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Meta Effect of Absorption Energy in Donor–Acceptor Substituted Benzenoids: A Computational Study of Its Dependence on Acceptor Strength, Solvent Polarity, and Conjugation Length

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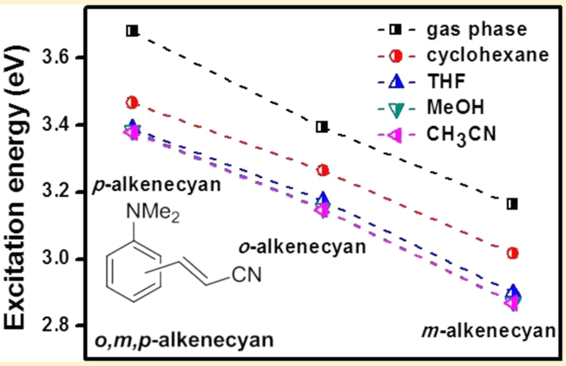
Ⓢ *Supporting Information*

ABSTRACT: The present work focuses on theoretical understanding of electronic absorption energies of *N,N*-dimethylaniline with different ortho-, meta-, and para-substituted acceptor groups. The meta isomers exhibit the lowest absorption energy compared to the ortho and para derivatives. This unusual behavior of absorption energies of the meta isomers is related to the "meta effect" well-known in organic photochemical reactions. The meta effect of absorption energy of the derivatives is found to depend on the strength of acceptors, solvent polarity, and conjugation length. The meta derivatives with strong acceptor groups generally exhibit the lowest absorption energy over the other isomers irrespective of solvent polarity. However, the meta isomers with weak acceptor groups exhibit the meta effect only in highly polar solvents. The trend of the lowest absorption energies of the meta isomers is observed to change if the acceptor group is bridged through π conjugation unit (n) with the core moiety. The normal pattern of absorption energy that is the para isomer is of lowest energy is observed to occur for the derivatives where the repeated conjugation units (n) are between 2 and 4. The normal pattern of absorption energy is continued to observe from $n > 4$ for all the derivatives.



1. INTRODUCTION

The term "meta effect" is used to describe an increased photochemical reactivity of meta benzenoid compounds over their ortho and para isomers in organic photochemical reactions. The high photochemical reactivity of the meta isomer was first noticed by Havinga et al. in 1956.[1] The phenomenon was then described by Zimmerman et al. in 1963 in the photochemical solvolysis of *m*, *p*-cyanophenyltrityl ethers[2] and *m*,*p*-methoxybenzyl acetate.[3] Since then, the effect has been well coined as the "meta effect" in literature. However, the mechanism of the meta effect had been a topic of debate for a long time. While Zimmerman et al. described the process through heterolytic cleavage, a different mechanism was proposed by Pincock et al. giving emphasize on homolysis.[4,5] The applicability of the meta effect was not only limited to solvolysis reactions in organic photochemistry but also utilized in photoreduction of benzophenone[6] and photolabile protection of carbonyl compounds.[7] While the aforementioned examples mainly dealt with organic photochemical reactions assisted by the meta effect, the dipole moment measurement of donor–acceptor substituted benzene derivatives by Sinha et al. contributed well to the concept of the meta effect. It described the charge migration from the donor part to the acceptor moiety in the meta isomer in the excited state, thus supporting the observed meta effect in various organic photochemical reactions.[8] The unusual observations of the photophysics of *m*-amino-substituted *trans*-1,2-diarylolefins by Lewis et al. on amino stilbene derivatives gave further insight into the notion of the meta effect.[9] Interestingly, they observed that the lowest energy absorption maxima of the *meta* isomer of diarylolefins was at a shorter wavelength compared to its para isomer, while the fluorescence maxima of the meta isomer was at longer wavelength compared to its para isomer and the fluorescence maxima of the meta isomer was found to be red-shifted with increasing solvent polarity.[9] Although the meta effect was demonstrated as an excited-state phenomenon by Zimmerman and subsequently by a school of chemists, recently, Foti et al. showed that the phenomenon might also occur in the ground state.[10] It was shown that *m*-methoxyphenol could undergo the homolytic cleavage of O–H bond even in the ground state.[10]

Thus, although a considerably large amount of literature on the meta effect related to organic photochemical reactions is documented, a detailed study of the meta effect in light of electronic absorption energy is lacking. On considering the importance of the meta effect observed in various photochemical reactions, a computational study of electronic absorption energies of a large number of meta-substituted donor–acceptor aromatic derivatives in addition to their ortho and para isomers may add knowledge to the understanding of the meta effect.

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The dimethylamino group (NMe_2) as a strong donating group is found in many donor−acceptor-substituted organic molecules, which find applications in various fields such as fluorescent probes,[11−13] nonlinear optical material,[14] laser dyes,[15] etc. Thus, here, we consider *N,N*-dimethylaniline as a parent derivative which is differentially substituted (ortho, meta, para) by various electron-withdrawing groups such as cyano (CN), alkyne, alkene, alkynyl cyano, and alkenyl cyano groups so as to compare the effect of substitutions on the electronic absorption energies in different solvents of varying polarities. Furthermore, the acceptor groups are conjugated with the core moiety through an increasing number of alkyne/alkene units as the conjugation linker to study the effect of chain length on the electronic absorption energies through time-dependent density functional theory (TD-DFT).[16−20]

2. COMPUTATIONAL DETAILS

All the computational work was carried out using the Gaussian 09 computational program.[21] The ground-state geometry of all of the *N,N*-dimethylaniline-containing donor−acceptor derivatives was optimized using the B3LYP[22]/6-311G(d,p) level of theory. The optimized geometries were used for vertical electronic absorption energy calculation using time-dependent density functional theory (TD-DFT) with B3LYP/6-311+G(d,p) and PBE0[23,24]/6-311+G(d,p) methods. Solvent contributions were introduced through self-consistent reaction field (SCRF) theory using a polarizable continuum model (PCM).[25] The B3LYP-optimized ground-state geometry was also used for the vertical excitation energy calculations with TD-CAM-B3LYP[26] methodology to compare its data with the results obtained from the previous methodologies. For CAM-B3LYP functional, standard parameters such as $\alpha = 0.19$, $\beta = 0.46$, and $\mu = 0.33$ were used for the calculations.

3. RESULTS AND DISCUSSION

3.1. Ground-State-Optimized Geometries and Solvent Effect.

A set of donor−acceptor substituted parent derivatives (Figure 1) was optimized with the B3LYP functional in the gas phase and in solvents of different polarities such as nonpolar cyclohexane, moderately polar tetrahydrofuran (THF), and highly polar methanol (MeOH) and acetonitrile (CH_3CN). A look at the change of structural parameter such C(Ph)−N(NMe_2) bond length with a dielectric constant of the solvents showed that the bond length decreased from gas phase to THF, and then the change was found to be minimal from THF to CH_3CN (Figure S1a, Supporting Information). The C(Ph)−N(NMe_2) bond length was found to be lowest for para-substituted molecules, followed by meta and next for ortho substitution. The observed higher C(Ph)−N(NMe_2) bond length for the ortho-substituted molecules could be attributed to steric interaction between the methyl groups of the dimethylamino moiety (NMe_2) and the adjacent ortho hydrogen of the phenyl ring, making the dimethylamino moiety out of plane of the phenyl ring. The general trend of decreasing C(Ph)−N(NMe_2) bond length with increasing solvent polarity probably indicated intramolecular charge-transfer (ICT) character of the substituted *N,N*-dimethylaniline derivatives. An investigation into the variation of the twist angle of the NMe_2 group with solvent polarity showed the highest twist angle for the ortho-substituted derivatives compared to the meta- and para-substituted derivatives (Figure S1b, Supporting Information). However, the twist angle was found to be almost unchanged with changing dielectric constant (Figure S1b, Supporting Information).

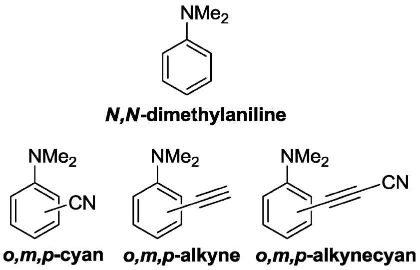

Figure 1. First set of parent derivatives under computational study.

3.2. Absorption Energy and Meta Effect.

The optimized ground-state geometries of the derivatives were used for vertical electronic absorption energy calculations. A gradual decrease in $S_0 \rightarrow S_1$ absorption energy with increasing solvent polarity was observed for all of the molecules with B3LYP functional (Figure 2a). However, the change of absorption energy was very low from THF to CH_3CN. The $S_0 \rightarrow S_1$ absorption energy of the parent derivative *N,N*-dimethylaniline[27−29] was found to be highest in the gas phase and also in all solvents of different polarities compared to its ortho-, meta-, and para-substituted derivatives. Interestingly, among the ortho-, meta-, and para-substituted derivatives, the $S_0 \rightarrow S_1$ absorption energy of the meta substituted derivatives was observed to be lowest. This unusual behavior of absorption energies of the meta-substituted derivatives is important to note given the fact that such unusual behavior of various meta isomers in terms of reactivity was observed in organic photochemical reactions.[1−3,6,7]A similar trend of absorption energy was also observed on employing the PBE0 functional for TD-DFT calculations (Figure 2b).

The unusual observation of lowest absorption energy of the meta isomer compared to its ortho and para isomers was understood from the frontier molecular orbitals. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) were mainly involved in the $S_0 \rightarrow S_1$ transition for the derivatives (Table S1, Supporting Information). It was observed that for the meta isomer, HOMO was mainly localized on the donor *N,N*-dimethylamino-substituted phenyl ring, whereas the LUMO was mainly concentrated on the acceptor group containing a phenyl ring (Figure 3). Thus, the phenyl ring was found to be the common in both the HOMO and LUMO. Such localization of HOMO and LUMO was not observed in the ortho (Figure S2, Supporting Information) and para (Figure S3, Supporting Information) substituted derivatives. In particular, for the para isomer, the HOMO and LUMO were observed to be completely delocalized over the whole molecule (Figure S3, Supporting Information). The localization of HOMO and LUMO on the donor and acceptor part, respectively, in the meta isomer probably led the $S_0 \rightarrow S_1$ transition to be of intramolecular charge-transfer character (ICT), thus lowering the absorption energy compared to its ortho and para isomers. The lowest absorption energy was also reported for *m*-cyanoaniline (λ_{max} 307 nm) compared to its para isomer (λ_{max} 270 nm) in water by Oshima and co-workers.[30] Lewis et al. observed such a meta effect for stilbene derivatives in fluorescence energy.[9,31] For example, *m*-amino-substituted 4′-(methoxycarbonyl)stilbene exhibited fluorescence maxima at λ_{max} 521 nm in CH_3CN, whereas the para isomer showed the fluorescence maxima at λ_{max} 501 nm in CH_3CN.[9] On the other hand, Ma et al. reported higher charge transfer coupling for

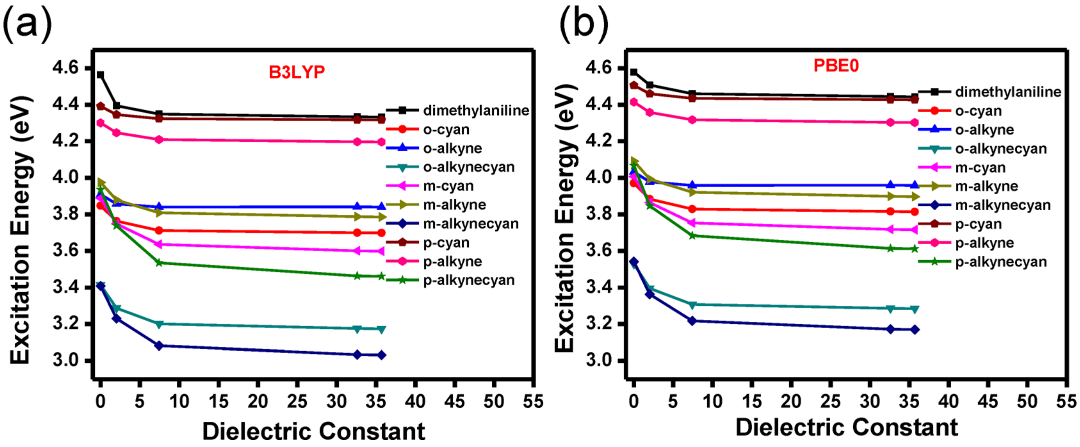

Figure 2. Correlation of $S_0 \rightarrow S_1$ excitation energy with a dielectric constant using (a) B3LYP/6-311+G(d,p) and (b) PBE0/6-311+G(d,p) levels of theory.

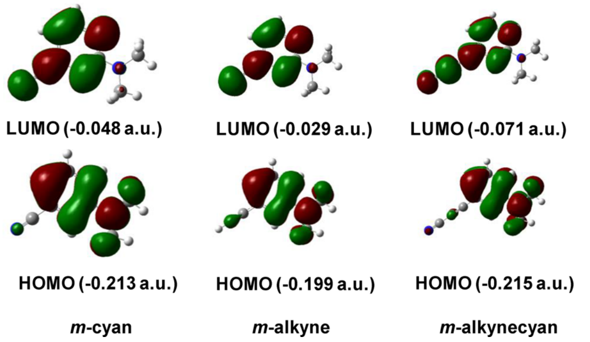

Figure 3. Frontier molecular orbitals involved in the $S_0 \rightarrow S_1$ transition of the meta derivatives using the B3LYP/6-311G(d,p) level of theory in the gas phase.

meta substituted donor−acceptor diphenylbutadienes and diphenylbutadiynes over their para isomers.[32]

3.3. Dependence of Meta Effect on Acceptor Strength and Solvent Polarity.

Figure 4 shows the correlation of $S_0 \rightarrow S_1$ absorption energy with different derivatives for a particular solvent. The observed meta effect in $S_0 \rightarrow S_1$ absorption energy for the derivatives was found to depend on the nature of the acceptor group and solvent polarity. To illustrate, it was found that the $S_0 \rightarrow S_1$ energy was lowest in all solvents as well as in the gas phase for a meta isomer containing alkynyl cyano as a strong acceptor group in the parent fluorophore. However, when the parent fluorophore was substituted with a comparatively weak acceptor group such as alkyne and cyano, the meta effect was observed to depend on polarity of solvent. In case of cyano substitution of the parent fluorophore, the meta effect was not observed in the gas phase but observed in solvents of different polarities. On the other hand, in the case of

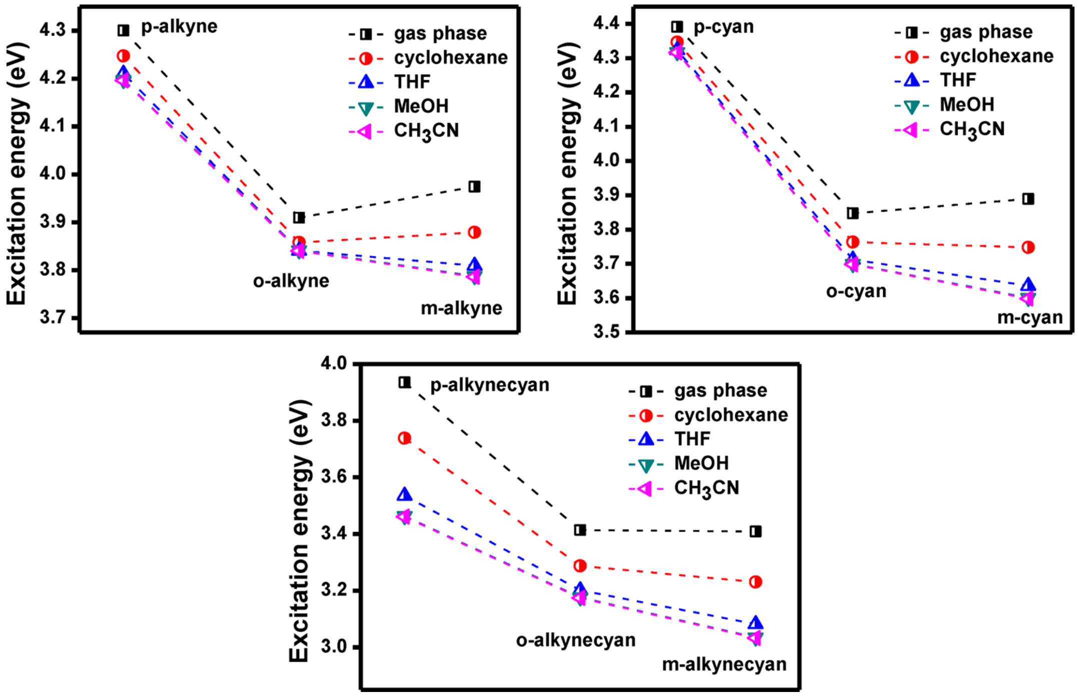

Figure 4. Correlation of $S_0 \rightarrow S_1$ absorption energy with different derivatives using the B3LYP/6-311+G(d,p) level of theory.

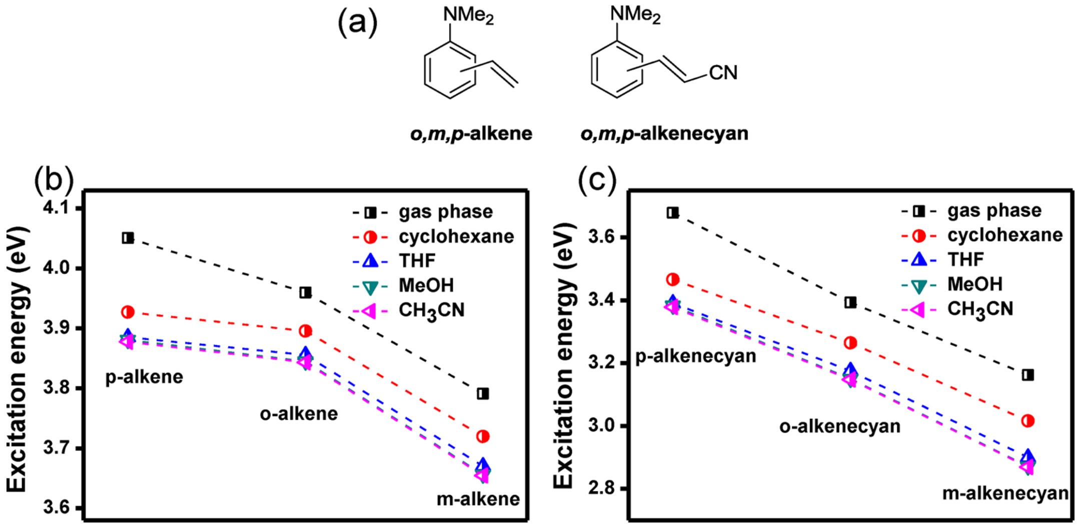

Figure 5. (a) Second set of derivatives under computational study and (b) correlation of $S_0 \rightarrow S_1$ absorption energy with *o,m,p*-alkene and (c) *o,m,p*-alkenecyan derivatives using the B3LYP/6-311+G(d,p) level of theory.

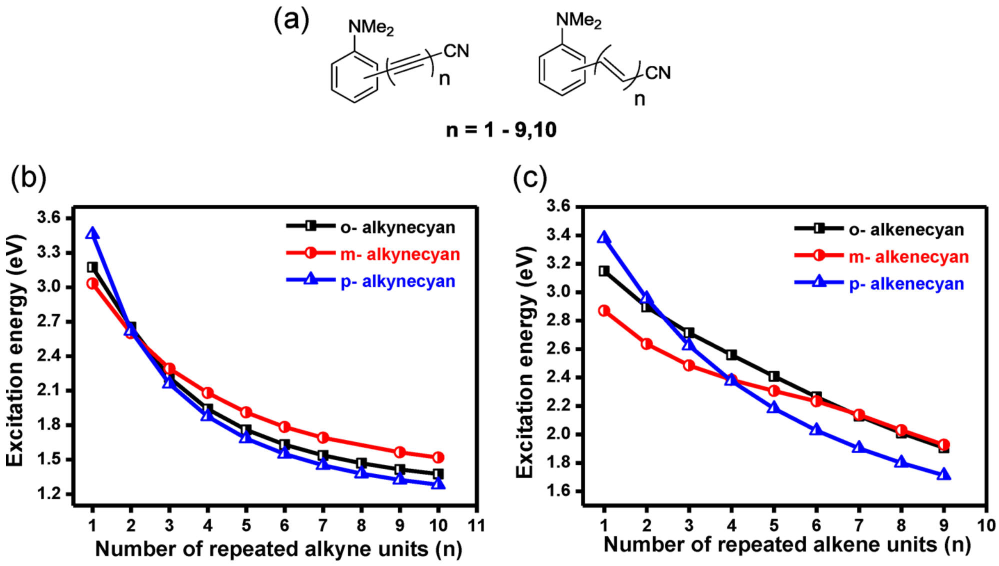

Figure 6. (a) Third set of derivatives under computational study and (b) correlation of $S_0 \rightarrow S_1$ absorption energy with repeated number of alkyne in alkynecyan and (c) alkene in alkenecyan derivatives using B3LYP/6-311+G(d,p) in cyclohexane.

alkyne substitution, the meta effect was noted in polar solvents like THF, MeOH, and CH_3CN but not in solvents of less polarity such as cyclohexane or in the gas phase. However, the meta effect remained unaffected by the polarity of the medium for a substitution with a strong acceptor group such as alkynyl cyano. A close observation was also found with the PBE0 functional (Figure S4, Supporting Information).

To ascertain the dependence of meta effect on acceptor strength and solvent polarity, a second set of derivatives (Figure 5a) was optimized in the gas phase, cyclohexane, THF, MeOH, and CH_3CN using the B3LYP/6-311G(d,p) level of theory. The computed $S_0 \rightarrow S_1$ absorption energies of the second set of derivatives were plotted for a particular solvent (Figure 5b,c). The $S_0 \rightarrow S_1$ absorption energy was found to be lowest for the meta isomers with alkene and alkenyl cyano-substituted derivatives, irrespective of the solvent polarity. This result indicates that the meta effect depends on acceptor strength as well as solvent polarity. Thus, the meta effect is more likely to occur for donor−acceptor derivatives with a strong acceptor group irrespective of the solvent polarity, whereas solvent polarity plays a crucial role for the derivatives substituted with a weak acceptor group.

3.4. Dependence of Meta Effect on Conjugation Length.

To study the effect of conjugation length on the meta effect of absorption energy, the acceptor group was bridged through an increasing number of alkene/alkyne units with the phenyl ring. Thus, a third set of derivatives (Figure 6a) containing an acceptor group with an increasing number of π units was optimized in nonpolar cyclohexane and polar CH_3CN solvents using previous methodology similar to the second set of derivatives. Figure 6b,c shows the variation of $S_0 \rightarrow S_1$ absorption energies with a number of repeating alkyne (Figure 6b) and alkene units in cyclohexane (Figure 6c) and CH_3CN (Figure S5, Supporting Information). The $S_0 \rightarrow S_1$ energy was generally found to be the lowest for meta isomers followed by ortho and the highest for para isomers of the derivatives when the value of n was less such as 1. Interestingly, when the value of *n* was high, a normal of trend of absorption energy that is the

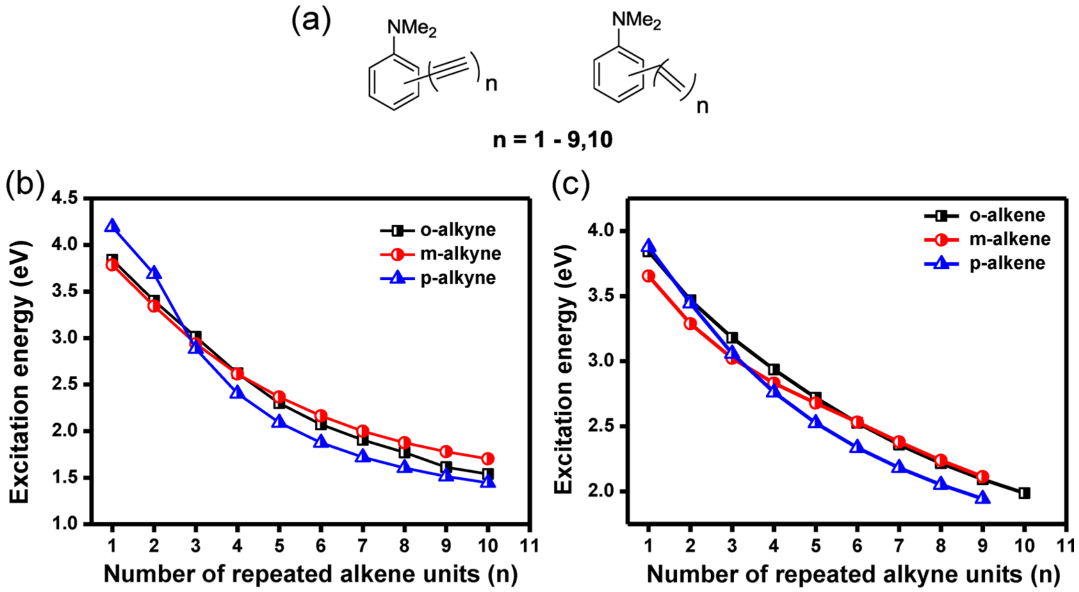

Figure 7. (a) Fourth set of derivatives under computational study and (b) correlation of $S_0 \rightarrow S_1$ absorption energy with repeated number of alkyne and (c) alkene using B3LYP/6-311+G(d,p) in cyclohexane.

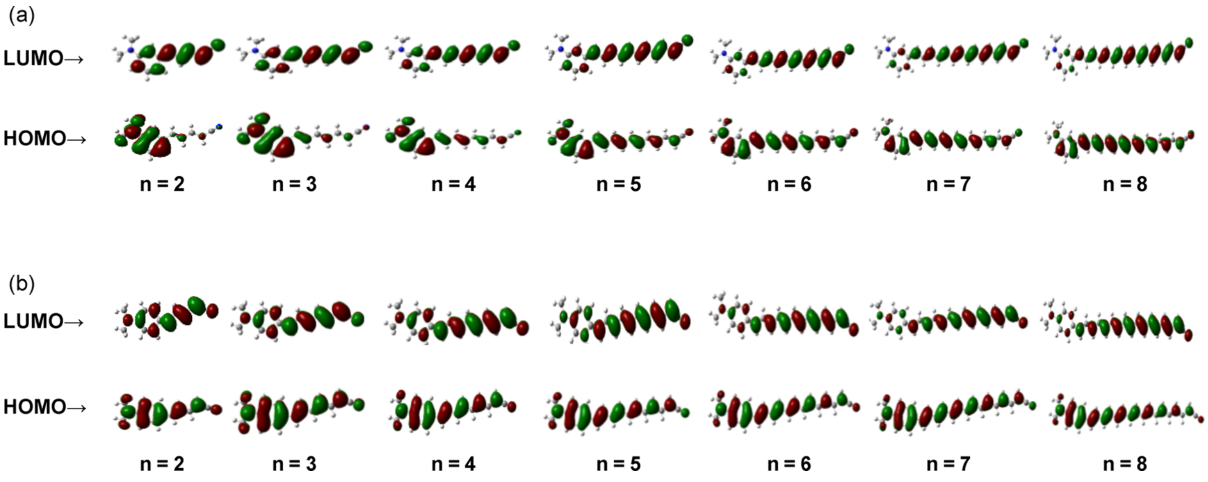

Figure 8. HOMO and LUMO of (a) *m*- and (b) *p*-alkenecyan derivatives from B3LYP/6-311G(d,p)-optimized geometries in CH_3CN.

para isomer is of lowest absorption energy was observed. Generally, the normal trend of absorption energies was observed to take place for the derivatives with repeated conjugation units (*n*) lying between 2 and 4. The normal trend was noticed to be continued from $n > 4$. Thus, the meta effect of absorption energies was found to depend on conjugation length.

The dependence of the meta effect of absorption energy on conjugation length was also verified with derivatives having no cyano acceptor group. Thus, a fourth set of derivatives (Figure 7a) was optimized using the previous methodology and used for vertical absorption energy calculations. It is worth mentioning that all of the double bonds considered in this study were trans in nature. TDDFT calculation of these optimized geometries in cyclohexane (Figure 7b,c) and CH_3CN (Figure S6, Supporting Information) showed a similar trend as observed in Figure 6. The breakdown of the meta effect of absorption energies at higher values of *n* could be related to the longer distance between the donor and acceptor parts. As the acceptor unit goes away from the donor part, the ICT for the meta isomer is unlikely to take place.

The absorption energy of the derivatives was also computed using the TD-CAM-B3LYP level of theory (Figure S7, Supporting Information) owing to the fact that the conventional hybrid DFT functional such as B3LYP is known to underestimate the excitation energy of donor−acceptor-substituted derivatives.[33−40] However, the primary aim of this study was focused on the understanding of trend of absorption energies among the ortho-, meta-, and para-substituted derivatives with conjugation length rather than focusing on actual estimation of their absorption energies. Figure S7 (Supporting Information) demonstrates that the absorption energy of the meta isomer is lowest for $n = 1$, but it starts increasing at $n > 1$, thus agreeing with the results obtained using B3LYP functional.

When the chain length is short, such as $n = 1$, the HOMO and LUMO of the meta isomers are found to be composed of donor (dimethylaniline substituted phenyl ring) and acceptor (cyano/alkyne/alkynyl cyano) moieties, respectively (Figure 3). On the other hand, the HOMO and LUMO of the para isomers are observed to be diffused over the whole molecular entity (Figure S3, Supporting Information). The localized

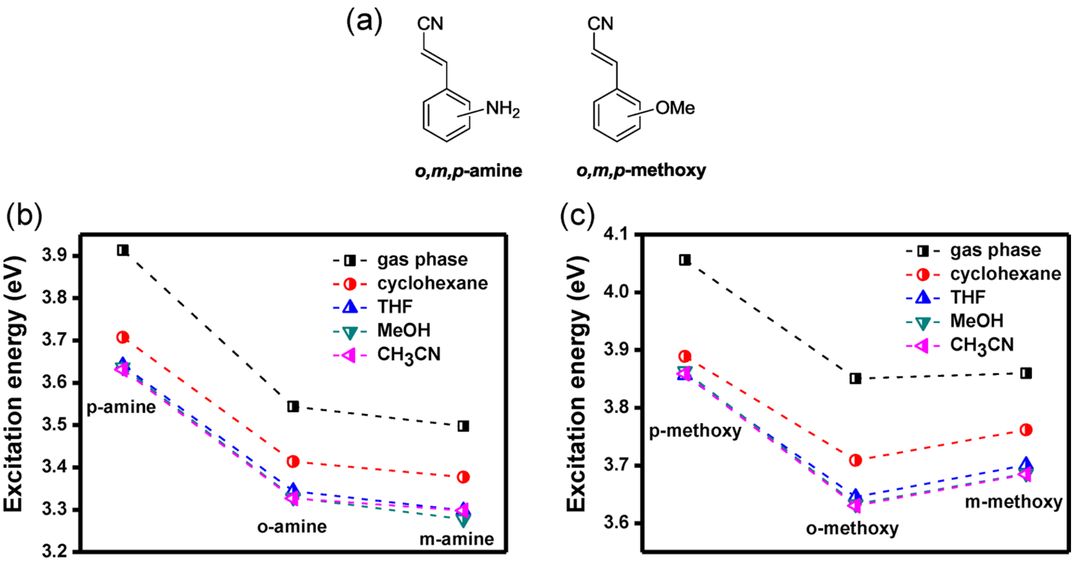

Figure 9. Fifth set of derivatives under computational study (a) and correlation of $S_0 \rightarrow S_1$ absorption energy with *o,m,p*-amine (b) and *o,m,p*-methoxy (c) derivatives using B3LYP/6-311+G(d,p) level of theory.

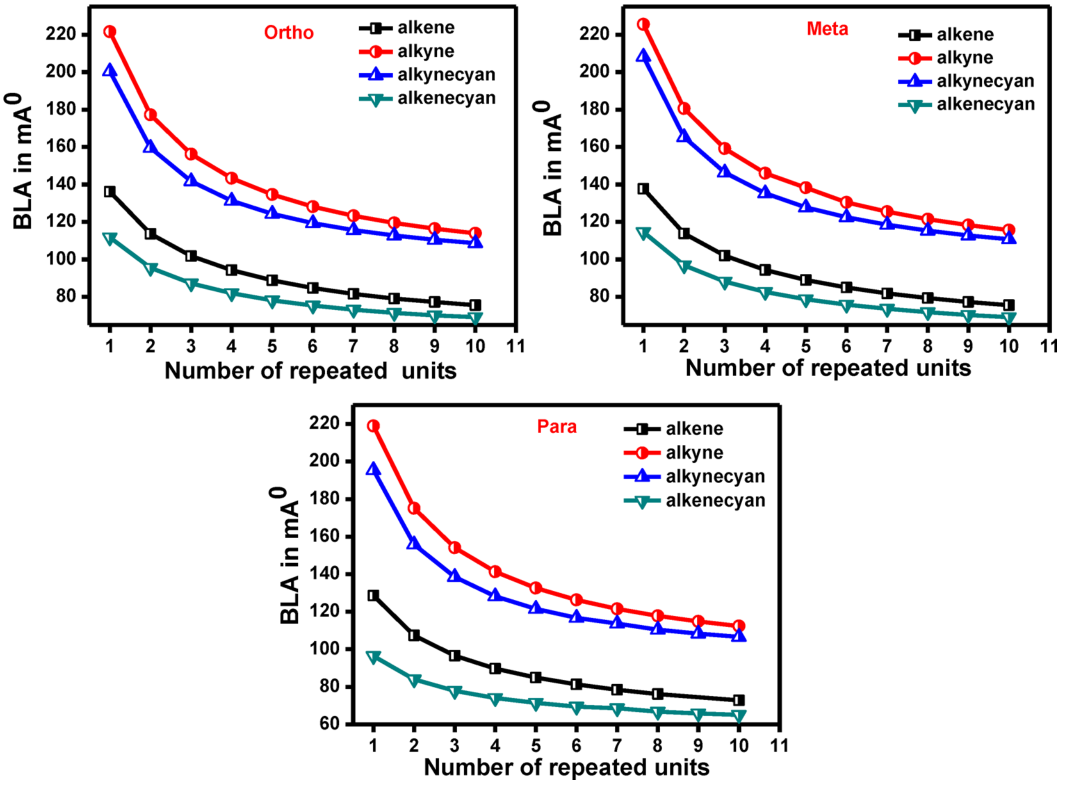

Figure 10. Correlation of BLA with repeated number of alkene/alkyne units for a fixed substitution of the derivatives using B3LYP/6-311+G(d,p) in cyclohexane.

HOMO and LUMO of the meta isomers induce intramolecular charge transfer (ICT) character and thus help in lowering the excitation energy of the meta isomers, as discussed previously. However, on increasing chain length, the characters of the HOMO and LUMO of the meta and para isomers are found to be changed. While the HOMO of the para isomers is observed to be delocalized on the entire molecular entity, the LUMO is localized on the acceptor part containing the alkene/alkyne chain at higher values of *n* (*n* > 3 or 4). Thus, the para isomers gain some charge-transfer character at higher values of *n*. On the other hand, unlike the HOMO and LUMO of the meta derivatives with shorter chain length, the HOMO of the meta isomers with higher chain length (*n* > 3 or 4) is observed to be diffused throughout the whole molecule and the LUMO is localized on acceptor group containing the alkene/alkyne chain (Figure 8). Thus, the meta isomers lose some charge character at higher values of *n* compared to the meta isomers with shorter values of *n*. A restoration of the ICT character of the para isomers on increasing chain length, coupled with the better donor−acceptor conjugation of the para isomers, probably helps in overcoming the ICT character of the meta isomers and, thus, assist in following the normal trend of excitation energy on increasing chain length.

3.5. Meta Effect and Donor Substituents. The meta effect was also observed to depend on the strength of donor moieties. A set of derivatives with alkenyl cyano as an acceptor group and different donor groups (Figure 9a) was optimized, and their absorption energies were computed. Figure 9b and Figure 6c show that the meta effect is present for derivatives with the strong donor substituents such as amine and dimethylamino moieties, respectively. However, the effect was not observed for the derivatives containing a weak donor such as methoxy substituent (Figure 9c). Further, the donor substituent (*N*,*N*-dimethylaniline) was bridged through varied alkyne chains (n) with the aromatic core to study its effect on the excitation energy. A slight meta effect was observed at $n = 1$ and 4, while the effect was not found at $n = 2$, 3, and 5. Thus, although the trend of the meta effect was not very consistent at shorter chain lengths; the normal trend of excitation energy was observed to be persistent at $n > 5$ (Figure S8, Supporting Information).

3.6. Bond Length Alternation Parameter and Acceptor Strength. Finally, a correlation of bond length alternation (BLA) parameter of the donor−acceptor substituted long chain π-conjugated derivatives with number of repeated alkyne/alkene units was studied. BLA is defined as the difference between the average of all homoatomic saturated bond lengths and the average of all homoatomic unsaturated bond lengths.[41,42] BLA values were calculated from the B3LYP ground state optimized geometries of the π conjugated derivatives in cyclohexane and were plotted against the number of repeating unit of alkyne/alkene (Figure S9, Supporting Information). Interestingly, a gradual decrease of BLA of the derivatives was observed with repeated number of conjugation units. Figure 10 shows the correlation of BLA with repeated number of conjugation units for a fixed substitution (ortho/meta/para) of all the derivatives. BLA was found to be lowest for the derivatives with alkenyl cyano as an acceptor group, whereas it was found to be highest for the alkyne containing derivatives, next was the alkynyl cyano containing derivatives and subsequently the derivatives with alkene as an acceptor group. Thus, from the BLA study the acceptor strength was found to follow the order of alkenyl cyano > alkene > alkynyl cyano > alkyne.

4. CONCLUSIONS

In summary, a detailed and systematic investigation of TDDFT vertical absorption energies of a series of ortho, meta and para substituted donor−acceptor derivatives with *N*,*N*-dimethylaniline as a core unit was carried out. The meta isomers were found to exhibit the lowest absorption energy, which was related to the meta effect observed in organic photochemical reactions. The meta effect was found to depend on acceptor strength as well as solvent polarity. The effect was observed in strong donor−acceptor-substituted derivatives, irrespective of solvent polarity. However, the effect was observed only in highly polar solvent when the acceptor was relatively weak such as alkene group. Interestingly, the meta effect of absorption energy was also found to depend on conjugation length when the acceptor group was bridged with π conjugation. The breakdown of the meta effect was observed to occur with a repeated conjugation unit (n) lying between 2 and 4. The geometrical parameter BLA was observed to decrease with the increase of repeated conjugation units in the long π conjugated derivatives providing the relative information on acceptor strength.

Thus, we believe that the observed meta effect of absorption energy in the present study can be used to tune photophysical properties of various fluorophores endeavoring its usage in various applications such as light emitting diode, field effect diodes, chemical sensors, etc.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Correlation of C(Ph)−N(NMe$_2$) bond length and twist angle of NMe$_2$ group with dielectric constant, oscillator strength, and orbital contributions of some parent derivatives, HOMO and LUMO of the ortho and para derivatives, correlation of $S_0 \rightarrow S_1$ absorption energy with different derivatives using PBE0/6-311+G(d,p) level of theory, correlation of $S_0 \rightarrow S_1$ absorption energy with repeated number of alkyne in *o,m,p*-alkynecyan and alkene in *o,m,p*-alkenecyan derivatives using B3LYP/6-311+G-(d,p) in CH_3CN, correlation of $S_0 \rightarrow S_1$ absorption energy with repeated number of alkyne in *o,m,p*-alkyne and alkene in *o,m,p*-alkene derivatives using B3LYP/6-311+G(d,p) in CH_3CN, correlation of $S_0 \rightarrow S_1$ absorption energy with repeated number of alkyne in *o,m,p*-alkyne and *o,m,p*-alkynecyan derivatives units using CAM-B3LYP/6-311+G(d,p) in cyclohexane, correlation of $S_0 \rightarrow S_1$ absorption energy with repeated number of alkyne (with respect to the donor group) units using B3LYP/6-311+G(d,p) in CH_3CN, correlation of BLA with repeated number of alkene/alkyne units using B3LYP/6-311+G(d,p) in cyclohexane and Cartesian coordinates of some selected derivatives. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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