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Stabilisation of alkylcarbamate anions using neutral hydrogen bond donors

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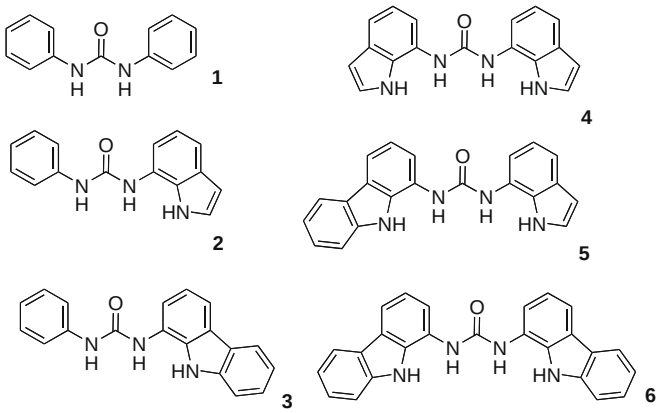
ABSTRACT

The interactions of a series of urea-based anion receptors and alkylcarbamate species formed by the reaction of carbon dioxide with primary amines have been investigated by ^{1}H NMR. Significant downfield shifts in the NH proton signals of the receptors in the presence of the alkylcarbamates were observed, consistent with classical host:anion hydrogen-bonding. This observation demonstrates that neutral hydrogen bond donor receptors can compete with ammonium cations to bind carbamates in DMSO-d_6 solution.

Carbon dioxide is a greenhouse gas, the anthropogenic emission of which has grown significantly since the start of the industrial revolution,[1] causing a rapid increase in atmospheric carbon dioxide levels.[2] This is forecast to have negative climatic consequences. Understandably, much work has been recently focussed upon many differing approaches to the capture,[3–9] activation or stabilisation[10–12] and use[13–16] of carbon dioxide with the aim of reducing the atmospheric concentration or using it as a chemical feedstock. Many industrial systems use aliphatic amines, which when exposed to carbon dioxide, rapidly form alkylammonium alkylcarbamate salts.[17–19] Weiss and co-workers have shown that, in solution, such salts rapidly exchange the carbon dioxide between two amines, such that only one species is observed on the NMR timescale (Scheme 1).[20]

We hypothesised that our recently reported neutral oxo-anion receptors[21,22] **3**–**6**, (and previously unreported compound **2**) which have a very high affinity for oxo-anions (e.g., compound **4** binds $^-$OAc with a stability constant K_a >10^4 M^{-1} in DMSO-d_6/0.5% H_2O) would bind, and hence stabilise alkylcarbamate anions via hydrogen-bonding interactions in organic solution. Proton NMR experiments were used to assess the interaction.

Each receptor was dissolved in DMSO-d_6 and the ^{1}H NMR spectrum acquired. Two equivalents of *n*-butylamine or one equivalent of 1,3-diaminopropane were then added, providing two amine groups per urea and giving one carbamate group per urea once the amine has reacted with CO_2. Carbon dioxide was then bubbled through each solution, before repeating the ^{1}H NMR experiments. This caused downfield shifts of the urea NH resonances for receptors **1**–**6**, compared to the initial sample (Tables 1 and 2). The downfield shift is consistent with host:anion hydrogen-bonding interactions, as shown in Scheme 2. Model studies conducted by passing CO_2 through a solution of the receptor in the absence of an amine showed no or insignificant shifts of the NH resonances so ruling out bicarbonate production and binding under the experimental conditions.



All the observed chemical shift changes are smaller than those seen upon addition of tetrabutylammonium acetate to solutions of the receptors,[21–23] presumably partly due to competition from the strong electrostatic and hydrogen-bonding association between the alkylcarbamate anion and alkylammonium cation. We attempted to perform NMR titrations with alkylammonium carba-

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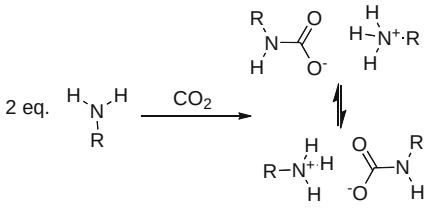


Scheme 1. The reaction of primary amines with carbon dioxide.

Table 1
Averaged downfield chemical shift changes/ppm for the one or two urea NH groups labelled as downfield or upfield, (with errors/%) for **1**–**6** in the presence of 2 equiv *n*-butylamine, satd with carbon dioxide

Receptor	Urea NH (downfield resonance)	Urea NH (upfield resonance)
1	0.11 (13)	
2	0.26 (6)	0.28 (6)
3	0.27 (13)	0.30 (15)
4	0.71 (7)	
5	0.67 (10)	0.68 (12)
6	0.63 (5)	

Change in given chemical shift is the mean of 3 repeats.

Table 2
Averaged downfield chemical shift changes/ppm, for the one or two urea NH groups labelled as downfield or upfield (with errors/%) for **1**–**6** in the presence of 1 equiv 1,3-diaminopropane, satd with carbon dioxide

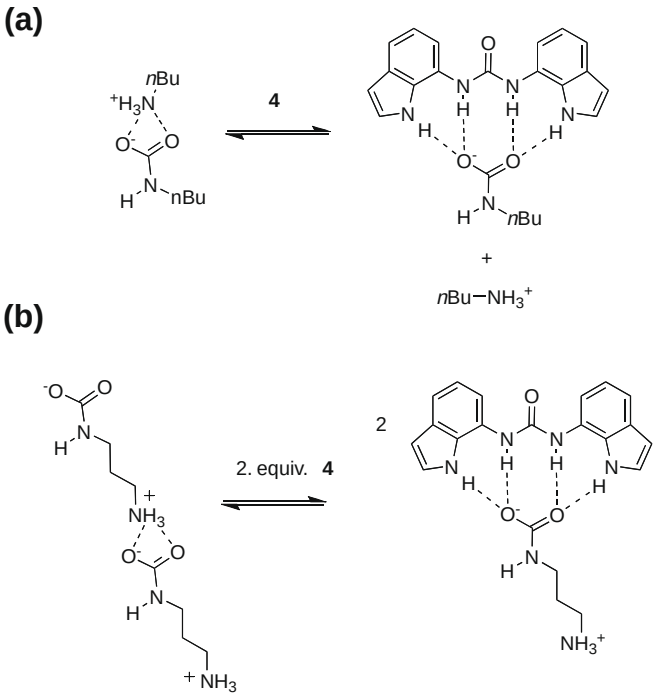
Receptor	Urea NH (downfield resonance)	Urea NH (upfield resonance)
1	0.08 (23)	
2	0.28 (14)	0.30 (15)
3	0.37 (9)	0.42 (10)
4	0.70 (10)	
5	0.50 (7)	0.51 (6)
6	0.56 (6)	

Change in given chemical shift is the mean of 3 repeats.

mates, however, whilst we observed significant downfield shifts, we could not reproducibly obtain stability constant values for carbamate binding. Loss of CO_2 during the titration or incomplete carbamate formation may be the cause of this irreproducibility.

These studies show that increasing the number of hydrogen bond donors in urea-based receptors from two to four causes a significant increase in the urea NH downfield shift in the presence of alkylcarbamate anions. This is indicative of the formation of a urea-alkylcarbamate complex. In order to form this complex, the receptor must compete with the primary ammonium cation generated upon alkylcarbamate formation. If we look at the series of compounds **1**, **2** and **4** where we have two, three and four hydrogen bond donors, respectively, the most downfield urea NH resonance shifts by 0.11, 0.26 and 0.71 ppm, respectively, in the presence of the carbamate formed from *n*-butylamine and carbon dioxide. Whilst the value of the shift is not necessarily indicative of the strength of the complex generated, analogy to our previous work on carboxylate complexation by these receptors would suggest that the diindolylurea **4** and dicarbazolyl urea **6** would bind the carbamates most strongly.

These results lead us to suggest that it is possible to stabilise alkylcarbamate anions with simple neutral indolyl- and carbazolyl-hydrogen bond donor arrays under competitive conditions. This finding may be of use in the production of new CO_2 capture technologies.



Scheme 2. Proposed interactions between receptor **4** and the alkylcarbamate: alkylammonium salt generated from (a) *n*-butylamine and CO_2 and (b) 1,3-diaminopropane and CO_2.

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Supplementary data

Supplementary data (synthesis and characterisation data for compound **2**. NMR stack plots for compounds and carbamate salts) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2009.06.058.

References and notes

1. Aresta, M.; Dibenedetto, A. *Dalton Trans.* **2007**, 2975.
2. *The Third Assessment Report of the Intergovernmental Panel on Climate Change*; Mertz, B., Davidson, O., Swart, R., Pan, J., Eds.; Cambridge University Press: Cambridge, 2001.
3. Banerjee, R.; Phan, A.; Wang, B.; Knobler, C.; Furukawa, H.; O'Keeffe, M.; Yaghi, O. M. *Science* **2008**, *319*, 939.
4. Endo, T.; Nagai, D.; Monma, T.; Yamaguchi, H.; Ochiai, B. *Macromolecules* **2004**, *37*, 2007.
5. Chen, Z.; Song, H.-S.; Portillo, M.; Jim Lim, C.; Grace, J. R.; Anthony, E. J. *Energy Fuels* **2009**, *23*, 1437.
6. Zhao, X.-X.; Xu, X.-L.; Sun, S.-B.; Zhang, L.-L.; Liu, X.-Q. *Energy Fuels* **2009**, *23*, 1534.
7. Zhao, C.; Chen, X.; Zhao, C.; Liu, Y. *Energy Fuels* **2009**, *23*, 1766.
8. Atwood, J. L.; Barbour, L. J.; Jerga, A. *Angew. Chem., Int. Ed.* **2004**, *43*, 2948.
9. Dalgarno, S. J.; Tian, J.; Warren, J. E.; Clark, T. E.; Makha, M.; Raston, C. L.; Atwood, J. L. *Chem. Commun.* **2007**, 4848.
10. Verdejo, B.; Blasco, S.; Gonzalez, J.; García-España, E.; Gavina, P.; Tatay, S.; Domenech, A.; Domenech-Carbo, M. T.; Jimenez, H. R.; Soriano, C. *Eur. J. Inorg. Chem.* **2008**, 84.
11. García-España, E.; Gavina, P.; Latorre, J.; Soriano, C.; Verdejo, B. *J. Am. Chem. Soc.* **2004**, *126*, 5082.
12. Brooks, S. J.; Gale, P. A.; Light, M. E. *Chem. Commun.* **2006**, 4344.
13. Byrne, C. M.; Allen, S. D.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **2004**, *126*, 11404.
14. Phan, L.; Jessop, P. G. *Green Chem.* **2009**, *11*, 307.
15. Brookes, N. J.; Ariafard, A.; Stranger, R.; Yates, B. F. *J. Am. Chem. Soc.* **2009**, *131*, 5800.
16. Xu, H.; Rudkevich, D. M. *Chem. Eur. J.* **2004**, *10*, 5432.
17. Diaf, A.; Garcia, J. L.; Beckman, E. J. *J. Appl. Polym. Sci.* **1994**, *53*, 956.

18. Diaf, A.; Enick, R. M.; Beckman, E. J. *J. Appl. Polym. Sci.* **1993**, *50*, 835.
19. Sartori, G.; Ho, W. S.; Savage, D. W. *Separ. Purif. Meth.* **1987**, *16*, 171.
20. George, M.; Weiss, R. G. *Langmuir* **2003**, *19*, 8168.
21. Caltagirone, C.; Hiscock, J. R.; Hursthouse, M. B.; Light, M. E.; Gale, P. A. *Chem. Eur. J.* **2008**, *14*, 10236.
22. Hiscock, J. R.; Caltagirone, C.; Light, M. E.; Hursthouse, M. B.; Gale, P. A. *Org. Biomol. Chem.* **2009**, *7*, 1781.
23. Caltagirone, C.; Gale, P. A.; Hiscock, J. R.; Brooks, S. J.; Hursthouse, M. B.; Light, M. E. *Chem. Commun.* **2008**, 3007.