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Crystalline hosts derived from pyrazole carboxylic acids. X-ray crystal structures of 4-nitropyrazole-3,5-dicarboxylic acid and its sodium salt including dioxane molecules

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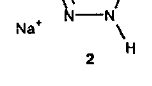
The pyrazole rings in the title compounds show a standard geometry with the substituents either coplanar (carboxylic groups) or perpendicular to the ring (nitro groups). Of the three acidic hydrogens of compound 1, the anion of the sodium salt involves the 3-carboxylic group. The crystal packing of both compounds is dominated by strong O-H...O and N-H...O hydrogen bonds. In the case of the salt, the Na cation is six-coordinated in an octahedral environment. An analysis of 169 sodium coordination geometries, retrieved from 123 structures in the Cambridge Structural Database, reveals coordination numbers from 2 to 8 when only nitrogen and oxygen atoms are involved. By far, coordination number 6 appears to be the most common one, about 75% of the reported cases, 50% of them being octahedral.

INTRODUCTION

We found, accidentally, that 3,5-dimethyl-4-nitropyrazole has non-linear optical properties due to the fact that it crystallizes in the form of a chiral helix and has a high dipole moment.[1] We decided then to explore the crystal structures of the other 4-nitropyrazoles bearing two identical substituents at positions 3 and 5. We report here the structure of one such compound, 4-nitropyrazole-3,5-dicarboxylic acid **1** and of its monosodium salt **2**.



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DISCUSSION

Molecular structure

The geometrical characteristics describing the molecular and crystal structures of compounds **1**·(dioxane)$_2$ and **2**·(dioxane)$_2$ are supplied in Table 1. Atom numbering follows the scheme indicated in Fig 1*a*. The anion in compound **2**·(dioxane)$_2$ involves the carboxylic group at the 3-position of the pyrazole ring, a fact probably related to the greater acidity of 3-COOH compared with 5-COOh.[2] This anion, located on a symmetry plane, places the oxygen atoms of both carboxylic groups on this plane and those of the nitro group perpendicular to it. The differences between the neutral pyrazole **1** and its anion **2**, as tested by half-normal probability plots[3] are mainly those concerning the different twisting of the nitro group and, to a lesser extent, the effect of the charge delocalization reflected in the C(4)-C(3)-C(6), C(6)-C(3)-C(4)-N(9) bond and torsion angles and in the C(6)-O(8)/C(3) and C(3)-C(4) bond lengths, Table 1. The carboxyl groups in **1**·(dioxane)$_2$ are not fully conjugated with the pyrazole being rotated by 12.0(3) and 8.1(3)°.

Comparison of the ring geometries with those of the parent pyrazole[4] (X-ray data at room temperature) shows the N(2)-C(3) and C(3)-C(4) bonds longer, mainly in **1**, than those of the pyrazole itself, probably due to the greater delocalization in **2**·(dioxane)$_2$ than in **1**·(dioxane)$_2$. The values of angles at C(4), C(3) and C(5) also reflect the influence of the substituents NO_2 and COOH (or COO^-) [pyrazole angles at N(1), N(2),...: 112.4(4), 103.8(4), 112.3(5), 105.0(5) and 106.6(5)°].

Another possibility of discussing the pyrazole geometries in compounds **1**·(dioxane)$_2$ and **2**·(dioxane)$_2$ is to compare them with the ensemble of NH-pyrazoles contained in the Cambridge Structural Database [CSD[5] hereinafter]. We have shown that the

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Table 1 Selected geometrical parameters (Å, °)

Compound	*1*	*2*		*1*	*2*
a) Host					
N(1)-N(2)	1.344(2)	1.347(7)	C(5)-C(12)	1.478(3)	1.503(8)
N(1)-C(5)	1.347(2)	1.339(8)	C(6)-O(7)	1.203(3)	1.232(8)
N(2)-C(3)	1.339(3)	1.342(7)	C(6)-O(8)	1.312(2)	1.263(7)
C(3)-C(4)	1.401(2)	1.386(8)	N(9)-O(10)	1.216(2)	1.198(5)
C(3)-C(6)	1.478(3)	1.495(8)	N(9)-O(11)	1.209(2)	1.198(5)
C(4)-C(5)	1.369(3)	1.363(8)	C(12)-O(13)	1.198(3)	1.205(7)
C(4)-N(9)	1.450(2)	1.449(7)	C(12)-O(14)	1.320(3)	1.299(8)
N(2)-N(1)-C(5)	113.2(2)	114.0(4)	N(1)-C(5)-C(12)	124.4(2)	122.9(4)
N(1)-N(2)-C(3)	104.9(1)	103.8(4)	C(3)-C(6)-O(8)	114.0(2)	113.8(4)
N(2)-C(3)-C(6)	123.7(2)	120.7(4)	C(3)-C(6)-O(7)	121.1(2)	119.0(4)
N(2)-C(3)-C(4)	110.0(2)	110.1(4)	O(7)-C(6)-O(8)	124.9(2)	127.2(5)
C(4)-C(3)-C(6)	126.3(2)	129.2(4)	C(4)-N(9)-O(11)	118.2(2)	118.7(2)
C(3)-C(4)-N(9)	127.6(2)	127.8(4)	C(4)-N(9)-O(10)	117.5(2)	118.7(2)
C(3)-C(4)-C(5)	106.5(2)	107.3(4)	O(10)-N(9)-O(11)	124.3(2)	122.7(2)
C(5)-C(4)-N(9)	125.9(2)	124.9(4)	C(5)-C(12)-O(14)	111.8(2)	111.1(4)
N(1)-C(5)-C(4)	105.5(2)	104.7(4)	C(5)-C(12)-O(13)	122.2(2)	120.3(4)
C(4)-C(5)-C(12)	130.0(2)	132.4(4)	O(13)-C(12)-O(14)	126.0(2)	128.5(5)
N(2)-C(3)-C(6)-O(8)	12.0(3)	0	C(6)-C(4)-C(3)-N(9)	3.7(3)	0
C(3)-C(4)-N(9)-O(10)	74.7(2)	90	C(12)-C(5)-C(4)-N(9)	−0.4(3)	0
C(4)-C(5)-C(12)-O(13)	8.1(3)	0			

b) Guest	*1*		*2*
O(21)-C(22)	1.431(3)	1.438(3)	1.438(7)
O(21)-C(26)	1.433(3)	1.442(3)	1.417(8)
C(22)-C(23)	1.495(3)	1.487(4)	1.494(8)
C(23)-O(24)	1.428(3)	1.422(4)	1.432(7)
O(24)-C(25)	1.434(3)	1.426(3)	1.431(7)
C(25)-C(26)	1.487(3)	1.477(4)	1.501(9)
C(22)-O(21)-C(26)	110.4(2)	109.9(2)	109.8(5)
O(21)-C(22)-C(23)	110.6(2)	111.0(2)	110.4(5)
C(22)-C(23)-O(24)	110.7(2)	111.1(2)	109.9(4)
C(23)-O(24)-C(25)	110.6(2)	110.2(2)	109.3(4)
O(24)-C(25)-C(26)	110.1(2)	111.5(2)	110.9(5)
O(21)-C(26)-C(25)	110.3(2)	110.8(2)	111.2(5)
C(22)-O(21)-C(26)-C(25)	−58.3(2)	−56.1(2)	56.4(6)
C(26)-O(21)-C(22)-C(23)	57.0(2)	56.1(3)	−58.1(6)
O(21)-C(22)-C(23)-O(24)	−56.4(2)	−57.1(3)	59.9(6)
C(22)-C(23)-O(24)-C(25)	56.9(2)	56.8(3)	−59.1(6)
C(23)-O(24)-C(25)-C(26)	−58.1(2)	−57.3(3)	57.5(6)
O(24)-C(25)-C(26)-O(21)	58.7(2)	57.3(3)	−56.9(6)
q2	0.015(3)	0.000(2)	0.023(6)
q3	0.564(2)	0.553(2)	0.569(5)
$\theta 2$	1.5(3)	0.0(2)	2.3(6)

c) Na coordination

Na-N(2)	2.657(5)	Na-O(24)ii	2.385(3)
Na-O(8)	2.478(5)	Na-O(24)iii	2.385(3)
Na-O(7)i	2.477(5)	Na-O(13)iv	2.606(4)
N(2)-Na-O(8)	63.0(1)	O(8)-Na-O(13)iv	72.5(1)
N(2)-Na-O(7)i	106.0(2)	O(7)i-Na-O(24)ii	85.6(1)
N(2)-Na-O(24)ii	94.1(1)	O(7)i-Na-O(24)iii	85.6(1)
N(2)-Na-O(24)iii	94.1(1)	O(7)i-Na-O(13)iv	118.5(2)
N(2)-Na-O(13)iv	135.5(2)	O(24)ii-Na-O(24)iii	169.3(2)
O(8)-Na-O(7)i	169.0(2)	O(24)ii-Na-O(13)iv	89.5(1)
O(8)-Na-O(24)ii	94.9(1)	O(24)iii-Na-O(13)iv	89.5(1)
O(8)-Na-O(24)iii	94.9(1)		

i = x, y − 1, z   ii = 1 − x, −y, 1/2 + z   iii = 1 − x, −y, −z   iv = 1/2 + x, 1/2 − y, z

Table 1 Table 1 continued

Compound	*1*	*2*		*1*	*2*
d) Hydrogen interactions					
Compound (**1**)					
N(1)-H(1)...O(24)(1 − x, −y, 1 − z)		0.91(3)	2.757(2)	1.86(3)	165(3)
O(8)-H(8)...O(21)(3/2 − x, −1/2 + y, 1/2 − z)		0.91(3)	2.643(2)	1.74(3)	170(3)
O(14)-H(14)...O(31)(1/2 − x, 1/2 + y, 1/2 − z)		0.92(4)	2.598(2)	1.68(4)	173(3)
Compound **2**					
N(1)-H(1)...O(10)(x, −1 + y, z)		0.81(8)	3.020(6)	2.33(8)	143(5)
N(1)-H(1)...O(10)(x, −1 + y, 1/2 − z)		0.81(8)	3.020(6)	2.33(8)	143(5)
O(14)-H(14)...O(8)(−1/2 + x, 1/2 − y, z)		0.79(8)	2.460(6)	1.68(8)	175(9)

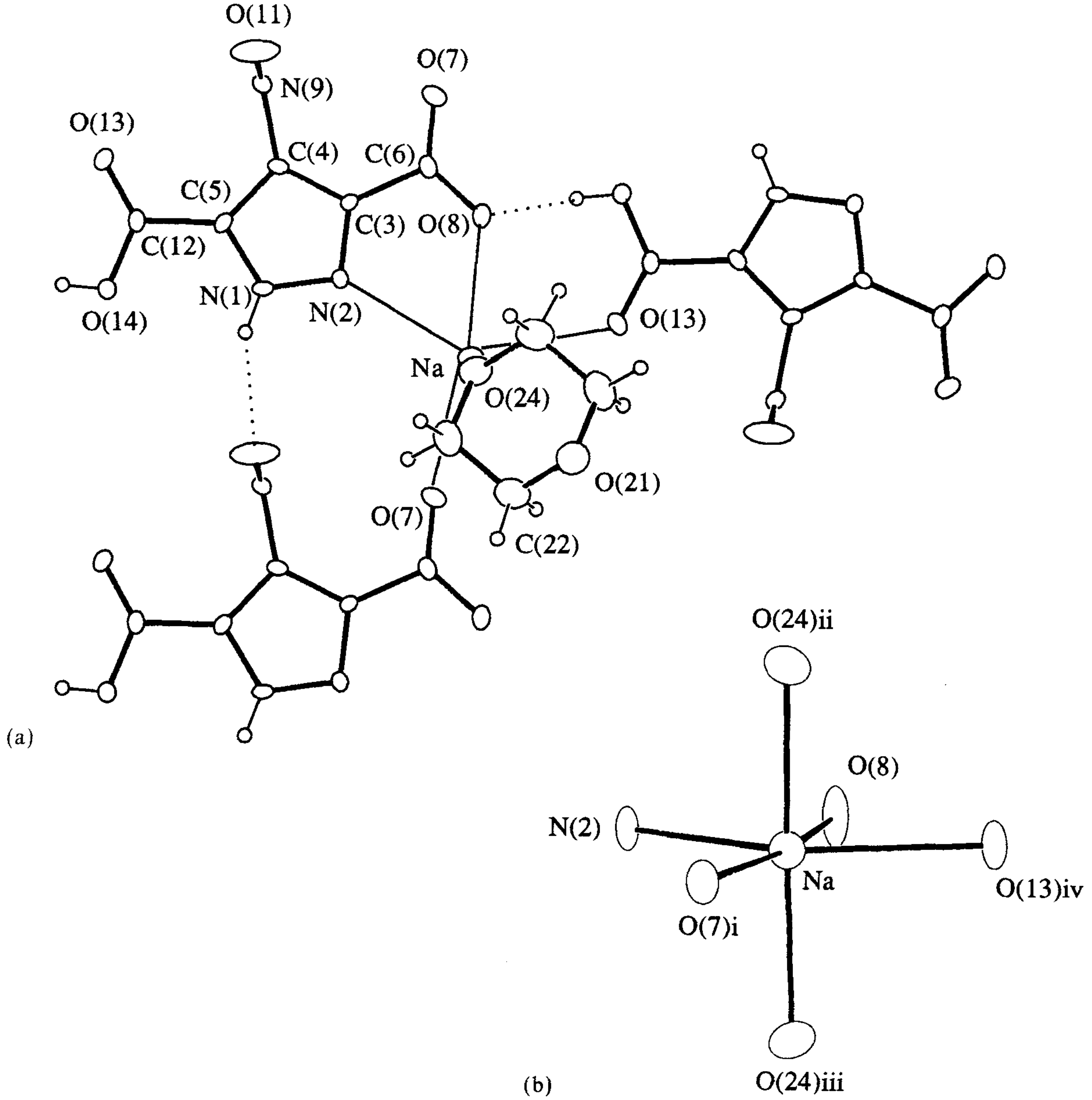

Figure 1 a) An Ortep[22] view perpendicular to the mirror plane of compound **2**·(dioxane)$_2$ showing the Na coordination (thin lines), *independent hydrogen bonds (dotted lines) and the atomic numbering. Ellipsoids are drawn at 30% probability level. The same* numbering scheme was used for compound **1**·(dioxane)$_2$. b) View of the octahedral sodium coordination.

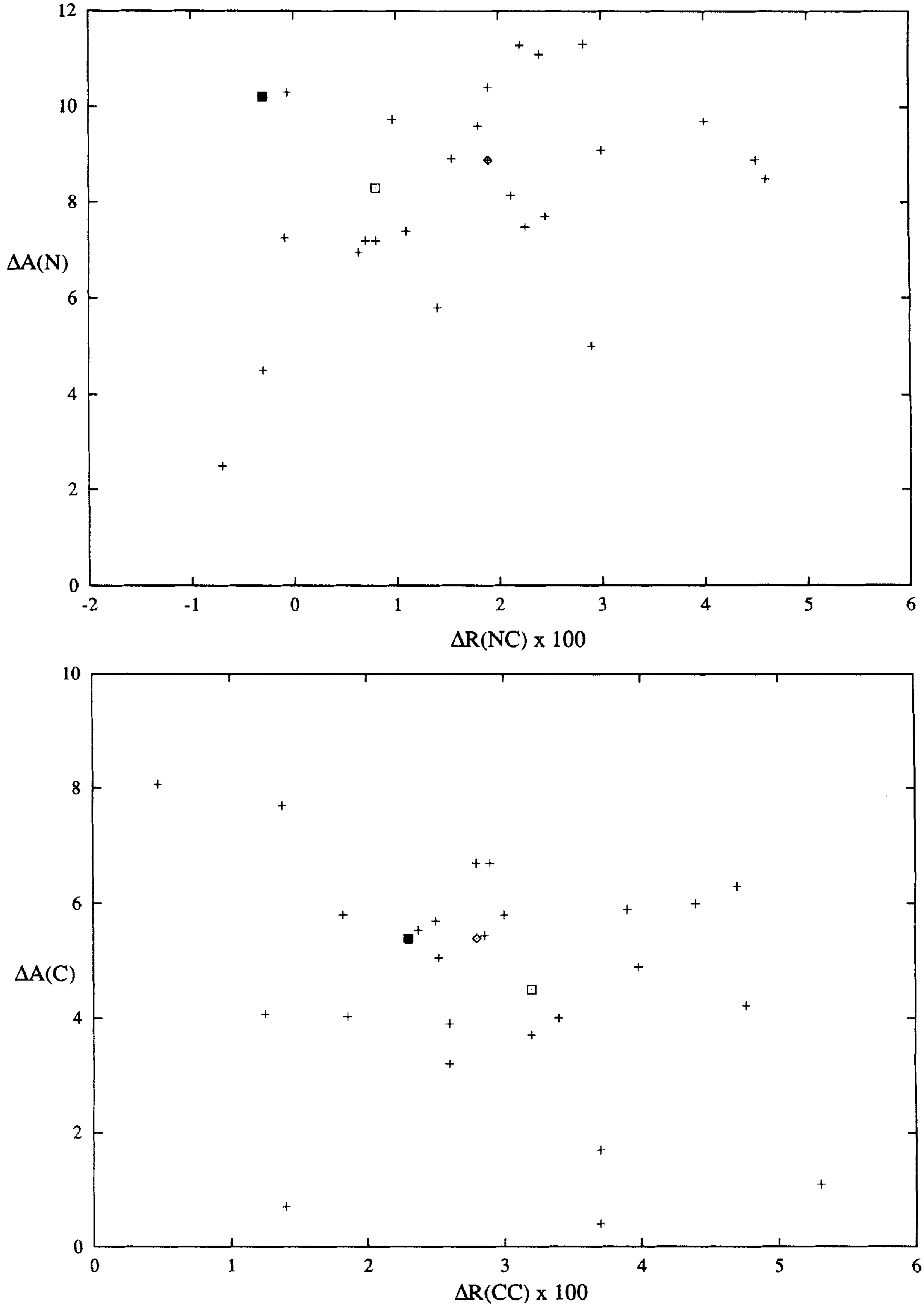

Figure 2 Paul-Curtin plots of NH-pyrazoles, a) ΔA(N) vs. ΔR(NC) × 100; b) ΔA(CC) vs. ΔR(CC) × 100. Crosses: literature data; diamond: average value of literature data; white square: **1**·(dioxane)$_2$; black square: **2**·(dioxane)$_2$. Definitions:[7] ΔA = N(1)-N(2); ΔA(C)-C(3)-C(5); ΔR(NC) = [N(1)-C(5)]-[N(2)-C(3)]; ΔR(CC) = [C(3)-C(4)]-[C(4)-C(5)]. ΔA(N) = [C(5)-N(1)-N(2)]-[N(1)-N(2)-C(3)]; ΔA(C) = [N(2)-C(3)-C(4)]-[N(1)-C(5)-C(4)].

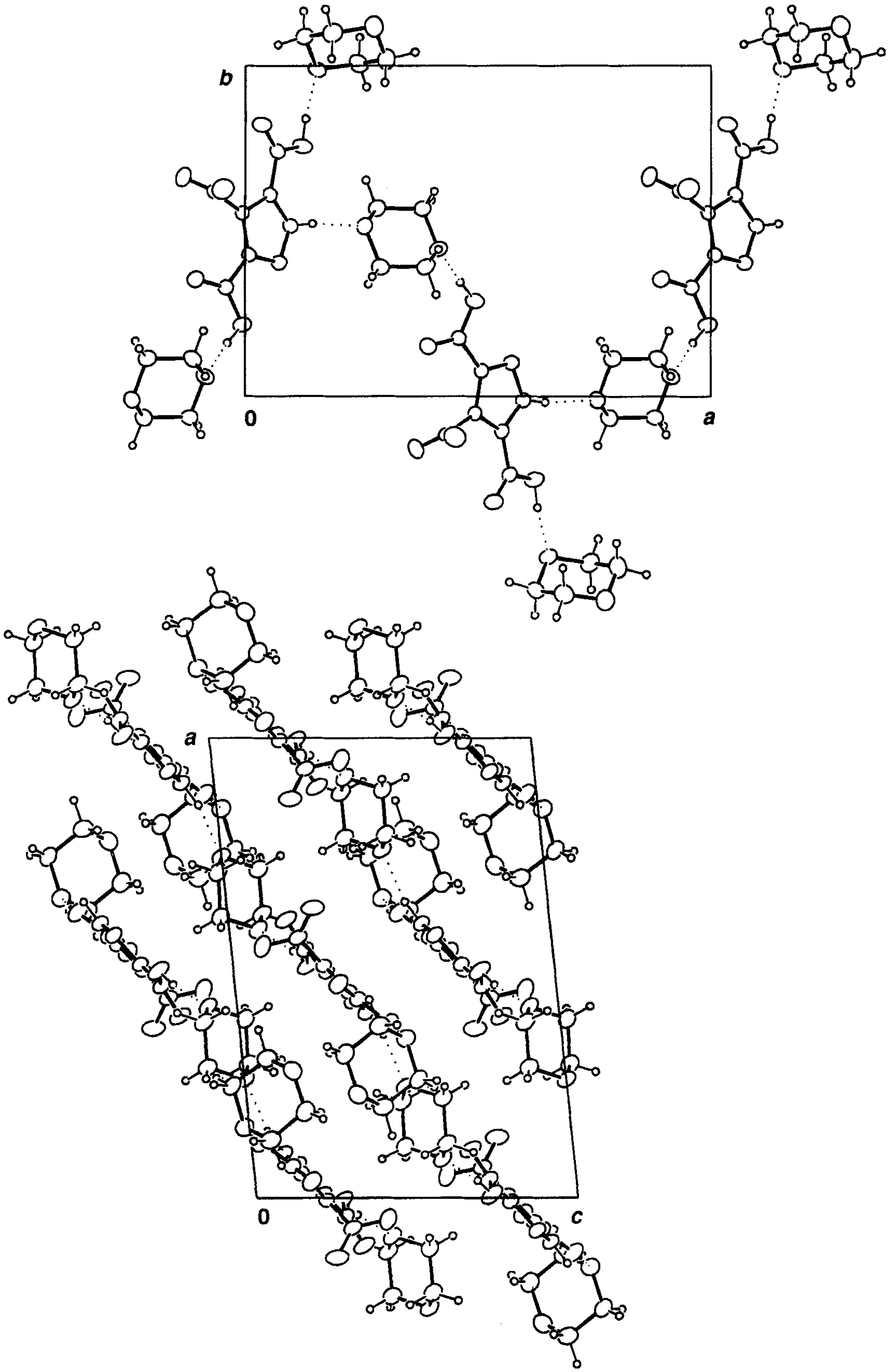

Figure 3 Crystal packing of compound **1**·(dioxane)$_2$: (a) an infinite chain projected down the *c* axis, (b) projection of the whole cell content along the *b* axis.

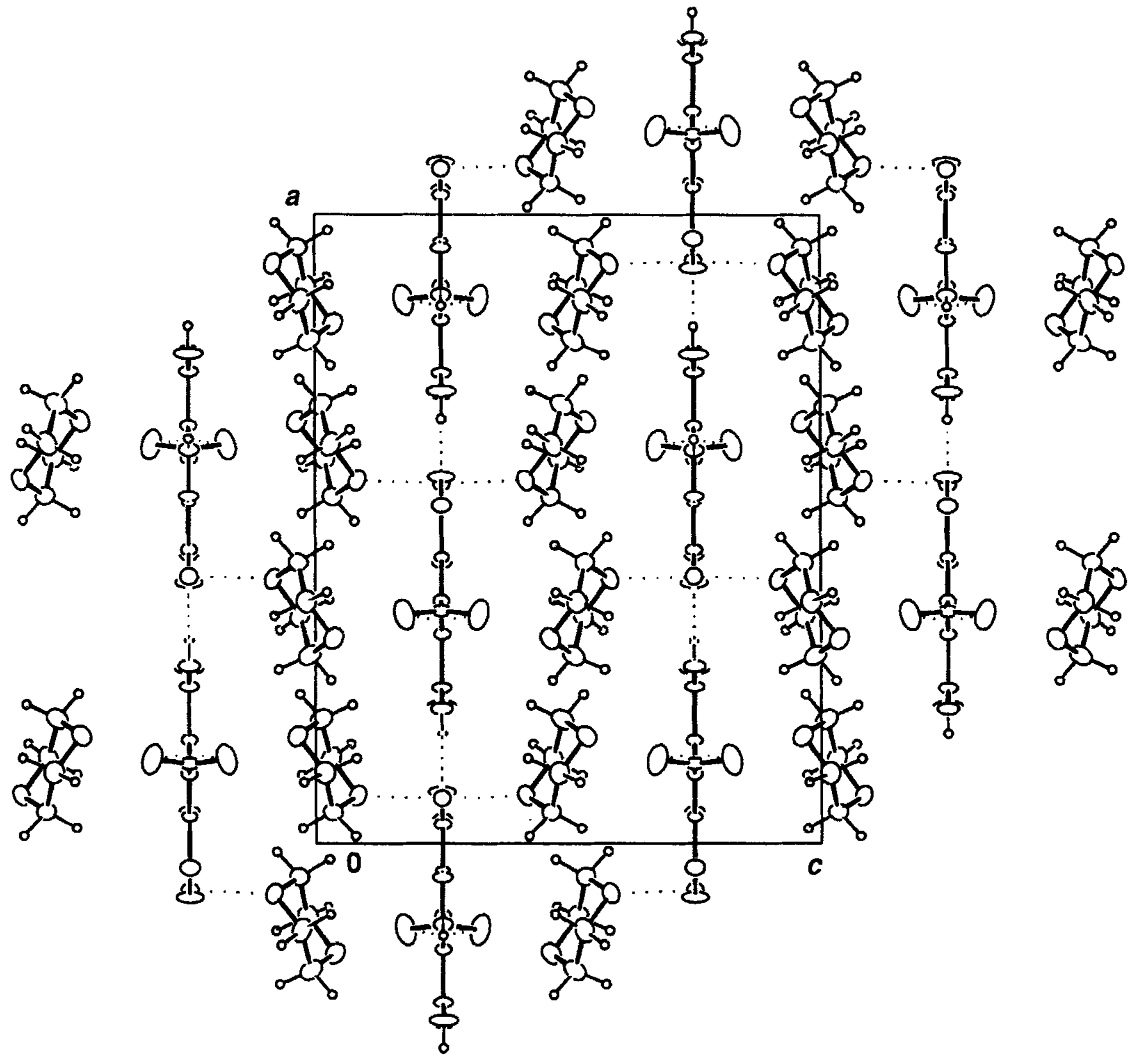

Figure 4 Crystal packing of compound **2**·(dioxane)$_2$ down the *b* axis.

representation in a space of differences in bond angles versus differences in bond lengths [the so called Paul-Curtin diagrams][6] is very useful to discuss pyrazole geometry,[7] Figs 2*a*, 2*b*. Plotting the geometries of compounds **1**·(dioxane)$_2$ and **2**·(dioxane)$_2$ in those diagrams, they appear as standard pyrazoles, with geometries near the averaged ones, the only anomaly being related to distances N(1)-C(5) and N(2)-C(3) in compound **2**·(dioxane)$_2$ [1.339(8) and 1.342(7) Å, Table 1]. Usually, the former is the longer which corresponds to its single and double-bond character, respectively. We assign this behavior to the presence of a carboxylate anion at C(3).

Regarding the dioxane guest molecules, one of the two independent molecules in **1**·(dioxane)$_2$ and that of **2**·(dioxane)$_2$ exhibits slightly distorted chair conformations (Table 1) while the second molecule in **1**·(dioxane)$_2$ exists as an ideal chair [Cremer and Pople's parameters:[8] $q2 = \theta 2 = 0°$].

Crystal packing

The pyrazole and the dioxane molecules in **1**·(dioxane)$_2$ form zig-zag chains, Fig 3*a*, running along (101), Fig 3*b*. One of the two independent dioxane guest molecules bonds pyrazole molecules through strong N-H...O and O-H...O hydrogen bonds. It is worth noticing that to the best of our knowledge,[7] compound **1** is the only pyrazole derivative in which the N(2) atom is not involved in hydrogen bonding interactions. The packing of these chains is only due to van der Waals forces. The crystal structure of **2**·(dioxane)$_2$ can be described as alternating layers, perpendicular to (001), of carboxylate and sodium ions on one hand and dioxane molecules on the other, Fig 4. The anion forms chains through strong O-H...O$^-$ bonds (Table 1) and the packing of these chains is governed by N-H...O=N three-centre interactions. The total packing coefficients[9] are 0.67 and 0.70 for **1**·(dioxane)$_2$ and **2**·(dioxane)$_2$, respectively.

Table 2 Database analysis of Na^+ coordination (oxygen and nitrogen ligands) (Å)

Coordination number	*No. of data*	*Polyhedra**	*Bond-range*
2	1	1 linear	2.352–2.358
3	1	1 equilateral triangle	2.244–2.588
4	6	6 tetrahedron 0 square-planar	2.198–2.544
5	21	3 trigonal bipyramid 3 regular square pyramid 4 distorted square pyramid 11 distorted square pyramid	2.219–2.857
6	127	63 octahedron 37 trigonal prism 27 trigonal antiprism	2.145–2.995
7	11	4 monocapped trigonal prism 0 capped octahedron 0 pentagonal bipyramidal 7 irregular	2.290–2.876
8	2	2 triangular dodecahedron/antiprism 0 body-centered cube	2.503–2.755

* See text for references.

The sodium cation coordination

The sodium cation is characterized by six-fold coordination. The polyhedron can be described as a distorted octahedron, Fig 1, partly due to the geometry of the pyrazole carboxylic acid derivative **2**, which acts as a bifentate ligand, N(2)-Na-O(8) = 63.0(1)°.

Using the CSD (April 1993 release),[5] 123 structures were retrieved corresponding to the following criteria: error free, no transition metals, non-disordered structures with $R < 0.050$; if several determinations of the same structure were performed, only that with the lower R factor was retained. Coordination numbers 2 to 8 have been found for the sodium cation if only oxygen and nitrogen atoms around the sodium ion were considered, as in **2**·$(dioxane)_2$. To analyze the sodium environment we have separated the angles L_i-Na^+-L_j from the $L_{i(j)}$-Na^+ distances. If all the ligands were situated in a sphere of radius 1 around the Na^+ centre, the geometry of the polyhedra could be described with a collection of angles L_i-Na^+-L_j. Table 2 contains the distribution of coordination environments found in the 169 geometries.

Coordination number 2 and 3 appear rather unusual with just one example each. Two symmetrically related nitrogen atoms [sodium bis(trimethylsilyl)amide, TMSIAS refcode] in a nearly linear arrangement (L_i-Na^+-L_j = 150.2°) are placed at 2.352 and 2.358 Å. In the structure of sodium tetraphenylallide diethylether solate (JEVPUV refcode), the centroid of two phenyl rings and the oxygen of the ether molecule are involved in an almost equilateral triangular planar coordination at 2.469, 2-588 and 2.244 Å and angles of 120.4 and 121.1° for the centroid-Na^+-O and 118.5° for centroid-Na^+-centroid angle, respectively.

Only two eight-coordinate examples were found (NABPEX and PUJNAC). The corresponding polyhedra can be regarded as intermediates between a triangular dodecahedron and an antiprism.

Within each ordination number, the geometries have been classified according to the main molecular shapes[11,12,13] (see Table 2) by means of a hierarchical cluster analysis.[10] Figure 5 shows the dendogram corresponding to the most common case, i.e. coordination 6. The L_i-Na^+-L_j angles corresponding to the ideal geometries of the prism **P**, the octahedron **Oc** and the antiprism **AP** were also introduced as well as that of **2**·$(dioxane)_2$. The horizontal axis represents the number of cases. It appears that the most frequent coordination geometry is octahedron (50% of the cases), then trigonal prism (29%) and finally, trigonal antiprism (21%). The vertical axis corresponds to the proximity between structures, the compound we have studied being one of the less distorted octahedra. Prisms and octahedra are more alike than antiprisms.

From Table 2 it appears that five-coordinate geometries are more common than any of those corresponding to coordination number 4 and 7. The geometries described in Table 2 as distorted square or trapezoidal pyramids (coordination number 5, 68% of the hits) correspond to a situation where the sodium cation lies above the plane of the four basal ligands (in a square or trapezoidal disposition).

In conclusion, 4-nitropyrazole-3,5-dicarboxylic acid **1** is a new host related to aromatic carboxylic

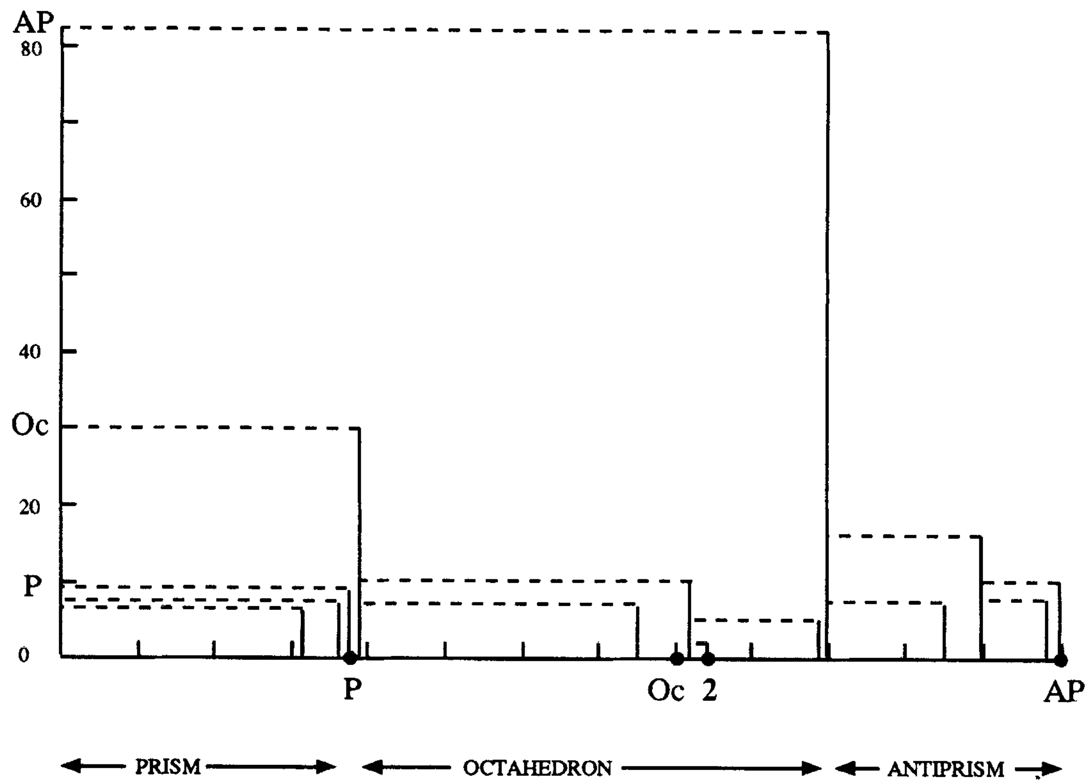

Figure 5 Dendogram corresponding to coordination number six.

acids [trimesic acid;[14] 1,1′-binaphthyl-2,2′-dicarboxylic acid[15]] able to include such guests as tetrahydrofuran and dioxane and, probably, other ethers as well.

EXPERIMENTAL

4-nitropyrazole-3,5-dicarboxylic acid was prepared in two ways.

a. From 3,5-pyrazoledimethanol. At 0 °C, 310 mg of 3,5-pyrazoledimethanol[16] are dissolved in 1 mL of conc. sulfuric acid. After adding 1 mL of fuming nitric acid (90%), the solution is stirred at 100 °C for four hours. Then it is poured on ice, the solution neutralized with sodium carbonate, and slightly acidified with HCl. Then the solvents are evaporated and the dry residue is extracted with THF yielding the diacid as a white solid, yield 73%. m.p.: 202–204 °C. Mass spectrum (m/z, %): 157 (20, $M^{+\cdot}$-CO_2), 113 (30, $M^{+\cdot}$-$2CO_2$), 44 (100, $CO_2^{+\cdot}$). Compound **1** has been prepared by oxidation by potassium permanganate of 3,5-dimethyl-4-nitropyrazole[17] with a m.p. 205 °C.

b. From diethylpyrazole-3,5-dicarboxylate. 830 mg of diethylester[18] are cooled in an ice-bath and 1.8 mL conc. sulfuric acid is added, followed by 2.2 mL fuming nitric acid (90%). The solution is then heated slowly to 50 °C and further to 110 °C. After ten hours it is cooled and poured on ice. The reaction is then worked up as described above yielding 640 mg of a 1:1 complex of tetrahydrofuran (THF) and compound **1**, $C_5H_3N_3O_6{\cdot}C_4H_8O$ (yield: 60%). ^1H NMR (DMSO-d_6, ppm): 8.5 – 6.5 (br, s, 3H, O-H, N-H), 3.62 (m, 4H, THF), 1.75 (m, 4H, THF). ^{13}C NMR (DMSO-d_6, ppm): 161.5 (CO-C_5), 159.0 (CO-C_3), 140.2 (br, C_5), 135.2 (C_4), 132.8 (br, C_3), 68.5 and 26.6 (THF).

When the crude product obtained according to the first procedure was crystallized in dioxane, a mixture of two 1:2 complexes was obtained: **1**·(dioxane)$_2$ [$C_5H_3N_3O_6{\cdot}2(C_4H_8O_2)$] and **2**·(dioxane)$_2$ [$C_5H_2N_3O_6Na{\cdot}2(C_4H_8O_2)$]. the origin of these two compounds is to be found in the experimental procedure, where an excess of sodium carbonate has probably been used. The surprising fact was that both kind of crystals were obtained simultaneously as a mixed crop and that both contain two molecules of dioxane of crystallization.

X-ray structure determination

Crystal data and experimental details are shown in Table 3. The structures were solved by direct methods[19] and refined by the least-squares procedure.

Table 3 Crystal analysis parameters at room temperature

	(1)	*(2)*
Crystal data		
Formula	$C_5H_3N_3O_6.2C_4H_8O_2$	$C_5H_2N_3O_6^-.2C_4H_8O_2.Na^+$
Crystal habit	Colourless, rhombic prism	Colourless, plate
Crystal size (m)	0.42 × 0.42 × 0.33	0.07 × 0.13 × 0.18
Symmetry	Monoclinic, $P2_1/n$	Orthorombic, Pnam
Unit cell determination:	Least-squares fit from 67 reflexions ($\theta < 45°$)	Least squares fit from 56 reflexions ($\theta < 45°$)
Unit cell dimensions (Å, °)	a = 15.2918(4) b = 10.7293(2) c = 10.7153(2) 90, 96.087(2), 90	a = 17.8423(6) b = 6.9373(1) c = 14.2474(4) 90, 90, 90
Packing: V(Å^3), Z	1748.2(1), 4	1763.5(1), 4
Dc(g/cm^3), M, F(000)	1.312, 345.31, 728	1.383, 367.29, 768
μ(cm^{-1})	9.04	11.58
Experimental data		
Technique	Four circle diffractometer: Philips PW1100, Bisecting geometry Graphite oriented monochromator: $\omega/2\theta$ scans Detector apertures 1 × 1°. 1 min./reflex.	
Radiation	CuKα	CuKα
Scan width:	1.5°	1.4°
θ_{max}	65°	60°
Number of reflexions:		
Independent	2975	1365
Observed	2594 ($3\sigma(I)$ criterion)	927 ($3\sigma(I)$ criterion)
Standard reflexions:	2 reflexions every 90 minutes 4.5% decay	No variation
Solution and refinement		
Solution	Sir88	
Refinement:		
Least-Squares on Fo	Full matrix	
Parameters:		
Number of variables	311	180
Degrees of freedom	2283	747
Ratio of freedom	8.3	5.2
Final shift/error	0.02	0.08
H atoms	From difference synthesis	
Weighting-scheme	Empirical as to give no trends in $\langle\omega\Delta^2F\rangle$ vs. $\langle\lvert Fobs\rvert\rangle$ and $\langle \sin\theta/\lambda\rangle$	
Max. thermal value (Å^2)	U22[O(11)] = 0.105(1)	U11[O(10)] = 0.131(4)
Final ΔF peaks (eÅ^{-3})	0.23	0.32
Final R and Rw	0.048, 0.057	0.054, 0.051

Two and one reflections were affected by secondary extinction and were considered as unobserved in the last cycles of refinement. Most of the calculations were performed on a VAX6410 computer using the XRAY80 System.[20] The atomic scattering factors were taken from the *International Tables for X-Ray Crystallography*, Vol. IV.[21] Fractional atomic coordinates are given in Tables 4 and 5.

SUPPLEMENTARY MATERIAL AVAILABLE

Thermal factors for the non-hydrogen atoms, hydrogen parameters, CSD refcodes and references and structure factors tables are available from C.F.-F.

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Table 4 Final atomic coordinates for compound **1**·(dioxane)$_2$

Atom	*x*	*y*	*z*
N(1)	0.40205(10)	0.01258(14)	0.39937(15)
N(2)	0.42737(10)	−0.09997(14)	0.36143(16)
C(3)	0.49156(11)	−0.07616(16)	0.28902(17)
C(4)	0.50542(11)	0.05260(16)	0.28241(16)
C(5)	0.44697(11)	0.10728(17)	0.35381(17)
C(6)	0.54089(12)	−0.17402(17)	0.22931(18)
O(7)	0.60620(10)	−0.14939(14)	0.18077(17)
O(8)	0.50625(10)	−0.28563(13)	0.23358(17)
N(9)	0.56677(10)	0.11754(14)	0.21109(17)
O(10)	0.54824(13)	0.12523(17)	0.09815(16)
O(11)	0.63222(10)	0.16148(17)	0.26746(19)
C(12)	0.43085(12)	0.24053(18)	0.37793(18)
O(13)	0.46427(10)	0.32212(13)	0.32312(15)
O(14)	0.37747(11)	0.25566(14)	0.46587(16)
O(21)	0.91473(10)	0.05882(13)	0.40933(14)
C(22)	0.88129(14)	−0.06521(19)	0.39205(24)
C(23)	0.78338(14)	−0.06613(22)	0.38934(23)
O(24)	0.75696(9)	−0.01156(13)	0.50100(14)
C(25)	0.79057(15)	0.11280(20)	0.51693(23)
C(26)	0.88812(15)	0.11185(21)	0.52211(21)
O(31)	0.15365(10)	−0.01235(13)	−0.01453(15)
C(32)	0.24301(16)	0.00626(24)	−0.04076(23)
C(33)	0.30291(16)	0.01864(29)	0.07732(28)
O(34)	0.27602(11)	0.11792(17)	0.15238(16)
C(35)	0.18754(17)	0.09927(26)	0.17884(25)
C(36)	0.12701(16)	0.08806(21)	0.06247(25)

Table 5 Final atomic coordinates for compound **2**·(dioxane)$_2$

Atom	*x*	*y*	*z*
Na	0.5745(1)	−0.0419(4)	0.2500
N(1)	0.3723(3)	0.1321(8)	0.2500
N(2)	0.4471(2)	0.1566(7)	0.2500
C(3)	0.4557(3)	0.3486(8)	0.2500
C(4)	0.3864(3)	0.4384(8)	0.2500
C(5)	0.3333(3)	0.2970(8)	0.2500
C(6)	0.5322(3)	0.4366(9)	0.2500
O(7)	0.5382(2)	0.6135(6)	0.2500
O(8)	0.5847(2)	0.3144(6)	0.2500
N(9)	0.3707(3)	0.6434(7)	0.2500
O(10)	0.3642(2)	0.7244(5)	0.1763(3)
C(12)	0.2491(3)	0.3032(9)	0.2500
O(13)	0.2167(2)	0.4556(6)	0.2500
O(14)	0.2209(2)	0.1305(7)	0.2500
O(21)	0.3267(2)	0.2875(5)	0.0359(3)
C(22)	0.3853(3)	0.3765(9)	−0.0181(5)
C(23)	0.4481(3)	0.2379(9)	−0.0337(4)
O(24)	0.4214(2)	0.0721(5)	−0.0834(2)
C(25)	0.3631(4)	−0.0181(9)	−0.0301(5)
C(26)	0.3004(3)	0.1208(10)	−0.0111(5)

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