

Computational modeling of phase-transfer catalyst 1-propyl-4-dimethylaminopyridinium

Gintautas Šaduikis²,

Laimutė Rastenytė¹,

Algirdas Matijoška¹,

Olegas Eicher-Lorka^{1*}

¹ Institute of Chemistry,
LT-01108 Vilnius, Lithuania

² Lithuanian Environmental
Protection Agency,
LT-01108 Vilnius, Lithuania

Computational structure modeling of 1-propyl-4-dimethylaminopyridinium cation (an active part of the phase-transfer catalyst) was carried out using the Gaussian 98W program. Analysis of the optimized structure evidenced an intense conjugation between dimethylamino group and pyridine ring as well as delocalization of a positive charge. 1-Alkyl-4-dimethylaminopyridinium quaternary salts can be defined as double-centered catalysts of "mixed" type. The calculated ¹H and ¹³C NMR spectra of the optimized structure are in good agreement with the experimental data.

Key words: phase-transfer catalysis, pyridinium salts, molecular modelling, B3LYP, NMR spectroscopy

INTRODUCTION

1-Alkyl-4-dialkylaminopyridinium halides examined in our previous works as phase-transfer (PT) catalysts at the two-phase liquid-liquid system [1, 2] demonstrated an outstanding catalytic performance in a number of α -elimination reactions. With a view to estimate the PT mechanism as well as the relationship between catalyst structure and catalytic properties, we aimed to establish the structure of an active catalyst form which takes part in the process of PT. Neither of these concerns has been covered in the literature for quaternary pyridinium salts; moreover, despite recent advances in computational chemistry, no reported attempts of the catalyst structure modeling by means of modern computational methods have been found. We opted for one of the most trivial of synthesized quats, 1-propyl-4-dimethylaminopyridinium bromide, as the subject for computational structure modeling using the GAUSSIAN 98W program [1].

Theoretically, either of the two nitrogens of quaternary dialkylaminopyridinium halide is able to play a role of cationic centre. For instance, the structure of 1-propyl-4-dimethylaminopyridinium cation is depicted as a resonance hybrid of two marginal structures (see Fig. 1, the values of certain bond lengths in angstroms (Å) are shown).

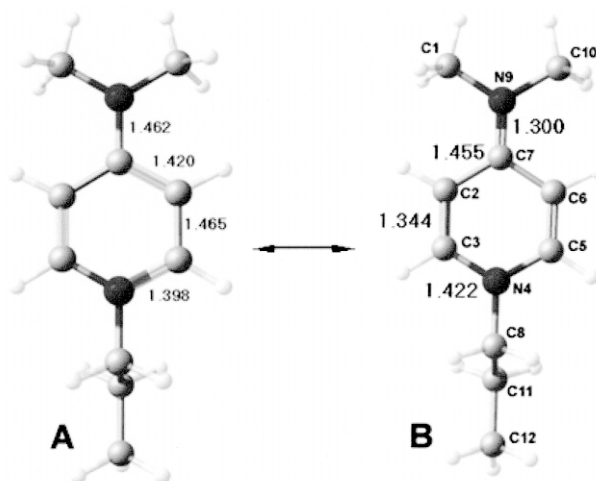


Fig. 1. Marginal structures of 1-propyl-4-dimethylaminopyridinium cation. A: entirely aromatic pyridine ring; single C7-N9 bond; positive charge localized on the ring nitrogen N4. B: 1,4-dihydropyridine ring; double C7-N9 bond; positive charge localized on the dimethylamino group nitrogen N9

EXPERIMENTAL

Different computational methods (HF, DFT) and levels were used. For the structure optimising, the optimal method was DFT (Density Functional Theory) at level B3LYP/6-311++G** [3]. For ¹H NMR spectra calculations, the best was the HF (Hartree-Fock)

*Corresponding author. E-mail: lorka@ktl.mii.lt

method at level 6-311+G (d, p). Magnetic shielding constants were calculated using GIAO (Gauge-Independent Atomic Orbital) and IGAIM methods (for ^1H and ^{13}C NMR spectra, respectively) [1].

RESULTS AND DISCUSSION

The results of structure optimization are presented in Fig. 2. For both marginal forms A and B, the final optimized structure C appeared to be identical. Hence the latter is the most stable in terms of molecule energy. The calculated atom charges are depicted in structure D. One can see that a positive charge on the pyridine nitrogen (N4) is more than twice as high as that on the amine nitrogen (N9). On the other hand, the pyridine nitrogen N4 is considerably more sterically hindered when compared to N9. Therefore, an active role of the dimethylamino nitrogen in the process of PT is highly presumable.

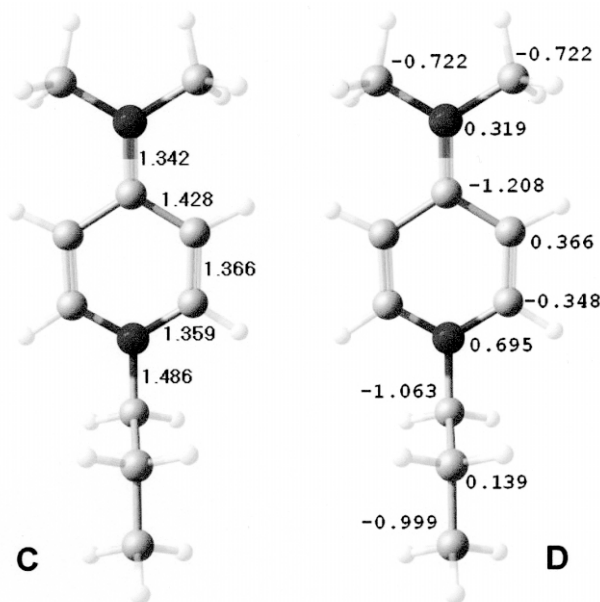


Fig. 2. The structure of the optimized molecule: C – bond lengths (Å); D – atom charges

The nature of C–N bonds of the optimized structure was further analyzed using NBO methods [1]. According to the results (see Fig. 3), an exocyclic C7–N9 bond has a character of a double bond planar with pyridine ring. The first bond C7–N9 (1) is

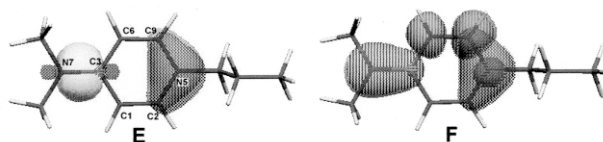


Fig. 3. The visualization of bonds [1]: E – the σ bond of C7–N9 (1); lone pair electrons of N4; F – the π bond of C7–N9 (2); lone pair electrons of N4 orbital interaction with pyridine ring – C5–C6 antibond orbital

formed by $0.6213 [sp^{2.23}]_C + 0.7836 [sp^{1.74}]_N$ electrons; the second bond C7–N9(2) is formed by $0.9325 [sp^{1.00}]_C + 0.9016 [sp^{1.00}]_N$ electrons. At the same time, the pyridine ring retains its aromaticity. This configuration is achieved by an intense conjugation between dimethylamino group and pyridine ring, which ensures an effective delocalization of the positive charge.

The accomplished calculations provide valuable information about the catalyst type. Depending on the characteristics of the cationic centre, all PT catalysts are defined as “soft” or “hard”, as suggested by E. Dehmlow [1]. From this viewpoint, the pyridine nitrogen N4, which features a marked sterical hindrance as well as a delocalized positive charge, is ascribed to the catalysts of “soft” type. Meanwhile, the dimethylamino nitrogen N9 adjacent with two short-chain alkyl groups is readily accessible, thus it is ascribed to the catalysts of “hard” type. Considering 1-alkyl-4-dimethylaminopyridinium quaternary salts as a whole in terms of the above classification, they can be defined as double-centered PT catalysts of “mixed” type. The role of dimethylamino group as a substantial contributor to the stabilization of quaternary pyridinium cation is evident. Obviously, 4-dialkylaminopyridinium quaternary salts should be superior than PT catalysts when compared to pyridinium quats without dialkylamino group in 4- (or 2-) position of the pyridine ring. The latter is clearly confirmed by the experiments [1].

^1H NMR spectra of 1-propyl-4-dimethylaminopyridinium bromide were recorded in neutral, acid, and alkali media. Negligible differences in the positions of chemical shifts (see Table 1) evidence the absence of any major structural changes by varying pH.

Both ^1H NMR and ^{13}C NMR spectra are in good correlation with the experimental data (see Fig. 4).

Table 1. ^1H NMR experimental spectra data of 1-propyl-4-dimethylaminopyridinium bromide

Solvent	^1H BMR spectra data (δ , ppm)					
	Py-2H (2H, d)	Py-3H (2H, d)	N ⁺ -CH ₂ (2H, t)	N-(CH ₃) ₂ (6H, s)	-CH ₂ - (2H, m)	CH ₃ (3H, t)
CD ₃ CN	8.10	6.94	4.14	3.22	1.89	0.93
D ₂ O	8.03	6.91	4.11	3.21	1.89	0.93
D ₂ O + CF ₃ COOH	7.97	6.86	4.08	3.20	1.83	0.89
D ₂ O + NaOD	7.98	6.85	4.06	3.17	1.79	0.87

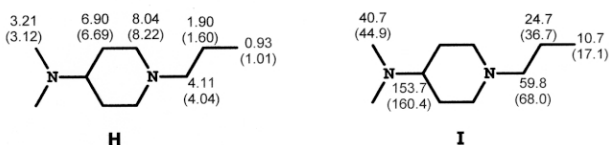


Fig. 4. ^1H NMR spectrum, chemical shifts (ppm); **I** – ^{13}C NMR spectrum, chemical shifts [first number – experimental, second number (in brackets) – calculated]

For ^1H NMR (**H**) and ^{13}C NMR spectra (**I**), respectively, correlation quotients of chemical shifts are: 0.998 and 0.9987; an average difference: 0.16 and 5.3 ppm; the maximum difference: 0.3 and 8.25 ppm.

The results of computational modelling demonstrate that the optimized structure **C** is very close to the structure of real 1-propyl-4-dimethylaminopyridinium cation, which takes part in the process of PT. The latter structural fragment is present in any of 4-dialkylaminopyridinium quaternary salts described in our previous articles [1]. There is evidence to postulate that the structures of an active cationic centre for the explored model and for the rest of 4-dialkylaminopyridinium quats are similar.

CONCLUSIONS

The structure of phase-transfer catalyst 1-propyl-4-dimethylaminopyridinium cation was evaluated by the computational DFT and ab-initio methods. The dimethylamino group is conjugated to a great extent with an aromatic ring; a positive charge is delocalized between two nitrogen atoms of pyridine and amino group. The calculated ^1H and ^{13}C NMR spectra of the optimized structure are in good correlation with experimental data.

Received 22 November 2005

Accepted 28 November 2005

References

1. G. K. Kupetis, G. Ąaduikis, O. Nivinskienė and O. Eicher-Lorka, *Monatsh Chem.*, **133**, 313 (2002).
2. G. K. Kupetis, G. Ąaduikis, O. Nivinskienė and O. Eicher-Lorka, *Chemija*, **12**, 246 (2001).
3. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzew-

ski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle and J. A. Pople, *Gaussian 98, Revision A. 7*, Gaussian, Inc., Pittsburgh, PA (1998).

4. M. J. Frisch, M. J. Frisch, *Gaussian 98 User's Reference, 2nd edition*, Gaussian, Inc, Pittsburgh, PA (1999).
5. E. O. Glendening, A. E. Reed, J. E. Carpenter, F. Weinhold, *NBO Version 3.1*.
6. E. V. Dehmlow and S. S. Dehmlow In: *Phase Transfer Catalysis*, Verlag Chemie, Weinheim (1983); E. V. Dehmlow, *Izv Akad Nauk, Ser Khim*, 2094 (1995).
7. D. J. Brunelle In: C. M. Starks (Ed) *Phase-Transfer Catalysis, New Chemistry, Catalysts, and Applications*, American Chemical Society, Washington, 38 (1987).
8. P. Flükiger, H. P. Lüthi, S. Portmann and J. Weber, *MOLEKEL 4.1*, Swiss Center for Scientific Computing, Manno, Switzerland, (2000–2001).

Gintautas Šaduikis, Laimutė Rastenytė,
Algirdas Matijočka, Olegas Eicher-Lorka

TARPFAZINIO KATALIZATORIAUS, 1-PROPIL-4-DIMETILAMINOPIRIDINIO, STRUKTŪROS MODELIAVIMAS

Santrauka

Kvantiniai *ab-initio* skaiėiavimo metodais (programa GAUSSIAN 98W) nustatyta aktyvaus (dalyvaujanėio tarpfaziniame perneėime) ketvirtinio katijono struktūra. Tarp 4-dimetilamino grupės ir aromatinio ėiedo yra stipri konjugacija, o teigiamas krėvis delokaliziuotas tarp piridininio ir amininio azoto atomė. Remiantis apskaiėiavimais, 1-alkil-4-dimetilaminopiridinio ketvirtinės druskos gali bėti traktuojamos kaip miėraus tipo TF katalizatoriai su dviem katijoniniais centrais. Optimizuotos struktūros apskaiėiuoti ^1H ir ^{13}C BMR spektrai gerai koreliuojasi su eksperimentiniais spektrais.