Short Note

Crystal Structure of Bis(1-butyl-1-methypryrolidinium) Perthiodicarbonate Complex

Noël Pinaud 1, Yann Danten 2, Mathieu Marchivie 3, Marcel Besnard 2, Isabel Cabaço 4 and Jean Guillon 5,*

1 ISM—CNRS UMR 5255, University of Bordeaux, 351 Cours de la Libération, F-33405 Talence, France; noel.pinaud@u-bordeaux.fr
2 GSM—ISM—CNRS UMR 5255, University of Bordeaux, 351 Cours de la Libération, F-33405 Talence, France; yann.danten@u-bordeaux.fr (Y.D.); marcel.besnard@u-bordeaux.fr (M.B.)
3 CNRS, Bordeaux INP, ICMMB, UMR 5026, University of Bordeaux, 87 Avenue du Docteur Schweitzer, F-33608 Pessac, France; mathieu.marchivie@u-bordeaux.fr
4 CeFEMA, Centro de Física e Engenharia de Materiais Avançados, Departamento de Física, Instituto Superior Técnico, Universidade de Lisboa, 1049-001 Lisboa, Portugal; isabelcabaco@tecnico.ulisboa.pt
5 ARNA Laboratory, INSERM U1213-UMR CNRS 5320, Faculty of Pharmacy, University of Bordeaux, 146 Rue Léo Saignat, F-33076 Bordeaux, France
* Correspondence: jean.guillon@u-bordeaux.fr; Tel.: +33-557-571-652

Abstract: Bis(1-butyl-1-methypryrolidinium) perthiodicarbonate was obtained by the reaction of carbon disulfide with 1-butyl-1-methypryrolidinium acetate ([BmPyrro][Ac]) in the liquid phase. Structural characterization of this original complex was achieved by single-crystal X-ray diffraction (SCXRD) analysis. The asymmetric unit of the title compound, C2S6·2C9H20N, consisted of two crystallographically 1-methyl-1-butyl pyrrolidinium cations and one perthiodicarbonate anion. The complex C2S6·2C9H20N crystallized in the monoclinic space group, C 2/c, and possessed the following cell parameters: a = 16.0970(10) Å, b = 14.7140(9) Å, c = 12.3280(8) Å, α = 90°, β = 112.3730(12)°, γ = 90°, V = 2700.11 Å3, and Z = 8, Z′ = 0.5.

Keywords: bis(1-butyl-1-methypryrolidinium) perthiodicarbonate; ionic liquid; single-crystal X-ray diffraction analysis

1. Introduction

Ionic liquids attract the attention of physical chemists due to their unique characteristics and wide spectrum of applications. As they have very good dissolution properties for most organic and inorganic compounds, they are increasingly used neutrally by chemists as substitutes for traditional organic solvents or as an excellent medium for the synthesis and stabilization of nanoparticles. They also may have a role in trapping small molecules such as CO2 [1,2]. In recent years, they have also been used for new crystallization strategies, including the crystallization of solids with high and low melting points, and they are found as additives in the crystallization conditions of macromolecules such as proteins [3].

In this study, we extended our previous work on understanding the molecular mechanisms involved in the addition of CO2, OCS, and CS2 in ionic liquids. Specifically, we focused on developing a crystallization strategy for the compounds formed during the reaction between 1-butyl-1-methypryrolidinium acetate ([BmPyrro][Ac]) 1 and CS2. These previous NMR analyses highlighted the formation of CO2, CH3COS−, and CS3− anions in the reaction medium [4,5]. Consequently, these anions could compete with the initial acetate to form either ([BmPyrro][CH3COS−]) 2 or (bis[BmPyrro][CS32−]) 3.

In this work, we aimed to determine, by crystallization and X-ray diffraction, which of these anions complexed the 1-butyl-1-methypryrolidinium cation. Surprisingly, a fascinating structure of bis(1-butyl-1-methypryrolidinium) perthiodicarbonate 4 was obtained (Figure 1).
2. Results and Discussion

2.1. Synthesis of Bis(1-butyl-1-methypyrrolidinium) Perthiodicarbonate 4

Upon the dissolution of CS₂ in [BmPyro] [Ac] 1, a blood-red solution was observed, showing that a reaction had occurred. This blood-red color of the CS₂-[BmPyro] [Ac] solution was due to the presence of CS₃²⁻ anions. Previous ¹H, ¹³C NMR, and UV–visible investigations conducted by our research team showed that the reaction of [BmPyro] [Ac] 1 with CS₂ led, via coupled complex reactions, to the degradation of this molecule to form several main adducts, namely, CO₂, OCS, thioacetate anion (CH₃COS⁻) 2, and, as a minor species, trithiocarbonate anion (CS₃²⁻) 3 (Scheme 1) [4,5]. Such products formed in this system have already been found in the solution of CS₂ in 1-butyl-3-methylimidazolium acetate ([Bmim] [Ac]) [6]. In order to isolate one of these 1-butyl-1-methypyrrolidinium salts, we investigated some crystallographic assays. The different tests made it possible to isolate a single crystalline form. Thus, orange crystals in the shape of a thick diamond were obtained. Surprisingly, the data of their measurement revealed the formation of a complex consisting of two 1-methyl-1-pyrrolidinium cations coupled with a single perthiodicarbonate anion (Scheme 1). This formation of perthiodicarbonate anion from a reaction medium containing CS₂ and CS₃²⁻ initially formed has already been described in the literature [7,8].

![Figure 1. Chemical structure of bis(1-butyl-1-methypyrrolidinium) perthiodicarbonate 4.](image)

**Scheme 1.** Synthesis of bis(1-butyl-1-methypyrrolidinium) perthiodicarbonate 4.

2.2. Crystallographic Structure

The title compound crystallized in the monoclinic C 2/c space group. The asymmetric unit of the title compound, C₂S₂·2CH₂H₂N, consisted of one 1-methyl-1-butyl pyrrolidinium cation and one half perthiodicarbonate anion; the whole anion was obtained by symmetry around a 2-fold rotation axis situated at 0,y,1/4. The cation was disordered into two positions, with the respective occupation of 86/14%, which corresponded approximately to a 90° rotation around the alkyl axis of the molecule. Both conformations were stabilized by different but similar S···H short contacts; however, a very short S···H contact and numerous H···H interactions, potentially repulsive, were found for the minor conformation. Only the main position is drawn in Figure 2 for clarity.
The bond distances and angles of our pyrrolidinium cation were all within normal ranges [9,10], with the butyl substituent adopting the energetically preferred anti conformation with an N1–C6–C7–C8 torsional angle of 173.0(2)°. The pyrrolidine heterocycle adopting the energetically preferred envelope (Cs) ring conformation with an interplanar dihedral angle between the C7A–10A–N1A and C9A–C8A–C10A–C7A planes in the pyrrolidine ring was found at 129.3(1)°. The torsion angle with 85.50(9)° (C1–S1–S1–C1) was also similar to the torsion angles in (Et4N)2C5S6 (86.92(16)° [11]. In our pyrrolidinium salt, the S–C–S angle was noticed at 32.9(3)°. Nevertheless, the C–S···H angle was far from the ideal value of 105°. The S···H contact with the methyl of the cation, Figure 3a; 2 with a double S···H short contact of the title compound fulfilled D–H···S angle > 140°. Nevertheless, the C–S···H angle was far from the ideal value of 105° and did not lie within the S–C–S plane, which most probably suggests the mainly electrostatic nature of these interactions.

The network cohesion was ensured by anion–cation interactions through close H···S contacts involving the methyl group, CH2 of the pyrrole ring of the pyrrolidinium cation, and the four sulfur atoms of the CS2− moiety of the anion. Each anion interacted with six cations (two with a double S···H contact with the methyl of the cation, Figure 3a; 2 with a single S···H contact with the methyl of the cation or the CH2 of the pyrrolidine ring, Figure 3b), whereas the cations interacted with three anions. All these interactions propagated in the three directions to form the crystal network. According to the classification of T. Steiner [13], the S···H short contacts can be considered weak hydrogen bonding, providing that the distance is close to or below the sum of Van der Waals radii and that the D–H···S angle is close to 180° (>110°). As the S···H short contacts of the title compound fulfilled these requirements, they could be considered as weak hydrogen bonding (S···H distance around 2.75 Å within the 2.2–3.2 range found in the CSD data for similar interactions and D–H···S angle > 140°). Nevertheless, the C–S···H angle was far from the ideal value of 105° and did not lie within the S–C–S plane, which most probably suggests the mainly electrostatic nature of these interactions.

Figure 2. ORTEP (Oak Ridge Thermal Ellipsoid Plot) drawing of the bis(1-butyl-1-methyppyrrrolidinium) perthiodicarbonate with thermal ellipsoids at the 50% level. The labeling scheme is shown for the asymmetric unit only. The minority part of the disordered cation is removed for clarity.
3. Materials and Methods

Commercial reagents were used as received, without additional purification. Crystallographic data were collected at 298 K on a Bruker APEX Duo diffractometer (Bruker France S.A.S., Champs-sur-Marne, France) using monochromatic Mo-Kα radiation (λ = 0.71073 Å).

3.1. Bis(1-butyl-1-methylypyrrolidinium) Perthiodicarbonate

CS₂ was dissolved in [BmPyrro][Ac] at a 0.02 mole fraction at room temperature. A slight release of heat was observed as well as a strong red coloring of the sample. The solution was then distributed into drops of different volumes (4 μL to 10 μL) on a siliconized glass slide. The glass plate was then placed in a vacuum desiccator (0.05 mbar) overnight to remove residual water traces and CO₂ and OCS forms during the chemical reaction between [BmPyrro][Ac] and CS₂ [4–6]; then, it was placed at 4 degrees Celsius for 72 h. Suitable green-orange diamond-shaped crystals 300 × 200 × 100 μm long were observed in the drops. The crystals were then preserved in paraton oil before being measured.

3.2. Crystal and Refinement Data

The structure of bis(1-butyl-1-methylypyrrolidinium) perthiodicarbonate was established using X-ray crystallography (Figure 2) [18]. The green-orange crystal of the title compound was obtained by slow evaporation under reduced pressure from the reaction solution mixture, as described above.

The collected data were reduced using SAINT software, version 6.45 (SAINT, Bruker AXS Inc., Madison, WI, USA), and all reflections were used for unit–cell refinement. The crystal structure was solved by direct methods and successive Fourier difference syntheses with the SHELXS program and refined on F² by anisotropic full-matrix weighted least square methods using SHELXL within the OLEX2 package [19–21]. All non-H atoms except those of the minority disordered part of the cation were refined anisotropically. H-atoms were analyzed according to the riding model and included for structure factor calculation, but not refined.

Figure 3. View of the anion–cation interaction showing the (a) double S···H contacts and (b) single S···H contacts.

It is worth noting that the structural description of this original dianion completes the very scarce crystal structures containing this perthiodicarbonate moiety, as only five entries were found in the CSD database [11,14–17]. It is interesting that the conformation of this molecular dianion is quasi-identical within all the published crystal structures as the RMSD (Root Mean Square Deviation) ranged from 0.065 Å to a maximum value of 0.136 Å between our dianion molecular structure and that of the bis(tetraphenylphosphonium) perthiodicarbonate [14].
Crystal data for bis(1-butyl-1-methylpyrrolidinium) perthiodicarbonate 4: monoclinic, space group C 2/c, a = 16.0970(10) Å, b = 14.7140(9) Å, c = 12.3280(8) Å, α = 90°, β = 112.3730(12)°, γ = 90°, V = 2700.11 Å³, Z = 8, Z' = 0.5, ρ(calcd) = 1.232 Mg.m⁻³, FW = 500.91 for C₂S₈·2C₃H₂O₂N, F(000) = 1080, crystal size = 0.30 × 0.20 × 0.10 mm, θ range = 3.892–52.744°, 23,027 reflections collected, 2745 independent reflections, Rint = 0.0238, R1 [1 > 2σ(I)] = 0.0341, wR2 (all data) = 0.0909, Δρmax = 0.25 eÅ⁻³, and Δρmin = −0.21 eÅ⁻³. Full crystallographic results were deposited at the Cambridge Crystallographic Data Centre (CCDC-995843), UK, as shown in the Supplementary X-ray Crystallographic Data.

4. Conclusions

By taking into account our previous research data in the domain of ionic liquid, and mainly during the reaction between 1-butyl-1-methylpyrrolidinium acetate ([BmPyrro][Ac]) and CS₂, we identified a new component, i.e., bis(1-butyl-1-methylpyrrolidinium) perthiodicarbonate 4, for which the structure was established and confirmed by X-Ray crystallography.

Supplementary Materials: ¹H-NMR and ¹³C-NMR spectra of 1-butyl-1-methylpyrrolidinium acetate ([BmPyrro][Ac]) 1 and 1-butyl-1-methylpyrrolidinium acetate ([BmPyrro][Ac]) 1 in reaction with CS₂ are available online. Figure S1: ¹H-NMR spectrum of 1-butyl-1-methylpyrrolidinium acetate ([BmPyrro][Ac]) 1. Figure S2: ¹³C-NMR spectrum of 1-butyl-1-methylpyrrolidinium acetate ([BmPyrro][Ac]) 1. Figure S3: ¹H-NMR spectrum of 1-butyl-1-methylpyrrolidinium acetate ([BmPyrro][Ac]) 1 with CS₂. Figure S4: ¹³C-NMR spectrum of 1-butyl-1-methylpyrrolidinium acetate ([BmPyrro][Ac]) 1 with CS₂. Figure S5: Zoom of ¹³C-NMR spectrum of 1-butyl-1-methylpyrrolidinium acetate ([BmPyrro][Ac]) 1 with CS₂. Table S1: Crystal data and structure refinement for the title compound 4. Table S2: Fractional atomic coordinates (×10⁴) and equivalent isotropic displacement parameters (Å² × 10⁴) for the title compound 4. Table S3: Bond lengths for the title compound 4. Table S4: Bond angles for the title compound 4. Table S5: Hydrogen bonds for the title compound 4. Table S6: Torsion angles for the title compound 4. Table S7: Atomic occupancy for the title compound 4.

Author Contributions: N.P., M.M. and J.G. conducted the synthesis and prepared and revised the manuscript; Y.D., M.B. and M.M. carried out the experiments; N.P. and I.C. carried out the crystallographic experiments. All authors have read and agreed to the published version of the manuscript.

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