



REGULAR ARTICLE

Mechanistic pathways for halogen dance reactions in bromothiophenes: a cascade-like pattern

NADER SAKHAE^{a,b,*} , SAHAR SAKHAE^c, AKBAR MOBARRAKI^d, AHMAD TAKALLOU^e and MOHAMMAD HOSSEIN SAKHAE^f

^aDepartment of Mathematics and Natural Sciences, Harris-Stowe State University, St. Louis, MO 63108, USA

^bDepartment of Chemistry, Southern Illinois University Edwardsville, Edwardsville, IL 62025, USA

^cIslamic Azad University, Mashhad Branch, Mashhad, Iran

^dDepartment of Chemistry, Tarbiat Modarres University, P.O. Box. 14115-175, Tehran, Iran

^eDepartment of Chemistry, Kharazmi University, Tehran, Iran

^fMashhad University of Medical Sciences, Mashhad, Iran

E-mail: SakhaeeN@hssu.edu; nsakhae@siue.edu

MS received 30 December 2019; revised 8 January 2020; accepted 3 March 2020

Abstract. Ever since the halogen dance reaction was discovered by Bunnet *et al*, synthetic chemists have utilized the transformation in many desirable ways to build substituted heterocyclic target molecules of all kind. Using DFT-Cam-B3LYP/land2dz computations and focused on Hannes Frohlich *et al*. Halogen Dance (HD) reactions of bromothiophenes, a new bromo-bridged Transition State (TS) is proposed. This bromo-bridged TS was then used to put forth eight possible isomerization as well as eight possible disproportionation paths. These mechanistic pathways were then carefully inspected based on TS's energy and protonation/deprotonation steps to find the most suitable pathways. Collectively these mechanistic pathways joined like a jigsaw puzzle to give, for the first-time, a fully comprehensive cascade-like pattern for base-catalyzed halogen dance in its entirety. The present work may well shed light on a dynamic domino mechanism which dominates the realm of nonaqueous strongly basic medium, organic chemistry, reactions.

Keywords. Dynamic domino mechanisms; nonaqueous strongly basic medium; substituted heterocyclic; cascade-like pattern; disproportionation paths; base-catalyzed halogen dance.

1. Introduction

Halogen dance reactions have so far challenged the minds of such great chemists like Bunnet to speculate about the underpinning mechanism. Yet to the deeper aspect of these reactions is the realm of strong nonaqueous basic media,^{1,2} the niches of which still invites those who dare to step into uncharted territories. Aryl halides reactions in basic media have appeared in the literature with different names like halogen scrambling, halogen migration³, halogen isomerization, halogen dance, or base catalyzed halogen dance,⁴⁻⁶ which implies the lack of a consensus for the underpinning mechanism.

In 1971 Joseph F Bunnet *et al*, wrote an invaluable report⁴ on the so-called base catalyzed Halogen dance

reaction.^{7,8} The report revolutionized our understanding of the reaction, ruled out then accepted benzyne mechanism and has tagged the name *base catalyzed Halogen dance* to this beautiful synthetically versatile reaction so far.^{2,9-17} Hereafter the Halogen dance (HD) reaction is used. In this paper we try to propose a mechanism that can explain the so-called HD reactions in great detail for the first time, and that is the pseudo nucleophilic attack on a halogen electrophilic center also recently referred to as SN@X mechanism.¹⁸

Bunnet points out the reluctance of aryl halides to react in organic chemistry texts back then.⁴ And among the more advanced reaction mechanisms, he points out SNAr mechanism which includes Aryl lithium compounds. He also correctly predicts the domain of aryl

*For correspondence

Electronic supplementary material: The online version of this article (<https://doi.org/10.1007/s12039-020-01786-1>) contains supplementary material, which is available to authorized users.

halide reactions to be much more versatile. But even today, at a time when these reactions are being exploited by synthetic chemists the reaction is largely realized as a *cascade of deprotonation (metal–hydrogen exchange) and metal–halogen exchange reactions ultimately leading to the most stable organometal species*.¹⁹ However, to this chaotic maze there is order and to explain it is the main purpose here.

2. Computational methods

All computations were done at DFT-Cam-B3LYP/lanl2dz level of theory,^{20–26} using gaussian g09 package,²⁷ the reliability of basis set is already proven to yield very similar to results obtained with CCSDT coupled cluster configurational methods,^{28–33} in particular for halogens and their long-range contact be it of parallel or orthogonal X–X interactions. Long-range interactions are of special interest in this work. All of the TS configurations and in particular dihedral between the planes of the two benzene rings (see Table 2 column 8) are significantly controlled by these sorts of interactions. The chosen DFT-Cam-B3LYP/lanl2dz level of computation was of prime importance and was actually one of the most reliable cost-effective methods, used in our test runs to yield reproducible results for TS structures. The bond lengths were in cases slightly corrected at MP2/aug cc-pVTZ level of theory. Frequency computations were done for all TS structures to estimate the smoothness and dynamics of the TS formation (ongoing research in this part as to address issues on Tunneling and QM charge transfer effects in TS complexes are in progress and deserve a separate assessment and report when completed). To further evaluate the role of HOMO-LUMO gaps in resonance and polarizability,^{34,35} conjugate anions of some derivatives were also computed. In many of the mechanistic cycles directionality is judged based on the basicity and nucleophilicity double checked via polarizabilities as well, confirming the reliable geometries regarding the reported C–H bond lengths in Table 1. The C–Br bond lengths though show slight changes but are a perfect measure as to address the electrophilicity of Bromine centers, again due to the promising Cam-B3LYP/lanl2dz method and basis set combinations for halogen-containing compounds.

3. Results and Discussion

First we will be pointing out to two important aspects of HD reactions and delving into the jumble of reactions trying to paint the big picture at the end. We

would focus on bromobenzene derivatives to make the discussion disciplined. When going from 3,4 to 2,5 positions and also slightly when going from bromothiophene to its poly brominated derivatives, firstly the C–H acidity increases, and secondly the bromine substituents become more and more electrophilic and susceptible to strong nucleophilic attack forming bridged anionic Transition States (TS) as the main mechanistic feature in all HD reactions. An ideal candidate for HD reaction is a bromothiophene derivative that poses a good balance towards both deprotonation of H and attack on electrophilic Br as well. Such candidates, however, are neither the tetra brominated nor mono brominated derivatives, but the specially substituted cases where two traits can be maximally or minimally manifested. One such case is the thermodynamically stable 3,4 dibromothiophene with inactive bromines which act as a sink to terminate HD reaction cycles. Other such cases are the 2,3,5 tribromothiophene and fully brominated tetrabromothiophene derivatives with both H acidity and Br electrophilicity, and enough stability to make it more of a catalyst nature, feeding the frenzy dance of halogens in these reactions. The autocatalytic activity of fully brominated tetrabromothiophene is the main driving force in cases reported by Hannes Frohlich *et al* back in 1990.

Acidity increases as the C–H bond becomes shorter making the conjugate anion more stable, also a smaller C–Br would imply more resonance interaction between the bromine and the aromatic system (this is reflected in HOMO-LUMO gaps), which makes the bromine center more susceptible to nucleophilic attack. These trends are all listed in Table 1 for bromothiophene derivatives along with their relative energies. It is important to note that energies are reported as the sum of CH and CBr units in each derivative with reference to the most stable CH/CBr units. Monobromothiophene, tetrabromobenzene and 2,3,5 tribromothiophene were set as $X+S+4Y$, $4X+S+Y$ and $2X+S+2Y$ equations respectively, and solved for reference X, S and Y. Using such a scheme made energy comparisons among different derivatives meaningful. The same approach is also used for relative energies of TS structures were an extra variable Z was added for the bridging bromine atom.

One main feature of the TS structures in relation to parent bromothiophene derivatives is that each TS can break into two bromothiophene derivatives one at a time. Based on this each bromothiophene derivative is labeled with a letter and since it can be attacked at all bromine centers all Br atoms are numbered (Figure 1). Thus, each TS can be uniquely defined by a two-letter

Table 1. Properties of bromothiophene derivatives based on their abilities to produce potent amphiphilic anions

Bromothiophene derivatives	Most acidic C-H bond length (Å)	Most electrophilic C-Br bond length (Å)	Homo-Lumo gap (ev)	E _{rel} (kcal)
2 mono	1.0794	1.919.2	8.38	3.8
3 mono	1.0790	1.9350	8.51	1.2
2,3 di	1.0790	1.9110	8.23	1.8
2,4 di	1.0788	1.9161	8.21	1.2
3,4 di	1.0785	1.9270	8.45	0.0
2,5 di	1.0823	1.9170	8.05	3.5
2,3,4 tri	1.0786	1.9100	8.11	1.2
2,3,5 tri	1.0817	1.9097	7.94	2.1

Most acidic hydrogens and most electrophilic bromines are listed as well as HOMO-LUMO gap indicating most conjugate systems.

Table 2. Lower energy Bromobridged TS structures (20 out of 48 is being listed and higher energy TSs more than 17 kcal where all ruled out) All in SN@Br mechanism for a cast of bromothiophene reactions in basic media. Stabilizing factors, like the S-S interaction and Br guides leading to linear pseudo Br₃⁻ feature, has been listed.

Bromo bridged TS structures	Br bridge length (Å)	Br deviation from center (Å)	Linear pseudo Br ₃ ⁻ (Å)	Other Br-Br	S-S length (Å)	S-Br	Dihed angel (°)	E _{rel} (kcal)
c ₁ c ₂	4.594	0.417	–	0	8.350	0	96	7.5
e ₁ e ₂	4.524	0.319	–	2	8.199	2	109	6.7
b ₂ b ₃	4.582	0.472	7.995	0	8.209	1	0	5.1
a ₃ a ₁	4.581	0.453	7.842	0	8.373	1	173	4.5
a ₃ e ₂	4.592	0.474	–	2	9.814	0	122	10.1
d ₁ e ₂	4.544	0.393	–	2	8.266	2	103	7.1
a ₂ e ₂	4.529	0.309	–	4	9.757	0	91	9.7
a ₁ e ₁	4.518	0.343	7.835	0	7.036	2	169	1.0
c ₁ e ₁	4.620	0.591	–	0	7.080	1	142	0.0
e ₁ d ₁	4.584	0.526	7.944	0	7.102	2	169	1.4
fe ₂	4.593	0.516	–	0	8.504	1	180	8.2
b ₂ e ₂	4.579	0.456	7.844	0	9.866	0	180	10.2
a ₁ e ₂	4.487	0.038	–	1	8.187	2	108	6.0
he ₂	4.651	0.604	–	1	9.859	0	109	7.9
a ₂ e ₁	4.580	0.487	–	2	8.266	2	123	4.4
a ₃ e ₁	4.627	0.573	7.862	0	8.413	1	176	4.2
he ₁	4.681	0.674	7.946	0	8.458	1	175	1.8
fe ₁	4.632	0.612	–	0	7.035	1	133	2.8
b ₂ e ₁	4.622	0.569	–	1	8.245	1	100	5.2
c ₁ e ₂	4.582	0.489	–	0	8.480	1	180	5.4

code regarding the parent bromobenzene derivatives at both sides while the two number-subscript give the bridging Br locus on both sides, respectively.

With the brief description given so far, we are now prepared to discuss two trends starting with monobromo, tribromothiophene and di bromothiophene derivatives. And then move on to possible disproportionation reactions including dibromo derivatives. Which will then highlight the big picture out of the jumble of HD reactions in bromothiophene derivatives.

The isomerization of monobromo and tribromothiophene derivative is less noticed in the literature but it can fit well into the realm of HD reactions if proper catalysts like 2,4 dibromothiophene, *c*, and fully brominated tetrabromothiophene, *e*, are present in trace amounts respectively. The reaction mechanism is much like that of a photochemical radical reactions where a single radical can run a cycle over a thousand times before quenching (Figure 2). Here the TS and *c* or *e* are repeatedly used and reproduced while the isomerization closes completion. The direction of the

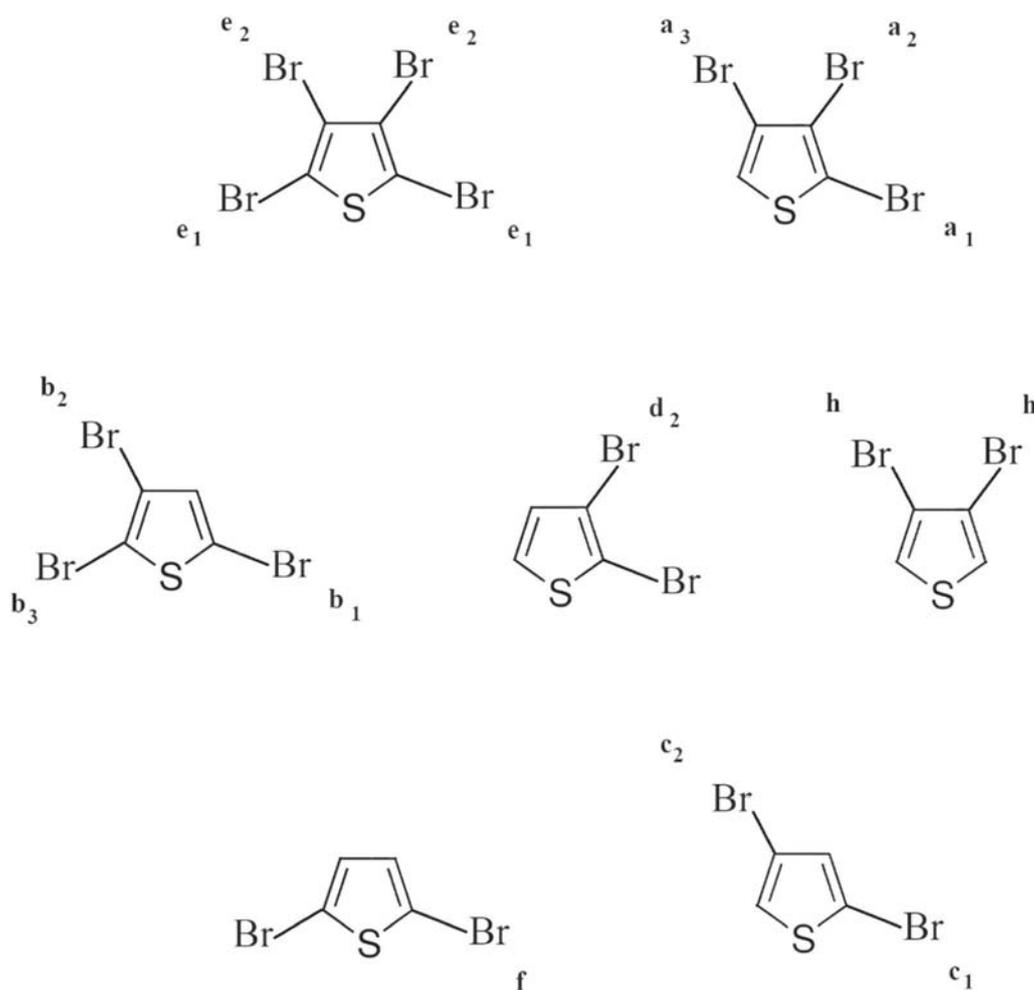


Figure 1. Donor acceptor moieties of $SN_{@}Br$ Intermediates labeled based on the bridged bromine atoms.

cycle depends on the basicity and nucleophilicity of the anions at the access points of the cycle. The more basic anion (marked MB) is protonated to form the product while the more nucleophilic anion (marked MN) will attack electrophilic bromines in the catalyst, here *c* or *e* to make TS and drive the cycle forward. The reactant is deprotonated to form the nucleophilic anion which then enters and isomerizes through the cycle into the final product.

In the case of dibromothiophenes both *a* and *b* can possibly serve as catalyst; however, *a* can only form high energy TS structures. And only TS structures having at least one *b*₂ moiety (two top cycles shown in Figure 3) are viable low energy mechanisms. TS structures involving *a* are all of high energies except for the one shown here which has low enough energy that could make it a mechanistic path. Figure 3 shows all the possible cycles with catalyst *b*, and on possible path involving *a*. These include 2,5 dibromothiophene (*f*) to 2,4 dibromothiophene (*c*) and 2,5 dibromothiophene (*f*) to 2,3 dibromothiophene (*d*) as well as 2,3

dibromothiophene (*d*) to 3,4 dibromothiophene (*h*) isomerizations. Energies of TS's as well as some other properties are listed in Table 2.

It becomes clear that for isomerization of a bromothiophene derivatives with *n* Br atoms a bromothiophene with *n*+1 Br can serve as catalyst among which *b* and *e* are the most active derivative capable of forming energetically favorable TS structures. A key point for a potential catalyst is thus, how good a source of electrophilic Bromine center the derivative is.

As can be clearly seen energetically favorable isomerizations are *f* to *c*, *f* to *d* and *d* to *h* as well. Among these isomerizations the first two are both kinetically favorable while the third one is a thermodynamically favorable transformation. It is also evident that *h* acts as a sink for HD reaction in bromothiophene derivatives. Figure 3 shows all the possible cycles for isomerization of dibromothiophene derivatives. Again, energies of TS's as well as some other properties are all listed in table 2.

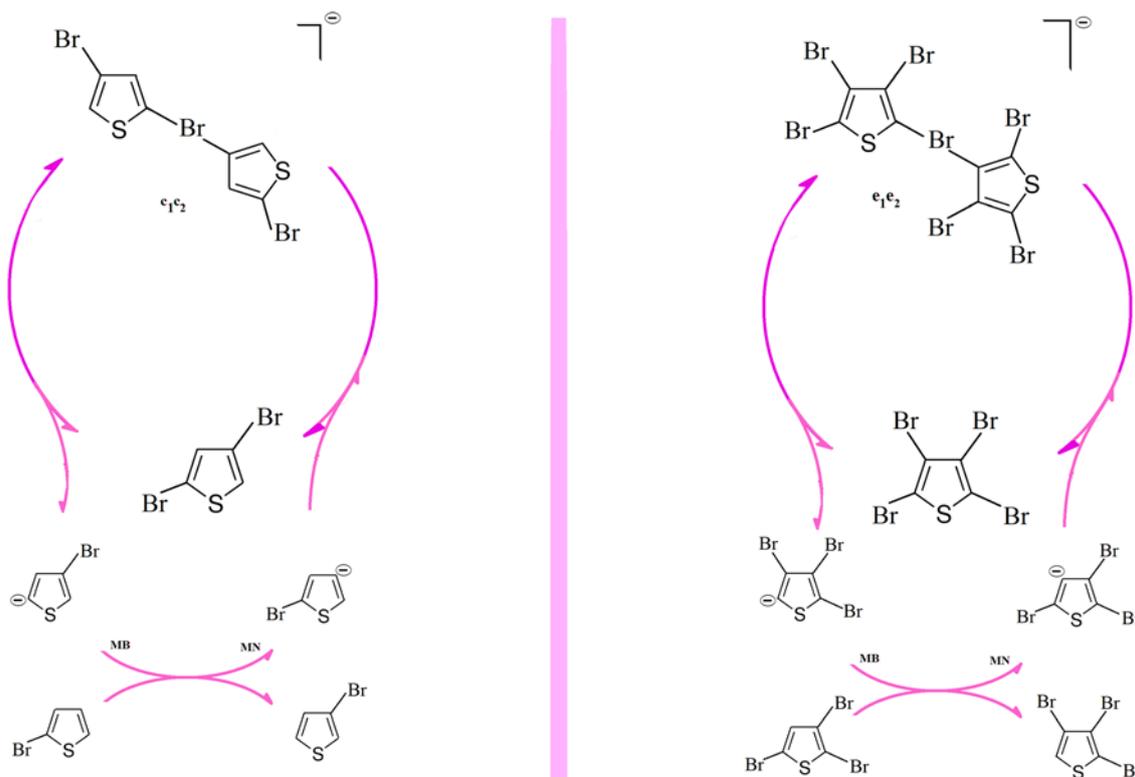


Figure 2. Possible monobromo and tribromo isomerization pathways via SN_{Br} mechanism, for dibromo thiophene derivatives.

AS mentioned in the beginning neither the fully brominated nor mono brominated derivatives are among the ideal candidate in driving the catalytic cycle in HD reactions; however, we have so far identified two potent such candidates in bromothiophene derivatives (*b* and *e*). And looking at tribromothiophenes at least eight possible pathways can be found that use two dibromothiophenes to yield a tribromothiophene along with a monobromothiophene derivative. These disproportionation reactions are the missing link in the trail to reveal the full pattern of HD reactions in bromothiophene derivatives. While only four of the most energetically favorable cycles are provided here (Figure 4). Interested readers can refer to SI for a detailed account on all eight possible pathways (see SI). Considering the disproportionation pathways the evident product of them is the catalytically active kinetically stable 2,3,5 tribromothiophene, *b*, which serves as kind of a lynchpin around which the frenzied halogen dance reactions took place. Before moving on to the full pattern however, some structural features of TS structures are also worth more elaborate attention. The first feature is the donor acceptor distance in the bromo bridged intermediate, and with it the deviation of bridging Br from the exact center. While comments of Br tunneling in these species are only reported for electron transfer reactions there

seems to be a clear relation of DAD and energy. This relation generally means an ideal DAD can be found as shorter and shorter contacts are reached and then a sharp rise is observed after a limit. The deviation from the center is also hard to achieve, there is a more deviation when C-Br strength is greatly different in both sides. Thus, one evident pattern of these HD reactions is their reversibility and that no perfect completion can be reached. Three Br-Br interactions are also considered here. While no single stabilizing feature can stand out interactions involving sulfur are likely to play a big role as both the S-S and S-Br interactions seem to stabilize the TS to a good extent. Linear alignment of two Br on both ends with the central bridging Br to form a pseudo Br_3^- linear substructure if present will further stabilize the TS structure. Other Br-Br interactions of orthogonal or at least nonlinear nature seems to play a minor role in stabilizing the TS structures. The number of TS structures are more than listed here and ongoing research is in progress to fully analyze all the data and in more depth, to fully understand these TS structures and their dynamics.

In the big pattern of HD reactions of bromothiophene derivatives (Figure 5) the dibromothiophene (*f*) take two upstream reactions yielding *c* and *d*, while *d* takes a main stream reaction all the way to *h*. There

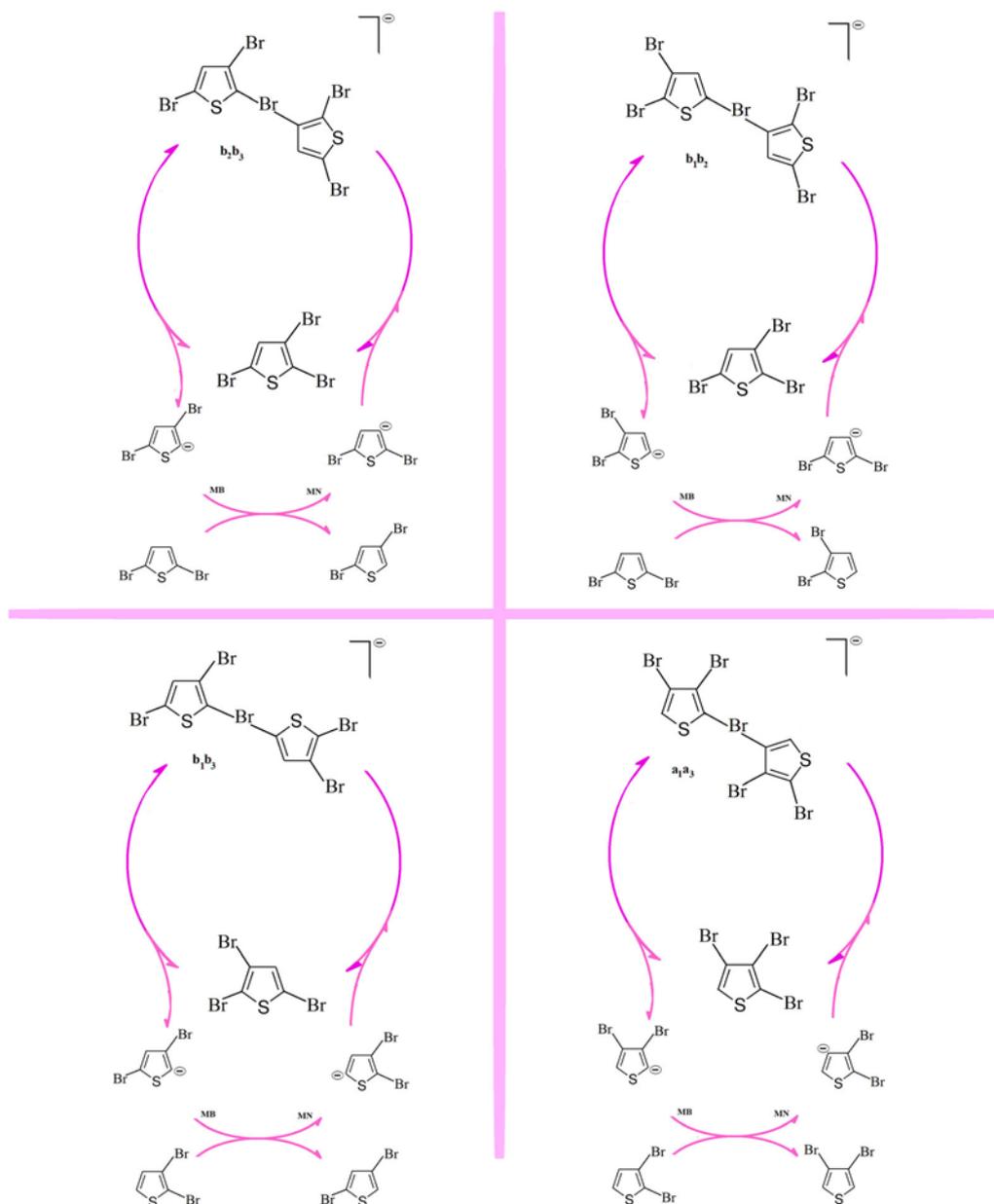


Figure 3. Possible isomerization pathways via $\text{SN}_{\text{a}}\text{Br}$ mechanism, for dibromo thiophene derivatives, used in various synthetic strategies to heterocyclic compounds.

are two downstream reactions with monoiodothiophene and tribromothiophene isomerizations leading to 3-monobromothiophene and 2,3,4 tribromothiophene (**a**). There are also three main stream reactions with dibromothiophene isomerizations all leading to the same products (3-monobromothiophene and 2,3,4 tribromothiophene (**a**)). These latter products then drain the cascade to the stable 3,4 dibromothiophene, **h**, derivative that plays the role of a chemical sink in these HD reactions.

The full picture with all its seemingly chaotic pathways and cycles of HD reactions present an ordered intricately connected maze that serves to convert 2,5

dibromothiophene (**a**) to 3,4 dibromothiophene (**h**) in its entirety. Three of the most stable computed TS structures also shown in Figure 6. Not all of these TS structures are kinetically viable based on H acidity and Br-nucleophilicity. See SI for full structurally possible pathways in dibromothiophene derivatives.

4. Conclusions

To summarize the present work tried to present a detailed mechanism of Halogen Dance, HD, reactions in bromothiophene derivatives based on the bromo-

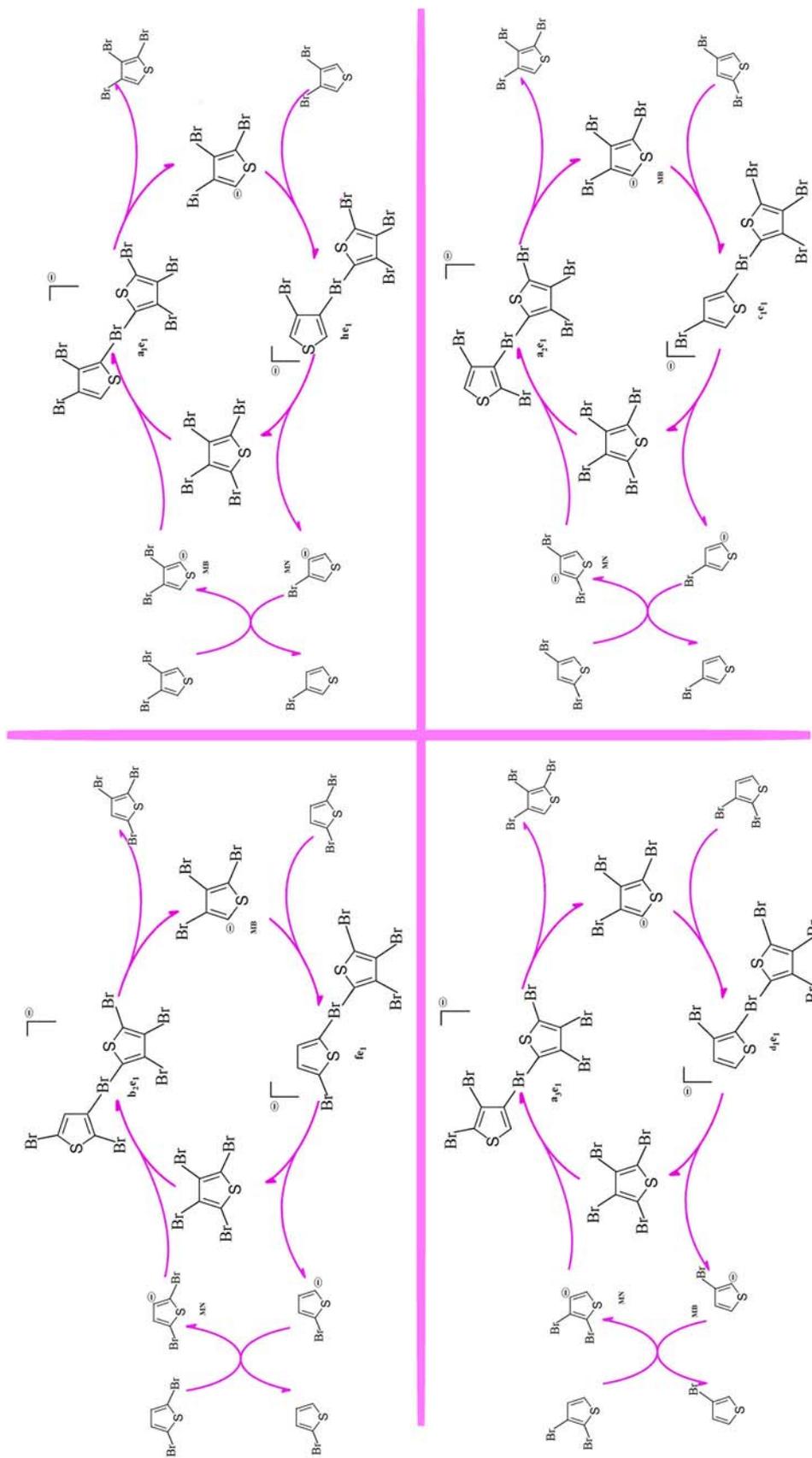


Figure 4. The most energetically favorable SN_@Br pathways for disproportionation of di bromothiophene derivatives yielding mono and tri bromothiophene products.

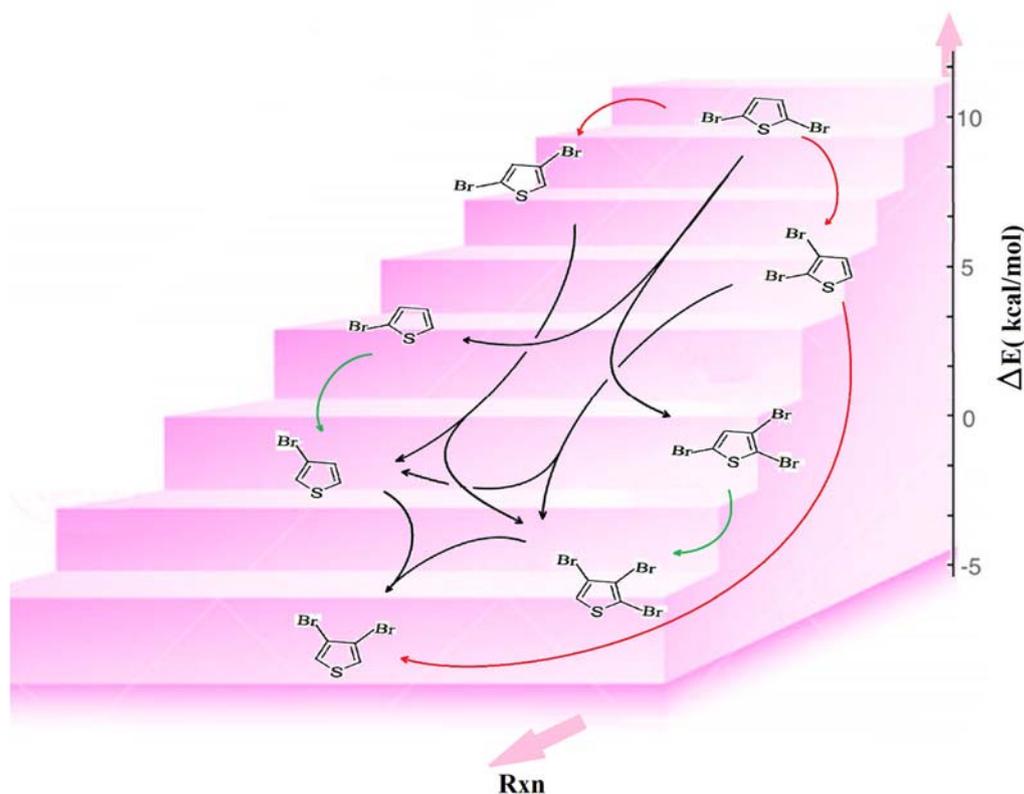


Figure 5. Cascade like reaction Coordinate for halogen dance in bromothiophene derivatives moving away from 2/5 substituents into 3/4 substituents. Dibromo isomerizations are shown in red, tribromo and monobromo isomerizations in green while, disproportionations are shown in black.

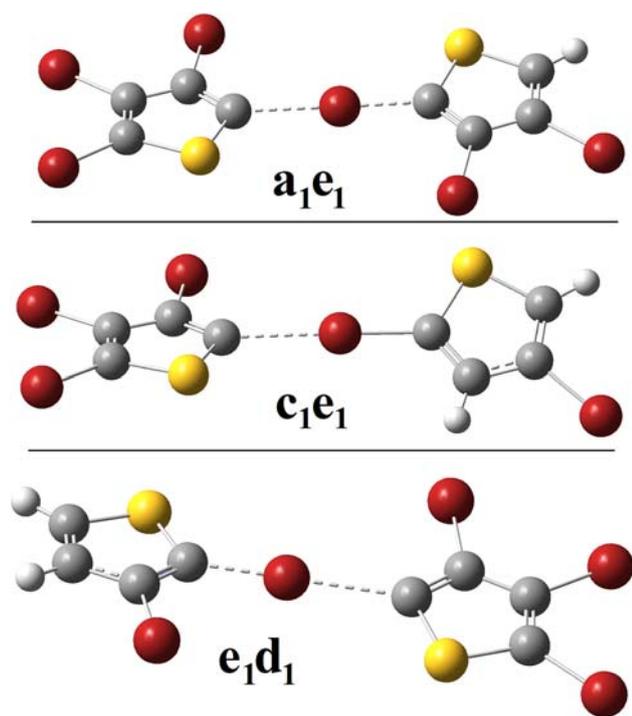


Figure 6. Three of the most stable TS structures. Not all of the three are kinetically formed based on H acidity and Br-nucleophilicity. See SI for full structurally possible pathways in di bromothiophene derivatives.

bridged transition state, TS, in lieu of all other mechanism. Bromo-bridged transition states can fully explain a cast of HD reactions. The basic concepts that are the main cornerstones of the suggested mechanism are acidity of aromatic C-H's and electrophilicity of aryl Bromides on their Br atoms. A resonance interaction with rather strong effects on C-Br bond lengths determines such electrophilic nature. The catalytic cycles not only include all previously reported HD reactions like the Hannes Frohlich type isomerization but well expand beyond them. The findings also suggest substantial autocatalytic activity for derivatives like 2,3,4 tribromothiophene or tetrabromothiophene, *b* and *e* respectively. Such catalytic edge is gained by a delicate balance between H acidity and Br electrophilicity which endows both, *b* and *e* a kinetic stability as well as their auto catalytic activity. Features of the TS structures are closely examined and a combined S-S and S-Br interaction seems to stabilize the TS. For the first time a full patterned trend of HD reactions is presented for bromothiophene derivatives. Further studies can illustrate the properties and dynamics of bromo-bridged structures that are shown to be at the heart of halogen dance reactions in this paper. Such studies could ultimately pave the path

toward a deeper more detailed understanding of reactions in strong nonaqueous basic media in organic chemistry, and shall guide synthetic chemists with a road-map to design and practice newer more efficient synthetic approaches in years to come.

Supplementary Information (SI)

Figures S1–S2, Z-Matrices and Table S1 are available at www.ias.ac.in/chemsci.

References

- Mubarak M S and Peters D G 1996 Electrochemical reduction of mono- and dihalothiophenes at carbon cathodes in dimethylformamide. First example of an electrolytically induced halogen dance *J. Organic Chem.* **61** 8074
- Fröhlich J 1994 *Substituted Heterocyclic Compounds by Selective Control of Halogen-Dance Reactions* H Suschitzky and E F V Scriven (Eds.), *Progress in Heterocyclic Chemistry* Vol. 6. (Elsevier) Ch. 1 p. 1
- Bailey W F and Patricia J J 1988 The mechanism of the lithium-halogen interchange reaction: A review of the literature *J. Organometallic Chem.* **352** 1
- Bunnett J F 1972 Base-catalyzed halogen dance, and other reactions of aryl halides *Acc. Chem. Res.* **5** 139
- Duan X-F and Zhang Z-B 2005 Recent progress of halogen-dance reactions in heterocycles *Heterocycles* **65** 2005
- Schlosser M 2005 The 2×3 toolbox of organometallic methods for regiochemically exhaustive functionalization *Angew. Chem. Int. Edit.* **44** 376
- Vaitiekunas A and Nord F 1951 Tetrabromothiophene from 2-bromothiophene by means of sodium acetylide in liquid ammonia *Nature* **168** 875
- Vaitiekunas A and Nord F 1953 Studies on the chemistry of heterocyclics. XXII Investigations on the mechanism of reactions of 2-thienyl halides with sodium amide and sodium acetylide in liquid ammonia *J. Am. Chem. Soc.* **75** 1764
- Stangeland E L and Sammakia T 2004 Use of thiazoles in the halogen dance reaction: application to the total synthesis of WS75624 B *J. Organic Chem.* **69** 2381
- Sammakia T, Stangeland E L and Whitcomb M C 2002 Total synthesis of caerulomycin C via the halogen dance reaction *Organic Lett.* **4** 2385
- Fröhlich J, Hametner C and Kalt W 1996 Synthesis of trisubstituted thiophenes via a halogen dance reaction at 2-bromo-5-methylthiophene *Monatsh. Chem.* **127** 325
- Getmanenko Y A, Tongwa P, Timofeeva T V and Marder S R 2010 Base-catalyzed halogen dance reaction and oxidative coupling sequence as a convenient method for the preparation of dihalo-bisheteroarenes *Organic Lett.* **12** 2136
- Stanetty P, Schnürch M, Mereiter K and Mihovilovic M D 2005 Investigations of the halogen dance reaction on N-substituted 2-thiazolamines *J. Organic Chem.* **70** 567
- Vinicius Nora de Souza M 2007 Halogen dance reaction and its application in organic synthesis *Curr. Organic Chem.* **11** 637
- Schnürch M 2011 *Recent progress on the halogen dance reaction on heterocycles*. In *Halogenated Heterocycles* (Springer) pp. 185–218
- Miller R E, Rantanen T, Ogilvie K A, Groth U and Snieckus V 2010 Combined Directed ortho Metalation—Halogen Dance (HD) Synthetic Strategies. HD—Anionic ortho Fries Rearrangement and Double HD Sequences *Organic Lett.* **12** 2198
- Gakh A A and Tuinman A A 2001 ‘Fluorine dance’ on the fullerene surface *Tetrahedron Lett.* **42** 7137
- Donham L L and Gronert S 2019 Substitution reactions on iodine and bromine—mechanisms for facile halogenations of heterocycles *J. Organic Chem.* **84** 5757
- Schnürch M, Spina M, Khan A F, Mihovilovic M D and Stanetty P 2007 Halogen dance reactions—A review *Chem. Soc. Rev.* **36** 1046
- Wang D, Lü R, Yuan M, Fu A and Chu T 2014 A DFT/TD-DFT study of thiazolidinedione derivative in dimethylformamide: Cooperative roles of hydrogen bondings electronic and vibrational spectra *Spectrochim. Acta Part A* **125** 131
- Bouzzine S, Salgado-Morán G, Hamidi M, Bouachrine M, Pacheco A G and Glossman-Mitnik D 2015 DFT study of polythiophene energy band gap and substitution effects *J. Chem.* **2015** 296386. <https://doi.org/10.1155/2015/296386>
- Torii H and Yoshida M 2010 Properties of halogen atoms for representing intermolecular electrostatic interactions related to halogen bonding and their substituent effects *J. Comput. Chem.* **31** 107
- Lu Y X, Zou J W, Fan J C, Zhao W N, Jiang Y J and Yu Q S 2009 Ab initio calculations on halogen-bonded complexes and comparison with density functional methods *J. Comput. Chem.* **30** 725
- Carrera E I and Seferos D S 2015 Efficient halogen photoelimination from dibromo dichloro and difluoro tellurophenes *Dalton Trans.* **44** 2092
- Lu Y, Zou J, Wang H, Yu Q, Zhang H and Jiang Y 2005 Triangular halogen trimers A DFT study of the structure, cooperativity, and vibrational properties *J. Phys. Chem. A* **109** 11956
- Siiskonen A and Priimagi A 2017 Benchmarking DFT methods with small basis sets for the calculation of halogen-bond strengths *J. Mol. Model.* **23** 50
- Gaussian G. 09, Revision A. 02, MJ Frisch, GW Trucks, HB Schlegel, GE Scuseria, MA Robb, JR Cheeseman, G. Scalmani, V. Barone, B. Mennucci, GA Petersson, H. Nakatsuji, M. Caricato, X. Li, HP Hratchian, AF Izmaylov, J. Bloino 2009
- Forni A, Pieraccini S, Rendine S, Gabas F and Sironi M 2012 Halogen-Bonding Interactions with π systems: CCSD (T), MP2, and DFT calculations *ChemPhysChem* **13** 4224
- Kolar M H and Hobza P 2016 Computer modeling of halogen bonds and other σ -hole interactions *Chem. Rev.* **116** 5155
- Mitin A V and van Wüllen C 2006 Two-component relativistic density-functional calculations of the dimers of the halogens from bromine through element 117 using effective core potential and all-electron methods *J. Chem. Phys.* **124** 064305
- Sedlak R, Riley K E, Řezáč J, Pitoňák M and Hobza P 2013 MP2.5 and MP2.X: approaching CCSD

- (T) quality description of noncovalent interaction at the cost of a single CCSD iteration *ChemPhysChem* **14** 698
32. Kato M, Hada M, Fukuda R and Nakatsuji H 2005 Relativistic configuration interaction and coupled cluster methods using four-component spinors: Magnetic shielding constants of HX and CH₃X (X= F, Cl, Br, I) *Chem. Phys. Lett.* **408** 150
 33. Liakos D G, Hansen A and Neese F 2010 Weak molecular interactions studied with parallel implementations of the local pair natural orbital coupled pair and coupled cluster methods *J. Chem. Theory Comput.* **7** 76
 34. Pearson R G 1986 Absolute electronegativity and hardness correlated with molecular orbital theory *Proc. Nat. Acad. Sci.* **83** 8440
 35. Duxbury D F 1993 The photochemistry and photophysics of triphenylmethane dyes in solid and liquid media *Chem. Rev.* **93** 381