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Ab initio study on *N,N′,N′′*-triaminoguanidine

Pansy Iqbal, Dhilon S. Patel and Prasad V. Bharatam*

Department of Medicinal Chemistry, National Institute of Pharmaceutical Education and Research (NIPER), S.A.S. Nagar (Mohali), 160 062 Punjab, India

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ABSTRACT: Electronic structure calculations and second-order delocalizations in *N,N′,N′′*-triaminoguanidine (**TAG**) have been studied by employing *ab initio* MO and density functional methods. There are total 10 rotational isomers on the potential energy (PE) surface of **TAG**. The effect of three amino groups substitution on guanidine (**Gu**) has been studied in terms of the primary and the secondary electron delocalizations in **TAG** by employing Natural Population Analysis (NPA). An increased electron delocalization is observed in protonated triaminoguanidine (**TAGP**) due to the three strong intramolecular hydrogen bonds and hence accounts for its extra stability. The increase in the electron delocalization upon protonation in **TAG** can be compared to that in guanidine. The absolute proton affinity (APA) of **TAG** is less than that of **Gu**. HOMA and NICS studies have been carried out to understand electron delocalization in **TAGP**. Copyright © 2007 John Wiley & Sons, Ltd.
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KEYWORDS: *N,N′,N″*-triaminoguanidine; electron delocalization; proton affinity; *ab initio* calculations; natural population analysis

INTRODUCTION

N,N′,N′′-triaminoguanidine (**TAG**) is known to have extensive applications in both chemical and biological systems.[1] It was first synthesized by Stollé in 1904[2] and since then the chemistry of **TAG** and its derivatives has been extensively studied. Due to the advantages like lower toxicity, lower corrosive product formation, higher specific impulse and less solid reaction products formation than the conventional composite propellants, triaminoguanidine nitrate is classified as an environmentally friendly and clean-burning rocket propellant for commercial applications.[3] The nitrate, perchlorate and carbonate derivatives of **TAG** are extensively used in fire extinguishers and vehicle air bags.[4] **TAG** carboxylates have been investigated for the design of anti-diabetic agents for the treatment of non-insulin-dependent diabetes mellitus (NIDDM).[5] As a guanidine derivative, **TAG** acts as a reversible inhibitor of cholinesterase and also demonstrates combined inhibition of monoamine oxidase.[6,7] *N,N*-dinitramide salts of **TAG** are used as solubilizing agents for biologically active agents such as medical imaging or diagnostic agents, pharmacologically active agents and agricultural agents such as pesticides,[8] and in the preparation of various biologically significant compounds.[9]

It is suggested that guanidine and its derivatives like aminoguanidine, diaminoguanidine, biguanides etc. mainly exist in their protonated form under physiological conditions, which accounts for their high basicity and also explains their various biological properties.[10–12] The electronic structure, proton affinity etc. on guanidine, aminoguanidine and diaminoguanidine have been studied earlier.[11,12] It was reported that the presence of an additional NH_2 unit in aminoguanidine is responsible for the reduction in the toxicity of guanidine.[12] Recently we studied the absolute proton affinities of guanidine, aminoguanidine and diaminoguanidine (Fig. 1), which suggest that the increased stabilization of the protonated species is a result of the strong intramolecular interactions rather than increased delocalization upon protonation.[13] Extensive studies on the electronic structure, isomerism, electron delocalization, rotational barriers etc. in guanidine, aminoguanidine and diaminoguanidine and their protonated structures were carried out.[13] The trends in the C—N barriers in guanidine, aminoguanidine, diaminoguanidine, urea, thiourea, selenourea, biguanide, formamide, thioformamide, selenoformamide etc. can be

**Correspondence to:* P. V. Bharatam, Department of Medicinal Chemistry, National Institute of Pharmaceutical Education and Research (NIPER), S.A.S. Nagar (Mohali), 160 062 Punjab, India.
E-mail: pvbharatam@niper.ac.in

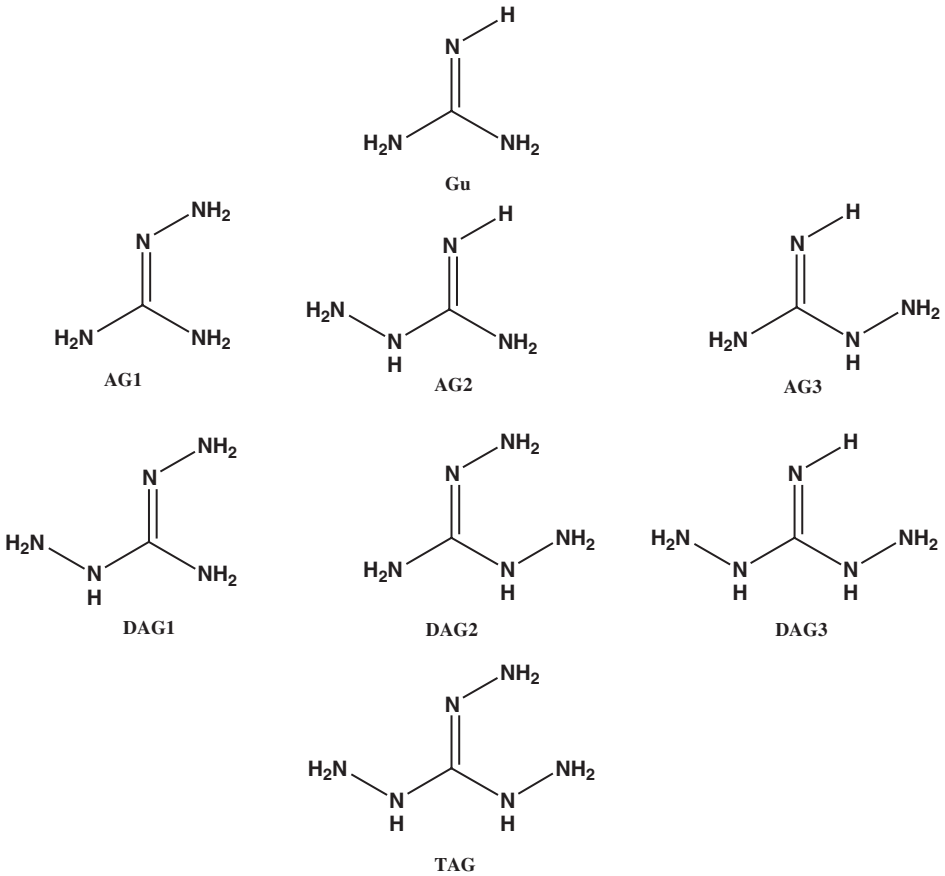

Figure 1. Guanidine (**Gu**), three different isomers of aminoguanidine (**AG1**, **AG2** and **AG3**), three different isomers of diaminoguanidine (**DAG1**, **DAG2** and **DAG3**) and *N,N′,N″*-triaminoguanidine (**TAG**)

traced to the primary and secondary electron delocalizations in these systems, which in turn are controlled by molecular orbital interactions.[14,15]

The three amino groups substitution on guanidine moiety yields one basic structure of **TAG** (Fig. 1) with 10 rotational isomers possible on its potential energy (PE) surface. In the present paper, the C—N and N—N rotational PE surface of **TAG** and its proton affinity has been studied and compared with that of guanidine using *ab initio* MO and DFT methods. The partial π character across C—N bonds is an important property in guanidine and its derivatives,[13,14] and this determines the conformational surface of these species. A study of the rotational PE surface in the gas phase provides information regarding the extent of electron delocalizations in this system, which is reported in this paper.

COMPUTATIONAL DETAILS

Ab initio MO[16] and density functional (DFT)[17] calculations have been performed using the GAUSSIAN98 package.[18] Complete optimizations have been performed on various isomers of **TAG** to understand the electronic structure, N—N and C—N bond rotations, and electron delocalization using HF, B3LYP[19] and MP2(full)[20] methods at the 6-31+G* basis set. To characterize each stationary point as a minimum or a transition state and to estimate the zero point vibrational energies (ZPE), frequencies for all optimized species were computed at all levels. The calculated ZPE values were scaled by a factor of 0.9153, 0.9806 and 0.9661 for HF, B3LYP and MP2(full) levels, respectively.[21] Higher accuracy G2MP2[22] method, which includes thermal and ZPE corrections, was employed to obtain more exact relative energies for all the structures and the G2MP2-free energy data has been used in the analysis of results (unless otherwise specifically mentioned).

Estimation of intramolecular hydrogen-bonding interactions has been performed using atoms in molecules (AIM)[23] calculations (wherever applicable). Natural bond orbital (NBO) approach[24] has been employed to quantitatively estimate the second-order interactions as: $E^{(2)} = -2F_{ij}/\Delta E_{ij}$, where $E^{(2)}$ is the energy due to second-order interactions; $\Delta E_{ij} = E_i - E_j$ is the energy difference between the interacting molecular orbitals i and j; F_{ij} is the Fock matrix element for the interaction between i and j.

The protonated structure of triaminoguanidine (**TAGP**) was also optimized using the same methods in order to

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study the protonation energies (Eqns 1 and 2), absolute proton affinity (APA) (Eqn 3) and evaluate their electron delocalization.

$$E_{\text{prot}} = [E(\text{BH}^+) - E(\text{B})] + [\text{ZPE}(\text{BH}^+) - \text{ZPE}(\text{B})] \quad (1)$$

$$G_{\text{prot}} = G_{298}(\text{BH}^+) - G_{298}(\text{B}) \quad (2)$$

$$\text{APA} = -\Delta H_{298} = H_{298}(\text{B}) + H_{298}(\text{H}^+) - H_{298}(\text{BH}^+) \quad (3)$$

where E_{prot} (Eqn 1)[12j] is the electronic energy of protonation reaction, G_{prot} (Eqn 2) is the Gibbs free energy of protonation and APA is the absolute proton affinity of a molecule (Eqn 3).[10f] $E(\text{B})$ and $E(\text{BH}^+)$ denote the total energies of the base and its conjugate acid, respectively; ZPE is the zero-point vibrational energy correction; G_{298} is the free energy at 298.15 K of the free base (B) and its conjugate ionic acid (BH^+); H_{298} is the enthalpy of the free base (B), its conjugate ionic acid (BH^+) and the proton (H^+) at 298.15 K. Equation (1) includes the changes in total energy and in ZPE, Eqn (2) includes the changes in total energy, in ZPE, in thermal energy and entropy change on going from 0 to 298.15 K and Eqn (3) gives the negative of enthalpy change ($-\Delta H_{298}$), which includes the changes in total energy, in ZPE, in vibrational energy on going from 0 to 298.15 K, and in rotational and translational energy and a work term (RT = 0.592 kcal/mol).[15c] For H^+, only the translational energy term is not equal to zero (H_{298} $\text{H}^+ = 3/2\text{RT} = 0.899$ kcal/mol at 298.15 K) and a work term (RT = 0.592 kcal/mol).[10f] In the present work, E_{prot}, G_{prot} and APA are calculated using energy, Gibbs free energy and enthalpy, respectively, obtained at the G2MP2 level of calculation.

Harmonic oscillator measure of aromaticity (HOMA),[25] a geometry-based aromaticity index (HOMA is defined in such way to give 0 for a model non-aromatic system and 1 for a system where full π-electron delocalization occurs), was applied to quantify the extent of π-electron delocalization of guanidinium ion and aminoguanidinium ion. HOMA is defined as follows:

$$\text{HOMA} = 1 - \frac{\alpha}{n}\sum \left(d_{\text{opt}} - d_{\text{i}}\right)^2 \quad (4)$$

where α is the normalization constant (93.52 for CN bonds), n is the number of bonds taken into account, d_{opt} is the optimum bond length which is assumed to be realized when full delocalization of π electrons occurs (1.334 for CN bonds) and d_{i} are the running bond lengths.

Nucleus-independent chemical shift (NICS) index, introduced by Schleyer *et al.*[26] related to the magnetic properties of the molecule, was applied to quantify the extent of π-electron delocalization of triaminoguanidinium ion. It is defined as the negative value of absolute shielding computed at a ring centre or any other interesting point of the system, determined by the non-weighted mean of the heavy atom coordinates. Aromatic systems are characterized by negative NICS, antiaromatic systems by positive NICS, as discussed in the study of many cyclic systems.[26]

RESULTS AND DISCUSSION

Potential energy surface of TAG

The complete electronic structure calculations have been carried out on **TAG** and on its C—N and N—N rotational isomers to generate a PE surface. **TAG1** is the most stable isomer having the least energy on a PE surface (Table 1). The C—N and N—N rotational processes in **TAG1** lead to nine additional minima **TAG2–TAG10** (Fig. 2). There are notably two strong intramolecular hydrogen-bonding interactions observed in **TAG1** between N5 and H15 and between N7 and H12 with distances being 2.161 Å and 2.312 Å, respectively (Fig. 2). However, AIM studies did not show any bond critical points to support these stabilizing interactions. The $n_{\text{N5}} \rightarrow \sigma^*_{\text{N4—H15}}$ ($E^{(2)}$: 5.33 kcal/mol) (Table 2) second-order interaction in **TAG1** corroborates the possible intramolecular hydrogen bond stabilizing interaction. In case of the other minima, only one such stabilizing attractive interaction can be possible. For example, in the case of **TAG2**, which is an N4—N7 rotamer of **TAG1** and is only 0.92 kcal/mol less stable than **TAG1** (Table 1), only one such attractive interaction between lone pair of electrons on N5 and H15 is observed. **TAG4** (3.49 kcal/mol) and **TAG10** (5.15 kcal/mol) are the C2—N4 rotamers while **TAG5** which is 3.57 kcal/mol less stable than **TAG3** is the C2—N3 rotamer, where all these isomers have no intramolecular H-bonding interactions. **TAG3** (2.63 kcal/mol), **TAG6** (4.51 kcal/mol), **TAG7**, **TAG8** and **TAG9** (3.12, 4.18 and 4.54 kcal/mol) are not purely N3—N6, N4—N7 and N1—N5 rotamers, respectively; instead of N—N rotation these isomers undergo conformational changes along with C—N bond rotations to generate these minima on the PE surface. Though there are several possible conformations for the TAG, the energy difference between these isomers are quite small; all of this fall within a range of about 5 kcal/mol. This indicates that in solution-state any of these conformations may exist or all of these might exist simultaneously. This observation is quite different from that of **AG** and **DAG** where one or two conformers are more energetically preferred over the others.

Electron delocalization in triaminoguanidine

Electron delocalization in **TAG1** can be understood as a function of N—N and C—N bond rotations. On the N1—N5, N3—N6 and N4—N7 rotational paths in **TAG1**,

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Table 1. Relative energies (kcal/mol, ZPE-corrected values, which have been scaled by a factor of 0.9153, 0.9806 and 0.9661 for HF, B3LYP and MP2(full) levels, respectively) of various conformers of triaminoguanidine (**TAG**) and protonated triaminoguanidine (**TAGP**) at 298.15 K using 6-31+G* basis set

Structure	HF (*E*)	B3LYP (*E*)	MP2(full) (*E*)	G2MP2 (*G*)	Chemical interpretation of the energy data
Triaminoguanidine					
TAG1	**0.00**	**0.00**	**0.00**	**0.00**	Global minimum
TAG2	3.20	2.82	3.07	0.92	Δ*E* from **TAG1**
TAG3	3.77	2.90	2.42	2.63	Δ*E* from **TAG1**
TAG4	4.46	3.38	3.15	3.49	Δ*E* from **TAG1**
TAG5	5.95	4.44	4.03	3.57	Δ*E* from **TAG1**
TAG6	7.70	4.91	4.29	4.51	Δ*E* from **TAG1**
TAG7	7.08	5.39	4.92	3.12	Δ*E* from **TAG1**
TAG8	7.28	5.96	5.11	4.18	Δ*E* from **TAG1**
TAG9	8.91	5.87	5.48	4.54	Δ*E* from **TAG1**
TAG10	8.22	5.79	5.75	5.15	Δ*E* from **TAG1**
TAG1-TS1	11.87	10.52	11.54	9.58	Rot. Bar. across N1–N5 in **TAG1**
TAG1-TS2	12.58	10.91	11.02	9.05	Rot. Bar. across N3–N6 in **TAG1**
TAG1-TS3	19.11	16.18	16.36	14.61	Rot. Bar. across N4–N7 in **TAG1**
TAG1-TS4	12.84	11.36	10.36	9.99	Rot. Bar. across C2–N3 in **TAG1**
TAG1-TS5	—	9.56	9.34	9.02	Rot. Bar. across C2–N4 in **TAG1**
Protonated triaminoguanidine					
TAGP1	**0.00**	**0.00**	**0.00**	**0.00**	Global minimum
TAGP2	7.29	6.59	7.44	5.85	Δ*E* from **TAGP1**
TAGP3	14.03	12.67	13.85	11.36	Δ*E* from **TAGP1**
TAGP4	13.86	12.34	13.17	11.65	Δ*E* from **TAGP1**
TAGP5	14.65	13.13	13.91	12.11	Δ*E* from **TAGP1**
TAGP6	19.51	17.64	18.39	16.37	Δ*E* from **TAGP1**
TAGP1-TS1	15.53	13.01	14.26	11.75	Rot. Bar. across N1–N5 in **TAGP1**
TAGP1-TS2	15.53	13.01	14.26	11.74	Rot. Bar. across N3–N6 in **TAGP1**
TAGP1-TS3	22.22	18.98	20.98	17.09	Rot. Bar. across N4–N7 in **TAGP1**
TAGP1-TS4	18.12	17.87	16.79	16.75	Rot. Bar. across C2–N3 in **TAGP1**
TAGP1-TS5	18.00	14.40	16.16	13.98	Rot. Bar. across C2–N4 in **TAGP1**

there are three different transition states **TAG1-TS1**, **TAG1-TS2** and **TAG1-TS3,** respectively (Fig. 3). The N1—N5, N3—N6 and N4—N7 rotational barriers for **TAG1** are 9.58, 9.05 and 14.61 kcal/mol, respectively (Table 3), which are higher than the N—N rotational barriers in hydrazine (7.8 kcal/mol) and aminoguanidine (**AG1**: 8.2 kcal/mol)[13] (Table 3). These rotations lead to the corresponding minima **TAG7**, **TAG3** and **TAG2,** respectively.

In aminoguanidine, the N1—N5 rotational barrier was characterized by the breaking of intramolecular hydrogen bond.[13] In case of **TAG1** during the N1—N5 rotation, there is a loss of the possible intramolecular attractive interaction. The N4—N7 and N3—N6 rotation also leads to a loss of the H-bonding interaction.

The C2—N3 rotational barrier (through the transition state **TAG1-TS4 –** Fig. 3) has been estimated to be about 9.99 kcal/mol (Table 3), which is comparatively smaller than the corresponding interaction in guanidine (**Gu1**: 10.84 kcal/mol) (Table 3). The C—N and N—N rotational barriers in **TAG** are not very large. They are only of the order of 9–14 kcal/mol. This suggests that at equilibrium interconversions among various conformations are quite practical. The NPA analysis shows stronger electron delocalization from N3 ($n_{N3} \rightarrow \pi^*_{C2—N1}$; $E^{(2)}$: 61.29 kcal/mol) in **TAG1**, which is larger than that in **Gu1** ($E^{(2)}$: 41.58 kcal/mol) (Table 2). **TAG1-TS5** (Fig. 3) depicts the C2—N4 transition state with an energy barrier of 9.02 kcal/mol. This barrier is higher in value than that of **Gu1** (6.82 kcal/mol) (Table 3) and also the $n_{N4} \rightarrow \pi^*_{C2—N1}$ delocalization in **TAG1** is ($E^{(2)}$: 50.78 kcal/mol), which is greater than the $n_{N4} \rightarrow \pi^*_{C2—N1}$ delocalization in **Gu1** ($E^{(2)}$: 46.09 kcal/mol).[13] Since both C2—N3 and C2—N4 rotations in **TAG1** correspond with the loss of possible attractive intramolecular interactions, thus these barriers to rotation in value are higher and the lone pair delocalization is also greater than that of guanidine.

Protonated triaminoguanidine

Protonation at the iminic nitrogen of all the isomers of **TAG** upon protonation give **TAGP**, which may exist in any of the six conformations – **TAGP1–TAGP6** (Fig. 4). Out of these conformations, **TAGP1** is the most stable and **TAGP2–TAGP6** are its rotational isomers. **TAGP1** is characterized by three very strong intramolecular hydrogen-bonding interactions between N5 and H15, N6 and H16 and N7 and H12 (which are confirmed by AIM analysis for bond path) with each of the distances being 2.26 Å (Fig. 5). All the other isomers have either two or

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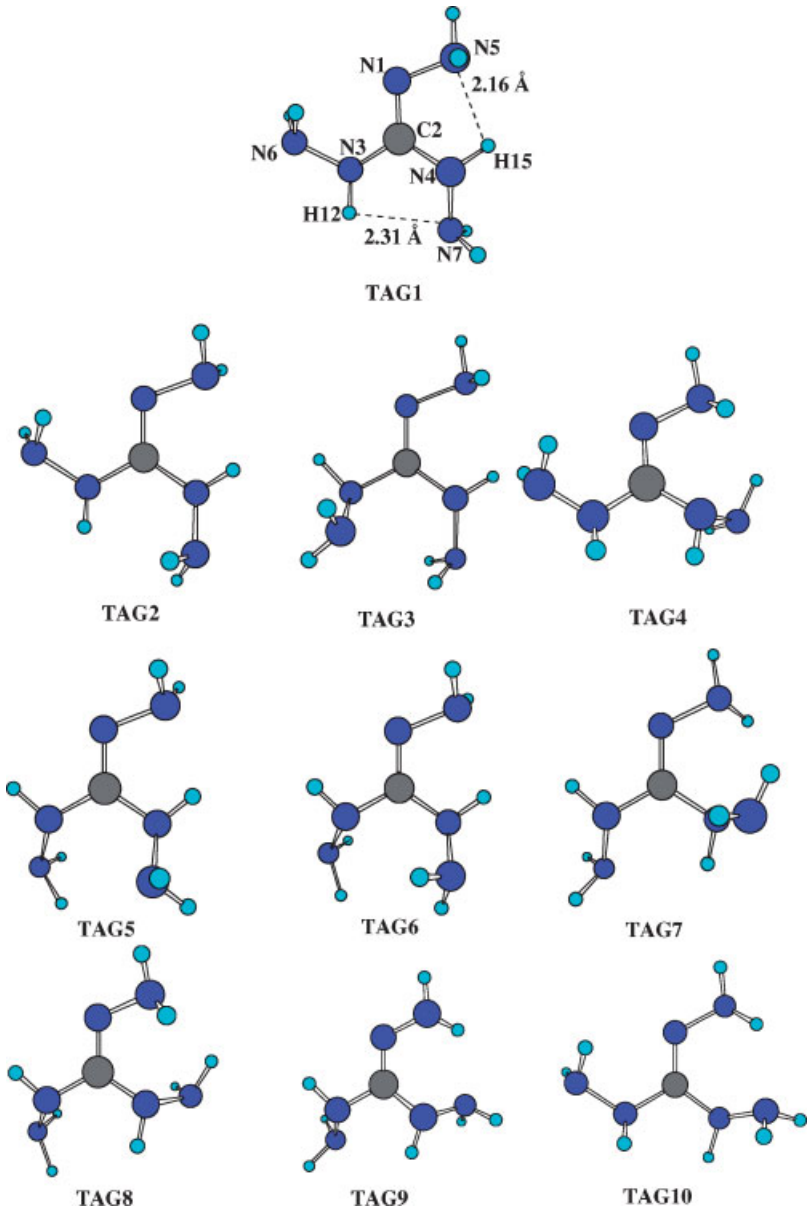

Figure 2. C—N and N—N rotational isomers of *N*,*N*′,*N*″-triaminoguanidine (**TAG**)

only one such intramolecular interaction. The energy difference between **TAGP1** and **TAGP2** is 5.85 kcal/mol at G2MP2 level favouring **TAGP1** (Table 1) and these two are different only by a N3—N6 rotation, however during this rotation there is a loss of strong intramolecular hydrogen bonding between N6 and H16. The other conformers have even higher energy differences owing to the loss of such attractive intramolecular interactions. The N1—N5, N3—N6, N4—N7, C2—N3 and C2—N4 rotational barriers in **TAGP1** are 11.75, 11.74, 17.09, 16.75 and 13.98 kcal/mol, respectively, at G2MP2 level (Table 3). It is interesting to note that under protonated conditions, **TAG** prefers a specific conformation, unlike the noted flexibility under unprotonated state. The relative stabilities of the rotational isomers of **TAGP** are quite less, C—N and N—N rotational barriers are high. The only possible low energy process is the inversion at N6 in **TAGP1** to give **TAGP2**, which goes through a barrier of about 5.85 kcal/mol but the reverse inversion from **TAGP2** to **TAGP1** is barrier-less path. Similarly, C—N and N—N rotations from any of the isomers to **TAGP1** are quite low energy processes. This analysis indicates that the possibility of finding isomers of **TAGP** in solution is quite low, precluding the possibility of interconversion among conformers. Thus, it may be concluded that there is only one possible conformation for the **TAGP** in solution. In the protonation study of **TAG** we have considered only iminic nitrogen as the potential protonation site because there can be complete delocalization of the electrons upon protonation at iminic nitrogen. To

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Table 2. NBO analysis of the most stable conformer of guanidine (**Gu**) and triaminoguanidine (**TAG**) and their protonated forms at the MP2(full)/6-31+G* level at 298.15 K

		Second-order interaction			Occupancy	
Structure	Interaction	$E^{(2)a}$	$E_i - E_j^b$	F_{ij}^b	$\rho n_{(N)}$	ρ_{π^*}
Gu1	$n_{N3} \rightarrow \pi^*_{C2-N1}$	41.58	0.67	0.153	$1.893_{(N3)}$	0.212
	$n_{N4} \rightarrow \pi^*_{C2-N1}$	46.09	0.68	0.162	$1.892_{(N4)}$	
	$n_{N1} \rightarrow \sigma^*_{C2-N4}$	23.56	1.22	0.152	$1.939_{(N1)}$	
GuP	$n_{N3} \rightarrow \pi^*_{C2-N1}$	112.48	0.48	0.220	$1.762_{(N3)}$	0.443
	$n_{N4} \rightarrow \pi^*_{C2-N1}$	112.49	0.48	0.220	$1.762_{(N4)}$	
TAG1	$n_{N1} \rightarrow \sigma^*_{C2-N4}$	16.11	1.28	0.128	1.949	
	$n_{N3} \rightarrow \pi^*_{C2-N1}$	61.29	0.61	0.179	1.841	0.276
	$n_{N4} \rightarrow \pi^*_{C2-N1}$	50.78	0.65	0.168	1.865	
	$n_{N5} \rightarrow \sigma^*_{N4-H15}$	5.33	1.20	0.072	1.975	
	$n_{N6} \rightarrow \sigma^*_{C2-N3}$	7.73	1.26	0.088	1.980	
	$n_{N7} \rightarrow \sigma^*_{N4-H15}$	7.89	1.21	0.087	1.976	
TAGP	$n_{N1} \rightarrow \pi^*_{C2-N4}$	118.83	0.49	0.227	1.754	0.461
	$n_{N3} \rightarrow \pi^*_{C2-N4}$	118.51	0.49	0.227	1.754	
	$n_{N5} \rightarrow \sigma^*_{N4-H15}$	9.58	1.21	0.096	1.969	
	$n_{N6} \rightarrow \sigma^*_{N3-H12}$	9.58	1.21	0.096	1.969	
	$n_{N7} \rightarrow \sigma^*_{N4-H15}$	9.58	1.21	0.096	1.969	

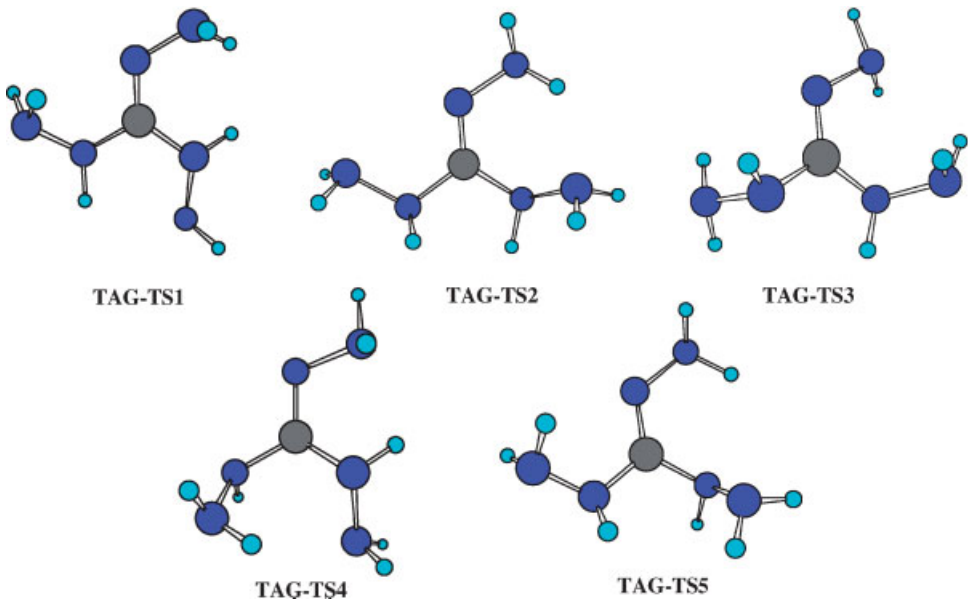

Figure 3. N—N and C—N rotational transition states in **TAG1**

Table 3. Barriers to rotation (kcal/mol) of the most stable conformers of guanidine (**Gu**), and triaminoguanidine (**TAG**) and their protonated forms of (**gup** and **TAGP**) obtained at MP2(full)/6-31G* and G2MP2 level

	C—N3		C—N4		N1—N5		N3—N6		N4—N7	
Structure	MP2(f)	G2MP2	MP2(f)	G2MP2	MP2(f)	G2MP2	MP2(f)	G2MP2	MP2(f)	G2MP2
Gu1	12.40	10.84	7.06	6.82	—	—	—	—	—	—
GuP	11.96	13.18	11.96	13.18	—	—	—	—	—	—
TAG1	10.36	9.99	6.89	9.02	11.54	9.58	16.36	9.05	11.02	14.61
TAGP	16.79	16.75	16.16	13.98	14.26	11.75	14.26	11.74	20.98	17.09

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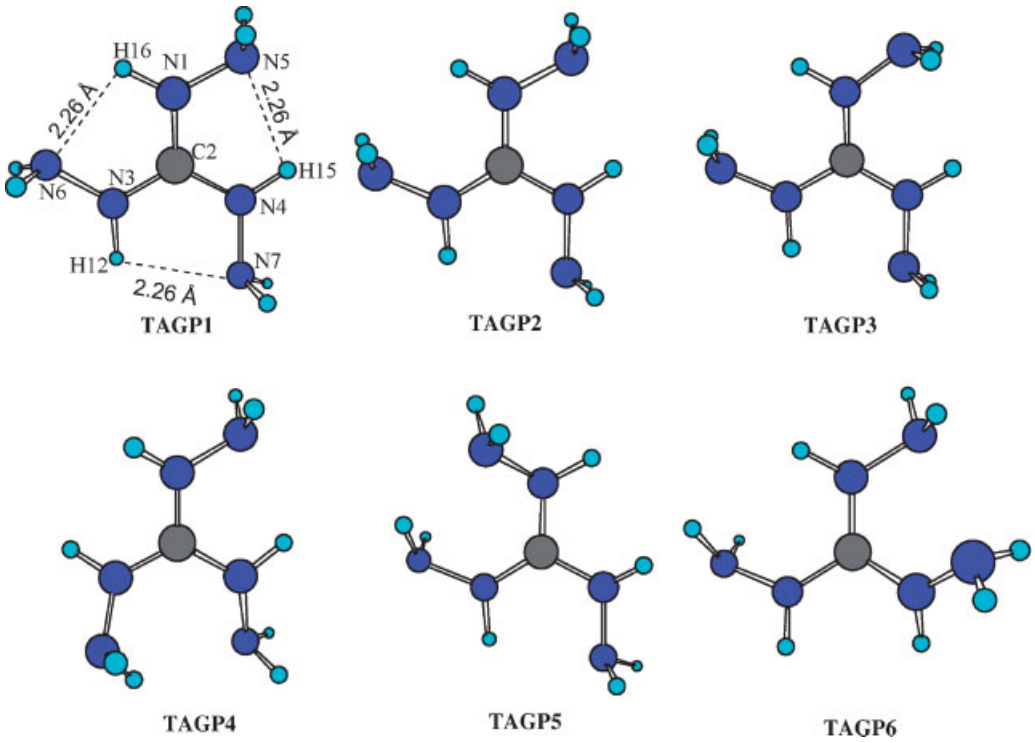
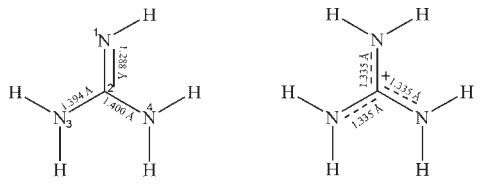
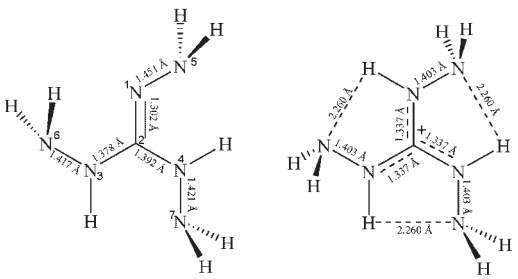


Figure 4. C—N and N—N rotational isomers of protonated triaminoguanidine (**TAGP**)



	Gu	GuP
Bond angles in degrees		
N1-C-N3	**120.2**	**120.0**
N1-C-N4	**128.2**	**120.0**
N3-C-N4	**111.7**	**120.0**
Sum of angles in degrees		
N3	**337.0**	**360.0**
N4	**339.0**	**360.0**



	TAG	TAGP
Bond angles in degrees		
N1-C-N3	**119.9**	**120.0**
N1-C-N4	**123.4**	**120.0**
N3-C-N4	**116.7**	**120.0**
Sum of angles in degrees		
N1	**------**	**360.0**
N3	**346.4**	**360.0**
N4	**342.8**	**360.0**

Figure 5. Comparative geometric features of guanidine and triaminoguanidine

check the possibility any of the amino nitrogen atoms compete with iminic nitrogen, we have carried out protonation study at amino nitrogen also. But all the amino nitrogen showed quite higher protonation energy (as expected) than the protonation at iminic nitrogen excluding the possibility of any close competition between the amino and iminic nitrogen for protonation under physiological condition.

The electronic energy of protonation (E_{prot}), Gibbs free energy of protonation (G_{prot}) and APA of triaminoguanidine (**TAG1**) are estimated to be −232.44, −226.12 and 233.78 kcal/mol, respectively, at G2MP2 level. The APA value of **TAG** is smaller than that of **Gu** (235.68 kcal/mol) and both aminoguanidine (**AG**) (235.94) value as well as diaminoguanidine (**DAG**) (239.27) value.[13] The increase in electron distribution upon protonation in **TAG** is similar to that of **Gu**, **AG** as well as **DAG**. In the latter cases, it was concluded that the observed differences in the proton affinities have no bearing on the increase in electron distribution upon protonation instead it is a result of the gain in the intramolecular hydrogen bonds.[13] However, there is a gain in the intramolecular hydrogen bonds in **TAG** (i.e. two intramolecular hydrogen bond in free base, **TAG1**, and three intramolecular hydrogen bond in the protonated form, **TAGP1**), the APA value is less than that of **Gu**, **AG** as well as **DAG** (Table 4).

Unlike **AG** and **DAG**, the protonation in case of **TAG** is more comparable to that in **Gu**. The presence of three electron-donating amino groups to the $C(N)_3$ frame-work does not perturb the existing strong π-electron deloca-

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Table 4. Protonation energies (E_{prot}, G_{prot}) and absolute proton affinity (APA) of triaminoguanidine at G2MP2 level of calculations (kcal/mol) at 298.15 K

Structure	E_{prot}	G_{prot}	APA
Gu[a]	−234.93	−229.42	235.68
AG1[a]	−234.84	−228.72	235.94
DAG1[a]	−238.54	−231.52	239.27
TAG1	−232.44	−226.12	233.78

[a] Reference 13.

lization of guanidinium moiety, instead their effect further strengthens the electron delocalization by increased resonance stabilization due to the formation of tripentacyclic system arising from the three strong intramolecular hydrogen bonds upon protonation. The C2—N3 and C2—N4 bond rotations in **GuP** and **TAGP1** (Table 3) shows a similar pattern. Upon protonation all hydrogens, that is, three guanidino hydrogens are equivalent and six amino hydrogens are equivalent, in **TAG** become equivalent, similar to that in **Gu**. The NPA analysis (Table 2) showed that in case of both **GuP** and **TAGP1**, the trend in electron delocalization is comparable ($n_{N3/4} \rightarrow \pi^*_{C2—N1}$; $E^{(2)}$: 112.48 kcal/mol in **GuP** and $n_{N1/3} \rightarrow \pi^*_{C2—N4}$; $E^{(2)}$: 118.83 kcal/mol in **TAGP**). The HOMA values for **GuP**[13] and **TAGP1** are exactly the same value as 0.999, while the NICS values for **GuP** and **TAGP1** are −44.1 and −39.4, respectively, which are also comparable and accounts for aromatic nature of both the ions. The geometric features also demonstrate a similarity pattern between guanidinium and triaminoguanidinium ion (Fig. 5). All these results clearly indicate that the presence of three amino groups on guanidine does not have a major effect on the electron delocalization of guanidine, instead **TAG** itself is electronically similar to guanidine.

CONCLUSIONS

Ab initio MO and DFT calculations on **TAG** showed that there are 10 conformational minima on the PE surface. **TAG1** is the most stable isomer characterized by two strong intramolecular hydrogen bonds. All other isomers arise due to C—N and N—N rotations, which lead to the loss of the attractive intramolecular interactions and hence have lower stability. The π electron delocalization upon protonation **TAGP** is comparatively different from that of protonated aminoguanidine (**AGP**) as well as diaminoguanidine (**DAGP**), but is comparable to that of guanidine (**GuP**) as indicated by differences in the C—N rotational barriers and the NPA second-order electron distributions. The effect of the three electron-donating amino groups to the $C(N)_3$ frame-work can be understood as the increase in the electron delocalization by increasing resonance due to the formation of tripentacyclic system arising from the three strong intramolecular hydrogen bonds upon protonation. The APA of **TAG** is 233.78 kcal/mol, only slightly smaller than that of guanidine (235.68 kcal/mol). The HOMA (0.999 for **GuP** and 0.999 for **TAGP1**) and NICS (−44.1 and −39.4 for **GuP** and **TAGP1**, respectively) studies also corroborate the similarity between the aromatic nature of both **GuP** and **TAGP1** ions.

Supporting information available

Tables S1 and S2 containing the ZPE-corrected absolute energy data of triaminoguanidine and its protonated form, the geometrical parameters (Table S3) and HOMA and NICS (Table S4) for various system is available free of charge via the internet at http://www.interscience.wiley.com/jpoc.

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REFERENCES

1. *The Chemistry of Guanidine*. American Cyanamid Co: Wayne, NJ, 1950.
2. (a) Stollé R. *Ber.* 1904; **37**: 3548; (b) Stollé R, Krauch K. *J. Prakt. Chem.* 1913; **88**: 306; (c) Pellizzari G, Gaiter A. *Gazz. Chim. Ital.* 1914; **44**: 72; (d) Prandtl W, Dollfus W. *Ber.* 1932; **65**: 754; (e) Schotte H. German Patent, 1926.
3. (a) Menke K, Gunser G, Schnoering M, Boehnlein-Mauss J, Weiser V. *Int. Ann. Conf. ICT 22* 2003; 1–19; (b) Eckl W, Ebeling H, Eisenreich N, Noetz J. 2002; DE 10204268; (c) Knowlton GD, Ludwig CP, Deppert TM, McFadden D, Dupont J, Salafia C. 2003; US 094225; (d) Mendenhall IV, Smith RG, Taylor RD. 2002; US 6436211; (e) Jadhav HS, Dhavale DD, Krishnamurthy VN, Chen L, Feng C. *4th Proc. Int. Autumn Seminar on Propellants, Explosives and Pyrotechnics*. 2001; 493; (f) Gadiot GMHJL, Hoffmans DW, Korting PAOG, Leenders APM. *4th Int. Symposium on Special Topics in Chemical Propulsion*. 1997; 430.
4. (a) Zeuner S, Hofmann A, Schropp R, Rodig K-H. 2001; DE 20111410; (b) Magnum MG, Ouart DC. 2001; US 0017175; (c) Scheffee RS, Neidert JB, Black RE, III, Lynch RD, Martin JD. 2001; WO 039839; (d) Hamilton BK, Harrington P. 2000; EP 995732; (e) Grzyll LR. 2000; US 6045637; (f) Yamato Y. 2000; WO 014032; (g) Cabrera R, Grzelczyk C. 1999; US 5985060.
5. Larsen SD, Vaillancourt VA, May PD, Tanis SP, Meglasson MD, Schostarez HJ. 1999; US 5994577.
6. Rozengart EV, Basova NE. *Doklady Biochem. Biophys.* 2002; **384**: 185–188.
7. Nikol'skaya EB, Yagodina OV, Khovanskikh AE. *Doklady Academii Nauk* 1999; **365**: 829–831.
8. Bottaro JC, Petrie MA, Penwell PE, Bomberger DC. 2003; WO 006371.
9. (a) Lemke H-D, Gehlen A. 2002; WO 008301; (b) Muller IM, Robson R. *Angew. Chem. Int. ed.* 2000; **39**: 4357–4359; (c) Savel'eva ZA, Romanenko GV, Sheludyakova LA, Larionov SV. *Polyhedron* 2000; **19**: 1737–1740; (d) Wagle DR, M. Lankin E, Hwang S-B. 1997; WO 9735849.
10. (a) Hannon CL, Anslyn EV. In *Bioorganic Chemistry Frontiers*, Dugas H (ed.). Springer-Verlag: Berlin, 1993; (b) Patai S. *The Chemistry of Amidines and Imidates*. Wiley: Chichester, 1975; (c) Patai S, Rapport Z. *The Chemistry of Amidines and Imidates*. Wiley: Chichester, 1991; (d) Ishikawa T, Isobe T. *Chem. Eur. J.*

DOI: 10.1002/poc

2002; **8**: 553–557; (e) Palagiano E, De Marino S, Minale L, Riccio R, Zollo F, Iorizzi M, Carré JB, Debitus C, Lucarain L, Provost J. *Tetrahedron* 1995; **51**: 3675–3682; (f) Raczynska ED, Cyrañski MK, Gutowski M, Rak J, Gal J-F, Maria P-C, Darowska M, Duczmal K. *J. Phys. Org. Chem.* 2003; **16**: 91–106.

11. (a) Koskinen JT, Koskinen M, Mutikainen I, Tilus P, Mannfors B, Elo H, Naturforsch Z. 1997; **52b**: 1259–1272; (b) Koskinen JT, Koskinen M, Mutikainen I, Tilus P, Mannfors B, Elo H. 1996; **51b**: 1771–1778.
12. (a) Sapse AM, Snyder G, Santoro AV. *J. Phys. Chem.* 1981; **85**: 662–665; (b) Sapse AM, Snyder G, Santoro AV. *Int. J. Quantum Chem.* 1981; **20**: 755–762; (c) Gobbi A, Frenking G. *J. Am. Chem. Soc.* 1993; **115**: 2362–2372; (d) Caminiti R, Pieretti A, Bencivenni L, Ramondo F, Sanna N. *J. Phys. Chem.* 1996; **100**: 10928–10935; (e) Wiberg KB, Rush DJ. *J. Am. Chem. Soc.* 2001; **123**: 2038–2046; (f) Wiberg KB, Rablen RR. *J. Am. Chem. Soc.* 1995; **117**: 2201–2209; (g) Wiberg KB, Breneman CM. *J. Am. Chem. Soc.* 1992; **114**: 831–840; (h) Wiberg KB. *J. Am. Chem. Soc.* 1990; **112**: 4177–4182; (i) Peeters D, Lewy G, Wilante C. *J. Mol. Struc.* 1997; **416**: 21–32; (j) Maksic ZB, Kovacevic B. *J. Org. Chem.* 2000; **65**: 3303–3309; (k) Amekraz B, Tortajada J, Morizur J-P, Gonzalez AI, Mo O, Yanez M, Leito I, Maria P-C, Gal J-F. *New J. Chem.* 1996; **20**: 1011–1021; (l) Hille B. *J. Gen. Physiol.* 1972; **59**: 637–658; (m) Hunter EP, Lias SG. *J. Phys. Chem. Ref. Data,* 1998; **27**: 413. http://webbook.nist.org; (n) Kovacevic B, Maksic ZB. *Org. Lett.* 2001; **3**: 1523–1526; (o) Kovacevic B, Glasovac ZZ, Maksic B. *J. Phys. Org. Chem.* 2002; **15**: 765–774; (p) Lieber E, Smith GBL. *Chem. Rev.* 1939; **25**: 213–271.
13. (a) Bharatam PV, Iqbal P, Malde A, Tiwari R. *J. Phys. Chem.* 2004; **108**: 10509–10517; (b) Bharatam PV, Iqbal P. *J. Comp. Chem.* 2006; **27**: 334–343.
14. (a) Bharatam PV, Moudgil R, Kaur D. *J. Phys. Chem.* 2003; **107**: 1627–1634; (b) Bharatam PV, Uppal P, Kaur AD. *J. Chem. Soc. Perkin Trans.* 2000; **2**: 43–50; (c) Bharatam PV, Kaur AD. *J. Phys. Org. Chem.* 2003; **16**: 183–189; (d) Moudgil R, Bharatam PV, Kaur R, Kaur D. *Proc. Ind. Acad. Sci. (Chem. Sci.)* 2002; **114**: 223–230; (e) Bharatam PV, Patel DS, Iqbal P. *J. Med. Chem.* 2005; **48**: 7615–7622; (f) Bharatam PV, Uppal P, Kaur D. *Chem. Phys. Lett.* 1997; **276**: 31–38; (g) Lammertsma K, Bharatam PV. *J. Org. Chem.* 2000; **65**: 4622–4630; (h) Bharatam PV, Uppal P, Kaur D. *J. Mol. Struc. (Theochem)* 1999; **458**: 227–237; (i) Kaur D, Sharma P, Kaur M, Kaur P, Bharatam PV. *J. Mol. Struc. (Theochem)* 2007; **805**: 119–125; (j) Kaur D, Sharma P, Bharatam PV. *J. Mol. Struc. (Theochem)* 2007; **805**: 119–125; (k) Bharatam PV, Sundriyal S. *J. Nanosci. Nenotechnol.* 2006; **6**: 3277–3282.
15. (a) Pople JA, Beveridge DL. *Approximate Molecular Orbital Theory.* McGraw Hill: New York, 1970; (b) Hehre WJ, Radom L, Schleyer PvR, J. Pople A. *Ab Initio Molecular Orbital Theory.* Wiley: New York, 1985; (c) http://gaussian.com/g_whitepap/thermo.htm.
16. (a) Parr RG, Yang W. *Density Functional Theory of Atoms and Molecules*. O.U.P: New York, 1989; (b) Bartolotti LJ, Fluchick K. In *Reviews in Computational Chemistry*, Lipkowitz KB, Boyd DB (eds). VCH Publishers: New York, 1996.
17. Gaussian-98 set of programs, Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Zakrzewski VG, Montgomery JA, Jr, Stratmann RE, Burant JC, Dapprich S, Millam JM, Daniels AD, Kudin KN, Strain MC, Farkas O, Tomasi J, Barone V, Cossi M, Cammi R, Mennucci B, Pomelli C, Adamo C, Clifford S, Ochterski J, Petersson GA, Ayala PY, Cui Q, Morokuma K, Malick DK, Rabuck AD, Raghavachari K, Foresman JB, Cioslowski J, Ortiz JV, Baboul AG, Stefanov BB, Liu G, Liashenko A, Piskorz P, Komaromi I, Gomperts R, Martin RL, Fox DJ, Keith T, Al-Laham MA, Peng CY, Nanayakkara A, Gonzalez C, Challacombe M, Gill PMW, Johnson B, Chen W, Wong MW, Andres JL, Gonzalez C, Head-Gordon M, Replogle ES, Pople JA. Gaussian Inc., Pittsburgh PA, 1998.
18. (a) Becke AD, *J. Chem. Phys.* 1993; **98**: 5648–5652; (b) Lee C, Yang W, Parr RG. *Phys. Rev.* 1988; **37b**: 785–789; (c) Perdew JP, Wang Y. *Phys. Rev.* 1992; **45b**: 13244–13249.
19. (a) Moller C, Plesset MS. *Phys. Rev.* 1934; **46**: 618–622; (b) Krishan R, Frisch MJ, Pople JA. *J. Chem. Phys.* 1980; **72**: 4244–4245.
20. Scott AP, Radom L. *J. Phys. Chem.* 1996; **100**: 16502–16513.
21. Curtiss LA, Raghavachari K, Pople JA. *J. Chem. Phys.* 1993; **98**: 1293–1298.
22. Bader RFW. *Atoms in Molecules: A Quantum Theory.* Oxford University Press: Oxford, 1990.
23. (a) Reed AE, Weinstock RB, Wienhold F. *J. Chem. Phys.* 1985; **83**: 735–746; (b) Reed AE, Wienhold FL, Curtiss A. *Chem. Rev.* 1988; **88**: 899–926.
24. (a) Onsager L. *J. Am. Chem. Soc.* 1936; **58**: 1486–1493; (b) Kirkwood JG. *J. Chem. Phys.* 1934; **2**: 351–361; (c) Wong MW, Frisch MJ, Wiberg KB. *J. Am. Chem. Soc.* 1991; **113**: 4776–4782; (d) Wong MW, Wiberg KB, Frisch MJ. *J. Am. Chem. Soc.* 1992; **114**: 523–529; (e) Wong MW, Wiberg KB, Frisch MJ. *J. Chem. Phys.* 1991; **95**: 8991–8998; (f) Wong MW, Wiberg KB, Frisch MJ. *J. Am. Chem. Soc.* 1992; **114**: 1645–1652.
25. (a) Krygowski TM. *J. Chem. Inf. Comput. Sci.* 1993; **33**: 70–78; (b) Cyrañski MK, Krygowski TM. *J. Chem. Inf. Comput. Sci.* 1996; **36**: 1142–1145; (c) Krygowski TM, Cyrañski MK. 1996; *Tetrahedron* 1996; **52**: 1713–1722; (d) Krygowski TM, Cyrañski MK. *Tetrahedron* 1996; **52**: 10255–10264; (e) Krygowski TM, Cyrañski MK, Czarnocki Z, Häfelinger G, Katritzky AR. *Tetrahedron* 2000; **56**: 1783–1796; (f) Cyrañski MK, Stêpieñ BT, Krygowski TM. *Tetrahedron* 2000; **56**: 9663–9667; (g) Krygowski TM, Cyrañski MK. *Chem. Rev.* 2001; **101**: 1385–1420; (h) Krygowski TM, Cyrañski MK, Anulewicz-Ostrowska R. *Pol. J. Chem.* 2001; **75**: 1939–1942.
26. (a) Schleyer PvR, Maerker C, Dransfeld A, Hommes NJRvE. *J. Am. Chem. Soc.* 1996; **118**: 6317–6318; (b) Cyrañski MK, Krygowski TM, Wisiorowski M, Hommes NJRvE, Schleyer PvR. *Angew. Chem., Int. Ed. Engl.* 1998; **37**: 177–180; (c) Subramanian G, Schleyer PvR, Jiao H. *Angew. Chem., Int. Ed. Engl.* 1996; **35**: 2638–2641; (d) Jiao H, Schleyer PvR. *Angew. Chem., Int. Ed. Engl.* 1996; **35**: 2383–2386; (e) Jiao H, Schleyer PvR, Mo Y, McAllister MA, Tidwell TT. *J. Am. Chem. Soc.* 1997; **119**: 7075–7083; (f) Schleyer PvR, Jiao H, Hommes NJRvE, Malkin VG, Malkina O. *J. Am. Chem. Soc.* 1997; **119**: 12669–12670; (g) Subramanian G, Schleyer PvR, Jiao H. *Organometallics* 1997; **16**: 2362–2369; (h) Jemmis ED, Kiran B. *Inorg. Chem.* 1998; **37**: 2110–2116.

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