along this reaction coordinate. The $CF_3Cl + e^- \rightarrow CF_3{}^{\bullet} + Cl^-$ reaction therefore appears, in polar solvents, as a concerted electron transfer–bond breaking process in agreement with what was previously suggested from the analysis of the kinetics of the electrochemical reduction of the perfluoroalkyl halides.[15]

Conclusions

The following conclusions emerge from the results described in the preceding sections. MP3 calculations using pseudo-potentials for the halogens and semidiffuse functions in the carbon orbital set indicate that in the series CH_3F, CH_3Cl, CH_3Br, CH_3I, the reaction $CH_3X + e^- \rightarrow CH_3{}^{\bullet} + X^-$ is a concerted electron transfer–bond breaking process in accord with previous experimental observations pertaining to the reductive cleavage of alkyl halides in the gas phase, in apolar or weakly polar solid matrixes and in their electrochemical reduction in polar solvents. The magnitudes of the activation barrier and the geometries of the transition state thus found are in good agreement with the application of a previously developed empirical model based on Morse curves approximation, in which the activation barrier is quadratically related to the driving force and the intrinsic activation barrier is equal to one-fourth of the CH_3–X bond dissociation energy. This validation of the empirical model reinforces the confidence in its general applicability to a vast class of organic and inorganic reductive cleavage reactions.

The comparison of the energy profiles obtained by means of full basis set calculations for CH_3Cl and CF_3Cl reveals that a shallow minimum appears on the anion profiles at large C–Cl distances in both cases. The stabilization energy vis-à-vis R• + Cl⁻ is, however, much larger with CF_3Cl than with CH_3Cl. Analysis of the charge density maps of these states shows that the bond between carbon and chlorine is of the electrostatic type and that the larger stabilization found with $CF_3Cl^{\bullet-}$ essentially derives from the polarization of the $CF_3{}^{\bullet}$ fragment as compared to the $CH_3{}^{\bullet}$ fragment.

Simulation of the effect of polar solvents on the energy profiles of CF_3Cl and $CF_3Cl^{\bullet-}$ shows that the energy minimum on the $CF_3Cl^{\bullet-}$ disappears. The $CF_3Cl + e \rightarrow CF_3{}^{\bullet} + Cl^-$ thus appears as a concerted electron transfer–bond breaking process in agreement with the conclusions previously derived from the kinetics of the electrochemical reduction of perfluoroalkyl halides in polar solvents. These results emphasize and rationalize the role of the solvent among the parameters that drive reductive cleavage reactions toward either the concerted or the stepwise mechanism.

Bond Alternation in Triannelated Benzenes: Dissection of Cyclic π from "Mills–Nixon" Effects

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Abstract: The structures of a number of triannelated benzenes are calculated at the ab initio 6-31G(D) and local density functional levels of theory. Their structures are discussed in terms of ring strain and cyclic π effects. The results offer no evidence for the "Mills–Nixon" postulate in simple annelated benzenes. A new motif in bond-alternating benzenes is proposed.

Classic examples of bond alternation in benzenoid structures are seen experimentally in the central ring of triphenylene (1)[2] and starphenylene (2) (Figure 1).[3,4] Speculation has been made that similar bond alternation exists in simple triannelated benzenes like tricyclobutabenzene.[5] Computations at the ab initio 3-21G level and below support these notions,[6] although the low-temperature X-ray analysis of perfluorotricyclobutabenzene (3) reveals no such alternation (Figure 2).[7] Ab initio 6-31G(D) computations provide a structural data base consistent with experiment. Dissecting this set into cyclic π and "Mills–Nixon" components dispels some notions and generates new speculations. From this vantage point, the present investigation begins.

Methods

The molecular structures of all stationary points have been determined with both the semiempirical AM1 method[8] and the split valence 6-31G(D) basis set at the restricted Hartree–Fock (RHF) self-consistent field (SCF) level of theory.[9] This basis set includes a set of six d polarization functions on all heavy atoms. For illustration purposes, several calculations were also performed using the 3-21G basis set[10] in order to supplement available literature calculations and, at the ab initio level, using the local density functional (LDF) approach.[11] Geometry optimizations

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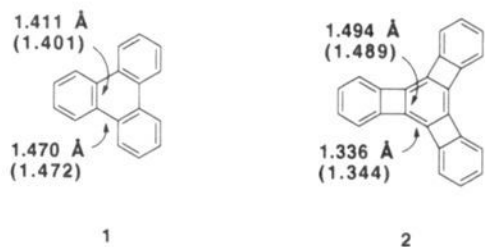
1.411 Å
(1.401)

1.470 Å
(1.472)

1

1.494 Å
(1.489)

1.336 Å
(1.344)

2

Figure 1. Structures of **1** and **2** including the X-ray determined value for the long and short bond length of the central ring; LDF value in parentheses.
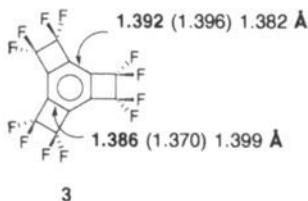

1.392 (1.396) 1.382 Å

1.386 (1.370) 1.399 Å

3

Figure 2. Structure of **3** showing the central ring bond lengths (X-ray, (6-31G(D)), 3-21G).

Table I. Selected Bond Lengths for Cycloalkanes and Cycloalkenes

	endo bond length, Å	
compd	exptl[c]	6-31G(D)
Cycloalkanes[a]		
cyclohexane	1.535 ± 0.016	1.532
cyclopentane	1.543 ± 0.018	1.540
cyclobutane	1.554 ± 0.021	1.546
cyclopropane	1.509 ± 0.026	1.497
Cycloalkenes[b]		
cyclohexene	1.326 ± 0.012	1.321
cyclopentene	1.324 ± 0.013	1.319
cyclobutene	1.335 ± 0.019	1.322
cyclopropene	1.288 ± 0.017	1.276

[a] Single bond length. [b] Double bond length. [c] Taken from ref 18; errors are standard deviations over a variety of compounds in which such ring systems are found.
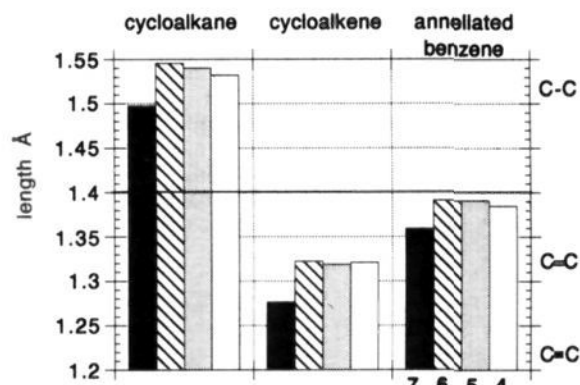

Figure 3. Comparison of the endo bond lengths in cycloalkanes, cycloalkenes, and triannelated benzenes **4–7** of ring size 3–6.

were performed with the aid of analytically determined gradients and the search algorithms contained in MOPAC (version 6.0),[12] GAMESS,[13] and DMOL.[14] The nature of each SCF-stationary point was established by calculating (analytically for ab initio Hartree–Fock wavefunctions, numerically for semiempirical and ab initio LDF methods) and diagonalizing the matrix of energy second derivatives (Hessian) to determine the number of imaginary frequencies. All minima are determined to have zero imaginary frequencies. All reported bond lengths in this work are rounded off to three decimal places.[15]

"Mills–Nixon" Effects

In the D_{6h} structure of benzene, symmetry requires that both Kekulé resonance structures contribute equally.[16] In C_s tetralin, no such symmetry requirement exists, and thus the ring annelation could induce bond-length alternation in the arene nucleus. Decreasing the size of the annelation increases the strain of the system[17] and is claimed to exacerbate the degree of bond alternation. This notion of strain-induced bond localization in benzenoid aromatics forms the basis of the Mills–Nixon postulate.[18]

Existing calculations at the semiempirical and ab initio 3-21G levels,[6] along with indirect experimental results[19] on annelated benzenes, have created a polemic in this general area. Although there have been several synthetic studies on small ring annelated

benzenes,[5b,20] a dearth of highly accurate structural data exists.[21] Those data which do exist show a dissonant relationship with the existing computational work. Diagnostic of the problem is the discrepency that one sees between the accurate X-ray geometry of **3**[7] and the interpretation of the published calculations.[6b,c]

Studies on small strained systems indicate that inferior results are obtained with computational levels lower than ab initio 6-31G(D).[22] Implementation of 6-31G(D) to solve the structure of **3** brings theory and experiment into agreement (cf. Figure 2). This casts doubts on the Mills–Nixon postulate for simple annelated benzenes. Therefore, a deeper and more general analysis of strain effects in cyclic hydrocarbons seems warranted.

Discussion of the relationship between strain and bond length in simple cycloalkanes started with the fiduciary works on hybridization.[23] Early theoretical studies predicted that in three- and four-membered rings the direction of the normally hybridized orbitals would lie off the internuclear axis (the "bent-bond" formalism[24]) and that to keep the orbital path length constant the internuclear distances would shorten. Dunitz observed bond elongation in cyclobutanes,[25] however, and in conjunction with Shoemaker[26] proposed the presently accepted view that there is

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(15) The extraction of geometries and structural evaluations were done with MacMoMo, an X-ray coordinate analysis program available through Dr. Max Dobler, Department of Organic Chemistry, ETH-Zürich.

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(20) For the synthesis of a variety of strained annelated benzenes, see: (a) Giovannini, E.; Vuilleumier, H. *Helv. Chim. Acta* **1977**, *60*, 1452. (b) Thummel, R. *J. Am. Chem. Soc.* **1976**, *98*, 628. (c) Thummel, R. P.; Nutakul, W. *J. Org. Chem.* **1977**, *42*, 300.

(21) (a) Boyko, E. R.; Vaughan, P. A. *Acta Crystallogr.* **1964**, *17*, 152. (b) Korp, J. D.; Thummel, R. P.; Bernal, I. *Tetrahedron* **1977**, *33*, 3069. (c) Boese, R.; Blaser, D. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 304. (d) Billups, E.; Rodin, W. A.; Haley, M. *Tetrahedron* **1988**, *44*, 1305.
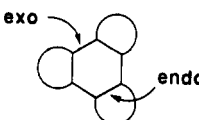
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(25) Dunitz, J. D. *Acta Crystallogr.* **1949**, *2*, 1.

Table II. Selected Bond Lengths for the Annelated Benzenes 1-12

|	endo bond length, Å					exo bond length, Å					Δ, pm
compd	exptl	6-31G(D)	LDF	3-21G	AM1	exptl	6-31G(D)	LDF	3-21G	AM1	$d_{endo}-d_{exo}$ [h]
1	1.411[a]	1.401				1.470[a]	1.472				-7.1
2	1.494[b]	1.481	1.489		1.525	1.336[b]	1.329	1.344		1.325	15.2
3	1.386[c]	1.370	1.406	1.399[d]	1.457	1.392[c]	1.396	1.396	1.382[d]	1.346	-2.6
4		1.385		1.384	1.400		1.410		1.404	1.410	-2.5
5	1.395[e]	1.391		1.386	1.428	1.378[e]	1.383		1.381	1.374	0.8
6	1.413[i]	1.391	1.408	1.408[f]	1.473	1.390[i]	1.378	1.380	1.361[f]	1.341	1.3
7		1.359		1.381[g]	1.482		1.356		1.338[g]	1.306	0.3
8		1.362			1.425		1.450			1.380	-8.8
9		1.489			1.492		1.280			1.295	20.9
10		1.374					1.408				-3.4
11		1.500	1.502	1.523[f]	1.530		1.317	1.336	1.309[f]	1.320	18.3
12		1.440	1.429		1.482		1.344	1.366		1.346	9.6

[a] Reference 1. [b] Reference 2. [c] Reference 7. [d] Reference 6b. [e] Reference 21a. [f] References 5 and 6a. [g] Reference 6d. [h] Difference between the endo and exo bond lengths, determined from 6-31G(D) geometries. [i] See Note Added in Proof.

a competition between nonbonded repulsions, which lengthen bonds, and the bent-bond formalism, which shortens bonds. Thus, they concluded that in cyclobutane the nonbonded term dominates, leading to a long bond, and in cyclopropane the nonbonded term vanishes, leading to a short bond.

Structures extracted from a recent survey of the Cambridge Crystallographic Data Base,[27] as well as a series of ab initio 6-31G(D) calculations (Table I) performed on simple cycloalkanes and cycloalkenes, corroborate the earlier studies. Using cyclohexane as the standard, one sees little change in bond length for cyclopentane, a slight elongation in bond length for cyclobutane, and a marked shortening in bond length for cyclopropane. The same trend holds for the double bond lengths in the cycloalkene series. This begs the question: Is the trend general for all bond types, specifically for those of annelated benzenes?

The figure heading of Table II shows a generic triannelated benzene. The benzene nucleus comprises two types of bonds, those contained within the annelation (endo bonds) and those connecting two annelations (exo bonds); the endo bonds are analogous to the bonds considered in the cycloalkane and cycloalkene series.

Considering first the endo bond length in tricyclohexa- (4), tricyclopenta- (5), tricyclobuta- (6), and tricyclopropabenzene (7),

4   5

6   7
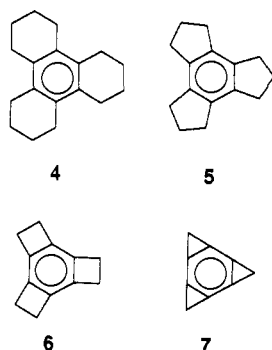
6-31G(D) calculations predict bond lengths of 1.385, 1.391, 1.391, and 1.359 Å, respectively (Table II). Comparison with the results for cycloalkanes and cycloalkenes shows no anomolous behavior for the benzene series (Figure 3). A Mills–Nixon distortion would have resulted in a significantly longer endo bond in 6 and 7. Thus, bent bonds must play an important role in determining the geometry of these systems.

The structural consequence of the Mills–Nixon postulate is ultimately bond alternation in annelated benzenes. Bond alter-
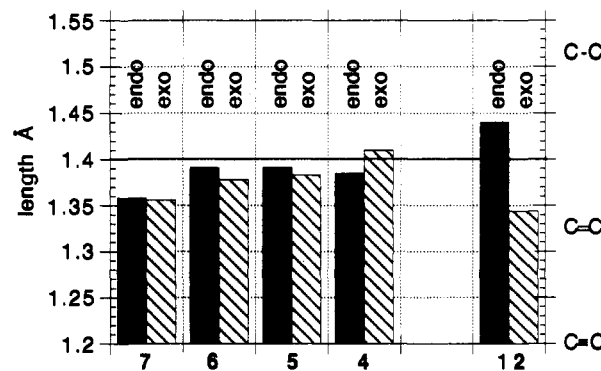

Figure 4. Comparison of endo to exo bond lengths in annelated benzenes 4–7 and 12.

nation is trivially defined by a ring geometry in which the bond lengths alternate long–short around the ring; the average aromatic bond length for alkyl-substituted benzenes is 1.397 ± 0.009 Å.[27] The case in which the endo bond set is longer than the exo bond set corresponds to a Mills–Nixon distortion. The opposite ordering corresponds to a reverse Mills–Nixon distortion.

Reviewing the series 4–7 for bond alternation, one finds the following endo/exo pairs: 4 (1.385/1.410), 5 (1.391/1.383), 6 (1.391/1.378), and 7 (1.358/1.356). From these data one can definitively conclude that no significant bond alternation and, hence, no significant Mills–Nixon distortion exists for these compounds (Figure 4).[28] From the data in Table II one sees that predictions made from 3-21G and semiempirical calculations would lead one astray.

Having dispelled the myth of significant Mills–Nixon distortions in simple triannelated benzenes, one is still left with the observed bond alternation in 1 and 2. Consideration of cyclic π effects illuminates this quandary.

Cyclic π Effects

One explanation for the bond alternation in 1 and 2 stems from the concept that Hückel cycles of $4n + 2$ electrons are more stable than isolated double bonds, which are in turn more stable than Hückel cycles of $4n$ electrons.[29] In both 1 and 2, the three endo

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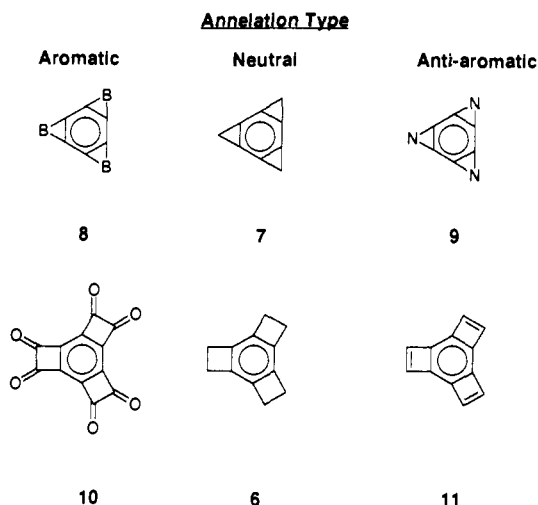
(28) Arguments have been made on the basis of the p overlap or computational bond order differences among bonds in compounds with minimal structural distortions; see: Hiberty, P. C.; Ohanessian, G.; Delbecq, F. *J. Am. Chem. Soc.* **1985**, *107*, 3095. Although there may be merit in their approach, the present study confines itself to experimentally verifiable structural parameters such as bond lengths.

(29) (a) Garratt, P. J. *Aromaticity*; Wiley-Interscience: New York, 1986. (b) Lloyd, D. *The Chemistry of Cyclic Compounds. To Be or Not to Be Like Benzene*; Wiley-Interscience: New York, 1989.

Annelation Type

| Aromatic | Neutral | Anti-aromatic |

8   7   9

10   6   11

Figure 5. Structures of 6–11. Headings indicate if annelation is $4n +$ 2, "neutral", or $4n$.
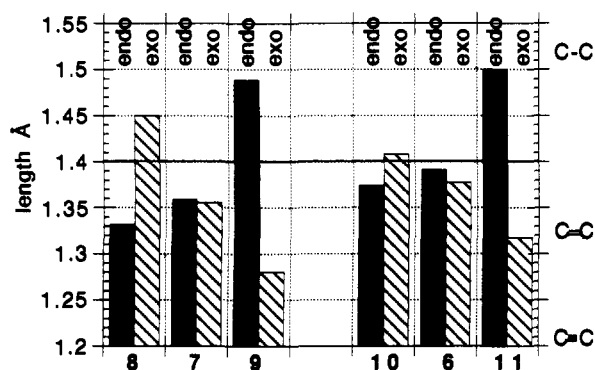

Figure 6. Comparison of endo to exo bond lengths in 6–11.

bonds of the central "benzene" are part of an annelated π system and the three exo bonds are not. For **1**, the annelation ring is a $(4n + 2)$-electron system and the endo bonds (1.41 Å) are shorter than the exo bonds (1.47 Å), indicative of greater bond order[16] in the endo bond. The structure of **2**, however, has $(4n)$-electron annelations, and the exo bonds (1.34 Å) are shorter than the endo bonds (1.49 Å), indicative of greater bond order[16] in the exo bonds.

From the series of simple annelated benzenes discussed above, **6** and **7** serve as useful reference structures to probe further this cyclic π effect. The annelations of **6** and **7** are designated "neutral" in that they do not constitute a cyclic π system. Ab initio calculations at the 6-31G(D) level show no appreciable bond alternation in **6** or **7**. Replacement of the methylene groups in **7** by BH (**8**) or NH (**9**) groups converts the neutral annelation into a $(4n + 2)$-electron or $(4n)$-electron annelation, respectively.[30] Replacement of the ethylidane groups in **6** by dicarbonyl bridges (**10**) or ethylidene groups (**11**) creates a similar series for the four-membered annelations (Figure 5).

Comparison of endo/exo pairs shows the following: **8** (1.362/1.450), **9** (1.489/1.280), **10** (1.374/1.408), and **11** (1.500/1.317).[31] In all cases, the structures distort to increase the importance of $4n + 2$ cycles and to decrease the importance of $4n$ cycles (Figure 6). Thus, aromatic character serves as the driving force of molecular structure in these compounds.

For **3–11**, changes in the π-electron count have a greater ability to induce bond-length alternations than do changes in simple

12

Figure 7. Left: benzene with constrained CCH angles; exo and endo bond lengths are calculated by 6-31G(D).[5a,31] Right: structure of **12** indicating the endo and exo bond lengths as calculated by ab initio 6-31G(D) and (LDF) methods.

annelation size. Simple annelations do not seem to have the leverage necessary to induce significant σ-based distortions. The geometrical ramifications of these annelations are attenuated by bent bonding à la Dunitz. In light of these results, it may be wise to think more deeply about the structural significance of σ versus π effects in determining the structures of molecules with extended π systems.[32]

Mills–Nixon Effects Revisited

On the basis of the results for **3–7**, one might conclude that strain-induced bond alternation in a benzenoid compound falls outside the realm of molecular possibilities. A 6-31G(D) calculation by Stanger on an artificially strained benzene speaks against this assertion.[5a,33] Stanger's study involves the optimization of the geometry of a constrained conformation of benzene, where the hydrogen–carbon–carbon bond angles are held at 90° (Figure 7). The endo bond length is 1.529 Å, and the exo bond length is 1.329 Å. Although hypothetical, Stanger's structure provides food for thought and raises questions as to the types of molecular structures that might share the qualities of this crimped benzene.

As previously mentioned, bent bonding attenuates some of the strain effect that simple annelated benzenes might be expected to exert on the geometry of the benzene nucleus. In Stanger's crimped benzene, bent bonding is not possible. Therefore, if one could create a strained annelation that resisted adopting a bent-bonding orbital geometry, then one should see Mills–Nixon distortions in the benzene ring.

Tribicyclo[2.1.1]hexabenzene **12** offers this unique type of strained annelation of benzene for which no investigations have been reported.[34] The bridgehead carbon of the bicyclic annelation cannot easily participate in a bent bond, making **12** an ideal test structure. Calculations on **12** at both 6-31G(D) and local density functional (LDF) levels of theory both reveal a bond-alternating structure (cf. Figure 7) with endo/exo bond lengths of 1.440/1.344 Å (6-31G(D)) and 1.429/1.366 Å (LDF). Comparison of this structure with the series **4–7** shows that the bond alternation in **12** is significant and well worth investigating (cf. Figure 4). This is a new structural motif in Mills–Nixon investigations, and the structure elucidation of this and related molecules is underway.

(30) Some computations at the 6-31G level have recently been done on aza- and oxacyclopropabenzene; see: Eckert-Maksic, M.; Maksic, Z. B.; Hodosek, M.; Poljanec, K. *Int. J. Quantum Chem.* **1992**, *42*, 869.

(31) The similarity in structure between **3** and **10** can be rationalized by application of Bent's rule to **3** (see: Bent, H. A. *Chem. Rev.* **1961**, *61*, 275). The greater p character of the electron-deficient α carbons endows the annelations in **3** with aromatic character, which accounts for the shorter endo bonds.
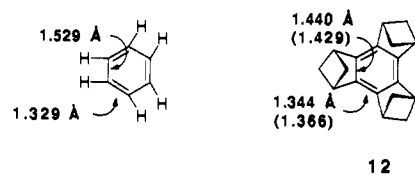
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Analogies between the Concepts of Molecular Chemistry and Solid-State Physics concerning Structural Instabilities. Electronic Origin of the Structural Modulations in Layered Transition-Metal Dichalcogenides

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Abstract: The concepts of both Fermi surface nesting and local chemical bonding were employed to analyze the electronic origin of the structural modulations of layered transition-metal dichalcogenides 1T-MX$_2$ and 2H-MX$_2$. Analogies between the two concepts and their complementary nature were examined. The concept of hidden Fermi surface nesting was used to explain the d-electron-count dependence of the structural modulations of the 1T-MX$_2$ layers containing d$^{4/3}$, d^2, and d^3 ions on the basis of their hidden one-dimensional Fermi surfaces. The latter are derived from the observations that these layers are made up of three different sets of edge-sharing octahedral chains and that strong σ-bonding interactions between the t$_{2g}$ orbitals occur along each chain direction. From the viewpoint of local chemical bonding, the driving force for the diamond-chain formation in the d^3 systems and the zigzag-chain formation in the d^2 systems is two-center, two-electron σ-bonding, but that for the ribbon-chain formation in the d$^{4/3}$ systems is three-center, two-electron σ-bonding. Several structural modulations of 1T-MX$_2$ and 2H-MX$_2$ layers, difficult to understand in terms of Fermi surface nesting, were examined by performing molecular orbital and tight-binding band electronic structure calculations. The $\sqrt{13} \times \sqrt{13}$ modulation of a d^1 1T-MX$_2$ layer is described as a superposition of linear, multicenter σ-bonding interactions which occur in three different directions around metal atoms. The 2 × 2 modulation of 1T-TiSe$_2$ results from a second-order Jahn–Teller instability of the TiSe$_6$ octahedra with d^0 ions. The 3 × 3 modulation of a d^1 2H-MX$_2$ layer occurs to enhance the extent of the metal–metal bonding interactions between adjacent MX$_6$ trigonal prisms. Structural modulations arising from Fermi surface nesting in low-dimensional metals are equivalent in nature to first-order Jahn–Teller distortions of molecules. Structural modulations of low-dimensional metals do not always originate from Fermi surface nesting, just as not all molecular distortions are caused by first-order Jahn–Teller distortions.

1. Introduction

Since the seminal work by Wilson, DiSalvo, and Mahajan[1] and by Williams, Parry, and Scruby[2] in the early 1970s on transition-metal dichalcogenides,[3] charge density wave (CDW) phenomena have become an important topic to study. Over the years, the research field of CDW phenomena has grown tremendously to include other transition-metal chalcogenides, transition-metal oxides, and organic charge-transfer salts.[4]

The CdI$_2$-type transition-metal dichalcogenides, 1T-MX$_2$ (M = transition metal; X = S, Se, or Te), consist of MX$_2$ layers obtained from MX$_6$ octahedra by sharing their edges (Figure 1a).[5] The metal atoms of an undistorted MX$_2$ layer form a hexagonal lattice (Figure 1b); this is observed for 1T-TiS$_2$, which contains d^0 ions. The 1T-MX$_2$ phases with d-electron counts from d^1 to d^3 exhibit various patterns of structural distortions resulting from their metal–metal bonding: The 1T-MX$_2$ (M = Ta, X = S or Se) systems, which have d^1 ions, exhibit a $\sqrt{13} \times \sqrt{13}$ metal-atom clustering (Figure 1c). The 1T-MTe$_2$ (M = V, Nb, or Ta) systems, for which the d-electron count is formally d^1 but actually close to d$^{4/3}$ because of a partial chalcogen-to-metal electron transfer,[6] have their metal ions clustered into "ribbon-chains" (Figure 1d). The metal ions of the 1T-MX$_2$ phases with d^2 electron count show "zigzag-chains" (Figure 1e), while those with d^3 electron count exhibit "diamond-chains" (Figure 1f). Thus the metal–metal bonding patterns of 1T-MX$_2$ phases depend critically

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