basis set (6s,5p,2d,1f) is used for the C atom in the Ni_3CH_3 calculations. As in their previous work,[14] Ni 3d orbitals are not explicitly included in ref 42.

VII. Conclusions

The conclusions of the present study of chemisorption of CH_3 on the (111) surface of nickel can be summarized as follows:

(1) Dissociated CH_3 binds strongly to the Ni(111) surface with adsorption energies of 39, 36, and 34 kcal/mol at the 3-fold, bridge, and atop atom sites, respectively. The two 3-fold adsorption sites have comparable stability. Compared to other CH_x fragments, the potential surface of the Ni(111) appears fairly flat for methyl radical adsorption.

(2) In the calculated equilibrium geometry of CH_3 on Ni(111), the hydrogens are in a plane parallel to the surface in a pyramidal configuration pointing in the direction above the nearest nickel atoms. The angle between the surface normal and the C–H bond is 112 ± 2°. Ni–C bond distances are 2.35, 2.34, and 2.03 Å for methyl at the 3-fold, bridge, and atop atom sites, respectively.

(3) Calculated CH_3–(Ni surface) stretching vibrational frequencies are 369, 296, and 416 cm^{-1} for the 3-fold, bridge, and atop sites. The C–H stretching frequency for CH_3 at the center of a 3-fold site is 2966 cm^{-1} for the equilibrium geometry.

(4) A low C–H frequency of methyl on Ni(111) is calculated at 2627 cm^{-1} if CH_3 is shifted away from the 3-fold center by 0.67 au and if one of the hydrogens is tilted to give a C–H bond parallel to the surface. This shift puts one of the hydrogens directly above a Ni atom. This geometry is only 1.6 kcal/mol higher in energy than the calculated equilibrium geometry.

(5) The reaction of $CH_2(ads) + H(ads) = CH_3(ads)$ on the surface is 13 kcal/mol exothermic. An energy barrier occurs when H and CH_2 are moved from infinite separation to adjacent 3-fold sites on the surface for the pathway investigated.

(6) Electron transfer occurs to carbon from the surface, primarily from the 4s band of Ni, accompanied by a work function increase of the lattice by about 0.2 eV. Ni 3d orbitals strongly interact with the 1e symmetry orbitals of CH_3. Covalent s and d bonding characterizes the bonding of methyl to the nickel surface.

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Registry No. Me•, 2229-07-4; Ni, 7440-02-0; CH_2, 2465-56-7; H, 12385-13-6.

Revival of an Old Structure Problem: Trithiapentalene—Real or Time-Averaged C_{2v} Symmetry?

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Abstract: The structures of 1,6,6aλ^4-trithiapentalene **1a** and the related compounds 1,6-dioxa-6aλ^4-thiapentalene **1b** and 1,6-diaza-6aλ^4-thiapentalene **1c** were examined on the basis of ab initio MO theory employing the 3-21G(*) and 6-31G* basis sets. In case of the trithia and dioxathia molecules, the bridged C_{2v} structures appear as most stable arrangements when the correlation energy is considered, whereas the corresponding open C_s forms are preferred at the SCF level. The same conclusions can be drawn for the 1,6-disubstituted diazathiapentalenes. Contrary to this, structure **4** with an aromatic isothiazole ring is the most stable form for the unsubstituted compounds.

The systematic study and discussion of the structure of 1,6,6aλ^4-trithiapentalene **1a** and of related compounds, e.g., of types **1b** and **c**, began in 1958[1] and has attracted much attention because of the unusual binding behavior in these systems.[2-5] Compounds belonging to this class had been obtained much earlier. Thus, the 2,5-dimethyl derivative of **1a** was already prepared in 1925, but the completely different structural formula **3** was proposed.[6] Nowadays, most experimental data for 1,6,6aλ^4-trithiapentalene are in agreement with the assumption of C_{2v} molecular symmetry corresponding to **1a**. Nevertheless, a final confirmation of this structure has not been given until now.[2-5] Alternatively to this structure proposition, which is based on the no-bond–single-bond resonance concept, valence tautomerization between the two alternate forms of **2** may be postulated for which the C_{2v} form represents a transition state. Provided that the energy barrier is too low to be observed by the experimental methods used, distinctions between real or time-averaged C_{2v} symmetry may be impossible. In Scheme I, both interpretation possibilities are illustrated by eq 1a and 1b.

Former attempts to contribute to a decision of this question by means of quantum chemical methods were significantly influenced by the type of approximation chosen.[2-5,7] Mostly, semiempirical MO methods and minimum basis set ab initio MO

Scheme I

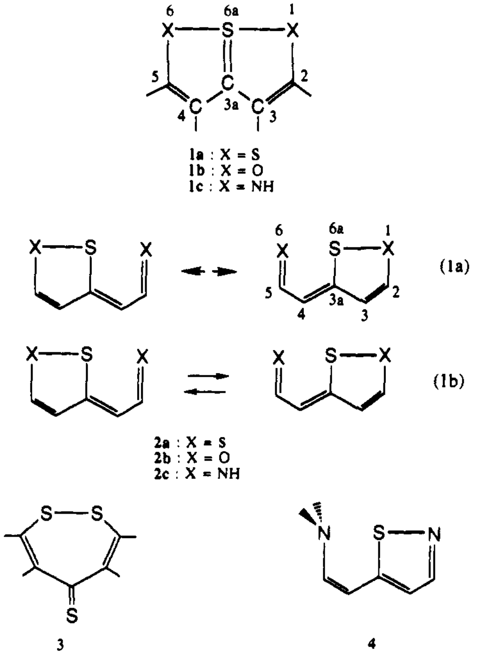

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Table I. 3-21G(*) and 6-31G* Optimized Geometries in Comparison with X-ray and Electron Diffraction Data for 1,6,$6a\lambda^4$-Trithiapentalene **1a**[a]

bond length[b]	3-21G(*)	6-31G*	X-ray[c]	ED[d]	bond angle[b]	3-21G(*)	6-31G*	X-ray[c]	ED[d]
S(1)C(2)	1.683	1.686	1.684	1.698	S(1)C(2)C(3)	120.5	120.3	120.1	118.7
C(2)C(3)	1.358	1.359	1.354	1.364	C(2)C(3)C(3a)	120.1	119.8	120.3	119.4
C(3)C(3a)	1.410	1.412	1.409	1.422	C(3)C(3a)S(6a)	119.5	119.5	118.5	119.2
C(3a)S(6a)	1.734	1.738	1.748	1.708	H(2′)C(2)S(3)	120.2	120.6		
S(1)S(6a)	2.403	2.386	2.363	2.328	H(3′)C(3)C(3a)	118.4	118.6		
C(2)H(2′)	1.073	1.076			C(3a)S(6a)S(1)	88.6	88.7	89.1	90.1
C(3)H(3′)	1.070	1.074			S(6a)S(1)C(2)	91.3	91.7	92.0	92.6

[a] C_{2v} symmetry, E_T(3-21G(*)) = −1377.536 783 au, E_T(6-31G*) = −1384.131 800 au. [b] Bond lengths in angstroms, bond angles in degrees. [c] Reference 9. [d] Reference 10.

Table II. 3-21G(*) and 6-31G* Optimized Geometries for the C_s Form **2a**[a]

bond length[b]	3-21G(*)	6-31G*	bond angle[b]	3-21G(*)	6-31G*
S(1)C(2)	1.729	1.734	S(1)C(2)C(3)	118.4	118.4
C(2)C(3)	1.328	1.329	C(2)C(3)C(3a)	118.3	118.4
C(3)C(3a)	1.453	1.453	C(3)C(3a)S(6a)	113.6	113.3
C(3a)C(4)	1.358	1.360	C(4)C(3a)S(6a)	124.8	125.1
C(3a)S(6a)	1.750	1.753	C(3a)C(4)C(5)	126.5	127.4
C(4)C(5)	1.416	1.423	C(4)C(5)S(6)	127.2	128.1
C(5)S(6)	1.634	1.635	H(2′)C(2)C(3)	123.9	124.5
S(1)S(6a)	2.095	2.089	H(3′)C(3)C(3a)	119.0	119.3
S(6)S(6a)	3.022	3.096	H(4′)C(4)C(3a)	116.5	116.0
C(2)H(2′)	1.070	1.073	H(5′)C(5)C(4)	114.4	114.0
C(3)H(3′)	1.070	1.074	C(3a)S(6a)S(1)	95.3	95.6
C(4)H(4′)	1.073	1.076	C(3a)S(6a)S(6)	80.1	79.3
C(5)H(5′)	1.077	1.079			

[a] Numbering scheme taken from **1**, E_T(3-21G(*)) = −1377.550 692 au, E_T(6-31G*) = −1384.148 873 au. [b] Bond lengths in angstroms, bond angles in degrees.

theory were employed. Frequently, the calculations were based on experimental or model geometries and tried to confirm the molecular structure in an indirect way by comparison between theoretical data, e.g., charge distributions, transition energies, dipole moments, orbital energies, etc., and corresponding experimental, in particular spectroscopic findings. Complete geometry optimization of the symmetric and asymmetric forms **1** and **2** was not performed. Only in a few cases, the consequences of a displacement of the central sulfur atom in **1** were examined with partially contradictory results.[2–5,7d–h] On the basis of the progress in ab initio MO theory,[8a] a reinvestigation of this problem seems to be justified, which considers more extended basis sets, complete geometry optimization, characterization of the stationary points on the energy hypersurface, and correlation energy.

Methodology

All calculations were performed by using the program packages GAUSSIAN86[8b] and HONDO7.[8c] The geometries of the various molecules were completely optimized by employing the 3-21G(*) and 6-31G* basis sets.[8a] Correlation energy was considered for selected molecular forms based on the Møeller–Plesset perturbation treatment up to the second order (basis set 6-31G*) and fourth order (basis set 3-21G(*)) with freezing of the innermost occupied and outermost virtual orbitals (20 for **1a**, 12 for **1b,c**).

Results and Discussion

Tables I and II summarize the 3-21G(*) and 6-31G* optimized geometries for the structures **1a** (C_{2v}) and **2a** (C_s). The comparison of the structure parameters for the C_{2v} symmetry with X-ray[9] and electron diffraction data[10] shows a good agreement; both basis sets are able to reproduce the geometry of the molecules. However, the calculated energy differences of 8.7 (3-21G(*)) and 10.7 kcal/mol (6-31G*) are both in favor of the C_s form **2a**, thus supporting the valence tautomerization assumption (eq 1b). This is additionally confirmed by the characterization of the C_{2v} form as a saddle point on the energy hypersurface. In both basis sets, one distinct negative eigenvalue of the force constants matrix was obtained.

Only consideration of the correlation energy changes the situation in favor of the C_{2v} form. On the basis of the 3-21G(*) geometries, the Møeller–Plesset perturbation treatment was brought to the fourth order (MP4/3-21G(*)//3-21G(*)) and provided an energy difference of 7.0 kcal/mol in favor of **1a** now. Because of computational limitations, the corresponding calculations for the 6-31G* geometries could only be realized up to the second order (MP2/6-31G*//6-31G*). Here, the C_{2v} form is more stable than the C_s form by 6.4 kcal/mol. Thus, the assumption of a single minimum curve for the three-sulfur bridge in **1a** seems to be justified as concluded from most experiments.[2–5] These results confirm another experience found for other compounds, e.g., various carbocations,[8a,11a–d] that correlation energy favors bridged or nonclassical structures over classical ones.

Stimulated by the reasonable results for trithiapentalene, we extended our studies to the related systems **1b** and **1c**, where the two outer sulfurs are replaced by oxygen and nitrogen atoms, respectively. In case of the 1,6-dioxa-$6a\lambda^4$-thiapentalene compound **1b**, we find a situation that is completely comparable with that for **1a**. Only after inclusion of correlation energy, the symmetric form **1b** is more stable than the open form **2b** by 4.5 kcal/mol in the MP4/3-21G(*)//3-21G(*) calculation and by 8.3 kcal/mol in the MP2/6-31G*//6-31G* one. Contrary to this, the SCF energy differences are in favor of **2b** with 3.9 (6-31G*) and 1.3 kcal/mol (3-21G(*)). The optimized geometries may well be compared with the experimental structure data from a microwave study[4,12] (Table III).

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Table III. 3-21G(*) and 6-31G* Optimized Geometries in Comparison with Microwave Data for Dioxathiapentalene **1b**[a]

bond length[b]	3-21G(*)	6-31G*	MW[c]	bond angle[b]	3-21G(*)	6-31G*	MW[c]
O(1)C(2)	1.296	1.265	1.326	O(1)C(2)C(3)	116.3	118.0	115.0
C(2)C(3)	1.366	1.371	1.370	C(2)C(3)C(3a)	111.2	110.9	113.4
C(3)C(3a)	1.399	1.398	1.390	C(3)C(3a)S(6a)	115.0	114.5	113.9
C(3a)S(6a)	1.739	1.737	1.732	H(2')C(2)C(3)	125.0	124.3	129.0
O(1)S(6a)	1.869	1.893	1.873	H(3')C(3)C(3a)	123.7	123.9	124.1
C(2)H(2')	1.071	1.079	1.074	C(3a)S(6a)O(1)	85.4	85.7	87.0
C(3)H(3')	1.065	1.070	1.089	S(6a)O(1)C(2)	112.1	110.9	110.7

[a] C_{2v} symmetry, E_T(3-21G(*)) = −735.097754 au, E_T(6-31G*) = −738.833512 au. [b] Bond lengths in angstroms, bond angles in degrees. [c] Reference 12.

Table IV. 3-21G(*) and 6-31G* Optimized Geometries for Diazathiapentalene **1c**[a]

bond length[b]	3-21G(*)	6-31G*	bond angle[b]	3-21G(*)	6-31G*
N(1)C(2)	1.312	1.302	N(1)C(2)C(3)	114.3	114.8
C(2)C(3)	1.378	1.381	C(2)C(3)C(3a)	112.9	112.9
C(3)C(3a)	1.396	1.397	C(3)C(3a)S(6a)	115.5	115.5
C(3a)S(6a)	1.755	1.758	H(2')C(2)C(3)	123.1	123.4
N(1)S(6a)	1.909	1.928	H(3')C(3)C(3a)	122.7	122.6
C(2)H(2')	1.073	1.078	C(3a)S(6a)N(1)	84.3	84.2
C(3)H(3')	1.067	1.071	S(6a)N(1)C(2)	113.0	112.6
N(1)H(1')	1.000	0.997	H(1')N(1)C(2)	122.7	121.5

[a] C_{2v} symmetry, E_T(3-21G(*)) = −695.648269 au, E_T(6-31G*) = −699.156778 au. [b] Bond lengths in angstroms, bond angles in degrees.

The 1,6-diaza-6aλ^4-thiapentalene molecule **1c** represents a further basic compound in the class of 6aλ^4-thiapentalenes. Compared with **1a**/**2a** and **1b**/**2b**, some additional points have to be considered describing the structure of the various molecular forms. Firstly, the possibility of pyramid structures at the nitrogens of **1c** was examined. Starting 6-31G* geometry optimizations for **1c** from the two different out-of-plane distortion possibilities of the N hydrogens with C_2 symmetry (both hydrogens point to opposite sides of the molecular plane) and C_s symmetry (the two hydrogens point to the same side), the planar C_{2v} form was obtained as the optimum geometry (Table IV). Secondly, geometry optimization of the two different molecular forms of **2c** with the hydrogen atom of the imino group pointing to or away from the central sulfur atom was performed. These calculations show that the latter structure is the more stable, representing an energy minimum at the SCF level, characterized by only positive eigenvalues of the force constants matrix. On the basis of the optimum geometries of **1c** and **2c**, the same energetic relation between both molecular forms was obtained as before for the dioxathia and trithia compounds. At the SCF level, the open form **2c** is preferred by 7.1 (6-31G*) and 1.1 kcal/mol (3-21G(*)). Considering the correlation energy, the energy difference is reversed in favor of the C_{2v} form and amounts to 2.5 (MP4/3-21G(*)//3-21G(*)) and to 7.3 kcal/mol (MP2/6-31G*//6-31G*). Thus, the results for the diazathiapentalenes seem to fit into the general picture about the structure of 6aλ^4-thiapentalenes at least for all 1,6-disubstituted diazathia derivatives. For the 1,6-unsubstituted molecule, the additional structure possibility **4** has to be considered, which contains the aromatic isothiazole ring. Trithia- and dioxathiapentalenes cannot form the corresponding heteroaromatic system. The calculations indicate in fact a distinctly higher stability of **4** in comparison to **1c** and **2c**. The energy differences related to the C_{2v} form are 9.9 and even 21.6 kcal/mol by employing the 3-21G(*) and 6-31G* basis sets. The optimized geometries for **4** are given in Table V. Even though the correlation energy stabilizes the bridged arrangement **1c** much more than the open isothiazole form **4**, the latter acquires a very small energy advantage of 0.5 kcal/mol at the MP4/3-21G(*)//3-21G(*) level and a larger one of 7.9 kcal/mol at the MP2/6-31G*//6-31G* level. The experimental findings[13-15] for 1,6-unsubstituted diazathia- and tetraazathiapentalenes indicate an interconversion between the two alternate forms of **4** passing through the C_{2v} arrangement **1c** as an intermediate.

Table V. 3-21G(*) and 6-31G* Optimized Geometries for the Isothiazole Form **4**[a] of the Diazathiapentalenes

bond length[b]	3-21G(*)	6-31G*	bond angle[b]	3-21G(*)	6-31G*
N(1)C(2)	1.296	1.284	N(1)C(2)C(3)	115.1	116.4
C(2)C(3)	1.430	1.429	C(2)C(3)C(3a)	110.9	110.7
C(3)C(3a)	1.357	1.355	C(3)C(3a)S(6a)	109.1	108.4
C(3a)C(4)	1.457	1.465	C(4)C(3a)S(6a)	125.7	126.8
C(3a)S(6a)	1.732	1.730	C(3a)C(4)C(5)	124.8	127.0
C(4)C(5)	1.319	1.322	C(4)C(5)N(6)	120.4	121.9
C(5)N(6)	1.433	1.422	H(2')C(2)C(3)	124.5	124.2
N(1)S(6a)	1.658	1.658	H(3')C(3)C(3a)	124.6	124.7
N(6)S(6a)	2.795	2.954	H(4')C(4)C(3a)	115.8	114.8
C(2)H(2')	1.068	1.076	H(5')C(5)C(4)	120.3	119.2
C(3)H(3')	1.068	1.073	C(3a)S(6a)N(1)	93.3	94.1
C(3)H(4')	1.074	1.076	C(3a)S(6a)N(6)	74.8	72.9
C(5)H(5')	1.076	1.080	H(6')N(6)C(5)[c]	115.2	111.4
N(6)H(6')	1.005	1.003			

[a] Numbering scheme taken from **1**, C_s symmetry, E_T(3-21G(*)) = −695.664110 au, E_T(6-31G*) = −699.191182 au. [b] Bond lengths in angstroms, bond angles in degrees. [c] Torsion angles $H_2N(6)C(5)H(5')$ = ±66.5 (3-21G(*)) and ±60.0 (6-31G*).

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