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Chiral aziridine-*trans*-2,3-dicarboxylic acid derivatives: exciting history, re-examination and structures

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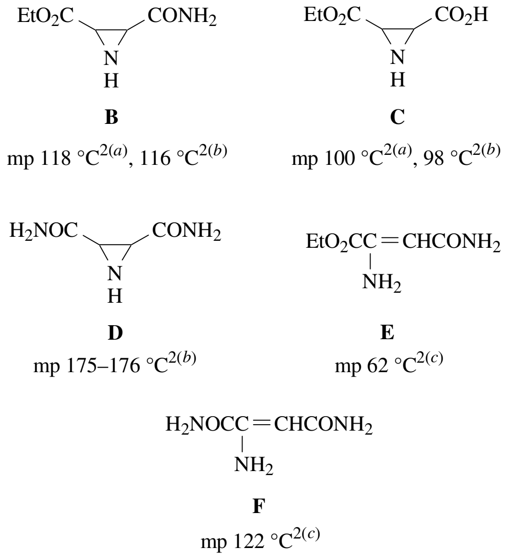
Chiral aziridines 5, 6 and enamine 7 were synthesised; compounds B, C and D, which were obtained over 100 years ago, were not aziridines; the product described as B was identified with isomeric enamine 7. The crystal structures of aziridines (±)- and (+)-6 were studied.

(2*S*,3*S*)-(+)-Aziridine-*trans*-2,3-dicarboxylic acid (**A**) is the first aziridine compound found in nature,[1] whereas the derivatives of (±)-**A** are the first aziridines described: **B**, **C** (Tübingen Universität, 1881)[2(*a*)] and **D** (Stuttgart Hochschule, 1892);[2(*b*)] in addition, the data on compounds **B**, **C**[2(*a*)] were confirmed elsewhere[2(*b*)] (Scheme 1).



Scheme 1

Compounds **B** and **D** were obtained by reactions of α,β-dibromosuccinic ester with NH_3 in EtOH at 100–130 °C, whereas compound **C** was obtained by acid hydrolysis of compound **B**;[2] the composition of the products was reliably confirmed by elemental analysis.[2] In subsequent studies of α,β-dibromosuccinic, monohalomaleic and fumaric esters under mild conditions, it was found that they always give mixtures of aziridines and the corresponding enamines.[3,4] In addition to enamines, aziridines are also formed upon epimination of dimethyl fumarate and dimethyl maleate;[1(*c*)] in turn, enamines undergo complex oxidative transformations;[5(*a*)] under acidic catalysis, the reaction smoothly gives substituted Δ^3-pyrrolidones-2.[5(*b*)] It was also reported that diethyl aziridine-*trans*-2,3-dicarboxylate on heating (1.5 h at 125 °C) is converted almost quantitatively into the corresponding enamine.[3(*a*)] Therefore, reasonable doubts regarding the study by Lehrfeld[2(*a*)] have been expressed a long time ago: '...it still remains uncertain whether he had aziridines (**B**, **C**) or the isomeric enamines, *e.g.* (**E**)'.[4]

However, the melting points of enamines **E**, **F**,[2(*c*)] which have been obtained from dialkyl chloromaleate and NH_3, characterised by elemental analyses and described as maleic acid derivatives, differ considerably from those of aziridines **B**[2(*a*),(*b*)] and **D**,[2(*b*)] respectively (Scheme 1). It is interesting that some of these papers[2(*a*),(*c*)] were presented by famous A. Pinner.

An intriguing question was raised in this study: what compounds have actually been obtained 122 years ago[2(*a*)] and 111 years ago?[2(*b*)] We synthesised authentic aziridines **B** and **D** using the published method[6(*a*)] and expanded for the synthesis of (2*S*,3*S*)-(+)-diisopropyl aziridine-*trans*-2,3-dicarboxylate[6(*b*)] (Scheme 2).[†]

Ammonolysis of (±)-**3** gave monoamide (±)-**5** and diamide (±)-**6**, and that of (2*S*,3*S*)-(+)-**3** gave diamide (2*S*,3*S*)-(+)-**6** (Scheme 3).[†]

[†] NMR spectra were recorded on a Bruker WM-400 spectrometer (^{1}H, 400.13 MHz and ^{13}C, 100.61 MHz). Optical rotation was measured on a Polamat-A polarimeter. Melting points were measured on a Boetius heating stage and corrected.

1: yield 94%, yellow liquid. ^{1}H NMR ($CDCl_3$) δ: 1.35 (t, 6H, 2Me, ^2J 7.2 Hz), 4.32 (m, 4H, 2CH_2O), 5.26 (d, 1H, ^3J 4.3 Hz), 5.72 (d, 1H, ^3J 4.3 Hz).

2: yield 72%, yellow liquid. ^{1}H NMR ($CDCl_3$) δ: 1.23 (br. t, 6H, 2Me), 3.81 (br. s, 1H, HO), 4.20 (m, 4H, 2CH_2O), 4.28 (d, 1H, HCN, ^3J 2.6 Hz), 4.58 (d, 1H, HCO, ^3J 2.6 Hz).

3: (±)-**3**, yield 24%, mp 52–54 °C (hexane), (2*S*,3*S*)-(+)-**3**, yield 30%, mp 53–54 °C (hexane), $[\alpha]_D^{20}$ +135° (*c* 1.0, EtOH). ^{1}H NMR (C_6D_6) δ: 0.77 (t, 3H, Me, ^3J 7.4 Hz), 0.82 (t, 3H, Me, ^3J 6.9 Hz), 1.60 (dd, 1H, H_a, $^3J_{ab}$ 9.5 Hz, $^3J_{ac}$ 8.5 Hz), 2.70 (dd, 1H, H_b, $^3J_{bc}$ 2.2 Hz), 2.97 (dd, 1H, H_c), 3.79 (q, 2H, CH_2O, ^3J 7.4 Hz), 3.84 (q, 2H, CH_2O, ^3J 6.9 Hz).

4: yield 7%, bp 103–105 °C (2 Torr). ^{1}H NMR ($CDCl_3$) δ: 1.28 (t, 3H, Me, ^3J 7.0 Hz), 1.34 (t, 3H, Me, ^3J 7.0 Hz), 4.17 (q, 2H, CH_2O), 4.31 (q, 2H, CH_2O), 5.50 (s, 1H, HC), 7.65 (br. s, 2H, H_2N).

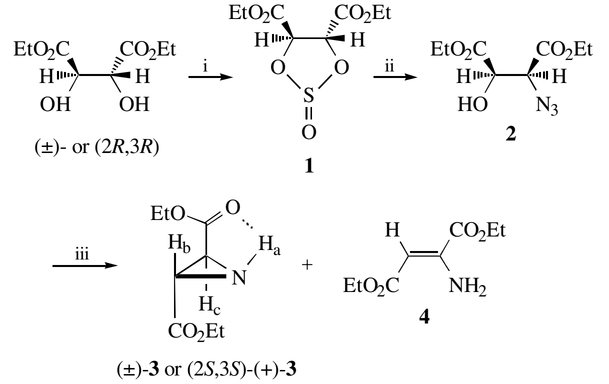
5: yield 32%, mp 100–101 °C (ethyl acetate). ^{1}H NMR (C_6D_6) δ, invertomer **5a**: 0.77 (t, 3H, Me, ^3J 7.2 Hz), 1.42 (dd, 1H, H_a, $^3J_{ab}$ 8.4 Hz, $^3J_{ac}$ 7.6 Hz), 2.33 (dd, 1H, H_b, $^3J_{bc}$ 2.0 Hz), 2.62 (dd, 1H, H_c), 3.70 (m, 2H, CH_2O, spectrum ABX_3), 5.65 and 5.98 (br. s, 2H, H_2N); invertomer **5b**: 0.89 (t, 3H, Me, ^3J 7.1 Hz), 1.98 (dd, 1H, H_a, $^3J_{ab}$ 10.9 Hz, $^3J_{ac}$ 9.2 Hz), 2.6 (dd, 1H, H_b, $^3J_{bc}$ 2.0 Hz), 2.76 (dd, 1H, H_c), 3.87 (q, 2H, CH_2O), 5.32 and 6.17 (br. s, 2H, HN), the ratio **5a**/**5b** = 4:1.

6: yield 85%, (±)-**6**, mp 199–201 °C (H_2O), (2*S*,3*S*)-(+)-**6**, mp 201–202 °C (MeOH), $[\alpha]_D^{20}$ +126.9° (*c* 0.84, H_2O). ^{1}H NMR ([$^2H_6$]DMSO/[$^2H_5$]Py, 1:1) δ: 2.30 (dd, 1H, H_a, $^3J_{ab}$ 8.5 Hz, $^3J_{ac}$ 8.1 Hz), 2.82 (dd, 1H, H_b, $^3J_{bc}$ 2.2 Hz), 2.96 (dd, 1H, H_c), 7.57 and 7.93 (br. s, 2H, H_2N), 7.60 and 8.49 (br. s, 2H, H_2N). ^{13}C NMR ([$^2H_6$]DMSO) δ: 35.51 (dd, C-3, ^1J 169.3 Hz, ^2J 9.7 Hz), 36.04 (dd, C-2, ^1J 172.1 Hz, ^2J 8.5 Hz), 170.76 and 170.93 (s, CO).

7, yield 67%, mp 117 °C (Pr^iOH). ^{1}H NMR ($CDCl_3$) δ: 1.29 (t, 3H, Me, ^3J 7.1 Hz), 4.17 (q, 2H, CH_2O), 5.00 (s, 1H, H_c). ^{13}C NMR (CD_3OD) δ: 15.00 (qt, Me, ^1J 127.0 Hz, ^2J 2.8 Hz), 60.20 (tq, CH_2O, ^1J 147.0 Hz, ^2J 4.2 Hz), 84.60 (d, 2-CH, ^1J 166.5 Hz), 152.50 (d, 1-C, ^2J 1.3 Hz), 168.00 (d, 3-C, ^3J 4.9 Hz), 171.5 (td, 4-C, ^3J 3.5 Hz, ^2J 1.4 Hz). Found (%): C, 45.82; H, 6.09; N, 17.69. Calc. for $C_6H_{10}N_2O_5$ (%): C, 45.56; H, 6.37; N, 17.71.

8: mp 30 °C. ^{1}H NMR (CD_3OD) δ: 3.64 (s, 3H, MeO_2C-4), 3.82 (s, 3H, MeO_2C-3), 5.32 (s, 1H, HC-2), 6.43 and 7.38 (br. s, H_2N). ^{13}C NMR (CD_3OD) δ: 51.08 (q, MeO_2C-4, ^1J 146.0 Hz), 53.45 (q, MeO_2C-3, ^1J 148.1 Hz), 87.95 (d, C-2, ^1J 170.3 Hz), 147.9 (s, C-1), 165.0 (dq, CO-3, $^3J_{CCCH}$ 4.9 Hz, $^3J_{COCH}$ 3.8 Hz), 171.24 (dq, CO-4, ^3J 3.8 Hz, ^2J 1.7 Hz).

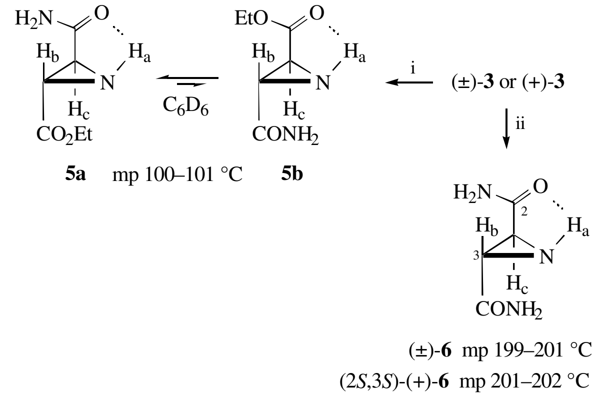
9: obtained from diamide of acetylenedicarboxylic acid and NH_3 in methyl cellosolve (4 days at 20 °C), yield 90%, mp 211–212 °C (MeOH). ^{1}H NMR ([$^2H_6$]DMSO) δ: 5.02 (s, 1H, H_c), 6.04 and 6.89 (2 br. s, 2H, H_2NCO), 6.96 (br. s, 2H, H_2NC), 7.41 and 7.69 (2 br. s, 2H, H_2NCO).



Scheme 2 *Reagents and conditions*: i, $SOCl_2$, CCl_4, refluxing for 2 h; ii, NaN_3, anhydrous DMF, 20 °C, 48 h; iii, Ph_3P, anhydrous DMF, 30 h at 120 °C, chromatography on SiO_2.

Product structures were confirmed by NMR spectra;[†] the signals were assigned on the basis of previous studies.[3(d)]

It is obvious from a comparison of the melting points of compounds (±)-**5** and **B**, as well as of (±)-**6** and **D**, that Lehrfeld,[2(a)] and Hell and Poliakoff[2(b)] had no aziridines **B** and **D** (and also **C** synthesised from compound **B**).



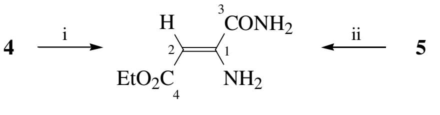
Scheme 3 *Reagents and conditions*: i, 10-fold excess of NH_3 in EtOH (8 days at 20 °C); ii, 15-fold excess of NH_3 and EtONa in EtOH (1 day at 20 °C).

Further, in order to check whether aziridine **B** corresponded to the other possible enamine structure, we synthesised authentic enamine **7** by the ammonolysis of diester **4** (Scheme 4).[†]

The composition and structure of enamine **7** were confirmed unambiguously by elemental analysis and ^{1}H and ^{13}C NMR spectra; its configuration was established by a comparison of the $^{3}J_{^{13}C^{1}H}$ coupling constants with those of previously studied enamines[7] and dimethyl aminofumarate **8**.[†]

Based on the coincidence of the melting points of the product described as aziridine **B**[2(a),(b)] (Scheme 1) and authentic enamine **7** (Scheme 4), we can state that it was enamine **7** that was actually obtained in those studies.[2(a),(b)]

We found that, contrary to the data by Berlin *et al.*,[3(a)] pure aziridines did not change on prolonged heating: **3** (in [$^{2}H_7$]DMF, 9.5 h at 120 °C), **5** (in C_5H_5N, 16.5 h at 115 °C), (±)-**6** (in methyl cellosolve, 16.5 h at 124 °C or solid, 6 h at 155 °C), whereas smooth isomerisation into the corresponding enamines occurred on heating in the presence of NH_4Cl (*i.e.*, under the same conditions as those used in the studies cited[2,3]) in methyl cellosolve, 3 h at 124 °C: compound **3** was completely converted into compound **4**, and compound **5**, into compound **7** (Scheme 4). Thus, we also managed to find out the source of enamine **7** in the previous studies.[2(a),(b)]



7, mp 117 °C

Scheme 4 *Reagents and conditions*: i, NH_3 in EtOH/H_2O, 12 h at 20 °C; ii, 3 h at 124 °C in the presence of NH_4Cl in methyl cellosolve.

A small amount of the compound described[2(b)] as **D** was obtained in only one experiment. However, its melting point did not match those of the *trans*-isomer of aziridine (±)-**6**, the sufficiently well characterised *cis*-**6** (mp 187–188 °C),[3(c)] and isomeric enamine **F**, the configuration of which was not established but the composition was confirmed by elemental analysis (mp 225 °C, decomp.).[3(c)] Finally, it was shown that authentic

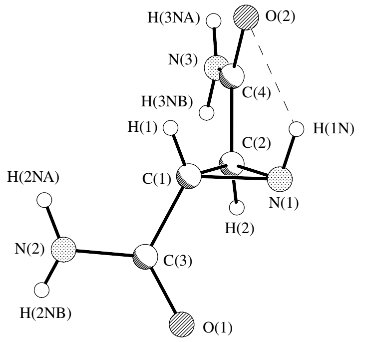


Figure 1 The general view of **6**. The selected geometrical parameters for (+)-**6** and (±)-**6** (values are given for two independent molecules). Bond lengths (Å): for (+)-**6**: N(1)–C(1) 1.458(2), N(1)–C(2) 1.464(2), C(1)–C(2) 1.495(2), C(1)–C(3) 1.489(2), C(2)–C(4) 1.499(2); for (±)-**6**: N(1)–C(1) 1.461(2)/1.470(2), N(1)–C(2) 1.471(2)/1.474(2), C(1)–C(2) 1.505(2)/ 1.497(2), C(1)–C(4) 1.498(2)/1.498(2), C(2)–C(3) 1.499(2)/1.494(2); bond angles (°): (+)-**6**: C(1)–N(1)–C(2) 61.57(9), N(1)–C(2)–C(1) 59.02(9), N(1)–C(1)–C(2) 59.41(9); for (±)-**6**: (values are given for two independent molecules): C(1)–N(1)–C(2) 61.75(9)/61.15(9), N(1)–C(2)–C(1) 58.78(9)/ 59.56(9), N(1)–C(1)–C(2)59.47(9)/59.29(9); torsion angles(°): for (+)-**6**: O(2)–C(4)–C(2)–N(1) 23.6, O(1)–C(3)–C(1)–N(1) 9.7, for (±)-**6**: O(2)–C(4)–C(2)–N(1) 17.1/23.6, O(1)–C(3)–C(1)–N(1) 24.2/36.2. Intramolecular N(1)–H(1N)···O(2) H-bond: for (+)-**6** N(1)···O(2) 2.891(2) Å, N(1)–H(1N)–O(2) 110°; for (±)-**6**: N(1)···O(2) 2.891(2)/2.879(2) Å, N(1)–H(1N)–O(2) 105/107°.

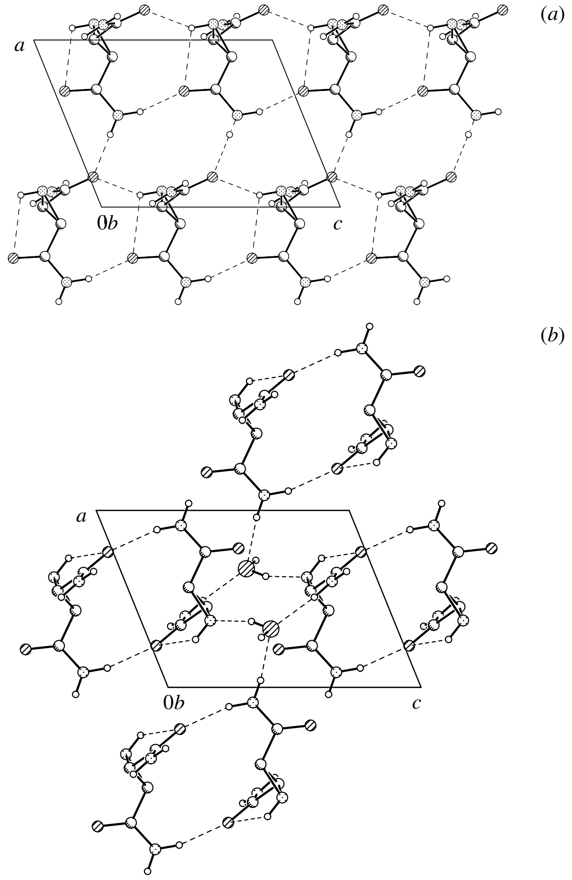


Figure 2 Supramolecular arrangement of two independent molecules in (±)-**6**.

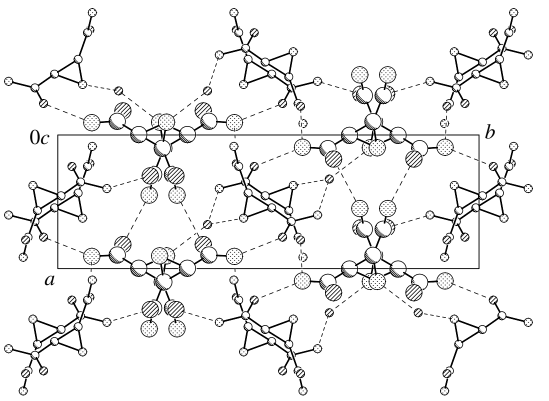


Figure 3 H-bonded three-dimensional framework in (±)-**6**. The radii of circles representing atoms for independent molecules are different; hydrogen atoms are omitted for clarity.

aziridine (±)-**6** did not isomerise into enamine even on heating with NH_4Cl in methyl cellosolve (3 h at 124 °C).

It is interesting to note that the same story, albeit reversed, occurred with the parent aziridine. It was originally obtained by S. Gabriel (1888) but described as vinylamine.[8(*a*)] Its real cyclic structure was revealed eleven years later.[8(*b*),(*c*)] Unsubstituted vinylamine was synthesised another 92 years later.[8(*d*)] Simultaneously, an unusually facile aziridine–enamine fragmentation of 1-(*tert*-alkylmethoxyamino)aziridine into the corresponding vinyldiazene was found in our laboratory.[9] The reverse enamine–aziridine rearrangement has only been described for one compound: 2-aminoacrylonitrile exposed to UV irradiation gives 2-cyanoaziridine (yield of 10–20%).[10] However, we showed that dimethyl aminofumarate **8**, as well as aminofumaric acid diamide **9**,[†] remained unchanged under UV irradiation (400 W lamp, in MeOH, 10 h at 50 °C).

In the case of aziridine **6**, the enantiomer and the racemate have almost equal melting points. In order to find a conglomerate, we studied the structures of crystals of (±)-**6** suitable for XRD studies and of (+)-**6** (for comparison).[‡] It was shown that the racemate crystallises as a monohydrate with two independent diamide molecules (space group $P2_1/c$, $Z = 8$, $Z' = 2$); *i.e.*, one diamide molecule corresponds to one-half of a solvate water molecule. A homochiral crystal of (+)-**6** (space group $P2_12_12_1$, $Z = 4$, $Z' = 1$) contains no solvate molecules. The bond lengths and angles in (±)-**6** are similar to those in (+)-**6**; the main distinction between the molecular structures consists in different orientations of the amide groups with respect to the aziridine ring (Figure 1). The intramolecular H-bond N(1)H(1N)···O(2) fixes the torsion angles O(2)C(4)–C(2)N(1), whereas the torsion angles O(1)C(3)C(1)N(1) in (±)-**6** and (+)-**6** differ significantly. Unusual packing exists in the racemic crystal with different supramolecular structures for independent molecules. One of them participates in the formation of H-bonded layers parallel to the crystallographic plane *ac* [Figure 2(*a*)], while the other one is involved in N–H···O bonded dimers combined into layers by water molecules [Figure 2(*b*)]. This results in a three-dimensional H-bound framework (Figure 3).

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[‡] *Crystallographic data*. Crystals of (+)-**6** ($C_4H_7N_3O_2$, $M = 129.13$) are orthorhombic, space group $P2_12_12_1$, at 150 K: $a = 7.089(2)$ Å, $b = 8.307(3)$ Å, $c = 9.732(3)$ Å, $V = 573.1(3)$ Å^3, $Z = 4$ ($Z' = 1$), $d_{calc} = 1.497$ g cm^{-3}, μ(MoKα) = 1.22 cm^{-1}, $F(000) = 272$. Intensities of 938 reflections were measured with a Siemens P3/PC diffractometer [λ(MoKα) = 0.71072 Å, $\theta/2\theta$-scans, $2\theta < 60°$] and 937 independent reflections were used in the further refinement.

Crystals of (±)-**6** ($C_4H_7N_3O_2 \cdot 1/2H_2O$, $M = 138.13$) are monoclinic, space group $P2_1/c$, at 110 K: $a = 7.005(1)$ Å, $b = 20.450(4)$ Å, $c = 9.268(2)$ Å, $\beta = 112.114(3)°$, $V = 1229.9(4)$ Å^3, $Z = 8$ ($Z' = 2$), $d_{calc} = 1.492$ g cm^{-3}, μ(MoKα) = 1.24 cm^{-1}, $F(000) = 584$. Intensities of 12720 [(±)-**6**] reflections were measured with a Smart 1000 CCD diffractometer [λ(MoKα) = 0.71072 Å, ω-scans with 0.3° step in ω and 10 s per frame exposure, $2\theta < 60°$] 3545 independent reflections ($R_{int} = 0.0819$) were used in the further refinement.

Both structures were solved by a direct method and refined by the full-matrix least-squares technique against F^2 in the anisotropic-isotropic approximation. Hydrogen atoms were located from the Fourier synthesis and refined in the isotropic approximation. The refinement converged to $wR_2 = 0.1204$ and GOF = 1.053 for all independent reflections [$R_1 = 0.0398$ was calculated against F for 905 observed reflections with $I > 2\sigma(I)$] for (+)-**6** and to $wR_2 = 0.1149$ and GOF = 0.999 for all independent reflections [$R_1 = 0.0501$ was calculated against F for 2810 observed reflections with $I > 2\sigma(I)$] for (±)-**6**. 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 223127 and 223128. For details, see 'Notice to Authors', *Mendeleev Commun*., Issue 1, 2003.