

DIMCARB – A Quantum Mechanics Study of its Structure

VALENTIN PLESU¹, GEORGE IULIU MARTON^{1*}, ANCA LIANA MARTON¹, PETRICA IANCU¹, ALEXANDRA ELENA BONET RUIZ¹, JORDI BONET-RUIZ²

¹University Politehnica of Bucharest, Centre for Technology Transfer in Process Industries (CTTPI), 1, Gh. Polizu Str., Bldg. A, Room A056, 011061 Bucharest, Romania

²University of Barcelona, Department of Chemical Engineering, 1, Martí i Franques Str., E-08028 Barcelona, Spain

The present paper describes the quantum mechanics study for dimethylammonium dimethylcarbamate, a ionic liquid (IL) successfully used as performant “green” reaction solvent, but also as extraction solvent for natural components. The dynamic equilibrium between dimethylamine and carbon dioxide in molecular ratio of 2:1, liquid up to 60 °C as ionic pair and dissociated beyond this temperature, but readily reforming the ionic dimethylammonium - dimethylcarbamate pair not only provides an environmentally-friendly reaction and extraction solvent, but allows an easy reaction working-up and a quantitative recovery/recycling of the solvent. The molecular modelling is performed with GAMESS at DFT M11/KTZVP level of theory, which provides geometries close to the ones determined by X-ray, in order to elucidate the most stable structure of the ionic liquid. A new mechanism of formation for DIMCARB is presented, demonstrating that the mechanism presented in literature is not possible. Dimer and tetramer configurations are considered and modelled, finding the most stable ones.

Keywords: DIMCARB, ionic liquids, molecular modeling, non-conventional solvents, dialcarb

Although not the main participant in a chemical reaction, the solvent plays a determining role for the outcome of the synthesis, in respect with the yield, distribution of products, reaction rate, reaction mechanism, stereoselectivity, thermodynamic aspects, etc.

In principal, the solvents are needed for getting reactants in close proximity in the same phase, achieving thus a reasonable reaction rate and yield. The solvent is chosen as a compromise between the reagents individual preferences for more or less polar media. A solvent should be powerful in dissolution process, polar, non-protic, cheap and easy to remove, in such a manner that the synthesis step and the solvent separation step to become parts of an integrated system.

Being the major quantitative component in an organic synthesis preparation, the solvent's removal during the work-up step of the synthesis may cause problems associated with its physical properties (e.g. toxicity, a too high boiling point, or a too low vapor pressure, inconvenient miscibility with other materials used during some work-up procedures, or environment protection precautions and cost when recovering or disposing the solvent).

Since most of reactions are studied not only at a laboratory scale, but also for industrial application, it is not only the development of reaction which is important, but also the toxicity and the recycling solutions for large amounts of solvents.

These are the reasons for which other options have been searched in respect with usage of solvents: solventless syntheses, choice of supercritical fluids [1], “green” solvents, etc., but none of these offered either the best solution or, even less, a universal key applicable to any type of chemical reaction.

Searching for proper solvents leads to the basic conditions that an ideal solvent should fulfil in respect with the reaction stage and with the work-up stage: in the reaction step the solvent should be liquid, best dissolve reagents and catalyst, chemically inert in respect with

them; in the separation step, triggered by changing a physical parameter, a change in the condition of the solvent should occur, switching the solvent to its constituting components as separable from the reaction mixture, but immediately recombining into the initial liquid state, to be thus completely recoverable.

Briefly, selecting the most convenient solvent for a synthesis is a challenging task for most researchers and within this general topic, the solution to use ionic liquids, as nonconventional solvents, is suitable for many applications.

Ionic liquids are non-volatile salts within one component is organic, with low melting point (<100 °C; or very low, in case of room temperature ionic liquids -RTILs), due to poor coordination of the constituent ions, with at least one ion showing a delocalized charge. They do not benefit of a stable crystal lattice, and their toxicity is reduced, compared to volatile solvents, as a consequence of their low volatility [2].

Subsequently, the properties that introduce ionic liquids (ILs) as very convenient solvents [3] are their easiness to be contained, reduced risk of combustion, thermal stability, tunable solvating capacity that may change the reactivity of certain species towards the substrates, ionic conductivity and electrochemical stability against oxidation [4], possibility to tailor their properties by modifying the action and/or the anion in their composition.

Although some of them may present inconvenient moisture sensitivity or even hygroscopicity, they are more and more considered due to some advantages: chemically inert, easy to remove by crystallization/sublimation/distillation, providing good solubilisation for a large class of organic & inorganic molecules as well as ionic complexes, good performance in asymmetric syntheses – when using chiral ILs – and the possibility of changing their miscibility properties by various combinations of ionic pairs in the IL, and, last but not least, their biodegradability [5, 6].

*email: g_marton@chim.upb.ro; phone: +40214023916

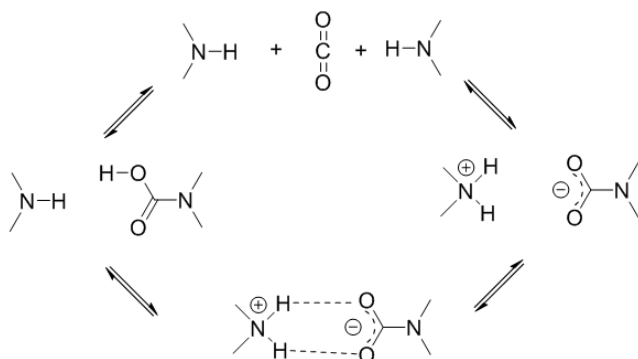
A remarkable utility of ionic liquids is their effectiveness in extracting metabolites and natural compounds (of diverse polarity from liquid samples, such as the extraction of polyunsaturated fatty acid methyl esters, organic acids, amino acids, phenols, alkaloids, and proteins from aqueous solutions), as well as their use as media for microwave and for enzymatic reactions, as stationary phase/ mobile phase additives in chromatography [7].

Dialkylammonium dialkylcarbamates (dialcarbs) are zwitterionic salts, resulted in the reaction of secondary alkylamines with carbon dioxide and are some of the first IL-s tested as non-conventional solvents. Their simplest representative is dimethylammonium dimethylcarbamate (DIMCARB). This is produced [8] and used for selective extraction of sulphur and aromatic hydrocarbons from crude oil [9], since the mid-XXth century.

DIMCARB and other similar distillable ionic liquids opened new routes for the *green chemistry*, both as performant solvents, and as catalysts in a holistic approach [10].

Starting from DIMCARB, by changing the alkyl moieties [11], other representatives in the class are synthesized, in order to obtain a scale of melting points and decomposition temperatures, both essential for solvent removal from the reaction mixture.

The dialcarbs [12] are easy to be produced by cooling the gaseous mixture of the secondary amine and carbon dioxide (in 2:1 molar ratio), the composition of the mixture passing from gaseous state to liquid state when chilled, and reversely when heated. This transition between states, in a dynamic equilibrium (scheme 1), creates the possibility of recovering them from the reaction mixture at the end of the reaction, the technique resembling to a *distillation*.



Scheme 1. Dynamic equilibrium of DIMCARB [13]

Liquid at room temperature, DIMCARB dissociates at 60 °C into the constitutive neutral molecules, therefore it can be distilled off from the reaction mixture, since the neutral components recombine in the attached condenser into the ionic liquid, ready for recovery/ recycling.

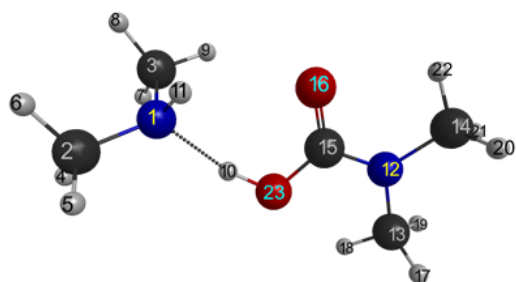
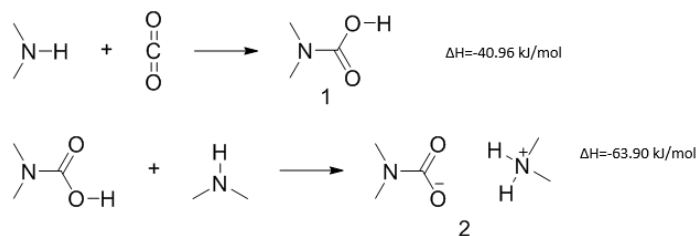
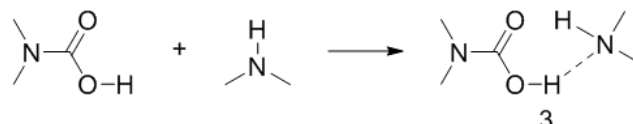


Fig 1. Association of dimethylamine with N,N-dimethylcarbamamic acid via a hydrogen bond



Scheme 2. The formation of DIMCARB.



Scheme 3. DIMCARB as an association based on a hydrogen bonding

Results and discussions

DIMCARB is modelled using GAMESS [14] at the DFT M11/KTZVP level of theory [15-17]. For structure of DIMCARB, the literature [11] reports an ion pair **2**, formed in two steps, firstly by addition of the dimethylamine to carbon dioxide leading to N,N-dimethylcarbamamic acid **1** and secondly by a proton transfer from the unstable adduct **1** to another molecule of dimethylamine (scheme 2).

Molecular simulations show that the reaction presented in scheme 2 is not possible, as the ion pair is highly unstable, and a transition state to the ion pair does not exist. While the intermediate **1** appears to be stable, the reaction with dimethylamine leads to an association **3** of two molecules by a hydrogen bond (scheme 3, and fig. 1).

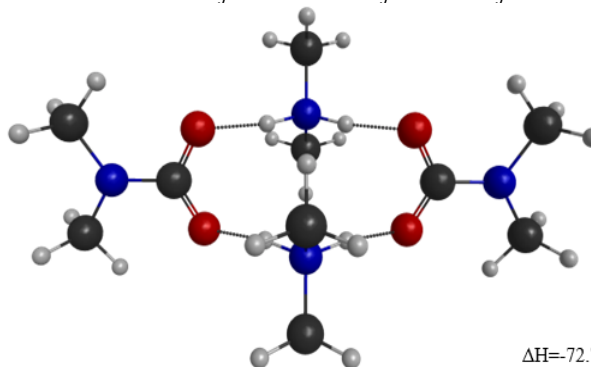
The reaction energy of -63.90 kJ/mol shows that the formation of DIMCARB is in fact controlled by association energy. The total energy of the two steps is -104.86 kJ/mol and shows a rather stable association compared with a physical mixture of dimethylamine and carbon dioxide.

Under these circumstances, a dimer of DIMCARB is considered next. In this case a stable product is found, whose most stable symmetrical conformation is shown in figure 2. The association energy of -72.726356 kJ/mol is quite large for a simple physical association. Relating this value to the formation energy of a hypothetical single molecule of DIMCARB, it appears that the formation of the dimer is irreversible at room temperature.

The simulations show that the dimer may present two conformations in terms of symmetry; the non-symmetrical conformation is presented in figure 3.

These results are checked against literature X-Ray (RX) data [18] as are presented in table 1.

As expected, the literature RX reported bonds and angles values and the calculated ones are quite different in the case of the single molecule. In the case of the dimer, again, significant differences in the lengths of the two N-H bonds in the dimethylamine moiety shown by RX data do not fit



ΔH=-72.726356 kJ/mol

Fig 2. Symmetrical conformation of DIMCARB dimer

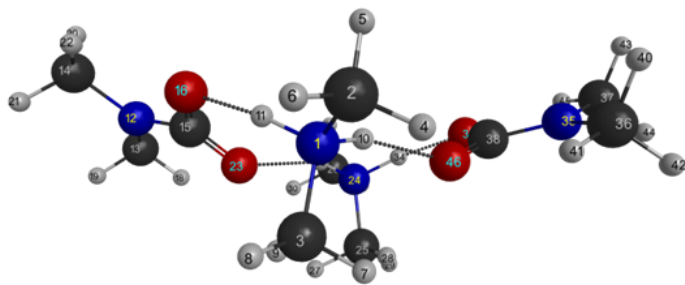


Fig 3. Non-symmetrical (twist) conformation of DIMCARB dimer to the equal lengths of the N-H bonds presumed by a symmetrical structure. This is the reason why the non-symmetrical (twist) conformation (fig 3) is considered and modelled. In the twisted conformation, the model shows different lengths for the two N-H bonds, matching therefore the RX data.

A tetramer is also modelled and its final structure is shown in figure 4. The association energy is -11 kJ/mol, showing a good stability of this molecular association.

The modelling of the tetramer leads to a final geometry corresponding to a macrocycle.

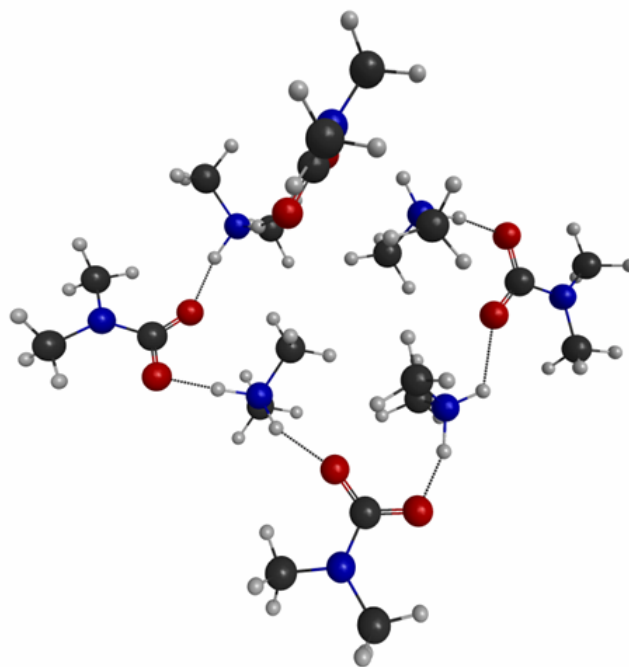


Fig 4. The final structure of the tetramer

Atoms	Lit. Data	Calculated for the single molecule	Calculated for the dimer (SYM)	Calculated for the dimer (non-SYM)
Bond Length (Å)				
O16-C15	1.2628 (15)	1.33217	1.26952	1.26787
O23-C15	1.2694 (15)	1.22478	1.26952	1.26819
N12-C15	1.3788 (17)	1.35785	1.37062	1.37354
N12-C13	1.4485 (19)	1.44749	1.44497	1.44321
N12-C14	1.4490 (16)	1.44854	1.44496	1.44529
N1-C2	1.4726 (17)	1.46576	1.47546	1.47252
N1-C3	1.4776 (17)	1.46570	1.47658	1.47613
N1-H10	0.899 (15)	1.64827	1.07233	1.04052
N1-H11	0.983 (16)	1.01392	1.07240	1.09380
Angles (°)				
C3-N1-C2	112.52 (11)	111.84	112.86	113.18
O16-C15-O23	124.33 (12)	122.74	123.50	123.83
O16-C15-N12	118.10 (12)	113.88	118.25	117.74
O23-C15-N12	117.57 (11)	123.39	118.24	118.43
C15-N12-C14	120.97 (11)	123.66	121.65	121.61
C15-N12-C13	121.84 (11)	119.70	121.64	121.83
C14-N12-C13	115.11 (11)	116.64	116.71	116.54

Table 1
COMPARISON BETWEEN CALCULATED DATA AND LITERATURE [18]

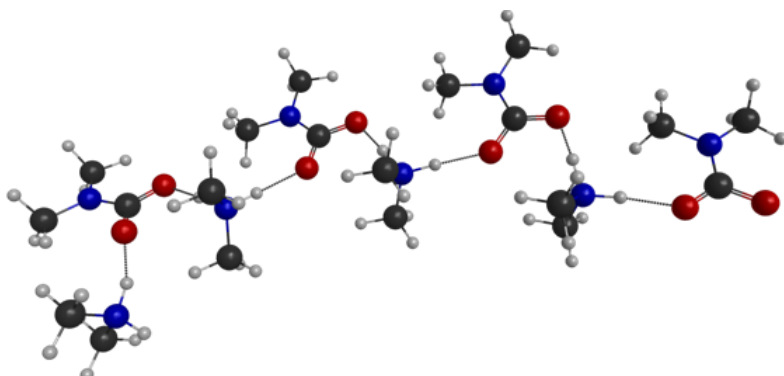


Fig 5. The starting geometry of the tetramer

It is worth being mentioned that the starting geometry is almost linear (fig 5).

Conclusions

The study showed that the molecular modelling with GAMESS of DIMCARB at DFT M11/KTZVP level of theory provides geometries close to the ones indicated by X-ray analysis.

The DIMCARB molecule exists only as supramolecular cyclic cluster of at least two molecules. Only in this case separated charges are observed.

The final geometry of the tetramer is a macrocycle showing a tendency to self-assemble in supramolecular clusters.

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