1480 reflections
183 parameters
All H-atom parameters refined

Atomic scattering factors from *International Tables for X-ray Crystallography* (1962, Vol. III)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)*

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

	x	y	z	U_{eq}
I	0.0000	0.64446 (1)	0.0000	0.04755 (5)
S(1)	0.4974 (4)	0.73177 (3)	0.5139 (3)	0.0541 (3)
N(1)	0.6536 (6)	0.6679 (1)	0.3733 (5)	0.043 (1)
N(3)	0.4592 (5)	0.6379 (1)	0.5282 (4)	0.038 (1)
C(2)	0.5290 (7)	0.6760 (1)	0.4816 (6)	0.042 (1)
C(3)	0.5447 (6)	0.6037 (1)	0.4505 (6)	0.036 (1)
C(4)	0.6621 (9)	0.7425 (2)	0.3768 (8)	0.066 (1)
C(5)	0.7296 (9)	0.7061 (2)	0.3131 (8)	0.061 (1)
C(6)	0.6667 (7)	0.6224 (1)	0.3532 (6)	0.041 (1)
C(7)	0.5025 (8)	0.5565 (1)	0.4703 (5)	0.038 (1)
C(8)	0.2718 (7)	0.5412 (2)	0.4300 (7)	0.047 (1)
C(9)	0.2395 (8)	0.4959 (2)	0.4440 (7)	0.052 (1)
C(10)	0.4197 (8)	0.4664 (1)	0.4884 (7)	0.048 (1)
C(11)	0.6401 (8)	0.4809 (2)	0.5212 (7)	0.052 (1)
C(12)	0.6810 (7)	0.5263 (2)	0.5150 (6)	0.044 (1)
C(13)	0.3360 (7)	0.6355 (2)	0.6580 (6)	0.053 (1)

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

S(1)—C(2)	1.716 (3)	C(3)—C(7)	1.461 (4)
S(1)—C(4)	1.747 (7)	C(4)—C(5)	1.327 (9)
N(1)—C(2)	1.350 (7)	C(7)—C(8)	1.426 (7)
N(1)—C(5)	1.384 (7)	C(7)—C(12)	1.371 (7)
N(1)—C(6)	1.382 (4)	C(8)—C(9)	1.387 (8)
N(3)—C(2)	1.321 (5)	C(9)—C(10)	1.365 (7)
N(3)—C(3)	1.388 (5)	C(10)—C(11)	1.370 (7)
N(3)—C(13)	1.460 (6)	C(11)—C(12)	1.393 (8)
C(3)—C(6)	1.367 (7)		
C(2)—S(1)—C(4)	88.3 (3)	N(1)—C(5)—C(4)	111.6 (6)
C(2)—N(1)—C(5)	113.6 (4)	N(1)—C(6)—C(3)	106.2 (4)
C(2)—N(1)—C(6)	108.5 (4)	C(3)—C(7)—C(8)	120.1 (4)
C(2)—N(3)—C(3)	108.0 (4)	C(3)—C(7)—C(12)	120.3 (4)
C(2)—N(3)—C(13)	122.3 (4)	C(8)—C(7)—C(12)	119.5 (4)
C(3)—N(3)—C(13)	129.3 (4)	C(7)—C(8)—C(9)	117.8 (4)
S(1)—C(2)—N(1)	112.7 (3)	C(8)—C(9)—C(10)	121.7 (5)
N(1)—C(2)—N(3)	109.4 (3)	C(9)—C(10)—C(11)	120.6 (4)
N(3)—C(3)—C(6)	107.9 (3)	C(10)—C(11)—C(12)	119.4 (5)
S(1)—C(4)—C(5)	113.8 (5)	C(7)—C(12)—C(11)	121.0 (4)

Table 3. *Contact distances (Å)*

I···N(3)	3.811 (2)	I···S(1$^{\text{i}}$)	3.722 (1)
I···C(4$^{\text{i}}$)	3.763 (6)	I···N(3$^{\text{ii}}$)	3.759 (2)

Symmetry codes: (i) $x - \frac{1}{2}, \frac{3}{2} - y, z - \frac{1}{2}$; (ii) $x - 1, y, z - 1$.

H atoms were located by difference Fourier synthesis and refined isotropically. Programs used were: *SDP* (Frenz, 1978), *PARST* (Nardelli, 1983), *PLUTO* (Motherwell, 1974) and *ORTEP*II (Johnson, 1976).

The authors are grateful to the Netherlands Organization for Scientific Research (NWO) for the support of this investigation.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry, together with the results of MNDO calculations on the cation, have been deposited with the IUCr (Reference: CR1172). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Hydrogen Bonding in 2-Methyl-1,2,3-propanetricarboxylic Acid, Ammonium Dihydrogen 1,2,3-Propanetricarboxylate Hemihydrate and Tetraammonium 1,2,3,4-Butanetetracarboxylate Monohydrate

HAZEL A. BARNES AND JOHN C. BARNES*

Department of Chemistry, University of Dundee, Dundee DD1 4HN, Scotland. E-mail: j.c.barnes@dundee.ac.uk

(*Received 21 June 1995; accepted 3 October 1995*)

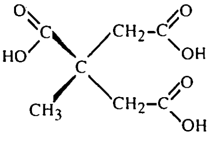
Abstract

The extensive hydrogen-bonded networks of the title compounds, $C_7H_{10}O_6$, (I), $NH_4^+.C_6H_7O_6^-.\frac{1}{2}H_2O$, (II), and $4NH_4^+.C_8H_6O_8{}^{4-}.H_2O$, (III), have been analyzed. In compound (I), layers are formed by eight-membered and 16-membered hydrogen-bonded rings. In compound (II), the anions are arranged into double chains of 30-membered rings through short hydrogen bonds. These chains are cross-linked by weaker hydrogen bonds to H_2O and NH_4^+. In compound (III), stacks of centrosymmetric anions are connected by hydrogen bonds to H_2O and NH_4^+.

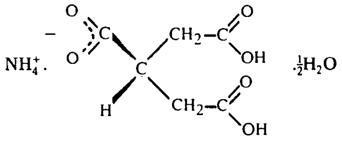
Comment

Hydrogen bonding to give supramolecular arrays is a major factor in the design of the crystal structures of polycarboxylic acids and their ammonium salts (Jeffrey & Saenger, 1994). The extensive literature on mono- and dicarboxylic acids has been codified by Etter, MacDonald & Bernstein (1990) and reviewed by Etter (1990) and Bernstein, Davis, Shimani & Chang (1995) using network analysis to describe the structural elements.

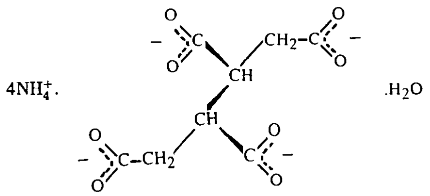
There are relatively few published structures of tri- or tetracarboxylic acids or their salts. In the present paper, we report the structures of β-methyl tricarballylic acid, (I), tricarballylic acid monoammonium salt hemihydrate, (II), and 1,2,3,4-butanetetracarboxylic acid tetraammonium salt monohydrate, (III).



(I)



(II)



(III)

Interest in these structures lies in the contribution of hydrogen bonding to the crystal packing; there are no unexpected bond lengths or bond angles within the molecules. Polycarboxylic acids and their ammonium salts can form many local hydrogen-bond networks, which must often be of similar energy. In consequence, many compounds form syrups which do not readily yield crystals. Only one of the possible ammonium salts was successfully crystallized for each of the acids in the present study. Crystal packing and hydrogen-bonding requirements can utilize the flexibility of the 1,2,3-propanetricarboxylate framework. For example, the C1—C2—C3—C10 torsion angle can adopt the three possible staggered positions, being approximately −60° in tricarballylic acid, 60° in compounds (I) and (II), and 180° in citric acid. The C—C—C—O torsion angles can also vary widely. The anions in compound (III) are centrosymmetric, restricting the possible torsional variation.

Dicarboxylic acids such as fumaric acid (Brown, 1966; Bednowitz & Post, 1966) or camphoric acid (Barnes, Paton, Blyth & Howie, 1991), in which the acid groups are back-to-back across the molecule, frequently form chains in which the molecules are joined by hydrogen-bonded carboxylic rings which are described in the Etter notation as $R_2^2(8)$. Camphoric acid is thus a $C(8)R_2^2(8)$ system. Variations in the packing of these chains leads to polymorphism in both of these acids. In addition to ordered monoclinic camphoric acid, there is an orthorhombic form with two chains in the asymmetric unit, one of which is ordered and the second of which is disordered by slippage in the chain direction.

On addition of excess ammonia to camphoric acid, the compound most readily crystallized is ammonium hydrogen camphorate monohydrate, which contains a hierarchy of hydrogen bonds (Barnes, Paton, Blyth & Howie, 1991). The hydrogen camphorate anions are assembled into spiral $C_3^3(24)$ chains about a threefold axis by strong hydrogen bonds [2.555 (9) Å]. These chains form pillars with the methyl groups pointing inwards and the carboxylate groups, exposed to form weaker hydrogen bonds to NH_4^+ and H_2O, occupying the spaces between pillars. NH_4^+ and H_2O each form four hydrogen bonds with distances in the range 2.71–2.93 Å.

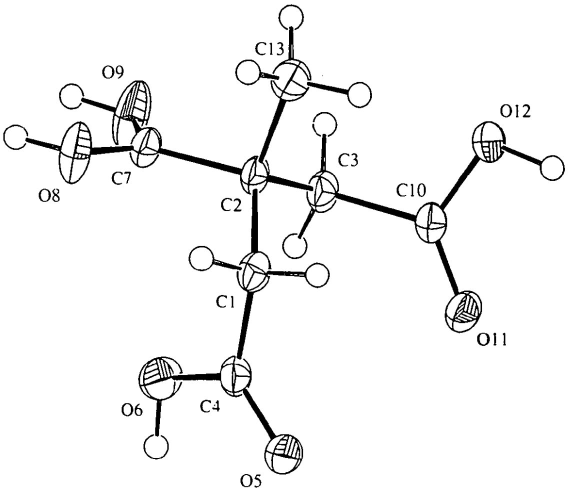


Fig. 1. View of β-methyl tricarballylic acid, (I), with ellipsoids plotted at the 50% probability level.

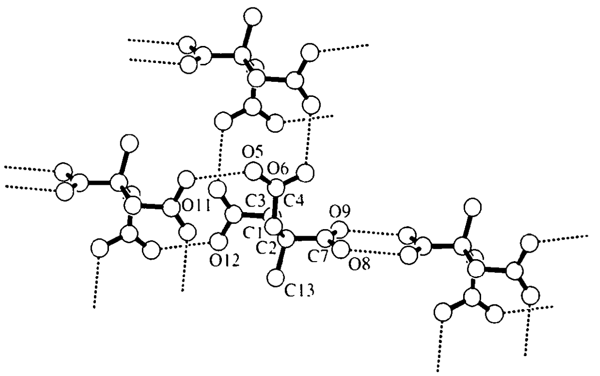


Fig. 2. Hydrogen bonding in (I). An $R_2^2(8)$ ring joins O8···O9^{i} and O9···O8^{i} [2.662 (2) Å]. $R_4^4(16)$ rings are formed by O11···O6^{ii} and O6···O11^{ii} [2.65 (2) Å] and by O5···O12^{iii} and O12···O5^{iii} [2.650 (2) Å]. For symmetry operations see *Comment*.

In 1,2,3-propanetricarboxylic acid (tricarballylic acid) (Barnes & Paton, 1988), each carboxylic acid group takes part in an intermolecular $R_2^2(8)$ ring, with hydrogen-bond lengths of 2.71 (2) Å, resulting in an extended structure of double layers containing $C_2^2(14)$ chains and larger frameworks such as $R_6^6(44)$ rings. The corresponding 2-methyl acid [(I); Fig. 1] is very different. Only the central carboxylic acid group forms an $R_2^2(8)$ ring. The outer acid groups link the molecules into layers by two sets of $R_4^4(16)$ rings (Fig. 2).

Compound (II) is the ammonium salt which crystallizes most readily from the reaction of excess ammonia with tricarballylic acid. The individual anions (Fig. 3) form double chains through short O9···H12^{i}—O12^{i} hydrogen bonds [2.518 (3) Å] in the **c** direction, crosslinked in the **a** direction by even shorter O6—H61···O6^{ii} bonds [2.456 (3) Å] (Fig. 4). The $R_4^4(30)$ ring thus formed from four anions provides a cavity for two NH_4^+ cations. These are hydrogen bonded to atoms O8^{iii} and O6^{iv} of one ring and O8 and O5^{ii} of the adjacent ring [2.87 (5) Å] in the **b** direction. Atom H61 lies on a special position at the centre of the O6···O6^{ii} bond. Thus, there are only half the protons required for COOH at C4. The O14 water molecule, also on a special position, must be formulated $\frac{1}{2}H_3O^+$, with disordered protons. Attempts to locate these protons were not successful. Atom O14 has contacts to two O9 atoms [2.907 (3) Å] and to two pairs of O11 atoms [2.818 (3) and 2.2906 (3) Å] and can thus link the double chains of anions in the **a** direction. [For compound (II); symmetry codes: (i) $x, y, 1+z$; (ii) $\frac{1}{2}-x, \frac{1}{2}-y, -z$; (iii) $x, 1-y, \frac{1}{2}+z$; (iv) $x, 1-y, z-\frac{1}{2}$.]

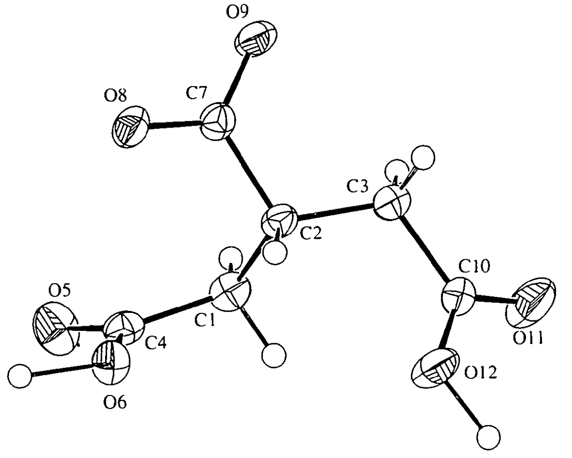


Fig. 3. View of the dihydrogen tricarballylate anion in compound (II) with ellipsoids plotted at the 50% probability level.

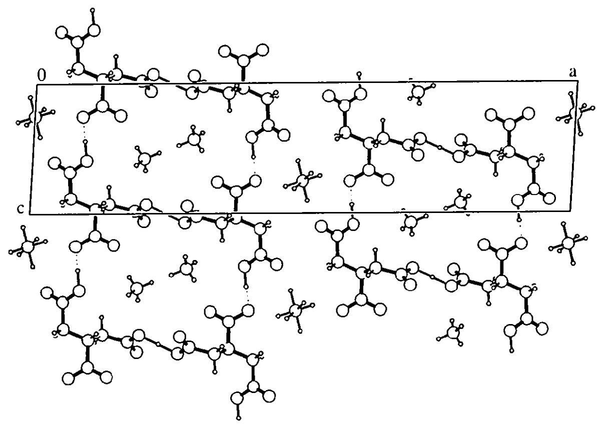


Fig. 4. Packing diagram for compound (II). View down **b** showing chains of $R_4^4(30)$ rings in the **c** direction enclosing NH_4^+ with disordered H_3O^+ at 0,0.1405,0.25.

As yet, structure quality crystals of 1,2,3,4-butanetetracarboxylic acid have not been obtained. In the tetraammonium salt, (III), the anion is found in the extended centrosymmetric (*trans*) form, with two very similar half anions in the asymmetric unit (Fig. 5). The six-C atom chain has an essentially flat herringbone conformation, with the inner carboxylate C4 groups staggered with respect to the adjacent protons and the outer carboxylate C3 groups arranged with atom O32 *trans* to H11. With no acidic protons for hydrogen bonding, the anions arrange in stacks parallel to **a**, with only van der Waals contacts. Fig. 6 shows that the NH_4^+ and H_2O groups connect these stacks through hydrogen bonds. Each H_2O molecule hydrogen bonds to carboxylate O31^{i} and O71^{ii} atoms at distances of 2.734 (2) and 2.777 (2) Å, respectively, and to NH_4^+ N12^{iii} and N9^{iv} atoms at distances of 2.799 (2) and 2.851 (2) Å, respectively. Two of the NH_4^+ cations form the expected four hydrogen bonds, but the other two each have five contacts in the range 2.73–2.95 Å. Although a description of this hydrogen bonding by network analysis would be possible, the result would be so complex as to be of very limited use. [For compound (III); symmetry codes: (i) $1-x, 1-y, 1-z$; (ii) $-x, 1-y, 1-z$; (iii) $1-x, 2-y, 1-z$; (iv) $x, 1+y, 1+z$.]

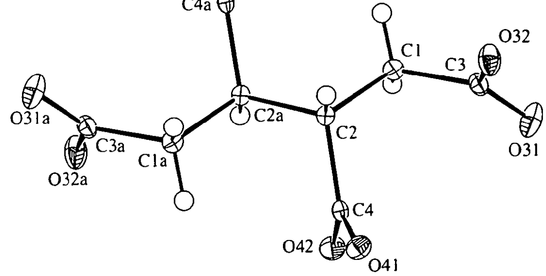


Fig. 5. View of the 1,2,3,4-butanetetracarboxylate anion in compound (III) with ellipsoids plotted at the 50% probability level.

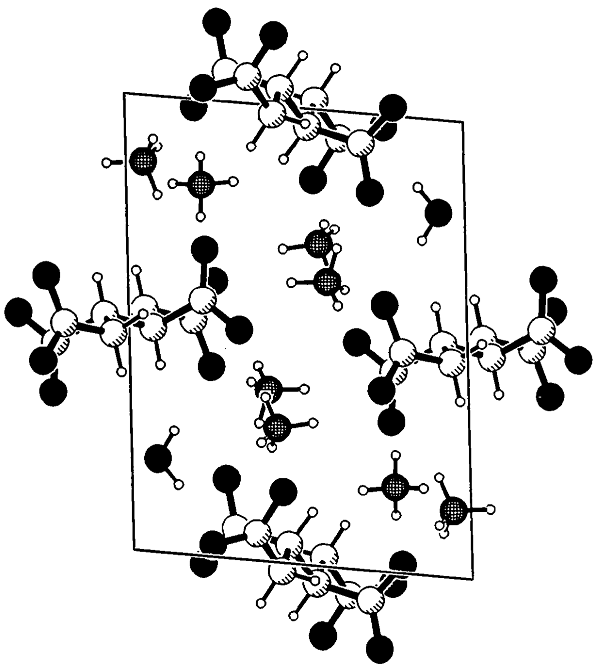


Fig. 6. The packing diagram for (III), viewed down **a** showing anion stacks parallel to **a** interconnected by hydrogen bonds to NH_4^+ and H_2O. C atoms are shaded, O atoms filled and N atoms netted.

Experimental

Compound (I), obtained from Aldrich, was recrystallized from water. Compounds (II) and (III) were prepared by the addition of excess saturated aqueous ammonia to the acid (1.0 mmol) in EtOH and allowing the solution to stand in air until crystals formed.

Compound (I)

Crystal data

$C_7H_{10}O_6$
$M_r = 190.15$
Triclinic
$P\overline{1}$
$a = 6.8350 (10)$ Å
$b = 6.995 (2)$ Å
$c = 8.5400 (10)$ Å
$\alpha = 86.770 (5)°$
$\beta = 88.663 (8)°$
$\gamma = 84.456 (13)°$
$V = 405.68 (14)$ Å^3
$Z = 2$
$D_x = 1.557$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 250 reflections
$\theta = 2–25°$
$\mu = 0.139$ mm^{-1}
$T = 150 (1)$ K
Prism
0.38 × 0.22 × 0.09 mm
Colourless

Data collection

Enraf–Nonius CAD-4 FAST diffractometer
Measurement method: area detector
Absorption correction: none
2233 measured reflections
1918 independent reflections

1159 observed reflections $[I > 2\sigma(I)]$
$R_{int} = 0.047$
$\theta_{max} = 30.02°$
$h = -6 \rightarrow 9$
$k = -9 \rightarrow 9$
$l = -5 \rightarrow 11$

Refinement

Refinement on F^2
$R(F) = 0.036$
$wR(F^2) = 0.117$
$S = 0.408$
1918 reflections
161 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0613P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = -0.03$
$\Delta\rho_{max} = 0.29$ e Å^{-3}
$\Delta\rho_{min} = -0.16$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

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

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

	x	y	z	U_{eq}
C1	0.1967 (2)	0.3353 (2)	0.6032 (2)	0.0238 (3)
C2	0.1897 (2)	0.2685 (2)	0.7781 (2)	0.0216 (3)
C3	0.2329 (2)	0.0478 (2)	0.8059 (2)	0.0245 (3)
C4	0.3707 (2)	0.2607 (2)	0.5077 (2)	0.0247 (3)
O5	0.3580 (2)	0.2059 (2)	0.37627 (13)	0.0385 (3)
O6	0.54112 (15)	0.2619 (2)	0.57612 (14)	0.0349 (3)
C7	0.3354 (2)	0.3672 (2)	0.8718 (2)	0.0241 (3)
O8	0.3482 (2)	0.5444 (2)	0.83800 (15)	0.0411 (3)
O9	0.4260 (2)	0.2743 (2)	0.9811 (2)	0.0481 (4)
C10	0.1006 (2)	−0.0630 (2)	0.7149 (2)	0.0227 (3)
O11	0.14593 (14)	−0.13538 (15)	0.59178 (12)	0.0305 (3)
O12	−0.0738 (2)	−0.0756 (2)	0.78150 (13)	0.0373 (3)
C13	−0.0159 (2)	0.3405 (2)	0.8419 (2)	0.0324 (3)

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

C1—C4	1.495 (2)	C4—O5	1.214 (2)
C1—C2	1.541 (2)	C4—O6	1.316 (2)
C2—C7	1.530 (2)	C7—O9	1.248 (2)
C2—C13	1.544 (2)	C7—O8	1.268 (2)
C2—C3	1.549 (2)	C10—O11	1.213 (2)
C3—C10	1.503 (2)	C10—O12	1.317 (2)
C4—C1—C2	117.48 (11)	O5—C4—C1	123.22 (13)
C7—C2—C1	111.05 (10)	O6—C4—C1	114.72 (12)
C7—C2—C13	105.49 (11)	O9—C7—O8	123.71 (13)
C1—C2—C13	106.75 (12)	O9—C7—C2	119.30 (12)
C7—C2—C3	108.67 (11)	O8—C7—C2	116.86 (12)
C1—C2—C3	112.94 (11)	O11—C10—O12	121.92 (13)
C13—C2—C3	111.70 (11)	O11—C10—C3	124.58 (12)
C10—C3—C2	112.83 (11)	O12—C10—C3	113.50 (12)
O5—C4—O6	122.05 (13)		
C4—C1—C2—C7	73.82 (14)	C2—C1—C4—O6	−43.9 (2)
C4—C1—C2—C13	−171.69 (11)	C1—C2—C7—O8	41.0 (2)
C4—C1—C2—C3	−48.5 (2)	C3—C2—C7—O8	165.86 (13)
C13—C2—C3—C10	65.7 (2)	C2—C3—C10—O12	−80.83 (15)

Compound (II)

Crystal data

$NH_4^+.C_6H_7O_6^-.\frac{1}{2}H_2O$
$M_r = 202.17$
Monoclinic
$C2/c$
$a = 30.9331 (12)$ Å
$b = 7.8035 (14)$ Å
$c = 7.4103 (3)$ Å
$\beta = 93.565 (4)°$
$V = 1785.3 (3)$ Å^3
$Z = 8$
$D_x = 1.504$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 250 reflections
$\theta = 2–25°$
$\mu = 0.138$ mm^{-1}
$T = 150 (1)$ K
Block
0.52 × 0.35 × 0.27 mm
Colourless

Data collection

Enraf–Nonius CAD-4 FAST diffractometer
Measurement method: area detector
Absorption correction: none
3797 measured reflections
1386 independent reflections
975 observed reflections $[I > 2\sigma(I)]$
$R_{\rm int} = 0.063$
$\theta_{\rm max} = 24.72°$
$h = -35 \rightarrow 35$
$k = -9 \rightarrow 5$
$l = -8 \rightarrow 8$

Refinement

Refinement on F^2
$R(F) = 0.040$
$wR(F^2) = 0.100$
$S = 0.889$
1381 reflections
174 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0437P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.09$
$\Delta\rho_{\rm max} = 0.29$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.18$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for* (II)

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

	x	y	z	$U_{\rm eq}$
C1	0.14488 (7)	0.1020 (3)	−0.0741 (3)	0.0275 (6)
C2	0.11991 (7)	0.2674 (3)	−0.0355 (3)	0.0226 (5)
C3	0.07362 (7)	0.2578 (4)	−0.1198 (3)	0.0297 (6)
C4	0.19270 (7)	0.1048 (3)	−0.0211 (3)	0.0257 (5)
O5	0.21067 (5)	−0.0170 (2)	0.0576 (2)	0.0394 (5)
O6	0.21305 (4)	0.2400 (2)	−0.0703 (2)	0.0284 (4)
C7	0.12184 (7)	0.2986 (3)	0.1689 (3)	0.0234 (5)
O8	0.15726 (5)	0.3384 (2)	0.2441 (2)	0.0328 (4)
O9	0.08760 (5)	0.2762 (2)	0.2519 (2)	0.0359 (5)
C10	0.06964 (7)	0.2427 (3)	−0.3234 (3)	0.0281 (6)
O11	0.03967 (6)	0.1620 (3)	−0.3981 (2)	0.0548 (6)
O12	0.09878 (5)	0.3180 (2)	−0.4115 (2)	0.0378 (5)
N13	0.20500 (8)	0.6007 (3)	0.0757 (4)	0.0313 (5)
O14	0	0.1405 (5)	1/4	0.0646 (8)

Table 4. *Selected geometric parameters (Å, °) for* (II)

C1—C4	1.507 (3)	C4—O6	1.292 (3)
C1—C2	1.540 (3)	C7—O8	1.238 (2)
C2—C3	1.528 (3)	C7—O9	1.270 (3)
C2—C7	1.532 (3)	C10—O11	1.224 (3)
C3—C10	1.510 (3)	C10—O12	1.288 (3)
C4—O5	1.230 (3)		
C4—C1—C2	115.8 (2)	O6—C4—C1	115.2 (2)
C3—C2—C7	113.0 (2)	O8—C7—O9	123.9 (2)
C3—C2—C1	110.5 (2)	O8—C7—C2	117.7 (2)
C7—C2—C1	109.1 (2)	O9—C7—C2	118.4 (2)
C10—C3—C2	115.4 (2)	O11—C10—O12	122.7 (2)
O5—C4—O6	123.4 (2)	O11—C10—C3	120.3 (2)
O5—C4—C1	121.3 (2)	O12—C10—C3	117.0 (2)
C4—C1—C2—C3	171.7 (2)	O6—C4—C1—C2	−46.7 (3)
C4—C1—C2—C7	−63.5 (3)	O8—C7—C2—C3	−167.5 (2)
C1—C2—C7—O8	69.1 (3)	C2—C3—C10—O12	−32.6 (3)

Compound (III)

Crystal data

$4NH_4^+.C_8H_6O_8^{4-}.H_2O$
$M_r = 320.31$
Triclinic
$P\overline{1}$
$a = 7.8714\ (7)$ Å
$b = 8.602\ (2)$ Å
$c = 12.043\ (2)$ Å
$\alpha = 94.454\ (8)°$
$\beta = 108.24\ (2)°$
$\gamma = 94.402\ (11)°$
$V = 767.7\ (2)$ Å^3
$Z = 2$
$D_x = 1.386$ Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 250 reflections
$\theta = 2$–$25°$
$\mu = 0.124$ mm^{-1}
$T = 150\ (1)$ K
Block
$0.61 \times 0.47 \times 0.32$ mm
Colourless

Data collection

Enraf–Nonius CAD-4 FAST diffractometer
Measurement method: area detector
Absorption correction: none
3874 measured reflections
3433 independent reflections
2151 observed reflections $[I > 2\sigma(I)]$
$R_{\rm int} = 0.048$
$\theta_{\rm max} = 29.70°$
$h = -8 \rightarrow 10$
$k = -11 \rightarrow 6$
$l = -16 \rightarrow 16$

Refinement

Refinement on F^2
$R(F) = 0.035$
$wR(F^2) = 0.120$
$S = 0.368$
3431 reflections
281 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.1000P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.32$
$\Delta\rho_{\rm max} = 0.27$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.18$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 5. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for* (III)

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

	x	y	z	$U_{\rm eq}$
C1	0.2224 (2)	0.4371 (2)	−0.01910 (10)	0.0125 (2)
C2	0.0772 (2)	0.46019 (14)	0.03956 (10)	0.0108 (2)
C3	0.3824 (2)	0.3654 (2)	0.05933 (11)	0.0136 (3)
C4	0.0030 (2)	0.30217 (15)	0.06636 (10)	0.0110 (2)
C5	−0.2234 (2)	0.0470 (2)	0.52916 (11)	0.0144 (3)
C6	−0.0544 (2)	0.07116 (15)	0.49100 (10)	0.0129 (3)
C7	−0.3268 (2)	0.1912 (2)	0.51596 (11)	0.0144 (3)
C8	0.0647 (2)	0.21956 (15)	0.55963 (11)	0.0138 (3)
O31	0.41649 (14)	0.23364 (12)	0.02528 (8)	0.0222 (2)
O32	0.47097 (14)	0.44581 (12)	0.15509 (8)	0.0205 (2)
O41	−0.08862 (13)	0.20461 (11)	−0.01844 (8)	0.0156 (2)
O42	0.03655 (13)	0.27840 (11)	0.17272 (7)	0.0154 (2)
O71	−0.37394 (14)	0.24115 (13)	0.41655 (8)	0.0225 (2)
O72	−0.3593 (2)	0.25521 (13)	0.60307 (8)	0.0244 (3)
O81	0.09836 (15)	0.32618 (12)	0.50189 (8)	0.0218 (2)
O82	0.1191 (2)	0.22860 (12)	0.66982 (8)	0.0236 (3)
N9	0.1029 (2)	0.05137 (15)	−0.14732 (10)	0.0172 (2)
N10	0.3258 (2)	0.4097 (2)	0.37652 (10)	0.0168 (2)
N11	0.1789 (2)	0.5673 (2)	0.70502 (10)	0.0173 (3)
N12	0.4278 (2)	0.7782 (2)	0.18792 (11)	0.0189 (3)
O13	0.39221 (15)	0.92308 (13)	0.79544 (9)	0.0212 (2)

Table 6. *Selected geometric parameters (Å, °) for* (III)

C1—C3	1.524 (2)	C5—C7	1.527 (2)
C1—C2	1.537 (2)	C5—C6	1.542 (2)
C2—C4	1.535 (2)	C6—C8	1.536 (2)

C2—C2^i	1.535 (2)	C6—C6^{ii}	1.538 (3)
C3—O31	1.252 (2)	C7—O72	1.253 (2)
C3—O32	1.262 (2)	C7—O71	1.258 (2)
C4—O41	1.257 (2)	C8—O81	1.254 (2)
C4—O42	1.2607 (14)	C8—O82	1.254 (2)
C3—C1—C2	112.30 (9)	C7—C5—C6	111.67 (11)
C1—C2—C4	110.57 (10)	C8—C6—C6^{ii}	109.92 (13)
C1—C2—C2^i	110.72 (12)	C8—C6—C5	110.01 (10)
C4—C2—C2^i	109.69 (13)	C6^{ii}—C6—C5	111.83 (13)
O31—C3—O32	125.04 (12)	O72—C7—O71	122.99 (13)
O31—C3—C1	118.74 (11)	O72—C7—C5	119.58 (12)
O32—C3—C1	116.22 (12)	O71—C7—C5	117.43 (11)
O41—C4—O42	123.76 (12)	O81—C8—O82	123.89 (13)
O41—C4—C2	118.42 (10)	O81—C8—C6	117.80 (11)
O42—C4—C2	117.81 (11)	O82—C8—C6	118.29 (11)
O31—C3—C1—C2	117.12 (13)	O71—C7—C5—C6	55.0 (2)
C3—C1—C2—C2^i	177.27 (12)	C7—C5—C6—C6^{ii}	177.63 (12)
C3—C1—C2—C4	−60.95 (13)	C7—C5—C6—C8	55.19 (14)
C1—C2—C4—O41	−68.07 (14)	C5—C6—C8—O81	−121.02 (13)

Symmetry codes: (i) $-x, 1-y, -z$; (ii) $-x, -y, 1-z$.

Using the area detector system, cell dimensions were refined from 250 reflections selected from two regions 90° apart and 5° wide at $\kappa = 0°$. For all compounds, the intensity standards were not measured by the area detector. Possible variations were checked by comparing intensities of common or symmetry-related reflections as they occurred during data collection. In this case, no variation was noted.

For all compounds, data collection: *MADNES* (Pflugrath & Messerschmidt, 1991); cell refinement: *MADNES*; data reduction: *MADNES*; program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *PLATON*92 (Spek, 1992*a*) and *PLUTON*92 (Spek, 1992*b*)

The authors thank EPSRC and Professor M. Hursthouse (University of Wales, Cardiff) for the data collections.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the IUCr (Reference: LI1138). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1996). C**52**, 736–739

3,12-Dimesityl-6,8-dimethyl-5,10-dioxa-1,2,4,11-tetraazatricyclo[7.3.1.0^{2,6}]trideca-3,7,11-triene and 3,12-Dimesityl-6,8,13-trimethyl-5,10-dioxa-1,2,4,11-tetraazatricyclo-[7.3.1.0^{2,6}]trideca-3,7,11-triene

M. Pierrot,[a] M. Giorgi,[a] M. El Messaoudi,[b]
A. Hasnaoui,[b] M. El Aatmani[c] and J. P. Lavergne[d]

[a]*LBS-URA 1409, Centre Scientifique Saint-Jérôme C12, 13397 Marseille, France,* [b]*Laboratoire des Substances Naturelles et Hétérocycles, Faculté des Sciences, Université Cadi Ayyad, BP S15 Marrakech, Morocco,* [c]*Laboratoire de Chimie du Solide Minéral, Faculté des Sciences, Université Cadi Ayyad, BP S15 Marrakech, Morocco, and* [d]*Laboratoire de Synthèse et d'Etudes physicochimiques d'aminoacides et peptides, URA 468, Université de Montpellier II, 34095 Montpellier, CEDEX 5, France*

(*Received 21 June 1995; accepted 21 September 1995*)

Abstract

X-ray crystallographic study of the title compounds, $C_{27}H_{32}N_4O_2$ and $C_{28}H_{34}N_4O_2$, respectively, allows us to establish the structures of the diadducts obtained from the condensation of nitrile oxides and 1,2-diazepines. The conformations of the five-, six- and seven-membered rings forming the tridecatriene are described.

Comment

As part of our program on the synthesis of bi- or triheterocyclic systems which have biological activity, we are studying cycloaddition reactions on seven-membered heterocycles (Hasnaoui, El Messaoudi & Lavergne, 1985; El Messaoudi, Hasnaoui, El Mouhtadi, Goupil & Lavergne, 1988; Hasnaoui, Baouid & Lavergne, 1991; El Messaoudi, Hasnaoui, El Mouhtadi & Lavergne, 1992; Baouid, Benharref, Hasnaoui & Lavergne, 1994). In a recent publication (El Messaoudi, Hasnaoui & Lavergne, 1994; El Messaoudi, Hasnaoui, Lavergne & Pierrot, 1995), we have described, in particular, the 1,3-dipolar cycloadditions of the 1,2-diazepines (I) and (II) with nitrile oxides, which lead to the title compounds (III) and (IV), respectively. X-ray diffraction study of compounds (III) and (IV) allows us to assign, without ambiguity, a structure of type *A*.