Revisiting Ag– π interactions with bis((pyrrol-2-yl)methylene)hydrazine: CC versus CN bond complexation

Stephane Baudron, Hubert Chevreau

► To cite this version:

Stephane Baudron, Hubert Chevreau. Revisiting Ag– π interactions with bis((pyrrol-2-yl)methylene)hydrazine: CC versus CN bond complexation. CrystEngComm, 2019, 21 (12), pp.1853-1856. 10.1039/C9CE00168A . hal-02290903

HAL Id: hal-02290903

<https://hal.science/hal-02290903>

Submitted on 13 Jan 2022

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Revisiting Ag- π interactions with bis((pyrrol-2-yl)methylene)hydrazine: CC versus CN bond complexation

Stéphane A. Baudron^{a,*} and Hubert Chevreau^b

^a *Laboratoire de Tectonique Moléculaire, UMR CNRS 7140, icFRC, Université de Strasbourg, F-67000, Strasbourg, France. Tel: 33 368851323; E-mail: sbaudron@unistra.fr.*

^b *Synchrotron SOLEIL, L'Orme des merisiers, BP 48, F-91192 Saint-Aubin, France ; Tel : 33 169359700 ; E-mail : hubert.chevreau@synchrotron-soleil.fr.*

Abstract: Reinvestigation of the assembly of bis((pyrrol-2-yl)methylene)hydrazine with Ag(I) salts suggests that, in the solid state, Ag- π interactions involve CC rather than CN pyrrolic bonds, in contrast with an earlier and unique report with this ligand.

Hypothesized about a century ago,¹ Ag- π interactions² have been experimentally demonstrated³ and since been employed as a tool in crystal engineering for the construction of complex architectures.⁴ Whereas assembly with alkenes, alkynes and arenes have been largely explored, systems involving pyrrolic derivatives have been the object of more recent development.⁵ Studies in solution and in the solid state have shown that these heterocyclic compounds can also bind Ag(I) cations via this mode of complexation. In particular, investigations in the crystalline state indicated that the metal center tends to interact with CC bonds of the pyrrolic backbone, especially with the β -carbon atoms.^{6,7} Contrastingly, the group of Ma has reported that the association of the bis((pyrrol-2-yl)methylene)hydrazine ligand **1** with AgNO₃ leads to the formation of a two-dimensional network (**1**(AgNO₃)₂), **2**, built by coordination of the central hydrazine nitrogen atoms and Ag- π interactions involving a pyrrolic CN bond (Fig. 1).⁶ This result is noteworthy, as it is, to the best of our knowledge, the first and only example describing complexation by the CN bond. In light of the unique character of this observation, it may be of interest to examine the assembly of this organic compound with other Ag(I) salts, in order to determine whether this mode of interaction is general and recurrent. We therefore report herein on the synthesis and crystal structure of networks based on **1** associated with AgX salts (X- =

TfO⁻, TsO⁻, SiF₆²⁻, NO₃⁻) as well as on theoretical calculations to put in perspective the results reported in the literature⁶ and in the present study.

Fig. 1 Representation of **1** and crystal structure of the 2D network **2**, obtained by assembly with AgNO₃ and showing Ag- π interaction (in purple dash lines) with a pyrrolic CN bond, as reported by Ma and co-workers (CSD refcode BEPWOJ/208759).⁶ Thermal ellipsoids are presented and CH hydrogen atoms have been omitted for clarity.

Ligand **1** has been prepared as described⁶ and crystallized as a water solvate **1**(H₂O), from slow evaporation of an EtOH solution. Since its structure had not been reported, it has been determined by X-ray diffraction (Monoclinic, *P2*/c) and is presented in Fig. 2. In this compound, the central fragment is organized in a *trans* fashion and the two pyrrolic moieties point in opposite directions. The earlier acts as a hydrogen bond acceptor, interacting with the water molecule ($d_{O\cdots N} = 2.886(1)$ Å; $\alpha_{O-H\cdots N} = 164.8^\circ$) and the latter as a donor ($d_{N\cdots O} = 2.886(2)$ Å; $\alpha_{N-H\cdots O} = 166.3^\circ$), leading to an overall two-dimensional arrangement.

Fig. 2 Crystal structure of ligand **1**. CH hydrogen atoms have been omitted for clarity.

The assembly of **1** with a variety of Ag(I) salts has been explored using the liquid-liquid diffusion method as reported for the AgNO₃ system, **2**,⁶ affording crystalline networks **3-5** incorporating respectively AgTfO, AgTsO and AgSiF₆ (starting from AgBF₄) (see ESI for experimental details).

Upon slow diffusion of an AcOEt solution of AgTfO into a CH₂Cl₂ solution of **1**, crystals of **3** (**1**(Ag(TfO)H₂O)₂) were obtained. In the structure of this 2D network (Triclinic, *P*-1), a Ag(I) cation is coordinated to a central nitrogen atom of **1** ($d_{\text{Ag-N}} = 2.277(2)$ Å), to two bridging triflate anions ($d_{\text{Ag-O}} = 2.362(3), 2.750(3)$ Å) and to a water molecule ($d_{\text{Ag-O}} = 2.3887(2)$ Å) (Fig. 3). In addition, it forms Ag- π interactions with the β -pyrrolic carbon atoms in a dissymmetrical η^2 fashion ($d_{\text{Ag-C}} = 2.580(2), 2.885(2)$ Å). Such a mode of interaction with similar distances is usually observed with pyrrolic derivatives.⁷ Here, the pyrrolic nitrogen atom is not involved in Ag(I) complexation, in contrast with the reported structure of **2**. The pyrrole NH is intramolecularly hydrogen bonded to the coordinated water molecule ($d_{\text{N}\cdots\text{O}} = 2.841(2)$ Å; $\alpha_{\text{N-H}\cdots\text{O}} = 159.3^\circ$).

Fig. 3 Crystal structure of network **3**. Ag- π interactions are highlighted in purple dash lines. CH hydrogen atoms have been omitted for clarity.

Upon slow diffusion of Et₂O vapour into a CHCl₃/MeOH solution of **1** with an excess of AgTsO, crystals of **4** (**1**(Ag(TfO)H₂O)₂) were isolated. As in the previous case, the Ag(I) cation is coordinated to a central nitrogen atom ($d_{\text{Ag-N}} = 2.290(3)$ Å), to two bridging tosylate anions ($d_{\text{Ag-O}} = 2.294(4), 2.391(5)$ Å) and here again interacts with β -pyrrolic carbon atoms in a dissymmetrical η^2 fashion ($d_{\text{Ag-C}} = 2.542(2), 2.715(4)$ Å) (Fig. 4). The pyrrolic NH is, as before, not involved in Ag(I) complexation but is hydrogen bonded to the uncoordinated oxygen atom

of the tosylate anion ($d_{N\cdots O} = 2.776(2)$ Å; $\alpha_{N-H\cdots O} = 161.5^\circ$). Interestingly, no Ag- π interactions are observed with the aromatic tosylate anion.

It is worth noting that, in the X-ray powder pattern of **4** synthesized via the above-mentioned solution route, the presence of an unidentified impurity could be detected. An alternative preparation method was thus developed using mechanochemistry.^{8,9} It was found that ball milling of **1** with two equivalents of AgTsO led to the formation of **4** in pure form as demonstrated by elemental analysis and X-ray diffraction on powder (see ESI for details).

In the course of our investigation, we have attempted to assemble **1** with AgBF₄. Few crystals of network **5** could be isolated upon standing of the crystallization solutions over several weeks. Compound **5**, formulated (1)₃Ag₂(SiF₆)(CH₂Cl₂) (Monoclinic, C2/c), does not incorporate BF₄[−] but the SiF₆^{2−} anion, resulting probably from reaction of the glass, as reported in other cases.¹⁰ Since only very few crystals of this compound could be obtained, it will not be further discussed herein. However, it should be noted that, in the structure of this network, the Ag(I) center interacts in a η^1 mode with one β -pyrrolic carbon atom albeit with a longer Ag-C distance than in **3** and **4** (3.076(3) Å) (Fig. ESI3). No interaction with the pyrrolic nitrogen atom could be observed in this material.

Fig. 4 Crystal structure of network **4**. Ag- π interactions are highlighted in purple dash lines. The tolyl group of the TsO[−] anion is shown in faded grey and CH hydrogen atoms have been omitted for clarity.

It is worth noting that **3** and **4** have the same stoichiometry as **2**: (1)Ag₂X₂. However, while the coordination of the central nitrogen atom and of the oxygen atoms of the anions is common to all three 2D networks, Ag- π interactions differ. They involve the pyrrolic nitrogen atom in **2**, but complexation takes place exclusively with the β -carbon atoms in the compounds presented herein. The latter observation is consistent with other pyrrole-based assemblies described in the literature.⁷ For structures **3-5**, the position of the nitrogen atom in the pyrrolic ring was ascertained by the better refinement parameters obtained with this arrangement and is supported by the above-mentioned hydrogen bonds consistent with the location of the NH. Interestingly, a closer look at the published structure of **2** indicates that the thermal ellipsoids of the C3 and N3 atoms differ from the rest of the atoms (Fig. 1) and analysis of the cif file by Checkcif also suggests that the attribution of these two atoms may be incorrect. We therefore sought to reinvestigate the synthesis of **2**, in order to redetermine its crystal structure. Upon slow diffusion of a MeOH solution of AgNO₃ in a CHCl₃ solution of **1**, two types of yellow crystals could be obtained. The first phase (Monoclinic, *P2₁/n*), named **2'** hereafter, has unit cell parameters corresponding to the ones reported for **2**. However, crystal structure determination of this network revealed that the location of the nitrogen atom is different to what has originally been described. In this compound, the pyrrolic NH is hydrogen bonded to the nitrate anion ($d_{\text{N}\cdots\text{O}} = 2.904(2)$ Å; $\alpha_{\text{N-H}\cdots\text{O}} = 143.0^\circ$) and Ag- π interaction takes place in a η^2 fashion with the β -pyrrolic CC bond rather than with the CN bond ($d_{\text{Ag-C}} = 2.632(2), 2.699(2)$ Å, Fig. 5a). This is consistent with what is observed for compounds **3-5** and other assemblies published with pyrrolic derivatives.^{5,7} Interestingly, the second phase obtained in the same crystallization batch is a MeOH solvate, **6** ((**1**)(AgNO₃)₂ MeOH). In this compound (Orthorhombic, *Pnma*), the silver cation is coordinated to the central nitrogen atom ($d_{\text{Ag-N}} = 2.283(2)$ Å) and to two bridging nitrate anions ($d_{\text{Ag-O}} = 2.368(3), 2.458(3)$ Å). Once again, Ag- π interactions are observed in a dissymmetrical η^2 fashion with the β -pyrrolic CC bond ($d_{\text{Ag-C}} = 2.633(2), 2.770(2)$ Å, Fig. 5b), leading to an overall two-dimensional organization. The pyrrolic NH is hydrogen bonded to the MeOH solvate molecule ($d_{\text{N}\cdots\text{O}} = 2.962(2)$ Å; $\alpha_{\text{N-H}\cdots\text{O}} = 144.0^\circ$). It is worth noting that crystals of **6** desolvated upon exposure to air.

Fig. 5. Crystal structure of network **2'** (a) and MeOH solvate **6** (b). Ag- π interactions are highlighted in purple dash lines and CH hydrogen atoms have been omitted for clarity. For **6**, the MeOH molecule and the disorder of one nitrate anion are not shown.

Since the interactions observed in **2'** and **3-6** differ from the ones reported for **2**, it appeared interesting to assess theoretically the relative energies of the arrangements involving either CC or CN bonds. In order to determine the most favourable interaction in these compounds, either Ag-CC or Ag-CN, density functional theory (DFT) calculations were performed using the exchange-correlation functional of Perdew-Burke-Ernzerhof (PBE)¹¹ as implemented in Quantum Espresso.¹² The DFT-D2 method of Grimme with modified dispersion correction was used to describe correctly van der Waals interactions.¹³ For each compound, two conformations of the pyrrol-2-yl group were investigated: i) the pyrrol-2-yl is facing the Ag atom with 2 C atoms: interaction Ag-CC and ii) the pyrrol-2-yl is rotated by 180° along its bond with the methylene group and facing the Ag atom with 1 C and 1 N atoms: interaction Ag-CN. Then ground-state total energy minimizations on opposite conformations were performed; the lattice parameters obtained from experimental measurements were used and kept constant. The resulting energies are presented in Table 1.

Table 1. Ground-state total electronic energy of compounds **2**, **2'**, **3**, **4**, **5** and **6** in either Ag-CN or Ag-CC conformations.

Compound	Energy (Ry)	
	<i>Ag-CC</i>	<i>Ag-CN</i>
2	-2651.21	-2651.14
2'	-2651.21	-2651.14
3	-1883.53	-1883.50
4	-3353.98	-3353.96
5	-4441.58	-4441.33
6	-5561.88	-5561.71

For all compounds, one can observe that the Ag-CC interaction leads to lower energies and thus a more stable conformation in comparison to the Ag-CN interaction, which is in good agreement with the single-crystal structure determination of compounds **2'**, **3**, **4**, **5** and **6**. Regarding the reported structure **2**, DFT calculations indicate that the Ag-CC interaction would be more favourable by 0.07 Ry, i.e. 92kJ/mol, than the Ag-CN interaction. The structures **2** and **2'** are thus most likely identical and exhibit preferentially an Ag-CC interaction.

In conclusion, we have shown that assembly of ligand **1** with AgTfO, AgTsO and AgSiF₆ proceeds by coordination of the central nitrogen atoms, the anions as well as by Ag- π interactions with the β -pyrrolic carbon atoms, in agreement with observation on other pyrrole-based ligands reported in the literature. These results are at variance with network **2**, based on AgNO₃, described to involve the pyrrolic nitrogen atom in the Ag(I) cation complexation. A closer look at the crystal data for this compound combined with theoretical calculations suggests that the location of the nitrogen atom in the structure determination may have been incorrectly attributed in the original report. It was further confirmed by reinvestigation of the structure of this network. In **2'**, reported herein, Ag- π interactions indeed involve β -pyrrolic carbon atoms, in line with the present results and other architectures.⁷ This study thus underlines that complexation of Ag(I) cations via CC bonds is a recurrent and general mode of Ag- π interactions for pyrrolic derivatives.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We thank the Université de Strasbourg, the Centre National de la Recherche Scientifique, the International centre for Frontier Research in Chemistry (icFRC), the Labex CSC within the Investissement d'Avenir program ANR-10-IDEX-0002-02 and the Ministère de l'Enseignement Supérieur, de la Recherche et de l'innovation for financial support. The SOLEIL synchrotron and the Centre de Calcul Recherche et Technologie are gratefully acknowledged for computational time.

References

- 1 A. E. Hill, *J. Am. Chem. Soc.*, 1921, **43**, 254.
- 2 (a) E. A. Hall Griffith and E. L. Amma, *J. Am. Chem. Soc.*, 1974, **96**, 743. (b) K. Shelly, D. C. Finster, Y. J. Lee, R. Scheidt and C. A. Reed, *J. Am. Chem. Soc.*, 1985, **107**, 5955. (c) J. C. Ma and D. A. Dougherty, *Chem. Rev.*, 1997, **97**, 1303. (d) S. V. Lindeman, R. Rathore and J. K. Kochi, *Inorg. Chem.*, 2000, **39**, 5707. (e) S. Liu, A. Yu Rogazhev, *ChemPhysChem.*, 2018, **19**, 2579.
- 3 (a) R. E. Rundle and J. E. Goring, *J. Am. Chem. Soc.*, 1950, **72**, 5337. (b) H. G. Smith and R. E. Rundle, *J. Am. Chem. Soc.*, 1958, **80**, 5075.
- 4 (a) M. Munakata, L. P. Wu and G. L. Ning, *Coord. Chem. Rev.*, 2000, **198**, 171. (b) A. N. Khlobystov, A. J. Blake, N. R. Champness, D. A. Lemenovskii, A. G. Majouga, N. V. Zyk and M. R. Schröder, *Coord. Chem. Rev.*, 2001, **222**, 155. (c) C. Janiak, *Dalton Trans.*, 2003, 2781. (d) A. Y. Robin and K. M. Fromm, *Coord. Chem. Rev.*, 2006, **250**, 2127. (e) T. C. W. Mak and L. Zhao, *Chem. Asian J.*, 2007, **2**, 456. (f) J. Burgess and P. J. Steel, *Coord. Chem. Rev.*, 2011, **255**, 2094.
- 5 S. A. Baudron, *Coord. Chem. Rev.*, 2019, **380**, 318.
- 6 L. Yang, X. Shan, Q. Chen, Z. Wang and J. S. Ma, *Eur. J. Inorg. Chem.*, 2004, 1474.

- 7 (a) D. Salazar-Mendoza, S. A. Baudron and M. W. Hosseini, *Chem. Commun.*, 2007, 2252. (b) D. Salazar-Mendoza, S. A. Baudron and M. W. Hosseini, *Inorg. Chem.*, 2008, **47**, 766. (c) G.-F. Chang, C.-H. Wang, H.-C. Lu, L.-S. Kan, I. Chao, W. H. Chen, A. Kumar, C.-H. Hung, L. Lo, M. A. C. dela Rosa and C.-H. Hung, *Chem. Eur. J.*, 2011, **17**, 11332. (d) A. Béziau, S. A. Baudron and M. W. Hosseini, *Dalton Trans.*, 2012, **41**, 7227. (e) H. Ruffin, S. A. Baudron, D. Salazar-Mendoza and M. W. Hosseini, *Chem. Eur. J.*, 2014, **20**, 2449. (f) D. Ghorai and G. Mani, *Inorg. Chem.*, 2014, **53**, 4117. (g) T. Guchhait, B. Barua, A. Biswas, B. Basak and G. Mani, *Dalton Trans.*, 2015, **44**, 9091. (h) S. A. Baudron and M. W. Hosseini, *Chem. Commun.*, 2016, **52**, 13000. (i) F. Zhang, S. A. Baudron and M. W. Hosseini, *CrystEngComm*, 2017, **19**, 4393. (j) O. Jana and G. Mani, *New J. Chem.*, 2017, **41**, 9361.
- 8 (a) M. K. Beyer and H. Clausen-Schaumann, *Chem. Rev.*, 2005, **105**, 2921. (b) J. L. Do and T. Friscic, *ACS Central Sci.*, 2017, 3, 13. (c) J. L. Howard, Q. Cao and D. L. Browne, *Chem. Sci.*, 2018, **9**, 3080.
- 9 S. L. James, C. J. Adams, C. Bolm, D. Braga, P. Collier, T. Friščić, F. Grepioni, K. D. M. Harris, G. Hyett, W. Jones, A. Krebs, J. Mack, L. Maini, A. G. Orpen, I. P. Parkin, W. C. Shearouse, J. W. Steed and D. C. Waddell, *Chem. Soc. Rev.*, 2012, **41**, 413.
- 10 (a) M. Maekawa, S. Kitagawa, T. Kuroda-Sowa and M. Munakata, *Chem. Commun.*, 2006, 2161. (b) Y.-P. Xie and T. C. W. Mak, *Inorg. Chem.*, 2012, **51**, 8640.
- 11 J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865.
- 12 P. Giannozzi, O. Andreussi, T. Brumme, O. Bunau, M. Buongiorno Nardelli, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, M. Cococcioni, N. Colonna, I. Carnimeo, A. Dal Corso, S. de Gironcoli, P. Delugas, R. A. DiStasio Jr, A. Ferretti, A. Floris, G. Fratesi, G. Fugallo, R. Gebauer, U. Gerstmann, F. Giustino, T. Gorni, J. Jia, M. Kawamura, H.-Y. Ko, A. Kokalj, E. Küçükbenli, M. Lazzeri, M. Marsili, N. Marzari, F. Mauri, N. L. Nguyen, H.-V. Nguyen, A. Otero-de-la-Roza, L. Paulatto, S. Poncé, D. Rocca, R. Sabatini, B. Santra, M. Schlipf, A. P. Seitsonen, A. Smogunov, I. Timrov, T. Thonhauser, P. Umari, N. Vast, X. Wu and S. Baroni, *J. Phys. Condens. Matter*, 2017, **29**, 465901.
- 13 S. Grimme, *J. Comp. Chem.*, 2006, **27**, 1787.