^{1}H NMR (CDCl$_3$), δ: 1.92 (s, 4 H, 2 CH$_2$); 3.82 (s, 12 H, 4 MeO). ^{13}C NMR (CDCl$_3$), δ: 28.3 (t, CH$_2$, ^1J = 133.7 Hz); 53.5 (q, MeO, ^1J = 148.2 Hz); 71.0 (s, CN$_3$); 167.16 (s, CO).

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3,7-Diaza-2,6-dioxobicyclo[3.3.1]nonane-1,5-dicarboxylates: complete autoassembly and NMR studies

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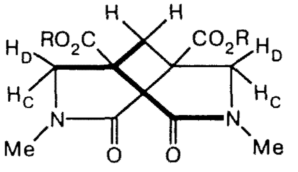
To develop further the principle of complete autoassembly of cage structures,[1] we have studied the synthesis of the bicyclic dilactam **1a** (*cf.* the known data[2]) by aminomethylation of methylenebismalonate.[3] The intermediate formation of the corresponding diamino tetraester was confirmed by the preparation of the sterically hindered analog **2** from ethylenebismalonate[3] under the same conditions (Scheme 1).

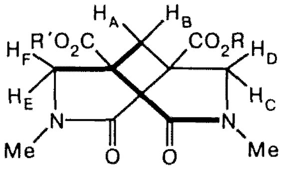
Diester **1a** readily undergoes transesterification to give its analog **1b** (MeOH/MeONa, 0.5 h at 20 °C, yield 84 %, m.p. 205—207 °C). Exhaustive alkaline hydrolysis of diester **1a** gave derivatives **1c**,**d**, and partial hydrolysis of **1a**,**b** yielded compounds **3a**,**b** and **4a**,**b**.

The compositions and structures of compounds **1**—**4** were confirmed by the data of elemental analysis and ^{1}H and ^{13}C NMR spectroscopy.



1b—d

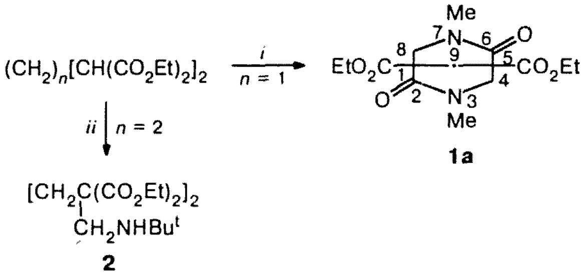
R = Me (**1b**), K (**1c**), H (**1d**)



3a,b, 4a,b

R = Et, R′ = K (**3a**), H (**3b**)
R = Me, R′ = Na (**4a**), H (**4b**)

Scheme 1



Reagents and conditions: *i.* 1 equiv. of 1,3,5-trimethylhexahydro-1,3,5-triazine in the presence of CF$_3$CO$_2$H, 20 h at 100 °C. *ii.* 1 equiv. of 1,3,5-tris(*tert*-butyl)hexahydro-1,3,5-triazine under the conditions described in *i.*

1a. Yield 75 %. M.p. 103—104 °C (*cf.* Ref. 2). **2.** Yield 75 %. M.p. 80 °C. ^{1}H NMR (CD$_3$OD), δ: 1.06 (s, 18 H, 2 Bu^t); 1.25 (t, 12 H, 4 Me, ^3J = 7.0 Hz); 1.83 (s, 4 H, 2 CH$_2$); 3.0 (s, 4 H, 2 CH$_2$N); 4.17 (q, 8 H, 4 CH$_2$O, ^3J = 7.0 Hz). ^{13}C NMR (CDCl$_3$), δ: 13.96 (qt, $\underline{C}$H$_3$CH$_2$O, ^1J = 127.2 Hz, ^2J = 2.2 Hz); 25.75 (tt, (CH$_2$)$_2$, ^1J = 132.2 Hz, ^2J = 3.6 Hz); 28.74 (q.sept., $\underline{Me}_3$C, ^1J = 125.0 Hz, ^3J = 4.4 Hz); 43.93 (t, CH$_2$N, ^1J = 138.1 Hz); 49.85 (br.s, $\underline{C}$(CO$_2$Et)$_2$); 58.22 (s, $\underline{C}$Me$_3$); 60.9 (tq, CH$_2$O, ^1J = 148.2 Hz, ^2J = 4.4 Hz); 170.83 (br.s, CO). Yield of the picrate 60 %, m.p. 177—178 °C. Found (%): N, 11.21. C$_{38}$H$_{54}$O$_{22}$N$_8$. Calculated (%): N, 11.49.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 4, pp. 1037—1039, April, 1996.

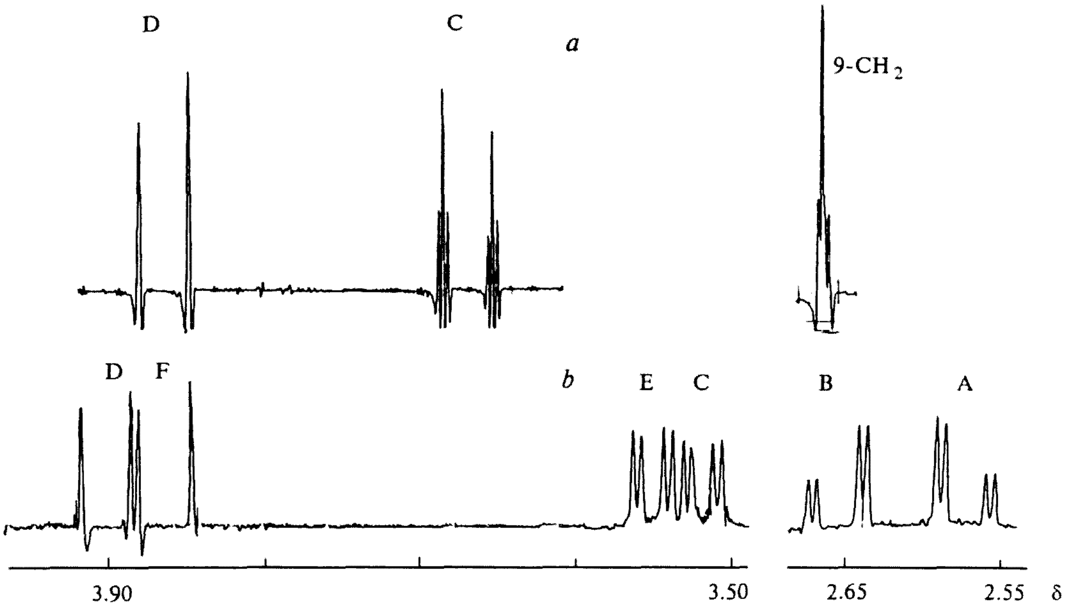


Fig. 1. ^{1}H NMR spectra under the conditions of line narrowing of the methylene protons in the symmetrical bicyclic compound **1a** in CDCl$_3$ (*a*) and in nonsymmetrical **3a** in CD$_3$OD (*b*).

1b. Yield 84 %, m.p. 205—207 °C. Found (%): N, 9.45. $C_{13}H_{18}O_6N_2$. Calculated (%): N, 9.39.

1c. Yield 90 %, m.p. >240 °C (decomp.).

1d. Yield 88 %, m.p. 190—191 °C. Found (%): N, 10.05. $C_{11}H_{14}O_6N_2$. Calculated (%): N, 10.37.

3a. Yield 71 %, m.p. >230 °C (decomp.).

3b. Yield 79 %, m.p. 171—173 °C (decomp.). Found (%): N, 9.51. $C_{13}H_{18}O_6N_2$. Calculated (%): N, 9.39.

4a. Yield 88 %, m.p. >235 °C (decomp.).

4b. Yield 72 %, m.p. 185—186 °C (decomp.). Found (%): N, 10.12. $C_{12}H_{16}O_6N_2$. Calculated (%): N, 9.86.

For symmetrical dilactams **1**, virtual spin-spin coupling[4] of the carbon atoms of the 4,8-CH$_2$ groups with the 9-CH$_2$ protons was detected (for example, for diesters **1a**,**b** under the conditions of decoupling from the MeN protons, $^3J_{\mathrm{C,H}}{}^{\mathrm{obs}}$ = 4.4 Hz); the spin-spin coupling of the protons of the 9-CH$_2$ group with the H$_\mathrm{C}$ protons in the 4,8-CH$_2$ groups was also observed, $^4J_{\mathrm{H,H}}{}^{\mathrm{obs}}$ = 1.2 Hz (Fig. 1). It is of interest that in the case of nonsymmetrical dilactams **3** and **4**, first-order spectra separate for each CH$_2$N bridge were observed, the corresponding true spin-spin coupling constants $^4J_{\mathrm{AC}}$ and $^4J_{\mathrm{BE}}$ being almost twice as great as the $^4J_{\mathrm{H,H}}{}^{\mathrm{obs}}$ constants in the spectra of symmetrical dilactams (see Fig. 1).

These examples clearly demonstrate that the virtual coupling is eliminated as the spin system becomes nonsymmetrical.

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