Anion-π Interaction in Four-Membered Rings

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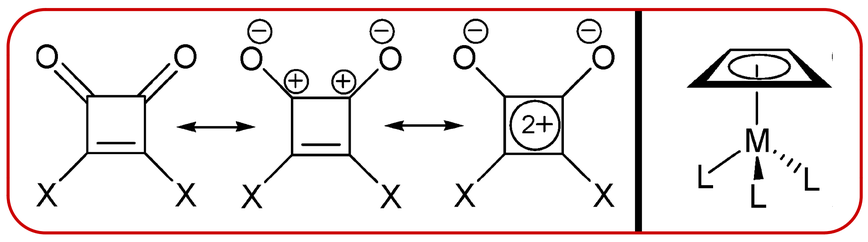
The importance of anion-*π* interactions in four-membered rings have not been previously described in the literature. Two kinds of rings have been found to be suitable for participation in anion-*π* interactions:

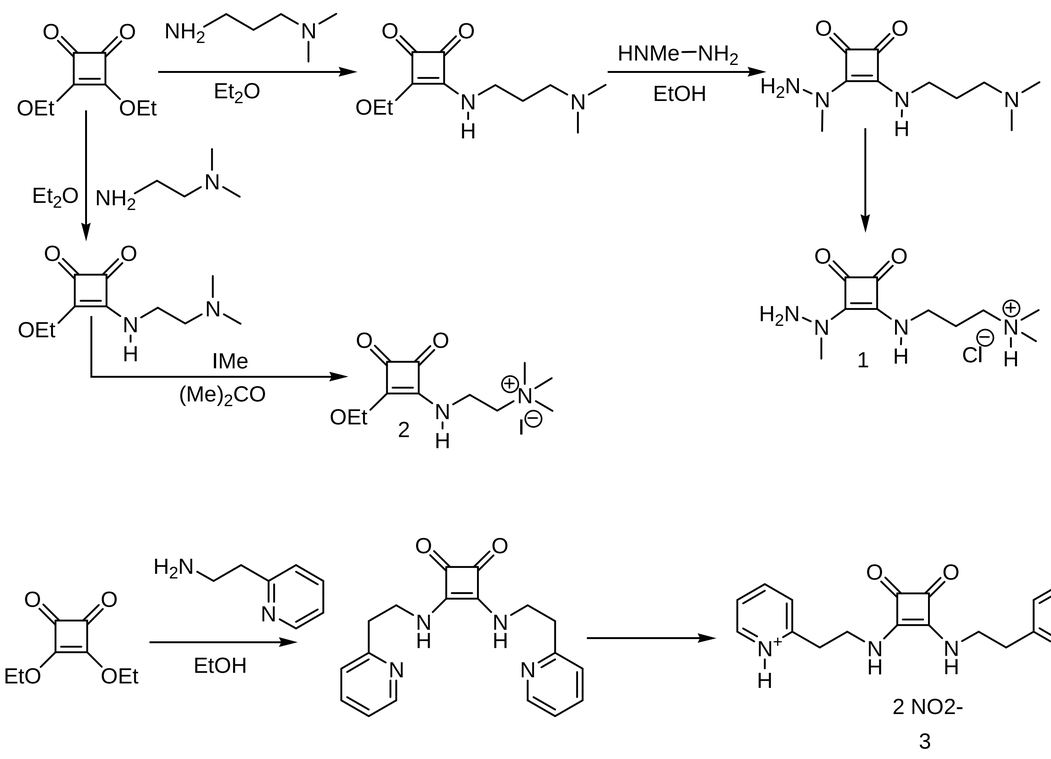
- ✓ different salts of cyclobuten-1,2-dione derivatives
- ✓ η^4-cyclobutadiene complexes with transition metals.

We have evidenced it by reporting the synthesis and X-ray characterization of three new squaramide salts that exhibit interesting anion-*π* interactions in the solid state. A search in the CSD has also provided further evidence of its importance. In addition, a high level ab initio investigation on squarate and thiosquarate salts has provided computational support for the experimental observations.

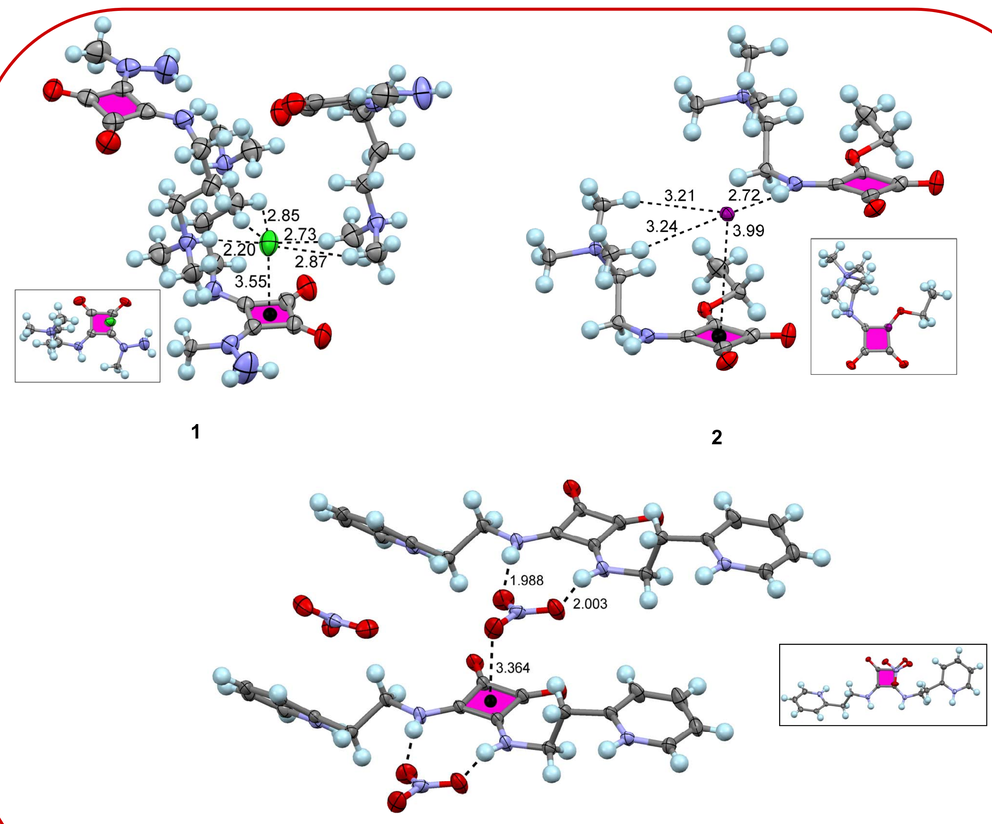
Four-membered rings suitable for anion-π interactions



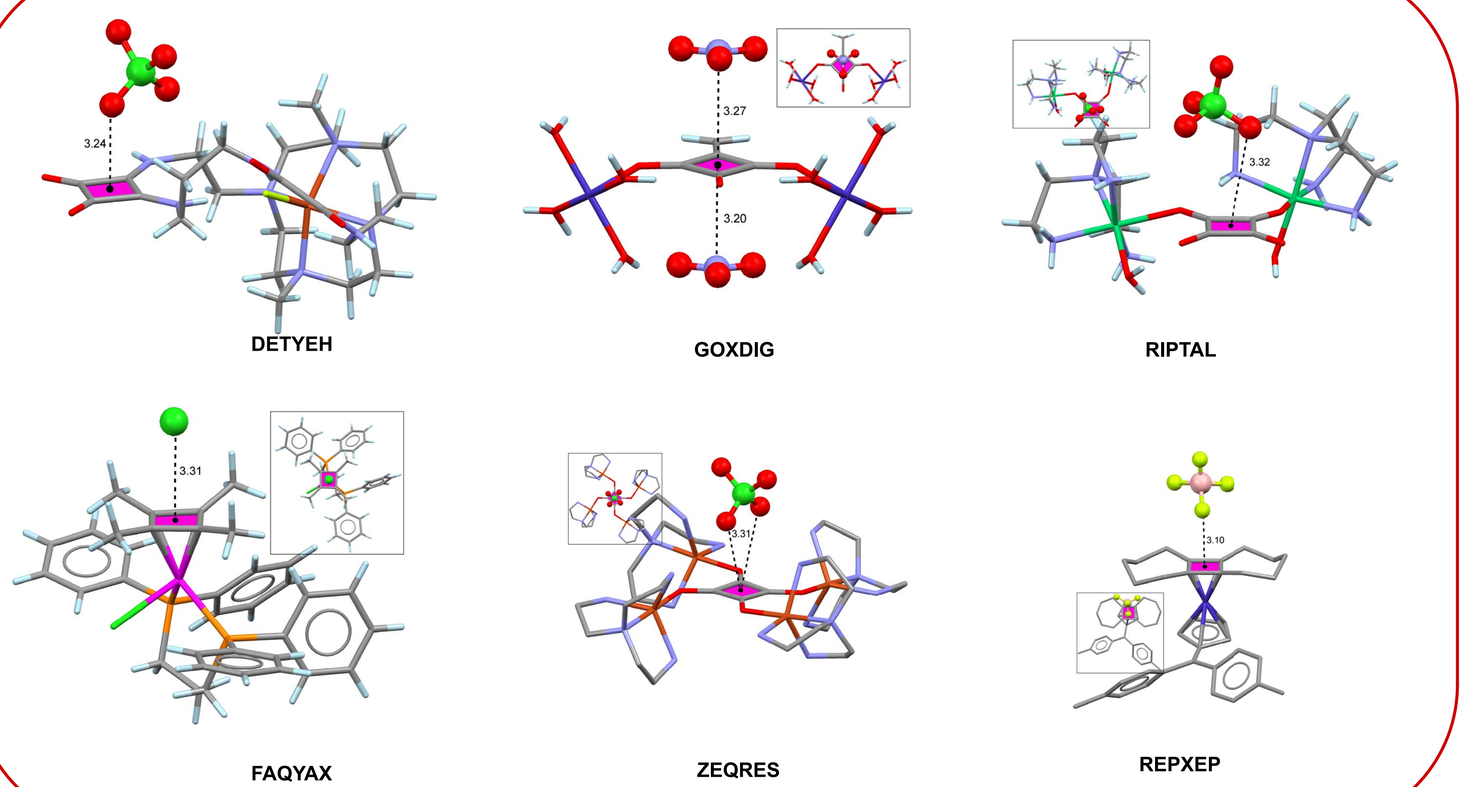
Squaramides Synthetic Route



Squaramide X-ray structures featuring anion-π interactions



Selected structures exhibiting anion–π interactions



Theoretical studies

Schematic representation of model compounds **4**–**5** and complexes **7**–**12**.

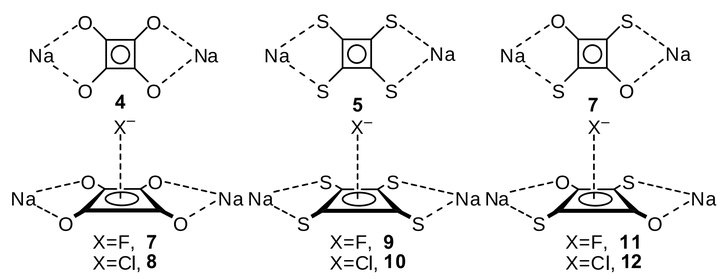


Table. Binding Energies without and with the BSSE Correction (E and E_{BSSE}, kcal/mol, respectively) and Equilibrium Distances (R_e, Å) at RI-MP2/aug–cc–pVTZ Level of Theory for Complexes **7**–**12** are Summarized.

Complex	E	E_{BSSE}	R_e
7 (**4**+F⁻)	–7.27	–4.66	2.596
8 (**5**+Cl⁻)	–6.09	–2.99	3.160
9 (**5**+F⁻)	–10.00	–5.49	2.319
10 (**5**+Cl⁻)	–6.23	–2.68	3.050
11 (**6**+F⁻)	–11.17	–7.43	2.425
12 (**7**+Cl⁻)	–8.10	–4.13	3.029

Structure **3** is published in:C. Rotger, B. Soberats, D. Quiñonero, A. Frontera, P. Ballester, J. Benet-Buchholz, P. M. Deyà, A. Costa. *Eur. J. Org. Chem*. **2008**, 1864-1868.
Structure **1** and **2** are published in C. Estarellas, M. C. Rotger, M. Capó, D. Quiñonero, A. Frontera, A. Costa, P. M. Deyà, *Org. Lett.* **2009**, *11*, 1987-1990