Available online at www.sciencedirect.com

ScienceDirect

Tetrahedron Letters 49 (2008) 2060–2062

Tetrahedron Letters

The relative stability of pyridinium and 1,7-diaza[12]annulenium quaternary salts

Ibon Alkorta *, José Elguero

Instituto de Química Médica (CSIC), Juan de la Cierva, 3, 28006 Madrid, Spain

Received 9 January 2008; revised 29 January 2008; accepted 1 February 2008
Available online 7 February 2008

Abstract

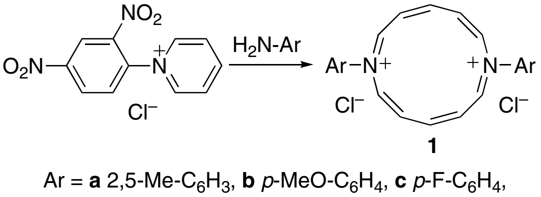
Theoretical calculations (energies and chemical shifts) at the B3LYP/6-311++G(d,p) level confirm that the compounds described as 1,7-diaza[12]annulenium quaternary salts are in fact pyridinium quaternary salts.

In synthetic organic chemistry there is a general principle that must be always followed: when a new compound is described, and if the structure is within the accepted paradigm few proofs are required; on the other hand, if the structure is an improbable one, then the proofs should be very convincing.[1]

Two authors recently reported a method to prepare the until this time unknown 1,7-diaza[12]annulenium quaternary salts **1**. Yamaguchi et al. in 2006 described the following reaction (Scheme 1).[2]

The seven compounds were characterized by ^{1}H and ^{13}C NMR as well as by their UV and oxidation potentials.

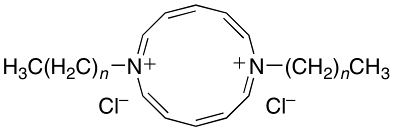
The following year, Shi et al. based on the previous work prepared a series of surfactants with the same structure (Scheme 2).[3] According to them, ^{1}H NMR and ^{13}C NMR spectroscopy, high-resolution mass spectrometry (HRMS), and elemental analysis left no doubt as to the structures. They even carried out geometry optimizations of several conformers of the *N*-methyl derivative [B3LYP/6-311+G(2d,p)] confirming their minimum-energy nature.



1

Ar = **a** 2,5-Me-C$_6$H$_3$, **b** *p*-MeO-C$_6$H$_4$, **c** *p*-F-C$_6$H$_4$, **d** *p*-Cl-C$_6$H$_4$, **e** *p*-Br-C$_6$H$_4$, **f** *p*-I-C$_6$H$_4$, **g** *n*-hexyl

Scheme 1. Yamaguchi et al. procedure.

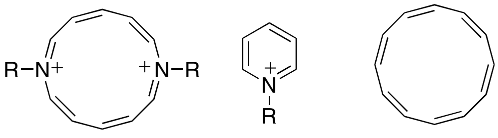


a, $n = 11$
b, $n = 13$
c, $n = 15$

2

Scheme 2. Menger et al. compounds.

Both papers were in error, as Christl has shown recently.[4] Christl suspected the reaction conditions given by Yamaguchi et al.[2] because these were virtually the same as those Zincke et al.[5,6] utilized to prepare the N-substituted pyridinium chlorides **4** (R = aryl) directly from



3 4 5

a, R = H; **b**, R = *p*-fluorophenyl

Scheme 3. Compounds **3**–**5**.

---

* Corresponding author.
E-mail address: ibon@iqm.csic.es (I. Alkorta).

0040-4039/$ - see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2008.02.002

dinitrophenylpyridinium salts and primary amines (for instance, anilines) more than one hundred years ago. The reaction has become the method of choice to prepare *N*-arylpyridinium chlorides (Scheme 3).[7–9]

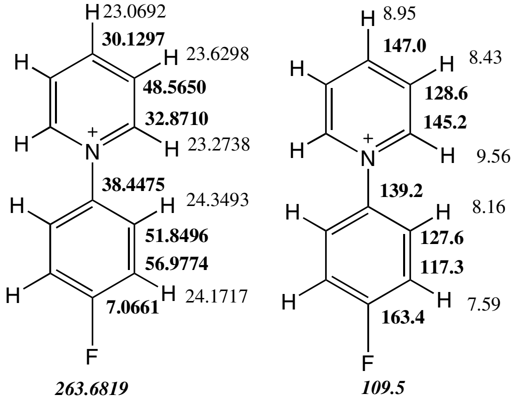
The controversy is now definitively settled,[4] and the authors[2,3] have withdrawn their papers recognizing that the compounds they claimed are actually the well-known pyridinium salts **4**. However, Christl wrote 'only for one alleged **3** (**3c**, R = 4-FC_6H_4), are there two deviations from the values of the corresponding **4′**. These deviations concern compound **3b** versus **4b** discussed, respectively, in Refs. 2 and 10. Unfortunately the NMR data corresponding to the Supplementary data of Ref. 2 is no longer available, having been withdrawn. Since we were part of the controversy,[10] we decided to examine this problem both from an energetic and a NMR point of view.

First we carried out B3LYP/6-311++G(d,p) calculations[11] using the GAUSSIAN 03 facilities[12] on **3a** and **4a** as model compounds. We have found two minima for compound **3a** using the reported most stable configurations of [12]annulene **3**.[13] Compared to two molecules of **2a** they are 602.9 and 623.3 kJ mol^{-1} less stable. The second step was to carry out GIAO calculations of absolute shieldings σ[14] on the optimized geometries of **1b** (two minima) and **2b**. Here again two molecules of **2b** are more stable than minimum 1 of **1b** (570.0 kJ mol^{-1}) and minimum 2 of **1b** (586.0 kJ mol^{-1}).

The GIAO σ values calculated for **2b** are very well correlated with the corresponding experimental values (Scheme 4).[14]

$$\delta^{1}\text{H (ppm)} = (33.3 \pm 1.3) - (1.04 \pm 0.05)\ \sigma^{1}\text{H (ppm)},\quad n = 9\ \text{(including TMS)},\ r^2 = 0.980 \tag{1}$$

$$\delta^{13}\text{C (ppm)} = (174.2 \pm 1.1) - (0.94 \pm 0.02)\ \sigma^{13}\text{C (ppm)},\quad n = 12\text{(including TMS)},\ r^2 = 0.997 \tag{2}$$

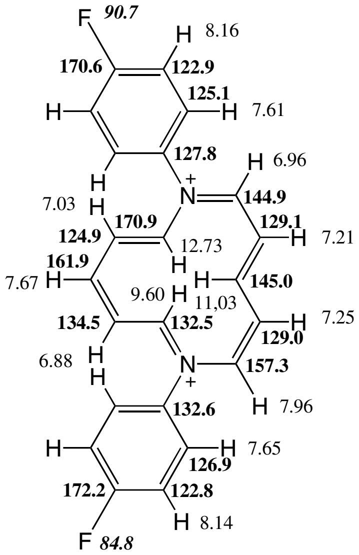


2b [calculated σ values]

2b [exp. values from ref. 4. Compound **Ic**. Solvent: DMSO-d_6]

References: ^{1}H TMS = 31.97
^{13}C TMS = 184.75 and ^{19}F;
$CFCl_3$ = 153.70 ppm

Scheme 4. Calculated absolute shieldings and experimental chemical shifts (all in ppm).



1b

Scheme 5. The predicted chemical shifts for 1,7-diaza[12]annulenium quaternary salt **1b**.

Eq. 2 is better because ^{1}H NMR chemical shifts are sensitive to solvent effects. The ^{19}F chemical shift (109.5 ppm)[4] differs from the calculated σ value (263.7 ppm) at 154.2 ppm, value almost identical to the reference $CFCl_3$ ($\delta = 0.0$, $\sigma = 153.7$ ppm).

Then, using these equations and the calculated σ of minimum 1 of **1b** we have estimated its chemical shifts (Scheme 5).

Depending on the barrier to the automerization of annulene **1b** some signals would be averaged at room temperature, but in any case they are very different from those of **2b** (experimental). The predictions for **1b** could be used to identify this compound in case it will be synthesized in the future.

Acknowledgments

This work was carried out with financial support from the Ministerio de Educación y Ciencia (Project No. CTQ2006-14487-C02-01/BQU) and Comunidad Autonoma de Madrid (Project MADRISOLAR, Ref. S-0505/PPQ/0225). Thanks are given to the CTI (CSIC) for allocation of computer time.

Supplementary data

Supplementary data (geometries, energies and GIAOs of **1a**, **2a**, **1b** and **2b**) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2008.02.002.

References and notes

1. Alkorta, I.; Goya, P.; Elguero, J.; Singh, S. P. *Natl. Acad. Sci. Lett.* **2007**, *30*, 139–159.
2. Yamaguchi, I.; Gobara, Y.; Sato, M. *Org. Lett.* **2006**, *8*, 4279–4281.

3. Shi, L.; Lundberg, D.; Musaev, D. G.; Menger, F. M. *Angew. Chem., Int. Ed.* **2007**, *46*, 5889–5891.
4. Christl, M. *Angew. Chem., Int. Ed.* **2007**, *46*, 9152–9153.
5. Zincke, T. *Justus Liebigs Ann. Chem.* **1904**, *330*, 361–374.
6. Zincke, T.; Heuser, G.; Möller, W. *Justus Liebigs Ann. Chem.* **1904**, *333*, 296–345.
7. Jones, G. In *Comprehensive Heterocyclic Chemistry I*; Katritzky, A. R., Rees, C. W., Eds.; Pergamon Press: Oxford, 1984; Vol. 2, Chapter 2.08, p 398.
8. Sanderson, K. *Nature News*, published online 4 December 2007, doi:10.1038/news.2007.341. Note that the figure selected to illustrate the comment is a [14] not a [12]annullene.
9. http://en.wikipedia.org/wiki/Zincke_reaction.
10. Claramunt, R. M.; Elguero, J. *Collect. Czech. Chem. Commun.* **1981**, *46*, 584–596.
11. Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648–5652; Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785–789; Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724–728; Frisch, M. J.; Pople, J. A.; Krishnam, R.; Binkley, J. S. *J. Chem. Phys.* **1984**, *80*, 3265–3269.
12. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J.A. GAUSSIAN *03*; Gaussian: Pittsburgh PA, 2003.
13. Castro, C.; Karney, W. L.; Vu, C. M. H.; Burkhardt, S. E.; Valencia, M. A. *J. Org. Chem.* **2005**, *70*, 3602–3609.
14. Ditchfield, R. *Mol. Phys.* **1974**, *27*, 789–807; London, F. *J. Phys. Radium* **1937**, *8*, 397–409.