SHORT PAPER

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^{1}H NMR study on the conformation of 5-dicyanomethylene-10,11-dihydro-5*H*-dibenzo[a,d]cycloheptene[†]

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It has been found that the central ring of 5-dicyanomethylene-10,11-dihydro-5*H*-dibenzo[a,d]cycloheptene, **1**, undergoes bond inversion which is slow on the NMR time scale at ambient temperature. The character of this conformational process has been established and its activation energy estimated.

Keywords: 5-dicynaomethylene-10,11dihydro-5*H*-dibenzo[a,d]cycloheptene

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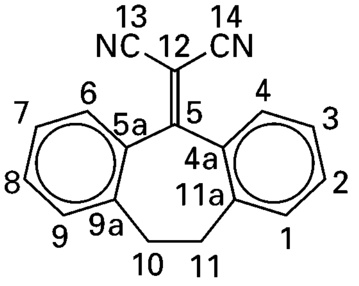
It has been observed that 5-dicyanomethylene-10,11-dihydro-5*H*-dibenzo[a,d]-cycloheptene, **1**, undergoes a conformational process which is slow on the NMR time scale. At room temperature the proton signal of CH_2 groups has a form of two broad, strongly overlapped singlets. We have found it interesting to explain which of the possible conformational processes is responsible for the dynamic character of the mentioned signal. For this purpose ^{1}H NMR spectra have been measured in the range –60 to 60°C. At the highest temperature used the signal is a slightly broadened singlet whereas at the lowest one it has a form of a symmetrical multiplet characteristic of an AA′BB′ spin system. As the basis of our conformational consideration we have assumed the structures of minimal energy predicted by the semi-empirical AM1 method implemented in the HyperChem 4 program. Two such structures have been found.

One of them, **1a**, possesses a C2 symmetry axis passing along the C=C double bond and through the centre of the single C–C bond. The other one, **1b**, has the central ring of the molecule in a boat-like form and its carbon atoms form three planes crossing at the C5 carbon atom. The planes are defined: the first by one aromatic ring and carbons C5 and C10, the second by the dicyanomethylene group and the third by the other aromatic ring and carbon atoms C5, C10 and C11 (C10-C11 bond is tilted only by *ca* 7° from the aromatic ring plane). Because the latter structure is 54 kJ/mol more stable we have assumed it to be this one we actually deal with. Although three processes which may affect the proton NMR spectrum are conceivable (see Scheme 1) the concerted inversion of the bonds in both the dicyanomethylene and the CH_2CH_2, fragments of the ring (equilibrium III) seems to be improbable. For this reason the process III has been excluded from further discussion. To obtain identical chemical shifts for all four CH_2 protons, as it is observed at high temperature, both the processes, I and II, have to be fast on the NMR time scale. On the other hand only one of them is to be stopped at low temperature to give the AA′BB′ but not the ABCD signal pattern. Having all the needed geometrical parameters for the assumed conformation **1b** we calculated the values of all the vicinal coupling constants between the four nonequivalent protons using the extended Karplus equation.[1] Then the expected mean values of these parameters have been calculated assuming process I to be fast and II slow and vice versa. The results are collected in Table 1 together with the experimental coupling constants obtained from the numerical analysis of the spectrum measured at –40 ^{0}C with the use of a Laokoon-type, iterative program (experimental and calculated spectra are shown in Fig. 1). The inspection of these data suggests that at low temperatures the process II is slowed down rather than the process I. The dynamic spectra could be then simulated. The rate of the conformational transformation has



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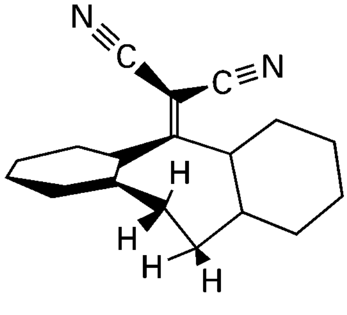
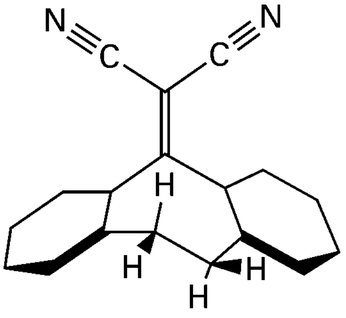


1a



1b

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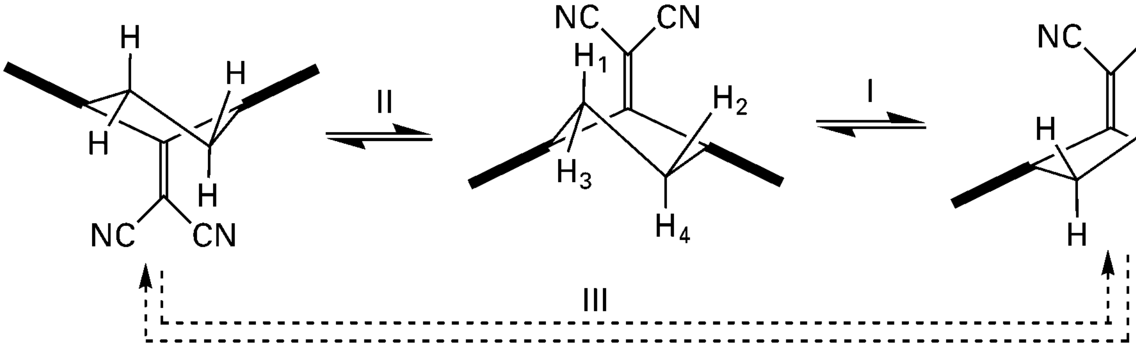

Scheme 1

been changed to obtain the best fit between the theoretical and experimental spectra. Depending on the appearance of the signal observed different criteria for the fitting accuracy have been assumed. These were the half-height width for singlet-like spectra, peak-to-valley intensities ratios when two overlapped, singlet-like signals were observed and visual comparison for the cases in which a discrete structure could be visible. In this way 16 points describing a rate–temperature relationship have been obtained. This relationship has been applied to the determination of the activation energy from the Arrhenius equation: $\lg(k) = A - E_a/(2.303RT)$ ($A = 10.21 \pm 0.06$, $E_a = -46.0 \pm 0.3$ kJ/mol, correlation coefficient $r = 0.9997$; error values quoted refer to statistical errors only). Using the Eyring equation the $\Delta G^{\neq}$ value has been calculated for each temperature. It changes monotonically from 62.6 kJ/mol at 331 K to 58.5 kJ/mol at 261 K.

Table 1 Coupling constants between protons of CH_2CH_2 group in **1**

	Vicinal coupling constants /Hz			
Proton numbers	Experimental values[a]	Calculated values		
		I slow, II slow[b]	I fast; II slow	I slow; II fast
1,2	3.1	3.1	3.1	3.2
1,4	9.2	12.7	8.5	12.7
2,3	9.2	4.4	8.5	4.4
3,4	3.1	3.3	3.3	3.2
1,3 and 2,4	–16.8			

[a]From analysis of the spectrum measured at –40 °C.
[b]From Karplus equation for conformation **1b** predicted by the AM1 method.

Experimental

The IR spectrum of **1** in KBr was measured using a Specord M80 spectrometer. The ESI mass spectrum was obtained on a Mariner (ESI-ToF) PerSeptive Biosystems instrument.

All NMR spectra of **1** solution in $CDCl_3$ were recorded using a Varian Gemini 2000 spectrometer operating at 4.7 T. The temperature of measurements was established with the use of methanol or ethylene glycol sample. It has been found that the chemical shifts of CH_2CH_2 protons do not change over the all range of temperature used. The same was assumed regarding proton-proton couplings. The iterative analysis of the static spectra and the simulation of the dynamic spectra were done using homemade programs for a personal computer based on the non-linear least squares optimization and the standard lineshape theory of coupled spin systems undergoing an intramolecular exchange.[2–4] The semi-empirical AM1 geometry optimizations were performed using the HyperChem 4 program.[5]

Synthesis of 5-dicyjanomethylene-10,11-dihydro-5H-dibenzo-[a,d]cycloheptene, **1**: The investigated compound was prepared by reaction of dibenzosuberone (Aldrich) with malononitrile in the presence of titanium tetrachloride as catalyst in 15% yield following the literature procedure.[6] Column chromatography (SiO_2, hexane/ethyl ether = 9/1, v/v) of the reaction mixture gave desired product slightly contaminated with dibenzosuberone (see signal at 3.22 ppm in Fig.1). A sample of **1** was purified by crystallisation from benzene; m.p. 210–211°C; ESI MS *m/z* calcd for $C_{18}H_{12}N_2Na$ ($M + Na^+$): 279.0893, found: 279.0872;

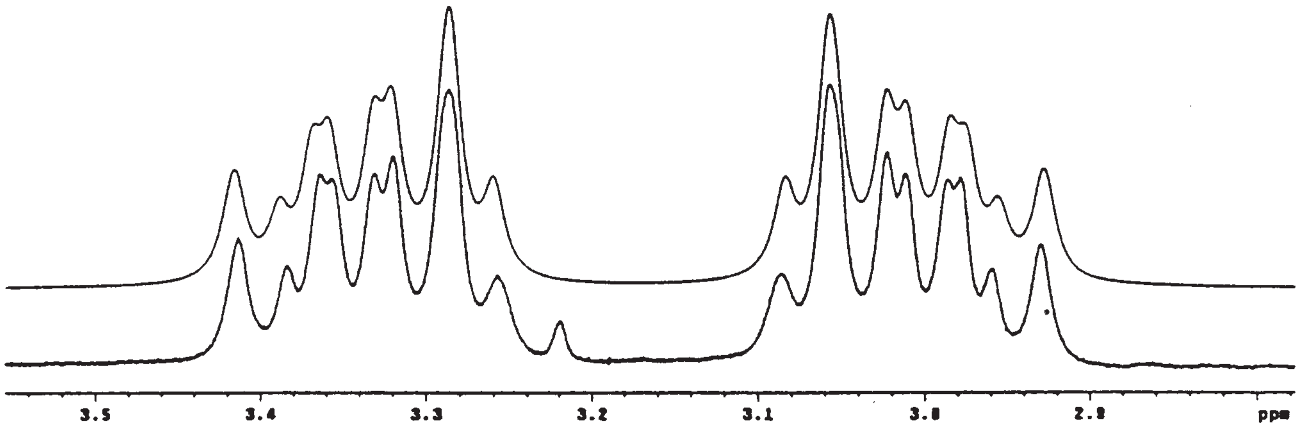

Fig. 1 Aliphatic part of experimental (lower plot) and calculated spectra of **1** at –40°C. Signal at 3.22 ppm originates from an impurity.

IR(KBr, ν/cm^{-1}): 3064, 2940, 2880, 2824, 2228, 1584, 1552, 1480, 1448, 1328, 1172, 776, 756.

^{1}H NMR ($CDCl_3$, 200 MHz, 60°C) 7.50–7.24 (m, 8H, H_{Ar}), 3.17 (bs, 4H, $2 \times CH_2$).

^{1}H NMR ($CDCl_3$, 200 MHz, –40°C) 7.48–7.26 (m, 8H, H_{Ar}), 3.34 (m, 2H, H1 and H2, $J_{H1,H2}$ = 3.1 Hz, $J_{H1,H3}$ = $J_{H2,H4}$ = -16.3 Hz, $J_{H1,H4}$ = $J_{H2,H3}$ = 9.3 Hz), 3.01 (m, 2H, H3 and H4, $J_{H3,H4}$ = 3.1 Hz, for proton enumeration see Scheme 1).

^{13}C NMR ($CDCl_{3,}$ 50.2 MHz) 178.94 (C12), 138.07 (C4a, C5a), 135.09 (C9a, C11a), 131.55 (C2, C8), 130.12 (C3, C7), 127.25 (C1, C9), 126.68 (C4, C6), 112.82 (CN), 85.85 (C12).

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