SCIENTIFIC RESEARCH JOURNAL,
VOL 18, NO 2 (2021) 119-128
HTTPS://DOI.ORG/10.24191/SRJ.V18I2.13040

SCIENTIFIC
RESEARCH
JOURNAL
SRJ
ISSN: 1675-7009
e-ISSN: 2289-649X

Theoretical Investigation of the Quasi-ring C–H···π Interactions

Lee Sin Ang[1*], Zaidi Ab Ghani[1], Mohd Hafiz Yaakob[1], Mohamed Ismail Mohamed-Ibrahim[2]

[1]Faculty of Applied Sciences, Universiti Teknologi MARA Perlis Branch Arau Campus, 02600 Arau, Perlis.
[2]School of Distance Education, Universiti Sains Malaysia, 11800 USM, Pulau Pinang.

[*]Corresponding author's e-mail: anglee631@uitm.edu.my

Received: 5 April 2021
Accepted: 7 August 2021
Online First: 31 August 2021

ABSTRACT

The quasi-ring C–H···π interactions have been reported to be responsible for the stability of crystalline materials. The statistical analysis, together with electronic structure calculations in the framework of density functional theory and Moller-Plesset have also provided positive data on the aforementioned interactions. However, improvements can be had in the theoretical calculations, where the basis set convergence is not explored. This is crucial as the interactions are of weak type, reported to be around 4 – 5 kcal mol^{-1}. In this investigation, the idea is to combine the geometry, potential energy surface, and bonding analysis to provide different insights into the interactions. Our results show that the original configurations of the crystals, even with the substitutions of linear chains, are more favorable than the rotated ones. Further calculations are needed to verify the involvements of the π orbitals of the N, C, Cl, S and the d-orbital of Cu, and the s-orbital of hydrogen atoms.

Keywords: C–H···π interactions, crystal structures, density functional theory

PENERBIT PRESS
UNIVERSITI TEKNOLOGI MARA

INTRODUCTION

Weak interactions are important in the study of materials science. Although their strengths are much lesser compared to covalent and ionic interactions, their existence help in stabilising the crystal structure, and is thus indispensable in the field of crystal engineering and the understanding of newly found materials. In this regard, C–H···π interactions have been shown to be a vital component in several chemical and biochemical processes. The interactions have been studied as a favourable force to stabilise the packing of molecules in crystals [1-6] and protein stability [7], to cite a few examples. Using data mining, the interactions that exist between lone pair of metals to the π of arenes in the case of thallium(I) occur in 13 % of their crystal structures [8]. Even though the C–H···π interactions are ubiquitous, the nature of these weak interactions means that the accurate predictions of the energies involved can only be obtained using high-level methods, and the field is still generating great interest among researchers [9, 10].

Our main objective is to investigate the existence of the "quasi-ring C–H···π" interactions as reported by Tiekink *et al.* [11-15]. Using a statistical method, Tiekink *et al.* reported that the C–H···π interactions are present in many crystal structures [11, 15]. Theoretical calculations had been performed to verify this claim on a compound ($C_{56}H_{42}Cu_1N_2P_2S_1$, with Cambridge Structural Database (CSD) refcode ZADBOV, labelled **4** here) in Reference 11. In that report, using the non-covalent interactions (NCI) analysis, the π-stacking (π-type interaction) is deduced to exist for **4**. It is an attractive interaction, albeit a weak one. This interaction is postulated to arise from the quasi-π system formed between the p-orbitals of N, C, Cl, S and the d-orbital of Cu, and the s-orbital of the hydrogen atom. The energy for the interaction was reported to be around 4 – 5 kcal mol^{-1} from DFT calculations [11].

Herein, we report the results of our theoretical investigations carried out on compound **4**. Since this is a weak interaction, the methods used will be crucial to the conclusion. In the current investigation, the objective is to improve upon the basis sets used and provide new insights using the potential energy surface calculations. Only preliminary results will be presented here.

METHODOLOGY

The structural coordinates of compound **4** were downloaded from the CSD database. We then performed geometry optimisations and scan calculations on the complete molecule. Calculations were also performed on compound **4**, with and without the quasi-ring (Qr). Our objective is to test whether the H attached to the ortho C of the phenyl ring (Phq) will move to the center of the Qr (its 'final' position in the crystal structure), even without the existence of the Qr. We also wanted to know the effect on an H that is not attached to a phenyl ring. To do this, we replaced the Phq with CH_2CH_3 and $CH_2CH_2CH_3$ chains. Between these two models, $CH_2CH_2CH_3$ has a longer chain and hence should be more flexible. It is used to model possible movements of an H atom on that chain to the center of the Qr.

We also rotated the Phq that has one of its hydrogen pointing towards the center of the Qr (the centroid). The rotations were performed to gauge whether the changes in the positions of the hydrogen, with or without the Qr, will affect the energy profile of the system. The calculations were performed by using the G09 suite of programmes [16], with Gaussview [17] as the visualiser. Functional BP86, together with the DEF2TZVP basis set is used in the optimisation and single-point energy calculations. This combination is as used in the previous work of Tiekink [11].

RESULTS AND DISCUSSION

Molecule **4** was optimised with all the other atoms fixed except for those in the Phq where the hydrogen is pointing towards the centroid. We labelled the hydrogen that is pulled towards the centroid as Hc. Following the movement of the Hc for each optimisation step, it was found that the Hc is attracted towards the centroid. The distance between the centroid and the Hc decreases from the original distance of 2.283 Å to 2.115 Å. The resulting structure is as shown in Figure 1.

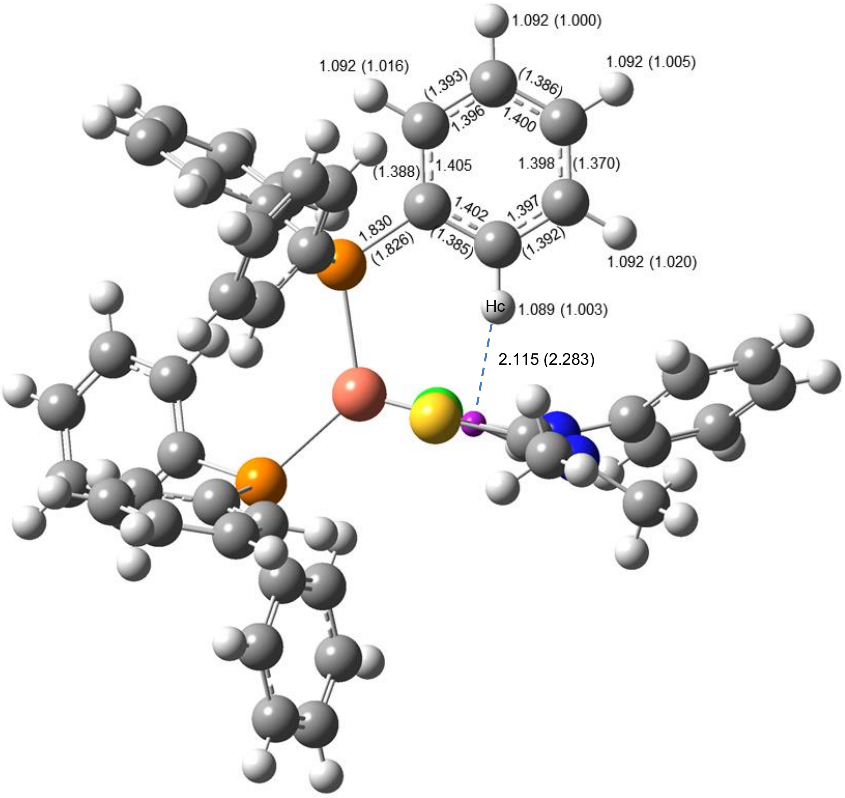

Figure 1: The Structure of 4, in which only the Atoms in the Phenyl Ring Phq and P–C are Allowed to Relax, Resulting in the Changes in the Bonds Lengths (Indicated Close to the Atoms (for Hydrogens) and Bonds (for Bonds Involving Carbons)). The Centroid is Indicated by a Purple Sphere. Bond Lengths from the Crystal Structure are Given in Brackets

Comparing the bond lengths of the Phq and the P–C (which is the only moiety that was optimised) with those from the crystal structure, it can be seen that they are all longer than those from the crystal structure. The shortened distance of 2.115 Å between the centroid and Hc can be attributed to the elongation of the C–P, C–C, and C–H bonds directly above the Qr. The angles P–C–C and C–C–H directly above the Qr (not shown) also decreased, hence pulling the Hc closer to the centroid, contributing to the decrease distance between Hc and centroid. Based on these observations, it is clear that the Qr does have some sort of interaction with the Hc. The longer C–H bonds opposite to this side of Phq may be seen as the expansion of the bonds as there are no constraint/interactions imposed by neighbouring molecules (whereas in the present calculation, we only used one molecule of **4**).

For the case of the two models where CH_2CH_3 and $CH_2CH_2CH_3$ were used to simulate Phq, their geometries were also optimised (the positions of the atoms were allowed to be relaxed, including the bond that attaches them to the P) while the positions of other atoms were fixed. Comparing with the initial arrangement of the CH_2CH_3 and $CH_2CH_2CH_3$, the results from the calculations showed that the end of these two chains have also moved towards the Qr. This can be seen in Figure 2. This means that the center of the Qr might be attracting the Hc attached to the end of these chains. The distances between the nearest H to the centroid of the Qr are tabulated in Table 1.

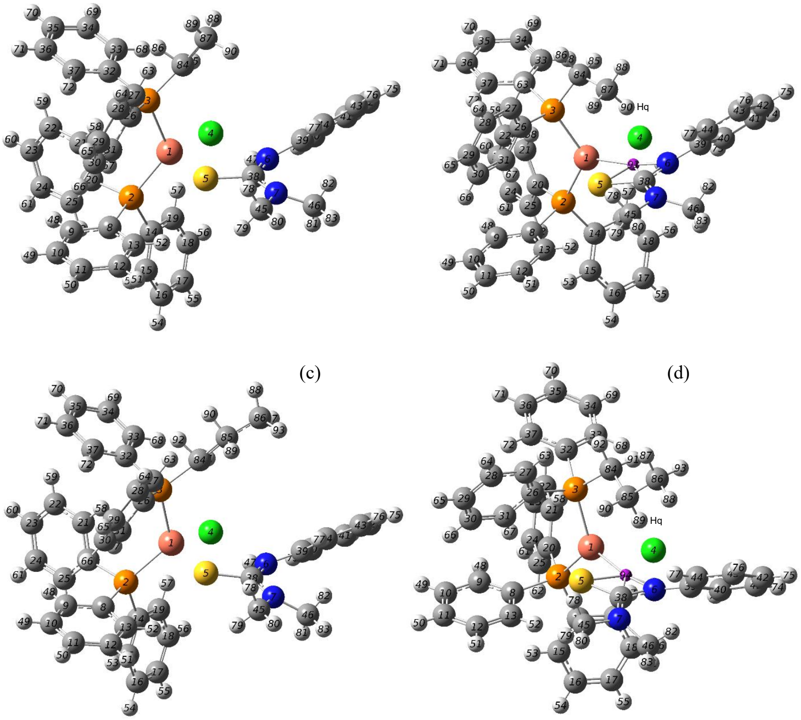

Figure 2: The Geometry of Linear Chains as a Substitute for the Phenyl Ring. The Initial Arrangement of the CH_2CH_3 is Shown in (a). After Optimisation, the Structure Obtained is as Shown in (b). The Original Configuration of $CH_2CH_2CH_3$ is in (c), and the Relaxed Geometry in (d)

Table 1. Equilibrium Distance (in Å) from the Nearest H to the Centroid of the Qr. The Corresponding Value in the Crystal Structure of 4 is 2.283 Å

System	Distance of nearest H to centroid (Å)		
	CH_2CH_3	$CH_2CH_2CH_3$	Phenyl ring
Qr	2.39	2.30	2.115
No Qr	2.19	2.16	2.016

Comparing with the optimisation of the Phq in Figure 1, where Hc is able to go even deeper into the Qr (2.115 Å), these results show that the models with the Phq replaced by the CH_2CH_3 and $CH_2CH_2CH_3$ do not show the interactions as found for the Phq. It seems that the Phq has electronic properties that allow for it to have special interactions with the quasi-ring, which the straight chain lacks.

The changes in the energy of the system as the Phq is rotated about the P–C bond are shown in Figure 3. As shown in Figure 3, the curves of the two potential energy surface (PES) with or without Qr are similar, especially of the peaks and valleys. The energetically most favorable arrangement of the Phq is at the original configuration, as found in the crystal structure. The minima at around 190° is the case where the H was directly opposite to the Hc atom now takes the position of the nearest distance to the centroid. This is the same with the original position from the crystal structure. The maxima of the PES happened when the Phq was rotated perpendicular to their original position, hence the Hc is the furthest at this rotated angle.

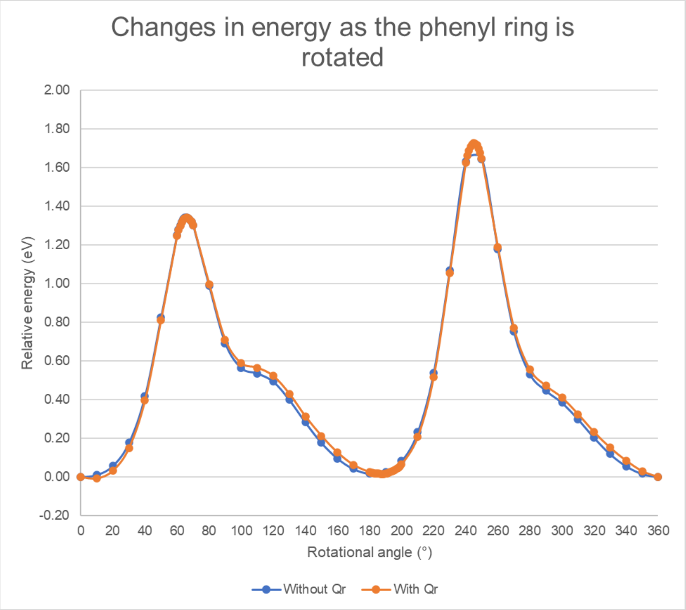

Figure 3. Changes in the Energy of the System when the Phq is Being Rotated

By comparing the PES for those with and without the Qr as shown in Figure 3, we can see that the Qr generates no effect for the rotational movement of the Phq.

CONCLUSION

Our current investigation on the existence of the quasi-ring C–H interactions are in agreement with the previous findings. Preliminary results on the geometry and potential energy surface do point to stable original configuration, even with the use of the linear chains to replace the ring. However, the involvements of the π orbitals of N, C, Cl, S and the d-orbital of Cu, and the s-orbital of hydrogen atoms are yet to be clarified. Further investigations should be performed using the non-covalent interactions (NCI) or the bonding analysis, together with the convergence of the basis sets. The knowledge acquired from research at microscopic level could be used to complement the experimental findings, especially in providing explanations for the macroscopic properties in the search of new materials.

REFERENCES

[1] H. Brunner and T. Tsuno, 2015. Cyclopentadienyl/Phenyl Attraction in CpM–L–E–Ph Compounds by CH/π Interactions, *Organometallics,* vol. 34, pp. 1287-1293. DOI: 10.1021/acs.organomet.5b00022

[2] M. A. M. Capozzi, G. Terraneo, and C. Cardellicchio, 2019. Structural insights into methyl- or methoxy-substituted 1-(α-aminobenzyl)-2-naphthol structures: the role of C-H···π interactions, *Acta Crystallogr C Struct Chem*, vol. 75, pp. 189-195. DOI: 10.1107/s2053229619001050

[3] A. Matsumoto, T. Tanaka, T. Tsubouchi, K. Tashiro, S. Saragai, and S. Nakamoto, 2002. Crystal Engineering for Topochemical Polymerization of Muconic Esters Using Halogen−Halogen and CH/π Interactions as Weak Intermolecular Interactions, *Journal of the American Chemical Society,* vol. 124, pp. 8891-8902. DOI: 10.1021/ja0205333

[4] M. Nishio, 2004. CH/π hydrogen bonds in crystals, *CrystEngComm*, vol. 6, pp. 130-158. DOI: 10.1039/B313104A

[5] N. Suzuki, T. Matsuda, T. Nagai, K. Yamazaki, and M. Fujiki, 2016. Investigation of the Intra-CH/π Interaction in Dibromo-9,9′-dialkylfluorenes, *Crystal Growth & Design*, vol. 16, pp. 6593-6599. DOI: 10.1021/acs.cgd.6b01290

[6] Y. Umezawa, S. Tsuboyama, H. Takahashi, J. Uzawa, and M. Nishio, 1999. CHπ interaction in the conformation of organic compounds. A database study, *Tetrahedron*, vol. 55, pp. 10047-10056. DOI: 10.1016/S0040-4020(99)00539-6

[7] A. Gil, V. Branchadell, and M. J. Calhorda, 2016. A theoretical study of methylation and CH/π interactions in DNA intercalation: methylated 1,10-phenanthroline in adenine–thymine base pairs, *RSC Advances*, vol. 6, pp. 85891-85902. DOI: 10.1039/C6RA15495F

[8] I. Caracelli, I. Haiduc, J. Zukerman-Schpector, and E. R. T. Tiekink, 2017. A new non-covalent bonding mode in supramolecular chemistry: Main group element lone-pair–π(arene) interactions, in *Aromatic Interactions: Frontiers in Knowledge and Application: The Royal Society of Chemistry*, 2017, pp. 98-123. DOI 10.1039/9781782626626-00098

[9] D. Chakraborty, K. Berland, and T. Thonhauser, 2020. Next-generation nonlocal van der Waals density functional, *Journal of Chemical Theory and Computation,* vol. 16, pp. 5893-5911. DOI: 10.1021/acs.jctc.0c00471

[10] P. Xu, M. Alkan, and M. S. Gordon, 2020. Many-Body Dispersion, *Chemical Reviews*, vol. 120, pp. 12343-12356. DOI: 10.1021/acs.chemrev.0c00216

[11] C. I. Yeo, S. N. A. Halim, S. W. Ng, S. L. Tan, J. Zukerman-Schpector, M. A. B. Ferreira, and E. R. T. Tiekink, 2014. Investigation of putative arene-C–H⋯π(quasi-chelate ring) interactions in copper(I) crystal structures, *Chemical Communications*, vol. 50, pp. 5984-5986. DOI: 10.1039/C4CC02040E

[12] C. I. Yeo, L. Y. Liew, J. Chew, S.-Y. Teow, and E. R. T. Tiekink, 2020. Crystal structure of chlorido-(O-ethyl phenylcarbamothioamide-κS)-bis(triphenylphosphane-κP)-silver(I), $C_{45}H_{41}AgClNOP_2S$, *Zeitschrift für Kristallographie - New Crystal Structures*, vol. 235, pp. 1477-1480. DOI: 10.1515/ncrs-2020-0363

[13] C. I. Yeo, S.-Y. Teow, L. Y. Liew, J. Chew, and E. R. T. Tiekink, 2020. Crystal structure of chlorido-(O-methyl phenylcarbamothioamide-κS)-bis(triphenylphosphane-κP)silver(I), $C_{44}H_{39}AgClNOP_2S$, *Zeitschrift für Kristallographie - New Crystal Structures,* vol. 235, pp. 1473-1475. DOI: 10.1515/ncrs-2020-0362

[14] C. I. Yeo and E. R. T. Tiekink, 2018. Crystal structure of the co-crystal O-isopropyl phenylcarbamothioate – 4,4′-bipyridine (2/1), $C_{15}H_{17}N_2OS$, *Zeitschrift für Kristallographie - New Crystal Structures,* vol. 233, pp. 491-492. DOI: 10.1515/ncrs-2017-0374

[15] J. Zukerman-Schpector, C. I. Yeo, and E. R. T. Tiekink, 2016. Supramolecular architectures sustained by arene-C–H···π(quasi-chelate ring) interactions in the crystal structures of copper(I) complexes, *Zeitschrift für Kristallographie - Crystalline Materials,* vol. 231, pp. 55-64. DOI: 10.1515/zkri-2015-1868

[16] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, 2016. Gaussian 09, Revision D.01, Wallingford CT, Gaussian, Inc.

[17] R. Dennington, T. A. Keith, and J. M. Millam, 2016. GaussView, Version 6.1, Shawnee Mission, KS, Semichem Inc.