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Understanding the Crystalline Formation of Triazene N-Oxides and the Role of Halogen $\cdots \pi$ Interactions

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ABSTRACT

The crystallization of a series of 1-(4-halophenyl)-3-phenyltriazenide N1-oxides (1-4) and 1-(phenyl)-3-phenyltriazenide N1-oxide (5) were evaluated using the supramolecular cluster approach. This method was an efficient tool to assess the crystallization mechanism of compounds and, consequently, the steps involved in crystal formation. Compounds 1 and 4 show crystallization in two main steps while compounds 2 and 3 present three main steps, in which column formation occurs in the first step. The crystallization process for 5 occurs in 3 main steps, starting from a robust dimer formation (-16.82 kcal mol⁻¹). Two new parameters – N_{CG}% (topological and energetic contribution percentage) and NG/NC (energetic parameter/topological parameter ratio) - assisted in the interpretation of crystal growth. Compounds 1-4 showed N_{CG} % = 50 in the first step while compound 5 only reached 50% of contribution in the second step. The differences in N_{CG} % were attributed to strong hydrogen bonds in the non-halogenated compound. The dominant parameter in each step of the crystallization process was indicated by the NG/NC parameter. The crystallization mechanism in all compounds was initially driven by an energetic process followed by a topological process. It was showed the existence of the X $\cdots\pi$ interactions and observed as a consequence of a topological process and without any major contributions to crystal formation. Thermal analysis and UV-Vis spectral data were also discussed regarding the properties of these compounds.

INTRODUCTION

The understanding of crystalline networks requires the use of certain parameters in order to understand the interactions that form the system. The geometric parameter has been a widely used tool for describing intermolecular interactions, including halogen interactions.^{1,2} Recognizing interactions helps elucidate the crystallization processes of different molecules whose final goal is to correlate characteristics of this process with final emergent properties. However, a broad approach using topological and energetic data parameters in addition to geometric data for the study of crystals remains scarce in the literature.

According to Kitaigorodskii³, the assembly route of molecules to crystals is governed by molecules approaching each other to form the first close-pack, which are then close-packed by other layers or chains of molecules. Because of this, the crystallization process can be viewed as a stepwise progression in which molecule association increases system complexity, leading to the final 3D crystal. This progression occurs analogously to Darwinian evolution⁴, where the process of selforganization blends competition, cooperation, and complementarity. The Darwinian process improves individual organization, which leads to the emergence of the crystalline arrangement.

Following this idea, our research group proposed a method in a previous study⁵ where crystallization mechanisms for isoxazoles were presented in order to better understand crystalline formation. This proposal was based on the observation of the energetic contributions of different dimers that formed the crystal and used the supramolecular cluster as portion of the study. Our findings show that the supramolecular cluster has an energetic hierarchy related to the formation of interactions; in that case, the hydrogen bond was the strongest interaction and the first to form. The π -interactions, on the other hand, were weaker and observed in other steps of the crystallization.

*T*riazene*1*-Oxide derivatives are an important class of molecules due to the hard basicity character of the coordinating atoms O and N. This characteristic imposes electronic properties that allow molecular self-organization via intermolecular secondary interactions⁶. These species have different applications in chemistry and biology, such as in sensors, electronic displays^{7,8}, as well as in antileukemic and anticancer drugs^{9,10}. Some of these applications are a result of non-covalent intermolecular interactions and the packaging behavior of these compounds.

Therefore, our aim is to assess the comprehension of the system by studying the analysis of crystal formation while considering the topological and energetic normalized data of the supramolecular cluster as a tool. In pursuance of this, a series of five *I*-oxide triazene was used, in addition to the proposal of crystallization mechanisms for each system in order to observe the contrasts between different substituents. Important information regarding the contribution of each crystallization step will be provided. This will be done by observing the dominant parameter of the process in addition to observing the influence of halogen… π interactions to crystal formation. Geometric and QTAIM data were used to answer the questions on the role of halogen… π interactions in crystal formation. Additionally, thermal analyses (TGA and DSC) and UV-Vis spectroscopy were carried out to determine the potential applications of these molecules.

RESULTS AND DISCUSSION

Molecular description

Crystals suitable for X-ray single crystal analysis of compounds **1-5** were obtained from the respective solutions by means of crystallization through slow evaporation of the solvent. Figure 1 shows the molecular structures of the compounds. Crystallographic data are shown in Table 5 and additional data regarding bond lengths (Å) and angles (°) are demonstrated in Table S1 (ESI[†]).



Figure 1. Projection of the molecular structures of compounds **1** to **5**. H atoms are represented with arbitrary radii. Non-hydrogen atoms are represented with thermal ellipsoids at the 50% probability level.

All compounds discussed in this study belong to the class of triazene N_1 -oxides, such as derivatives from the classical triazenes, in which the double-bonded terminal Natom in the nitrogen triad is substituted by an "oxo" group in the solid state. In solution, these compounds are in a chemical equilibrium with the respective tautomer form in which the *oxo* group is protonated resulting in a *hydroxyl* functional group. The diazo(oxide)amine [-N=N(\rightarrow O)-N(H)-] functional group can be stabilized by substitution of the terminal N atoms with alkyl, phenyl, or aryl substituents. In the present study, 1-phenyl-3-*para*-halophenyl (*p*-F, *p*-Cl, *p*-Br and *p*-I) substitution was selected in view of the comparison of its crystallographic features with that of the unsubstituted 1,3-*bis*(phenyl)triazene N_1 -oxide.

Compound 1 belongs to a monoclinic crystal system in a primitive three-dimensional lattice corresponding to *Bravais* type *P* and chiral space group $P2_1$ (*Z*=2; *Z*'=1). Given that compound 1 does not present a heavy atom with anomalous scattering, we were unable to determine its absolute configuration. Thus, the selected molecular

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configuration was based on the lowest Flack value observed, which was 0.1(3). An attempt to solve the structure considering the centrosymmetric space group $P2_1/m$ in comparison with the acentric space group $P2_1$ was fruitless. Compounds 2 and 3 are isostructural and belong to the centrosymmetric monoclinic space group $P2_1/c$ (Z = 4; Z' = 1). Compound 4 belongs to the orthorhombic and chiral $P2_12_12_1$ space group (Z=4; Z=1), and its molecular configuration was selected based on the lowest Flack value observed, which was 0.048(18). Compound 5 crystallizes in the centrosymmetric monoclinic space group $P2_1/n$ (Z=4; Z'=1). All molecules present the expected trans stereochemistry regarding the N=N double bond in the [-N=N(\rightarrow O)-N(H)-] diazoamine N₁-oxide moiety and an almost planar shape. Molecules 1-5 deviate slightly from planarity [r.m.s. deviation from the least-squares plane through the non-hydrogen atoms: 0.0857 Å (1), 0.0353 Å (2), 0.0318 Å (3), 0.0466 Å (4), 0.0468 Å (5), respectively]. The N13-N12-N11-O dihedral angle in the molecules {[$-0.3(2)^{\circ}(1)$], [$-0.9(4)^{\circ}(2)$], [$-1.1(4)^{\circ}(3)$], [$1.4(12)^{\circ}(4)$] and [$0.5(3)^{\circ}(5)$], respectively]} are similar to the angle [N13-N12-N11-O1 = $0.7(5)^{\circ}$] found in 3phenyl-1-methyltriazene 1-oxide, and contribute to the near-planar conformation of the molecules¹¹. The average value of 1.295 Å for the N11-O bond distance observed in the molecules 1 to 5 (ESI \dagger , Table S1) is in agreement with the N11-O1 bond distance of 1.246(4) Å observed in the similar compound 3-phenyl-1-methyltriazene 1-oxide, which indicates that the molecules adopt the N-oxide tautomeric form in the solid state¹¹. The angles between the planes of the rings presented values of 10.32, 3.01, 2.16, 5.93, and 3.53 for 1 to 5, respectively. These values are a result of the influence of the crystal packing on the different intermolecular interactions of each structure.

Supramolecular cluster

The supramolecular cluster approach¹² - grown from the neighboring molecules around a reference molecule (M1) - was used to obtain information on the contact surface (topologic parameter) and energy of interaction (energetic parameter) between the molecules in the crystalline arrangement of each structure (see ESI[†], Figures S2-S7 and Tables S2-S6). The cluster was speculated since we are considering a 3D portion of the crystal that provides all the necessary information of the involved

interactions in the whole crystal. This method can assess the understanding of crystal formation without neglecting molecules that are important to the system.

The neighboring molecules around M1 represent the molecular coordination number (MCN). These dimers are represented by the interaction between the M1 and MN molecules (*e.g.*, M1····M2, M1····M3, ..., M1····M15). All molecules which share surface contact area of the van der Waals radii with the reference molecule M1 are considered part of the cluster. The supramolecular cluster with the surface contact area of each dimer was obtained using the Voronoi-Dirichlet Polyhedra (VDP) with the ToposPro 4.0 software¹³. This method has already been reported^{5,14–16} as an efficient tool to assess crystalline understanding, especially regarding the steps involved in crystal formation, *i.e.* the crystallization mechanism⁵.

The different supramolecular clusters can be compared by the normalization¹² of raw topological and energetic data in order to observe the distinct behavior of the dimers in the formation of each crystalline structure. Normalization is a tool that places all the different data in the same scale, allowing precise comparisons and interpretations of different systems. Hence, all N molecules in the cluster contribute in some way to the whole system, and it is necessary to assess the contribution of each one in relation to a standard, in our case, in relation to the number of molecules present in the cluster (around reference molecule M1).

For example, in a cluster with an MCN of 16, all dimers must have an ideal contribution of 1 for all considered parameters (*e.g.* energy), which leads to a 100% contribution of 16. However, this is not the reality of most molecules where distinct interactions occur, leading to different dimeric contributions. Therefore, all raw data should be reduced to the same scale using the MCN as reference for this normalization.

From normalized values, intermolecular interactions can be divided into four types¹². Type I represents a molecular dimer with high interaction energy on a small contact surface (*e.g.* hydrogen bonds). Type II corresponds to high interaction energy on a large contact surface (*e.g.*, $\pi \cdots \pi$ interactions). Type III corresponds to both small interaction energy and contact surfaces with a maximum difference of \pm 0.5 between the both parameters, and Type IV is a contribution based on large contact surfaces with low interaction energy.

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Topological and energetic normalized data of each dimer from the supramolecular cluster of compounds 1, 2, and 5 (for 3 and 4, see ESI[†], Figure S1) with the respective dimer classification are described in Figure 2.



Figure 2. Topological and energetic normalized data of each dimer from the supramolecular cluster of compounds 1, 2, and 5.

Figure 2 demonstrates that compound **1** has two type-I dimers and two type-II dimers, which corresponds to dimers involved in hydrogen interactions and stacking, respectively. The remaining dimers exhibited a type-III behavior with low area and energy values. Notably, data from compound **1** is similar to data from compound **4** (see ESI[†], Figure S1). Compound **2** (for compound **3**, see ESI[†], Figure S1) had only one dimer with type I behavior and one dimer with type II, which is different from what was observed in compounds **1** and **4**. These data provide important information on the formation of the crystalline structure, especially concerning the first dimers formed (the most energetic ones). Finally, compound **5** displayed a distinct characteristic when compared to compounds **1-4**. The supramolecular cluster only presented one type-I dimer of the highest energetic contribution of all systems, and

two type-II dimers with lower contribution regarding stacking interactions when compared to 1-4. This normalized data approach provides significant data of the characteristics of the dimers and enables the understanding of the crystal formation, which is discussed in the following section.

Crystallization mechanism

Since crystallization is a stepwise process that takes into account energy hierarchies, crystallization mechanisms have been proposed for a series of compounds in order to understand crystal formation. The normalized data previously presented was used to assess the proposed crystallization mechanism⁵ for each structure. The main difference between these proposed mechanisms and the earlier study³ is that the normalized values were used in all steps and in the interpretation of the mechanisms.

Firstly, individual dimer data regarding stabilization energy was used to define the highest and lowest dimer hierarchies in order to assess the steps of crystal formation. Then, the main steps were defined, where in some cases more than one hierarchy is present in the same crystallization step. The proposed crystallization mechanism for compounds **1**, **4**, and **5** are presented in Figure 3, 4, and 5.

Once the main steps were determined, we returned to the data of the normalized dimer in order to obtain two main parameters to assess the elucidation of the process:

- The topological and energetic contribution for each step of the crystal growth. The percentage of contribution (N_{CG}%) from each given step can be found by the sum of the normalized topological and energetic data (NC+NG) of each step. As a result, we are able establish the steps with the highest contribution for both parameters, *i.e.* surface area and energy. The step contribution can indicate where the definitive step towards the considered crystalline structure is.
- The ratio between NG and NC to find the parameter that rules each step. The NG/NC provides important information on the governing parameter in each step, in which values over 1.0 indicate higher energetic contribution and values under 1.0 indicate dominant topologic parameter. Values near 1.0 indicate a balance between parameters. Thus, it is possible to inform where the changes between the dominant parameters occur.

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Figure 3 presents the steps of the crystallization mechanism for compound 1. Compound 4 also presents the same general steps, and an illustration can be found in the ESI† (Figure S8). The cluster molecules involved in the steps were depicted and its normalized energy values were highlighted.



Figure 3. Proposal of crystallization mechanism of compound **1**. NG = normalized energy. The shaded area represents the portion in the previous step.

The proposal of the crystallization mechanism for structures **1** and **4** shows two major steps (Figure 3). The first step occurs with the formation of interconnected columns by hydrogen interactions with stabilization energy of -9.78 kcal mol⁻¹ (NG = 2.99) for each of the two dimers involved and energy of -8.85 kcal mol⁻¹ (NG = 2.71) for the molecule stacking of each dimer. The dimers involved in this step present the highest portion of surface contact area and stabilization energy in relation to the whole supramolecular cluster (see Figure 2). This step contributes 53.4% to crystal formation when both stabilization energy (NG) and surface contact area (NC) are considered, namely the topological and energetic parameters are taken into consideration in the final contribution (N_{CG}%).

Step 2 presents the final crystal formation (3D growth) with the interaction between the columns formed in step 1. These dimer interactions occur when stabilization energy is below -2.7 kcal mol⁻¹ (NG < 0.83). However, despite the higher number of dimers involved, the remaining 46.6% of topological and energetic contribution for the crystallization mechanism is occurs to form the 3D network.

A value of 1.46 was found for the first step, regarding the second parameter (NG/NC), which indicates a strong impact from the energetic parameter in this step of crystal growth, *i.e.* almost 50% more influence than the topologic factor. Moreover, a value of 0.65 was found for the second step, demonstrating a change in the dominant parameter in this step of the crystallization where topology plays a more relevant role than stabilization energy.

Compounds 2 and 3 present similar clusters with isostructural behavior, which leads to identical proposals of crystallization mechanism. Figure 4 depicts the mechanism of compound 2 (for compound 3, see ESI[†], Figure S9).



Figure 4. Proposal of the crystallization mechanism of compound 2. NG = normalized energy. The shaded area represents the portion in the previous step.

There are three main steps in the proposal of crystallization mechanism for compounds **2** and **3**. In the first step, the two main energetic dimers form the displaced columns. The dimer involved in a hydrogen interaction of -15.17 kcal mol⁻¹ (NG = 3.31) and the stacking dimer -13.65 kcal mol⁻¹ (NG = 2.98). Two dimers from

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the supramolecular cluster with stabilization energy of -4.48 kcal mol⁻¹ (NG=1.96) appear in this step due to the formation of the displaced columns. The dimers considered in the first step had a N_{CG} % of 54.6%, indicating that this first step is a point of no return for the crystal since over 50% of all stabilization energy and surface contact area of the crystal rely on this first step.

The second step is the interaction between the columns (formed in step 1) with interaction energy of -6.34 kcal mol⁻¹, which leads to the 2D growth of the crystal. In this step, crystallization is increased by a N_{CG}% of 9.6%. Finally, the third step is responsible for the formation of the 3D crystal network. In this final step, the 2D columns interact through dimers with lower stabilization energy below -3.2 kcal mol⁻¹ (NG < 0.69). This final step represents the remaining 35.8% of the topological and energetic contribution. The NG/NG parameter presented values of 1.17, 1.06, and 0.77 for the first, second, and third steps, respectively. These data demonstrate the evolution of the dominant parameter through the crystallization process with a slight dominance of the stabilization energy in the first step, and the subsequent rise of topological governance in the other two steps.

Figure 5 demonstrates the proposal for the crystallization mechanism of compound **5**, which differs from the other supramolecular structures.



Figure 5. Crystallization mechanism of compound **5**. NG = normalized energy. The shaded area represents the portion in the previous step.

The first step for compound **5** (Figure 5) differs from the previous compounds due to the formation of a dimer with a robust stabilization energy of -16.82 kcal mol⁻¹. The

normalized data (NG = 4.49) shows the magnitude of this dimer with a value four and a half times greater than expected, which represents a strong hydrogen interaction. This first step corresponds to 19.2% of contribution of the whole crystal, even though it is only one dimer. The second step is the stacking interaction of these dimers in order to form columns with stabilization energy of -9.44 kcal mol⁻¹ (NG = 2.52) and -3.89 kcal mol⁻¹ (NG = 1.04). At this moment, there is an increase of 37% in contribution. The third step is similar to that of compounds 1 and 4, where the columns interact with each other with energies below -2.6 kcal mol⁻¹ (NG < 0.69) in order to form the 3D crystal lattice. The last step contributes with a N_{CG} % of 43.8. The crystallization behavior of this structure differs from the others in the contribution of each step, since there is a unique first step with a strong hydrogen interaction between the two molecules. The G/C ratio showed values of 2.72, 1.05, and 0.63 for steps 1, 2, and 3, respectively. This data clearly demonstrates the transition between the dominant parameter in each step. The first step with high energy in a smaller surface area had a value almost three times higher, thus, highlighting the importance of the energetic parameter. The transition in the dominant parameters in the second step indicated a balance between the surface and energy parameters. The last step, due to the presence of lower stabilization energies in column approximation, was highly influenced by the topological parameter.

For better visualization, the three proposed mechanisms of crystallization for compounds **1-5** are summarized in Figure 6.



Figure 6. Summary of crystallization steps for compounds 1-5 with the topologic and energetic contribution (N_{CG} %). NG/NC parameter is also demonstrated for each stage.

The data presented in Figure 6 shows the main event in each step for compounds 1-5 until 3D crystal growth. In each step, the combined contribution considering topological and energetic parameters is described in order to have a comprehensive view of the steps in all the studied supramolecular structures. Compounds 1-4 had contributions of over 50% in the first step. Compound 5, which formed a strong first dimer, only reached a contribution of 50% when the first and second stages were considered. However, it is possible to state that the first dimer is formed irreversibly, since the hydrogen interaction formed corresponds to almost 20% of the entire interaction energy of the crystal.

The NG/NC parameter allows us to observe the transition between the dominant parameter during the crystallization process. Compounds **1-5** behaved similarly during the steps, in other words the first dominance of the stabilization energy of the interactions involved in the considered dimers, its subsequent decrease, and the increase of the topological relevance to the crystal growth. The final step of the crystallization process relies almost exclusively on a topological dependent process.

Thus, based on such findings, differences between the angles of the rings in each structure mentioned in the molecular description section can be better understood. Compounds 1 and 4 have the highest angles, which is unexpected due to the differences between F and I. However, the influence on these torsion angles relies on crystal packing, and it was possible to observe that 1 and 4 have similar mechanisms of crystallization achieving a similar 3D crystal network. Structures 2 and 3 are isostructural and consequently present similar torsion values. The structure without substituent (5) has an intermediate value, which is distinct from the others and consistent with its different crystal packing.

Intermolecular interactions

The supramolecular cluster aided in comprehending the differences in the crystal packing of the studied systems. From this approach, it is possible look even further into specific interactions to assess if considered dimers are relevant to crystal packing. In view of studies that conventionally focus on intermolecular interactions in a geometric perspective, we will first discuss this parameter and afterwards advance to a broader view using the supramolecular cluster as the essential portion of the study.

This discussion will focus mainly on halogen interactions and its importance to crystal packing. These intermolecular interactions were identified according to the standardization of the *Platon* program¹⁷. The arrangements involving halogen… π interactions for compounds 1–4 are shown in ESI† (Figure S40), where a supposed prominence of these intermolecular interactions is demonstrated. Figure 7 presents the orientation of the halogen atoms for compounds 1-4 in relation to the plane of the aromatic ring forming the halogen… π interactions. The geometric parameters for all halogen… π interactions are presented in Table 1.



Figure 7. Orientation of the halogen atoms in relation to the plane of the aromatic ring forming the halogen $\cdots \pi$ type interactions for compounds 1-4.

1-4.					
Parameter	1	2	3	4	
Dist. r _a (Å)	3.2654(5)	3.5379(4)	3.5332(1)	3.6053(1)	
Dist. r _b (Å)	3.4127(5)	3.4023(4)	3.4054(1)	3.9080(2)	
Dist. r _r (Å)	4.1018(7)	3.7591(5)	3.7499(1)	3.9080(2)	
β (°)	91.443(5)	154.064(7)	154.457(2)	170.601(1)	
α (°)	44.757(4)	70.169(8)	70.344(2)	49.518(1)	
Symmetry operators	$2-x, -\frac{1}{2}+y, -z$	$1+x, -\frac{1}{2}-y, \frac{1}{2}+z$	$1+x, \frac{1}{2}-y, \frac{1}{2}+z$	$1-x, -\frac{1}{2}+y, 1\frac{1}{2}-z$	

 Table 1. Geometric parameters for the halogen interactions observed in compounds

 1-4.

 $\alpha = X$...Centroid–plane. $\beta = C - X$...Centroid.

The interactions presented in **1** and **4** are classified as localized and type (L)^{1,2}. This is due to their parameter r_a (distance from halogen to a specific carbon) as the shortest distance when compared to the parameters r_r (distance from the halogen to the centroid) and r_b (distance from the halogen to the bond between two carbons of the aromatic ring). Table 4 shows r_a values equal to 3.2654 (5) and 3.6053 (1) Å for compounds **1** and **4**. The distance of the van der Waals radii for F…C and I…C are 3.17 and 3.68 Å, indicating a strong halogen… π interaction for compound **4**, whereas values for distance r_a are lower than the sum of the van der Waals I…C radii.

Compounds 2 and 3 are classified as semi-localized and type (SL). Their distances of lower values registered for parameter r_b are 3.4023 (4) and 3.4054 (1) Å, respectively, where the distance of the interactions Cl… π and Br… π are 3.4023 (4) and 3.4054 (1) Å. In this sense, values below the sum of the van der Waals radii, which are 3.45 and 3.55 Å, respectively, for Cl…C and Br…C, indicating a significant interaction. The halogen… π interaction nomenclature for compounds 1 - 4 can also be attributed to the geometric criteria. For compound 1, the F… π interaction shows angle β (C-F…Centroid) as 91.443 (5)°, a value very close to the orthogonal one, thus indicating that it is a lone pair… π type interaction according to Mooibroek *et al.*¹⁸. For compounds 2, 3, and 4, the halogen… π interactions have a β angle of 154.064 (7), 154.457 (2), and 170.601 (1), respectively, and present values close to linearity (180°). This indicates that these are σ -hole type interactions.

In this geometric approach, it is possible to assess some magnitude of the $X \cdots \pi$ interactions using only the atom-atom distances, in accordance with the established literature. However, how can the existence of the $X \cdots \pi$ interactions be assured only by means of raw geometric data? And what about the strength of those interactions, how can it be assessed without considering an energetic approach? How can it be properly assessed that these type of interactions are relevant to crystal formation?

QTAIM approach

The Quantum Theory of Atoms in Molecules $(QTAIM)^{19}$ analysis was carried to assess the identification and strength of the intermolecular interactions. This was done to corroborate the intermolecular interactions observed by the geometric parameter and to attempt to answer some of the earlier questions. Bond critical points (BCPs) were obtained to confirm the existence of the interactions. The intermolecular $X \cdots \pi$ interactions were confirmed for structures **1-4** (Figure 8), corroborating the observed data in the geometric discussion in addition to other interactions observed. In the case of structure **1**, two different types of interactions ($X \cdots \pi$ and $C-H \cdots \pi$) were observed, which were different from compounds **2-4** that presented only $X \cdots \pi$ interaction. Structure **5**, which had no replacement in the phenyl ring, presented, in a similar dimer, two C-H $\cdots \pi$ interactions.

The first question regarding the existence of the intermolecular interactions is then answered: each interaction involved in the considered dimer has been identified by

the BCPs in the QTAIM. The second and third questions are still pendent and, thus, it is necessary to go beyond the energy calculation of the dimer and observed interaction. A referential is necessary to assess the relevance of this dimer/interaction, and the supramolecular cluster can aid us in acquiring this information. Therefore, the energy involved in each interaction was obtained through the fragmentation of the energy from the considered dimer using a method previously reported^{5,14}, which is highlighted in Figure 8.



Figure 8. Representation of X… π (1-4) and C-H… π (1 and 5) interactions through the BCPs observed by QTAIM analysis. The energy involved in each interaction is highlighted (in kcal mol⁻¹).

The QTAIM data regarding the interactions involved in those dimers are presented in Table 2. These interactions observed by the BCPs, in a separate form, can induce the

observer to conclude that $X \cdots \pi$ interactions are relevant to crystal formation. However, when considering the energy of the involved dimers that range from -1.76 to -2.69 kcal mol⁻¹, it becomes clear that these dimers have low energetic value when considering total crystal energy. Consequently, this information helps answer the two remaining questions.

Table 2. QTAIM data and atom interaction energy $(G_{AI})^b$ for dimers with $H^{\dots}\pi$ and $X^{\dots}\pi$ interactions for compounds 1–5.

Comp.	Dimer	$\begin{array}{c} G_{M1\cdots MN} \\ (kcal \ mol^{-1})^a \end{array}$	Interaction	$\rho_{\rm INT}$ (u.a.) ^b	$\begin{array}{c} G_{AI(x\cdots Y)} \\ (kcal \ mol^{-1})^c \end{array}$	% ^d
1	M1…M12	2.60	$F \cdots \pi$	0.004047	-1.10	3.7
1	M1…M13	-2.09	$\mathrm{H}{\cdots}\pi$	0.005811	-1.59	5.4
2	M1…M9	1 76	$C1\cdots\pi$	0.006136	1 76	55
<u></u>	M1…M14	-1.70		0.000130	-1.70	5.5
3	M1…M9	-2 61	$\operatorname{Br}\cdots\pi$	0.007093	-2 61	79
5	M1…M14	2.01		0.007075	2.01	1.9
4	M1…M16	-2 56	$I \cdots \pi$	0.005375	-2 56	7.0
	M1…M19	2.00	1 //	0.000070	2.30	7.0
5	M1…M9	-2.33	$H\cdots\pi$	0.002655	-0.83	2.8
	M1…M16		$H\cdots \pi$	0.004812	-1.50	5.0

^aStabilization energy obtained by DFT calculation. ^bObtained using QTAIM. ^cInteraction energy involved in each interaction obtained by the fragmentation. ^dInteraction contribution regarding the total energy cluster.

The fragmentation of the interaction energy of the dimer in the different interactions provides important additional data. The contribution of $X \cdots \pi$ interactions are discernible when the whole system is considered. Moreover, $X \cdots \pi$ interactions are responsible for less than 7.9% of the entire stabilization energy of the supramolecular cluster, contributing 3.7, 5.5, 7.9, and 7.0% for compounds 1 to 4, respectively. This data provides an important insight on $X \cdots \pi$ interactions and allows us to answer the previous question of the importance of this kind of interaction for crystal formation. This broad analysis has shown us that in these series of crystal molecules, halogen $\cdots \pi$ interactions are a topological consequence of the crystallization process because they are present in the last steps of the crystallization process in the approximation of the columns. The systematic approach, which is not solely dependent on geometric parameters, enabled us to confidently assess that halogen $\cdots \pi$ interactions do not drive the crystallization process.

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Using the molecular electrostatic potential (MEPs), it is possible to observe the regions with negative and positive potential in the molecules²⁰. In the case of compounds 2-4, it is possible to observe the positive region in the halogen atom (σ -hole) (Figure 9), which allows the interaction σ -hole… π observed in the previous section to occur. Compound 1 with the fluorine atom, on the other hand, does not present the σ -hole, which leads to a lone-pair… π interaction.²⁰ Additional MEPs regarding the involved dimers are presented in ESI† (Figure S10).



Figure 9. Molecular electrostatic potential for compounds 1-4. The V_{max} is highlighted.

Thermal Analysis

Thermal analytical techniques can provide important information of storage and stability of different compounds. As previously reported in the literature, triazenes are compounds with excellent biological activity against tumor cells (*e.g.* TLX5 lymphoma and L1210 leukemia cells)^{9,10,21}. Thus, understanding the thermal behavior of these compounds is an important and integral part of developing stable drugs²².

DSC and TGA analysis were carried out to elucidate the thermal performance of these structures in a broad range of temperature. Firstly, TGA screening was carried out for compounds 1-4 in a temperature range of 25 to 900 °C in order to observe the decomposition steps and decomposition temperature of the structures as a function of the halogen p-substituted in the aromatic ring (see ESI[†]; Figures S11-S15). The decomposition percentage indicates that the decomposition of the samples is almost complete (> 90%) in the evaluated temperature range. Nevertheless, Figure 10 shows the TGA thermograms of compounds 1-4 in a range from 100 to 400 °C, in which the main changes in weight loss *versus* temperature were observed. For a better visualization, the TGA thermogram of **5** was omitted from Figure 10 and depicted in the ESI.



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Figure 10. Overlap of TGA thermograms of 1-4 at heating rate of 10 °C min⁻¹.

From Figure 10, it is possible to note that these structures decompose in two main steps, the first from 90 to 220 °C and the second from 150 to 450 °C, approximately. Furthermore, by peak differences in the derivative weight as a function of temperature plots, it can be note that the halogens influence the decomposition pattern of triazene *N*-oxides. Table 3 demonstrates data regarding initial decomposition temperature (T_i), final decomposition temperature (T_f), decomposition percentage (%), and temperature of maximum decomposition (T_d). T_i shows the temperature in which the compound starts to lose mass and indicates that no thermal degradation based on mass loss occurs in temperatures below T_i . T_f indicates the temperature in which mass loss is complete. T_d corresponds to the temperature of the maximum peaks in the derivative weight (%) as a function of temperature (T) in the TGA thermogram (Figure 10).

Compound	Step	$T_i^a(^{\circ}C)$	$T_{f}^{b}(^{\circ}C)$	$T_d^{c}(^{\circ}C)$	% ^d
1	1	129.36	155.16	143.97	52.50
	2	155.16	396.20	177.54	41.47
2	1	137.24	173.59	159.96	67.77
	2	173.59	400.05	241.27	23.68
3	1	94.92	207.79	160.92	63.34
	2	207.79	449.78	254.66	27.58
4	1	121.70	217.35	162.83	66.61
	2	217.35	455.52	282.40	20.45
5	1	128.40	154.26	138.76	60.49
	2	154.26	312.88	166.60	35.84

Table 3. Thermogravimetric data obtained by TGA in a heating rate of 10 °C min⁻¹.

^aInitial decomposition temperature. ^bFinal decomposition temperature. ^cTemperature of maximum decomposition. ^dDecomposition percentage.

Halogens, in general, tend to increase the stability of triazene compounds as observed in Table 3. An order for decomposition temperatures can be estimated for the compounds in this study, in which: 5 < 1 < 2 < 3 < 4. This order in relation to compounds in which X = halogen corresponds to: F < Cl < Br < I.

In the literature, halogen compounds exhibit a pattern of decomposition behavior generally related to the strengths of the carbon-halogen (C–X) bonds. The greater the C–X bond dissociation enthalpies, the more thermally stable the halogenated compounds²³. For alkyl halides, for example, the bond dissociation enthalpies are 106, 81, 69, and 54 kcal mol⁻¹ for C–F, C–Cl, C–Br and C–I, respectively, in which the stability order is: $I < Br < Cl < I^{24}$. This order represents the opposite trend found in this study. We suppose that the order found for triazene *N*-oxides is a result of two mutual factors: (*i*) halogen electronegativity and (*ii*) atomic radius. An increase in decomposition temperatures of the compounds as the halogens atomic radius increase and electronegativity decrease can be highlighted. Unexpectedly, this indicates that triazene *N*-oxides substituted in the *para* position by hard substituents (lower atomic radius and greater electronegativity, *i.e.* F atom) decomposed in lower temperatures than the same compounds with soft substituents in the same position (greater atomic

radius and lower electronegativity, *i.e.* I atom) that possess a more polarizable electronic cloud.

Compounds were submitted to DSC analysis in order to determine their thermal events (*e.g.* melting and crystallization temperatures). Each sample was subjected to three cycles of heating and cooling in a safe temperature range varied according to the decomposition temperature of the compounds present in the sample. This was done to avoid decomposition within the DSC equipment. However, no thermal events were observed for **1-4** in all cycles within the temperature ranges evaluated (see ESI[†]; Figures S16-S19). This leads us to believe that the melting point of the compounds is likely very close to the point at which they decompose. This assumption is in accordance with the study reported by Serebryanskaya *et al.*²⁵. The authors observed thermal decompositions for 1,3-Bis(2-alkyltetrazol-5-yl)triazenes and their Fe(II), Co(II), and Ni(II) complexes using DSC, in addition to finding that the triazene complexes decomposed without melting at temperatures above 240 °C.

UV-Vis

The absorption of electromagnetic radiation of the ultraviolet-visible by molecules, atoms, or ions is usually associated with electronic transitions. The development of semi-conductor materials with optical properties can result in optical electronic devices, such as light emitting diode (LED) displays, applications in optical communication, and biological labeling^{7,8}. Therefore, the optical behavior of compounds **1-4** in ethanol were evaluated from spectroscopy of molecular absorption in the UV-Visible region (in a range of 200 to 600 nm). All the compounds show three distinct peaks of absorbance in a range of 190 to 400 nm, which corresponds to the UV region (Figure 11(a)). These peaks of absorbance occur when an electron is promoted from a low energy state to a high-energy electronic state by the interaction of the absorbance as a function of wavelength (λ) in different concentrations of compound **1**, which presents three peaks at 200, 234, and 348 nm (black arrows). From this data, an absorbance *versus* concentration plot can be constructed for each absorption peak. Figure 11(b) demonstrates this plot for compound **1** at 200 nm.



Figure 11. (a) Absorbance *versus* wavelength (λ) and (b) absorbance *versus* concentration for 1 at 200 nm in ethanol at 25 °C.

By using the Lambert-Beer law, the angular coefficient of the straight line observed in Figure 11(b) corresponds to the molar absorptivity (ε) of compound **1** in ethanol at 200 nm. The absorbance *versus* λ for **2-4** and the absorbance *versus* concentration plots for **1** at 238 and 348 nm and **2-4** in all λ of absorption are depicted in SI. The straight lines of all experimental data were obtained with an excellent determination coefficient. Molar absorptivity (ε) measures the ability of a mole of substance to attenuate a light incident on a given wavelength. It is an intrinsic property of substances and provides an estimation of how strongly a substance absorbs radiation of a given frequency. Table 4 shows the λ_1 , λ_2 , and λ_3 of absorption peaks and the molar absorptivity (ε) in each λ for compounds **1-4**.

 λ_2 λ_1 λ_3 ε1 **E**₂ 83 Compound $(L \text{ mol}^{-1} \text{ cm}^{-1})$ $(L \text{ mol}^{-1} \text{ cm}^{-1})$ $(L \text{ mol}^{-1} \text{ cm}^{-1})$ (nm)(nm) (nm) 15289 1 348 238 200 23098 26757 2 12562 6424 11531 360 240200 3 352 238 200 21238 12257 23963 4 360 241 203 25083 12874 21899

Table 4. Wavelengths $(\lambda_1, \lambda_2, \lambda_3)$ and molar absorptivity (ε) in each λ for compounds **1-4** in ethanol.

^a ε_1 , ε_2 and ε_3 correspond to molar absorptivity in λ_1 , λ_2 , λ_3 , respectively.

From Table 4, λ_1 , λ_2 , and λ_3 were assigned to $n \to \pi^*$, $n \to \sigma^*$ and $\pi \to \pi^*$ electron transitions, respectively. The triazene chemical groups probably involved in these

transitions are N=N, -N=N-N, and C=C, respectively. The absorption transition of these triazene*1*-oxide are in agreement with data previously reported in the literature for triazene structures without coordinated oxygen^{26,27}. Furthermore, the ε of **1-4** demonstrates that all compounds possess a strong absorbance capacity, which shows promising optical properties.

Domingues *et al.*²⁶ reported an *ortho*-substituted triazene with a fluorine atom possessing greater ε value than the *ortho*-substituted analogue compound with a chlorine atom. In this study, compound 1 with an aromatic ring *p*-F substituted shows significantly larger ε_1 , ε_2 , and ε_3 values than the *p*-Cl substituted analogue compound (2). Nevertheless, the ε_1 , ε_2 , and ε_3 values for compounds 2 and 3 were similar to values found for compound 1. This indicates that the electron transitions associated with the absorbance phenomena in triazene *N*-oxides is not highly dependent on electronic effects caused by different halogens bond in the aromatic ring.

Conclusions

Triazene N-oxide were successfully used as a model to contribute to the understanding of crystallization mechanisms and the importance of certain interactions, such as halogen π interactions to crystal growth. Proposals of crystallization mechanisms were presented for the series of molecules using topological and energetic data obtained from the supramolecular cluster. Two new parameters were presented to interpret the crystal formation, the CG% and the NG/NC. It was possible to observe that compounds 1-4 (X = halogen) presented contributions of over 50% in the first step. Compound 5 (X = H), which formed a strong first dimer in the first step, only reached 50% of contribution when considering the first and second step. The NG/NC parameter enabled us to observe the transition between the dominant parameters during the crystallization process. All compounds presented similar behavior during the steps, *i.e.* first a dominance of the stabilization energy of the interactions and the final step of the crystallization process relying almost exclusively on a topological process. With a broad analysis, it was possible to assure the existence of $X^{\dots}\pi$ interactions and assess their participation in crystal formation, showing that the formation of this kind of interaction in these molecules is a consequence of a topological process. UV-Vis and thermal analysis (TGA and DSC) were also carried out to observe the special properties of these molecules. In addition

to halogens influencing the decomposition pattern, it was also possible to assess that these structures are stable (mass loss at T > 129 °C) and decompose in two main stages. An increase in the decomposition temperature of the compounds as the atomic radius of the halogens increase and electronegativity decrease can be highlighted. No thermal events (*e.g.* melting and/or crystallization temperatures) were observed for the compounds in the temperature range evaluated (below decomposition temperatures). Furthermore, the ε of the halogenated compounds showed that all compounds possess strong absorbance capacity, indicate promising optical properties.

Experimental

Materials and Methods

The infrared absorption spectra were performed as KBr pellets using 3 to 5 mg of sample per 100 mg of KBr in the Bruker IR spectrophotometer. UV/Visible spectra were recorded using a Shimadzu UV-2600 spectrophotometer. For this analysis, a standard solution with concentration of 0.5 mM was made for compounds 1-4. From these standards solutions, 5.00 μ L volumes were extracted and diluted in the cuvette containing 3 mL of ethanol. Samples were analyzed at 25 °C. The spectra were recorded within a range of 190-600 nm at a scanning rate of 600 nm min⁻¹ (0.1 s integration per 1.0 nm). The ¹H and ¹³C NMR spectra were obtained on Bruker DPX (600MHz) spectrometers using DMSO-d6 as solvent. Raman spectra were performed on Bruker MultiRAM devices with laser at 1064 nm wavelength and exposure time of 3 s. Thermal analysis were performed on a TGA Q5000 (TA Instruments Inc., USA). The heating rate used was 10 °C.min⁻¹ and inert atmosphere of N₂ (50 ml.min⁻¹). Elemental analysis technique was performed using a Perkin - Elmer CHN 2400. DSC experiments were performed using a MDSC Q2000 (T-zero[™] DSC Technology, TA Instruments Inc., USA). Dry high purity (99.999%) nitrogen gas was used as the purge gas (50 mL min⁻¹). The instrument was initially calibrated in standard MDSC mode using the extrapolated onset temperatures of melting indium (156.60°C) at a heating rate of 10°C min⁻¹ and the heat from the fusion of indium (28.71 J g⁻¹). Heat capacity calibration was carried out by running standard sapphire (IJa-Al2O3) measurement at the experimental temperature. The heating rate was 5 °C min⁻¹. The instrument was initially calibrated in standard DSC mode with Indium (99.99%). The

masses of the reference pots and lids and the samples weighed 51 ± 0.02 mg. The samples were enclosed in aluminum pots with lids. The masses of the samples were weighed on a Sartorius scale (M500P) with an accuracy of (± 0.001 mg). Data were treated using TA Universal Analysis 2000 Software, version 4.5 (TA Instruments Inc., USA).

Synthesis

Solvents and reagents were used without prior treatment. The triazene N_1 -oxide compounds were synthesized starting from the diazotization reaction of the respective 4-halophenylamine in acidic medium with sodium nitrite (1:1) at 0 °C to obtain the respective diazonium salt and, subsequent coupling with β -phenylhydroxylamine, previously synthetized²⁸, according to the methodology described in²⁹ (Scheme 1).



Scheme 1. Synthesis path for triazene N1-oxide compounds 1-4.

Synthesis of 1-(4-fluorphenyl)-3-phenyltriazenide N₁-oxide (1)

For the synthesis of **1**, a solution of NaNO₂ (1.25 g, 17.9 mmol) in 20 mL of water was added to a solution of 4-fluoraniline (2.0 g, 17.9 mmol) in 15 mL of a mixture of concentrated HCl and water (1:1) cooled to 0°C, thus forming the diazonium salt. After 20 minutes, the β -phenylhydroxylamine solution (2.2 g, 17.9 mmol) in 15 mL of concentrated acetic acid was added and the reaction mixture stirred for 40 minutes at 0 °C. The reaction mixture was carefully pH-adjusted to about 5 and the yellow opaque precipitate was vacuum filtered and recrystallized from a fraction of ethanol/pyridine solvents, which after approximately five days of slow evaporation resulted in yellow crystals in the form of needles. Compound **1** C₁₂H₁₀FN₃O shows a yield of 75%. Elementar analysis % C₁₂H₁₀FN₃O: Calculated: C 63.40; H 5.32; N 17.06; Experimental: C 62.27; H 4.36; N 18.19. *IR* (KBr): v (N-H) 3132.26; v (C-H) 3055; v (C=C) 1604.71; δ (N-H) 1515.99; v (N=N) 1429.19; v (N-N-N) 1332.76; v (N → O) 1298.13; v (C_{ar}-Halog) 1220.25; v (N-N) 1195.40 cm⁻¹. *Raman*: v (N-H) 3080; v (C-H) 3050; v (C=C) 1606; δ (N-H) 1003; v (N=N) 1431; v (C-C) 1401; v (N=N-N)ring 100; v (C_{ar}-Halog) 381; v (C-N) 1204 cm⁻¹. NMR ¹H (400 MHz DMSO – d₆) δ = 12.04 (s, 1H, OH); δ = 8.09 (d, J=8.8Hz, 2H, ArH); δ = 7.60-5.53 (m, 5H, ArH); δ = 7.22 ppm (t, J=8.1Hz, 2H, ArH); NMR ¹³C (400 MHz DMSO – d₆); δ = 159.9 (d, ¹J_C. F=238.9Hz, C₄); δ = 142.8 (C₇); δ =137.1 (C₁⁴J_{C-F} = 2.1Hz,); δ = 129.5 (C₁₀); δ = 129.1 (C₉, C₁₁); δ = 119.5 (C₈, C₁₂); δ = 116.4 (d, ³J_{C-F} = 7.9Hz, C₂, C₆); δ =115.8 ppm (d, ²J_{C-F} = 22.7Hz, C₃, C₅). UV/Vis: λ = 360 nm, attributed n → π*, group (N-N), ε_{276} = 28153 L mol⁻¹.cm⁻¹; λ = 238 nm, attributed π → π *, group (C=C), ε_{238} = 32551 L mol⁻¹ cm⁻¹.

Synthesis of 1-(4-chlorophenyl)-3-phenyltriazenide N₁-oxide (2)

Compound **2** was synthesized according to the procedure described for compound **1**, but using 4-chloroaniline (2.0 g; 15.74 mmol) as the primary amine. Compound **2** $C_{12}H_{10}ClN_{3}O$ shows a yield of 83%. Elementar Analysis % $C_{12}H_{10}ClN_{3}O$: Calculated: C 58.19; H 4.07; N 16.97; Experimental: C 58.34; H 4.27; N 16.64. *IR* (KBr): *v* (N-H) 3186.07; *v* (C-H) 3100; *v* (C=C) 1598.74; δ (N-H) 1509.44; *v* (N=N) 1418.37; *v* (N-N-N) 1330.07; *v* (N \rightarrow O) 1296.74; *v* (Car-Halog) 636.90; *v* (N-N) 1168.33 cm⁻¹. *Raman*: *v* (N-H) 3078; *v* (C-H) 3070; *v* (C=C) 1598; δ (N-H) 1005; *v* (N=N) 1420; *v* (C-C) 1396 cm⁻¹; *v* (N=N-N)-*ring* 93; *v* (Car-Halog) 410; *v* (C-N) 1213 cm⁻¹. NMR ¹H (600 MHz DMSO – d₆) δ = 12.13 (*s*, 1H, OH); δ = 8.09 (*d*, *J* = 7.8 Hz, 2H, *Ar*H); δ = 7.60 – 7.51 (*m*, 5H, *Ar*H); δ = 7.41 ppm (*d*, *J* = 8.6 Hz, 2H, *Ar*H); NMR ¹³C (600 MHz DMSO – d₆); δ = 142.86 (*C*₁); δ = 139.50 (*C*₇); δ = 129.82 (*C*₄); δ = 129.17 (*C*₃, *C*₅); δ = 129.08 (*C*₉, *C*₁₁); δ = 126.13 (*C*₁₀); δ = 119.65 (*C*₂, *C*₆); δ = 116.49 ppm (*C*₈, *C*₁₂). UV/Vis: λ = 360 nm, attributed n $\rightarrow \pi^*$, group (N=N), ε_{360} = 12562 Lmol⁻¹ cm⁻¹; λ = 240 nm, attributed n $\rightarrow \sigma^*$, group (-N = N-N), ε_{240} = 6424 L mol⁻¹ cm⁻¹; λ = 200 nm, attributed $\pi \rightarrow \pi^*$, group (C=C), ε_{200} = 11531 Lmol⁻¹ cm⁻¹.

Synthesis of 1-(4-bromophenyl)-3-phenyltriazenide N₁-oxide (3)

By repeating the same preparation used for compound 1, but substituting 4fluorophenyl for 4-bromophenyl (2 g; 11.76 mmol) for compound 3. Compound 3 $C_{12}H_{10}BrN_{3}O$ had a yield of 80%. Elementar Analysis % $C_{12}H_{10}BrN_{3}O$: Calculated: C 49.34; H 3.45; N 14.38; Experimental: C 49.58; H 3.48; N 13.98. *IR* (KBr): *v* (N-H) 3188.96; *v* (C-H) 3090; *v* (C=C) 1584.85; δ (N-H) 1505.15; *v* (N=N) 1414.72; *v* (N-N-N) 1329.03; *v* (N → O)1296.70; *v* (C_{ar}-Halog) 609.23; *v* (N-N) 1169.23 cm⁻¹. *Raman*: *v* (N-H)3075; *v* (C-H)3069; *v* (C=C) 1596; δ (N-H)1006; *v* (N=N)1417; *v* (C-C)1394; *v* (N=N-N)-*ring*92; *v* (C_{ar}-Halog)553; *v* (C-N)1212 cm⁻¹. NMR ¹H (600 MHz DMSO – d₆) δ = 12.13 (*s*, 1H, OH); δ = 8.09 (*d*, *J* = 7.4 Hz, 2H, *Ar*H); δ = 7.54 ppm (ddd, *J* = 41.4, 23.7, 7.8 Hz, 7H, *Ar*H); NMR ¹³C (600 MHz DMSO – d₆); δ = 142.85 (*C*₁); δ = 139.88 (*C*₇); δ = 131.94 (*C*₃, *C*₅); δ = 129.84 (*C*₁₀); δ = 129.18 (*C*₉, *C*₁₁); δ = 119.65 (*C*₂, *C*₆); δ = 116.91 (*C*₈, *C*₁₂); δ = 114.05 ppm (*C*₄). UV/Vis: λ = 352 nm, a attributed n → π^* , group (N=N), ϵ_{352} = 21238 Lmol⁻¹ cm⁻¹; λ = 200 nm, attributed n → σ^* , group (-N=N-N), ϵ_{238} = 12257 Lmol⁻¹ cm⁻¹; λ = 200 nm, attributed $\pi \rightarrow \pi^*$, group (C=C), ϵ_{200} = 23963 Lmol⁻¹ cm⁻¹.

Synthesis of 1-(4-iodophenyl)-3-phenyltriazenide N₁-oxide (4)

Compound 4 was obtained by beginning with 4-iodophenyl (2 g; 9.13 mmol) as the primary amine and following the same procedure used for the synthesis of compound 1. Compound 4 $C_{12}H_{10}IN_{3}O$ shows a yield of 68%. Elementary Analysis % C₁₂H₁₀IN₃O: Calculated: C 42.50; H 2.97; N 12.39; Experimental: C 40.71; H 3.08; N 11.51. IR (KBr): v (N-H) 3068.15; v (C-H) 3050; v (C=C) 1588.52; δ (N-H) 1500.44; v (N=N) 1417.09 cm⁻¹; v (N-N-N) 1331.55; v (N \rightarrow O) 1298.04; v (C_{ar}-Halog) 611.30; v (N-N) 1086.98 cm⁻¹. Raman: v (N-H) 3072; v (C-H) 3072; v (C=C) 1592; δ (N-H) 1003; v (N=N) 1420; v (C-C) 1394; v (N=N-N)-ring 100-77; v (C_{ar}-Halog) 1060; v (C-N) 1210 cm⁻¹. NMR ¹H (600 MHz DMSO – d_6) δ = 12.10 (s, 1H, OH); δ = 8.09 (d, J = 7.5Hz, 2H, ArH); $\delta = 7.68$ (d, J = 8.2 Hz, 2H, ArH); $\delta = 7.61 - 7.52$ (m, 3H, ArH); $\delta = 7.35$ ppm (d, J = 8.1 Hz, 2H, ArH); NMR ¹³C (600 MHz DMSO - d₆); $\delta = 142.84$ (C_1) ; $\delta = 140.33 (C_7)$; $\delta = 137.70 (C_3, C_5)$; $\delta = 129.82 (C_{10})$; $\delta = 129.15 (C_9, C_{11})$; $\delta =$ 119.64 (C₂, C₆); $\delta = 117.24$ (C₈, C₁₂), $\delta = 85.56$ ppm (C₄). UV/Vis: $\lambda = 360$ nm, attributed n $\rightarrow \pi^*$, group (N=N), $\varepsilon_{360} = 25083$ L mol⁻¹ cm⁻¹; $\lambda = 241$ nm, attributed n \rightarrow σ^* , group (-N=N-N), $\varepsilon_{241} = 12874$ Lmol⁻¹ cm⁻¹; $\lambda = 203$ nm, attributed $\pi \rightarrow \pi^*$, group (C=C), $\varepsilon_{203} = 21899$ Lmol⁻¹ cm⁻¹.

Spectroscopic analysis

Absorptions observed in the infrared spectra of compounds 1-4 at 3132 cm⁻¹, 3186, 3189, and 3068 cm⁻¹, respectively, correspond to the v_{as} (N-H) stretches of the respective diazo(oxide)amine $[-N=N(\rightarrow O)-N(H)-]$ chain of each compound, which is in accordance with what was found at 3140 cm⁻¹ for compound 5^1 . In addition, the bands observed at 1298, 1296, 1297, and 1298 cm⁻¹, respectively, correspond to the characteristic stretches of the $vN(\rightarrow O)$ dative bond in accordance with what was found at 1339 cm⁻¹ in compound 5^1 and demonstrate that the compounds show the tautomeric form of the triazene N_1 -oxide in the solid state. In the Raman spectra of compounds 1-4, the observed bands at 3080, 3078, 3075, and 3072 cm⁻¹ were attributed to the characteristic v_{s} (N-H) stretches in triazene compounds. On the other hand, the vibrations observed at 381, 410, 553, and 1060 cm⁻¹ for compounds 1, 2, 3, and 4, were attributed to the aromatic carbon-halogen [$\nu_s(C_{ar}-X)$; X = F, Cl, Br, and I], respectively^{30,31}. In the ¹³C NMR spectrum, the "C4" carbons bond to the respective halogens for compound 1, 2, 3, and 4 correspond to the peak with a chemical shift at δ 159.9 (d, ${}^{1}J_{C-F}=238,9\text{Hz}$), δ 129.31, δ 114.58, and δ 85.06, respectively. It is possible to highlight the decreasing disbanding effect as it decreases along group 17 in the periodic table, an expected effect due to the electronegativity (I inductive effect) decreasing from fluorine to iodine and also because of the effect of the heavy atom that increases from fluorine to iodine. Electronic absorption spectra of compounds 1, 2, 3, and 4 were recorded in ethanol, which exhibits a strong absorption at 348 nm (1) and 352 nm (2, 3, and 4) (Figs. S28-S31). When compared with usual electronic absorption spectra of classical triazene derivatives [RN=N-N(H)R], these absorptions observed at the region of 348-352 nm where assigned to the partly forbidden $(n \rightarrow \pi^*)$ transition and attributed to the (N=N) chromophore group.³² Additionally, medium intensity absorptions were observed at 234 nm (1), 240 nm (2), 238 nm (3), and 241 nm for (4). These absorptions at 234-241 nm were assigned to the $(n \rightarrow \sigma^*)$ transition, also in analogy of that attributed to the (N=N) chromophore group when compared with the triazenes.³² A third strong band is observed at 200 nm for all compounds that were assigned to the expected and characteristic $(\pi \rightarrow \pi^*)$ transition of the phenyl and *p*-halophenyl substituents.

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Crystal Structure Determination

X-ray diffraction data for 1–5 are listed in Table 5. The X-ray diffraction technique was performed using the Bruker APEXII-CCD diffractometer with an area detector, graphite monochromator, and Mo-K α radiation source with wavelength (λ) of 0.71073 Å³³. Data reduction and absorption correction involved the SAINT and SADABS³⁴ software programs, respectively. The structures were solved via Direct Methods ³⁵ and the refinement of the data included square squares (F2) and the method of least squares including complete matrices using anisotropic thermal parameters for non-hydrogenic atoms. The hydrogen atoms are set as geometric for all compounds. Crystallographic data for the structural analysis of the compounds have been deposited at the Cambridge Crystallographic Data Center with the deposition numbers of 1570873 (1), 1570875 (2), 1570876 (3), 1570877 (4), and 759893 (5). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB21EZ, United Kingdom; Fax: +44 1223 336033 or deposit@ccdc.cam.ac.uk.

2		1			
Compound	1	2	3	4	5
Moiety formula	$C_{12}H_{10}FN_3O$	$C_{12}H_{10}CIN_3O$	$C_{12}H_{10}BrN_3O$	$C_{12}H_{10}IN_3O$	$C_{12}H_{11}N_3O$
Sum formula	$C_{12}H_{10}FN_3O$	$C_{12}H_{10}CIN_3O$	$C_{12}H_{10}BrN_3O$	$C_{12}H_{10}IN_3O$	$C_{12}H_{11}N_{3}O$
Mw	231.23	247.68	292.14	339.13	213.24
Crystal system	Monoclinic	Monoclinic	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_1$	$P2_{1}/c$	$P2_{1}/c$	$P2_{1}2_{1}2_{1}$	$P2_1/n$
<i>a</i> [Å]	9.6487(15)	6.1680(9)	6.2398(3)	4.7465(3)	5.4917(5)
<i>b</i> [Å]	5.2866(7)	9.5740(16)	9.7185(5)	9.9491(6)	16.1419(13)
<i>c</i> [Å]	11.1382(19)	19.477(3)	19.5527(10)	26.6177(14)	12.4976(10)
α[°]	90	90	90	90	90
β[°]	110.361(5)	96.539(9)	96.462(2)	90	100.382(7)
γ[°]	90	90	90	90	90
$V[Å^3]$	532.65(14)	1142.7(3)	1178.17(10)	1256.98(13)	1090.20(16)
Z	2	4	4	4	4
$D_{\text{calcd}}[\text{g cm}^{-3}]$	1.442	1.440	1.647	1.792	1.299
μ [mm ⁻¹]	0.108 (Mo-	0.320 (Mo-	3.475 (Mo-	2.535 (Mo-	0.087 (Mo-
	K_{α})	K_{α})	K_{α})	K_{α})	K_{α})
<i>F</i> (000)	240	512	584	656	448
T[K]	293(2)	293(2)	293(2)	293(2)	295(2)
Reflections	19621	9904	11495	14579	11977
collected					
Independent	2392	2379	2602	2719	3451
reflections					
$R_{\rm int}$	0.0533	0.0638	0.0475	0.0470	0.0587
Observed	2125	1489	1813	1758	1177
reflections [
$I > 4\sigma(F)$]					
Parameters refined	154	154	155	154	145
Flack x parameter	0.1(3)	-	-	0.048(18)	-
R(F) reflections [0.0351	0.0660	0.0337	0.0466	0.0687
$I > 4\sigma(F)$]					
$wR(F^2)$	0.0870	0.1660	0.0688	0.1145	0.1464
S	1.058	1.015	1.007	1.037	0.998
$\Delta \rho_{\rm min} \left[e {\rm \AA}^{-3} \right]$	+0.235	+0.506	+0.228	+0.373	+0.164
$\Delta \rho_{max} \left[e \text{\AA}^{-3} \right]$	-0.248	-0.664	-0.220	-0.1.031	-0.148

 Table 5. Crystal data and refinement parameters for compounds 1–5.

Topological Analysis

Voronoi-Dirichlet Polyhedra (VDP) was used in the ToposPro¹³ software for the construction of the supramolecular cluster. The molecular coordination number (MCN) found for each cluster was 18 for compounds **1** and **4**, 14 for compounds **2** and **3**, and 16 for compound **5**. The face of the molecular VDP was considered to be a set of atomic VDP faces corresponding to the adjacent contacts between the atoms of

two molecules. Thus, it was established that the area of the face of a VDP corresponds to a molecular M1…MN interaction, and the considered topological parameter was the contact surface area between the dimers provided by the software.³⁶

Stabilization Energy Calculation

The intermolecular interaction energy of the dimers from the supramolecular clusters of compounds 1–5 were determined by single-point calculations performed with geometries obtained from X-Ray diffraction. The optimization of the molecular geometry was not performed. Density functional theory (DFT) at the ω B97X-D/cc-pVDZ level of theory was used for the calculation. Calculations for compound **4** were carried out with ω B97X-D/cc-pVDZ-PP because the relativistic effects of the iodine atom needed to be corrected. All calculations were performed with the aid of the Gaussian 09³⁷ software package. The counterpoise method of Boys and Bernardi³⁸ was employed in order to minimize the BSSE. The stabilization energy for M1····MN was given by the energy values of the considered dimer minus the sum of the monomer energies of M1 and MN.

Competing financial interest

The authors declare no competing financial interest.

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