Extension of Saunders' Isotopic Perturbation Method as Probe for the Structures in Solution of 2,4,6,8-Substituted Barbaralanes – NMR-Spectroscopic Evidence for the Coexistence of Localised and Delocalised States[1]

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Keywords: Cope rearrangements / Isotope effects / Solvent effects / Thermochromism / Transition states / Valence Isomerisation

The deuterium-labelled 2,4,6,8-substituted barbaralanes [D_5]-**1a** and **b**, and the two model barbaralanes **15** und **19** for the estimation of ^{13}C chemical shifts in the slow-exchange limit are synthesised from bicyclo[3.3.1]nona-3,7-diene-2,6-dione (**5**). – The extension of Saunders' isotopic perturbation method bridges the gap between the limiting cases "perturbation of shift equivalence in delocalised systems" and "perturbation of degeneracy" by considering the *simultaneous* presence of delocalised species of higher symmetry and skewed equilibria between localised molecules that are degenerate in the absence of the isotopic perturbation. An equation (Equation 7) is derived for such multi-component systems which describes the temperature dependence of the relative isotopic splittings in ^{13}C spectra with three parameters, viz. the isotopic perturbation parameters ΔH^P and ΔS^P of the skewed equilibria and the enthalpy difference ΔH^0 between the delocalised and localised species. – Relative isotopic splittings $\Delta\delta^P/\Delta\delta$ are calculated from estimated chemical shifts in the slow-exchange limit ($\Delta\delta$) and isotopic splittings ($\Delta\delta^P$) of signals in variable-temperature 151-MHz ^{13}C NMR spectra recorded for solutions of [D_5]-**1a** and **b** in [D_8]toluene and *N,N'*-dimethylpropylene urea. The results obtained from [D_5]-**1a** in both solvents and from [D_5]-**1b** in the former are compatible with either a skewed equilibrium between localised valence tautomers alone or the simultaneous presence of localised and *small amounts* of delocalised valence tautomers. In striking contrast, the small isotopic splittings themselves and their small temperature dependence, observed for solutions of [D_5]-**1b** in *N,N'*-dimethylpropylene urea, demonstrate that one half of the solvated compound exists in the delocalised state [D_5]-**1b***, which is more stable by 2 kJ mol^{-1} than the equilibrating localised species [D_5]-**1b** $\rightleftharpoons$ [D_5]-**1b'**.

Introduction

The structures of the 2,4,6,8-substituted barbaralanes **1** have been determined by X-ray diffraction analyses.[2,3,4] Both compounds exist as static valence tautomers which do *not* undergo Cope rearrangement in the solid state, contrary to a number of other degenerate barbaralanes and semibullvalenes.[5][6] By contrast, the ^{13}C spectra recorded for solutions of **1** at room temperature may arise from *truly* symmetrical species **1a*** (C_{2v}) and **1b*** (C_2) or *apparently* symmetrical systems that exhibit time-averaged symmetry due to a very fast exchange. Signal broadening, which might indicate the onset of slowing down of the exchange, cannot be observed, however, even at a spectrometer frequency of 151 MHz and the lowest accessible temperatures. Therefore, no experimental evidence exists so far, that supports the *bona fide* assumption of very fast Cope rearrrangements and hence the existence of symmetric double-well systems in solution, except for the two nitrile bands in the IR spectrum of **1b** which have been attributed to a localised valence tautomer.[3]

Saunders' isotopic perturbation method is the method of choice for the distinction between single-minimum and symmetrical double-minimum systems.[7,8,9] In an extension of this technique, we demonstrate here that equilibrating *localised valence tautomers may coexist with delocalised, symmetrical species* in solutions. According to ones point of view, these species may be considered as vibronic states, transition states, or transition structures of degenerate Cope rearrangements, or as bishomoaromatic barbaralanes. Our analysis of the data takes into account the recent detection of temperature- and solvent-dependent fractions that occupy the delocalised state **1***.[10] Therefore, the isotopic perturbation is considered for three-component equilibria that involve a skewed degenerate two-site exchange *and* a third, delocalised species of higher symmetry, viz. **1** $\rightleftharpoons$ **1*** $\rightleftharpoons$ **1'**. Furthermore, we describe the syntheses of the model barbaralanes **15** and **19** which were designed for the estimation of ^{13}C chemical shifts in the absence of exchange.

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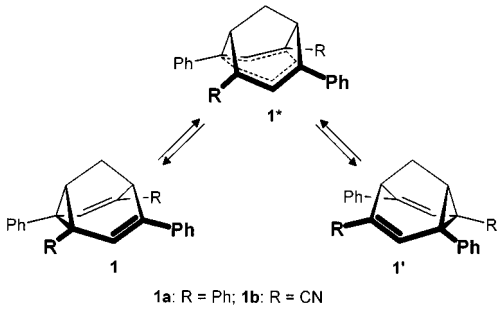
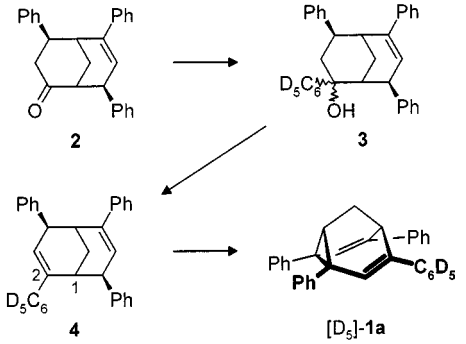


Results and Discussion

Syntheses of Deuterium-Labelled 2,4,6,8-Substituted Barbaralanes

In principle, any minor modification of one of the phenyl groups of **1a** and **b** is sufficient for the application of Saunders′ method. The modification could be, for example, introduction of an alkyl group or formal exchange of the protons for deuterium atoms. An important advantage of the latter perturbation is the opportunity to recognize the position of the skewed equilibria in ^{13}C spectra on the basis of $^{13}C,D$ couplings, a reduction of signal intensity due to quadrupolar and reduced dipole-dipole relaxation, and intrinsic deuterium isotope effects on chemical shifts.[8][11] Therefore, we synthesised the pentadeuterophenyl barbaralanes [D_5]-**1a** and **b**. To the best of our knowledge, perturbations of degenerate equilibria by deuterium atoms at phenyl rings have not yet been exploited.

The preparation of [D_5]-**1a** began with the cerium(III)-mediated addition of [D_5]phenyllithium to the triphenylketone **2**, which is an intermediate in the first synthesis of **1a**.[2] The subsequent dehydration of the resulting diastereomeric alcohols *exo*- and *endo*-**3** was performed with boron trifluoride–diethyl ether[12] instead of sulphuric acid in acetic acid used originally.[2] Cyclisation of the tetraphenyldiene **4** to [D_5]-**1a** was achieved with the *N*-bromosuccinimide bromination–zinc-copper couple debromination sequence, which is superior to the original deprotonation–oxidation protocol.[2][13]



The synthesis of [D_5]-**1b** turned out to be much more difficult than anticipated. The execution of the deceptively simple synthesis of the deuterated diphenyldiketone [D_5]-**7** by conjugate addition of *one* mol of a phenylcuprate reagent at the dienedione **5**[14] followed by the conjugate addition of a perdeuterated phenylcuprate reagent met with unexpected obstacles. A stoichiometric amount of the cyano Gilman reagent[15] that was prepared from phenyllithium, copper(I) cyanide, and boron trifluoride–diethyl ether yielded a mixture of **5**, **7**, and small amounts of **6**. Only a little of the diphenyldiketone **7** was formed along with **6**, when stoichiometric amounts or less of the phenyl cuprate reagent $(PhLi)_2{\cdot}CuCN$ were employed, but the desired phenyldiketone **6**, detected by HPLC at low temperatures, disappeared on warming of the reaction mixture. Eventually, quenching of the cold reaction mixture after a short reaction period allowed us to isolate **6** in moderate yield. An X-ray diffraction analysis of **6** confirmed the expected *exo* configuration[3][4] and showed that the cyclohexanone moiety adopts the chair conformation with an axial position of the phenyl group (Figure 1).

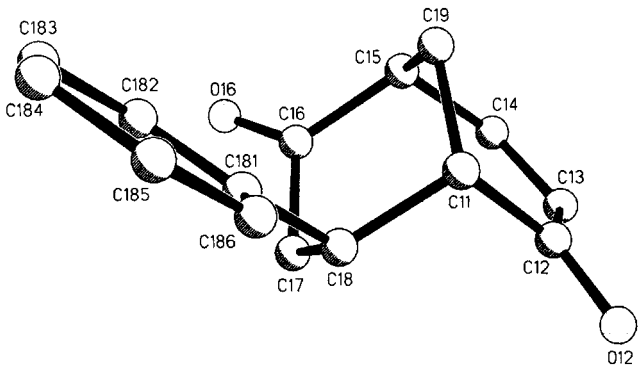
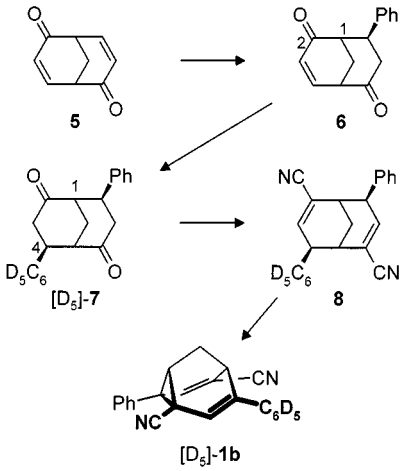


Figure 1. Perspective drawing of molecule A of the unsaturated phenyldiketone **6** showing the numbering of the atoms. The numbering of the independent molecule B (not shown) differs by the digit 2 instead of the 1 placed ahead of each atomic number of molecule A

The yield of the second conjugate addition was even worse. A slight excess of the cyano Gilman reagent $(C_6D_5Li)_2{\cdot}CuCN$ in the presence of boron trifluoride–diethyl ether converted **6** into a complex mixture from which a small amount of [D_5]-**7** could be separated by flash chromatography. These results contrast strikingly with the smooth formation of **7** from **5** in one step.[13] Apparently, **6** itself is *not* an intermediate in this sequence. While the enolate that is formed by the conjugate addition of the first equivalent of the cuprate is obviously stable enough to allow the second conjugate addition, **6** appears to be prone to decomposition under a variety of conditions. Three further steps completed the synthesis of [D_5]-**1b** as described for the protio compound **1b**.[4]

Syntheses of Model Barbaralanes

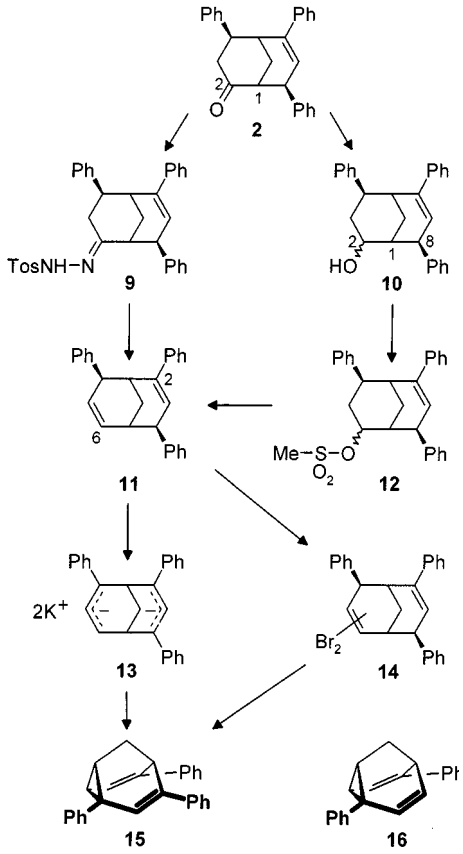
The calculation of relative splittings from equilibrium isotope splittings of ^{13}C signals necessitates knowledge of the ^{13}C chemical shifts for non-exchanging valence tautomers (Equation 4, *vide infra*). As for certain semibullval-



enes,[16] slow-exchange spectra could not be obtained for the tetrasubstituted barbaralanes **1**. Therefore, values for the required shift differences $\Delta\delta$ had to be estimated from model compounds. One of the most suitable of all conceivable models for non-rearranging tetraphenylbarbaralane [D_5]-**1a** appeared to be the triphenylbarbaralane **15** because it certainly can be expected to exist only as the valence tautomer **15**, in which *two* phenyl groups are conjugated with double bonds.

The synthesis of **15** from the known triphenylketone **2** followed an obvious route via triphenyldiene **11**. While the Shapiro reaction of **9**[17] gave **11** only in moderate yield (31% for two steps), the longer sequence, involving reduction of **2** to the secondary alcohols *exo*- and *endo*-**10**, mesylation, and elimination, was superior and afforded **11** in 63% overall yield. Reduction of **2** with sodium borohydride afforded a mixture of the two diastereomeric alcohols *exo*- and *endo*-**10** (1:2). Partial separation by medium-pressure liquid chromatography allowed us to assign the NMR signals to individual diastereomers and thus their configurations (Tables 7 and 8). Attempts at the direct dehydration of the alcohols **10** met with little success. Therefore, their mixture was converted into the mesylates **12**. Elimination with activated, neutral aluminium oxide[18] from the mesylates **12** afforded the triphenyldiene **11** in good yield and excellent purity, when diethyl ether was employed as solvent. In tetrahydrofuran solution, the elimination occurred much more slowly and was incomplete even after extended periods of time.

Cyclisation of **11** to triphenylbarbaralane **15** was achieved with both methods that were employed previously for the syntheses of 2,6-diphenylbarbaralane (**16**)[19][20] and tetraphenylbarbaralane **1a**.[2][13] The first method involves bromination of the bicyclic dienes with *N*-bromosuccinimide in cyclohexane as solvent and subsequent ring-closure by debromination of the dibromides with the zinc-copper couple.[13] Despite of painstaking exclusion of molecular oxygen and careful monitoring of both steps by reversed-phase HPLC, the yield of **15** was low, most probably because a number of decomposition products formed in the bromination step besides **14**.



In the first step of the second cyclisation protocol, the bicyclic dienes are deprotonated twice with Lochmann-Schlosser base to afford crystalline, deeply coloured dipotassium bicyclo[3.3.1]nonadienediides, e.g. **13**. Oxidation of the dipotassium salts at low temperatures with 1,2-dibromoethane[2][20] or iodine[13] furnishes the phenyl-substituted barbaralanes in moderate yields. This procedure gave a somewhat better yield of **15** than the bromination–debromination sequence (Table 1).

Triphenylbarbaralane **15** forms pale yellow, weakly thermochromic crystals whose surface slowly turns bright red even on storage at −20°C in the dark. The UV/Vis spectra (Figure 2) show that **15** resembles diphenylbarbaralane **16** and significantly differs from tetraphenylbarbaralane **1a**. A study of the ^{13}C chemical shifts over a wide temperature range (Table 8) showed only a minor dependence on temperature − hence triphenylbarbaralane **15** exists as a single valence tautomer.

Insufficient solubility in appropriate solvents presents a limiting problem in kinetic studies by dynamic ^{13}C spectroscopy at low temperatures. The solubility of 2,6-diphenylbarbaralane (**16**) could be improved by the formal introduction of *tert*-butyl groups at the *para* position of the phenyl rings.[16] Therefore, we synthesised bis-2,6-(*4-tert-butylphenyl*)barbaralanedicarbonitrile (**19**) from the dienedione **5** by the same route that had led us to the corresponding di*phenyl*barbaralanedicarbonitrile **1b**.[3][4] We note in passing that the intermediate diaryldiketone **17** also adopts the chair-boat conformation (Figure 3) which had

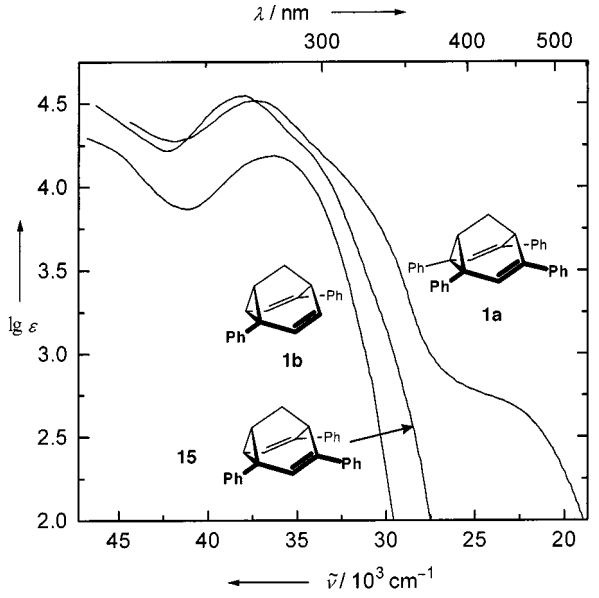


Figure 2. UV/Vis spectra of the phenyl-substituted barbaralanes **1a**, **15**, and **16** taken from solutions in ethanol/diethyl ether/2-methylbutane (2:5:5),[2] acetonitrile, and *trans*-decalin,[19] respectively, at 295 K

been found for **7**[3] and (1*S*)-**7**.[4] Unfortunately, signal-broadening that could be attributed to slower exchange was not observed, even at 172 K, the lowest temperature that allowed recording of an acceptable ^{13}C spectrum (Table 9).

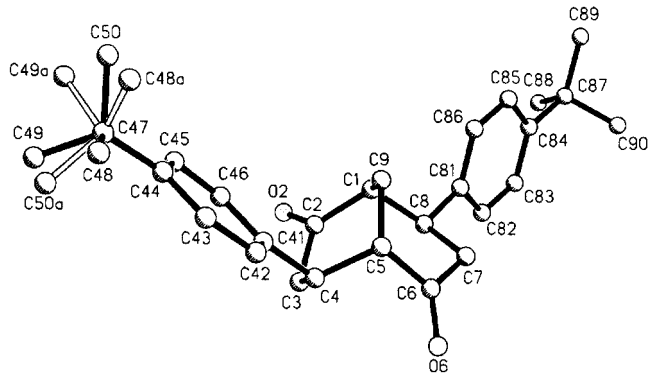


Figure 3. Perspective drawing of the diaryldiketone **17** showing the numbering of the atoms

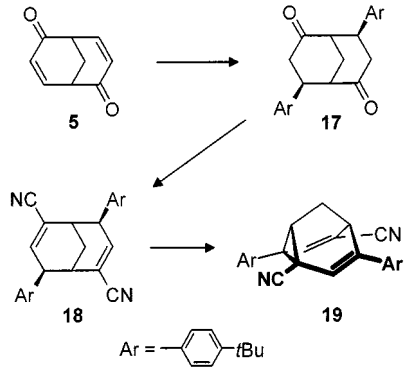


Table 1. Reagents, yields, melting points, solvents used for recrystallisation, and IR data. Data for the non-deuterated compounds are given in square brackets

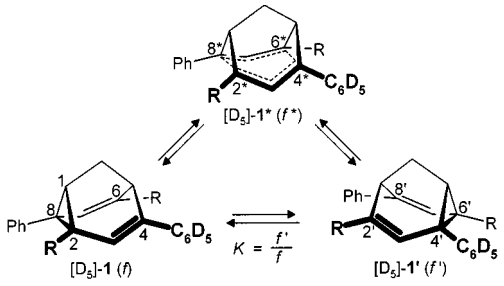
Cpd.	Starting material	Reagent Solvent	Yield [%]	M.p. [°C]	IR (KBr) [cm^{-1}] C=O	C=C	OH
x-**3**, *n*-**3** (1 : 2)	**2**	C_6D_5Li–$CeCl_3$ THF	95				
x-**3**·2MeOH			28 [49	100 (MeOH) 183–184][2]			
n-**3**			67 [40	155–157 (PE) 155–156][2]			
4	**3**	BF_3–Et_2O, CH_2Cl_2 [H_2SO_4, HOAc	88 98	188–190 (AcOEt) 184–185][2]			
6	**5**	PhLi, CuCN, THF	33	88–90 (MeOH)	1715 1664	1607	
[D_5]-**7**	**6**	C_6D_5Li, CuCN BF_3–Et_2O, THF	16	140–141 (EtOH) [135–137][3]			
9	**2**	$TosNHNH_2$ EtOH	85	195–196 (dec.) (THF/EtOH)		1599	3210[a]
x-**10**, *n*-**10** (1 : 2)	**2**	$NaBH_4$ MeOH	92	50–60		1599	3400 3560
x-**12**, *n*-**12** (1 : 2)	**10**	$MeSO_2Cl$ NEt_3, CH_2Cl_2	92	55–60		1599	
11	**9**	MeLi, Et_2O	37				
	12	Al_2O_3, Et_2O	75	129–130 (AcOEt)		1599	
15	**11**	1. BuLi, *t*BuOK 2. I_2, THF	19	99–100 (PE)		1598	
	11	1. NBS, C_6H_{12} 2. Zn/Cu, THF	11				C≡N
17	**5**	CuCN, $tBuC_6H_4Li$ BF_3–Et_2O, THF	60	231–233	1694		
18	**17**	1. Me_3SiCN, KCN–18-crown-6 2. HF–Py, $POCl_3$, Py	50	263–264		1624	2215
19	**18**	NaOH, $Bu_4N^+OH^-$, C_2Cl_6	19	182 (dec.)			2237 2207

[a] NH. – [b] 1170, 1330, 1353 cm^{-1} (Me–SO_2–O).

Deuterium Isotopic Perturbation of Degenerate Equilibria between Localised Valence Tautomers that Coexist with a Symmetrical, Delocalised Isomer

Extension of Saunders' Isotopic Perturbation Method

Some twenty years ago, Saunders and coworkers developed isotopic perturbation as a new method for distinguishing between static (single-minimum) and equilibrating (double-well) structures. They based their method on the isotopic splittings $\Delta\delta^P$ of NMR signals for nuclei that are equivalent in the absence of the isotopic perturbation. The size of the *relative* isotopic splittings $\Delta\delta^P/\Delta\delta$ (where $\Delta\delta$ are the chemical shift differences in localised species) was suggested as criterion for the distinction between "isotopic perturbation of degeneracy"[7a] and "isotopic perturbation of resonance".[7b,c] Furthermore, while the latter gives rise to *temperature-independent*, *small* isotopic splittings, *sizeable temperature-dependent* isotopic splittings were considered as unequivocal evidence of a thermodynamic isotope effect characteristic of a degenerate dynamic equilibrium.[7,8] Recently, Balzer and Berger have shown that deuterium-induced splittings of carbon-13 signals of delocalised carbocations that are symmetrical in the absence of the deuterium are purely intrinsic. As a consequence, they discourage use of Saunders' term "isotopic perturbation of resonance".[9] Following their recommen-



dation, we refer to the temperature-independent small isotopic splittings characteristic of single-minimum species as "*isotopic perturbation of shift equivalence in delocalised systems*".

The recent discovery of the equilibrium between localised (**1**, **1**′) and delocalised (**1***) states of thermochromic barbaralanes[10] necessitates an extension of Saunders' method, which considers only one or the other possible structure but not an equilibrium between them. In the general case of the coexistence of both, the observed isotopic splitting will be the average over those molecules that are delocalised (fraction f^*) and those that are localised (fractions f and f').

The weighted average $\bar{\delta}_i$ of the chemical shifts δ_i, $\delta_{i'}$, and δ_{i^*} of a ^{13}C atom C_i in three different environments is given by Equation 2. Because $\delta_i = \delta_{j'}$ and $\delta_j = \delta_{i'}$, provided intrinsic isotope effects are neglected, the shift difference $\Delta\delta^P_{ij}$ between two carbon atoms C_i and C_j that are equivalent in the absence of the isotopic perturbation is given by Equation 3 where $\Delta\delta_{ij}$ denotes the difference in the chemical shifts of C_i and C_j in the limit of slow exchange. The shift difference $\delta_{i^*} - \delta_{j^*} = \Delta\delta^*$ is the isotopic perturbation of shift equivalence in delocalised systems.

$$f + f' + f^* = 1 \qquad (1)$$

$$\bar{\delta}_i = f\delta_i + f'\delta_{i'} + f^*\delta_{i^*} \qquad (2)$$

$$\Delta\delta^P_{i,j} = \bar{\delta}_i - \bar{\delta}_j = (f - f')\,\Delta\delta_{i,j} + f^*\Delta\delta^* \qquad (3)$$

The *relative* isotopic splitting (Equation 4) is obtained from Equation 3 and recognised as the difference between the fractions of the equilibrating localised molecules plus a second term which accounts for the presence of the delocalised species.

$$\frac{\Delta\delta^P}{\Delta\delta} = (f - f') + f^*\frac{\Delta\delta^*}{\Delta\delta} \qquad (4)$$

$$= (1 - f^*)\frac{1-K}{1+K} + f^*\frac{\Delta\delta^*}{\Delta\delta} \qquad (5)$$

Defining the equilibrium constants K such that they are less than unity ($K = f'/f$) yields Equation 5, which comprises Saunders' relative splittings for the isotopic perturbation of degeneracy ($f^* = 0$)[7a] and shift equivalence in delocalised systems ($f^* = 1$)[7b,c] as limiting cases. The second terms in Equation 3−5 only play a role, if both the fraction f^* of the delocalised species *and* the isotopic perturbation of shift equivalence in delocalised systems, $\Delta\delta^*$, assume sizeable values. The latter is much smaller than the isotopic perturbation of degeneracy.[7−9] Therefore we neglect the last term.

Recent studies of the thermochromism of **1a** and **b** have not only disclosed an equilibrium between localised and delocalised structures but also afforded the enthalpy differences ΔH^0 between them, from which f^* values may be calculated according to Equation 6.[10]

$$f^* \approx \left(1 + 2\cdot\exp\frac{\Delta H^0}{R\cdot T}\right)^{-1} \qquad (6)$$

Considering the well-known temperature dependence of the equilibrium constant $K = \exp(\Delta S^P/R - \Delta H^P/RT)$, where ΔH^P and ΔS^P (the perturbation parameters) are the differences between the thermodynamic parameters of the two labelled localised valence tautomers, we obtain from Equation 5 and 6 an expression for the temperature dependence of the relative splitting, Equation 7. Application of Equation 7 is superior to the traditional calculation of equilibrium parameters with the linear relationship $\ln K$ vs. $1/T$, because Equation 7 correctly weights the experimental data.

$$\frac{\Delta\delta^P}{\Delta\delta} = \left(1 - \frac{1}{1 + 2\exp\left(\Delta H^0/RT\right)}\right)\frac{1 - \exp\left(\Delta S^P/R - \Delta H^P/RT\right)}{1 + \exp\left(\Delta S^P/R - \Delta H^P/RT\right)} \qquad (7)$$

Equation 7 may be used to calculate enlightening curves in relative splitting vs. temperature diagrams *that are characterised by a certain pair of perturbation parameters* ΔH^P *and* ΔS^P. Besides Saunders' limiting cases $f^* = 0$ and $f^* = 1$, there exists a third interesting situation, in which the localised and the delocalised species possess the same enthalpy, i.e. $\Delta H^0 = 0$ and $f^* = 1/3$ (Equation 6). This is the borderline that cuts each of these certain $(\Delta\delta^P/\Delta\delta)-$temperature diagrams into an upper section between the limit $f^* = 0$ and the borderline $f^* = 1/3$ − the area where ΔH^0 is positive − and a lower section between borderline $f^* = 1/3$ and the limit $f^* = 1$ − the area where ΔH^0 is negative, in other words, the delocalised species more stable than the two equilibrating localised valence tautomers. Thus, a cursory inspection of the observed relative splitting vs. temperature data in these diagrams (Figures 6−9) immediately reveals the relative stability of the coexisting species.

Deuterium Isotopic Splittings in Carbon-13 Spectra of the Barbaralanes [D5]-1a and b

Variable-temperature 151-MHz ^{13}C spectra were recorded for solutions of [D5]-**1a** and **b** in two widely different solvents. Our recent study of thermochromic semibullvalenes and barbaralanes has shown that the localised structures **1a** and **b** are preferred in nonpolar solvents while dipolar solvents, in particular *N*,*N*′-dimethylpropylene urea, render the delocalised structure **1b*** even more stable than **1b**.[10b]

Deuterium isotopic splittings in ^{13}C spectra of [D5]-**1a** in [D8]toluene solutions are displayed in Figure 4. The assignment of the signals is immediately obvious. Most importantly, Figure 4 provides unequivocal evidence for the pre-

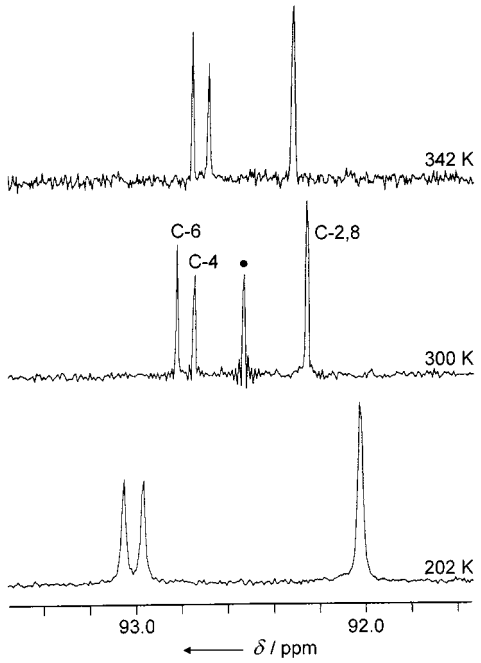


Figure 4. Deuterium isotope splittings in 151-MHz ^{13}C spectra recorded for a solution of [D_5]-**1a** in [D_8]toluene at various temperatures. The signal marked with a dot stems from added unlabelled tetraphenylbarbaralane **1a**

ferred position of the pentadeuterophenyl group, viz. the vinyl position (C-4). Thus [D_5]-**1a** is slightly more stable than [D_5]-**1a′**. It is unnecessary to consider the cumulative isotope effect on the chemical shift of C-4, because the isotopic splitting can be measured directly using the signal of C-6, which is separated by five bonds from the next deuterium atoms. That these do not influence the shift of C-2, which is also five bonds away, is seen from the single high-field signal which has double intensity and hence is assigned C-2 and C-8. The isotopic splittings observed for a solution of [D_5]-**1a** in *N*,*N*′-dimethylpropylene urea (DMPU) are of similar size (Table 2).

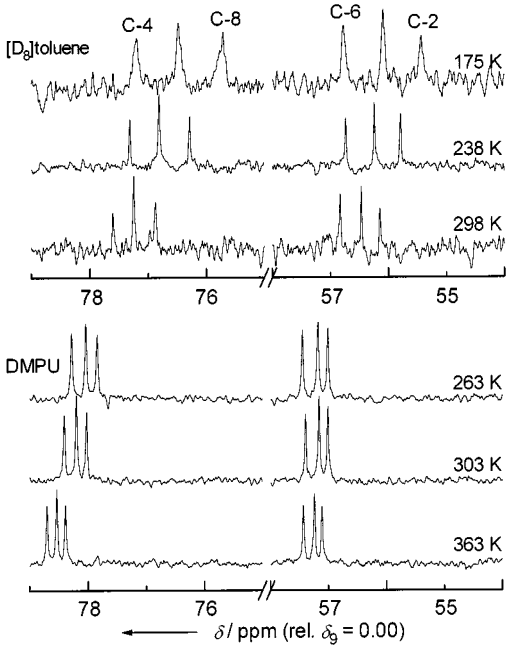


Figure 5. Deuterium isotope splittings in 151-MHz ^{13}C spectra recorded for solutions of a mixture of **1b** (middle signals) and [D_5]-**1b** in [D_8]toluene and *N*,*N*′-dimethylpropylene urea at various temperatures

Table 2. Deuterium isotopic splittings $\Delta\delta_{i,j}^{P}$ [ppm] in 151-MHz ^{13}C spectra taken from solutions of the barbaralanes [D_5]-**1a** and **b** in [D_8]toluene and *N*,*N*′-dimethylpropylene urea at various temperatures

Cpd.	*T* [K]	$\Delta\delta_{6,2}^{P}$	$\Delta\delta_{4,8}^{P}$
[D_5]-**1a**	202.3	1.008	
in	224.2	0.88	
[D_8]toluene	247.2	0.782	
	269.1	0.656	
	297.3	0.551	
	321.2	0.485	
	342.2	0.439	
in DMPU	265.3	0.738	
	300.4	0.591	
	330.1	0.491	
	344.9	0.449	
	359.8	0.411	
	370.1	0.387	
[D_5]-**1b**	174.9	1.339	1.559
in	195.4	1.166	1.378
[D_8]toluene	216.6	1.057	1.229
	237.9	0.943	1.097
	268.7	0.806	0.940
	298.4	0.684	0.803
in DMPU	263.0	0.440	0.508
	283.0	0.411	0.478
	303.0	0.387	0.451
	323.0	0.363	0.428
	343.0	0.340	0.405
	363.0	0.322	0.385

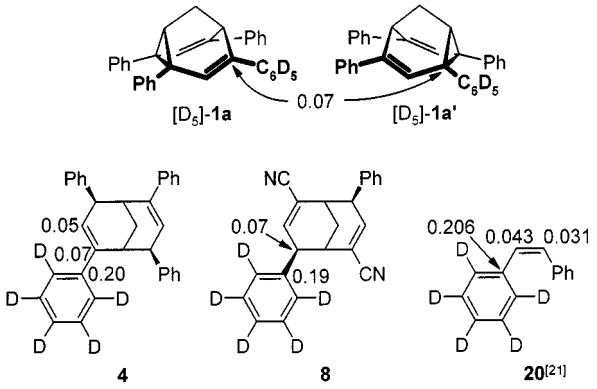
The deuterium isotopic splittings in ^{13}C spectra of [D_5]-**1b** are shown in Figure 5. The assignment of the signals is based on the assumption that the pentadeuterophenyl group prefers the same position as in [D_5]-**1a** and, therefore, [D_5]-**1b** is more stable than [D_5]-**1b′**. Inspection of Figure 5 reveals a dramatic difference between the two solvents, not only in the absolute size of the splittings $\Delta\delta^{P}$ but also in their temperature dependence which is much larger in [D_8]toluene (−0.53 ppm/100 K for $\Delta\delta_{6,2}^{P}$ and −0.61 ppm/100 K for $\Delta\delta_{4,8}^{P}$) than in *N*,*N*′-dimethylpropylene urea (−0.12 ppm/100 K for $\Delta\delta_{6,2}^{P}$ and $\Delta\delta_{4,8}^{P}$).

The isotopic splitting is not perfectly symmetric relative to the time-averaged signal of **1b** between the components of each pair of signals that result from isotopic splitting. Instead, the average shift of each pair is slightly changed towards lower field. Scrutiny of Figure 4 uncovers the same effect for [D_5]-**1a**.

On the basis of the generally accepted vibrational explanation of equilibrium isotope effects,[8] it is difficult to rationalise the position of the equilibria **1** ⟹ **1′** which are skewed by the presence of deuterium atoms that are three, four and five bonds away from the carbon atom involved in the Cope rearrangement. We restrain ourselves from any attempts because they are beyond the scope of the present paper.

Cumulative Instrinsic Isotope Effects of Pentadeuterophenyl Groups

An evaluation of equilibrium isotopic splittings in ^{13}C spectra requires consideration of intrinsic deuterium isotope effects on ^{13}C chemical shifts. While the five deuterium atoms of the phenyl group at C-4 of [D_5]-**1a** and **b** do *not* influence the chemical shifts of ^{13}C atoms that are distant by five and more bonds (C-2,6,8, Figure 4), they certainly shift to higher field the signal of C-4, which is distant by only *three* bonds from the next deuterium atoms. Therefore, we measured this shift for [D_5]-**1a** and some precursors (**4**, **8**) relative to the equivalent non-deuterated site in the same molecules. In all three cases, the high-field shift was 0.07 ppm, a value which is close to the corresponding high-field shift reported recently for [D_5]-*cis*-stilbene (**20**).[21] Accordingly, the values of the isotopic splittings $\Delta\delta_{4,8}^{P}$, which are listed for [D_5]-**1b** in Table 2, have been corrected by the addition of 0.070 ppm.

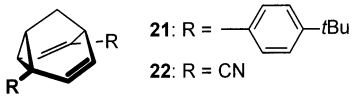


Cumulative intrinsic deuterium isotope effects of pentadeuterophenyl groups (upfield shifts [ppm]), measured for [D_5]-**1a**, **4**, and **8** relative to the equivalent non-deuterated site in the same molecule

Estimation of Carbon-13 Chemical Shifts for Non-exchanging Valence Tautomers

Shift differences $\Delta\delta$ between exchanging carbon atoms, measured in the limit of slow exchange at low temperatures, are required for the calculation of relative isotopic splittings (Equation 4, 5) and the thermodynamic parameters of the skewed equilibria (Equation 7). Unfortunately, extremely low energy barriers and insufficient solubility in suitable solvents of both tetrasubstituted barbaralanes **1a** and **b**, and also the bis(4-*tert*-butylphenyl)barbaralanedicarbonitrile **19**, precluded such measurements. Therefore, the calculations necessitated the use of *estimated* values for $\Delta\delta$. Triphenylbarbaralane **15** was employed as model for a non-exchanging valence tautomer of tetraphenylbarbaralane **1a**. Assuming that the carbon atoms C-4 of **15** and non-rearranging **1a** absorb at the same field, because the attached phenyl groups may adopt very similar conformations, we used Saunders' original method[7a] and estimated the shift difference for non-exchanging **1a** at $\Delta\delta_{6,2}$ = 91.6 by doubling the difference between the averaged value for the signals of C-4 and C-6 of **15** (δ = 138.5, Table 8) and the value for the time-averaged signal of C-2,4,6,8 of **1a** (δ = 92.7).

Carbon-13 spectra of two barbaralanes that are related to **1b**, viz. **21** and **22**, could be obtained in the limit of slow exchange, affording shift differences of $\Delta\delta_{6,2}$ = 100.1 and 91.4 ppm, respectively.[16] Use of these values as estimates for $\Delta\delta_{4,8}$ and $\Delta\delta_{6,2}$ of **1b** gave unsatisfactory results, however. The calculated values for $\Delta\delta_{4,8}^{P}/\Delta\delta_{4,8}$ were larger than those for $\Delta\delta_{6,2}^{P}/\Delta\delta_{6,2}$, a result that, of course, cannot be true. Therefore, the estimated values for $\Delta\delta_{4,8}$ and $\Delta\delta_{6,2}$ were adjusted by a correction term (3.1 ppm) which was calculated by setting $\Delta\delta_{4,8}^{P}/\Delta\delta_{4,8}$ and $\Delta\delta_{6,2}^{P}/\Delta\delta_{6,2}$ equal at ca. 300 K. The relative splittings were then calculated from the isotopic splittings of [D_5]-**1b** in Table 2 with the *corrected* estimated values ($\Delta\delta_{4,8}$ = 103.2 and $\Delta\delta_{6,2}$ = 88.3).



Finally we note that an error of 5 ppm in the estimated values of $\Delta\delta$ translates into only small errors in the perturbation parameters ΔH^{P} (5 to 6%) and ΔS^{P} (10 to 21%). These errors are somewhat larger than the errors resulting from the neglect of the delocalised species [D_5]-**1a*** and **b*** in [D_8]toluene solutions (*vide infra*, Table 3).

Thermodynamic Parameters of the Isotopic Perturbed Equilibria [D_5]-1 $\rightleftharpoons$ [D_5]-1′

In principle, all three parameters ΔH^{0}, ΔH^{P} and ΔS^{P} of Equation 7 should be available by fitting of Equation 7 to the relative splitting vs. temperature data. Attempts at this goal, using the data of Table 2, met with failure, however.[22] Therefore, only the perturbation parameters ΔH^{P} and ΔS^{P} were calculated by fitting Equation 7 to the data with the method of least squares, while ΔH^{0} were kept constant at $\Delta H^{0} = \infty$ (corresponding to the complete absence of delocalised species **1***, $f^{*} = 0$) and at reported values from the study of thermochromism.[10] The results are listed in Table 3.

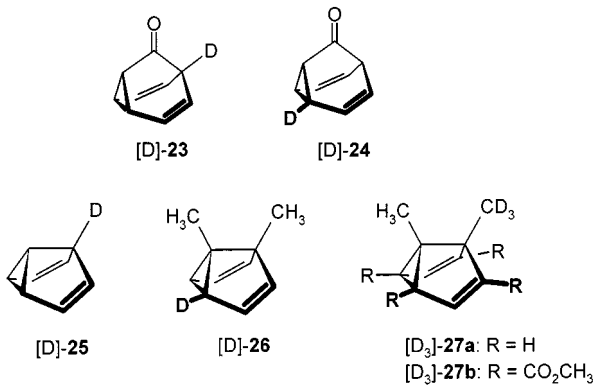
Neglect of the small amounts of the delocalised species that are present in [D_8]toluene solution, viz. 1−5% [D_5]-**1a*** and 3−9% [D_5]-**1b***, results in an increase of ΔH^{P} by 2 and 4.5%, whereas ΔG^{P}(300 K) decreases by 3.5 and 9%, respectively. The presence of larger amounts of [D_5]-**1a*** (17−21%) in the solvent *N,N′*-dimethylpropylene urea has a more noticeable effect, but the differences between the perturbation parameters that were calculated for ΔH^{0} = 1.9 kJ mol^{-1} and $\Delta H^{0} = \infty$ are still not very large ($\Delta\Delta H^{P}$ = −13%, $\Delta\Delta G^{P}$ = −18%). Actually, all enthalpy and entropy data for the skewed equilibria of [D_5]-**1a** and of [D_5]-**1b** in [D_8]toluene fall into the range reported for the trideuteromethyl semibullvalenes [D_3]-**27a** and **b**, whose deuterium atoms are separated from the Cope system by three bonds (Table 3). Apparently, this distance is an important factor

Table 3. Thermodynamic parameters ΔH^P, ΔG^P (300 K) [J mol^{-1}], and ΔS^P [J mol^{-1} K^{-1}] for the isotopic perturbed equilibria between deuterated valence tautomers of barbaralanes and semibullvalenes. Values that are printed *in italics* were calculated by fitting of Equation 7 to the experimental data.

Cpd.[a]	[b]	T [K]	ΔH^0	f^* [%] (eq. 6)	ΔH^P [c]	ΔS^P [c]	$\Delta G^P_{300\,K}$	Fig.	Ref.
[D$_5$]-**1a**	T	202 – 342	6.5[d]	1 – 5	*51.35 ± 1.35*	*0.0672 ± 0.0052*	*31.2*	6	[e]
			∞	0	*52.40 ± 1.32*	*0.0743 ± 0.0051*	*30.1*		
	U	265 – 370	1.9[10]	17 – 21	*68.65 ± 0.18*	*0.0964 ± 0.0006*	*39.7*	7	[e]
			∞	0	*59.81 ± 0.34*	*0.0917 ± 0.0011*	*32.4*		
[D$_5$]-**1b**	T	175 – 298	4.1[10]	3 – 9	*48.91 ± 0.80*	*0.0193 ± 0.0037*	*43.1*	8	[e]
			∞	0	*51.12 ± 0.73*	*0.0396 ± 0.0033*	*39.2*		[e]
	U	263 – 363	∞	0	*20.05 ± 0.47*	*–0.0064 ± 0.0015*	*22.0*		
			–1.6	51 – 46	49	0.02	43	8	[e]
			–2.2	58 – 51	70	*0.07*	49	9	
[D]-**23**	T	303 – 353			453.4 ± 29.0	0.674 ± 0.088	251		[24]
[D]-**25**					353	0.423	226		[8a]
[D]-**26**	C	220 – 302			485 ± 2.5	0.75 ± 0.01	260		[8a]
[D$_3$]-**27a**	D	187 – 302			40.0	0.044	27		[8a]
[D$_3$]-**27b**	D	181 – 302			74	0.123	37		[25]

[a] More stable valence tautomer. – [b] Solvent: C = [D]trichloromethane; D = [D$_2$]dichloromethane; T = [D$_8$]toluene; U = *N*,*N*′-dimethylpropylene urea. – [c] For the numbers of significant digits see ref.[23] – [d] The unknown ΔH^0 value for solutions of [D$_5$]-**1a** in [D$_8$]toluene is approximated by the average of the ΔH^0 values obtained for solutions in butyronitrile (5.5 kJ mol^{-1}) and methylcyclohexane (7.5 kJ mol^{-1}).[10b] – [e] This work.

for the extent of the isotopic perturbation of the degenerate equilibria of semibullvalenes and barbaralanes. This conclusion is supported by a comparison with systems that bear a deuterium atom nearer to the rearranging allylic moiety, viz. [D]-**23**,[24] [D]-**25**, and [D]-**26**:[8a] The isotopic perturbation as expressed by the thermodynamic parameters is larger by one order of magnitude than in the other cases (Table 3).



More stable valence tautomers of deuterium-labelled barbaralones and semibullvalenes

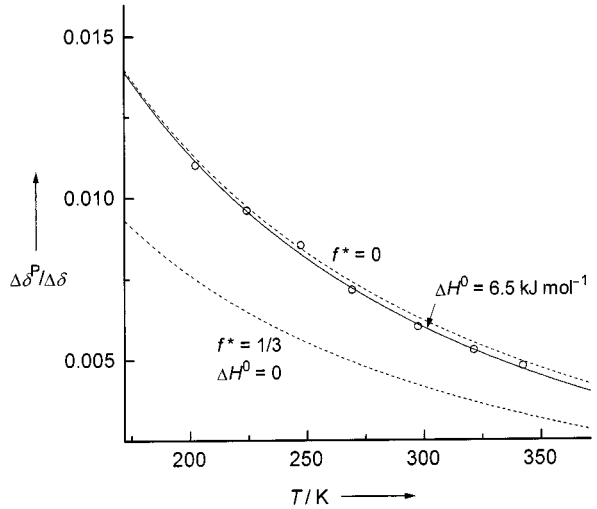


Figure 6. Diagram of relative isotopic splittings vs. temperature. The $\Delta\delta^P/\Delta\delta$ values are calculated from isotopic splittings $\Delta\delta_{6,2}{}^P$ in ^{13}C spectra recorded for solutions of [D$_5$]-**1a** in [D$_8$]toluene (Figure 4, Table 2). All three curves are calculated according to Equation 7 with the same isotopic perturbation parameters ΔH^P = 52 J mol^{-1} and ΔS^P = 0.07 J mol^{-1} K^{-1} (Table 3). The broken curves denote the limiting case in which $f^* = 0$ ($\Delta H^0 = \infty$) and the borderline case where f^* is 1/3 ($\Delta H^0 = 0$)

The effect of the presence of delocalised species **1*** on the measured relative splittings may be visualised by considering the experimental data points and computed curves (Equation 7) in relative splitting vs. temperature diagrams *that are characterised by a certain pair of ΔH^P and ΔS^P* values (Figures 6–9). The data for [D$_5$]-**1a** in [D$_8$]toluene solution (Figure 6) lie close to the limiting curve computed for the absence of the delocalised species [D$_5$]-**1a*** ($\Delta H^0 = \infty$, $f^* = 0$). The corresponding data for [D$_5$]-**1b** in [D$_8$]toluene are further away from the upper limiting curve (Figure 8). Eventually, the presence of about 20% of [D$_5$]-**1a*** in *N*,*N*′-dimethylpropylene urea gives rise to relative splittings that are closer to the borderline ($\Delta H^0 = 0$, $f^* = 1/3$, Figure 7).

NMR Evidence for the Coexistence of [D$_5$]-1b* and [D$_5$]-1b in Solutions in *N*,*N*′-Dimethylpropylene Urea

We emphasise that the preferred interpretation of the experimental results discussed so far is *in accord* with the presence of small to moderate amounts of symmetrical, delocalised species as inferred from the work on thermochromism[10] but *none of these three experiments provides per se independent evidence* for the coexistence of delocalised val-

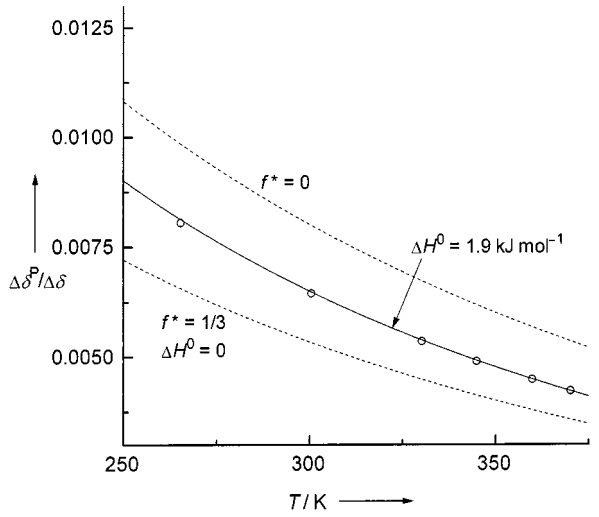


Figure 7. Diagram of relative isotopic splittings vs. temperature. The $\Delta\delta^P/\Delta\delta$ values are calculated from isotopic splittings $\Delta\delta_{6,2}{}^P$ in ^{13}C spectra recorded for solutions of [D_5]-**1a** in *N*,*N*′-dimethylpropylene urea (Table 2). All three curves are calculated according to Equation 7 with the same isotopic perturbation parameters ΔH^P = 70 J mol^{-1} and ΔS^P = 0.1 J mol^{-1} K^{-1} (Table 3). The broken curves denote the limiting case in which $f^* = 0$ ($\Delta H^0 = \infty$) and the borderline case where f^* is 1/3 ($\Delta H^0 = 0$)

ence tautomers, because reasonable thermodynamic parameters may also be obtained without them (Table 3). The situation is totally different, however, in case of the experiment performed with solutions of [D_5]-**1b** in *N*,*N*′-dimethylpropylene urea: The measured isotopic splittings themselves as well as their temperature dependence are very small (Table 2) and indicative of a phenomenon that is *not* evident from [D_8]toluene solutions. In fact, calculation of ΔH^P and ΔS^P *without* consideration of the delocalised species [D_5]-**1b*** ($\Delta H^0 = \infty$, $f^* = 0$) leads to very small values (Table 3) which are *not* compatible with the effects of solvents and structure on the isotopic perturbation that are observed in the other cases. Therefore, we have to consider the presence of [D_5]-**1b***, which is evident from thermochromism,[10] and assess ΔH^0, which could not be derived from thermochromism for this system, in two different ways.

We base the calculation with Equation 7 of ΔH^0 for [D_5]-**1b** in *N*,*N*′-dimethylpropylene urea on two extreme pairs of perturbation parameters ΔH^P and ΔS^P that are assumed to be constant. The first pair is taken from the experiment with [D_5]-**1b** in [D_8]toluene solution, the second from the experiment with [D_5]-**1a** in *N*,*N*′-dimethylpropylene urea as solvent (Table 3). The foundation for this procedure is the generally accepted explanation of equilibrium isotope effects.[8][26] Within the framework of the Born-Oppenheimer approximation, isotopic substitution does not change the shape of the potential energy hypersurface for equilibrating, degenerate molecules, which remains a symmetric double-well potential, but only alters the position of vibrational levels within each well. The greater mass of deuterium gives rise to lower levels with small differences between the two wells. Thus the greater mass skews the equilibrium that is degenerate in the absence of deuterium. For these reasons, the cumulative equilibrium isotope effect of pentadeuterophenyl groups that are located at equivalent positions can be expected to be very similar for the tetrasubstituted barbaralanes [D_5]-**1a** and **b**. Second, it may be anticipated that the effects of solvents translate only into small changes of equilibrium isotope effects because solvation only slightly modifies the shape of the potential energy surface in regions that belong to the perdeuterophenyl groups.

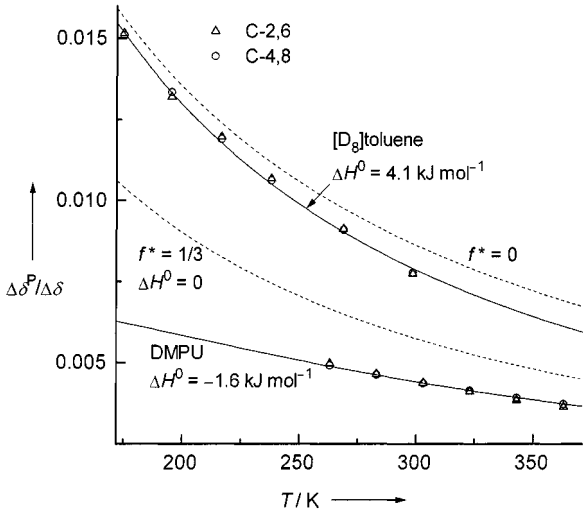


Figure 8. Diagram of relative isotopic splittings vs. temperature. The $\Delta\delta^P/\Delta\delta$ values are calculated from isotopic splittings in ^{13}C spectra recorded for solutions of [D_5]-**1b** in [D_8]toluene (above) and *N*,*N*′-dimethylpropylene urea (Figure 5, Table 2). All four curves are calculated according to Equation 7 with the same isotopic perturbation parameters ΔH^P = 49 J mol^{-1} and ΔS^P = 0.02 J mol^{-1} K^{-1} (Table 3). The broken curves denote the limiting case in which $f^* = 0$ ($\Delta H^0 = \infty$) and the borderline case where f^* is 1/3 ($\Delta H^0 = 0$)

Our first interpretation of the small isotopic splittings of [D_5]-**1b** in *N*,*N*′-dimethylpropylene urea and their little temperature dependence neglects the effects of different solvation on the potential of the pentadeuterophenyl groups. Thus, the pair of parameters ΔH^P = 49 J mol^{-1} and ΔS^P = 0.02 J mol^{-1} K^{-1} that have been derived for [D_5]-**1b** in [D_8]toluene solutions is employed as *constant* parameters in the fit of Equation 7 to the relative splitting vs. temperature data for *N*,*N*′-dimethylpropylene urea solutions (Figure 8). Variation of the third parameter ΔH^0 yields a negative value $\Delta H^0 = -1.6$ kJ mol^{-1} which indicates that about 50% exist as the delocalised valence tautomer [D_5]-**1b***.

The second interpretation rests on the assumption that the equilibrium isotope effect of pentadeuterophenyl groups is the same for [D_5]-**1a** and **b**. The pair of parameters ΔH^P = 70 J mol^{-1} and ΔS^P = 0.1 J mol^{-1} K^{-1} that describes the isotopic perturbation for [D_5]-**1a** in *N*,*N*′-dimethylpropylene urea solution (Figure 7) was the starting point for the fit of Equation 7 to the relative splitting vs. temperature data of [D_5]-**1b** in the same solvent. When ΔS^P was fixed at 0.1 J mol^{-1} K^{-1}, no curve could be adapted to the data, however. Simultaneous variation of ΔH^0 *and* ΔS^P yielded a somewhat smaller value ΔS^P = 0.07 J mol^{-1} K^{-1} and again a negative value for the enthalpy difference between the localised and delocalised valence tautomers, $\Delta H^0 = -2.2$ kJ mol^{-1}, which corresponds to the presence of about 55% of [D_5]-**1b*** (Figure 9). The agreement be-

tween the results, which are based on the two different limiting approximations, is very satisfactory. Any other intermediate values for the perturbation parameters ΔH^P and ΔS^P are expected to result in enthalpy differences ΔH^0 between −1.6 and −2.2 kJ mol^{-1} and to confirm that *one half of the compound exists as C_2 symmetric, delocalised valence tautomer [D_5]-**1b*** in N,N′-dimethylpropylene urea solution at room temperature.*

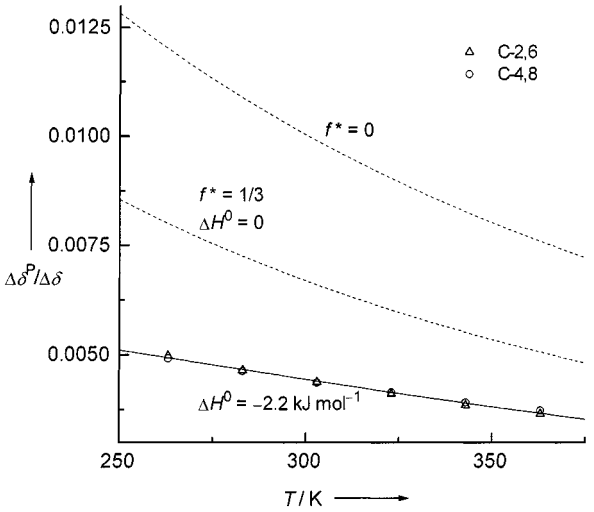


Figure 9. Diagram of relative isotopic splittings vs. temperature. The $\Delta\delta^P/\Delta\delta$ values are calculated from isotopic splittings in ^{13}C spectra recorded for solutions of [D_5]-**1b** in *N,N′*-dimethylpropylene urea (Figure 5, Table 2). All three curves calculated according to Equation 7 with the same isotopic perturbation parameters ΔH^P = 70 J mol^{-1} and ΔS^P = 0.07 J mol^{-1} K^{-1} (Table 3). The broken curves denote the limiting case in which f^* = 0 ($\Delta H^0 = \infty$) and the borderline case where f^* is 1/3 (ΔH^0 = 0)

The simultaneous presence of rapidly equilibrating, asymmetric species, whose equilibrium is skewed by isotopic labelling, and an isomer of higher symmetry has been invoked previously. Perrin and Nielson demonstrated with the ^{18}O isotopic perturbation method that the hydrogen bond in the monoanions of dicarboxylic acids is asymmetric (double-well potential) in both water and organic solvents. As one possible explanation for the observed smaller ^{18}O-induced isotope shift in the latter, they proposed a range of solvation states. The weaker forces in organic solvents should allow locally symmetric environments to coexist with asymmetric ones.[27]

Temperature and Solvent Dependence of Carbon-13 Chemical Shifts

The inference of variable amounts of delocalised barbaralanes from thermochromism[10] and isotopic splittings raised the question whether their presence is also reflected by a particular temperature and solvent dependence of ^{13}C chemical shifts. If a delocalised valence tautomer (chemical shift δ_i*) coexists with a rapidly equilibrating pair of degenerate valence tautomers (time-averaged chemical shift $\bar{\delta}_{i,i'}$), the observed chemical shift $\bar{\delta}_i$ is the weighted average as expressed by Equation 8.

$$\bar{\delta}_i = \bar{\delta}_{i,i'} + f^*(\delta_{i^*} - \bar{\delta}_{i,i'}) \quad (8)$$

Chemical shifts of the equilibrating localised valence tautomers and the delocalised valence tautomer have been calculated recently for the parent semibullvalene (**25** ⟹ **25′** and C_{2v}-**25***).[28] Similar calculations have been carried out by H. Jiao for 4,8-*dimethyl*barbaralane-2,6-dicarbonitrile (**28** ⟹ **28′** and C_2-**28***),[29] which was taken as model for 4,8-*diphenyl*barbaralane-2,6-dicarbonitrile (**1b**). The results are compiled in Table 4.

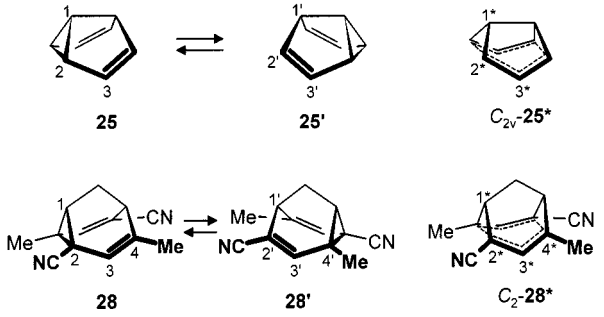


Table 4. Calculated time-averaged ^{13}C chemical shifts $\bar{\delta}_{i,i'}$ (δ values, relative TMS) for the equilibrating localised valence tautomers and chemical shifts δ_{i^*} for the delocalised structures of the parent semibullvalene (**25**, IGLO/DZ/Becke3LYP/6−31G*) and 4,8-dimethylbarbaralane-2,6-dicarbonitrile (**28**, GIAO-SCF/6−311G*//Becke3-LYP/6−31G*)

C_i	$\bar{\delta}_{i,i'}$	δ_{i^*}	$\delta_{i^*} - \bar{\delta}_{i,i'}$	Ref.
	25⇌25′	**25***		[28]
C-1	52.0	50.2	1.8	
C-2	85.5	96.7	11.2	
C-3	119.0	125.4	−6.4	
	28⇌28′	**28***		[29]
C-1	31.8	34.3	2.5	
C-2	71.5	80.0	8.5	
C-3	136.1	127.3	−8.8	
C-4	89.9	112.1	22.2	
C-9	18.5	16.3	−2.2	
CN	128.2	128.7	0.5	
CH_3	21.7	22.4	0.7	

Both calculations predict that noticeable changes of ^{13}C chemical shifts are to be expected only for the rearranging allylic moieties. Because the temperature-driven changes of the fractions f^* of delocalised valence tautomers **1a*** and **b*** are less than 7% per 100 K (Table 3), the resulting temperature dependence of ^{13}C chemical shifts are anticipated to fall in the range of the inherent temperature dependence, which is usually less than 2 ppm/100 K.[30] This expectation is born out by a comparison of the temperature gradients which may be calculated from the ^{13}C chemical shifts for [D_5]-**1a** and **b** that are listed in Table 6.

Variation of the solvent has a much more pronounced influence on the fraction f^* of the delocalised valence tautomers than temperature (Table 3).[10b] The changes of the ^{13}C chemical shifts that are caused by an exchange of

Table 5. Differences in chemical shifts (δ values, expressed relative to that of C-9) in ^{13}C spectra recorded for solutions of the tetrasubstituted barbaralanes **1a** and **b** in *N,N'*-dimethylpropylene urea and [D_8]toluene at 300 K

	δ(DMPU) − δ([D_8]toluene) at 300 K	
	1a	**1b**
C-1,5	−0.92	−0.60
C-2,6	0.16	0.70
C-3,7	−0.56	−0.14
C-4,8		1.30
C-9	(0.00)	(0.00)

[D_8]toluene for *N,N'*-dimethylpropylene urea are listed in Table 5. The signals of the rearranging allylic moieties do indeed show low-field (C-2,6, C-4,8) and high-field shifts (C-3,7) as expected, on the basis of the estimates in Table 4, for an increase of the delocalised species, but the unexpected high-field shifts of the bridgehead signals (C-1,5) point to other solvent effects of the same order of magnitude. Therefore, while the experimental observations are not contradictory, they do not provide evidence for the existence of delocalised valence tautomers.

Conclusion

The extension of Saunders' isotopic perturbation method described here enables the calculation of temperature-dependent relative isotopic splittings of NMR signals in cases where delocalised species of higher symmetry coexist with rapidly equilibrating classical isomers (Equation 7). Equilibria in similar multi-component systems that are skewed by other perturbations, e.g. by different substituents, may be treated in the same way. We note that unequivocal evidence for the coexistence of delocalised species may be obtained only if they are more stable than the localised valence tautomers. Otherwise, the relative splitting vs. temperature data suggest ambiguous interpretations. In case of the tetrasubstituted barbaralanes **1a** and **b**, the changes of ^{13}C chemical shifts that may be caused by temperature- or solvent-induced variations of the fractions of the delocalised isomers **1a*** and **b*** are too small for an unequivocal distinction from the inherent temperature dependence of the ^{13}C chemical shifts and different solvent effects. The present extension of Saunders' isotopic perturbation method should be useful in the future quest for homoaromatic barbaralanes and semibullvalenes, and other delocalised (non-classical) species that coexist with equilibrating classical structures.

Experimental Section

General Remarks: Yields, melting points, and IR: Table 1. − ^1H NMR: Table 7, 9. − ^{13}C NMR: Table 2, 4−6, 8, 9. Signals of ^{13}C atoms that are equivalent by virtue of symmetry or fast exchange are given only once in the Tables. Similar chemical shifts of ^{13}C atoms that bear the same number of protons are printed in *italics* and may be exchanged. − Molecular formulae and masses, and elemental analyses: Table 10. − Melting points: Kofler apparatus from Reichert, Vienna, Austria. − IR: Perkin−Elmer 1420. − ^1H and ^{13}C NMR: Bruker AC 250, WM 400 and DMX 600. Carbon-13 signals were assigned on the basis of DEPT and $^{13}C,^1H$ COSY spectra. Proton signals were assigned on the basis of $^1H,^1H$ COSY spectra. − Carbon-13 spectra at variable temperatures: Bruker DMX 600. Temperatures were calculated from shift differences in proton spectra of methanol (202−269 K) and ethylene glycol (297−342 K) with the help of van Geet's equations.[31] Lower temperatures were calibrated with the recently developed high-precision ^{13}C shift thermometer.[32] − 70-eV MS: Finnigan MAT 8200. − UV: Perkin−Elmer 330, [ε] = L mol^{-1} cm^{-1}.

HPLC was performed on (250 × 4.6) mm stainless-steel columns: Bruker-Franzen LC 21-C equipped with UV detector Knauer 87.00 (λ = 254 nm), reversed-phase silica gel Europrep 60−30 C18, 10 μm (Knauer), 2.0 mL/min methanol/water (95:5), retention times t_R [min] = 3.6 (*endo*-**3**), 3.8 (**2**), 4.0 (*exo*-**3**), 4.8 (**1a**), 5.2 (**15**), 7.4 (**11**), 9.5 (**4**). − Reversed-phase silica Prodigy 5μ ODS (3) 100 Å (Phenomenex), 1.5 mL/min acetonitrile t_R = 3.1 (**19**). − Ultremex 3μ silica (Phenomenex), 1.5 mL/min petroleum ether (50−70°C) (PE)/ethyl acetate (EA) (80:20), t_R = 3.1 (**8**), 5.2 ([D_5]-**7**), 6.9 ([D_5]-**1b**) 8.5 (**6**), 11.9 (**5**); (90:10), t_R = 6.6 (**17**), 8.5 (**19**). − Waters M-6000 A equipped with UV detector 440 (λ = 254 nm) and RI detector R 401, silica gel LiChrosorb Si60, 5 μm (Knauer), 1.5 mL/min PE/EA (80:20), t_R = 4.4 (*endo*-**12**), 4.9 (*exo*-**12**), 5.4 (*exo*-**10**), 6.4 (*endo*-**10**).

Flash chromatography: UV detector Knauer 87.00 (λ = 254 nm), (40 × 4) and (30 × 3)cm glass column packed with silica gel 32−63 μm (ICN Biomedicals), PE/EA, 1.8 bar N_2. − MPLC[33]: Pump FC1 equipped with pump head K 110 and 0.2-l pulse damper (Lewa, D-71229 Leonberg), UV detector Knauer 87.00 (λ = 254 nm), and (40 × 4) cm glass column packed with LiChroprep Si60, 15−25 μm (Merck), PE/EA (8 : 2), 50 mL/min, 13.5 bar, t_R [min]: 14.3 (*exo*-**10**), 16.8 (*endo*-**10**), 11.8 (*endo*-**12**), 12.8 (*exo*-**12**).

Debrominations were performed with freshly prepared zinc-copper couple. − Under Ar (99.998%), benzene, cyclohexane and diethyl ether were distilled from NaH, CH_2Cl_2, EA and PE (50−70°C) from P_2O_5, triethylamine from CaH_2, methanol from magnesium methoxide, and tetrahydrofuran and pentane from Na/K alloy. − Potassium *tert*-butoxide was sublimed twice at 10^{-2} Torr and handled under Ar. − Copper(I) cyanide was dried at 55−60°C/10^{-2} Torr over powdered KOH. − Dry cerium(III) chloride,[34] KCN−18-crown-6,[35] phenyllithium,[36] 1-bromo-4-*tert*-butylbenzene,[37] **2**,[2] and **5**[14] were prepared according to known procedures. − Boron trifluoride−diethyl ether was distilled immediately before use.

2,4,6,8-(Pentadeuterophenyl)triphenylbarbaralane [D_5]-1a

[D_5]Phenyllithium: A 25-mL two-necked flask equipped with a sintered-glass funnel[36] was filled with Ar and charged with [D_5]bromobenzene (99.5% deuteration, 5.00 g, 30.9 mmol) and benzene (7.5 mL). A solution of butyllithium in hexane (2.38 M, 11.3 mL, 26.8 mmol) was added during 15 min via syringe to the stirred solution to yield a pale yellow precipitate. Stirring was continued for 16 h. The precipitate was collected by filtration and washed carefully with pentane (3 × 10 mL). Drying at 10^{-2} Torr afforded a colourless powder (1.84 g, 77%).

***exo*- and *endo*-2-Hydroxy-2-[D_5]phenyl-4,6,8-triphenylbicyclo[3.3.1]-non-6-ene (*exo*- and *endo*-3):**[2] A suspension of dry cerium(III) chloride (5.42 g, 22 mmol) in tetrahydrofuran (40 mL) was stirred under Ar for 17 h. A freshly prepared, cold (−40°C) solution of [D_5]phenyllithium (1.84 g, 21 mmol) in tetrahydrofuran (20 mL) was rapidly added to the cooled suspension (−78°C) via syringe

followed by stirring for 1.5 h at −78°C. A solution of **2** (5.00 g, 14 mmol) in tetrahydrofuran (20 mL) was added during 45 min at −78°C, and stirring was continued for 2 h until the conversion was complete (HPLC). The cooling bath was removed, and the suspension was allowed to attain 20−25°C. Sat. aq. NH_4Cl (100 mL) was added to the suspension. The aq. layer was extracted with diethyl ether (3 × 50 mL). The combined org. layers were extracted with sat. aq. NH_4Cl (2 × 50 mL) and NaCl (50 mL), and dried with $MgSO_4$. Distillation of the solvent i. vac. afforded a solid which consisted of *exo*- and *endo*-**3** (1:2, ^{1}H NMR). Flash chromatography with PE/EA (95:5) yielded two fractions. Recrystallisation of the first fraction from methanol yielded colourless needles (*exo*-**3**, 1.96 g, 28%, m.p. 100°C) containing two mol of methanol (^{1}H NMR) which could not be removed by drying over P_2O_5 for 24 h at 60°C/10^{-2} Torr. Recrystallisation of the second fraction from PE gave colourless needles (*endo*-**3**, 4.11 g, 67%, m.p. 155−157°C). − ^{13}C NMR: The assignment of the signals for the ^{13}C atoms C-2, 6 and *ipso*-C, reported in ref.[2] for the nondeuterated compound, must be exchanged.

2-[D_5]Phenyl-4,6,8-triphenylbicyclo[3.3.1]nona-2,6-diene (4): According to the method by Posner et al.,[12] A stirred solution of **3** (5.11 g, 11.4 mmol) in CH_2Cl_2 (180 mL) was cooled at 0°C under Ar. Boron trifluoride−diethyl ether (1.7 mL, 14 mmol) was added at this temperature during 15 min. The solution was stirred at 20−25°C for 2.5 h and cooled again at 0°C. Sat. aq. $NaHCO_3$ (180 mL) was added to the vigorously stirred solution. The aq. layer was extracted with CH_2Cl_2 (2 × 40 mL). The combined org. layers were extracted with sat. aq. NaCl (50 mL) and dried with $MgSO_4$. Distillation of the solvent i. vac. yielded a pale yellow powder. Recrystallisation from EA afforded colourless needles (4.34 g, 88%, m.p. 188−190°C).

2,4,6,8-[D_5]Phenyltriphenyltricyclo[3.3.1.$0^{2,8}$]nona-3,6-diene ([D_5]-1a):[13] All operations were performed under Ar. A suspension of **4** (1.00 g, 2.33 mmol), *N*-bromosuccinimide (1.50 g, 8.43 mmol) and azodiisobutyronitrile (ca.10 mg) in cyclohexane (100 mL) was heated under reflux for 40 min while the initial orange colour slowly faded. Powdered CaH_2 (0.5 g) was added to the vigorously stirred, cold suspension, and a stream of Ar was introduced which helped to remove HBr (ca. 20 min). The solid material was removed by filtration through a glass sinter funnel. The pale yellow filtrate was diluted with tetrahydrofuran (50 mL), and zinc-copper couple (2.5 g) was added. The vigorously stirred suspension was heated under reflux for 40 min while the formation of the product was monitored by reversed-phase HPLC. After cooling to 20−25°C, the mixture was filtered through a pad of silica gel (32−63 μm, 2 × 3 cm) which was rinsed with tetrahydrofuran (50 mL). The solvent was distilled i. vac. until the final volume was ca. 10 mL. Enough EA was added to dissolve the precipitate. Flash chromatography with PE/EA (95: 5) afforded orange-red coloured crystals (568 mg, 57%, m.p. 143−147°C).

4,8-(Pentadeuterophenyl)phenylbarbaralane-2,6-dicarbonitrile ([D_5]-1b)

***exo*-8-Phenylbicyclo[3.3.1]non-3-ene-2,6-dione (6):** A stirred suspension of dry copper(I) cyanide (6.58 g, 73.5 mmol) in tetrahydrofuran (160 mL) was cooled at −78°C under Ar. Under vigorous stirring, phenyllithium (12.4 g, 147 mmol) was added slowly enough to keep the temperature below −50°C. The resulting olive-green solution was stirred at −78°C for 2 h, allowed to warm rapidly to −15°C, and cooled again at −78°C. A solution of **5** (10.9 g, 73.5 mmol) in tetrahydrofuran (60 mL) was added *very rapidly*, whereupon the reaction mixture turned deep red. After stirring at −78°C for 50 min, a mixture of sat. aq. NH_4Cl (160 mL) and aq. NH_3 (2 M, 20 mL) was added followed by stirring for 15 min. The aq. layer was extracted with diethyl ether (4 × 100 mL). The combined org. layers were extracted with sat. aq. NH_4Cl (2 × 200 mL) and NaCl (2 × 200 mL) and dried with $MgSO_4$. Distillation of the solvent i. vac. gave a honey-coloured, oily residue [12.5 g, **6**:**7** = 9:1 (HPLC)]. Flash chromatography with PE/EA (3:1) and recrystallisation of the orange-yellow solid (5.33 g, 32%) from methanol afforded colourless crystals (m.p. 88−90°C). − ^{1}H NMR (250 MHz, [D]trichloromethane): δ = 2.21 (br. d, J = 13.6 Hz, 9-H), 2.34 (br. d, J = 13.6 Hz, 9-H′), 2.69 (br. d, J = 16.4 Hz, 7-H_{exo}), 2.80 (m, 1-H), 3.19 (dd, J = 16.4, 7.9 Hz, 7-H_{endo}), 3.36 (m, 5-H), 3.70 (br. d, J = 7.9 Hz, 8-H), 6.33 (d, J = 9.7 Hz, 3-H), 7.11 (ddd, J = 9.7, 7.0, 1.7 Hz, 4-H), 7.2−7.4 (m, Ph). − MS, *m*/*z* (%): 226 (20) [M^+], 132 (24), 131 (100), 104 (25), 103 (15), 95 (14), 77 (8).

***exo*,*exo*-4-[D_5]Phenyl-8-phenylbicyclo[3.3.1]nonane-2,6-dione ([D_5]-7):** As described in the preceding experiment, an olive-green solution was prepared from copper(I) cyanide (3.03 g, 34 mmol) and [D_5]phenyllithium (6.02 g, 68 mmol) in tetrahydrofuran (130 mL) and cooled at −78°C. Boron trifluoride−diethyl ether (7.2 g, 6.4 mL, 51 mmol) was added dropwise to the solution, which was stirred for 20 min at that temperature. A solution of **6** (5.33 g, 23.6 mmol) in tetrahydrofuran (25 mL) was added dropwise during 5 min, whereupon the mixture turned red-brown. The stirred mixture was allowed to attain room temperature overnight. Workup as described in the preceding experiment, flash chromatography of the yellow-brown oil with PE/EA (4:1) and recrystallisation of the pale yellow solid from ethanol gave pale yellow, long needles (1.20 g, 16%, m.p. 140−141°C). − MS, *m*/*z* (%): 310 (22), 309 (100) [M^+], 131 (22), 122 (58), 117 (59), 91 (18), 82 (4), 77 (10), 55 (19).

***exo*,*exo*-4-[D_5]phenyl-8-phenylbicyclo[3.3.1]nona-2,6-diene-2,6-dicarbonitrile (8):** As described for the nondeuterated compounds,[4] [D_5]-**7** (1.20 g, 3.9 mmol) was converted with trimethylsilyl cyanide in the presence of KCN−18-crown-6 into a mixture of diastereomeric *O*-trimethylsilyl cyanohydrins (colourless noncrystalline solid, 1.45 g, 74%). Treatment of the crude product with hydrogen fluoride−pyridine in $POCl_3$ followed by heating with $POCl_3$ in pyridine and workup yielded colourless crystals (0.62 g, 66%, m.p. 225−227°C).

4,8-[D_5]Phenylphenyltricyclo[3.3.1.$0^{2,8}$]nona-3,6-diene-2,6-dicarbonitrile ([D_5]-1b): As described for **1b**,[4] brick-red needles (0.20 g, 38%, m.p. 213−217°C) were obtained from **8** (0.53 g, 1.6 mmol). Concentrated solutions must be degassed and kept under argon to avoid autoxidation.[13]

2,4,6-Triphenylbarbaralane (15)

4,6,8-Triphenylbicyclo[3.3.1]non-6-en-2-one *p*-Toluenesulphonylhydrazone (9): To a stirred suspension of **2** (1.00 g, 2.74 mmol) and *p*-toluenesulphonylhydrazine (0.61 g, 3.3 mmol) in ethanol (95%, 20 mL), one drop of aq. conc. HCl was added, and the mixture was heated under reflux for 2 h. After cooling to 20−25°C, the precipitate was isolated by filtration and washed with cold ethanol/water (1:1, 2 × 5 mL) and methanol (2 mL) to yield a colourless powder [1.24 g, 85%, m.p. 190°C (dec.)], which was sufficiently pure for the next step. Recrystallisation from ethanol/tetrahydrofuran (1:3) afforded a colourless, microcrystalline powder [0.95 g, 65%, m.p. 195−196°C (dec.)]. The loss of material on recrystallisation was due to the sensitivity of **9** toward air. − MS, *m*/*z* (%): 533 (1) [M^+], 348 (43), 257 (26), 231 (49), 156 (16), 130 (32), 91 (100) [$C_7H_7^+$], 65 (25).

***exo*- and *endo*-2-Hydroxy-4,6,8-triphenylbicyclo[3.3.1]non-6-ene (*exo*- and *endo*-10):** Sodium borohydride (0.65 g, 17 mmol) was ad-

ded in several portions under Ar at −10−0°C to a stirred suspension of powdered **2** (2.50 g, 6.86 mmol) in methanol (100 mL). The mixture was allowed to warm to 20−25°C, and stirring was continued for 2 d. Water (50 mL) was added, and the solution was slightly acidified with aq. conc. HCl (pH 5). After distillation of the solvent i. vac., the colourless solid residue was dissolved in ether (100 mL) and water (50 mL). The aq. layer was extracted with ether (2 × 50 mL). The combined org. layers were dried with $MgSO_4$. Distillation of the solvent i. vac., followed by flash chromatography of the residue with PE/EA (70:30) afforded a colourless powder (2.31 g, 92%, m.p. 50−60°C), which consisted of *exo*- and *endo*-**10** (1:2, ^{1}H NMR). − MS, *m*/*z* (%): 366 (1) [M^+], 348 (4) [$M^+ - H_2O$], 230 (99), 105 (99), 77 (68).

***exo*- and *endo*-2-(Methylsulphonyl)oxy-4,6,8-triphenylbicyclo[3.3.1]-non-6-ene (*exo*- and *endo*-12):** Triethylamine (1.1 g, 1.5 mL, 11 mmol) was added at 0°C under N_2 to a stirred solution of *exo*- and *endo*-**10** (1:2, 2.00 g, 5.46 mmol) in CH_2Cl_2 (30 mL). Methanesulphonyl chloride (0.94 g, 0.64 mL, 8.2 mmol) was added via syringe during 10 min, and stirring was continued at 0°C for 2.5 h. Ether (100 mL) and water (20 mL) were added. The org. layer was extracted with aq. HCl (2 M, 2 × 25 mL), aq. $NaHCO_3$ (5%, 2 × 25 mL), and water (2 × 25 mL), and dried with $MgSO_4$. Distillation of the solvent i. vac., followed by flash chromatography of the residue with PE/EA (80:20) afforded a colourless powder (2.23 g, 92%, m.p. 55−60°C), which consisted of *exo*- and *endo*-**12** (1:2, ^{1}H NMR). − MS, *m*/*z* (%): 348 (5) [$M^+ - MeSO_3H$], 96 (44), 94 (47), 79 (68). − Partial separation of a sample by MPLC (PE/EA, 80:20) afforded enriched fractions of the diastereomers from which the NMR spectra were taken.

2,4,8-Triphenylbicyclo[3.3.1]nona-2,6-diene (11): a) A solution of methyllithium in diethyl ether (1.3 M, 3.5 mL, 4.6 mmol) was added via syringe during 5 min under Ar to a stirred suspension of powdered **9** (1.00 g, 1.88 mmol) in diethyl ether (25 mL) kept at −78°C. The pale yellow suspension was allowed to attain 20−25°C overnight and kept at that temperature until the evolution of N_2 had ceased (21 h). The deep red solution was cooled at 0°C. Water (10 mL) was added cautiously resulting in the formation of a pale yellow org. layer which was extracted with sat. aq. NaCl (3 × 10 mL). The combined aq. layers were extracted with ether (2 × 20 mL). The combined org. layers were dried with $MgSO_4$. Distillation of the solvent yielded a viscous, yellow oil. Flash chromatography with PE/EA (80:20) and recrystallisation from EA and little methanol afforded colourless prisms (240 mg, 37%, m.p. 128−129°C). − MS, *m*/*z* (%): 348 (100) [M^+], 257 (57), 231 (69), 218 (56), 115 (41), 91 (73).

b) A solution of *exo*- and *endo*-**12** (1: 2, 2.50 g, 5.62 mmol) in diethyl ether (40 mL) was added under Ar during 15 min to a stirred suspension of neutral aluminium oxide (ICN Biomedicals, activity I, ca. 40 g) in diethyl ether (40 mL). The suspension was stirred vigorously at 20−25°C for 3 d while the formation of **11** was monitored by HPLC. The suspension was filtered through a pad of kieselguhr (2 × 3 cm), which was rinsed with diethyl ether (120 mL). Distillation of the solvent i. vac. and recrystallisation from EA and little methanol afforded colourless prisms (1.47 g, 75%, m.p. 129−130°C).

2,4,6-Triphenyltricyclo[3.3.1.0^{2,8}]nona-3,6-diene (15): All operations were performed under Ar. Solvents, water, Na_2SO_4, and silical gel

Table 6. Chemical shifts (δ values) in ^{13}C spectra taken from solutions of the barbaralanes [D_5]-**1** and their precursors. The chemical shifts in ^{13}C spectra that were recorded for solutions in [D_8]toluene and *N*,*N*′-dimethylpropylene urea are expressed relative to that of C-9. The numbers of the carbon atoms of the barbaralanes refer to the more stable valence tautomers **1**

Cpd.	[a]	Temp. [K]	quat. C C-2 C-8	quat. C C-4 C-6	CH C-1 C-5	CH C-3 C-7	CH C-4 C-8	CH C-3 C-7	CH_2 C-9	CN	*ipso*-C	*o*-, *m*-C		*p*-C
[D_5]-**1a**	C	295	92.49	92.97 93.04	30.92 30.97	123.87 123.90			19.86		141.06 140.87	128.05	127.54 [b]	126.21
	T	202	72.24	73.17 73.25	10.57 10.67	104.66 104.69			0.00					
	T	342	73.16	73.53 73.60	11.49 11.53	103.55 103.58			0.00					
	U	265	72.75	73.42 73.49	9.90 9.95	103.40 103.42			0.00					
	U	370	73.55	73.87 73.94	11.05 11.07	103.05 103.07			0.00					
4	C	295	142.36	142.43	38.00	124.60 124.65	45.80		19.00		144.39 140.99 140.80[c]	128.60 128.48	126.53 128.24	127.33 126.23
[D_5]-**1b**	C	295	73.27 94.48	93.80 72.63	31.4	127.20 127.42			17.3	118.3	136.83 136.64[c]	127.23	129.24	150.7 128.87
	T	175	55.44 75.73	77.22 56.78	13.88	[d]			0.00					
	T	298	56.15 76.88	77.62 56.84	14.48 14.51	110.08 110.29			0.00					
	U	263	57.02 77.86	78.30 57.46	13.53	109.96 110.28			0.00					
	U	363	57.12 78.40	78.72 57.44	14.36	109.86 110.17			0.00					
6	C	295	200.0	207.1	49.13 49.65	132.0	148.2 43.8	37.6	29.3		142.7	127.32	128.79	126.94
8	C	295	*117.95*		37.9	143.4	44.908 44.984		16.7	*118.33*	139.186 138.997[c]	128.34	128.99	127.70

[a] Solvent: C = [D]trichloromethane, T = [D_8]toluene, U = *N*,*N*′-dimethylpropylene urea. − [b] δ = 127.53, 127.07 (*o*-, *m*-C), 125.69 (*p*-C) [three (1:1:1) triplets, $^1J_{C,D}$ = 23.5 Hz]. − [c] The signal is lower and somewhat broadened. − [d] Measurement of the chemical shifts was precluded by overlap with solvent signals.

Table 7. Chemical shifts (δ values) and coupling constants (absolute values [Hz]) in proton spectra of triphenylbarbaralane **15** and its precursors, recorded for [D]trichloromethane solutions. Indices of protons: *x* = *exo*, *n* = *endo*

Cpd.	1-H 5-H	2-H	3-H$_x$ 3-H$_n$	4-H 8-H	7-H	9-H 9-H'	Ph (m)	CH_3 (s)	NH (s)	^2J 3*x*,3*n*	 9,9'	 1,2	^3J 2,3*x* 2,3*n*	 1,9 1,9'	 5,9 5,9'	 3*x*,4*n* 3*n*,4*n*	^4J 7,8	 5,7	 4*n*,9
9	2.87 br. s		2.74 d	3.16 br. d	6.14 d	1.62 br. s	6.8 – 8.0	2.42	10.53 br.	16.6							4.2		
	3.03 br. s		2.41 dd	3.25 d					OH							7.0			
exo-**10**	2.04 m	4.08 q	*2.31* ddd	2.90 m	6.25 dd	*2.21* br. dt	7.2 – 7.6		2.05	15.1	13.3	3.2	3.8	3.1	3.1	6.6	4.1	0.8	[a]
	3.44 m		*2.21* [a]	3.43 d		*1.67* br. dt							3.8	3.1	3.1	[a]			
endo-**10**	2.10 m	4.25 dt	2.22 br. dd	3.12 br. d	6.32 dd	1.77 ddt	7.2 – 7.6		2.07	13.7	13.5	5.0	5.0	3.1	3.1	7.0	3.9	0.8	1.4
	3.25 m		2.02 dt	3.91 d		1.54 dt							12.2	2.7	2.7	[a]			
exo-**12**	2.33 m	5.12 q	*2.47* br. dt	2.98 m	6.26 d	*2.29* br. dt	7.2 – 7.6	2.56		15.7	13.1	3.2	3.2	3.6	3.6	3.5	4.0	[a]	[a]
	3.52 m		*2.37* ddd	3.52 d		*1.78* dtm							3.2	[a]	[a]	6.6			
endo-**12**	2.40 m	5.27 dt	2.47 br. dd	3.20 br. d	6.35 dd	1.81 ddt	7.2 – 7.6	3.12		13.7	13.4	5.3	5.3	3.6	3.6	[a]	4.1	0.9	1.7
	3.29 m		2.34 dt	3.92 d		1.58 dt							12.1	2.7	2.7	5.8			
		3-H	6-H							$^2J_{9,9'}$	$^3J_{5,6}$	$^3J_{6,7}$							$^4J_{1,3}$
11	3.06 br. s	6.08 dd	6.25 ddt	3.55 d	5.72 ddt	*1.67* ddd	7.2 – 7.6			12.8	5.7	9.9		2.5	3.5		4.5	0.8	0.3
	2.51 br. s			3.23 d		*1.56* dt					$^3J_{1,8}$			1.9	1.9	4.7			
15[b]	2.51 dq	6.27 d			6.12 dd	*1.52* br. dt	6.9 – 7.4			12.3	7.5			2.1	2.3		7.0	1.3	
	3.85 m			2.40 br. t		*1.43* dtm								2.1	2.7			$^4J_{1,5}$ 2.1	$^4J_{3,5}$ 1.1

[a] Poorly resolved signals. – [b] Solvent [D_6]benzene.

Table 8. Chemical shifts (δ values) in ^{13}C spectra recorded for solutions of triphenylbarbaralane **15** and its precursors in [D]trichloromethane

	quat. C			CH			CH_2						
Cpd.	C-2 C-8	C-4 C-6	C-1 C-5	C-2 C-6	C-3 C-7	C-4 C-8	C-3	C-9	CH_3	*ipso*-C	*o*-, *m*-C		*p*-C
11	*141.18*		38.7		124.5	46.7		18.3		*144.28*	128.64	128.19	127.29
			36.3	132.9	126.9	43.7				*144.14*	128.57	126.56	126.18
										143.08	128.40		126.14
15	37.10	*137.76*	25.12		123.56			20.36		145.47	128.49	128.19	126.56
		138.31	36.36		119.45	32.04				140.63	128.40	125.63	126.32
										140.49	128.35	125.54	
(366 K)[a]	16.95	*118.11*	5.14		102.64			0.00					
		117.70	16.62		98.58	11.98							
(248 K)[a]	16.48	*117.56*	4.27		102.96			0.00					
		117.18	15.69		98.97	11.61							
										ipso-C	*o*-, *m*-, *p*-C		
9	163.6		45.3			41.6	24.9	20.0	21.6	*144.00*	129.85	128.85	127.39
		140.02	38.6		126.3	47.8				*143.89*	129.27	128.30	127.02
										143.28	128.98	128.05	126.73
										142.42			
										135.47			
exo-**10**			42.7	73.0		37.4	30.5	17.2		*145.15*	128.52	128.08	126.28
		140.43	34.3		126.25	45.8				*144.49*	128.47	127.48	125.92
										142.42	128.36	127.33	125.84
endo-**10**			42.8	69.3		41.6	29.9	21.7		*145.88*	128.31	127.20	125.76
		140.68	36.1		128.55	39.3				*143.48*	128.28	125.96	
										141.90	127.40	125.84	
exo-**12**			40.6	81.4		37.4	29.4	17.6	38.1	*144.07*	128.60	128.11	126.63
		139.92	33.5		125.55	45.1				*143.97*	128.51	127.57	125.88
										142.84	128.23	127.29	125.72
endo-**12**			41.1	81.0		41.6	27.8	21.5	38.9	*144.50*	128.69	127.54	126.39
		140.21	36.0		127.84	39.9				*142.01*	128.46	127.28	126.20
										141.95	128.23	127.13	125.85

[a] Solvent [D_8]toluene; the chemical shifts are expressed relative to that of C-9 (δ_9 = 20.70 relative TMS at 300 K).

were degassed and saturated with Ar. a) A 250-mL two-necked flask equipped with a sintered glass funnel[36] was charged with **11** (1.00 g, 2.87 mmol) and potassium *tert*-butoxide (0.98 g, 8.8 mmol). A solution of butyllithium in hexane (2.4 M, 5.3 mL, 13 mmol) was slowly added via syringe to the stirred mixture. The deep red suspension was diluted with pentane (20 mL) and stirred for 17 h. The microcrystalline, black-red precipitate (**13**) was collected by filtration, washed with pentane (4 × 20 mL), dried for 10 min in a stream of Ar, and cooled to −70°C. Tetrahydrofuran (70 mL) was added dropwise at −70°C. The resulting deep violet solution was stirred at −70°C for 1 h and added dropwise during 1.5 h through a narrow PTFE tubing to a vigorously stirred solution of iodine (1.00 g, 3.94 mmol) in tetrahydrofuran (150 mL) kept at −70°C. Each drop was immediately decolourised. The resulting pale brown solution was allowed to attain 20−25°C during 1 h. Diethyl ether (300 mL) and water (200 mL) were added. The org. layer was extracted with water (2 × 200 mL). Drying of the org. layer with Na_2SO_4, distillation of the solvent i. vac. to a final volume of 2 mL, and flash chromatography of the concentrated solution with PE yielded a yellow oil. Crystallisation from PE at −20°C afforded pale yellow crystals (190 mg, 19%, m.p. 99−100°C). − MS, *m/z* (%): 346 (100) [M^+], 268 (30), 255 (50), 192 (22), 115 (22), 91 (27). − UV (acetonitrile): λ_{max} [nm] (lg ε): 220 (4.401) (sh), 258 (4.555) (Figure 2).

b) A suspension of **11** (0.50 g, 1.43 mmol), *N*-bromosuccinimide (0.77 g, 4.3 mmol) and azodiisobutyronitrile (ca.10 mg) in cyclohexane (50 mL) was heated under reflux. After 30 min, a second portion of *N*-bromosuccinimide (0.77 g, 4.33 mmol) was added, and stirring and heating were continued for 30 min. To the vigorously stirred, cold suspension, powdered CaH_2 (0.2 g) was added, and a stream of Ar introduced which helped to remove HBr (ca. 15 min). After filtration through a sintered-glass funnel, the orange-coloured filtrate was diluted with tetrahydrofuran (25 mL). Zinc-copper couple (1.77 g) was added, and the vigorously stirred suspension heated under reflux for 45 min, while the formation of **15** was monitored by reversed-phase HPLC. After cooling to 20−25°C, the mixture was filtered through a pad of silica gel (2 × 3 cm), which was rinsed with tetrahydrofuran (50 mL). The solvent was distilled i. vac. until the final volume was 5 mL. Enough EA was added to dissolve the precipitate. Flash chromatography with PE and crystallisation at −20°C afforded pale yellow crystals (56 mg, 11%, m.p. 98−100°C).

4,8-Bis(4-*tert*-butylphenyl)barbaralane-2,6-dicarbonitrile (19)

4-*tert*-Butylphenyllithium: A 500-mL two-necked flask equipped with a coarse sintered-glass funnel[36] was filled with Ar and charged with 1-bromo-4-*tert*-butylbenzene (51.1 g, 0.24 mol) and benzene (90 mL). A solution of butyllithium in hexane (1.45 M, 145 mL, 0.21 mol) was added during 2 h to the stirred solution. Stirring was continued for 2 d. The colourless precipitate was collected by filtration, washed with pentane (2 × 50 mL), and dried at 10^{-2} Torr to afford a colourless powder (26.5 g, 90%).

***exo*,*exo*-4,8-Bis(4-*tert*-butylphenyl)bicyclo[3.3.1]nonane-2,6-dione (17):** As described for [D_5]-**7**, a cold (−78°C) mixture was prepared from a stirred suspension of copper(I) cyanide (13.8 g, 154 mmol) in tetrahydrofuran (0.5 L), 4-*tert*-butylphenyllithium (43.0 g, 307 mmol), and boron trifluoride−diethyl ether (37 g, 32 mL, 0.26 mol). A solution of **5** (8.42 g, 56.8 mmol) in tetrahydrofuran (60 mL) was added dropwise during 1.5 h at that temperature to the stirred mixture, which was subsequently allowed to attain room temperature overnight. Workup as described for **6** gave a dark brown crude product which was dissolved in a minimum amount of boiling EA. Finely dispersed inorganic material was removed by filtration of the hot suspension. Addition of the same volume of ethanol to the filtrate and crystallisation overnight at −20°C yielded pale yellow crystals (14.3 g, 60%). Recrystallisation from

Table 9. Chemical shifts (δ values) in proton and ^{13}C spectra taken from solutions of the 4,8-diarylbarbaralane-2,6-dicarbonitrile **19** and its precursors in [D]trichloromethane

Cpd.	1-H 5-H	9-H 9-H'	3-H_{exo} 3-H_{endo}	4-H 8-H	*t*Bu (s)	Ph (m)	$^2J_{3x,3n}$	$^3J_{3,4}$	$^3J_{3x,4}$	$^3J_{3n,4}$	$^3J_{1,9}$=$^3J_{5,9}$
17	2.83 m	2.15 br. t	2.81 dd 2.89 dd 3-H 7-H	3.52 br. t	1.31	7.2 – 7.4	16.3		7.1	5.6	2.8
18	2.71 br. t	1.62 br. t	6.73 d	3.73 d	1.32	7.1 – 7.5		4.8			3.1
19	3.61 br. t	1.58 br. t	6.52 m		1.34	7.4 – 7.5					2.7

	C-1 C-5	C-2 C-6	C-3 C-7	C-4 C-8	C-9	CN	*ipso*-C *p*-C	*o*-, *m*-C		C(—CH_3)$_3$
17	50.8	212.4	42.1	41.3	22.8		140.2 149.9	126.77 125.77	34.4	31.9
18	37.7	*117.23*	143.7	44.6	16.9	*118.47*	136.1 150.7	125.9 128.0	34.5	31.3
19[a]	31.41	73.4	126.97	94.6	17.3	118.6	133.7 152.0	126.17 126.87	34.7	31.20
(298.6 K)[c]	17.329	56.482	109.819	77.508	0.000	[b]	117.505 135.139	109.929 108.978	14.806	13.385
(171.6 K)[c]	17.785	55.500	111.629	76.300	0.000	109.717	117.640 135.023	110.210 109.584	14.199	13.947

[a] Solvent [D_2]dichloromethane. − [b] The signal of the cyano groups collapses with that of C-3,7 at this temperature. − [c] Solvent chlorodifluoromethane−[D_6]dimethyl ether (3:1); the chemical shifts are expressed relative to that of C-9 (δ_9 = 16.70 relative TMS at 298.6 K).

EA gave colourless crystals, m.p. 231−233°C. − MS, *m/z* (%): 417 (31), 416 (100) [M$^+$], 401 (41), 359 (31), 228 (27), 193 (59), 57 (76).

***exo*,*exo*-4,8-Bis(4-*tert*-butylphenyl)bicyclo[3.3.1]nona-2,6-diene-2,6-dicarbonitrile (18):** As described for the diphenyl compounds,[4] **17** (2.20, 5.3 mmol) was converted with trimethylsilyl cyanide in the presence of KCN−18-crown-6 (reaction period 16 h at 60°C) into a mixture of diastereomeric *O*-trimethylsilyl cyanohydrins (colourless, noncrystalline solid, 2.24 g, 69%). Treatment of the crude product with hydrogen fluoride−pyridine in $POCl_3$ followed by heating with $POCl_3$ in pyridine, workup, and recrystallisation of the crude product from PE/EA (4:1) at −20°C yielded colourless crystals (0.79 g, 50%, m.p. 263−264°C). − MS, *m/z* (%): 435 (25) [(M + 1)$^+$], 419 (37), 378 (40), 322 (17), 202 (27), 188 (15), 148 (20), 91 (10), 57 (100), 41 (21).

Table 10. Molecular formulae and masses, and elemental analyses

Cpd.		Molecular mass		Elemental analysis C	H	N	S
6	$C_{15}H_{14}O_2$	226.3	Calcd.	79.62	6.24		
			Found	79.90	6.40		
9	$C_{34}H_{32}N_2O_2S$	532.7	Calcd.	76.66	6.05	5.26	
			Found	76.87	6.02	5.12	
exo-**10**,	$C_{27}H_{26}O$	366.5	Calcd.	88.48	7.15		
endo-**10**			Found	88.62	7.33		
11	$C_{27}H_{24}$	348.5	Calcd.	93.06	6.94		
			Found	92.73	7.22		
exo-**12**,	$C_{28}H_{28}O_3S$	444.6	Calcd.	75.64	6.35		7.21
endo-**12**			Found	73.54	6.42		7.18
15	$C_{27}H_{22}$	346.5	Calcd.	93.60	6.40		
			Found	93.47	6.46		
17	$C_{29}H_{36}O_2$	416.6	Calcd.	83.61	8.71		
			Found	83.29	8.81		
18	$C_{31}H_{34}N_2$	434.6	Calcd.	85.67	7.88	6.45	
			Found	85.24	8.15	6.41	
19	$C_{31}H_{32}N_2$	432.6	Calcd.	86.07	7.46	6.48	
			Found	86.34	7.47	6.24	

Table 11. Experimental details and results of the X-ray diffraction analyses

Cpd.		**6**	**17**
Molecular formula		$C_{15}H_{14}O_2$	$C_{29}H_{36}O_2$
Molecular mass		226.27	416.60
Crystal system		orthorhombic	monoclinic
Space group		*Pna*2$_1$	*C*2/*c*
a [pm]		1271.3(1)	3743.5(5)
b [pm]		689.7(1)	664.2(1)
c [pm]		2681.7(3)	2164.7(4)
β [°]			110.489(9)
V [10^{-6}·pm^3]		2351.5(6)	5041(2)
Z		8	8
d(calcd.) [g cm^{-3}]		1.278	1.098
Size of crystal [mm]		0.6 × 0.75 × 0.2	0.2 × 0.25 × 0.35
Range	*h*	−1 → 8	−48 → 0
	k	−16 → 1	0 → 8
	l	−34 → 34	−26 → 28
No. of measured reflections		7605	6389
symmetry-independent refl.		5389	4914
Observed refl. $F > 3\sigma(F)$		3888	2531
Lin. absorpt. coeff. [mm^{-1}]		0.08	0.07
Absorption correction		ψ-scan	ψ-scan
Ratio F_{obs}/parameters		12.71	8.01
R		0.067	0.111
R_w		0.060	0.095
Diff. Four.	$\Delta\rho_{max}$[a] [eÅ^{-3}]	0.44	0.32
	$\Delta\rho_{min}$[b]	0.38	0.30

[a] Maximum and [b] minimum of the remaining electron density in the final differential Fourier synthesis.

4,8-Bis(4-*tert*-butylphenyl)tricyclo[3.3.1.0^{2,8}]nona-3,6-diene-2,6-dicarbonitrile (19): As described for **1b**,[4] brick-red crystals (0.15 g, 19%, dec. above 182°C) were obtained from **18** (0.79 g, 1.8 mmol) after flash chromatography of the crude product with PE/EA (9:1). Concentrated solutions must be degassed and kept under argon to avoid autoxidation.[13] − MS, *m/z* (%): 433 (100) [(M + 1)$^+$], 417 (22), 375 (15), 361 (15), 319 (12), 201 (27), 173 (14), 157 (20), 57 (93), 41 (23).

X-Ray Diffraction Analyses were performed on transparent, colourless crystals of **6** and **17**. The cell parameters were determined on the basis of 70 reflections. The number of reflections reported in Table 10 were obtained with Mo-K_α radiation and 2 Θ_{max} = 55° (graphite monochromator, ω-scan). Measurements were carried out with a system Siemens P4. The programme SHELXTL PLUS[38] was employed. The structure was solved by direct methods and refined anisotropically by the least-squares method. The weighting scheme for R_w is $1/\sigma^2$. The positions of the hydrogen atoms were calculated by the riding model and included with isotropic descriptions.[39]

Acknowledgments

We are indepted to Dr. H. Jiao, University of Erlangen-Nürnberg, for the permission to quote his calculation of the ^{13}C chemical shifts of 4,8-dimethylbarbaralane-2,6-dicarbonitrile (**28**). We thank Dr. G. Lange and Mr. F. Dadrich for recording the mass spectra. Financial support of this work by the Fonds der Chemischen Industrie, Frankfurt am Main, is gratefully acknowledged.

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[39] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-122163 (**6**), -122164 (**17**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. code +44(1223)336−033, E-mail: deposit@ccdc.cam.ac.uk].

Received May 25, 1999
[O99295]