

## Structure of 6,6-Diethylperhydro-1,4-diazepine-5,7-dione

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**Abstract.**  $C_9H_{16}N_2O_2$ ,  $M_r = 184.36$ , orthorhombic,  $Pbca$ ,  $a = 12.275$  (4),  $b = 20.280$  (3),  $c = 7.937$  (2) Å,  $V = 1975.9$  (9) Å<sup>3</sup>,  $Z = 8$ ,  $D_x = 1.239$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 0.053$  mm<sup>-1</sup>,  $F(000) = 800$ , room temperature,  $R = 0.056$  for 1276 observed reflections. The two lactam groups are planar. The seven-membered ring adopts a flattened twist-chair conformation. The ethyl groups, both in the staggered conformation, are in *anti* orientation and situated on either side of the mean plane of the seven-membered ring.

**Introduction.** Since the synthesis of barbituric acid, its derivatives have been widely used as therapeutic agents with soporific, tranquillizing, anticonvulsant or narcotic effectiveness. Such a wide spectrum of biological action and its duration depends on the nature of substituents at position 5 of the barbituric acid ring and on the substituents at the lactam groups. However, barbituric acid derivatives also have a high toxicity so the search is still on for new drugs which are less toxic and more differentiated in the duration of their action. The role of the ring size in the biological activity of barbiturates needs to be checked, so Bobrański (1986) and co-workers have synthesized several seven-membered analogs. Here we present the structure of 6,6-diethylperhydro-1,4-diazepine-5,7-dione.

**Experimental.** Crystals grown from methyl alcohol by slow evaporation; crystal system and approximate cell dimensions determined from oscillation and Weissenberg photographs; crystal specimen  $0.8 \times 0.6 \times 0.3$  mm; Syntex  $P2_1$  four-circle diffractometer, graphite-monochromated Mo  $K\alpha$  radiation,  $\theta$ - $2\theta$  scan mode, background and intensity of reflections determined by peak-profile analysis (Lehmann & Larsen, 1974; Jaskólski, 1979), accurate cell parameters refined from setting angles of 15 reflections with  $19 < \theta < 25^\circ$ ;  $[(\sin\theta)/\lambda]_{\max} = 0.704$  Å<sup>-1</sup>,  $0 \leq h \leq 14$ ,  $0 \leq k \leq 22$ ,  $0 \leq l \leq 10$ , 3000 unique reflections measured, 1276 considered observed [ $I > 2\sigma(I)$ ].  $L_p$  correction but no absorption correction. Structure solved by direct methods with *MULTAN78* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978), best set of

phases enabled location of all non-H atoms. Structure refined by full-matrix least squares with *SHELX76* (Sheldrick, 1976), function minimized  $\sum w(|F_o| - |F_c|)^2$ ,  $w^{-1} = \sigma^2(F_o) + 0.001F_o^2$ ,  $\sigma(F_o)$  based on counting statistics. Non-H atoms refined anisotropically, all H atoms located from difference synthesis and refined isotropically; empirical isotropic extinction parameter  $x$  used to correct  $F_c$  according to  $F'_c = F_c(1 - xF_c^2/\sin\theta)$ ,  $x$  converged at 0.0141 (5). Final  $R = 0.056$ ,  $wR = 0.069$ ,  $S = 1.56$ ,  $(\Delta/\sigma)_{\max} = 0.03$  in final cycle; largest peak in final  $\Delta F$  map 0.12, largest hole  $-0.14$  e Å<sup>-3</sup>; atomic scattering factors from *International Tables for X-ray Crystallography* (1974). Other computer programs used: *ORTEP* (Johnson, 1976); *PLUTO* (Motherwell & Clegg, 1978).

**Discussion.** The positional parameters and  $U_{eq}$  for non-H atoms are given in Table 1.† A stereoview of the molecule with atom labelling is given in Fig. 1. Bond lengths, bond angles and some torsion angles are given in Table 2. The seven-membered ring contains two lactam groups. The C–N bonds differ in length. Those involved in the lactam groups are shorter; the mean value of N(1)–C(7) and N(4)–C(5) distances is 1.330 (2) Å, and is the same as in the caprolactam molecule (Winkler & Dunitz, 1975). The above fact and the increase in the values of the C(7)–N(1)–C(2) and C(5)–N(4)–C(3) angles are characteristic of a lactam function and demonstrate  $\pi$  delocalization along each lactam fragment, which is further confirmed by the planarity of the N(1), C(7), O(8), C(6) (I) and N(4), C(5), O(9), C(6) (II) fragments. The distances of these atoms from their least-squares planes are  $\leq 0.020$  (2) Å in (I) and  $\leq 0.026$  (2) Å in (II); the angle between (I) and (II) is  $151.1$  (1)°. The ring closing together with the planar lactam fragments cause the angular deformations at C(6): the endocyclic angle C(5)–C(6)–C(7) has been enlarged to  $124.4$  (2)° and, in consequence, the exocyclic C(6) angles are significantly

† Lists of structure factors, anisotropic thermal parameters, torsion angles, H-atom parameters, bond lengths and angles involving H atoms and least-squares-planes data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51639 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. Final fractional coordinates and equivalent isotropic thermal parameters ( $\text{\AA}^2$ )
$$U_{eq} = (U_{11}U_{22}U_{33})^{1/3}.$$

|       | x          | y           | z          | $U_{eq}$   |
|-------|------------|-------------|------------|------------|
| N(1)  | 0.2561 (2) | 0.1736 (1)  | 0.3306 (3) | 0.0450 (8) |
| C(2)  | 0.2099 (3) | 0.1238 (2)  | 0.2210 (4) | 0.054 (1)  |
| C(3)  | 0.0916 (3) | 0.1132 (2)  | 0.2518 (4) | 0.062 (1)  |
| N(4)  | 0.0702 (2) | 0.0715 (1)  | 0.3970 (3) | 0.0522 (8) |
| C(5)  | 0.1197 (2) | 0.0711 (1)  | 0.5457 (3) | 0.0418 (8) |
| C(6)  | 0.1941 (2) | 0.1269 (1)  | 0.6100 (3) | 0.0407 (8) |
| C(7)  | 0.2458 (2) | 0.1799 (1)  | 0.4970 (3) | 0.0382 (7) |
| O(8)  | 0.2841 (1) | 0.22906 (9) | 0.5664 (2) | 0.0497 (6) |
| O(9)  | 0.1005 (2) | 0.0255 (1)  | 0.6455 (2) | 0.0557 (7) |
| C(10) | 0.1212 (3) | 0.1641 (2)  | 0.7399 (4) | 0.065 (1)  |
| C(11) | 0.0293 (4) | 0.2027 (2)  | 0.6629 (7) | 0.081 (2)  |
| C(12) | 0.2907 (3) | 0.0943 (2)  | 0.7028 (4) | 0.063 (1)  |
| C(13) | 0.3678 (3) | 0.0581 (2)  | 0.5873 (7) | 0.083 (2)  |

Table 2. Bond lengths ( $\text{\AA}$ ), bond angles ( $^\circ$ ) and some torsion angles ( $^\circ$ ) with e.s.d.'s in parentheses

|                     |           |                     |           |
|---------------------|-----------|---------------------|-----------|
| N(1)—C(2)           | 1.449 (4) | C(7)—O(8)           | 1.232 (3) |
| N(1)—C(7)           | 1.333 (3) | C(5)—O(9)           | 1.239 (3) |
| C(2)—C(3)           | 1.488 (5) | C(6)—C(10)          | 1.559 (4) |
| C(3)—N(4)           | 1.453 (4) | C(10)—C(11)         | 1.503 (6) |
| N(4)—C(5)           | 1.327 (3) | C(6)—C(12)          | 1.545 (4) |
| C(5)—C(6)           | 1.542 (4) | C(12)—C(13)         | 1.508 (6) |
| C(6)—C(7)           | 1.537 (3) |                     |           |
|                     |           |                     |           |
| N(1)—C(2)—C(3)      | 112.6 (3) | N(4)—C(5)—O(9)      | 119.1 (2) |
| C(2)—C(3)—N(4)      | 113.0 (2) | C(6)—C(5)—O(9)      | 116.6 (2) |
| C(3)—N(4)—C(5)      | 128.8 (2) | C(5)—C(6)—C(12)     | 107.3 (2) |
| N(4)—C(5)—C(6)      | 124.1 (2) | C(7)—C(6)—C(10)     | 106.5 (2) |
| C(5)—C(6)—C(7)      | 124.4 (2) | C(7)—C(6)—C(12)     | 105.1 (2) |
| C(6)—C(7)—N(1)      | 123.4 (2) | C(5)—C(6)—C(10)     | 103.6 (2) |
| C(7)—N(1)—C(2)      | 128.6 (2) | C(10)—C(6)—C(12)    | 109.4 (2) |
| N(1)—C(7)—O(8)      | 119.0 (2) | C(6)—C(12)—C(13)    | 113.6 (3) |
| C(6)—C(7)—O(8)      | 117.5 (2) | C(6)—C(10)—C(11)    | 114.5 (3) |
|                     |           |                     |           |
| N(1)—C(2)—C(3)—N(4) | -79.9 (3) | C(2)—C(3)—N(4)—C(5) | 40.6 (3)  |
| C(3)—N(4)—C(5)—C(6) | 15.3 (3)  | N(4)—C(5)—C(6)—C(7) | -17.6 (3) |
| C(5)—C(6)—C(7)—N(1) | -18.5 (3) | C(6)—C(7)—N(1)—C(2) | 9.8 (3)   |
| C(7)—N(1)—C(2)—C(3) | 48.1 (3)  |                     |           |

smaller than the tetrahedral ones, C(12)—C(6)—C(7) and C(10)—C(6)—C(5) being  $105.1(2)$  and  $103.6(2)^\circ$ , respectively. The bond lengths N(1)—C(2) and N(4)—C(3), with a mean value of  $1.451(3)$   $\text{\AA}$ , are in agreement with the N( $sp^2$ )—C( $sp^3$ ) distance (Grand & Rey, 1979). The relatively short C(2)—C(3) distance of  $1.488(5)$   $\text{\AA}$  is probably due to the thermal motions or disorder of this fragment of the ring. Nevertheless, the C(2) and C(3) ring bond angles with a mean of  $112.9(2)^\circ$  are close to the theoretical values given for the twist-chair conformation of cycloheptane,  $114.1^\circ$  (Bixon & Lifson, 1967) and  $114.7^\circ$  (Hendrickson, 1967). The conformation of the seven-membered ring is controlled by the planarity of the lactam groups and can be described as a flattened twist-chair (Bixon & Lifson, 1967; Hendrickson, 1967; Bocian, Pickett, Rounds & Strauss, 1975; Flapper & Romers, 1975; Ponnuswamy & Trotter, 1985). The local pseudotwofold axis passes through C(6) and the midpoint of the C(2)—C(3) bond. The low values of the torsional

angles along N(1)—C(7) and N(4)—C(5) are due to the planarity of the lactam groups. The N(1)—C(2)—C(3)—N(4) torsion angle [ $-79.6(3)^\circ$ ] shows a significant extra twisting from a staggered conformation. Ethyl groups, both in the staggered conformation, are in *anti* orientation and situated on either side of the mean plane of the seven-membered ring. Nevertheless, some steric hindrance due to the ethyl groups exists, which is manifested in short intramolecular distances depicting the environment of the C(5)—C(6)—C(7) ring fragment.

The crystal structure (Fig. 2) is built of infinite helices along the *b* axis. Every molecule in the helix is involved in four hydrogen bonds, two of which are characterized in Table 3. Two other hydrogen bonds are related by the symmetry of the space group.

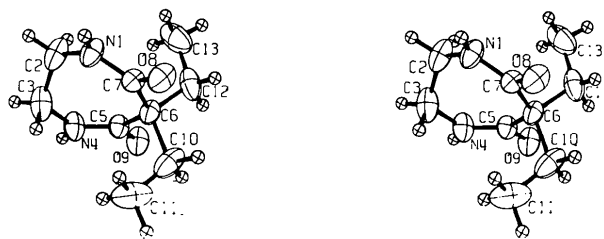


Fig. 1. A stereoview of the molecule.

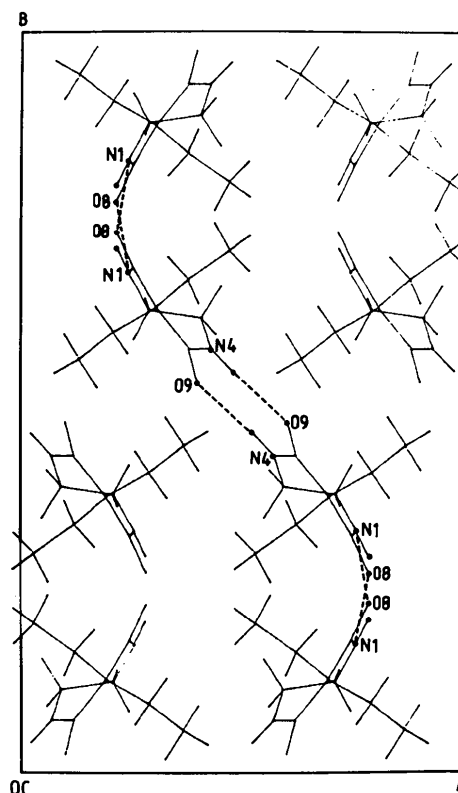


Fig. 2. The crystal packing.

Table 3. *Intermolecular hydrogen bonds*

|                               |             |                                |             |
|-------------------------------|-------------|--------------------------------|-------------|
| N(1)⋯O(8 <sup>i</sup> )       | 2.900 (3) Å | N(4)⋯O(9 <sup>ii</sup> )       | 2.895 (3) Å |
| N(1)–H(11)                    | 0.84 (3) Å  | N(4)–H(41)                     | 0.87 (3) Å  |
| H(11)⋯O(8 <sup>i</sup> )      | 2.16 (3) Å  | H(41)⋯O(9 <sup>ii</sup> )      | 2.08 (3) Å  |
| N(1)–H(11)⋯O(8 <sup>i</sup> ) | 147 (2)°    | N(4)–H(41)⋯O(9 <sup>ii</sup> ) | 174 (2)°    |

Symmetry code: (i)  $x, \frac{1}{2}-y, z-\frac{1}{2}$ ; (ii)  $-x, -y, 1-z$ .

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## Functionalized Bicyclo[4.4.0]decane from Double Michael Addition Reaction

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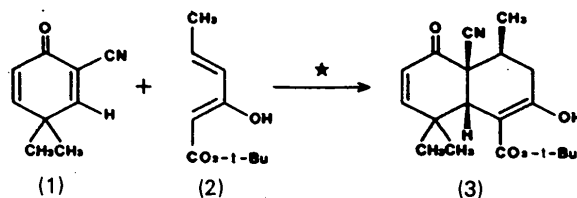
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**Abstract.** *rel*-(1*R*,5*S*,6*R*)-*tert*-Butyl 6-cyano-3-hydroxy-5,10,10-trimethyl-7-oxobicyclo[4.4.0]deca-2,8-diene-2-carboxylate.  $C_{19}H_{25}NO_4$ ,  $M_r = 331.41$ , triclinic,  $P\bar{1}$ ,  $a = 8.0554$  (15),  $b = 11.9774$  (24),  $c = 20.361$  (4) Å,  $\alpha = 87.585$  (18),  $\beta = 86.941$  (16),  $\gamma = 75.015$  (18)°,  $Z = 4$ ,  $V = 1894.12$  Å<sup>3</sup>,  $D_x = 1.162$  Mg m<sup>-3</sup>,  $\lambda(\text{Cu } K\alpha) = 1.54056$  Å,  $\mu = 0.62$  mm<sup>-1</sup>,  $F(000) = 711.90$ , room temperature, final  $R = 0.065$ ,  $wR = 0.037$ ,  $S = 2.467$  for 4473 observed reflections. The bicyclic compound (3) is obtained from the double Michael addition reaction between a diene and a dienophile with total control of relative stereochemistry at carbons 1, 5 and 6. The relative stereochemistry is *cis* for the *AB* ring junction and *syn* between C6-cyano and C5-methyl.

**Introduction.** The synthesis of complex organic molecules of biological interest such as steroids is partic-

ularly attractive when synthetic strategies give the possibility of reaching a high level of chemo-, regio-, diastereo- and enantioselectivity. The Michael addition reaction is a very useful reaction in organic synthesis, and a few studies (Stork, Winkler & Saccomano, 1983; Toma, 1981) have been made to point out which are the important factors involved when this reaction is used in cyclization. A study of the intramolecular Michael addition reaction was reported recently (Lavallée &



\*  $\text{Cs}_2\text{CO}_3$  in  $\text{CH}_3\text{CN}$ , 16 h at room temperature, 95% yield

Fig. 1. Synthesis scheme.

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