Alkyl and Alkenyl Substituent Effects on Nonbonded Interactions of Hexatriene

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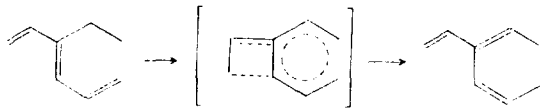
Alkyl and alkenyl substituent effects on nonbonded interactions of hexatriene were examined using CNDO/2 method. The results showed that: (1) rapid rate of thermal electrocyclization of 3-vinyl hexa-1, 3, 5-triene is due to increased overlap population between atom pair reacting resulting from strong electron repelling interaction of vinly group on the triene moiety; (2) stability of a conformer is determined by additive effect of composite π structures; (3) a substituent on positions 2 and 3 increases the HOMO AO coefficient of sites 1 and 4 considerably and activates interactions with these sites.

Introduction

Recently Spangler and his co-workers[1] have reported effects of alkyl and alkenyl substitution on the rate of thermal electrocyclization of 1,3,5-hexatriene (HTE) to cyclohexa-1,3-diene.

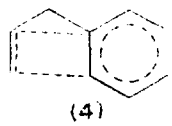
Their study showed the extremely fast thermal electrocyclization of 3-vinyl substituted HTE, which was over 30 times faster than the rate of ring closure of the ethyl substituted HTE.

They have attributed the accelerative effect of the 3-vinyl substituted to anchimeric π-bond participation of the vinyl group in the electrocyclization transition state, (2).



(1) (2) (3)

However they found no such π-bond anchimeric rate enhancement with 3-allyl substituent for which homoallylic π-bond participation[2], (4), may be expected; electrocyclization rate and activation parameters for 3-allyl and 3-propyl



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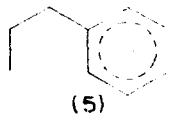
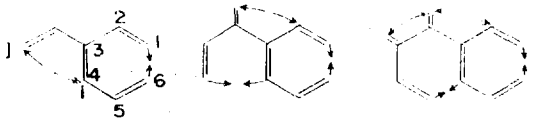


(5)

analogues were very nearly the same although in the latter, (5), homoallylic π-bond participation is not possible (see Table 1). Thus anchemeric π-bond participation does not offer a completely satisfactory explanation of the extraordinary rate enhancement of the 3-vinyl substituent.

We have recently developed simple rules for predicting intramolecular nonbonded interactions based on the frontier orbital (FMO) theory[3]: (1) nonbonded interactions between end-to-end atoms are significant only in crowded forms; (2) nonbonded interactions become appreciable only in crowded π-conjugated (or π-isoconjugate) systems; (3) nonbonded interactions can be assessed by the signs of the products of AO coefficients of two end atoms in the highest occupied (HO)MO. The $4N+2$ π electron system has attractive, while $4N$ π electron system has repulsive interactions. Systems with $4N+1$ and $4N-1$ π electrons are attractive but stabilizing effects are smaller than that for $4N+2$ system. we have also pointed out that the interacting atom pair may be considered to form a loose center (or bond) which acts either as an electron source (donating) when there is a repulsive interaction, or as an electron sink (withdrawing) when the interaction is attractive. We have adopted a notation of $(n\pi/m)$ to represent $n\pi$ electrons delocalized over m atoms or centers, and have shown that the effect of stabilizing (attractive interaction) and destabilizing (repulsive interaction) composite π structures within a molecule is additive. According to these rules, 3-vinyl group on HTE[6] forms a $(4\pi/4)$ repulsive center (triene moiety itself forms a $(6\pi/6)$ attractive center) which will act as an electron repelling center (shown by arrows as $\longleftrightarrow$) at the interacting site i (which is position 4 in this case) and



(6) (7) (8)

hence will increase the overlap population, P^{π}_{16}, of the electrocyclization center. On the other hand 3-allyl, (7), and 3-propyl, (8), substituents, when isoconjugate π structures of methylene groups are taken into consideration, give a repulsive site at position 2 from a $(4\pi/4)$ structure and an attractive (shown by arrows as $\longleftrightarrow$) site at position 4 from $(5\pi/5)$ and $(6\pi/6)$ respectively.

Attractive interaction leads to electron withdrawl from the main triene moiety and hence decreases overlap population, $p_{16}{}^{\pi}$, of the electrocyclization center.

Note that there is an extra $(4\pi/4)$ system in (8), which does not interact directly with the triene moiety; it will

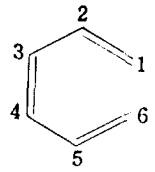
have only secondary effect on P_{16}^{π}.

In this work we report effects of vinyl, methyl, ethyl, allyl and *n*-propyl substitutions at positions 2 and 3 of the HTE on energy components and overlap populations by applying the rules presented earlier.

Calculations

The geometry of hexatriene was optimized($d_{C_1-C_2}=d_{C_3-C_4}=d_{C_5-C_6}=1.34$Å, $d_{C_2-C_3}=d_{C_4-C_5}=1.47$Å, $\angle C_1C_2C_3=\angle C_4C_5-C_6=155.0°$, $\angle C_2C_3C_4=\angle C_3C_4C_5=130.0°$) but standard geometries were adopted for substituents.[4]

All calculations were performed using CNDO/2 method. Conjugated and isoconjugate structures studied in this work had planar heavy atom skeletons and crowded conformations as preferred forms in all cases.



Coordinate system and numbering scheme.

Results and Discussion

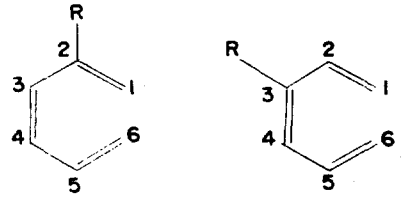
All except vinyl were found to behave as electron donators in the sense that they raised levels of FMO's; vinyl group had inter-frontier level narrowing effect as expected from a conjugative substituent.[5]

According to the frontier orbital theory, AO coefficients of HOMO will have dominant influence on eigenvector properties of a molecule[3]. The AO coefficients (absolute values) of the HOMO of HTE were $C_2(C_5)=0.276$, $C_3(C_4)=0.455$ and $C_1(C_6)=0.466$. These indicate that substituent interacting at position 1 of the triene will have the strongest interaction, *i.e.*, the largest p_{ij}^{π}, while interaction at position 2 will be the weakest, and at position 3 and 4 the intermediate.

In general, however, we found that position 1 and 4 are preferentially activated (absolute values of AO coefficient increase) by a neighboring substituent at positions 2 and 3 respectively; AO coefficient of the HOMO at position 1 becomes larger when a substituent is on position 2, while that at position 4 increases when a substituent is on position 3. This effect of activating positions 1 and 4 by substituents at positions 2 and 3 respectively was found to be quite general irrespective of the nature of substituents.[6] We can therefore expect exceptionally strong interactions at sites (*i*) 1 and 4.

For all the substituent studied, the 3-substituted analogues were preferred to the 2-substituted ones energetically. Table 1 shows π-overlap populations P_{16}^{π}, and experimental rate data for the most stable conformations of 2- and 3-substituted HTE. All P_{16}^{π} values are positive, and hence end-to-end (1 to 6) attractive and bonding.[3] The 3-vinyl compound has the largest P_{16}^{π} while it is nearly the same for 3-ethyl, 3-allyl and 3-propyl compounds. This trend is in good agreement with the experimental rates and enthalpies of activation[1]. It is therefore clear that the extremely fast rate of thermal cyclization of 3-vinyl HTE is a direct consequence of an increase in the overlap population of the reaction center, P_{16}^{π}, due to a strong electron repulsion ($P_{ij}^{\pi}<0$) at position 4 of the triene from a ($4\pi/4$)

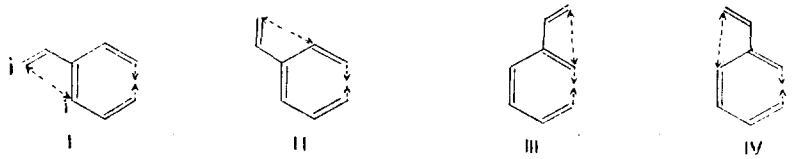
TABLE 1: π-Overlap Populations, P_{16}^{π}, and Rate Data (at 135.0 °C) for the Most Stable form of 2-R and 3-*R* Systems



Substituent (R)	Position of R for stable form	P_{16}^{π} ($\times 10^4$)	K ($\times 10^4$)[1]	$\Delta H^{\neq}$[1] kcal/mol
Vinyl	3	1.421	45.9[a]	22.0
Ethyl	3	1.410	4.24	24.2
Allyl	3	1.409	3.72	24.5±0.3
Propyl.	3	1.409	3.69	23.5±0.1

[a]122.1 °C

TABLE 2: Energy Analysis and π-Overlap Populations of 2- and 3-Methyl Substituted Systems

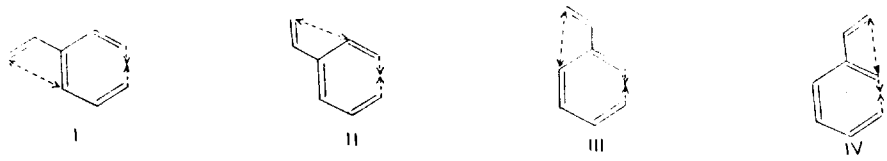


I II III IV

Form	Composite[a] π-structures	E_{tot}(a.u)	$2\sum^{occ}\epsilon_i$(a.u)	P_{ij}^{π} Rep.($\times 10^3$)	P_{16}^{π} ($\times 10^4$)	$\Delta(2\sum^{occ}\epsilon_i)$[b]	$\Delta(V_{nn}-V_{ee})$[b]	ΔE_{tot}[b]
I	($4\pi/4$)	−57.0405	−34.2570	−5.1352	1.438	2.0 (1.0)	−0.1	1.9
II	($4\pi/4$)	−57.0435	−34.2602	−0.6441	1.409	0.0 (0.0)	0.0	0.0
III	($4\pi/4$)	−57.0327	−34.2990	−8.0450	1.434	−24.4 (1.5)	31.2	6.8
IV	($4\pi/4$)	−57.0373	−34.3108	−0.5896	1.385	−31.8 (−2.5)	35.7	3.9

[a]Except the main ($6\pi/6$) system of triene moiety; [b]Relative energies (to the form II) are in kcal/mol. Values in parenthesis are for π-orbital energies.

TABLE 3: Energy Analysis and π-Overlap Populations of 2- and 3-Vinyl Substituted Systems



Form	Composite[a] π-structures	E_{tot} (a.u)	$2\sum^{occ}\epsilon_i$(a.u)	P_{ij}^{π} Rep($\times 10^3$)	P_{16}^{π} ($\times 10^4$)	$\Delta(2\sum^{occ}\epsilon_i)^b$	$\Delta(V_{nn}-V_{ee})^b$	ΔE_{tot}^b
I	$(4\pi/4)$	−63.9913	−38.0186	−4.8378	1.421	0.0	0.0	0.0
						(0.0)		
II	$(4\pi/4)$	−63.9912	−38.0100	−0.5038	1.368	5.4	−5.3	0.1
						(0.4)		
III	$(4\pi/4)$	−63.9477	−38.0562	−0.2968	1.326	−23.6	51.0	27.4
						(−3.1)		
IV	$(4\pi/4)$	−63.9442	−38.0350	−8.5523	1.434	−10.3	39.8	29.6
						(2.4)		

[a]Except the main $(6\pi/6)$ system of the triene moiety; [b]Relative energies to the form I are in kcal/mol. Values in parenthesis are for π-orbital energies.

TABLE 4: Energy Analysis and π-Overlap Populations of 2-Ethyl Substituted Systems

Form	Composite[a] π-structures	E_{tot}(a.u)	$2\sum^{occ}\epsilon_i$(a.u)	$P_{ij}^{\pi\,b}$ Rep.($\times 10^3$)	P_{ij}^{π} Attr.($\times 10^3$)	P_{16}^{π} ($\times 10^4$)	$\Delta(2\sum^{occ}\epsilon_i)^c$	$\Delta(V_{nn}-V_{ee})^c$	ΔE_{tot}^c
I	$(5\pi/5)$	−65.6943	−39.7798	−7.7062	3.3299	1.431	−14.4	18.9	4.5
	$(4\pi/4)$						(−1.5)		
II	$(5\pi/5)$	−65.7014	−39.7568	−0.4717	3.4843	1.386	0.0	0.0	0.0
	$(4\pi/4)$						(0.0)		
III	$3\times(4\pi/4)$	−65.4823	−39.7006	−7.8725		1.433	35.1	102.2	137.5
				(−15.8)			(24.5)		
IV	$3\times(4\pi/4)$	−65.5213	−39.6824	1.1477		1.385	46.7	66.3	113.0
				(−16.5)			(23.1)		

[a]Except the main $(6\pi/6)$ system of the triene moiety; [b]Values in parenthesis are those for secondary repulsive centers which are not on the triene moiety; [c]Relative energies to the form II are in kcal/mol. Values in parenthesis for π-orbital energies.

center formed by the vinyl group. Other substituents, *i.e.*, ethyl, allyl and propyl, form attractive centers at position 4 or 2 of the triene, which lead to decreases in P_{16}^{π}. We will now examine individual 2- and 3-substituted trienes in more detail.

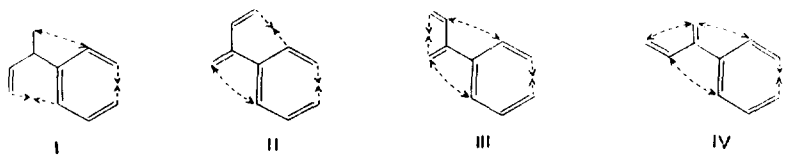
Methyl-Substituted Hexatrienes. Let us consider four isoconjugate structures of interest which are shown in Table 2, together with energy and population analysis. Methyl group forms a $(4\pi/4)$ repulsive system with the triene moiety in each case. The most stable form is II with a $(4\pi/4)$ which interact weakly with position 2. Repulsive interactions with positions 1 (form III) and 4 (form I) are an order of magnitude larger than those with positions 2 (form II) and 3 (form IV), and electron donating powers reflected on p_{16}^{π} are accordingly greater for the former pair. It should be noted that strong repulsions in forms I and III lead to unfavorable π-one-electron factor, $2\sum^{\pi}\epsilon_i$.

Vinyl-Substituted Hexatrienes. The four conjugate structures of vinyl substituted hexatriene are topologically the same as the four isoconjugate structures of methyl substituted hexatriene, as given in Table 3. Here again repulsive interactions of $(4\pi/4)$ systems formed with positions 1 (form IV) and 4 (form I) are stronger than those with positions 2 (form II) and 3 (form III).

Ethyl-Substituted Hexatrienes. Four isoconjugate structures can be considered for 2-ethyl substituted hexatriene as shown in Table 4; forms I and II have a $(5\pi/5)$ and a $(4\pi/4)$ systems each and forms III and IV have three $(4\pi/4)$ systems. The former two are more stable than the latter two forms, since $(5\pi/5)$ system (a $4N+1$ π electron system) is attractive and stabilizing whereas $(4\pi/4)$ system (a $4N$ π electron system) is repulsive and destabilizing[3]. The active site 1 is repulsive in form I, whereas it is attractive in form II; the form I has greater P_{16}^{π} but the form II has more stability. Repulsive $(4\pi/4)$ centers in structures III and IV which do not interact directly with the triene moiety have only secondary effects on energies and P_{16}^{π}.

For 3-ethyl substituted hexatriene, composite-π-isoconjugate structures are the same as in 2-substituted hexatriene as presented in Table 5. Structures I and II are more

TABLE 5: Energy Analysis and π-Overlap Populations of 3-Ethyl Substituted Systems

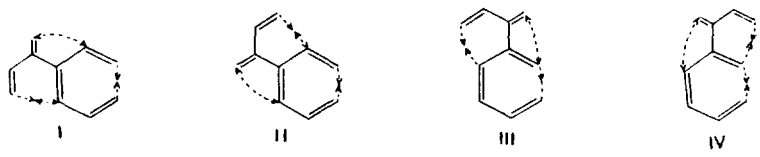


I II III IV

Form	Composite[a] π-structures.	E_{tot}(a.u)	$2\sum^{occ}\epsilon_i$(a.u)	P_{ij}^{π}[b] Rep.($\times 10^3$)	P_{ij}^{π} Attr($\times 10^3$)	P_{16}^{π} ($\times 10^4$)	$\Delta(2\sum^{occ}\epsilon_i)$[c]	$\Delta(V_{nn}-V_{ee})$[c]	ΔE_{tot}[c]
I	(5π/5)	−65.7284	−39.6968	−0.5876	1.1474	1.410	0.0	0.0	0.0
	(4π/4)						(0.0)		
II	(5π/5)	−65.7236	−39.6974	−4.9666	0.8932	1.437	−0.4	3.4	3.0
	(4π/4)						(1.8)		
III	3×(4π/4)	−65.6658	−39.6650	−4.8295		1.437	20.0	19.3	39.3
				(−17.0)			(12.8)		
IV	3×(4π/4)	−65.6875	−39.6690	−0.4069		1.409	17.4	8.2	25.7
				(−16.6)			(10.0)		

[a]Except the main (6π/6) system of the triene moiety; [b]Values in parenthesis are those for secondary repulsive centers which are not on the triene moiety; [c]Relative energies to the form I are in kcal/mol. Values in parenthesis for π-orbital energies.

TABLE 6: Energy Analysis and π-Overlap Populations of 2- and 3-Allyl Substituted Systems



I II III IV

Form	Composite[a] π-structures	E_{tot}(a.u)	$2\sum^{occ}\epsilon_i$(a.u)	P_{ij}^{π} Rep.($\times 10^3$)	P_{ij}^{π} Attr.($\times 10^3$)	P_{16}^{π} ($\times 10^4$)	$\Delta(2\sum^{occ}\epsilon_i)$[b]	$\Delta(V_{nn}-V_{ee})$[b]	ΔE_{tot}[b]
I	(5π/5)	−72.3704	−43.3808	−0.5843	1.5881	1.409	0.0	0.0	0.0
	(4π/4)						(0.0)		
II	(5π/5)	−72.3614	−43.3970	−4.9431	1.1629	1.440	−10.2	15.8	5.6
	(4π/4)						(0.5)		
III	(5π/5)	−71.9693	−43.5210	−7.6754	4.5935	1.442	−88.0	339.7	251.7
	(4π/4)						(−6.7)		
IV	(5π/5)	−72.1243	−43.4406	−0.4770	4.8686	1.384	−37.5	192.0	154.4
	(4π/4)						(−1.0)		

[a]Except the main (6π/6) system of the triene moiety; [b]Relative energies to the form I are in kcal/mol. Values in parenthesis are for π-orbital energies.

stable than III and IV, since I and II contain an attractive (5π/5) center each whereas III and IV have two repulsive (4π/4) centers each instead. Here again interactions on sites 1 and 4 are stronger than those on sites 2 and 3; the form has highly attractive interaction at site 4 while the form II has highly repulsive interaction at site 4, which are accordingly reflected as decrease and increase in P_{16}^{π}.

Allyl-Substituted Hexatrienes. Four isoconjugate structures, I∼IV, are of interest for 2- and 3-allyl substituted hexatriene as shown in Table 6. All four have the same composite π structures; a (5π/5) and a (4π/4). Three-substituted analogues are in general most stable than 2-substituted ones. The P_{16}^{π} value is the resultant sum of the composite repulsive and attractive interactions with sites on the triene moiety[7]. Thus combination of strong repulsive (at site 1 or 4) and weak attractive (at site 2 or 3) interactions leads to greater P_{16}^{π}, as can be seen for the the forms II and III.

Propyl-Substituted Hexatrienes. For 2-propyl hexatriene there are one attractive (6π/6) and two repulsive (4π/4) systems in I and II, and one attractive (5π/5) and two repulsive (4π/4) systems in III and IV as shown in Table 7. Since 4N+2 π electron system, (6π/6) is more stabilizing relative to 4N+1 π electron system, (5π/5), I and II are more stable than III and IV[3]. Strong repulsive (site 1) and weak attractive (site 3) interactions in forms I and III lead to large P_{16}^{π}.

For 3-propyl hexatriene, composite π structures formed by the substituent are the same as in 2-propyl hexatriene as presented in Table 8. Forms I and II contain a (6π/6) while forms III and IV contain a (5π/5) systems each and hence the former pair becomes more stable than the latter. Forms II and IV have a strong repulsive (site 4) and a weak attractive (site 2) interactions, which lead to greater P_{16}^{π} for the two forms.

we conclude that:

(1) the extremely rapid thermal electrocyclization of 3-vinyl-1,3,5-hexatriene to 2-vinylcyclohexa-1,3-diene is a direct consequence of increased overlap population be-

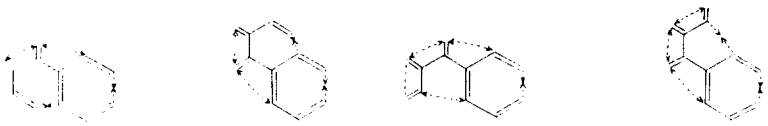
TABLE 7. Energy Analysis and π-Overlap Populations of 2-Propyl Substituted Systems

I II III IV

Form	Composite π-structures[a]	E_{tot}(a. u)	$2\sum^{occ}\epsilon_i$(a. u)	P_{ij}^{π}[b] Rep.($\times 10^3$)	P_{ij}^{π} Attr.($\times 10^3$)	P_{16}^{π} ($\times 10^4$)	$\Delta(2\sum^{occ}\epsilon_i)$[c]	$\Delta(V_{nn}-V_{ee})$[c]	ΔE_{tot}[c]
I	$(6\pi/6)$	−74.1908	−45.4548	−7.9279	10.3000	1.431	−50.6	78.1	27.5
	$2\times(4\pi/4)$			(−19.8)			(−12.4)		
II	$(6\pi/6)$	−74.2347	−45.3742	−0.5521	8.2050	1.386	0.0	0.0	0.0
	$2\times(4\pi/4)$			(−19.8)			(0.0)		
III	$(5\pi/5)$	−73.9331	−45.2482	−7.9218	2.9571	1.437	79.1	110.2	189.3
	$3\times(4\pi/4)$			(−42.1)			(21.1)		
IV	$(5\pi/5)$	−73.9328	−45.1644	−0.5253	2.5650	1.386	131.7	57.8	189.4
	$3\times(4\pi/4)$			(−41.6)			(38.0)		

[a]Except the main $(6\pi/6)$ system of the triene moiety; [b]Values in parenthesis are the sum of those for secondary repulsive centers which are not on the triene moiety; [c]Relative energies to the form II are in kcal/mol. Values in parenthesis are for π-orbital energies.

TABLE 8. Energy analysis and π-Overlap Populations of 3-Propyl Substituted Systems



I II III IV

Form	Composite π-structures[a]	E_{tot}(a. u)	$2\sum^{occ}\epsilon_i$(a. u)	P_{ij}^{π}[b] Rep.($\times 10^3$)	P_{ij}^{π} Attr.($\times 10^3$)	P_{16}^{π} ($\times 10^4$)	$\Delta(2\sum^{occ}\epsilon_i)$[c]	$\Delta(V_{nn}-V_{ee})$[c]	ΔE_{tot}[c]
I	$(6\pi/6)$	−74.3703	−45.1954	−0.6175	3.1330	1.409	0.0	0.0	0.0
	$2\times(4\pi/4)$			(−20.1)			(0.0)		
II	$(6\pi/6)$	−74.3550	−45.2174	−5.0882	3.5070	1.434	−13.8	23.4	9.6
	$2\times(4\pi/4)$			(−19.9)			(−1.3)		
III	$(5\pi/5)$	−74.1313	−45.1294	−0.6109	0.7504	1.411	41.4	108.6	150.0
	$3\times(4\pi/4)$			(−42.3)			(22.1)		
IV	$(5\pi/5)$	−74.1194	−45.1536	−5.0803	0.7497	1.437	26.2	131.2	157.4
	$3\times(4\pi/4)$			(−42.5)			(20.3)		

[a]Except the main $(6\pi/6)$ system of the triene moiety; [b]Values in parenthesis are the sum of those for secondary repulsive centers which are not on the triene moiety; [c]Relative energies to the form I are in kcal/mol. Values in parenthesis are for π-orbital energies.

tween atom pair reacting, P_{16}^{π}, due to strong electron-repelling interaction of vinyl group by forming a $(4\pi/4)$ center with site 4 of the triene moiety.

(2) Stability of a conformer can be assessed by considering resultant sum of repulsive and attractive interactions of composite π structures in the form (additivity rule)[7]; the more attractive, the more stabilizing.

(3) Side chain interactions with a site of the triene moiety increase in the order $2<3\ll4<1$ because the magnitude of AO coefficients of HOMO increases in the same order.

(4) Composite π structures which are not interacting directly with a site of the triene moiety have only secondary effects on overlap population of atom pair 1, 6 (P_{16}^{π}).

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The Vacancies-in-Solid Model Applied to Sublimation Pressure, Enthalpies and Entropies of Sublimation, and Enthalpies and Entropies of Solid Krypton and Xenon

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Thermodynamic properties such as sublimation pressures, enthalpies and entropies of sublimation, enthalpies and entropies of solid krypton and xenon are calculated from 0 °K to the triple point, using the vacancies-in-solid model. The Mie-Lennard-Jones 12,6 potential in uniform potential field is used. The results are compared with the calorimetric and sublimation pressure values, and are in a good agreement with the available calorimetric and sublimation pressure values.

Introduction

During the past, thermodynamic properties of the rare gas solids have theoretically created much interest because their atoms are characterized by the tightly bound, closed-shell structure, spherical symmetry, and weak interatomic force, and interatomic forces between their atoms are relatively accurately described. Highly accurate data of thermodynamic properties for the solids are necessary because they can be compared with theoretical predictions based on proposed models. Sublimation pressures of solid krypton and xenon have been measured by some investigators over past scores of years. Chen *et al.*[1,2] have measured sublimation pressures of solid argon, krypton and xenon, and obtained their semi-empirical enthalpies of sublimation which were derived from their sublimation pressure measurements via the Clausius-Clapeyron equation. Schwalbe *et al.*[3] have determined the calorimetric enthalpy and entropy of solid argon, krypton and xenon by the following thermodynamic relationships.

$$H_{cal}(T,P)=H_R+\int_{T_R}^{T} C_{sat}dT+\int_{P_R}^{P} VdP \tag{1}$$

$$S_{cal}(T,P)=\int_0^T (C_{sat.}/T)dT \tag{2}$$

where C_{sat} is the saturated heat capacity of the condensed phase along the saturated sublimation pressure curve, and V the molar volume of the condensed phase at arbitrary point (T, P). H_R denotes the enthalpy at some reference temperature T_R.

Although there have been numerous experimental studies of solid krypton and xenon, few theories can explain their thermodynamic properties quantitatively from 0 °K up to the triple point. In previous papers,[4-6] we have derived a solid partition function for monatomic crystals on the basis of the vacancies-in-solid model which have taked account of lattice vacancy defects and two maximum phonon frequencies for perfect crystals, and used the modified Mie-Lennard-Jones 12,6 potential. We have also studied the sublimation pressures of solid argon and xenon, and molar volumes and isothermal compressibilities of solid krypton and xenon. In this paper, we have used the same vacancies-in-solid model and evaluated sublimation pressures, enthalpies and entropies of sublimation, and ehthalpies and entropies of solid krypton and xenon from 0 °K to the triple point. And also, we have compared our results with observed data, available calorimetric data and semi-empirical values derived from sublimation pressures. Finally, we are to test for availability of our vacancies-in-solid model.

The Partition Function

According to the vacancies-in-solid model,[4-6] the canonical ensemble partition function $Q(N, x, T)$ for monatomic crystals is written as

$$\begin{aligned} Q(N,x,T)&=\frac{(N+N_h)!}{N!N_h!}q_c^{xN}(q_\alpha+q_\beta)^{(1-x)N} \\ &=\frac{(N+N_h)!}{N!N_h!}q_c^{N}(1+\Delta)^{(1-x)N} \end{aligned} \tag{3}$$

where

$$q_c=q_\alpha=\left(2\sinh\frac{\theta_c}{2T}\cdot 2\sinh\frac{\theta_D}{2T}\right)^{-3/2}e^{-\phi_c/kT},$$

$$q_\beta=q_n=\left(2\sin h\frac{\theta_c}{2T}\right)^{-3}e^{-\phi_\beta/kT},$$

$$x=V_0/V=(a_0/a)^3$$

$$\Delta=q_\beta/q_\alpha$$

and

$$-\Phi_c(x)=-N\phi_c(x)=U_e+D_e(2x^2-x^4).$$

Here q_c, q_α and q_β represent the molecular partition functions of the perfect oscillator of the perfect crystal-like part, the imperfect oscillator of the imperfect crystal-like part in α-state and β-state, respectively. θ_D is the Debye temperature, and θ_c is given in order to (4/7) $\theta_D\cdot\phi_c$ and ϕ_β are the