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Mononitro-monoperchlorylbenzenes - A DFT Treatment

Lemi Türker

Department of Chemistry, Middle East Technical University, Üniversiteler, Eskişehir Yolu No: 1, 06800 Çankaya/Ankara, Turkey; e-mail: lturker@gmail.com; lturker@metu.edu.tr

Abstract

Perchloryl derivatives, especially aromatic ones have some explosive character and decompose explosively when they are initiated. In the present study, *ortho*, *meta* and *para* nitro isomers of perchlorylbenzene have been considered within the framework of density functional theory at the level of B3LYP/6-311++G(d,p). The results have indicated that they are electronically stable such that the *para* isomer is more stable than the others whereas the ortho isomer is the least stable of all. Various quantum chemical properties of these isomers are harvested and discussed. The calculated UV-VIS spectra of the isomers have been obtained and the impact sensitivity order is estimated as *meta* < *para* < *ortho*. Also nucleus independent chemical shifts values for the isomers are calculated which yield the aromaticity order of *ortho* > *meta* > *para*.

1. Introduction

Since perchlorates or perchloryl derivatives have some explosive character, for many years the wide use of perchloric acid in organic synthesis has been hindered by greatly exaggerated ideas. Although, work with the anhydrous acid is in fact not without danger, the use of an aqueous solution (30, 60, and 72%) involves practically no risk of explosion. Also, solutions of the anhydrous acid in acetic acid or acetic anhydride containing less than 55% of $HC1O_4$ by volume (which are frequently used) are also quite safe [1].

The introduction of the $C1O_3$ group into organic compounds by the action of perchloric acid on aromatic compounds is not possible. Perchlorylation of organic

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compounds directly was not developed until 1958 [2,3]. However, perchloryl compounds of the aromatic series are easily formed by the action of $FC1O_3$ (in the presence of $AlCl_3$ or $AlBr_3$) on benzene and other aromatic hydrocarbons containing no electron-acceptor groups. Investigations on the spectra [2] and chemical properties of the perchloryl compounds confirm that they have the $ArClO_3$ and not the ester structure $ArOClO_2$ [2-4]. The synthesis and oxidation of certain perchlorylbenzenes were achieved by Gardner and coworkers [5]. Perchlorylation of benzene and synthesis of perchlorylbenzene-d_5 have been achieved by Lunelli [6].

The perchlorylarenes are generally stable liquids or solid compounds, some of them can be distilled without decomposition. They are entirely stable in neutral and acid media, but in concentrated alkali solutions they are hydrolyzed to phenols. The perchloryl compounds decompose explosively when they are initiated by a sharp blow or when the temperature is raised [7,8]. The action of nucleophilic reagents on perchloryl compounds has been studied [3].

Perchloric acid and its derivatives may be used in the halogenation [9-12], nitration [13,14], nitrosation [15,16], and diazotization [17] of organic compounds. Polarity and polarizability of certain perchloryl compounds were determined [18]. Perchlorobenzenes, like other similar compounds have greater energies then the corresponding nitro compounds because the central chlorine atom within the perchloryl group possesses greater energy then do the corresponding nitro groups[8]. This greater energy provides overall superior explosive power along with significant energy output. Some nitro perchloryl compounds were synthesized by nitrating the suitable perchloryl compounds and are used as explosives, such as 3-nitroperchlorylbenzene [8]. It is another interesting substance having explosive properties suitable for use in a variety of applications including high explosives, gun propellants and high energy-fuel additive for solid rocket fuels [8]. Perchlorylamino furazans and their salts were available and constitute new high-energy-density materials with high sensitivity [19].

In the present treatment *ortho*, *meta* and *para* nitro isomers of perchlorylbenzene have been considered within the framework of density functional theory (DFT). Although the *meta* isomer has been synthesized [2,5], up to the best knowledge of the author the other isomers have not been synthesized yet. Also any quantum chemical calculations on them have not appeared in the literature.

2. Method of Calculation

The geometry optimizations of all the present structures leading to energy minima have been achieved initially by using molecular mechanics (MM2) method followed by semi-empirical PM3 self consistent fields molecular orbital (SCF MO) method [20,21] at the restricted level [22,23]. Subsequent optimizations were achieved at Hartree-Fock level employing various basis sets successfully. Then, geometry optimizations were managed within the framework of density functional theory [24,25] at the level of B3LYP/6-311++G(d,p) [22,26]. The exchange term of B3LYP consists of hybrid Hartree-Fock and local spin density (LSD) exchange functions with Becke's gradient correlation to LSD exchange [25,27]. Note that the correlation term of B3LYP consists of the Vosko, Wilk, Nusair (VWN3) local correlation functional [28] and Lee, Yang, Parr (LYP) correlation correction functional [29]. Also, vibrational analyses have been done on the optimized structures. The total electronic energies are corrected for the zero point vibrational energy (ZPE). The normal mode analysis for each structure yielded no imaginary frequencies for the $3N–6$ vibrational degrees of freedom, where N stands for the number of atoms in the system. Consequently, this has indicated that the structure of each molecule corresponds to at least a local minimum on the potential energy surface. All these calculations have been done by using the Spartan 06 package program [30]. Whereas the NICS calculations were performed by using Gaussian 03 program [31].

3. Results and Discussion

Nitro and perchloryl groups are both inductively and mesomerically electron withdrawing in character. Measurement of the dipole moment of $FC1O_3$ has shown that, although the molecule is electrically neutral, the $C1O_3$ group is the electropositive end of a dipole and the fluorine atom is the electronegative end [32]. However, perchlorylbenzene is nitrated in the *meta*-position and its nitro-compound can be reduced to the amine [2]. Thus, ClO_3 group is a *meta*-directing group like NO_2. Hence, the NO_2 and ClO_3 substituents on benzene molecule will exert similar types of effects, at different extents, but might be opposing depending on their positions.

Figure 1 shows the top and side views of the isomers considered as well as the direction of their dipole moment vectors. The direction of the vectors in the figure demonstrate the effects of the substituents, such that the positive end of the vectors originate from the phenylene ring in the *ortho* and *meta* cases due to strong electron attracting powers of the substituents. In the *para* case, the positive end lies on the NO_2

group indicating that perchloryl moiety is stronger electron withdrawing effect as compared to nitro substituent. It is worth noting that in the *ortho* case the nitro group is not coplanar with the ring probably arising from electronic repulsion between the oxygen atoms of the substituents.

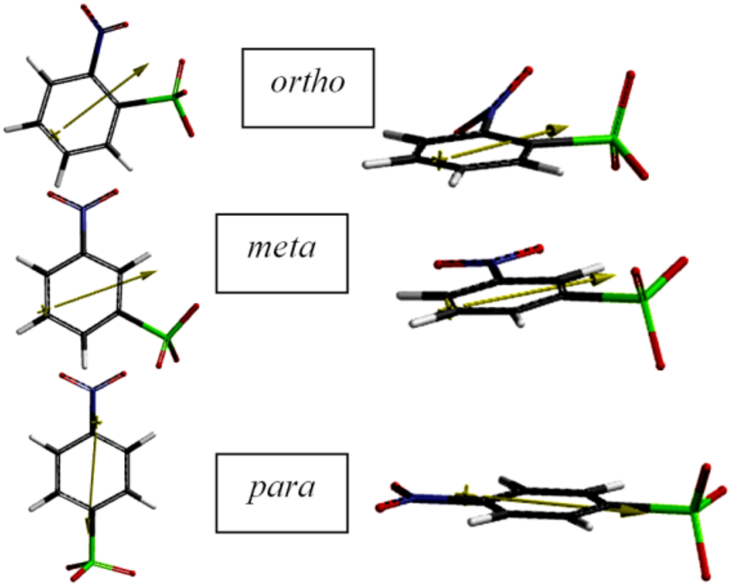

Figure 1. Top and side views of the isomers considered.

Figure 2 displays the calculated bond lengths of the isomers considered. In the *ortho*

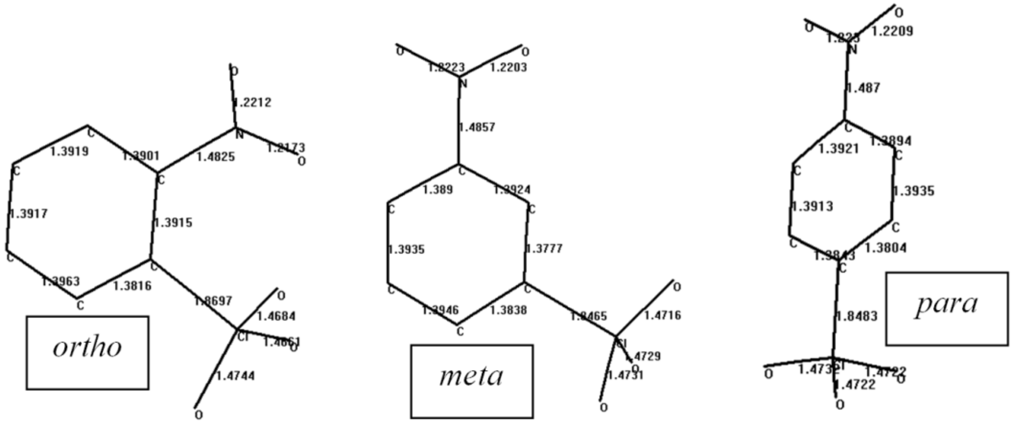

Figure 2. Calculated bond lengths of the isomers considered.

isomer, bond lengths of the ring are almost constant (about 1.39 Å) which indicates that the ring is highly aromatic (see NICS section below). In the cases of the *meta* and *para* isomers, some slight bond length variations occurs. The C-NO_2 bond lengths are about 1.48 Å in all the isomers considered. As for the C-ClO_3 bond lengths, they are 1.869, 1.846 and 1.848 Å, respectively for the o-, m- and p-isomers. The Cl-O bond lengths are about 1.47 Å in all the three isomers.

Figure 3 shows numbering of atoms (which are key to Tables 1-3) in the isomers considered.

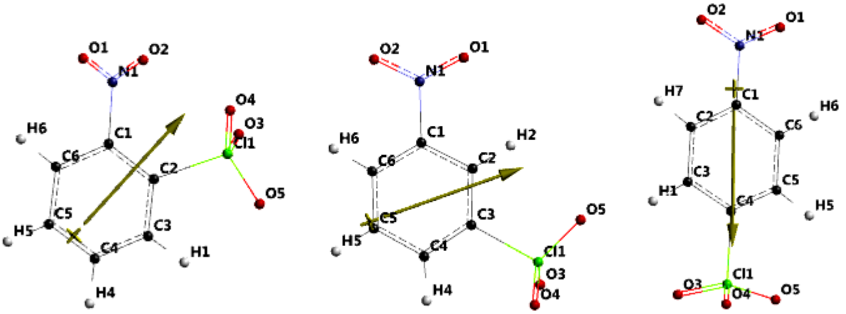

Figure 3. Numbering of atoms in the isomers considered.

Tables 1-3 show the Mulliken and Lowdin bond orders and bond lengths as well as the types of the bonds (as single, double or conjugated) for the isomers considered. They indicate some long-range hydrogen bondings (not shown in the tables) between some carbon atoms. Lowdin approach also predicts long oxygen-oxygen single bond between the nitro oxygen atoms in all the cases. On the other hand, both approaches predict single C-Cl bonding having bond order of ca. 0.650- 790. As for the Cl-O bonds, the Mulliken approach predicts two of them to be double, the other one delocalized in the ortho isomer. Whereas for the other isomers Cl-O bonds are predicted to be delocalized. In contrast to the Mulliken treatment Lowdin predicts all Cl-O bonds as double in all the cases.

Table 1. Mulliken and Lowdin bond orders and bond lengths for the *ortho* isomer.

	Mulliken		**Lowdin**	
Bond	Order	Length	Order	Length
C1 C2	1.45	1.3914 [deloc]	1.352	1.3914 [deloc]
C1 C6	1.377	1.3903 [deloc]	1.398	1.3903 [deloc]
C1 N1	0.477	1.4831 [single]	0.956	1.4831 [single]
C4 C5	1.581	1.3912 [deloc]	1.473	1.3912 [deloc]
C4 C3	1.401	1.3958 [deloc]	1.438	1.3958 [deloc]
C4 H4	0.933	1.0831 [sing-H]	0.874	1.0831 [sing-H]
C2 C3	1.416	1.3810 [deloc]	1.452	1.3810 [deloc]
C2 Cl	0.690	1.8695 [single]	0.751	1.8695 [single]
C6 C5	1.525	1.3919 [deloc]	1.455	1.3919 [deloc]
C6 H6	0.897	1.0824 [sing-H]	0.849	1.0824 [sing-H]
C5 H5	0.944	1.0831 [sing-H]	0.079	1.0831 [sing-H]
C3 H1	0.902	1.0821 [sing-H]	0.844	1.0821 [sing-H]
N1 O1	1.9	1.2208 [double]	2.006	1.2208 [double]
N1 O2	1.952	1.2169 [double]	2.022	1.2169 [double]
Cl O3	1.706	1.4657 [double]	1.802	1.4657 [double]
Cl O4	1.719	1.4687 [double]	1.778	1.4687 [double]
Cl O5	1.587	1.4746 [deloc]	1.748	1.4746 [double]

For numbering of atoms see Figure 3.

Table 2. Mulliken and Lowdin bond orders and bond lengths for the *meta* isomer.

	Mulliken		**Lowdin**	
Bond	Order	Lengths	Order	Lengths
C1 C2	1.598	1.3920 [deloc]	1.373	1.3920 [deloc]
C1 C6	1.443	1.3900 [deloc]	1.397	1.3900 [deloc]
C1 N1	0.524	1.4859 [single]	0.968	1.4859 [single]
C4 C5	1.493	1.3942 [deloc]	1.456	1.3942 [deloc]
C4 C3	1.216	1.3841 [single]	1.421	1.3841 [deloc]
C4 H4	0.922	1.0827 [sing-H]	0.968	1.0827 [sing-H]
C2 C3	1.356	1.3777 [deloc]	1.456	1.3777 [deloc]
C2 H2	0.889	1.0815 [sing-H]	1.421	1.0815 [sing-H]
C6 C5	1.561	1.3936 [deloc]	0.968	1.3936 [deloc]
C6 H6	0.913	1.0812 [sing-H]	1.456	1.0812 [sing-H]
C5 H5	0.891	1.0827 [sing-H]	0.872	1.0827 [sing-H]
C3 Cl	0.641	1.8460 [single]	0.78	1.8460 [single
N1 O1	1.912	1.2209 [double]	2.008	1.2209 [double]
N1 O2	1.879	1.2220 [double]	2.003	1.2220 [double]
Cl O3	1.689	1.4729 [deloc]	1.779	1.4729 [double]
Cl O4	1.600	1.4730 [deloc]	1.769	1.4730 [double]
Cl O5	1.609	1.4716 [deloc]	1.771	1.4716 [double]

For numbering of atoms see Figure 3.

Table 3. Mulliken and Lowdin bond orders and bond lengths for the *para* isomer.

	Mulliken		Lowdin	
Bond	Order	Lengths	Order	Length
C1 C2	1.782	1.3895 [double]	1.401	1.3895 [deloc]
C1 C6	1.726	1.3924 [double]	1.384	1.3924 [deloc]
C1 N1	0.616	1.4871 [single]	0.969	1.4871 [single]
C4 C5	1.363	1.3839 [deloc]	1.422	1.3839 [deloc]
C4 C3	1.449	1.3805 [deloc]	1.442	1.3805 [deloc]
C4 Cl	0.710	1.8479 [single]	0.780	1.8479 [single]
C2 C3	1.256	1.3940 [deloc]	1.44	1.3940 [deloc]
C2 H7	0.882	1.0812 [sing-H]	0.849	1.0812 [sing-H]
C6 C5	1.261	1.3908 [deloc]	1.46	1.3908 [deloc]
C6 H6	0.877	1.0812 [sing-H]	0.849	1.0812 [sing-H]
C5 H5	0.875	1.0824 [sing-H]	0.854	1.0824 [sing-H]
C3 H1	0.879	1.0817 [sing-H]	0.848	1.0817 [sing-H]
N1 O1	1.887	1.2218 [double]	2.005	1.2218 [double]
N1 O2	1.897	1.2218 [double]	2.005	1.2218 [double]
Cl O3	1.619	1.4726 [deloc]	1.766	1.4726 [double]
Cl O4	1.655	1.4726 [deloc]	1.778	1.4726 [double]
Cl O5	1.622	1.4725 [deloc]	1.775	1.4725 [double]

For numbering of atoms see Figure 3.

Figure 4 shows electrostatic potential (ESP) charges on the atoms of the isomers considered. Note that the ESP charges are obtained by the program based on a numerical method that generates charges that reproduce the electrostatic potential field from the entire wavefunction [30]. In the figure note that the carbon atoms having the substituents possess negative partial charges in the *ortho* and *para* cases in contrast to the *meta* isomer.

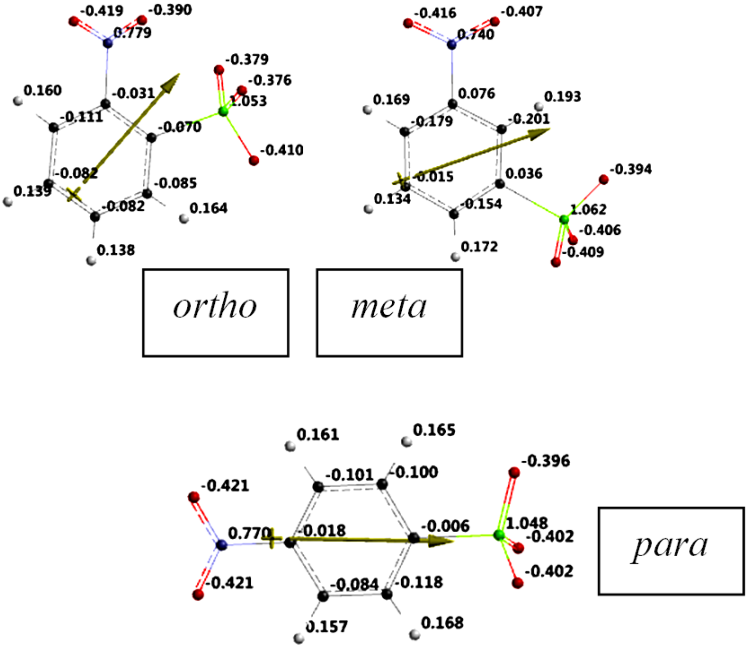

Figure 4. The ESP charges on the atoms of the isomers considered.

Figure 5 depicts the electrostatic potential maps of the isomers where the blue regions

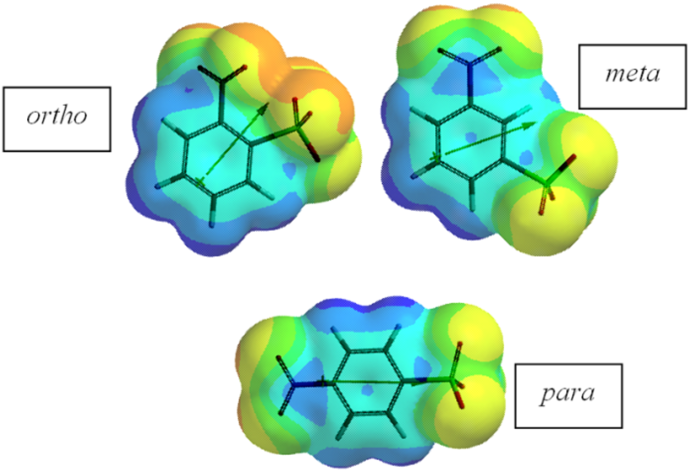

Figure 5. The ESP maps of the isomers considered.

relatively stand for the most positive potential field and red ones, if exists any, the most negative ones. As seen in the figure, in all the cases, positive potential region overlaps with the peripheral hydrogen atoms and less intensely with the aromatic kernel. The oxygen atoms of the substituents engender certain negative potential regions at different extents.

Figure 6 shows the local ionization maps of the isomers considered. In the local ionization potential map conventionally red regions (if any exists) on the density surface indicate areas from which electron removal is relatively easy, meaning that they are subject to electrophilic attack. In the present case, the presence of two electron attracting groups make the systems of interest rather electron poor.

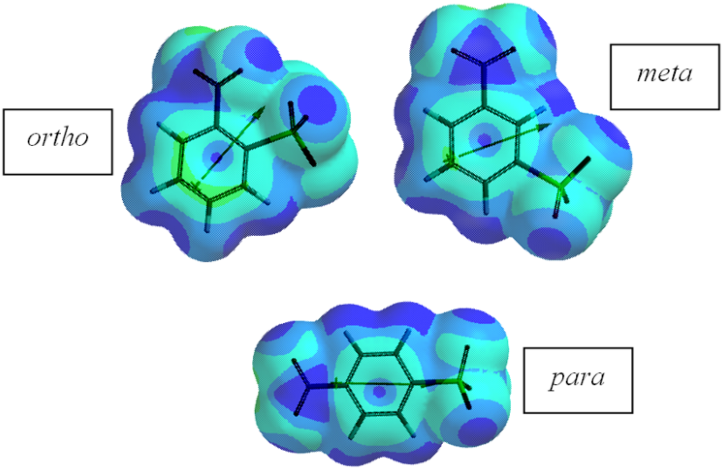

Figure 6. Local ionization maps of the isomers considered.

Figure 7 stands for the LUMO maps of the isomers considered. A LUMO map

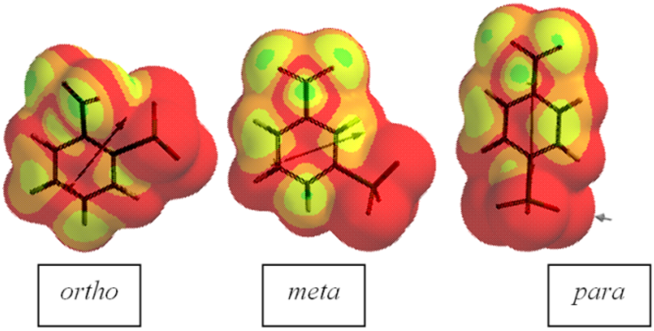

Figure 7. The LUMO maps of the isomers considered.

displays the absolute value of the LUMO on the electron density surface. The blue color stands for the maximum value of the LUMO and the color red, the minimum value.

Table 4 tabulates the dipole moment components as well as the resultant values of the moments for the isomers considered. The order of dipole moments is *ortho*> *meta*> *para.* Since dipole moment is a vectorial quantity, in the case of the *para* isomer two similar type substituents present exert electron attracting effects opposingly to diminish the dipole moment as compared to the other isomers. The polarizability values for the isomers are 52.96, 52.92 and 52.93 (units of 10^{-30} m^3), respectively.

Table 4. Dipole moment components and the resultant moment values for the isomers considered.

Isomer	X	Y	Z	Resultant
Ortho	-0.899003	5.836954	4.881098	7.661812
Meta	-0.954238	4.410895	2.258982	5.046738
Para	0.016246	0.917010	-0.629465	1.112383

In debye units.

Table 5 displays some energies of the isomeric structures considered where E, ZPE and E_C stand for the total electronic energy, zero point vibrational energy and the corrected total electronic energy, respectively. The data indicate that electronically the *para* isomer is more stable than the others whereas the ortho isomer is the least stable of all.

Table 5. Some energies of the isomers considered.

Isomer	E	ZPE	E_C
ortho	-2945411.14	273.30	-2945137.84
meta	-2945455.06	272.88	-2945182.18
para	-2945455.97	272.81	-2945183.16

Energies in kJ/mol.

Figure 8 displays some of the molecular orbital energies of the isomers considered. The *ortho* isomer is characterized with comparatively higher HOMO and LUMO energy levels than the respective energy levels of the other isomers (see Table 6).

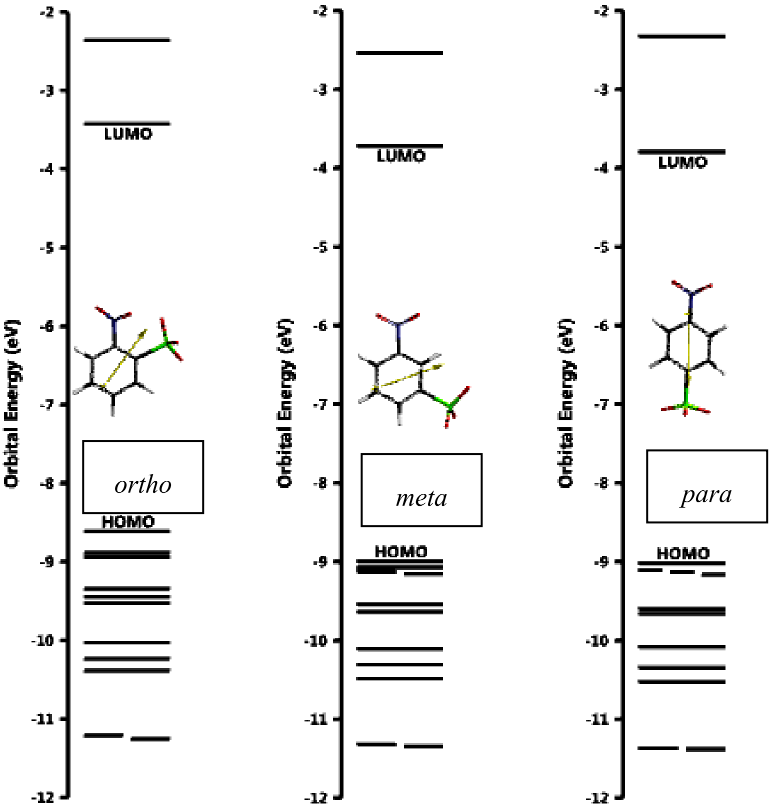

Figure 8. Some of the molecular orbital energies of the isomers considered.

Table 6 lists the HOMO, LUMO energies and Δε (Δε = ε_{LUMO} - ε_{HOMO}) values (interfrontier molecular orbital energy gap) of the structures presently considered. The HOMO and LUMO energy levels follow the same order of *para* < *meta* < *ortho*. Note that both of the present substituents are electron attracting type inductively and mesomerically. However, due to the size mismatch between the orbitals of carbon and chlorine atoms, the conjugative effect of ClO_3 group should be highly diminished as compared to the nitro group. Also note that both of the Mulliken and Lowdin bond orders predict the C-ClO_3 bonds to be single. An additional factor should be worth mentioning that is in the case of the *meta* isomer these substituents are crossly conjugated, thus they do not interact conjugatively with each other. All these effects collectively dictate the physical, chemical and quantum chemical properties of these isomers. The Δε values follow the order of *ortho* < *para* < *meta*. Thus, in terms of impact sensitivity, a reverse order is to be expected, because there exists a reverse correlation between the impact sensitivity and Δε values [33,34].

Table 6. The HOMO, LUMO energies and Δε values of the isomers considered.

Isomer	HOMO	LUMO	Δε
Ortho	-830.95	-330.31	500.64
Meta	-868.20	-358.95	509.25
Para	-870.29	-366.39	503.90

Energies in kJ/mol.

Figure 9 shows the calculated UV-VIS time-dependent density functional (TDDFT) spectra of the isomers considered. The appearance of the spectra implies the existence of better extended conjugation in the *ortho* case as compared to the others.

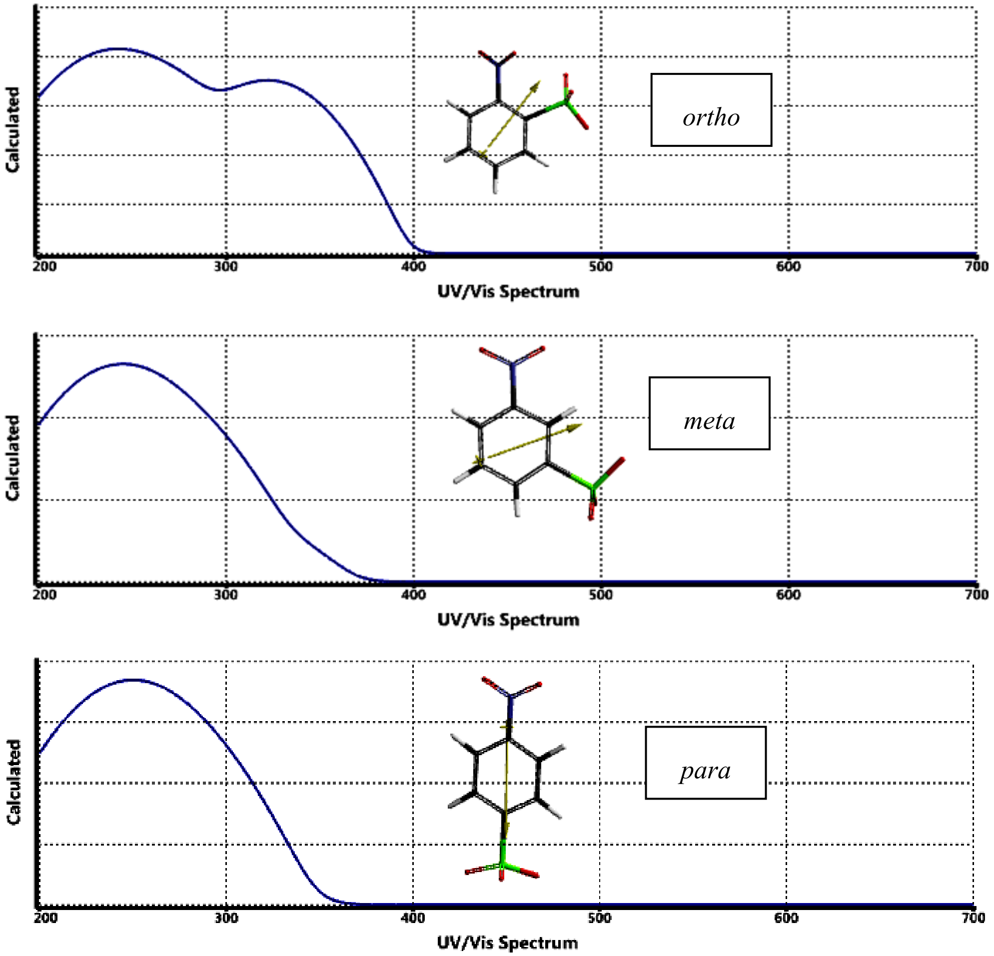

Figure 9. Calculated UV-VIS (TDDFT) spectra of the isomers considered.

Figure 10 depicts the HOMO and LUMO patters of the species considered. As seen in the figure, the nitro group greatly contributes to the HOMO and LUMO in the *ortho* isomer whereas the contribution from the perchloryl group is rather low. In the case of the *meta* isomer contribution of the nitro group in to the HOMO is lesser than the perchloryl group but the perchloryl moiety contributes nil in to the LUMO. The HOMO of the *para* isomer has low contributions from both of the substituents whereas in to the LUMO the predominant contribution comes from the nitro group.

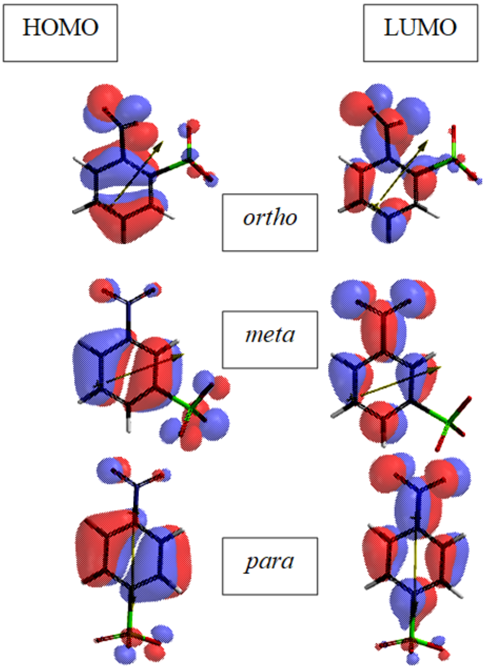

Figure 10. The HOMO and LUMO patterns of the isomers considered.

NICS

In the literature, generally aromaticity has been discussed in terms of energetic, structural and magnetic criteria [35-40]. A simple but efficient probe has been introduced for aromaticity that is "nucleus-independent chemical shift" (NICS) [41]. It is the computed value of the negative magnetic shielding at some selected point in space (generally, at a ring or cage center). Through the years the calculated data piled in the literature which indicate that negative NICS values denote aromaticity (-11.5 for benzene, -11.4 for naphthalene) whereas positive NICS values denote antiaromaticity (28.8 for cyclobutadiene) while small NICS values indicate non-aromaticity (-2.1 for cyclohexane, -1.1 for adamantine). NICS has been proved to be an effective probe for local aromaticity of individual rings of polycyclic systems although couple of contradictory results exist [41].

Table 7 shows the NICS(0) values of the isomers considered. The aromaticity order of these isomers is *ortho* > *meta* > *para*. Since, for the existence and strengths of aromaticity ring current is an essential factor, the above order implies that in the ortho isomer more pronounced ring current prevails than the others and a less effective one exists in the *para* isomer. These are the outcome of overall perturbation effects of the substituents arising from their positions and electronic effects.

Table 7. NICS(0) values of the isomers considered.

Structures		
ortho	*meta*	*para*
-12.1694	-11.7754	-11.5376

4. Conclusion

The present density functional treatment, within the restrictions of the theory and the basis set employed, has indicated that the positional variations of the substituents in nitro perchlorylbenzenes result electronically stable isomers in all the cases. The *para* and *ortho* isomers are the most and the least stable ones, respectively. The impact sensitivity order is estimated as *meta* < *para* < *ortho*. As compared to the *ortho* isomer, perchloryl group at the *meta* or *para* position lowers both the HOMO and LUMO energy levels while the interfrontier molecular orbital energy gaps somewhat expands.

References

[1] Burton, H., & Praill, P.F.G. (1955). Perchloric acid and some organic perchlorates. *Analyst*, *80*, 4-15. https://doi.org/10.1039/AN9558000004

[2] Inman, C.B., Oesterling, R.E., & Tyszkowsky, E.A. (1958). Reactions of perchloryl fluoride with organic compounds. I. Perchlorylation of aromatic compounds. *J. Amer. Chem. Soc.*, *80*(19), 5286-5288. https://doi.org/10.1021/ja01552a069

[3] Scott, F.L., & Oesterling, R.E. (1960). Production of benzyne intermediates from perchloryl aromatic compounds. *J. Amer. Chem. Soc.*, *82*(19), 5247-5249. https://doi.org/10.1021/ja01504a061

[4] Scott, F.L., & Oesterling, R.E. (1960). Communication-Hydrogenolysis of perchloryl aromatic compounds. *J. Org. Chem.*, *25*(9), 1688-1689. https://doi.org/10.1021/jo01079a620

[5 Gardner, D.M., Oesterling, R.E., & Scott. F.L. (1963). The synthesis and oxidation of certain perchlorylbenzenes. *J. Org. Chem.*, *28*(10), 2650-2652. https://doi.org/10.1021/jo01045a040

[6] Lunelli, B. (1976). Perchlorylation of benzene and synthesis of perchlorylbenzene-d_5. *Ind. Eng. Chem. Prod. Res. Dev.*, *15*(4), 278-282. https://doi.org/10.1021/i360060a011

[7] Krivun, G.N.S.V., Dulenko, V.I., & Zhdanov, Yu.A. (1965). Perchloric acid and its compounds in organic synthesis. 34(2) *Russian Chemical Reviews*, *34*(2) 88-104. https://doi.org/10.1070/RC1965v034n02ABEH001416

[8] Ledgard, J. (2007). *The preparatory manual of explosives* (3rd ed.). Jared Ledgard.

[9] Mihre, P.C. (1960). Influence of steric hindrance on the isotope effect in aromatic substitution. *Acta Chem. Scand.*, *14*, 219- 221. https://doi.org/10.3891/acta.chem.scand.14-0219

[10] de la Mare, P.B.D., & Maxwell, J.L. (1962). The kinetics and mechanisms of aromatic halogen substitution. Part XV. Reagents involved in bromination by hypobromous acid in aqueous acetic acid. *Chem. and Ind.*, *553*, 4829-4835. https://doi.org/10.1039/JR9620004829

[11] de la Mare, P.B.D., & Hilton, I.C. (1962). The kinetics and mechanisms of aromatic halogen substitution. Part XIII. Bromination by hypobromous acid in concentrated mineral acids. *J. Chem. Soc.*, 997-1005. https://doi.org/10.1039/JR9620000997

[12] Fischer, A., Packer, J., & Vaughan, J. (1962). The acid-catalyzed bromination of substituted benzyl phenyl ketones. *J. Chem. Soc.*, 3318-3321. https://doi.org/10.1039/JR9620003318

[13] Kuhn, S.J., & Olah, G.J. (1961). Aromatic substitution. VII.1 Friedel-Crafts type nitration of aromatics. *J. Amer. Chem. Soc.*, *83*(22), 4564-4571. https://doi.org/10.1021/ja01483a016

[14] Olah, G.A., & Kuhn, S.J. (1962). Aromatic substitution XII. Steric effects in nitronium salt nitrations of alkylbenzenes and halobenzenes. *J. Amer. Chem. Soc.*, *84*(19), 3684-3687. https://doi.org/10.1021/ja00878a018

[15] Morrison , D.A., & Turney, T.A. (1960). The nitrosation of phenol in aqueous perchloric acid. *J. Chem. Soc.*, 4827-4828. https://doi.org/10.1039/JR9600004827

[16] Challis, B.C., & Ridd, J.H. (1962). Nitrosation, diazotization, and deamination. Part XI.

The acid-catalyzed diazotization of the anilinium and related ions in aqueous perchloric acid (up to 3·0M). *J. Chem. Soc.*, 5208-5217. https://doi.org/10.1039/JR9620005208

[17] Larkworthy, L.F. (1959). Nitrosation, diazotization, and deamination. Part VII. The reactivities of some aromatic amines towards dinitrogen trioxide. *J. Chem. Soc.*, 3116-3122. https://doi.org/10.1039/JR9590003116

[18] Vereshchagin, A.N., Vigalok, I.V., Aleksandrova, L.K., & Petrova, G.G. (1981). Polarity and polarizability of certain perchloryl compounds. *Russian Chemical Bulletin*, *30*(2) 190-193. https://doi.org/10.1007/BF00953561

[19] Sheremetev, A.B. (2020). Perchlorylamino furazans and their salts: new high-energy-density materials with high sensitivity. *Mendeleev Communications*, *30*(4), 490-493. https://doi.org/10.1016/j.mencom.2020.07.028

[20] Stewart, J.J.P. (1989). Optimization of parameters for semi empirical methods I. Method. *J. Comput. Chem*., *10*, 209-220. https://doi.org/10.1002/jcc.540100208

[21] Stewart, J.J.P. (1989). Optimization of parameters for semi empirical methods II. Application. *J. Comput. Chem*., *10*, 221-264. https://doi.org/10.1002/jcc.540100209

[22] Leach, A.R. (1997). *Molecular modeling*. Essex: Longman.

[23] Fletcher, P. (1990). *Practical methods of optimization*. New York: Wiley.

[24] Kohn, W., & Sham, L. (1965). Self-consistent equations including exchange and correlation effects. *J. Phys. Rev.*, *140*, A1133-A1138. https://doi.org/10.1103/PhysRev.140.A1133

[25] Parr R.G., & Yang, W. (1989). *Density functional theory of atoms and molecules*. London: Oxford University Press.

[26] Cramer, C.J. (2004). *Essentials of computational chemistry*. Chichester, West Sussex: Wiley.

[27] Becke, A.D. (1988). Density-functional exchange-energy approximation with correct asymptotic behavior. *Phys. Rev. A*, *38*, 3098-3100. https://doi.org/10.1103/PhysRevA.38.3098

[28] Vosko, S.H., Wilk, L., & Nusair, M. (1980). Accurate spin-dependent electron liquid correlation energies for local spin density calculations: a critical analysis. *Can. J. Phys.*, *58*, 1200-1211. https://doi.org/10.1139/p80-159

[29] Lee, C., Yang, W., & Parr, R.G. (1988). Development of the Colle-Salvetti correlation energy formula into a functional of the electron density. *Phys. Rev. B*, *37*, 785-789. https://doi.org/10.1103/PhysRevB.37.785

[30] SPARTAN 06 (2006). Wavefunction Inc., Irvine CA, USA.

[31] Gaussian 03, Frisch, M.J., Trucks, G.W., Schlegel, H.B., Scuseria, G.E., Robb, M.A., Cheeseman, J.R., Montgomery, Jr., J.A., Vreven, T., Kudin, K.N., Burant, J.C., Millam, J.M., Iyengar, S.S., Tomasi, J., Barone, V., Mennucci, B., Cossi, M., Scalmani, G., Rega, N., Petersson, G.A., Nakatsuji, H., Hada, M., Ehara, M., Toyota, K., Fukuda, R., Hasegawa, J., Ishida, M., Nakajima, T., Honda, Y., Kitao, O., Nakai, H., Klene, M., Li, X., Knox, J.E., Hratchian, H.P., Cross, J.B., Bakken, V., Adamo, C., Jaramillo, J., Gomperts, R., Stratmann, R.E., Yazyev, O., Austin, A.J., Cammi, R., Pomelli, C., Ochterski, J.W., Ayala, P.Y., Morokuma, K., Voth, G.A., Salvador, P., Dannenberg, J. J., Zakrzewski, V.G., Dapprich, S., Daniels, A.D., Strain, M.C., Farkas, O., Malick, D. K., Rabuck, A.D., Raghavachari, K., Foresman, J.B., Ortiz, J.V., Cui, Q., Baboul, A.G., Clifford, S., Cioslowski, J., Stefanov, B.B., Liu, G., Liashenko, A., Piskorz, P., Komaromi, I., Martin, R.L., Fox, D.J., Keith, T., Al-Laham, M.A., Peng, C.Y., Nanayakkara, A., Challacombe, M., Gill, P.M.W., Johnson, B., Chen, W., Wong, M. W., Gonzalez, C., and Pople, J.A., Gaussian, Inc., Wallingford CT, 2004.

[32] Dorofeenko, G.N., Krivun, S.V., Dulenko, V.I., & Zhdanov, Yu.A. (1965). Perchloric acid and its compounds in organic synthesis. *Russian Chemical Reviews*, *34*(2), 88-104. http://dx.doi.org/10.1070/RC1965v034n02ABEH001416

[33] Anbu, V., Vijayalakshmi, K.A., Karunathan, R., Stephen, A.D., & Nidhin, P.V. (2019). Explosives properties of high energetic trinitrophenyl nitramide molecules: A DFT and IM analysis. *Arabian Journal of Chemistry*, *12*(5), 621-632. https://doi.org/10.1016/j.arabjc.2016.09.023

[34] Badders, N.R., Wei, C., Aldeeb, A.A., Rogers, W.J., & Mannan, M.S. (2006). Predicting the impact sensitivities of polynitro compounds using quantum chemical descriptors. *Journal of Energetic Materials*, *24*, 17-33. https://doi.org/10.1080/07370650500374326

[35] Minkin, V.I., Glukhovtsev, M.N., & Simkin, B.Y. (1994). *Aromaticity and antiaromaticity: Electronic and structural aspects*, New York: Wiley.

[36] Schleyer, P.R., & Jiao, H. (1996). What is aromaticity?. *Pure Appl. Chem.*, *68*, 209-218. https://doi.org/10.1351/pac199668020209

[37] Glukhovtsev, M.N. (1997). Aromaticity today: energetic and structural criteria. *J. Chem. Educ*., 74, 132-136. https://doi.org/10.1021/ed074p132

[38] Krygowski, T.M., Cyranski, M.K., Czarnocki, Z., Hafelinger, G., & Katritzky, A.R. (2000). Aromaticity: a theoretical concept of immense practical importance. *Tetrahedron, 56*, 1783-1796. https://doi.org/10.1016/S0040-4020(99)00979-5

[39] Schleyer, P.R. (2001). Introduction: aromaticity. *Chem. Rev*., *101*, 1115-1118. https://doi.org/10.1021/cr0103221

[40] Cyranski, M.K., Krygowski, T.M., Katritzky, A.R., & Schleyer, P.R. (2002). To what extent can aromaticity be defined uniquely?. *J. Org. Chem.*, *67*, 1333-1338. https://doi.org/10.1021/jo016255s

[41] Schleyer, P.R., Maerker, C., Dransfeld, A., Jiao, H., & Hommes, N.J.R.E. (1996). Nucleus independent chemical shifts: a simple and efficient aromaticity probe. *J. Am. Chem. Soc.*, *118*, 6317-6318. https://doi.org/10.1021/ja960582d