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Diethyl 6(*R*)-3-(4-Chlorophenyl)-6-(tetra-*O*-acetyl-D-*arabino*-threitol-1-yl)-1,2,3,6-tetrahydro-1,2,3,4-tetrazine-1,2-dicarboxylate, $C_{26}H_{33}ClN_4O_{12}$

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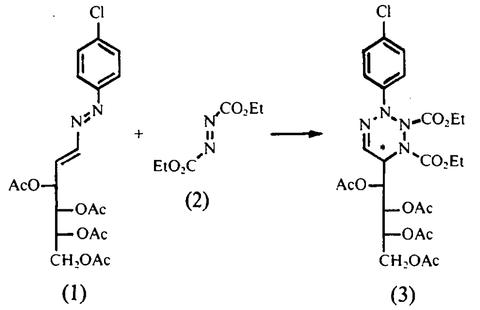
Abstract

The configurations around the chiral centres C53, C52, C51 and C5 are *R*, *S*, *R* and *R*, respectively, corresponding to a D-*arabino* conformation. The tetrahydrotetrazine ring has a conformation close to that of a half-boat. Packing of the molecules is governed by normal van der Waals contacts.

Comment

The title compound, (3), was prepared (Avalos, Babiano, Cintas, Jiménez, Molina, Palacios & Sánchez, 1991) by reaction of the azoalkene (1) with the diethyl azodicarboxylate, (2), in benzene at room temperature.



An X-ray investigation was carried out in order to elucidate unequivocally the molecular conformation of the title compound. A new chiral centre is produced (marked with an asterisk) to which Avalos *et al.* (1991) assigned the absolute configuration *S*. The results of our crystal structure determination indicate that the new chiral centre is *R*. A drawing of the molecule with the atomic numbering is shown in Fig. 1.

In the chlorophenyl group, the mean value of the C—C bond lengths is 1.39 (2) Å and the C—Cl bond length is 1.741 (17) Å. This group is planar, with a maximum deviation from the least-squares plane of 0.021 (11) Å and the substituent N2 displaced by 0.115 (10) Å. In the tetrahydrotetrazine ring, the mean N—N bond length is 1.391 (13) Å, C5—C6 is 1.509 (15) Å and the C—N single and double bonds are 1.455 (13) and 1.244 (14) Å, respectively. The ring conformation is near to a half boat. Puckering parameters (Cremer & Pople, 1975) are $\theta = 57$ (1)°, $Q = 0.417$ (7) Å and $\varphi = 147$ (2)° for the sequence N1, N2, N3, N4, C5 and C6. The Nardelli (1983*a*) asymmetry parameters are ΔC_2(N2) 0.107 (3) and ΔC_2(N1–C6) 0.013 (4). The substituents C21, C31, C41 and C51 are at 0.769 (10), −1.503 (10),

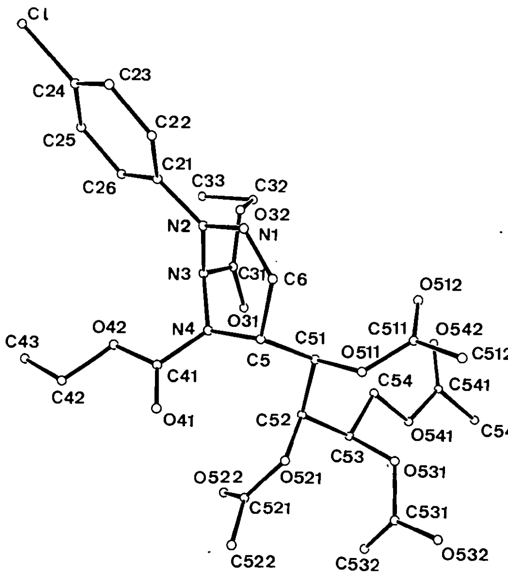


Fig. 1. An *ORTEP*II (Johnson, 1976) view of (3) showing the atomic numbering.

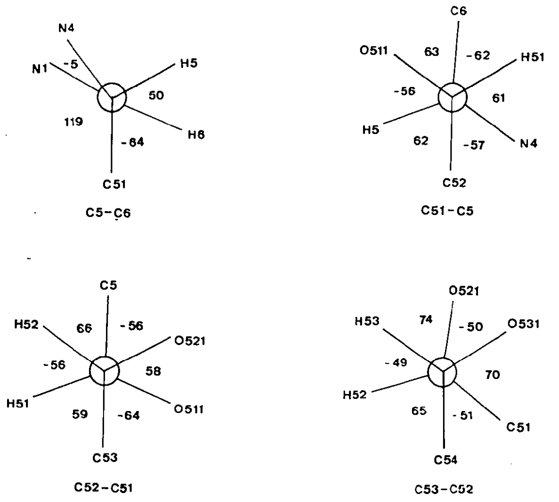


Fig. 2. Some Neuman projections.

1.399 (10) and −1.540 (9) Å from the least-squares ring plane.

The terminal C atom of the *arabino* chain deviates significantly from the least-squares plane of C5—C51—C52—C53. The Newman projections corresponding to the C—C bonds are shown in Fig. 2. According to the Klyne & Prelog (1960) rules, the configurations of the chiral centres C53, C52, C51 and C5 are *R*, *S*, *R* and *R*, respectively, in accordance with the structure determined here. The dihedral angle between the tetrahydrotetrazine best plane and the chlorophenyl group is 153.2 (4)°, and that between the tetrahydrotetrazine best plane and the sugar-chain plane is 71.3 (5)°. Crystal packing is governed by van der Waals contacts.

Experimental

The title compound, (3), was prepared according to the procedure of Avalo, Babiano, Cintas, Jiménez, Molina, Palacios & Sanchez (1991) by reaction of azoalkenes with diethylazodicarboxylates in benzene at room temperature. Crystals were grown form benzene solution.

Crystal data

$C_{26}H_{33}ClN_4O_{12}$
$M_r = 629$
Orthorhombic
$P2_12_12_1$
$a = 13.673$ (2) Å
$b = 28.300$ (2) Å
$c = 8.314$ (5) Å
$V = 3216$ (2) Å^3
$Z = 4$
$D_x = 1.29$ Mg m^{-3}
$D_m = 1.30$ Mg m^{-3}
D_m measured by flotation in bromobenzene–ethanol

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 25 reflections
$\theta = 5$–$15°$
$\mu = 0.177$ mm^{-1}
$T = 293$ K
Prism
0.63 × 0.12 × 0.10 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical
$T_{\min} = 0.664$, $T_{\max} = 1.068$
5199 measured reflections
5199 independent reflections

3471 observed reflections [$I \geq 2\sigma(I)$]
$\theta_{\max} = 30°$
$h = 0 \rightarrow 19$
$k = 0 \rightarrow 39$
$l = 0 \rightarrow 11$
3 standard reflections
frequency: 60 min
intensity variation: 3%

Refinement

Refinement on F
$R = 0.060$
$wR = 0.060$
$S = 2.22$
3471 reflections
388 parameters
H-atom parameters not refined

Unit weights applied
$(\Delta/\sigma)_{\max} = 0.007$
$\Delta\rho_{\max} = 0.3$ e Å^{-3}
$\Delta\rho_{\min} = -0.3$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Cl	0.0788 (4)	0.9151 (2)	0.3953 (8)	0.114 (3)
O31	−0.3083 (6)	0.9179 (3)	1.1700 (9)	0.072 (3)
O32	−0.2637 (6)	0.9560 (2)	0.9391 (9)	0.074 (3)
O41	−0.3114 (6)	0.7622 (3)	1.0626 (12)	0.085 (3)
O42	−0.1804 (6)	0.8081 (2)	1.0678 (11)	0.072 (3)
O511	−0.5933 (5)	0.8498 (2)	0.9887 (9)	0.061 (2)
O512	−0.6241 (8)	0.9251 (3)	0.9355 (14)	0.109 (4)
O521	−0.5093 (6)	0.7945 (2)	1.2283 (8)	0.054 (2)
O522	−0.4018 (9)	0.7859 (3)	1.4277 (12)	0.109 (5)
O531	−0.6587 (6)	0.8534 (3)	1.3152 (9)	0.068 (3)
O532	−0.6518 (9)	0.8050 (4)	1.5263 (13)	0.128 (5)
O541	−0.6164 (7)	0.9379 (3)	1.4760 (10)	0.078 (3)
O542	−0.6002 (8)	1.0104 (3)	1.3906 (13)	0.106 (4)
N1	−0.3626 (7)	0.8683 (4)	0.6937 (11)	0.068 (3)
N2	−0.2772 (7)	0.8795 (4)	0.7733 (10)	0.068 (3)
N3	−0.2763 (6)	0.8781 (3)	0.9408 (10)	0.053 (3)
N4	−0.3254 (6)	0.8384 (3)	0.9990 (10)	0.054 (3)
C5	−0.4261 (7)	0.8344 (4)	0.9436 (13)	0.056 (3)
C6	−0.4315 (8)	0.8508 (4)	0.7713 (13)	0.063 (4)
C21	−0.1891 (9)	0.8863 (4)	0.6867 (13)	0.060 (4)
C22	−0.1929 (9)	0.8785 (4)	0.5168 (14)	0.070 (4)
C23	−0.1094 (11)	0.8889 (4)	0.4261 (17)	0.084 (5)
C24	−0.0257 (11)	0.9043 (5)	0.5075 (21)	0.094 (6)
C25	−0.0220 (10)	0.9097 (5)	0.6714 (20)	0.091 (6)
C26	−0.1045 (9)	0.9002 (5)	0.7597 (16)	0.080 (5)
C31	−0.2878 (8)	0.9187 (4)	1.0301 (13)	0.059 (3)
C32	−0.2456 (14)	0.9999 (4)	1.0270 (19)	0.097 (5)
C33	−0.1432 (11)	1.0023 (5)	1.0824 (24)	0.120 (7)
C41	−0.2735 (8)	0.7986 (3)	1.0419 (14)	0.061 (4)
C42	−0.1210 (10)	0.7714 (4)	1.1351 (23)	0.106 (7)
C43	−0.0258 (12)	0.7878 (5)	1.1754 (23)	0.123 (8)
C51	−0.4989 (7)	0.8622 (3)	1.0547 (12)	0.053 (3)
C52	−0.4920 (8)	0.8456 (3)	1.2290 (12)	0.054 (3)
C53	−0.5610 (8)	0.8688 (4)	1.3463 (13)	0.060 (3)
C54	−0.5600 (9)	0.9212 (4)	1.3423 (14)	0.072 (4)
C511	−0.6514 (9)	0.8852 (4)	0.9411 (15)	0.072 (4)
C512	−0.7459 (10)	0.8676 (5)	0.8759 (19)	0.099 (6)
C521	−0.4585 (11)	0.7696 (4)	1.3383 (14)	0.081 (5)
C522	−0.4868 (15)	0.7196 (5)	1.3235 (18)	0.115 (7)
C531	−0.6939 (11)	0.8178 (5)	1.4088 (19)	0.091 (6)
C532	−0.7847 (12)	0.7977 (6)	1.3307 (24)	0.133 (8)
C541	−0.6342 (10)	0.9855 (5)	1.4791 (16)	0.081 (5)
C542	−0.6992 (11)	1.0025 (5)	1.6172 (18)	0.102 (6)

Table 2. *Selected geometric parameters* (Å, °)

Cl—C24	1.741 (17)	N2—C21	1.415 (15)
O31—C31	1.198 (13)	N3—N4	1.392 (11)
O32—C31	1.339 (12)	N3—C31	1.378 (13)
O32—C32	1.462 (14)	N4—C5	1.455 (13)
O41—C41	1.168 (12)	N4—C41	1.382 (12)
O42—C41	1.321 (13)	C5—C6	1.509 (15)
O42—C42	1.437 (16)	C5—C51	1.564 (14)
O511—C51	1.444 (12)	C21—C22	1.430 (15)
O511—C511	1.342 (14)	C21—C26	1.362 (17)
O512—C511	1.190 (14)	C22—C23	1.396 (19)
O522—C521	1.169 (17)	C23—C24	1.403 (22)
O531—C53	1.431 (13)	C24—C25	1.369 (25)
O531—C531	1.364 (16)	C25—C26	1.375 (20)
O532—C531	1.186 (19)	C32—C33	1.476 (24)
O541—C54	1.430 (14)	C42—C43	1.427 (22)
O541—C541	1.369 (17)	C51—C52	1.532 (14)
O542—C541	1.130 (17)	C52—C53	1.507 (14)
O521—C52	1.467 (11)	C53—C54	1.485 (15)
O521—C521	1.349 (14)	C511—C512	1.492 (18)
N1—N2	1.381 (13)	C521—C522	1.472 (18)
N1—C6	1.244 (14)	C531—C532	1.514 (23)
N2—N3	1.399 (11)	C541—C542	1.510 (20)
C52—O521—C521	115.3 (8)	O31—C31—N3	121.6 (10)
C31—O32—C32	114.5 (9)	O31—C31—O32	128.2 (10)
C41—O42—C42	117.1 (8)	O32—C32—C33	112.5 (12)

C51—O511—C511	117.2 (8)	O42—C41—N4	111.4 (8)
C53—O531—C531	117.0 (9)	O41—C41—N4	122.2 (10)
C54—O541—C541	115.6 (9)	O41—C41—O42	126.0 (9)
N2—N1—C6	118.9 (9)	O42—C42—C43	111.5 (10)
N1—N2—C21	120.5 (8)	O511—C51—C5	103.2 (7)
N1—N2—N3	118.6 (8)	C5—C51—C52	111.4 (8)
N3—N2—C21	120.3 (8)	O511—C51—C52	109.9 (7)
N2—N3—C31	120.3 (8)	O521—C52—C51	106.4 (7)
N2—N3—N4	111.3 (7)	C51—C52—C53	116.2 (8)
N4—N3—C31	116.0 (8)	O521—C52—C53	109.4 (7)
N3—N4—C41	120.1 (8)	O531—C53—C52	109.6 (8)
N3—N4—C5	114.2 (7)	C52—C53—C54	114.6 (9)
C5—N4—C41	120.1 (8)	O531—C53—C54	108.1 (9)
N4—C5—C51	112.2 (8)	O541—C54—C53	107.6 (9)
N4—C5—C6	108.8 (8)	O511—C511—O512	122.7 (11)
C6—C5—C51	111.8 (8)	O512—C511—C512	125.3 (12)
N1—C6—C5	125.2 (10)	O511—C511—C512	111.4 (10)
N2—C21—C26	122.2 (10)	O521—C521—O522	124.7 (10)
N2—C21—C22	116.7 (10)	O522—C521—C522	126.8 (12)
C22—C21—C26	121.0 (11)	O521—C521—C522	108.3 (11)
C21—C22—C23	118.2 (11)	O531—C531—O532	121.5 (13)
C22—C23—C24	117.6 (13)	O532—C531—C532	129.6 (14)
Cl—C24—C23	117.7 (12)	O531—C531—C532	108.6 (12)
C23—C24—C25	123.7 (4)	O541—C541—O542	122.5 (12)
Cl—C24—C25	118.4 (12)	O542—C541—C542	122.4 (13)
C24—C25—C26	118.0 (14)	O541—C541—C542	115.3 (11)
C21—C26—C25	121.1 (13)	O32—C31—N3	109.8 (8)

Preliminary Weissenberg photographs indicated that the crystal belonged to the orthorhombic system with systematic absences consistent with the $P2_12_12_1$ space group. Corrections were made for Lorentz and polarization effects. An empirical absorption correction following the *DIFABS* procedure (Walker & Stuart, 1983) was applied to anisotropically refined data. The structure was solved by direct methods using *SIR*88 (Burla, Camalli, Cascarano, Giacovazzo, Polidori, Spagna & Viterbo, 1989). After anisotropic refinement by full-matrix least squares of all of the 43 non-H atoms in the asymmetric unit, the H atoms were assigned the same isotropic displacement parameters as the atoms to which they were bonded and were included but not refined in the final stage of refinement. Refinement was over nine parameters per atom plus one for scale; the over-determination ratio was 4.8 reflections/parameter. All calculations were carried out with crystallographic programs of the *XRAY*70 System (Stewart, Kundell & Baldwin, 1970). Bond lengths and angles were calculated by the program *PARST* (Nardelli, 1983*a*).

We thank Dr Palacios for supplying the crystals and the Junta de Andalucía and DGICYT (PB89–0540) for financial support.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: LI1072). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Aminoguanidinium Nitrate

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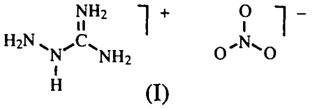
Abstract

The structure of aminoguanidinium nitrate, $CH_7N_4^+.-NO_3^-$, has been determined by single-crystal X-ray methods. The structure is a salt complex containing discrete aminoguanidinium and nitrate ions. The O atoms of the nitrate group are involved in intermolecular bonds with the H atoms of the aminoguanidinium ion.

Comment

As part of a program aimed at synthesizing new optical materials having significant birefringence, we have prepared the compound aminoguanidinium nitrate, (I). Several guanidinium salts have been studied over the last two decades (Adams & Small, 1974) and the chloride (Bryden, 1957), dihydrogenphosphate (Adams, 1977) and sulfate (Mullen & Hellner, 1978) salts have been structurally characterized. In the oxoanion salts, multiple hydrogen bonds to O atoms are present, each O atom accepting three H atoms. Similar hydrogen-bond interactions are observed in the present structure.



(I)

A labeled drawing of the molecular units is given in Fig. 1. The aminoguandinium moiety is nearly planar with C—N distances and interatomic angles similar to those found in other guanidinium and substituted guanidinium salts [torsion angle N1—C1—N3—N4 is 4.0 (3)°]. A packing diagram is given in Fig. 2. The nitrate and guanidinium moieties are approximately coplanar. Within the same plane the nitrate groups are linked through hydrogen bonds to the N atoms of the guanidinium portion of the molecule. Above and below this plane, the groups are bonded intermolecularly