



You have downloaded a document from
RE-BUS
repository of the University of Silesia in Katowice

Title: Spectroscopic characterization and crystal structures of two cathinone derivatives : N-ethyl-2-amino-1-phenylpropan-1-one (ethcathinone) hydrochloride and N-ethyl-2-amino-1-(4-chlorophenyl)propan-1-one (4-CEC) hydrochloride

Author: Piotr Kuś, Joachim Kusz, Maria Książek, Ewelina Pieprzyca, Marcin Rojkiewicz

Citation style: Kuś Piotr, Kusz Joachim, Książek Maria, Pieprzyca Ewelina, Rojkiewicz Marcin. (2017). Spectroscopic characterization and crystal structures of two cathinone derivatives : N-ethyl-2-amino-1-phenylpropan-1-one (ethcathinone) hydrochloride and N-ethyl-2-amino-1-(4-chlorophenyl)propan-1-one (4-CEC) hydrochloride. "Forensic Toxicology" (Vol. 35, iss. 1 (2017), s. 114-124), doi 10.1007/s11419-016-0345-6



Uznanie autorstwa - Licencja ta pozwala na kopiowanie, zmienianie, rozprowadzanie, przedstawianie i wykonywanie utworu jedynie pod warunkiem oznaczenia autorstwa.



UNIwersYTET ŚLĄSKI
W KATOWICACH



Biblioteka
Uniwersytetu Śląskiego



Ministerstwo Nauki
i Szkolnictwa Wyższego

Spectroscopic characterization and crystal structures of two cathinone derivatives: *N*-ethyl-2-amino-1-phenylpropan-1-one (ethcathinone) hydrochloride and *N*-ethyl-2-amino-1-(4-chlorophenyl)propan-1-one (4-CEC) hydrochloride

Piotr Kuś¹  · Joachim Kusz² · Maria Książek² · Ewelina Pieprzyca³ · Marcin Rojkiewicz¹

Received: 2 October 2016 / Accepted: 13 October 2016 / Published online: 31 October 2016
© The Author(s) 2016. This article is published with open access at Springerlink.com

Abstract Comprehensive chemical characterization for two cathinone derivatives, *N*-ethyl-2-amino-1-phenylpropan-1-one (ethcathinone) hydrochloride and *N*-ethyl-2-amino-1-(4-chlorophenyl)propan-1-one (4-chloroethcathinone, 4-CEC) hydrochloride, in material seized by drug enforcement agencies was performed by nuclear magnetic resonance (NMR) spectroscopy, infrared spectroscopy, gas chromatography–mass spectrometry in positive electron ionization mode, liquid chromatography–mass spectrometry in positive electrospray ionization mode and X-ray crystallography. The examined samples of these two compounds proved to be very pure for ethcathinone and mixed with very small quantities of other substances for 4-CEC by NMR spectroscopy and mass spectrometry. X-ray crystallographic studies confirmed the occurrence of both compounds as racemic mixtures. These spectroscopic and crystallographic data seem very useful for their identification. Especially for 4-CEC, this is the first description on its spectroscopic characterization in a scientific context to our knowledge.

Keywords Ethcathinone · 4-Chlorocathinone · 4-CEC · NMR · MS · X-ray crystallography

Introduction

Synthetic cathinones are based on naturally occurring cathinone, one of the psychoactive compounds present in khat (*Catha edulis*), a plant growing in the Arabian Peninsula, Ethiopia and Somalia, as well as cultivated in other East African countries. The plant is variably called Arabian Tea, Abyssinian Tea, Chat Tree, Khat or Cafta. Its leaves contain ca. 1% alkaloids. The main ones are: cathinone (2-amino-1-phenylpropan-1-one, α -aminopropiophenone), *L*-ephedrine and cathin [(1*S*, 2*S*)-2-amino-1-phenylpropan-1-ol, (+)-nor- ψ -ephedrine].

Synthetic cathinones first appeared on the European illicit drug market in 2005 and today they make up one of the largest categories of novel psychoactive substances (NPSs) as over 80 synthetic cathinone derivatives were detected via the EU Early Warning System between 2005 and 2014 [1]. Cathinone derivatives are claimed to have effects similar to those of cocaine, amphetamine or MDMA (ecstasy), but little is known about their toxicity and pharmacokinetic properties. Synthetic cathinones most often are sold as powders or tablets through physical retail shops or via the Internet labeled as ‘plant feeders’, ‘plant food’, ‘research chemical’, or ‘bath salts’. Various products are labeled with such warnings as ‘not for human consumption’ or ‘not tested for hazards or toxicity’. The availability of high-quality and pure synthetic cathinones has sometimes been reported as offering direct competition to low-quality and relatively more expensive established drugs. The most common administration routes include insufflation (snorting) and oral ingestion of capsules, tablets or powder wrapped in a cigarette paper (so-called ‘bombing’). Rectal insertion and intravenous, subcutaneous and intramuscular injections were also reported [2–4].

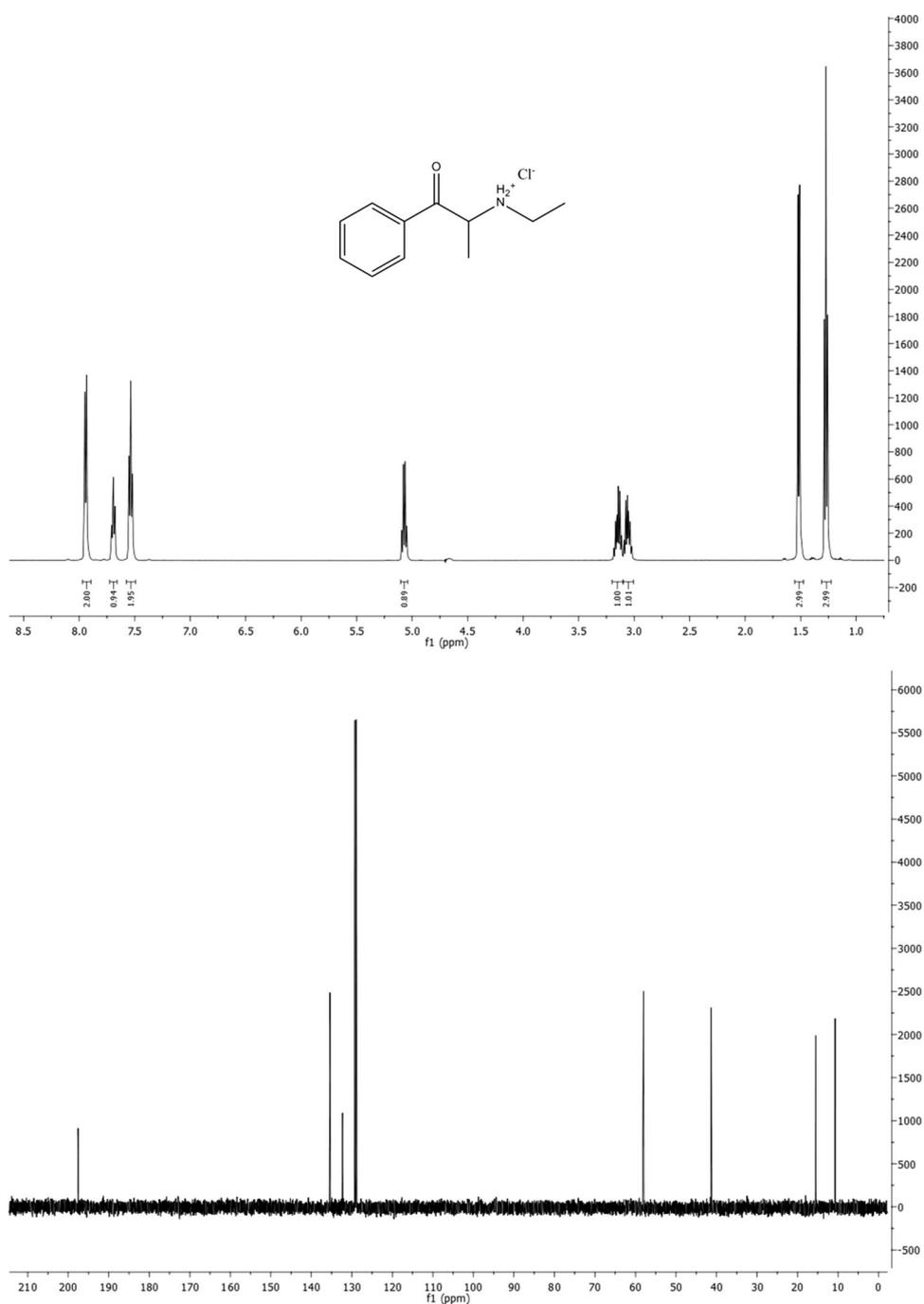
✉ Piotr Kuś
pkus@ich.us.edu.pl

¹ Department of Chemistry, University of Silesia, 9 Szkolna Street, 40-006 Katowice, Poland

² Institute of Physics, University of Silesia, 4 Uniwersytecka Street, 40-007 Katowice, Poland

³ Department of Forensic Medicine, Medical University of Silesia, 15 Poniatowskiego Street, 40-055 Katowice, Poland

Fig. 2 ^1H Nuclear magnetic resonance (NMR; *upper*) and ^{13}C NMR (*lower*) spectra of compound **1** in D_2O

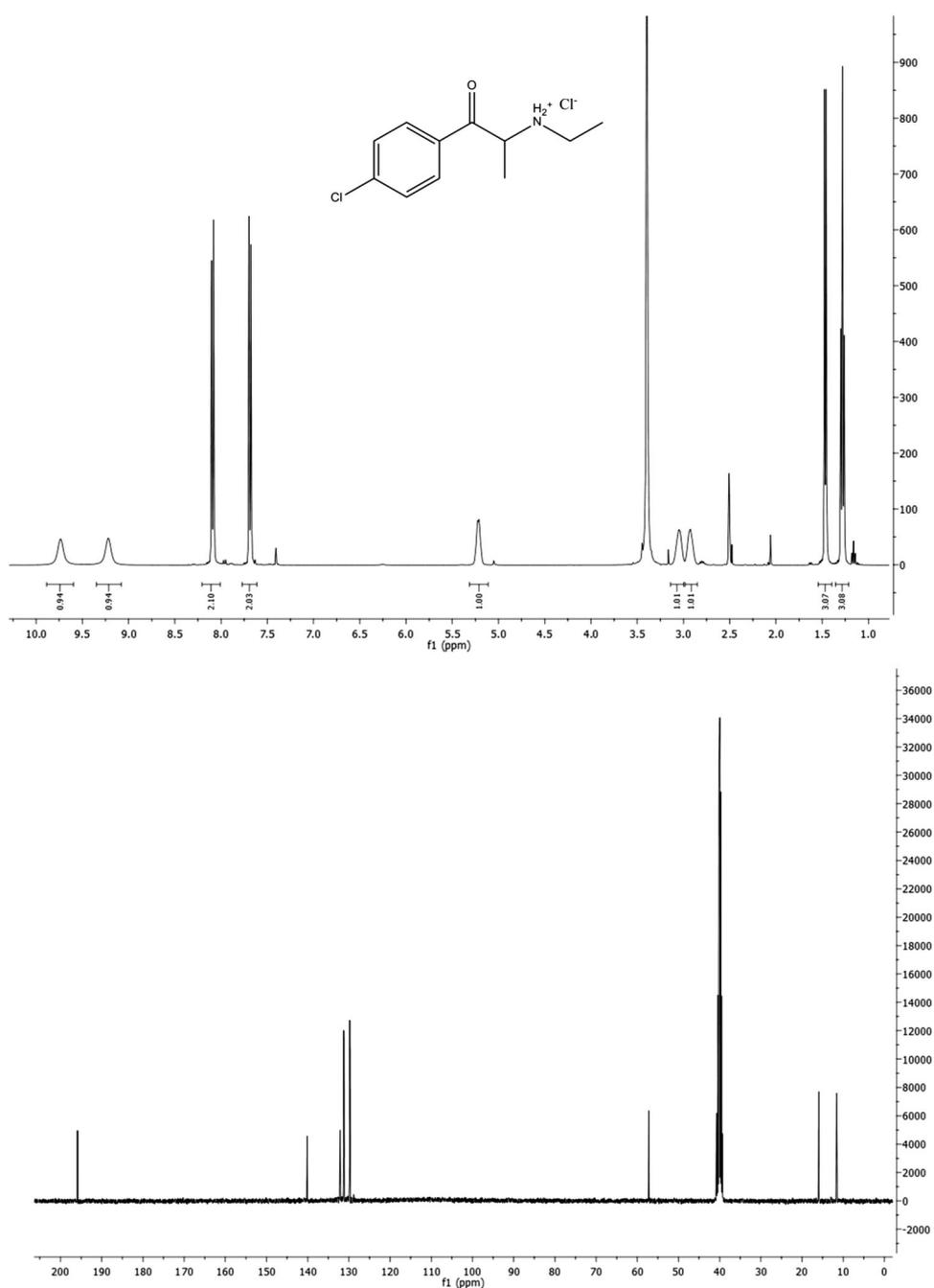


initial column temperature ($75\text{ }^\circ\text{C}$) was maintained for 1 min, then was increased linearly at $25\text{ }^\circ\text{C}/\text{min}$ up to $280\text{ }^\circ\text{C}$, and maintained for 20.8 min. The mass detector was set to positive electron ionization (EI) mode, and the electron beam energy was 70 eV. The mass detector was operating in a full scan mode in the range of m/z 40–450.

The single crystal X-ray experiments were performed at room temperature. The data were collected using a SuperNova kappa diffractometer with an Atlas charge coupled device (CCD) detector and a Xcalibur

diffractometer with a Sapphire3 CCD detector (Oxford Diffraction Ltd., Yarnton, England). For the integration of the collected data, the CrysAlis RED software (version 1.171.32.29; Agilent Technologies, Santa Clara, CA, USA) was used. The solving and refining procedures were similar for both compounds. The structures were solved using direct methods with the SHELXS97 software and the solutions were refined using the SHELXL-2014/7 program [16]. CCDC 1481895 (**1**) and 1481896 (**2**) contain supplementary crystallographic data for this paper. These data

Fig. 3 ^1H NMR (*upper*) and ^{13}C NMR (*lower*) spectra of compound **2** in dimethyl sulfoxide- d_6



can be obtained free of charge from The Cambridge Crystallographic Data Centre via: www.ccdc.cam.ac.uk/data_request/cif.

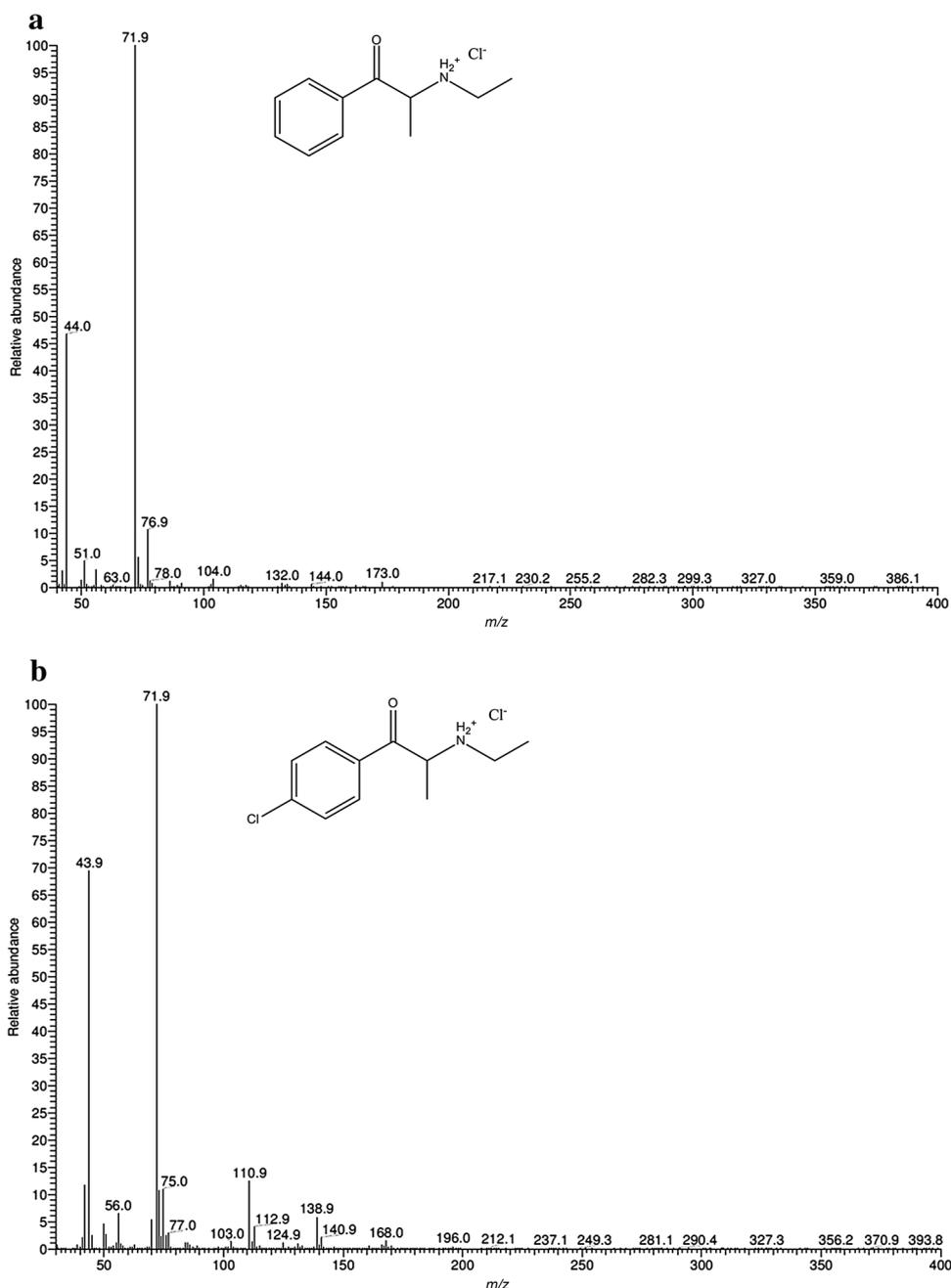
Results and discussion

NMR spectra

Samples of both compounds received for analysis were examined by ^1H and ^{13}C NMR and IR spectroscopy, and

ESI-MS, which confirmed that they were cathinone derivatives. Figures 2 and 3 show NMR spectra of compounds **1** and **2**, respectively. They fully confirm the predicted structures of the examined species. At the same time, they demonstrate that the examined substances are nearly pure cathinones. No other signals were detected which would imply the presence of other impurities in the examined sample of compound **1**. The ^1H NMR spectrum of compound **2** showed signals at 7.95, 7.40, 5.05, 3.45, 3.16, 2.48, 2.06 and 1.18 ppm of very low intensities reflecting some undefined

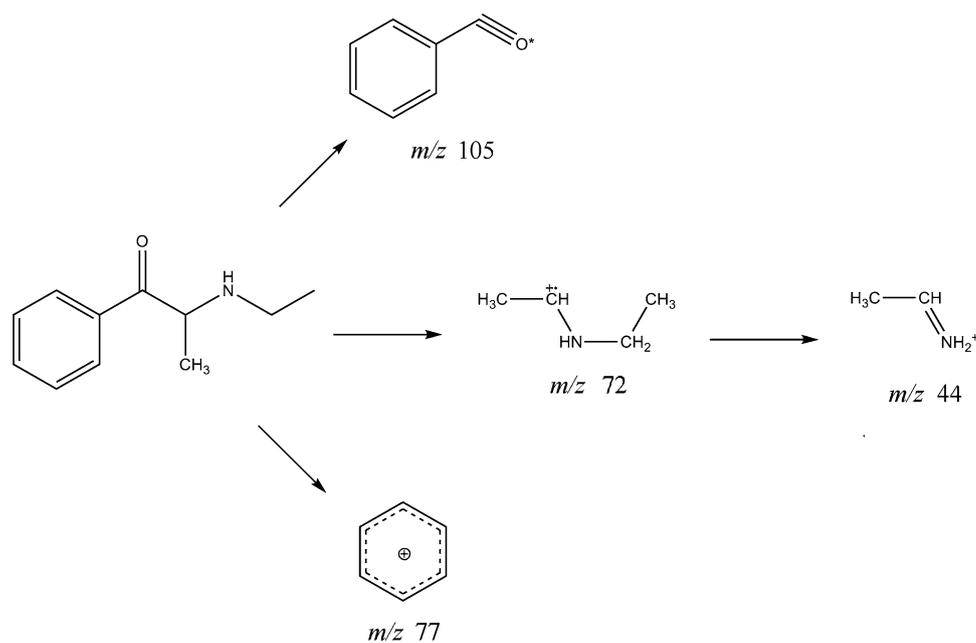
Fig. 4 Electron ionization (EI) mass spectra of **a** compound **1** and **b** compound **2**



impurities (approximate content of impurities <1%; Fig. 3, upper panel). The N–H protons in the hydrochloride salt of compound **2** are diastereotopic (chemically inequivalent). These protons were observed as two broad singlets at $\delta = 9.74$ and 9.22 ppm but only in DMSO- d_6 solution (Fig. 3, upper panel). In D $_2$ O or CD $_3$ OD solutions, these signals were not observed (Fig. 2, upper panel). The ^1H NMR spectra of both compounds confirmed the presence of a substituted benzene ring, which was mono-substituted (compound **1**) and di-substituted (*para*, compound **2**). The methinic protons in compounds **1** and **2** appeared as quintets at

5.07 and 5.21 ppm, respectively (see below). The *N*-ethyl side chains yielded two multiplets for methylene protons centered at 3.05 and 3.15 ppm for compound **1**, and two broad multiplets (like broad singlets) centered at 2.93 and 3.05 ppm for compound **2**. Terminal methyl groups yielded triplets centered at 1.27 and 1.28, for compounds **1** and **2**, respectively.

The ^{13}C NMR spectra displayed carbonyl resonance at 197.6 and 195.9 ppm for compounds **1** and **2**, respectively (Figs. 2, 3, lower panels, also see below). The six aromatic carbons appearing as four signals for both compounds showed greater differences because they reflect chemical

Fig. 5 EI fragmentation pathways of compound **1**

and structural differences. The methylene carbons of *N*-ethyl groups were found at 41.3 and 40.8 ppm for compounds **1** and **2**, respectively. The methinic carbons resonated at 58.0 and 57.2 ppm for compounds **1** and **2**, respectively. The up-field two signals in both spectra correspond to both methyl carbons of each compound.

Compound **1** (ethcathinone hydrochloride)

^1H NMR (D_2O), δ (ppm): 7.94 (d, 2H), 7.69 (t, 1H), 7.53 (t, 2H), 5.07 (q, 1H), 3.15 (m, 1H), 3.05 (m, 1H), 1.52 (d, 3H), 1.27 (t, 3H).

^{13}C NMR (D_2O), δ (ppm): 197.6, 135.4, 132.3, 129.3, 128.9, 58.0, 41.3, 15.5, 10.7.

Compound **2** (4-CEC hydrochloride)

^1H NMR ($\text{DMSO}-d_6$), δ (ppm): 9.74 (bs, 1H), 9.22 (bs, 1H), 8.09 (d, 2H), 7.68 (d, 2H), 5.21 (q, 1H), 3.05 (bs, 1H), 2.93 (bs, 1H), 1.47 (d, 3H), 1.28 (t, 3H).

^{13}C NMR ($\text{DMSO}-d_6$), δ (ppm): 195.9, 140.1, 132.1, 131.2, 129.8, 57.2, 40.8, 15.9, 11.6.

IR spectra

Only IR spectra of compound **1** were previously published [9]. The IR spectra showed strong C=O absorption bands at 1694 and 1686 cm^{-1} for compounds **1** and **2**, respectively. The shift of the C=O absorption band for one compound relative to the other is a result of a substituent in a *para* position of the aromatic ring in compound **2**. Spectra of both compounds showed characteristic bands associated with

their salt forms. These included a broad pattern from 2300 to 3100 cm^{-1} corresponding to amine salt absorption bands and combination of aromatic and aliphatic C–H stretches. The main NH_2^+ stretch absorption for both compounds appeared at 2694 cm^{-1} . The aromatic C=C ring stretch vibrations appeared at 1597 and ca. 1590 cm^{-1} for compounds **1** and **2**, respectively. A strong band at 839 cm^{-1} in the spectrum of compound **2** was characteristic for two adjacent free hydrogen atoms in an aromatic *para*-di-substituted ring (aromatic C–H out-of-plane bend). Two bands at 768 and 698 cm^{-1} in compound **1** were characteristic for an aromatic C–H out-of-plane bend of a mono-substituted benzene ring. All other absorption peaks are listed below.

Compound **1** (ethcathinone hydrochloride)

IR (KBr; cm^{-1}): 3417, 2934, 2803, 2742, 2480, 1694, 1597, 1439, 1387, 1338, 1314, 1237, 1194, 1128, 1105, 1025, 978, 861, 792, 768, 698, 684, 657, 537.

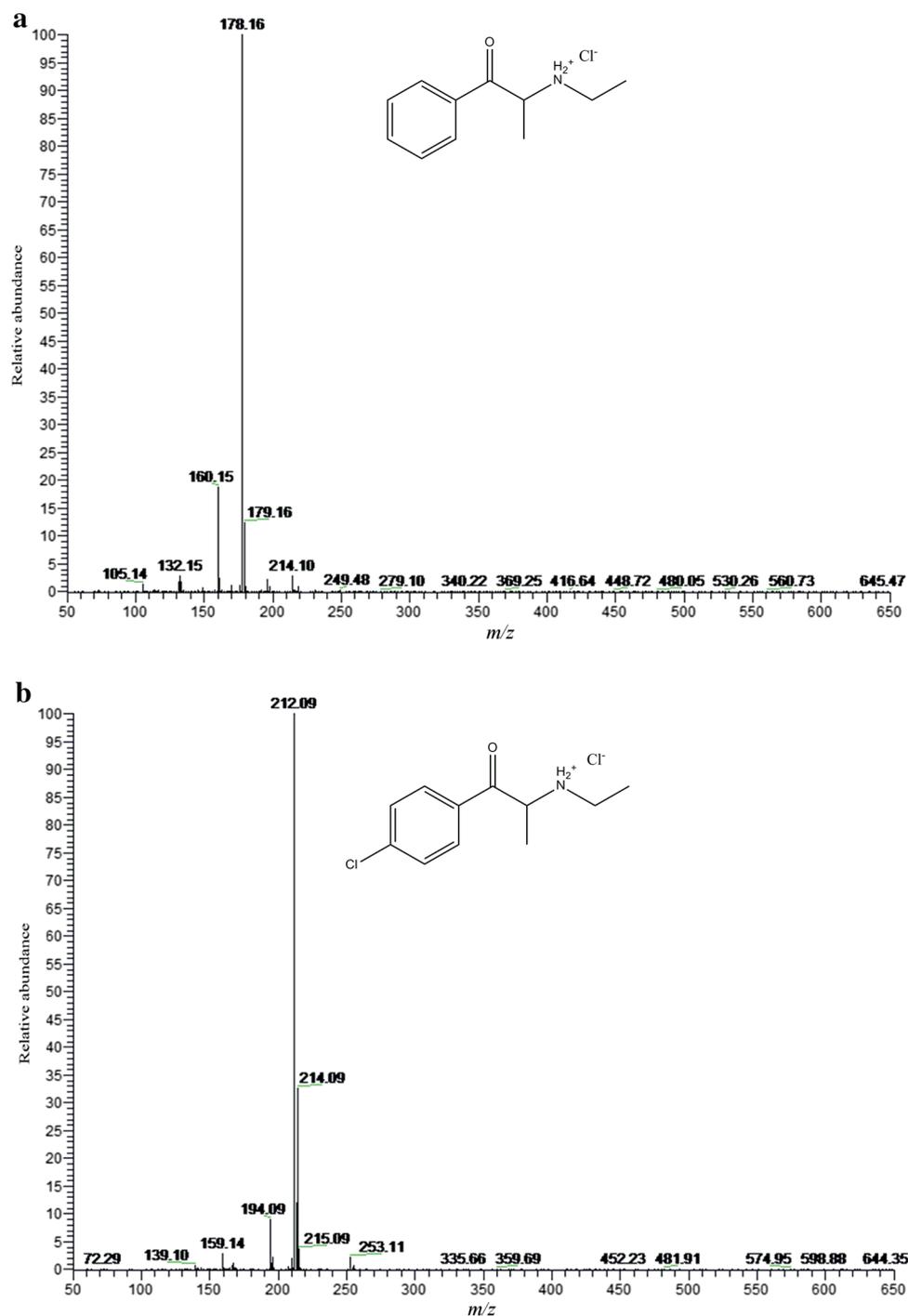
Compound **2** (4-CEC hydrochloride)

IR (KBr; cm^{-1}): 3530, 3430, 2983, 2795, 2694, 2447, 1687, 1590sh, 1554, 1462, 1392, 1292, 1234, 1164, 1094, 1051, 974, 919, 839, 794, 748, 684, 479.

GC–MS and ESI–MS spectrometry

Figure 4 shows the EI mass spectra of compounds **1** and **2**. Figure 5 shows EI fragmentation pathways of compound **1**. For compound **2**, fragmentation pathways was identical (with respect to the Cl substituent). The molecular ions for

Fig. 6 Electrospray ionization (ESI) mass spectra of **a** compound **1** and **b** compound **2**



both compounds were not visible. Base peaks for compounds **1** and **2** at m/z 72 probably resulted from formation of *N*-ethylethano-1-iminium cation via the initiated benzoyl unit cleavage and by the loss of a hydrogen molecule. For compound **1**, after cleavage of the β -ketone unit, the benzoyl cation at m/z 105 was formed with subsequent loss of a CO molecule to form a phenyl cation at m/z 77. Similarly, for compound **2**, the same process led to the 4-chlorobenzoyl cation at m/z 139 and the next

4-chlorophenyl cation at m/z 111. These types of fragmentation are consistent with previously reported data [9, 17–19].

Figure 6a shows the ESI mass spectrum of compound **1** upon HPLC–MS analysis. A base peak appeared at m/z 178.16 in good accordance with the calculated value for $[M + H]^+$ [calc. for M ($C_{11}H_{15}NO$); m/z 178.12]. Figure 6b shows the ESI mass spectrum of compound **2**. Base peaks appeared at m/z 212.09 and 214.09 (for isotopic ^{37}Cl atom).

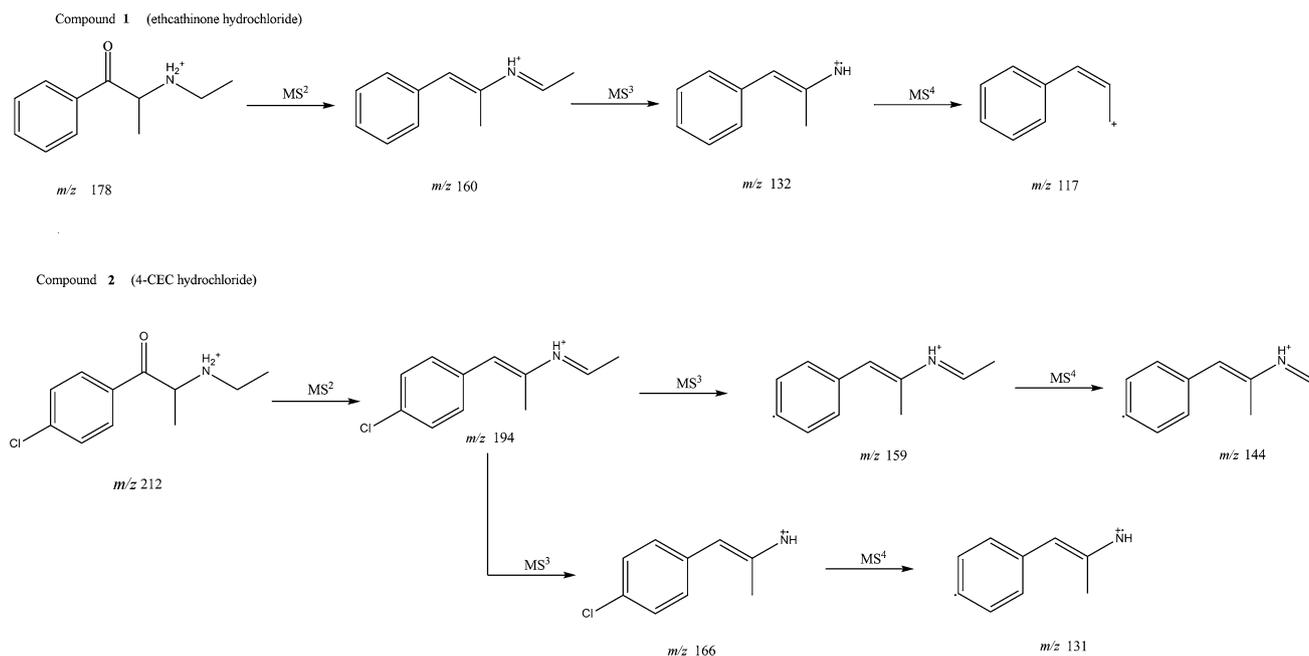


Fig. 7 Proposed fragmentation pathways of compounds 1 and 2 in ESI-MSⁿ modes

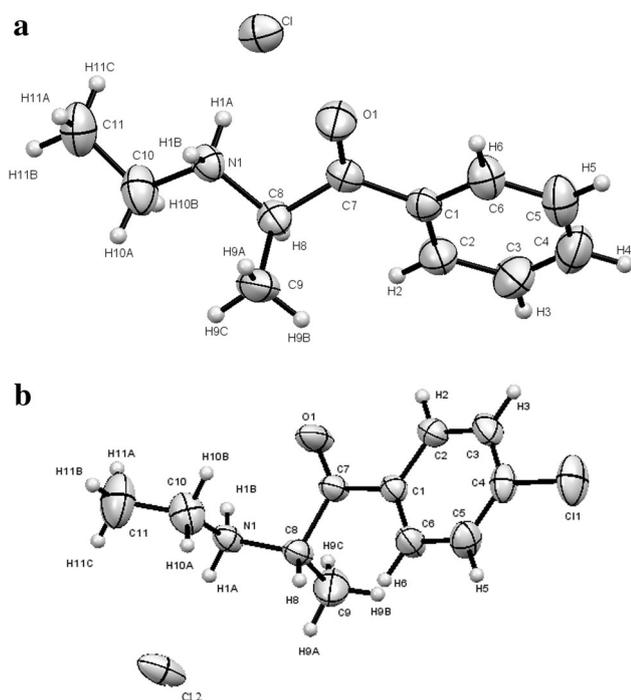


Fig. 8 **a** The molecule of an (*S*) enantiomer of compound 1 in the crystal. **b** The molecule of an (*R*) enantiomer of compound 2 in the crystal. Ellipsoids correspond to 50% probability levels

Both peaks were in good accordance with calculated values for $[M + H]^+$ ions [calc. for $M(C_{11}H_{14}ClNO)$; m/z 212.08 and 214.08 for ^{35}Cl and ^{37}Cl , respectively]. Isomer ratio occurring in nature was ca. 76/34 ($^{35}Cl/^{37}Cl$) which is almost ideally reflected by the intensities of both basic peaks.

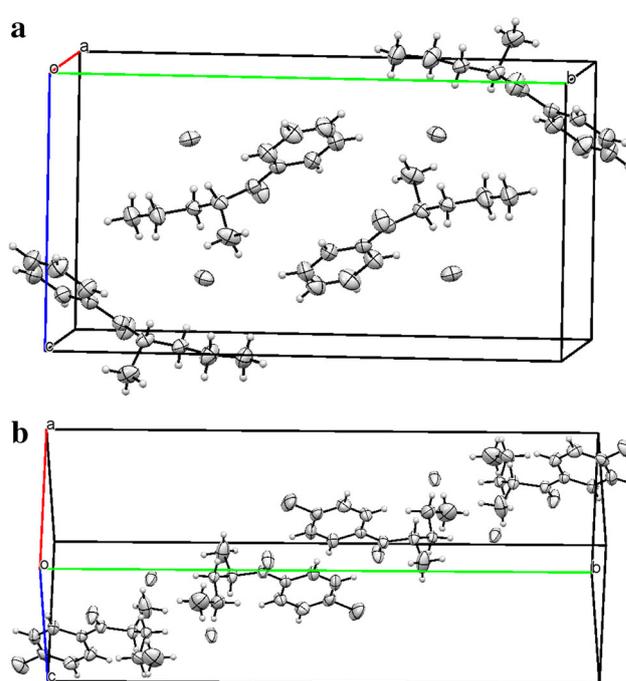


Fig. 9 Packing diagrams of **a** compound 1 and **b** compound 2

The elimination of one water molecule from the protonated molecular ion is very characteristic for cathinones, especially in the tandem mode [19]. For both described compounds, this phenomenon appeared in MS¹ spectra. In Fig. 7, we present proposed fragmentation pathways for ESI in MS², MS³ and MS⁴ modes for compound 1 and compound 2 as well.

Table 1 Crystal data and structure refinement for ethcathinone hydrochloride (compound **1**) and 4-CEC hydrochloride (compound **2**)

	Compound 1	Compound 2
Molecular formula	C ₁₁ H ₁₆ NOCl	C ₁₁ H ₁₅ NOCl ₂
Molecular weight	213.70	248.14
Crystal system	Monoclinic	Monoclinic
Space group	P2 ₁ /c	P2 ₁ /c
Temperature (K)	290	290
a (Å)	5.6558(1)	7.3569(3)
b (Å)	19.7808(6)	26.1246(5)
c (Å)	10.5559(2)	7.2462(2)
β (°)	97.570(2)	112.454(4)
V (Å ³)	1170.66(5)	1287.11(8)
Z	4	4
D _x (g cm ⁻³)	1.212	1.281
Absorption coeff. (mm ⁻¹)	2.64	0.48
F (000)	456	520
Crystal size (mm)	0.13 × 0.07 × 0.02	0.60 × 0.24 × 0.20
Data collection and structure solution		
Data collected	12,532	18,874
Independent reflections	2381	2615
Observed reflections [I > 2σ(I)]	2065	2407
R(int.)	0.021	0.018
Completeness (%)	99.8	99.5
T _{max} /T _{min}	1.000/0.838	1.000/0.858
No of parameters	154	138
R1[I > 2σ(I)]	0.0323	0.0394
wR2 (all data)	0.0918	0.0976
S	1.04	1.05
Largest difference peak and hole (eÅ ⁻³)	0.25, -0.14	0.37, -0.47

Table 2 Hydrogen bonds in compound **1** (Å and deg)

D-H...A	D-H	H...A	D...A	D-H...A
N1-H1A...Cl1	0.883(19)	2.25(2)	3.1307(13)	174.4(15)
N1-H1B...Cl1 ⁱ	0.887(18)	2.299(19)	3.1692(13)	167.0(14)
C8-H8...Cl1 ⁱⁱ	0.957(16)	2.919(16)	3.8234(14)	158.0(13)
C9-H9B...O1 ⁱⁱ	0.95(2)	2.54(2)	3.183(2)	125.2(17)
C9-H9C...Cl1 ⁱⁱⁱ	0.96(2)	2.88(2)	3.7320(18)	148.3(18)
C11-H11A...Cl1 ⁱ	0.99(3)	2.95(3)	3.712(2)	134.6(18)

Symmetry codes: (i) $x, -y + 3/2, z - 1/2$; (ii) $x + 1, y, z$; (iii) $x + 1, -y + 3/2, z - 1/2$

X-ray studies

Both hydrochloride salts crystallize in a monoclinic (P2₁/c) space group. The molecular structures of both compounds are shown in Fig. 8. Packing diagrams for both compounds are shown in Fig. 9. Crystal data and structure refinement for compounds **1** and **2** are presented in Table 1. The ring systems in both compounds were planar. All distances and

Table 3 Hydrogen bonds in compound **2** (Å and deg)

D-H...A	D-H	H...A	D...A	D-H...A
N1-H1A...Cl2	0.91(2)	2.20(2)	3.1064(15)	174.3(17)
N1-H1B...Cl2 ⁱ	0.88(2)	2.31(2)	3.1372(15)	157.3(18)
C8-H8...Cl2 ⁱⁱ	0.94(2)	2.62(2)	3.5488(18)	167.6(17)
C10-H10B...Cl1 ⁱⁱⁱ	0.98(3)	2.94(3)	3.610(2)	126.5(17)

Symmetry codes: (i) $x, -y + 1/2, z - 1/2$; (ii) $x, -y + 1/2, z + 1/2$; (iii) $-x, -y + 1, -z + 1$

angles in the molecular structures were normal. Hydrogen bonds in compounds **1** and **2** are listed in Tables 2 and 3, respectively. Selected geometric parameters for compounds **1** and **2** are presented in Table 4.

Compound **1**

Both compounds occurred in the examined crystals as paired enantiomers. The pairs were mutually linked by

Table 4 Selected geometric parameters for compounds **1** and **2** (Å, °)

	Compound 1	Compound 2
O1-C7	1.2080(16)	1.210(2)
N1-C10	1.4917(19)	1.488(2)
N1-C8	1.4921(18)	1.485(2)
C7-C8	1.5143(19)	1.522(2)
C8-C9	1.523(2)	1.514(3)
C10-C11	1.497(3)	1.481(3)
O1-C7-C1	121.34(12)	121.99(15)
O1-C7-C8	119.14(12)	119.10(15)
C1-C7-C8	119.44(11)	118.87(13)
N1-C8-C7	107.94(11)	109.47(13)
N1-C8-C9	111.03(12)	109.22(15)
C7-C8-C9	108.46(13)	109.34(16)
N1-C10-C11	110.72(15)	111.50(18)
C2-C1-C7-O1	-165.45(14)	-8.7(3)
C6-C1-C7-O1	12.8(2)	168.50(18)
C2-C1-C7-C8	17.7(2)	168.87(16)
C6-C1-C7-C8	-164.05(13)	-13.9(3)
C10-N1-C8-C7	165.77(13)	-69.25(19)
C10-N1-C8-C9	-75.47(16)	171.06(18)
O1-C7-C8-N1	25.19(18)	-26.5(2)
C1-C7-C8-N1	-157.87(11)	155.85(14)
O1-C7-C8-C9	-95.20(16)	93.1(2)
C1-C7-C8-C9	81.74(15)	-84.5(2)
C8-N1-C10-C11	-174.37(15)	-179.8(2)

hydrogen bonds formed with chloride ions occurring between these molecules. For compound **1**, all short contacts were linked to methyl groups (in position 2, and in ethyl group) and chloride ions freely located between molecules of the compound as well as with a ketone group of oxygen atoms. Chloride ions were placed at almost equal distance from two ammonium groups from the adjacent molecules (3.131 and 3.169 Å, respectively, Fig. 9a); at the same time, hydrogen atoms C–H9 and C–H8 from two surrounding molecules formed close contacts with the same chloride ion (2.88 and 2.918 Å, respectively, Fig. 10). Torsional angles C7C8N1C10 were identical in both enantiomers present in the elementary cell (165.77°).

Compound **2**

Compound **2** stereoisomers occurred pairwise forming hydrogen bonds with chloride ions (Fig. 11). Torsional angles C7C8N1C10 are identical in both enantiomers (69.25°). Distances between N–HA, as well as N–HB, and chloride ion present between these molecules were 2.221 and 2.322 Å, respectively.

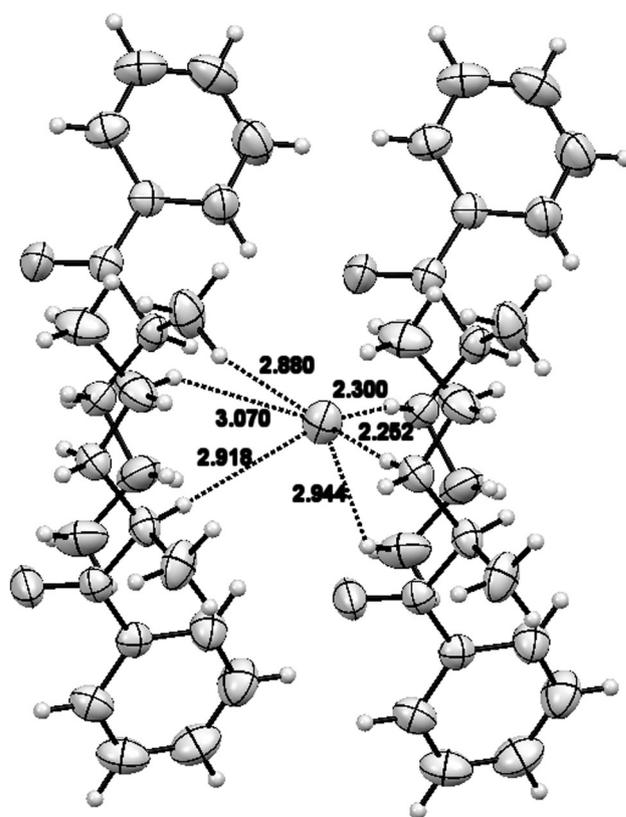


Fig. 10 Schematic representation of a single chloride ion surrounded by compound **1** molecules. The dotted lines show short contacts of the chloride ion with hydrogen atoms from four nearest molecules

Crystallographic structures of both compounds can be characterized by the distance between the chloride ion and the surrounding molecules of cathinone cation. In the case of compound **1**, the chloride ion was surrounded by four different cationic species (Fig. 10), whereas in compound **2**, this ion was surrounded by three adjacent cations (Fig. 11b). This finding is corroborated by short distances between the chloride ion and various fragments of surrounding molecules (<3Å).

Conclusions

In this paper, we report spectroscopic (IR, NMR and MS) and crystallographic characteristics of two designer drugs: ethcathinone and 4-chloroethcathinone (4-CEC), both present on the illicit drug market either as pure substance or mixed with other species (to be confirmed chromatographically as well as by using NMR and MS). The examined samples of these two compounds proved, indeed, to be either very pure (compound **1**) or mixed with other

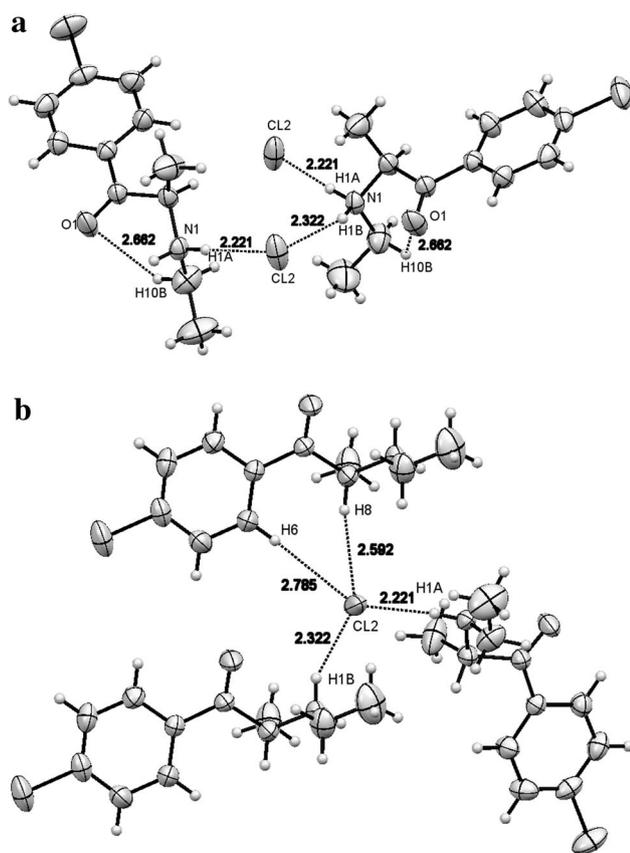


Fig. 11 **a** Two molecules forming half an elementary cell of compound **2** with short interatomic distances are shown. **b** Three molecules of compound **2** surrounding the chloride anion in the crystallographic structure. The *dotted lines* show short contacts of chloride ion with hydrogen atoms from three adjacent molecules

substances (compound **2**). NMR and MS spectra can be used to differentiate between both compounds. Crystallographic studies confirmed the occurrence of both compounds as racemic mixtures which would rather be expected considering the possible method of synthesizing these compounds.

Compliance with ethical standards

Conflict of interest The authors have no financial or other relations that could lead to a conflict of interest.

Ethical approval This article does not contain any studies with human participants or animals performed by any of the authors.

Open Access This article is distributed under the terms of the Creative Commons Attribution 4.0 International License (<http://creativecommons.org/licenses/by/4.0/>), which permits unrestricted use, distribution, and reproduction in any medium, provided you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made.

References

- European Monitoring Centre for Drugs and Drug Addiction (2015) European drug report. http://www.emcdda.europa.eu/attachelements.cfm/att_239505_EN_TDAT15001ENN.pdf. Accessed June 2015
- Zawilska J, Wojcieszak J (2013) Designer cathinones—an emerging class of novel psychoactive substances. *Forensic Sci Int* 231:42–53
- Valente MJ, Geudes de Pinho P, Carvalho F, Carvalho M (2014) Khat and synthetic cathinones: a review. *Arch Toxicol* 88:15–45
- Prosser JM, Nelson LS (2012) The toxicology of bath salts: a review of synthetic cathinones. *J Med Toxicol* 8:33–42
- http://gis.gov.pl/images/%C5%9Brodki_zast%C4%99pcze/%C5%9Bz/gis_raport_2013-2014.pdf. Accessed June 2015
- Adamowicz P, Geroń J, Gil D, Lechowicz W, Skulska A, Tokarczyk B (2016) The prevalence of new psychoactive substances in biological material—a three-year review of casework in Poland. *Drug Test Anal* 8:63–70
- Yu H, Rothman RB, Dersch CM, Partilla JS, Rice KC (2000) Uptake and release effects of diethylpropion and its metabolites and biogenic amine transporters. *Bioorg Med Chem* 8:2689–2692
- Rosen E, Free SM, Heil GC (1971) Reduced side effects following administration of a new anorectic agent, 4'-chloro-2-(ethylamino)propiofenone, in timed-release form. *J Pharm Sci* 60:1900–1903
- Dal Cason TA (2007) Synthesis and identification of *N*, *N*-dimethylcathinone hydrochloride. *Microgram J* 5:3–12
- National Forensic Laboratory, Slovenia (2016) Analytical report: 4-CEC. http://www.policija.si/apps/nfl_response_web/0_Analytical_Reports_final/4-CEC-ID-1501-16-report_final.pdf. Accessed Feb 2016
- Nycz JE, Małecki G, Zawiązalec M, Paździorek T (2011) X-ray structures and computational studies of several cathinones. *J Mol Struct* 1002:10–18
- Power JD, McDermott SD, Talbot B, O'Brien JE, Kavanagh P (2012) The analysis of amphetamine-like cathinone derivatives using positive electrospray ionization with in-source collision-induced dissociation. *Rapid Commun Mass Spectrom* 26:2601–2611
- Fornal E (2013) Formation of odd-electron product ions in collision-induced fragmentation of electrospray-generated protonated cathinone derivatives: aryl α -primary amino ketones. *Rapid Commun Mass Spectrom* 27:1858–1866
- Hyde JF, Browning E, Adams R (1928) Synthetic homologs of *d*, *l*-ephedrine. *J Am Chem Soc* 50:2287–2292
- Kavanagh P, O'Brien JE, Fox J, O'Donnell C, Christie R, Power JD, McDermott SD (2012) The analysis of substituted cathinones. Part 3. Synthesis and characterization of 2,3-methylenedioxy substituted cathinones. *Forensic Sci Int* 216:19–28
- Sheldrick GM (2008) A short history of SHELX. *Acta Cryst A* 64:112–122
- Camilleri A, Johnson MR, Brennan M, Davis S, Caldicott DGE (2010) Chemical analysis of four capsules containing the controlled substance analogues 4-methylmethcathinone, 2-fluoromethamphetamine, α -phthalimidopropiofenone and *N*-ethylcathinone. *Forensic Sci Int* 197:59–66
- Awad T, Clarke CR, DeRuiter J (2006) Chromatographic and mass spectral studies on methoxymethcathinones related to 3,4-methylenedioxyamphetamine. *J Chromatogr Sci* 44:155–161
- Majchrzak M, Rojkiewicz M, Celiński R, Kuś P, Sajewicz M (2016) Identification and characterization of new designer drug 4-fluoro-PV9 and α -PHP in the seized materials. *Forensic Toxicol* 34:115–124