LEJEUNE, R., VANDENBALCK, J. L., PATRIARCHE, G. J. & LAPIÈRE, C. L. (1981*b*). *Anal. Lett.* **14**(B15), 1279–1295.
LEJEUNE, R., VANDENBALCK, J. L., PATRIARCHE, G. J. & LAPIÈRE, C. L. (1981*c*), *Anal. Lett.* **14**(A16), 1311–1325.
MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J. P. & WOOLFSON, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. de York, Angleterre, et de Louvain-la-Neuve, Belgique.
NORTH, A. C. T., PHILLIPS, D. C. & MATHEWS, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
PORTYAGINA, V. A. & KARPP, V. R. (1966), *Ukr. Khim. Zh.* **32**, 1306–1310.
SHELDRICK, G. M. (1976). *SHELX76*, Program for crystal structure determination. Univ. de Cambridge, Angleterre.
THUNUS, L. (1981). *J. Pharm. Belg.* **36**, 237–242.
THUNUS, L. & LAPIÈRE, C. L. (1982). *Ann. Pharm. Fr.* **40**, 259–267.

Acta Cryst. (1983). C**39**, 1410–1412

Structure of 1-Acetyl-7-benzylamino-6*H*-1,2,3,4-tetrahydropyrido[2,3-*c*]azepine, $C_{18}H_{21}N_3O$

BY JOHN C. BARNES,* WIGEN GOLNAZARIANS, JOHN IBALL AND JOHN D. PATON

Chemistry Department, The University, Dundee DD1 4HN, Scotland

AND THOMAS MCC. PATERSON AND HANS SUSCHITZKY

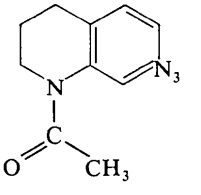
The Ramage Laboratories, Department of Chemistry and Applied Chemistry, University of Salford, Salford M5 4WT, England

(*Received* 25 *March* 1983; *accepted* 20 *June* 1983)

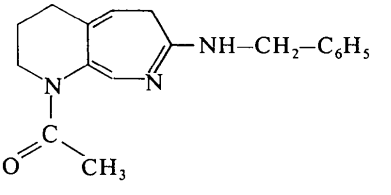
Abstract. $M_r = 295{\cdot}4$, monoclinic, $P2_1/c$, $a = 8{\cdot}737\ (8)$, $b = 20{\cdot}198\ (15)$, $c = 9{\cdot}624\ (8)$ Å, $\beta = 107{\cdot}94\ (6)°$, $U = 1615{\cdot}8$ Å^3, $Z = 4$, $D_x = 1{\cdot}21$ Mg m^{-3}, Cu $K\alpha$ radiation, $\lambda = 1{\cdot}5418$ Å, $\mu = 0{\cdot}53$ mm^{-1}, $F(000) = 632$, $T = 293$ K, $R = 0{\cdot}097$ for 1437 reflexions. The product of a ring-expansion reaction on *N*-acetyl-7-azido-1,2,3,4-tetrahydroquinoline has been identified as the title compound. The tetrahydroquinoline ring is found in both chair and skew-boat conformations in the crystal.

Introduction. In previous studies we have demonstrated that photolysis and thermolysis of bicyclic aromatic azides in the presence of amines is a preparative route to bicyclic azepines. We have also given guidelines for predicting the structure of the resulting azepines (Suschitzky, 1980; Iddon, Meth-Cohn, Scriven, Suschitzky & Gallacher, 1979). By contrast there appears to be no literature report about analogous ring expansion of bicyclic azides in which one of the rings is partially saturated. The success of such a reaction would substantially widen the scope of azepine formation.

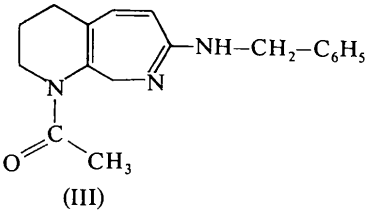
We have now photolysed *N*-acetyl-7-azido-1,2,3,4-tetrahydroquinoline (I) in dioxane in the presence of benzylamine and obtained an azepine (58%) shown by analysis and H NMR to be either (II) or (III). X-ray structural analysis has now shown the product to be (II).



(I)



(II)



(III)

Experimental. Full details of the preparation of (II) will be reported elsewhere. Crystals pale yellow plates with ill-defined faces, data collected during the rebuilding of a Wooster four-circle diffractometer, incorporating a CAMAC control system with an LSI 11 microprocessor, fixed-χ mode, $\theta_{max} \leq 75°$ for 4 octants, $180 \geq \chi \geq 140°$, two crystals ($0{\cdot}2 \times 0{\cdot}3 \times 0{\cdot}5$ mm) accurately mounted on *b* and *c* axes, respectively, lattice parameters from centring high 2θ axial reflexions by hand at $(2\theta, \omega)$ and $(-2\theta, \omega-2\theta)$; diffractometer not entirely reliable at that time, many χ layers collected several times; repeated measurements of standard planes of $\chi = 180°$ showed no intensity variation;

* Author for correspondence.

0108-2701/83/101410-03$01.50

out of 29 layers measured only the 19 which had individual internal consistency indices below 0·13 were used in the solution; 3315 measured reflexions with internal consistency index 0·084, 2634 unique reflexions, 1437 with $F > 6\sigma(F)$ used in the refinement; no absorption corrections. All calculations performed on the Dundee University DEC 10 computer, *SHELX*76 (Sheldrick, 1976), *XANADU* (Roberts & Sheldrick, 1975) and *PLUTO* (Motherwell & Clegg, 1978); atomic scattering factors from *International Tables for X-ray Crystallography* (1974). Structure solved by direct-methods routine *TANG*; an *E* map showed the seven-membered ring and the phenyl group; structure extended by least-squares refinement and Fourier synthesis, all non-hydrogen atoms located, $R = 0{\cdot}29$, refinement with anisotropic non-H atoms, $R = 0{\cdot}12$.

At this point C(2)–C(3) = 1·43 (1), C(3)–C(4) = 1·38 (1) Å although both are single bonds. C(2), C(4) and particularly C(3) had high thermal parameters. These factors are consistent with the saturated six-membered ring occurring in both chair and boat conformations in the crystal. C(3) was divided into two partially occupied sites with the constraints C(2)–C(3),[C(31)] = 1·51 (1) Å; C(3),[C(31)]–C(4) = 1·51 (1) Å; C(3)–C(31) = 1·06 (3) Å. This model refined to $R = 0{\cdot}097$ with 58(3)% occupancy of C(31). C(2) and C(4) will occupy slightly different sites in the two conformers; this was not allowed for in the model but can be seen in the anisotropic thermal parameters. Most of the H atoms were located and refined with grouped isotropic thermal parameters. Not all H atoms at C(2),C(3),C(4) were observed and, because of the disorder, those missing were not introduced by calculation; final refinement (minimizing $\sum w|F_o - |F_c||^2$): 272 refined parameters, $wR = 0{\cdot}100$, $w = 5{\cdot}2716/[\sigma(F) + 0{\cdot}001981F^2]$, $(\Delta/\sigma)_{av} = 0{\cdot}037$, $(\Delta/\sigma)_{max} = 0{\cdot}198$ [H(201)], max. $\Delta\rho$ peak 0·32 e Å^{-3}.*

Table 1. *1-Acetyl-7-benzylamino-6H-1,2,3,4-tetrahydropyrido[2,3-c]azepine coordinates* ($\times 10^4$) *for non-hydrogen atoms with e.s.d.'s in parentheses*

$U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq} (Å^2 × 10^3)
N(1)	8597 (5)	3733 (3)	−954 (4)	71 (1)
C(2)	9377 (8)	3155 (5)	−1386 (5)	98 (3)
C(3)	10384 (20)	2727 (7)	−163 (11)	95 (10)
C(31)	11068 (13)	3128 (12)	−335 (8)	107 (8)
C(4)	11128 (7)	3106 (5)	1216 (5)	112 (3)
C(5)	10184 (5)	3741 (3)	3011 (4)	61 (1)
C(6)	9008 (5)	4174 (4)	3395 (4)	69 (2)
C(7)	7510 (5)	3785 (3)	3198 (4)	62 (2)
N(8)	6557 (4)	3614 (3)	1932 (3)	67 (1)
C(9)	6988 (5)	3708 (3)	684 (4)	64 (2)
C(10)	9926 (5)	3534 (3)	1629 (4)	67 (2)
C(11)	8454 (5)	3683 (3)	514 (4)	56 (1)
C(12)	8389 (6)	4295 (4)	−1728 (4)	67 (2)
C(13)	7792 (7)	4895 (5)	−1194 (5)	85 (2)
O(14)	8696 (5)	4313 (3)	−2913 (3)	93 (2)
N(15)	7193 (4)	3598 (3)	4435 (3)	70 (2)
C(16)	5833 (7)	3184 (4)	4442 (6)	78 (2)
C(17)	4882 (5)	3488 (4)	5350 (4)	61 (2)
C(18)	4526 (5)	3112 (4)	6419 (5)	72 (2)
C(19)	3602 (6)	3397 (6)	7213 (5)	85 (3)
C(20)	3057 (7)	4035 (6)	6959 (7)	90 (3)
C(21)	3408 (6)	4393 (4)	5894 (7)	87 (2)
C(22)	4322 (6)	4130 (5)	5094 (6)	72 (2)

* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38670 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *1-Acetyl-7-benzylamino-6H-1,2,3,4-tetrahydropyrido[2,3-c]azepine interatomic distances* (Å) *and angles* (°)

C(2)–N(1)	1·475 (11)	C(9)–N(8)	1·378 (6)
C(11)–N(1)	1·460 (6)	C(11)–C(9)	1·342 (6)
C(12)–N(1)	1·339 (9)	C(11)–C(10)	1·430 (5)
C(3)–C(2)	1·505 (14)	C(13)–C(12)	1·472 (11)
C(31)–C(2)	1·512 (11)	O(14)–C(12)	1·250 (6)
C(31)–C(3)	1·049 (25)	C(16)–N(15)	1·455 (9)
C(4)–C(3)	1·497 (13)	C(17)–C(16)	1·510 (9)
C(4)–C(31)	1·478 (10)	C(18)–C(17)	1·389 (8)
C(10)–C(4)	1·505 (10)	C(22)–C(17)	1·382 (12)
C(6)–C(5)	1·481 (8)	C(19)–C(18)	1·396 (9)
C(10)–C(5)	1·345 (6)	C(20)–C(19)	1·369 (16)
C(7)–C(6)	1·488 (7)	C(21)–C(20)	1·363 (11)
N(8)–C(7)	1·293 (5)	C(22)–C(21)	1·374 (10)
N(15)–C(7)	1·357 (6)		

C(11)–N(1)–C(2)	113·8 (5)	C(11)–C(9)–N(8)	128·9 (3)
C(12)–N(1)–C(2)	120·7 (5)	C(5)–C(10)–C(4)	121·4 (4)
C(12)–N(1)–C(11)	124·0 (6)	C(11)–C(10)–C(4)	117·6 (4)
C(3)–C(2)–N(1)	116·3 (7)	C(11)–C(10)–C(5)	121·0 (5)
C(31)–C(2)–N(1)	106·3 (9)	C(9)–C(11)–N(1)	119·0 (3)
C(31)–C(2)–C(3)	40·7 (10)	C(10)–C(11)–N(1)	114·6 (4)
C(31)–C(3)–C(2)	70·0 (10)	C(10)–C(11)–C(9)	126·0 (4)
C(4)–C(3)–C(2)	112·9 (10)	C(13)–C(12)–N(1)	120·3 (5)
C(4)–C(3)–C(31)	68·4 (9)	O(14)–C(12)–N(1)	120·1 (6)
C(3)–C(31)–C(2)	69·3 (10)	O(14)–C(12)–C(13)	119·6 (6)
C(4)–C(31)–C(2)	113·6 (8)	C(16)–N(15)–C(7)	123·5 (4)
C(4)–C(31)–C(3)	70·3 (9)	C(17)–C(16)–N(15)	111·4 (6)
C(31)–C(4)–C(3)	41·3 (10)	C(18)–C(17)–C(16)	119·6 (7)
C(10)–C(4)–C(3)	112·3 (8)	C(22)–C(17)–C(16)	120·5 (6)
C(10)–C(4)–C(31)	116·0 (8)	C(22)–C(17)–C(18)	119·8 (5)
C(10)–C(5)–C(6)	120·8 (4)	C(19)–C(18)–C(17)	118·6 (7)
C(7)–C(6)–C(5)	107·8 (5)	C(20)–C(19)–C(18)	121·2 (7)
N(8)–C(7)–C(6)	123·2 (4)	C(21)–C(20)–C(19)	119·1 (7)
N(15)–C(7)–C(6)	116·4 (3)	C(22)–C(21)–C(20)	121·4 (8)
N(15)–C(7)–N(8)	120·4 (5)	C(21)–C(22)–C(17)	119·8 (6)
C(9)–N(8)–C(7)	121·0 (4)		

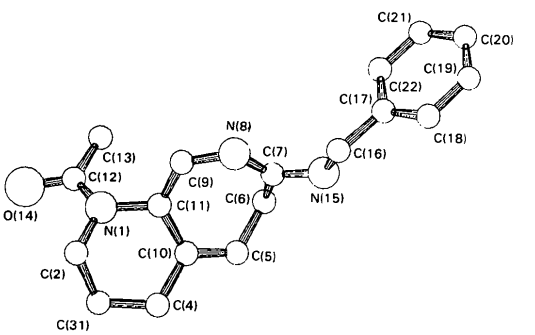


Fig. 1. 1-Acetyl-7-benzylamino-6*H*-1,2,3,4-tetrahydropyrido[2,3-*c*]-azepine viewed perpendicular to the plane C(2), C(4), C(11), showing the chair conformer only.

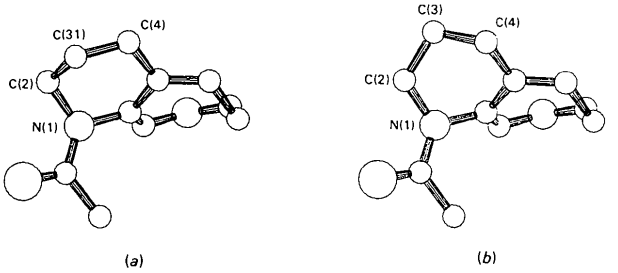


Fig. 2. The tetrahydropyridoazepine fragment showing: (*a*) the chair conformer, (*b*) the skew-boat conformer.

Discussion. Atomic coordinates are given in Table 1 with bond lengths and angles in Table 2. The molecule lies on a plane perpendicular to **b** at $y = 0{\cdot}4$, along the line 0,0·4,1;1,0·4,0. The dimensions about C(5) and C(6) show unambiguously that the correct formulation for the azepine ring is (II). The phenyl group is rotated by 70·0 (4)° from the plane C(5),C(10),C(11),C(9). The majority conformer of the saturated ring has the torsion angle C(11)–C(10)–C(4)–C(31) = 26·8 (9)°, indicating a distorted chair conformation (Fig. 2*a*). The minority conformer has the corresponding torsion angle of −18·5 (8)° for the skew-boat isomer (Fig. 2*b*). N(1)–C(12) = 1·339 (9) Å and thus must be a partial double bond. This is confirmed by the planar geometry at N(1) [$\sum$ angles at N(1) = 358·5°]. The torsion angle C(12)–N(1)–C(11)–C(10), −113·5 (8)°, shows that the N(1)–C(12) vector lies between the axial and equatorial directions at N(1). All other bond lengths and angles have typical values. There is a hydrogen bond between N(15) and O(14) of the molecule related by (0,0,1).

References

IDDON, B., METH-COHN, O., SCRIVEN, E. F. V., SUSCHITZKY, H. & GALLACHER, P. T. (1979). *Angew. Chem. Int. Ed. Engl.* **18**, 900–915.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

MOTHERWELL, W. D. S. & CLEGG, W. (1978). *PLUTO*. Program for molecular drawings. Univ. of Cambridge, England.

ROBERTS, P. & SHELDRICK, G. M. (1975). *XANADU*. Program for crystallographic calculations. Univ. of Cambridge, England.

SHELDRICK, G. M. (1976). *SHELX*76. Program for crystal structure determination. Univ. of Cambridge, England.

SUSCHITZKY, H. (1980). *Heterocycl. Lect.* S-1–14.

Acta Cryst. (1983). C**39**, 1412–1414

Acétyl-1 Triméthyl-2,3,5 Dihydro-2,3 1*H*-Benzazépine-1-(2*R**, 3*R**), $C_{15}H_{19}NO$ (2*a*), et Acétyl-1 Triméthyl-2,3,5 Dihydro-2,3 1*H*-Benzazépine-1-(2*R**,3*S**), $C_{15}H_{19}NO$ (2*b*). Deux Benzazépines Diastéréoisomères

PAR LOÏC TOUPET

Groupe de Physique Cristalline, ERA au CNRS n° 07015, *Université de Rennes, Campus de Beaulieu,* 35042 *Rennes CEDEX, France*

ET PHILIPPE URIAC

Laboratoire de Chimie Pharmaceutique, UER Médico-Pharmaceutiques, avenue L. Bernard, 35043 *Rennes CEDEX, France*

(*Reçu le* 7 *février* 1983, *accepté le* 13 *juin* 1983)

Abstract. (2*a*): $M_r = 229{\cdot}3$, monoclinic, $P2_1/c$, $a = 7{\cdot}318$ (2), $b = 13{\cdot}664$ (3), $c = 14{\cdot}646$ (3) Å, $\beta = 119{\cdot}1$ (2)°, $V = 1279{\cdot}6$ Å^3, $Z = 4$, $D_x = 1{\cdot}189$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 0{\cdot}069$ mm^{-1}, $F(000) = 496$, $T = 298$ K, $R_w = 0{\cdot}068$ for 1271 observations. (2*b*): $M_r = 229{\cdot}3$, monoclinic, $P2_1/c$, $a = 9{\cdot}425$ (2), $b = 17{\cdot}341$ (3), $c = 9{\cdot}063$ (2) Å, $\beta = 114{\cdot}6$ (2)°, $V = 1346{\cdot}8$ Å^5, $Z = 4$, $D_x = 1{\cdot}131$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 0{\cdot}066$ mm^{-1}, $F(000) = 496$, $T = 298$ K, $R_w = 0{\cdot}051$ for 1025 observations. These two X-ray analyses allow the elucidation of the stereochemistry of these benzazepines and a comparison with biologically active benzodiazepines. The results of the NMR studies are also explained.

Introduction. Les deux benzazépines diastéréoisomères (2*a*) et (2*b*) sont obtenues à partir de la benzazépine (1) par transposition allylique puis *N*-acétylation (Bonnic, Huet, Lattes & Bouget, 1968; Uriac, 1982). L'étude cristallographique de ces deux isomères (2*R**, 3*R**) et (2*R**, 3*S**) a été nécessaire pour confirmer les attributions de configuration relative basées sur les constantes de couplage ^{1}H RMN J[H(2)H(3)] et les études

0108-2701/83/101412-03$01.50