10^4$; for H $\times 10^3$), with e.s.d.'s in parentheses

| | <i>x</i> | <i>y</i> | <i>z</i> |
|--------|-----------|-----------|-----------|
| C(1) | -490 (5) | 3132 (3) | 958 (2) |
| C(2) | 1529 (6) | 3501 (3) | 1679 (2) |
| C(3) | 1068 (6) | 3168 (3) | 2580 (2) |
| C(4) | 3290 (6) | 3606 (3) | 3235 (2) |
| C(5) | 2883 (6) | 3328 (3) | 4157 (2) |
| C(6) | 1987 (6) | 2018 (3) | 4241 (2) |
| C(7) | 3601 (7) | 1229 (3) | 3941 (2) |
| C(8) | 2656 (7) | -77 (4) | 3992 (3) |
| C(9) | 250 (7) | -624 (3) | 3442 (2) |
| C(10) | 218 (6) | -490 (3) | 2476 (2) |
| C(11) | -2236 (6) | -1008 (3) | 1977 (2) |
| C(12) | -2505 (7) | -809 (3) | 1021 (3) |
| C(13) | -1951 (6) | 494 (3) | 855 (2) |
| C(14) | -3311 (6) | 1260 (3) | 1357 (2) |
| C(15) | -2967 (5) | 2529 (3) | 1122 (2) |
| C(16) | 2119 (6) | 4111 (3) | -868 (2) |
| C(17) | -277 (6) | 3697 (3) | -2327 (2) |
| C(18) | -2568 (6) | 3223 (3) | -2737 (2) |
| C(19) | -3059 (6) | 3183 (3) | -3628 (2) |
| C(20) | -1282 (6) | 3616 (3) | -4126 (2) |
| C(21) | 987 (6) | 4098 (3) | -3716 (2) |
| C(22) | 1512 (6) | 4139 (3) | -2823 (2) |
| N(1) | -305 (4) | 3333 (3) | 174 (2) |
| N(2) | 1909 (5) | 3898 (3) | -28 (2) |
| N(3) | 77 (5) | 3694 (3) | -1423 (2) |
| O | 4021 (4) | 4614 (2) | -1093 (1) |
| H(21) | 209 (6) | 441 (3) | 174 (2) |
| H(22) | 263 (6) | 313 (3) | 150 (2) |
| H(31) | -15 (6) | 352 (3) | 282 (2) |
| H(32) | 57 (6) | 225 (3) | 254 (2) |
| H(41) | 455 (6) | 320 (3) | 302 (2) |
| H(42) | 364 (6) | 448 (3) | 323 (2) |
| H(51) | 177 (6) | 381 (3) | 442 (2) |
| H(52) | 436 (6) | 363 (3) | 456 (2) |
| H(61) | 43 (6) | 170 (3) | 389 (2) |
| H(62) | 175 (6) | 195 (3) | 487 (2) |
| H(71) | 388 (6) | 134 (3) | 332 (2) |
| H(72) | 497 (6) | 147 (3) | 426 (2) |
| H(81) | 376 (6) | -53 (3) | 382 (2) |
| H(82) | 245 (6) | -25 (3) | 459 (2) |
| H(91) | -90 (6) | -22 (3) | 367 (2) |
| H(92) | -11 (6) | -154 (3) | 347 (2) |
| H(101) | 129 (6) | -97 (3) | 219 (2) |
| H(102) | 62 (6) | 35 (3) | 239 (2) |
| H(111) | -333 (6) | -63 (3) | 229 (2) |
| H(112) | -261 (6) | -187 (3) | 199 (2) |
| H(121) | -146 (6) | -126 (3) | 66 (2) |
| H(122) | -422 (6) | -119 (3) | 74 (2) |
| H(131) | -20 (6) | 91 (3) | 98 (2) |
| H(132) | -226 (6) | 55 (3) | 25 (2) |
| H(141) | -291 (6) | 130 (3) | 200 (2) |
| H(142) | -503 (6) | 91 (3) | 123 (2) |
| H(151) | -403 (6) | 248 (3) | 61 (2) |
| H(152) | -344 (6) | 310 (3) | 160 (2) |
| H(181) | -376 (6) | 290 (3) | -239 (2) |
| H(191) | -460 (6) | 282 (3) | -388 (2) |
| H(201) | -152 (6) | 361 (3) | -473 (2) |
| H(211) | 216 (6) | 441 (3) | -407 (2) |
| H(221) | 310 (6) | 455 (3) | -247 (2) |
| H(N3) | -107 (6) | 336 (3) | -117 (2) |
| H(N2) | 301 (6) | 428 (3) | 40 (2) |

Table 3. Bond lengths (Å) and angles (°)

E.s.d.'s are in parentheses.

| | | | |
|-------------------|-----------|-------------------|-----------|
| C(1)–C(2) | 1.504 (4) | C(15)–C(1) | 1.516 (4) |
| C(2)–C(3) | 1.522 (5) | C(1)–N(1) | 1.273 (4) |
| C(3)–C(4) | 1.528 (4) | N(1)–N(2) | 1.392 (4) |
| C(4)–C(5) | 1.529 (5) | N(2)–C(16) | 1.365 (4) |
| C(5)–C(6) | 1.529 (5) | C(16)–N(3) | 1.367 (4) |
| C(6)–C(7) | 1.519 (6) | N(3)–C(17) | 1.400 (4) |
| C(7)–C(8) | 1.519 (5) | C(17)–C(18) | 1.393 (4) |
| C(8)–C(9) | 1.543 (5) | C(18)–C(19) | 1.383 (5) |
| C(9)–C(10) | 1.523 (5) | C(19)–C(20) | 1.385 (5) |
| C(10)–C(11) | 1.528 (5) | C(20)–C(21) | 1.384 (5) |
| C(11)–C(12) | 1.526 (6) | C(21)–C(22) | 1.386 (5) |
| C(12)–C(13) | 1.538 (5) | C(22)–C(17) | 1.392 (5) |
| C(13)–C(14) | 1.518 (5) | C(16)–O | 1.233 (4) |
| C(14)–C(15) | 1.537 (5) | | |
| C(2)–H(21) | 1.03 (3) | C(11)–H(111) | 0.98 (4) |
| C(2)–H(22) | 0.90 (4) | C(11)–H(112) | 0.98 (3) |
| C(3)–H(31) | 0.97 (4) | C(12)–H(121) | 1.04 (4) |
| C(3)–H(32) | 1.04 (3) | C(12)–H(122) | 1.04 (3) |
| C(4)–H(41) | 1.01 (4) | C(13)–H(131) | 1.02 (3) |
| C(4)–H(42) | 1.00 (3) | C(13)–H(132) | 0.95 (3) |
| C(5)–H(51) | 1.03 (4) | C(14)–H(141) | 1.00 (3) |
| C(5)–H(52) | 0.99 (3) | C(14)–H(142) | 0.99 (3) |
| C(6)–H(61) | 0.99 (3) | C(15)–H(151) | 0.96 (3) |
| C(6)–H(62) | 1.01 (4) | C(15)–H(152) | 1.04 (3) |
| C(7)–H(71) | 1.01 (4) | C(18)–H(181) | 0.95 (3) |
| C(7)–H(72) | 0.87 (3) | C(19)–H(191) | 0.94 (3) |
| C(8)–H(81) | 0.95 (4) | C(20)–H(201) | 0.93 (3) |
| C(8)–H(82) | 0.99 (4) | C(21)–H(211) | 0.95 (3) |
| C(9)–H(91) | 0.97 (4) | C(22)–H(221) | 1.03 (3) |
| C(9)–H(92) | 1.05 (4) | N(2)–H(N2) | 0.88 (3) |
| C(10)–H(101) | 1.03 (4) | N(3)–H(N3) | 0.85 (3) |
| C(10)–H(102) | 0.98 (3) | | |
| C(1)–C(2)–C(3) | 117.9 (3) | C(2)–C(1)–N(1) | 123.6 (3) |
| C(2)–C(3)–C(4) | 111.3 (3) | C(1)–N(1)–N(2) | 117.9 (2) |
| C(3)–C(4)–C(5) | 113.1 (3) | N(1)–N(2)–C(16) | 118.1 (2) |
| C(4)–C(5)–C(6) | 115.1 (3) | N(2)–C(16)–O | 121.7 (3) |
| C(5)–C(6)–C(7) | 114.7 (3) | N(2)–C(16)–N(3) | 114.2 (3) |
| C(6)–C(7)–C(8) | 114.5 (3) | O–C(16)–N(3) | 124.2 (3) |
| C(7)–C(8)–C(9) | 114.8 (3) | C(16)–N(3)–C(17) | 128.7 (3) |
| C(8)–C(9)–C(10) | 114.6 (3) | N(3)–C(17)–C(18) | 116.9 (3) |
| C(9)–C(10)–C(11) | 111.9 (3) | N(3)–C(17)–C(22) | 123.8 (3) |
| C(10)–C(11)–C(12) | 115.7 (3) | C(17)–C(18)–C(19) | 120.5 (3) |
| C(11)–C(12)–C(13) | 115.2 (3) | C(18)–C(19)–C(20) | 120.4 (3) |
| C(12)–C(13)–C(14) | 114.3 (3) | C(19)–C(20)–C(21) | 119.0 (3) |
| C(13)–C(14)–C(15) | 114.6 (3) | C(20)–C(21)–C(22) | 121.3 (3) |
| C(14)–C(15)–C(1) | 116.9 (3) | C(21)–C(22)–C(17) | 119.5 (3) |
| C(15)–C(1)–C(2) | 121.9 (3) | C(22)–C(17)–C(18) | 119.3 (3) |
| C(15)–C(1)–N(1) | 114.4 (3) | | |

Table 3 (cont.)

| | | | |
|-------------------|---------|---------------------|---------|
| C(1)–C(2)–H(21) | 108 (2) | C(11)–C(10)–H(101) | 104 (2) |
| C(1)–C(2)–H(22) | 104 (2) | C(11)–C(10)–H(102) | 106 (2) |
| C(3)–C(2)–H(21) | 107 (2) | H(101)–C(10)–H(102) | 113 (3) |
| C(3)–C(2)–H(22) | 107 (2) | C(10)–C(11)–H(111) | 105 (2) |
| H(21)–C(2)–H(22) | 113 (3) | C(10)–C(11)–H(112) | 108 (2) |
| C(2)–C(3)–H(31) | 113 (2) | C(12)–C(11)–H(111) | 109 (2) |
| C(2)–C(3)–H(32) | 108 (2) | C(12)–C(11)–H(112) | 107 (2) |
| C(4)–C(3)–H(31) | 106 (2) | H(111)–C(11)–H(112) | 111 (3) |
| C(4)–C(3)–H(32) | 109 (2) | C(11)–C(12)–H(121) | 111 (2) |
| H(31)–C(3)–H(32) | 110 (3) | C(11)–C(12)–H(122) | 110 (2) |
| C(3)–C(4)–H(41) | 107 (2) | C(13)–C(12)–H(121) | 109 (2) |
| C(3)–C(4)–H(42) | 103 (2) | C(13)–C(12)–H(122) | 107 (2) |
| C(5)–C(4)–H(41) | 109 (2) | H(121)–C(12)–H(122) | 104 (3) |
| C(5)–C(4)–H(42) | 109 (2) | C(12)–C(13)–H(131) | 115 (2) |
| H(41)–C(4)–H(42) | 115 (3) | C(12)–C(13)–H(132) | 111 (2) |
| C(4)–C(5)–H(51) | 111 (2) | C(14)–C(13)–H(131) | 107 (2) |
| C(4)–C(5)–H(52) | 110 (2) | C(14)–C(13)–H(132) | 108 (2) |
| C(6)–C(5)–H(51) | 110 (2) | H(131)–C(13)–H(132) | 101 (3) |
| C(6)–C(5)–H(52) | 108 (2) | C(13)–C(14)–H(141) | 112 (2) |
| H(51)–C(5)–H(52) | 102 (3) | C(13)–C(14)–H(142) | 110 (2) |
| C(5)–C(6)–H(61) | 111 (2) | C(15)–C(14)–H(141) | 108 (2) |
| C(5)–C(6)–H(62) | 108 (2) | C(15)–C(14)–H(142) | 106 (2) |
| C(7)–C(6)–H(61) | 107 (2) | H(141)–C(14)–H(142) | 107 (3) |
| C(7)–C(6)–H(62) | 110 (2) | C(14)–C(15)–H(151) | 105 (2) |
| H(61)–C(6)–H(62) | 107 (3) | C(14)–C(15)–H(152) | 112 (2) |
| C(6)–C(7)–H(71) | 109 (2) | C(1)–C(15)–H(151) | 109 (2) |
| C(6)–C(7)–H(72) | 108 (2) | C(1)–C(15)–H(152) | 105 (2) |
| C(8)–C(7)–H(71) | 109 (2) | H(151)–C(15)–H(152) | 108 (3) |
| C(8)–C(7)–H(72) | 109 (2) | C(17)–C(18)–H(181) | 118 (2) |
| H(71)–C(7)–H(72) | 107 (3) | C(19)–C(18)–H(181) | 121 (2) |
| C(7)–C(8)–H(81) | 111 (2) | C(18)–C(19)–H(191) | 117 (2) |
| C(7)–C(8)–H(82) | 113 (2) | C(20)–C(19)–H(191) | 122 (2) |
| C(9)–C(8)–H(81) | 108 (2) | C(19)–C(20)–H(201) | 124 (2) |
| C(9)–C(8)–H(82) | 106 (2) | C(21)–C(20)–H(201) | 117 (2) |
| H(81)–C(8)–H(82) | 104 (3) | C(20)–C(21)–H(211) | 117 (2) |
| C(8)–C(9)–H(91) | 107 (2) | C(22)–C(21)–H(211) | 121 (2) |
| C(8)–C(9)–H(92) | 107 (2) | C(21)–C(22)–H(221) | 125 (2) |
| C(10)–C(9)–H(91) | 108 (2) | C(17)–C(22)–H(221) | 115 (2) |
| C(10)–C(9)–H(92) | 105 (2) | N(1)–N(2)–H(N2) | 120 (2) |
| H(91)–C(9)–H(92) | 116 (3) | C(16)–N(2)–H(N2) | 120 (2) |
| C(9)–C(10)–H(101) | 111 (2) | C(16)–N(3)–H(N3) | 112 (2) |
| C(9)–C(10)–H(102) | 110 (2) | C(17)–N(3)–H(N3) | 119 (2) |

cular to the plane in order to allow the insertion of the 15th C atom. The C₁₄ ring is surprisingly intact and all eclipsing is concentrated in the vicinity of the sp² atom (eclipsing being less unfavourable at such a C atom). In Dale's notation we can refer to the found quadrangular conformation as [3435]; the dihedral angles between the all-*anti* parts are given in Table 5.

Table 4. Torsion angles (°)

E.s.d.'s are in parentheses. The torsion angle A(1)–A(2)–A(3)–A(4) is viewed along A(2)–A(3), with a clockwise rotation of A(1) to A(4) taken to be positive.

| | | | | | |
|------------------------|------------|-------------------------|------------|------------------------|------------|
| C(1)–C(2)–C(3)–C(4) | 179.9 (3) | C(10)–C(11)–C(12)–C(13) | –58.2 (4) | C(2)–C(1)–N(1)–N(2) | 1.9 (5) |
| C(2)–C(3)–C(4)–C(5) | 178.0 (3) | C(11)–C(12)–C(13)–C(14) | –53.4 (4) | C(15)–C(1)–N(1)–N(2) | 179.3 (3) |
| C(3)–C(4)–C(5)–C(6) | 57.6 (4) | C(12)–C(13)–C(14)–C(15) | –173.9 (3) | C(1)–N(1)–N(2)–C(16) | 179.7 (3) |
| C(4)–C(5)–C(6)–C(7) | 58.6 (4) | C(13)–C(14)–C(15)–C(1) | –39.2 (4) | N(1)–N(2)–C(16)–O | 179.6 (3) |
| C(5)–C(6)–C(7)–C(8) | –177.6 (3) | C(14)–C(15)–C(1)–C(2) | –69.5 (4) | N(1)–N(2)–C(16)–N(3) | –2.1 (4) |
| C(6)–C(7)–C(8)–C(9) | 59.8 (4) | C(15)–C(1)–C(2)–C(3) | 4.6 (5) | N(2)–C(16)–N(3)–C(17) | –175.5 (3) |
| C(7)–C(8)–C(9)–C(10) | 56.8 (4) | C(3)–C(2)–C(1)–N(1) | –178.2 (3) | C(16)–N(3)–C(17)–C(18) | –179.3 (3) |
| C(8)–C(9)–C(10)–C(11) | –177.8 (3) | C(14)–C(15)–C(1)–N(1) | 113.0 (3) | C(16)–N(3)–C(17)–C(22) | 0.8 (5) |
| C(9)–C(10)–C(11)–C(12) | 174.2 (3) | | | | |

Table 5. Dihedral angles between all-anti parts in the C_{15} ring ($^{\circ}$)

| E.s.d.'s are in parentheses. | |
|------------------------------|----------|
| C(12)···C(15),C(8)···C(12) | 87.7 (4) |
| C(8)···C(12),C(5)···C(8) | 88.8 (4) |
| C(5)···C(8),C(1)···C(5) | 88.4 (4) |
| C(1)···C(5),C(12)···C(15) | 88.8 (4) |
| C(1)···C(5),C(8)···C(12) | 1.8 (5) |
| C(5)···C(8),C(12)···C(15) | 21.9 (5) |

The most striking aspect of the molecular packing is the H-bonding between molecules related by a centre of symmetry. This interaction, which certainly contributes

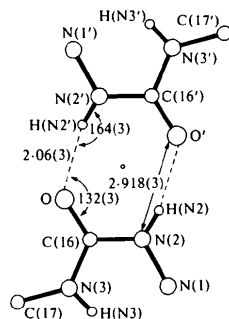


Fig. 3. Hydrogen-bonding scheme. Some distances (Å) and angles ($^{\circ}$) are shown, with their e.s.d.'s in parentheses.

to the existence of an ordered large-ring structure, is illustrated in Fig. 3.

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The Accuracy of Refined Protein Structures: Comparison of Two Independently Refined Models of Bovine Trypsin

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Abstract

The structure of diisopropyl-fluorophosphate-inhibited bovine trypsin has been refined to a standard crystallographic residual of $R = 0.157$ at 1.5 Å resolution for a constrained model (C&S coordinates). Benzamidine-inhibited bovine trypsin has also been independently refined ($R = 0.229$ at 1.8 Å) by Bode & Schwager [*J. Mol. Biol.* (1975), **98**, 693–717] (B&S coordinate set). Comparison of these structures after suitable correction for the different inhibitors and consequent structural

differences permits an experimental determination of the differences in structure, which places an upper limit on the errors in the refined coordinate sets. The models are remarkably similar in well determined regions. The average positional difference between internal main-chain atoms is 0.146 Å (0.163 Å r.m.s.); however, there are some differences as large as 3–9 Å associated mostly with poorly determined external side chains. The magnitude of the deviations is strongly dependent on the region of the structure compared, and is closely related to refined thermal parameters in our analysis.