The Degenerate Cope Rearrangement in 2,6-Barbaralanedicarbonitrile

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The ^{1}H and ^{13}C NMR spectra of 4-bromo-2,6-barbaralanedicarbonitrile (**2b**) were completely analysed and the molecule is shown to exist as a single valence tautomer. The ^{13}C chemical shifts of **2b** serve as estimates of the analogous shifts in the non-exchanging valence tautomer of 2,6-barbaralanedicarbonitrile (**2a**) itself. The barrier for the degenerate Cope rearrangement of **2a** in [D$_2$]dichloromethane has been determined from line width measurements in the temperature range 204 – 249 K to be $\Delta G_{206}^{\pm}$ = 24.2 kJ · mol^{-1}. The solid state ^{13}C NMR spectrum of **2a** indicated that the bulk of the sample is not undergoing rapid rearrangement at room temperature.

Die entartete Cope-Umlagerung des 2,6-Barbaralandicarbonitrils

Die ^{1}H- und ^{13}C-NMR-Spektren von 4-Brom-2,6-barbaralandicarbonitril (**2b**) wurden vollständig analysiert. Das Molekül existiert nur in einer einzigen valenztautomeren Form. Die chemischen Verschiebungen im ^{13}C-NMR-Spektrum von **2b** dienen zur Abschätzung der analogen Verschiebungen des nicht-umlagernden Valenztautomeren des 2,6-Barbaralandicarbonitrils (**2a**). Die Barriere der entarteten Cope-Umlagerung von **2a** in [D$_2$]Dichlormethan wurde durch Messungen der Linienbreite im Temperaturbereich 204 – 249 K zu $\Delta G_{206}^{\pm}$ = 24.2 kJ · mol^{-1} bestimmt. Das Festkörper-^{13}C-NMR-Spektrum von **2a** zeigt, daß sich der größte Teil der Probe bei Raumtemperatur nicht rasch umlagert.

Much has been written about the possibility of homoaromaticity in neutral molecules[1] and *Dewar*[2] and *Hoffmann*[3] added significantly to the subject when they reported their theoretical investigations of the effects of substituents on the Cope rearrangement in molecules of type **1**, for which the transition state is a 6π-electron homoaromatic system. One prediction of their theory is that electron withdrawing substituents at the 2, 4, 6, and 8 positions should stabilize the transition state and weaken the 2,8-bond. They further suggested that the combined effect of substituents might so modify the system that the homoaromatic arrangement would in fact become the ground state of the molecule.

Although some fragmentary evidence is available which suggests the qualitative correctness of the predicted substituent effect[4,5], no truly definitive example permitting quantitative evaluation of the effect has been reported. The ideal substituent for this

purpose is the cyano group since, as well as being strongly electron withdrawing, it possesses the further merit that it introduces neither conformational ambiguities nor severe steric crowding which might otherwise mask its intrinsic electronic contribution. We have chosen to study the effect of the cyano substituent in the barbaralane system [**1** (n = 1)][6] since, unlike the semibullvalene system [**1** (n = 0)][7], the barrier could be anticipated to be sufficiently high to allow determination by ^{13}C NMR spectroscopy. The compound chosen for study was 2,6-barbaralanedicarbonitrile (**2a**), the synthesis of which we have already reported[8].
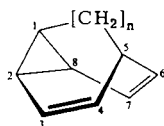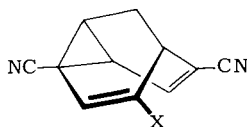
1: n = 0,1,2   **2a**: X = H   **2b**: X = Br

The ^{13}C spectrum at 100 MHz of 2,6-barbaralanedicarbonitrile (**2a**) was examined as a function of temperature. Below −20 °C there is clear evidence of line broadening due to the degenerate Cope rearrangement and at 100 MHz and −140 °C, the lowest temperature achievable with the spectrometers available to us, the only observable, discrete signal is that of C-9 which is unaffected by the exchange process. Thus, in order to extract the rates of exchange from line broadening in the "fast exchange" region it was necessary to obtain estimates of the chemical shifts for the non-exchanging valence tautomer. A preliminary study of the ^{13}C spectrum of 4-bromo-2,6-barbaralanedicarbonitrile suggested that this molecule might exist as only the non-degenerate valence tautomer **2b** and, if so, it would serve as a model for the chemical shifts in 2,6-barbaralanedicarbonitrile (**2a**) itself. Accordingly, a detailed study of the NMR spectra of the bromo compound **2b** was undertaken.

In order to assign the ^{13}C spectrum of 4-bromo-2,6-barbaralanedicarbonitrile it was necessary to analyse its proton spectrum. Although most of the protons are weakly coupled, 1-H and 8-H remain tightly coupled even at 360 MHz and a total analysis was therefore performed. A comparison of the calculated and observed spectra is presented in Fig. 1 and the chemical shifts and absolute values of the coupling constants are listed in Table 1. With the proton assignments available, the ^{13}C absorptions of the protonated carbons were readily assigned by single frequency, medium power decoupling experiments. Assignments of the fully substituted carbon atoms were less obvious and required analysis of the fully coupled spectrum. This was achieved by selective, low power decoupling of each proton (except 1-H and 8-H) in turn and by simulation of the multiplets in the fully coupled spectrum. The final set of chemical shifts and coupling constants are assembled in Table 2. The assignments of the absorptions of C-4 and C-6, which are of particular importance for the problem in hand, are based on long range couplings with the methylene protons. The nucleus C-2 is coupled (J = 7.8 Hz) to one of these protons (δ = 1.445) but not to the other (δ = 1.653). The former is therefore *trans* to C-2, the sizeable coupling being a result of a nearly perfect antiperiplanar relation between the interacting nuclei. This proton also shows a large coupling (J =
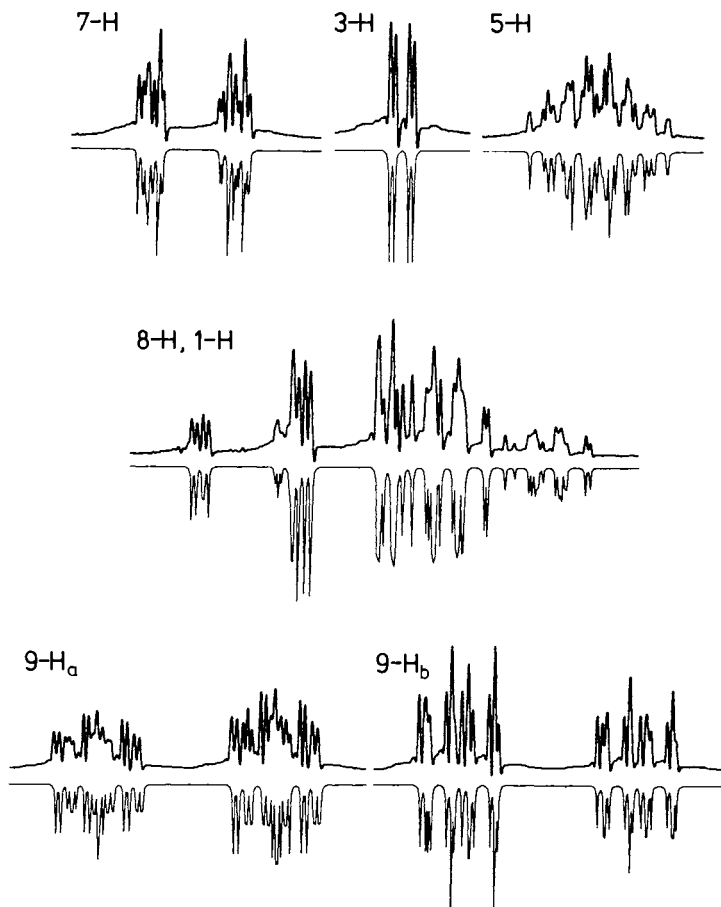
Fig. 1. Experimental and theoretical (inverted) proton spectrum of 4-bromo-2,6-barbaralanedi-carbonitrile (2b) in [D₂]dichloromethane at 19 °C and 360 MHz. The fit of the theoretical spectrum is a function of the digital resolution of the plotting routine and therefore depends on the frequency of the first point in each plot. In greatly expanded spectra (unsuitable for reproduction) the apparent fit is much better. The plotted regions are for protons absorbing at δ = 6.66 (7-H); 6.14 (3-H); 3.25 (5-H); 3.00 (8-H) and 2.96 (1-H); 1.65 (9-H$_a$); 1.44 (9-H$_b$)

11.2 Hz) with the carbon at δ = 116.3 and a smaller one (J = 3.9 Hz) with that at δ = 112.3. The former is therefore assigned to C-4. In agreement with this assignment, the proton at δ = 1.653 which is *cis* to C-2, is coupled with J = 2.0 and 10.0 Hz to C-4 (δ = 116.3) and C-6 (δ = 112.3), respectively.

A study of the carbon-13 chemical shift over a wide temperature range (183 – 293 K) showed that the bromo compound 2b exists as a single valence tautomer. Inspection of the data in Table 3 reveals that the chemical shifts relative to that of C-9, which should be virtually the same in the two valence tautomers, have only a minor dependence on temperature. In particular, there is no change in the difference between the chemical shifts of C-2 and C-6. That the shifts of C-2 and C-6 for the bromo compound 2b are

Table 1. Proton chemical shifts (ppm, principal diagonal elements) and absolute values[a] of coupling constants (Hz, other elements) of 4-bromo-2,6-barbaralanedicarbonitrile (2b) in [D$_2$]dichloromethane at 292 K

	1-H	3-H	5-H	7-H	8-H	9-H$_a$[b]	9-H$_b$
1-H	2.962	0.00	1.96	0.00	7.80	2.36	2.17
3-H		6.142	1.44	0.06	0.00	0.39	0.00
5-H			3.250	1.12	0.05	2.93	3.27
7-H				6.664	7.00	0.04	0.40
8-H					2.999	0.88	0.56
9-H$_a$[b]						1.653	13.59
9-H$_b$							1.445

[a] Inclusion of the expected relative signs for the large coupling constants had a negligible effect on the calculated spectrum. – [b] Proton on the same side as bromine.

Table 2. Carbon chemical shifts (ppm) and carbon hydrogen coupling constants (Hz) of 4-bromo-2,6-barbaralanedicarbonitrile (2b) in [D$_2$]dichloromethane at 292 K

	δ [ppm]	1-H	3-H	5-H	7-H	8-H	9-H$_a$[a]	9-H$_b$
C-1	25.8	174.9	3.2	9.0	3.2		3.2	3.2
C-2	23.7	2.4				2.4	~0	7.8
C-3	120.6	1.3	174.1	3.8		1.3		
C-4	116.3		5.9	9.1	2.0		2.0	11.2
C-5	41.5	3.7	6.4	145.9	7.6		3.7	3.7
C-6	112.3			7.2[b]		3.9[b]	10.0	2.5[b]
C-7	136.5	2.2		4.5	170.2			
C-8	31.3	2.4			3.4	174.2	7.4	
C-9	18.3	3.5		3.5		3.5	136.2	136.2
2-CN	120.1		4.7		4.7	4.7		
6-CN	117.4			4.3	7.2			

[a] Proton on the same side as bromine. – [b] These couplings have not been unambigously assigned.

Table 3. Effect of temperature on the ^{13}C chemical shifts in 4-bromo-2,6-barbaralanedicarbonitrile (2b) in [D$_2$]dichloromethane. The shifts are expressed relative to that of C-9

	Shift (ppm)		
	293 K	183 K	Difference
C-1	7.5	7.7	– 0.2
C-2	5.4	5.4	0.0
C-3	102.3	102.5	– 0.2
C-4	98.0	97.9	0.1
C-5	23.1	22.5	0.6
C-6	93.9	93.9	0.0
C-7	118.4	119.6	– 1.2
C-8	13.1	13.0	0.1
C-9	(0.0)	(0.0)	(0.0)
2-CN	101.8	102.3	– 0.5
6-CN	99.2	99.9	– 0.7

indeed appropriate for the analogous nuclei in 2,6-barbaralanedicarbonitrile (2a) itself is confirmed by agreement between the observed shift ($\delta = 66.9$) for C-2/C-6 in this compound and the average ($\delta = 68.0$) of the two shifts in the model 2b.

Table 4. Line widths (Hz) at half height of the ^{13}C signals of C-2/C-6, C-4/C-8, and 2-CN/6-CN of 2,6-barbaralanedicarbonitrile (2a) and solvent (CD_2Cl_2) as a function of temperature

Temp. [K]	C-2/C-6	C-4/C-8	2-CN/6-CN	CD_2Cl_2
249	3.50	7.13	1.75	2.73
239	4.75	7.92	1.75	2.82
229	9.05	13.17	1.55	2.57
219	16.71	20.30	1.31	2.59
209	29.37	33.43	1.62	2.67

The C-2 and C-6 signals in the broad band decoupled spectrum provide the best information about the rate of the Cope rearrangement of 2a. This is because of their large chemical shift difference (≈ 8000 Hz at 8.46 T) and because, having no attached protons, their effective line widths in the absence of exchange are not very dependent on the efficiency of broad band decoupling. The line widths at half height (Table 4) were determined by least squares fitting the observed signal to a Lorentzian line shape. The solvent ([D_2]dichloromethane) lines and the signal of the nitrile carbons remained constant (2.67 ± 0.21 and 1.60 ± 0.16 Hz, respectively) over the temperature range 209 – 249 K. The rate constant for exchange is given by the equation[9]

$$k = \pi(\Delta\nu)^2/2(W_{exchn} - W_0)$$

Calculations of enthalpies and entropies of activation from rates determined by this equation can lead to serious errors[10] and we therefore restrict our discussion of the barrier for the Cope rearrangement in 2a to a consideration of $\Delta G^{\pm}_{206}$ which can be obtained from the data in Table 4 by a short extrapolation using the equation

$$W_{exchn} = a + b\, e^{c/T}$$

with values of a, b and c determined by the method of non-linear least squares. The data for C-2/C-6 ($\Delta\nu = 8025$ Hz) gives $\Delta G^{\pm}_{206} = 24.2 \pm 3.2$ kJ · mol^{-1} ($a = -1.2$; $b = 1.3 \times 10^{-4}$; $c = 2580$) while those for C-4/C-8 ($\Delta\nu = 7650$ Hz) give an almost identical value but with a lower precision ($\Delta G^{\pm}_{206} = 24.2 \pm 4.2$ kJ · mol^{-1}; $a = 2.2$; $b = 1.5 \times 10^{-4}$; $c = 2600$).
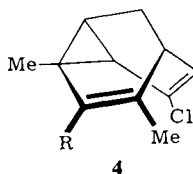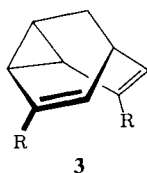

Table 5 lists rates and free enthalpies of activation of the Cope rearrangement for barbaralane [3a = 1 (n = 1)] and some simple substituted derivatives. It is seen that

substituents can change the rate of rearrangement by at least four orders of magnitude. Most strikingly, the introduction of the cyano groups at the two opposite corners [C-2 and C-6] lowers the barrier in barbaralane by approximately 8 kJ · mol^{-1}. In fact the 2,6-barbaralanedicarbonitrile (2a) rearranges at a rate similar to semibullvalene [1 (n = 0)][7]. A similar lowering of the barrier by cyano groups is found for 2,6-disubstitution in 1,5-dimethylsemibullvalene although in this system it has not yet been possible to evaluate the contribution accurately[5]. Nevertheless, the predictions regarding the effect of substitution[2,3] at the corners appear to be general for the systems 1. We note that even if the effect of cyano substitution is additive 2,4,6,8-semibullvalenetetra-carbonitrile would still not have a homoaromatic ground state. It thus appears that the combination of electron acceptors at C-2, C-4, C-6 and C-8 *and* donors at C-1 and C-5, as suggested by *Hoffmann*[3], offers the best approach for realizing neutral ground state homoaromaticity.

Table 5. Rate constants [s^{-1}] and the free enthalpies of activation $\Delta G^{\pm}$ [kJ · mol^{-1}] for the degenerate Cope rearrangement of some barbaralanes

Cpd.	R	Temp. [K]	$10^{-2} \cdot k$ [s^{-1}]	$\Delta G^{\pm}$ [kJ · mol^{-1}]	Temperature Range [K]	Ref.
3a	H	206	296[a]	32.2	184 – 204	[6]
		206	423	31.6[b]	148 – 263	[11]
3b	Me	206	18	36.8	[c]	[12]
		206	3.7	39.8[b]	148 – 263	[11]
3c	Ph	206	70	34.7	[c]	[12]
2a		206	31000	24.2 ± 3.2	209 – 249	this work
4a	H	175	1.2	35.1	[c]	[13]
4b	OMe	178	1.0	36.0	[c]	[13]
4c	OSiMe$_3$	192	0.8	39.3	[c]	[13]

[a] Extrapolated from the reported T_2^{exchn} *vs.* T data[6] using the method described (in the text). –
[b] Calculated from the Eyring and Arrhenius parameters kindly supplied by Professor *Günther*. –
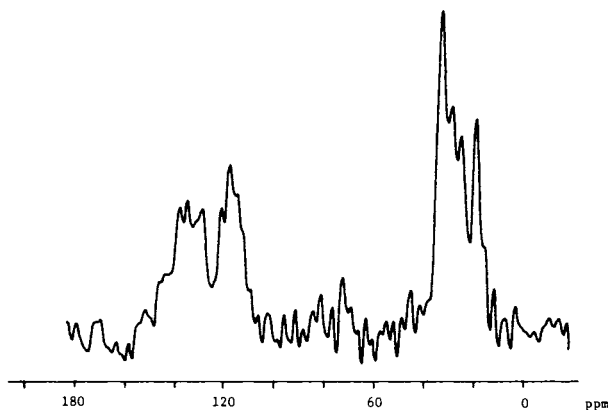[c] Single measurement at the stated temperature.

Figure 2. 15 MHz ^{13}C spectrum of solid 2,6-barbaralanedicarbonitrile (2a) at 298 K. Spinning rate 1.5 kHz, contact time 2.00 ms, pulse delay 5 s

We have also examined the ^{13}C spectrum of solid 2,6-barbaralanedicarbonitrile (2a) (Fig. 2). At room temperature the Cope rearrangement is slow on the NMR time scale although there is perhaps some evidence of the presence of a minor component which is exchanging rapidly and giving the weak absorption near 70 ppm. This behavior in the solid is similar to that observed by *Miller* and *Yannoni*[14,15] for solid semibullvalene [1(n = 0)] in which the Cope rearrangement is at least a thousand times slower than in solution.

Experimental Part

The NMR spectra were obtained using Bruker WM 400, WM 360 and WP 200 NMR spectrometers. The solid state spectrum was obtained with a JEOL FX 60 Q spectrometer using a CP-MAS probe.

The proton spectrum of 4-bromo-2,6-barbaralanedicarbonitrile (4-bromotricyclo[3.3.1.0^{2,8}]-nona-3,6-diene-2,6-dicarbonitrile, 2b) was obtained using a solution in [D$_2$]dichloromethane (20 mg/ml). The FID was obtained with 32 K data points, gaussian multiplied (line broadening −1.0 Hz), and zero filled to 128 K before Fourier transformation. A spectrum with selective irradiation of 1-H was also obtained. The analyses of both the six and seven spin systems were carried out using the program LAME[16]. For the latter, 422 transitions were assigned and fitted with an RMS error of 0.059 Hz.

The variable temperature ^{13}C spectra were carried out using solutions in [D$_2$]dichloromethane. The temperatures were measured by switching to ^{31}P observation and determining the separation of the two lines of a standard solution of triphenylphosphane and triphenylphosphane oxide using the same ^{1}H decoupling power. The Lorentzian line shape least squares fitting routine, which is part of the Bruker software package, was used to determine line widths.

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