positional molecular parameters are lower when molecular flexibility is included, but a higher value of the overall molecular rotation is observed in this case. The torsional angles of selected molecular fragments show in some cases (the ethyl group and two of the acetyl chains) a larger deviation for the experimental values but inclusion of the Coulombic term does not appreciably improve the fit. These discrepancies between experimental and theoretical parameters of molecular subrotations and the above-cited cell expansion could be attributed to limitations of the force-field approach, in particular the assumed transferability of potential parameters.

The authors thank Professor J. A. Galbis-Pérez for supplying the crystals and for helpful discussion on chemical aspects and Professor A. López-Castro for collecting the diffractometer data. The present work is part of a research project supported by the CAICYT of the Spanish Government.

References

BURGOS, E. & BONADEO, H. (1977). *Chem. Phys. Lett.* **49**, 475–478.

CONDE, C. F., MILLÁN, M., CONDE, A. & MÁRQUEZ, R. (1985*a*). *Acta Cryst.* C**41**, 277–280.

CONDE, C. F., MILLÁN, M., CONDE, A. & MÁRQUEZ, R. (1985*b*). *Acta Cryst.* C**41**, 1658–1662.

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

ESTRADA, M. D., CONDE, A. & MÁRQUEZ, R. (1983). *Acta Cryst.* C**39**, 1418–1421.

ESTRADA, M. D., CONDE, A. & MÁRQUEZ, R. (1984). *Acta Cryst.* C**40**, 898–901.

ESTRADA, M. D., CONDE, A. & MÁRQUEZ, R. (1986). *Acta Cryst.* C**42**, 454–457.

GALBIS-PÉREZ, J. A., PALACIOS-ALBARRÁN, J. C., JIMÉNEZ-REQUEJO, J. L. & AVALOS-GONZÁLEZ, M. (1984). *Carbohydr. Res.* **129**, 131–142.

GOVERS, H. A. J. (1975). *Acta Cryst.* A**31**, 380–385.

HAMILTON, W. C. (1959). *Acta Cryst.* **12**, 609–601.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

MASON, A. & KREEVOY, M. M. (1955). *J. Am. Chem. Soc.* **77**, 5808–5814.

MIRSKAYA, K. V. (1973). *Tetrahedron*, **29**, 679–682.

MURRAY-RUST, P. & MOTHERWELL, S. (1978). *Acta Cryst.* B**34**, 2534–2546.

NARDELLI, M. (1983). *Acta Cryst.* C**39**, 1141–1142.

SKORCZYCK, R. (1976). *Acta Cryst.* A**32**, 447–452.

STEWART, J. M., MACHIN, P. A., DICKINSON, C. W., AMMON, H. L., HECK, H. & FLACK, H. (1976). The XRAY76 system. Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland.

TAYLOR, R. & KENNARD, O. (1982). *J. Am. Chem. Soc.* **104**, 5063–5070.

WILLIAMS, D. E. (1972*a*). *Acta Cryst.* A**28**, 84–88.

WILLIAMS, D. E. (1972*b*). *Acta Cryst.* A**28**, 629–635.

WILLIAMS, D. E. (1974). *Acta Cryst.* A**30**, 71–77.

Acta Cryst. (1987). C**43**, 1138–1142

Structure of 5-(β-D-Glucopyranosyl)barbituric Acid Trihydrate*

BY M. MILLAN, C. F. CONDE, A. CONDE AND R. MÁRQUEZ

Departamento de Optica y Sección de Física del Centro Coordinado del CSIC, Universidad de Sevilla, Spain

(*Received* 17 *September* 1985; *accepted* 6 *January* 1987)

Abstract. $C_{10}H_{15}N_3O_7.3H_2O$, $M_r = 343{\cdot}3$, monoclinic, $P2_1$, $a = 10{\cdot}883$ (3), $b = 12{\cdot}497$ (20), $c = 10{\cdot}553$ (4) Å, $\beta = 91{\cdot}05$ (3)°, $V = 1435$ (2) Å^3, $Z = 4$, $D_m = 1{\cdot}57$ (2), $D_x = 1{\cdot}589$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}7107$ Å, $\mu = 0{\cdot}13$ mm^{-1}, $F(000) = 728$, $T = 300$ K, $R = 0{\cdot}064$ for 2692 observed independent reflexions. The compound presents a zwitterionic structure in which the negative charge is delocalized in the system formed by the two carbonyl groups at C4 and C6 and the carbon atom C5 of the barbituric ring. In the two independent molecules in the asymmetric unit the pyranose ring adopts a $^4C_1$ conformation and the dihedral angles between the pyranose and barbituric rings for the two molecules are 80·9 (3) and 90·3 (3)°. The molecules are linked by an extensive three-dimensional hydrogen-bonding network, involving the water hydration molecules, which stabilize the crystal structure.

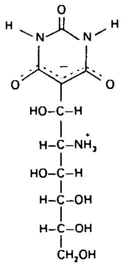
Introduction. The structure determination of the title compound (II) was undertaken as part of a continuing project on conformational details of *C*-nucleosides in the solid state. An easy synthesis of *C*-nucleoside derivatives of barbituric acids by reaction of aldoses with the barbituric acid has been reported (Avalos-González, 1981; Galbis-Pérez, Avalos-González, Jiménez-Requejo & Palacios-Albarrán, 1983). In this way, the reaction of barbituric acid with D-glucose

---

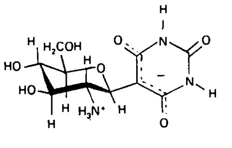
* Barbituric acid is 2,4,6(1*H*,3*H*,5*H*)-pyrimidinetrione.

0108-2701/87/061138-05$01.50

yields the acyclic *C*-glycoside (I) or its cyclic analogue (II) by dehydration of the sugar side chain. After acetylation, the cyclic form was established from spectral data (UV, IR and ^{1}H NMR). For the non-acetylated compound the acyclic form was initially supposed and an X-ray analysis was suggested to elucidate the molecular form; finally, the cyclic *C*-nucleoside structure was established. The X-ray structure of the analogous 5-β-D-galactopyranosyl-1,3-dimethylbarbituric acid monohydrate has been reported (Millán, Conde, Conde & Márquez, 1985) and the cyclic form was also established in that X-ray analysis.



(I)



(II)

Experimental. Crystals of the title compound, prepared as previously described in the Organic Chemistry Department of the University of Extremadura, were kindly supplied by Professor J. Galbis. Colourless crystals in the form of prisms elongated along [001]. D_m by flotation method. Crystal 0·04 × 0·14 × 0·17 mm. Enraf–Nonius CAD-4 diffractometer equipped with graphite monochromator; cell dimensions obtained from 25 reflexions in the range $2 < \theta < 20°$. Total of 3768 independent reflexions ($-14 \leq h \leq 14$, $0 < k \leq 15$, $0 \leq l \leq 16$) measured in the $2 \leq \theta \leq 30°$ range using ω–2θ scan technique. Three standard reflexions (600, 060, 006) monitored; variation in intensity less than 4% of mean values. 1076 reflexions considered as unobserved [$I < 2\sigma(I)$]. No correction for absorption or extinction. Structure solved by direct methods using *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). The absolute configuration was assumed on the basis of the configurations of the compounds used in the synthesis. Full-matrix least-squares refinement; function minimized $\sum w(|F_o| - |F_c|)^2$ with weighting scheme based on the statistical count criterion ($w = 1/\sigma^2$). Difference Fourier synthesis revealed the H-atom positions; isotropic temperature factor for each equal to that of the atom bonded to it. Further least squares including positional parameters of the H atoms. At final convergence $\Delta/\sigma < 0{\cdot}03$ (for non-hydrogen atoms) with $R = 0{\cdot}064$, $wR = 0{\cdot}073$, $S = 2{\cdot}2$ for 541 variables refined. Max. and min. values in final difference density map 0·35 and $-0{\cdot}30$ e Å^{-3}. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). Calculations carried out on a Univac 1100; crystallographic programs of the *XRAY*70 system (Stewart, Kundell & Baldwin, 1970) used throughout.*

Discussion. Fractional atomic coordinates and equivalent isotropic temperature factors (Hamilton, 1959) for non-hydrogen atoms are given in Table 1. A projection of the molecule *A* with lettering is shown in Fig. 1. Bond lengths and angles involving non-hydrogen atoms are shown in Table 2. For bonds involving H atoms, the mean values found are 1·07 (4) Å for C—H distances, 0·93 (5) Å for O—H bond lengths and 1·08 (3) Å for N—H distances.

Table 1. *Atomic coordinates and equivalent isotropic thermal parameters*

$$U_{\text{eq}} = \tfrac{1}{3}\sum_i \sum_j a_i^* a_j^* a_i a_j \cos(\mathbf{a}_i . \mathbf{a}_j).$$

	x	*y*	*z*	U_{eq}(Å^2 × 10^3)
Molecule *A*				
C1	0·5868 (10)	0·8315 (11)	0·8174 (10)	30 (3)
C2	0·7982 (9)	0·8652 (11)	0·8946 (9)	26 (3)
C3	0·8420 (8)	0·7926 (11)	0·8078 (9)	21 (2)
C4	0·7631 (8)	0·7475 (11)	0·7180 (9)	23 (3)
C5	0·9755 (7)	0·7626 (11)	0·8158 (8)	20 (2)
C6	0·9954 (9)	0·6415 (11)	0·8233 (8)	23 (3)
C7	1·1304 (8)	0·6123 (10)	0·8237 (8)	21 (2)
C8	1·1945 (8)	0·6681 (11)	0·7143 (9)	23 (3)
C9	1·1657 (8)	0·7884 (11)	0·7212 (10)	26 (3)
C10	1·2277 (10)	0·8532 (11)	0·6178 (10)	31 (3)
N1	0·6388 (7)	0·7683 (11)	0·7271 (8)	29 (3)
N2	0·6702 (8)	0·8813 (10)	0·8966 (8)	29 (3)
N3	0·9366 (7)	0·6021 (10)	0·9420 (8)	27 (2)
O1	0·4793 (7)	0·8423 (11)	0·8249 (9)	43 (3)
O2	0·8615 (7)	0·9174 (10)	0·9727 (8)	40 (3)
O3	0·7956 (6)	0·6859 (9)	0·6291 (6)	28 (2)
O4	1·0365 (6)	0·8038 (9)	0·7081 (6)	26 (2)
O5	1·2012 (7)	0·8038 (9)	0·4954 (7)	34 (2)
O6	1·3186 (7)	0·6430 (10)	0·7250 (8)	39 (3)
O7	1·1430 (7)	0·5000	0·8102 (7)	30 (2)
Molecule *B*				
C11	0·7144 (9)	0·0615 (11)	0·6741 (9)	25 (3)
C21	0·9205 (9)	0·0410 (11)	0·5907 (9)	23 (3)
C31	0·9692 (8)	0·1062 (10)	0·6887 (8)	21 (2)
C41	0·8881 (8)	0·1454 (11)	0·7821 (9)	22 (3)
C51	1·0994 (8)	0·1394 (10)	0·6854 (8)	21 (2)
C61	1·1172 (7)	0·2588 (10)	0·6657 (8)	20 (2)
C71	1·2526 (8)	0·2874 (10)	0·6595 (9)	22 (3)
C81	1·3198 (8)	0·2456 (11)	0·7771 (9)	21 (2)
C91	1·2961 (7)	0·1254 (10)	0·7887 (8)	21 (3)
C101	1·3589 (10)	0·0717 (11)	0·8981 (10)	30 (3)
N11	0·7654 (7)	0·1196 (10)	0·7688 (8)	26 (2)
N21	0·7947 (8)	0·0200 (10)	0·5892 (8)	28 (3)
N31	1·0560 (7)	0·2926 (10)	0·5456 (8)	26 (2)
O11	0·6043 (6)	0·0463 (10)	0·6637 (7)	34 (2)
O21	0·9830 (7)	0·0045 (9)	0·5014 (7)	30 (2)
O31	0·9202 (6)	0·2028 (9)	0·8741 (7)	28 (2)
O41	1·1665 (6)	0·1078 (9)	0·7974 (6)	23 (2)
O51	1·3303 (6)	0·1223 (10)	1·0144 (7)	32 (2)
O61	1·4439 (6)	0·2730 (10)	0·7647 (8)	38 (3)
O71	1·2718 (6)	0·3982 (8)	0·6379 (7)	24 (2)
Water molecules				
O8	0·4718 (7)	0·7032 (10)	0·5264 (8)	40 (3)
O9	0·3793 (8)	0·7517 (12)	1·0469 (9)	51 (3)
O10	0·4551 (8)	0·5010 (11)	0·8810 (9)	50 (3)
O12	0·5055 (7)	0·4240 (11)	0·5360 (8)	41 (3)
O13	0·8091 (9)	0·3979 (10)	0·8952 (10)	48 (3)
O14	0·7237 (9)	0·4726 (10)	0·6584 (9)	48 (3)

---

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43704 (29 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

In the glucopyranose ring the mean values for the C—C and C—O bond lengths are 1·527 (10) and 1·423 (11) Å, respectively, for molecule *A*, and 1·522 (5) and 1·433 (10) Å, respectively, for molecule *B*, in agreement with the mean values 1·522 (2) and 1·426 (2) Å obtained from 57 pyranose compounds (Ohanessian, Longchambon & Arene, 1978). The mean value of the endocyclic C—C—C angles is 110·1 (9)° for molecule *A* and 110·0 (9)° for molecule *B*, in agreement with an sp^3 hybridization of the C atoms. The angles O4—C9—C10 and C8—C9—C10 show a difference of 5·2 (13)° and the analogous difference for molecule *B* is 6·8 (12)°, both values in the range 5–9° reported for oligosaccharides. This angular distortion is due to interactions between the substituents at C8 and C9.

The glucopyranose ring adopts a ${}^4C_1$ conformation as in most D-pyranoses. In terms of ring-puckering coordinates (Cremer & Pople, 1975) the values of the amplitude–phase pair (q_2,φ_2) and puckering coordinate q_3 for molecule *A* are 0·078 (9) Å, −34 (8)° and 0·588 (9) Å [$Q = 0\cdot593$ (9) Å and $\theta = 7\cdot6$ (9)°] for the sequence O4—C5—C6—C7—C8—C9. The corresponding values for molecule *B* are $q_2 = 0\cdot032$ (10) Å, $\varphi_2 = -49$ (18)° and $q_3 = 0\cdot588$ (9) Å [$Q = 0\cdot589$ (9) Å and $\theta = 3\cdot1$ (10)°] for the analogous sequence. The asymmetry parameters of Nardelli (1983) are $\Delta C_s(\mathrm{O4}) = 0\cdot031$ (5), $\Delta C_s(\mathrm{C5}) = 0\cdot062$ (5), $\Delta C_s(\mathrm{C6}) = 0\cdot031$ (5), $\Delta C_2(\mathrm{O4{-}C9}) = 0\cdot001$ (4), $\Delta C_2(\mathrm{C5{-}O4}) = 0\cdot004$ (4), $\Delta C_2(\mathrm{C6{-}C5}) = 0\cdot004$ (4) for molecule *A* and $\Delta C_s(\mathrm{O41}) = 0\cdot017$ (5), $\Delta C_s(\mathrm{C51}) = 0\cdot027$ (5), $\Delta C_s(\mathrm{C61}) = 0\cdot011$ (5), $\Delta C_s(\mathrm{O41{-}C91}) = 0\cdot004$ (4), $\Delta C_2(\mathrm{C51{-}O41}) = 0\cdot021$ (4), $\Delta C_2(\mathrm{C61{-}C51}) = 0\cdot018$ (4) for molecule *B*.

The mean values of the intracyclic torsion angles are 58·5 (8)° for molecule *A* and 58·4 (8)° for molecule *B* [values range from 50·5 (12) to 67·9 (11)° and from 54·4 (11) to 64·1 (11)°, respectively; the smallest value being about C6—C7 and the largest value about C9—O4 for molecule *A* and similarly for molecule *B*]. As observed generally in pyranose rings, a greater puckering occurs about the C5—O4, O4—C9 and C8—C9 bonds and a smaller puckering about C5—C6, C6—C7 and C7—C8 bonds in comparison with the torsional angle of 55° in cyclohexane. However, for molecule *B*, the torsion angle about C51—C61 is slightly greater than 55°.

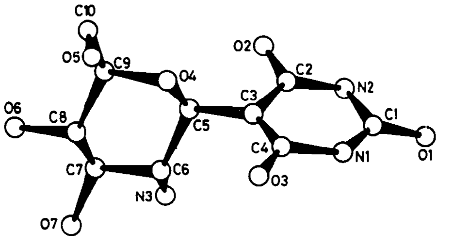


Fig. 1. A projection of molecule *A* with lettering.

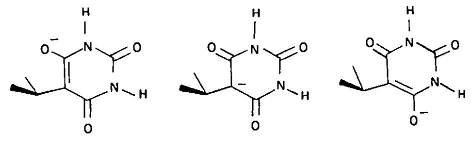
The torsion angles C8—C9—C10—O5 = 51·0 (13) and O4—C9—C10—O5 = −69·9 (12)° for molecule *A*, and the corresponding values of 54·8 (13) and −67·7 (12)° for molecule *B*, indicate a *gauche–gauche* conformation for the exocyclic bond in both molecules. This *gg* conformation is not the most frequent adopted for pyranoses (*gg*: 37·6%; *tg*: 2·7%; *gt*: 59·5%) (Longchambon, Ohanessian, Avenel & Newman, 1975); the *gauche* angles differ from the ideal value of 60° by less than 10°.

In the barbituric moiety the mean values for the endocyclic N—C bond lengths are 1·383 (12) Å for molecule *A* and 1·371 (12) Å for molecule *B* in agreement with those reported for barbituric acid derivatives (Craven, Vizzini & Rodrigues, 1969; Shimizu, Nishigaki, Nakai & Osaki, 1982).

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

Molecule *A*		Molecule *B*	
C1—N1	1·368 (16)	C11—N11	1·346 (15)
C1—N2	1·371 (15)	C11—N21	1·365 (14)
C1—O1	1·182 (13)	C11—O11	1·216 (12)
C2—C3	1·380 (16)	C21—C31	1·412 (15)
C2—N2	1·409 (13)	C21—N21	1·393 (13)
C2—O2	1·248 (14)	C21—O21	1·258 (13)
C3—C4	1·386 (14)	C31—C41	1·422 (14)
C3—C5	1·502 (12)	C31—C51	1·478 (13)
C4—N1	1·383 (12)	C41—N11	1·378 (12)
C4—O3	1·268 (14)	C41—O31	1·252 (14)
C5—C6	1·530 (19)	C51—C61	1·520 (18)
C5—O4	1·423 (12)	C51—O41	1·433 (11)
C6—C7	1·514 (13)	C61—C71	1·519 (12)
C6—N3	1·500 (13)	C61—N31	1·482 (12)
C7—C8	1·528 (14)	C71—C81	1·521 (13)
C7—O7	1·417 (13)	C71—O71	1·420 (17)
C8—C9	1·538 (19)	C81—C91	1·530 (18)
C8—O6	1·389 (12)	C81—O61	1·402 (11)
C9—C10	1·526 (16)	C91—C101	1·490 (15)
C9—O4	1·423 (11)	C91—O41	1·432 (10)
C10—O5	1·455 (14)	C101—O51	1·419 (14)
N2—C1—O1	123·6 (11)	N21—C11—O11	121·5 (10)
N1—C1—O1	122·3 (11)	N11—C11—O11	122·9 (10)
N1—C1—N2	114·1 (9)	N11—C11—N21	115·6 (9)
N2—C2—O2	116·7 (10)	N21—C21—O21	117·9 (9)
C3—C2—O2	126·1 (9)	C31—C21—O21	123·8 (9)
C3—C2—N2	117·2 (9)	C31—C21—N21	118·2 (9)
C2—C3—C5	118·2 (9)	C21—C31—C51	119·5 (8)
C2—C3—C4	120·3 (9)	C21—C31—C41	118·5 (8)
C4—C3—C5	121·5 (9)	C41—C31—C51	121·8 (9)
C3—C4—O3	125·1 (9)	C31—C41—O31	124·5 (8)
C3—C4—N1	118·0 (9)	C31—C41—N11	117·5 (9)
N1—C4—O3	116·8 (8)	N11—C41—O31	118·0 (8)
C3—C5—O4	109·2 (7)	C31—C51—O41	112·2 (8)
C3—C5—C6	112·6 (8)	C31—C51—C61	113·8 (8)
C6—C5—O4	109·4 (9)	C61—C51—O41	108·6 (9)
C5—C6—N3	107·8 (9)	C51—C61—N31	109·9 (9)
C5—C6—C7	112·0 (10)	C51—C61—C71	111·3 (10)
C7—C6—N3	110·3 (8)	C71—C61—N31	108·5 (7)
C6—C7—O7	109·5 (8)	C61—C71—O71	112·5 (8)
C6—C7—C8	110·1 (8)	C61—C71—C81	109·7 (8)
C8—C7—O7	109·2 (8)	C81—C71—O71	113·3 (8)
C7—C8—O6	107·0 (8)	C71—C81—O61	106·8 (8)
C7—C8—C9	108·3 (8)	C71—C81—C91	108·9 (8)
C9—C8—O6	114·5 (10)	C91—C81—O61	114·3 (10)
C8—C9—O4	109·2 (10)	C81—C91—O41	108·9 (10)
C8—C9—C10	113·1 (9)	C81—C91—C101	115·4 (9)
C10—C9—O4	107·9 (9)	C101—C91—O41	108·6 (8)
C9—C10—O5	109·1 (10)	C91—C101—O51	111·4 (10)
C1—N1—C4	125·0 (9)	C11—N11—C41	125·9 (9)
C1—N2—C2	124·8 (10)	C11—N21—C21	124·2 (9)
C5—O4—C9	110·3 (7)	C51—O41—C91	113·1 (7)

However, the values of the intracyclic C—C distances [mean values of 1·383 (13) and 1·417 (14) Å, respectively, for molecules *A* and *B*] are significantly shorter than those reported for barbituric acid derivatives, revealing an appreciable double-bond character. In a valence-bond description, based on the use of Pauling's formula (Pauling, 1960), the percentage of double-bond character comes to 57% and 36% respectively (C—C: 1·504, C=C: 1·334 Å). On the other hand, the mean values of the bond distances O2—C2 and O3—C4 are 1·258 (14) and 1·255 (13) Å, respectively, for molecules *A* and *B*, both higher than the adopted value for C=O. The resulting percentage of double-bond character is 65% and 67%, respectively (C—O: 1·43, C=O: 1·21 Å). These features are consistent with the resonance forms:



(*a*) (*b*) (*c*)

and confirm a zwitterionic structure for the compound in which the negative charge is delocalized in the system formed by the two carbonyls at C2 and C4 and the carbon atom C3 of the barbituric ring of molecule *A*, and the corresponding atoms of molecule *B*. This structure had been proposed on the basis of IR spectra showing bands associated with the $^{+}NH_3$ group (~3000 and ~1600 cm^{-1}) (Galbis-Pérez, Avalos-González, Jiménez-Requejo & Palacios-Albarrán, 1983).

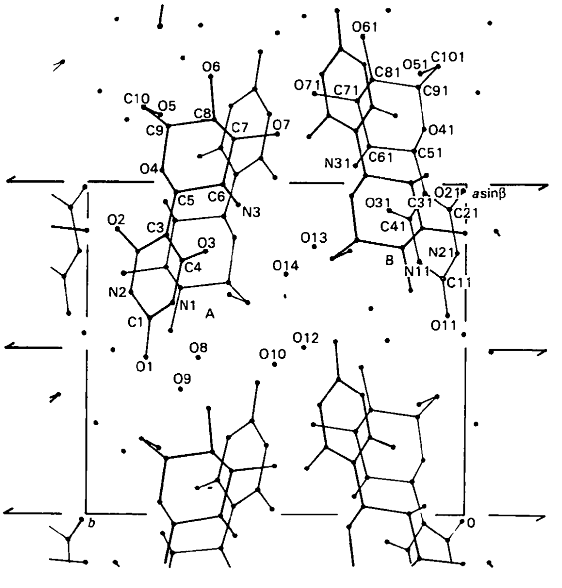


Fig. 2. A view of the structure along [001].

Table 3. *Possible hydrogen bonds*

X—H···Y	X—H	X···Y	H···Y	∠X—H···Y
O9—HO91···O1	0·91 (5) Å	2·84 (1) Å	2·03 (6) Å	148 (6)°
O13—HO132···O14	0·89 (5)	2·81 (1)	2·02 (6)	147 (6)
O13—HO131···O31	0·90 (7)	2·73 (2)	1·89 (7)	154 (5)
O14—HO141···O3	0·96 (7)	2·80 (2)	2·00 (8)	139 (4)
O14—HO142···O12	0·95 (5)	2·75 (1)	1·86 (6)	156 (6)
O71 HO71···O7	0·96 (6)	2·64 (1)	1·68 (6)	175 (5)
N1—HN1···O8	1·07 (6)	2·88 (1)	1·84 (6)	165 (5)
O10—HO102···O51$^{\rm i}$	0·88 (6)	2·98 (1)	2·16 (6)	154 (5)
N3—HN31···O51$^{\rm i}$	1·09 (6)	2·96 (1)	1·90 (5)	161 (5)
N3—HN32···O31$^{\rm i}$	1·11 (6)	2·77 (1)	1·68 (6)	163 (5)
O5—HO5···O14$^{\rm ii}$	0·89 (7)	2·79 (2)	1·91 (7)	172 (5)
N31—HN313···O21$^{\rm ii}$	1·13 (7)	2·73 (2)	1·68 (7)	150 (5)
O6—HO6···O8$^{\rm iii}$	1·03 (6)	2·80 (1)	1·85 (6)	153 (5)
O9—HO92···O13$^{\rm iv}$	0·84 (7)	2·82 (2)	2·16 (6)	135 (6)
N2—HN2···O10$^{\rm iv}$	1·03 (6)	3·12 (1)	2·12 (6)	165 (5)
O51—HO51···O10$^{\rm v}$	0·92 (6)	2·98 (1)	2·07 (6)	167 (5)
O7—HO7···O2$^{\rm v}$	0·89 (6)	2·51 (1)	1·67 (6)	157 (5)
O61—HO61···O9$^{\rm v}$	0·98 (5)	2·75 (1)	1·79 (5)	165 (7)
N31—HN312···O5$^{\rm vi}$	1·06 (6)	2·83 (1)	1·86 (6)	149 (5)
N21—HN21···O71$^{\rm vi}$	1·07 (6)	2·92 (1)	1·87 (6)	164 (5)
N31—HN311···O3$^{\rm vi}$	1·07 (6)	2·81 (1)	1·79 (6)	158 (5)
O8—HO81···O11$^{\rm vii}$	0·93 (6)	2·91 (1)	2·01 (6)	162 (5)
O12—HO121···O11$^{\rm vii}$	0·94 (7)	2·85 (1)	1·96 (6)	156 (6)
O8—HO82···O12$^{\rm vii}$	1·00 (7)	2·85 (2)	1·99 (8)	142 (4)
O10—HO101···O6$^{\rm viii}$	0·94 (6)	2·82 (1)	1·93 (6)	160 (5)
O12—HO122···O71$^{\rm viii}$	0·90 (6)	2·80 (1)	1·94 (5)	159 (5)
N11—HN11···O9$^{\rm ix}$	1·07 (6)	3·02 (2)	2·00 (7)	158 (5)

Symmetry code: none x, y, z; (i) $-x+2, y+\frac{1}{2}, -z+2$; (ii) $-x+2, y+\frac{1}{2}, -z+1$; (iii) $x+1, y, z$; (iv) $-x+1, y+\frac{1}{2}, z+2$; (v) $-x+2, y-\frac{1}{2}, -z+2$; (vi) $-x+2, y-\frac{1}{2}, -z+1$; (vii) $-x+1, y+\frac{1}{2}, -z+1$; (viii) $x-1, y, z$; (ix) $-x+1, y-\frac{1}{2}, -z+2$.

The ring adopts a small boat deformation in molecule *A* [$\sum(\Delta/\sigma)^2 = 31{\cdot}4$, χ^2 at 95% = 7·8] and a small twist–boat deformation in molecule *B* [$\sum(\Delta/\sigma)^2 = 10{\cdot}0$, χ^2 at 95% = 7·8]. The dihedral angle between pyranose and barbituric rings is 80·9 (3)° for molecule *A* and 90·3 (3)° for molecule *B*.

Crystal packing

Fig. 2 shows a view along [001] of the structure, stabilized by an extended three-dimensional hydrogen-bonding network in which water molecules are involved. The packing of the structure consist of chains of molecules along [001]. These chains consist of a sequence of molecules *A* and *B* alternating and aligned head-to-tail, each molecule being linked to its neighbours by hydrogen bonds.

The water molecules are located between these chains and involved in hydrogen bonds linking the neighbouring chains. The chains are joined together not only by the water molecules, but also by the O7—HO7···O2 ($-x+2$, $y-\frac{1}{2}$, $-z+2$) and N21—H21···O71 ($-x+2$, $y-\frac{1}{2}$, $-z+1$) bonds to give a three-dimensional extended packing scheme. Details of the geometry of the possible hydrogen bonds are given in Table 3.

Values of the H···O distance for the O—H···O bonds are in the range 1·67–2·16 Å and values of the O—H···O angle agree with the statistical result (Allen, Kennard & Taylor, 1983) that short hydrogen bonds tend to be more linear than long ones. For the three bonds with O···H < 1·81 Å the mean value of the donor–proton–acceptor angle is 166 (5)°, in agreement with the mean value 168·4 (9)° reported (Allen, Kennard & Taylor, 1983), but for bonds with O···H > 1·81 Å the mean value found is 150 (3)°, lower than the mean value 165·8 (12)° reported in the above-cited statistical study. For the N—H···O bonds the mean value of the H···O distance is 1·86 (5) Å and the mean N—H···O angle is 159 (4)°.

We thank Professor J. A. Galbis for supplying the crystals and for helpful discussions on chemical aspects and Professor A. López Castro for collecting the diffraction data. The present work is part of a project supported by a grant of the Comisión Asesora de Investigación Científica y Técnica of the Spanish Government.

References

Allen, F. H., Kennard, O. & Taylor, R. (1983). *Acc. Chem. Res.* **16**, 146–153.

Avalos-González, M. (1981). Doctoral Thesis. Univ. of Extremadura, Spain.

Craven, B. M., Vizzini, E. A. & Rodrigues, M. M. (1969). *Acta Cryst.* B**25**, 1978–1993.

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

Galbis-Pérez, J. A., Avalos-González, M., Jiménez-Requejo, J. L. & Palacios-Albarrán, J. C. (1983). *Carbohydr. Res.* **124**, C15–C17.

Hamilton, W. C. (1959). *Acta Cryst.* **12**, 609–610.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

Longchambon, F., Ohanessian, J. Avenel, D. & Newman, A. (1975). *Acta Cryst.* B**31**, 2623–2627.

Main, P., Fiske, S., Hull, S. E., Lessinger, L., Germain, P., Declercq, J.-P. & Woolfson, M. M. (1980). *MULTAN*80. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

Millán, M., Conde, C. F., Conde, A. & Márquez, R. (1985). *Acta Cryst.* C**41**, 274–277.

Nardelli, M. (1983). *Acta Cryst.* C**39**, 1141–1142.

Ohanessian, J., Longchambon, F. & Arene, C. (1978). *Acta Cryst.* B**34**, 3666–3671.

Pauling, L. (1960). *The Nature of the Chemical Bond.* Ithaca: Cornell Univ. Press.

Shimizu, N., Nishigaki, S., Nakai, Y. & Osaki, K. (1982). *Acta Cryst.* B**38**, 2309–2311.

Stewart, J. M., Kundell, F. A. & Baldwin, J. C. (1970). The *XRAY*70 system. Computer Science Center, Univ. of Maryland, College Park, Maryland.

Acta Cryst. (1987). C**43**, 1142–1145

1,1′,3,3′-Tetrakis(dimethylamino)-4*H*,4′*H*-4,4′-biisoquinolyldiium Diperchlorate (II) and 1,1′,3,3′-Tetrakis(dimethylamino)-4,4′-biisoquinolyl (III)

By Peter F. Lindley and Adrial R. Walton

*Department of Crystallography, Birkbeck College, Malet St., London WC*1*E* 7*HX, England*

Gerhard V. Boyd and George A. Nicolaou

*Department of Chemistry, King's College London, Kensington Campus, London W*8 7*AH, England*

and Ole Hammerich

Department of General and Organic Chemistry, The H. C. Ørsted Institute, 2100 *Copenhagen, Denmark*

(*Received* 14 *October* 1986; *accepted* 19 *January* 1987)

Abstract. (II): $C_{26}H_{34}N_6^{2+}.2ClO_4^-$, $M_r = 629{\cdot}5$, monoclinic, $I2/a$, $a = 14{\cdot}580\ (1)$, $b = 10{\cdot}760\ (1)$, $c = 18{\cdot}634\ (1)$ Å, $\beta = 90{\cdot}693\ (3)°$, $U = 2923{\cdot}1\ (4)$ Å^3, $Z = 4$, $D_x = 1{\cdot}43$ Mg m^{-3}, Cu $K\alpha$, $\lambda = 1{\cdot}54178$ Å, $\mu = 2{\cdot}381$ mm^{-1}, $F(000) = 1320$, $T = 293\ (1)$ K, $R = 0{\cdot}068$ for 2606 unique reflections. (III): $C_{26}H_{32}N_6$, $M_r = 428{\cdot}6$, monoclinic, $P2_1/c$, $a = 9{\cdot}844\ (9)$, $b = 10{\cdot}580\ (9)$, $c = 24{\cdot}355\ (21)$ Å, $\beta = 109{\cdot}860\ (8)°$, $U = 2386\ (4)$ Å^3, $Z = 4$, $D_x = 1{\cdot}19$ Mg m^{-3}, Cu $K\alpha$, $\lambda = 1{\cdot}54178$ Å, $\mu = 0{\cdot}496$ mm^{-1}, $F(000) = 920$, $T = 293\ (1)$ K, $R = 0{\cdot}055$ for 4056 unique reflections. The symmetry-related halves of the cation in (II) are nearly parallel and are joined by an exceptionally long [1·597 (2) Å] bond; in the conjugate base (III) this bond is 1·496 (7) Å, the normal length for a single bond between sp^2-hybridized C atoms, and the planes of the halves of the molecule form a dihedral angle of 62·8 (3)°.

Introduction. The work reported herein arose from an investigation into the chemistry of the readily available 1,3-bis(dimethylamino)isoquinolines (I). Oxidative dimerization of (I) with aqueous silver perchlorate or cyclic voltammetry resulted in the formation

0108-2701/87/061142-04$01.50