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Synthesis and crystal structure of chiral hydroquinoxaline derivatives

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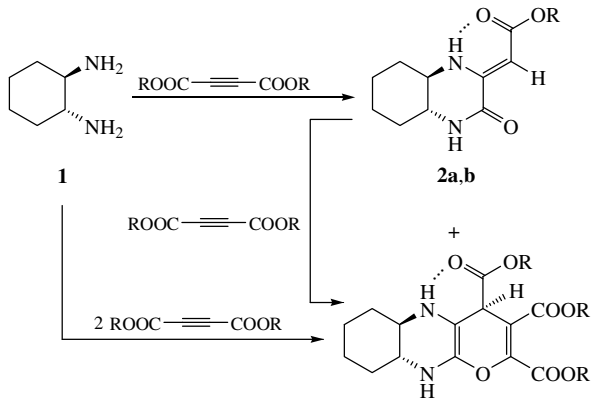
The addition of dialkyl acetylenedicarboxylate and 1,2-dibenzoylacetylene to *trans*-(1*R*,2*R*)-diaminocyclohexane afforded quinoxaline derivatives. The reaction of *trans*-(1*R*,2*R*)-*N*,*N*′-diisopropyldiaminocyclohexane with dimethyl acetylenedicarboxylate gave a new chiral compound.

Quinoxalines serve as a source of pharmaceutical agents.[1–4] These nitrogen heterocycles are useful intermediates in organic syntheses.[5]

Acetylenic esters are versatile reagents for heterocyclization, and many products can be prepared from the addition of these compounds to nitrogen-, oxygen- and sulfur-containing compounds.[6,7]

trans-(1*R*,2*R*)-Diaminocyclohexane (DACH)[8] derivatives are now well established as anticancer drugs.[9] The enantiomeric pairs of this compound exhibit different biological activities. For example, the 1*R*,2*R* isomers of DACH derivatives have somewhat higher antitumor activity than that of the 1*S*,2*S* isomer.[10]



a R = Me
b R = Et

Scheme 1

We are interested in the chemistry of heterocyclic compounds containing nitrogen and sulfur atoms.[11] We first carried out the reaction of dimethyl acetylenedicarboxylate[12] with *trans*-(1*R*,2*R*)-DACH **1** (1:1) in methanol to obtain a single compound, which was characterized to be 3-(methoxycarbonylmethylene)-1,4,4a*R*,5,6,7,8,8a*R*-octahydroquinoxalin-2-one **2a**, in 65% yield. The structure of **2a** was determined by NMR and IR spectroscopy, mass spectrometry and microanalysis (Scheme 1).†

Compound **2a** exhibited two broad lines at δ 6.52 and 8.02 ppm arising from NH protons along with a sharp signal from the C=CH proton at about δ 5.54 ppm. Further, we obtained a single crystal suitable for an X-ray diffraction study to confirm the structure.‡

An ORTEP diagram of **2a** is shown in Figure 1. [The absolute configuration of the reagent used *trans*-(1*R*,2*R*)-DACH was determined in another context.[8]]

Compound **2a** in the solid state shows dimers linked by hydrogen bonds [N(1)–H(1)···O(4) and N(3)–H(3)···O(1)]. In addition, there are intramolecular hydrogen bonds [N(2)–H(2)···O(3) and N(4)–H(4)···O(6)] which fix the α,β-unsaturated sequences

† *trans*-(1*R*,2*R*)-DACH was purchased from Aldrich. The other chemicals and solvents were purchased from Merck. 1,2-Dibenzoylacetylene was prepared by the published method.[11] The melting points were obtained using an Electrothermal IA 9100 Digital melting point apparatus. The IR spectra were recorded on a Bruker IFS-88 instrument (the samples as KBr disks for the range 4000–400 cm^{-1}). The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC-300 spectrometer (^{1}H, 300.134 MHz; ^{13}C, 75.469 MHz) using TMS as an internal standard. Mass-spectrometric measurements were made on an Agilent 6890 N Network GC system. The C, H, N analyses were performed by the microanalytical service of the N.I.O.C. Research Institute of Petroleum Industry.

*Synthesis of 3-(methoxycarbonylmethylene)-1,4,4a*R*,5,6,7,8,8a*R*-octahydroquinoxalin-2-one* **2a**: *trans*-(1*R*,2*R*)-DACH (10 mmol, 1.14 g) and dimethyl acetylenedicarboxylate (10 mmol, 1.42 g) in 40 ml of MeOH was heated at reflux for 30 min. The solution was cooled and the reaction vessel set aside overnight. The crystals formed were separated. Colourless prism crystals from methanol. Yield 65%, mp 187–188 °C. $[\alpha]_D^{25}$ –248.4 (*c* 0.40, $CHCl_3$). FT-IR (ν/cm^{-1}): 3314, 3188 (NH), 1691, 1659 (CO), 1615 (C=C), 1214 (C–O), 1153 (C–N). ^{1}H NMR ($CDCl_3$) δ: 1.31 (m, 4H, CH_2), 1.83 (m, 4H, CH_2), 3.02 (m, 1H, CH), 3.04 (m, 1H, CH), 3.62 (s, 3H, OMe), 5.54 (s, 1H, =CH), 6.52 (s, 1H, NH), 8.02 (br. s, 1H, NH). ^{13}C NMR ($CDCl_3$) δ: 23.5 (CH_2), 23.8 (CH_2), 29.5 (CH_2), 29.8 (CH_2), 50.7 (CH), 55.2 (CH), 55.6 (OMe), 86.4 (=CH), 149.1 (C=), 161.2 (CO), 170.9 (CO_2). MS, *m*/*z* (%): 224 (100) (M^+), 193 (53) ($C_{10}H_{13}N_2O_2^+$), 165 (15) ($C_9H_{13}N_2O^+$), 136 (8) ($C_8H_{12}N_2^+$), 149 (22) ($C_9H_{13}N_2^+$). Found (%): C, 58.87; H, 7.69; N, 12.36. Calc. for $C_{11}H_{16}N_2O_3$ (%): C, 58.93; H, 7.14; N, 12.5.

*3-(Ethoxycarbonylmethylene)-1,4,4a*R*,5,6,7,8,8a*R*-octahydroquinoxalin-2-one* **2b** was synthesised analogously to **2a**. Colourless plate crystals from ethanol. Yield 68%, mp 194–195 °C, $[\alpha]_D^{25}$ –210.2 (*c* 0.36, $CHCl_3$). FT-IR (ν/cm^{-1}): 3321, 3172 (NH), 1692, 1657 (CO), 1602 (C=C), 1211 (C–O), 1132 (C–N). ^{1}H NMR ($CDCl_3$) δ: 1.22 (t, 3H, Me, *J* 7.5 Hz), 1.35 (m, 4H, CH_2), 1.94 (m, 4H, CH_2), 2.96 (m, 1H, CH), 3.11 (m, 1H, CH), 4.13 (q, 2H, OCH_2, *J* 7.5 Hz), 5.66 (s, 1H, =CH), 6.58 (s, 1H, NH), 8.12 (br. s, 1H, NH). ^{13}C NMR ($CDCl_3$) δ: 14.9 (Me), 24.2 (CH_2), 24.8 (CH_2), 29.1 (CH_2), 30.4 (CH_2), 50.8 (CH), 55.1 (CH), 55.0 (OCH_2), 86.8 (=CH), 149.1 (C=), 162.4 (CO), 169.7 (CO_2). MS, *m*/*z* (%): 238 (M^+), 193 (48) ($C_{10}H_{13}N_2O_2^+$), 165 (20) ($C_9H_{13}N_2O^+$), 136 (5) ($C_8H_{12}N_2^+$), 73 (38) ($C_3H_5O_2^+$). Found (%): C, 60.11; H, 7.59; N, 11.75. Calc. for $C_{12}H_{18}N_2O_3$ (%): C, 60.05; H, 7.56; N, 11.76.

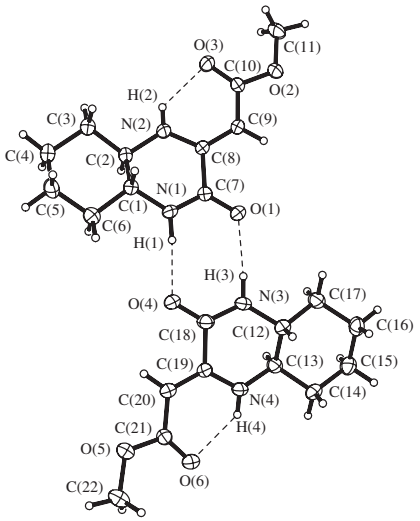
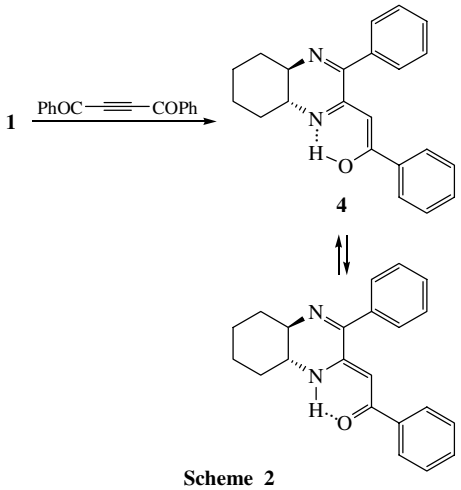


Figure 1 ORTEP drawing of **2a** dimer. Selected bond lengths (Å): O(1)–C(7) 1.243(2), O(3)–C(10) 1.222(2), N(1)–C(1) 1.471(2), N(1)–C(7) 1.327(2), N(2)–C(8) 1.354(2), N(2)–H(2) 0.82(2), O(5)–C(22) 1.446(2), N(4)–C(13) 1.461(2), N(4)–C(19) 1.345(2), N(3)–H(3) 0.86(2). Selected bond angles (°): C(1)–N(1)–C(7) 122.9(2), C(2)–N(2)–C(8) 123.7(2), N(1)–C(1)–C(2) 108.7(1), N(1)–C(1)–C(6) 112.0(1), N(2)–C(8)–C(7) 116.3(2), N(2)–C(8)–C(9) 124.8(2), O(2)–C(10)–O(3) 121.5(2), C(1)–N(1)–H(1) 121.(1), N(4)–C(19)–C(18) 116.9(2), C(12)–N(3)–H(3) 120.(1), C(18)–N(3)–H(3) 116.(1), C(19)–N(4)–H(4) 114.(1). Selected hydrogen bonding dimensions (Å): [N(1)···O(4) 2.840(2), N(3)···O(1) 2.912(2), N(2)···O(3) 2.722(2), N(4)···O(6) 2.767(2)].

in the plane of the six-membered heterocyclic ring. The dihedral angle between the 'best planes' of the two molecules in the dimer of **2a** is 15°.

The reaction of compound **2** with dialkyl acetylenedicarboxylate (1:1) or the reaction of *trans*-(1*R*,2*R*)-DACH with dialkyl acetylenedicarboxylate (1:2) afforded trialkyl-4*S*,5a*R*,9a*R*-4*H*-pyrano[2,3-*b*]-1,4,4a,5,6,7,8,8a-octahydroquinoxaline-2,3,4-tricarboxylate **3** (Scheme 1).§

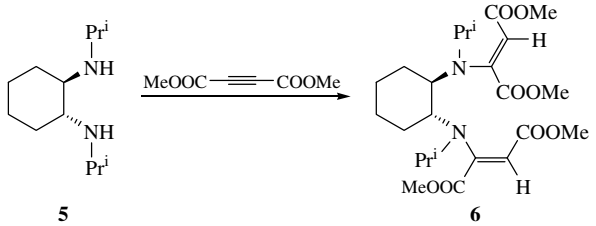
Because of the NH···O=C intramolecular hydrogen bond, the ^{1}H NMR spectra of **3a** exhibited one NH proton (br. s, δ 9.08 ppm) more deshielded than the other (br. s, δ 6.18 ppm). Compound **3** contains three centers of chirality and two diastereomers are possible but TLC and NMR spectra of this compound exhibited only a single, pure structure. These data indicated that a Michael type addition and Diels–Alder [4 + 2] cycloaddition reaction have occurred to afford **2** and **3**, respectively. As the Diels–Alder transition state involves the diene and dienophile, if one or both of these components are chiral, an asymmetric synthesis becomes possible. The reaction of chiral diene **2** with DMAD afforded chiral compound **3**. In compound **3**, the absolute configuration at C-4 depends on which face of the diene was attacked. The NH···O=C hydrogen bond in compound **2** blocked one face of the diene and



Scheme 2

controlled the reaction. This reaction was directed to other face of the diene by the C-4a*R*, C-8a*R* and NH···O=C hydrogen bond in compound **2** to give compound **3**.

The reaction of **1** with 1,2-dibenzoylacetylene[15] gave 3-(2-hydroxy-2-phenylvinyl)-2-phenyl-4a*R*,5,6,7,8,8a*R*-hexahydroquinoxaline **4** in 73% yield. The ^{1}H NMR spectra of **4**¶



Scheme 3

‡ *X-ray diffraction analysis*: at 193 K crystals of **2a** ($C_{11}H_{16}N_2O_3$) are monoclinic, space group $P2_1(4)$,[13] a = 10.663(1), b = 9.928(1) and c = 11.318(2) Å, β = 106.19(1)°, V = 1150.6(3) Å^3, Z = 4, M = 224.26, d_{calc} = 1.295 g cm^{-3}, μ = 0.9 cm^{-1}, $2\theta_{max}$ = 51.93°, $-13 \le h \le 13$, $-12 \le k \le 12$, $-13 \le l \le 13$, 16273 measured reflections, 4460 unique, R_{int} = 0.0437 [$F_0 > 4\sigma(F_0)$ = 3221], number of parameter, 307. The structure was solved by a directed method using SHELXS-97 program[14] and refined against F^2 (SHELXL-97).[14] H atoms = free refinement, Flack-parameter = 0.1(7), R_1 = 0.0279 [$F_0 > 4\sigma(F_0)$], R_1 = 0.0439 (all data), wR_2 = 0.0526 (all data), $w = 1/[\sigma^2(F_0^2) + (0.0256P)^2]$; $P = [\max(F_0^2, 0) + 2F_c^2]/3$, max. residual electron density 0.14 eÅ^{-3}.

CCDC 635031 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2008.

§ *Synthesis of trimethyl-4S,5a*R*,9a*R*-4*H*-pyrano[2,3-*b*]-1,4,4a,5,6,7,8,8a-octahydroquinoxaline-2,3,4-tricarboxylate* **3a**: compound **2a** (10 mmol, 2.24 g) and dimethyl acetylenedicarboxylate (10 mmol, 1.42 g) or compound **1** (10 mmol, 1.14 g) and dimethyl acetylenedicarboxylate (20 mmol, 2.84 g) in 40 ml of MeOH were heated at reflux for 1 h. The progress of reaction was monitored by TLC using *n*-hexane–ethyl acetate (4:1). The solvent was removed on a rotary evaporator. The crude product was subjected to column chromatography on silica gel using *n*-hexane–ethyl acetate (4:1) as an eluent affording pure compound **3a** as yellow powder. Yield 82%, mp 137–138 °C, $[\alpha]_D^{25}$ –357.9 (*c* 0.17, $CHCl_3$). FT-IR (ν/cm^{-1}): 3290, 3182 (NH), 1722 (CO), 1589, 1435 (C=C), 1208 (C–O), 1158 (C–N). ^{1}H NMR ($CDCl_3$) δ: 1.31 (m, 4H, CH_2), 1.94 (m, 4H, CH_2), 3.05 (m, 1H, CH), 3.17 (m, 1H, CH), 3.56 (s, 3H, OMe), 3.58 (s, 3H, OMe), 3.62 (s, 3H, OMe), 6.18 (s, 1H, NH), 6.58 (s, 1H, CH), 9.08 (br. s, 1H, NH). ^{13}C NMR ($CDCl_3$) δ: 23.4 (CH_2), 23.7 (CH_2), 28.7 (CH_2), 29.5 (CH_2), 39.2 (CH), 51.4 (CH), 53.6 (OMe), 54.5 (CH), 54.8 (OMe), 55.2 (OMe), 96.4 (C=C), 112.7 (C=C), 130.9 (C=C), 152.1 (C=C), 164.2 (CO_2), 165.9 (CO_2), 169.2 (CO_2). MS, *m*/*z* (%): 366 (19) (M^+), 307 (100) ($C_{15}H_{19}N_2O_5^+$), 224 (4) ($C_{11}H_{16}N_2O_3^+$), 275 (83) ($C_{14}H_{15}N_2O_4^+$), 59 (38) ($C_2H_3O_2^+$). Found (%): C, 55.79; H, 6.08; N, 7.69. Calc. for $C_{17}H_{22}N_2O_7$ (%): C, 55.74; H, 6.01; N, 7.65.

*Triethyl-4S,5a*R*,9a*R*-4*H*-pyrano[2,3-*b*]-1,4,4a,5,6,7,8,8a-octahydroquinoxaline-2,3,4-tricarboxylate* **3b** was synthesised analogously to **3a**. Yellow powder. Yield 88%, mp 155–156 °C, $[\alpha]_D^{25}$ –218.4 (*c* 0.57, $CHCl_3$). FT-IR (ν/cm^{-1}): 3285, 3180 (NH), 1718 (CO), 1593, 1482 (C=C), 1211 (C–O), 1142 (C–N). ^{1}H NMR ($CDCl_3$) δ: 1.25 (t, 3H, Me, *J* 7.5 Hz), 1.29 (m, 4H, CH_2), 1.79 (m, 2H, CH_2), 1.83 (m, 2H, CH_2), 3.04 (m, 1H, CH), 3.07 (m, 1H, CH), 3.95 (q, 2H, OCH_2, *J* 7.5 Hz), 6.05 (s, 1H, NH), 6.51 (s, 1H, CH), 8.99 (br. s, 1H, NH). ^{13}C NMR ($CDCl_3$) δ: 14.3 (Me), 15.5 (Me), 15.7 (Me), 23.1 (CH_2), 23.8 (CH_2), 28.3 (CH_2), 29.4 (CH_2), 39.8 (CH), 50.6 (CH), 54.5 (CH), 58.9 (OCH_2), 59.2 (OCH_2), 59.7 (OCH_2), 95.0 (C=C), 110.5 (C=C), 130.3 (C=C), 151.7 (C=C), 162.4 (CO_2), 165.8 (CO_2), 170.1 (CO_2). MS, *m*/*z* (%): 408 (9) (M^+), 335 (100) ($C_{17}H_{23}N_2O_5^+$), 238 (6) ($C_{12}H_{18}N_2O_3^+$), 290 (13) ($C_{15}H_{18}N_2O_4^+$), 73 (41) ($C_3H_5O_2^+$). Found (%): C, 58.78; H, 6.88; N, 6.86. Calc. for $C_{20}H_{28}N_2O_7$ (%): C, 58.82; H, 6.86; N, 6.86.

exhibited one proton (s, δ 10.82 ppm), and the FT-IR spectra exhibited a broad vibration bond at 3434 cm^{-1} (not the C=O bond). It was concluded that there is proton transfer across the N···OH hydrogen bond, a tautomeric enaminone structure (Scheme 2).

We expected that the reaction of *trans*-(1*R*,2*R*)-*N*,*N*′-diisopropyldiaminocyclohexane **5** with dimethyl acetylenedicarboxylate gives a product with a structure analogous to that of **2**, but the reaction of these compounds afforded a pure *trans*-(1*R*,2*R*)-*N*,*N*′-diisopropyl-*N*,*N*′-bis{(*E*)-dimethyl but-2-enedioate}DACH **6** (Scheme 3). The ^{1}H NMR spectra of **6**¶ exhibited a sharp signal at δ 4.91 ppm for the two olefinic protons of C=CH in (*E*) geometrical isomer. The structure of compound **6** was deduced from its elemental analyses and IR, ^{1}H and ^{13}C NMR spectra. The mass spectra of this compound displayed a molecular ion peak at *m*/*z* 482. Any initial fragmentation involves loss from or complete loss of the side chain and section of the diaminocyclohexyl ring system.

In summary, the presented reactions carried the advantage of being performed under neutral conditions and occurred under mild conditions to provide high levels of stereoselectivity.

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¶ *Synthesis of 3-(2-hydroxy-2-phenylvinyl)-2-phenyl-4a*R,*5,6,7,8,8a*R-*hexahydroquinoxaline* **4**: *trans*-(1*R*,2*R*)-DACH (10 mmol, 1.14 g) and 1,2-dibenzoylacetylene (10 mmol, 2.34 g) in 40 ml of MeOH were heated at reflux for 3 h. The solution was cooled and the reaction vessel set aside overnight. Compound **4** was separated as yellow needles crystals from methanol, yield 73%, mp 187–188 °C, $[\alpha]_D^{25}$ –477.6 (*c* 0.12, $CHCl_3$). FT-IR (ν/cm^{-1}): 3434 (OH), 1612 (C=N), 1565, 1538 (C=C). ^{1}H NMR ($CDCl_3$) δ: 1.54 (m, 4H, CH_2), 1.91 (m, 2H, CH_2), 2.20 (m, 1H, CH_2), 2.48 (m, 1H, CH_2), 2.99 (m, 1H, CH), 3.19 (m, 1H, CH), 5.81 (s, 1H, =CH), 7.51 (m, 6H, H_{Ar}), 7.51 (m, 4H, H_{Ar}), 10.82 (s, 1H, NH). ^{13}C NMR ($CDCl_3$) δ: 22.5 (CH_2), 22.8 (CH_2), 28.6 (CH_2), 28.8 (CH_2), 53.6 (CH), 55.4 (CH), 75.9 (=CH), 125.3 (C_{Ar}), 125.8 (C_{Ar}), 126.4 (C_{Ar}), 127.7 (C_{Ar}), 128.8 (C_{Ar}), 129.3 (C_{Ar}), 134.9 (C_{Ar}), 136.7 (C_{Ar}), 163.8 (HOC=), 163.3 (C=N), 164.9 (C=N). MS, *m*/*z* (%): 330 (94) (M^+), 314 (78) ($C_{22}H_{22}N_2^+$), 225 (100) ($C_{15}H_{17}N_2^+$), 147 (98) ($C_9H_{11}N_2^+$), 77 (69) (Ph^+). Found (%): C, 80.05; H, 6.69; N, 8.46. Calc. for $C_{22}H_{22}N_2O$ (%): C, 80.00; H, 6.67; N, 8.48.

Synthesis of trans-*(1*R*,2*R*)*-N,N′-*diisopropyl*-N,N′-*bis{(*E*)-dimethyl but-2-enedioate}-DACH* **6**: *trans*-(1*R*,2*R*)-*N*,*N*′-diisopropyldiaminocyclohexane **5** (10 mmol, 1.98 g) and dimethyl acetylenedicarboxylate (20 mmol, 2.84 g) in 40 ml of MeOH were heated at reflux for 3 h. The solution was cooled and the reaction vessel set aside overnight. Compound **6** was separated as yellow crystals from methanol, yield 85%, mp 166–167 °C, $[\alpha]_D^{25}$ +132.3 (*c* 0.46, $CHCl_3$). FT-IR (ν/cm^{-1}): 1742, 1697 (CO), 1573 (C=C), 1214 (C–O), 1156 (C–N). ^{1}H NMR ($CDCl_3$) δ: 0.90 (d, 6H, 2Me, *J* 7.0 Hz), 0.95 (d, 6H, 2Me, *J* 7.0 Hz), 1.15 (m, 2H, CH_2), 1.25 (m, 4H, $2CH_2$), 1.62 (m, 2H, CH_2), 3.07 (m, 2H, 2CH), 3.09 (m, 2H, 2CH), 3.23 (s, 6H, 2OMe), 3.47 (s, 6H, 2OMe), 4.91 (s, 2H, =CH). ^{13}C NMR ($CDCl_3$) δ: 14.2 (Me), 31.5 (CH_2), 46.5 (CH_2), 48.8 (CH), 50.9 (CH), 64.5 (OMe), 87.2 (OMe), 136.4 (C=), 151.8 (=CH), 165.0 (CO_2), 166.0 (CO_2). MS, *m*/*z* (%): 482 (2) (M^+), 423 (1) ($C_{22}H_{35}N_2O_6^+$), 266 (2) ($C_{15}H_{24}NO_3^+$), 216 (100) ($C_{10}H_{18}NO_4^+$), 81 (21) ($C_6H_9^+$), 43 (22) ($C_3H_7^+$). Found (%): C, 59.87; H, 7.89; N, 5.78. Calc. for $C_{24}H_{38}N_2O_8$ (%): C, 59.75; H, 7.88; N, 5.81.