Journal of Molecular Structure 929 (2009) 125–127

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc

# The computational study of the complex between 4-nitrophenyl[bis(methylsulfonyl)]methane and TBD base in acetonitrile and tetrahydrofuran solution

Iwona Binkowska *, Jacek Koput, Arnold Jarczewski

*Faculty of Chemistry, Adam Mickiewicz University, Grunwaldzka 6, 60-780 Poznań, Poland*

A R T I C L E  I N F O

*Article history:*
Received 27 February 2009
Received in revised form 3 April 2009
Accepted 6 April 2009
Available online 17 April 2009

*Keywords:*
4-Nitrophenyl[bis(methylsulfonyl)]methane
4-Nitrophenyl[bis(ethylsulfonyl)]methane
TBD
Carbon acid
Acetonitrile
Tetrahydrofuran

A B S T R A C T

The electronic spectra of the complex between 4-nitrophenyl[bis(methylsulfonyl)]methane and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) in acetonitrile and tetrahydrofuran solvent are predicted at the CIS(D)/cc-pVDZ and PBE0/cc-pVDZ levels of theory taking into account the macroscopic solvent effect. The obtained results for 4-nitrophenyl[bis(methylsulfonyl)]methane/TBD system are discussed taking into consideration the experimental data for 4-nitrophenyl[bis(ethylsulfonyl)]methane/TBD system.

## 1. Introduction

The proton abstraction reaction from carbon acids induced by strong organic bases in solution has attracted our attention for many years involving the nature of the products, stabilization of the transition state and mechanism of these reactions. The electron withdrawing groups such as: cyano, nitro or sulfonyl change the properties of the molecule of methane derivative in such a way that its proton donor properties are changed in a wide range making carbon acid (C-acid) [1–10]. The family of disulfonyl carbon acids, have a strong acidic character [5,11] due the presence of two sulfonyl groups attached to the central α-carbon atom. In our previous paper [12], four feasible conformations in the ground electronic state were discussed and energetics of the ion-pair hydrogen bonded complexes of 4-nitrophenyl[bis(methylsulfonyl)]methane with 1,5,7-triazabicyclo[4.4.0]dec-5-ene in vacuum and acetonitrile solvent are predicted at the MP2/cc-pVDZ level of theory. In the gas phase, the energies of four possible ion-pair complexes are calculated to be −92.0, −100.4, −100.7 and −75.3 kcal mol$^{-1}$, relative to the energy of the separated ions. In acetonitrile solvent, the corresponding relative energies are predicted to be −109.6, −116.0, −114.8 and −105.7 kcal mol$^{-1}$ [12].

However, in the previous experimental paper dealing with the formation of carbanions of C-acids activated by ethylsulfonyl or benzylsulfonyl groups in the presence of different organic bases, we found that the electronic spectra taken in acetonitrile solvent for 4-nitrophenyl[bis(ethylsulfonyl)]methane/TBD system has the intense absorption maxima around $\lambda_{max} \sim 444$ nm. The spectra for this complex in tetrahydrofuran solvent has intense absorption band with $\lambda_{max} \sim 440$ nm. However, the change of the solvent from acetonitrile to less polar tetrahydrofuran causes quite unexpectedly the batochromic, instead hipsochromic, shift for 4-nitrophenyl[bis(benzylsulfonyl)]methane/TBD 1:1 complex, amounting to $\Delta\lambda_{max} = \sim 16$ nm. The reverse tendency was visible, however smaller, $\Delta\lambda_{max} = \sim 6$–8 nm, for other complexes formed between 4-nitrophenyl[bis(benzylsulfonyl)]methane and MTBD, DBU, and TMG bases in acetonitrile solvent. The unusual trend suggest that the complexes formed retain more ionic character in the lower polarity solvent.

To shed some light on this problem, we performed the computational study, in the hope that the calculated electronic transition energies for the 4-nitrophenyl[bis(methylsulfonyl)]methane/TBD complex in acetonitrile and tetrahydrofuran solvent will confirm the previous, unexpected experimental data for 4-nitrophenyl [bis(ethylsulfonyl)]methane/TBD complex [10]. Because of the large size of the complexes in question, 4-nitrophenyl[bis(methylsulfonyl)] methane was considered instead of 4-nitrophenyl[bis(ethylsulfonyl)]methane used in the spectrophotometric measurements [10].

---

* Corresponding author. Tel.: +48 61 829 1479/80; fax: +48 61 829 1505.
*E-mail address:* iwonakal@amu.edu.pl (I. Binkowska).

0022-2860/$ - see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.molstruc.2009.04.006

## 2. Experimental

### 2.1. Synthesis

4-nitrophenyl[bis(ethylsulfonyl)]methane was originally synthesized according to the method described by Aiken and Cronyn [7,13]. The melting point and NMR spectroscopy confirmed the purity of the obtained compound (mp = 202 °C). 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) from Fluka was used as a commercial reagent.

Acetonitrile, the isocratic grade solvent from J.T. Baker, was stored over $CaH_2$, distilled over $P_4O_{10}$ and finally, fractionally distilled over $CaH_2$. The fraction of 81.5–82 °C was collected and stored under argon to prevent $CO_2$ and moisture. Tetrahydrofuran (Aldrich) was stored and next distilled from blue sodium/benzophenone ketyl**,** under argon atmosphere. All solutions for spectrophotometric measurements were freshly prepared before experiments and handled with precautions to protect them from atmospheric carbon dioxide and moisture.

### 2.2. Calculation

The electronic excited state energies and transition oscillator strengths of the complexes were determined using the configuration interaction methods, CIS and CIS(D) [14,15], both in conjunction with the cc-pVDZ basis set [16]. In the CIS approach, the calculations included all singly-excited configurations within the valence active space. The CIS(D) method includes additionally a second-order perturbational correction to the CIS excitation energy and, therefore, it is analogous to the MP2 approach for the ground electronic state. The solvent effects were accounted for within the conductor-like polarizable continuum model (CPCM) [17] at the CIS/cc-pVDZ level of theory. To estimate the electronic transitions energies in solution, the solvent shifts determined at the CIS level were added to the transitions energies in vacuo determined at the CIS(D) level. Electronic transition energies of the complexes were also calculated by means of the time-dependent density functional theory (TD-DFT) using the PBE0 hybrid functional [18] in conjunction with the cc-pVDZ basis set. The calculations were performed using the Gaussian 03 package [19].

### 2.3. Spectrophotometric measurements

The electronic spectra in acetonitrile and tetrahydrofuran were recorded on a Hewlett Packard Diode Array Spectrophotometer (HP 8452) fitted with thermostated cell holder to keep the temperature constant within ±0.1 °C.

## 3. Results and discussion

The formula of studied compounds is presented in Fig. 1.

Recently, we discussed the crystallographic, NMR and FT-IR results for the complexes of 4-nitrophenyl[bis(ethylsulfonyl)]methane and TBD and MTBD bases in solution and in the solid state [20,21]. In the crystal form of the 1:1 complex, the N–H protons of the protonated molecule of TBD are hydrogen bonded with two sulfonyl groups of carbon acid by two weak hydrogen bonds. A similar structure of the complex was proposed in chloroform solution whereas in acetonitrile it changed and the complex with two intermolecular hydrogen bonds of protonated TBD with the oxygen atoms of the nitro group of carbon acid appeared. The FT-IR results demonstrate that the negative charge after deprotonation of 4-nitrophenyl[bis(ethylsulfonyl)]methane C-acid is delocalized in such a way that the nitro groups are strongly engaged in this conjugation process. Furthermore, the strong shift of the bands of the $\nu(SO_2)$ vibrations indicates that also the sulfonyl groups are involved in the delocalization process of the electron lone pair after the abstraction of the proton from carbon acid takes place.

The same conclusions were drawn from the ab initio calculations for 4-nitrophenyl[bis(methylsulfonyl)]methane, where the complexes with double hydrogen NHO bonds were found [11]. These results in the solid state indicate that the ion-pair complexes are formed between the oxygen atoms of the sulfonyl groups and TBD molecule. It appear, that the lowest relative energy has been found for two structures having double hydrogen NHO bonds. First one is formed between nitrogen atoms of TBD base and the oxygen atom of one sulfonyl group. In the second one, two NHO bonds involve the oxygen atoms of both sulfonyl groups. However, in acetonitrile the probability of formation of the complex with the hydrogen bonds between oxygen atoms of the nitro group of carbon atom and TBD base certainly rises, as indicated by the reduced relative energy values.

However, the most astonishing fact that the absorption maximum for the ionized complex in acetonitrile ($\lambda_{max} \sim 444$ nm) has been changed, after acetonitrile was replaced with tetrahydrofuran, showing the batochromic, instead hipsochromic, shift required additional support. Therefore, the theoretical ab initio CIS(D)/cc-pVDZ and TD-DFT PBE0/cc-pVDZ methods were used to estimate the electronic excitation energies of the complexes and to determine the maximum absorption position $\lambda_{max}$ (the transition to the lowest excited state $S_1$) in solvents in question. The calculated values of $\lambda_{max}$ for the complexes of interest are given in Table 1. The electronic excited state $S_1$ is predicted to have the $\pi, \pi^*$ character. The solvent shift of the $S_1 \leftarrow S_0$ transition was determined at the CIS/cc-pVDZ level to be $-390$ and $-440\ cm^{-1}$ for acetonitrile and tetrahydrofuran, respectively. At the PBE0/cc-pVDZ level, the coresponding solvent shifts were predicted to be $-680$ and $-720\ cm^{-1}$, respectively. Apparently, there is no difference between the calculated solvent shifts and the estimated $\lambda_{max}$ values for the 4-nitrophenyl[bis(methylsulfonyl)]methane (1)/TBD complex in acetonitrile and tetrahydrofuran solutions. For comparison, the experimental $\lambda_{max}$ values for the 4-nitrophenyl[bis(ethylsulfonyl)]methane (2)/TBD complex in both solvents are shown.

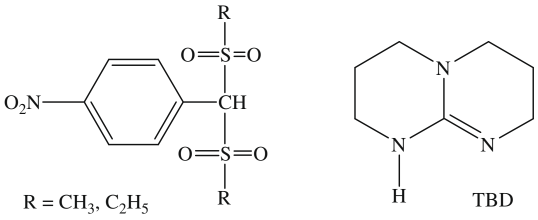

**Fig. 1.** Formula of the carbon acids and organic base used in this work.

**Table 1**
The calculated and experimental values of $\lambda_{max}$ for the complexes between TBD base and 4-nitrophenyl[bis(methylsulfonyl)]methane (1) and 4-nitrophenyl[bis(ethylsulfonyl)]methane (2) carbon acids in acetonitrile and tetrahydrofuran solvent.

| Products | (1)–TBD PBE0/cc-pVDZ | (1)–TBD CIS(D)/cc-pVDZ | (2)–TBD Spectrophotometric method |
|---|---|---|---|
| $\lambda_{max}$ (nm) in MeCN | 413 | 337 | 444-6 |
| $\lambda_{max}$ (nm) in THF | 414 | 337 | 440 |

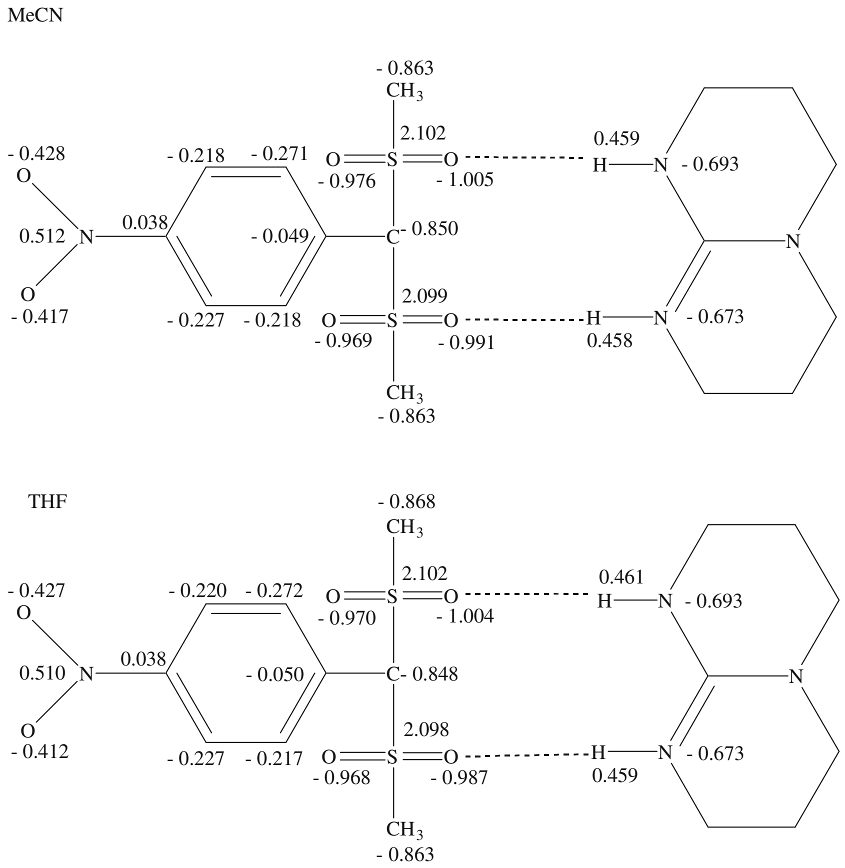

**Fig. 2.** Atomic charges (*e*) determined by natural-bond-orbital (NBO) population analyses of the Hartree–Fock electron density for 4-nitrophenyl[bis(methylsulfonyl)]methane (1)–TBD complex in acetonitrile (MeCN) and tetrahydrofuran (THF).

The change of the solvent from acetonitrile to tetrahydrofuran shifts the maximum absorption position $\lambda_{max}$ by just 4–6 nm toward the shorter wavelength. The $\lambda_{max}$ values for the (1)/TBD complex estimated by means of the TD-DFT method PBE0/cc-pVDZ are in a much better agreement with the experimental data for the (2)/TBD complex than those obtained by the ab initio method CIS(D)/cc-pVDZ.

The $\lambda_{max}$ value for 4-nitrophenyl[bis(methylsulfonyl)]methane (1)/TBD complex calculated by TD-DFT method without consideration of solvent environment was ~402 nm, while this value obtained by means of CIS(D)/cc-pVDZ method was only ~332 nm. It is noteworthy that the calculated values of $\lambda_{max}$ taking into account both acetonitrile and tetrahydrofuran solvents are comparable (Table 1), although their macroscopic characteristics as dielectric constants are very different ($\varepsilon_{MeCN} = 36.6$ and $\varepsilon_{THF} = 7.6$). Then, in conclusion, we can speculatively assume that the explanation already given in the previous paper that the complex has very similar ionic character in both solvents. Atomic charges determined by NBO population analyses of the Hartree–Fock electron density for (1)/TBD complex in both THF and MeCN solvents, despite of their different polarity are alike (Fig. 2).

It seems to be obvious that in THF solvent the anion is strongly stabilized by its dipoles. Therefore it seems to be likely that this unusual trend of the shifts previously observed [10] is due to lower salvation of the product in THF solution, what is strongly suggested by very similar distribution of electron densities in both solvents demonstrated in Fig. 2. Hence the anion of this C-acid in THF may have the structure similar to that found in the gas phase as previously estimated in the DFT calculations [12,22].

## Acknowledgements

We gratefully acknowledge the financial support from MNiSW Grant No. N204 087 32/2496. The calculations were performed at the Poznań Supercomputer Center PCSS.

## References

[1] A. Jarczewski, C.D. Hubbard, J. Mol. Struct. 649 (2003) 287.
[2] W. Gałęzowski, I. Grześkowiak, A. Jarczewski, J. Chem. Soc. Perkin Trans. 2 (1998) 1607.
[3] Z. Wisłocka, I. Nowak, A. Jarczewski, J. Mol. Struct. 788 (2006) 152.
[4] K. Minksztym, A. Jarczewski, J. Mol. Struct. 691 (2004) 203.
[5] M. Stańczyk-Dunaj, W. Gałęzowski, A. Jarczewski, Can. J. Chem. 80 (2002) 1259.
[6] W. Gałęzowski, I. Grześkowiak, A. Jarczewski, Can. J. Chem. 77 (1999) 1042.
[7] F. Aiken, B.G. Cox, P.E. Sørensen, J. Chem. Soc. Perkin Trans. 2 (1993) 783.
[8] K.P. Ang, F.F. Tan, W.S. Lee, Aust. J. Chem. 30 (1977) 2473.
[9] I. Binkowska, A. Jarczewski, J. Mol. Struct. 797 (2006) 61.
[10] I. Binkowska, A. Jarczewski, J. Mol. Struct. 875 (2008) 86.
[11] I. Nowak, I. Binkowska, M. Stańczyk-Dunaj, A. Jarczewski, Wiadomości Chemiczne 62 (2008) 1.
[12] I. Binkowska, J. Koput, A. Jarczewski, J. Mol. Struct. 876 (2008) 344.
[13] M. Cronyn, J. Chem. Soc. 47 (1952) 1225.
[14] J.B. Foresman, M. Head-Gordon, J.A. Pople, M.J. Frisch, J. Phys. Chem. 96 (1992) 135.
[15] M. Head-Gordon, R.J. Rico, M. Oumi, T.J. Lee, Chem. Phys. Lett. 219 (1994) 21.
[16] T.H. Dunning Jr., J. Chem. Phys. 90 (1989) 1007.
[17] V. Barone, M. Cossi, J. Phys. Chem. A 102 (1998) 1995.
[18] C. Adamo, V. Barone, J. Chem. Phys. 110 (1999) 6158.
[19] M.J. Frisch et al., Gaussian 03, Revision D.01, Gaussian Inc., Pittsburgh, PA, 2003.
[20] I. Binkowska, A. Jarczewski, A. Katrusiak, G. Wojciechowski, B. Brzezinski, J. Mol. Struct. 597 (2001) 101.
[21] A. Huczyński, I. Binkowska, A. Jarczewski, B. Brzezinski, J. Mol. Struct. 841 (2007) 133.
[22] A. Jarczewski, J. Koput, I. Nowak, J. Mol. Struct. 788 (2006) 138.