Tetrahedron Letters No.1, pp. 67-72, 1970. Pergamon Press. Printed in Great Britain.

CONFIGURATION AND CONFORMATIONAL MOBILITY OF [12]ANNULENE FROM NMR STUDIES AT VARIOUS TEMPERATURES[1]

by

Jean F.M. Oth, J.-M. Gilles
Union Carbide European Research Associates, Bruxelles 18
and
G. Schröder
Institut fur Organische Chemie der Universität Karlsruhe.

(Received in UK 27 November 1969; accepted for publication 4 December 1969)

As shown in the preceding note[2], a 75% pure [12]annulene can be synthesized by UV irradiation of syn-tricyclo[8.2.0.0$^{2.9}$]dodeca-3.5.7.11-tetraene at -110°C. We have investigated the temperature dependent NMR spectrum of this compound in order

i) to establish its configuration in terms of the number and the sequence of cis and trans double bonds, and
ii) to study the reversible dynamic process occurring in this molecule.

The most suitable sample for very low temperature NMR studies was obtained by irradiating at -120°C for five days in a sealed quartz NMR tube a solution containing 30 mg of syn-tricyclo[8.2.0.0$^{2.9}$]dodeca-3.5.7.11-tetraene in 0.5 ml of a mixture of THF-d_8 and CD_3-O-CD_3 (1:1 by volume). The 60 MHz NMR spectrum was recorded at five degree intervals from -170°C to -80°C [3]. Some of the spectra are shown in figure 1.

The spectrum at the lowest temperature (-170°C) consists of two broad bands centred at δ = -0.56 ppm and δ = 1.39 ppm (internal reference C_6H_6 [4]) with intensities approximately in the ratio 3 to 9. With increasing temperature the low-field band coalesces with a component of the high-field signal ($T_{coalesc.}$ = -165.7°C). A new broad band then develops at δ = +0.4 ppm. This band sharpens progressively with increasing temperature while the remaining high-field signal sharpens much faster without any appreciable frequency shift. The resolved spectrum corresponding to the condition of fast exchange is observed already at -110°C ; it consists of two signals of the same intensity : one, a quartet, is centred at δ = 0.43 ppm (i.e. the mean of the δ values observed at -170°C), the second signal is also a quartet, but with greater separation of the central lines and appears at δ = 1.34 ppm.

The low field-signal in the -170°C spectrum must be assigned to the internal protons of a cyclic molecule which sustains a paramagnetic ring current[5], i.e. to a [12]annulene with three internal and nine external protons. Since it is not possible to close a dodecahexaene chain containing two adjacent trans double bonds and since three internal protons

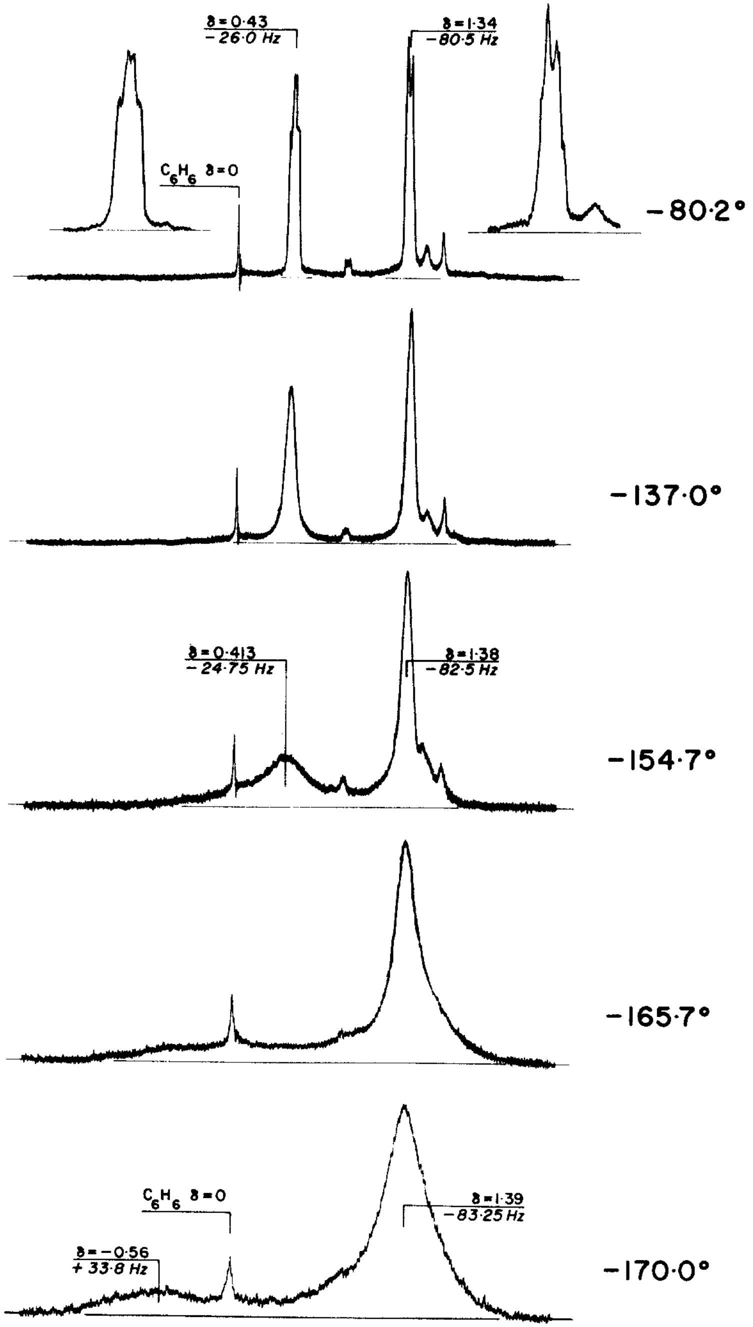
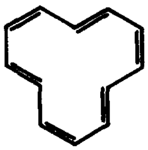


Figure 1 : NMR spectra (at 60 MHz) of [12]-21-annulene at different temperatures.

require the presence of three trans double bonds, the only possible configuration is that in which cis (C) and trans (T) double bonds alternate, i.e. CTCTCT or 21 in our binary representation[6]:



CTCTCT
010101 → 21
[12]-21-ANNULENE

This configuration is also supported by the analysis of the temperature dependence of the NMR spectrum. [12]-21-annulene may undergo an isodynamical[7] conformation change[8]; this reversible process K occurs by simultaneous rotation around all single bonds and permutes magnetic sites 1 and 2 as well as 3 and 4 as can be seen on the exchange diagram shown in figure 2.

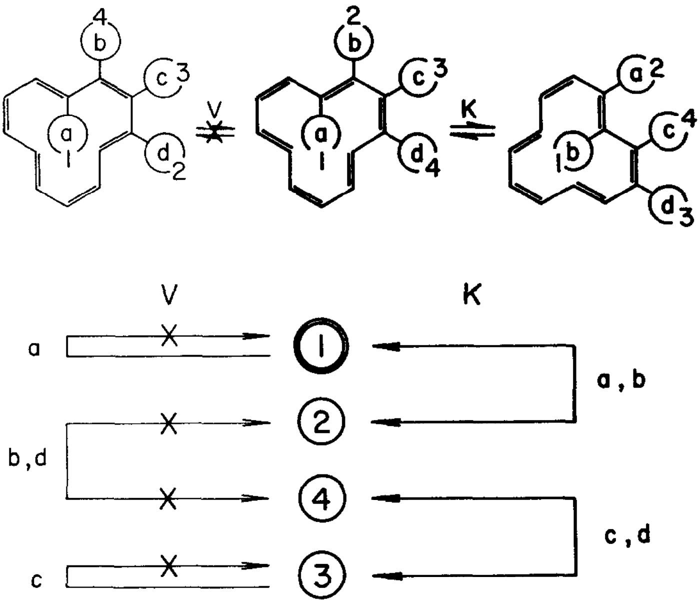


Figure 2 : Exchange diagram for the [12]-21-annulene ; the letters identify the protons, the numbers the magnetic sites. K is the rate for a conformation change, V the rate for a bond shift (valence bond isomerism).

Consequently, under the conditions of fast exchange, all the protons on trans double bonds become isochronous as do all the protons on cis double bonds so that only two chemical shifts (with 6 protons on each) are observed. The high temperature spectrum is thus immediately understood on the basis of this exchange mechanism. In fact, the structure of each resonance signal as observed at -80° C may be regarded, to a first approximation, as the A part of an AA'BB' system.

We were unable to observe the spectrum of [12]-21-annulene in the complete absence of exchange ; this spectrum is expected to consist of a quartet at low field of relative intensity 3 centred at $\delta_1 = -0.75$ ppm (transitions of protons on site 1) and three quartets, each of relative intensity 3, centred at $\delta_2 = +1.62$, $\delta_{3(4)} = 1.09$ and $\delta_{4(3)} = 1.66$ ppm and corresponding to the transitions of protons on sites 2, 3 (or 4) and 4 (or 3), respectively[9].

Using the method of Anderson-Kubo-Sack[10] we have computed the NMR line shape and fitted the calculated to the experimental spectra recorded between -170°C and -137°C. These calculations were based on a simplified spectrum (under condition of no exchange) consisting of a quartet, a doublet and two singlets for the transitions of protons on magnetic sites 1, 2, 3 and 4, respectively. The conformational mobility exchanges the lines of the quartet (site 1) with those of the doublet (site 2) on the one hand and the two singlets together (sites 3 and 4) on the other hand. By an iterative fitting procedure (for an example, cf. fig.3), we have determined the chemical shifts in the absence of exchange (as given above) and the rates of conformation change (fitting of 13 spectra between -170°C and -136.7°C). In view of the approximations introduced in such an analysis and of the presence of impurities affecting the experimental line shape (cf. fig.3), a high accuracy cannot be expected ; nevertheless, a good Arrhenius plot could be obtained from which the following kinetic parameters were deduced (with standard deviations indicated[11]) :

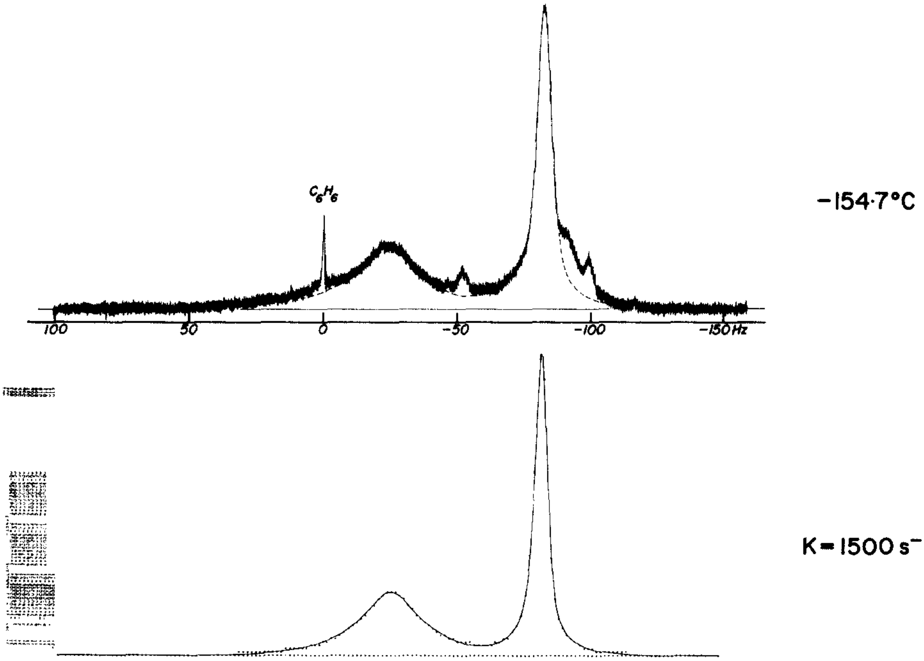
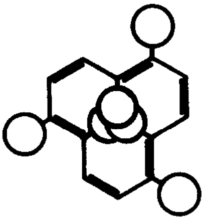


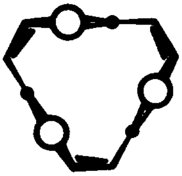
Figure 3 : NMR spectrum observed at -154.7°C and the corresponding calculated spectrum (K = 1500 s^{-1}).

$\log_{10} A$	E_a kcal mole^{-1}	K (-100°) s^{-1}	$\Delta G^{\ddagger}$ (-100°) kcal mole^{-1}	$\Delta H^{\ddagger}$ (-100°) kcal mole^{-1}	$\Delta S^{\ddagger}$ (-100°) cal mole^{-1}deg^{-1}
10.7 (±0.4)	4.1 (±0.2)	$4 (\pm 1) \times 10^5$	5.5 (±0.1)	3.7 (±0.2)	- 10 (± 2)

The very low activation enthalpy results certainly from the severe overcrowding of the internal hydrogens :



The molecule in the most stable conformation cannot be planar ; in fact, model considerations indicate that, in order to accommodate the three inner protons with minimum non bonding interactions and minimum angle strain, the mean absolute torsion angle around the single bonds $\langle |\theta| \rangle$ would have to be as high as 50-60° so that the energy necessary to reach the transition state is reduced. The observed isodynamical conformation change implies that the trans double bonds are not perpendicular to the mean plane of the ring ($\mathcal{D}_3$ symmetry - absolute torsion angles close to 90°) as was suggested by Staab et al.[12] in the case of the tribenzo[12]annulene :



$\mathcal{D}_3$

In fact, this geometry is that of one of the possible transition states.

The negative entropy of activation seems to indicate that the transition state(s) is (are) more rigid than the ground state(s) ; one should not overlook, however, the possible contribution which may result from a difference in multiplicity between ground and transition states.

The strong deviation from planarity explains also the relatively small paramagnetic shift of the signal of the inner protons (δ_1 = -0.75, i.e. τ_1 = 1.93) ; in [16]-85-annulene, in which four single bonds are already twisted by 40° [13] (the mean absolute torsion angle $\langle |\theta| \rangle$ around the eight single bonds is thus 20°), the inner protons appear at τ = -0.56.

In principle [12]-21-annulene may undergo an isodynamical valence bond isomerization V. Would this process be present simultaneously with the conformation change, one would observe a complete magnetic equivalence of all the protons at high temperature as is the case in [16]annulene$^{5,14)}$ (cf. the exchange diagram on figure 2). In fact, we have not detected any broadening of the high temperature signals up to -40°, where a permanent rearrangement takes place$^{2)}$. This would mean that the overcrowding of the inner hydrogens which prevents the formation of a planar transition state also impedes the valence bond isomerization.

We gratefully acknowledge the technical assistance of Mr. J. Braibant.
G.S. thanks Badische Anilin- & Soda Fabrik, Deutsche Forschungsgemeinschaft and Fond der chemischen Industrie.

References

1) Contribution X on annulenes. Part IX : see ref. 2).

2) J.F.M. Oth, H. Röttele and G. Schröder, Tetrahedron Letters, preceding publication.

3) The NMR spectra were recorded on a Varian spectrometer model DP-60 equipped with external lock. The temperature control system was modified to allow temperature reading during the recording ; the sample temperature is generally known to ± 0.2°C.

4) Benzene is formed in small amounts during the irradiation of the starting compound. Note that the line width of the benzene signal is ~ 4 Hz at -170°C.

5) J.A. Pople and K.G. Untch, J. Amer. Chem. Soc., 88, 4811 (1966).
H.C. Longuet-Higgins, Special Publication no. 21, The Chemical Society, London, 109 (1967)
F. Baer, H. Kuhn and W. Regel, Z. Naturforschung 22a, 103 (1967).

6) J.F.M. Oth and J.-M. Gilles, Tetrahedron Letters, 60, 6259 (1968).

7) By an isodynamical conformation change, the molecule passes from one conformation to an identical one ; the nuclei are redistributed among the various chemical (magnetic) sites. Cf. S.L. Altmann, Proc. Roy. Soc., A 298, 184 (1967).

8) Cf. also the conformational mobility of 1.5-bisdehydro- and of 5-bromo-1.9-bisdehydro-[12]annulene :
R. Wolowsky and F. Sondheimer, J. Amer. Chem. Soc., 87, 5720 (1965).
K.G. Untch and D.C. Wysocki, J. Amer. Chem. Soc., 89, 6386 (1967).

9) The magnetic sites are numbered as indicated on figure 2.

10) P.W. Anderson, J. Phys. Soc. Japan, 9, 316 (1954)
R. Kubo and K. Tomita, J. Phys. Soc. Japan, 9, 888 (1954)
R.A. Sack, Mol. Phys., 1, 163 (1958).

11) Systematic errors could be as high as two times the standard errors.

12) H.A. Staab, F. Graf and B. Junge, Tetrahedron Letters, 7, 743 (1966).

13) I.C. Paul, S.M. Johnson and G.S.D. King, submitted for publication in J.Amer.Chem.Soc.

14) G. Schröder and J.F.M. Oth, Tetrahedron Letters, 34, 4083 (1966).