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THE CRYSTAL AND MOLECULAR STRUCTURE OF 3,9,12,18-TETRA-*t*-BUTYL-DIDEHYDRO[18]ANNULENE

Chizuko Kabuto and Yoshio Kitahara[†]
Department of Chemistry, Faculty of Science, Tohoku University
Sendai 980, Japan
Masahiko Iyoda and Masazumi Nakagawa
Department of Chemistry, Faculty of Science, Osaka University
Osaka 560, Japan

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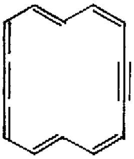
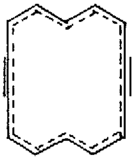
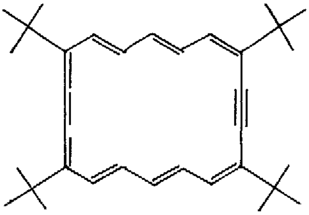
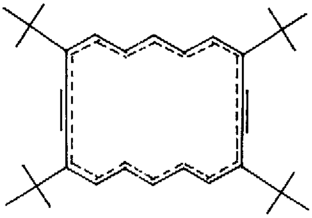
Among a wide variety of dehydroannulenes, didehydro[4n+2]annulenes containing formal acetylenic and cumulenic bonds are especially interesting, because the structure of didehydro[14]annulene (1) revealed by the X-ray crystallographic study[2] indicates that the molecule can be properly represented by the symmetrical structural formula (I) with the highly delocalized π-bonds.


(1)


(I)


(2)


(II)

Successful synthesis and recognition of the high conformational stability and strong diamagnetic ring current of tetra-*t*-butyldidehydro[18]annulene (2)[3] prompt us to the X-ray structural study of the compound.

A single crystal of prism shape with the dimensions of 0.2x0.2x0.25 mm placed in a thin-walled glass capillary with dry nitrogen was mounted on a Rigaku automated four circle diffractometer.

[†] Deceased, Feb. 4th, 1976.

The unit cell, having the dimensions of a=10.165, b=15.908, c=9.914 Å, and β=108.54°, belong to the space group $P2_1/n$. The unit cell contains two molecules, indicating that the resulting structure must have a center of symmetry. A total od 3059 reflections within 2θ=55° were measured using Mo-Kα radiation. During the period of data collections, three standard reflections monitored periodically showed no significant variation of the intensities. The structure was solved by the direct method and refined by the block-diagonal least-squares method. The refinement for the 17 carbon atoms (half of the molecule) was recycled to give an R-factor to 0.13 and then a difference Fourier map located all hydrogen atoms. The parameters for the 5 hydrogen atoms bonded directly to the ring were refined in the successive stages; however, the parameters for the hydrogen atoms in the methyl groups, appearing a rather wide distribution of the electron density, were not refined but included only in the structure factor calculation. Several cycles of refinement with the anisotropic temperature parameters for the carbon atoms and the isotropic for the hydrogen atoms gave the final R-factor of 0.09.

The bond lengths and angles in the molecule are shown in Fig. 1. These results can lead reasonably to the conclusion that the molecule of (2) is essentially in the same nature of bonding as the case of the didehydro[14]annulene (1). It seems that the slight variations observed among a total of six bonds, which were independently determined of each other in the polyene part, are of no significance. The range of the lengths is 1.383 to 1.391 Å, and the average value is 1.387 Å which is close to that for benzene. These bonds, therefore, are represented by the formal C(sp^2)====C(sp^2) bond. On the other hand, the linear C-C-C-C linkage, which has the unique short bond of 1.209 Å and the other two longer bonds of average 1.373 Å, can be properly defined neither by teh acetylenic nor by the cumulenic bond. It is rather reasonable to consider their resonance hybrid by assigning the formal C(sp)====C(sp) and C(sp)====C(sp^2) bonds, respectively. Thus, the structure is consistent with the formula (II). In the molecule of (1), the corresponding bonds are observed in the lengths of av. 1.396, av. 1.377, and 1.200 Å, respectively.

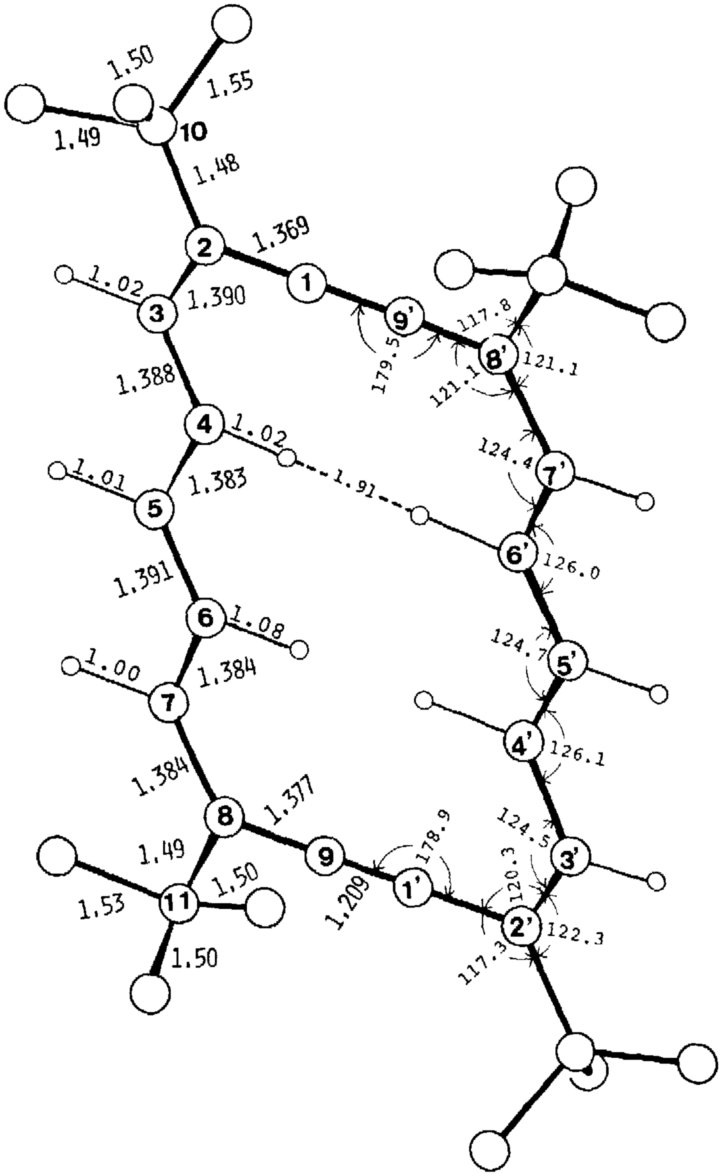


Fig. 1. Bond lengths (Å) and angles (°) of the molecule (2).
The standard deviations are as follows : 0.6-0.7° in the bond angles, 0.008-0.009 Å in the innercyclic C-C bond and the exocyclic C-C bond lengths, and 0.010-0.011 Å in the methyl C-C bond lengths.

In order to see the molecular planarity of (2), the least-squares plane through the ring nine carbon atoms was calculated. The deviations of atoms are as follows:

C(1)	-0.007 Å
C(2)	-0.008 Å
C(3)	-0.007 Å
C(4)	0.017 Å
C(5)	0.010 Å
C(6)	-0.005 Å
C(7)	-0.007 Å
C(8)	0.006 Å
C(9)	-0.010 Å

The deviations of the exocyclic carbon atoms in the *t*-butyl groups from the same plane are:

C(10)	-0.041 Å
C(11)	-0.010 Å.

These results indicate that the molecule has essentially a planar conformation. A planar conformation of this system must bring about the abnormally short contacts between inner hydrogen atoms, which may be suggested by the fact that the observed distance of 1.91 Å is fairly shorter than the sum of van der Waals radii(2.4 Å for H---H contact)[4]. The distortions of 124-126° from the sp^2 hybridization angle of 120° are observed in the ring CCC angles, which should be rationalized as a means of lessening some of the repulsion.

It should be pointed out that the ring forces toward a planar conformation, despite of the presence of such repultions. This fact suggests that the inherent stabilization energy provided by the complete delocalization is sufficiently great even in the 18-membered system as well as the 14-membered system.

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