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## Methanetriacetic and methylmethanetriacetic acids, their precursors and derivatives: NMR and X-ray diffraction studies

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The NMR spectra and crystal structures of triacid 2b, triamide 4b and diastereomers 7, 8 were studied; the crystal structure of 2b is the first example of an H-bonded totally interlocked and percatenated homochiral structure.

Methanetriacetic acid (MTA) and methylmethanetriacetic acid (MMTA) are of great interest as the  $C_3$  symmetric synthons.<sup>1</sup> However, the structural and spectroscopic characteristics of MTA, MMTA and their derivatives were not described. Only limited <sup>1</sup>H NMR data for the  $\alpha, \alpha', \alpha''$ -tribromo-substituted trimethyl ester of MTA was reported.<sup>2</sup>

Starting from MTA, tris(benzoylmethyl)methane,<sup>1(h)</sup> tris(diazoacetonyl)methane<sup>1(h),(k)</sup> and tris(haloacetonyl)methanes (Hal = = Cl, Br)<sup>1(h)</sup> were synthesised. Two latter compounds were used for synthesis of cage compounds: 2,4,9-trioxaadamantanes,<sup>1(h)</sup> 'bullvalenetrione' and bullvalene.<sup>1(k)</sup> A chiral tridentate tris(oxazolidine) ligand was synthesised based on MTA for the efficient copper-mediated asymmetric allilic oxidation of cycloalkenes.<sup>3(a)</sup> MTA is also used as a linker to control the assembly and cyclooligomerization of amino acids.<sup>3(b)</sup> Based on MMTA and  $C_3$  symmetric tripodal aminopyridine receptors, two types of supramolecular complexes were obtained and characterised by NMR spectroscopy, XRD analysis and high-level *ab initio* calculations.<sup>4</sup>

In this work, we reproduced the preparation of MTA, MMTA and their known derivatives<sup>1,2</sup> and synthesised new compounds **4a,b, 6** (Scheme 1).<sup> $\dagger$ </sup>

All of the products were characterised by NMR spectroscopy.<sup>†</sup> The NMR spectra of compounds **1a,b**, **6** and **8** show diastereotopy of all the protons ( $H_a$ ,  $H_b$  in **6**) and carbons of substituents **A** and **B** in the field of the asymmetric centre of the substituent **C**. Whereas in the case of homochiral isomer **7** the protons and carbons of the three CHCO<sub>2</sub>Me substituents are equivalent. This convincing criterion of the configuration assignment of **7**, **8** diastereomers is unambiguosly proven by an XRD study.

The magnitudes of vicinal coupling constants  $({}^{3}J_{\rm HH})$  for **8** and **7** differ significantly (8.2, 4.0 and 4.5 Hz, respectively),<sup>†</sup> witnessing a substantial conformation change of one of the substituents (**A** or **B**) in solution. Addition of the chiral shift



**Scheme 1** *Reagents and conditions*: i, MeONa in MeOH (EtONa in EtOH for **1b**), boiling for 12 h (6 h for **1b**), then 12 h at 20 °C, neutralization by MeCO<sub>2</sub>H, separation of MeCO<sub>2</sub>Na and vacuum distillation; ii, 20% HCl, boiling for 12 h and 35 h for **2a** and **2b**, respectively; iii, excess SOCl<sub>2</sub> in abs. MeOH, 0.5 h at 25 °C, boiling for 5 h, and vacuum distillation; iv, excess NH<sub>3</sub> in MeOH (cat. MeONa), 1 week at 25 °C for **4a**, 2 weeks at 25 °C, 20 h at 90 °C in a sealed glass tube, and 2 weeks at 25 °C for **4b**; v, excess SOCl<sub>2</sub> in CCl<sub>4</sub>, boiling for 15 h, 3 days at 25 °C and recrystallization from CCl<sub>4</sub>; vi, excess NH<sub>3</sub> in MeCN, 1 h at 25 °C, separation of NH<sub>4</sub>Cl, and evaporation of the solvent in a vacuum; vii, PCl<sub>5</sub>, Br<sub>2</sub>, heating under reflux for 42 h, then 12 h at 20 °C, and isolation of the products by crystallization.

reagent  $Eu(tfc)_3$  to the racemic solution of 7 results in splitting of the <sup>1</sup>H NMR spectrum to the full sets of the signals of two enantiomers.<sup>†</sup>

In order to analyse the crystal packing of this tripodal structures, XRD analysis was performed. Unfortunately, in the case of **2a**, **3a**, **4a** and **6**, single crystals suitable for XRD were not obtained; thus, the analysis of supramolecular organization in crystals was performed only for **2b** and **4b**.

Surprisingly, the achiral molecules of **2b** crystallise in the chiral space group  $P4_32_12$  with two independent molecules per unit cell. Each of carboxylic groups participate in two intermolecular O–H…O bonds [2.621(4)–2.691(4) Å] with the formation of expected H-bonded rings. All of these H-bonded rings are coplanar and the molecules are assembled into infinite

<sup>†</sup> NMR spectra were measured on a Bruker WM-400 spectrometer (<sup>1</sup>H 400.13 MHz; <sup>13</sup>C 100.62 MHz); melting points were determined on a Boetius heating stage and corrected.

**1a**: yield 63%, bp 180–185 °C (3–4 Torr) [lit.,<sup>1(g)</sup> bp 203–205 °C (11 Torr)]. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 2.56 (m, 2H, A-CH<sub>2</sub>, AB part of ABX spectrum,  $\Delta \nu$  29.0 Hz, <sup>2</sup>J<sub>AB</sub> –16.8 Hz, <sup>3</sup>J<sub>AX</sub> 8.4 Hz, <sup>3</sup>J<sub>BX</sub> 5.5 Hz), 2.58 (m, 2H, B-CH<sub>2</sub>, AB part of ABX spectrum,  $\Delta \nu$  50.5 Hz, <sup>2</sup>J<sub>AB</sub> –17.1 Hz, <sup>3</sup>J<sub>AX</sub> 8.7 Hz, <sup>3</sup>J<sub>BX</sub> 5.4 Hz), 3.07 (m, 1H, HC, X part of ABX spectra), 3.68 (s, 3H, A-Me), 3.69 (s, 3H, B-Me), 3.82 (s, 3H, C-MeO), 4.19 (d, 1H, HCCN, <sup>3</sup>J 4.7 Hz).

**1b**: yield 45%, bp 185–188 °C (17 Torr) [lit.,<sup>1(b)</sup> bp 210 °C (21 Torr)]. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 1.25 (t, 3H, Me, <sup>3</sup>J 7.1 Hz), 1.26 (t, 3H, Me, <sup>3</sup>J 7.1 Hz), 1.32 (t, 3H, Me, <sup>3</sup>J 7.1 Hz), 1.34 (s, 3H, Me), 2.72 (br. s, 2H, CH<sub>2</sub>), 2.80 (m, 2H, CH<sub>2</sub>, AB spectrum,  $\Delta v$  32.0 Hz, <sup>2</sup>J –16.1 Hz), 4.130 (q, 2H, CH<sub>2</sub>O, <sup>3</sup>J 7.1 Hz), 4.135 (q, 2H, CH<sub>2</sub>O, <sup>3</sup>J 7.1 Hz), 4.26 (q, 2H, CH<sub>2</sub>O, <sup>3</sup>*J* 7.1 Hz), 4.49 (s, 1H, HC). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>) δ: 0.77 (t, 3H, C-Me, <sup>3</sup>J 7.1 Hz), 0.87 (t, 3H, A-Me, <sup>3</sup>J 7.2 Hz), 0.88 (t, 3H, B-Me, <sup>3</sup>J 7.2 Hz), 1.33 (s, 3H, Me), 2.82 (br. s, 2H, CH<sub>2</sub>), 2.86 (m, 2H, CH<sub>2</sub>, AB spectrum,  $\Delta v$  27.5 Hz,  $^{2}J$  –16.3 Hz), 3.71 (q,  $\tilde{2}$ H, CH<sub>2</sub>O,  $^{3}J$  7.1 Hz), 3.832 (q, 2H, CH<sub>2</sub>O, <sup>3</sup>J 7.1 Hz), 3.836 (q, 2H, CH<sub>2</sub>O, <sup>3</sup>J 7.1 Hz), 4.52 (s, 1H, HC). <sup>13</sup>C NMR ( $C_6D_6$ )  $\delta$ : 13.83 (q, C-Me, <sup>1</sup>J 126.5 Hz), 14.10 (q, A,B-Me, <sup>1</sup>J 126.2 Hz), 22.91 (q, D-Me, <sup>1</sup>J 126.5 Hz), 37.86 (br. s, CMe-D), 40.03 (t, A-CH<sub>2</sub>, <sup>1</sup>J 128.5 Hz), 40.74 (t, B-CH<sub>2</sub>, <sup>1</sup>J 128.4 Hz), 45.42 (d, CH, <sup>1</sup>J 138.10 Hz), 60.57 (t, A-CH<sub>2</sub>O, <sup>1</sup>J 146.7 Hz), 60.61 (t, B-CH<sub>2</sub>O, <sup>1</sup>J 146.6 Hz), 62.61 (t, C-CH<sub>2</sub>O, <sup>1</sup>J 148.0 Hz), 115.68 (d, CN, <sup>2</sup>J 9.7 Hz), 165.01 (d, C-CO, <sup>2</sup>J 8.3 Hz), 170.56 (s, A,B-CO).

**2a**: yield 70%, mp 128 °C (Et<sub>2</sub>O) (lit.,<sup>1(g)</sup> mp 126 °C; lit.,<sup>4(a)</sup> mp 127–128 °C; lit.,<sup>4(b)</sup> mp 125.6 °C). <sup>1</sup>H NMR ([<sup>2</sup>H<sub>6</sub>]acetone)  $\delta$ : 2.51 (d, 6H, 3CH<sub>2</sub>, <sup>3</sup>J 6.6 Hz), 2.69 (hept., 1H, HC, <sup>3</sup>J 6.6 Hz).

**2b**: yield 92%, mp 170–172 °C (Et<sub>2</sub>O) (lit., $^{1(g)}$  mp 172 °C). <sup>1</sup>H NMR (CD<sub>3</sub>OD)  $\delta$ : 1.20 (s, 3H, Me), 2.61 (s, 6H, 3CH<sub>2</sub>), 5.15 (br. s, CO<sub>2</sub>H, H<sub>2</sub>O).

**3a**: yield ~100%, bp 156 °C (13 Torr). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 2.45 (d, 6H, 3CH<sub>2</sub>, <sup>3</sup>J 6.6 Hz), 2.75 (hept., 1H, HC, <sup>3</sup>J 6.6 Hz), 3.65 (s, 9H, 3MeO).

**3b**: yield 58%, bp 152–153 °C (10 Torr). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 1.18 (s, 3H, Me), 2.62 (s, 6H, 3CH<sub>2</sub>), 3.65 (s, 9H, 3MeO).

**4a**: yield ~100%, mp 248–252 °C (MeOH). <sup>1</sup>H NMR ([<sup>2</sup>H<sub>6</sub>]DMSO)  $\delta$ : 2.07 (d, 6H, 3CH<sub>2</sub>, <sup>3</sup>*J* 6.0 Hz), 3.40 (hept., 1H, HC, <sup>3</sup>*J* 6.0 Hz), 6.77 and 7.30 (2s, 6H, 3NH<sub>2</sub>).

**4b**: yield 10%, mp 232–234 °C (MeOH). <sup>1</sup>H NMR ([<sup>2</sup>H<sub>6</sub>]DMSO)  $\delta$ : 1.01 (s, 3H, Me), 2.16 (s, 6H, 3CH<sub>2</sub>), 7.00 and 7.68 (2s, 6H, 3NH<sub>2</sub>).

**5**: yield 40%, mp 93–94 °C (CCl<sub>4</sub>). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 1.27 (s, 3H, Me), 2.80 (m, 4H, 2CH<sub>2</sub>, AB spectrum,  $\Delta\nu$  36.2 Hz, <sup>2</sup>*J* –16.7 Hz), 3.06 (s, 2H, CH<sub>2</sub>COCl).

**6**: yield 50%, mp 193–197 °C (MeCN). <sup>1</sup>H NMR ([<sup>2</sup>H<sub>6</sub>]DMSO) δ: 1.04 (s, 3H, Me), 2.21 (m, 4H, 2CH<sub>2</sub>, AB spectrum,  $\Delta\nu$  24.4 Hz, <sup>2</sup>J –13.3 Hz), 2.35 (s, 2H, CH<sub>2</sub>CO<sup>-</sup>), 3.4 (br. s, NH<sub>4</sub><sup>+</sup>, H<sub>2</sub>O), 6.97 and 7.70 (2s, 4H, 2NH<sub>2</sub>).

7: total yield of **7** + **8** is equal to 58%, for **7**, yield 30%; needle-shaped crystals, mp 97–98 °C (isopropanol) (lit., <sup>2</sup> mp 97–98 °C). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$ : 3.27 (s, 9H, 3MeO), 3.82 (q, 1H, HC, <sup>3</sup>J 4.5 Hz), 5.16 (d, 3H, 3CHBr, <sup>3</sup>J 4.5 Hz); a 9 mg sample of **7** added with 0.45 mg of Eu(tfc)<sub>3</sub>, <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$ : 3.32, 3.34 (2s, 9H, 3Me,  $\Delta \nu$  8.0 Hz), 4.13, 4.18 (2br. q, 1H, HC,  $\Delta \nu$  20.0 Hz), 5.29, 5.31 (2d, 3H, 3CHBr,  $\Delta \nu$  8.0 Hz, <sup>3</sup>J 4.4 and 4.3 Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$ : 46.20 (ddt, CHBr, <sup>1</sup>J 156.2 Hz, <sup>2</sup>J 4.4 Hz, <sup>3</sup>J 4.6 Hz), 46.36 (dq, CH, <sup>1</sup>J 138.0 Hz, <sup>2</sup>J 3.2 Hz), 53.30 (q, MeO, <sup>1</sup>J 148.4 Hz), 168.16 (dq, CO, <sup>2</sup>J 4.8 Hz, <sup>3</sup>J 4.5 Hz).

**8**: yield 20%, prismatic crystals, mp 111–112 °C ( $C_6H_6$ ) (lit.,<sup>2</sup> mp 113–114 °C). <sup>1</sup>H NMR ( $C_6D_6$ )  $\delta$ : 3.19 (s, 3H, **A**-MeO), 3.23 (s, 3H, **B**-MeO), 3.26 (s, 3H, **C**-MeO), 4.01 (dt, 1H, CH, <sup>3</sup>J 8.2 Hz, <sup>3</sup>J 4.0 Hz), 4.98 (d, 1H, **C**-CH, <sup>3</sup>J 8.2 Hz), 5.01 (d, 1H, **A**-CH, <sup>3</sup>J 4.0 Hz), 5.11 (d, 1H, **B**-CH, <sup>3</sup>J 4.0 Hz). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>)  $\delta$ : 45.37, 45.75, 45.88 (CHBr), 48.40 (CH), 53.48, 53.60, 53.67 (MeO), 167.2, 167.4, 168.3 (CO).



Figure 1 H-bonded layer of the 'seine' type in the crystal of 2b.

layers of the 'seine type' with a distance between parallel layers equal to 5.946 Å. The unit of this seine is a regular rectangle  $(8.85 \times 17.45 \text{ Å})$  composed of six molecules of **2b** (Figure 1). Due to high symmetry in a crystal, there are two series of equivalent orthogonal layers parallel to the *ac* and *bc* crystallographic planes, respectively (Figure 2). As the result, the crystal of **2b** can be described as the three-dimensional totally interpenetrated orthogonal infinite seines (Figure 3). Clearly, the 'stitch' of this 'supramolecular H-bonded netting' is the catenane (Figure 4); thus, compound **2b** can be regarded as a self-assembled homochiral infinite polycatenane.



Figure 2 The orthogonality of H-bonded layers (see Figure 1) in the crystal of 2b.

Although the catenanes and interpenetrated structures were described previously, the chiral supramolecular organization including all of the above features was unknown before.<sup>5(a),(b)</sup> Similar structures described are achiral: H-bonded (trimesic acid)<sup>5(c)</sup> and metal-coordinated.<sup>5(d)-(g)</sup> Thus, we found previously that a bicyclic chiral bis(lactam) crystallises in the chiral space group  $I4_1$  (Z' = 3) with the formation of an unbalanced threefold interpenetrated diamondoid H-bonded network.<sup>6</sup> This compound undergoes spontaneous resolution by crystallization.<sup>6</sup> Recently, the spontaneous resolution of two covalently bonded catenanes was described.<sup>7</sup>



Figure 3 Schematic view of the interpenetration of the H-bonded layers in 2b.



Figure 4 Catenane element in the crystal of 2b.

In a crystal of 4b, NH<sub>2</sub> groups are involved in not only intermolecular [2.927(3)-2.935(3) Å] but also intramolecular H-bonds [2.884(3)–3.043(3) Å] probably, due to an excess of proton donors over proton acceptors (Figure 5). The intermolecular H-bonds assemble molecules into a three-dimensional network

In order to obtain direct information on the configuration of asymmetric centres in 7 and 8, XRD analysis<sup>‡</sup> was undertaken.

The XRD of 7 and 8 demonstrated that both compounds crystallise as racemates; in 7, the configurations of all centres were the same (S,S,S or R,R,R) (Figure 5), while 8 is characterised by (S,S,R) or (R,R,S) configuration (Figure 6). Compound 7 crystallises in space group  $P2_1/c$  with two independent molecules the difference in the geometry of which is negligible.

Note that, although 7 and 8 are different diastereomers, the mutual orientation of Br and the C=O group in CHBr-CO<sub>2</sub>Me fragments is practically the same (Figure 6). Thus, the torsion angles Br-C-C=O for three chains in 7 and 8 are equal to



Figure 5 General view of 4b.

ŧ Crystallographic data for 2b, 4b, 7, 8. Intensities of reflections for 4b, 7 and 8 were measured on a Smart 1000 CCD diffractometer at 120 K  $[\lambda(MoK\alpha) = 0.71072 \text{ Å}, \omega$ -scans] and for **2b** at Siemens P3/PC diffractometer at 298 K [ $\lambda$ (MoK $\alpha$ ) = 0.71072 Å,  $\theta$ /2 $\theta$ -scans]. The structures were solved by direct method and refined by the full-matrix leastsquares technique against  $F^2$  in the anisotropic-isotropic approximation.

**2b**  $(C_8H_{12}O_6)$  at 298 K is tetragonal, space group  $P4_32_12$  (or  $P4_12_12$ ), a = 11.893(2), c = 27.113(5) Å, V = 3835(1) Å<sup>3</sup>, Z = 16 (Z' = 2), M = 100= 204.18,  $d_{\text{calc}} = 1.415 \text{ g cm}^{-3}$ ,  $\mu(\text{MoK}\alpha) = 1.23 \text{ cm}^{-1}$ , F(000) = 1728,  $wR_2 = 0.1210$  and GOF = 1.000 for 3080 independent reflections with arrow 3 (a) Y. Kohmura and T. Katsuki, Tetrahedron Lett., 2000, 41, 3941;  $2\theta < 50^\circ$ ,  $R_1 = 0.0393$  for 2368 observed reflections with  $I > 2\sigma(I)$ .

**4b** (C<sub>8</sub>H<sub>15</sub>N<sub>3</sub>O<sub>3</sub>) is monoclinic, space group  $P2_1/n$ , a = 6.692(2), b == 6.328(2), c = 23.935(7) Å,  $\beta = 94.92(2)^{\circ}$ , V = 1009.8(5) Å<sup>3</sup>, Z = 4 (Z' = 1), M = 201.23,  $d_{\text{calc}} = 1.324$  g cm<sup>-3</sup>,  $\mu$ (MoK $\alpha$ ) = 1.02 cm<sup>-1</sup>, F(000) = 432,  $wR_2 = 0.0895$  and GOF = 1.000 for 2676 independent reflections with  $2\theta < 58^\circ$ ,  $R_1 = 0.0417$  for 2219 observed reflections with  $I > 2\sigma(I)$ .

7 ( $C_{10}H_{13}Br_{3}O_{6}$ ) is monoclinic, space group  $P2_{1}/c$ , a = 7.312(2), b = 100= 16.087(3), c = 25.131(5) Å,  $\beta = 94.818(5)^{\circ}$ , V = 2945.7(1) Å<sup>3</sup>, Z = 8 $(Z' = 2), M = 468.93, d_{calc} = 2.115 \text{ g cm}^{-3}, \mu(\text{MoK}\alpha) = 8.234 \text{ cm}^{-1}, F(000) = 8.234 \text{ cm}^{-1}$ = 1808,  $wR_2$  = 0.1685 and GOF = 1.075 for 4161 independent reflections with  $2\theta < 54^\circ$ ,  $R_1 = 0.0743$  for 3420 observed reflections with  $I > 2\sigma(I)$ .

8 ( $C_{10}H_{13}Br_{3}O_{6}$ ) is orthorhombic, space group  $Pna2_{1}$ , a = 12.321(2), b = 15.812(2), c = 7.457(1) Å, V = 1452.9(4) Å<sup>3</sup>, Z = 4 (Z' = 1), M = 468.93,  $d_{\text{calc}} = 2.144 \text{ g cm}^{-3}, \mu(\text{MoK}\alpha) = 8.347 \text{ cm}^{-1}, F(000) = 904, wR_2 = 0.0670$ and GOF = 1.057 for 6292 independent reflections with  $2\theta < 60^\circ$ ,  $R_1 = 1000$ = 0.0331 for 4457 observed reflections with  $I > 2\sigma(I)$ .

All calculations were performed using SHELXTL PLUS 5.0.

Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). These data can be obtained free of charge via www.ccdc.cam.uk/ conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or deposit@ccdc.cam.ac.uk). Any request to the CCDC for data should quote the full literature citation and CCDC reference numbers 283410-283413. For details, see 'Notice to Authors', Mendeleev Commun., Issue 1, 2005.



Figure 6 General view of 7 (one independent molecule is shown) and 8.

23.3, 7.9, 97.5 and 22.1, 3.8, 92.5°, respectively. In addition, the H–C(1)–C–H torsion angles in 7 and 8 are also very close to each other and equal to 72, 91, 180 and 63, 105, 175°, respectively, witnessing the significant difference from the conformation in solution<sup>†</sup> established on the basis of the vicinal spin coupling constants  ${}^{3}J_{\rm HH}$ .

The analysis of crystal packing demonstrated that molecules are assembled into a three-dimensional framework (7) and chains (8) by means of C-Br···Br and C-Br···O contacts. In spite of the acidity of central hydrogen atoms in 7 and 8, all intermolecular C-H…Br distances correspond to typical van der Waals contacts. Taking into account that the type and strengths of intermolecular contacts in 7 and 8 are different, it is assumed that the similarities in conformation are governed by intramolecular C-H···O=C and C-H···Br contacts.

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