CHEMISTRY LETTERS, pp. 1515-1518, 1977. Published by the Chemical Society of Japan

^{13}C NMR SPECTRUM AND SPIN-LATTICE RELAXATION TIMES (T_1) OF A [14]ANNULENO[14]ANNULENE DERIVATIVE AND THE SIGNAL ASSIGNMENTS BY THE T_1 METHOD

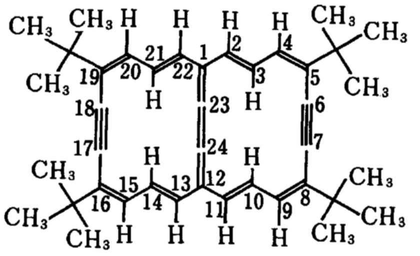
Hiroshi NAKANISHI,* Shuzo AKIYAMA,** and Masazumi NAKAGAWA**

**National Chemical Laboratory for Industry, 1-1-5, Honmachi, Shibuya-ku, Tokyo 151*

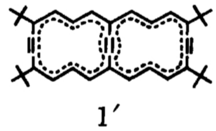
***Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka 560*

^{13}C NMR spectrum of a [14]annuleno[14]annulene derivative (1) and the spin-lattice relaxation times (T_1) were studied. The assignments of the signals of four quaternary ring carbons were successfully made by comparing the observed T_1's with the calculated ones. The chemical shifts of 1 were compared with those of corresponding [14] and [22]annulene derivatives.

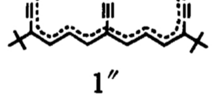
5,8,16,19-Tetra-t-butyl-6,17,23-trisdehydro[10.10.2][14]-annuleno[14]annulene (1), which was recently synthesized,$^{1)}$ is a new type of condensed nonbenzenoid aromatic compounds and has two 14-π-electron systems. It is very important to clarify the electronic structure of 1, because this is a new type of annulenes. There are two modes of π-electron delocalization in 1: (a) delocalization within two separate 14-carbon ring systems (1'), or (b) within a 22-carbon ring system (1''). These are shown below. To distinguish between 1' and 1'', NMR spectra are expected to be useful. In contrast to the previously investigated annulenes, the chemical shifts of the ring protons of 1 do not correlate with the numbers of ring carbon atoms.$^{1)}$ The ^{13}C NMR spectrum of 1, which is shown in Fig. 1,$^{2)}$ consists of only eight peaks. This indicates the presence of a bond system of acetylenes and cumulenes in which several carbon atoms have become equivalent through resonance (1a - 1c). It is difficult to assign the signals of the ring carbons of 1, especially those of the quaternary carbon atom signals A, B, C and F (see Fig. 1), only by com-



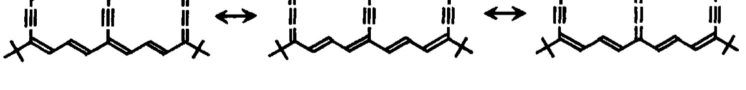
1



1′



1″



1a 1b 1c

paring the chemical shifts with those of the related monocyclic annulene analogues, because 1 is a new type of annulene compounds and its electronic structure has not been determined as yet, and it is not certain at present that the chemical shift analogy is fully valid for the assignments. A ^1H coupled ^{13}C spectrum cannot give sufficient information about the signal assignments. On the other hand, the spin-lattince relaxation method has recently become known to be powerful and useful for the assignments of ^{13}C signals in several organic molecules,[3,4] because T_1 is a quantity closely related to the molecular structure and motion.

In this paper, we present the successful application of the T_1 method to the assignments of ^{13}C signals of 1. The chemical shifts and T_1 values of 1 are given in Table I.[5] Becuase the T_1 values of the methyl and ring CH carbons are very short (< 1.3 sec), and those of the quaternary ring carbons are shorter than 56 sec, it can be safely said that the relaxation of these carbons occurs mainly by a dipole-dipole mechanism, and that the contribution of the spin-rotation is negligibly small. The T_1 due to the former can be described by the following equation:

$$\frac{1}{T_1} = \hbar^2 \gamma_H^2 \gamma_C^2 \sum_j \sum_i \frac{N_i}{r_i^6} \tau_{cj}, \qquad (1)$$

where γ is the gyromagnetic ratio, N_i is the number of equivalent nuclei, r is the internuclear distance between the carbon and hydrogen atoms, and τ_c is the correlation time. Since T_1's of the signal D and E are much shorter than those of the singnals A, B, C, and F, they are assigned to the ring CH carbons, which are bonded directly to one hydrogen atom, respectively. Because the distances between the quaternary carbons and the other unattached hydrogen atoms are longer than those of the C-H bonds, the quaternary

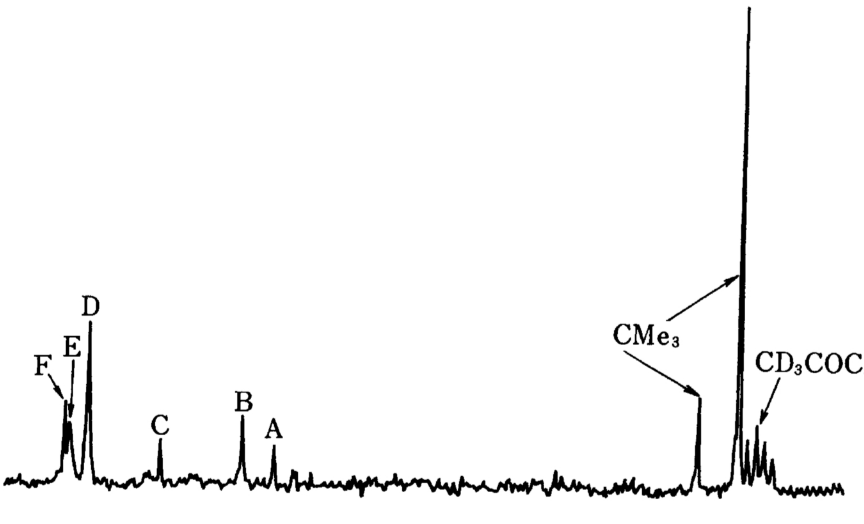


Fig. 1. The total ^{13}C spectrum of 1 at 31.2°C. The concentration is 150 mg/3 ml in CS_2 + CD_3COCD_3 (10:1).

Table I. ^{13}C chemical shifts, peak intensities, and observed and calculated T_1 values of carbons in 1 ($*T_1$ values at 40.4°C).

peak	Me	Me_3C	A	B	C	D	E	F
(PPM from TMS)	32.2	38.0	102.4	107.1	119.6	130.8	133.7	134.4
Intensity	12	4	2	4	2	8	4	4
T_1(obsd.) (sec)*	1.3		42.1	55.8	27.3	1.0	1.0	33.6
T_1(calcd.) (sec)			72.4	89.0	28.1			37.4
Carbons			23,24	6,7 17,18	1,12	2,4,9 11,13,15 20,22	3,10 14,21	5,8 16,19

carbons have much longer T_1 values. Thus, peaks A, B, C, and F are assigned to the four kinds of quaternary ring carbons [(1,12), (5,8,16,19), (6,7,17,18), and (23,24)]. Since the quaternary carbons are located at different positions in the molecules, their r_i and N_i are different from each other and so they have unequal T_1 values.

Compound 1 has four t-butyl groups at the four corners of the annulene ring and a symmetrical molecular shape, and so one may assume that its tumbling motion is almost isotropic. Therefore, all quaternary carbons on the ring have a common correlation time $\tau_c(r)$ on the basis of the tumbling motion of the ring. In the case of the carbons on the periphery of the ring [e.g., C(8) and C(6)], relaxation occurs via hydrogen atoms of the methyl groups as well as those bonded to ring carbons. Thus, another correlation time, which is calculated from the correlation times $\tau_c(m)$ of the methyl carbons, should be taken into account in addition to $\tau_c(r)$.

Using the obtained T_1 values of the ring CH and methyl carbons, bond distances and bond angles determined from an X-ray analysis of 1,[6] $\tau_c(r)$ and $\tau_c(m)$ determined from eq. 1 are 3.3×10^{-11} and 1.1×10^{-11} sec, respectively. The T_1 values of the four kinds of quaternary ring carbons are now calculated* from eq. 1 using these $\tau_c(r)$ and $\tau_c(m)$ values and the X-ray data. The results are given in Table I. The assignments of the ring quaternary carbons in Table I are made on the basis of the relative magnitudes of the calculated and experimentally obtained T_1 values. The assignments thus determined by the T_1 method correlate with the numbers of carbon atoms represented by the four peaks in the spectrum, which are shown in Table I.

---

*The calculations are made assuming the absence of the cross correlation between $\tau_c(r)$ and $\tau_c(m)$.

Although the calculated and experimentally obtained T_1 values of signals, C and F, are in excellent agreement, the experimentally obtained T_1 values of the signals, A and B, which are longer than those of the signals C and F, are considerably different from the calculated ones. This may be clue to a short pulse delay time (150 sec) and probably due to a few assumptions descrived above.

It is very interesting to note from the assignments that the signal of the centered carbons [C(23), C(24), δ:102.4] is at a higher field than that of the peripheral carbons [C(6), C(7), C(17), C(18), δ:107.1]. This fact may signify that the electronic states and/or the degree of the ring current effects are different from each other in the two kinds of ring carbons. It is also worth pointing out that the ^{13}C signals of the corresponding carbons in bisdehydro[14]- and bisdehydro[22]annulene derivatives are at much lower field (δ:116.7 and 116.8, respectively) than those in <u>1</u>. These results strongly suggest that <u>1</u> does not have the structure <u>1</u>", and that the aromaticity in <u>1</u> is different from that in the corresponding bisdehydro[14]annulene derivatives.

The authors wich to express their hearty thanks to Dr. O. Yamamoto of National Chemical Laboratory for Industry for his helpful discussion.

References and Notes

1) S. Akiyama, M. Iyoda, and M. Nakagawa, J. Am. Chem. Soc., <u>98</u>, 6410 (1976). 2) The ^{13}C NMR spectra were measured on a Varian XL-100-15A and a NEVA NV-14 spectrometers operating at 25.16 and 15.09 MHz, respectively, with a Varian 620/L computer (16k). 3) F. W. Wehri, ed. by G. C. Levy, "Topics in Carbon-13 NMR Spectroscopy", Vol. 2, p. 343, John Wiley & Sons Inc., New York, (1976) and references cited herein. 4) T. Hayashi and H. Nakanishi, Bull. Chem. Soc. Jpn., to be submitted. 5) Parameters in the measurements of ^{13}C spectra to determine the T_1 values were as follows: for the signals A, B. C and F, spectral width (SW): 2000 Hz, pulse delay (PD) 150 sec, and pulse width (PW): 41 μsec. Accumulation number (NT): 130, and sensitivity enhancement factor (SE): 0.1 sec. For the signals D and E, SW: 2000 Hz, PD: 6 sec, PW: 41 μsec, NT: 200, and SE: 0.1 sec. The sample tube was sealed after oxygen contained in the sample was excluded by purging with N_2 gas stream. The T_1 values were determined by the usual 180°-τ-90° pulse sequence method. The T_1 values were evaluated from 8 - 10 data by means of the least squares method. 6) The details of the X-ray data will be soon published elsewhere.

(Received September 2, 1977)