The Search for Homoaromatic Semibullvalenes. 5.[1] 1,5-Dimethyl-2,4,6,8-semibullvalenetetracarboxylic Dianhydride

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The synthesis and study of a novel bisannelated semibullvalene that is calculated to be a neutral homoaromatic ground state molecule is presented. Through variable-temperature X-ray, ^{13}C solution-phase NMR, and ^{13}C solid-state CP-MAS NMR studies and by a modified Saunders' isotopic perturbation method, 1,5-dimethyl-2,4,6,8-semibullvalenetetracarboxylic dianhydride is shown to be a highly fluxional molecule that is not homoaromatic in the solution or solid states. The barrier to the Cope rearrangement of this dianhydride, in solution, is estimated (from 125 MHz ^{13}C NMR data) to be less than 14 kJ mol^{-1}.

Introduction

The concept of homoaromaticity was advanced more than four decades ago,[2] and since that time the area has remained one of intense interest and extensive investigation.[3] Despite this extreme activity, there is to date no well-accepted example of an electrically neutral ground state homoaromatic molecule.[3,4] The phenomenon is well founded, as many homoaromatic cationic species are known.[3] From the results of calculations on the trimerization of acetylene to give benzene, Houk et al. postulated that it was very unlikely that any closed-shell neutral homoaromatic system could ever exist.[5] However, recent calculations, at a much higher level of theory, suggest that there is weak (homo)aromatic stabilization of the planar D_{3h} transition state for the trimerization of acetylene to benzene.[6] Subsequently, Liebman et al. presented thermochemical evidence for neutral homoaromaticity in triquinacene **1**.[7] Using similar techniques, Scott et al. have suggested that permethyl [5]pericyclyne **2** is a neutral homoaromatic,[8] and Rogers et al. assert that 1,3,5-cycloheptatriene is homoaromatic.[9] Roth et al. also conclude from heats of hydrogenation data and comparison of experimental and calculated, using force field methods (MM2ERW), heats of formation that a series of cycloheptatrienes and norcaradienes are homoaromatic.[10] Calculations by us[11] and others[12] do not support the claims that either triquinacene or the [5]pericyclynes should be considered as neutral homoaromatics. It is believed that the nonconjugated models and inappropriate force fields used to account for strain energy differences in these thermochemical studies are inadequate for the reliable assignment of homoaromaticity.[3,12a−d] The case of cycloheptatriene is controversial. Early work was equivocal, whereas our more recent calculations do not support homoaromaticity for this system[1b] and those of Schleyer[13] and Cremer[14] et al. suggest some homoaromatic stabilization as do the thermochemical studies of Roth et al.[10]

The semibullvalenes have long been recognized as the system most closely approaching neutral homoaromaticity.[3,4,15] It has even been suggested that the homoconjugative interactions in semibullvalenes may be viewed as the open-shell through-space (homoconjugative) in-

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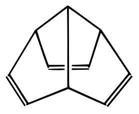

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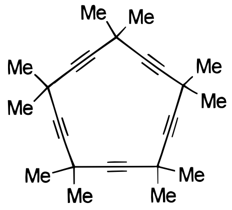

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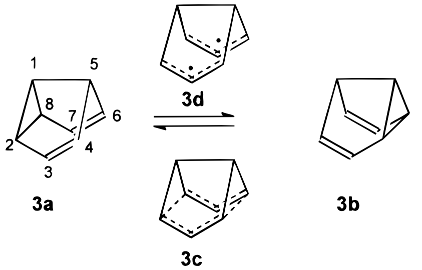
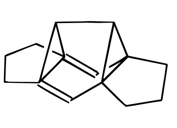
teraction of two allyl radicals (e.g., **3d**),[16] which thus avoids the destabilization predicted for closed-shell systems.[5] The degenerate Cope rearrangement of semibullvalene (**3a** $\rightleftarrows$ **3b**) proceeds through the homoaromatic transition state (**3c**) with a very low activation barrier ($\Delta G^{\ddagger}_{298} = 25.94$ kJ mol^{-1},[17a] $\Delta G^{\ddagger}_{173} = 24.27$ kJ mol^{-1},[17a] $\Delta G^{\ddagger}_{123} = 23.01$ kJ mol^{-1} [17b]).[18,19] There have been many experimental and theoretical investigations aimed at lowering this barrier even to the point of eliminating it and achieving a ground state homoaromatic semibullvalene analogue of (**3c**).[3,4] One approach to this goal is by small-ring annelation of the semibullvalene nucleus.[1,3,4,19,20] Paquette and Chamot suggested that in the bisannelated semibullvalene **4** the "breathing motion" of the Cope process would be inhibited, and this would perhaps lead to a homoaromatic molecule.[21] Early extended Hückel investigations by Hoffmann and Stohrer suggested that the Cope rearrangement of the bisethenoannelated semibullvalene **5** would be strongly inhibited and that the perturbed transition state would be the strained cyclodecapentaene **6**.[22] Very recent high-order ab initio and density functional theory calculations[12e,19] completely validate our earlier semiempirical calculations on several annelated semibullvalenes.[1a,c] These calculations clearly demonstrate that small ring annelation at the 1,5, 2,8, or 2,8:4,6 position(s) results in homoaromatic semibullvalenes. Supporting the contention that suitable small-ring annelation of the semibullvalene nucleus will result in homoaromaticity is the fact that the Cope rearrangement of **7** is still fast on the NMR time scale at −160 °C.[23] **7** is not an ideal candidate for neutral homoaromaticity as it is well-known that substitution at the 3,7-positions of the semibullvalene[4,17a,24a,b] and barbaralane[4,16,24c] nuclei increases the activation barrier for the Cope rearrangement. Thus, the NMR results for **7** bode well for the prospect of neutral homoaromatic systems based on appropriately designed bisannelated semibullvalenes. Using a set of semiempirical discriminators for the detection of energy-lowering homoconjugative interactions,[1b] we predicted that the annelated semibullvalenes **8**−**10** will have a homoaromatic ground state.[1a,c] These predictions are confirmed, for **8** and **9**, by recent high-order ab initio and density functional theory results.[12e,19] This paper contains a full account of our studies on the bisannelated semibullvalenes 1,5-dimethyl-2,4,6,8-semibullvalenetetracarboxylic dianhydride **10** and (1,5)-ethyl,methyl-2,4,6,8-semibullvalenetetracarboxylic dianhydride **11**.[25]





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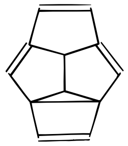

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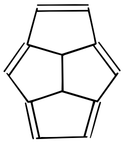

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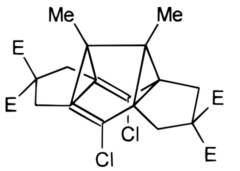

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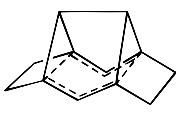

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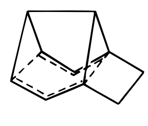

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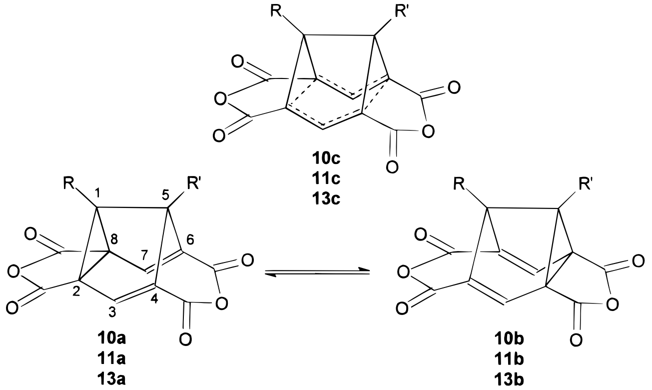

10 R = R' = Me; **11** R = Me, R' = Et; **13** R = R' = H

Results and Discussion

The known[26] tetraester **12** (R = Me) (Scheme 1A) appeared to be the ideal starting material for the synthesis of a variety of bisannelated semibullvalenes. In particular, the dianhydride **10** was considered to be a readily accessible synthetic target. Initially, only a single minimum corresponding with **10c** was located by semiempirical calculations on **10**.[1d] During a recent reinvestigation of this system, a higher energy minimum corresponding with the localized forms (**10a**,**b**) was discovered. Using our discriminators,[1a−c] the ground state species

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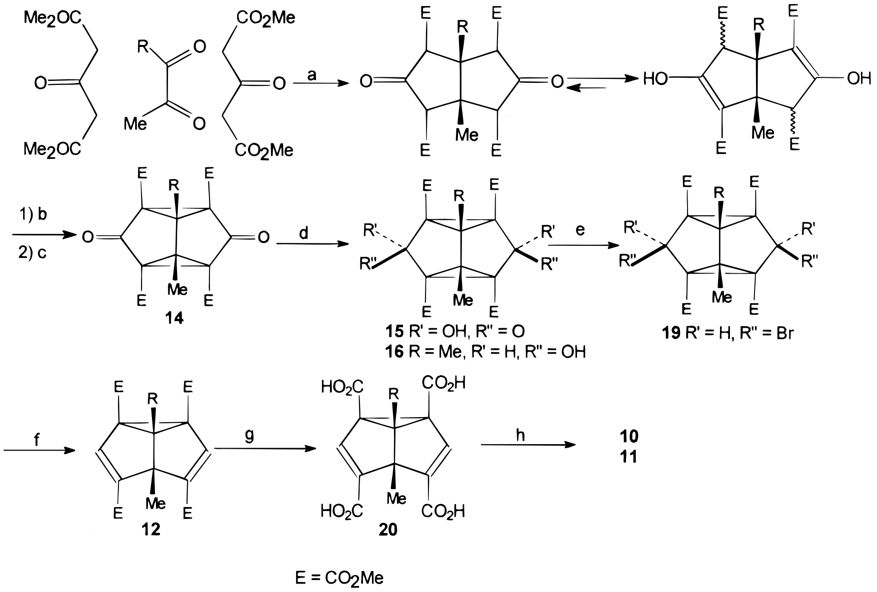
Scheme 1[a]



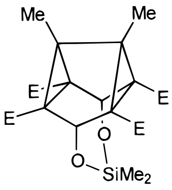
[a] Key: (A, R = Me) (a) $NaHCO_3$, H_2O (82%), (b) Br_2, $CHCl_3$ (88%), (c) Et_3N, $CHCl_3$ (78%), (d) *i*-Bu_3Al, toluene, ambient, 4 h, $R' = H$, $R'' = OH$ (76%), (e) MsCl, Et_3N, CH_2Cl_2, 5 °C → ambient, 40 h, $R' = H$, $R'' = OMs$ (83%), (f) NaI, acetone, reflux, 3.5 h (63%); (B, R = Me) (a) $NaHCO_3$, H_2O (82%), (b) Br_2, $CHCl_3$ (88%), (c) Et_3N, $CHCl_3$ (78%), (d) $NaBH_4$, THF, H_2O, <0 °C, 5 h, $R' = OH$, $R'' = H$ (82%), (e) PBr_3, benzene, H_2O, 45 °C, 48 h, $R' = H$, $R'' = Br$ (81%), (f) NaI, acetone, reflux, 5 h (85%), (g) NaOH, H_2O, ambient, 18 h (88%), (h) TFAA, ambient, 24 h (79%); (C, R = Et) (a) $NaHCO_3$, $MeOH/H_2O$ (86%), (b) Br_2, $CHCl_3$, (c) Et_3N, $CHCl_3$ (76% for steps b and c combined), (d) $NaBH_4$, THF, H_2O, <0 °C, 14 h, $R' = OH$, $R'' = H$ (79%); (e) PBr_3, benzene, H_2O, 48 °C, 48 h, $R' = H$, $R'' = Br$ (72%); (f) NaI, acetone, reflux, 6 h (55%), (g) NaOH, H_2O, ambient, 24 h (50%), (h) TFAA, ambient, 24 h (32%).

Table 1. AM1 Results for the Bisanhydrides 10 and 13

compd	AM1 method	ΔH_f (kJ/mol)	distance (Å) C(2,8)	distance (Å) C(4,6)	two-center energy (eV) C(2,8)	two-center energy (eV) C(4,6)
10a/b	SCF	−413.5	1.597	2.270	−10.08	0.24
10a/b	CI2	−416.4	1.516	2.268	−10.05	0.23
10c	SCF	−390.4	2.204	2.205	−1.26	−1.25
10c	CI2	−434.8	2.291	2.291	−0.80	−0.79
13a/b	SCF	−375.1	1.601	2.277	−10.02	0.23
13a/b	CI2	−376.2	1.604	2.276	−9.97	0.23
13c	SCF	−359.2	2.224	2.221	−1.81	−1.21
13c	CI2	−407.9	2.312	2.310	−0.71	−0.72

10c was judged to be homoaromatic. There was a significant decrease in energy between the SCF and correlated (CI2) calculations, and the two-center energy partitioning terms between C(2)−C(8) and C(4)−C(6) showed a significant favorable interaction (Table 1).[1a−c] Similar results were obtained for 2,4,6,8-semibullvalenetetracarboxylic dianhydride (**13**) (Table 1).

Using Grohmann's procedure[26] (Scheme 1A) we were able to obtain **12** (R = Me) in 24% overall yield from 2,3-butanedione. However, we wished to avoid the use of the pyrophoric triisobutylaluminum for the reduction of diketone **14** (R = Me). In their paper, Grohmann et al. note that with reducing agents other than triisobutylaluminum **14** (R = Me) gave different stereoisomers or mixtures of diols.[26] We found that reduction of **14** (R = Me) with sodium borohydride in wet THF at less than 0 °C resulted in the exclusive formation of **15** (R = Me) in excellent yield (Scheme 1B). If the reduction was carried out at higher temperatures, then a mixture of stereoisomers resulted. Comparison of an authentic sample of Grohmann's diol **16** (Scheme 1A) with **15** (R = Me) clearly revealed the isomeric nature of the two diols. The highly symmetrical structure of **15** (R = Me), proposed on the basis of NMR spectroscopy, was confirmed by its easy conversion to the cyclic silyl ether **17**. Initial concern that the *endo,endo* configuration of the diol **15** (R = Me) would preclude the formation of the dimesylate **18** was unfounded. Treatment of **18** with sodium iodide in acetone under reflux produced the desired tetraester **12** (R = Me) in 61% yield. Although acceptable, the yield for these steps was poorer than for the corresponding steps in Grohmann's synthesis (Scheme 1A). In an effort to improve the overall yield, while maintaining the advantage of reduction with the easily handled sodium borohydride, diol **15** (R = Me) was converted to the dibromide **19** (R = Me) (81%) by reaction with phosphorus tribromide in wet benzene. Grob fragmentation of **19** (R = Me) proceeded smoothly to give **12** (R = Me) in 85% yield (32% overall from 2,3-butanedione, Scheme 1B). Not only does this modification result in higher yields of **12** (R = Me), but also we find it to be operationally much simpler than Grohmann's route. Starting from 2,3-butanedione, multigram quantities of tetraester **12** (R = Me) are simply and routinely available by our route (Scheme 1B) in about 1 week. Hydrolysis of **12** (R = Me) to the tetraacid **20** (R = Me) was easily accomplished with aqueous sodium hydroxide. It is interesting to note that the tetraacid **20** (R = Me) is much more thermally labile than the tetraester **12** (R = Me), yielding the corresponding cyclooctatetraene on warming. Reaction of **20** (R = Me) with oxalyl chloride produced the monoanhydride diacid **21**, while treatment with trifluoroacetic anhydride gave the desired dianhydride **10**. The dianhydride **10** proved to be remarkably stable. It could be purified by sublimation (200 °C at ambient pressure) and showed no sensitivity to ambient oxygen. This contrasts with the behavior of other semibullvalenes, which frequently undergo thermolysis to the corresponding cyclooctatetraene under relatively mild conditions[26,27] and often tend to react with oxygen.[23,27a,b] On prolonged deliberate exposure of **10** to the atmosphere it was recovered unchanged along with the product of partial hydrolysis (**21**, $\sim$10% after 24 h).



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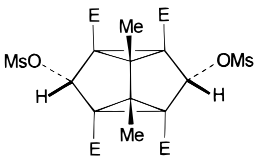

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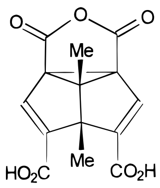

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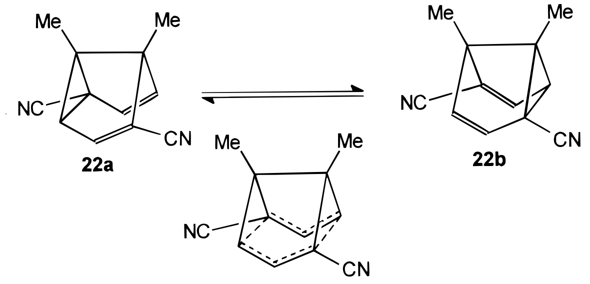
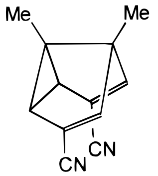
With **10** in hand, an extensive study of its properties was undertaken with the prime objective of determining the nature of the ground state − localized equilibrating Cope system (**10a** ⇄ **10b**) or delocalized homoaromatic species (**10c**). The variable-temperature X-ray structural studies proved to be the most illuminating in resolving this question (in the solid state). X-ray structure determination would appear to be the ideal means to solve this problem. The homoaromatic species **10c** should have high symmetry with an equalization of bond/interatomic distances, which would be readily apparent from the crystal structure. However, the β form of the dinitrile **22** displayed apparent C_2 symmetry (from X-ray crystallography).[28] The usual conclusion from this observation is that **22** exists as the neutral homoaromatic species **22c**. However, variable-temperature (solids) ^{13}C CP-MAS NMR studies clearly showed that **22** was a Cope system equilibrating between nondegenerate tautomers (**22a** and **22b**) through a homoaromatic transition state (**22c**).[28] At ambient temperature, there is accidental degeneracy of **22a** and **22b** that results in the apparent C_2 symmetry at this temperature.[28] These results nicely explain the perplexing structural changes observed, by variable-temperature X-ray crystallography, in **23** where the C(2,8) distance decreases and the C(4,6) distance increases with decreasing temperature.[29] As the temperature is lowered, the population of the low-energy tautomer increases and the C(2,8) and C(4,6) distances reflect this change in population. It has been proposed that the anomalous interatomic distances observed in the X-ray structures of many semibullvalenes are explained by similar Cope rearrangements between nondegenerate tautomers.[30] Thus, in the X-ray analyses of equilibrating semibullvalenes it is to be expected that the time-averaged bond/internuclear distances will vary with temperature and parallel the increasing population of the low-energy tautomer. However, for homoaromatic species C_2 symmetry should be maintained at all temperatures. Of course, in systems displaying such fine energy balances, crystal packing forces may be of importance in determining the nature of the ground states. It might be anticipated that the barrier to the solid-state Cope rearrangement will be higher or, at least, equivalent to that in the solution phase.[31] Therefore, if the Cope rearrangement can be frozen out in the solid state then the molecule is not homoaromatic (in the solid) and most likely will not be so in the solution or gas phases (unless the energy difference between the localized and delocalized forms is extremely small and of the same order as the crystal packing forces). However, if the Cope rearrangement cannot be frozen out it is virtually assured that the molecule is homoaromatic under all conditions.



22a **22b** **22c**



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X-ray structure determination was carried out on **10** at 293, 243, 163, 148, and 123 K. At the three higher temperatures, a highly symmetric structure was obtained (C(2,8) = C(4,6) $\sim$ 1.96 Å); however, at the lower temperatures symmetry was broken with the C(2,8) distance contracting and the C(4,6) distance expanding (C(2,8) = 1.679(4) and C(4,6) = 2.197(4) Å at 123 K).[1d] The X-ray results provided the first indication that **10** was not homoaromatic.

Quast considers the sum of the C(2,8) and C(4,6) internuclear distances (Σ_r) in semibullvalenes to be a molecular property and an indicator of the magnitude of the activation barrier for the Cope process.[30] The sum of the C(2,8) and C(4,6) internuclear distances in the more rapidly rearranging semibullvalenes (3.97−3.99 Å) is significantly higher than the corresponding Σ_r (3.85−3.93 Å) in the less fluxional semibullvalenes.[30] These values, for "open" (not annelated) systems, cannot be directly compared with Σ_r for **10** as annelation across the terminii of the semibullvalene nucleus must surely result in considerable perturbation of distances. Similarly, the estimated limiting values (for a single tautomer) of the C(2,8) ($\sim$1.578 Å) and C(4,6) (Σ_r −1.578 Å) distances used by Quast et al. in the assessment of the equilibrium constant for a variety of open semibullvalenes[30] are inappropriate for the bisannelated **10**. However, the sum of the C(2,8) and C(4,6) distances (3.93 Å at 293 K and 3.97 Å at 123 K) certainly suggest an extremely low activation barrier for the Cope rearrangement in **10**. A comparison of the calculated C(2,8) and C(4,6) distances (Table 1, 1.52−1.60 and 2.27 Å, respectively) and Quast's estimated values[30] for C(2,8) and C(4,6) (1.578 and 2.15−2.41 Å, respectively) with the corresponding distances determined for **10** at 123 K[1d] suggests that the experimental value for C(2,8) is quite long (1.679 Å) and that for C(4,6) rather short (2.197 Å). These anomalous distances clearly indicate that at 123 K either equilibra-

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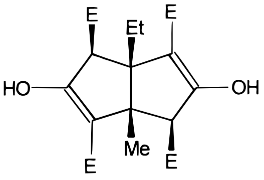
tion is still occurring between **10a** and **10b** or there is a frozen population distribution of these nondegenerate tautomers.

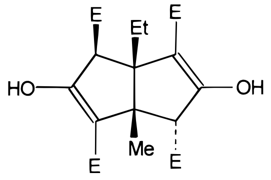
Previously, variable-temperature ^{13}C CP-MAS NMR spectroscopy was extremely successful in revealing the solid-phase characteristics of semibullvalenes. Such studies on one crystalline modification of the parent molecule demonstrated that the localized forms (**3a**,**b**) were not degenerate.[31] Similarly, and of even greater interest, the β form of the dinitrile **22** was shown not to be a neutral homoaromatic ground state molecule, but an equilibrating Cope system with nondegenerate localized forms.[28]

Unusually, for rapidly equilibrating semibullvalenes, there was no change in the variable-temperature solid CP-MAS spectra of **10** between 293 and 223 K.[1d] It is impossible to distinguish between a homoaromatic or localized ground state for **10** from these VT CP-MAS spectra. However, in the solid state it is evident, from X-ray crystallography, that the dianhydride **10** is not homoaromatic. The variable-temperature solution-phase ^{13}C spectra of **10** (at both 75 and 125[32] MHz) were inconclusive, supporting either a homoaromatic species (**10c**) or a localized system (**10a**,**b**) undergoing rapid (on the NMR time scale) degenerate Cope rearrangement. At 75 MHz, no change was observed in the spectra between 297 and 190 K (the solubility limit), and an upper limit to the activation barrier for the Cope rearrangement (**10a** $\rightleftarrows$ **10b**) was estimated at 17 kJ mol^{-1}.[1d] Due to the increased sensitivity of the 125 MHz instrument, a more dilute solution of **10** could be used for the determination of its variable-temperature ^{13}C NMR spectra, and it was possible to reach 183 K without undue precipitation. Again, no line broadening of the C(2,4,6,8) signal was detected. Thus, the upper limit for the Cope process, if equilibration is occurring, can be further refined. Once more assuming a chemical shift difference of ~100 ppm between C(2,8) and C(4,6) in **10a** and a limit of observable broadening due to exchange of 0.5 Hz,[1d] $\Delta G^{\ddagger}$ is estimated to be <14 kJ mol^{-1}.[33]

To distinguish between a homoaromatic ground state (**10c**) or a rapidly equilibrating Cope system (**10a** $\rightleftarrows$ **10b**) in the solution phase, Gompper's[34] modification of the Saunders[35] isotopic perturbation method was employed. In Gompper's method, the degeneracy of the localized forms of a semibullvalene (e.g., **10a**,**b**) is lifted by different alkyl group substitution at C(1) and C(5) (e.g., **11**). If **11** is homoaromatic (single minimum potential energy surface), then its NMR spectra will be essentially temperature independent. However, if **11** exists as a Cope system (double minimum surface), then the two tautomers (**11a** and **11b**) will not be degenerate and their populations will parallel the temperature changes resulting in a tracking of the time-averaged chemical shift with temperature. The first step in the synthesis of **11** was the Weiss–Cook condensation of 2,3-pentanedione with dimethyl 1,3-acetonedicarboxylate, which has been reported in detail elsewhere.[36] This reaction resulted in surprising stereoselectivity, giving only **24** and **25** in 86% overall yield. The mixture or the individual isomers (**24** and **25**) were carried through to **11** (Scheme 1). Unfortunately, the variable-temperature solution-phase ^{13}C NMR spectra of **11** showed a clear, equilibration driven, tracking of the C(2,8) and C(4,6) chemical shifts with temperature. To account for the inherent variation of chemical shifts with temperature, an internal standard of the C(2,4,6,8) signal of the symmetrical analogue **10** was used as a reference for all signals at each temperature. The observed temperature dependence for the C(2,8) and C(4,6) signals of **11** was +0.0250 and −0.0248 ppm/deg, respectively (these values were unfortunately erroneously reported as +0.250 and −0.248 ppm/deg in our original paper[1d]). Consequently, it must be concluded that **11** (and by analogy **10**) is not homoaromatic in solution.

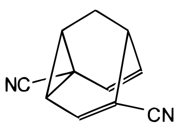


24

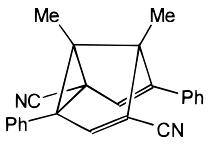


25

An alternative for studying the solution-phase properties of semibullvalenes is IR spectrometry. The time scale of the IR experiment renders it more amenable than NMR to the investigation of extremely rapid processes.[4,27b,c,37] The observation of two nitrile bands in the IR spectra of **22**,[27c] **26**,[37a] **27**,[27b] and **28**[37b] supported the conclusion of Quast et al. that these molecules were highly fluxional, but not homoaromatic. It would appear that the carbonyl region of the IR spectrum of **10** could be used in a similar diagnostic manner. Unfortunately, the carbonyl region of **10** is broad and complex and cannot be reliably used in the assessment of the nature of the ground state of **10**. Part of the reason for the complexity in the carbonyl absorptions of **10** may arise from an exceptionally low barrier to the Cope rearrangement. Quast et al. observed a temperature dependence (a broadening and some coalescence of the bands) of the nitrile bands in **28**, which they speculate may be due to the extremely high rate of the Cope process in **28**.[37b]



26



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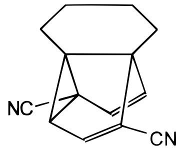

28

Although there is apparently no appropriate classical chromophore, the dianhydrides **10** and **11** are vivid yellow crystalline solids at ambient temperature. When the pure solid or a solution of either semibullvalene is cooled, the color decreases in intensity and by about −78 °C the color is greatly diminished. Quast et al. observed similar results in their most fluxional semibullvalenes

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[32] The 125 MHz spectra were kindly recorded by Varian Associates, Inc. Palo Alto, California.

[33] A reviewer suggested that a more conservative estimate of 1 or 2 Hz be used for the exchange broadening which results in $\Delta G^{\ddagger}$ < 15 or 16 kJ mol^{-1}, respectively.

[34] Gompper, R.; Schwarzensteiner, M.-L.; Wagner, H.-U. *Tetrahedron Lett.* **1985**, *26*, 611.

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[37] (a) Quast, H.; Görlach, Y.; Stawitz, J.; Peters, E.-M.; Peters, K.; von Schnering, H. G. *Chem. Ber.* **1984**, *117*, 2745. (b) Quast, H.; Mayer, A.; Peters, E.-M.; Peters, K.; von Schnering, H. G. *Chem. Ber.* **1989**, *122*, 1291. (c) Win, W. W.; Grohmann, K. G.; Todaro, L. *J. Org. Chem.* **1994**, *59*, 2803.

and barbaralanes and have correlated this reversible thermochroism with a very flat double minimum potential energy surface and an exceptionally low activation barrier to the Cope rearrangement.[27b]

The extremely wide temperature range over which **10**, in the solid state, displays apparent degeneracy is perhaps also a reflection of the exceptionally low barrier to the Cope process (**10a** $\rightleftarrows$ **10b**). All other solid-state studies on equilibrating symmetrical semibullvalenes have revealed a narrow temperature range for degeneracy of the tautomers.

The bisannelated semibullvalene **10** is not homoaromatic in the solution or solid states. However, all of the experimental data lead to the conclusion that the activation barrier for the Cope rearrangement is exceedingly low and, in any event, is estimated to be less than 14 kJ mol^{-1}. Quantum mechanical calculations, which, of course, strictly only apply to the isolated molecule in the gas phase, clearly predict that **10** is homoaromatic. Some gas-phase properties of **10** are currently under investigation.

Experimental Section

Mass spectra were determined at 70 eV (EI) or using methane chemical ionization (CI). Melting points were determined on a hot stage apparatus and are uncorrected. Microanalyses were performed by M-H-W Laboratories and Desert Analytics.

Tetramethyl 1,5-Dimethyltetracyclo[3.3.0^{1,5}.0^{2,8}.0^{4,6}]octane−3,7-dione-2,4,6,8-tetracarboxylate (14, R = Me).[26] A solution of tetramethyl 1,5-dimethyl-*cis*-bicyclo[3.3.0]octane-3,7-dione-2,4,6,8-tetracarboxylate[38] (22 g, 0.055 mol) in chloroform (300 mL) was added dropwise to a stirred solution of bromine (19.45 g, 0.122 mol) in chloroform (50 mL) at ambient temperature. The mixture was kept at ambient temperature for 3 h and then cooled in an ice bath. Triethylamine (24.6 g, 0.244 mol) was added dropwise to this cooled stirred solution. The mixture was allowed to warm to ambient temperature and then kept for 4 h before all volatile materials were removed by evaporation in vacuo. The residue was triturated with warm (50 °C) water and the resulting solid collected by vacuum filtration (17.8 g, 82% overall). Recrystallization from methanol gave the pure diketone **14** (R = Me) (15.2 g, 70% overall) as white prisms: mp 184−185 °C; ^{1}H NMR (CDCl$_3$) δ 3.78 (s, 12H), 1.73 (s, 6H); ^{13}C NMR (CDCl$_3$) 189.0, 162.0, 53.24, 48.1, 30.0, 8.4; IR (KBr) 2985, 1754, 1747, 1718, 1436, 1317, 1300, 1237, 1145.

Tetramethyl 1,5-Dimethyltetracyclo[3.3.0^{1,5}.0^{2,8}.0^{4,6}]octane-3-*exo*,7-*exo*-diol-2,4,6,8-tetracarboxylate (16).[26] The diketone **14** (R = Me) (1.9 g, 0.0048 mol) was added portionwise over 15 min to a stirred cooled (0 °C) solution of triisobutylaluminum (1 M, 12 mL, 0.012 mol) in toluene under N$_2$. The mixture was allowed to warm to ambient temperature over 4 h. Ether (5 mL), methanol (2 mL), and dilute hydrochloric acid (15 mL) were added to this solution, which was then extracted with ethyl acetate (3 × 50 mL). The extracts were washed with water (2 × 25 mL), dried (MgSO$_4$), and evaporated in vacuo. The crude product (1.65 g, 86%) was recrystallized from ethyl acetate to give pure diol **16** (1.45 g, 76%) as white prisms: mp 214−216 °C; ^{1}H NMR (CDCl$_3$) δ 4.60 (s, 2H), 3.87 (bs, 2H), 3.66 (s, 12H), 1.66 (s, 6H); ^{13}C NMR (CDCl$_3$) 167.38, 71.59, 52.27, 49.35, 47.51, 9.29.

Tetramethyl 1,5-Dimethyltetracyclo[3.3.0^{1,5}.0^{2,8}.0^{4,6}]octane-3-*exo*,7-*exo*-dimesyl-2,4,6,8-tetracarboxylate.[26] Methanesulfonyl chloride (3.0 g, 0.026 mol) was added dropwise to an ice-cold stirred solution of diol **16** (3.0 g, 0.007 54 mol) and triethylamine (8 mL) in dichloromethane (25 mL). The mixture was allowed to warm to ambient temperature and kept for 40 h. Dichloromethane (200 mL) was added, and the solution was washed with dilute hydrochloric acid (50 mL) and water (2 × 50 mL), dried (MgSO$_4$), and evaporated in vacuo. The crude product (3.99 g, 96%) was recrystallized from acetone−hexane to give the pure dimesylate (3.5 g, 83%) as white prisms: mp 139−140 °C; ^{1}H NMR (CDCl$_3$) δ 5.63 (s, 2H), 3.67 (s, 12H), 2.99 (s, 6H), 1.74 (s, 6H); ^{13}C NMR (CDCl$_3$) 164.85, 79.49, 52.63, 47.97, 47.92, 39.34, 9.13; IR (KBr) 3200, 2960, 1750, 1345, 1250.

Tetramethyl 1,5-Dimethyl-2,4,6,8-semibullvalenetetracarboxylate (12, R = Me)[26] **from *exo*,*exo*-Dimesylate.** A stirred solution of sodium iodide (2.0 g, 0.0133 mols) and tetramethyl 1,5-dimethyltetracyclo[3.3.0.^{1,5}0.^{2,8}0^{4,6}]octane-3-*exo*,7-*exo*-dimesyl-2,4,6,8-tetracarboxylate (2.0 g, 0.003 61 mol) in acetone (25 mL) was heated under reflux under nitrogen for 2 h. Sodium iodide (1 g, 0.0065 mol) was added to the solution, which was heated under reflux for an additional 1.5 h. The acetone was removed in vacuo, and a saturated solution of sodium thiosulfate (10 mL) was added followed by water (75 mL) and then extraction with ether (3 × 25 mL). The extracts were washed with water (25 mL), dried (MgSO$_4$), and evaporated in vacuo to give a quantitative yield of the crude semibullvalene. Recrystallization from hexanes−ethyl acetate gave the pure semibullvalene (0.82 g, 63%) as lustrous yellow cubes: mp 103−104 °C (lit.[26] mp 102.5−103 °C).

Tetramethyl 1,5-Dimethyltetracyclo[3.3.0^{1,5}.0^{2,8}.0^{4,6}]octane-3-*endo*,7-*endo*-diol-2,4,6,8-tetracarboxylate (15, R = Me). Sodium borohydride (2.96 g, 0.078 mols) was added portionwise to a cooled (in an ice/salt bath) stirred suspension of the diketone **14** (R = Me) (31.0 g, 0.0787 mol) in THF (400 mL) and water (40 mL). The mixture was kept cold for 8 h, never allowing the temperature to rise above −5 °C. The solvent was removed in vacuo and water (500 mL) and concentrated HCl (5 mL) were added to the solid residue. The crude product (30.5 g, 97%) was collected by filtration. Recrystallization from ethyl acetate gave the pure diol **15** (R = Me) (27.47 g, 88%) as white plates: mp 182−183 °C; ^{1}H NMR (CDCl$_3$) δ 5.20 (d, J = 7.4 Hz, 2H), 4.30 (d, J = 7.4 Hz, 2H), 3.67 (s, 12H), 1.38 (s, 6H); ^{13}C NMR (CDCl$_3$) 167.57, 74.02, 52.43, 48.34, 45.48, 8.76; IR (KBr) 3545, 2956, 2927, 1730, 1437, 1260, 1190, 1057; MS m/z CI 381 (1.6), 380 (3.3), 368 (6.7), 367 (39.5), 349 (42.6), 348 (55.6), 337 (34.8), 317 (77.7), 316 (41.6), 307 (26.5), 306 (20.8), 305 (100), 289 (80.3), 261 (56.4); EI 368 (4.9), 367 (26.5), 348 (50.6), 321 (28.2), 320 (21.1), 316 (46.1), 307 (26.7), 305 (18.2), 289 (100), 288 (33.2), 261 (74.9). Anal. Calcd for $C_{18}H_{22}O_{10}$: C, 54.27; H, 5.57. Found: C, 54.54; H, 5.66.

Silyl Ether 17. Dimethyldichlorosilane (1.3 mL, 0.011 mol) was added dropwise to a stirred cooled (in an ice/salt bath) solution of the diol **15** (R = Me) (3.98 g, 0.01 mol) and triethylamine (7 mL, 0.045 mol) in dichloromethane (50 mL). The mixture was allowed to slowly warm to ambient temperature and kept with stirring for 18 h. It was evaporated in vacuo, water (200 mL) was added, and the mixture was extracted with ethyl acetate (3 × 30 mL). The extracts were washed with water (50 mL) and saturated brine (50 mL), dried (Na$_2$SO$_4$), and evaporated in vacuo to give the crude product (4.5 g, 96%), which was purified by recrystallization from ethyl acetate to give the ether **17** (4.21 g, 92.5%) as white cubes: sublimes >160 °C; ^{1}H NMR (CDCl$_3$) δ 5.44 (s, 2H), 3.68 (s, 12H), 1.38 (s, 6H), 0.17 (s, 6H); ^{13}C NMR (CDCl$_3$) 166.53, 76.46, 76.0, 51.82, 49.32, 46, 93, 8.27, 0.0; IR (KBr) 3002, 2958, 1747, 1432; MS m/z EI 454 (7), 439 (100), 423 (37), 395 (63), 363 (46), 335 (44), 245 (33), 89 (84), 75 (52), 59 (34.5). Anal. Calcd for $C_{20}H_{26}O_{10}Si$: C, 52.85; H, 5.77. Found: C, 53.02; H, 5.95.

Tetramethyl 1,5-Dimethyltetracyclo[3.3.0^{1,5}.0^{2,8}.0^{4,6}]octane-3-*endo*,7-*endo*-dimesyl-2,4,6,8-tetracarboxylate (18). A stirred mixture of the diol **15** (R = Me) (4 g, 0.0101 mol), methanesulfonyl chloride (3 g, 0.032 mol), pyridine (2 mL), and dry dichloromethane (30 mL) was kept under N$_2$ at 38 °C for 36 h. The solvent was removed in vacuo, and the residue was poured into methanol (10 mL). The resulting solid was collected and purified by recrystallization from methanol to give the dimesylate **18** (2.4 g, 43%) as white prisms: mp 154−155 °C; ^{1}H NMR (CDCl$_3$) δ 6.14 (s, 2H), 3.79 (s, 12H), 3.11 (s,

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[38] Bertz, S. H.; Cook, J. M.; Gawish, A.; Weiss, U. *Org. Synth.* **1985**, *64*, 27.

6H), 1.46 (s, 6H); ^{13}C NMR (CDCl$_3$) 167.5, 80, 53, 48, 46, 40, 9.7; IR (CHCl$_3$) 3023, 2955, 1730, 1440, 1360, 1261, 1173, 965.

Tetramethyl 1,5-Dimethyl-2,4,6,8-semibullvalenetetracarboxylate (12, R = Me)[26] from *endo,endo*-Dimesylate 18. A stirred solution of sodium iodide (3.0 g, 0.02 mol) and dimesylate **18** (2.8 g, 0.005 05 mol) in dry acetone (30 mL) was heated under reflux under nitrogen for 40 h. The acetone was removed in vacuo, water (75 mL) was added, and the mixture was extracted with ether (3 × 25 mL). The extracts were washed with sodium bisulfite solution (10%, 3 × 25 mL) and water (25 mL), dried (MgSO$_4$), and evaporated in vacuo. The crude material was purified by column chromatography (silica, ethyl acetate/hexanes 1:3) to give the pure semibullvalene **12** (R = Me)[26] (1.1 g, 60%).

Tetramethyl 1,5-Dimethyltetracyclo[3.3.0^{1,5}.0^{2,8}.0^{4,6}]octane-3-*exo*,7-*exo*-dibromo-2,4,6,8-tetracarboxylate (19, R = Me). A stirred mixture of the diol **15** (R = Me) (12 g, 0.0303 mol), PBr$_3$ (8.17 g, 0.0301 mol), benzene (300 mL), and water (0.12 g, 0.0067 mol) was kept at 45 °C under nitrogen for 48 h. It was evaporated in vacuo, and the solid residue was treated with saturated NaHCO$_3$ solution (100 mL) and extracted with CH$_2$Cl$_2$ (4 × 75 mL). The extracts were washed with water (100 mL), dried (MgSO$_4$), and evaporated in vacuo to give the crude dibromide **19** (R = Me) (13.34 g, 84%), which upon recrystallization from CH$_2$Cl$_2$−hexanes gave pure **19** (R = Me) (12.86 g, 81%) as white prisms: mp 183−184 °C; ^{1}H NMR (CDCl$_3$) δ 4.86 (s, 2H), 3.69 (s, 12H), 1.83 (s, 6H); ^{13}C NMR (CDCl$_3$) 165.65, 52.51, 52.21, 50.27, 47.89, 9.11; IR (KBr) 3030, 3000, 2954, 1739, 1437, 1344, 1243, 1200, 1064, 960; MS *m/z* CI 495 (3.0), 493 (9.4), 491 (5.2), 445 (5.1), 443 (8.3), 415 (4.5), 414 (17.8), 413 (91.1), 412 (32), 411 (100), 410 (10.1), 381 (50), 379 (44.6), 364 (6.1), 333 (46); EI 493 (5), 445 (8.5), 443 (5.2), 414 (21), 413 (79.5), 412 (28.4), 411 (91.3), 410 (7), 385 (9.7), 383 (11), 382 (8), 381 (46.5), 380 (10), 379 (46), 364 (6.3), 333 (22), 272 (100). Anal. Calcd for C$_{18}$H$_{20}$Br$_2$O$_8$: C, 41.24; H, 3.84. Found: C, 41.27; H, 3.85.

Tetramethyl 1,5-Dimethyl-2,4,6,8-semibullvalenetetracarboxylate (12, R = Me)[26] from *exo,exo*-dibromide 17. A stirred solution of sodium iodide (8.0 g, 0.0533 mol) and the dibromide **19** (R = Me) (5.24 g, 0.01 mol) in dry acetone (65 mL) was heated under reflux under nitrogen for 5 h. The acetone was removed in vacuo, water (100 mL) was added to the residue, and the mixture was extracted with ether (4 × 25 mL). The extracts were washed with water (25 mL) and saturated brine (25 mL), dried (MgSO$_4$), and evaporated in vacuo to give a quantitative yield of the crude semibullvalene. Recrystallization from hexanes−ethyl acetate gave the pure semibullvalene (3.1 g, 85%) as lustrous yellow cubes: mp 104−105 °C (lit.[26] mp 102.5−103 °C).

1,5-Dimethyl-2,4,6,8-semibullvalenetetracarboxylic Acid (20, R = Me). A stirred solution of the tetraester **12** (R = Me) (8.0 g, 0.022 mol) and sodium hydroxide (8 g, 0.2 mol) in THF (100 mL) and water (40 mL) was kept at ambient temperature under nitrogen for 18 h. The solution was cooled in an ice bath and acidified with concentrated HCl. The resulting precipitate (5.95 g, 88%) was collected, dried, and used without further purification. A small batch of the precipitate was recrystallized from water to give the tetraacid **20** (R = Me) as yellow plates: mp 182−183 °C dec; ^{1}H NMR (DMSO-d_6) δ 6.2 (s, 2H), 3.1 (br s, 4H), 1.4 (s, 6H); ^{13}C NMR (DMSO-d_6) 166.1, 130.3, 104.1, 67.8, 10.7; IR (KBr) 3850, 3000, 1704, 1594, 1409, 1251, 1150, 900; MS *m/z* CI 319 (1), 307 (2), 293 (3), 291 (64), 273 (77), 265 (100), 247 (90), 229 (98), 213 (95), 203 (96), 190 (25), 175 (64), 147 (28), 131 (84), 91 (62), 77 (39), 63 (35); EI 272 (36), 228 (13), 213 (16), 200 (24), 184 (52), 156 (40), 128 (80), 69 (42), 63 (68), 51 (65), 44 (100). Anal. Calcd for C$_{14}$H$_{12}$O$_8$: C, 54.54; H, 3.93. Found: C, 54.45; H, 3.87.

1,5-Dimethyl-4,6-semibullvalenedicarboxy-2,8-dicarboxylic Anhydride (21). A stirred mixture of the tetraacid **20** (R = Me) (0.558 g, 0.0181 mol), oxalyl chloride (2 mL), and dry THF (25 mL) was kept under nitrogen at 50 °C for 12 h. All volatile material was removed in vacuo to give the crude anhydride **21** (estimate 85% yield from NMR). This solid was recrystallized from dry ethyl acetate/hexanes to give the pure product (0.08 g) and a waxy residue, which still contained much anhydride **21**. Anhydride **21**: mp 240−242 °C dec; ^{1}H NMR (acetone-d_6) δ 6.6 (s, 2H), 1.53 (s, 3H), 1.40 (s, 3H); ^{13}C NMR (acetone-d_6) 164.5, 163.9, 144.4, 127.1, 80.7, 65.9, 64.9, 13.8, 10.0; IR (KBr) 3400, 3065, 1735, 1694, 1494, 1351, 1202, 1143; MS *m/z* EI 290 (8), 272 (15), 246 (100), 218 (65), 202 (71), 174 (55), 128 (65), 115 (71), 91 (72), 77 (71), 63 (27). Anal. Calcd for C$_{14}$H$_{10}$O$_7$: C, 57.94; H, 3.47. Found: C, 57.73; H, 3.66.

1,5-Dimethyl-2,4,6,8-semibullvalenetetracarboxylic Dianhydride (10). A stirred mixture of trifluoroacetic anhydride (20 mL) and the tetraacid **20** (R = Me) (1.0 g, 0.00325 mol) was kept under nitrogen at ambient temperature for 24 h. The suspended tetraacid slowly dissolved in the trifluoroacetic anhydride. The volatile materials were removed by distillation at ambient pressure, and the resulting viscous dark oil solidified on cooling. The solid was recrystallized from dry ethyl acetate/hexanes to give the dianhydride **10** (0.695 g, 79%) as yellow prisms. In an alternative workup, the residue remaining after removal of the volatile materials was triturated with ethyl acetate/hexanes and the resulting solid was purified by sublimation. Dianhydride **10**: sublimes (ambient pressure) above 200 °C; ^{1}H NMR (acetone-d_6) δ 6.39 (s, 2H) and 1.52 (s, 6H); ^{13}C NMR (acetone-d_6) 161.5, 125.0, 105.0, 68.9, 11.3; IR (KBr) 3030, 2948, 1875, 1836, 1802, 1768, 1758, 1560, 1452, 1222, 1123, 1084, 945, 881, 762, 736 cm^{-1}; MS *m/z* EI 272 (25), 244 (2), 228 (15), 200 (25), 184 (65), 156 (55), 128 (100), 102 (48), 87 (33), 74 (45). Anal. Calcd for C$_{14}$H$_8$O$_6$: C, 61.77; H, 2.96. Found: C, 62.00; H, 3.13.

Tetramethyl 1-Ethyl-5-methyltetracyclo[3.3.0^{1,5}.0^{2,8}.0^{4,6}]octane-3,7-dione-2,4,6,8-tetracarboxylate (14, R = Et). (a) From Tetramethyl 1-Ethyl-5-methyl-*cis*-bicyclo[3.3.0]octa-2,6-diene-3,7-diol-4-*exo*,8-*exo*-2,6-tetracarboxylate (25), the Major Isomer from the Weiss−Cook Condensation of Dimethyl 1,3-Acetonedicarboxylate with 2,3-Pentanedione.[36] A solution of bromine (0.9 g, 0.0054 mol) in chloroform (1 mL) was added to a stirred solution of the dienol **25** (1.0 g, 0.002 45 mol) at ambient temperature. After 5 h, the mixture was cooled in an ice bath and triethylamine (1.6 mL, 1.1 g, 0.011 mol) was added. The mixture was allowed to warm to ambient temperature and kept for a further 5 h. The solvent was removed in vacuo, and the residue was dissolved in ether (25 mL). The etheral solution was washed with water (25 mL), dried (MgSO$_4$), and evaporated in vacuo. The resulting solid was recrystallized from methanol/water to give the tetracyclic diketone **14** (R = Et) (0.76 g, 76%) as white prisms: mp 127−128 °C; ^{1}H NMR (CDCl$_3$) δ 3.77 (s, 6H), 3.76 (s, 6H), 2.21 (q, J = 7.3 Hz, 2H), 1.78 (s, 3H), 1.11 (t, J = 7.3 Hz, 3H); ^{13}C NMR (CDCl$_3$) 189.67, 162.19, 161.99, 53.53, 53.23, 50.09, 47.58, 16.45, 12.25, 8.55; IR (KBr) 3013, 2960, 2895, 1744, 1721, 1434, 1386, 1340, 1329, 1260, 1200, 1108, 1089; MS *m/z* CI 437 (6), 409 (20), 381 (36), 377 (100), 349 (36), EI 409 (2), 364 (14), 317 (27), 285 (46), 115 (26), 59 (100).

(b) From Tetramethyl 1-Ethyl-5-methyl-*cis*-bicyclo[3.3.0]octa-2,6-diene-3,7-diol-4-*endo*,8-*exo*-2,6-tetracarboxylate (25), the Minor Isomer from the Weiss−Cook Condensation of Dimethyl 1,3-Acetonedicarboxylate with 2,3-Pentanedione.[36] The above procedure was used with the dienol **25** (1.0 g, 0.002 45 mol), bromine (0.9 g, 0.0054 mol), and triethylamine (1.6 mL, 1.1 g, 0.011 mol) to give the tetracyclic diketone **14** (R = Et) (0.229 g, 23%).

(c) From a Mixture of 24:25 (∼3:2), the Mixture Isolated Directly from the Weiss−Cook Condensation of Dimethyl 1,3-Acetonedicarboxylate with 2,3-Pentanedione.[36] A similar procedure as above was used with the mixture of **24**/**25** (42.6 g, 0.1034 mol) in chloroform (150 mL), bromine (11.7 mL, 36.4 g, 0.227 mol) in chloroform (50 mL), and triethylamine (72 mL, 50.4 g, 0.499 mol) in chloroform (50 mL). After removal of all volatile material in vacuo, the residue was triturated with ether and the solid collected and resuspended in water. The product was collected, washed with water, and dried. The resulting tetracyclic diketone **14** (R = Et) (25 g, 59%) was of sufficient purity to use directly in the next step.

Tetramethyl 1-Ethyl-5-methyltetracyclo[3.3.0^{1,5}.0^{2,8}.0^{4,6}]octane-3-*endo*,7-*endo*-diol-2,4,6,8-tetracarboxylate (15, R = Et). Sodium borohydride (1.07 g, 0.029 mol) was added portionwise to a cooled (in an ice/salt bath), stirred solution of the diketone **14** (R = Et) (11.5 g, 0.028 mol) in THF (175 mL) and water (2.5 mL). The mixture was allowed to warm to ambient temperature and kept for 18 h. The solvent was removed in vacuo, and the residue was extracted into dichloromethane (150 mL). The extract was washed with water (3 × 10 mL), dried ($MgSO_4$), and evaporated in vacuo. The resulting viscous oil was crystallized from methanol−water to give the diol **15** (R = Et) (9.5 g, 79%) as white cubes: mp 120−121 °C; ^{1}H NMR ($CDCl_3$) δ 5.23 (d, J = 7.3 Hz, 2H), 4.12 (d, J = 7.3 Hz, 2H), 3.72 (s, 6H), 3.71 (s, 6H), 1.95 (q, J = 7.4 Hz, 2H), 1.49 (s, 3H), 0.91 (t, J = 7.4 Hz, 3H); ^{13}C NMR ($CDCl_3$) 167.73, 167.60, 74.07, 52.52, 52.50, 48.62, 48.33, 44.99, 16.37, 12.49, 8.80; IR (KBr) 3342, 2954, 2887, 1725, 1438, 1328, 1277, 1257, 1200, 1189, 1146, 1134, 1086; MS *m*/*z* EI 381 (26), 362 (70), 333 (31), 303 (100), 289 (37), 275 (83). Anal. Calcd for $C_{19}H_{24}O_{10}$: C, 55.34; H, 5.86. Found: C, 55.53; H, 5.83.

Tetramethyl 1-Ethyl-5-methyltetracyclo[3.3.0^{1,5}.0^{2,8}.0^{4,6}]octane-3-*exo*,7-*exo*-dibromo-2,4,6,8-tetracarboxylate (19, R = Et). A stirred mixture of the diol **15** (R = Et) (4.12 g, 0.01 mol), PBr_3 (1 mL, 2.85 g, 0.0105 mol), benzene (35 mL), and water (0.180 g, 0.01 mol) was kept at 42 °C under nitrogen for 48 h. It was evaporated in vacuo, and the solid residue was treated with ice-cold saturated $NaHCO_3$ solution (50 mL). The resulting precipitate was collected and recrystallized from dichloromethane−hexanes to give **19** (R = Et) (3.76 g, 72%) as white prisms: mp 181−182 °C; ^{1}H NMR ($CDCl_3$) δ 4.88 (s, 2H), 3.76 (s, 6H), 3.70 (s, 6H), 2.38 (q, J = 8.0 Hz, 2H), 1.92 (s, 3H), 1.16 (t, J = 8.0 Hz, 3H); ^{13}C NMR ($CDCl_3$) 165.70, 165.64, 53.43, 52.95, 52.56, 52.52, 52.09, 50.09, 50.35, 47.70, 15.99, 13.00, 8.9; IR (Nujol) 2900, 1751, 1728, 1457, 1377, 1306, 1262, 1247, 1216. Anal. Calcd for $C_{19}H_{22}Br_2O_8$: C, 42.40; H, 4.12. Found: C, 42.55; H, 4.32.

Tetramethyl (1,5)-Ethyl,methyl-2,4,6,8-semibullvalenetetracarboxylate (12, R = Et). A stirred solution of sodium iodide (6.0 g, 0.04 mol) and the dibromide **19** (R = Et) (6.0 g, 0.011 mol) in dry acetone (50 mL) was heated under reflux under nitrogen for 6 h. The acetone was removed in vacuo, water (100 mL) was added to the residue, and the mixture was extracted with ether (4 × 25 mL). The extracts were washed with 10% sodium thiosulfate solution (25 mL), water (25 mL), and saturated brine (25 mL), dried ($MgSO_4$), and evaporated in vacuo. The resulting residue was purified by column chromatography (silica) and recrystallized (methanol−water) to give the semibullvalene (2.29 g, 55%) as yellow cubes: mp 94−94.5 °C; ^{1}H NMR ($CDCl_3$) δ 6.36 (s, 2H), 3.77 (s, 6H), 3.74 (s, 6H), 2.10 (q, J = 8.1 Hz, 2H), 1.58 (s, 3H), 0.804 (t, J = 8.1 Hz, 3H); ^{13}C NMR ($CDCl_3$) 167.0, 165.08, 131.76, 114.0, 96.0, 74.69, 67.99, 52.20, 51.99, 11.50, 11.22; IR (KBr) 3030, 2955, 2934, 1744, 1729, 1713, 1599, 1456, 1429, 1387, 1378, 1331, 1287, 1274, 1243, 1232, 1202, 1195, 1168, 1121, 1073, 1045. Anal. Calcd for $C_{19}H_{22}O_8$: C, 60.31; H, 5.86. Found: C, 60.22; H, 5.80.

(1,5)-Ethyl,methyl-2,4,6,8-semibullvalenetetracarboxylic Acid (20, R = Et). A cooled (−10 °C) solution of sodium hydroxide (1 g, 0.025 mol) in water (4 mL) was added to a stirred solution of the tetraester **12** (R = Et) (0.8 g, 0.0021 mol) in THF (8 mL). The mixture was allowed to warm to ambient temperature and was kept for 24 h. The solvent was removed in vacuo and the resulting residue cooled to −20 °C and then acidified with concentrated HCl. The resulting yellow precipitate (0.341 g, 50%) was collected, washed with ice-cold water, dried, and used without further purification. A small batch of the precipitate was recrystallized from acetone−hexane to give the tetraacid **20** (R = Et): mp 194−195.5 °C dec; ^{1}H NMR ($CDCl_3$) δ 6.40 (s, 2H), 2.11 (q, J = 7.6 Hz, 2H), 1.60 (s, 3H), 0.82 (t, J = 7.6 Hz, 3H). Anal. Calcd for $C_{15}H_{14}O_8$: C, 55.90; H, 4.38. Found: C, 55.79; H, 4.50.

(1,5)-Ethyl,methyl-2,4,6,8-semibullvalenetetracarboxylic Dianhydride (11). A stirred mixture of trifluoroacetic anhydride (10 mL) and the tetraacid **20** (R = Et) (0.5 g, 0.001 55 mol) was kept under nitrogen at ambient temperature for 24 h. The suspended tetraacid dissolved in the trifluoroacetic anhydride within 1 h to give a pale yellow solution. The volatile materials were removed in vacuo. The solid residue was recrystallized from dry dichloromethane/hexanes to give the dianhydride **11** (0.160 g, 32%) as yellow prisms: sublimes (ambient pressure) above 165 °C; ^{1}H NMR ($CDCl_3$) δ 6.35 (s, 2H), 1.91 (q, J = 6.5 Hz, 2H), 1.56 (s, 3H), 0.96 (t, J = 6.5 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 159.5, 158.8, 122.8, 110.0, 101.9, 72.7, 67.5, 19.7, 11.7, 11.0; IR (KBr) 3069, 2992, 2970, 2938, 2881, 1837, 1806, 1762, 1557, 1481, 1388, 1229, 1122, 940, 877, 735 cm^{-1}; MS *m*/*z* EI 286 (37), 227 (28), 198 (45), 170 (34), 141 (72), 115 (58), 67 (100). Anal. Calcd for $C_{15}H_{10}O_6$: C, 62.94; H, 3.52. Found: C, 63.03; H, 3.60.

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