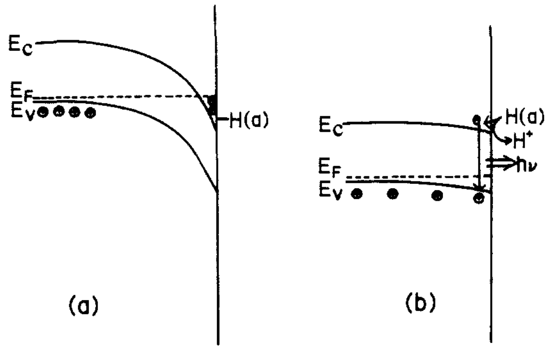

Figure 8. Proposed model for the EL caused by electron injection: (a) under strong cathodic bias; (b) near the flat band potential.

thermore, Auger Electron Spectroscopic measurements of the n-GaAs electrode on which hydrogen evolution reaction took place for 30 min at −1.5 V (current density = ca. 1 Å·cm^{-2}) provided evidence of no enrichment of Ga at the surface region.[16] In addition, there is no possibility that the amount of adsorbed hydrogen exceeds one monolayer. Therefore, with all the evidence presented above, we propose that the most probable species responsible for the EL generation is the adsorbed hydrogen atom. The model which explains the EL generation is shown in Figure 8. Thus, H(a), the energy of which is higher than that of the bottom of the conduction band *at the surface*, is generated when p-GaAs is kept under strong negative bias (reaction 1 or 5) and injects electron into the conduction band (reaction 3 or 7) when the potential is pulsed to the positive potential limit which is close to the flat band potential. Some of the injected electrons recombine radiatively with holes in the valence band (reaction 9) which is the majority carrier of p-GaAs. The results of Ru^{3+} treated p-GaAs can also be explained by this mechanism. Thus, the energy level of H(a) at the Ru^{3+} treated p-GaAs surface should be within the energy gap and, therefore, no EL should be observed.[17] The increase of dark hydrogen evolution current is caused by the lowering of the H(a) energy level as proposed by Bard for the effect of Pt on the photoelectrochemical hydrogen evolution reaction.[18]

Acknowledgment. Prof. A. B. Ellis and Dr. W. S. Hobson are acknowledged for the donation of p-GaAs single crystals. This work was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture.

Registry No. GaAs, 1303-00-0; H, 12385-13-6; H_2, 1333-74-0; Ru^{3+}, 22541-88-4; $RuCl_3$, 10049-08-8.

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[16] Kaneko, S.; Uosaki, K.; Kita, H., unpublished result.

[17] There may be a possibility of sub-band emission in this case. Our detection system, however, can measure the emission only up to 1100 nm and no sub-band gap EL was detected within this region.

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Topologically Determined Charge Distributions and the Chemistry of Some Cage-Type Structures Related to Adamantane

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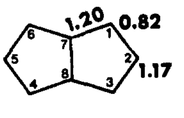
Contribution from the Department of Chemistry, University of South Carolina, Columbia, South Carolina 29208. *Received July 29, 1985*

Abstract: The rule of topological charge stabilization says that nature prefers to locate heteroatoms at those positions in a molecular structure where connectivity and electron filling level tend to accumulate or deplete electron density in an isoelectronic, isostructural, homoatomic system. The rule can be rationalized on the basis of first-order perturbation theory. Here we apply the rule to some cage-type structures related to adamantane. Examples include P_4S_3, P_4S_4, P_4S_5, and P_4S_6, as well as many others. Extended Hückel calculations of Mulliken atom populations in homoatomic systems correlate with the positions of atoms of different electronegativities in these structures. Topologically determined charge distributions can explain some of the chemistry of these systems.

A recent survey of planar conjugated molecules has demonstrated that connectivity and the number of electrons occupying the molecular orbital system determine the patterns of charge densities in homoatomic systems.[1] The *rule of topological charge stabilization* says that nature prefers to locate heteroatoms at those positions where connectivity and electron filling level tend to accumulate or deplete electron density. An example from planar conjugated molecules is pentalene (1) shown with charge densities for 8 π electrons calculated by the simple Hückel method. Charge densities at positions 1, 3, 4, and 6 are considerably smaller than those at the other sites. The rule of topological charge stabilization says that less electronegative atoms would be favored in those positions with low charge density. Pentalene is known only as the heavily substituted 1,3,5-tri-*tert*-butyl derivative,[2] but the isoelectronic inorganic analogs (2, 3) have been prepared.[3,4] In 2 and 3 borons are located at positions 1, 3, 4, and 6, and more electronegative nitrogens or sulfurs occupy the other sites, arrangements in which the electronegativities of the constituent atoms match the distribution of charge densities determined by connectivity in 1, the homoatomic, isoelectronic structure which we refer to as the *uniform reference frame*. That the pattern of charge densities is also a function of the number of valence electrons can be seen by comparing the charges for the pentalene dianion (4, 10 π electrons) with those of pentalene itself (1). In



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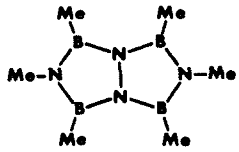

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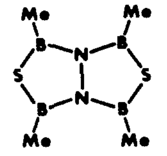

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[1] Gimarc, B. M. *J. Am. Chem. Soc.* **1983**, *105*, 1979.

[2] Hafner, K.; Süss, H. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 576.

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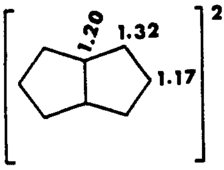
4, positions 1, 3, 4, and 6 have the largest charge densities, a pattern consistent with the known heteroatomic system (**5**).[5]



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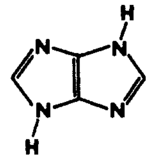


5

Over the years there have been a few specific applications of the concept of topological charge stabilization. The idea was mentioned as early as 1950 when Longuet-Higgins, Rector, and Platt studied the π-electronic structure of porphine.[6] As their zero-order electron distribution in porphine, those authors used simple Hückel charge densities calculated for the hydrocarbon that is isostructural and isoelectronic with porphine. Muetterties and Hoffmann have shown that in trigonal-bipyramidal molecules such as PF_2Cl_3, the more electronegative fluorines prefer the axial positions while the less electronegative chlorines go to the equatorial sites, an arrangement that is in accord with extended Hückel charge distributions calculated for the PF_5 reference frame.[7,8] Gimarc[9] and Burdett[10] have described trends in site preferences for atoms of different electronegativities in linear and bent triatomic molecules and ions with 10 to 22 valence electrons. Burdett has pointed out that charge distributions calculated for an appropriate homoatomic system can correlate the different positions taken by atoms from groups VA (15)[70] and VIA (16)[70] in the cage-type structures of S_4N_4 and P_4S_4.[11] Except for the triatomic molecules and ions mentioned above and our earlier survey of two-dimensional systems,[1] topological charge stabilization has not been applied in a systematic way to the study of large groups of molecules that share related structures, and few chemists are aware of the utility of this concept for organizing a large amount of chemical information about structures and relative stabilities.

Theoretical Rationale

First-order perturbation theory gives a simple justification for the rule of topological charge stabilization. Consider the uniform reference frame as the unperturbed system with Hamiltonian H°, wave function Ψ°, and total energy $E(0)$ related by the Schrödinger wave equation

$$H^\circ\Psi^\circ = E(0)\Psi^\circ$$

Now introduce heteroatoms as a perturbation, keeping the structure and the number of electrons fixed. The perturbing Hamiltonian H' can be expressed as a sum of changes in the Coulomb nuclear–electron attraction terms due to changes in nuclear charge ΔZ that result from the heteroatoms:

$$H' = -\sum_{\alpha,i} \Delta Z_\alpha / r_{i\alpha}$$

where α labels the nuclei and i labels the electrons. For the perturbed system, $\mathcal{H} = H^\circ + H'$ and the total energy E can be calculated as the zeroth-order energy plus correction terms to higher order:

$$E = E(0) + E(1) + E(2) + ...$$

The first-order perturbation correction to the energy is given by

$$E(1) = \langle \Psi^\circ | H' | \Psi^\circ \rangle$$

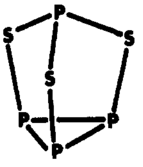
Since the operator H' involves only simple multiplication, the Ψ° factors can be combined within the integral to give the electron density, $\rho = (\Psi^\circ)^*\Psi^\circ$. Then

$$E(1) = \langle \rho H' \rangle$$

Therefore, to give maximum stability or energy lowering from $E(1)$, the heteroatoms should be those for which the largest ΔZ match positions where ρ is already large in the unperturbed reference frame. For qualitative considerations it is convenient to assume valence electrons only and to replace ΔZ by changes in effective nuclear charge $\Delta\zeta$, or, even more simply, to use electronegativity as a measure of $\Delta\zeta$.

Tetrahedral Structures

In order to extend our appreciation of the utility, scope, and limitations of the rule of topological charge stabilization, we have examined a number of molecules of the representative elements that have cage-type structures related to the tetrahedron. The simplest of these are molecules such as P_4S_3 and As_4S_3. The four phosphorus atoms of P_4S_3 are at the four corners of a distorted tetrahedron with an apical phosphorus linked by bridging sulfurs to a basal triangle of phosphorus atoms (**6**).[12] As_4S_3 has an analogous structure.[13] The known anion P_7^{3-} serves as the uniform reference frame for P_4S_3 and As_4S_3.[14] Structure **7** displays the Mulliken net atomic populations (or more simply, atomic charges) for P_7^{3-} calculated from extended Hückel wave functions[15] based on the experimental structure. The extended Hückel method is known to yield exaggerated charges,[16] but experience shows that they are adequate for the purposes here which require only a qualitative pattern of charge distributions. In some test cases we found that the charge iteration modification of the extended Hückel method gave charges that were undoubtedly more realistic but with the same sense or pattern as those from the non-iterative procedure.



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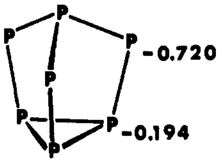

7

The homoatomic uniform reference frames for 3-dimensional systems are often hypothetical and have very large total charge Q. Since we are interested only in charge differences, we introduce *normalized charges*. Imagine a system of N atoms with a total charge Q. The individual atomic charges q_r sum to Q:

$$\sum_{r=1}^{N} q_r = Q$$

Suppose we subtract the quantity Q/N from each atomic charge to define normalized charges q_r':

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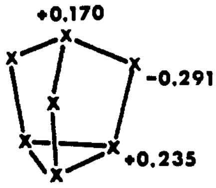
$$q_r' = q_r - Q/N$$

The normalized charges sum to zero. Applying this procedure to the P_7^{3-} charges in **7** yields the normalized charges in **8**. Since the reference frame in **8** is no longer composed of real atoms, we have introduced the symbol X to label atoms. Normalized charges emphasize charge differences by creating quantities that have differences in sign, thereby making relative charges easier to appreciate.



8

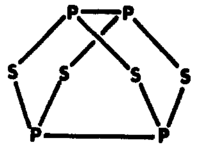
The normalized charges in **8** show that the bridging positions are negative compared to apical and basal sites. Hence the more electronegative sulfurs should prefer to occupy the bridges with less electronegative P or As atoms in the apex and basal triangle as observed P_4S_3 and As_4S_3.

Topological charge stabilization offers a beautiful explanation for the driving force to equilibrium in the system P_4S_3/As_4S_3. Blachnik and Wickel have reported the results of their experimental studies of this system.[17] They found that when the reactants are mixed in the stoichiometric ratio (1:3), the equilibrium lies predominately to the side of the PS_3As_3 product:

$$P_4S_3 + 3\ As_4S_3 \rightleftarrows 4PS_3As_3$$

The structure of the product PS_3As_3 presumably has a phosphorus atom at the apex, three bridging sulfurs, and a basal triangle of arsenic atoms. Blachnik and Wickel attribute the stability of the product to the greater strength of PS compared to AsS bonds and to the increase in number of PS bonds from 6 in the reactants to 12 in the product. Topological charge stabilization offers an alternative explanation.[18] In arranging atoms among reactant and product molecules, the electronegative S atoms should occupy the bridges, the less electronegative P atom should occupy the apical site, and the still less electronegative As atoms should prefer the basal positions as determined by relative charges in the uniform reference frame (**8**).

The molecule P_4S_4 (**9**) has a cage structure.[19] The phosphorus atoms are at the corners of a slightly distorted tetrahedron, and sulfurs bridge four of the tetrahedral edges with the two remaining edges being P–P bonds. A different description places four equivalent sulfur atoms at the corners of a square plane and bonded to pairs of phosphorus atoms above and below the plane. Burdett has pointed out that charge distributions calculated for an appropriate homoatomic, isoelectronic system can correlate the different positions in the cage taken by atoms from elements of groups VA (15) and VIA (16).[11] For example, in P_4S_4 the group VIA element occupies the plane with the group VA element above and below. However, in S_4N_4 the situation is just reversed;[20] the nitrogens (group VA) occupy the plane with sulfurs (group VIA) paired above and below. These molecules contain 44 valence electrons, and the hypothetical ion O_8^{4+} might serve as a uniform reference frame with model bond distances and angles chosen for calculation of charge densities from extended Hückel wave functions. Normalized charges have been chosen for representation in **10**. The four atoms at the corners of the square plane are negative with respect to the pairs above and below. Therefore the more electronegative atoms prefer the plane positions with the less electronegative atoms occupying sites above and below the plane, an arrangement that is realized in the structures of the known examples of this series. In S_4N_4 and Se_4N_4 the group VA element N occupies the square[20,21] and in P_4S_4, As_4S_4, and As_4Se_4 the group VIA elements are on the plane.[19,22,23]



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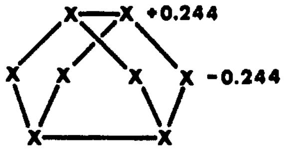
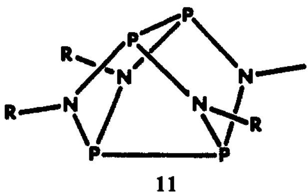


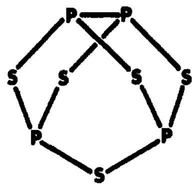
10

A related structure is $P_4N_4R_4$ (**11**) where the R groups (*tert*-butyl) are substituted on the square-planar nitrogens and the phosphorus atoms are bonded in pairs above and below the plane,[24] again in agreement between the relative electronegativities of N and P and the relative charges of the uniform reference frame (**10**).



11

The P_4S_5 cage (**12**) is related to that of P_4S_4 (**9**) with an additional sulfur bridging one pair of phosphorus atoms.[25] Normalized charges for the O_9^{4+} uniform reference frame appear in **13**. With much lower symmetry than **10**, structure **13** has four different kinds of positions. But again, the more electronegative sulfurs occupy the negative sites while the less electronegative phosphorus atoms take the positive positions. Similarly, in the related structures P_4Se_5 and As_4S_5, the more electronegative group



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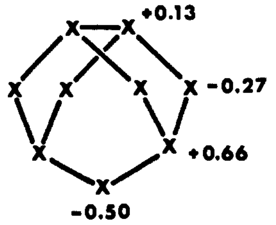

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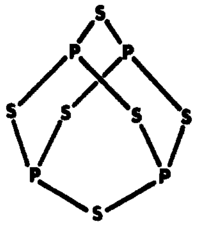
(25) P_4S_5: Griffin, A. M.; Sheldrick, G. M. *Acta Crystallogr.* **1975**, *31B*, 2738.

Table I. Adamantane Analogues

A	B	C
P_4O_6	$P_4(NMe)_6$	$(HC)_4(CH_2)_6$
As_4O_6	$As_4(NMe)_6$	$N_4(CH_2)_6$
As_4S_6	$(HC)_4S_6$	$P_4(SiMe_2)_6$
Sb_4O_6	$(HSi)_4S_6$	$P_4(GeMe_2)_6$
	$(HSi)_4Se_6$	

VIA atoms (S or Se) are in the negative sites and the less electronegative group VA atoms (P or As) take up the positive locations.[26,27] But the positions of group VA and group VIA elements are reversed in $S_4N_5^-$ because N is more electronegative than S.[28]

The insertion of still another sulfur between the bonded pair of phosphorus atoms in **12** leads to the structure which one anticipates for P_4S_6 (**14**), this particular molecule being as yet unknown. But the highly symmetrical structure is that of adamantane of which there are many examples.[29-40] The structure has only two different kinds of positions, numbered and with the structure drawn in a different orientation in **15**. The 1, 3, 5, and 7 sites are referred to as tertiary, 3-coordinate, or bridgehead sites. The 2, 4, 6, 8, 9, and 10 positions are the secondary, 2-coordinate, or bridging sites. Normalized charges for an appropriate oxygen uniform reference frame (**16**) show that the 3-coordinate or bridgehead sites are positive relative to the 2-coordinate or bridging positions. The rule of topological charge stabilization predicts that the bridgehead atoms should be less electronegative than those in the bridges. Table I lists thirteen molecules that have the full adamantane symmetry. In nine of these (columns A and B) the less electronegative atoms occupy the bridgeheads while the more electronegative atoms form the bridges. In three others (column C), such as $N_4(CH_2)_6$, the situation is reversed in opposition to the topological charge stabilization rule. The remaining compound is adamantane itself in which both bridges and bridgeheads are carbons.



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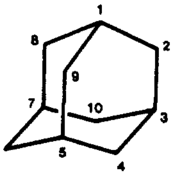

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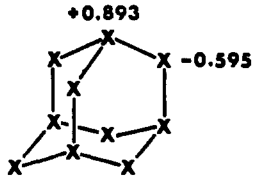
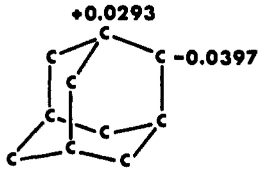


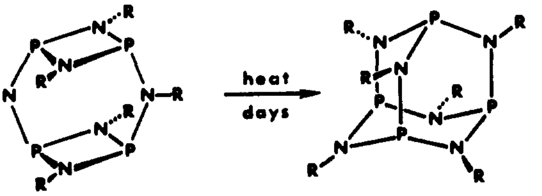
16

The charge densities of the carbon framework of adamantane $(HC)_4(CH_2)_6$ appear in **17**. The calculated charges of the hydrogens themselves are not shown in **17**. These charges still have the same signs but are much reduced compared to the normalized charges of the bare frame **16**. Substituent hydrogens smooth out charge differences on the frame to which they are attached. This smoothing effect of substituents may explain the exceptional cases in column C of Table I. All of the exceptions contain substituents on bridges, bridgeheads, or both. Substituents add more atomic orbitals to the basis set as well as additional sites for charge so a redistribution of charges should be easier in those cases, making bridgehead and bridge sites more adaptable to the acceptance of atoms in opposition to the rule of topological charge stabilization.

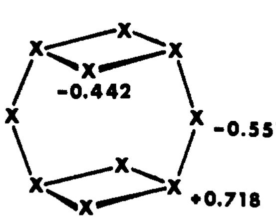


17

The compound $P_4(NR)_6$ is known to exist in two isomers, the "double decker" cage (**18**)[41] and the adamantane structure (**19**).[33] $P_4(NR)_6$ (R = *i*-Pr) is known to rearrange rather easily and quantitatively from **18** to **19** which presumably is the more stable of the two forms. The normalized charge densities for the uniform reference frame of the "double decker" form are shown in **20**. Once more, the 3-coordinate sites are positive relative to the 2-coordinate sites. In the "double decker" isomer the less electronegative phosphorus atoms occupy the 3-coordinate positions. A comparison of charges in isomeric uniform reference frames **16** and **20** reveals a smaller separation of charges in **20**. The sum of positive $q' = 3.57$ in **16** and 2.87 in **20**. This suggests that the isomeric structure **20** might be more acceptable for systems in which electronegativities of atoms are closer to each other, such as P and N in $P_4(NR)_6$, than it would be in P_4O_6 which has a



18 **19**



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(26) P_4Se_5: Penney, G. J.; Sheldrick, G. M. *J. Chem. Soc. A* **1971**, 245.

(27) As_4S_5: Whitfield, H. J. *J. Chem. Soc., Dalton Trans.* **1973**, 1740.

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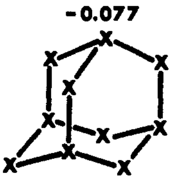
Table II. Bridgehead Substituted Adamantane Analogues

A	B	C	D
P_4O_{10}	$Sn_4S_{10}^{4-}$	$P_4S_6O_4$	$(MeC)_4(CH_2)_6$
P_4S_{10}	$Sn_4Se_{10}^{4-}$	$P_4O_6S_4$	$Si_4O_6(t\text{-Bu})_4$
P_4Se_{10}	$B_4S_{10}^{8-}$	$Ge_4S_6Br_4$	$Si_4S_6Me_4$
$Si_4S_{10}^{4-}$	$Ga_4S_{10}^{8-}$	$Ge_4S_6I_4$	$Ge_4S_6Me_4$
$Si_4Te_{10}^{4-}$	$Ga_4Se_{10}^{8-}$	$Ge_4Se_6I_4$	$Sn_4S_6Me_4$
$Ge_4S_{10}^{4-}$	$In_4S_{10}^{8-}$	$Si_4(CH_2)_6Cl_4$	$Sn_4Se_6Me_4$
$Ge_4Se_{10}^{4-}$	$In_4Se_{10}^{8-}$		

much larger difference in electronegativities between P and O and for which a structure of the type **20** is unknown.

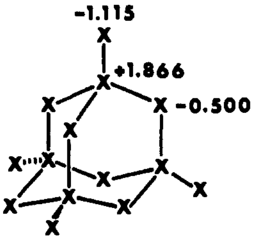
The molecules $(HC)_4(BR)_6$, where R = Me, Cl, or Br, also have adamantane structures,[42,43] but they are not isoelectronic with adamantane. In $(HC)_4(BR)_6$ the six borons are in bridging positions and the four carbons are at the bridgeheads. If we take R = H, then $(HC)_4(BR)_6$ is a 44 valence electron system while adamantane and P_4O_6 have 56 valence electrons. These systems allow us to compare charge distributions in systems with the same structure but different numbers of electrons. The normalized charges for the 44 electron case (**21**) although small show a reversal of polarity compared to those for the 56 electron system (**16**). The order of charges in **21** is perfectly consistant with the more electronegative carbon being located at the bridgehead and the less electronegative boron as the bridge.



21

Bridgehead Substituted Adamantanes

Table II lists 26 molecules that have the basic adamantane framework but with a non-hydrogen substituent atom or group at each bridgehead[44-66] as in **22** which shows the normalized charges q_r' for the uniform reference frame O_{14}^{4+}. As in the unsubstituted system (**16**) the bridge sites are negative with respect to the bridgeheads, but in **22** the most negative positions are the substituent, terminal, or exo sites. The topological charge stabilization rule predicts that $P_4S_6O_4$, in which oxygens are exo and sulfurs are bridges, should be more stable than $P_4O_6S_4$ which has oxygen bridges and sulfur substituents. Synthetic history, however, casts some doubt on this conclusion. $P_4O_6S_4$ was first prepared in the late 19th century.[67] Its structure is well-known.[57] Although the synthesis of $P_4S_6O_4$ was reported nearly 20 years ago,[56] more recent investigations have noted the failure of attempts to repeat the original synthesis.[68] Recently, Wolf and Meisel[69] have described the preparation, though not the structural characterization, of $P_4S_6O_4$. They reacted mixtures of P_4O_{10} and P_4S_{10} in stoichiometric ratios appropriate for the synthesis of $P_4O_6S_4$ and of $P_4O_2S_8$ and found $P_4S_6O_4$ as a minor product in both cases along with other $P_4O_{10-n}S_n$ products. An experiment with P_4O_{10}/P_4S_{10} = 2:3, the stoichiometric ratio for $P_4S_6O_4$, was not reported. Thus the topological charge stabilization rule reveals the $P_4O_6S_4$, $P_4S_6O_4$ case as an interesting problem for further theoretical and experimental investigation.



22

Of the 26 molecules and ions in Table II only five examples in column C strictly follow the pattern of declining electronegativities specified by the charge distribution in **22**: exo > bridge > bridgehead. Fourteen more molecules (columns A and B) are composed of only two elements, such as P_4O_{10} and $Si_4Te_{10}^{4-}$, but in each case the less electronegative element occupies the bridgehead sites. Another 5 examples (column D) have bridging oxygens or sulfurs with less electronegative group IVA atoms at the bridgeheads and alkyl groups at bridgehead substituents. Notice that all of these exceptional cases bear hydrogen or methyl substituents on the bridging and exo atoms. As we saw previously, these substituents produce a smoothing of charge distributions and therefore they may make exceptions to the rule more stable than they would be without substituents.

Conclusion

Atomic charge in a molecule is an old and useful concept. Even the notion that charges can be determined by connectivity goes back at least 35 years.[6] The main idea here is that, based on a calculation for a single reference structure, conclusions can be drawn concerning the relative stabilities of many possible isoelectronic molecules and ions with related structures. The rule can be rationalized by first-order perturbation theory without reference to the molecular orbital model. The rule can guide synthetic efforts and point out problems that merit further study

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by both theory and experiment. Topological charge stabilization is a useful generalizing principle for understanding the relative stabilities of individual molecules within structural classes.

Acknowledgment. We are grateful to Professor Robert G. Parr of the University of North Carolina for pointing out to us the simple perturbation argument that rationalized the rule of topological charge stabilization.

Registry No. P_4O_6, 12440-00-5; As_4O_6, 12505-67-8; As_4S_6, 65113-28-2; Sb_4O_6, 72926-13-7; $P_4(NMe)_6$, 10369-17-2; $As_4(NMe)_6$, 2030-90-2; $(HC)_4S_6$, 281-40-3; $(HSi)_4S_6$, 7343-45-5; $(HSi)_4Se_6$, 7265-91-0; $(HC)_4(CH_2)_6$, 281-23-2; $N_4(CH_2)_6$, 100-97-0; $P_4(SiMe_2)_6$, 67684-77-9; $P_4(GeMe_2)_6$, 28133-43-9; P_4O_{10}, 16752-60-6; P_4S_{10}, 15857-57-5; P_4Se_{10}, 102436-55-5; $Si_4S_{10}{}^{4-}$, 102436-56-6; $Si_4Te_{10}{}^{4-}$, 102436-57-7; $Ge_4S_{10}{}^{4-}$, 34274-80-1; $Ge_4Se_{10}{}^{4-}$, 102436-48-6; $Sn_4S_{10}{}^{4-}$, 102492-33-1; $Sn_4Se_{10}{}^{4-}$, 102436-49-7; $B_4S_{10}{}^{8-}$, 102436-50-0; $Ga_4S_{10}{}^{8-}$, 102436-51-1; $Ga_4Se_{10}{}^{8-}$, 102492-34-2; $In_4S_{10}{}^{8-}$, 102436-52-2; $In_4Se_{10}{}^{8-}$, 102436-53-3; $P_4S_6O_4$, 12143-41-8; $P_4O_6S_4$, 15780-31-1; $Ge_4S_6Br_4$, 58356-00-6; $Ge_4S_6I_4$, 80134-82-3; $Ge_4Se_6I_4$, 102436-58-8; $Si_4(CH_2)_6Cl_4$, 18222-89-4; $(MeC)_4(CH_2)_6$, 1687-36-1; $Si_4O_6(t\text{-Bu})_4$, 18407-92-6; $Si_4S_6Me_4$, 5372-65-6; $Ge_4S_6Me_4$, 39873-50-2; $Sn_4S_6Me_4$, 20814-45-3; $Sn_4Se_4Me_4$, 80167-11-9.

Predictions of Relative Stabilities among Series of Carborane Isomers by the Criterion of Topological Charge Stabilization

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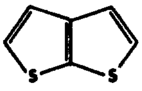
Abstract: We have used topological charge stabilization considerations to predict the qualitative ordering of stabilities of positional isomers among the various classes of *closo*-carboranes, $C_2B_{n-2}H_n$, $5 \le n \le 12$. The rule of topological charge stabilization states that the positions of heteroatoms in a structure are related to the distribution of atomic charges that are determined by connectivity or topology for an isoelectronic, isostructural, homoatomic reference system. For charges we used Mulliken net atomic populations calculated from extended Hückel wave functions. The order of stabilities we predict agrees perfectly with what can be deduced from experimental data and matches reasonably well with the results of detailed calculations.

The *rule of topological charge stabilization* states that heteroatoms prefer to be located at sites that conform to the pattern of relative electron densities determined by connectivity or topology in an isoelectronic, isostructural, homoatomic system that we call the *uniform reference frame*.[1] An example from planar conjugated molecules is the series of thienothiophene positional isomers (**1–4**). For these structures the pentalene dianion (**5**) serves as the uniform reference frame. Charge densities shown in **5** are π electron charge densities from simple Hückel calculations.



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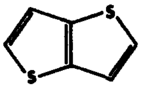

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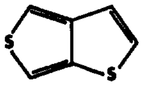

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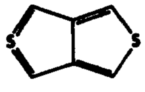

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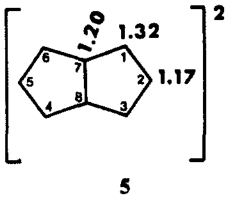

5

The largest charge densities in **5** are at equivalent positions 1, 3, 4, and 6. Therefore, placement of electronegative heteroatoms at these positions would be favored. It follows, then, that structures **1** and **2** would be expected to be the most stable isomers, **3** somewhat less so, and **4** the least stable, an ordering that agrees with the known reactivities and calculated resonance energies of the thienothiophenes.[1]

Although the relative thermodynamic stabilities of positional isomers are surely determined by relative total energies of the individual molecules, the rule of topological charge stabilization, focusing on a single common homoatomic reference structure, can point out what is right or wrong with a particular heteroatomic structure, and it allows one to order quickly the relative stabilities of a group of heteroatomic positional isomers. Simple first-order perturbation theory relates charge density distributions to total energy differences.[2]

The concept of topological charge stabilization was introduced as early as 1950 when Longuet-Higgins, Rector, and Platt[3] pointed out that the locations of nitrogens in porphine are those corresponding to positions of high π charge densities in the corresponding isoelectronic hydrocarbon. Meutterties and Hoffmann accounted for the structure of PCl_3F_2, with axial fluorines and equatorial chlorines, as a result of charge distributions established by topology in PF_5.[4,5] Gimarc[6] and Burdett[7] have discussed the arrangement of heteroatoms in linear and bent triatomic molecules and ions. Burdett mentioned charge densities calculated for a homoatomic reference structure as the basis for explaining the different positions taken by elements from groups VA (15)[55] and VIA (16)[55] in S_4N_4 and P_4S_4.[8] Gimarc has surveyed the structures of a large collection of planar conjugated systems.[1] Finally, Gimarc and Ott have used the rule of topological charge stabilization to rationalize the structures and properties of a group of cage-type molecules related to adamantane.[2,9] Only in these most

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