KÁLMÁN, A., ARGAY, GY. & VASSÁNYI, I. (1977). *Tetrahedron Lett.* pp. 4237–4240.
KÁLMÁN, A. & PÁRKÁNYI, L. (1980). *Acta Cryst.* To be published.
KAPECKI, J. A., BALDWIN, J. E. & PAUL, I. C. (1968). *J. Am. Chem. Soc.* **90**, 5800–5805.
LOZAC'H, N. (1971). *Adv. Heterocycl. Chem.* **13**, 161–234.
MELLOR, I. P. & NYBURG, S. C. (1971). *Acta Cryst.* B**27**, 1954–1958.
PINEL, R., MOLLIER, Y., LLAGUNO, E. C. & PAUL, I. C. (1971). *Chem. Commun.* pp. 1352–1353.
SHELDRICK, G. M. (1976). *SHELX*. Program for crystal structure determination. Univ. of Cambridge, England.
SÓLYOM, S., SOHÁR, P., TOLDY, L., KÁLMÁN, A. & PÁRKÁNYI, L. (1977). *Tetrahedron Lett.* pp. 4245–4248.
STANKOVIĆ, S., RIBÁR, B., KÁLMÁN, A., ARGAY, GY., TOLDY, L., TÓTH, I. & WHITE, D. N. J. (1980). *Acta Cryst.* In the press.

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Structure of 7-Chloro-2-methylamino-5-phenyl-3*H*-1,4-benzodiazepin-3-ol

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Abstract. $C_{16}H_{14}ClN_3O$, M_r = 299·76, monoclinic, $P2_1/c$, a = 14·29 (1), b = 20·72 (2), c = 10·27 (1) Å, β = 93·30 (5)°, U = 3034 Å^3, Z = 8, D_c = 1·312 Mg m^{-3}, $F(000)$ = 1248, Mo $K\alpha$ radiation, λ = 0·71069 Å, μ(Mo $K\alpha$) = 0·21 mm^{-1}. Final R = 6·1% for 2302 observed counter amplitudes. E.s.d.'s average 0·009 Å for bond lengths and 0·55° for bond angles not involving H atoms. The angles between the 5-phenyl ring and the C(6)–(11) phenyl moiety of the 1,4-benzodiazepine system are 60·8 (5) and 65·4 (5)° for the two independent molecules.

Introduction. The crystal structure of the title compound (Sternbach, Reeder, Stempel & Rachlin, 1964) has been determined as part of an investigation of structure–activity relationships for 1,4-benzodiazepine derivatives. Certain of these compounds exhibit marked anxiolytic and anti-convulsant activity in man (Randall, Schallek, Sternbach & Ning, 1974).

A crystal 0·4 × 0·3 × 0·2 mm was mounted along the direction of elongation which coincided with c. Cell dimensions and intensities were measured on a Stoe Stadi-2 diffractometer with graphite-monochromatized Mo $K\alpha$ radiation. For layers 0–2, 140 counts of 1 s at intervals of 0·01° in ω were taken, backgrounds being measured for 30 s at each end of the scan. For the higher layers (3–10), the scan range was calculated from $[A + (B\sin\mu/\tan\theta')]$ where μ is the equi-inclination angle, $2\theta'$ is the azimuth angle and A and B were assigned values of 1·0 and 0·6, respectively. 2302 independent reflexions in the range $0·10 < \sin\theta/\lambda < 0·59$ Å^{-1} were considered to be observed $[I > 2·5\sigma(I)]$. The intensities of four zero-layer reflexions were remeasured after each layer and showed no significant variation.

The structure was solved by direct methods with *SHELX* (Sheldrick, 1976) and refined by least squares until all calculated shifts were $<0·1\sigma$ and R = 6·1% for the 2302 observed reflexions. H atoms were included in the calculations but their coordinates were not refined. The H atoms bonded to N(12) and O(3) were located from a difference synthesis and the others were placed in theoretical positions. Anisotropic temperature factors were used for the heavier atoms and one overall isotropic temperature factor for H.

The weighting scheme was $w = 1/[\sigma^2(F)]$ where $\sigma(F)$ is the e.s.d. in the observed amplitudes derived from counting statistics. Final atomic coordinates are listed in Table 1.*

Computations were carried out on the CDC 7600 computer at the University of Manchester Regional Computer Centre and on the Birmingham University ICL 1906A.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35032 (15 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. *Fractional atomic coordinates* ($\times 10^4$) *with e.s.d.'s in parentheses*

	Molecule *A*			Molecule *B*		
	x	*y*	*z*	*x*	*y*	*z*
Cl(7)	−6847 (1)	1082 (1)	−2105 (2)	2295 (1)	−3710 (1)	−2216 (2)
C(2)	−2624 (4)	−369 (3)	−2294 (6)	−2017 (4)	−2329 (3)	−3147 (5)
C(3)	−2966 (4)	−292 (3)	−3710 (6)	−1492 (4)	−2070 (3)	−4268 (5)
C(5)	−4492 (4)	−682 (3)	−3444 (5)	−77 (4)	−1870 (3)	−3037 (5)
C(6)	−5580 (4)	174 (3)	−2710 (6)	979 (4)	−2801 (3)	−2657 (6)
C(7)	−5764 (4)	689 (3)	−1930 (6)	1141 (4)	−3439 (3)	−2357 (6)
C(8)	−5118 (4)	913 (3)	−976 (6)	410 (5)	−3857 (3)	−2162 (6)
C(9)	−4252 (4)	619 (3)	−850 (6)	−505 (4)	−3629 (3)	−2225 (6)
C(10)	−4011 (4)	102 (3)	−1639 (5)	−705 (4)	−2970 (3)	−2504 (5)
C(11)	−4688 (4)	−125 (3)	−2604 (5)	59 (4)	−2564 (3)	−2739 (5)
C(12)	−1402 (5)	−804 (4)	−752 (7)	−3414 (4)	−2200 (3)	−1866 (6)
C(1′)	−5222 (4)	−1181 (3)	−3730 (6)	646 (4)	−1400 (3)	−2515 (5)
C(2′)	−5907 (4)	−1329 (3)	−2876 (6)	1048 (4)	−1453 (3)	−1247 (6)
C(3′)	−6533 (5)	−1834 (4)	−3110 (8)	1688 (4)	−992 (3)	−766 (6)
C(4′)	−6481 (6)	−2192 (4)	−4231 (10)	1968 (4)	−503 (3)	−1558 (7)
C(5′)	−5813 (6)	−2046 (4)	−5102 (8)	1601 (5)	−457 (3)	−2838 (7)
C(6′)	−5175 (5)	−1547 (3)	−4870 (7)	923 (4)	−901 (3)	−3304 (6)
N(1)	−3124 (3)	−170 (2)	−1359 (5)	−1631 (3)	−2773 (2)	−2377 (4)
N(4)	−3697 (3)	−777 (2)	−3929 (4)	−787 (3)	−1622 (2)	−3694 (4)
N(12)	−1777 (3)	−642 (2)	−2069 (5)	−2867 (3)	−2091 (2)	−3007 (4)
O(3)	−2265 (3)	−400 (2)	−4592 (4)	−2097 (2)	−1722 (2)	−5138 (3)
H(3)	−3188	214	−3857	−1158	−2429	−4772
H(6)	−6101	10	−3381	1589	−2457	−2817
H(8)	−5271	1328	−339	581	−4330	−1933
H(9)	−3733	807	−86	−1044	−3927	−2027
H1(12)	−761	−1085	−772	−3960	−1876	−2203
H2(12)	−1218	−358	−182	−3634	−2651	−1628
H3(12)	−1923	−1057	−281	−3069	−1961	−954
H(2′)	−5943	−1021	−1996	879	−1818	−607
H(3′)	−7033	−1932	−2400	2002	−994	260
H(4′)	−6940	−2573	−4404	2509	−125	−1160
H(5′)	−5770	−2307	−5974	1864	−46	−3426
H(6′)	−4636	−1421	−5537	644	−825	−4253
H[N(12)]	−1382	−781	−2690	−3053	−1758	−3641
H[O(3)]	−1970	−903	−4569	−2008	−1794	−6067

Table 2. *Molecular dimensions*

	A	*B*		*A*	*B*		*A*	*B*
(*a*) Bond lengths (Å)								
N(1)–C(10)	1·402 (7)	1·399 (7)	C(5)–C(1′)	1·486 (8)	1·497 (7)	C(1′)–C(2′)	1·386 (9)	1·397 (8)
N(1)–C(2)	1·296 (8)	1·313 (7)	C(6)–C(11)	1·415 (8)	1·402 (8)	C(2′)–C(3′)	1·388 (10)	1·392 (9)
C(2)–N(12)	1·343 (7)	1·327 (7)	C(6)–C(7)	1·368 (8)	1·374 (9)	C(3′)–C(4′)	1·375 (13)	1·374 (9)
N(12)–C(12)	1·464 (8)	1·463 (8)	C(7)–Cl(7)	1·748 (6)	1·740 (6)	C(4′)–C(5′)	1·378 (13)	1·389 (10)
C(2)–C(3)	1·516 (8)	1·509 (8)	C(7)–C(8)	1·386 (8)	1·381 (9)	C(5′)–C(6′)	1·391 (11)	1·400 (9)
C(3)–O(3)	1·406 (7)	1·406 (6)	C(8)–C(9)	1·379 (9)	1·389 (9)	C(6′)–C(1′)	1·399 (9)	1·385 (8)
C(3)–N(4)	1·458 (7)	1·469 (7)	C(9)–C(10)	1·398 (9)	1·421 (8)	N(12)–H[N(12)]	0·92	0·98
N(4)–C(5)	1·283 (8)	1·293 (7)	C(10)–C(11)	1·424 (8)	1·408 (8)	O(3)–H[O(3)]	1·12	0·98
C(5)–C(11)	1·477 (8)	1·480 (8)						
(*b*) Bond angles (°) (e.s.d.'s are 0·4–0·7°)								
C(10)–N(1)–C(2)	120·5	121·0	C(11)–C(5)–C(1′)	120·3	118·6	C(5)–C(11)–C(6)	119·8	117·6
N(12)–C(2)–N(1)	122·4	123·4	C(11)–C(6)–C(7)	119·9	119·7	C(6)–C(11)–C(10)	118·8	120·9
N(1)–C(2)–C(3)	121·1	119·9	C(6)–C(7)–Cl(7)	120·1	118·4	C(6′)–C(1′)–C(2′)	118·7	119·1
N(12)–C(2)–C(3)	116·5	116·7	C(6)–C(7)–C(8)	122·2	121·2	C(6′)–C(1′)–C(5)	118·4	119·4
C(2)–N(12)–C(12)	122·3	124·3	C(8)–C(7)–Cl(7)	117·8	120·4	C(2′)–C(1′)–C(5)	122·8	121·4
C(2)–C(3)–N(4)	105·3	106·2	C(7)–C(8)–C(9)	118·4	119·8	C(1′)–C(2′)–C(3′)	121·9	120·3
C(2)–C(3)–O(3)	113·5	110·7	C(8)–C(9)–C(10)	122·2	120·9	C(2′)–C(3′)–C(4′)	119·1	120·2
O(3)–C(3)–N(4)	108·7	108·2	C(9)–C(10)–C(11)	118·4	117·4	C(3′)–C(4′)–C(5′)	119·9	120·2
C(3)–N(4)–C(5)	118·5	117·2	C(9)–C(10)–N(1)	116·0	116·2	C(4′)–C(5′)–C(6′)	121·5	119·7
N(4)–C(5)–C(11)	123·3	125·8	C(11)–C(10)–N(1)	125·5	126·1	C(5′)–C(6′)–C(1′)	118·9	120·4
N(4)–C(5)–C(1′)	116·3	115·6	C(5)–C(11)–C(10)	121·3	121·4			
(*c*) Selected torsion angles (°) (e.s.d.'s are 0·6–0·9°)								
C(10)–N(1)–C(2)–C(3)	2·2	5·9	C(11)–C(10)–N(1)–C(2)	40·7	41·2	C(12)–N(12)–C(2)–C(3)	−173·8	−169·3
N(1)–C(2)–C(3)–N(4)	−74·3	−76·7	N(4)–C(5)–C(1′)–C(2′)	149·0	136·7	N(4)–C(3)–C(2)–N(12)	106·8	104·0
C(2)–C(3)–N(4)–C(5)	73·7	72·5	C(11)–C(5)–C(1′)–C(2′)	−28·9	−41·6	N(1)–C(2)–C(3)–O(3)	166·9	166·1
C(3)–N(4)–C(5)–C(11)	−3·9	−4·3	C(9)–C(10)–N(1)–C(2)	−142·5	−146·2	N(12)–C(2)–C(3)–O(3)	−12·1	−13·2
N(4)–C(5)–C(11)–C(10)	−40·1	−34·6	C(6)–C(11)–C(5)–N(4)	143·0	147·4	C(5)–N(4)–C(3)–O(3)	−164·4	−168·7
C(5)–C(11)–C(10)–N(1)	−1·3	−7·5	C(12)–N(12)–C(2)–N(1)	7·3	11·4	C(10)–N(1)–C(2)–N(12)	−178·9	−174·8

Discussion. The two independent molecules in the unit cell are closely similar as regards bond lengths and angles (Table 2). The conformations of the 1,4-benzodiazepine rings are also broadly similar, as illustrated in Fig. 1; nevertheless, significant differences in torsion angles of 3–6° occur for the N(1)—C(2), N(1)—C(10), C(10)—C(11) and C(5)—C(11) bonds. Larger differences of 12–13° occur for C(5)—C(1′) which defines the orientation of the 5-phenyl ring with respect to the 1,4-benzodiazepine system [Table 2(*c*)]. The angles between the mean planes of phenyl rings C(6)–(11) and C(1′)–(6′) are 60·8 and 65·4° for molecules *A* and *B*, respectively (Table 3). Similar interplanar angles ranging from 54 to 67° occur in the related 5-phenyl-1,4-benzodiazepines: oxazepam (Gilli, Bertolasi, Sacerdoti & Borea, 1978), medazepam hydrochloride (Chananont, Hamor & Martin, 1980) and diazepam (Camerman & Camerman, 1972). In clonazepam, where the 5-phenyl ring carries a chloro substituent in the *ortho* position, the interplanar angle is larger, 83·7 and 77·8° for the two independent molecules (Chananont, Hamor & Martin, 1979). As expected, the seven-membered ring adopts a boat conformation with C(3) as the bow and C(10) and C(11) forming the stern (Table 3, planes III–V).

The formal double bond, N(1)—C(2), mean length 1·304$_5$ Å, is significantly longer than the expected value of 1·274 Å. The adjacent C(2)—N(12) formal single bond, mean length 1·335 Å, is significantly shorter than a C(sp^2)—N single bond and corresponds in length

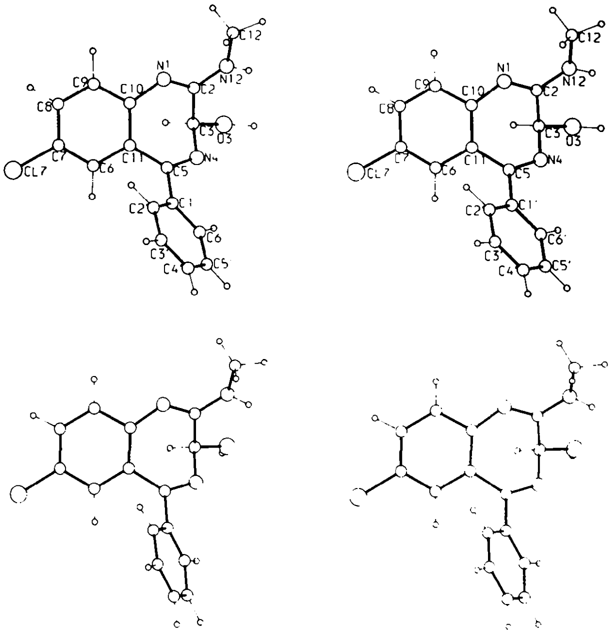

Fig. 1. The two independent molecules in the unit cell each viewed in a direction perpendicular to the mean plane through C(5)–(11), N(1). Upper diagram, molecule *A*, lower diagram, molecule *B*.

Table 3. *Mean-plane calculations*

(*a*) Deviations of atoms from planes (Å)

Distances marked with an asterisk refer to atoms defining the plane. E.s.d.'s are *ca* 0·006 Å.

Plane (I)	*A*	*B*
N(1)	0·064	0·195
C(2)	−0·608	−0·386
N(12)	−0·557	−0·169
C(3)	−1·519	−1·368
O(3)	−2·386	−2·100
N(4)	−0·627	−0·565
C(5)	0·029	0·003
C(6)	0·016*	−0·002*
C(7)	−0·014*	0·013*
C(8)	0·005*	−0·010*
C(9)	0·003*	−0·002*
C(10)	−0·001*	0·012*
C(11)	−0·008*	−0·010*
Cl(7)	−0·058	0·072
C(1′)	0·891	0·764
C(2′)	2·068	2·021
C(3′)	2·916	2·734
C(4′)	2·570	2·176
C(5′)	1·395	0·906
C(6′)	0·545	0·214

Plane (IV)	*A*	*B*
C(2)	0*	0*
C(3)	0*	0*
N(4)	0*	0*

Plane (II)	*A*	*B*
N(4)	0·710	0·855
C(5)	0·116	0·035
C(11)	−0·398	−0·828
C(1′)	0·004*	0·007*
C(2′)	−0·007*	−0·021*
C(3′)	0·003*	0·015*
C(4′)	0·003*	0·005*
C(5′)	−0·006*	−0·018*
C(6′)	0·002*	0·012*

Plane (III)	*A*	*B*
N(1)	0·003*	−0·007*
C(2)	−0·004*	0·009*
C(3)	−0·777	−0·780
N(4)	0·004*	−0·009*
C(5)	−0·003*	0·007*
C(10)	−0·670	−0·646
C(11)	−0·694	−0·610

Plane (V)	*A*	*B*
N(1)	0·003*	0·015*
C(5)	−0·002*	−0·013*
C(10)	−0·005*	−0·031*
C(11)	0·005*	0·029*

(*b*) Interplanar angles (°)

E.s.d.'s are *ca* 0·5°.

	A	*B*
Plane (I)–Plane (II)	60·8	65·4
Plane (III)–Plane (IV)	59·5	60·7
Plane (III)–Plane (V)	34·6	31·6

to C—N bonds in heteroaromatic systems. Appreciable electron delocalization therefore occurs here. The disposition of bonds from N(12) is near-planar, the sum of the bond angles at N(12) being 359·9° in *A* and 358·8° in *B*.

The N(4)—C(5) formal double bond, mean length 1·288 Å, and the C(sp^2)—C(sp^2) single bonds, C(11)—C(5) and C(1′)—C(5), mean lengths 1·478$_5$ and 1·491$_5$ Å, do not differ significantly from standard values. The C(3)—O(3) bond, 1·406 Å in both molecules, is, however, somewhat shorter than the value of 1·426 Å cited for a C—O single bond by Sutton (1965). This difference of 0·02 Å is probably significant.

A and *B* are linked by one O···O and two N···N hydrogen bonds (Table 4). *A*···*B* dimers related by the *c* glide plane are hydrogen bonded through N(1) of *B* acting as acceptor and O(3) of a symmetry-related *B* molecule acting as donor. All other intermolecular contacts correspond to normal van der Waals interactions.

Table 4. *Hydrogen-bond geometry*

Superscript (I) refers to equivalent position $x, -\frac{1}{2}-y, \frac{1}{2}+z$. E.s.d.'s for distances not involving hydrogen atoms are *ca* 0·01 Å.

	Molecule		Molecule	Distance (Å)	Angle (°)	
N(1)	*B*	···O(3)	*B*$^{\rm I}$	2·65	H[O(3)]*B*$^{\rm I}$–O(3)*B*$^{\rm I}$···N(1)*B*	17
		···H[O(3)]	*B*$^{\rm I}$	1·73		
O(3)	*B*	···O(3)	*A*	2·81	H[O(3)]*A*–O(3)*A*···O(3)*B*	21
		···H[O(3)]	*A*	1·80		
N(4)	*B*	···N(12)	*A*	3·03	H[N(12)]*A*–N(12)*A*···N(4)*B*	24
		···H[N(12)]	*A*	2·22		
N(4)	*A*	···N(12)	*B*	3·10	H[N(12)]*B*–N(12)*B*···N(4)*A*	24
		···H[N(12)]	*B*	2·24		

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References

Camerman, A. & Camerman, N. (1972). *J. Am. Chem. Soc.* **94**, 268–272.

Chananont, P., Hamor, T. A. & Martin, I. L. (1979). *Cryst. Struct. Commun.* **8**, 393–400.

Chananont, P., Hamor, T. A. & Martin, I. L. (1980). *Acta Cryst.* B**36**, 898–902.

Gilli, G., Bertolasi, V., Sacerdoti, M. & Borea, P. A. (1978). *Acta Cryst.* B**34**, 2826–2829.

Randall, L. O., Schallek, W., Sternbach, L. H. & Ning, R. Y. (1974). *Psychopharmacological Agents*, Vol. 3, edited by M. Gordon, pp. 175–281. New York: Academic Press.

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

Sternbach, L. H., Reeder, E., Stempel, A. & Rachlin, A. I. (1964). *J. Org. Chem.* **29**, 332–336.

Sutton, L. E. (1965). *Tables of Interatomic Distances and Configuration in Molecules and Ions*. Spec. Publ. No. 18. London: The Chemical Society.

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The Structure of (±)-Methyl 4,5-Dimethoxy-2-(2,6-dimethoxy-1-oxo-9-phenyl-5-phenalenyl)-1-oxo-8-phenyl-1,2-dihydro-2-acenaphthylenecarboxylate

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Abstract. $C_{43}H_{32}O_8$, $M_r = 676{\cdot}72$, m.p. 447–449 K, *Pbca*, $a = 19{\cdot}874$ (5), $b = 29{\cdot}835$ (8), $c = 11{\cdot}569$ (2) Å, $Z = 8$, $D_x = 1{\cdot}310$, D_m (flotation H_2O/KI) = 1·304 Mg m^{-3}; 4345 reflections, $2\theta < 110°$, $741 < 3\sigma(F_o)$. The structure was solved by direct methods. Full-matrix least-squares refinement converged at R = 0·045. The points of attachment of the two monomeric units were established.

Introduction. While the pigments of *Lachnanthes tinotoria* Ell. (Haemodoraceae) contain either an intact or a modified 9-phenylphenalenone ring system (Harmon, Edwards & Highet, 1977, and previous papers in this series) one pigment isolated from the seeds of the plant appeared to contain both. Although considerable chemical and physical data have been developed for this unique, amorphous, dimeric pigment and its derivatives, the nature of the modified segment and the points of attachment of the two monomeric units remained obscure. For this reason, a permethylated, crystalline derivative, (I), was subjected to X-ray analysis.

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