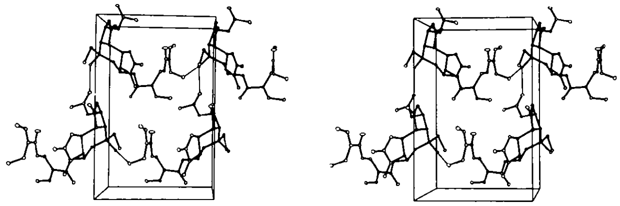

Fig. 4. Packing diagram for the hydrogen bromide adduct of spicatine with **a** horizontal, **b** vertical and **c** upwards, perpendicular to the plane of the paper.

O(19) and O(16)^{i}, and 2·82 Å between O(31) and O(19)^{ii} [(i) $2-x$, $y-\frac{1}{2}$, $1-z$; (ii) $x-1$, y, z]; H(O19)–O(16)^{i} = 1·91 Å, O(19)–H(O19)–O(16)^{i} = 150°, H(O31)–O(19)^{ii} = 1·76 Å and O(31)–H(O31)–O(19)^{ii} = 168°. All intermolecular C–O distances are longer than 3·25 Å; Br–O(31)^{iii} = 3·32 Å [(iii) $x+1$, y, $z-1$]. The intramolecular distance Br–O(19) is 3·22 Å.

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References

Asher, J. D. M. & Sim, G. A. (1965). *J. Chem. Soc.* pp. 1584–1594.

Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.

Germain, G., Main, P. & Woolfson, M. M. (1970). *Acta Cryst.* B**26**, 274–285.

Hanson, H. P., Herman, F., Lea, J. D. & Skillman, S. (1964). *Acta Cryst.* **17**, 1040–1044.

Hendrickson, J. B. (1961). *J. Am. Chem. Soc.* **83**, 4537–4547.

Herz, W., Poplawski, J. & Sharma, R. P. (1975). *J. Org. Chem.* **40**, 199–206.

Hewson, A. T., Pettersen, R. C. & Kennard, O. (1972). *Cryst. Struct. Commun.* **1**, 383–388.

Hughes, E. W. (1941). *J. Am. Chem. Soc.* **63**, 1737–1752.

International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.

Ito, T., Shimizu, T., Fujimoto, Y. & Tatsuno, T. (1978). *Acta Cryst.* B**34**, 1009–1011.

Karlsson, B., Pilotti, A.-M., Wiehager, A.-C., Wahlberg, I. & Herz, W. (1975). *Tetrahedron Lett.* pp. 2245–2248.

McPhail, A. T. & Sim, G. A. (1973). *Tetrahedron*, **29**, 1751–1758.

Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Thiessen, W. E. & Hope, H. (1970). *Acta Cryst.* B**26**, 554–562.

Acta Cryst. (1979). B**35**, 247–249

Structure of 1,2-Bis(1,3,7-trimethyl-6-lumazinyl)-*threo*-1,2-butanediol

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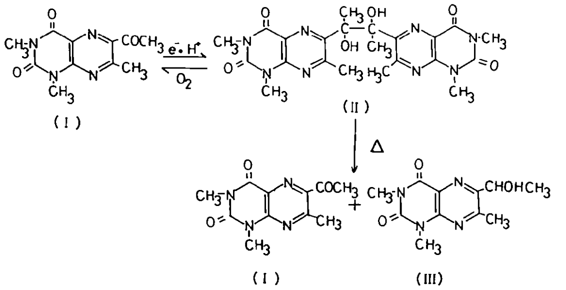
Abstract. $C_{22}H_{26}N_8O_6$, M_r = 498·56, monoclinic, $C2/c$, a = 17·840 (8), b = 14·860 (8), c = 18·121 (8) Å, β = 107·98 (1)°, V = 4569·3 Å^3, Z = 8, D_x = 1·45 Mg m^{-3}. The molecule consists of two lumazine derivatives linked together through a butanediol group. The central C–C bond of the butanediol group was found to be much longer than usual C–C bonds; this explains the unusual properties of this compound.

Introduction. During electrochemical studies with various 6- and 7-acyl-1,3-dimethyllumazines it was found that 6-acetyl-1,3,7-trimethyllumazine (I) dimerizes in slightly alkaline solution to the appropriate pinacol in a one-electron reduction process. This reaction resembles those in the literature known as electrohydrodimerizations of aromatic aldehydes and ketones (Fry, 1972) and led to only one stereochemical isomer which was believed, according to analogous findings (Fry, 1972), to be a *threo* form. Furthermore, this molecule, 1,2-bis(1,3,7-trimethyl-6-lumazinyl)-*threo*-1,2-butanediol (II), showed unusual properties due to some steric strain along the C–C glycol bond which is extremely sensitive to chemical modifications. Autoxidation takes place in alcoholic solution back to the starting material (I) and heating above the melting point results in a disproportionation reaction to (I) and 6-(1-hydroxyethyl)-1,3,7-trimethyllumazine (III).



In order to confirm the structure of (II) and to find a plausible explanation for the weak glycolic bond an X-ray analysis was undertaken.

The lattice parameters were determined from the setting angles of 19 reflections ranging from 36 to 79° in 2θ, measured on a Philips PW 1100 diffractometer. The reflection data were collected with Cu $K\alpha$ radiation monochromated by a graphite plate. The θ–2θ scanning technique was used with a scan speed of 6° min^{-1} in θ. The scans were repeated twice when the total counts during the first scan were less than 5000. The background was measured at each end of the scan for half the total scan time. 3889 independent reflections were measured within $\theta = 3 \sim 78°$. No absorption correction was applied. The crystal structure was solved by the multi-solution method with *MULTAN* (Germain, Main & Woolfson, 1971) based on 342 reflections with $E \geq 1{\cdot}7$. Difference Fourier and least-squares calculations gave all the atoms except for the methyl H atoms on the lumazine groups which had not been found in difference electron density maps. The refinement was carried out by the block-diagonal least-squares method with weights: $w^{1/2} = 0{\cdot}5$ when $F_o \leq 2$, $w^{1/2} = 1$ when $F_o \leq 20$ and $w^{1/2} = 20/F_o$ when $F_o > 20$. The R value reduced to 0·072. The final atomic coordinates are listed in Table 1.*

Discussion. A stereoscopic drawing of the molecule is given in Fig. 1. Bond lengths and angles in the two pteridine ring systems are similar (Figs. 2 and 3, and Table 2): the maximum and mean differences in the corresponding bond lengths are 0·016 and 0·007 Å and

Table 1. *Positional parameters* ($\times 10^4$ *for* C, N, O *and* $\times 10^3$ *for* H)

	x	*y*	*z*
N(1)	383 (2)	4477 (2)	1685 (2)
N(3)	−580 (2)	3792 (2)	644 (2)
N(5)	656 (1)	2057 (2)	1817 (1)
N(8)	1276 (2)	3591 (2)	2630 (2)
N(1′)	3095 (2)	1571 (2)	−41 (1)
N(3′)	3924 (2)	2425 (2)	989 (2)
N(5′)	2452 (1)	1282 (2)	1650 (1)
N(8′)	2092 (2)	682 (2)	143 (1)
C(2)	−236 (2)	4576 (2)	1023 (2)
C(4)	−345 (2)	2915 (2)	891 (2)
C(4a)	339 (2)	2866 (2)	1574 (2)
C(6)	1280 (2)	1996 (2)	2441 (2)
C(7)	1575 (2)	2785 (2)	2877 (2)
C(8a)	676 (2)	3634 (2)	1971 (2)
C(9)	782 (2)	5292 (2)	2087 (3)
C(10)	−1241 (3)	3903 (3)	−79 (3)
C(11)	2229 (2)	2795 (3)	3653 (2)
C(12)	1594 (2)	1039 (2)	2677 (2)
C(13)	1172 (2)	682 (2)	3238 (2)
C(2′)	3727 (2)	2140 (2)	218 (2)
C(4′)	3552 (2)	2147 (2)	1519 (2)
C(4a′)	2875 (2)	1558 (2)	1196 (2)
C(6′)	1860 (2)	721 (2)	1380 (2)
C(7′)	1680 (2)	391 (2)	604 (2)
C(8a′)	2677 (2)	1262 (2)	432 (2)
C(9′)	2921 (3)	1226 (3)	−844 (2)
C(10′)	4614 (3)	3044 (3)	1271 (3)
C(11′)	1065 (2)	−308 (3)	235 (2)
C(12′)	1435 (2)	388 (2)	1950 (2)
C(13′)	1746 (2)	−551 (2)	2215 (2)
O(1)	−484 (2)	5307 (2)	771 (2)
O(2)	−705 (1)	2267 (2)	539 (1)
O(3)	2411 (1)	1053 (2)	3098 (1)
O(1′)	4096 (2)	2396 (2)	−196 (2)
O(2′)	3774 (2)	2393 (2)	2196 (1)
O(3′)	615 (1)	289 (1)	1575 (1)
H(C13)	119 (3)	120 (4)	362 (3)
H′(C13)	58 (3)	53 (3)	291 (3)
H″(C13)	150 (3)	9 (4)	352 (3)
H(C13′)	161 (2)	−94 (3)	167 (2)
H′(C13′)	229 (3)	−56 (3)	250 (3)
H″(C13′)	146 (3)	−78 (4)	249 (3)
H(O3)	263 (3)	145 (4)	285 (3)
H(O3′)	35 (5)	81 (6)	118 (5)

Table 2. *Bond lengths* (Å) *and angles* (°) *involving* H *atoms*

C(13)–H(C13)	1·02 (6)	C(13′)–H′(C13′)	0·95 (4)	N(5)···H(O3′)	2·16 (9)
C(13)–H′(C13)	1·06 (4)	C(13′)–H″(C13′)	0·88 (6)	N(5′)···H(O3)	2·12 (5)
C(13)–H″(C13)	1·10 (5)	O(3)–H(O3)	0·89 (6)		
C(13′)–H(C13′)	1·11 (4)	O(3′)–H(O3′)	1·05 (8)		
H(C13)–C(13)–C(12)	105 (3)	H′(C13)–C(13)–H″(C13)	112 (4)	C(12′)–C(13′)–H″(C13′)	109 (4)
H(C13)–C(13)–H′(C13)	111 (4)	H(C13′)–C(13′)–C(12′)	104 (2)	H(C13′)–C(13′)–H″(C13′)	111 (5)
H(C13)–C(13)–H″(C13)	113 (4)	H(C13′)–C(13′)–H′(C13′)	112 (4)	H(O3)–O(3)–C(12)	106 (4)
C(12)–C(13)–H′(C13)	108 (3)	H(C13′)–C(13′)–H″(C13′)	107 (4)	H(O3′)–O(3′)–C(12′)	115 (5)
C(12)–C(13)–H″(C13)	107 (3)	C(12′)–C(13′)–H′(C13′)	114 (3)		

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* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33942 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Deviations* (Å) *of atoms from the least-squares planes through the pteridine ring systems*

$Z \parallel c$, $Y \parallel b$, $X \perp a^*$, and X, Y and Z are measured in Å.

Unprimed pteridine ring system				Primed pteridine ring system			
N(1)	0·030	C(7)	−0·030	N(1′)	0·030	C(7′)	−0·033
N(3)	0·004	C(8a)	−0·013	N(3′)	−0·020	C(8a′)	0·006
N(5)	0·032	C(9)*	0·131	N(5′)	0·030	C(9′)*	−0·045
N(8)	−0·053	C(10)*	0·051	N(8′)	−0·025	C(10′)*	−0·030
C(2)	0·053	C(11)*	−0·150	C(2′)	0·008	C(11′)*	−0·157
C(4)	−0·073	O(1)*	0·104	C(4′)	−0·049	O(1′)*	−0·011
C(4a)	−0·024	O(2)*	−0·172	C(4a′)	0·009	O(2′)*	0·110
C(6)	0·075			C(6′)	0·025		

$0{\cdot}6244X + 0{\cdot}0606Y - 0{\cdot}7787Z = -1{\cdot}4349$ $\qquad$ $-0{\cdot}6223X + 0{\cdot}7762Y - 0{\cdot}1014Z = -1{\cdot}3072$

* Omitted from the calculations of the least-squares planes.

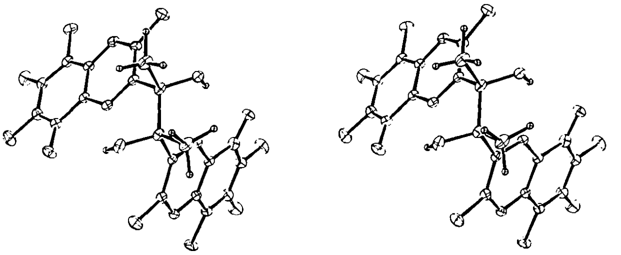

Fig. 1. Stereoscopic drawing of the molecule.

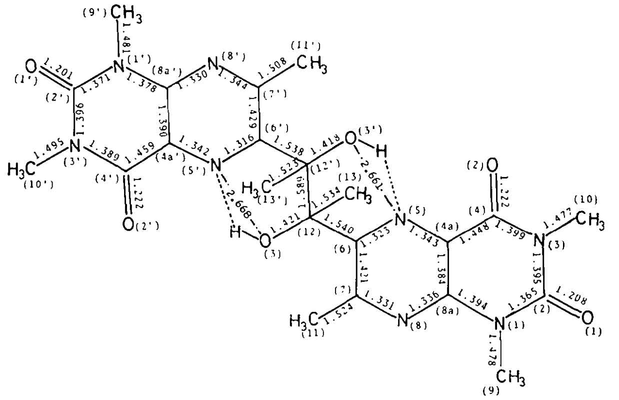

Fig. 2. Bond lengths (Å) of the molecule.

those of bond angles 0·8 and 0·3° respectively. The average standard deviations excluding H atoms are 0·004 Å and 0·3°. The deviations of the atoms from the least-squares planes are listed in Table 3. The two pteridine ring systems make an angle of 124·2° and the C chain connecting the two ring systems takes a *gauche* conformation with an internal rotation angle C(6)–C(12)–C(12′)–C(6′) of 61·9°. The bond lengths and angles in the pteridine ring systems are very similar to those found in lumazine (maximum differences: 0·037 Å, 3·9°; mean differences: 0·011 Å, 1·7°) (Norrestam, Stensland & Söderberg, 1972). The molecule has a *threo* configuration about C(12) and C(12′) and two intramolecular hydrogen bonds [N(5)···O(3′) 2·661 (3) and N(5′)···O(3) 2·668 (4) Å] are found. It is very interesting that the three C–C bonds connecting the two lumazine groups are not equal in length: the central C(12)–C(12′) bond is much longer (1·589 Å) than the others (1·540, 1·538 Å) which have the normal C–C single-bond length. It should also be noted that the conformation about the C(12)–C(12′) bond is such that the two hydroxyl groups, O(3)H and O(3′)H, are oriented *trans* to each other. It follows that the two methyl groups, C(13)H$_3$ and C(13′)H$_3$, as well as the two pteridine C(6) atoms are oriented *gauche* to each other. The torsion angles about the C(12)–C(12′) bond are: O(3)–C(12)–C(12′)–O(3′) = 173·5, C(6)–C(12)–C(12′)–C(6′) = 61·9, C(13)–C(12)–C(12′)–C(13′) = −60·4°. As a result of this *gauche* conformation, the interatomic distances C(6)···C(6′) and C(13)···C(13′) are very short [3·096 (5) and 3·003 (6) Å respectively], which may cause the strain at the C(12)–C(12′) bond, making it longer. As mentioned before, this molecule is chemically very labile and easily splits into two lumazine groups. Unstable properties of this compound must be explained by this long C–C bond. The orientation of the pteridine ring system with respect to the C(12)–C(12′) bond is a twist form. The torsion angles about the C(12)–C(6) and C(12′)–C(6′) bonds, N(5)–C(6)–C(12)–C(12′) and N(5′)–C(6′)–C(12′)–C(12), are 30·2 and 20·1° respectively. As is seen in Fig. 1, the six-membered rings formed by the two intramolecular hydrogen bonds [N(5), C(6), C(12), C(12′), O(3′), H(O3′) and N(5′), C(6′), C(12′), C(12), O(3), H(O3)] take a half-chair form and the conformation of the molecule is stabilized by these hydrogen bonds.

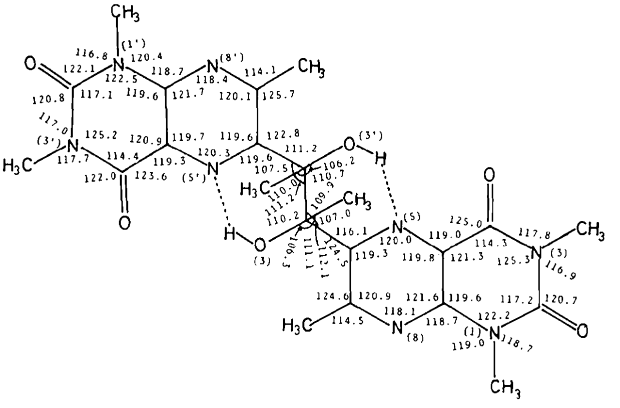

Fig. 3. Bond angles (°) of the molecule.

References

Fry, A. J. (1972). *Top. Curr. Chem.* **34**, 27.

Germain, G., Main, P. & Woolfson, M. M. (1971). *Acta Cryst.* A**27**, 368–376.

Norrestam, B., Stensland, B. & Söderberg, E. (1972). *Acta Cryst.* B**28**, 659–666.