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CRYSTAL STRUCTURE OF 4-(*N*-ACETYL-2,3,4-TRI-*O*-ACETYL-β-L-ARABINOPYRANOSYLAMINO)AZOBENZENE

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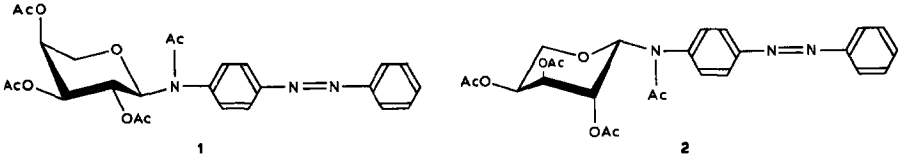
ABSTRACT

The crystals of the title compound, $C_{25}H_{27}N_3O_8$ (M_r 497.55), are monoclinic, space group $P2_1$ with a = 11.680(2), b = 8.089(1), c = 13.804(3) Å, β = 92.52(2)°, V = 1302.7 Å^3, and Z = 2; D_c = 1.27 g.cm^{-3}. The structure was solved by using direct methods. The refinement of all non-hydrogen atom parameters yielded R = 0.050. The compound has normal geometry with the $^1C_4$ conformation of the pyranoid ring and the extended *trans* conformation of the azobenzene moiety.

INTRODUCTION

In solutions, pyranoses and their derivatives occur mostly as an equilibrium of chair conformations ($^4C_1 \rightleftharpoons {}^1C_4$). In the solid state, however, only one of these conformers is usually obtained. We obtained two isomers of 4-(*N*-acetyl-2,3,4-tri-*O*-acetyl-L-arabinopyranosylamino)azobenzene as crystalline solids, an α-$^4C_1$ isomer (**1**) and a β-$^1C_4$ isomer (**2**). The structure of these compounds was established on the basis of their ^{1}H-n.m.r. spectra[1]. The isolation of the $^1C_4$ isomer is noteworthy, as only L-arabinose derivatives with the $^4C_1$ structure have been obtained so far.

In order to confirm unambiguously the ^{1}H-n.m.r. spectral evidence as to the configuration and conformation of **2**, its X-ray crystal structure was solved and is now reported.



1 2

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EXPERIMENTAL

Compound **2** was prepared by a method previously reported[1]. Red crystals were grown from anhydrous acetic acid. The space group was determined from oscillation and Weissenberg photographs. All measurements for a crystal 0.35 × 0.35 × 0.60 mm were made on a Syntex $P2_1$ diffractometer, using Mo-K_α radiation (λ = 0.71069 Å). The cell parameters were determined from a least-squares refinement of the setting angles of 15 reflections; 4038 independent reflections were measured in the range $4.0 < 2\theta < 60.0°$ with the variable θ–2θ scan technique. The scan rate varied from 2.0 to 29.3°/min, depending on the intensity. The intensities were not corrected for absorption (μMoK_α = 1.0 cm^{-1}).

The *E*-map, based on the phases produced by MULTAN-80[2], showed the positions of all heavy atoms, which were refined by a block diagonal least-squares routine with isotropic and subsequently anisotropic temperature factors. using 2293 reflections with $I > 1.96\sigma(I)$. The methyl H atoms were found from ΔF synthesis, and the positions of the remaining H atoms were calculated on the basis of the geometry of the molecule (C–H and N–H = 0.95 Å). Full-matrix least-squares refinement of the heavy atom parameters was then performed. The resulting agreement factors R ($=\Sigma \| F_o| - |F_c \| / \Sigma |F_o|$) and wR $[=\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2]^{1/2}$ were 0.050 and 0.046, respectively. The function minimised was $\Sigma w(|F_o| - |F_c|)^2$ with $w = \sigma^{-2}(F)$, where $\sigma^2(F) = \sigma^2(F_o) + (0.005F_o)^2$, and $\sigma(F_o)$ was taken from the counting statistic. Neutral atom scattering factors were those listed in International Tables for X-ray Crystallography[3]. The anomalous dispersion was included for O atoms. The programs Syntex XTL/XTLE[4], PUCK 2[5], and ORTEP[6] were also used for calculation.

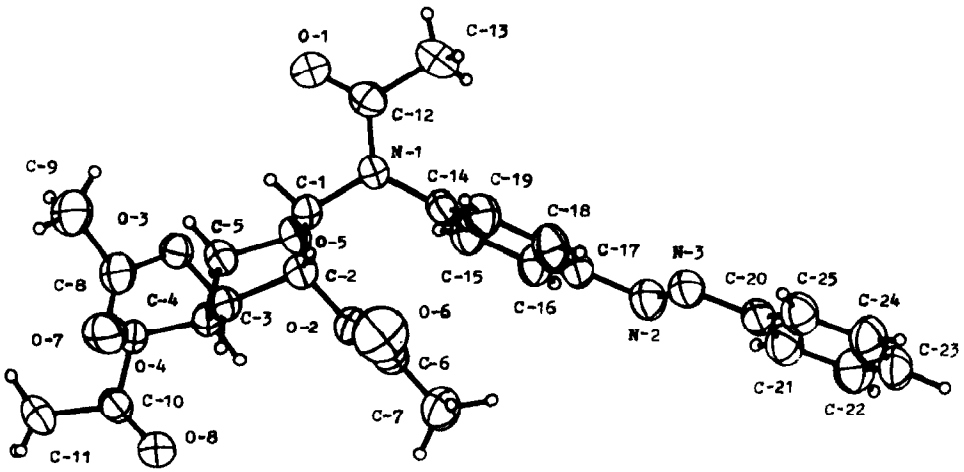

Fig. 1. ORTEP drawing showing atom numbering in 4-(*N*-acetyl-2,3,4-tri-*O*-acetyl-β-L-arabinopyranosylamino)azobenzene. The non-hydrogen atoms are represented by 50% probability ellipsoids and the hydrogen atoms are drawn as spheres of arbitrary size.

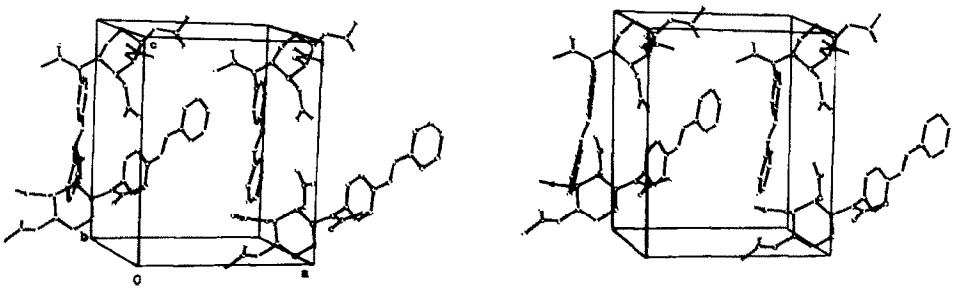

Fig. 2. Stereoview of the unit cell. The hydrogen atoms have been removed for clarity.

RESULTS AND DISCUSSION

The atom numbering scheme, overall molecular conformation, and stereoview of the unit cell are shown in Figs. 1 and 2. Tables I–IV list the atomic positional and thermal parameters, bond distances and angles, and selected torsion angles.

The pyranoid ring has the $^1C_4$ conformation. The Cremer and Pople ring-puckering parameters[7,8] q = 0.580(3) Å, θ = 173.2(3)° and Φ = 196(3)° indicate some distortion of this chair conformation in the direction between $B_{3,0}$ and $^1S_3$ geometry. All bond lengths and valency angles in the carbohydrate moiety and in the aglycon group are in good agreement with similar values for other compounds. The azobenzene moiety has the *trans* conformation with a C–N=N–C torsion angle of −178.5(3)°. The deviation from coplanarity of both aromatic rings is small. The angle between normals to the best planes of both rings (plane C-14,C-15,C-16, C-17,C-18,C-19, equation: $0.9747X + 0.2116Y - 0.0721Z - 1.8959 = 0$; plane C-20,C-21,C-22,C-23,C-24,C-25, equation: $0.9580X + 0.2173Y - 0.1872Z - 1.4164 = 0$) is 6.7°. There were no intramolecular steric interactions, but there were some intermolecular contacts, correponding to weak van der Waals forces.

TABLE I

ATOMIC PARAMETERS[a]

Atom	x	y	z	B_{eq} *or* B_{iso} (Å^2)
O-1	2402(2)	4036(4)	1136(2)	5.2(2)
O-2	−513(2)	373(4)	2583(2)	4.0(2)
O-3	−1425(2)	4236(4)	1485(2)	3.6(2)
O-4	−2542(2)	2177(4)	129(1)	3.4(1)
O-5	420(2)	1139(—)	758(1)	3.4(2)
O-6	−713(3)	1288(6)	4101(2)	8.1(4)
O-7	−3318(2)	4581(4)	1684(2)	5.7(2)
O-8	−3783(2)	537(4)	853(2)	5.1(2)
N-1	1729(2)	1903(4)	2006(2)	3.4(2)
N-2	2890(2)	−3816(5)	4162(2)	4.5(2)
N-3	3225(2)	−3551(5)	5011(2)	4.4(2)
C-1	591(2)	2193(5)	1573(2)	3.2(2)
C-2	−389(2)	2045(5)	2254(2)	3.3(2)

Table I (continued)

Atom	x	y	z	B_{eq} *or* B_{iso} *(Å²)*
C-3	−1512(2)	2505(5)	1698(2)	3.3(2)
C-4	−1613(2)	1545(5)	744(2)	3.1(2)
C-5	−552(2)	1682(5)	168(2)	3.4(2)
C-6	−674(3)	158(7)	3557(3)	5.4(4)
C-7	−755(4)	−1611(8)	3808(4)	7.6(5)
C-8	−2414(3)	5137(5)	1488(2)	4.0(3)
C-9	−2180(3)	6871(6)	1210(3)	5.6(3)
C-10	−3585(2)	1522(5)	247(2)	3.8(2)
C-11	−4435(3)	2223(6)	−478(3)	5.7(3)
C-12	2598(3)	2903(5)	1684(2)	3.8(3)
C-13	3792(3)	2526(6)	2068(3)	5.5(3)
C-14	1970(2)	445(5)	2575(2)	3.4(2)
C-15	2115(3)	−1056(5)	2122(2)	4.0(3)
C-16	2396(3)	−2453(5)	2670(3)	4.2(3)
C-17	2539(3)	−2321(5)	3668(2)	3.9(3)
C-18	2360(3)	−837(6)	4121(2)	4.5(3)
C-19	2069(3)	556(5)	3575(2)	4.2(3)
C-20	3611(3)	−5027(5)	5518(2)	4.0(3)
C-21	3739(3)	−6554(6)	5097(3)	4.8(3)
C-22	4110(3)	−7899(6)	5667(3)	5.2(3)
C-23	4345(3)	−7668(7)	6644(3)	5.3(3)
C-24	4227(3)	−6160(7)	7049(3)	5.4(4)
C-25	3861(3)	−4815(6)	6493(2)	4.8(3)
H–C-1	57	331	138	5
H–C-2	−25	227	280	5
H–C-3	−218	221	206	5
H–C-4	−175	37	93	5
H-1–C-5	−62	95	−40	5
H-2–C-5	−46	275	−5	5
H-1–C-7	−18	−202	428	10
H-2–C-7	−152	−201	373	10
H-3–C-7	−43	−230	332	10
H-1–C-9	−279	742	131	8
H-2–C-9	−150	733	143	8
H-3–C-9	−209	695	60	8
H-1–C-11	−505	197	−52	8
H-2–C-11	−421	313	−82	8
H-3–C-11	−524	251	−11	8
H-1–C-13	393	143	196	8
H-2–C-13	389	280	267	8
H-3–C-13	430	312	172	8
H–C-15	202	−114	142	6
H–C-16	250	−355	233	6
H–C-18	241	−78	483	6
H–C-19	193	155	390	6
H–C-21	359	−667	442	8
H–C-22	421	−901	536	8
H–C-23	460	−864	706	8
H–C-24	439	−608	774	8
H–C-25	378	−375	680	8

[a]Estimated standard deviations in parentheses. Values of positional parameters are × 10^4 for non-H atoms and × 10^3 for the H atoms. $B_{eq} = {}^1/_3 B_{ii}$. The *y* co-ordinate of O-5 was not refined.

TABLE II

BOND LENGTHS (Å)[a]

O-1–C-12	1.203(5)	C-2–C-3	1.537(4)
O-2–C-2	1.436(5)	C-3–C-4	1.529(4)
O-2–C-6	1.377(5)	C-4–C-5	1.505(4)
O-3–C-3	1.435(5)	C-6–C-7	1.476(9)
O-3–C-8	1.366(4)	C-8–C-9	1.483(6)
O-4–C-4	1.442(4)	C-10–C-11	1.490(5)
O-4–C-10	1.345(4)	C-12–C-13	1.502(5)
O-5–C-1	1.421(3)	C-14–C-15	1.379(6)
O-5–C-5	1.436(3)	C-14–C-19	1.384(4)
O-6–C-6	1.185(7)	C-15–C-16	1.391(6)
O-7–C-8	1.190(4)	C-16–C-17	1.384(5)
O-8–C-10	1.185(5)	C-17–C-18	1.375(6)
N-1–C-1	1.452(4)	C-20–C-21	1.376(6)
N-1–C-12	1.386(4)	C-20–C-25	1.376(5)
N-1–C-14	1.439(5)	C-21–C-22	1.400(6)
N-2–N-3	1.237(4)	C-22–C-23	1.377(6)
N-2–C-17	1.439(5)	C-23–C-24	1.352(7)
N-3–C-20	1.445(5)	C-24–C-25	1.388(6)
C-1–C-2	1.517(4)		

[a]Estimated standard deviations in parentheses.

TABLE III

VALENCY ANGLES (DEGREES)[a]

C-2–O-2–C-6	116.7(3)	O-3–C-8–C-9	109.8(3)
C-3–O-3–C-8	116.9(3)	O-7–C-8–C-9	126.3(4)
C-4–O-4–C-10	116.8(3)	O-4–C-10–O-8	123.8(3)
C-1–O-5–C-5	110.2(2)	O-4–C-10–C-11	110.4(3)
C-1–N-1–C-12	116.4(3)	O-8–C-10–C-11	125.8(3)
C-1–N-1–C-14	120.7(3)	O-1–C-12–N-1	121.7(3)
C-12–N-1–C-14	121.7(3)	O-1–C-12–C-13	121.5(3)
N-3–N-2–C-17	112.0(3)	N-1–C-12–C-13	116.8(3)
N-2–N-3–C-20	113.2(3)	N-1–C-14–C-15	120.0(3)
O-5–C-1–N-1	108.9(2)	N-1–C-14–C-19	119.8(3)
O-5–C-1–C-2	111.2(2)	C-15–C-14–C-19	120.2(3)
N-1–C-1–C-2	115.7(3)	C-14–C-15–C-16	120.0(3)
O-2–C-2–C-1	111.1(3)	C-15–C-16–C-17	119.6(3)
O-2–C-2–C-3	106.9(3)	N-2–C-17–C-16	115.3(3)
C-1–C-2–C-3	108.8(3)	N-2–C-17–C-18	124.3(3)
O-3–C-3–C-2	105.8(3)	C-16–C-17–C-18	120.4(3)
O-3–C-3–C-4	108.8(3)	C-17–C-18–C-19	120.0(4)
C-2–C-3–C-4	109.8(3)	C-14–C-19–C-18	119.8(3)
O-4–C-4–C-3	110.8(3)	N-3–C-20–C-21	125.1(3)
O-4–C-4–C-5	106.1(3)	N-3–C-20–C-25	114.8(3)
C-3–C-4–C-5	112.6(3)	C-21–C-20–C-25	120.1(4)
O-5–C-5–C-4	109.1(2)	C-20–C-21–C-22	119.9(4)
O-2–C-6–O-6	122.1(4)	C-21–C-22–C-23	119.2(4)
O-2–C-6–C-7	111.4(4)	C-22–C-23–C-24	120.5(4)
O-6–C-6–C-7	126.5(5)	C-23–C-24–C-25	120.9(4)
O-3–C-8–O-7	123.9(3)	C-20–C-25–C-24	119.4(4)

[a]Estimated standard deviations in parentheses.

TABLE IV

SELECTED TORSION ANGLES (DEGREES)[a]

O-5–C-1–C-2–C-3	−59.0(3)
C-1–C-2–C-3–C-4	50.1(4)
C-2–C-3–C-4–C-5	−50.5(3)
C-3–C-4–C-5–O-5	56.1(3)
C-4–C-5–O-5–C-1	−63.3(3)
C-5–O-5–C-1–C-2	66.4(3)
C-5–O-5–C-1–N-1	−164.9(3)
O-5–C-1–N-1–C-14	−75.3(4)
O-5–C-1–C-2–O-2	58.4(3)
C-1–C-2–C-3–O-3	−67.2(3)
C-2–C-3–C-4–O-4	−169.1(3)
C-17–N-2–N-3–C-20	−178.5(3)
C-18–C-17–N-2–N-3	−13.0(4)
N-2–N-3–C-20–C-21	7.6(4)

[a]Estimated standard deviations in parentheses.

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