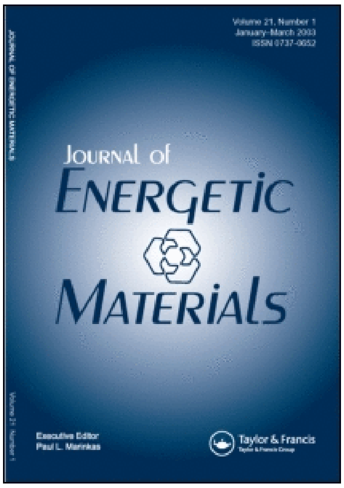

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AM1 Studies on the Mechanism of Hydrolysis of Dinitro semi-glycoluril

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Abstract

Theoretical calculations on the hydrolyses of dinitro semi-glycoluril in neutral, acidic and alkaline media, have been performed by using AM1 method. The geometries of reactant, activated, and product complex for the hydrolysis processes have been fully optimized. Both in neutral and acidic media, activated complexes with four-membered ring structure have been obtained, and reaction-coordinate eigenvectors reveal their concerted feature of component processes involved. In contrast, in alkaline media, the hydrolysis is relatively easy, since it proceeds without activation of reactant complex, and the potential energy curve of this hydrolysis process obtained is also indicative of this. The calculated activation energies for the hydrolyses of dinitro semi-glycoluril in neutral and acidic media are 217.233 kJ/mol and 218.856 kJ/mol respectively.

Introduction

It is well known that cyclic urea nitroamines are important energetic materials with many advantages such as high density, high energy, high expiosive speed and the like. However, the bad hydrostability of cyclic urea nitroamines Limits their practical use. Obviously theoretical study of their hydrolysis mechanism has certain significance in guiding the design of cyclic urea nitroamines with good characters. With reference to the

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theoretical study concerning their hydrostability, only one example involving the quantum chemical calculations on the molecules of cyclic urea nitroamines was reported by our group[1], the results show that their hydrostabilities are in relation to net charge on carbonyl carbon atom and influenced by steric hindrance, the presence of electron-withdrawing group bonded with the nitrogen atom adjacent to the carbonyl carbon atom is favourable to the hydrolysis. In order to investigate the hydrolyses of cyclic urea nitroamines further, the AM1 semi-empirical MO method was used to calculate the dynamic property of hydrolysis of dinitro semi-glycoluril, one of cyclic urea nitroamines, in neutral, acidic and alkaline media, the mechanism of the hydrolysis was discussed in this paper.

Computational Method and Results

Semi-empirical quantum-chemical calculations have been performed with $MOPAC_5$ program[2], as implemented locally on a Hp-9000-842 computer at the National key laboratory of our university, using the AM1 hamiltonian[3]. At this level, the geometry optimization was performed. saddle points were located with use of a combination of the SADDLE[4] and NLLSQ[5] algorithms, and confirmed by vibrational frequency analysis.

The optimized structures for the reactant complex, activated complex and product complex for each of the hydrolysis processes of dinitro semi-glycoluril are shown in Figure 1, 1R, 1T and 1P (first row) for the hydrolysis process in neutral medium and 2R, 2T, 2P(second row) in acidic medium; The potential energy curve and optimized geometry of product complex for the hydrolysis of dinitro semi-glycoluril in alkaline medium are shown in Figure 2. Also shown are the lengths (in Å)of the making and breaking bonds and the angles(in degree) between these bonds. Although all internal degrees of freedom were optimized, the values of the remaining geometrical parameters are not listed here for brevity' s sake. Table 1 contains the heats of formation for various species optimized with AM1 method.

Figure 3 shows pauling bond orders[6] for making and breaking bonds of the activated complex, these are calculated from the data of Figure 1, according to:

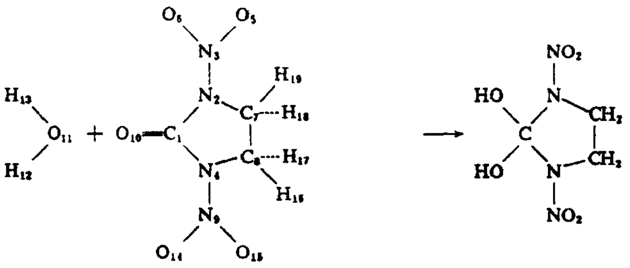
$$B=\exp\{[R(1)-R(B)]/0.3\}$$

where R(B) is the length of a bond of order B and values of R(1) for bonds with orders assumed to be unity, are taken from $O_{11}-H_{12}$ in 1R and from $O_{11}-C_1$, C_1-O_{10}, $O_{10}-H_{12}$ in 1P for 1T; from $O_{18}-H_{19}$ in 2R and from $O_{18}-C_2$, C_2-N_1, N_1-H_{19} in 2P for 2T; Figure 3 also shows net atomic charges from Mulliken population analyses at the AM1 level for the optimized structures 1T and 2T. Figure 4 shows net atomic charges for AM1 optimized neutral and carbonyl oxygen protonated dinitro semi-glycoluril, also include the structure parmeters mentioned in the paper

Discussion

1. Hydrolysis in neutral medium.

Calculation on the neutral moleculer of dinitro semi-glycoluril slows that the net charge in carbonyl carbon atom is as high as 0.41 (see Figure 4), this is because both nitrogen atoms adjacent to this carbon atom are bonded with strongly electron-withdrawing nitro group, obviously, the carbon atom is liable to be attacked by nucleophiles. So the addition of water to carbonyl in dinitro semi-glycoluril may be the key step of the hydrolysis of this compound.



(1)

Recently, we have carried out the AM1 calculations on the hydrolysis of nitrourea[7], and found that the hydrolysis of nitrourea in neutral medium features four-center carbonyl-addition reaction, in this reaction, bonding of nucleophile (H_2O) with carbonyl carbon atom and transfer of one proton of the nucleophile to carbonyl oxygen proceed simultaneously, activated complex formed has cyclic structure, and this indicates a concerted reaction. Ab initial and AM1 studies on the addition of neutral nucleophiles to carbonyls have been reported by I. H. Williams, et al[8-9], they obtained similar results. It is expected that the hydrolysis of dinitro semi-glycoluril occurs according to the mechanism similar to the above-mentioned one due to the similar structure feuture between dinitro semi-glycoluril and nitrourea

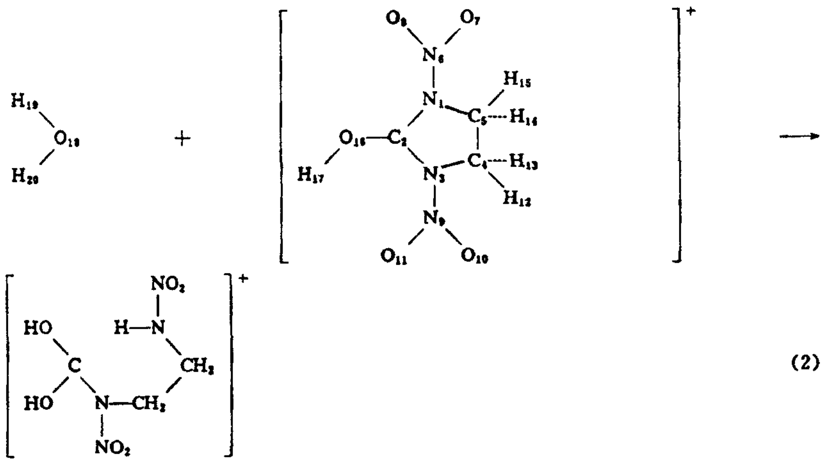
Calculation on reaction show that in the process of this reaction, with the attack of water to the carbonyl carbon atom, the distance $O_{11}-C_1$ decreases, $O_{11}-H_{12}$ increases, $H_{12}-O_{10}$ decreases and $O_{10}-C_1$ increases gradually. When the distance $O_{11}-C_1$ equal to 1.584 Å, the activated complex with four-membered ring (Figure 1, 1T) forms, which has only one negative eigenvalue in force constant matrix and only one imaginary vibration, the activation energy was calculated to be 217.233 kJ/mol. With continuing of the reaction, the distance $O_{11}-C_1$ decreases further, when it is equal to 1.400 Å, the reaction ends to produce the relatively stable intermediate. Obviously, in the whole process of the reaction, from reactant complex to activated complex, to final product complex, with the decrease of the distance $O_{11}-C_1$ from 3.101 Å to 1.

584 Å to final 1. 400 Å, the distance $O_{11}-H_{12}$ from 0. 964 Å to 1. 251 Å to final 2. 115 Å and the distance $O_{10}-H_{12}$ from 2. 228 to 1. 402 Å to 0. ,nj974 Å. In other words, two component processes involved by reaction 1: PT or proton transfer (the transfer of the proton from the nucleophilic reactant to the carbonyl oxygen) and HAR, or heavy-atom reorganization (the formation of carbon-nucleophile bond and the concomitant fission of carbonyl π-bond) are concerted. This is also shown by eigenvectors of the reaction coordinates of the activated complex 1T whose bond-order data (Figure 3) suggest that PT and HAR have occurred to the extent of 24% and 54% respectively.

It is also noted that from reactant complex to activated complex to final product complex, the dihedral angle involving the oxygen of attacking water $O_{11}-C_1-N_2-N_4$ changes from 126° to 117° to 124°, the related angle $O_{11}-C_1-N_2$ from 82° to 115° to finial 119°; the dihedral angle involving the oxygen atom of carbonyl $O_{10}-C_1-N_2-N_4$ changes from −180° to −140° to −120° the related angle $O_{10}-C_1-N_2$ changes from 126° to 117° to 107°. Obviously, the hybrization state of carbonyl carbon atom changes from initial sp^2 in reactant complex to the final sp^3 in product complex.

2. Hydrolysis in acidic media

In acidic medium, protonation of some electron-donating atoms such as oxygen and nitrogen should be considered firstly. Calculation on the protonation of dinitro semi-glycoluril shows that carbonyl oxygen atom other than the other atoms is protonated predominately. So the hydrolysis of dinitro semi-glycoluril in acidic medium is, in fact ,a reaction between water and protonated dinitro semi-glycoluril. The determining step should be the nucleophile attack of water to the protonated carbonyl group, since the protonation of carbonyl is more favorable to such a attack (net charge on the protonated carbonyl carbon is as high as 0. 44, as shown in Figure 4)

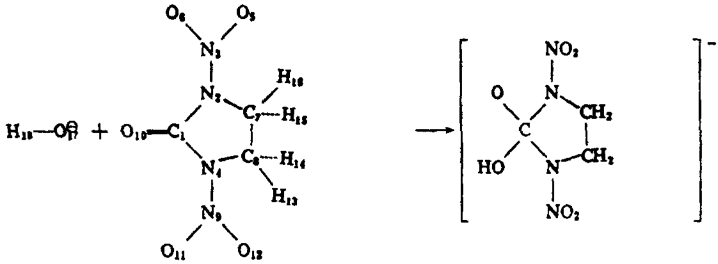


(2)

AM1 calculation on the reaction (2) show that with the attack of water, namely decrease of the distance $O_{18}-C_2$, the distance C_2-N_1 increases, N_1-H_{19} decreases, $H_{19}-O_{18}$ increases. When the distance $O_{18}-C_2$ is equeal to 1.480 Å, activated complex with four-membered ring structure forms, which is confirmed by only one negative eigenvalue in force constant matrix and only one imaginary vibration, the activation energy was calculated to be 218.856 kJ/mol. With the continuing of the reaction, the distance $O_{18}-C_2$ decreases further, when it is equal to 1.336 Å, obtaining relatively stable intermediate. Obviously, during the whole process of the reaction, with the distance $O_{18}-C_2$ decrease progressively from 2.699 Å to 1.480 Å to final 1.336 Å, the distance $O_{18}-H_{19}$ changes from 0.965 Å to 1.352 Å to final 4.581 Å, the distance C_2-N_1 changes from 1.387 Å to 1.533 Å to 3.174 Å, the distance $H_{19}-N_1$ changes from 4.610 Å to 1.359 Å to final 1.016 Å simultaneously. In other wards the three component processes involved: ①the attack of oxygen atom of water to carbonyl carbon atom, ②transfer of one proton of water to the one amine nitrogen connected with nitro group, ③the fisson of the bond between carbonyl carbon atom and nitrogen atom to whom the proton is transferred take plact at the same. Additionly, the bond-order data of the activated complex. as marked in Figure 3, suggest that the above-mentioned three component, have occurred to the extent 62%, 28% and 38%, respectively. It can be concluded from these studies that the hydrolysis of dinitro semi-glycoluril in acidic medium is also a typical concerted reaction.

3. Hydrolysis in alkaline medium

$OH^{\ominus}$ is a well-known strong nucleophile reagent, therefore, the hydrolysis of dinitro semi-glycoluril in alkaline medium is the reaction between $OH^{\ominus}$ and dinitro semi-glycoluril.



(3)

During the calculation on the reaction, it is found that as the attacking reagent $OH^{\ominus}$ approaches to the carbonyl carbon atom, the energy of the reactant complex decreases until the formation of product complex, no transition state forms. The potential curve for the hydrolysis is shown in Figure 2.

The optimized structure for the product complex and dinitro semi-glycoluril are noted in Figure 2 and Figure 4 respectively. It is also noted that, from reactant complex to product complex, the bond length between carbonyl oxygen and its carbon in dinitro semi-glycoluril changes from 1.227 Å to 1.264 Å; the dihedral angle involving the oxygen atom of carbonyl $O_{10}—C_1—N_2—N_4$ changes from —177° to —116°; the related angle $O_{10}—C_1—N_2$ changes from 126° to 113°, remarkablely, the hybrization state of carbonyl carbon atom changes from sp^2 to sp^3.

Conclusion

As expected, the hydrolysis of dinitro semi-glycoluril is similar to that of nitrourea in some cases. But in alkaline medium, the hydrolysis of dinitro semi-glycoluril is quite different from that of nitrourea, in former case, hydrolysis can proceed without the activation of reactant complex, while the activation energy required for the hydrolyses in latter case is calculated to be 245.333 kJ/mol. The hydrolysis of dinitro semi-glycoluril in neutral or acidic media involve activated complexes with four-membered ring structure, and can be regarded as concerted reactiones. The remarkable difference between the hydrolysis in neutral medium and in acidic medium is that one proton of attacking water transfers to carbonyl oxygen atom in neutral medium, while in acidic medium the corresponding proton to one of the two nitrogen atoms bonded with nitro group in dinitro semi-glycoluril.

Acknowledgment

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References

[1] Xiao Heming, Tang Zehua, Chen Li, Deng Ya, Acta Physico Chimica Sinica, (4), 1990

[2] Stewart, J. J. P. MOPAC, A General Molecular Orbital Package (QCPE 455), 5th ed., 1988

[3] Dewar, M. J. S., Zoebisch, E. G., Healy, E. F., Stewart, J. J. P., J. Amer. Chem. Soc., 1985(107), 3902—3909

[4] Dewar, M. J. S.; Healy, E. F,; stewart, J. J. P., J. Chem. Soc., Faraday Trans. 2, 1984, 80, 227.

[5] P. K. Weiner, ph. D. Dissertation, The University of Texas at Austin, Austin, Texas, 1975

[6] Sim, L. B.; Lewis, D. E., In Isotopes in Organic Chemistry; Bun-

cel, E. , lee, C. C. , Eds. ; Elsevier: Amsterdem, 1984; vol. 6.

[7] Li Yuming, Xiao Heming, manuscript in prepation.

[8] Ian H. Williams, Dale Spangler, Gerald M. Maggiora, and Richard L, Schowen, J. Am. Chem. Soc, 1985, 107, 7717—7723

[9] Ian H, Williams, J. Am. Chem. Soc. 1987, 109, 6299—6307

Table 1. Heat of formation (HF) for AM1 optimized structure(kJ/mol)

species HF reaction	reactant complex	activated complex	product complex
1	−71.647	−145.586	81.111
2	659.248	878.104	600.827
2593960			

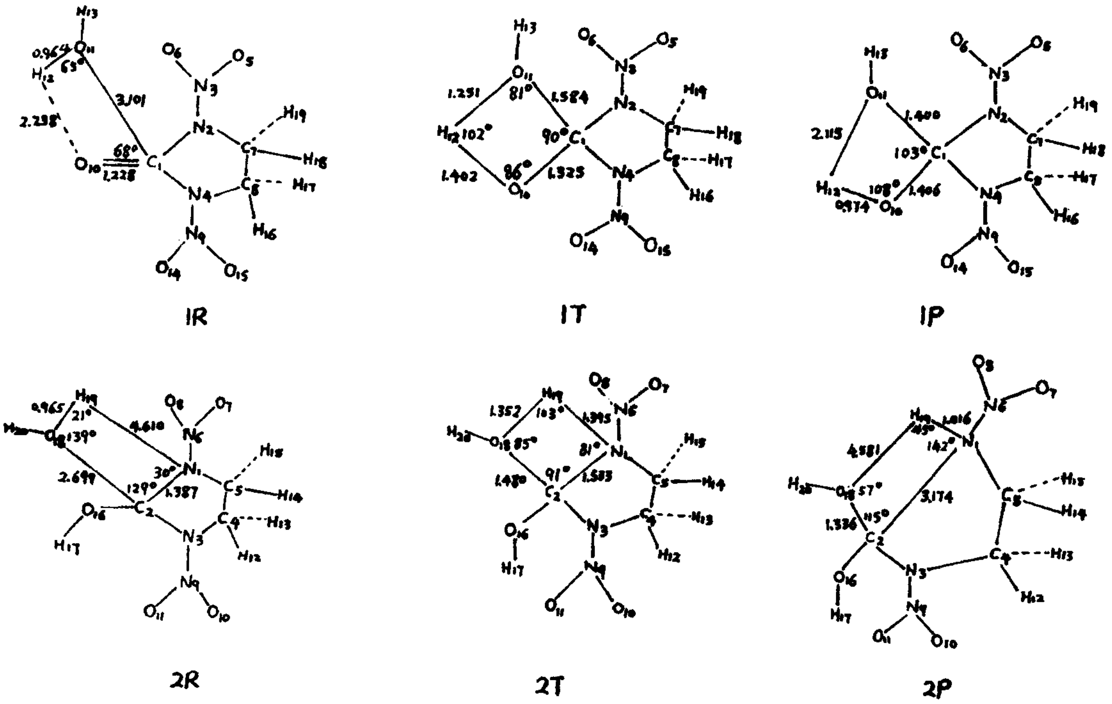


Figure 1. AM1 optimized geometries for reagent, activated and product complex for hydrolysis in neutral and acidic media

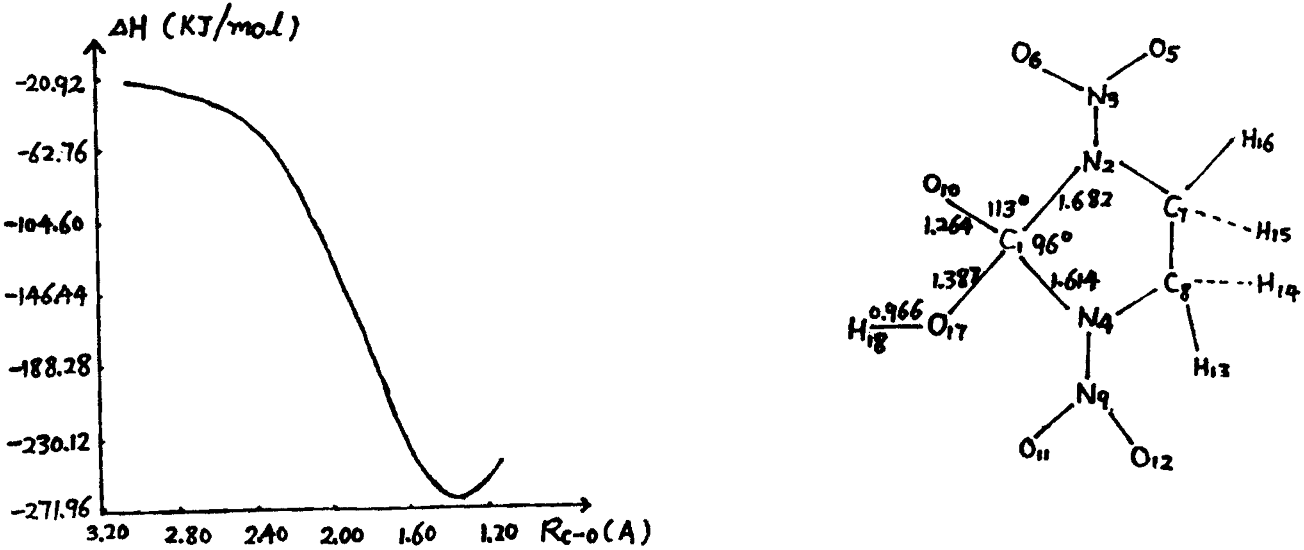
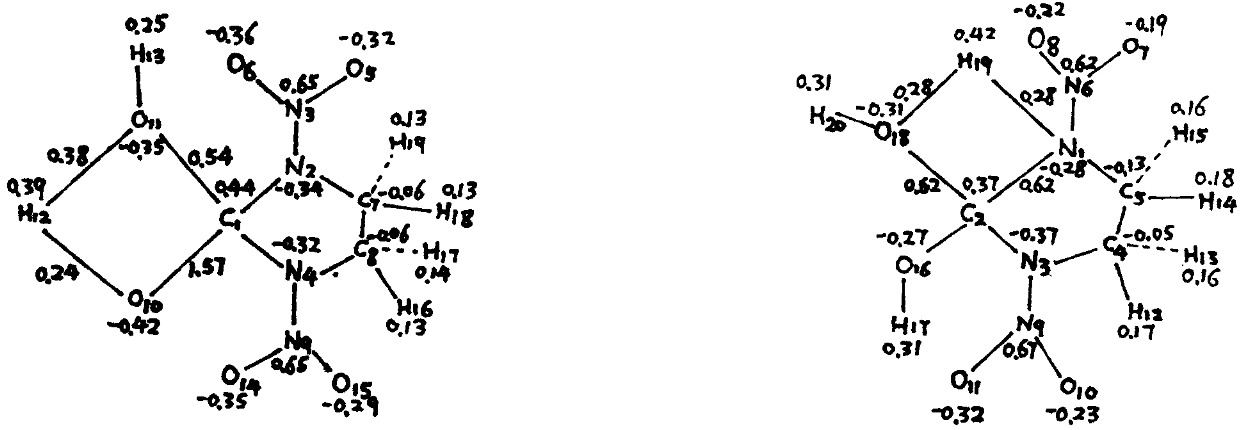


Figure 2. Potential energy curve and optimized geometry of product complex for hydrolysis in alkaline medium



1T

2T

Figure 3. Pauling bond orders (inside ring) for mainly changed bonds and net atomic charges for AM1 optimized activated complex 1T and 2T

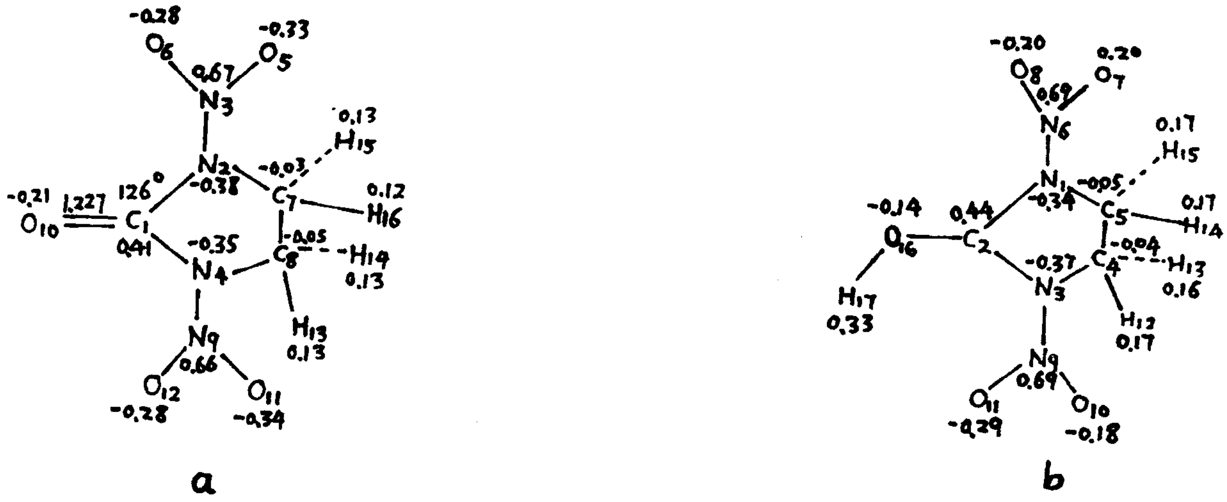


Figure 4. Net atomic charges for AM1 optimized neutral dinitro semi-glycoluril(a) and protonated dinitro semi-glycoluril(b)