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Notes on the Modeling of 3,3′,4,4′-Tetrakis(alkylthio)-2,2′,5,5′-tetrathiafulvalenes by Molecular Mechanics and Parametrized MO Calculation

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Introduction

The polycyclic species of 3,3′,4,4′-tetrakis(alkylthio)-2,2′,5,5′-tetrathiafulvalenes, which we will abbreviate BADT, are of experimental significance in the design and development of molecular solid-state conductors.[1] They are effective electron donors in general, but we can expect details of their behavior to depend on details of their structure. We refer explicitly to the length of the alkyl chain. Singh[2] and others[3] have mounted a systematic experimental study of the family, with emphasis on structures and electrochemical behavior of the tetrathiafulvalenes in the condensed phase.

Here we address the question whether widely available modeling methods, such as the molecular mechanics scheme MM2 and approximate molecular orbital packages including MNDO, AM1, and PM3, are able to capture structural and chemical details of these species. If modeling methods prove to be accurate or at least consistent and reliable in their representation of tetrathiafulvalenes, they can serve to guide experimental studies of these and related species. Modeling seeks to represent one or more of the following molecular properties: equilibrium structure, charge distribution, relative energy, optical spectrum.

Estimates of tetrathiafulvalenes' ionization potentials and the structural consequences of ionization are also of interest. In the following sections we describe the performance and predictions of modeling of each of these properties.

Equilibrium Structures

General Remarks. One may view the tetrathiafulvalenes' structure as composed of an essentially D_{2h} (planar-rectangular) C_6S_8 core of dimension 3.65 Å × 9.00 Å (Figure 1) with alkyl chains of length n connecting sites at the corners of the rectangle. Geometric parameters for the core and its connectors are defined in Table 1.

The core is essentially invariant for all species $n = 1$, 2, 4, and 6 so long as the chains span the shorter edges of the rectangle. When $n = 6$ the species produced by synthesis appears to have alkyl connectors across the longer edges; this forces the core out of planarity and has other structural effects detailed below.

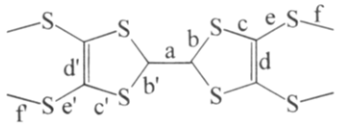

Figure 1. Definition of bond vectors for the central thia-substituted tetrathiafulvalene core.

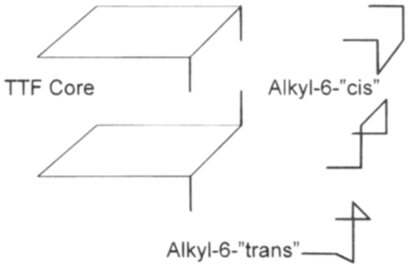

Figure 2. Building elements for the non-cyclophane structures.

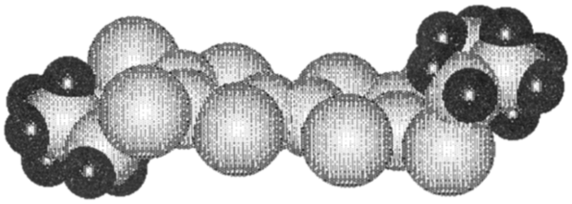

Figure 3. Butyl system in anti conformation.

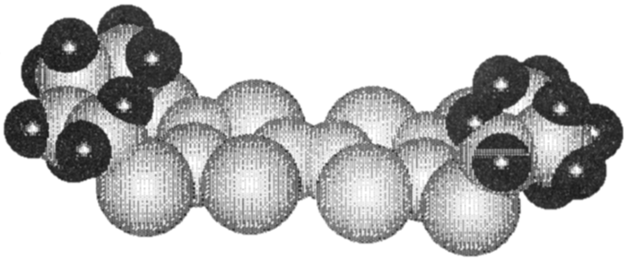

Figure 4. Butyl system in the "syn" conformation.

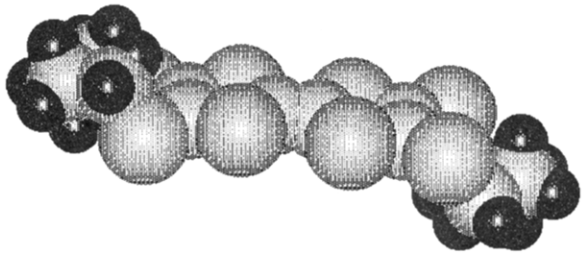

Figure 5. Butyl system in the "C-2" conformation.

For the shortest alkyl chain ($n = 1$) the system is constrained to overall planarity, symmetry D_{2h}. But for $n = 2$, the chain is already sufficiently long that it might be gauche-twisted out of plane to relieve H···H nonbonded repulsion. The twists of the chains at left and right may be related by a reflection plane perpendicular to the plane of the TTF core, or by a two-fold rotation about an axis perpendicular to the TTF plane and lying in the reflection plane just defined. These isomers may be called ethyl-C_s and ethyl-C_2, respectively.

The longer hydrocarbon rings may be arranged in a

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[1] Williams, J. M.; Kuroda, H.; Eds. *Mol. Cryst. Liq. Cryst.* **1990** *181* 1−367.

[2] Kumar, S. K.; Singh, H. B.; Jasinski, J.; Paight, E. S.; Butcher, R. J. *J. Chem. Soc., Perkin Trans 1* **1991**, 3341.

[3] Varma, K. S; Underhill, A. E. *Physica B* **1986**, *143*, 321. Wallis, J. D.; Karrer, A.; Dunitz, J. D. *Helv. Chim. Acta* **1986**, *69*, 69. Varma, K. S.; Evans, J.; Edge, S.; Underhill, A. E.; Bojesen, G.; Becher, J. *J. Chem. Soc., Chem. Comm.* **1989**, 257.

0022-3263/95/1960-5708$09.00/0

Table 1. Definition of Structural Features and and Typical PM3-Computed Values of Structural Parameters for the Family of TTF Species[a]

label	definition	mean values in TTF “D_{2h}” core	mean values in TTF “D_{2h}” cation
a	internal double bond linking five-rings	1.349	1.369
b and *c*	C−S single bonds in the five-ring (*b* is adjacent to the central double bond)	1.758	1.720
d	double bond in the TTF five-membered rings	1.357	1.370
e and *f*	C−S single bonds in the n+m ring (*e* is connected to the TTF core)	1.750 and 1.830	1.745 and 1.833
A	CCS angle between central C═C and the connecting CS bond = $a{\cdot}b = ab \cos A$	123	123
B	CSC angle between CS bonds in the five-ring = $b{\cdot}c$	96.4	96.4
C	SCS angle between SC bond in five-ring and CS bond in the n+m ring = $e{\cdot}f$	112	117
D	CSC angle between SC bond attaching n+m ring to the TTF core and its neighbor in the n+m ring = $f{\cdot}g$	106	106
T1	torsion angle defined by $b{\otimes}c{\cdot}e$	180 ± 5	180 ± 5
T2	torsion angle defined by $c{\otimes}e{\cdot}f$	varies with chain length and type of isomer	generally similar with values for neutral species

[a] Units are angstroms and degrees.

Table 2. Molecular Mechanics Survey of Butyl TTF[a]

chain length	SC orientation	chain orientation	symmetry operation	descriptive name	potential energy	relative *E*
4	parallel	gauche	reflection	syn	225.727	0
4	parallel	gauche	rotation	anti	230.690	4.93
4	antiparallel	trans	reflection	Cs-twist	228.615	2.89
4	antiparallel	trans	rotation	Ci-twist	228.610	2.89

[a] Energy units are kcal/mol.

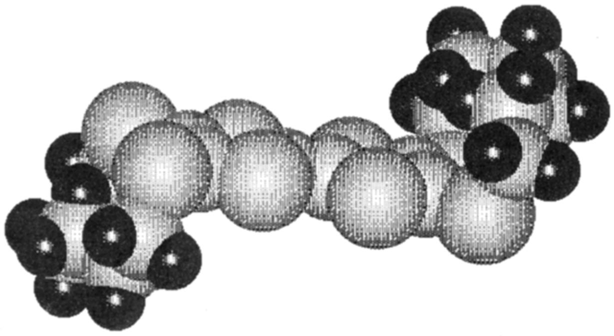

Figure 6. Hexyl system in the “anti” conformation.

large number of conformations. We may visualize these with the help of Figure 2. The tetrathiafulvalene core is represented by a rectangle, and the sulfur valences may be directed parallel (top left) or antiparallel (bottom left). The alkyl chains which link the sulfur valences may be arranged “gauche” (top and center right) or “trans” (bottom right). [The “gauche” chains are sketched in a simplified way which does not distinguish the sense of the twist from a “cis” orientation.]

The ring closing may be called parallel-gauche, parallel-trans, or antiparallel-trans. The remaining possibility, antiparallel-gauche, is energetically infeasible.

There are two edges to be connected by the alkyl chains of length *n*. For $n \leq 5$ only the shorter edges can be spanned. The connections on the two edges may be related by symmetry operations. These include a reflection in the plane perpendicular to the TTF core, a $C_2(z)$ rotation about an axis perpendicular to the TTF core, or a $C_2(y)$ rotation in the plane of the TTF core. In the gauche chain connection the $C_2(z)$ and reflection operation produce indistinguishable species, while for the trans chain, the resulting structures are distinguishable. The two alkyl connections need not be symmetry-related in principle, but in the absence of X-ray structures for examples of asymmetric connections, we leave this avenue unexplored. Structures of species for $n = 4$ are shown in Figures 3−5.

Alkyl chains of length six have further degrees of freedom. The gauche chain may be connected in an “up” orientation (top right in Figure 2) so the structure resembles a stair, or in a “down” orientation (right center). The array of possible model structures has already become unwieldy, and at this point we have made no energetic predictions. A preliminary refinement of the modeling, including estimates of relative energies, can be obtained relatively quickly by molecular mechanics, if a force field suitable to these systems is available.

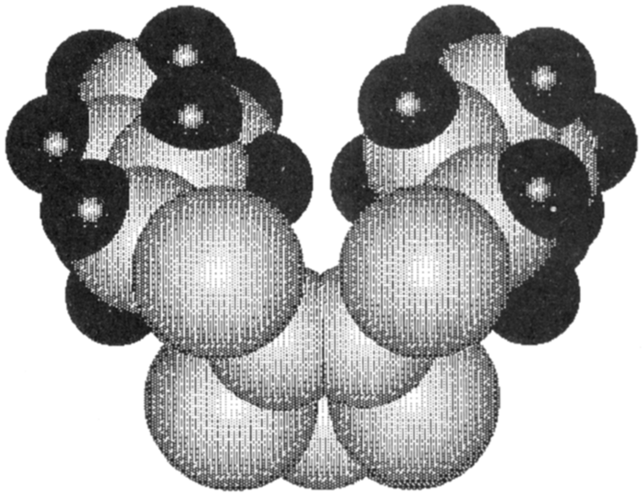

Figure 7. Hexyl system in the “cyclophane” structure.

Molecular Mechanics

We used the MM+ implementation provided in Hyperchem II and III[4] to represent plausible structures of the tetrathiafulvalenes.[5] CSC bond angles are not well-described in the potential field supplied, but constraining

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(4) HyperChem is a suite of modeling programs adapted to the Windows environment and distributed by HyperCube Inc., Waterloo, Ontario, Canada.

Table 3. Abbreviations for Computational Methods

RHF(opt)	UHF(opt)	RHF CI	ROHF CI
restricted Hartree–Fock SCF LCAO MO method, single determinant, no spin polarization. (Geometry is optimized.)	unrestricted Hartree–Fock SCF LCAO MO methods, single determinant, diffferent orbitals for different spins. (Geometry is optimized.)	RHF as defined in column 1, with configuration interaction but no further geometry optimization.	restricted open shell Hartree–Fock: single determinant, with identical space orbitals for spin-paired electrons, with configuration interaction

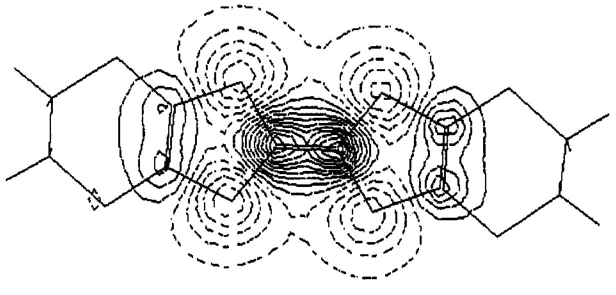

Figure 8. Contours of the highest occupied MO in the TTF core (ethyl example). Contours of the HOMO amplitude in a plane 0.5 Å above the core plane.

Table 4. PM3 Ionization Energies (kcal/mol) for TTF Species

species identifier	butyl	hexyl
syn	176	177
anti	187	200
twist C_i	174	175
twist C_s	174	
cyclophane	–	191

these angles to 90° improves the predicted structures substantially. We also observed very weak resistance to twisting of the five-membered rings of the TTF core. During optimization this “flexibility” often delayed and even prevented the arrival at the near-planar geometry of the TTF core known from X-ray studies. Constraining the torsion angles C=C–S–C in the TTF core removed this distraction. Relaxing the constraint on torsion angles after optimization was nearly complete produced the lowest energy, essentially planar structures. Relative energies are reported in Table 2 for butyl systems.

The first impression given by these exercises is that the chain orientation is of minor energetic significance. A more thorough investigation would find a large number of chain conformations of comparable energy. The situation promises to be more unwieldy for the structures formed with six-carbon chains.

Rather than construct a large number of model structures and let optimization methods find nearby structures, we have chosen to start with a few distinct structures and watch their evolution as they are “warmed” in the course of a molecular mechanics calculation. This capability is provided in the Hyperchem III package. Starting with syn, anti, and two twisted model structures of the hexyl species (similar to the forms found by MM+ optimization in the butyl species), we watched their motion through one thousand steps totaling 1 ps. After this thermal agitation, we reoptimized the energy starting from the last computed structure. The newly refined “equilibrium” structure was tested by another warming–reoptimization cycle. We accepted as reasonable the structure which survived several of these cycles. This persistence was usually apparent in the plots of potential energy in the course of the molecular dynamics run; the potential would be nearly constant, apart from typical periodic fluctuations if the structure were stable. A conformational change would be attended by a clear passage of the potential energy to a lower persistent value.

A candidate for the lowest energy structure for a TTF in which the short sides of the core rectagle are spanned by a hexyl chain is shown in Figure 6. A candidate for the “cyclophane” structure, which results when the longer sides of the core rectangle are spanned by a hexyl chain is shown in Figure 7.

These persistent structures were to be the starting point for structural investigations using approximate molecular orbital methods. We can get a preliminary view of the bonding in the TTF core by Hückel theory. The highest occupied MO has the form verified by more sophisticated calculations and shown in Figure 8.

We used the MNDO package of programs as expressed in Hyperchem III which is capable of finding least-energy geometries by gradient search within RHF or UHF models, with the possibility of imposing constrains on bond lengths, angles, or torsion angles. In some cases we used MNDO 6.0 as compiled for the 486 microprocessor, supplied by ARSoftware.[6] This implementation can optimize geometry for systems described by multiconfigurational wave functions.

AM1

The description of the BADT species within the AM1 parametrization is disappointing. The most significant flaws are the unrealistic value predicted for SC bonds, which are typically computed to be shorter than experimental studies would suggest by as much 0.10 Å. The AM1 parametrization also confuses the order of high-lying molecular orbitals, populating an orbital which extends the interior C=C bond to about 1.38 Å. This has the side effect of allowing the TTF core to twist out of planarity. Constraints can inhibit this behavior; for example one may force the occupation of the C=C bonding MO in the initial assignment; still the stability of the description is unsatisfactory.

PM3

Stewart's extensive study[7] of the performance of MNDO/AM1/PM3 establishes the clear superiority of the PM3 parameterization over its predecessors. This derives from the effort to optimize the parameter values to provide the best possible description of the molecular

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(5) The MM2 force field does not contain a number of the parameters necessary for description of the tetrathiafulvalenes. The HyperChem package proceeds to substitute “default” parameters as follows. Consider a chain A-B-C-D. If the parameters for torsion of the chain are not in the database, parameters for chains with three matches are sought. If this search fails, parameters for chains with two matches are sought, and in the last resort, chains with a single match are sought. This procedure may produce useful results in some cases, but clearly requires care.

(6) ARSoftware, Landover, MD. This package includes multiconfigurational descriptions of systems, but in contrast to HyperChem permits geometry optimization of systems described by several configurations.

(7) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 209.

Table 5. PM3 Computed and X-ray Structures of Smaller Alkyltetrathiafulvalenes

species: label and symmetry	energy: heat of formation, kcal/mol	model (see Table 4)	geometric parameters (see Table 1, Figure 1) (Å and deg) *a, A*	*b, B*	c, C	*e, D*	*f*, T1	*d*, T2
ethyl-C_2	93.14	RHF(opt)	1.351	1.759	1.756	1.736	1.821	1.358
	92.57	RHF-CI	122.8	95.7	114.9	103.5	180 ± 2	167 ± 3
	269.32	ROHF-CI						
Ethyl-C_s	93.10	RHF(opt)	1.351	1.759	1.756	1.736	1.821	1.358
	92.53	RHF-CI	122.8	95.7	114.9	103.6	180 ± 2	167 ± 2
	269.29	ROHF-CI						
ethyl X-ray structure[a]	partially oxidized	AuI_2^- counterion	1.362	1.746	1.754	1.749	1.814	1.358
			122.4	95.4	114.5	100.7		
ethyl X-ray structure[b]	neutral	"tub"	1.319					
propyl X-ray structure[c]	neutral	"twisted	1.341	1.759	1.763	1.750	1.818	1.336
		chair"	122.5	93.7	115.8	103.3		
methyl	105.54	RHF(opt)	1.352	1.767	1.737	1.736	1.826	NA
D_{2h}	105.25	RHF-CI	122.5	94.8	123.8	95.7	180 ± 1	
	285.96	ROHF-CI						
core	71.71	RHF(opt)	1.350	1.765	1.741	NA	NA	1.342
D_{2h}	70.86	RHF-CI	123.0	95.3				NA
	250.15	ROHF-CI						
SH-substituted	95.46	RHF(opt)	1.350	1.768	1.759	1.736	NA	1.359
core	95.10	RHF-CI	123.0	96.4	120.5	[99.4]	180 ± 1	NA
D_{2h}[d]	278.90	ROHF-CI						

[a] Geiser, U.; Wang, H. H.; Webb, K. S.; Firestone, M. A.; Beno, M. A.; Williams, J. M. *Acta Crystallogr.* **1987**, *C43*, 996; isolated linear AuI_2^- fragments with partly oxidized TTF; shortened S···S contacts (<3.60 Å). [b] Kobayashi, H.; Kobayashi, A.; Sasaki, Y.; Saito, G.; Inokuchi, H. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 301. [c] Porter, L. C.; Kini, A. M.; Williams, J. M. *Acta Crystallogr.* **1987**, *C43*, 998; "twisted chair" neutral species. [d] This is not the lowest energy species: a C_{2h} form with alternating 0,180 torsion angles "T2" (in this case applying to the CCSH chain) and bond-length nonequivalences on the third decimal, lies at 91.80 kcal/mol. We report this structure for its consistency with larger systems.

Table 6. PM3-Computed Structural Parameters for Larger Alkyltetrathiafulvalenes

species: label and symmetry	energy: heat of formation (kcal/mol)	model (see Table 4)	geometric parameters (see Table 1, Figure 1) (Å and deg) *a, A*	*b, B*	*c, C*	*d, D*	*e, T1*	*f, T2*	first optical transition: λ (nm)
hexyl 10	69.73	RHF(opt)	1.349	1.758	1.758	1.752	1.833	1.357	235
(syn) C_2	69.26	RHF-CI	123.7	96.4	117.6	104.9			
(E-cation)	247.25	ROHF-CI							
hexyl 10	69.04	RHF(opt)	1.349	1.759	1.757	1.748	1.827	1.356	234
(anti) C_i	68.56	RHF-CI	123.4	96.6	111.9	105.6			
(E-cation)	269.32	ROHF-CI							
hexyl 10	70.23	RHF(opt)	1.349	1.757	1.758	1.745	1.833	1.356	234
(twist) C_s		RHF-CI	123.2	96.4	111.8	106.5	180 ± 5	108 and 139	
		ROHF-CI							
hexyl 10	70.93	RHF(opt)	1.350	1.757	1.761	1.747	1.833	1.356	234
(twist) C_2		RHF-CI	123.2	96.4	111.5	106.4	180 ± 5		
(E-cation)	245.71	ROHF-CI							
hexyl 16	79.81	RHF(opt)	1.347	1.765	1.773	1.738	1.838	1.361	259
cyclophane	79.42	RHF-CI	122.5	92.8	121.8	107.9	162	46 and 57	
(E-cation)	271.26	ROHF-CI							
butyl	84.75	RHF(opt)	1.349	1.759	1.755	1.746	1.824	1.356	233
twist ≈ D_2		RHF-CI	123.5	96.3	112.8	108 ± 2	180 ± 5	108 and 139	
(E-cation)	258.83	ROHF-CI							
butyl	88.36	RHF(opt)	1.349	1.758	1.758	1.744	1.829	1.355	238
syn (C_2)		RHF-CI	123.2	96.4	112 ± 2	105 ± 3	180 ± 5	112 and 132	
(E-cation)	264.49	ROHF-CI							
butyl	88.61	RHF(opt)	1.349	1.758	1.755	1.744	1.829	1.356	235
anti (C_i)		RHF-CI	123.5	96.4	113	105 ± 2	180 ± 5	102 and 119	
(E-cation)	275.44	ROHF-CI							
butyl	84.68	RHF(opt)	1.350	1.757	1.764	1.738	1.827	1.355	230
twist C_s		RHF-CI	123.1	96.3	110	107	180 ± 5	144 ± 7	
(E-cation)	258.62	ROHF-CI							
butyl anti		X-ray	1.337	1.761	1.750	1.749	1.820	1.341	
		structure[a]	123.0	95.6	117.5	101.5	180 ± 5		

[a] Das, K.; Sinha, U. C.; Kumar, S. K.; Singh, H. B.; Mishnev, A. *Acta Crystallogr.* **1992**, *C48*, 488.

geometry and heats of formation of molecules involving C and S in environments not very different from those of tetrathiafulvalenes. The most striking improvement is in molecules with adjacent lone-pair bearing atoms and in hypervalent molecules. Perhaps of more interest in this study, PM3 reproduces CS bond lengths within 0.04 Å, a considerable improvement on the AM1 systematic *under*estimate of these lengths by about 0.10 Å.

The tendency to twist about the TTF central double bond (marked in AM1) is less problematic in PM3. As in molecular mechanics studies, one may find an optimum structure efficiently by constraining the tetrathiafulvalene core to be planar in early states of the optimization and then relaxing the constraint after the optimization was nearly complete. In each case vibrational analysis showed that the structure was an equilibrium point, though deformation (arching, not twisting) was very easy. This device was not needed in the larger systems ($n > 3$). Since there are a great many alternative conformations in the macrocyclic rings, we do not guarantee that our structures are global minima.

Hyperchem III permits configuration interaction (CI)

Table 7. PM3-Computed Structure of Selected Monocations

species: label and symmetry	energy: heat of formation (kcal/mol)	model (see Table 4)	geometric parameters (see Table 1, Figure 1) (Å, deg)					
			a, *A*	*b*, *B*	*c*, *C*	*d*, *D*	*e*, *T1*	*f*, *T2*
hexyl 10	242.0	UHF(opt)	1.396	1.720	1.740	1.746	1.833	1.369
(syn) C_2			122.6	96.5	117.0	106.2	180 ± 5	90 and 70
(E-dication)	510.9	RHF						
hexyl 10 (anti)	241.4	UHF(opt)	1.396	1.721	1.738	1.747	1.833	1.369
			122.6	96.6	116.9	106.5	180 ± 5	90 and 70
(E-dication)	507.5	RHF						
hexyl 16	239.4	UHF(opt)	1.395	1.711	1.744	1.743	1.843	1.370
twist C_i			122.5	96.4	111.7	107.6	180 ± 5	
(E-dication)	500.6	RHF						
hexyl 16	264.9	UHF(opt)	1.390	1.723	1.748	1.743	1.843	1.380
cyclophane			122.2	94.0	120.6	95.9		
(cation)	536.3	RHF						
butyl	253.3		1.397	1.719	1.745	1.730		1.370
twist C_s				96.2	111.4	108.2		
dication	513.8							

or mixing of excited states into the ground state determinant. This calculation is a useful precaution against misleading behavior in the Restricted Hartree–Fock calculations which lead to optimized geometries. If CI proves extensive, the single determinant used in RHF may not lead to a reliable geometry. This is often the case in systems with diradical character, for example, or for any systems in which low-lying virtual orbitals are present. Generally a multiconfigurational SCF function is required for a satisfactory description of these systems.

We had suspected that CI would be extensive in these species, which have numerous high-lying MOs derived from sulfur lone pairs and local π bonds. However the task of modeling was considerably simplified by the modest extent of CI in the neutral systems. The energetic impact was always less than 1 kcal/mol. CI is indispensable to the description of the cations, and there are bound to be at least minor differences between the UHF-optimized and ROHF-CI-optimized structures. Spot tests showed these differences always to be small.

Relative Energetics of Neutral Species

The large number of conformers available in the BADT systems, especially for longer alkyl chains, makes us hesitate to claim that we have found absolute minima in the potential energy surfaces. However we have some confidence in the following statements.

1. Molecular mechanics calculations, constrained so that reasonable CSC angles are achieved in small systems, can be said to agree with the most effective PM3-MNDO calculations in the sense that all plausible structures lie within 10 kcal/mol of one or another for the butyl species. (There is disagreement in details of energetic ordering; orbital methods favor twisted (antiparallel) forms.)

2. In the hexyl-chain species, the orientation of the chains is of little energetic significance. Essentially strain free conformations are available for all structural types in which the shorter edges of the TTF rectangle are spanned.

Spectra of Neutral Species

We used the semiempirical program of M. Zerner (ZINDO/S) as provided in Hyperchem III. In this program excited states are described as combinations of singly excited states derived from the ground state (single) determinant. Parameters are chosen to produce reasonable spectra rather than ground state properties, so we used PM3-optimized molecular structures. Transition energies in these calculations are systematically overestimated, but accurate within 0.2–0.4 eV; differences between calculated results for related systems are probably more reliable, owing to cancelation of similar errors in the description of each system. The results of this exercise are simply the following: the TTF core defines the spectrum; the persistent neutral core has a persistent optical spectrum dominated by excitation from the HOMO (Figure 7), with computed transitions all lying in the range of 230 to 240 nanometers for $n = 2$, 4, and 6; the cyclophane, in which the TTF core is bowed out of planarity, is red-shifted by about 20 nm.

This latter point is not inconsistent with the observation that the cyclophane is colored, while other species are not.

(Vertical) Ionization Energies

The simplest estimate of the vertical ionization energy is given by Koopmans' theorem, in which the MO energies correspond to ionization energies. This gives a helpful first impression of large effects. Alternatively, we may compute the energy of the 2n - 1 electron system and report the difference. This has semiquantitative utility.

One may describe the open shell radical cation by the unrestricted Hartree–Fock (UHF) method, wherein electrons of different spins can occupy orbitals differing in spatial distribution, or we can restrict the doubly-occupied MOs to have the same spatial form, as in the RHF method. The UHF method is convenient, but does not represent a pure spin state of the radical cation. We used this restricted open-shell Hartree–Fock method (ROHF) even though this wave function does not obey Brillouin's theorem; certain singly-excited states do mix with the ROHF ground determinant. We chose to include these singles, using the ROHF-CI method (with 300 microstates) to represent the vertically-ionized state's wave function. A guide to these abbreviations is provided in Table 3.

PM3 calculations provide an account of ionization energies which are generally superior to estimates by AM1, but one should not expect accuracy greater than about 0.25–0.5 eV (12 kcal/mol) in the systems we describe. Our results are collected in Table 4. As usual we presume that differences in computed ionization energies in isomers are more reliable than absolute values. Alkane thiols are described very well; thiophene is described poorly, in the results reported by Stewart. The (gas phase, "vertical") ionization energies are typically overestimated for sulfur systems.

Geometric Consequences of Ionization

We optimized the geometry of the cations using the UHF model, in order to make a slightly more realistic estimate of the oxidation potentials of these species and in part to prepare the system for a second vertical ionization. As one would have predicted in view of the orbital from which charge is extracted (Figure 8) the local C=C double bonds are lengthened and the CS bonds connecting local C=C bonds are shortened; effects are ca. 0.02 Å. The systems are not changed in symmetry, though one may expect easier twisting about the weakened C=C bonds.

This addresses the problem of the distinct oxidation potentials observed for the local-ring species, and the single (but broadened) oxidation potential observed for the cyclophane.

Detailed Results and Conclusions on PM3 Computed Structures

Tables 5–7 contain values for the geometric parameters obtained within the PM3 parametrization using the several forms of the wave function. Table 1 defines the geometric parameters (See Figure 1 for a pictorial version). Table 4 summarizes the abbreviations for the forms of the wave function. On the basis of these details, we offer the following general remarks.

Comparison of the PM3 computed optimum structures with experimental structures of BADT with the alkyl chain length $n = 1-4$ show agreement of computed bond lengths with X-ray values within 0.02 Å. We were surprised only by the C=C interior bond reported in an X-ray study[8] to be very short, equal to 1.31 Å.

Conclusions

Modeling permits the following general statements: (1) Within the family of 3,3′,4,4′-tetrakis(alkylthio) substituted species, the tetrathiafulvalene core is essentially structurally invariant with approximate D_{2h} symmetry. (2) The alkyl rings can occupy a number of conformations of roughly comparable energy. The number of these conformations increases exponentially with chain length. (3) The highest occupied molecular orbital (HOMO), from which ionization occurs, is an antibonding combination of bonding local CC π bonding MO of symmetry b_{1u} in the core symmetry group D_{2h}. There is considerable sulfur lone pair amplitude in the HOMO. (4) The "vertical" ionization energies (lacking any representation of structural relaxation or medium effects) range from 170 to 200 kcal/mol. Values drift slowly downward as the size of the alkyl ring increases. For the butyl and hexyl systems the syn form is easier to ionize than the anti form. (5) For the hexyl system, a "cyclophane" structure can be formed, though it is less stable than the "D_{2h}" form by approximately 10 kcal/mol. In this species the tetrathiafulvalene is forced well out of the persistent (approximate) D_{2h} structure shown in all other members of the family. (6) The cyclophane is harder to ionize than the more stable hexyl isomers. (7) The optical spectra of all species are similar, with the exception of the "cyclophane". This species has low-energy electronic transitions which suggest that the species should be colored.

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Supporting Information Available: Cartesian coordinates for all species described here, in the PM3-optimized equilibrium geometry, are available from the authors as PDB files. Those who wish copies should supply a 3.5 inch diskette.

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[8] Kobayashi, H.; Kobayashi, A.; Sasaki, Y.; Saito, G.; Inokuchi, H. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 301.