J. Org. Chem. **1999,** *64,* 1311−1318

Aromatic Character of Tria- and Pentafulvene and Their Exocyclic Si, Ge, and Sn Derivatives. An ab initio Study

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Received November 17, 1998

The structures and dipole moments have been calculated for both methylenecyclopropene (triafulvene) and pentafulvene and their exocyclic Si, Ge, and Sn analogues **1a**−**d** and **2a**−**d**, respectively. Ab initio calculations employing the HF, DFT, and MP2 methods, each using split valence plus polarization and triple split valence with two sets of polarization functions basis sets, have been performed. The results of these six levels of theory on each of the eight molecules were compared, and the aromatic character of these systems was examined. The structures **1a**−**d** exhibited pronounced bond alternation in the ring suggesting the existence of only weak cyclopropenyl cation-like resonance contribution. However, very large dipole moments were predicted in the direction that would be expected from an aromaticity contribution. Since Si, Ge, and Sn are less electronegative than C, the large dipole moments in the direction of the exocyclic heteroatom were surprising. The most striking finding was that, while **1a** is planar, 4-sila-, 4-germa-, and 4-stannatriafulvene were nonplanar with trans-bent structures in which the exocyclic double bond is bent slightly out of the cyclopropene ring plane and out of the HXH plane (X = Si, Ge, Sn) by large angles. Thus, the Si, Ge, and Sn atoms exhibit pyramidal geometries. The dipole moment of pentafulvene, **2a,** (oriented toward the ring) was substantially smaller than that of its Si, Ge, and Sn analogues, **2b**−**d,** The large dipoles of **2b**−**d** were due to greater charge separation resulting from the lower electronegativities of Si, Ge, and Sn versus that of C. The cyclopentadienyl rings exhibited strong bond alternation indicating only a modest cyclopentadienyl anion-like contribution in **2b**−**d**.

Introduction

Aromaticity is a seminal concept in organic chemistry. According to Hückel's $4n + 2$ rule and experimental studies, the cyclopropenyl cation[1] as well as the cyclopentadienyl anion[2] are stabilized by their aromaticity. The parent cyclopropenyl and cyclopentadienyl compounds with an exocyclic double bond are triafulvene[3−5] (i.e., methylenecyclopropene), **1a**, and pentafulvene,[6−10] **2a**. Both can be portrayed with dipolar resonance structures (**B** and **C**; **F** and **G**) shown in Figure 1. These dipolar resonance hybrids are usually discussed as being stabilized to some small degree by aromaticity.[11−16] Cyclopropenone,[17−20] **3**, the oxo analogue of **1a**, exhibits a very large (4.39 D) dipole moment[21] attributed to a substantial aromatic dipolar contribution (Figure 1). Its structure[21,22] consists of relatively long $C{=}C$ and $C{=}O$

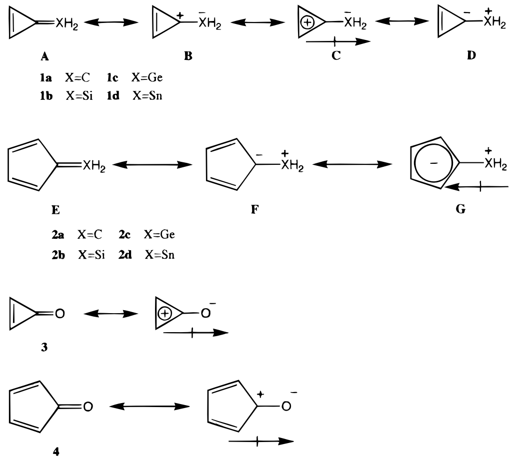

Figure 1. Resonance structures of triafulvene, **1**, and petafulvene, **2**, and their Si, Ge, and Sn derivatives versus cyclopropenone, **3**, and cyclopentadienone, **4**.

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10.1021/jo982279w CCC: $18.00

bonds and short ring C−C bonds (for a review see ref 23). The corresponding "aromatic" contribution to **1a** (structure **C**) should be substantially less than that in **3** given the far larger electronegativity of oxygen versus CH$_2$. However, **1a** is predicted[11] by simple Hückel MO theory to exhibit a MO resonance energy of 0.96β (β = 18 kcal/mol) and C−C π-bond orders of 0.752 (to the exocyclic C), 0.454, and 0.818 (ring double bond).[12] The 4-heterosubstituted analogues of triafulvene, 4-sila-, 4-germa-, and 4-stannatriafulvene (**1b**−**d**, respectively) are unique because the exo C═XH$_2$ (X = Si, Ge, Sn) double bond is intrinsically polarized as $^-$C−X$^+$H$_2$. This contribution would reduce aromatic-type contributions. Alternatively, the inherent polarity of this bond should be reduced by the contributions from hybrid structures of **1b**−**d** shown in Figure 1.

Triafulvene, **1a,** was first synthesized in 1984.[3−5] Its molecular structure and dipole moment have been determined by microwave spectroscopy.[24] The electric dipole moment of 1.90 D was the largest dipole moment determined for a hydrocarbon in the gas phase[24] indicating that the dipolar resonance form contributes significantly to its electronic structure. However, the exocyclic double bond was 1.332 Å long. This length is equal, within the experimental uncertainty (of 0.005 Å), to the corresponding bond length in methylenecyclopropane.[25] Ab initio calculations predicted that the exocyclic double bond in triafulvene would be 0.005 Å longer than in methylenecyclopropane.[24] Furthermore, the cyclopropene ring in triafulvene exhibits significant bond alternation with bond distances of 1.323 and 1.441 Å. Therefore, it was concluded that the dipolar resonance form only contributed by about one-fifth to the ground state of triafulvene and that the molecule basically was nonaromatic.[24] Whether or not triafulvene can be described as somewhat aromatic, however, is still debated in the literature. The potential aromatic character has stimulated a large number of theoretical studies on triafulvene[23,26−36] as well as its 4-hetero-substituted analogues,[23,36−41] and triafulvene has variously been characterized as aromatic,[26−29] nonaromatic,[30−32] and antiaromatic.[33]

We are interested in the effect of exocyclic heteroatom substitution on the electronic and molecular structure of triafulvene. Specifically, substitution of C by the other group IVA elements (silicon, germanium, and tin) was studied herein. When carbon is replaced by one of these elements, the exocyclic bond distance increases and the electronegativity of the exocyclic atom decreases. Si, Ge, and Sn have virtually the same electronegativity, tabulated as 1.8, 1.9, and 1.8, respectively,[42] versus 2.5 for carbon. This should decrease the dipolar contributions by hybrid structures **B** and **C** in Figure 1. The recent experimental generation of a 4-silatriafulvene derivative (as a fleeting intermediate) confirmed this structure's exceptional reactivity.[43] Recent ab initio calculations[44,45] on 4-silatriafulvene predicted that the planar form was a transition state between two degenerate bent structures with silicon being nonplanar. The distortion of the C═Si bond out of the SiH$_2$ plane, in fact, resembles the trans-bent geometries predicted for ethylene derivatives where both carbon atoms were replaced by other group IVA elements.[44,45] When only one carbon atom was replaced by another group IVA element, however, the calculations[44,45] yielded planar structures which is in agreement with a recent theoretical and experimental study of 1,1-dimethyl-1-germene.[46]

Pentafulvene, **2a,** was first described 92 years ago,[6] and simple Hückel MO theory predicts that **2a** has a resonance energy of 1.44β. The molecule is planar with C_{2v} symmetry and has a dipole moment of 0.42 D[47,48] pointing (negative end) into cyclopentadiene ring (see Figure 1). The structure of pentafulvene, determined by microwave spectroscopy,[47] exhibits significant bond alternation, and the dipolar resonance form was estimated to contribute only 7% to the electronic ground state. Thus, this molecule was considered nonaromatic.[47] Electron diffraction studies confirmed strong bond alternation existed in the 6,6′-dimethyl derivative.[49] Several theoretical studies[27−29,31,32,34] on the structure and aromaticiy of pentafulvene conclude that this molecule essentially is nonaromatic. Heat of combustion measurements on the 6,6-dimethyl and 6,6′-diphenyl derivatives suggest a resonance energy of about 12 kcal/mol.[7] 6-Sila-, 6-germa-, and 6-stannapentafulvene (**2b**, **2c**, and **2d**, respectively) might have higher aromatic contributions because the group IVA heteroatoms could, on the basis of their lower electronegativity, favor a more cyclopentadienyl anion-like ring structure as depicted by the dipolar hybrid structure, **G**, shown in Figure 1. The dipolar contributions of **2b**−**d** operate in a direction opposite to that of

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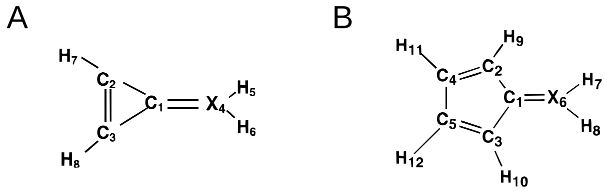

Figure 2. Numbering of the atoms for triafulvenes (A) and pentafulvenes (B).

cyclopentadienone, **4**, a very unstable pseudo-4π-electron system[50] (see Figure 1).

Triafulvenes and pentafulvenes are important systems for organic chemists, and they are widely discussed in most major graduate teaching textbooks in organic chemistry. These molecules have also been discussed in the early classic studies on MO theory.[11,51] A study of these classic systems using modern and more accurate computational methods would therefore be important for many organic chemists. In this study, modern, accurate MO-based methods were employed; however, the potential aromaticity of the compounds were discussed in terms of geometries, dipole moments, and resonance-theoretical language commonly used by organic chemists.

In this paper, we report the results of a series of calculations on triafulvene, **1a**, pentafulvene, **2a,** and their derivatives where the exocyclic atom X = C, Si, Ge, and Sn, respectively (Figure 1). These eight molecules were studied using several well-established ab initio methods (see below). The main objective of our investigation was to study the effect of heteroatom substitution (**1b**−**d** vs **1a** and **2b**−**d** vs **2a**) on the structures and dipole moments and to evaluate the aromatic character of these systems.

Throughout this paper, bond lengths are given in angstroms, angles are in degrees, dipole moments are in Debyes, total energies are in Hartrees, and relative energies are in kcal/mole (see Figure 2 for atom numbering scheme).

Computational Details

It is important that all molecules in a group are calculated at a consistent level of theory in studies of any series of related molecules. Preliminary calculations using smaller basis sets (e.g., STO-3G[52] and 3-21G[53]) were carried out using both density functional and Hartree−Fock methods. The results of these calculations are not reported here. Widely used basis sets such as 6-31G[54] and 6-311G[55] or even Dunning's correlation consistent basis sets[57−59] have to our knowledge not been extended to the heavier elements in this study, Ge and Sn, although the sila- and germatropylium cations were studied[60] at the MP2/6-31G(d) level of theory. We therefore chose the basis sets compiled by Huzinaga[40] for atoms from $Z = 3$ (lithium) to $Z = 86$ (radon). The calculations reported here employed one basis set of split valence plus polarization quality, called spV+P, and a triple split basis set augmented with two sets of polarization functions, called tsV+2P. For the Sn analogue of triafulvene, **1d**, the number of contracted basis functions was 103 and 160 for the spV+P and the tsV+2P basis sets, respectively, and for the Sn derivative of pentafulvene 141 and 224, respectively.

All species were completely optimized at the Hartree−Fock, MP2,[61−64] and B3-LYP[65,66] levels using both basis sets. (Explanations of the abbreviations for the various computational methods are given in ref 67.) In addition, harmonic vibrational frequencies were calculated for all optimized species at all six levels of theory. Initially, all species were assumed to be planar. However, the vibrational analysis revealed that the planar forms of the Si, Ge, and Sn derivatives of triafulvene, **1b**−**d**, respectively, were transition states on the molecular potential surfaces. These systems were therefore reoptimized from nonplanar start geometries yielding the nonplanar (trans-bent) minima reported here.

Compounds **1a**−**d** are strained species and **1b**−**d** and **2b**−**d** have unknown geometrical and electronic properties. Some of our results may be difficult to rationalize with simple hybridization or electrostatic arguments. In theoretical investigations of unknown systems, where very limited results are available for similar molecules, a series of high-quality computational techniques should be employed. The convergence in our results with improved level of theory was not satisfactory, in particular for the relative energies of the planar and nonplanar forms of the triafulvene derivatives. Therefore, selected single-point energy calculations at the MP3, and MP4(SDQ),[61−64] and QCISD levels[68] were carried out. It would have been desirable to have employed a correlation method which included the effect of triple substitutions in these calculations; however, for the series of molecules presented here this was not feasible with our present computational facilities.

All calculations were carried out using the program Gaussian-94[69] on Cray-YMP and Cray J-916, Cray C-90, and Silicon Graphics computers.

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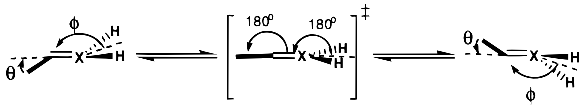
Table 1. Optimized Geometries and Dipole Moments for Triafulvene, 1a, and Its Si, Ge, and Sn Derivatives, 1b−d

	basis set method					
	spV+P^b			tsV+2P^b		
parameter^a	HF	B3LYP	MP2	HF	B3LYP	MP2
1a, X = C (planar form, M)^c						
$R(C_1C_4)$	1.3354	1.3461	1.3550	1.3206	1.3285	1.3323
$R(C_1C_2)$	1.4407	1.4617	1.4698	1.4231	1.4398	1.4464
$R(C_2C_3)$	1.3190	1.3399	1.3559	1.2997	1.3160	1.3277
$R(C_2H_7)$	1.0686	1.0795	1.0785	1.0723	1.0770	1.0761
$R(C_4H_5)$	1.0745	1.0844	1.0819	1.0667	1.0812	1.0795
$\angle C_1C_2H_7$	148.8	149.3	149.3	149.0	149.4	149.5
$\angle C_1C_2C_3$	62.8	62.7	62.5	62.8	62.8	62.7
$\angle H_5C_4H_6$	119.0	118.6	119.7	118.6	118.2	118.8
μ	2.48	2.11	2.01	2.48	2.14	2.05
1b, X = Si (nonplanar form, M)^c						
$R(Si_4C_1)$	1.9333	1.7441	1.7705	1.8853	1.7914	1.7441
$R(C_1C_2)$	1.4044	1.4576	1.4741	1.3884	1.4316	1.4576
$R(C_2C_3)$	1.3306	1.3169	1.3471	1.3102	1.3138	1.3169
$R(C_2H_7)$	1.0685	1.0789	1.0775	1.0665	1.0762	1.0752
$R(Si_4H_5)$	1.5202	1.5043	1.4873	1.5019	1.4915	1.4754
$\angle C_1C_2H_7$	147.6	147.3	147.1	148.0	147.7	147.1
$\angle C_1C_2C_3$	61.7	62.6	62.8	61.8	62.7	63.1
$\angle H_5Si_4H_6$	101.0	108.9	113.8	103.0	109.6	115.4
$\angle C_1Si_4H_5$	95.9	106.2	112.0	97.9	106.7	115.1
$\angle Si_4C_1C_2$	150.1	149.7	150.3	150.1	149.9	151.1
Out1^d	10.5	13.5	12.5	10.5	13.2	11.2
Out2^e	77.4	61.4	46.7	77.3	60.1	37.4
μ	7.14	4.44	3.20	6.57	3.90	2.54
1b, X = Si (planar form, TS)^c						
$R(Si_4C_1)$	1.7332	1.7328	1.7321	1.7167	1.7206	1.7211
$R(C_1C_2)$	1.4450	1.4701	1.4832	1.4314	1.4499	1.4632
$R(C_2C_3)$	1.3091	1.3290	1.3429	1.2894	1.3052	1.3148
$R(C_2H_7)$	1.0691	1.0780	1.0772	1.0653	1.0754	1.0749
$R(Si_4H_5)$	1.4739	1.4801	1.4744	1.4649	1.4712	1.4682
$\angle C_1C_2H_7$	146.4	146.7	146.7	146.6	147.0	146.9
$\angle C_1C_2C_3$	63.1	63.1	63.1	63.2	63.3	63.3
$\angle H_5Si_4H_6$	120.5	120.1	120.3	119.8	119.6	119.3
μ	3.07	2.84	2.83	2.69	2.36	2.50
1c, X = Ge (nonplanar form, M)^c						
$R(Ge_4C_1)$	2.0708	1.9407	1.8852	2.0280	1.9178	1.8391
$R(C_1C_2)$	1.3997	1.4417	1.4581	1.3818	1.4196	1.4449
$R(C_2C_3)$	1.3336	1.3442	1.3545	1.3142	1.3199	1.3224
$R(C_2H_7)$	1.0688	1.0795	1.0778	1.0667	1.0767	1.0754
$R(Ge_4H_5)$	1.5867	1.5741	1.5494	1.5693	1.5571	1.5245
$\angle C_1C_2H_7$	147.8	147.7	147.7	148.2	148.1	147.7
$\angle C_1C_2C_3$	61.6	62.2	62.3	61.6	62.3	62.8
$\angle H_5Ge_4H_6$	97.2	102.6	106.7	99.1	104.2	111.3
$\angle C_1Ge_4H_5$	92.0	98.9	103.9	93.4	99.9	108.7
$\angle Ge_4C_1C_2$	150.3	148.2	148.0	150.2	148.5	148.7
Out1^d	8.8	16.0	16.7	9.4	15.5	16.5
Out2^e	87.0	75.7	66.4	84.8	73.8	55.3
μ	7.72	5.57	4.83	7.24	4.85	3.42
1c, X = Ge (planar form, TS)^c						
$R(Ge_4C_1)$	1.8009	1.7967	1.7879	1.7906	1.7890	1.7805
$R(C_1C_2)$	1.4375	1.4650	1.4792	1.4226	1.4440	1.4590
$R(C_2C_3)$	1.3128	1.3320	1.3455	1.2936	1.3091	1.3176
$R(C_2H_7)$	1.0673	1.0782	1.0774	1.0654	1.0751	1.0751
$R(Ge_4H_5)$	1.5182	1.5234	1.5140	1.5075	1.5116	1.5026
$\angle C_1C_2H_7$	146.7	147.2	147.2	147.1	147.5	147.4
$\angle C_1C_2C_3$	62.8	63.0	62.9	63.0	63.0	63.2
$\angle H_5Ge_4H_6$	122.6	121.8	121.9	121.8	121.5	120.8
μ	3.65	3.17	3.34	3.14	2.50	2.83
1d, X = Sn (nonplanar form, M)^c						
$R(Sn_4C_1)$	2.3233	2.1925	2.1881	2.3148	2.1925	2.1672
$R(C_1C_2)$	1.4000	1.4397	1.4436	1.3794	1.4118	1.4175
$R(C_2C_3)$	1.3339	1.3560	1.3617	1.3157	1.3235	1.3327
$R(C_2H_7)$	1.0690	1.0797	1.0782	1.0669	1.0770	1.0757
$R(Sn_4H_5)$	1.7819	1.7720	1.7572	1.7770	1.7682	1.7505
$\angle C_1C_2H_7$	147.6	147.5	147.7	148.0	148.0	147.9
$\angle C_1C_2C_3$	61.6	62.2	61.9	61.5	62.1	62.0
$\angle H_5Sn_4H_6$	96.0	95.2	99.6	96.6	99.1	100.9
$\angle C_1Sn_4H_5$	88.6	95.2	93.9	89.0	93.9	94.9
$\angle Sn_4C_1C_2$	151.1	148.7	149.0	151.0	149.1	148.9
Out1^d	5.1	15.0	13.7	5.6	13.7	14.1
Out2^e	87.9	81.8	83.9	88.5	84.0	82.3
μ	7.88	5.60	6.33	7.86	5.80	6.15

Table 1 (Continued)

	basis set method					
	spV+P[b]			tsV+2P[b]		
parameter[a]	HF	B3LYP	MP2	HF	B3LYP	MP2
	1d, X = Sn(planar form, TS)[c]					
$R(Sn_4C_1)$	2.0241	2.0104	1.9962	2.0244	2.0094	1.9880
$R(C_1C_2)$	1.4344	1.4677	1.4860	1.4144	1.4419	1.4626
$R(C_2C_3)$	1.3153	1.3323	1.3448	1.2970	1.3097	1.3162
$R(C_2H_7)$	1.0675	1.0784	1.0779	1.0655	1.−757	1.0753
$R(Sn_4H_5)$	1.7055	1.7119	1.7024	1.7017	1.7055	1.6972
$\angle C_1C_2H_7$	146.7	147.1	147.0	147.1	147.6	147.3
$\angle C_1C_2C_3$	62.7	63.0	63.1	62.7	63.0	63.3
$\angle H_5Sn_4H_6$	124.8	123.2	122.2	106.4	122.9	121.5
μ	3.81	2.68	3.21	4.02	2.87	3.40

[a] See text. [b] See Figure 2 for numbering of the atoms. [c] M minimum (no imaginary frequencies), TS transition state (one imaginary frequency). [d] Angle between the $X{=}C_1$ bond and the cyclopropene ring. [e] Angle between the $C_1{=}X$ bond and the $X-H_5-H_6$ plane.



		θ	φ
1b	X=Si	11.2	142.6
1c	X=Ge	16.5	124.7
1d	X=Sn	14.1	97.7

Figure 3. The *trans*-bent conformations (schematic) for the 4-heterosubstituted triafulvenes calculated at the MP2/ts+2P level.

Results and Discussion

Triafulvene, 1a, and its Si, Ge, and Sn Analogues, 1b−d. The optimized structures and dipole moments of triafulvene, **1a**, 4-silatriafulvene, **1b,** 4-germatriafulvene, **1c**, and 4-stannatriafulvene, **1d,** calculated using the Hartree−Fock, B3-LYP, and MP2 methods and the spV+P and tsV+2P basis sets are given in Table 1. The minimum energy geometry of triafulvene, **1a**, was planar with C_{2v} symmetry. However, the silicon, **1b,** germanium, **1c,** and tin, **1d,** analogues each exhibited nonplanar minima with trans-bent structures of C_s symmetry. The planar forms of these 4-heteroatom systems, **1b**−**d**, represented transition states for the interconversion between two equivalent trans-bent forms. The trans-bent structures of **1b**−**d** are schematically shown in Figure 3 along with their planar transition states. The inversion barriers for these systems calculated at different levels of theory are given in Table 2.

Conformation and Inversion Barriers in Triafulvene Derivatives 1a−d. There is a clear tendency for increased nonplanarity around the exocyclic center going through the triafulvene series from C to Sn as reflected by the increased barrier to inversion. The barriers increase smoothly going from Si to Ge to Sn at all levels of theory. This can be rationalized by the smaller tendency to form double bonds (or increased tendency toward sp^3-type hybridizations) going to higher atomic number within group IVA. Poorer π-orbital overlap with carbon occurs going from C to Si, Ge, and Sn, decreasing the bond energy of such π-bonds. This trend should increase the importance of the dipolar resonance forms **B** and **C** (Figure 1), and it is also reflected in the geometries and dipole moments discussed below.

The calculated barriers, however, appear to be quite sensitive to the level of theory with the exception of triafulvene which is predicted to be planar at all levels. At the Hartree−Fock level, the energy barriers are clearly too large and the effect of electron correlation is significant and much larger than for most inversion barriers.[70] In these systems, electron correlation always reduces the magnitude of the barrier, and this correlation effect is clearly exaggerated at the MP2 level. At the B3-LYP level, the correlation effects are smaller and the inversion barriers are larger compared to those obtained at the MP2 level. Since the differences in the calculated inversion barriers at the B3-LYP and MP2 levels are quite large, a set of three different single-point calculations, with improved treatment of electron correlation, was performed. The MP2-optimized geometries were used for these calculations. The results, which are included in Table 2, were reassuring, yielding very similar results. The contribution to the barrier from electron correlation was about halfway between the contribution from the MP2 and B3-LYP levels. The MP2 method therefore seems to overestimate, and the B3-LYP level seems to underestimate the effect of electron correlation on the inversion barriers for these systems. The inversion barriers are estimated to be about 1.5, 5, and 10 kcal/mol for the Si, Ge, and Sn analogues of triafulvene, respectively.

Structures and Dipole Moments of Triafulvene Derivatives 1a−d. A main goal of this investigation was to identify trends when the exocyclic carbon atom was substituted with the heavier group IVA elements Si, Ge, and Sn. The discussion below will focus on these trends. The tendency to form double bonds decreases going down the group which increasingly favors the dipolar resonance forms because less energy is required to partially disrupt the π-bond. There is also a large increase in the molecular dipole moments for this series ranging from about 2 D for planar triafulvene, **1a**, to over 6 D for 4-stannatriafulvene, **1d**. In every case the negative end of the dipole points toward the exocyclic C, Si, Ge, and Sn. The dipole moments for the optimized nonplanar geometries of **1b**−**d** are remarkably large. The dipole moment for triafulvene has been determined experimentally[24] to be 1.90 D which is among the largest dipole moments to be measured for a hydrocarbon. The MP2 and B3-LYP methods yield dipole moments for triafulvene in excellent agreement with the experiment. The calculated dipole moments are largest at the SCF level for all species. It is also interesting to note that forcing molecules **1b**−**d** into a planar structure is accompanied by a decrease in

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(70) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; John Wiley & Sons: New York, 1986; p 266

Table 2. Total Energies and Inversion Barriers for Triafulvene Derivatives, 1a−d Calculated at Different Levels of Theory

	total energy, ΔE											
	SCF/SCF		B3-LYP/B3-LYP		MP2/MP2		MP3/MP2[a]		MP4(SDQ)/MP2		QCISD/MP2	
sv+P Basis Set												
C	−153.685843	0.0	−154.703255	0.0	−154.171702	0.0						
Si	−404.615247	7.9	−405.979191	2.8	−405.058565	1.0						
Ge	−2189.220091	17.1	−2191.696308	9.0	−2189.818627	3.6						
Sn	−6134.197237	27.4	−6137.518457	15.1	−6134.684288	8.5						
tsV+2P Basis Set												
C	−153.716707	0.0	−154.751223	0.0	−154.272956	0.0						
Si	−404.656177	6.1	−406.036110	2.8	−405.169839	0.6	−405.197459	1.1	−405.203166	1.4	−405.204895	1.6
Ge	−2189.292945	14.1	−2191.790406	8.3	−2190.016685	2.5	−2190.011749	4.0	−2190.030833	4.6	−2190.030800	5.1
Sn	−6134.269863	26.7	−6137.606734	14.9	−6134.849294	6.6	−6134.873362	10.7	−6134.881768	10.0	−6134.883942	10.0

[a] MP3/MP2 means that the energy was calculated at the MP3 level using the MP2-optimized geometry.

the dipole moment and by a significant shortening of the C−X bond lengths at every level of theory. Planarity, therefore, decreases the contribution from the dipolar resonance forms **B** and **C**. It should be pointed out, however, that with exception of the nonplanar form of **2d**, the calculated C−X bond lengths are significantly shorter than known typical C−X single bond lengths.[71] This is a manifestation of significant remaining double bond character and thus significant contribution from the nonaromatic resonance forms.

The calculated inversion barriers, dipole moments, and bond lengths demonstrate significant dipolar resonance contributions to the ground-state configuration of these molecules. Only part of the dipole moment increase through the series can be explained simply from the longer C−X bond lengths. The dipolar resonance forms have a formal negative charge on X. However, the decrease in electronegativity (going from C to Si, Ge, and Sn) favors the opposing nonaromatic resonance form, **D**, shown in Figure 1. Thus, the large dipoles pointing in the direction represented in hybrids **B** and **C** are surprising especially since Si, Ge, and Sn are not planar which decreases π-overlap. The bond alternations in the cyclopropene fragments are significant, 0.10−0.15 Å. In every case they were slightly greater in the planar form than in the corresponding trans-bent form. The small reduction in the magnitude of ring bond alternation going from planar to trans-bent structures suggests that Si, Ge, and Sn can better accommodate excess electron density from the ring as the heteroatom hybridization becomes more nonplanar. The bond alternations in the cyclopropene ring decrease slightly from silicon to tin. The dipolar resonance form, **D** (favored by the electronegativities of Si, Ge, and Sn relative to C) weakens the amount of contribution from aromaticity which would, otherwise, occur. So the reduction in ring bond length alternation (which means some aromatic-like contribution) is, at first glance, surprising.

On the whole there appears to be clear evidence for some contribution from resonance forms **B** and **C** in **1b**−**d** which is enhanced as the heteroatom becomes pyramidal. These molecules could, therefore, be described as partly aromatic. Norden and co-workers[24] estimated that the dipolar resonance form contributed about 20% to the electronic ground state of triafulvene, and they characterized this molecule as nonaromatic. Does the aromatic character increase when the exocyclic carbon atom is replaced by larger and less electronegative group IVA elements and as Si, Ge, and Sn deform away from planarity? Less π-bond character exists between the exocyclic heteroatom and the ring. Thus, less π-electron polarization toward the ring as represented by hybrid structures **D** (based on the lower hetroatom electronegativity) actually takes place in the trans-bent geometry. This renders the ring a little more aromatic-like than would be expected, although the exocyclic bond to the heteroatom is distorted a small amount out of the ring plane. Keep in mind that pronounced ring bond alternation exists in triafulvene analogues **1b**−**d** as well as in **1a**. Only in **1d** is the alternation slightly decreased, suggesting only a weak “aromatic” contribution to the structure.

Pentafulvene and Its Si, Ge, and Sn Analogs. The results for pentafulvene, **2a,** 6-silapentafulvene, **2b**, 6-germapentafulvene, **2c**, and 6-stannapentafulvene, **2d**, are given in Table 3. The calculated structures and dipole moments for this series do not vary significantly with the level of calculation. The effect of electron correlation on the calculated dipole moments is, in contrast to the triafulvene systems, small. The experimental bond lengths for pentafulvene, determined by microwave spectroscopy,[47] are 1.3485, 1.470, 1.355, and 1.476 Å for $C_1{-}C_6$, $C_1{-}C_2$, $C_2{-}C_3$, and $C_3{-}C_4$, respectively, in excellent agreement with our calculated structures (see Figure 2b for numbering). The relatively small dipole moment of pentafulvene of 0.42 D[47] is also in good agreement with our calculated values (0.41−0.66 D).

Geometry optimizations of the pentafulvene derivatives yielded, in contrast to the triafulvene systems, planar structures for all molecules (**2a**−**d**) in the series at all levels of theory. This fact combined with the short $X{-}C_1$ bond lengths show that the $X{-}C_1$ bonds are basically double bonds, indicating small contribution from the aromatic-like dipolar resonance forms. Furthermore, the cyclopentadiene rings exhibited significant bond alternations. However, the degree of bond alternation decreases when the exocyclic carbon atom is replaced by silicon, germanium, or tin. This indicates more contribution from such resonance hybrids as **F** and **G** (Figure 1) which represent the ring as an aromatic cyclopentadienyl anion.

The calculated dipole moments for the Si, Ge, and Sn analogues, pointing (negative end) toward the cyclopentadiene ring, were significantly larger than that of the parent pentafulvene molecule. Using the tsV+2P basis set the calculated dipole moments ranged from 2.25 to 2.61 D for Si (**2b**), 2.31 to 2.70 D for Ge (**2c**), and 2.85 to 3.54 D for Sn (**2d**). This can be explained by increased

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(71) On the basis of tabulated covalent radii (ref 42), the C−X single bond lengths are 1.95, 1.99, and 2.17 Å for X = Si, Ge, and Sn, respectively.

Table 3. Optimized Geometries[a] and Dipole Moments for Pentafulvene and Its Si, Ge, and Sn Derivatives, 2a–d

	basis set method					
	spV+P			tsV+2P		
parameter[b]	HF	B3-LYP	MP2	HF	B3-LYP	MP2
2a, X = C						
$R(C_6C_1)$	1.3374	1.3585	1.3705	1.3229	1.3401	1.3480
$R(C_1C_2)$	1.4871	1.4853	1.4829	1.4733	1.4710	1.4668
$R(C_2C_4)$	1.3436	1.3672	1.3805	1.3303	1.3508	1.3610
$R(C_4C_5)$	1.4896	1.4850	1.4833	1.4766	1.4721	1.4702
$R(C_2H_9)$	1.0726	1.0816	1.0812	1.0706	1.0793	1.0801
$R(C_4H_{11})$	1.0734	1.0828	1.0821	1.0715	1.0804	1.0806
$R(C_6H_7)$	1.0769	1.0870	1.0855	1.0739	1.0830	1.0828
$\angle C_2C_1C_3$	105.7	106.4	107.2	105.5	106.2	106.8
$\angle C_4C_2C_1$	108.0	107.7	107.3	108.2	107.9	107.6
$\angle C_5C_4C_2$	109.1	109.1	109.1	109.1	109.0	109.0
$\angle H_7C_6H_8$	117.6	117.9	118.8	117.3	117.1	117.8
$\angle C_1C_2H_9$	124.4	124.5	124.9	124.4	124.5	124.9
$\angle C_2C_4H_{11}$	126.5	126.4	126.1	126.5	126.4	126.2
μ	0.44	0.57	0.65	0.41	0.58	0.66
T.E.[c]	−230.673868	−232.202726	−231.416480	−230.713793	−232.265242	−231.562523
2b, X = Si						
$R(Si_6C_1)$	1.7267	1.7447	1.7509	1.7130	1.7320	1.7396
$R(C_1C_2)$	1.4724	1.4721	1.4715	1.4597	1.4587	1.4569
$R(C_2C_4)$	1.3546	1.3778	1.3911	1.3422	1.3625	1.3732
$R(C_4C_5)$	1.4725	1.4714	1.4700	1.4570	1.4552	1.4519
$R(C_2H_9)$	1.0726	1.0813	1.0814	1.0711	1.0793	1.0808
$R(C_4H_{11})$	1.0733	1.0825	1.0821	1.0717	1.0804	1.0810
$R(Si_6H_7)$	1.4795	1.4862	1.4804	1.4684	1.4757	1.4722
$\angle C_2C_1C_3$	106.0	107.0	107.7	105.6	106.5	107.1
$\angle C_4C_2C_1$	108.1	107.5	107.1	108.3	107.9	107.5
$\angle C_5C_4C_2$	108.9	109.0	109.0	108.9	108.9	108.9
$\angle H_7Si_6H_8$	115.5	115.6	116.3	114.8	115.4	115.4
$\angle C_1C_2H_9$	125.0	125.3	125.7	125.0	125.2	125.5
$\angle C_2C_4H_{11}$	126.3	126.1	125.8	126.1	126.1	125.8
μ	1.92	1.40	1.84	2.61	2.25	2.50
T.E.	−481.594571	−483.479965	−482.31012	−481.649678	−483.553262	−482.469656
2c, X = Ge						
$R(Ge_6C_1)$	1.7888	1.8093	1.8083	1.7799	1.8000	1.8010
$R(C_1C_2)$	1.4683	1.4676	1.4686	1.4551	1.4536	1.4527
$R(C_2C_4)$	1.3558	1.3789	1.3914	1.3436	1.3637	1.3738
$R(C_4C_5)$	1.4722	1.4718	1.4713	1.4560	1.4551	1.4518
$R(C_2H_9)$	1.0725	1.0812	1.0814	1.0710	1.0792	1.0807
$R(C_4H_{11})$	1.0732	1.0825	1.0822	1.0716	1.0804	1.0810
$R(Ge_6H_7)$	1.5292	1.5349	1.5241	1.5162	1.5217	1.5113
$\angle C_2C_1C_3$	106.5	107.6	108.3	106.0	107.1	107.5
$\angle C_4C_2C_1$	107.8	107.2	106.8	108.1	107.6	107.3
$\angle C_5C_4C_2$	109.0	109.0	109.1	108.9	108.9	108.9
$\angle H_7Ge_6H_8$	115.5	115.6	116.5	114.8	115.5	115.9
$\angle C_1C_2H_9$	125.1	125.5	125.9	125.1	125.3	125.7
$\angle C_2C_4H_{11}$	126.2	126.1	125.9	126.1	126.1	125.8
μ	1.72	1.16	1.52	2.70	2.31	2.50
T.E.	−2266.184791	−2269.189643	−2267.068757	−2266.273975	−2269.301794	−2267.316608
2d, X = Sn						
$R(Sn_6C_1)$	1.9941	2.0166	2.0187	1.9922	2.0139	2.0125
$R(C_1C_2)$	1.4649	1.4662	1.4702	1.4503	1.4496	1.4502
$R(C_2C_4)$	1.3611	1.3827	1.3937	1.3481	1.3678	1.3765
$R(C_4C_5)$	1.4637	1.4653	1.4658	1.4505	1.4520	1.4490
$R(C_2H_9)$	1.0731	1.0817	1.0820	1.0713	1.0793	1.0811
$R(C_4H_{11})$	1.0734	1.0827	1.0825	1.0717	1.0805	1.0813
$R(Sn_6H_7)$	1.7178	1.7249	1.7124	1.7138	1.7185	1.0775
$\angle C_2C_1C_3$	106.2	107.3	107.7	106.1	107.2	107.5
$\angle C_4C_2C_1$	108.1	107.4	107.1	108.2	107.6	107.4
$\angle C_5C_4C_2$	108.8	108.9	109.0	108.8	108.8	108.9
$\angle H_7Sn_6H_8$	114.3	115.1	115.6	113.4	114.2	114.8
$\angle C_1C_2H_9$	125.3	125.7	126.0	125.3	125.6	125.9
$\angle C_2C_4H_{11}$	126.2	126.1	125.8	126.1	126.1	125.8
μ	3.61	2.82	2.89	3.54	2.85	3.08
T. E.	−6211.144729	−6215.003825	−6212.928720	−6211.227944	−6215.107308	−6212.145024

[a] All structures planar with C_{2v} symmetry. [b] See Figure 2 for numbering of the atoms. [c] T.E. = total energy.

contributions from the dipolar hybrids **F** and **G** as the exocyclic carbon was replaced by the less electronegative Si, Ge, or Sn atoms. Also a portion of the dipole moment increase results from the longer ring carbon to exocyclic heteroatom bond distances.

It appears that the pentafulvene series exhibits evidence for a relatively small contribution from aromatic-like resonance structures. This contribution increases slightly when the carbon atom is replaced by the less electronegative elements in group IVA. The lowest B_1

vibrational frequencies, which can be assigned as the XH_2 wagging mode, were calculated at the B3-LYP/ts+2P level to be 225.3, 151.3, 145.2, and 126.8 cm^{-1} for **2a**, **2b**, **2c**, and **2d**, respectively, indicating decreasing sp^2 character of X going through the series C to Sn.

In summary, the calculations show that the contribution from the dipolar (aromatic) resonance forms to the electronic structure of the pentafulvene species is small but increases when the exocyxlic carbon atom is replaced by less electronegative and larger atoms from group IVA.

Acknowledgment. This work has been supported by the NSF EPSCoR program (OSR-9452857, ESR-9452857) and the state of Mississippi. Some of the calculations were carried out on a Silicon Graphics Computer System purchased with funds from a grant from the National Science Foundation (CHE-9205329). Computer time for this research was provided by The Mississippi Center for Supercomputing Research.

JO982279W