Pasteur-like resolution of quasi-racemates in solid and gas phases

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10.1070/MC2003v013n03ABEH001801

Isotopomeric quasi-racemates (IQR), *i.e.*, 1:1 mixtures of enantiomers one of which contains an isotopic label, can undergo crystallisation as conglomerates or true quasi-racemates. In the former case, each single crystal contains, predominantly or exclusively, either labelled or non-labelled enantiomers, whereas in the latter case, it contains both enantiomers (1:1). If solution sputtering is used to ionise quasi-racemates, the formation of homochiral protonated and metallated enantiomers and their homochiral oligomers in the gas phase is detected in ion cyclotron resonance (ICR) mass spectra; these compounds differ in their *m*/*z* values; hence, Pasteur-like 'manual sorting' can be employed to catch them successively in the ion trap of the spectrometer.

Louis Pasteur was the first to report[1] quasi-racemates, *i.e.*, the mixtures (1:1) of chiral compounds with close structures but opposite absolute configurations.[2] The examples of these include the mixtures of monoammonium (+)-tartrate and (–)-malate[1,2] or the dimethyl esters of (+)-dicarboxylic acids and the diethyl (or diisopropyl) esters of their (–)-enantiomers.[3(a)–(d)] Quasi-racemic mixtures of enantiomers, one of which contains an isotopic label,[3(a),(b),(e)] *e.g.*, (+)-alaninamide and (–)-alaninamide-^{15}N,[3(a),(b)] are most similar to racemates. Unlike true racemates and conglomerates, the components of such isotopomeric quasi-racemates (IQRs) can be detected by not only chiroptical methods or chiral chromatography but also many 'achiral' spectral methods (MS,[3(a),(b),(e)] NMR,[3(c),(d)] IR, *etc*.). Therefore, IQRs can be used to study the self-association of chiral molecules in solid and gas phases, as well as in solutions. In many cases, the isotopic label should probably not change the crystal structure, and the single crystals of IQRs can be used in tests for conglomerate formation or racemic twinning and also for studying other crystal properties by spectral methods. IQRs have previously been used to determine the enantiomeric composition by ^{1}H NMR in a study of absolute asymmetric synthesis by photodimerisation in a chiral crystal.[4(a)] Recently, IQRs have been employed in an elegant study of the chiral self-assembly of (±)-Lys and (±)-Glu derivatives into two-dimensional crystallites at the air–water interface using MS (and other techniques).[4(b)–(d)] This method is widely used in studies on the chiroselective self-assembly of IQR molecules.[5]

In this work, we studied three IQRs. The first one, IQR-**1**, was obtained on the basis of asparagine (Asn) forming a conglomerate (space group $P2_12_12_1$, $Z = 4$),[6] whose ICR mass spectra contained the following ions: [2AsnCu^{II} + H$^+$],[5(b)] as well as [Asn + H$^+$], [2Asn + H$^+$], [4Asn + H$^+$] and [Asn + M$^+$], [2Asn + M$^+$] (M = Na, K)[6] upon electrospray ionisation (ESI) of solutions.[7] Using known procedures,[8] (*S*)-(–)-Asn-(^{15}N-amide) was obtained from (*S*)-(+)-Asp and $^{15}NH_3$;† (*R*)-(+)-Asn was obtained by spontaneous resolution of (±)-Asn.[6,†]

As expected, crystallisation of their equimolar mixture (IQR-**1**) from water gives optically pure or highly enriched crystals containing labelled (*S*)-Asn or non-labelled (*R*)-Asn. This was confirmed by ^{1}H NMR spectra and ICR mass spectra of solutions of these crystals (Figure 1) and by the measurement of optical rotation angles.† The ICR mass spectrum‡ of the equi-

† NMR spectra were measured on a Bruker WM-400 spectrometer (400.13 MHz for ^{1}H and 100.61 MHz for ^{13}C); optical rotation was measured on a Polamat-A polarimeter; melting points were determined on a Boetius heating stage and corrected.

IQR-**1**. (*R*)-Asn was obtained by spontaneous resolution of (±)-Asn (see ref. 6). (*S*)-Asn (^{15}N-amide) was synthesised from (*S*)-(+)-Asp and $^{15}NH_3$ (isotopic enrichment 98.7%) (see ref. 8). ^{1}H NMR spectrum ([$^2H_6$]DMSO, at 60 °C) δ: 2.52 (m, 2H, CH_2, AB part of ABX spectrum, $\Delta\nu$ 380.0, $^2J_{AB}$ –16.1 Hz, $^3J_{AX}$ 8.7 Hz, $^3J_{BX}$ 4.0 Hz), 3.40 (dd, 1H, HC, X-part), 7.02 (dd, 1H, HN, $^1J_{HN}$ 87.4 Hz, $^2J_{HH}$ 2.3 Hz), 7.69 (dd, 1H, HN, $^1J_{HN}$ 88.7 Hz, $^2J_{HH}$ 2.3 Hz) (*cf.* with the spectrum of formamide-^{15}N).[14] The spectra of HC protons of the isotopomers coincide, whereas those of HN do not overlap (*cf.* ref. 6); this makes it possible to determine their ratio. (*R*)- and (*S*)-Asn (18 mg of each) were dissolved in 2 ml of distilled water and kept at 18–20 °C. After 11 days, six crystals with a total mass of 30 mg were obtained. For a crystal with a mass of 14 mg: $[\alpha]^{20}_{578}$ –29.4°, $[\alpha]^{20}_{546}$ –37.7°, $[\alpha]^{20}_{436}$ –53.6°, $[\alpha]^{20}_{406}$ –67.1° (*c* 0.3, 1N HCl); the ^{1}H NMR spectrum ([$^2H_6$]DMSO) does not contain signals of $^{15}NH_2$ protons; the mass spectrum contains only the signal of an ion with *m*/*z* 133 [M + H$^+$] but no signal with *m*/*z* 134. It follows that the crystal contains only (*R*)-Asn. For another crystal with a mass of 7 mg: $[\alpha]^{20}_{578}$ +27.6°, $[\alpha]^{20}_{546}$ +35.6°, $[\alpha]^{20}_{436}$ +50.5°, $[\alpha]^{20}_{406}$ +63.5° (*c* 0.2, 1N HCl). The peak of labelled (*S*)-Asn with *m*/*z* 134 [M + H$^+$] predominates in the mass spectrum.

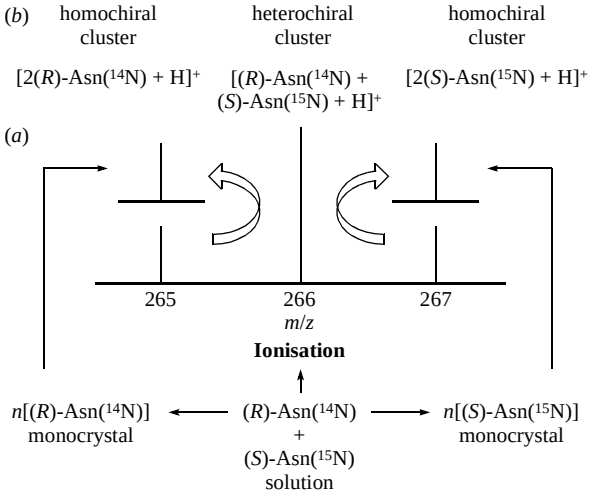
IQR-**2**. Betaines **1** and **1**-d_5 were obtained by reactions of maleic acid with pyridine and pyridine-d_5 in water (three weeks at 20 °C) in 98 and 90% yields, respectively; mp of separate crystals are 214 (decomp.) and 200–204 °C (decomp.), respectively.

1: ^{1}H NMR (D_2O) δ: 3.4 (m, 2H, CH_2, AB part of ABX spectrum, $\Delta\nu$ 68.0, $^2J_{AB}$ –18.0 Hz, $^3J_{AX}$ 9.9 Hz, $^3J_{BX}$ 4.4 Hz), 5.6 (dd, 1H, HC, X-part), 8.0 (dd, 2H-β, ^3J 7.8 Hz, ^3J 6.1 Hz), 8.5 (t, 1H, H-γ, ^3J 7.8 Hz), 8.9 (d, 2H, 2H-α, ^3J 6.1 Hz). ^{13}C NMR (D_2O) δ: 37.0 (t, CH_2, ^1J 131.0 Hz), 71.3 (d, CH, ^1J 144.2 Hz), 127.6 (d, CH-γ, ^1J 175.7 Hz), 144.2 (d, CH-β, ^1J 193.7 Hz), 146.0 (d, CH-α, ^1J 171.5 Hz), 168.1 (s, CO_2), 170.8 (s, CO_2H).

1-d_5: ^{1}H NMR (D_2O) δ: 3.4 (m, 2H, CH_2, AB part of ABX spectrum, $\Delta\nu$ 68.0, $^2J_{AB}$ –18.0 Hz, $^3J_{AX}$ 9.9 Hz, $^3J_{BX}$ 4.4 Hz), 5.6 (dd, 1H, HC, X-part). The spectrum of a **1**/**1**-d_5 (1:1) mixture is identical to the spectrum of **1**, but the integral intensity of signals in the region δ 8–8.9 is two times lower. Crystallisation of **1** and **1**-d_5 from distilled water and separation of crystals according to the sign of optical rotation gave portions of crystals of (*R*)-(+)-**1** with $[\alpha]^{20}_D$ +71.5° (*c* 0.8, H_2O) and (*S*)-(–)-**1**-d_5 with $[\alpha]^{20}_D$ –69.9° (*c* 0.8, H_2O). Subsequent co-crystallisation of their equimolar amounts gave six crystals with total masses of 1.5 to 6.7 mg. Based on mass spectra, the *ee* was found to be 100% in one crystal, only a peak of **1**-d_5 with *m*/*z* 201 [M + H$^+$] was observed; in another three crystals, the *ee* was 56, 50 or 35% with predominance of **1**: the peak with *m*/*z* 196 was observed. Based on ^{1}H NMR of solutions of two more crystals, the *ee* was found to be 66.6 and 60% for **1**-d_5 and **1**, respectively, from the signal ratio at δ 5.6 (HC) and 8.5 (H-γ).

IQR-**3**. (*R*,*R*)-(+)-Dimethyl tartrate (+)-**2** {mp 58–61 °C, $[\alpha]^{20}_D$ +21.0° (*c* 1.0, H_2O)} and (*S*,*S*)-(–)-dimethyl tartrate (–)-**2** [mp 59–60 °C, $[\alpha]^{20}_D$ –20.9° (*c* 1.0, H_2O)] from Fluka were used.

(*S*,*S*)-(–)-Dimethyl tartrate-d_6 (–)-**2**-d_6 was obtained by transesterification: concentrated HCl (five drops) was added to a solution of (–)-**2** (1.3 g) in 30 ml of methanol-d_4, and the solution was kept for four days. The mixture was treated with an ethereal suspension of $NaHCO_3$, filtered, dried with anhydrous Na_2SO_4, filtered again, concentrated and evacuated. The product was recrystallised three times from CCl_4 to give 1 g of anhydrous crystals, mp 50 °C, $[\alpha]^{20}_D$ –21.7° (*c* 1.0, H_2O). ^{1}H NMR ($CDCl_3$) δ: 3.20 (d, 2H, 2HO, ^3J 6.5 Hz), 4.56 (d, 2H, 2HC, ^3J 6.5 Hz). Equimolar amounts of (+)-**2** and (–)-**2**-d_6 were dissolved in hot CCl_4; crystals of IQR-**3** were obtained, mp 90–92 °C. For a separate crystal, ^{1}H NMR ($CDCl_3$) δ: 3.20 (d, HO, ^3J 6.5 Hz), 3.87 (s, MeO), 4.55 (d, HC, ^3J 6.5 Hz); the integral intensity ratio of the signals at δ 3.87 and 4.55 is 3:2.



Scheme 1 (*a*) Spontaneous crystallization resolution of (±)-IQR-**1** by the Pasteur method and its ICR control. (*b*) Resolution of (±)-IQR-**1** in the form of enantiomeric protonated dimers by Pasteur-like manual sorting.

molar mixture (IQR-**1**) shows the formation of three protonated dimers: two homochiral dimers with *m*/*z* 265 and 267 and a heterochiral dimer with *m*/*z* 266. The successive removal of ions makes it possible to catch only the protonated (*R*)-enantiomer dimer with *m*/*z* 265 or the (*S*)-enantiomer with *m*/*z* 267 in the ion trap (Figure 1).‡ These operations are summarised in Scheme 1.

The next IQR, referred to as IQR-**2**, was obtained on the basis of pyridinium-betaine **1**, which was originally synthesised by O. Lutz [Schemes 2(*a*)[9(*a*)–(*c*),(*f*)] and (*b*)[9(*d*)–(*f*)]. According to X-ray diffraction data, (±)-**1** crystallises as a conglomerate (space group $P2_12_12_1$, $Z = 4$).[10] We have previously studied its spontaneous resolution,[11(*a*)] as well as its spectral and association properties.[11(*b*)] The reaction between (–)-bromosuccinic acid and C_5H_5N gave (+)-**1** [Scheme 2(*c*)]; therefore, based on the known (*S*)-(–)-configuration of the brominated acid and the Walden inversion in the reaction, it can be considered that the betaine has the (*R*)-(+)-**1** absolute configuration.

Spontaneous resolution according to Schemes 2(*b*) and 2(*d*) gave[11(*a*)] enantiomers of betaines **1** and **1**-d_5; IQR-**2** was prepared by mixing equimolar amounts of (*R*)-(+)-**1** and (*S*)-(–)-**1**-d_5. Its crystallisation from water gives a mixture of well-formed crystals. Based on the ESI-ICR mass spectra‡ of the solutions, the *ee* was found to be 100% in one crystal {only a peak at *m*/*z* 201 [(*S*)-(–)-**1**-d_5 + H]$^+$ was observed} and 55 and 50% in the other two crystals. In other two crystals, ^{1}H NMR showed *ee* 66.6 and 60.0% [by integrating the signals at δ 5.6 (HC) and 8.5 (γ-H)].

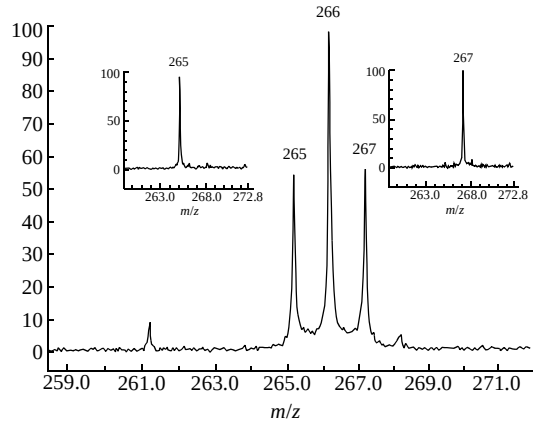


Figure 1 ESI-ICR mass spectrum of a protonated dimer of IQR-**1** [(*R*)-Asn(^{14}N) + (*S*)-Asn(^{15}N)]. Inserts: spectra of protonated homochiral dimers after removing all other ions.

Judging from the ESI-ICR spectrum of IQR-**2**, protonated monomers, dimers and trimers of **1** are formed (Figure 2). Like the previous example (IQR-**1**), Pasteur-like sorting makes it possible to catch purely ions of monomeric (with *m*/*z* 196 or 201), dimeric (with *m*/*z* 391 or 401) or trimeric (with *m*/*z* 586 or 601) protonated quasi-enantiomers in the ion trap. Thus, we performed the Pasteur-type spontaneous crystallisation resolution of IQRs-**1**,**2**, which form conglomerates, and also manual Pasteur-like sorting of quasi-enantiomeric cluster ions in the gas phase.

Finally, we studied IQR-**3**, *i.e.*, an equimolar mixture of (*R*,*R*)-(+)-dimethyl tartrate (DMT) and (*S*,*S*)-(–)-dimethyl tartrate-d_6 (DMT-d_6). X-Ray diffraction data are available for only the (*R*,*R*)-(+)-form.[12] However, it is known[13] that the melting point of the racemate (polymorphs with mp 84 and 90 °C) is higher than that of the enantiomer (polymorphs with mp 48, 50 and 61 °C). Therefore, it may only be assumed that the racemate does not form a conglomerate. We have proved this unambiguously: the crystallisation of IQR-**3** gave separate crystals containing both labelled and non-labelled quasi-enantiomers in a ratio close to 1:1. This was determined by ^{1}H NMR,† based on the ratio of integral intensities of signals at δ 3.87 (MeO) and 4.55 (HC) and by ICR spectra,‡ based on the ratio of peaks with *m*/*z* 201 [(+)-DMT + Na]$^+$ and *m*/*z* 207 [(–)-DMT-d_6 + Na]$^+$. Like the above cases, these ions can be caught successively in the ICR ion trap. Thus, manual Pasteur-like sorting makes it possible to separate quasi-enantiomeric cluster ions IQR-**3**, which do not form conglomerates.

Note that Asn is a second (after the Pasteur salt) example of the compound, in which hemihedry (enantiomorphism) was

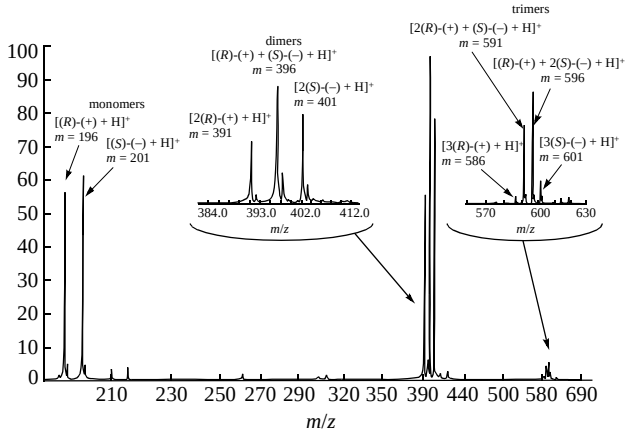
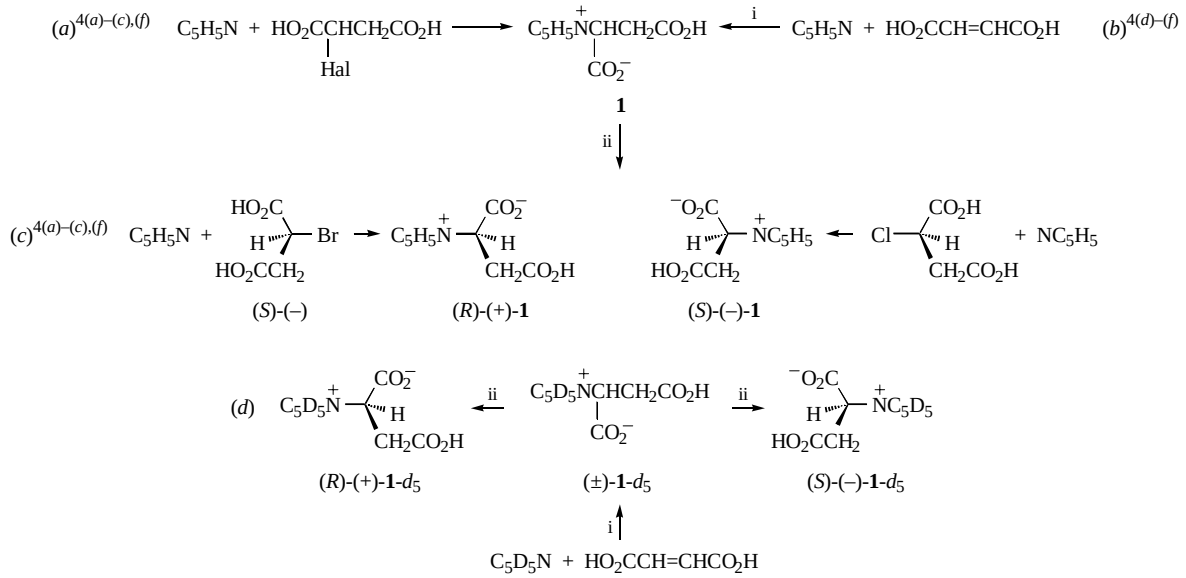


Figure 2 ESI-ICR mass spectrum of IQR-**2**.

‡ Experiments were performed on a Bruker Spectrospin CMS-47 based Fourier transform mass spectrometer equipped with a 4.7 T superconducting solenoid with a home made electrospray ionization (ESI) ion source and a multistage quadrupole ion transfer system with four stage differential pumping. Sample solution in H_2O–MeOH (1:1) with a ~10^{-5} mol dm^{-3} concentration were electrosprayed into a metal capillary of 0.5 mm internal diameter heated to 100 °C. After declasterization in the capillary, ions were collected by an RF ion funnel at ~1 Torr and transferred into a collisional quadrupole for futher cooling and axialization. From the collisional quadrupole, ions were transferred to an FT ICR cell for mass measurement. A conventional cylindrical ICR cell was used. A gas assisted trapping technique was used to trap ions in the cell. Ion kinetic energy in the laboratory system did not exceed 3 eV; thus, ion fragmentation was excluded. Combination of the ion funnel with the system of quadrupole ion guides provides fragmentation free conditions for ion transfer from the ESI ion source to the ICR cell. RF frequencies and amplitudes of voltages applied to quadrupole rods were chosen to keep low mass cut off below *m*/*z* 50. A chirp excitation mode was used to excite cyclotron motion of ions in the ICR cell without ion discrimination to permit quantitative measurements of peak intensities. A chirp rate (rate of frequency scanning during the excitation procedure) was chosen to be equal to 300 MHz s^{-1} with a total excitation time of 3 ms for the whole mass range *m*/*z* 100–500. For ejection of particular *m*/*z* ions excitation voltage was applied at the frequency corresponding to the position of the peak maximum on the frequency scale of the ion to be ejected from the cell.



Scheme 2 *Reagents and conditions*: i, 2 weeks in H_2O at 20 °C from maleic acid and pyridine; ii, sorting of crystals according to the sign and magnitude of the optical rotation angle.

observed.[15(a)] (+)-Asn was prepared by M. A. Puitti and was found to have a sweet taste as distinct from the natural (–)-Asn.[15(b)] L. Pasteur explained this distinction as arising from differential interaction of the two enantiomers with dissymmetric nerve tissue.[15(c)] For the first time the spontaneous resolution of (±)-Asn was carried out by I. Ostromisslensky,[16(a)] who also described its triboluminescence (which is also characteristic of the Pasteur salts[17]) and proposed this crystal property as a test for conglomerate formation. Studies on the triboluminescence phenomenon were reported in ref. 18.

We are grateful to Professor O. Neilands (Riga Polytechnical University) for his assistance in preparing this manuscript.

This work was supported by the Russian Foundation for Basic Research (grant nos. 03-03-32019, 02-03-3231a and 00-03-81187Bel), INTAS (grant no. 99-00157), and the Russian Academy of Sciences.

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Received: 22nd May 2003; Com. 03/2127