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Interaction of nitrogen dioxide with free base phthalocyanine

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Quantum chemical *ab initio* method was used to investigate interactions between NO_2 and H_2Pc. Four possible sites for NO_2 adsorption were considered. Full geometry optimisation together with frequency calculation was performed for the isolated molecules and the NO_2–H_2Pc complexes with the use of 6-31*g*(*d*, *p*) and minimal basis sets, respectively. Two stable and two transition states were found. The H_2Pc molecular structure was found to be largely affected under the influence of NO_2. It was found that for a certain chemisorption site H_2Pc molecule might disintegrate and its building blocks could react with NO_2 forming other species.

Keywords: phthalocyanine, gas sensors, *ab initio* calculations.

1. Introduction

Free base phthalocyanine (H_2Pc) and its metal substituted derivatives are well known materials used in many fields of industry due to their exceptional thermal and chemical stability and attractive electrical properties [1]. Since the electrical conductivity of Pc-based materials changes considerably under the influence of ambient gases, they are successfully applied in gas-sensing devices [1]. The sensors constructed with the Pc complexes are very well characterised as far as their macroscopic features are concerned [2–4]. However, there are still some questions difficult to answer on the basis of the experimental results. One of the problems is stability of Pc under oxidising conditions. It is known that the structure of the Pc macrocycle may be largely affected under the influence of oxidants. It was observed that high concentrations of NO_2 caused a disintegration of Pc molecules [5]. However, it is not evident whether or not at lower concentrations NO_2 chemisorbs irreversibly on a Pc surface. It is thought, on the basis of experimental work, that NO_2 molecules attack the weakest site of Pc ring, and break apart the isoindole units of the molecule forming in consequence phthalimide, which was registered in UV-VIS spectra [6]. It is difficult to get an insight on the nature of the interaction bewteen gaseous molecules and H_2Pc surface with the use of experimental methods only. A theoretical approach using quantum chemical methods can be helpful to explain the interactions.

We applied quantum chemical *ab initio* method in order to investigate the process of interaction of NO_2 with H_2Pc molecule. Our purpose was to examine possible sites for NO_2 chemisorption on H_2Pc surface and the changes that the interaction between the two species may cause in the chemical structure of the gas sensing molecule.

2. Methodology

In order to obtain results for a well defined system we have first performed full geometry optimisation of H_2Pc and NO_2 molecules. The results of the calculations reported here were obtained with the use of Gaussian 03 programme package [7]. Hartree–Fock (HF) method for the closed-shell systems with the 6-31*G*(*d*, *p*) split valence basis set was applied. The initial geometry of H_2Pc was taken from literature data [8]. The nature of the stationary point found in the process of energy minimisation

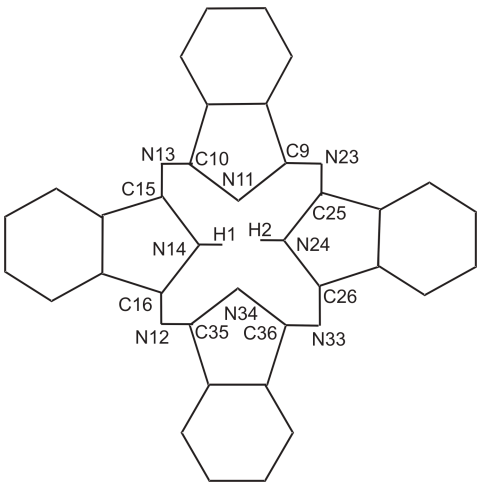

Fig. 1. Schematic view of H_2Pc molecule with atom labels as appears in the text.

was tested by doing a frequency calculation at the obtained geometry. After finding the true minimum we have investigated interactions between two NO_2 molecules and H_2Pc. Since it was suggested by experimentalists that oxidants might extensively alter the structure of Pc, we decided to perform full geometry optimisation also when NO_2 molecules were attached to the investigated system. However, the presented results for the NO_2 interacting with H_2Pc were obtained with the use of STO-3*G* minimal basis set. We shall refer here after to the atoms building H_2Pc molecule according to the labels shown in Fig. 1.

3. Results and discussion

In the process of H_2Pc geometry optimisation the true minimum was found, which was confirmed through a frequency calculation (no imaginary frequencies were obtained).

The obtained bond lengths appeared to be identical with those calculated with the use of the same method by DAY *et al*. [9]. The calculations let us find the net atomic charge of the atoms within the H_2Pc molecule. Although the values of charge obtained with the use of HF method are very much basis dependent, they give qualitatively good information about electronegativity of the atoms in the investigated system. It was found that the most electronegative atoms were the nitrogens: N14, N24 bonded to the inner hydrogen atoms, with their net charge –0.772 and –0.848, respectively. The other nitrogen atoms are overcharged by about 0.7 electron each. Therefore, these sites could be the most probable places for the chemisorption of NO_2 molecule.

Four positions for possible interactions between two NO_2 molecules and H_2Pc were considered. NO_2 molecules were placed symmetrically either over the two of the bridged nitrogen atoms (N12, N23) or close to the isoindole nitrogen atoms (N14, N24) bonded with the inner hydrogens, which is shown schematically in Fig. 2. NO_2 molecules in positions 1 and 2, as denoted in the figure, were put in such a way that only one oxygen atom of a molecule could potentially create a bond with a neighouring N atom of H_2Pc inner or outer ring, while in the other two positions both oxygen atoms could possibly interact with nearby nitrogens (N12, N13 and N23, N33). The initial bond length (1.165 Å) and the angle (136°) within the NO_2 molecule were the values obtained through its geometry optimisation (HF/6-31*g*(*d*, *p*)).

In the result of geometry optimisation we have found true minima (no imaginary frequencies) for the systems denoted as position 1 and 2. The total electron energy of the system 1 was –2039.962 hartree, slightly lower (by 0.12 eV) than the energy of the system 2, which suggests that the first one is more stable. In both cases a large deformity of H_2Pc molecule was observed, especially its distortion from planarity. Similar deformation was predicted earlier in the calculational semiempirical study of the interaction of NO with H_2Pc [10].

It is remarkable that in the position 2 the interaction of NO_2 molecules with N14 and N24 atoms caused that the inner hydrogens changed their postion inside the ring and bonded with N11 and N34. It is evident that when the interaction of NO_2 with H_2Pc is considered, the inner hydrogens cannot be treated as localised atoms. Hence, another initial position for NO_2 chemisorption, *i.e*., over N11 and N34 atoms, would give much similar results as far as the shared-hydrogen model is considered.

In the cases labeled as position 3 and 4, in the result of geometry optimisation one imaginary frequency was obtained. This might suggest that the obtained geometries are transition states. However, the resulting geometry of position 3 indicates rather repulsive interaction between H_2Pc and the two NO_2 molecules. This is probably because the NO_2 molecules were placed just over the H_2Pc inner ring close to each other (the initial distance between them was 2.037 Å) and they were able to form dinitrogen tetraoxide (N_2O_4). The system was treated as inseparable and was pushed far out of the H_2Pc plane, which molecular structure was not at all disrupted.

The final structure of the position 4 saddle point and the components of the mode corresponding to the imaginary frequency with a value 518*i* cm^{-1} shown in Fig. 3 is especially interesting. The largest components of this mode are those responsible for

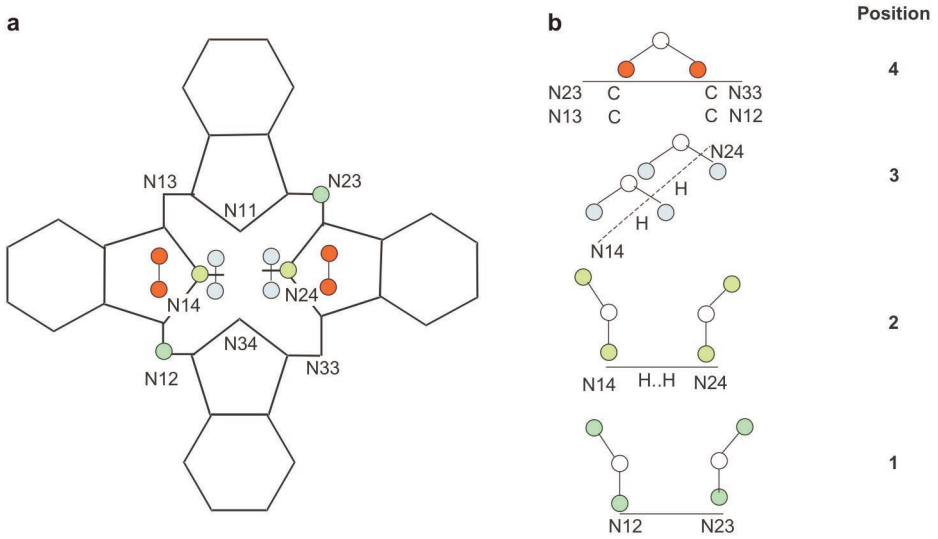

Fig. 2. Schematic view of H_2Pc molecule and four examined positions for $2NO_2$ adsorption together with the position numbering as appears in the text: top view (**a**) and side view (**b**).

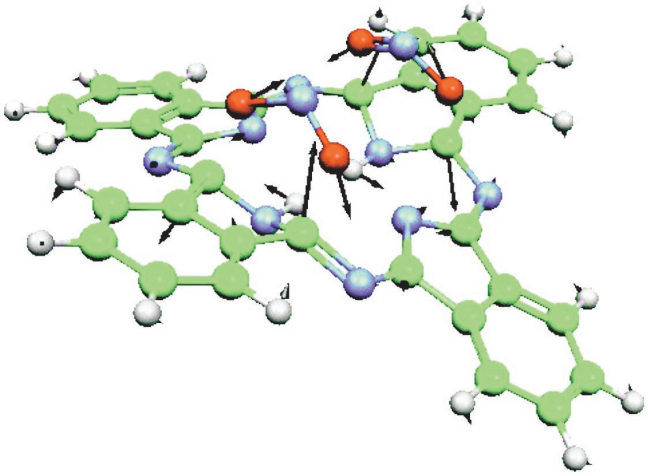

Fig. 3. Saddle point geometry for the H_2Pc–$2NO_2$ (position 4) system. The components of the normal mode corresponding to the single imaginary frequency are indicated.

the stretching of N–O bond and displacement of C15, C16, C25, C26 atoms of isoindole units. The direction of the vibration is such that it could break the bonds within the H_2Pc macrocycle and lead to a substitution of a bridged nitrogen with an oxygen atom creating a molecule of phthalimid. The fact that the bonds of N33-C26 type, as well as the bonds within NO_2 molecule, are becoming weaker when NO_2 interacts with

H_2Pc surface (they are longer by about 5 and 12%, respectively) supports that conclusion.

4. Conclusions

We have studied the interaction of NO_2 molecules with H_2Pc. Through the careful geometry optimisation of the investigated systems we have found that the process of adsorption of NO_2 on H_2Pc surface may differ considerably dependingly on the adsorption site. The most stable system is formed when oxygen atoms of NO_2 molecule are bonded with H_2Pc through the bridged nitrogens. In such a case binding energy is found to be –4.30 eV. Slightly less favorable process is chemisorption of NO_2 molecules being initailly over the pyrole nitrogens (calculated binding energy in that case is –4.13 eV). In the other examined cases transition states rather than stable systems were obtained. However, there are some clues coming from frequency calculations that H_2Pc molecule could be desintegrated under the inflence of NO_2 and other molecular species could be formed, for example phtalimid.

The obtained results indicate that at low concentration of NO_2 the molecules would chemisorb on H_2Pc surface creating bonds with the bridged nitrogen atoms. When the concentration of NO_2 in ambient atmosphere increases, the molecules would probably tend to create bonds with the other nitrogens of H_2Pc ring. There is a possibility that H_2Pc molecule building blocks would separate because of breaking the bonds between them, and other molecules, such as phthalimid, would be formed. Some more investigations should be done in order to find whether the described process of chemisorption is reversible.

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