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# Probing intramolecular interactions using molecular electrostatic potentials: Changing electron density contours to unveil both attractive and repulsive interactions

Goedele Roos<sup>1</sup> & Jane S. Murray\*<sup>2</sup>

<sup>1</sup>Univ. Lille, CNRS, UMR 8576 - UGSF - Unité de Glycobiologie Structurale et Fonctionnelle, F-59000 Lille, France

<sup>2</sup>Department of Chemistry, University of New Orleans, New Orleans, LA 70148 USA

## Abstract

We focus on intramolecular interactions, using the electrostatic potential plotted on iso-density surfaces to lead the way. We show that plotting the electrostatic potential on varying iso-density envelopes much closer to the nuclei than the commonly-used 0.001 a. u. contour can reveal the driving forces for such interactions, whether they be stabilizing or destabilizing. Our approach involves optimizing the structures of molecules exhibiting intramolecular interactions and then finding the contour of the electronic density which allows the interacting atoms to be separated; we call this the nearly-touching contour. The electrostatic potential allows then to identify the intramolecular interactions as either attractive or repulsive. The discussed 1,5- and 1,6-intramolecular interactions in *o*-bromophenol and *o*-nitrophenol are attractive, while the interactions between terminal methyl hydrogens in diethyl disulfides (as shown recently) and those between the closest hydrogens in planar biphenyl and phenanthrene are clearly repulsive in nature. For the attractive 1,4-interactions in trinitromethane and chlorotrinitromethane, and the 1,3-S---N and Si---O interactions in the ClH<sub>2</sub>Si(CH<sub>2</sub>)<sub>n</sub>NH<sub>2</sub> series, the lack of (3,-1) bond critical points was often cited as reason to not identify the 1,3-Si---N interactions as attractive in nature. Here, by looking at the nearly-touching contours we see that bond critical points are neither necessary nor sufficient for attractive interactions, as others have pointed out, and in some instances also pointing to repulsive interactions, as the examples of planar biphenyl and phenanthrene discussed in this work show.

## Intramolecular Interactions

In this work our focus is upon intramolecular interactions, interactions occurring within a molecule or ionic species. Intramolecular interactions can be either attractive, as in hydrogen bonding,<sup>1-3</sup> halogen bonding<sup>4-6</sup> and other  $\sigma$ -hole and  $\pi$ -hole interactions,<sup>7,8</sup> or repulsive, an area that has received less recognition in the literature.

Intramolecular interactions are very important in areas ranging from biochemistry and medicinal chemistry to energetic materials, but are more difficult to quantify than

intermolecular interactions A---B.<sup>9,10</sup> For the latter, one can compute interaction energies quite easily at high levels, simply because one can obtain energies for both the A and B parts and for the complex A---B to obtain an interaction energy  $\Delta E$ , where  $\Delta E = E(A---B) - [E(A) + E(B)]$ . This is not possible in a straightforward manner for intramolecular interactions because there are no separated A and B fragments, but simply one molecular or molecular ion.

One can also look at the distances between “interacting” atoms for the identification of both intermolecular and intramolecular interactions. If this distance is less or roughly equal to the sum of the van der Waals radii of the two atoms, then there is likely an attractive interaction. This criterion is not perfect because of the approximate nature of van der Waals radii<sup>11–13</sup> and because attractive interactions are often between portions of molecules, not particular atoms.<sup>14–16,12</sup>

The distance criterion also does not answer important questions. When two formally non-bonded atoms in a molecule are in close contact (close to or less than the sum of the van der Waals radii) does this suggest an attractive interaction or is this close contact simply there because of the structure of the molecule? Could such close contacts be repulsive?

In this work, we shall show that intramolecular interactions can be identified, be they stabilizing or destabilizing, by ‘simple’ electrostatics by plotting the electrostatic potential  $V(\mathbf{r})$  on varying iso-density envelopes much closer to the nuclei than the commonly-used 0.001 a. u. contour found for atoms not involved in an interaction. Varying contours of the electronic density have been used in earlier work to assess *intermolecular* interactions,<sup>17,18</sup> and also, to repulsive intramolecular interactions in disulfides.<sup>19</sup>

We search for the nearly-touching contours for which the interacting parts show their typical features. The approach of finding the nearly-touching points, which is a singularity when two densities approach, is parallel to finding the critical points of the electron density ( $\nabla\rho = 0$ ) (*cf.* QTAIM<sup>20,21</sup>) or to isolate regions with low density and low reduced gradient (*cf.* NCI-plot<sup>22,23</sup>); the strength of our approach is in its simplicity. We let the electrostatic potential lead the way to probe intramolecular interactions, unveiling both attractive (stabilizing) and repulsive (destabilizing) contacts.

## Theory and Methodology

### *Electrostatic potential*

The electrostatic potential  $V(\mathbf{r})$  is a tool to look at interactions between molecules or ions before they occur.  $V(\mathbf{r})$  that is produced at any point  $\mathbf{r}$  by the nuclei and electrons of a molecule is expressed rigorously by eq. (1):

$$V(\mathbf{r}) = \sum_A \frac{Z_A}{|\mathbf{R}_A - \mathbf{r}|} - \int \frac{\rho(\mathbf{r}')d\mathbf{r}'}{|\mathbf{r}' - \mathbf{r}|} \quad (1)$$

$Z_A$  is the charge on nucleus A, located at  $\mathbf{R}_A$  and  $\rho(\mathbf{r})$  is the molecule's electronic density. Eq. (1) shows that  $V(\mathbf{r})$  is the sum of a positive contribution due to the nuclei and a negative one from the electrons; its sign in any particular region depends, therefore, upon whether the effects of the nuclei or electrons are dominant in that region.<sup>24</sup> The electrostatic potential is physical observable, which can be determined experimentally as well as computationally. Its significance has been discussed in detail earlier.<sup>25–27</sup>

Since the early 1990's it has become commonplace to plot  $V(\mathbf{r})$  on iso-density surfaces, such as the 0.001 a. u., 0.002 a. u., or 0.003 a. u. contours of the electronic densities, following Bader *et al.*<sup>21</sup> We label such surfaces  $V_S(\mathbf{r})$ , with the surface local maxima and minima, called  $V_{S,\max}$  and  $V_{S,\min}$ , respectively.<sup>28</sup> Such surfaces provide a shape for the molecule, and allow atomic anisotropies within molecules, stemming from lone pairs,  $\pi$ -regions, strained bonds and  $\sigma$ - and  $\pi$ -holes, to be easily visualized.

The surface electrostatic potentials are very useful for predicting future interactions of the molecules. One can clearly “see” the driving forces for ensuing interactions. However,  $V_S(\mathbf{r})$  computed on 0.001 a. u., 0.002 a. u. and 0.003 a. u. contours of the electronic density masks the driving forces for intramolecular interactions. What we will show here is that the electrostatic potential plotted on iso-density contour envelopes closer to the nuclei than the 0.001 a. u. contour unveil the driving forces for intramolecular interactions, be they attractive or repulsive. Our search has been to find the nearly-touching contours for which a) the surface electrostatic potential doesn't show overlap between atoms or functional groups and b) the typical features are visible ( $\sigma$ -hole, lone pair, hydrogen  $V_{S,\max}$ ). The nearly-touching contours are contours where the interacting parts, be they molecules or parts of molecules, are not quite touching. For intermolecular interactions A---B, they allow one to look at the separate volumes of A and B.<sup>17,18</sup>

### *Calculation method*

We have computed optimized geometries for the molecules presented in this paper at the B3PW91/6-31G(d,p) level using Gaussian 09,<sup>29</sup> unless otherwise noted. The Wave Function Analysis – Surface Analysis Suite (WFA-SAS)<sup>30</sup> has been used to compute electrostatic potentials on iso-density surfaces, also at the B3PW91/6-31G(d,p) level. This method/basis set has been shown to provide reliable electron densities and electrostatic potentials.<sup>31</sup>

## Results & Discussion

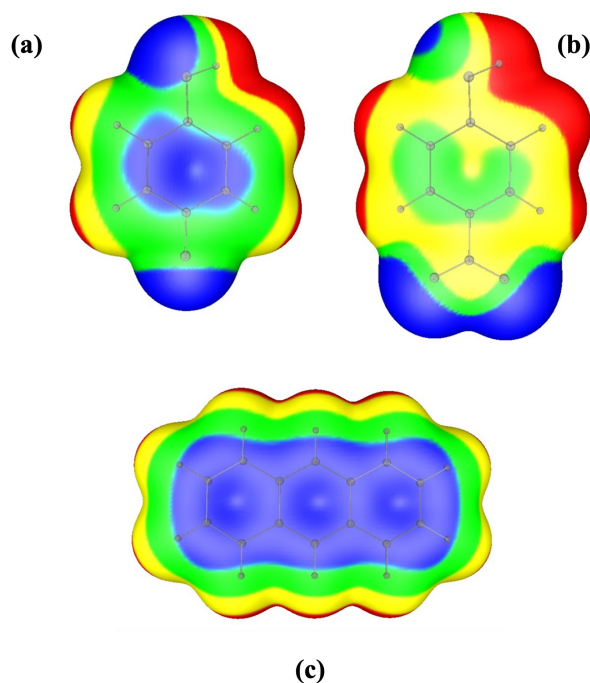
### *Typical features of the electrostatic potential when no intramolecular interactions are present*

Following the Hellmann-Feynman theorem,<sup>32–34</sup> the intramolecular forces that hold the atoms together within a molecule or molecular complex, whether they be ionic, covalent or metallic bonds or the weaker interactions, are Coulombic in nature.<sup>20,35–39</sup> It has been pointed out before in intermolecular contexts<sup>17,18,37</sup> - for example the attractive interaction in complexes between

aromatic molecules and HCN<sup>40</sup> - , as well as in intramolecular contexts<sup>8</sup> that the classical Coulombic forces are indeed able to capture “all” information. Coulomb’s law is thus sufficient to explain both covalent and non-covalent interactions.

For organic molecules, unless the hydrogen atoms are involved in an intramolecular interaction, it is anticipated that the surface electrostatic potential for each hydrogen will have an accessible hemispherical positive region of electrostatic potential with a surface maximum, or  $V_{S,max}$ ,<sup>3,28,41</sup> that the surface electrostatic potential will not show significant overlap between atoms or functional groups, and that typical features ( $\sigma$ -holes, lone pairs,  $\pi$  regions) are visible.<sup>9,42</sup> The 0.001 a. u. iso-density surface was historically chosen for the following reasons: **1)** The 0.001 a. u. surface is generally farther from the atoms than the often-used van der Waals radii (except for hydrogen); and **2)** There was a slightly better correlation between hydrogen  $V_{S,max}$  values and the Kamlet-Taft hydrogen-bond donating parameters at the 0.001 a. u. contour.<sup>43</sup> However, Bader *et al.* showed that the space within the 0.003 a. u. iso-density surface envelope was found to well represent the molecular volume of organic molecules,<sup>21</sup> and therefore, the 0.003 a. u. density envelope is also often used.

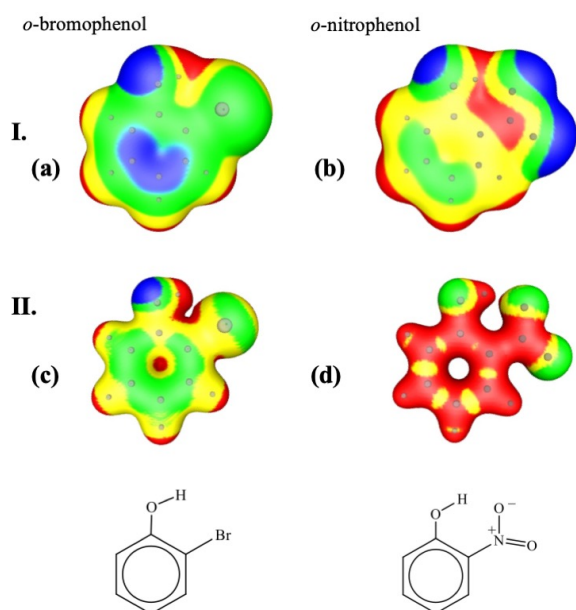
Figure 1 shows  $V_S(\mathbf{r})$  on the 0.001 a. u. contours of *p*-fluorophenol, *p*-nitrophenol and anthracene. Each hydrogen has a hemispherical region of positive electrostatic potential associated with it, and the -OH, fluorine and nitro-groups in *p*-fluorophenol and *p*-nitrophenol have their typical shapes. Notice that the phenolic hydrogen in *p*-nitrophenol is more positive than that of *p*-fluorophenol (cfr. red-colored region), consistent with the greater electron-attracting power of the nitro group in Figure 1(b) vs. the fluoro substituent in Figure 1(a). In a reverse manner, the phenolic oxygen in Figure 1(a) is more negative than that in Figure 1(b) (cfr. blue-colored region). Also, the  $\pi$ -regions of *p*-fluorophenol and anthracene are more negative than that of *p*-nitrophenol. As to be expected, the  $V_S(\mathbf{r})$  of the fluorine in Figure 1(a) and the nitro oxygens in Figure 1(b) show negative potentials.



**Figure 1:** Electrostatic potentials plotted on the 0.001 au contours of the electronic densities of *p*-fluorophenol (a), *p*-nitrophenol (b) and anthracene (c). The frameworks for the molecules are shown in gray. Color ranges, in kcal/mol, are: red, greater than 10; yellow, between 10 and 0; green, between 0 and -10; blue, more negative than -10.

*Driving forces for intramolecular interactions are hidden within the 0.001 a. u. contour.*

For molecules in which intramolecular interactions are present, the driving forces for the intramolecular interactions, either attractive or repulsive, are hidden within the 0.001 a. u. envelopes. In cases where the hydrogen is involved in an intramolecular interaction, there is either no visible  $V_{S,max}$  on the surface or one that has a smaller than expected magnitude; as in, for example, *o*-bromophenol and *o*-nitrophenol shown in Figures 2-I(a) and 2-I(b).



**Figure 2:** I. Electrostatic potentials plotted on the 0.001 a. u. contours of *o*-bromophenol (a) and *o*-nitrophenol (b), with color ranges, in kcal/mol: red, greater than 10; yellow, between 10 and 0; green, between 0 and -10; blue, more negative than -10. II. Electrostatic potentials plotted on the 0.0197 au contour for *o*-bromophenol (c) and the 0.055 au contour of *o*-nitrophenol (d). The color ranges for (c) are: red, greater than 60; yellow, between 60 and 30; green, between 30 and 0; blue, negative; for (d) are: red, greater than 100; yellow, from 100 to 60; green, from 60 to 0; blue, negative.

At the 0.001 a. u. contour, the four phenyl hydrogens of *o*-bromophenol (Figure 2-I(a)) and *o*-nitrophenol (Figure 2-I(b)) each have hemispherical surfaces around them, while the hydroxyl hydrogens do not. This is a clue that these hydrogens are involved in an intramolecular interaction, in these cases with the sides of the bromine or nitro oxygen. Here, the information is hidden within the 0.001 a. u. contour envelope and so, accordingly, we need to plot the electrostatic potential on contours closer to the nuclei to ‘free’ the hydrogen atoms. More electron density must be excluded from the surface envelopes to separate the electrostatic potentials and to make sure that all H-atoms, the bromine and the nitro group have their typical shapes. These contours are referred to in this paper as the nearly-touching contours; for *o*-bromophenol, this is the 0.0197 a. u. contour (Figure 2-II(c)), and for *o*-nitrophenol, the 0.055 a. u. contour (Figure 2-II(d)). On these contours, the electron densities of the hydroxyl hydrogens have hemispherical shapes and the bromine and nitro group can be easily identified.

From both plotting  $V_s(\mathbf{r})$  on the 0.001 a. u. contours and the nearly-touching contours, it can easily be seen if an interaction is repulsive or attractive. In the examples in Figure 2, the electrostatic potentials reveal attractive forces; see the red color for positive H-atoms, while the bromine and the nitro oxygens are primarily green and/or blue, respectively, at the 0.001 a. u. contours. At the nearly-touching contours (Figures 2-II(c) and 2-II(d)),  $V_s(\mathbf{r})$  is more positive

everywhere, because the surfaces are closer to the nuclei. The hydrogens are “free”, as is the bromine in Figure 2-II(c) and the upper nitro oxygen in Figure 2-II(d). In the next section, we will discuss a repulsive case.

*Intramolecular repulsion: do (3,-1) bond-critical points invariably indicate attractive interactions?*

Recognizing chemical bonds in a molecule’s geometry has been subject to long standing discussions in literature. A wealth of mathematical formalisms exists [to name a few of the today’s most common ones: energy decomposition analysis (EDA), symmetry-adapted perturbation theory (SAPT), quantum theory of atoms-in-molecules (QTAIM)], each of which has a particular chemical interpretation, linking the formalism to well-known chemical concepts such as the chemical bond<sup>44,45</sup>. Inconsistencies between alternative bonding analyses<sup>46–49</sup> and possibly also misinterpretations<sup>50</sup> have been the source of many controversies<sup>51,52</sup>.

In QTAIM, from the continuous electron density  $\rho(r_c)$ , critical points are defined. These are the points for which the gradient (first derivative) of  $\rho(r_c)$  vanishes and are either maxima, minima or saddle points. Bond critical points (BCPs) labeled as (3,-1) BCPs represent a maximum in  $\rho(r_c)$  in 2 directions and a minimum in the third one and are thus saddle points of the density. (3,-1) BCPs are found between nuclei, and are typically associated with noncovalent interactions, with some controversy as to whether these nuclei are always linked by a chemical bond or not and if a (3,-1) BCP is necessary to have a bonding interaction. For a comprehensive overview on QTAIM, see Kumar *et al.*<sup>53</sup>

In the next section, we will explore the necessity and sufficiency of (3,-1) BCPs for there to be attractive interactions. In many instances such BCPs do correspond to attractive interactions; however this is not universal, as will be discussed for the the diethyl disulfide “staples”, introduced recently<sup>19</sup> as cases of intramolecular repulsion, and for the long-standing question regarding the H-H interactions in planar biphenyl and phenanthrene.

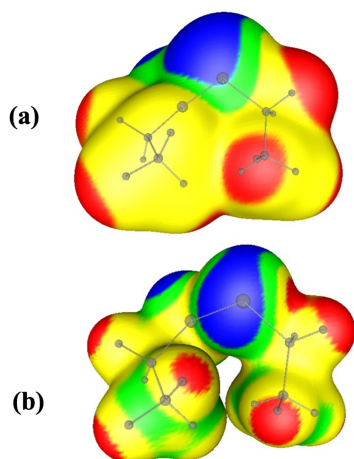
### ***Diethyldisulfide “staples”***

In our previous publication<sup>19</sup>, for a series of diethyl disulfide conformations, the nearly-touching contours of the electrostatic potential plotted on iso-density molecular surfaces allowed the assessment of intramolecular repulsion. For conformers with conformational energy near zero (relative to the conformer in its lowest energy conformation), the hydrogens and terminal methyl groups are separated at the 0.001 a. u., the 0.002 a. u. and 0.003 a. u. contours. However, for conformers obtaining “staple-like” conformations and having high conformational energies, the electron densities of the ethyl groups overlap on the 0.001 a. u. contour envelope. Figure 3 (a) shows DEDS4 as an example, having a relative conformational energy of 6.98 kcal/mol.<sup>19</sup> Electron density must be excluded from the surface envelopes in order to make the  $V_{S,max}$  visible on each H-atom and to separate the electrostatic potentials of



the terminal methyl groups. Accordingly, the electrostatic potential has to be plotted on a contour closer to the nuclei, in the given example, the 0.0105 a. u. contour. (Figure 3 (b)).

Furthermore, we can see that the nearly touching groups have positive potentials (indicated by the green/yellow/red color in Figure 3(b)), repelling each other. As such, in DEDES4 in Figure 3, the end methyl groups are involved in a repulsive interaction. It is noteworthy that a (3,-1) BCP is present between the closest hydrogens in DEDES4. (Not all of the diethyl disulfides with larger conformational energies have (3,-1) BCPs; for the ones that do, however, they are found between hydrogens of the terminal methyl groups.)



**Figure 3:** Electrostatic potentials plotted on the 0.001 a. u. contour (a) and 0.0105 a. u. contour (b) of a diethyl disulfide staple, DEDES4, having a relative conformational energy of 6.98 kcal/mol.<sup>19</sup> Color ranges are, in kcal/mol: for (a) red, greater than 10; yellow, between 10 and 0; green, between 0 and -10; blue, more negative than -10; for (b) red, greater than 30; yellow, between 30 and 15; green, between 15 and 0; blue, negative.

### *The H-H problem in planar biphenyl and phenanthrene*

Hydrogen-hydrogen bonding is a popular topic and it has been widely discussed whether a stabilizing interaction exists between adjacent H-atoms in, for example, planar biphenyl and phenanthrene. It has been shown before that a (3,-1) BCP does exist between the adjacent hydrogen atoms in planar biphenyl and the phenanthrene, which has led to the interpretation of H-H bonding,<sup>49</sup> and accordingly to many controversies.<sup>46-48</sup>

Here, we will show, based on the search for the nearly-touching contours in planar biphenyl and phenanthrene, that indeed, the adjacent H-atoms are involved in interactions, but as the electrostatic potentials plotted on these nearly-touching contours show, this interaction is destabilizing. This gives a new interpretation to the BCP: the existence of a (3,-1) BCP is not sufficient for there to be an attractive interaction. The presence of a (3,-1) BCP indicates that

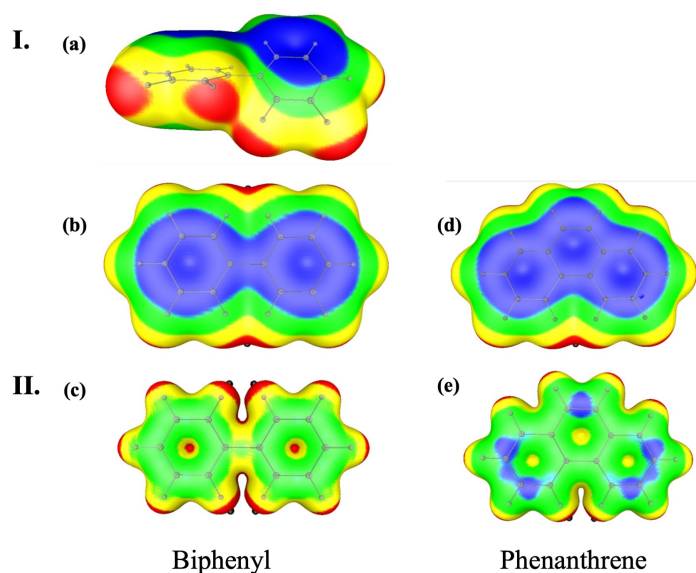
the atoms between which such a BCP is found are indeed involved in an interaction, but not necessarily a stabilizing one. Apparently, as we are finding, (3,-1) BCPs do not discriminate between stabilizing and destabilizing interactions.

Biphenyl in its lowest energy geometry has no (3,-1) BCPs between the closest hydrogens, which are around 2.38 Å apart (dihedral angle between rings about 39 degrees). Also, the electrostatic potential plots show a  $V_{S,max}$  on each H-atom at the 0.001 a. u. contour, indicating none of the H-atoms is involved in an interaction (Figure 4-I(a)).

This picture changes when you go to planar biphenyl. The typical hemispherical shapes of the electron density around the closest hydrogens, now about 1.85 Å apart, have disappeared at the 0.001 a. u. contour (Figure 4-I(b)). Only one  $V_{S,max}$  in between these two pairs of H-atoms is found, designated by black hemispheres, instead of two (one for each H-atom, which would be the case if these H-atoms were not in ‘interaction’). One needs to go to the 0.0178 a. u. contour (Figure 4-II(c)) to resolve the overlapping electron density and to find a  $V_{S,max}$  on each of the H-atoms. The plotted electrostatic potentials however show that they participate in repulsive contacts (red colored regions on the H’s; Figure 4-I(b) and 4-II(c)). Thus, indeed, the (3,-1) BCPs between the adjacent H-atoms reveal correctly that these H-atoms are interacting. However these BCPs are unable to identify whether the nature of the interaction is attractive or repulsive.

Similarly, for the phenanthrene example, the adjacent H's are about 2.00 Å apart and a BCP is found between them. Also here, we need to go closer to the nuclei, to the 0.01295 a. u. contour (Figure 4-II(e)), to resolve the overlapping electron density around these H-atoms found at the 0.001 a. u. contour (Figures 4-I(d)). These results suggest, in accordance with the BCP, that these adjacent H-atoms do interact; the electrostatic potential plotted on the nearly-touching contour reveals that they participate in a repulsive contact (*cfr.* red colored region on both H’s).

Note that Figure 4 is showing the positions of the  $V_{S,max}$  near interacting hydrogens in the planar cases (b), (c), (d) and (e), indicated by the black hemispheres. This shows clearly that adjacent H’s have overlapping positive regions that result in a single  $V_{S,max}$  until one goes to closer to the nuclei contours, where they then have separate  $V_{S,max}$ .



**Figure 4:** I. Electrostatic potentials plotted on the 0.001 a. u. contours of biphenyl (a), planar biphenyl (b) and phenanthrene (d). II. Electrostatic potentials plotted on the nearly-touching contour at 0.0178 a. u. for planar biphenyl (c) and at 0.01295 a. u. for phenanthrene (e). Color ranges, in kcal/mol, for (a), (b) and (d) are: red, greater than 10; yellow, between 10 and 0; green, between 0 and -10; blue, more negative than -10. Color ranges, in kcal/mol, for (c) and (e) are: red, greater than 50; yellow, between 50 and 25; green, between 25 and 0; blue, negative. Black hemispheres indicate the positions of the  $V_{S,max}$  near interacting hydrogens in (b), (c), (d) and (e).

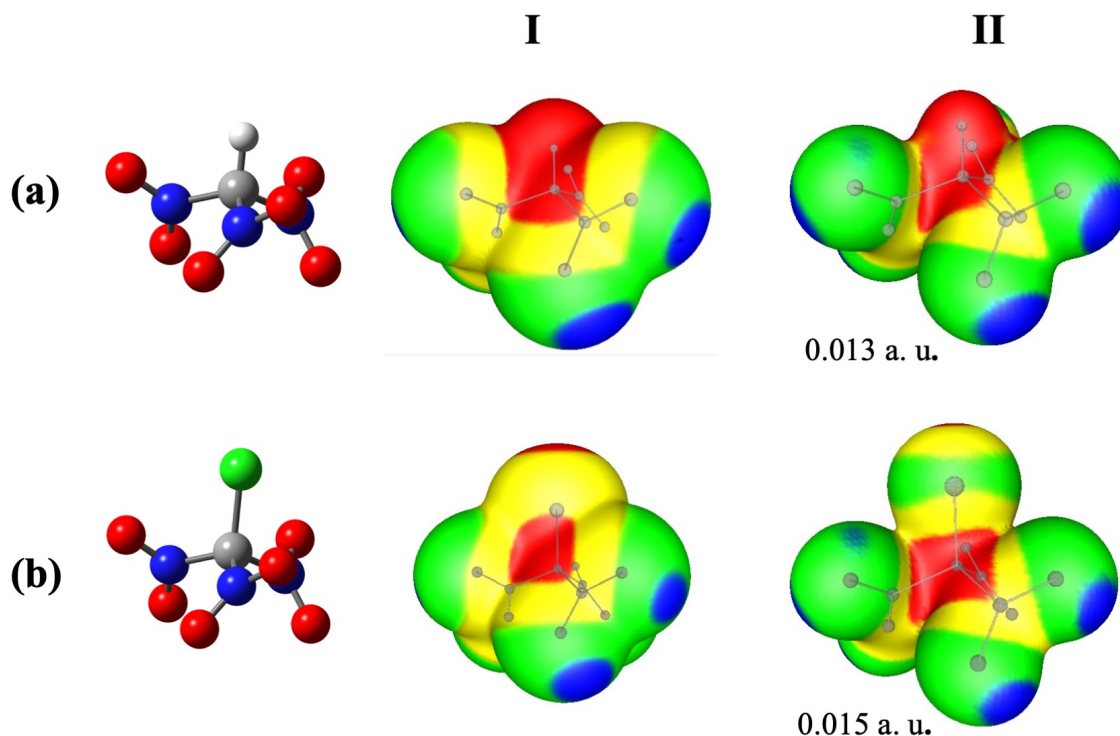
*Intramolecular attraction: are (3,-1) BCPs necessary for an attractive interaction?*

### ***Trinitromethane and chlorotrinitromethane***

The propeller-like molecules trinitromethane and chlorotrinitromethane are of special interest, as has been discussed earlier.<sup>9,42,54,55</sup> Looking at their structures, one can see the propeller-like orientations of the three nitro groups in each molecule, with three oxygens above the plane formed by the three nitro group nitrogens, and the other three oxygens below this plane. The carbon-hydrogen of trinitromethane (Figure 5 (a)) and carbon-chlorine of chlorotrinitromethane (Figure 5 (b)) form the vertical axes of the rotors.

Trinitromethane has a lower than might be anticipated acidity for its single hydrogen<sup>54</sup> and chlorotrinitromethane has the shortest carbon-chlorine single bond found in the Cambridge Structural Database<sup>42</sup>. Both facts can be explained quite simply as the result of attractive intramolecular interactions.<sup>9,42,54,55</sup> Indeed, the plots of the electrostatic potentials at the 0.001 a. u. contours show the hydrogen (Figure 5 I(a)) and chlorine (Figure 5 I (b)) in these molecules to have entirely positive surface potentials; this is what might be expected for the hydrogen, but not for the chlorine. There is clearly overlap at the 0.001 a. u. contour between the electron

densities of the positive hydrogen/chlorine and the three closest nitro oxygens, having negative electrostatic potentials, suggesting attractive intramolecular interactions. Going to larger contours closer to the nuclei, the 0.013 a. u. contour for trinitromethane and the 0.015 a. u. contour for chlorotrinitromethane, these overlapping electron densities are separated, and allow the hydrogen, chlorine and nitro groups to be better identified; see Figures 5 II (a-b).

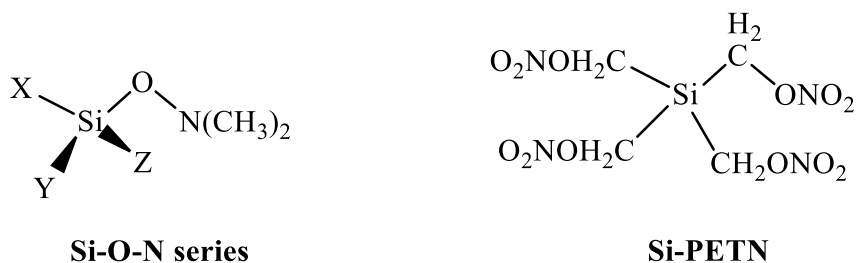


**Figure 5** Structures and computed electrostatic potentials on the 0.001 a. u. (**I**) contour and closer-to-the nuclei (**II**) contours for: (a) trinitromethane and (b) chlorotrinitromethane. Color ranges at the 0.001 a. u. contours, in kcal/mol, are: red, greater than 20; yellow, between 20 and 0; green, between 0 and -10; blue, more negative than -10. Color ranges at the 0.013 a. u. and 0.015 a. u. contours are: red, greater than 90; yellow, between 90 and 45; green, between 45 and 0; blue, negative.

An interaction is also suggested from the distances between H and the closest O's in trinitromethane, which are 2.92 Å, while the sum of the H and O vdW radii is ~3.0 Å. For chlorotrinitromethane, the distances between Cl and the closest O's are 2.92 Å, while the sum of the Cl and O vdW radii is ~3.3 Å. The suggested intramolecular 1,4-interactions (three H---O and three Cl---O), masked within the 0.001 a. u. surface, give explanations for the lower than expected acidity of the hydrogen in trinitromethane and for the short C-Cl bond distance in chlorotrinitromethane<sup>9,42,54,55</sup>. The closest oxygens to the hydrogen and chlorine in trinitromethane and chlorotrinitromethane can be envisioned as "clamps" holding the hydrogen and chlorine closer than might be expected to the carbon atoms to which they are bonded. Neither for trinitromethane nor for chlorotrinitromethane are there (3,-1) BCPs corresponding to these 1,4-interactions. We will return to this in a later section.

### ***Attractive intramolecular Si---O and Si---N interactions***

A series of molecules corresponding to the formula  $XYZSiON(CH_3)_2$  was synthesized by Mitzel *et al.*<sup>56-60</sup>, of which the structure is shown in Scheme 1 together with the structure of silicon pentaerythritol tetranitrate (Si-PETN)<sup>61</sup>.



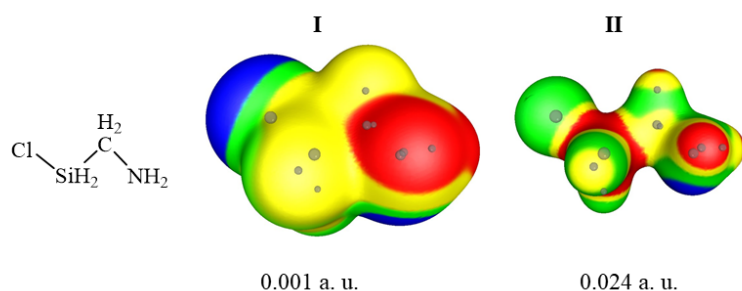
*Scheme 1*

Si-PETN is an analogue of pentaerythritol tetranitrate (PETN), where the central carbon is replaced by a silicon. Detailed computational studies have shown that the Si and O atoms in Si-PETN and the Si and N atoms in  $XYZSiON(CH_3)_2$  molecules participate in 1,3-attractive intramolecular interactions<sup>61,62,63</sup> held responsible for both the extreme lability of Si-PETN<sup>62,63</sup> and the contracted Si-O-N bond angles, short Si---N distances and reduced basicities of the amine nitrogens of the  $XYZSiON(CH_3)_2$  and similar molecules<sup>50,56-60,64,65</sup>. The electrostatic potentials of these molecules computed on 0.001 a. u. molecular surfaces do not reveal the driving forces for these attractive 1,3-interactions; these are happening within the 0.001 a.u. envelopes<sup>50,63-65</sup>, similar to the 1,4-interactions of trinitromethane and chlorotrinitromethane (Figure 5).

Table 1 lists the Si-N separations for the series  $ClH_2Si(CH_2)_nNH_2$  where  $n = 1 - 4$  and the nearly-touching contours of the electronic density which allow the driving forces of these interactions to be seen. In each case, the Si---N separation is considerably less than the sum of the van der Waals radii of Si and N, which is  $\sim 3.8 \text{ \AA}$ .<sup>66</sup> Figure 6 shows for the first molecule in this series,  $ClH_2SiCH_2NH_2$ , the structures and electrostatic potentials at the 0.001 a. u. contour (I) and a closer to the nuclei contour, 0.024 a. u. (II).

**Table 1.** Computed data for  $\text{ClH}_2\text{Si}(\text{CH}_2)_n\text{NH}_2$ , where  $n = 1 - 4$ . The contour X corresponds to the contour of the electronic density which separates the interacting Si and N atoms.

Molecule	Si---N separation (+++)	Contour X (a. u.)	Presence/absence of (3,-1) BCP
$\text{ClH}_2\text{SiCH}_2\text{NH}_2$	2.65	0.024	absent
$\text{ClH}_2\text{Si}(\text{CH}_2)_2\text{NH}_2$	2.69	0.023	absent
$\text{ClH}_2\text{Si}(\text{CH}_2)_3\text{NH}_2$	2.40	0.038	present
$\text{ClH}_2\text{Si}(\text{CH}_2)_4\text{NH}_2$	2.34	0.041	present



**Figure 6.** Structures and computed electrostatic potentials on the 0.001 a. u. contour (**I**) and the 0.024 a. u. contour (**II**) for  $\text{ClH}_2\text{SiCH}_2\text{NH}_2$ . Color ranges at the 0.001 a. u. contour, in kcal/mol, are: red, greater than 20; yellow, between 20 and 0; green, between 0 and -10; blue, more negative than -10. Color ranges at the 0.02 a. u. contour are: red, greater than 100; yellow, between 100 and 60; green, between 60 and 0; blue, negative.

Table 1 shows that not in all cases are (3,-1) BCPs found, only in the  $\text{Si}-(\text{CH}_2)_n\text{-N}$  systems with  $n = 3, 4$ . These BCPs are found only when a 1,5- or 1,6- interaction is present, not for the molecules in which the Si and N form an 1,3- or 1,4-interaction (i. e.  $n = 1$  or 2). This stresses again, as was the case for trinitromethane and chlorotrinitromethane, discussed in the previous section, and before extensively questioned in the literature,<sup>37,50,52</sup> that the presence of (3,-1) BCPs is not strictly necessary or sufficient to indicate the presence of an attractive interaction.

#### *Gauging the strength of intramolecular interactions*

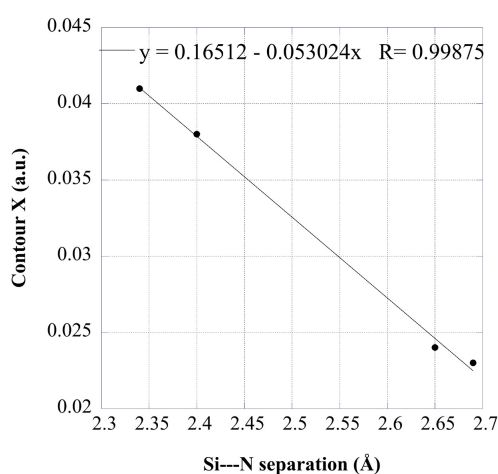
For stronger interactions, whether they be attractive or repulsive, it seems intuitive that one must exclude more electronic density to free the interacting atoms, or differently stated, that the nearly-touching contours are closer to the nuclei (thus higher in value). It is this excluded density that is responsible for the intramolecular interaction. We looked at this quantitatively before for a series of intermolecular interactions<sup>17,18</sup> and to a lesser extent, also for intramolecular interactions using a series of diethyl disulfides having different conformations.<sup>19</sup> For this series<sup>19</sup> we estimated the conformational energy by establishing the quantitative relationships between volumes at the nearly-touching contour X and relative conformational

energy and between the values of the nearly-touching contour X and relative conformational energy. This gives a clue and reasonable credence for a novel methodology to estimate intramolecular interaction energy, previously called an ‘indefinable quantity’<sup>10</sup>.

In this work, one point to notice is that the contour X to obtain the nearly-touching points for planar biphenyl and phenanthrene and are around 0.0178 a. u. and 0.01295 a. u. (Figure 4 (c) (e)), respectively. This is suggesting that the repulsion between positive hydrogens is greater for the planar biphenyl than for phenanthrene, following the distances between these adjacent H atoms of 1.85 Å and 2.00 Å for planar biphenyl and phenanthrene, respectively. So we are seeing that the contour X has some relationship, as we found for the disulfides, to the repulsion between hydrogens.

The values of the nearly-touching contours in Figure 2(c) and 2(d), 0.0197 a. u. for *o*-bromophenol and 0.055 au for *o*-nitrophenol, suggest that the intramolecular interaction between the phenolic hydrogen and the adjacent bromine of *o*-bromophenol is weaker than that of the similar hydrogen in *o*-nitrophenol and the closer nitro oxygen. As is expected, the  $V_s(\mathbf{r})$  on the 0.055 a. u. contour of *o*-nitrophenol is much more positive than that on the 0.0197 a. u. contour of *o*-bromophenol because the former contour is closer to the nuclei.

Also for the Si-N interactions in  $\text{ClH}_2\text{Si}(\text{CH}_2)_n\text{NH}_2$ , contour X increases (making the electron density envelope closer to the nuclei) as the Si---N separation becomes smaller (Figure 7). This suggests that the contour X can be used as an indicator of the strength of these attractive Si---N intramolecular interactions, as has been shown earlier for a variety of intermolecular interactions.<sup>17,18</sup>



**Figure 7** Plot of the electron density contour X vs. Si---N separation for the series  $\text{ClH}_2\text{Si}(\text{CH}_2)_n\text{NH}_2$ , where  $n = 1 - 4$ , using the data shown in Table 1. The R value is 0.999.

The nearly-touching contour approach for studying intramolecular interactions is not flawless, as it is not always easy to find the exact point of separation and thus to extract the exact value of the nearly-touching contour. When there are BCPs, it is very easy to find the nearly-touching contours; see Figures 2 – 4. For the 1,3- and 1,4- intramolecular interactions, however, it is a matter of trying to find the contour that allows the functional groups to be "seen", and thus also the driving forces for the interactions, whether they be repulsive or attractive. We will look at the topic of intramolecular interaction strength in more detail in further work.

## Concluding comments

Our major focus in this paper has been upon intramolecular interactions, a topic of extreme importance in a myriad of areas in chemistry, biochemistry and materials research. Our story however goes into other territories of computational chemistry, touching on intermolecular interactions as well<sup>17,18</sup> and bringing in Bader's elegant QTAIM<sup>20</sup>.

We computed the electrostatic potential on varying contours of the electronic density. The driving forces for interactions within a complex A---B or for intramolecular interactions are hidden within 0.001 a. u. iso-density envelopes. By going to contours of the electronic density closer to the nuclei, one can unveil these driving forces, using trial-and-error to obtain the nearly-touching contours for these interactions. The electrostatic potentials reveal the natures of the interactions. In the examples shown in Figures 2, 5 and 6, negative potentials are attracted to positive regions of electrostatic potential, yielding attractive interactions. In Figures 3 and 4, positive regions are interacting with positive regions, leading to repulsive interactions.

Our nearly-touching contours are by definition very similar to the values of the density at Bader's (3,-1) BCPs for molecules that have them. Our plots give three-dimensional views of the electrostatic potentials on the iso-density contours at these points, providing a novel way of looking at these interactions.

BCP's are found for 1,5- and 1,6- and greater intramolecular interactions in Figures 2 – 4. However only those for the intramolecular interactions of *o*-bromophenol and *o*-nitrophenol in Figure 2 are attractive. Those in the diethyl disulfide staple DEDS4 (Figure 3) and planar biphenyl and phenanthrene (Figure 4) are clearly repulsive. Our data suggests here that the presence of (3,-1) BCPs does not ensure an attractive interaction.

The 1,4- and 1,3-interactions shown in Figures 5 and 6 do not exhibit (3,-1) BCPs, yet there is strong evidence of attractive intramolecular interactions in both trinitromethane<sup>54</sup> and chlorotrinitromethane<sup>42,55</sup> (Figure 5) and in the many synthesized XYZSiON(CH<sub>3</sub>)<sub>2</sub> molecules<sup>56–60,64,65</sup>, Si-PETN<sup>62,63</sup> and the series of ClH<sub>2</sub>Si(CH<sub>2</sub>)<sub>n</sub>NH<sub>2</sub> molecules and analogues. Our conclusion here is that (3,-1) BCPs are not necessary to have an interaction; the topology of the electronic density is the determining factor as to whether there are (3,-1) BCPs<sup>37–39,44,50,52</sup>.



Thus, (3,-1) BCPs are not necessary or sufficient for the existence of attractive or repulsive intramolecular interactions.

For a series of similar interactions, the value of the nearly-touching contour  $X$  often correlates with the strength of the intramolecular interaction, as has been demonstrated in this paper. We have found this also to be the case for intuitive and counter-intuitive attractive intermolecular interactions<sup>17,18</sup>. It would certainly make an interesting point for a full study to extend our analyses and test our proposed methodology to other types of both inter- and intramolecular interactions, e. g. the interactions in diradical anions, which are somewhat counter-intuitive.

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