*Open Journal of Physical Chemistry*, 2012, 2, 15-22
http://dx.doi.org/10.4236/ojpc.2012.21003 Published Online February 2012 (http://www.SciRP.org/journal/ojpc)

# A Computational Evaluation of Bond Order and Charge Distributions in Isomeric Aminotroponiminiums and Their Benzo-Fused Derivatives

**S. Natarajan Balasubrahmanyam[1,2*], Irishi Narayanan Namboothiri[3], Kuruvilla Pius[4]**
[1]Department of Organic Chemistry, Indian Institute of Science, Bangalore, India
[2]Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore, India
[3]Department of Chemistry, Indian Institute of Technology, Mumbai, India
[4]Department of Chemistry, Mahatma Gandhi University, Kottayam, India
Email: *snb@orgchem.iisc.ernet.in

Received July 6, 2011; revised August 24, 2011; accepted October 10, 2011

## ABSTRACT

This paper reports the results on the nature of bond-order and net charge distributions predicted by *ab initio* Hartree-Fock procedures for 1-amino-2-iminio-, 1-amino-3-iminio- and 1-amino-4-iminiotropylium cations that incorporate, in order, the 1,7-, 1,3- and 1,5-diazapentadienium (vinamidinium) elements. There appears to be very little contribution from tropylium-type charge distribution, the positive charges residing largely in the nitrogen atoms. The partial bond fixations and charge distributions show interesting variation in the three isomers. The 1,3-isomer in which the 1,3-diazapentadienium element is preserved in the favoured zigzag conformation appears to be relatively the best stabilized. The six isomeric benzo-fused derivatives arising from the three amino-iminiotropylium cations show similar differences in patterns of behaviour. Interestingly, the isomer in which a zigzag 1,3-diazapentadienium element is conjugated with a styrene moiety receives the deepest stabilization. While showing that the element largely contributes to the relative stabilization among the systems studied, contribution from certain stereochemical destabilizing factors may not be insignificant.

**Keywords:** Vinamidinium Element; Amino-Iminiotropylium Cations; Benzo-Fused Amino-Iminiotropylium Derivatives; *Ab initio* Hartree-Fock Procedures; Partial Bond Fixations; Net Charge Distributions; Stereochemical Factors

## 1. Introduction

An evaluation of bond localizations and charge redistributions by theoretical methods when the amino (poly) vinyliminium (vinamidinium) structural element **1** (for the wide application of this element in chemistry see [1-11]) is made part of a cyclic system (e.g. aminotropon-2-, -3- & -4-iminiums **2a**-**c**; n = 3, 1 & 2 in **1**; the numbering indicated for **2a** applies to all structures **2**) was of interest because differences in energy content among these possibilities can arise for a number of reasons: While it is possible to conceive of a formal "diaminotropylium"-type charge distribution (**a**, **b**, **c**) for all three cases, only **2a**, which has the N *ipso*-carbons directly linked, can participate as a whole in a vinamidinium-type delocalization (**2'a**). In the cases of its analogues **2b** and **2c** passage of π-information between the nitrogens for delocalization of that type would be, apparently, confined to their "odd" sides (**2'b** and **2'c**) even while both have alternate vinylogous connectivity between the nitrogen *ipso* carbons.

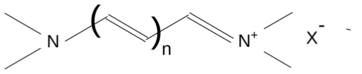
- Available experimental evidence [12] has shown that vinamidinium chains **1**, including those with 1,3-disubstitution, generally prefer *anti*-periplanar (*i.e.* zigzag) conformations. While such a conformation (**2'b**) can be maintained in the vinamidinium part of **2b**, *syn*-periplanar conformations are forced on **2a** and the vinamidinium part of **2c** (**2'c**). Differences in the degree of destabilization may, therefore, be expected to depend on the delocalization that comes into effect on cyclization into forms **2a**-**c**.
- Angle strain would be introduced when the internal angles open out beyond 120° to accommodate a planar 7-membered cyclic structure. Relief of strain can be expected to depend on the specific partial bond fixations that come about in **2a**-**c**.
- Alternatively, bond localization could be such as would permit the 7-membered cycles to assume specific puckered conformations, minimizing angle strain

---

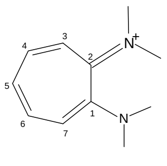
[*]Corresponding author.

while affecting the nature of the delocalization at the same time.

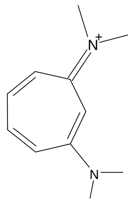
- The N-C-C-N array may not be uniplanar in the 1,2-system **2a** in order that *syn*-periplanar interaction be relieved, causing it to be different from the 1,3- and 1,4-systems **2b** and **2c** both of which may prefer to be entirely planar.



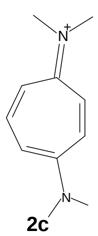
**1**



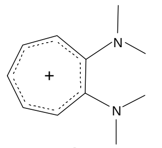
**2a**



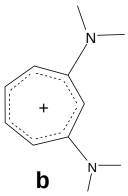
**2b**



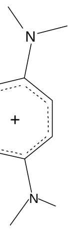
**2c**



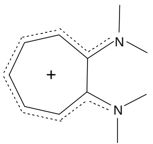
**a**



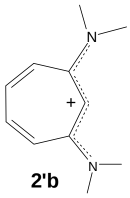
**b**



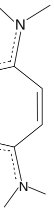
**c**



**2'a**



**2'b**

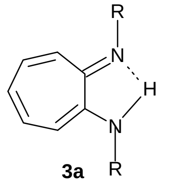


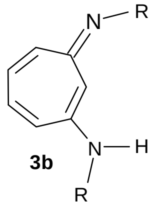
**2'c**

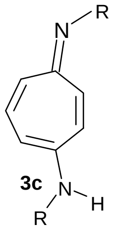
## 2. Structures with Aminotroponiminium Elements

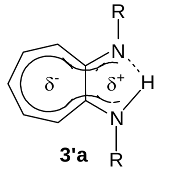
Attempts to synthesize the aminotroponimines structured like **2a-c** were made at a time when interest in comparing them, in order, with $\alpha$-, $\beta$- and $\gamma$-tropolones was running high [13-17]. Ionic representation **2a**/**2'a** would definitely have been that of the N,N'-tetramethylated primary product when one of the methods developed for the synthesis of the 1,2-free base N,N'-dimethyl derivative **3a** (R=Me) and salts thereof was suitably adapted [13]. The products were found to be highly unstable compared with **3a** which shows unusual stability and appreciable "aromatic" character: it undergoes facile nuclear electrophilic substitution and shows IR absorption bands for the presence of strong intramolecular N-H---N bridging. However, it exhibits its ring proton resonances upfield of those of $\alpha$-tropolone (**4**) and its dipole moment is in the opposite direction. An initial interpretation of these pieces of evidence was that they were consistent with the establishment of a 10π-electron circuit (**3a'**) involving hybridization of non-bonding electrons of the NHR substituent. (*cf.* the case of N-*tert.* butyl-3-(*tert.* butylamino)-2-nitroprop-1-en-1-amine for which X-ray evidence [18] can be said to accord with "through-resonance" of this type.) It should be noted, however, that a canonical structure (akin to **4**) where negative charge resides mostly on oxygen and the positive charge is distributed in a "tropylium" manner is not a large contributor to resonance in tropone. X-ray diffraction measurements and analysis of dipole moments and NMR spectra have disclosed that tropones and tropolones display appreciable partial bond fixation and must be regarded essentially as non-aromatic although some aromatic character can be accorded because of a susceptibility to aromatic-type substitution. The $^{1}$H and $^{13}$C spectra of the N,N'-isopropyl derivative of corresponding to **3a** (R=*i*Pr), have been stated to show better consistency with the presence of rapid tautomeric equilibrium in the solution state. However, X-ray crystallographic data have disclosed that the two C-N bonds differ significantly in length (N=C: 1.314 Å; N-C: 1.342 Å), showing that in the solid state the structure is not symmetric on the whole even while the seven-membered ring and the two nitrogen atoms are nearly uniplanar.

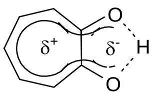
Structures **3b** and **3c** can only be just presumed to have been those of the primary products in their attempted synthesis [16,17]. The instability of **3b** and **3c** is in accord with the absence of possibility in them of intramolecular N-H---N bridging. While a hydrochloride of the 1,3-system **3b** is hygroscopic and unstable, both the 1,3- and 1,4-systems (**3b** and **3c**) are said to give stable, crystlline picrates associated with waters of crystallization. The authors of reference [16] managed to record the $^{1}$H NMR spectrum of the 1,3-system **3b** and found that the ring protons appear at fields higher than the "aromatic region", the shifts being even less than those of the protons of $\beta$-tropolone. While this may be seen as according well with an absence of possibility of establishing a H-bond mediated peripheral circuit the authors do not say explicitly whether the $^{1}$H NMR spectrum is or is not consistent with a symmetric structure [16,17]. The ethylene bridged free base **5**, where N-H---N bridging is not possible, has been synthesized [19]. The cycloheptimidazolonium salt **6**, where the two nitrogen atoms that bear partial positive charges are bonded to a carbonyl, is an interesting precursor in a synthesis of N,N'-disubstituted 1-amino-2-imino-cycloheptatrienes [20]. This system and the cycloheptaquinoxalinium salts **7** [15], are among those that formally retain the 1-aminotropon-2-iminium cationic element **2a** *per se*. The electronic structure of cation **7a** has spawned an interesting debate. It was first put forward as an example of a stable anti-aromatic with a peripheral 16π-electron circuit (form **7'a**) [21]. However, an estimation of resonance and circuit resonance energies and ring currents (employing graph theoretical methods [22-25]) showed that it would be more realistic to regard it and its other hetero-analogues **7b-d** as 6π-tropylium-6π-benzo systems **7”a**. π-Electron distributions calculated by MNDO and $^{13}$C NMR chemical shifts [26-28] have been found to accord with this structure.

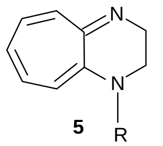

**3a**

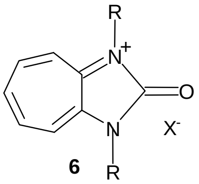

**3b**

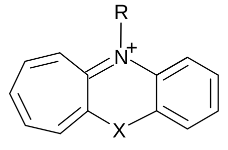

**3c**

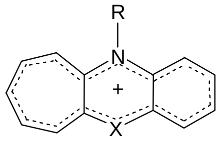

**3'a**

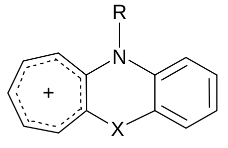

**4**


**5**


**6**


**7a: X = NH 7c: X = O**
**7b: X = NMe 7d: X = S**


**7'a**


**7''a**

## 3. Computational

### 3.1. Aminotroponiminiums

*Ab initio* MO procedures were applied to systems **2** [with amino (-NH$_2$) and iminium ($=\mathrm{NH}_2^+$) groups] in the attempt to obtain information on the possibilities raised above. Algorithms of the well-known GAUSSIAN procedures of various levels HF/3-21G, HF/6-31G$^*$and MP2/6-31G$^*$ (including one that takes into account electron correlation, all available in our laboratories) were used for implementing the calculations. The MO procedures yield somewhat different relative energies for each case (**Table 1**) for the possible reason that they take into account electron correlation in different ways. MO procedures are generally not regarded as suitable for direct comparison of stabilities on the basis of (small) differences in energy content. We hope to show, at least by implication, that the on-the-average lesser stabilization of the 1,2-system **2a** has significance.

### 3.2. Benzo Fusion

A strategy adopted in the investigation of mechanisms of reactions of tropolones has been predicated on a possibility that double bond character can be localized at certain positions within the 7-cycle by benzo-fusion [29].

Benzo-fusion to systems **2a-c** yields six isomeric benzo-analogues, formally represented by particular sets of canonical structures **8a-f** shown in **Figure 1** below, that may be expected to differ in the modes of electron delocalization.

**Table 1. *Ab initio* relative energies (kcal/mol) of aminotroponiminiums 2a-2c.**

| Species | HF/3-21G | HF/6-31G$^*$ | MP2/6-31G$^*$ |
|---|---|---|---|
| **2a** | 0.5 | 11.1 | 2.5 |
| **2b** | 0.0 | 0.0 | 0.0 |
| **2c** | 2.6 | 3.2 | –0.2 |

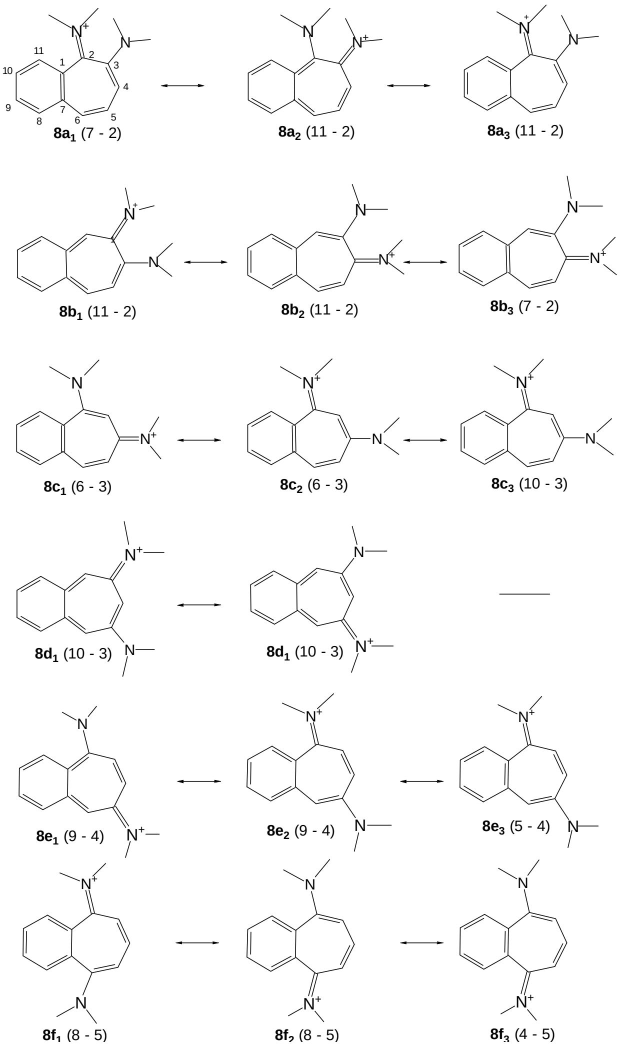


**Figure 1. Structures resulting from benzo-fusion of 1, 2-, 1, 3- and 1,4-amino-iminiocycloheptatrienes. Odd numbers in parentheses denote possible “vinamidic” pathways. The numbering indicated for 8a applies also to 8b-f.**

It was of interest to examine in what way the MO procedures would reflect the electron redistributions and structural features. The relative energies of the isomeric systems **8** are assembled in **Table 2**.

We discuss possible factors that may underlie why the non-symmetric 1,3-diamino system **8c**, derived from the diaminotropylium **2b**, the most stabilized among the monocyclic systems, is predicted also to be the most stabilized one. The structures were geometry optimized in the two sets of cases. Net atomic charges and HF calculated bond lengths (Å; in italics), shown in the structures in **Figures 2** and **3** below, were chosen to serve as the parameters relevant to making qualitative comparisons among each set of the systems.

**Table 2. *Ab initio* relative energies (kcal/mol) of Aminobenzotroponiminiums 8a-8f.**

| Species | HF/3-21G | HF/6-31G$^*$ | MP2/6-31G$^*$ |
|---|---|---|---|
| **8a** | 11.6 | 12.8 | 8.6 |
| **8b** | 5.0 | 5.6 | 4.6 |
| **8c** | 0.0 | 0.0 | 0.0 |
| **8d** | 13.6 | 12.5 | 10.3 |
| **8e** | 12.4 | 13.4 | 9.5 |
| **8f** | 12.5 | 12.6 | 8.0 |

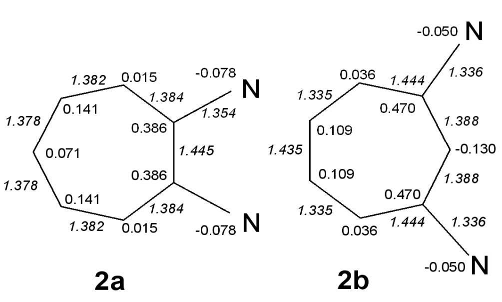


**Figure 2. HF bond lengths and net charge distributions in aminotroponiminiums.**

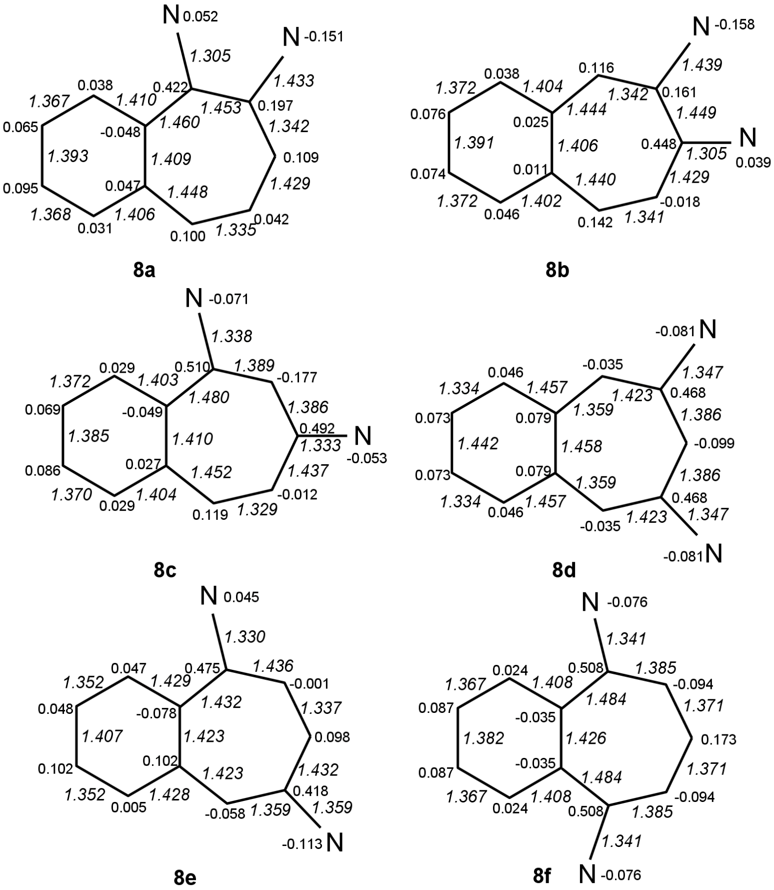


**Figure 3. HF bond lengths and net charge distributions in benzo-aminotroponiminiums.**

## 4. Results and Discussion

### 4.1. The Aminotroponiminiums 3

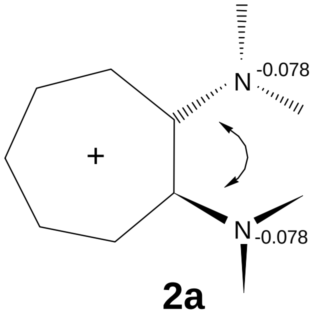
There seems to be good indication that stabilization correlates inversely with the length of the vinamidinium chain (**2’a** > **2’c** > **2’b**). Differences in the energies of formation of systems **2** apparently depend on maintenance of the zigzag conformation, as is the case in **2b**. Energy changes on the account that one and two *syn*-periplanar conformations are forced on the vinamidinium chains in **2c** and **2a** may not be strictly additive, however.

Factors of further interest are:

- Protonation of nitrogen draws electron density away from the nitrogen-*ipso* carbons to appreciable extents in all these aminotroponiminiums. High positive charges at the nitrogen-*ipso* carbons and build-up of electron density at the $\alpha$ carbons are seen.
- Consequent “vinyl cation” delocalization leads to charge alternation on the vinamidinium parts, the “odd” sides of aminotroponiminiums **2b** and **2c**.
- High bond orders are found at adjacent bonds in **2b** and **2c**.
- Vinamidinium character is well-preserved in **2b** and **2c**.
- Partial bond fixation is clearly seen on the “even” sides of **2b** and **2c** in the form of appreciable shortening of the C(4)-C(5) & C(6)-C(7) bonds in **2b** (1.335 Å) and the C(2)-C(3) bond in **2c** (1.338 Å).
- The pairs connecting the vinylic part with the vinamidic part [C(3)-C(4) & C(7)-C(1) in **2b** (1.444 Å) and C(1)-C(2) and C(3)-C(4) in **2c** (1.441 Å)] remain long (>1.40 Å), emphasizing suppression of delocalization on the “even” sides.

These characteristics are not strictly shared by the vinamidinium system that encompasses the whole of **2a**. While the bond connecting the nitrogen-*ipso* carbons [C(1) & C(2)] is long (1.445 Å) and there is a progresssive decrease in bond lengths along the half cycle, there is no charge alternation but only an alternate placement of low and high residual positive charges, in the form of equal partial positive charges on the symmetrically placed carbons. A similar polarization is found on the “even” sides of **2b** and **2c**: high positive charges at the nitrogen-*ipso* carbons cause a build-up of electron density at the $\alpha$ carbons but successive carbons bear decreasing amounts of positive charges; there is no charge alternation.

“Steric interactions” between the two vicinal nitrogens seem clearly present: atom co-ordinates show out-of-plane movements of the two nitrogen atoms (**Figure 4**). Puckering of the ring preserves $C_{2v}$ symmetry. The C-N bonds are lengthened compared with the values in **2b** or **2c** (1.395 Å in **2a** vs 1.363 Å in **2b** and 1.365 Å in **2c**). The increase in the negative charge at the nitrogens indicates a more amine-like and pyramidal than iminio-like and planar character.



**2a**

**Figure 4. Steric interaction between vicinal amino groups in 1,2-aminotroponiminium.**

While these factors can account for some of the differences in the energies of formation among systems **2** it appears that the roughly inverse correlation of stabilization with the length of the vinamidinium chain (**2b** ≅ **2c** > **2a**) must derive from what was anticipated in the “Introduction” section. While the zigzag conformation is maintained in **2b**, one and two *syn*-periplanar conformations are forced on the vinamidinium chains when they take the cyclic forms, respectively **2c** and **2a**, the proviso being energy changes on this account may not be strictly additive, as already noted.

### 4.2. The Benzo-Aminotroponiminiums

For carrying through qualitative comparisons conveniently features of systems **8** salient from the MO calculations have been assembled in **Table 3** overleaf.

- System **8c**, the nonsymmetric one of the two 1,3-systems, emerges as the most stabilized. All systems **8** share the feature of having the C(8)-C(9) and C(10)-C(11) bonds short and C(7)-C(1) bonds long making it appear that partial bond fixation in the benzo parts accords with a large contribution from *o*-quinonoid canonical structures, including the cases **8c** and **8f** for which such structures cannot be set down without charge separation.
- That the fixation is really not *o*-quinonoid in any of the cases except **8d** is clear from the increase in the lengths of both C(1)-C(2) and C(6)-C(7) bonds.
- While N(A) in **8a** and N(B) in **8b** bear partial positive charges, the partial charges at N(B) in **8a** and N(A) in **8b** are negative.
- The negative charges are much larger than at the negatively charged nitrogens of the other systems. The C-N bond lengths associated with the negative nitrogens are much longer than the ones associated with the positive nitrogens C(A)-N(A)—1.305 & C(B)-N(B)—1.433 Å in **8a** and C(A)-N(A)—1.439 & C(B)-N(B)—1.305 Å in **8b**, betokening amino and

**Table 3. Features of systems 8 qualitatively compared.**

| System | Position of Benzannulation and Minimum Length of Vinamidinium | Sign of Charge on Nitrogen and C-N Bond Length | Specific C-C Bond Lengths | Residual Positive Charges on Nitrogen-*ipso* Carbons | Signs of Charges at *α*-Carbons | Vertical (Y) Component of Dipole Moment[a] |
|---|---|---|---|---|---|---|
| **8a** | Vin.[b] (7C) | +N(A) – N(B)<br>short long | (A)-C-C-N-(B) long | Large Difference | Negative at C(*α*)-C-N(A)<br>Positive at C(*α*)-C-N(B) | Non-zero |
| **8b** | Vin. (7C) | –N(A) + N(B)<br>long short | (A)-C-C-N-(B) long | Large Difference | Positive at C(*α*)-C-N(A)<br>Negative at C(*α*)-C-N(B) | Non-zero |
| **8c**[c] | Even (3C) | –N(A & B) short, small diff. | Vin. part isolated by long bonds | Small Difference | Negative; small difference | Zero[d] |
| **8d** | Even (3C) | –N(A & B) short, equal | Vin. part isolated by long bonds | Equal | Negative; equal | Zero |
| **8e** | Vin. (5C) | –N(A & B) short, small diff. | Unequal pairs on Vin. side | Small Difference | Negative; larger at C(*α*)-C-N(A) | Zero[d] |
| **8f** | Even (5C) | –N(A & B) short, equal | Long bonds on even side | Equal | Negative; equal | Zero |

[a]See **Figure 5**. [b]Vin. = Vinamidinium. [c]The most stabilized system **8c** is styrene-like and vinamidic character appears best preserved. [d]No evidence of N---(benzo)H *peri*-interaction.

iminio C-N partial bond fixation in the respective cases.

- The ionic positive charge appears redistributed over the entirety of systems **8**. However, the largest residual positive charges are concentrated at the nitrogen-*ipso* carbons. While these charges are equal in the symmetric cases (**8d** & **8f**) and not very different in their non-symmetric analogues **8c** & **8e**, systems **8a** & **8b** are exceptional in that the charge differences are large, those at carbons *ipso* to the negative (amino-type) nitrogens, C(3) in **8a** and C(4) in **8b**, being much lower. The gathering of positive charges at both the nitrogen and carbon of the iminio-type C-N groups could be a destabilizing factor in these systems.
- Carbons *α* to the nitrogen-*ipso* carbons bear small negative charges in all cases. A part of this feature could be normal to the vinamidinium-type charge redistribution but there are three exceptions: carbons α to those bearing low positive charges in systems **8a** and **8b** and C(4) on the "even" side of **8e** bear positive charges.
- Neighbouring carbons on the "even" side of **8f** [C(1) & C(7)] bear negative charges.
- Low bond order (length > 1.45 Å) of the N(A)-C-C-N(B) bond, found in the precursor **2a**, is maintained in both of the benzo systems **8a** and **8b** derived from it. The lengthening arises, presumably, from an accumulation of high residual positive charges at vicinal carbons, C(2) & C(3) in **8a** and C(3) & C(4) in **8b**. It is manifest in a different form in systems **8c-8f**, leading to virtual isolation of the "odd" vinamidinium part from the "even" part—bonds C(1)-C(2) & C(4)-C(5)in **8c**, C(2)-C(3) &C(5)-C(6) in **8d**, C(2)-C(3) & C(4)-C(5) in **8e** and C(1)-C(2) & C(6)-C(7) in **8f** are long.
- The lengthening of the C(1)-C(7) bridging bond in systems **8**, coupled with partial bond fixation within the benzo ring, may or may not always accord with the bond order distribution natural to vinamidinium in those cases where benzo-substitution is on the vinamidinium side, as in **3e**.
- This factor is important if systems **8c** and **8e** or **8e** and **8f** are compared. **8c** is stabilized relative to **8d** despite the cyclizing entity being styrene-like in **8c** and *o*-quinonoid-like in **8d**.
- Absence of an iminio-type C-N group, with its in-plane hydrogens is presumably necessary for any out-of-plane movement of the constituent atoms or puckering of the 7-membered cycle. Systems other than **8a** and **8b** show zero orthogonal component of dipole moment (**Table 4**) even though the possibility of *peri*-interaction exists [30,31], one in each of **8c** and **8e** and two in **8f**.
- A component of dipole moment orthogonal to the general planes is present in both **8a** and **8b** and absent in the others (**Figure 5**). Atom co-ordinate data have indicated that the component arises both from a puckering of

**Table 4. Dipole moment components (debyes).**

| | X | Y | Z |
|---|---|---|---|
| **8a**[a] | −0.4707404 | −0.3161992 | 0.9706146 |
| **8b**[a] | −0.5218589 | 0.0001089 | 1.2733497 |
| **8c** | −0.6376398 | 0.0000000 | −1.2426583 |
| **8d**[b] | 0.0000000 | 0.0000000 | −1.3905561 |
| **8f** | 0.1818975 | 0.0000000 | 1.3918996 |
| **8e**[b] | 0.0000000 | 0.0000000 | −0.1339071 |

[a] Non-zero component of dipole moment orthogonal to the general molecular plane (see **Figure 5**) in **8a** & **8b** could be evidence of out-of-plane placements of the nitrogens and/or puckering of the 7-membered ring. [b] $C_{2v}$ symmetry is present.

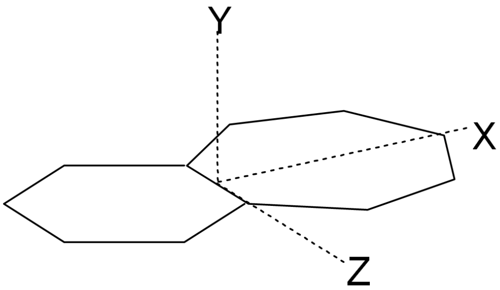


**Figure 5. Co-ordinate system for the benzo-aminotroponiminiums.**

the 7-membered ring and from out-of-plane placement of the nitrogens. The greater magnitude of the component in **8a** could arise from a larger out-of-plane movement of N(A) from a need to minimize not only *peri*-interaction of the *syn* iminio hydrogen on planar N(A) with the C(11) hydrogen but also the interaction of the *anti* iminio hydrogen with the amine-like N(B). However, the need to maintain uniplanarity of H-N(A)-H with C(1)-C(2)-C(3) in the system seems met partly by puckering of the ring whereby N(A) is moved above the general plane and partly by lengthening of the C(11)-C(1) bond.

- A point of similarity exists between systems **3f** and **3d** even though *o*-quinonoid bond order distribution, available to **3d**, is not very likely for **3f**. The symmetrically placed bonds between the vinamidinium and the rest of the system are lengthened; the latter are the longest bonds encountered in all of systems **8**. This symmetric distortion of the 7-membered cycle may prevent the accumulation of angle strain.

## 5. Conclusion

The three formalisms employed for the computations HF/3-21G, HF/6-31G$^*$ and MP2/6-31G$^*$ are in agreement in predicting system **2b** as relatively the best stabilized among the three isomeric aminotroponiminiums compared and system **8c** as the most stabilized among their six positional isomeric benzo analogues. It appears safe to state that the 3-carbon length of the vinamidinium moiety and the freedom it has to assume the preferred zigzag conformation are paramount among the stabilizing factors. The destabilization of **2a** and **8a** relative to the others of its kind likely arises from twists around bonds of low bond order. The lengthening of the C(1)-C(7) bond in all of the systems **8**, coupled with the implied partial bond fixation within the benzo ring, may or may not always accord with the bond order distribution natural to the vinamidinium chain in cases where benzo-substitution is on the vinamidinium side. This appears to be a factor when system **8c** is compared with system **8e** or **8e** with **8f**. The stabilization of **8c** relative to **8d** is of particular interest because the cyclizing entity is vinyl benzene-like (styrene-like) in the former whereas it is *o*-quinonoid in the latter. Of equal interest is a point of similarity between systems **8f** and **8d** even though bond order distribution of the *o*-quinonoid type, available to the latter, is not very likely for the former. The implied symmetric distortion of the 7-membered cycle seems to prevent either system from accommodating angle strain in a manner that prevents them from reaching the level of energy minimization possible for **8c** on this account.

## REFERENCES

[1] D. Lloyd and H. McNab, “Vinamidines and Vinamidinium Salts—Examples of Stabilized Push-Pull Alkenes,” *Angewandte Chemie International Edition*, Vol. 15, No. 8, 1976, pp. 459-468. doi:10.1002/anie.197604591

[2] S. S. Malhotra and M. C. Whiting, “Researches on Polyenes. VII. Preparation and Electronic Absorption Spectra of Homologous Series of Simple Cyanines, Merocyanines, and Oxonols,” *Journal of the Chemical Society*, Vol. 756, 1960, pp. 3812-3822. doi:10.1039/jr9600003812

[3] C. Jutz, “C-C Bond Forming Reactions of Chloromethinium Ions,” In: H.-G. Viehe and H. Bohm, Eds., *Iminium Salts in Organic Chemistry*, Wiley, New York, Vol. 9, 1976, pp. 225-343.

[4] J. Zemlicka and Z. Arnold, “Synthetic Reactions of Dimethylformamide. XI. Polyformylation of Ketones of Other Types and the Problem of the Reaction Course,” *Collection of Czechoslovak Chemical Communications*, Vol. 26, 1961, pp. 2852-2864.

[5] Z. Arnold, “Synthetic Reactions of Dimethyl Formamide. XII. Formylation of Some Carboxylic Acids and Their Derivatives,” *Collection of Czechoslovak Chemical Communications*, Vol. 26, 1961, pp. 3051-3057.

[6] I. M. Mallick and S. N. Balasubrahmanyam, “$\sigma$-Correlations and Steric Effects,” *Organic Magnetic Resonance*, Vol. 19, No. 3, 1982, pp. 160-163. doi:10.1002/mrc.1270190311

[7] S. N. Balasubrahmanyam, B. Jeyashri and I. N. N. Namboothiri, “Selectivities in the Formation of Pyridines and

Pyrimidines by Ammonia-Induced Cyclocondensations of Vinamidiniums," *Tetrahedron*, Vol. 50, No. 27, 1994, pp. 8127-8142. doi:10.1016/S0040-4020(01)85295-9

[8] R. Gompper and C. Schneider, "New (Dialkylamino)Allenes, -Thiophenes, and -Pyrroles from Vinamidinium Salts," *Synthesis*, No. 3, 1979, pp. 213-215. doi:10.1055/s-1979-28624

[9] J. T. Gupton, D. K. Krolikowski, R. H. Yu, S. W. Riesinger and J. A. Sikorski, "Application of 2-Substituted Vinamidinium Salts to the Synthesis of 2,4-Disubstituted Pyrroles," *Journal of Organic Chemistry*, Vol. 55, No. 15, 1990, pp. 4735-4740. doi:10.1021/jo00302a047

[10] K. Hafner, K. F. Bangert and K. Orgafos, "1,3-Bis(dimethylamino)pentalene," *Angewandte Chemie International Edition*, Vol. 6, No. 5, 1967, pp. 451-452. doi:10.1002/anie.196704511

[11] J. T. Gupton, J. Coury, M. Moebius and S. Fitzwater, "The Reaction of Organometallic Reagents with Unsymmetrically Substituted Vinamidinium and Chloropropeniminium Salts," *Synthetic Communications*, Vol. 16, No. 12, 1986, pp. 1575-1586. doi:10.1080/00397918608056411

[12] M.-L. Filleux-Blanchard and D. le Botlan, "Conformational Isomerism about the Carbon-Carbon Bond in Propenylylidene Ammonium Salts," *Organic Magnetic Resonance*, Vol. 9, 1977, pp. 618-620. doi:10.1002/mrc.1270091103

[13] W. R. Brasen, H. E. Holmquist and R. E. Benson, "Novel Analogs of Tropolone," *Journal of the American Chemical Society*, Vol. 82, No. 4, 1960, pp. 995-996. doi:10.1021/ja01489a055

[14] W. R. Brasen, H. E. Holmquist and R. E. Benson, "N,N'-Disubstituted 1-Amino-7-imino-1,3,5-cyclo Heptatrienes, a Non-Classical Aromatic System," *Journal of the American Chemical Society*, Vol. 83, 1961, pp. 3125-3135. doi:10.1021/ja01475a031

[15] N. Soma, J. Nakazawa, T. Watanabe, Y. Sato and G. Sunagawa, "Seven-Membered Ring Compounds. XV. Preparations of Troponimine Derivatives," *Chemical & Pharmaceutical Bulletin*, Vol. 13, 1965, pp. 457-464. doi:10.1248/cpb.13.457

[16] M. Cavazza and F. Pietra, "Synthesis of 3-Aminocycloheptatrienylidenamines," *Journal of the Chemical Society, Chemical Communications*, Vol. 11, 1976, 412-413. doi:10.1039/c39760000412

[17] M. Cavazza and F. Pietra, "A Synthetic Approach to 4-Amino-1-imino-2,4,6-cycloheptatrienes," *Synthesis*, No. 3, 1977, 204-205. doi:10.1055/s-1977-24326

[18] D. L. Ostercamp, L. M. Preston and K. D. Onan, "The Synthesis and Crystal Structure of N-Tert-butyl-3-(tert-butylimino)-2-nitropropen-1-amine," *Zeitschrift für Naturforschung B*, Vol. 48, 1993, pp. 1138-1142.

[19] T. Nozoe, S. Ishikawa and K. Shindo, "Synthesis and Reactions of 2,3-Dihydro-cyclohepta[b][1,4] Thiazines and 2,3-Dihydro-1H-cyclohepta [b] Pyrazines," *Heterocycles*, Vol. 28, 1989, pp. 733-744.

[20] H. Nakao, "Seven-Membered Ring Compounds. XVIII. Reactions of Quaternary Ammonium Salts of Cycloheptimidazole Derivatives," *Chemical & Pharmaceutical Bulletin*, Vol. 13, No. 7, 1965, pp. 810-818. doi:10.1248/cpb.13.810

[21] T. Nozoe, "Cyclohepta[b][1,4]benzoxazine and Related Compounds—Some Novel Aspects in Troponoid Chemistry," *Pure and Applied Chemistry*, Vol. 54, 1982, pp. 975-986. doi:10.1351/pac198254050975

[22] J. Aihara, "A New Definition of Dewar-Type Resonance Energies," *Journal of the American Chemical Society*, Vol. 98, No. 7, 1976, pp. 2750-2758. doi:10.1021/ja00426a013

[23] J. Aihara, "Resonance Energies of Nonbenzenoid Hydrocarbons," *Bulletin of the Chemical Society of Japan*, Vol. 51, No. 12, 1978, pp. 3540-3543. doi:10.1246/bcsj.51.3540

[24] J. Aihara, "Graph-Theoretical Formulation of London Diamagnetism," *Journal of the American Chemical Society*, Vol. 101, No. 20, 1979, pp. 5913-5917. doi:10.1021/ja00514a009

[25] J. Aihara and T. Horikawa, "Graph-Theoretical Formula for Ring Currents Induced in a Polycyclic Conjugated System," *Bulletin of the Chemical Society of Japan*, Vol. 56, No. 6, 1983, pp. 1853-1854. doi:10.1246/bcsj.56.1853

[26] T. Kurihara, K. Shindo, S. Ishikawa and T. Nozoe, "Benzo[b]cyclohepta[e][1,4]thiazines and Their Diazine Analogues. III. π-Electronic Structures of 5H,11H+- Cyclohepta[b]quinoxalinium Ions and Their O- and S-Analogues," *Bulletin of the Chemical Society of Japan*, Vol. 64, No. 9, 1991, pp. 2668-2676. doi:10.1246/bcsj.64.2668

[27] T. Nozoe, T. Kitahara, K. Takase and M. Sasaki, "Syntheses of Benzo[b]tropazines," *Proceedings of the Japan Academy*, Vol. 32, No. 5, 1956, pp. 349-352.

[28] J. Aihara, "A New Definition of Dewar-Type Resonance Energies," *Journal of the American Chemical Society*, Vol. 98, No. 10, 1976, pp. 2750-2758. doi:10.1021/ja00426a013

[29] F. Pietra, "Revival of Troponoid Chemistry," *Accounts of Chemical Research*, Vol. 12, 1979, pp. 132-138. doi:10.1021/ar50136a004

[30] I. N. N. Naboothiri and S. N. Balasubrahmanyam, "Transformations in Bromo- and Alkoxybenzotropones," *Journal of the Indian Institute of Science*, Vol. 74, 1994, pp. 473-486.

[31] I. N. N. Namboothiri and S. N. Balasubrahmanyam, "On the Temperature-Dependence of Regioselectivity in the Amination of Bromobenzotropones," *Indian Journal of Chemistry—Section B*, Vol. 32, 1994, pp. 1029-1034.