Discussion. The chemical structures of the title compound and mitomycin A are shown in Fig. 1. Bond lengths, angles and selected torsion angles are shown in Table 2. An *ORTEP*II (Johnson, 1976) drawing of the molecule is shown in Fig. 2.

N(1) is bonded to C(4a) and an H atom is bonded to C(8a). Therefore the molecule curls up and takes a more compact shape than mitomycin A. The quinone ring in mitomycin A is not present in albomitomycin A and the dihydroquinone ring takes a half-chair conformation. C(8a) deviates by 0·421 (1) Å from the least-squares plane defined by C(4a), C(5), C(6), C(7) and C(8). O(5) and O(8) deviate by 0·148 (2) and 0·379 (2) Å, respectively, from the plane on the opposite side as in mitomycin A (Hirayama & Shirahata, 1989). The significant deviation of this six-membered ring from planarity is obviously the main reason for the achromaticity of albomitomycin A.

Mitomycin A can be transformed to albomitomycin A in a protic solvent (Kono, Saitoh, Shirahata, Arai & Ishii, 1987). The transformation may occur through an intramolecular Michael reaction. In the crystal structure of mitomycin A (Hirayama & Shirahata, 1989), the lone-pair electrons of the N atoms of azirizine rings in the two independent molecules point towards C(4a) atoms. The average

C(4a)···N(1)—C(1) angle and the average distance between C(4a) and N(1) in mitomycin A are 76·9° and 3·323 Å, respectively. In albomitomycin A they are 100·9° and 1·497 Å, respectively. These geometrical parameters suggest that the intramolecular reaction is not only governed by the geometrical prerequisite in the molecule but also by the electronic characteristics of the C(4a) atom.

There is an intermolecular hydrogen bond between the N(10a)(x, y, z) and O(10a)(−x, −1/2+y, 2−z) atoms [N(10a)···O(10a) = 2·948 (3) Å and N(10a)—H···O(10a) = 141 (3)°].

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Structure of the Biimidazole Dimer Obtained from a Bridged N,N'-Diimidazolyl Sulfone

BY J. PAUL STREET

*Department of Chemistry, University of Houston, Houston, Texas 77204-5641, USA*

Abstract. (±)-4,4'-Bi(2-thia-1,3,6,12-tetraazatricyclo[9.3.0.0^{3,7}]tetradeca-4,6,11,13-tetraene 2,2-dioxide) (1), $C_{18}H_{18}N_8O_4S_2$, M_r = 470·52, monoclinic, C2/c, a = 24·444 (9), b = 5·468 (2), c = 15·282 (7) Å, β = 98·82 (4)°, V = 2018 Å^3, Z = 4, D_x = 1·55 g cm^{-3}, λ(Mo Kα) = 0·71073 Å, μ = 2·96 cm^{-1}, F(000) = 968, T = 296 K, R = 0·043 for 1190 observed [I > 3σ(I)] data. The title compound (1) is obtained from a copper-mediated homo-coupling of two symmetrical 2,2'-trimethylene-1,1'-diimidazolyl sulfone units. Only one diastereomer is obtained from this reaction, which is the racemic form. Each half of the molecule, containing the diimidazolyl sulfone groups, comprises an eight-membered ring in a boat–chair conformation. The two N—S bonds of (1) are statistically different, 1·645 (3) *versus* 1·672 (3) Å, and shorter than analogous imidazole N—S bond lengths in related structures. The standard deviation from planarity of the imidazole ring atoms in the biimidazole moiety is 0·006 Å, with a 78·3° dihedral angle between the rings. The S-bonded N atoms in the biimidazole group are slightly pyramidal, with the sum of the internal angles 356·8°. The other imidazole rings in the structure have a standard deviation from planarity of 0·007 Å, and there is no N-pyramidalization.

Introduction. In connection with synthetic efforts towards the preparation of macrocyclic ligands that

contain imidazole donor groups, we have recently prepared the bridged diimidazolyl sulfone (3). This was the starting material for an attempted cyclization involving a copper-mediated imidazole–imidazole coupling reaction. The procedure gave a single product whose NMR spectrum was consistent with either of the two expected diastereomers (1) or (2) obtained from the successful coupling of only one side of compound (3). In reapplying the coupling reaction procedure to this product, we have not been able to complete the cyclization. In this regard, diastereomer (1) might be expected to cyclize; however, (2) cannot do so because this would require a superpositioning of two sulfonyl O atoms. At this point we decided to obtain the crystal structure of the initial product.

(1)   (2)

(3)
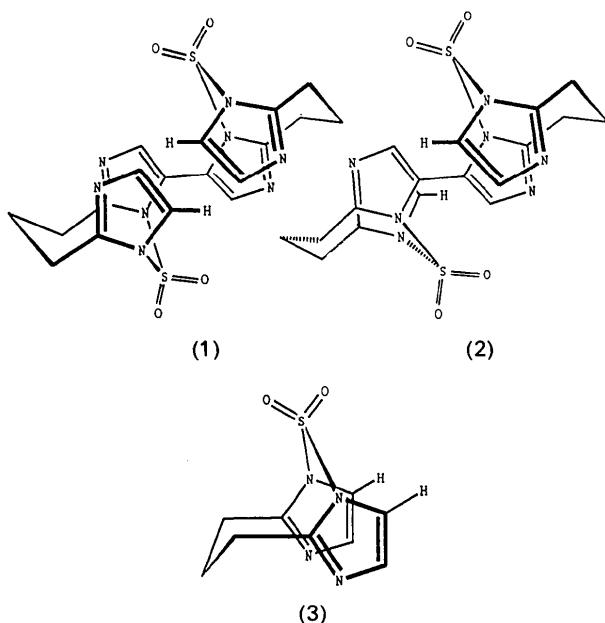
Experimental. A colorless columnar parallelepiped ($0.44 \times 0.18 \times 0.10$ mm) was selected from crystals obtained by slow evaporation of a $CDCl_3$ solution. Data collection was performed on a Nicolet $R3m/V$ diffractometer using graphite-monochromated Mo $K\alpha$ radiation. Intensities were measured using the ω-scan technique. The scan rate varied over the range $2.0–15.0°$ min^{-1}, depending on the count from rapid pre-scans of each reflection. Unit-cell parameters from setting angles of 25 reflections ($15 \le 2\theta \le 30°$). The collection range was $4 \le 2\theta \le 50°$. Two standard reflections, specifically $\overline{3}1\overline{5}$ and $\overline{8}22$, were monitored either every 2 h, or every 100 data collected, whichever occurred first throughout data collection. These showed no significant variation. $-28 \le h \le 28$, $0 \le k \le 6$, $0 \le l \le 18$. Lorentz and polarization corrections were applied to the data; however, no absorption correction was made because of the

small absorption coefficient ($\mu = 2.96$ cm^{-1}). Of 1785 independent data collected, 1190 had $I > 3\sigma(I)$. The Laue symmetry was determined to be $2/m$, and the space group was shown to be either Cc or $C2/c$ from systematic absences (hkl with $h + k$ odd, $h0l$ with l odd).

All calculations were made with the Nicolet *SHELXTL-Plus* (Sheldrick, 1987) series of crystallographic programs, on a MicroVAX II computer. Direct-methods structure solution revealed positions of all non-H atoms in the asymmetric unit, consisting of one half molecule situated about a twofold axis. After a normal sequence of isotropic and anisotropic refinement, all hydrogens were entered in calculated ideal positions and constrained to riding motion, with a single variable isotropic temperature factor. Full-matrix least-squares refinement of 146 parameters showed no unusually high correlations in the last cycle, and the final difference density map showed a maximum peak of ~ 0.2 e Å^{-3}. The function minimized was $\Sigma w \Delta F^2$, with individual weights $w = \sigma(F)^{-2}$. Final $R = 0.043$, $wR = 0.038$, $S = 1.99$. $(\Delta/\sigma)_{max} = 0.1$. The scattering factors used were those of *International Tables for X-ray Crystallography* (Cromer & Waber, 1974).

Discussion. The atomic parameters are given in Table 1* with the numbering scheme as shown in Fig. 1. Bond distances, angles and torsion angles are given in Table 2. The average S—O bond distance, 1.414 (3) Å, is essentially the same as the average [1.418 (3) Å] found in other *N*-arylsulfonylimidazole derivatives such as *N*-toluenesulfonylimidazole (Cesario & Guilhem, 1977) and 1-(4-imidazolylsulfonyl)-4-phenylimidazole (Guggenberger, 1975). The S—N(1) bond [1.645 (3) Å] is statistically shorter ($\ge 3\sigma_{diff}$, $\sigma_{diff} = 0.0042$ Å) than the S—N(4) bond [1.662 (3) Å]. Both S—N bond distances are shorter than the analogous bond in *N*-tosylimidazole [1.690 (4) Å]. Additionally, the S—N(1) bond is shorter than the 1.672 (4) Å S—N bond in 1-(4-imidazolylsulfonyl)-4-phenylimidazole. The bond angles around sulfur do not differ significantly from those in the related compounds.

The two distinguishable imidazole rings in the structure are essentially planar. The calculated least-squares-weighted plane comprising C(1), C(2), C(3), N(1), N(2) has a standard deviation from planarity of 0.006 Å, with a χ^2 value of 10, while the plane comprising C(7), C(8), C(9), N(3), N(4) has a standard deviation of 0.007 Å, with a χ^2 value of 13. The

Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic displacement parameters* ($\mathring{A}^2 \times 10^3$)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
S	5760 (1)	6832 (2)	3609 (1)	38 (1)
O(1)	5214 (1)	7186 (6)	3793 (2)	50 (1)
O(2)	6114 (1)	8806 (5)	3506 (2)	49 (1)
N(1)	5714 (1)	5141 (6)	2696 (2)	32 (1)
N(2)	6037 (1)	2609 (7)	1758 (2)	47 (1)
N(3)	6708 (2)	2620 (8)	5133 (2)	51 (2)
N(4)	6071 (1)	5011 (7)	4386 (2)	40 (1)
C(1)	5280 (2)	3499 (8)	2373 (3)	35 (1)
C(2)	5491 (2)	2030 (9)	1807 (3)	47 (2)
C(3)	6169 (2)	4440 (8)	2290 (3)	36 (1)
C(4)	6729 (2)	5599 (9)	2430 (3)	44 (2)
C(5)	7139 (2)	4629 (9)	3215 (3)	47 (2)
C(6)	7084 (2)	5550 (9)	4144 (3)	47 (2)
C(7)	6639 (2)	4393 (9)	4564 (3)	41 (2)
C(8)	6191 (2)	1978 (9)	5329 (3)	55 (2)
C(9)	5795 (2)	3397 (9)	4882 (3)	46 (2)

Table 2. *Bond lengths* ($\mathring{A}$), *angles* ($°$) *and torsion angles* ($°$)

S—O(1)	1·419 (3)	S—O(2)	1·408 (3)
S—N(1)	1·662 (3)	S—N(4)	1·645 (3)
N(1)—C(1)	1·421 (5)	N(1)—C(3)	1·406 (5)
N(2)—C(2)	1·384 (5)	N(2)—C(3)	1·299 (6)
N(3)—C(7)	1·296 (6)	N(3)—C(8)	1·388 (6)
N(4)—C(7)	1·413 (5)	N(4)—C(9)	1·401 (6)
C(1)—C(2)	1·340 (6)	C(1)—C(1')	1·477 (5)
C(3)—C(4)	1·495 (5)	C(4)—C(5)	1·535 (5)
C(5)—C(6)	1·532 (6)	C(6)—C(7)	1·487 (6)
C(8)—C(9)	1·343 (6)		

O(1)—S—O(2)	122·1 (2)	O(1)—S—N(1)	107·4 (2)
O(2)—S—N(1)	107·2 (2)	O(1)—S—N(4)	106·5 (2)
O(2)—S—N(4)	108·6 (2)	N(1)—S—N(4)	103·5 (2)
S—N(1)—C(1)	126·4 (3)	S—N(1)—C(3)	124·5 (2)
C(1)—N(1)—C(3)	105·9 (3)	C(2)—N(2)—C(3)	106·9 (4)
C(7)—N(3)—C(8)	107·7 (4)	S—N(4)—C(7)	128·0 (3)
S—N(4)—C(9)	124·3 (3)	C(7)—N(4)—C(9)	106·6 (3)
N(1)—C(1)—C(2)	105·2 (3)	N(1)—C(1)—C(1')	125·5 (3)
C(2)—C(1)—C(1')	129·3 (3)	N(2)—C(2)—C(1)	111·6 (4)
N(1)—C(3)—N(2)	110·5 (3)	N(1)—C(3)—C(4)	126·1 (4)
N(2)—C(3)—C(4)	123·4 (4)	C(3)—C(4)—C(5)	116·1 (4)
C(4)—C(5)—C(6)	118·0 (4)	C(5)—C(6)—C(7)	115·8 (4)
N(3)—C(7)—N(4)	109·4 (4)	N(3)—C(7)—C(6)	125·3 (4)
N(4)—C(7)—C(6)	125·2 (4)	N(3)—C(8)—C(9)	110·7 (4)
N(4)—C(9)—C(8)	105·6 (4)		

O1—S—N1—C1	−24·7 (2)	N1—C3—N2—C2	−0·8 (4)
O1—S—N1—C3	178·6 (2)	C4—C3—N2—C2	179·5 (4)
O2—S—N1—C1	−157·6 (2)	C5—C4—C3—N1	86·5 (4)
O2—S—N1—C3	45·8 (2)	C5—C4—C3—N2	−93·9 (4)
N4—S—N1—C1	87·72 (2)	C3—C4—C5—C6	−79·5 (4)
N4—S—N1—C3	−69·0 (2)	C7—C6—C5—C4	78·8 (4)
O1—S—N4—C7	−170·4 (2)	N4—C7—N3—C8	1·4 (4)
O1—S—N4—C9	23·3 (2)	C6—C7—N3—C8	−176·9 (4)
O2—S—N4—C7	−37·1 (2)	S—N4—C7—N3	−169·9 (4)
O2—S—N4—C9	156·6 (2)	S—N4—C7—C6	8·5 (4)
N1—S—N4—C7	76·6 (2)	C9—N4—C7—N3	−1·6 (4)
N1—S—N4—C9	−89·7 (2)	C9—N4—C7—C6	176·7 (4)
S—N1—C1—C2	−161·4 (4)	C5—C6—C7—N3	98·0 (4)
S—N1—C1—C1'	18·8 (4)	C5—C6—C7—N4	−80·0 (4)
C3—N1—C1—C2	−1·2 (4)	C7—N3—C8—C9	−0·7 (4)
C3—N1—C1—C1'	178·9 (4)	S—N4—C9—C8	169·9 (4)
C3—N2—C2—C1	0·0 (4)	C7—N4—C9—C8	1·1 (4)
N1—C1—C2—N2	0·8 (4)	N4—C9—C8—N3	−0·3 (4)
C1'—C1—C2—N2	−179·4 (4)	N1—C1—C1'—N1'	78·1 (4)
S—N1—C3—N2	161·9 (4)	N1—C1—C1'—C2'	−101·7 (4)
S—N1—C3—C4	−18·4 (4)	C2—C1—C1'—N1'	−101·7 (4)
C1—N1—C3—N2	1·3 (4)	C2—C1—C1'—C2'	78·5 (4)
C1—N1—C3—C4	−179·1 (4)		

Primed atoms represent those across the C_2 molecular axis.

sums of internal angles around N(1) and N(4) are 356·8 and 358·9°, respectively, indicating slight pyramidalization of N(1) (Beddoes, Dalton, Joule, Mills, Street & Watt, 1986).

The ring conformation of the eight-membered bridged diimidazolyl sulfone group, comprising each half of the molecule, is a boat–chair structure. This is in line with the most stable ring conformer determined by NMR and molecular-mechanics calculations for a closely related analogue of (1), 1,2-4,5-dibenzo-5,7-dithia-5,5-dioxo-1,4-cyclooctadiene (Cellatly, Ollis & Sutherland, 1976). Torsion angles within the trimethylene bridge are −79·5 (4) [C(3)C(4)C(5)C(6)], 78·8 (4) [C(7)C(6)C(5)C(4)], 86·5 (4) [C(5)C(4)C(3)N(1)] and −80.0 (4)° [C(5)C(6)C(7)N(4)], showing the near symmetry of this portion of the ring reflected across the local pseudomirror which passes through C(5) and S. The remaining portion of the ring is asymmetric with respect to this mirror due to the different S—N bond lengths, and to the greater pyramidalization of N(1) compared to N(4). This is seen in the greater absolute SN(1)C(3)C(4) torsion angle [−18·4 (4)°] *versus* the SN(4)C(7)C(6) angle [8·5 (4)°].

The molecule is in an extended conformation with a biimidazole dihedral angle of 78·3°, rather than being in the folded conformation as was drawn for structure (1). The folded form would be obtained by rotation about the biimidazole bond. Since product (1) is the ($\pm$) diastereomer, our inability to complete the cyclization suggests a large barrier for this rotation, which is borne out by molecular-mechanics calculations ($\sim$376 kJ mol^{-1}), and arises from severe non-bonded interaction of the two C(2) hydrogens with the two O(1) O atoms at the peak of the conformational barrier.
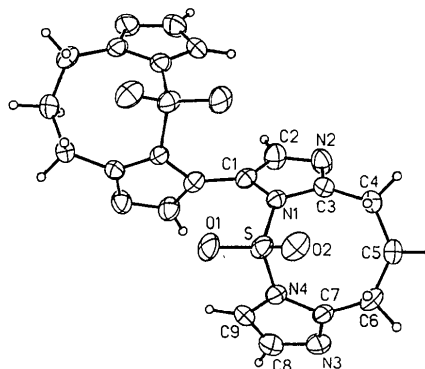
Fig. 1. View of the molecule showing the atom-numbering scheme. Thermal ellipsoids are 50% equiprobability envelopes, with hydrogens as spheres of arbitrary diameter.

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The Structure of 2-(3'-Hydroxy-2',3'-dimethylbutan-2'-yl)pyrazolo[3,4-d]pyrimidin-4(5H)-one Hydrate, a Photoadduct of Allopurinol with 2-Propanol

BY R. BRIAN LAMONT,* R. JEREMY H. DAVIES† AND JOHN F. MALONE*

Departments of Chemistry and Biochemistry, Queen's University, Belfast BT9 5AG, Northern Ireland

Abstract. $C_{11}H_{16}N_4O_2.H_2O$, $M_r = 254.3$, monoclinic, $P2_1/c$, $a = 13.343 (13)$, $b = 6.885 (7)$, $c = 13.334 (13)$ Å, $\beta = 91.76 (10)°$, $V = 1224.4$ Å^3, $Z = 4$, $D_x = 1.38$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 0.064$ mm^{-1}, $F(000) = 544$, $T = 293$ K, final $R = 0.038$ for 1191 unique reflections with $I > 3\sigma(I)$. The structure of the title compound, which is obtained by UV-irradiation of allopurinol in aqueous 2-propanol, is described. The crystals contain one molecule of water per asymmetric unit which is involved in a network of hydrogen bonding.

Introduction. Owing to its inhibition of the enzyme xanthine oxidase, the purine analogue allopurinol (1)

(1)
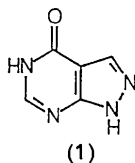
is an important therapeutic agent in the treatment of hyperuricaemic conditions, including gout. It also exhibits anti-trypanosomal activity (Marr, Berens & Nelson, 1978). When purines are irradiated with ultraviolet light in the presence of 2-propanol they undergo photoalkylation in which H atoms attached to ring C atoms are substituted by a 2-hydroxy-propyl group (Elad, 1976). However, similar irradia-

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* Department of Chemistry.
† Department of Biochemistry.

tion of allopurinol with 2-propanol (Bose & Davies, 1980) gave as the major photoproduct a compound identified, on the basis of spectroscopic inference, as 2-(3'-hydroxy-2',3'-dimethylbutan-2'-yl)pyrazolo[3,4-d]pyrimidin-4(5H)-one (2). This assignment is confirmed by the crystal structure analysis reported here. A feature of the molecule distinguishing it from allopurinol (Prusiner & Sundaralingam, 1972) and related pyrazolo[3,4-d]pyrimidine derivatives whose structures have been reported (Gadret, Goursolle & Leger, 1974; Sprang, Scheller, Rohrer & Sundaralingam, 1978; Srikrishnan, Parthasarathy, De & Chheda, 1983) is the requirement imposed by the substitution at N(2) for the distribution of π electrons in the allopurinol nucleus to reflect a 'quinonoid' arrangement of the conjugated double bonds.

(2)
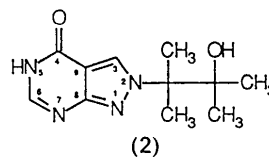
Experimental. Crystals were obtained from water. Colourless rectangular plates, crystal dimensions 1.0 × 0.25 × 0.10 mm, Stöe-Stadi-2 two-circle diffractometer, graphite-monochromated Mo $K\alpha$ radiation; unit-cell dimensions from 25 centred axial reflections in the range $3 < \theta < 20°$; the transformation (010/ −10−1/−101) gives a metrically orthorhombic A-centred cell but Weissenberg photographs taken