Crystal and Molecular Structure of 1-Methyl-4-phenyl-1*H*-2,3-benzodiazepine

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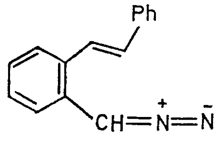
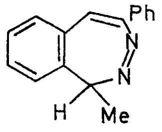
The title compound is the product of the cyclisation of an α-(*o*-alkenylaryl)diazoalkane, and the structure determination establishes the isomer formed in this reaction. All hydrogen atoms were located, and C(1) is shown to be tetrahedrally substituted. The seven-membered heterocyclic ring is biplanar, being bent about a line through C(1) with an interior interplanar angle of 110°. The N–N distance in the ring is 1·255 Å.

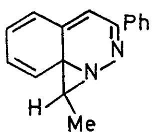
THE preparation of 1*H*-2,3-benzodiazepines by the cyclisation of α-(*o*-alkenylaryl)diazoalkanes has been reported by Reid *et al.*[1] who discuss various possible structures for the products. The present work was undertaken in particular to confirm that the product of the cyclisation of (I) was (II) rather than (III), which would have been expected by analogy with similar compounds lacking an annulated benzene ring.[2]



(I)



(II)



(III)

EXPERIMENTAL

Crystal Data.—$C_{16}H_{14}N_2$, $M = 234$. Monoclinic, $a = 7{\cdot}62$, $b = 14{\cdot}49$, $c = 11{\cdot}83$ Å, $\beta = 94{\cdot}1°$, $U = 1302$ Å^3, $Z = 4$, $D_c = 1{\cdot}19$ g cm^{-3}, $F(000) = 496$. Space group $P2_1/c$ from systematic absences, Cu-K_α radiation, $\lambda = 1{\cdot}5418$ Å, μ(Cu-K_α) = $5{\cdot}7$ cm^{-1}.

The crystals are yellow, and approximately equi-dimensional with many facets. The space group and cell dimensions were deduced from precession and Weissenberg photographs of a crystal mounted about [01$\bar{1}$]. Another crystal, with a mean diameter of 0·25 mm was mounted about the *a* axis, and used to collect multiple film packs of Weissenberg photographs for layers 0—5*kl*. Intensities were estimated from these films using a Saab film scanner, mark II.[3] Only a few intensities were observed for $\sin\theta/\lambda > 0{\cdot}5$, and of those observed, the 200 weakest were re-estimated visually, as the values determined by the scanner had large estimated errors. Lorentz and polarisation corrections, but no absorption or extinction corrections were applied. The final data set consisted of 794 reflections.

Approximate scale factors for the individual layers were obtained statistically, and normalised structure factors were estimated using the programs of the *X*-Ray system.[4]

The structure was solved by direct methods, applying the multi-solution method of Germain *et al.*,[5] to 257 reflections with $|E| \geqslant 1{\cdot}3$. Of eight sets of phases based on three origin-fixing reflections and three others, arbitrarily assigned phases of 0 or π, one set was easily selected as giving the best fit to the relationships. An *E* map based on this set gave the position of all carbon and nitrogen atoms, and a subsequent Fourier map phased by these atoms gave significant peaks near estimated positions for all hydrogen atoms. The structure was refined isotropically, allowing individual layer scale factors to vary, minimising the value of the function $\Sigma w(|F_o| - |F_c|)^2$. Initially, unit weights were used, but for the final cycles, a scheme of the form $w = (|F_o|/24)^2$ for $|F_o| \leqslant 24$, and $w = (24/|F_o|)^2$ for $|F_o| > 24$. Hydrogen positions were varied, but their temperature factors were kept fixed ($B = 6$ for methyl hydrogens and 4 for all others.) At convergence, R was 0·107. Two further cycles of refinement were carried out, allowing the non-hydrogen atoms to vary anisotropically but varying only a single scale factor. At this stage, no parameter shifts were $>0{\cdot}3$ times their errors, and refinement was terminated with R 0·093. For the scanner data alone, R was 0·076. Positional and thermal parameters for the atoms are given in Table 1.

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[1] A. A. Reid, J. T. Sharp, H. R. Sood, and P. B. Thorogood, *J.C.S. Perkin I*, 1973, 2543.

[2] M. Krieger and C. J. Fritchie, in G. Heinrichs, H. Krapf, B. Schroder, A. Steigel, T. Troll, and J. Sauer, *Tetrahedron Letters*, 1970, 1617.

[3] H. P. Drummond, R. O. Gould, and M. M. Harding, 'Programs for Evaluating Intensities Using the Saab Film Scanner, Mark II,' Edinburgh Regional Computing Centre, to be published.

[4] J. M. Stewart *et al.*, 'The *X*-Ray System,' Technical Report TR72-192, Computer Science Center, University of Maryland, 1972, implemented for the I.B.M. 370–155 at Edinburgh Regional Computing Centre.

[5] P. Main, M. M. Woolfson, and G. Germain, 'MULTAN, a Computer Programme for the Automatic Solution of Crystal Structures,' University of York, York, 1971.

TABLE 1

Positional parameters for carbon and nitrogen atoms with their substituent hydrogen atoms

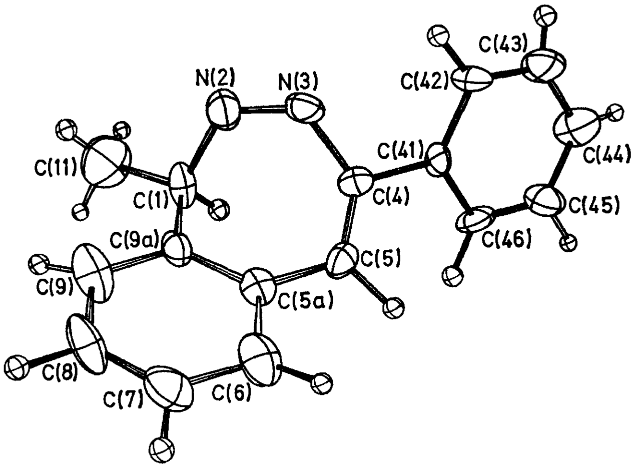
	10^4x	10^4y	10^4z		10^3x	10^3y	10^3z
C(1)	4879(15)	4506(5)	2447(8)	H(1)	472(15)	393(7)	292(8)
N(2)	6445(13)	4383(5)	1793(6)				
N(3)	7792(13)	3987(5)	2230(6)				
C(4)	7981(13)	3718(6)	3383(7)				
C(5)	7696(13)	4309(6)	4234(7)	H(5)	821(15)	412(7)	507(9)
C(5a)	6786(14)	5166(5)	4098(7)				
C(6)	7230(14)	5876(6)	4885(8)	H(6)	833(16)	584(7)	539(9)
C(7)	6364(16)	6728(7)	4727(9)	H(7)	665(15)	727(7)	527(8)
C(8)	5096(16)	6869(6)	3871(10)	H(8)	452(15)	753(7)	379(8)
C(9)	4594(14)	6173(6)	3090(9)	H(9)	335(15)	619(7)	268(8)
C(9a)	5399(15)	5299(6)	3220(7)				
C(11)	3233(17)	4585(8)	1653(9)	H(11)	342(17)	511(8)	110(10)
				H(12)	301(17)	339(9)	125(10)
				H(13)	226(18)	475(8)	213(10)
C(41)	8961(13)	2834(5)	3554(6)				
C(42)	10068(13)	2494(6)	2778(7)	H(42)	1023(14)	301(7)	209(8)
C(43)	10889(15)	1634(6)	2971(8)	H(43)	1166(15)	138(7)	235(8)
C(44)	10704(16)	1143(6)	3940(8)	H(44)	1112(15)	48(7)	398(8)
C(45)	9656(15)	1478(7)	4698(8)	H(45)	949(14)	110(7)	542(8)
C(46)	8753(14)	2306(6)	4533(6)	H(46)	798(16)	225(7)	574(8)

Thermal parameters ($\times 10^3$ Å^2) of the non-hydrogen atoms

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	26(8)	23(5)	51(6)	6(6)	−6(6)	3(5)
N(2)	32(8)	36(5)	42(5)	5(5)	6(5)	7(4)
N(3)	47(7)	29(4)	27(4)	11(5)	11(5)	−3(4)
C(4)	33(8)	30(6)	24(6)	−2(5)	1(5)	−3(5)
C(5)	27(8)	35(6)	27(5)	1(6)	−5(5)	2(5)
C(5a)	22(8)	20(5)	35(6)	−7(5)	8(6)	6(5)
C(6)	28(8)	41(6)	60(7)	−1(6)	11(6)	6(6)
C(7)	32(10)	53(7)	52(7)	3(6)	11(7)	−12(6)
C(8)	34(9)	18(5)	88(8)	5(6)	31(7)	−5(6)
C(9)	32(9)	33(6)	85(9)	−1(6)	5(6)	2(6)
C(9a)	37(8)	33(6)	34(6)	15(6)	13(6)	11(5)
C(11)	58(11)	81(8)	70(8)	−5(8)	−11(8)	−8(7)
C(41)	29(8)	13(4)	25(5)	7(5)	−0(5)	2(4)
C(42)	38(8)	41(6)	28(6)	0(6)	14(6)	−0(5)
C(43)	55(9)	38(6)	33(6)	13(7)	6(6)	−6(5)
C(44)	75(10)	25(5)	44(7)	13(6)	5(7)	−2(5)
C(45)	36(9)	47(7)	36(7)	0(7)	11(7)	−1(5)
C(46)	50(9)	32(6)	13(7)	7(7)	3(7)	3(5)

Temperature factors are in the form: $\exp(-2\pi^2\sum_i\sum_j a^*_i a^*_j h_i h_j U_{ij})$

The structure factor table is deposited as Supplementary Publication No. SUP 20997 (2 pp.).*



Perspective view of the structure, showing 50% probability thermal ellipsoids. Hydrogen atoms (unlabelled) are given arbitrary radii of 0·1 Å

DISCUSSION

Bond distances and angles are given in Table 2, and the Figure shows a thermal ellipsoid plot[6] of a molecule. The N–N bond length is comparable with the mean value for the N–N double bonds in *trans*-azobenzene and *trans*-azo-*p*-methylbenzene,[7] 1·245 Å. In those compounds, the adjacent C–N bond lengths are 1·433 Å, which is similar to C(4)–N(3) here, but not to C(1)–N(2), which has a normal value for a C–N single bond. All the other bond lengths in the ring systems, except those to C(1), are close to values found for aromatic systems, and all bond angles not involving C(1) or C(11) are *ca.* 120°. The saturated nature of C(1) is thus plain. The alternation of bond lengths in the seven-membered ring is consistent with structure (II).

The two carbocyclic rings are planar, no carbon atom deviating more than 0·026 for the fused or 0·019 Å for the phenyl ring from the best plane. The plane defined by C(5), C(5a), C(9a), and C(1) (maximum

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* For details of Supplementary Publications see Notice to Authors No. 7 in *J.C.S. Perkin II*, 1973, Index issue. Items less than 10 pp. are supplied as full-size copies.

[6] C. K. Johnson, 'ORTEP, A Fortran Thermal-ellipsoid Plot Program,' Oak Ridge National Laboratory, Tennessee, 1965, implemented at University of Newcastle Computing Service.

[7] C. J. Brown, *Acta Cryst.*, 1966, **21**, 146, 153.

deviation 0·006 Å) is not quite coplanar with the fused ring plane, the interior angle being 177°. The seven-membered ring is far from planar. In addition to the plane just described, a plane may be passed through C(1), N(2), N(3), and C(4) with a maximum deviation of 0·026 Å. The ring may thus be considered to be folded about a line between C(1) and a point beneath the C(4)–C(5) bond, the interior angle between the planes being 110°.

The pendant hydrogens of the phenyl and benzo-rings are within 0·2 Å of the best planes defined above. The methyl hydrogen atoms are also in plausible positions, all torsion angles about the C(1)–C(11) bond being between 50 and 70° or >170°. The methyl group is in the expected *exo*-position relative to the heterocyclic ring.

TABLE 2

Bond distances (Å) and bond angles (deg.) for 1-methyl-4-phenyl-1*H*-2,3-benzodiazepine

Bond distances

C(1)–N(2)	1·477(14)	C(1)–H(1)	1·01(10)
C(1)–C(11)	1·516(16)	C(5)–H(5)	1·07(11)
C(1)–C(9a)	1·505(12)	C(6)–H(6)	0·99(11)
N(2)–N(3)	1·255(13)	C(7)–H(7)	1·03(10)
N(3)–C(4)	1·415(11)	C(8)–H(8)	1·06(10)
C(4)–C(5)	1·351(12)	C(9)–H(9)	1·04(10)
C(5)–C(5a)	1·426(12)	C(11)–H(11)	1·02(13)
C(5a)–C(9a)	1·441(13)	C(11)–H(12)	1·00(12)
C(5a)–C(6)	1·411(13)	C(11)–H(13)	0·99(13)
C(6)–C(7)	1·407(14)	C(42)–H(42)	1·11(10)
C(7)–C(8)	1·364(16)	C(43)–H(43)	1·04(11)
C(8)–C(9)	1·402(14)	C(44)–H(44)	1·01(11)
C(9)–C(9a)	1·410(13)	C(45)–H(45)	1·03(10)
C(4)–C(41)	1·490(12)	C(46)–H(46)	1·02(12)
C(41)–C(42)	1·381(13)		
C(42)–C(43)	1·405(13)		
C(43)–C(44)	1·365(13)		
C(44)–C(45)	1·334(15)		
C(45)–C(46)	1·391(13)		
C(41)–C(46)	1·405(11)		

TABLE 2 (*Continued*)

Bond angles

N(2)–C(1)–C(11)	110·4(8)	N(2)–C(1)–H(1)	109(5)
N(2)–C(1)–C(9a)	102·9(8)	C(9a)–C(1)–H(1)	109(4)
C(11)–C(1)–C(9a)	119·2(8)	C(11)–C(1)–H(1)	106(5)
C(1)–N(3)–C(4)	123·2(9)	C(5a)–C(5)–H(5)	118(6)
N(3)–C(4)–C(5)	122·2(8)	C(7)–C(6)–H(6)	120(6)
N(3)–C(4)–C(41)	112·6(7)	C(5a)–C(6)–H(6)	121(6)
C(5)–C(4)–C(41)	123·3(8)	C(6)–C(7)–H(7)	121(6)
C(4)–C(5)–C(5a)	124·8(8)	C(8)–C(7)–H(7)	117(6)
C(5)–C(5a)–C(6)	117·9(8)	C(7)–C(8)–H(8)	118(6)
C(5)–C(5a)–C(9a)	121·6(8)	C(9)–C(8)–H(8)	120(6)
C(6)–C(5a)–C(9a)	120·5(8)	C(4)–C(5)–H(5)	117(6)
C(15)–C(6)–C(7)	117·6(9)	C(8)–C(9)–H(9)	120(5)
C(5a)–C(9a)–C(9)	119·3(8)	C(9a)–C(9)–H(9)	117(5)
C(6)–C(7)–C(8)	122·1(9)	C(1)–C(11)–H(11)	108·(6)
C(7)–C(8)–C(9)	121·8(9)	C(1)–C(11)–H(12)	109(7)
C(8)–C(9)–C(9a)	118·5(9)	C(1)–C(11)–H(13)	107(7)
C(1)–C(9a)–C(5a)	118·9(8)	H(11)–C(11)–H(12)	112(9)
C(1)–C(9a)–C(9)	121·7(9)	H(11)–C(11)–H(13)	110(9)
C(4)–C(41)–C(42)	112·7(7)	H(12)–C(11)–H(13)	111(10)
C(4)–C(41)–C(46)	119·7(8)	C(41)–C(42)–H(42)	110(6)
C(42)–C(41)–C(46)	117·6(8)	C(43)–C(42)–H(42)	130(6)
C(41)–C(42)–C(43)	119·6(8)	C(42)–C(43)–H(43)	118(6)
C(42)–C(43)–C(44)	121·9(9)	C(44)–C(43)–H(43)	120(6)
C(43)–C(44)–C(45)	118·5(9)	C(43)–C(44)–H(44)	119(5)
C(44)–C(45)–C(46)	122·2(8)	C(45)–C(44)–H(44)	121(5)
C(45)–C(46)–C(41)	120·1(8)	C(44)–C(45)–H(45)	119(5)
C(1)–N(2)–N(3)	120·4(8)	C(46)–C(45)–H(45)	119(5)
		C(45)–C(46)–H(46)	120(7)
		C(41)–C(46)–H(46)	120(7)

There are no intermolecular contacts, not involving hydrogen atoms, <3 Å, and there are only two involving a single hydrogen atom <2·7 Å. These are N(3) · · · H(45), at $x, \frac{1}{2} - y, z - \frac{1}{2}$ (2·58 Å) and N(2) · · · H(44), at $2 - x, \frac{1}{2} + y, \frac{1}{2} - z$ (2·65 Å). These together with the intramolecular non-bonded contacts N(3) · · · H(48) (2·35 Å) and H(5) · · · H(46) (2·29 Å) probably determine the tilt of the phenyl ring.

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