A number of short intramolecular H···H contacts influence the conformation of the molecule. The H(6a)···H(8$a$) and H(10$a$)···H(9$b$) distances are 2·24 (2·47) and 2·34 (2·38) Å, respectively. The folding of the six-membered ring along the C(7)···C(10) axis gives an interplanar angle of 111·4 (3) (113·8)°. The short intramolecular contacts cannot be relieved by any significant expansion of this interplanar angle due to contacts H(13$a$)···H(8$b$) and H(13$a$)···H(9$a$) = 2·59 (2·64) and 2·57 (2·62) Å, respectively. The interplanar angles for C(10)C(13)C(7) with C(7)C(8)C(9)C(10) and C(6a)C(7)C(10)C(10a) are 122·5 (3) (121·8)° and 126·1 (3) (124·5)°. The 126·1 and 130·8° interior interplanar angles indicate a significant contact between H(13$b$) and the N(12) lone pair. Other close contacts are H(7)···H(20$b$) = 2·25 (2·45), H(1)···H(21$a$) = 2·20 (2·37) and H(4)···H(5) = 2·39 (2·44) Å. The short contacts involving the C(20) and C(21) methyl groups force them out of the C(6)N(12)C(11) plane by 0·199 (4) (0·318) and 0·264 (4) (0·304) Å, respectively.

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# Structures of Diazapolycyclic Compounds. IX. 1,3-Dimethyl-1,4-dihydrobenzo[$g$]pyridazino[1,2-$b$]phthalazine-6,13-dione

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**Abstract.** $C_{18}H_{16}N_2O_2$, $M_r = 292\cdot33$, triclinic, $P\bar{1}$, $a = 11\cdot2747$ (5), $b = 9\cdot0849$ (2), $c = 7\cdot7367$ (2) Å, $\alpha = 109\cdot903$ (2), $\beta = 83\cdot234$ (2), $\gamma = 108\cdot492$ (3)°, $V = 706\cdot62$ (4) Å$^3$, $Z = 2$, $D_x = 1\cdot37$ Mg m$^{-3}$, $\lambda$(Cu $K\alpha$) = 1·5418 Å, $\mu = 0\cdot692$ mm$^{-1}$, $F(000) = 308$, room temperature, 2396 unique reflections, $R = 0\cdot050$. The pyrazine ring exhibits a distorted envelope conformation with N(14) at the flap. The methyl group bonded to C(1) occupies an axial position. As expected, the deformations in the amide groups are greater at the N atoms. The diazaquinone ring is nearly planar, with the O atoms out of this plane. All bond distances and angles, within the molecule, are normal.

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**Introduction.** As part of a project on analogues of tetracycline compounds (Beurskens, Beurskens, Apreda, Foces-Foces, Cano & García-Blanco, 1984), we have determined the structure of the title compound, in order to clarify some conformational aspects for future reactivity studies in the search for compounds with pharmacological activity.

**Experimental.** Table 1 summarizes the experimental data and structure-solution parameters, together with the refinement procedures. The structure was solved by means of the *TRADIR* program (*DIRDIF* system, Beurskens *et al.*, 1983), using a three-ring-system model taken from *MULTAN*80 (Main *et al.*, 1980). After application of the first translation vector, the remaining non-H atoms were located on a Fourier map.

**Discussion.** Fig. 1 displays the atomic numbering scheme (*ORTEP*, Johnson, 1965). Table 2 shows the final coordinates for the heavy atoms.* Some selected geometrical features are collected in Table 3.

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\* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42658 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

### Table 1. *Experimental data and structure-refinement procedures*

| | |
|---|---|
| Crystal habit | Prismatic. Yellow. Transparent |
| Size (mm) | 0·45 × 0·23 × 0·10 |
| Technique, bisecting geometry | Four-circle diffractometer (Philips PW 1100); graphite-monochromator; $\omega/2\theta$ scan mode |
| Unit-cell determination | Least-squares fit from 77 reflections ($\theta < 45°$) |
| Total measurements | Up to $\sin\theta/\lambda = 0.59$ Å$^{-1}$ |
| Range of $h,k,l$ | $\bar{1}3$–$\bar{1}3$, 10–10, 0–9 |
| Standard reflections | $2\bar{1}2$, $\bar{2}1\bar{2}$. No variation detected |
| Number of reflections: | |
| measured | 2396 |
| independent | 2396 |
| observed | 2148 |
| Criterion for observed | $I \geq 2\sigma(I)$ |
| Absorption correction | None |
| Computer programs | *XRAY*76 system (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976) |
| Solution | *MULTAN*80 and *DIRDIF*83 |
| Atomic scattering factors | *International Tables for X-ray Crystallography* (1974) |
| Refinement method | Full-matrix least squares on observed *F*'s |
| H atoms | From difference synthesis |
| Parameters refined: | |
| non-H atoms | 198 (coordinates and $U_{ij}$) |
| H atoms | 64 (coordinates and isotropic temperature factors) |
| Values for $R$, $wR$ | 0·050, 0·058 |
| Max./average $\Delta/\sigma$ in final refinement cycle | 0·12/0·009 |
| Weighting scheme | Empirical as to give no trends in $\langle w\Delta^2F \rangle$ *vs* $\langle F_o \rangle$ or $\langle \sin\theta/\lambda \rangle$ |
| $\Delta\rho_{max}$ (e Å$^{-3}$) | 0·18 |
| Secondary-extinction correction | None |
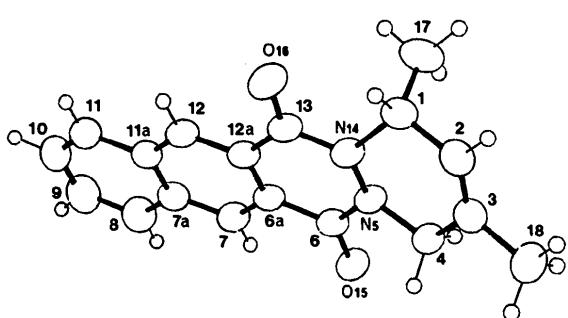


Fig. 1. *ORTEP* drawing of the compound showing the atomic numbering.

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The conformation of the pyrazine ring can be described using the model for flexible six-membered rings proposed by Cano, Foces-Foces & Garcia-Blanco (1977). According to the parameters found\* [$\tau_m$

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\* $\tau_m$ is the mean torsion in the ring, $q$ is the amplitude of pseudorotation modulating the mean torsion, $\Sigma/2$ is the pseudorotation phase, $\alpha_1 + \alpha_2 = \Sigma$ and $\alpha_1 - \alpha_2 = \delta$.

### Table 2. *Final atomic parameters for the heavy atoms*

$$U_{eq} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j \cos(a_i, a_j).$$

| | $x$ | $y$ | $z$ | $U_{eq}(\text{Å}^2 \times 10^4)$ |
|---|---|---|---|---|
| C(1) | 0·1204 (2) | 0·2038 (3) | 0·6281 (3) | 475 (8) |
| C(2) | 0·0958 (2) | 0·2991 (3) | 0·8207 (3) | 514 (9) |
| C(3) | 0·1848 (2) | 0·4127 (3) | 0·9306 (3) | 487 (8) |
| C(4) | 0·3176 (2) | 0·4544 (3) | 0·8684 (3) | 472 (8) |
| N(5) | 0·3440 (1) | 0·3501 (2) | 0·6848 (2) | 419 (6) |
| C(6) | 0·4667 (2) | 0·3770 (2) | 0·6339 (3) | 419 (7) |
| C(6a) | 0·5004 (2) | 0·2481 (2) | 0·4804 (2) | 408 (7) |
| C(7) | 0·6217 (2) | 0·2714 (3) | 0·4179 (3) | 463 (8) |
| C(7a) | 0·6575 (2) | 0·1474 (2) | 0·2761 (3) | 461 (8) |
| C(8) | 0·7818 (2) | 0·1679 (3) | 0·2069 (3) | 588 (10) |
| C(9) | 0·8125 (2) | 0·0446 (3) | 0·0694 (4) | 657 (11) |
| C(10) | 0·7209 (2) | −0·1066 (3) | −0·0071 (3) | 588 (10) |
| C(11) | 0·6016 (2) | −0·1307 (3) | 0·0555 (3) | 530 (9) |
| C(11a) | 0·5650 (2) | −0·0060 (2) | 0·1999 (3) | 439 (7) |
| C(12) | 0·4418 (2) | −0·0269 (2) | 0·2661 (3) | 453 (8) |
| C(12a) | 0·4090 (2) | 0·0963 (2) | 0·4038 (2) | 415 (7) |
| C(13) | 0·2778 (2) | 0·0745 (2) | 0·4620 (3) | 448 (7) |
| N(14) | 0·2511 (1) | 0·2002 (2) | 0·6028 (2) | 444 (6) |
| O(15) | 0·5447 (1) | 0·5037 (2) | 0·7205 (2) | 520 (6) |
| O(16) | 0·1924 (1) | −0·0478 (2) | 0·3860 (2) | 601 (6) |
| C(17) | 0·0851 (2) | 0·2660 (4) | 0·4882 (4) | 654 (12) |
| C(18) | 0·1629 (3) | 0·5104 (4) | 1·1249 (4) | 674 (12) |

### Table 3. *Bond distances* (Å) *and angles* (°) *for the heavy atoms and torsional angles* (°) *for the non-benzene rings*

| | | | | |
|---|---|---|---|---|
| C(1)–C(2) | 1·491 (3) | | C(7)–C(7a) | 1·407 (3) |
| C(1)–N(14) | 1·473 (3) | | C(7a)–C(8) | 1·418 (3) |
| C(1)–C(17) | 1·519 (5) | | C(7a)–C(11a) | 1·428 (2) |
| C(2)–C(3) | 1·319 (3) | | C(8)–C(9) | 1·361 (4) |
| C(3)–C(4) | 1·488 (3) | | C(9)–C(10) | 1·413 (3) |
| C(3)–C(18) | 1·500 (3) | | C(10)–C(11) | 1·351 (3) |
| C(4)–N(5) | 1·472 (2) | | C(11)–C(11a) | 1·424 (3) |
| N(5)–C(6) | 1·360 (2) | | C(11a)–C(12) | 1·400 (3) |
| N(5)–N(14) | 1·421 (2) | | C(12)–C(12a) | 1·372 (3) |
| C(6)–C(6a) | 1·469 (3) | | C(12a)–C(13) | 1·466 (3) |
| C(6)–O(15) | 1·232 (2) | | C(13)–N(14) | 1·369 (2) |
| C(6a)–C(7) | 1·371 (3) | | C(13)–O(16) | 1·232 (2) |
| C(6a)–C(12a) | 1·414 (2) | | | |

| | | | | |
|---|---|---|---|---|
| C(2)–C(1)–N(14) | 111·3 (2) | | N(5)–C(6)–O(15) | 119·6 (2) |
| C(2)–C(1)–C(17) | 112·2 (2) | | C(6a)–C(6)–O(15) | 122·9 (2) |
| N(14)–C(1)–C(17) | 111·4 (2) | | C(6)–C(6a)–C(12a) | 119·9 (2) |
| C(1)–C(2)–C(3) | 123·0 (2) | | C(7)–C(6a)–C(12a) | 120·0 (2) |
| C(2)–C(3)–C(4) | 121·5 (2) | | C(6a)–C(12a)–C(13) | 120·1 (2) |
| C(2)–C(3)–C(18) | 124·2 (2) | | C(12a)–C(13)–N(14) | 117·2 (2) |
| C(4)–C(3)–C(18) | 114·3 (2) | | C(12a)–C(13)–O(16) | 122·9 (2) |
| C(3)–C(4)–N(5) | 115·6 (2) | | N(14)–C(13)–O(16) | 119·8 (2) |
| C(4)–N(5)–C(6) | 116·0 (2) | | C(1)–N(14)–N(5) | 116·5 (2) |
| C(4)–N(5)–N(14) | 118·1 (2) | | C(1)–N(14)–C(13) | 118·0 (2) |
| C(6)–N(5)–N(14) | 122·5 (2) | | N(5)–N(14)–C(13) | 122·4 (2) |
| N(5)–C(6)–C(6a) | 117·5 (2) | | | |

| | | | |
|---|---|---|---|
| C(4)–N(5)–N(14)–C(1) | 39·8 (2) | C(6)–C(6a)–C(12a)–C(13) | 7·4 (3) |
| N(5)–N(14)–C(1)–C(2) | −42·9 (2) | C(6a)–C(12a)–C(13)–N(14) | −5·8 (3) |
| N(14)–C(1)–C(2)–C(3) | 23·5 (3) | C(12a)–C(13)–N(14)–N(5) | 3·3 (3) |
| C(1)–C(2)–C(3)–C(4) | 0·2 (4) | C(13)–N(14)–N(5)–C(6) | −2·5 (3) |
| C(2)–C(3)–C(4)–N(5) | −5·8 (3) | N(14)–N(5)–C(6)–C(6a) | 3·8 (3) |
| C(3)–C(4)–N(5)–N(14) | −14·4 (3) | N(5)–C(6)–C(6a)–C(12a) | −6·3 (3) |
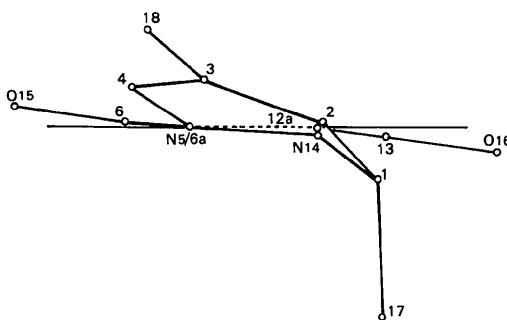
Fig. 2. Frontal view of the pyrazine ring along the overall molecular plane.

least-squares plane. The atoms O(15) and O(16) are slightly out of this plane, $-0.129$ (2) and $0.114$ (2) Å respectively. All bond distances and angles within the molecule compare well with those values previously reported for analogous compounds (Beurskens *et al.*, 1984, and references therein).

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$= 19.1$ (1), $q = 26.0$ (2), $\Sigma = -79.7$ (2), $\delta = 85.4$ (3), $\alpha_1 = 2.9$ (2), $\alpha_2 = -82.6$ (2)°] the ring exhibits an envelope conformation, with N(14) at the flap, distorted towards a diplanar one at the C(2)—C(3) and C(4)—C(5) bonds. Interestingly, a half-chair conformation has been described for a closely related compound with no methyl group at C(3) (Apreda, Foces-Foces, Cano & García-Blanco, 1978). The orientation of the methyl group bonded to C(1) is axial (see Fig. 2).

The distortion parameters for the 'amide groups' (Winkler & Dunitz, 1971) have been calculated from the torsion angles around the N(5)—C(6) and N(14)—C(13) bonds. As expected, the deformations with respect to $sp^2$ hybridization are greater at the N [$\chi_N = 21.4$ (4), $20.8$ (4)°] than at the C atoms [$\chi_C = -2.5$ (4), $-2.4$ (4)°]. The average angles around N(5) and N(14) are $118.9$ (1) and $119.0$ (1)°, values confirming the $sp^2$ hybridization.

The diazaquinone ring is nearly planar, with no atomic deviation greater than $0.033$ (2) Å from its

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# Structure of the Methanol Solvate of 13-Ethyl-18,19-dinor-17α-pregn-4-en-20-yn-17β-ol (13-Ethyl-18-norlynestrenol)

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**Abstract.** $C_{21}H_{30}O.CH_4O$, $M_r = 330.51$, monoclinic, $P2_1$, $a = 13.179$ (1), $b = 7.554$ (1), $c = 10.371$ (1) Å, $\beta = 93.535$ (3)°, $V = 1030.54$ (8) Å$^3$, $Z = 2$, $D_x = 1.065$ g cm$^{-3}$, $\lambda(Cu\,K\alpha) = 1.5418$ Å, $\mu = 4.41$ cm$^{-1}$, $F(000) = 364$, room temperature, $R = 0.044$ for 1488 unique reflections with $I \geq 2.5\sigma(I)$. The crystal was twinned by pseudomerohedry with a twin fraction of $0.146$ (8); *hkl* data with $l = 0$ were corrected for this