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Synthesis, Chemical and Physical Properties, X-ray Crystal Structure, and Theoretical Calculations of 9-[1-(2,4,6-Cycloheptatrienylidene)]xanthene[†]

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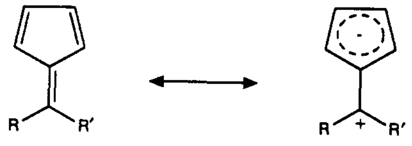
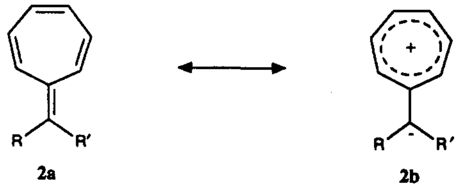
The title heptafulvalene (**3**) was synthesized in high yield by treatment of (9*H*-xanthyl)tropylium tetrafluoroborate (**11**) with either methanol, *N*,*N*-diisopropylethylamine, or dimethyl sulfoxide (DMSO). A single-crystal X-ray diffraction structure determination and MNDO, AM1, PM3 semiempirical molecular orbital and molecular mechanics theoretical calculation studies indicate that the geometry of title compound **3** is distorted into a nonplanar "S" shape around the exocyclic double bond connecting the two rings. This is due to the nonbonded steric interactions occurring between the peri hydrogens on the xanthyl portion of the molecule and those at the 2- and 7-positions on the cycloheptatrienyl ring. UV-visible spectral studies and the lack of reactivity toward lithium aluminum hydride clearly indicate polyolefin character and a minimal polar nature for compound **3**. These results are in good agreement with the low dipole moment calculated by the semiempirical methods.

The fulvenes have been recognized as intriguing compounds since they were first prepared and reported by Thiele nearly a century ago.[1] The realization that such compounds might possess aromatic character stimulated their preparation and led to investigation of the relationships between their structures and their chemical and physical properties. During the last three decades, several general reports have reviewed the progress of fulvene chemistry with special consideration to the question of the nature and origin of the aromatic character of fulvenes.[2] The results arising from these studies indicate that the nature of the bonding in fulvenes can be described on the basis of valence bond formalism as a resonance hybrid of the covalent resonance structure **1a** and the dipolar structure **1b**. Resonance structure **1b** contributes relatively more to the resonance hybrid than does **1a** in compounds with electron-donating substituents at the exocyclic carbon atom (R or R′).[3]



1a **1b**

This phenomenon can be explained in terms of stabilization through the cyclic conjugated system in accordance with Hückel's rule.[4] In agreement with this concept, the behavior of fulvenes can be shifted toward systems with either polyolefinic or conjugated character depending on the variation of the substituents at the exocyclic carbon atom. Recently, the chemistry of fulvenes with a cycloheptatriene moiety, namely heptafulvalenes, has become of considerable interest due to the tendency of cycloheptatriene to form a stable cation. This could offer a fulvene system with a high degree of dipolar character, as suggested by the resonance forms **2a** and **2b**.[2d,3a]



2a **2b**

On the other hand, little is known about the chemistry of heptafulvalenes containing hetero atoms in the ring adjacent to the cycloheptatriene moiety. There is a brief report describing the synthesis of some hetero analogues of heptafulvalene in very low yields.[5] The characterization of these analogues was based only on their ^{1}H NMR spectra. For example, it was reported that heptafulvalene **3**, which was obtained in 8% yield by reacting xanthone with 7-cycloheptatrienyl carbonyl chloride in the presence of triethylamine, is an unstable compound in the solid phase and that its elemental analysis could not be performed.[5]

During the course of our studies on 9-xanthyl systems,[6] we became intrigued with the fact that heptafulvalene **3** was not formed as a product under any of the reaction conditions which we produced. We have now found that **3** is, in fact, a very stable compound in the solid phase. In this paper, we report the synthesis, X-ray structure, and the chemical and physical properties of heptafulvalene **3** as well as its gas-phase geometry as calculated by MNDO, AM1, and PM3 semiempirical molecular orbital and molecular mechanics methods. We then compare these values with those of some known heptafulvalenes that do not contain heteroatoms in their rings.

Results and Discussion

General synthetic entries to heptafulvalenes and related compounds can be planned according to the nature of appropriate key starting compounds. The classical approach through addition of a suitable organomagnesium or related organometallic compound to a carbonyl carbon followed by dehydration is not feasible in the case of the cycloheptatrienylxanthyl system studied here. This is because of the great difficulty in generating a tropylium anion equivalent[7] to add to 9-xanthone. In fact, dehy-

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[†] Dedicated to Professor Paul von Ragué Schleyer on the occasion of his 60th birthday.

(1) Thiele, J. *Chem. Ber.* **1900**, *33*, 3359.

(2) (a) Day, J. H. *Chem. Rev.* **1953**, *53*, 167. (b) Bergman, E. D. *Chem. Rev.* **1968**, *68*, 41. (c) Prinzbach, H. *Pure Appl. Chem.* **1971**, *28*, 287. (d) Pietra, F. *Chem. Rev.* **1973**, *73*, 293.

(3) (a) Halton, B.; Buckland, S. J.; Mei, Q.; Stang, P. J. *Tetrahedron Lett.* **1986**, *27*, 5159. (b) Halton, B.; Randall, C. J.; Gainsford, G. J.; Stang, P. J. *J. Am. Chem. Soc.* **1986**, *108*, 5949. (c) Halton, B.; Randall, C. J.; Stang, P. J. *Ibid.* **1984**, *106*, 6108.

(4) Hückel, E. *Z. Physik* **1931**, *70*, 204.

(5) Kato, K.; Kitahara, Y.; Morita, N.; Asao, T. *Chem. Lett.* **1977**, *8*, 873.

(6) (a) Badejo, I. T.; Karaman, R.; Lee, N. W. I.; Lutz, E. C.; Mamanta, M. T.; Fry, J. L. *J. Chem. Soc., Chem. Commun.* **1989**, 566. (b) Badejo, I. T.; Karaman, R.; Fry, J. L. *J. Org. Chem.* **1989**, *54*, 4591. (c) Karaman, R.; Badejo, I. T.; Fry, J. L. *J. Am. Chem. Soc.* **1989**, *102*, 7926.

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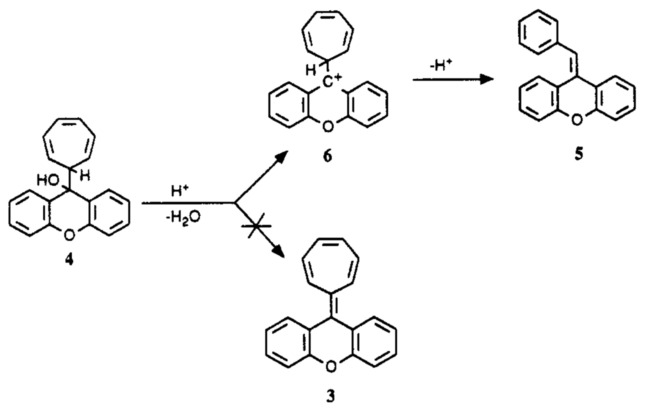
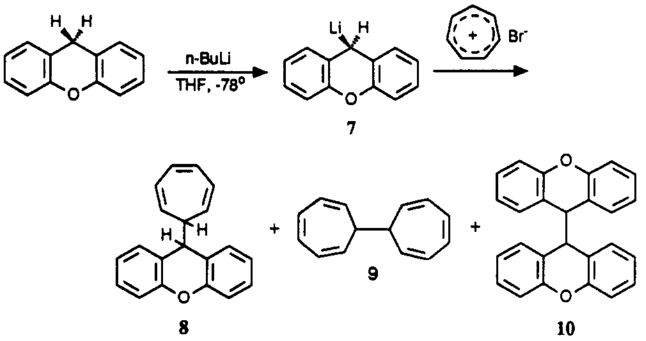
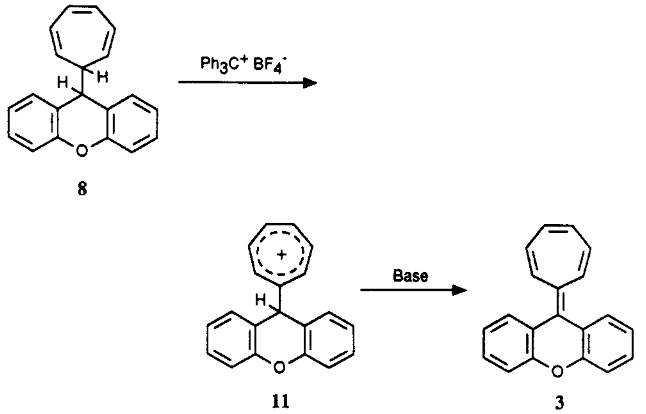
Scheme I



Scheme II



Scheme III



dration of 9-[1-(2,4,6-cycloheptatrienyl)]-9-xanthydrol (**4**), recently synthesized by a novel umpolung method, produced 9-benzylidenexanthene (**5**) as the exclusive dehydration product. It failed to give any heptafulvalene **3** (Scheme I).[6b] This appeared to be due to the relatively high thermodynamic stability of **5** and the relatively low energy barrier for the ring contraction rearrangement reaction of carbocation **6** to **5**.

The successful synthetic sequence to **3** which we have now employed involved first the generation of 9-lithioxanthene (**7**) from 9*H*-xanthene and *n*-butyllithium followed by addition of tropylium bromide to give a 45% yield of 9-[1-(2,4,6-cycloheptatrienyl)]-9*H*-xanthene (**8**) along with 17% of ditropyl (**9**) and 20% of dixanthene (**10**) (Scheme II) upon quenching with water.

The formation of ditropyl (**9**) and dixanthene (**10**) could have occurred via single-electron transfer (SET) from 9-lithioxanthene into tropylium bromide to generate 9-xanthyl and tropyl radicals. Subsequent dimerization of the radicals would give the respective dimeric products. It is also likely that the formation of **8** could have occurred by indiscriminate dimerization, but up to now there is no sharp evidence to support or to reject this notion. The recent study of Kochi and co-workers on the electron donor–acceptor (EDA) properties of the tropylium cation indicates that this carbocation has a great ability to accept an electron from neutral arenes, so an SET process from 9-lithioxanthene seems like a reasonable pathway for these reactants to follow.[8]

Hydride abstraction from **8** could lead to the formation of either of the carbocations **6** or **11**, where carbocation **11** is derived from hydride abstraction of allylic hydrogen of the cycloheptatrienyl moiety and carbocation **6** from that of the allylic/benzylic hydrogen in the xanthene ring. The results of MNDO calculations for both carbocations indicate that carbocation **11** should be 8.7 kcal/mol more stable than carbocation **6** (ΔH_f° = 224.9 vs 233.6 kcal/mol).[9] Moreover, we have found that the MNDO and PM3[10] calculated activation energies for the isomerization process **6** → **11** (1,2-hydride shift) are very high (73.0 and 85.0 kcal/mol, respectively). These results suggest that hydride abstraction of **8** could lead only to the formation of **11**, which ought to be resistant to further rearrangement.

As expected, treatment of **8** with triphenylcarbenium tetrafluoroborate ($Ph_3C^+BF_4^-$) in dichloromethane at room temperature gave, in addition to triphenylmethane, only one product in 84% yield. The ^{1}H NMR and ^{13}C NMR spectra for this compound were consistent with the structure of carbocation **11** but not with carbocation **6** (see Scheme III and the Experimental Section). Not unexpectedly, when the brownish yellow powder of **11** was refluxed in either dichloromethane or acetonitrile for more than 4 h, no decomposition was observed. This result is in accord with the results of the MNDO and PM3 calculations. Finally, treatment of **11** with either absolute methanol (MeOH) or dimethyl sulfoxide (DMSO) for 1 h at room temperature gave heptafulvalene **3** in 66% and 95% yields, respectively. When *N*,*N*-diisopropylethylamine was used as a base, it gave only a 48% yield of **3** (Scheme III). The structure identification of the bright yellow solid **3** was based on its ^{1}H NMR and ^{13}C NMR spectra and single-crystal X-ray diffraction structure.

Because fulvalenes can potentially exhibit the properties of species having highly dipolar structures, we measured the ultraviolet–visible spectrum of heptafulvalene **3** in different solvents. An almost total lack of solvent effect was observed. The fact that there was no significant shift in the absorption maximum of the electronic spectrum of **3** with a change of solvent polarity (from absolute ethanol to cyclohexane) indicates that the polarity of the electronic excited state is similar to that of the ground state.[11,12]

Since fulvalenes bearing a highly polar central bond have been reported to be reduced by lithium aluminum hydride,[2b] we treated heptafulvalene **3** with $LiAlH_4$ in ether for 12 h. After workup, the starting material was recovered. No reduction product was observed. This lack

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(7) (a) Dauben, H. J., Jr.; Rifi, M. R. *J. Am. Chem. Soc.* **1963**, *85*, 3041. (b) Doering, W. von E.; Gaspar, P. *Ibid.* **1963**, *85*, 3043. (c) Maltz, H.; Kelly, B. A. *J. Chem. Soc., Chem. Commun.* **1971**, 1390. (d) Deganello, G.; Boschi, T.; Toniolo, L. *J. Organomet. Chem.* **1975**, *97*, C46.

(8) Takahashi, Y.; Sankararaman, S.; Kochi, J. *J. Am. Chem. Soc.* **1989**, *111*, 2954.

(9) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899, 4907.

(10) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 209, 221.

(11) The $\lambda_{max}^{solvent}$ nm (log ϵ) values are: CH_2Cl_2, 366 (4.32); cyclohexane, 364 (4.32); $CHCl_3$, 368 (4.31); CH_3CN, 364 (4.29); absolute C_2H_5OH, 364 (4.30).

(12) Williams, D. H.; Fleming, I. *Spectroscopic Methods in Organic Chemistry*, 4th ed.; McGraw-Hill (UK): London, 1987.

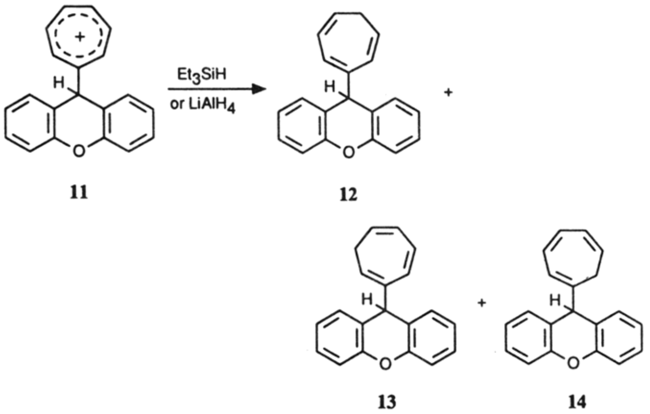
Table I. Bond Distances for 3 Determined by X-ray and Calculated

		bond distances, Å				
atom 1	atom 2	X-ray	MNDO	AM1	PM3	MMX
O1	C5	1.374	1.371	1.392	1.387	1.374
C1	C2	1.389	1.406	1.394	1.391	1.400
C1	C6	1.395	1.410	1.401	1.396	1.404
C2	C3	1.381	1.405	1.395	1.392	1.399
C3	C4	1.374	1.400	1.390	1.390	1.400
C4	C5	1.380	1.416	1.401	1.398	1.400
C5	C6	1.396	1.434	1.410	1.408	1.410
C6	C7	1.478	1.488	1.462	1.468	1.487
C7	C8	1.362	1.371	1.362	1.359	1.373
C8	C9	1.467	1.480	1.455	1.459	1.474
C9	C10	1.336	1.360	1.340	1.340	1.356
C10	C11	1.442	1.459	1.439	1.444	1.453
C11	C11′	1.326	1.357	1.347	1.342	1.358
H1	H9′	2.38	2.92	2.33	2.44	2.46
H9	H1′	2.39	2.93	2.36	2.47	2.45

Table II. Bond Angles for 3 Determined by X-ray and Calculated

atoms			bond angles, deg				
1	2	3	X-ray	MNDO	AM1	PM3	MMX
C2	C1	C6	121.2	120.8	120.5	120.0	120.5
C1	C2	C3	120.1	120.6	120.7	120.6	120.1
C2	C3	C4	119.7	120.4	120.2	120.6	119.8
C3	C4	C5	119.9	118.7	118.6	118.5	120.3
O1	C5	C4	116.2	118.0	115.9	116.1	119.3
O1	C5	C6	121.8	120.4	122.0	122.4	120.6
C4	C5	C6	122.0	121.6	122.0	121.5	120.1
C1	C6	C5	116.9	117.6	117.8	118.6	119.1
C1	C6	C7	125.6	125.9	123.8	124.0	124.7
C5	C6	C7	117.6	116.5	118.3	117.4	116.1
C6	C7	C8	123.8	125.0	123.8	124.0	125.6
C7	C8	C9	122.4	123.2	121.7	121.6	119.9
C8	C9	C10	127.6	126.5	127.0	126.5	128.1
C9	C10	C11	127.8	127.1	127.5	126.3	128.1
C9	C8	C9′	114.2	113.7	116.2	116.3	119.5
C5	O1	C5′	117.2	116.4	114.3	113.8	111.1
C6	C7	C6′	112.4	109.8	112.3	112.0	108.7
C10	C11	C11′	125.7	125.7	125.8	126.0	127.3

Scheme IV



of reactivity of **3** toward LiAlH$_4$ again indicates a low polarity of the central bond. This, in turn, reflects the relatively small contribution of a dipolar structure to the physical and chemical properties of **3**.

When heptafulvalene **3** was treated with methanesulfonic acid in CD$_2$Cl$_2$ at room temperature, a solution of brownish color was immediately formed. The ^{1}H NMR and ^{13}C NMR spectra of the brown solution were identical to those of a known solution of carbocation **11** and remained unchanged after 24 h. Addition of either triethylsilane (Et$_3$SiH) or lithium aluminum hydride produced three products in equal amounts with a combined yield of 91%. Analysis by ^{1}H NMR and GC/MS techniques indicated that the mixture was composed of three isomers (**12**, **13**, **14**, Scheme IV). Attempts to physically separate them failed.[13]

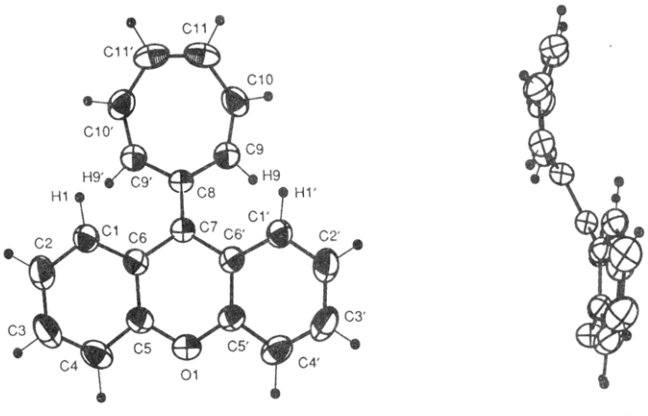


Figure 1. Full and side ORTEP views of the structure of 9-[1-(2,4,6-cycloheptatrienylidene)]xanthene (**3**) as determined by single-crystal X-ray diffraction.

X-ray Crystallography and Theoretical Calculations. The X-ray crystal structure for heptfulvalene **3** is depicted in Figure 1 in both full and side ORTEP views. The corresponding PLUTO views of the optimized AM1 structure are shown in Figure 2. Selected observed and calculated (MNDO, AM1, PM3, and MMX) bond distances, bond angles, and torsion angles appear in Tables

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[13] The spectroscopic data of these compounds compared well with those of similar isomers: Takahashi, K.; Suzuki, T.; Toda, H.; Takase, K.; Koseki, S.; Nakajima, T. *J. Org. Chem.* **1987**, *52*, 2666.

Table III. Torsion Angles for 3 Determined by X-ray and Calculated

atoms				Torsion Angles, deg				
1	2	3	4	X-ray	MNDO	AM1	PM3	MMX
C5′	O1	C5	C4	−158.1	−149.4	−154.9	−153.6	−139.7
C1	C6	C7	C6′	149.8	140.0	149.1	146.9	138.3
C6	C1	C2	C3	−0.2	0.7	0.3	−0.2	1.5
C2	C1	C6	C5	−3.6	−4.9	−3.1	−3.3	−3.6
C2	C1	C6	C7	176.0	176.4	177.8	177.6	179.7
C1	C2	C3	C4	2.8	2.4	2.0	2.6	0.7
C2	C3	C4	C5	−1.5	−1.2	−1.2	−1.3	−0.8
C3	C4	C5	O1	177.6	176.4	178.9	178.3	179.8
C3	C4	C5	C6	−2.4	−3.2	−1.8	−2.3	−1.3
O1	C5	C6	C1	−175.2	−173.4	−176.8	−176.0	−177.5
O1	C5	C6	C7	5.2	5.4	2.4	3.1	−0.9
C4	C5	C6	C1	4.9	6.2	3.9	4.5	3.5
C4	C5	C6	C7	−174.7	−175.0	−176.9	−176.3	−179.9
C1	C6	C7	C8	−33.5	−47.1	−35.5	−37.9	−40.7
C5	C6	C7	C8	146.1	134.2	145.4	143.0	142.9
C6	C7	C8	C9	−172.0	−174.4	−173.8	−173.3	−176.3
C7	C8	C9	C10	−146.8	−132.2	−141.2	−139.1	−153.1
C6	C7	C8	C9′	−4.3	2.3	0.7	0.8	−5.1
C9′	C8	C9	C10	44.5	50.9	45.4	48.0	35.8
C9	C10	C11	C11′	−28.9	−28.7	−27.1	−30.1	−21.2

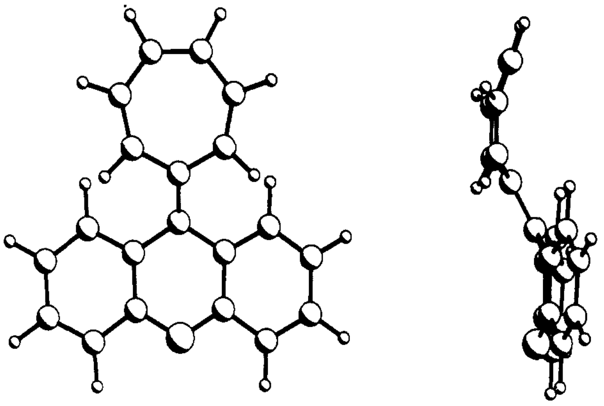

Figure 2. Full and side PLUTO views of the energy-optimized structure of 9-[1-(2,4,6-cycloheptatrienylidene)]xanthene (**3**) as determined by AM1 calculations (numbering same as in Figure 1).[14]

I–III for comparison purposes.[14] The observed bond lengths, bond angles, and torsion angles all fall within a reasonable range expected for similar compounds.[15] As may be seen, the agreement between the experimental and calculated values is fairly good for all computational methods. The alternation of single and double bonds in the cycloheptatriene ring, for example, is correctly predicted by each of the computational methods.[16]

Nevertheless, the discrepancies, which range up to 0.03 Å for bond lengths, 3° for bond angles, and nearly 15° for torsion angles, are clearly outside the experimental errors. There are, however, several structural features which should be pointed out. The most interesting feature is the S-shaped appearance of the molecule as shown in Figure 1. This distortion is caused primarily by nonbonded steric repulsions between the peri hydrogens on the xanthyl moiety and those adjacent to the exocyclic double bond on the 7-membered ring which project directly toward them (i.e., H1–H9′ and H1′–H9 interactions). This conclusion is supported by MNDO, AM1, and PM3 calculation results which indicate that the S-shaped conformation is 35–45 kcal/mol more stable than the totally planar structure, depending upon the method used (Table IV).[17] The calculated interatomic distance between H1 and H9′ for a planar structure is 1.42 Å (MNDO), whereas the experimental distance between these two atoms in the S-shaped geometry is 2.38 Å.

Table IV. Heats of Formation and Dipole Moments Calculated for 3

geometry	MNDO	AM1	PM3	MMX
optimized				
$\Delta H_f°$, kcal/mol	75.0	89.9	85.9	82.9
μ, Debye	1.04	1.31	1.09	0.22
planar cycloheptatrienyl				
$\Delta H_f°$, kcal/mol	82.1	95.9	91.8	
μ, Debye	1.20	1.47	1.26	
totally planar				
$\Delta H_f°$, kcal/mol	120.3	135.3	121.1	

Another significant structural feature of **3** is the distortion of the cycloheptatriene ring from planarity (the torsion angle C9–C10–C11–C11′ is −28.9°). This distortion may be due to the packing forces. This is as judged by the results of the semiempirical MO calculations which yield an estimated energy difference between the X-ray structure and that with a planar cycloheptatriene ring of only about 6 kcal/mol (Table IV). These calculations reveal that there is a fair amount of conformational flexibility, which should be manifested in the solution structure of the molecule. This conclusion is also supported by the observation that in solution heptafulvalene **3** behaves as a conjugated system. This is evident from its reactivity with alkenes[5] and its relatively long wavelength UV–visible absorption maximum (λ_{max}^{EtOH} = 364 nm). It is interesting to note that 1,3,5-cycloheptatriene is also nonplanar as determined by microwave in the gas phase,[18] whereas the X-ray crystal structure of tropone was found to be essentially planar at −60 °C.[19]

The dipole moments of fulvenes can be obtained by experimental measurements as well as by theoretical calculations. It has been shown that calculated values of

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[14] The observed and calculated geometrical parameters appear in the tables of supplementary material along with the PLUTO drawings of the energy-minimized structures of **3** calculated by MNDO, PM3, and MMX methods.

[15] Thomas, R.; Coppens, P. *Acta Crystallogr.* **1972**, *B28*, 1800.

[16] Cf. Nakajima, T. *Top. Curr. Chem.* **1972**, *32*, 1.

[17] The calculation of the planar structure was made by imposing the cycloheptatrienyl and xanthyl rings in the plane of the central bond while optimizing all bond lengths and angles. For the S shape conformation (X-ray structure), the torsion angles were forced while all other parameters were optimized. The heats of formation of the X-ray structure and the gas-phase optimal structures are almost identical. These and related values are listed in Table IV.

[18] Butcher, S. S. *J. Chem. Phys.* **1965**, *42*, 1833.

[19] Barrow, M. J.; Mills, O. S.; Filippini, G. *J. Chem. Soc., Chem. Commun.* **1973**, 66.

dipole moments of a variety of compounds by semiempirical methods, such as MNDO, are often in good accord with experimental data.[9] The magnitude of the dipole moment in fulvenes has proved to be a useful tool in predicting qualitatively the dipolar nature of the structure.[2,3,20] The calculated dipole moment of heptafulvalene **3** was found to be greatly dependent on its conformation. The calculated values for the X-ray structure and the gas-phase optimal conformation are very close (0.9 and 1.04 D, respectively) and larger than the values which we obtained by MNDO (0.07 D), AM1 (0.37 D), or PM3 (0.40 D) for heptafulvene (**2**, R = R′ = H).[21] When the cycloheptatriene ring is forced to rotate from its optimal arrangement,[22] other conformations with high dipole moments are populated. For example, the calculated dipole moment for the conformation with torsion angle $\phi_{C6-C7-C8-C9'} = 325°$ is 5.11 D. However, this conformation is energetically expensive and not accessible ($\Delta H_f° = 140.4$ kcal/mol). In contrast, rotations up to ±35° from the optimal arrangement do not lead to a significant change in either the energies (less than 4 kcal/mol) or the dipole moments (less than 0.2 D) of the resulting conformers.

Finally, the problem of finding globally optimized minima by computational methods must be mentioned. The molecular mechanics structural parameters reported in the tables for compound **3** were derived by using the experimental X-ray structure as input. When a planar structure was used as input for **3**, the MMX calculations produced an energy-minimized structure in which the C7–C8 bond was elongated to 1.41 Å, the torsion angle $\phi_{C6-C7-C8-C9'} = 56.95°$, and the H1–H9′ distance was 2.49 Å.

Conclusions

The combined experimental/theoretical study reveals the following. (1) In contrast to a previous report, heptafulvalene **3** is a stable compound, but its physical and chemical properties suggest little, if any, aromatic character beyond that in the two phenyl rings. (2) The polyolefinic nature of **3** is dominant and the characteristics of a dipolar structure are very small, similar to that found for simple heptafulvalenes. This is presumably due to the relatively low stability of a xanthyl anion. (3) In heptafulvalene **3** there is a fair amount of conformational flexibility, but the barrier to formation of the completely planar conformation is very high. (4) The observation that protonation of **3** led to the formation of only tropylium ion **11** to the exclusion of xanthyl cation **6** provides additional experimental credibility to our earlier postulated explanation for the behavior of alcohol **4** under acid conditions and lends credence to the computationally estimated large kinetic barrier separating the two ions.[6b]

Experimental Section

Methods of Calculation. All molecular orbital computations were done on a CRAY X-MP/28 computer with the use of MOPAC 5.0. The starting geometries were constructed by the PCMODEL program.[23] The molecular mechanics calculations were performed using the MMX software program on a Zenith 286 microcomputer and treated all non-hydrogens as π atoms without planar constraints.[23] The calculations carried out on the MNDO,[9] AM1,[24] and PM3[10] programs were based on the restricted Hartree-Fock (RHF) method. Total geometry optimizations were done with estimations of the second derivatives (Hessian Matrix) for each of the $3n - 6$ parameters in each species. Since an optimized geometry may turn out to be a local minimum, the optimization was begun from at least two starting geometries in order to verify global minima. The activation energy of a certain pathway was checked by the "reaction coordinate" method.[25]

X-ray Crystallography. X-ray intensity data collection was carried out with an Enraf-Nonius CAD4 automatic diffractometer. All calculations were carried out on a VAX 11/750 using VAXSDP. Scattering factors for the neutral atoms and anomalous scattering coefficients were taken from standard tabulations. The structure was solved by direct methods and refined by full-matrix least-squares to R = 0.035. Details are given in the supplementary material.

General nuclear magnetic resonance spectra were obtained on a Varian VXR-400 spectrometer. The solvent used was $CDCl_3$ (pretreated with basic alumina) unless otherwise indicated. Chemical shifts (ppm) were referenced to Me_4Si. Infrared spectra were determined on a Nicolet 60 SX FTIR instrument. The GC/MS experiments were performed on a Hewlett-Packard 5988A instrument using a 12-m methyl silicone capillary column. UV-visible spectra were run on a Hewlett-Packard 8452A diode array spectrophotometer. Mass spectra were recorded as m/z (relative intensity). Elemental analyses were carried out by Spang Microanalytical Laboratory, Eagle Harbor, MI. Melting points were taken on a Thomas-Hoover melting point apparatus and are uncorrected.

Reaction of 9-Lithioxanthene with Tropylium Bromide and the Synthesis of 9-[1-(2,4,6-Cycloheptatrienyl)]-9*H*-xanthene (8). A solution of xanthene (Aldrich, 3.00 g, 16.5 mmol) in dry THF (40 mL) under argon, was cooled to −78 °C. *n*-BuLi (1.55 M in hexane, 12.2 mL, 18.9 mmol) was added dropwise; the color of reaction mixture turned blood red.[26] The reaction was kept at −78 °C for 1 h. After 1 h at −78 °C, solid tropylium bromide (2.82 g, 16.5 mmol) was quickly added. The reaction was warmed and kept at 0 °C for 1 h, followed by warming up to room temperature for 1 h. After 1 h at room temperature, the reaction was diluted with CH_2Cl_2 and quenched with water. The aqueous layer was extracted twice with CH_2Cl_2, the combined CH_2Cl_2 layer was washed with brine and dried over anhydrous $MgSO_4$, filtered, and concentrated by rotary evaporation to give 6.00 g of crude product. Purification by elution from a silica gel column (230–400 mesh, 400 g) with hexanes gave three fractions. The first fraction gave 0.50 g (17%) of ditropyl, mp 60–61 °C (lit.[27] mp 61 °C). The ^1H NMR spectrum showed signals at δ 6.72 (t, 4 H, $J = 2.97$ Hz), 6.30 (t, 2 H, $J = 2.67$ Hz), 6.29 (t, 2 H, $J = 3.15$ Hz), 5.33 (d, 2 H, $J = 4.03$ Hz), 5.30 (d, 2 H, $J = 4.03$ Hz), and 1.98 (br s, 2 H) ppm. The ^{13}C NMR spectrum showed signals at δ 131.0, 125.7, 125.0, and 42.0 ppm. The IR spectrum (CCl_4) showed strong absorptions at 3016 and 2833 cm^{-1}. The mass spectrum m/z 182 (M^+, 0.5), 165 (8), 152 (4), 104 (16), 91 (100), 78 (19), 65 (15), and 39 (11). These data are consistent with the structure of ditropyl. The second fraction gave 2.00 g (45%), mp 93–95 °C. The ^1H NMR spectrum showed signals at δ 7.33–7.11 (m, 8 H), 6.68 (t, 2 H, $J = 2.97$ Hz), 6.27 (t, 1 H, $J = 3.11$ Hz), 6.25 (t, 1 H, $J = 2.89$ Hz), 5.42 (d, 1 H, $J = 6.67$ Hz), 5.40 (d, 1 H, $J = 6.60$ Hz),

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4.10 (d, 1 H, J = 7.33 Hz), and 2.20 (q, 1 H, J = 6.87 Hz) ppm. The ^{13}C NMR spectrum showed signals at δ 153.1, 130.6, 129.6, 127.7, 125.5, 124.7, 124.2, 124.1, 123.0, 116.4, 47.4, and 39.8 ppm. The IR spectrum (CCl_4) showed strong absorptions at 3071, 3027, 2890, 1601, 1578, 1477, 1253, and 746 cm^{-1}. The mass spectrum, m/z 272 (M$^+$, 1), 181 (100), 152 (12), 91 (23), and 65 (6). Anal. Calcd for $C_{20}H_{16}O$: C, 88.21; H,5.92. Found: C, 87.97; H, 5.86. These data are consistent with the structure of 9-[1-(2,4,6-cycloheptatrienyl)]-9*H*-xanthene. The third fraction gave 1.20 g (20%), mp 205–207 °C (lit.[28] mp 209 °C), of dixanthene. The ^{1}H NMR spectrum showed signals at δ 7.20 (t, 4 H, J = 6.96 Hz), 6.93 (t, 4 H, J = 7.32 Hz), 6.87 (d, 4 H, J = 8.14 Hz), 6.66 (d, 4 H, J = 7.41 Hz), and 4.20 (s, 2 H) ppm. The ^{13}C NMR spectrum showed signals at δ 153.0, 129.1, 128.1, 122.6, 121.8, 115.8, and 49.5 ppm. The IR spectrum (CCl_4) showed strong absorptions at 3027, 2907, 1621, 1554, 1459, 1221, and 1096 cm^{-1}. The mass spectrum, m/z 227 (1), 181 (100), 152 (13), 91 (12), and 65 (5). These data are consistent with the structure of dixanthene.

Synthesis of (9-Xanthyl)tropylium Tetrafluoroborate (11). Triphenylcarbenium tetrafluoroborate (Aldrich, 0.91 g, 2.76 mmol) was added to a solution of 9-[1-(2,4,6-cycloheptatrienyl)]-9*H*-xanthene (**8**, 0.50 g, 1.84 mmol) in 5.0 mL of dry CH_2Cl_2. The reaction was stirred under argon for 27.5 h, and then the CH_2Cl_2 was removed under vacuum (water aspirator). The resulting solid was washed with 125 mL of dry ether and filtered dry to give 0.56 g (84%) of a brownish-yellow powder, mp 127–128 °C. The solid was stable when kept under inert atmosphere at 0 °C. The ^{1}H NMR spectrum (CD_2Cl_2) showed signals at δ 9.05 (2 H, m, $-C_7H_6^+$), 9.02 (4 H, m, $-C_7H_6^+$), 7.36 (t, 2 H, J = 7.30 Hz), 7.26 (d, 2 H, J = 8.10 Hz), 7.20 (d, 2 H, J = 7.00 Hz), 7.08 (t, 2 H, J = 7.30 Hz), and 6.10 (s, 1 H) ppm. The ^{13}C NMR spectrum (CD_2Cl_2) showed signals at δ 176.4, 155.4, 154.8, 154.2, 150.9, 130.63, 130.60, 125.0, 121.0, 118.1, and 49.8 ppm. The IR spectrum (KBr) showed strong absorptions at 3020, 1623, 1531, 1541, 1255, 1082, 1032 (BF_4^-), 839, 751 and 699 cm^{-1}. Mass spectrum, m/z 270 (6), 238 (25), 181 (23), 165 (9), 105 (100), and 77 (35). UV–vis (CH_2Cl_2) λ_{max} (log ϵ) 234 (4.68), 282 sh (4.05), and 364 (3.95) nm. Anal. Calcd for $C_{20}H_{15}OBF_4$: C, 67.07; H, 3.92. Found: C, 66.85; H, 4.24. These data are consistent with the structure of (9-xanthyl)tropylium tetrafluoroborate.

Synthesis of 9-[1-(2,4,6-Cycloheptatrienylidene)]xanthene (11): Reaction of (9-Xanthyl)tropylium Tetrafluoroborate with Methanol. (9-Xanthyl)tropylium tetrafluoroborate (**11**, 20 mg, 0.056 mmol) was dissolved in anhydrous methanol (2 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 5 min and then warmed up to room temperature. After 1 h at room temperature, the stirring was stopped, and the solvent was removed (water aspirator). The solid was recrystallized in methanol to give 10 mg (66%) of bright-orange, needlelike solid, mp 125–127 °C. The ^{1}H NMR spectrum showed signals at δ 7.70 (dd, 2 H, J = 7.73, 1.47 Hz), 7.23 (tt, 2 H, J = 7.04, 1.51 Hz), 7.15 (dd, 2 H, J = 8.07, 1.32 Hz), 7.06 (tt, 2 H, J = 8.10, 1.22 Hz), 6.34 (d, 2 H, J = 11.03 Hz), 6.27 (t, 2 H, J = 3.68 Hz), 6.07 (dd, 1 H, J = 4.30, 1.18 Hz), and 6.04 (dd, 1 H, J = 4.32, 1.20 Hz) ppm. The ^{13}C NMR spectrum showed signals at δ 153.5, 132.5, 131.9, 130.5, 128.1, 126.8, 125.1, 122.3, 120.5, and 116.3 ppm. The IR spectrum (CCl_4) had sharp absorptions at 3064, 3029, 1594, 1572, 1470, 1445, 1300, 1257, 738, and 723 cm^{-1}. The mass spectrum, m/z 271 (M$^+$ + 1, 12), 270 (M$^+$, 57), 269 (M$^+$ − 1, 100), 239 (16), 134 (21), and 120 (11). UV–vis (CH_2Cl_2) λ_{max} (log ϵ) 230 (4.42), 248 (4.25), 292 sh (3.75), 312 sh (3.68), and 366 (4.32) nm. Anal. Calcd for $C_{20}H_{14}O$: C, 88.86; H, 5.22. Found: C, 88.75; H, 5.14. These data are consistent with the structure of 9-[1-(2,4,6-cycloheptatrienylidene)]xanthene.[5]

Deprotonation of (9-Xanthyl)tropylium Tetrafluoroborate (11) in Dimethyl Sulfoxide (DMSO). (9-Xanthyl)tropylium tetrafluoroborate (**11**, 0.50 g, 1.40 mmol) was dissolved in DMSO (10 mL) at room temperature. The reaction mixture was kept at room temperature for 5 min, diluted with CH_2Cl_2, washed first with water and then with brine, and dried over anhydrous $MgSO_4$. It was then filtered and concentrated by rotary evaporation and kept under vacuum overnight to give 0.36 g (95%) of product. Spectral analyses were consistent with the structure of 9-[1-(2,4,6-cycloheptatrienylidene)]xanthene.

Deprotonation of (9-Xanthyl)tropylium Tetrafluoroborate (11) with *N,N*-Diisopropylethylamine. To a solution of (9-xanthyl)tropylium tetrafluoroborate (**11**, 20 mg, 0.056 mmol) in dry CH_2Cl_2 (1 mL) at 0 °C was added *N,N*-diisopropylethylamine (40 μL, 0.22 mmol). The reaction mixture was stirred at 0 °C for 10 min and warmed up to room temperature. After 3 h, the solvent was removed by rotary evaporation. Preparative TLC purification gave 7.2 mg (48%) of product. Column chromatography purification using silica gel and elution with hexanes led to considerable decomposition. The spectral analyses were consistent with the structure of 9-[1-(2,4,6-cycloheptatrienylidene)]xanthene.

Reaction of (9-Xanthyl)tropylium Tetrafluoroborate (11) with Et_3SiH: Et_3SiH Reduction of (9-Xanthyl)tropylium Tetrafluoroborate. Triethylsilane (67 μL, 0.42 mmol) was added to a solution containing (9-xanthyl)tropylium tetrafluoroborate (**11**, 30 mg, 0.084 mmol) in dry CH_2Cl_2 (15 mL) at 0 °C. The reaction was kept at 0 °C for 10 min and then kept at room temperature for 1 h. The reaction mixture was diluted with CH_2Cl_2 and washed with water, and the aqueous layer was twice extracted with CH_2Cl_2. The combined organic layer was dried with anhydrous $MgSO_4$, filtered, and concentrated by rotary evaporation to give 21 mg (91%) of product. The ^{1}H NMR spectral analysis of the aliphatic region revealed three products in equal ratios. The ^{1}H NMR spectrum showed signals in the aliphatic region at δ 2.35 (t, 2 H, J = 6.80 Hz), 2.24 (t, 2 H, J = 6.78 Hz), and 2.20 (d, 2 H, J = 6.91 Hz) ppm.[13]

Lithium Aluminum Hydride Reduction of (9-Xanthyl)tropylium Tetrafluoroborate (11). Anhydrous diethyl ether (1 mL) was added to a mixture of (9-xanthyl)tropylium tetrafluoroborate (**11**, 20 mg, 0.056 mmol) and lithium aluminum hydride (4.7 mg, 0.112 mmol) at 0 °C. The reaction mixture was kept at 0 °C and then warmed up and kept at room temperature for an additional 1.5 h. The reaction mixture was diluted with CH_2Cl_2 and quenched with 1 N HCl (2 mL). The aqueous layer was extracted twice more with saturated aqueous $NaHCO_3$ solution and then brine. It was then dried over anhydrous $MgSO_4$, filtered, and concentrated by rotary evaporation to give 13.6 mg (90%) of product. The spectral analyses revealed three products, identical with those obtained with silane reduction and in the same ratio.

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Supplementary Material Available: Text of X-ray data collection and reduction, structure solution and refinement, and references, tables of crystal structure data, positional parameters, bond distances, bond angles, torsional angles, hydrogen positional parameters, and anisotropic temperature factors for compound **3** as well as the PLUTO representations of the MNDO, PM3, and MMX structures of **3** calculated for minimum energy (16 pages). Ordering information is given on any current masthead page.

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