J. Org. Chem. **2001,** *66,* 1949−1960

Lifting of the Degeneracy in Semibullvalenes by Remote and Direct Substituents: A Quantitative Study Using Variable-Temperature Carbon-13 NMR Spectroscopy†

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Received July 14, 2000

A series of six 1,5-(ethylmethyl)semibullvalenes (**1a** $\rightleftharpoons$ **1a′**, **2** $\rightleftharpoons$ **2′**, **3** $\rightleftharpoons$ **3′**) and two 4(2)-substituted semibullvalenes (**4** $\rightleftharpoons$ **4′**), each undergoing Cope equilibria between nondegenerate valence tautomers, was investigated by carbon-13 NMR spectroscopy at a range of temperatures in several different solvents. Gompper's treatment of substituent perturbation was extended, specifically accounting for the effects of the substituents on chemical shifts, to allow the determination of the thermodynamic parameters for these skewed equilibria. These new treatments were used to determine the population difference ($f - f'$) between the valence tautomers and the perturbation thermodynamic quantities ΔH^p, ΔS^p, and ΔG^p. The slow-exchange limit was reached for the parent 1,5-(ethylmethyl)semibullvalenes **3a** $\rightleftharpoons$ **3a′** from which it was established that the preferred valence tautomer is **3a** with the ethyl group on the cyclopropane ring. Despite considerable effort, the slow-exchange limit could not be reached in any of our other remotely substituted semibullvalenes. Provided that the ethyl group always prefers the cyclopropyl position as in **3a**, the 1-ethyl-5-methylsemibullvalenes **1a, 2,** and **3** are more stable by $\Delta H^p = 0.7{-}1.7$ kJ mol^{-1} than their valence tautomers **1a′, 2′,** and **3′**. In the directly substituted semibullvalenes (**4** $\rightleftharpoons$ **4′**), the preferred valence tautomers **4a** and **4b** have the bromine atom or the nitrile group on the vinyl position (C_4) rather than on the cyclopropane ring (C_2) and are more stable than **4a′** and **4b′** by $\Delta H^p = 4.8$ and 7.0 kJ mol^{-1}, respectively.

Introduction

Many substituted semibullvalenes undergo *degenerate* Cope rearrangements via transition structures, which may exhibit C_2, C_S, or C_{2v} symmetry.[2,3] There are also semibullvalenes that are completely locked in one of the two possible valence tautomeric structures, e.g., benzosemibullvalenes.[4,5] Between these limiting cases, a considerable number of semibullvalenes exist whose Cope equilibria are more or less skewed by virtue of appropriately placed substituents (including monoannelation),[2,6−12] deuterium atoms,[13] or heteroatoms[14]. These nondegenerate semibullvalenes merit renewed interest for several reasons.

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† Dedicated to Professor Leo A. Paquette on the occasion of his 65th birthday

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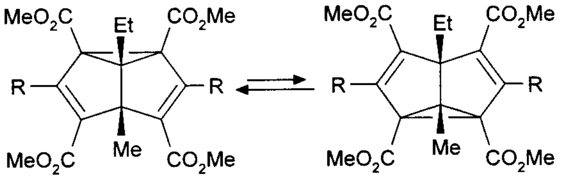
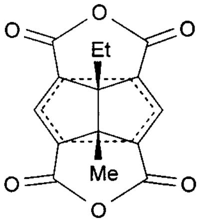
10.1021/jo001062a CCC: \$20.00

In an extension of Saunders' isotopic perturbation method,[15a−e] substituents other than isotopes may be employed to distinguish single-minimum systems from those that are characterized by symmetrical double-well potentials. Perturbation by ethyl vs. methyl substituents was used by Sorensen et al. to characterize the 1,6-dimethylcyclodecyl cation as a μ-hydrido bridged system rather than as a pair of rapidly equilibrating classical ions.[15f] This method, adopted by Gompper et al. [11a] using the tetramethyl 1,5-(ethylmethyl)semibullvalene tetracarboxylates **1b** ⇌ **1b′**, **1c** ⇌ **1c′**,[16] is particularly attractive for systems where isotopic substitution would involve an enormous synthetic effort.[13d] Recently, we used this method to probe the nature of the ground state, a delocalized (**2a***) or a localized system, of the semibullvalene bisanhydrides **2a** ⇌ **2a′**.[11e,f] The slow-exchange limit could not be reached in this system, and consequently the position of the skewed equilibrium could not be determined. Similarly, Gompper et al. could not determine the position of the equilibria in **1b** ⇌ **1b′** and **1c** ⇌ **1c′**, and consequently they were only able to estimate *absolute* values of the thermodynamic parameters.[11a] No such data are available for the semibullvalene bisanhydrides **2a** ⇌ **2a′**. The availability of 151-MHz carbon-13 spectra recorded at definite temperatures allowed us to obtain precise equilibrium data. In addition, an advanced treatment that avoids the compression associated with the standard logarithmic methods correctly weights the experimental data ensuring increased accuracy.

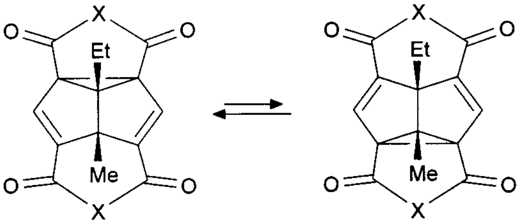


1 **1'**

1a: R = H; **1b**: R = OMe; **1c**: R = O-CO-Ph



2a*



2 **2'**

2a: X = O; **2b**: X = NPh

Manz and co-workers considered substituted semibullvalenes with skewed Cope equilibria as candidates for a pump−dump−probe strategy for the spectroscopic observation of the transition structure during a laser-controlled isomerization.[11b−d,17]

Their theoretical model simulations suggest that the Cope rearrangement may be controlled by two infrared picosecond laser pulses: The pump pulse excites the reactant to the transition state whose transient population may be monitored by another ultrashort, yet weak, probe laser pulse. The dump pulse stabilizes the product. Their favored candidate for the laser-driven Cope rearrangement is the system consisting of the two semibullvalene-2,6-dicarbonitriles **3b** and **3b′**.[11b−d] Knowledge of their relative stabilities is, of course, a prerequisite for the experimental realization of this proposal.

We have exploited the enormous equilibrium-driven temperature dependence of the substituent-induced splitting of carbon-13 signals, measured for the semibullvalene-2,6-dicarbonitriles **3b** ⇌ **3b′**, for the development of a high-precision carbon-13 shift thermometer in the temperature range 100−300 K.[11g] We now report the thermodynamic parameters for this equilibrium.

We confine our studies to representative examples from two different classes of nondegenerate semibullvalenes. In the first, (**1** ⇌ **1′**)−(**3** ⇌ **3′**), the equilibrium is perturbed by a *remote* substituent which we define as being separated from the terminal carbon atoms $C_{2,4,6,8}$ by several bonds. The second class, **4** ⇌ **4′**, involves *direct* substitution at one of the terminal atoms.

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(16) We use the abbreviation 1,5-(ethylmethyl)semibullvalenes to denote the mixture of the valence tautomers composed of the 1-ethyl-5-methylsemibullvalene and 5-ethyl-1-methylsemibullvalene moieties. Each carbon atom that undergoes exchange of the environment due to the Cope rearrangement of the two valence tautomers is given the *same* number in *both* valence tautomers. A prime is added to this number if the carbon belongs to the minor valence tautomer.

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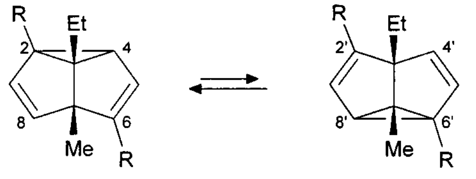
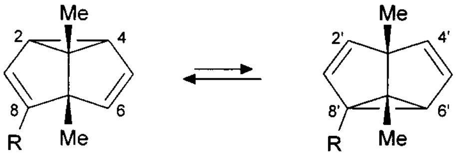


3 **3'**

3a: R = H; **3b**: R = CN; **3c**: R = CO_2Me



4 **4'**

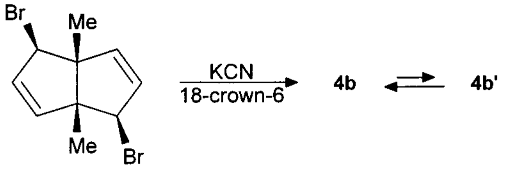
4a: R = Br; **4b**: R = CN

Results and Discussion

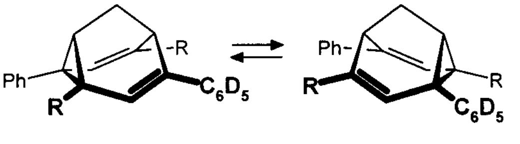
Synthesis of the Compounds Studied. The syntheses of the tetraesters **1a** $\rightleftharpoons$ **1a′** and the bisanhydrides **2a** $\rightleftharpoons$ **2a′** have been reported previously.[11e,f] The bisimides **2b** $\rightleftharpoons$ **2b′** are prepared from the bisanhydrides **2a** $\rightleftharpoons$ **2a′** by reaction with aniline to give a mixture of isomeric diacid–diamide intermediates which are not isolated but directly converted to the imides **2b** $\rightleftharpoons$ **2b′** by acetic anhydride-mediated dehydration.

Detailed protocols for the syntheses of the 1,5-dimethylsemibullvalenes **5a**,[18] **5b**,[19,20] and **5c**[20] corresponding with the (1,5)-ethylmethylsemibullvalenes **3** $\rightleftharpoons$ **3′** have been published. These protocols were followed in the syntheses of the latter semibullvalenes. Of course, the unsymmetrical substitution pattern resulted in the formation of more complex mixtures of isomeric intermediates (as shown in Schemes 1 and 2). In general, the mixed intermediates were carried through to the pure tautomeric mixtures of **3** $\rightleftharpoons$ **3′**.

We have previously published experimental details for the conversion of dibromide **21** to the monobromides **4a** $\rightleftharpoons$ **4a′**[10c] first reported by Askani.[9a] Askani also prepared solutions of the mononitriles **4b** $\rightleftharpoons$ **4b′** from these monobromides.[9c] However, the mononitriles were not purified or isolated and were only characterized by 60 MHz proton NMR spectra. We developed an improved one-step synthesis of these mononitriles from the dibromide **21**. After isolation of **4b** $\rightleftharpoons$ **4b′** by preparative gas chromatography, high-field proton and carbon-13 NMR spectra were recorded; this confirmed Askani's previous assignment of **4b** as the predominant isomer.

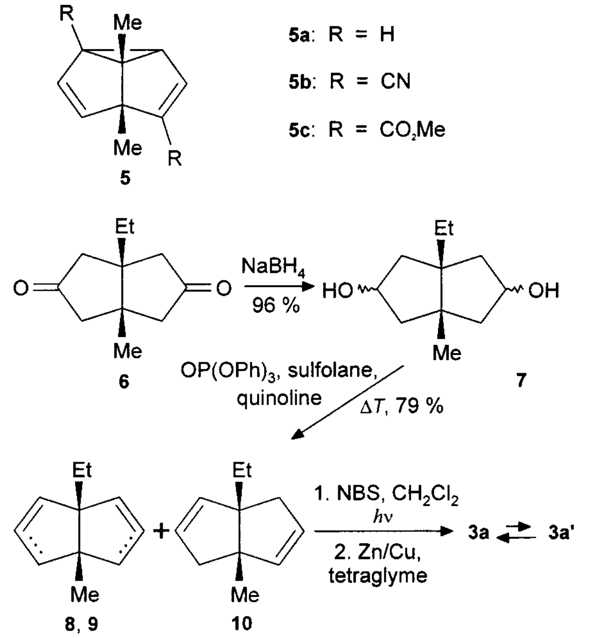


21



22a: R = Ph; **22b**: R = CN

Scheme 1



Perturbation of Degeneracy by Substituents Observed Through Variable-Temperature Carbon-13 NMR Spectroscopy. Saunders et al. developed isotopic perturbation as a method for distinguishing between static (single-minimum) and equilibrating (double-minimum) structures.[15] We have recently extended this technique to establish the solution structures of barbaralanes **22** $\rightleftharpoons$ **22′**.[21]

An advantage of deuterium isotopic perturbation is the opportunity to recognize the position of the skewed equilibria from the well-known isotope effects upon carbon-13 signals.[13e] Unfortunately, the long-range effects on carbon-13 signals of remote perturbing substituents do not permit unequivocal recognition of the dominant valence tautomer unless slow-exchange is attained and *both* valence tautomers can be observed.

Even with the availability of a 151 MHz carbon-13 NMR spectrometer capable of temperatures down to 100 K,[11g] slow-exchange spectra could only be obtained for the hydrocarbons **3a** $\rightleftharpoons$ **3a′** (Figures 1 and 2) despite considerable effort expended on our other 1,5-(ethylmethyl)semibullvalenes. At slow exchange for **3a** $\rightleftharpoons$ **3a′**, the two time-averaged signals for the carbon atoms $C_{2,8}$ ($C_{2',8'}$) and $C_{4,6}$ ($C_{4',6'}$) (observed at higher temperatures) are split into two pairs of signals. These new signals are of different intensities that correspond to the ratio of the valence tautomers at the slow-exchange limit.

The well-known γ gauche effect exerted by the remote methyl substituent ($Me-CH_2$) shifts the γ carbon resonances to higher field.[22] An inspection of Figure 1 immediately reveals that the *cyclopropyl* carbon-13 signals of the *major* valence tautomer (**3a**) are shifted to

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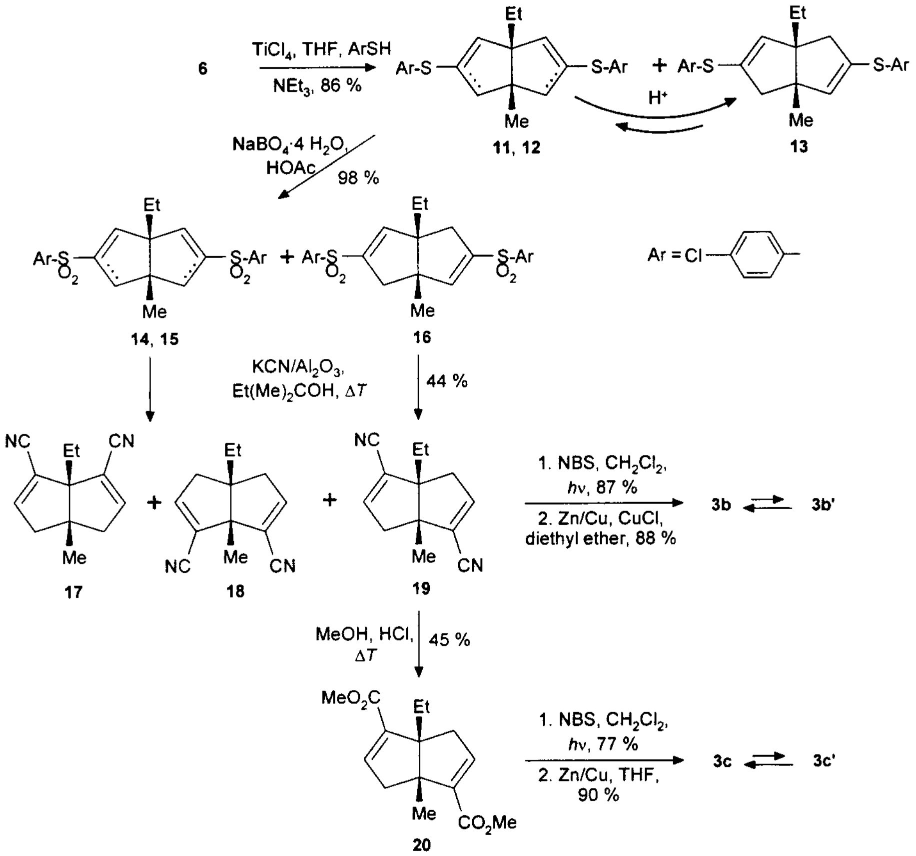
Scheme 2



higher field while this effect is observed for the *vinyl* carbon-13 signals of the *minor* isomer (**3a′**). These findings unequivocally establish the position of the equilibrium between **3a** and **3a′**. It seems reasonable to assume this same preference for the other 1,5-(ethylmethyl)semibullvalenes.

The temperature-dependent splitting of the time-averaged carbon-13 signals of **3a** $\rightleftharpoons$ **3a′** is demonstrated over the temperature range 150−360 K in Figure 2. In the region of coalescence between 150 and 120 K, the signals of interest disappear in the noise and are further obscured by the solvent signals. Below 120 K, the slow-exchange signals are observed and the splittings thus obtained are used in the calculation of the perturbation parameters ΔH^{P} and ΔS^{P} (vide infra).

Direct substitution on one of the terminal carbon atoms ($C_{2,4,6,8}$) results, in general, in more pronounced perturbations which cause stronger equilibrium imbalances. As a consequence, the minor valence tautomer may not be observed at temperatures below the coalescence region. The slow-exchange NMR spectrum instantly reveals the structure of the major isomer, viz **4a** (Figures 3 and 4).

There is yet another situation where the minor valence tautomer virtually disappears on cooling *before* any signal broadening and coalescence can be detected. In this case, the chemical shifts smoothly become temperature-independent as shown for **4b** $\rightleftharpoons$ **4b′** in Figures 5 and 6.

The Perturbation Parameters ΔH^{P} and ΔS^{P}. We define ΔH^{P} and ΔS^{P} as the differences between the thermodynamic parameters of the equilibrating valence tautomers. For the calculation of these differences from variable-temperature carbon-13 spectra, we adopt Saunders' expression (eq 1) which relates the difference between the fractions of the equilibrating species (the population excess $f - f'$) to the relative splitting $\Delta\delta^{\mathrm{P}}/\Delta\delta$ induced by the *isotopic* substitution.

$$f - f' = \frac{\Delta\delta^{\mathrm{P}}}{\Delta\delta} \qquad (1)$$

$\Delta\delta^{\mathrm{P}}$ is the equilibrium-driven difference in chemical shifts between the positions that would be time-averaged to equivalence in the absence of the perturbation. $\Delta\delta$ is the corresponding chemical shift difference for the *unperturbed* system in the slow-exchange limit; f and f' are the fractions of the two components present, where $f + f' = 1$.

Defining the equilibrium constant $K = f'/f$ such that its value is less than unity at low temperatures, we relate the population excess with the equilibrium constant by eq 2.

$$f - f' = \frac{1 - K}{1 + K} \qquad (2)$$

Introduction of the well-known temperature dependence of K relates the population excess with the temperature as in eq 3, the use of which correctly weights the experimental data. Fitting eq 3 to the experimental data using the nonlinear least-squares method affords the perturbation parameters.[21]

$$f - f' = \frac{1 - \exp\left(\frac{\Delta S^{\mathrm{P}}}{R} - \frac{\Delta H^{\mathrm{P}}}{RT}\right)}{1 + \exp\left(\frac{\Delta S^{P}}{R} - \frac{\Delta H^{\mathrm{P}}}{RT}\right)} \qquad (3)$$

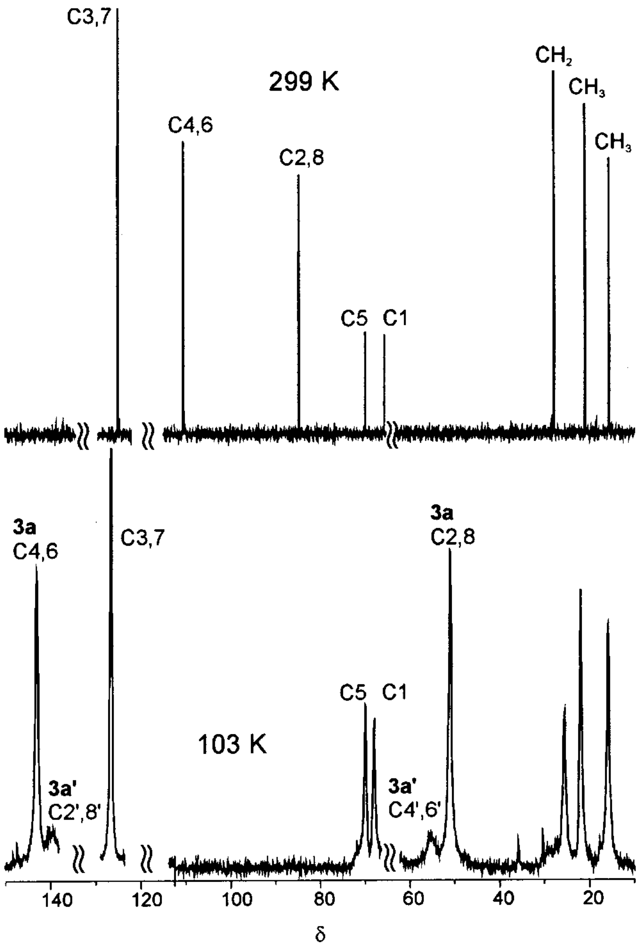


Figure 1. Carbon-13 spectra of the 1,5-(ethylmethyl)semibullvalenes **3a** $\rightleftharpoons$ **3a′** recorded for a solution in bromotrifluoromethane/chlorodifluoromethane/perdeuterated dimethyl ether (3:2:1) in the limit of fast (at 299 K, above) and slow exchange (at 103 K, below); for the sake of clarity, solvent signals have been omitted.

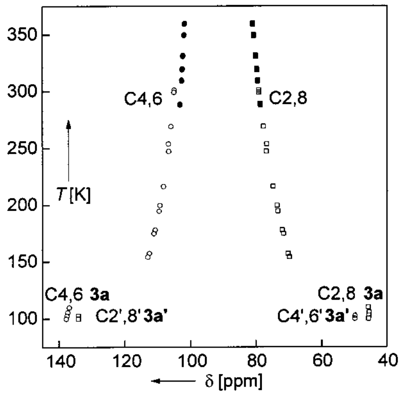


Figure 2. Chemical shifts vs temperature for the carbon atoms $C_{2,8}$ and $C_{4,6}$ of the 1,5-(ethylmethyl)semibullvalenes **3a** $\rightleftharpoons$ **3a′**. The filled symbols stem from experiments performed without a solvent, the hollow ones from carbon-13 spectra recorded for solutions as described in Figure 1.

If the perturbation is caused by substituents other than isotopes, the expression for the population excess (eq 1) must be modified to account for intrinsic substituent effects on chemical shifts. Consider two exchange-related carbon atoms C_i, C_j, say C_2 and C_6 of **1**−**4**, with limiting chemical shifts δ_i, $\delta_{i'}$, and δ_j, $\delta_{j'}$, respectively, in the slow-exchanging valence tautomers (Figure 7). The time-averaged chemical shifts of C_i and C_j are given by eqs 4a and b.

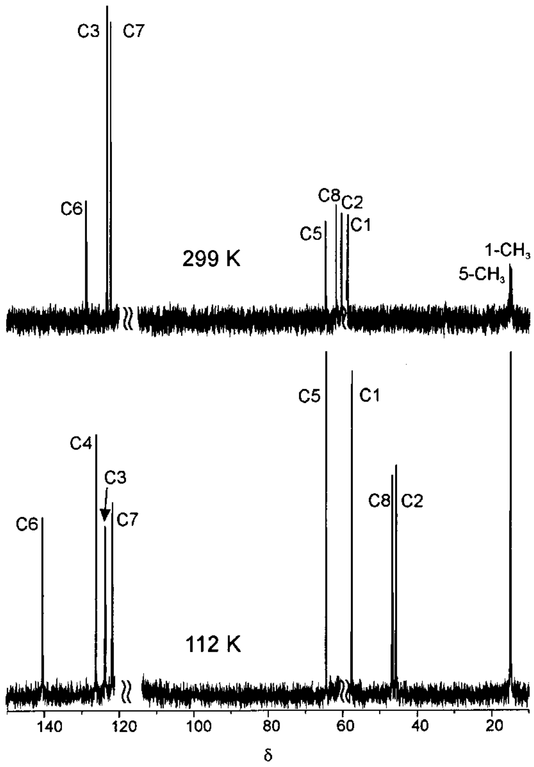


Figure 3. Carbon-13 spectra of the bromo-1,5-dimethylsemibullvalenes **4a** $\rightleftharpoons$ **4a′** recorded for a solution in chlorodifluoromethane/perdeuterated dimethyl ether (5:1) in the limit of fast (at 299 K, above) and slow exchange (at 112 K, below); for the sake of clarity, solvent signals have been omitted. At a temperature of 299 K, the signals of C1 and C4 are partially obscured by the signals of perdeuteriodimethyl ether and chlorodifluoromethane, respectively.

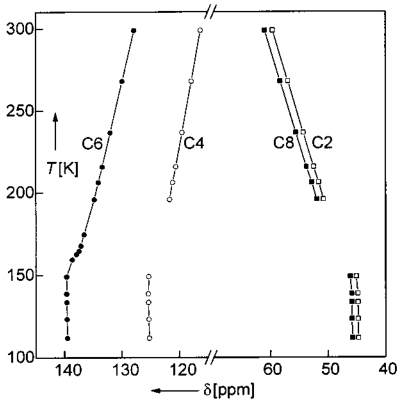


Figure 4. Chemical shifts vs temperature for the carbon atoms $C_{2,4,6,8}$ of the bromo-1,5-dimethylsemibullvalenes **4a** $\rightleftharpoons$ **4a′**. The spectra were taken from solutions as described for Figure 3.

$$\bar{\delta}_i = f\,\delta_i + f'\,\delta_{i'} \tag{4a}$$

$$\bar{\delta}_j = f\,\delta_j + f'\,\delta_{j'} \tag{4b}$$

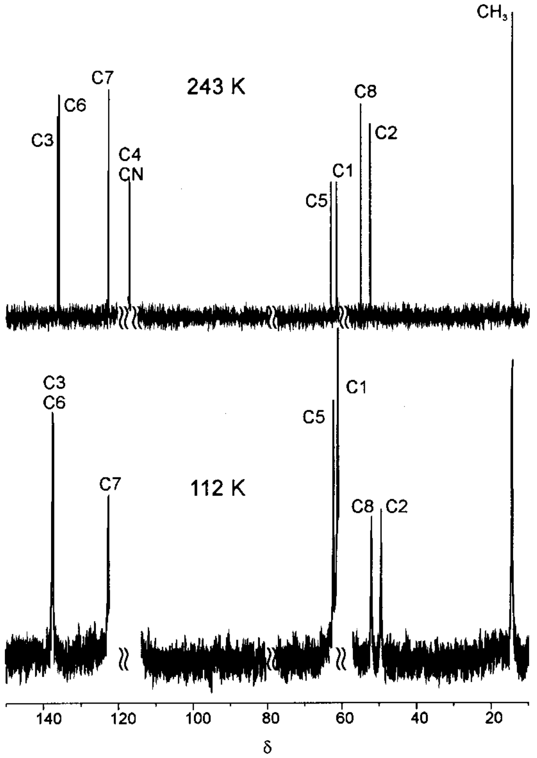


Figure 5. Carbon-13 spectra of the 1,5-dimethylsemibullvalenecarbonitriles **4b** $\rightleftharpoons$ **4b′** recorded for a solution in chlorodifluoromethane/deuteriochloroform/perdeuterated dimethyl ether (8:1:2) at a temperature of 243 K (above) and 112 K (below); for the sake of clarity, solvent signals have been omitted. At a temperature of 112 K, the signals of C_4 and the cyano group are obscured by the triplet of chlorodifluoromethane.

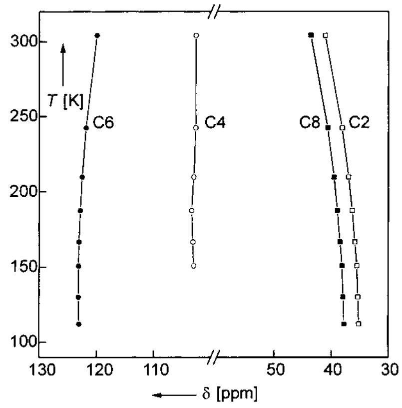
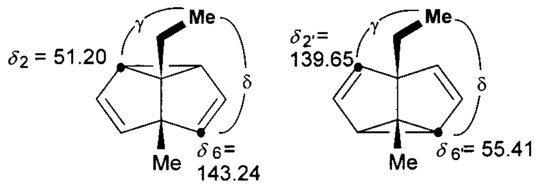


Figure 6. Chemical shifts vs temperature for the carbon atoms $C_{2,4,6,8}$ of the 1,5-dimethylsemibullvalenes **4b** $\rightleftharpoons$ **4b′**. The spectra were taken from solutions as described for Figure 5.

The population excess may then be expressed in terms of the limiting and the averaged chemical shifts by eq 5.

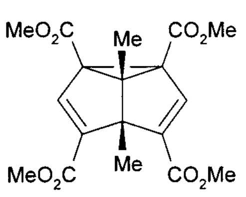
$$f - f' = \frac{\bar{\delta}_j - \delta_{j'}}{\delta_j - \delta_{j'}} - \frac{\bar{\delta}_i - \delta_i}{\delta_{i'} - \delta_i} \qquad (5)$$

The precise calculation of the population excess according to eq 5 hence requires the recording of NMR spectra in the slow-exchange limit for *both* valence tautomers. Unfortunately, this was only possible for the parent hydrocarbons **3a** and **3a′** (Figure 1). Therefore, the following approximate equation was derived for the *substituted* 1,5-(ethylmethyl)semibullvalenes **1a** $\rightleftharpoons$ **1a′**, **2** $\rightleftharpoons$ **2′**, **3b** $\rightleftharpoons$ **3b′**, and **3c** $\rightleftharpoons$ **3c′**. Provided that the differences $\delta_{j'} - \delta_i$ and $\delta_j - \delta_{i'}$ between the two long-range effects (δ and γ) exerted by the remote methyl substituent, of the ethyl group, are equal for the cyclopropyl (C_i, $C_{j'}$) and the vinyl position ($C_{i'}$, C_j), we can equate the two denominators in eq 5 with the corresponding shift difference $\Delta\delta$ for the *unperturbed* valence tautomers **5**, **23**, and **24** observable, in principle, in the slow-exchange limit. Thus, the approximate eq 6 results from the exact eq 5.

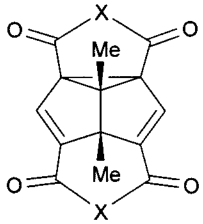


3a **3a'**

Figure 7. γ and δ effects of the remote methyl substituent on the chemical shifts of vinyl and cyclopropyl carbons of the 1,5-(ethylmethyl)semibullvalenes **3a** $\rightleftharpoons$ **3a′**. The spectra were taken at a temperature of ca. 100 K from solutions as described for Figure 1.



23



24

24a: X = O; **24b**: X = NPh

$$f - f' \approx \frac{\Delta\delta_{\text{obs}} - \Delta\delta_{\text{intr}}}{\Delta\delta} = \frac{\Delta\delta^{\text{P}}}{\Delta\delta} \qquad (6)$$

$\Delta\delta_{\text{obs}} = \bar{\delta}_j - \bar{\delta}_i$ is the *observed* splitting, $\Delta\delta_{\text{intr}} = \delta_{j'} - \delta_i \approx \delta_j - \delta_{i'}$ the difference between the intrinsic δ and γ effects of the remote methyl substituent upon equivalent positions of **3a** (Figure 7), and $\Delta\delta^{\text{P}}$ the *equilibrium-driven* shift difference between C_j and C_i.

Clearly, consideration of the intrinsic shift effects of the perturbing substituent is necessary to afford eq 6 which is equivalent to Saunder's expression (eq 1) derived for isotopic perturbation. Whereas eq 5 also holds for perturbations by *direct* substituents, e.g., as in **4** $\rightleftharpoons$ **4′**, the assumptions used in the derivation of eq 6 are certainly invalid in this case.

The carbon-13 NMR spectra of the parent 1,5-(ethylmethyl)semibullvalenes **3a** $\rightleftharpoons$ **3a′** could be recorded for both valence tautomers in the limit of slow exchange and thus provided an opportunity to probe the assumption used in the derivation of eq 6. Examination of the entries for **3a** $\rightleftharpoons$ **3a′** in Table 1 reveals that the perturbation parameters are essentially identical whether obtained using the exact eq 5 or the approximate eq 6. The agreement lends support for the use of the approximate eq 6 in determining the perturbation parameters for our other 1,5-(ethylmethyl)semibullvalenes. As can be cal-

Table 1. Thermodynamic Parameters ΔH^{P} (in kJmol^{-1}), ΔS^{P} (in Jmol^{-1}K^{-1}), and ΔG^{P} (kJ mol^{-1} at 300 K) of Skewed Cope Equilibria of Semibullvalenes and Population Excess $f - f'$ (in % at 300 K) as Measured by the Substituent-Induced Saunders' Relative Splittings $\Delta\delta^{\mathrm{P}}/\Delta\delta$ of NMR Signals from Carbon-13 Atoms that Are Time-averaged to Equivalence in the Absence of the Perturbing Substituents

cpd	T/K	solvent	ΔH^{P} (eq 3)	ΔS^{P} (eq 3)	eq[a]	ΔG^{P} (300 K)	$f - f'$ [b] (300 K)
1a $\rightleftharpoons$ **1a′**	185−289	CD_2Cl_2	1.678 ± 0.025	3.08 ± 0.11	6	0.75	15.0
1b $\rightleftharpoons$ **1b′**	233−306	$CDCl_3$	2.51 ± 0.17	5.0 ± 0.2	*c*	1.0	20
1c $\rightleftharpoons$ **1c′**	233−306	$CDCl_3$	1.55 ± 0.17	2.1 ± 0.2	*c*	0.9	18
2a $\rightleftharpoons$ **2a′**	185−289	[D_8]toluene	0.723 ± 0.005	1.51 ± 0.02	6	0.27	5.4
	279−340	DMPU	0.835 ± 0.011	1.76 ± 0.04	6	0.31	6.1
2b $\rightleftharpoons$ **2b′**	185−289	CD_2Cl_2	0.737 ± 0.019	1.26 ± 0.09	6	0.36	7.2
	279−361	DMPU	0.869 ± 0.010	1.62 ± 0.03	6	0.38	7.7
3a $\rightleftharpoons$ **3a′**	288−360	neat liquid	1.078 ± 0.012	−0.22 ± 0.04	5	1.14	22.5
			1.080 ± 0.013	−0.20 ± 0.04	6	1.14	22.5
	154−301	$CBrF_3/CHClF_2/D_3COCD_3$ (3:2:1)	1.181 ± 0.014	−0.31 ± 0.07	5	1.27	25.0
			1.184 ± 0.010	−0.29 ± 0.05	6	1.27	25.0
3b $\rightleftharpoons$ **3b′**	104−301	$CHClF_2/D_3COCD_3$ (3:1)	0.774 ± 0.006	−0.28 ± 0.04	6	0.86	17.0
			0.774 ± 0.006	−0.26 ± 0.03	6[d]	0.85	16.9
	265−370	DMPU	0.826 ± 0.016	0.50 ± 0.05	6	0.68	13.5
3c $\rightleftharpoons$ **3c′**	171−304	$CHClF_2/D_3COCD_3$ (5:1)	0.807 ± 0.035	−0.88 ± 0.15	6	1.07	21.1
4a $\rightleftharpoons$ **4a′**	196−299	$CHClF_2/D_3COCD_3$ (5:1)	4.775 ± 0.030	2.32 ± 0.12	7	4.08	67.4
	213−313	$CDCl_3$			*e*	4.4	71
	150−233	$CHClF_2/CD_2Cl_2$ (4:1)			*e*	3.9	66
4b $\rightleftharpoons$ **4b′**	242−304	$CDCl_3$	7.709 ± 0.237	0.30 ± 0.82	7	7.6	91
	130−304	$CHClF_2/CDCl_3/D_3COCD_3$ (8:2:1)	7.019 ± 0.098	0.40 ± 0.38	7	6.9	88

[a] Equation used in the calculation of the values for the population excess $f - f'$ from the NMR data reported in the Supporting Information. [b] Calculated from ΔG^{P} (300 K). [c] The absolute values for the perturbation parameters have been reported by Gompper et al.[11a] [d] Calculated from published $\Delta\delta_{6,2}$ values that have been determined at 37 temperatures (range 104−301 K) which were measured with calibrated platinum resistance thermometers.[11g] [e] Ref 10c.

culated from the chemical shifts given in Figure 7, the differences $\delta_{6'} - \delta_2$ (4.21 ppm) and $\delta_6 - \delta_{2'}$ (3.59 ppm) are indeed not very far apart. Consequently, their rounded average (4 ppm) was taken as the value of $\Delta\delta_{\mathrm{intr}}$ in eq 6 employed for our substituted 1,5-(ethylmethyl)-semibullvalenes.

We examined the sensitivity of the perturbation parameters ΔH^{P} and ΔS^{P} to the value of $\Delta\delta_{\mathrm{intr}}$ by calculating them for the equilibrium between the semibullvalenedicarbonitriles **3b** $\rightleftharpoons$ **3b′** according to eq 6 using $\Delta\delta_{\mathrm{intr}} = (4 \pm 1)$ ppm. The results show that variation of $\Delta\delta_{\mathrm{intr}}$ by 1 ppm translates into variations in ΔH^{P} of less than 1% and into variations of ± 0.2 J mol^{-1} K^{-1} in the value for the entropy term ΔS^{P} (−0.3 J mol^{-1} K^{-1}).

Besides eqs 5 and 6, there is a third way for the calculation of the population excess $f - f'$ from experimental data. This approach is based on chemical shifts of a *single* carbon atom C_i instead of two as in eqs 5 and 6. Equation 4a may be solved for f'. Because $f = 1 - f'$, the population excess is expressed by eq 7.

$$f - f' = 1 - 2f' = 1 - 2\frac{\bar{\delta}_i - \delta_i}{\delta_{i'} - \delta_i} \qquad (7)$$

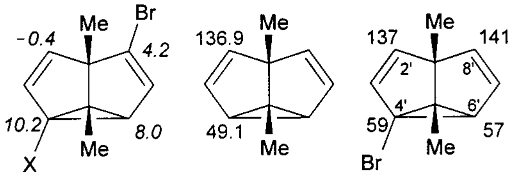
The parameters in eq 7 are the limiting chemical shift δ_i of that carbon atom in one of the two exchanging environments and the difference $\delta_{i'} - \delta_i$ between its limiting shifts in both valence tautomers.

Estimation of Carbon-13 Chemical Shifts for Valence Tautomers in the Slow-Exchange Limit. As has already been emphasized above, carbon-13 spectra of both valence tautomers, in the slow exchange limit, could be recorded only for the parent 1,5-(ethylmethyl)-semibullvalenes (**3a** and **3a′**, Figures 1, 2, and 7). Hence only these were suited to the application of the exact eq 5, which only neglects the inherent temperature dependence of the limiting chemical shifts. For all other nondegenerate semibullvalenes studied here, estimates of carbon-13 chemical shifts were necessary.

Use of eq 6 requires knowledge of the limiting shift differences $\Delta\delta$ of the corresponding *unperturbed* semibullvalene. Estimates for the degenerate semibullvalenes **5b** and **5c** have recently been reported[3]. Independent use, in eq 6, of $\Delta\delta_{6,2}$ and $\Delta\delta_{4,8}$ (estimated for **5b**: $\Delta\delta_{6,2} = 75.7$, $\Delta\delta_{4,8} = 83.7$ ppm; estimated for **5c**: $\Delta\delta_{6,2} = 80.6$, $\Delta\delta_{4,8} = 87.7$ ppm) gave rise to two somewhat differing sets of values for the population excess of each system **3b** $\rightleftharpoons$ **3b′** and **3c** $\rightleftharpoons$ **3c′**; a result that, of course, cannot be true. Therefore, both pairs of estimated limiting shift differences $\Delta\delta$ were adjusted by correction terms of 2.4 ppm for **5b** and of 2.6 ppm for **5c**, which were calculated by setting $\Delta\delta^{\mathrm{P}}_{6,2}/\Delta\delta_{6,2}$ and $\Delta\delta^{\mathrm{P}}_{4,8}/\Delta\delta_{4,8}$ equal at ca. 300 K. The corrected parameters eventually employed in eq 6 are $\Delta\delta_{6,2} = 78$ and $\Delta\delta_{4,8} = 81$ ppm for **5b** and $\Delta\delta_{6,2} = 83$ and $\Delta\delta_{4,8} = 85$ ppm for **5c**.

It is very difficult to estimate the $\Delta\delta$ values for the tetraester **23**, the bisanhydride **24a**, and the bisimide **24b**. We assume that the required $\Delta\delta$ values are in the range $\Delta\delta = 80-100$ ppm as all $\Delta\delta$ values determined for degenerate 1,5-dimethylsemibullvalenes fall within this range.[3,10f] We probed the sensitivity of the values of the perturbation parameters toward variation of the limiting shift differences $\Delta\delta$. Toward this end, values for the population excess $f - f'$ were calculated according to eq 6 for **1a** $\rightleftharpoons$ **1a′** and **2** $\rightleftharpoons$ **2′** from values of $\Delta\delta = (90 \pm 10)$ ppm and employed in the fits of eq 3. The results show that variation of $\Delta\delta$ by 10 ppm corresponds with changes in ΔH^{P} of less than 13% and in ΔS^{P} of less than 1 JK^{-1}mol^{-1}. The perturbation parameters listed in Table 1 were calculated with the admittedly rough estimate $\Delta\delta = 90$ ppm.

The minor valence tautomers **4a′** and **4b′** could not be observed by carbon-13 NMR spectroscopy at low temperatures, consequently their chemical shifts must be estimated for the calculation of the population excess according to eq 7. The estimates for the bromosemibullvalene **4a′** are based on the chemical shifts of **4a**, **5a**, and the 2,6-dibromosemibullvalene **25** (Figure 8).[10f] We assume

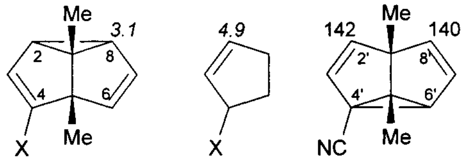


4a: X = H
25: X = Br

5a

4a'

Figure 8. Changes of carbon-13 chemical shifts ([ppm], *in italics*) by formal introduction of a bromine atom at the cyclopropane ring of **4a** (→**25**), observed chemical shifts of **5a**, and estimated chemical shifts for **4a′**.



5a: X = H
4b: X = CN

26a: X = H
26b: X = CN

4b'

Figure 9. Changes of carbon-13 chemical shifts ([ppm], *in italics*) by formal introduction of a carbonitrile group at a vinyl position of **5a** (→**4b**) and an allylic position of cyclopentene (**26a** → **26b**), and estimated chemical shifts for **4b′**.

that formal introduction of a bromine atom at the cyclopropane ring of **4a**, affording **25**, changes the chemical shifts of **4a** in the same way and magnitude as the analogous formal conversion of **5a** into the bromosemibullvalene **4a′**, which was not observed.

Estimation of carbon-13 chemical shifts for semibullvalenecarbonitrile **4b′** presents a more difficult problem because there are no reports of chemical shifts for closely related mononitriles that might provide the basis for this task. Formal substitution of cyclopentene (**26a**) by a cyano group, affording **26b**, is accompanied by a shift to low field of the γ vinyl signal by 4.9 ppm.[22] Addition of this value to the shift of C_4 of the hydrocarbon **5a** yields an estimate for $C_{2'}$ of **4b′**. Assuming that the δ effect of the cyano group in **4b** upon the shift of C_8 (3.1 ppm) is similar to the analogous δ effect of the cyano group in **4b′** upon the shift of $C_{8'}$, we estimate the shift of the latter carbon at 140 ppm (Figure 9). The assumption invokes a certain similarity of a double bond and a cyclopropane ring in the transmission of polar substituent effects,[23] which enables the cyano group to generate a similar polarization pattern in both valence tautomers **4b** and **4b′**.

As we did for the estimated shift differences in the slow-exchange limit of the 1,5-(ethylmethyl)semibullvalenes **3b** ⇌ **3b′** and **3c** ⇌ **3c′**, the internal consistency of the estimated limiting shifts of the minor valence tautomers **4a′** and **4b′** was probed. Toward this end, values of the population excess $f - f'$ were calculated according to eq 7 from the time-averaged chemical shifts $\bar{\delta}_2$, $\bar{\delta}_4$, $\bar{\delta}_6$, $\bar{\delta}_8$ of **4a** ⇌ **4a′** and $\bar{\delta}_2$, $\bar{\delta}_8$ of **4b** ⇌ **4b′** at a temperature of ca. 300 K, and the corresponding estimated parameters (Figures 8 and 9). The values obtained from the shifts of those sites that are separated from the perturbing substituent by three (C_2, $C_{2'}$) and four bonds (C_8, $C_{8'}$) agreed within 0.6% for both **4a** ⇌ **4a′** and **4b** ⇌ **4b′**. The values calculated from the shifts of the *directly* bonded (C_4, $C_{4'}$) and the *vicinal* sites (C_6, $C_{6'}$) of **4a** ⇌ **4a′** also agreed with each other but were larger by 9% than those calculated from the shifts of the remote sites C_2, $C_{2'}$, and C_8, $C_{8'}$. The agreement between the values that were obtained from the remote sites of both systems **4a** ⇌ **4a′** and **4b** ⇌ **4b′** led us to conclude that the limiting shifts estimated for the distant carbons are reasonably realistic, and we employed only these for the calculation of the perturbation parameters.

Calculation of the Perturbation Parameters ΔH^{P} and ΔS^{P}. Variable-temperature 151 MHz carbon-13 spectra were recorded for **1a** ⇌ **1a′**, **2** ⇌ **2′**, **3** ⇌ **3′**, and **4** ⇌ **4′**. The observed splittings $\Delta\delta_{\mathrm{obs}}$ and chemical shifts $\bar{\delta}_i$ are listed in Tables 1−7 included in the Supporting Information. Additional carbon-13 NMR data of **3b** ⇌ **3b′**, recorded in the temperature range 104−301 K, have been published in our recent paper describing a new high-precision carbon-13 shift thermometer for the temperature range 100−300 K.[11g]

To avoid signal referencing problems with different solvents and with chemical shift standards at varying temperatures, we standardized the spectra with the methyl signals of the semibullvalenes themselves (for details, see Table 8 included in the Supporting Information). Furthermore, we necessarily assumed that the chemical shifts of these methyl signals do not depend on the temperature and the particular solvent employed. Thus, the low-temperature chemical shifts could subsequently be translated to the common TMS scale by adding the values of the methyl shifts that were measured for deuteriochloroform solutions relative to TMS at ca. 300 K. A complete list of carbon-13 chemical shifts for **3a**, **3a′**, **4a**, **4b**, **5a**, and **23** is given in Table 8 included in the Supporting Information.

Depending on the availability of experimental carbon-13 chemical shifts in the slow-exchange limit, the population excess $f - f'$ values required for the calculation of the perturbation parameters were calculated with three different equations, viz eq 5 and eq 6 for **3a** ⇌ **3a′**, eq 6 for **1a** ⇌ **1a′**, **2** ⇌ **2′**, **3b** ⇌ **3b′**, and **3c** ⇌ **3c′**, and eq 7 for **4** ⇌ **4′**. The values of $f - f'$ are included in Tables 1−7 of the Supporting Information. The perturbation parameters ΔH^{P} and ΔS^{P} were calculated by nonlinear least-squares fits of eq 3 to the $f - f'$ vs temperature data. The squares of the correlation coefficients, calculated for a 95% confidence limit, were greater than 0.995 for all fits. The calculated values of the perturbation parameters and of $f - f'$ are listed in Table 1[24]. Graphs of the population excess $f - f'$ vs temperature for all 1,5-(ethylmethyl)semibullvalenes studied here are displayed in Figures 10−12.

The data compiled in Table 1 for the 1,5-(ethylmethyl)-semibullvalenes confirm that these are localized, classical molecules which are characterized by slightly unsymmetrical double-well potentials under the conditions employed.[11] The Figures 10−12 display the perturbations, as measured by the differences of the fractions $f - f'$ of the valence tautomers, i.e., the populations excess, over the useful temperature range 100−400 K. Inspection of these curves offers the opportunity to select a system which, at a certain given temperature, is characterized

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(23) (a) Tidwell, T. T. In *The Chemistry of the Cyclopropyl Group, Part 1*; Rappoport, Z., Ed.; Wiley: New York, 1987; p 565. (b) Cremer, D.; Childs, R. F.; Kraka, E. In *The Chemistry of the Cyclopropyl Group*; Rappoport, Z., Ed.; Wiley: New York, 1995; Vol. 2, p 339.

(24) For the numbers of significant digits see: Moore, J. W.; Pearson, R. G. *Kinetics and Mechanism*, 3rd ed.; Wiley: New York, 1981; p 33.

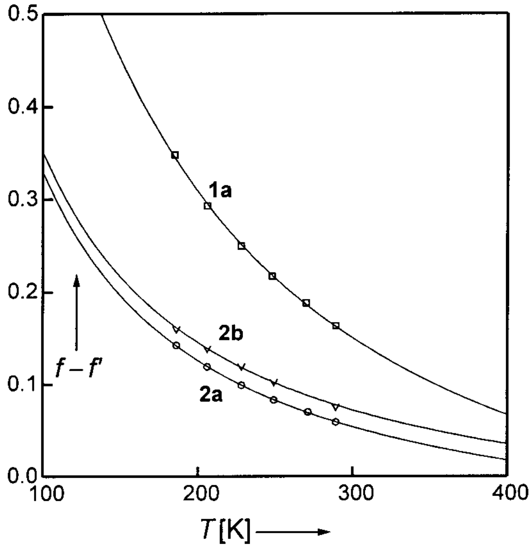

Figure 10. Substituent-induced population excess $f - f'$, as measured by Saunders' relative splitting $\Delta\delta^P/\Delta\delta$ of carbon-13 NMR signals, vs temperature for the tetramethyl 1,5-(ethylmethyl)semibullvalenetetracarboxylates **1a** ⇌ **1a′** (solvent deuterated dichloromethane) and the doubly bracketed 1,5-(ethylmethyl)semibullvalenes **2a** ⇌ **2a′** (solvent, perdeuteriotoluene) and **2b** ⇌ **2b′** (solvent, deuterated dichloromethane).

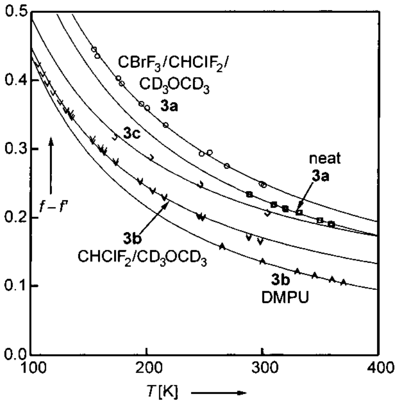

Figure 11. Substituent-induced population excess $f - f'$, as measured by Saunders' relative splitting $\Delta\delta^P/\Delta\delta$ of carbon-13 NMR signals, vs temperature for the 1,5-(ethylmethyl)-semibullvalenes **3** ⇌ **3′** (the solvents employed for **3a** ⇌ **3a′** and **3b** ⇌ **3b′** are given in the diagram, the solvent for **3c** ⇌ **3c′** was chlorodifluoromethane/perdeuterated dimethyl ether, 5:1).

by a particular population excess. This should foster the experimental realization of the pump−dump−probe strategy proposed by Manz and co-workers.[11b−d,17]

The results obtained with the limited number of different solvents used show that the perturbations by the substituents are only slightly affected by the nature of the solvent employed. Even changing from a nonpolar solvent to the highly dipolar solvent *N*,*N′*-dimethyl propylene urea (DMPU), which dramatically reverses the relative stabilities of the coexisting localized and delocalized structures of 4,8-diphenylbarbaralane-2,6-dicarbonitrile and favors the delocalized homoaromatic form,[21,25] results in only minor variations of the perturbation parameters ΔH^P and ΔS^P.

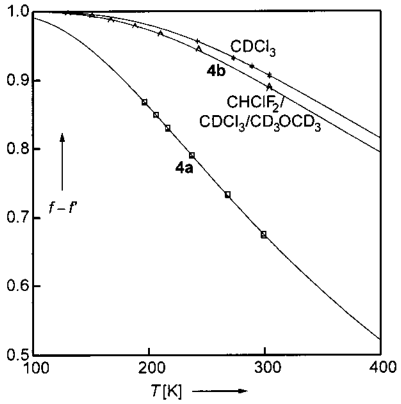

Figure 12. Substituent-induced population excess $f - f'$, as measured by Saunders' relative splitting $\Delta\delta^P/\Delta\delta$ of carbon-13 signals, vs temperature for the bromo-1,5-dimethylsemibullvalenes **4a** ⇌ **4a′** (solvent, chlorodifluoromethane/perdeuterated dimethyl ether, 5:1) and the 1,5-dimethylsemibullvalenedicarbonitriles **4b** ⇌ **4b′** (solvents given in the diagram).

The remote methyl group renders the valence tautomer **3a** with the ethyl group at the cyclopropyl carbon more stable by about 1 kJ mol^{-1} than the valence tautomer **3a′** with the ethyl group at the allylic carbon. It can be inferred that the same relative stability prevails in all other 1,5-(ethylmethyl)semibullvalenes because the *order of stability* is rooted in the different hyperconjugative electron donor capabilities of the two alkyl groups involved and the higher electron demand of a cyclopropyl carbon compared to that of an allylic carbon.[23] Both features are, of course, independent of the particular semibullvalene under consideration. Scrutiny of the data compiled in Table 1 reveals, however, that the *extent of the perturbations* caused by the difference between the two alkyl groups depends on the substitution pattern of the allylic systems involved in the Cope rearrangements. The perturbations of the doubly bracketed semibullvalenes **2** ⇌ **2′** are the smallest, while the population excesses of both **1** and **3** are close to 20% at room temperature.

A number of studies report, in more qualitative terms, the influence of a single directly bonded bromine atom or a nitrile group on the positions of Cope equilibria. Those valence tautomers of semibullvalenes[2,6,9g,10,12c] (including **4a** ⇌ **4a′** [9a,10c,f] and **4b** ⇌ **4b′** [9c]), 2,6-diazasemibullvalenes,[12h,i] barbaralanes,[26] and bullvalenes[27] predominate or even exist exclusively [26b,d] in which the perturbing substituent is on the double bond. Table 1 discloses the thermodynamic data (the perturbation parameters) that govern the Cope equilibria between the bromosemibullvalenes **4a** ⇌ **4a′** and the semibullvalenedicarbonitriles **4b** ⇌ **4b′**. The order of the ΔG^P values at room temperature agrees qualitatively with that of Hine's *D* values for a bromine atom ($D = 3.1$ kJ mol^{-1}) and the nitrile group ($D = 14.5$ kJ mol^{-1}).[28,29] In both cases, the

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[26] (a) Quast, H.; Görlach, J.; Stawitz, J. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 93. (b) Jackman, L. M.; Ibar, G.; Freyer, A. J.; Görlach, Y.; Quast, H. *Chem. Ber.* **1984**, *117*, 1671. (c) Quast, H.; Görlach, Y.; Stawitz, J.; Peters, E.-M.; Peters. K.; von Schnering, H. G. *Chem. Ber.* **1984**, *117*, 2745. (d) Quast, H.; Geissler, E.; Mayer, A.; Jackman, L. M.; Colson, K. L. *Tetrahedron* **1986**, *42*, 1805. (e) Quast, H.; Mayer, A. *Liebigs Ann. Chem.* **1989**, 515. (f) Jefford, C. W.; Rossier, J.-C.; Zuber, J. A. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 549.

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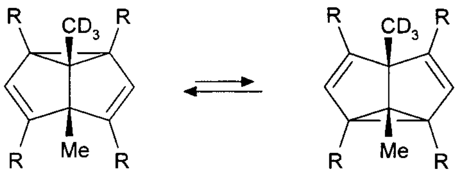
entropy terms are small compared to the relatively large enthalpy differences due to the electronic substituent effects and thus do not contribute significantly to the perturbation of the equilibria at room temperature. This holds also for the hydrocarbons **3a** $\rightleftharpoons$ **3a′** and the semibullvalenecarbonitriles **3b** $\rightleftharpoons$ **3b′** but not for the 2,4,6,8-substituted 1,5-(ethylmethyl)semibullvalenes **1** $\rightleftharpoons$ **1′**, **2** $\rightleftharpoons$ **2′** and the dimethyl semibullvalenedicarboxylates **3c** $\rightleftharpoons$ **3c′**, where the perturbation due to entropy differences cannot be neglected.

It is interesting to compare the perturbation by substituents, which skew the double-minimum potential, with the deuterium isotopic perturbation, which, assuming the Born–Oppenheimer approximation holds, does not change the symmetric double-well potential but only alters the positions of vibrational levels within each well. The equilibrium parameters that result from the latter are much smaller ($\Delta H^{\mathrm{P}} = 0.05-0.5$ kJ mol^{-1}) than those due to the former (Table 1),[13, 30] and hence the methods are complementary with respect to the size of the perturbation. Similarly, with the "remotely" deuterated semibullvalenes **27a** and **27b** the perturbation parameters are extremely small (ΔH^{P} = 0.040 and 0.074, respectively, kJ mol^{-1}).[13d]



27 **27′**

27a: R = H; **27b**: R = CO$_2$Me

Conclusions

The 1,5-(ethylmethyl)semibullvalenes in this study show a clear equilibrium-driven variation of chemical shift with temperature unequivocally demonstrating the classical nature of their ground states. In addition, refinement of Gompper's treatment of substituent perturbation [11a] allowed the precise determination of the thermodynamic parameters for equilibria skewed by substituents other than isotopes. We used these treatments with semibullvalenes **1a** $\rightleftharpoons$ **1a′**, **2** $\rightleftharpoons$ **2′**, **3** $\rightleftharpoons$ **3′**, and **4** $\rightleftharpoons$ **4′** to determine the population difference between the valence tautomers and the perturbation thermodynamic quantities ΔH^{P}, ΔS^{P}, and ΔG^{P}. While the preference for a particular valence tautomer **(3a)** could only be demonstrated for the parent 1,5-(ethylmethyl)semibullvalenes **3a** $\rightleftharpoons$ **3a′**, we assume that in each pair of the other 1,5-(ethylmethyl)semibullvalenes the same thermodynamic preference will be observed for the tautomer with the ethyl substituent on the cyclopropane ring. The treatments developed in this work are general and applicable to any system undergoing rapid nondegenerate equilibration, e.g., homotropilidenes, barbaralanes, bullvalenes, and other semibullvalenes and appropriately substituted cyclobutadienes and 5-indacenes.

Experimental Section

Instrumentation.[18,20,21] Preparative GC was performed with a 3 m × 2 mm glass column packed with Volaspher A2 (Merck) which was coated with 20% silicon oil SE30. NMR signals were assigned with the help of DEPT, ^{1}H,^{1}H COSY, ^{13}C,^{1}H COSY, NOESY, and NOE experiments. The deuterium lock of ^{13}C NMR spectra recorded for solutions in DMPU was provided by perdeuteriotoluene contained in a sealed, coaxial capillary tube. Temperatures below 300 K were calibrated according to ref 11g, temperatures above 300 K with ethylene glycol.[31] ^{13}C NMR spectra for neat **3a** $\rightleftharpoons$ **3a′** were recorded using simultaneously a sealed capillary tube with **3a** $\rightleftharpoons$ **3a′** and one with a liquid crystal for temperature calibration.[32] Both tubes were immersed in an NMR sample tube filled with perdeuteriotoluene. The temperatures just above and below the clearing point of the particular liquid crystal employed are given in Table 3, the clearing points of the liquid crystals are listed in Table 9 of the Supporting Information.

1,5-(Ethylmethyl)-2,4,6,8-semibullvalenetetracarboxylic Bisimides 2b $\rightleftharpoons$ **2b′.** A stirred mixture of the bisanhydride **2a** (0.30 g, 0.00105 mol) and aniline (0.30 g, 0.00315 mol) in dry diethyl ether (15 mL) was heated under reflux under nitrogen for 12 h. The resulting precipitate of the mixture of isomeric diamide–diacids was collected by filtration and dried under suction. The precipitate was suspended in dichloromethane (10 mL), and acetic anhydride (0.54 g, 0.00525 mol) and triethylamine (1.1 g, 0.0105 mol) were added. The orange solution slowly became pale yellow upon heating under reflux under nitrogen for 3 h. The volatile materials were removed in vacuo. The solid residue was purified by chromatography (silica, chloroform) and recrystallized from dry chloroform/hexanes to give the bisimide **2b** (0.124 g, 27%) as yellow prisms, mp 312 °C (dec): ^{1}H NMR (CDCl$_3$) δ 7.55–7.50 and 7.30–7.28 (m, 10H), 6.32 (s, 2H), 2.07 (q, J = 7.5 Hz, 2H), 1.71 (s, 3H), and 1.07 (t, J = 7.5 Hz, 3H); ^{13}C NMR (CDCl$_3$) δ 166.0, 165.4, 132.7, 132.2, 129.4, 129.2, 129.1, 127.8, 127.6, 121.2, 110.5, 99.3, 75.7, 69.9, 19.5, 11.7, 11.3; IR (KBr) 3060, 1736, 1708, 1594, 1493, 1404, 1383, 1202, 1145, 767, 746, 691, 660 cm^{-1}; MS (70 eV) m/z (%) 436 (87), 369 (100), 368 (63), 198 (59), 115 (31), 77 (88), 65 (39). Anal. Calcd for C$_{27}$H$_{20}$N$_2$O$_4$: C, 69.22; H, 4.30; N, 5.98. Found: C, 69.34; H, 4.09; N, 6.14.

1-Ethyl-5-methylbicyclo[3.3.0]octane-3,7-dione (6). Modified from the *Organic Syntheses* procedure for the 1,5-dimethyl compound.[33,34] A mixture of dimethyl 3-oxoglutarate (168 g, 0.97 mol), pentane-2,3-dione (48 g, 0.49 mol), water (3.5 L), and sodium carbonate (14.2 g) was stirred for 67 h at room temperature. The white solid formed was isolated by filtration and washed with ice-cold water (150 mL). The white powder was heated under reflux in a mixture of dilute hydrochloric acid (1M, 1.2 L) and acetic acid (0.24 L) until the gas evolution had subsided (ca. 3.5 h). The yellow solution was allowed to cool and extracted with chloroform (5 × 250 mL). Distillation of the solvent in vacuo afforded an orange-colored oil which was dissolved in chloroform (300 mL). The solution was extracted with a saturated aqueous solution of sodium bicarbonate (5 × 60 mL), followed by drying with sodium sulfate and distillation of the solvent in vacuo. Sublimation of the residue at 60 °C/10^{-2} Torr yielded a colorless, waxy solid (49.5 g, 56%), mp 85 – 93: ^{1}H NMR (400 MHz, CDCl$_3$) δ 0.94 (t, J = 7.5 Hz, 3H), 1.22 (s, 3H), 1.56 (q, J = 7.5 Hz, 2H), 2.28, 2.43 (AB system, J = 19.0 Hz, 4H), 2.34, 2.41 (AB system, J = 18.9

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(29) Recent use by Hagen et al. of Hine's D values to predict the position of the equilibrium in the Cope rearrangement of multiply substituted 1,5-dienes also afforded only a fair agreement: Hagen, J. P.; Lewis, K. D.; Lovell, S. W.; Rossi, P.; Tezcan, A. Z. *J. Org. Chem.* **1995**, *60*, 7471.

(30) For a summary of the equilibrium parameters resulting from deuterium isotopic perturbation of degenerate barbaralanes and semibullvalenes see ref 21.

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Hz, 4H). A wrong description of the spectrum of the ring protons has been reported in ref 35.

1-Ethyl-5-methylbicyclo[3.3.0]octane-3,7-dioles (7, Mixture of Diastereomers). Modified from a procedure described for the 1,5-dimethyl compounds.[36] Sodium borohydride (40 g, 1.1 mol) was added in portions to a stirred, cooled (0−20 °C) solution of **6** (36.0 g, 0.2 mol) in methanol (0.8 L). Stirring was continued for 3 d. Water (0.4 L) was added, and the solution was acidified with concentrated hydrochloric acid (120 mL) to attain a pH value of 5. The solvent was distilled in vacuo. The residue was dissolved in water (1.4 L). The solution was extracted for 24 h with diethyl ether in a continuous ether/water extractor.[37] The solvent was distilled in vacuo. The remaining solid was dried at 10^{-2} Torr. Recrystallization from petroleum ether (1 L) with the help of an extraction apparatus[38] afforded a white powder (35.5 g, 96%), mp 79−83 °C.

1-Ethyl-5-methylbicyclo[3.3.0]octadienes 8−10. The general procedure for the dehydration of secondary alcohols with triphenyl phosphate in hot sulfolane in the presence of quinoline was followed.[39] The mixture of the diols **7** (18.4 g, 0.1 mol) yielded a colorless liquid (11.7 g, 79%), bp 44−48 °C/10 Torr.

1,5-(Ethylmethyl)semibullvalenes 3a $\rightleftharpoons$ 3a′. The allylic bromination with NBS of the mixture of dienes **8**−**10** (7.41 g, 0.05 mol) was performed according to the general procedure described for similar 1,5-dialkylbicyclo[3.3.0]octadienes.[18] The combined crude products of three experiments (yellow oil) were distilled in a sublimation apparatus (bath temp 70 °C/4 × 10^{-5} Torr, coldfinger kept at −70 °C) to afford a pale yellow, waxy solid (35.7 g). Recrystallization from pentane (50 mL) at −25 °C yielded a colorless solid, mp 55−65 °C, which was a mixture of 4 isomeric dibromides containing <1% of monobromo and 3% of tribromo compounds (GC).

Reductive cyclization of the isomeric dibromides (3.8 g, 0.012 mol) to give **3a** $\rightleftharpoons$ **3a′** was performed with the zinc−copper couple in tetraglyme as solvent according to the optimized procedure for **5a**.[18] A pale yellow liquid (1.28 g) was obtained with a purity of 85% (GC), yield 62%. Distillation through a 20-cm Spaltrohr column (Fischer, D-53340 Meckenheim, Germany) at 20°C/10^{-2} Torr (receiver cooled at −78 °C), followed by repeated preparative GC (45 mL H_2/min, column temp 135 °C), yielded a colorless liquid consisting of **3a** $\rightleftharpoons$ **3a′** (97%) and the dienes **8**−**10** (3%, GC): ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.83 (t, $J = 7.5$ Hz, 3H), 1.09 (s, 3H), 1.45 (q, $J = 7.5$ Hz, 2H), 3.90 (m, 2H), 4.54 (m, 2H), 5.11 (m, 2H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 10.6 (CH_3), 15.8 (CH_3), 21.8 (CH_2), 60.0 (quat C), 64.3 (quat C), 79.5 (CH), 103.8 (CH), 119.0 (CH); MS (70 eV) *m*/*z* (%) 146 (44, M^+), 131 (100), 117 (46), 116 (33), 115 (56), 91 (75).

3,7-Bis(4-chlorophenylthio)-1-ethyl-5-methylbicyclo-[3.3.0]octadienes 11−13. According to the procedure reported for the preparation of the corresponding 1,5-dimethyl compounds,[19] the reaction of diketone **6** (43.5 g, 0.24 mol) with 4-chlorothiophenol (75 g, 0.52 mol) in tetrahydrofuran as solvent (0.9 L) in the presence of titanium tetrachloride (56 mL, 0.51 mol) and triethylamine (142 mL, 1.0 mol) yielded, after flash chromatography of the crude product on silica with petroleum ether (30−50 °C)/ethyl acetate (97:3), pale yellow crystals (90 g, 86%), mp 86−91 °C. Acid-catalyzed equilibration **11**, **12** $\rightleftharpoons$ **13**, as described for the corresponding dimethyl compounds,[20] afforded pale yellow crystals (86 g, 95%), mp 87−91 °C, in which the desired 2,6-diene **13** was enriched to 74% (HPLC).

3,7-Bis(4-chlorophenylsulfonyl)-1-ethyl-5-methylbicyclo[3.3.0]octadienes 14−16. The equilibrated mixture of **11**−**13** (92 g, 0.21 mol) was oxidized with sodium perborate tetrahydrate (196 g, 1.28 mol), as decribed for the corresponding dimethyl compounds,[19,20] to yield a colorless powder (103 g, 98%), mp 234−236 °C.

1-Ethyl-5-methylbicyclo[3.3.0]octa-2,6-diene-2,6-dicarbonitrile 19. As described for the corresponding 1,5-dimethyl compound,[20] the reaction of the mixture of sulfones **14**−**16** (73 g, 0.146 mol) in refluxing *tert*-amyl alcohol (2.5 L) with potassium cyanide (51.5 g, 0.78 mol) supported on basic alumina (440 g), followed by flash chromatography of the product mixture on silica with dichloromethane and subsequent medium-pressure liquid chromatography on silica with petroleum ether (30−50 °C)/ethyl acetate (9:1), afforded pale yellow crystals (9.43 g, 44%, based on 74% of **16** present in the starting mixture), mp. 98−101 °C. Sublimation at 80 °C bath temp/5 × 10^{-6} Torr yielded a colorless powder, mp 102 °C: ^{1}H NMR (400 MHz, C_6D_6) δ 0.65 (s, 3H), 0.60 (H_X), 0.93 (H_A), 1.10 (H_B) (ABX_3 system, $J_{AB} = 14.3$, $J_{AX} = J_{BX} = 7.5$ Hz), 1.52 (m, 8-H_{exo}), 1.58 (m, 4-H_{exo}), 2.21 (m, 8-H_{endo}), 2.22 (m, 4-H_{endo}), 5.52 (m, 7-H), 5.64 (m, 3-H), $J_{3,4x} = 2.0$, $J_{3,4n} = 3.0$, $J_{4x,4n} = 19.0$, $J_{4x,8x} = 1.1$, $J_{4n,8n} = 0.9$, $J_{7,8x} = 2.0$, $J_{7,8n} = 3.0$, $J_{8x,8n} = 19.0$ Hz; ^{13}C NMR ($CDCl_3$) δ 9.7 (CH_3), 19.3 (CH_3), 27.5 (CH_2), 41.8 (CH_2), 43.4 (CH_2), 58.6 (quat C), 62.0 (quat C), 115.1 (CN), 115.7 (CN), 121.4 (quat C), 123.7 (quat C), 144.0 (CH), 146.0 (CH); UV (CH_3CN) λ_{max} 207 nm, lg ϵ 4.268; MS (70 eV) *m*/*z* (%) 198 (39, M^+), 197 (10), 183 (28), 169 (100), 156 (19), 143 (12), 142 (46), 116 (16), 115 (29). Anal. Calcd for $C_{13}H_{14}N_2$: C, 78.75; H, 7.12; N, 14.13. Found: C, 78.38; H, 7.12; N, 14.34.

***exo,exo*-4,8-Dibromo-1-ethyl-5-methylbicyclo[3.3.0]octa-2,6-diene-2,6-dicarbonitrile.** A stirred solution of **19** (5.00 g, 0.025 mol) and *N*-bromosuccinimide (NBS) (10.8 g, 0.060 mol) in dichloromethane (140 mL) was heated under reflux and irradiated with a 250-W daylight lamp (Philips ML). The conversion was monitored by HPLC and was complete after 40 min. Dichloromethane (80 mL) was added, and the clear, orange-colored solution was extracted with aqueous sodium hydroxide (0.5 M, 5 × 50 mL) and dried with sodium sulfate. Distillation of the solvent in vacuo afforded a yellow powder. Flash chromatography on silica with petroleum ether (30−50 °C)/ethyl acetate (9:1) yielded pale yellow crystals (7.77 g, 87%), mp 139−140 °C: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.51 (s, 3H), 1.19 (H_X), 1.95 (H_A), 2.05 (H_B) (ABX_3 system, $J_{AB} = 14.4$ Hz, $J_{AX} = J_{BX} = 7.4$ Hz), 5.23 (dd, 4-H), 5.33 (dd, 8-H), 6.66 (d, 7-H), 6.72 (d, 3-H), ($J_{3,4} = J_{7,8} = 3.0$ Hz, $J_{4,8} = 0.9$ Hz); ^{13}C NMR ($CDCl_3$) δ 9.4 (CH_3), 18.7 (CH_3), 27.1 (CH_2), 55.6 (CH), 56.2 (CH), 61.8 (quat C), 64.1 (quat C), 113.5 (CN), 114.6 (CN), 121.7 (quat C), 122.9 (quat C), 143.7 (CH), 145.7 (CH); MS (70 eV) *m*/*z* (%) 358, 356, 354 (1.3, 2.9, 1.6, M^+), 277, 275 (43, 45), 196 (71), 195 (100), 181 (46), 168 (41), 154 (41), 140 (35). Anal. Calcd for $C_{13}H_{12}Br_2N_2$: C, 43.85; H, 3.40; N, 7.87. Found: C, 44.17; H, 3.49; N, 7.56.

1,5-(Ethylmethyl)semibullvalene-2,6-dicarbonitriles 3b $\rightleftharpoons$ 3b′. According to the procedure described for **5b**,[19] the dibromide of the foregoing experiment (5.34 g, 0.015 mol) was allowed to react with the zinc−copper couple (21 g) in the presence of cuprous chloride (1.9 g, 0.019 mol) in boiling diethyl ether (0.6 L) under argon. Workup afforded a yellow powder, which was sublimed at 70 °C bath temp/5 × 10^{-5} Torr. Recrystallization from ethyl acetate at −5 °C yielded pale yellow crystals (2.06 g, 70%), mp 111−112 °C. Concentration of the mother liquor in vacuo and cooling at −28°C gave a second crop (0.53 g, 18%), mp 111−112 °C: ^{1}H NMR (400 MHz, C_6D_6) δ 0.76 (s, 3H), 0.52 (H_X), 1.12 (H_A), 1.20 (H_B), (ABX_3 system, $J_{AB} = 15.0$ Hz, $J_{AX} = J_{BX} = 7.5$ Hz), 3.63 (d, $J = 4.0$ Hz, 1H), 4.07 (d, $J = 4.4$ Hz, 1H), 4.83 (d, $J = 4.4$ Hz, 1H), 4.87 (d, $J = 4.0$ Hz, 1H); ^{13}C NMR[11g]; UV (CH_3CN) λ_{max} 246 nm (lg ϵ 3.806), 366 (sh) (lg ϵ 1.592); MS (70 eV) *m*/*z* (%) 196 (47, M^+), 195 (29), 181 (95), 167 (37), 154 (100), 141 29), 140 (65), 127 (25). Anal. Calcd for $C_{13}H_{12}N_2$: C, 79.56; H, 6.16, N, 14.27. Found: C, 79.50; H, 6.08; N, 14.19.

Dimethyl 1-Ethyl-5-methylbicyclo[3.3.0]octa-2,6-diene-2,6-dicarboxylate (20). Modified from the procedure de-

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scribed for the corresponding 1,5-dimethyl compound.[20] A stirred solution of **19** (2.97 g, 0.015 mol) in dry methanol (180 mL) was saturated with dry hydrogen chloride. The solution was heated under gentle reflux. Every 24 h, the evaporated methanol was replenished and the solution was saturated again with hydrogen chloride. The procedure was repeated until the conversion was ca. 95% (7 d, HPLC). Water (75 mL) and dichloromethane (150 mL) were added to the solution which was cooled at room temperature, followed by stirring of the mixture for 1 h. The aqueous layer was extracted with dichloromethane (2 × 60 mL). The combined organic layers were extracted with saturated aqueous solutions of sodium bicarbonate (60 mL) and sodium chloride (60 mL) and dried with sodium sulfate. Distillation of the solvent in vacuo yielded a pale yellow oil which was separated by medium-pressure liquid chromatography on silica with petroleum ether (30−50 °C)/ ethyl acetate (9:1) to afford **20** as a colorless oil (1.12 g, 29%) besides a second fraction (1.01 g, 29%, colorless oil, presumably a mixture of mononitrile esters) and unchanged **19** (0.18 g, 6%). Treatment of the combined last two fractions with methanol and hydrogen chloride for 3 d as described above afforded, after chromatography, a second crop of **20** (0.65 g, 16%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.27 (s, 3H), 0.72 (H_X), 1.58 (H_A), 1.98 (H_B), (ABX_3 system, $J_{AB} = 15.4$ Hz, $J_{AX} = J_{BX} = 7.4$ Hz), 2.24 (8-H_{exo}), 2.26 (4-H_{exo}), 2.95 (8-H_{endo}), 2.99 (4-H_{endo}), 3.66 (s, 3H), 3.67 (s, 3H), 6.62 (7-H), 6.97 (3-H), ($J_{3,4x} = 2.1$, $J_{3,4n} = 3.2$, $J_{4x,4n} = 19.4$, $J_{4x,\ 8x} = 1.1$, $J_{4n,8n} = 0.8$, $J_{7,8x} = 2.1$, $J_{7,8x} = 3.2$, $J_{8x,8n} = 19.4$ Hz); ^{13}C NMR ($CDCl_3$) δ 10.0 (CH_3), 19.6 (CH_3), 27.0 (CH_2), 41.5 (CH_2), 42.8 (CH_2), 50.93 (2 CH_3), 57.1 (quat C), 61.5 (quat C), 138.4 (quat C), 141.2 (quat C), 142.0 (CH), 143.8 (CH), 164.57 (CO), 164.92 (CO); UV (CH_3CN) λ_{max} 214 nm (lg ϵ 4.193); MS (70 eV) *m*/*z* (%) 264 (35, M^+), 233 (25), 232 (100), 217 (17), 203 (31), 173 (25), 145 (27), 115 (17). Anal. Calcd for $C_{15}H_{20}O_4$: C, 68.16; H, 7.63. Found: C, 68.47; H, 7.92.

Dimethyl *exo,exo*-Dibromo-1-ethyl-5-methylbicyclo-[3.3.0]octa-2,6-diene-2,6-dicarboxylate. According to the procedure described for the corresponding dicarbonitrile, vide supra, irradiation of a stirred mixture of **20** (1.00 g, 0.004 mol) and NBS (1.66 g, 0.0093 mol) in dichloromethane (150 mL) for 1.5 h under reflux (HPLC), followed by workup and flash chromatography of the resulting light brown powder on silica with petroleum ether (30−50 °C)/ethyl acetate (94:6), afforded colorless crystals (1.25 g, 77%), mp 85−86 °C: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.50 (s, 3H), 0.91 (H_X), 1.88 (H_A), 2.12 (H_B), (ABX_3 system, $J_{AB} = 14.4$ Hz, $J_{AX} = J_{BX} = 7.6$ Hz), 3.75 (s, 3H), 3.76 (s, 3H), 5.45 (dd, 4-H), 5.72 (dd, 8-H), 6.75 (d, 3-H), 6.79 (d, 7-H) ($J_{3,4} = J_{7,8} = 2.9$ Hz, $J_{4,8} = 0.8$ Hz); ^{13}C NMR ($CDCl_3$) δ 10.7 (CH_3), 19.5 (CH_3), 27.1 (CH_2), 51.85 (CH_3), 51.96 (CH_3), 58.6 (CH), 59.5 (CH), 61.1 (quat C), 64.6 (quat C), 139.0 (quat C), 140.7 (quat C), 141.5 (CH), 142.2 (CH), 163.8 (CO), 164.5 (CO); MS (70 eV) *m*/*z* (%) 424, 422, 420 (15, 31, 15, M^+), 392, 390, 388 (6, 12, 6), 343, 341 (48, 49), 311, 309 (57, 56), 262 (46), 230 (66), 202 (74) 171 (50), 143 (100), 128 (54). Anal. Calcd for $C_{15}H_{18}Br_2O_4$: C, 42.68; H, 4.30. Found: C, 42.34 H, 4.25.

Dimethyl 1,5-(Ethylmethyl)semibullvalene-2,6-dicarboxylates 3c $\rightleftharpoons$ 3c′. A stirred mixture of the dibromide obtained in the foregoing experiment (1.11 g, 0.00272 mol) and the zinc−copper couple in dry THF (30 mL) was heated under argon and under reflux for 20 min. The conversion was monitored by HPLC. The mixture was filtered through silica (50 g, 32−63 μm) which was rinsed with dichloromethane (70 mL). Drying of the solution with sodium sulfate, distillation of the solvent in vacuo, and flash chromatography of the remaining yellow oil on silica with petroleum ether (30−50 °C)/ethyl acetate (9:1) afforded a yellow oil (0.61 g, 90%): ^{1}H NMR (400 MHz, C_6D_6) δ 1.47 (s, 3H), 0.85 (H_X), 1.86 (H_A), 1.98 (H_B) (ABX_3 system, $J_{AB} = 14.6$ Hz, $J_{AX} = J_{BX} = 7.4$ Hz), 3.48 (s, 3H), 3.49 (s, 3H), 4.67 (d, $J = 3.9$ Hz, 1H), 5.21, (d, $J = 4.4$ Hz, 1H), 5.92 (d, $J = 4.4$ Hz, 1H), 5.99 (d, $J = 3.9$ Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 11.5 (CH_3), 12.6 (CH_3), 19.5 (CH_2), 51.53 (CH_3), 51.77 (CH_3), 65.5 (quat C), 71.8 (quat C), 89.4 (CH), 90.6 (quat C), 109.5 (CH), 110.0 (quat C), 124.3 (CH), 126.8 (CH), 166.8 (CO), 168.5 (CO); UV (CH_3CN) λ_{max} 255 nm (lg ϵ 3.829), 384 (sh, lg ϵ 1.923); MS (70 eV), *m*/*z* (%) 262 (45, M^+), 230 (62), 203 (51), 202 (66), 171 (50), 143 (100) 128 (49), 115 (32). Anal. Calcd for $C_{15}H_{18}O_4$: C, 68.69; H, 6.92. Found: C, 68.33; H, 7.02.

4(2)-Bromo-1,5-dimethylsemibullvalenes 4a $\rightleftharpoons$ 4a′. These compounds were prepared as described.[10c] Purification by distillation through a 20-cm Spaltrohr column at 20°C/ 10^{-2} Torr followed by preparative GC (130 mL H_2/min, column temp 140 °C) afforded a pale yellow oil with a purity of >98% (GC).

1,5-Dimethylsemibullvalene-4(2)-carbonitriles 4b $\rightleftharpoons$ 4b′. Potassium cyanide (3.4 g, 0.0525 mol) was added to a stirred solution of **21**[10c] (5.10 g, 0.0175 mol) and the 18-crown-6/potassium cyanide complex (11.5 g, 0.035 mol) in dry acetonitrile (150 mL). With exclusion of light, stirring was continued until the conversion was >95% [ca. 15 h, reversed-phase HPLC with acetonitrile/water (7:3) on a Prodigy 5μ ODS column by Phenomenex]. The mixture was filtered through a 5-cm layer of kieselguhr, and the solvent was distilled in vacuo. The black residue was three times stirred for 1 h together with a mixture of a saturated aqueous solution of potassium dihydrogen phosphate and water (1:2, 15 mL). The resulting dark brown oil was distilled twice in a sublimation apparatus at 80 °C bath temp/5 × 10^{-4} Torr (coldfinger at −78 °C) to afford a light yellow oil (0.82 g, 16%) with ca. 80% purity (GC). Purification by preparative GC (130 mL H_2/min, column temp 140 °C) yielded a pale yellow oil with a purity of >90% (GC); IR (neat liquid) 2207 cm^{-1} (CN); ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.075 (3H), 1.227 (3H), 2.977 (m, 2-H), 3.170 (m, 8-H), 5.323 (m, 7-H), 5.644 (m, 6-H), 5.911 (m, 3-H), $J_{2,3} = 3.2$, $J_{2,8} = 6.3$, $J_{6,7} = 4.8$, $J_{7,8} = 2.6$ Hz.

Acknowledgment. We are indebted to Dr. G. Lange and Mr. F. Dadrich for measuring the mass spectra and Mrs. E. Ruckdeschl and Dr. D. Scheutzow for technical support. We thank the Merck KGaA, Darmstadt, for a gift of liquid crystals. Part of this work was funded by the Fonds der Chemischen Industrie, Frankfurt am Main. This work was also supported, in part, by a University of Idaho Seed Grant, an Idaho State Board of Education-Specific Research Grant and the NSF-Idaho EPSCoR project Cooperative Agreement Number OSR-9350539. T. D. thanks the Fonds der Chemischen Industrie, Frankfurt am Main, for a doctoral fellowship. We express our gratitude for a NATO Collaborative Research Grant (No. CRG.CRG 973044, to R.V.W. and H.Q.) which has greatly facilitated the cooperation.

Supporting Information Available: Seven tables of variable-temperature carbon-13 NMR data and calculated population excess; one table of carbon-13 chemical shifts recorded for a number of semibullvalenes in the limit of slow exchange; one table of liquid crystal data used for the temperature calibration in NMR experiments. This information is available free of charge via the Internet at http://pubs.acs.org.

JO001062A