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Short Note

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

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Abstract: Bis(1-butyl-1-methylpyrrolidinium) perthiodicarbonate was obtained by the reaction of carbon disulfide with 1-butyl-1-methylpyrrolidinium 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, $C_2S_6 \cdot 2C_9H_{20}N$, consisted of two crystallographically 1-methyl-1-butyl pyrrolidinium cations and one perthiodicarbonate anion. The complex $C_2S_6 \cdot 2C_9H_{20}N$ crystallized in the monoclinic space group, $C 2/c$, and possessed the following cell parameters: $a = 16.0970(10) \text{ \AA}$, $b = 14.7140(9) \text{ \AA}$, $c = 12.3280(8) \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 112.3730(12)^\circ$, $\gamma = 90^\circ$, $V = 2700.11 \text{ \AA}^3$, and $Z = 8$, $Z' = 0.5$.

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



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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 CO_2 [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 CO_2 , OCS , and CS_2 in ionic liquids. Specifically, we focused on developing a crystallization strategy for the compounds formed during the reaction between 1-butyl-1-methylpyrrolidinium acetate ([BmPyrro][Ac]) **1** and CS_2 . These previous NMR analyses highlighted the formation of CO_2 , CH_3COS^- , and CS_3^- anions in the reaction medium [4,5]. Consequently, these anions could compete with the initial acetate to form either ([BmPyrro][CH_3COS^-]) **2** or (bis[BmPyrro][CS_3^{2-}]) **3**.

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

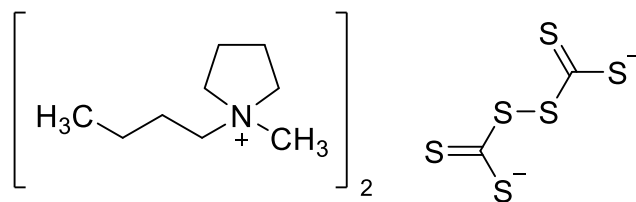
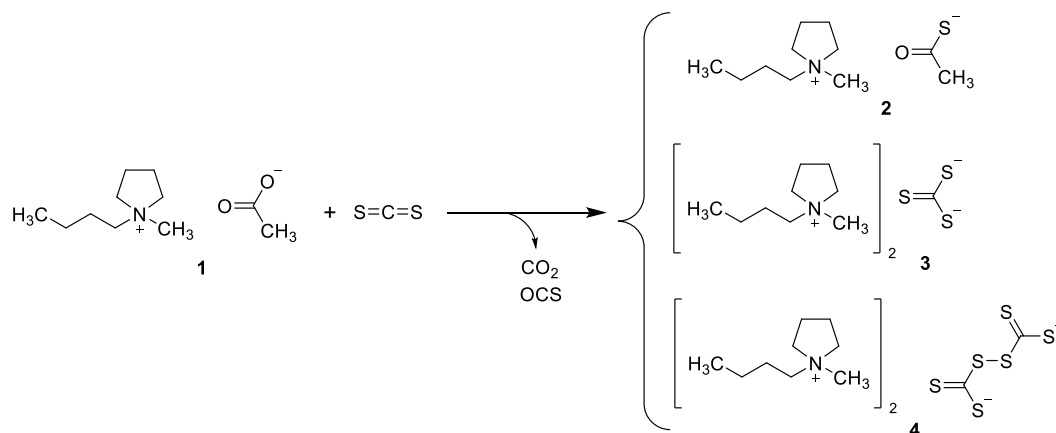


Figure 1. Chemical structure of bis(1-butyl-1-methylpyrrolidinium) perthiodicarbonate **4**.

2. Results and Discussion

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

Upon the dissolution of CS_2 in [BmPyrro] [Ac] **1**, a blood-red solution was observed, showing that a reaction had occurred. This blood-red color of the CS_2 -[BmPyrro] [Ac] solution was due to the presence of CS_3^{2-} anions. Previous ^1H , ^{13}C NMR, and UV-visible investigations conducted by our research team showed that the reaction of [BmPyrro] [Ac] **1** with CS_2 led, via coupled complex reactions, to the degradation of this molecule to form several main adducts, namely, CO_2 , OCS , thioacetate anion (CH_3COS^-) **2**, and, as a minor species, trithiocarbonate anion (CS_3^{2-}) **3** (Scheme 1) [4,5]. Such products formed in this system have already been found in the solution of CS_2 in 1-butyl-3-methylimidazolium acetate ([Bmim] [Ac]) [6]. In order to isolate one of these 1-butyl-1-methylpyrrolidinium 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 CS_2 and CS_3^{2-} initially formed has already been described in the literature [7,8].



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

2.2. Crystallographic Structure

The title compound crystallized in the monoclinic $C2/c$ space group. The asymmetric unit of the title compound, $\text{C}_2\text{S}_6 \cdot 2\text{C}_9\text{H}_{20}\text{N}$, 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 $\text{S} \cdots \text{H}$ short contacts; however, a very short $\text{S} \cdots \text{H}$ contact and numerous $\text{H} \cdots \text{H}$ interactions, potentially repulsive, were found for the minor conformation. Only the main position is drawn in Figure 2 for clarity.

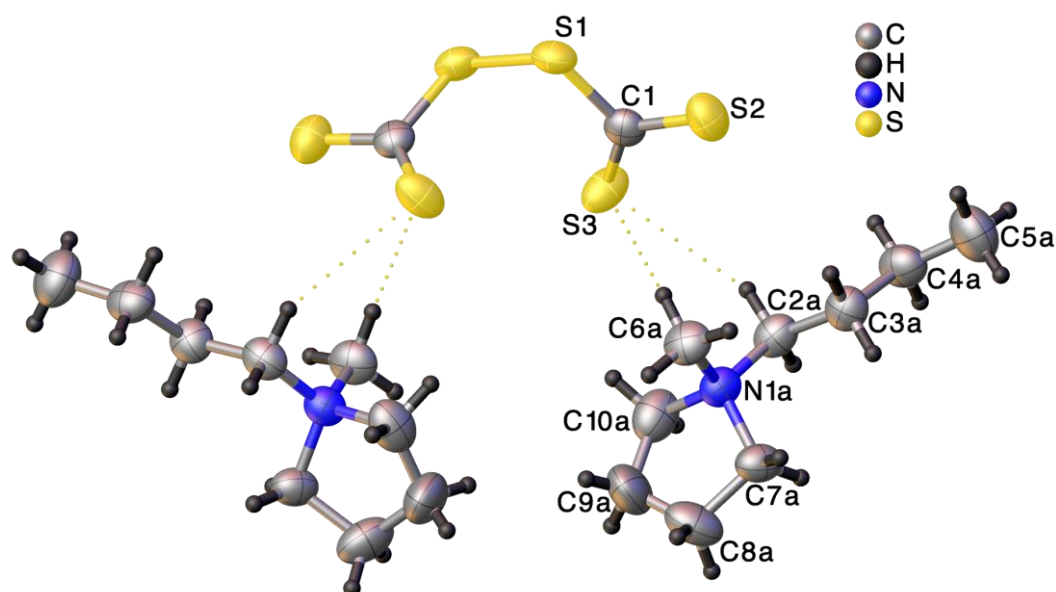


Figure 2. ORTEP (Oak Ridge Thermal Ellipsoid Plot) drawing of the bis(1-butyl-1-methylpyrrolidinium) perthiodicarbonate with thermal ellipsoids at the 50% level. The labeling scheme is shown for the asymmetric unit only. The minority part of the disordered cation is removed for clarity.

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 (*C_s*) 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 32.9(3)°.

The anion had *C₂* symmetry in the crystal (Figure 2). The bond distances 1.794(2) Å (C1–S1), 1.676(2) Å (C1–S2), 1.654(2) Å (C1–S3), and 2.0405(10) Å (S1–S1) were in the typical range for the C–S and conjugated C=S and S–S bonds in the $C_2S_6^{2-}$ anion [11,12]. The torsion angle with 85.50(9)° (C1–S1–S1–C1) was also similar to the torsion angles in $(Et_4N)_2C_2S_6$ (86.92(16)° [11]. In our pyrrolidinium salt, the S–C–S angle was noticed at 129.3(1)° for S2–C1–S3, which was a significant increase from the ideal 120° in the trithiocarbonate geometry. The dihedral angle between the two CS_3 moieties via the perthio bridge was found at 85.5(1)° in $C_2S_6 \cdot 2C_9H_{20}N$, which is comparable with other ammonium perthiodicarbonate salts [11,12].

The network cohesion was ensured by anion–cation interactions through close H···S contacts involving the methyl group, CH_2 of the pyrrole ring of the pyrrolidinium cation, and the four sulfur atoms of the CS_2^- 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 CH_2 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.

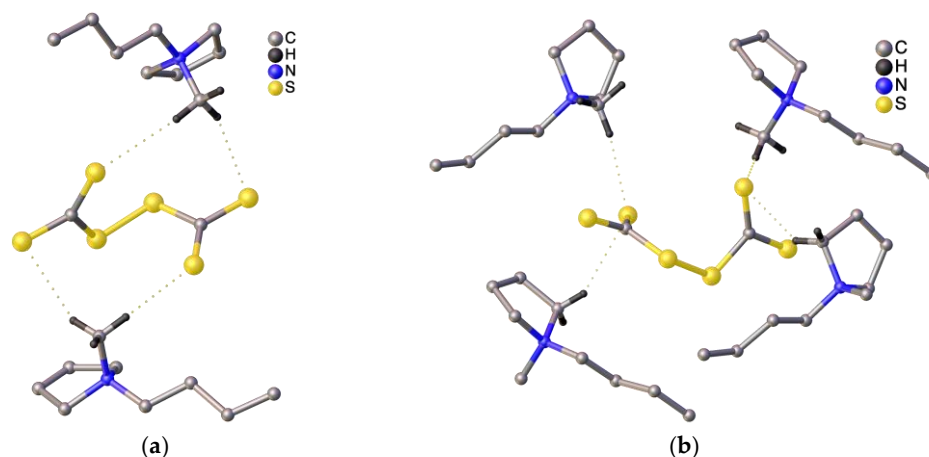


Figure 3. View of the anion–cation interaction showing the (a) double S···H contacts and (b) single S···H contacts.

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].

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-K α radiation ($\lambda = 0.71073$ Å).

3.1. Bis(1-butyl-1-methylpyrrolidinium) 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 μ L to 10 μ L) 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 \times 200 \times 100 μ m long were observed in the drops. The crystals were then preserved in paratone oil before being measured.

3.2. Crystal and Refinement Data

The structure of bis(1-butyl-1-methylpyrrolidinium) 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.

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, $\alpha = 90^\circ$, $\beta = 112.3730(12)^\circ$, $\gamma = 90^\circ$, $V = 2700.11$ Å³, $Z = 8$, $Z' = 0.5$, $\rho(\text{calcd}) = 1.232$ Mg.m⁻³, $\text{FW} = 500.91$ for C₂S₆·2C₉H₂₀N, $F(000) = 1080$, crystal size = $0.30 \times 0.20 \times 0.10$ mm, θ range = 3.892 – 52.744° , 23,027 reflections collected, 2745 independent reflections, $R_{\text{int}} = 0.0238$, $R_1 [I > 2\sigma(I)] = 0.0341$, wR_2 (all data) = 0.0909, $\Delta\rho_{\text{max}} = 0.25$ eÅ⁻³, and $\Delta\rho_{\text{min}} = -0.21$ 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: Crystallographic data of bis(1-butyl-1-methylpyrrolidinium) perthiodicarbonate **4**. Table S1: Crystal data and structure refinement for the title compound **4**. Table S2: Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å² $\times 10^3$) for the title compound **4**. U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij} tensor. 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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