The ^{1}H and ^{13}C NMR of 9,10-Bis(phenylethynyl)anthracene Dianion

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The formation of 9,10-bis(phenylethynyl)anthracene dianion by contact of tetrahydrofuran-d_8 solution of its precursor with sodium in vacuo, is confirmed by the ^{1}H and ^{13}C NMR spectra and its reactivity. The excess π-charge-density distribution estimated by the CNDO/2 calculation for the dianion, is consistent with the observed ^{1}H and ^{13}C chemical shift values.

The NMR studies of the π-dianions of polycyclic aromatics and annulenes have so far been largely served to investigate the electronic structures of these π-conjugated systems,[1] as well as ESR studies on the corresponding anion radicals. It has been suggested that the ease of the formation of π-dianion correlates well with the resonance energy per atom in a dianion molecule.[2] However, in practice the line broadening due to spin exchange with a corresponding anion radical in equilibrium with dianion in solution often prevents an observation of high-resolution NMR signals of dianion. On the other hand, it may be significant that a substituent effect on π-conjugated system can be discussed in terms of the excess charge distribution of the corresponding π-dianion. However, a discussion from this point of view has not generally been of interest. In the anthracene dianion, excess charge relative to its neutral precursor has been known to be extraordinarily large at the 9 and 10 positions;[3] this observation prompted us to discuss the effect of several kinds of substituents at these positions on the excess charge distribution.

The present paper reports on the formation of the dianion of 9,10-bis(phenylethynyl)anthracene (**1**) as a unique anthracene derivative and on its electronic structure on the basis of an observation of its ^{1}H and ^{13}C NMR and charge density distribution estimated by a MO calculation.

Experimental

Compound **1** (Aldrich Co. Ltd.) was used without further purification and tetrahydrofuran-d_8 (THF-d_8) (Canada MSD Co. Ltd.) was vacuum-distillated after drying with sodium/potassium alloy in a high-vacuum tube. 1 ml of a 0.2 mol dm^{-3} THF-d_8 solution of **1** was introduced into a 10 mm Pyrex tube connected to high-vacuum line and degassed. A small amount of sodium metal was placed in the upper part of an NMR tube connected to the vacuum line. After the solution was transferred into the sample tube, the tube was cut off from the vacuum line. By turning the tube, the solution was brought into contact with the metal at room temperature for controlled periods of time. The NMR spectra were measured on a Varian VXR-300 pulsed FT spectrometer operating at 300 and 75 MHz for ^{1}H and ^{13}C, respectively, at room temperature. The ESR spectra and mass spectra were recorded on a JES-FE1XG ESR spectrometer (X-band, 100 kHz modulation) and a JMS DX-300 mass spectrometer, respectively. A calculation of the charge density distribution was performed by the MO method with Y4CB04 of the library programs in the Computer Center of the University of Tokyo on HITAC M-240H of Ibaraki University.

Results and Discussion

Immediately after the contact of the THF-d_8 solution of **1** with sodium metal in vacuo at room temperature, the solution turned green, which gave an ESR spectrum of the anion radical of **1**. Upon further contact, the color of the solution gradually became purple, while the ESR disappeared and new NMR lines developed. The ^{1}H spectrum of the purple

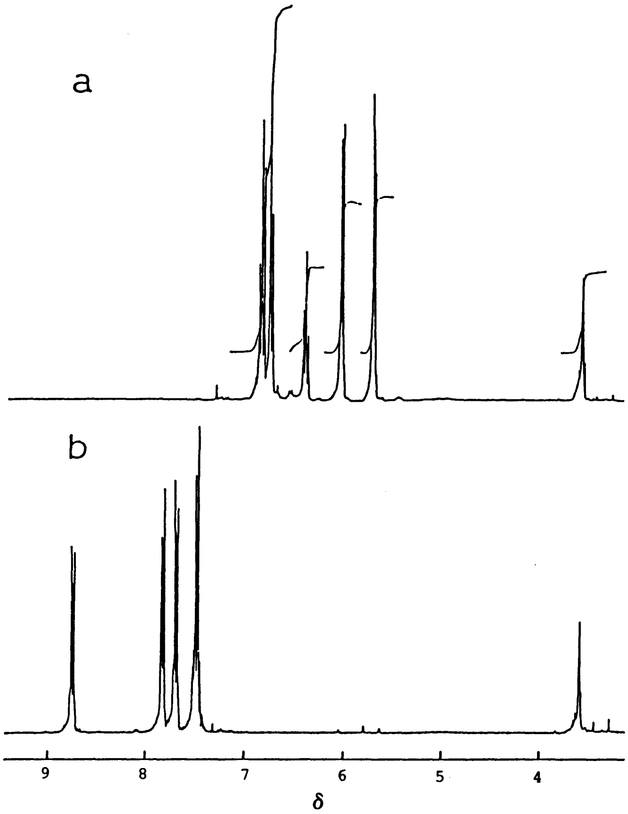


Fig. 1. ^{1}H NMR spectra of $\mathbf{1}^{2-}$ (a) and its neutral precursor (b) in THF-d_8.

solution measured after contact for 24 h is shown in Fig. 1, together with that of the neutral precursor **1** in THF-d_8. This spectrum exhibited the same pattern as that of **1**, which consists of an AA′BB′ and an AA′BB′C systems. The center of gravity of ^{1}H signals was shifted toward 1.53 ppm higher than that for **1**. Furthermore, in order to investigate whether this species is a diamagnetic monoanion formed by subtracting a proton from the solvent or not, after a purple solution was prepared in THF with the same technique, THF was excluded by evaporation and a resulting purple residue was solved in THF-d_8. The ^{1}H spectrum of the resulting purple solution was completely identical with that produced first by contact with sodium metal in THF-d_8; that is, the latter spectrum has no other lines than the former. One can thus rule out the possibility of the formation of a monoanion. The ^{13}C spectrum of the purple species (Fig. 2) is consistent with that expected from the ^{1}H spectrum, consisting of lines of five tertiary and five quaternary carbons as well as those of **1**. The high-field shift of the center of gravity of ^{13}C signals from **1** to the purple species is 5.26 ppm.[4] Thus, from these results, one may anticipate that the purple species is identified to a π-dianion of **1**, $\mathbf{1}^{2-}$ (or a disodium salt of dianion ($\mathbf{1}^{2-}\cdot 2\mathrm{Na}^+$)).

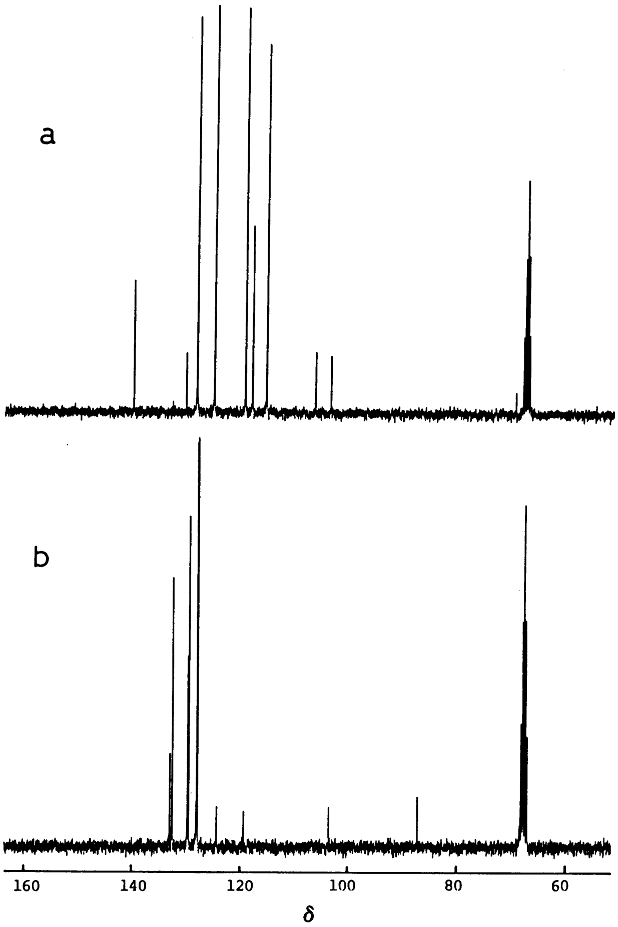


Fig. 2. ^{13}C NMR spectra of $\mathbf{1}^{2-}$ (a) and its neutral precursor (b) in THF-d_8.

For the ^{1}H spectrum of **1**, the lower-field group of the AA′BB′ system was assigned to H_1, in analogy with the case of 9,10-diphenylanthracene,[5] which is similar to **1** in view of containing π-type substituents at the 9 and 10 positions. The *o*-, *m*-, and *p*-protons of phenyl groups could be straightforwardly assinged due to their coupling patterns. For the ^{1}H spectrum of $\mathbf{1}^{2-}$, the lower-field group of the AA′BB′ pattern was assigned to H_1 on the basis of a combination of a C–H shift correlation 2D NMR (Fig. 4) and the ^{13}C assignment determined from a comparison of shift difference from **1** ($\Delta\delta$) with the calculated excess

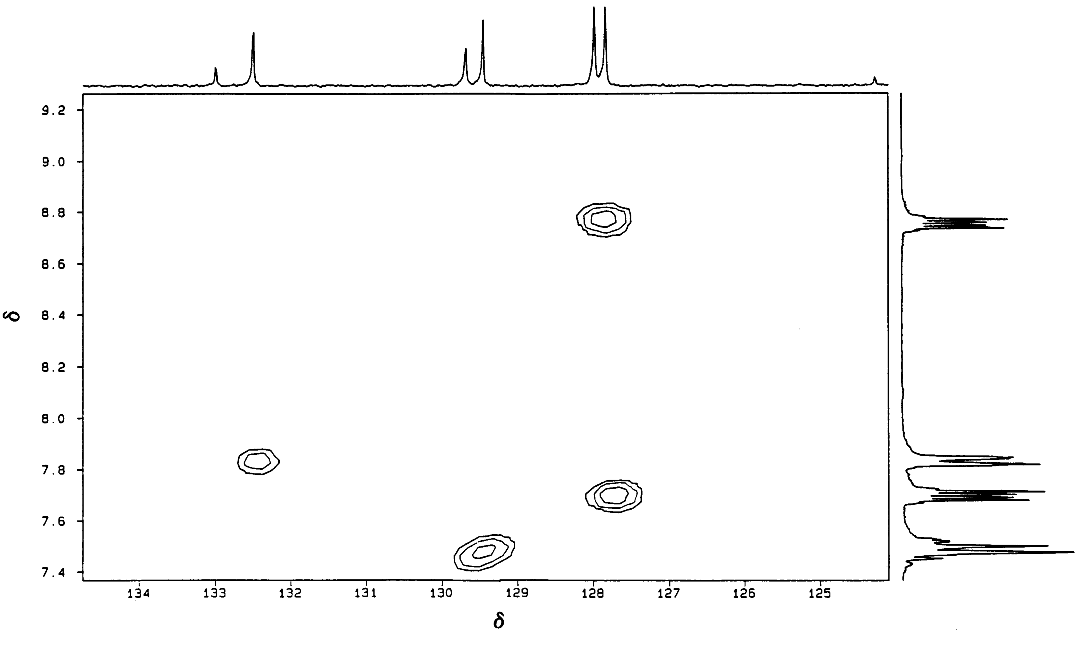


Fig. 3. H–C shift correlation 2D NMR of **1**.

charge (Δq_c^π) described later. The phenyl protons was easily assigned as well as **1**. For both **1** and **1**$^{2-}$, all of tertiary carbons were assigned on the basis of the C–H shift correlation 2D NMR (Figs. 3 and 4) and ^{1}H assignments. Since assignments of the quaternary carbons of both **1** and **1**$^{2-}$ are quite difficult, they were tentatively made by analogy with those of several phenyl derivatives of acetylene and by a comparison with the calculated excess π-charge-densities Δq_c^π's (Table 1).

It was then confirmed by measuring the ESR that addition of a reducible aromatic compound, *m*-dinitrobenzene, to the purple solution in vacuo gives the anion radical of this compound. A quenching experiment with oxygen afforded a neutral precursor, while with water and deutrium oxide the dihydro (*m/z* 380) and dideuterio derivatives (*m/z* 382) of **1** were formed, respectively, as shown by mass spectrometry. All these results strongly support the above expectation that the purple species is a π-dianion of **1** or its disodium salt.

The observed mean high-field ^{13}C shift, 5.26 ppm, of **1**$^{2-}$ from **1** is only about a half of 10.67 ppm estimated by using a commonly used value of k_c, 160 ppm/electron, in the correlation of ^{13}C shift with charge density, $\Delta\delta_c = k_c \cdot \Delta q_c^\pi$.[6] Recently, it was found by Eliasson et al.[7] that for $4n\pi$-systems the anisotropic high-field shift of a ring proton due to a paratropic ring current correlates well with a k_c value for ring carbons determined experimentally and that the anomalous deshielding of ring carbons for such a system is explained in terms of the average electronic excitation energy. For the anthracene dianion, 89 ppm/electron is given as k_c from their analysis. Since in our present system about 80% of the total excess π-charge occupies the anthracene moiety as calculated later, it may be plausible to consider that the anthracene ring carbons are affected by such the anomalous deshielding effect. Thus, this reason may explain the considerable reduction in the high-field shift of the center of gravity of ^{13}C signals from 10.67 ppm.

The MO calculations of electron density distributions were then performed on **1** and **1**$^{2-}$ by the CNDO/2 method.[8] Since an available crystal structure of **1** has not been found in the literature, a possible molecular geometry for **1** was estimated by a combination of the crystal structures of diphenylacet-

Table 1. Observed ^{1}H and ^{13}C Chemical Shifts for **1** and **1**$^{2-}$ a)

	δ_N	δ_D	$\Delta\delta_{obsd}$
H_1	8.75	6.05	−2.70
H_2	7.70	5.72	−1.98
H_{18}	7.83	6.76	−1.07
H_{19}	7.49	6.86	−0.63
H_{20}	7.49	6.42	−1.07
C_1	128.00	115.48	−12.52
C_2	127.85	119.39	−8.46
C_9 b)	133.00	69.40	−63.60
C_{11} b)	103.56	106.50	2.94
C_{15} b)	119.31	132.00	12.69
C_{16} b)	86.97	103.60	16.63
C_{17} b)	124.27	140.12	15.85
C_{18}	132.51	125.15	−7.36
C_{19}	129.47	128.41	−1.06
C_{20}	129.70	118.10	−11.60

a) Measured in ppm relative to the lower-field multiplet of THF and referred to TMS. δ_N and δ_D are shifts for **1** and **1**$^{2-}$, respectively. $\Delta\delta_{obsd}$ is shift of **1**$^{2-}$ relative to that of **1**. Positive signs denote low field shifts. b) Assigned tentatively.

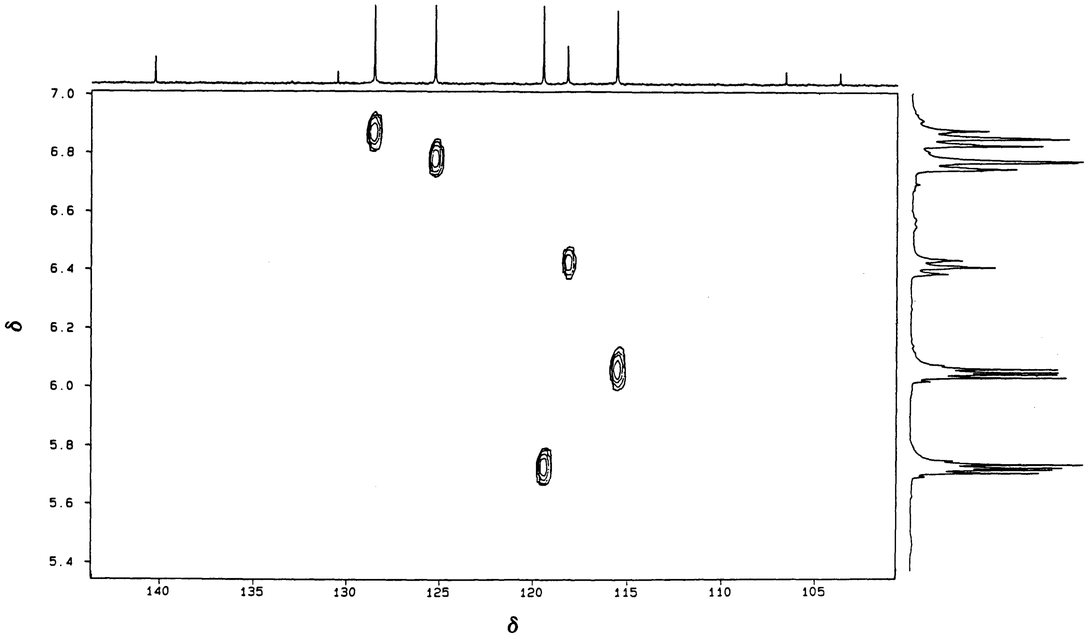
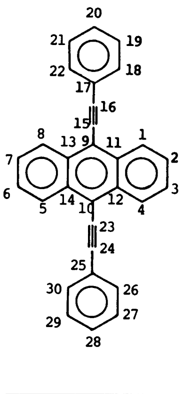


Fig. 4. H–C shift correlation 2D NMR of **1**$^{2-}$.

Table 2. Comparison of Changes of Calculated and Observed ^1H and ^{13}C Shifts of $\mathbf{1}^{2-}$ from $\mathbf{1}$[a)]



	Δq_c[b)]	$\Delta\delta_{calcd}$[c)]	$\Delta\delta_{obsd}$
H_1		−0.92	−2.70
H_2		−0.46	−1.98
H_{18}		−0.58	−1.07
H_{19}		−0.04	−0.63
H_{20}		−1.17	−1.07
C_1	0.0858	−13.73	−12.52
C_2	0.0429	−6.86	−8.46
C_9	0.4700	−75.20	−63.60
C_{11}	0.0349	−5.58	2.94
C_{15}	−0.0458	(7.33)[d)]	12.69
C_{16}	0.1318	(−21.09)[d)]	16.63
C_{17}	−0.1037	16.59	15.85
C_{18}	0.0543	−8.69	−7.36
C_{19}	0.0041	−0.66	−1.06
C_{20}	0.1090	−17.44	−11.60

a) In ppm. Positive signs denote low-field shifts. b) Excess π-charge density of $\mathbf{1}^{2-}$ relative to that of $\mathbf{1}$. c) Shifts of $\mathbf{1}^{2-}$ from those of $\mathbf{1}$ calculated using k_H=10.7 ppm/electron and k_c=160 ppm/electron in $\Delta\delta_H = -k_H \cdot \Delta q_c^\pi$ and $\Delta\delta_c = -k_c \cdot \Delta q_c^\pi$, respectively. d) Shift values in parentheses are not reliable because the standard k_c value (160 ppm/electron) may not be applied to sp-hybridized carbons.

ylene[9)] and anthracene[10)] as a planar structure.[11)] The distance between C_9 and C_{15}, R_{9-15}, was taken as the equal magnitude to R_{16-17}, by taking into account the considerable stability of the anthracene moiety.[12)] The electron density at the $2p_z$ orbital of carbon is denoted by q_c^π and its change from $\mathbf{1}$ to $\mathbf{1}^{2-}$ by Δq_c^π. ^1H and ^{13}C chemical shifts of $\mathbf{1}^{2-}$ relative to those of $\mathbf{1}$, $\Delta\delta_{calcd}$, were estimated using the relation $\Delta\delta_H = k_H \cdot \Delta q_c^\pi$[13)] and $\Delta\delta_c = k_c \cdot \Delta q_c^\pi$, respectively. As can be seen from Table 2, the observed shifts of $\mathbf{1}^{2-}$ from $\mathbf{1}$, $\Delta\delta_{obsd}$, for the anthracene ring protons are anomalously larger (3—4 times) than $\Delta\delta_{calcd}$ obtained using the standard k_H value, 10.7 ppm/electron, in contrast to those of the phenyl protons. This may be ascribed to a contribution of the partially paratropic ring current effect of the anthracene moiety.[14)] It may be plausible to consider that the change of the anisotropy of the triple bond from $\mathbf{1}$ to $\mathbf{1}^{2-}$ scarecely affects the $\Delta\delta_{obsd}$ of all the ring protons owing to its location far from protons. On the other hand, for C_1 and C_2 $\Delta\delta_{obsd}$ corresponds comparatively well to $\Delta\delta_{calcd}$; this seems to imply that an anomalous deshielding was not remarkably observed. Also for C_{18}, C_{19}, and C_{20}, the pattern of $\Delta\delta_{obsd}$ approximately corresponds to that of $\Delta\delta_{obsd}$. Since for the sp-hybridized C_{15} and C_{16}, a relevant k_c value has been unknown so far, the shifts of these carbons can not sufficiently be discussed here. For C_{17}, $\Delta\delta_{obsd}$ corresponds well to $\Delta\delta_{calcd}$; while for both C_9 and C_{11} $\Delta\delta_{obsd}$ is much smaller than $\Delta\delta_{calcd}$; that is, these two carbons are much more subject to the anomalous paramagnetic ring current than the other ring carbons. On the other hand, the calculation result that most of the excess π-charge in the anthracene moiety is concentrated on the central ring of anthracene allows us to consider that the central ring may contribute considerably to the partial paratropicity of the anthracene moiety. Thus, all the shifts, except for C_{15} and C_{16}, could be consistently explained, though qualitatively, with tentative assignments for the quaternary carbons.

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11) The geometric parameters used for CNDO/2 calculations are as follows: C_1C_2=1.3639 Å, C_2C_3=1.4180 Å, C_1C_{11}=1.4312 Å, C_9C_{11}=1.3968 Å, $C_{11}C_{12}$=1.4340 Å, C_9C_{15}=1.4384 Å, $C_{15}C_{16}$=1.1911 Å, $C_{16}C_{17}$=1.4384 Å, $C_{17}C_{18}$=1.3890 Å, $C_{18}C_{19}$=1.3907 Å, $C_{19}C_{20}$=1.3854 Å, $\angle C_1C_2C_3$=120.68°, $\angle C_{11}C_1C_2$=120.59°, $\angle C_1C_{11}C_{12}$=118.73°, $\angle C_9C_{11}C_{12}$=121.12°, $\angle C_{11}C_9C_{13}$=120.88°, $\angle C_{18}C_{17}C_{22}$=119.80°, $\angle C_{17}C_{18}C_{19}$=120.09°, $\angle C_{18}C_{19}C_{20}$=119.84°, $\angle C_{19}C_{20}C_{21}$=120.32°.

12) In order to examine an effect of excess π-electrons on the conjugated system, an attempt was then made of calculation of Δq_c^π with slight changes of each value of R_{9-15} and R_{15-16}. It was then found that Δq_c^π pattern is very sensitive to each of these two distances all through the molecule. However, no set of these two distances afforded Δq_c^π pattern which explaines $\Delta\delta_{obsd}$ better than original values of distances (R_{9-15}=1.4384 Å and R_{15-16}=1.1911 Å).

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