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THE MOLECULAR STRUCTURE OF A TRISDEHYDRO[10.10.2][14]ANNULENO[14]ANNULENE

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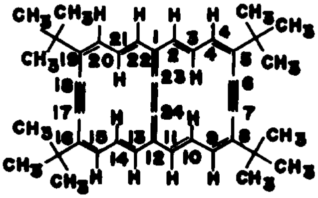
5,8,16,19-Tetra-t-butyl-6,17,23-trisdehydro[10.10.2][14]annuleno[14]annulene (1), which was recently synthesized[1], is a new type of condensed nonbenzenoid aromatic compounds with 14-π-electron systems. There are two models of π-electron delocalization in this compound; (a) delocalization within two separate 14-carbon ring system (1'), or (b) within a 22-carbon ring system (1''). To clarify the electronic structure of (1), the X-ray crystal structure analysis has been carried out at -150°C.



(1)

(1')

(1'')

Because of the poor solubility of (1) in the organic solvent, it was very difficult to obtain a suitable crystal for X-ray experiment. After a large number of recrystallizations, a dark-purple crystal with dimensions of 0.25 x 0.25 x 0.35 mm was cut out from a very fragile crystal with relatively large size. The determination of unit cell parameters and measurement of integrated intensities were carried out on a Rigaku four-circle X-ray diffractometer with the low temperature equipment by the gas flow method of liquid nitrogen. The crystal data are listed in Table 1, which shows the molecule locates on a crystallographic center of symmetry. A total of 3722 reflections were measured by the θ-2θ scan technique within a sphere of $\sin\theta/\lambda = 0.639$, among which 2876 were above the background. Intensity data were corrected for Lorentz and polarization effects but not for absorption.

Table 1. Crystal data of

5,8,16,19-tetra-*tert*-butyl-6,17,23-tris-dehydro[10.10.2][14]annuleno[14]annulene

Monoclinic	$C_{40}H_{48}$
Space Group $P2_1/n$	M = 528.8
$F(000)$ = 576	$\mu(MoK\alpha)$ = 0.58 cm^{-1}

	[-150°C]	[22°C]
a =	9.600(1) Å	9.762(1) Å
b =	9.888(2)	9.900(1)
c =	17.918(3)	17.993(1)
β =	95.75(1)°	94.71(1)°
V =	1692.3(4) $Å^3$	1733.2(1) $Å^3$
Z =	2	2
Dx =	1.037 g cm^{-3}	1.013 g cm^{-3}
Dm =		1.011

The structure was solved by the MULTAN74 program[2] using 350 $|E|$ values greater than 1.60. From the E map calculated by the set of phases which gave the highest combined figure of merit, 19 carbon atoms out of 20 independent ones were easily located. Subsequent Fourier synthesis revealed the remaining one. The refinement of the molecular structure was carried out by the block-diagonal least-squares method with HBLS-V[3]. After an anisotropic refinement of carbon atoms a difference Fourier map was calculated, from which all the hydrogen atoms were located and were included in the later refinement assuming isotropic temperature factors. The atomic scattering factors for carbon atom were taken from *International Tables for X-ray Crystallography*[4] and those for hydrogen atom were from Stewart et al[5]. The final R value for non-zero reflections is 0.110. The final atomic coordinates are listed in Table 2. A list of atomic thermal parameters and that of observed and calculated structure factors may be obtained from the author's laboratory upon request.

Table 2. Fractional atomic coordinates for carbon ($x10^4$) and hydrogen ($x10^3$) atoms

The numbering of carbon atoms are shown in Fig. 1, and that of hydrogen atoms follows the carbon atoms to which they are attached. The estimated standard deviations, given in parentheses, refer to the last significant figures.

	x	y	z		x	y	z
C(1)	-246(3)	1076(4)	-2723(2)	H(3)	-159(4)	379(4)	-199(2)
C(2)	-882(4)	2363(4)	-2670(2)	H(4)	-36(4)	135(5)	-131(2)
C(3)	-1149(4)	2883(4)	-1987(2)	H(5)	-153(4)	355(5)	-55(2)
C(4)	-841(4)	2202(4)	-1296(2)	H(8)	-161(5)	327(5)	81(3)
C(5)	-1119(4)	2639(4)	-610(2)	H(9)	-50(6)	75(6)	140(3)
C(6)	-848(4)	1850(4)	58(2)	H(10)	-164(5)	295(5)	218(3)
C(7)	-254(3)	555(4)	17(2)	H(14A)	-120(4)	505(4)	-302(2)
C(8)	-1188(4)	2353(4)	771(2)	H(14B)	-214(5)	495(5)	-381(3)
C(9)	-941(4)	1629(4)	1422(2)	H(14C)	-266(5)	441(5)	-312(3)
C(10)	-1237(4)	2071(4)	2142(2)	H(15A)	84(5)	366(5)	-345(3)

C(11)	-928(4)	1319(4)	2792(2)	H(15B)	-3(5)	376(5)	-426(3)
C(12)	-297(4)	31(4)	2752(2)	H(15C)	61(5)	233(5)	-389(3)
C(13)	-1249(4)	3093(4)	-3424(2)	H(16A)	-322(5)	204(6)	-360(3)
C(14)	-1871(5)	4502(4)	-3321(2)	H(16B)	-198(5)	145(5)	-400(3)
C(15)	112(4)	3263(4)	-3809(2)	H(16C)	-286(6)	258(6)	-437(3)
C(16)	-2296(5)	2230(5)	-3916(2)	H(18A)	-285(5)	309(5)	321(3)
C(17)	-1249(4)	1791(4)	3574(2)	H(18B)	-135(5)	397(6)	329(3)
C(18)	-1937(4)	3186(4)	3558(2)	H(18C)	-215(5)	344(5)	402(3)
C(19)	-2242(4)	767(4)	3881(3)	H(19A)	-303(4)	68(4)	346(2)
C(20)	114(5)	1843(5)	4094(2)	H(19B)	-177(5)	-17(6)	395(3)
				H(19C)	-252(5)	102(5)	437(3)
				H(20A)	68(5)	244(6)	394(3)
				H(20B)	57(5)	109(5)	413(3)
				H(20C)	-15(5)	206(5)	462(3)

The selected bond distances and angles are given in Fig. 1, which is the molecular projection on the least-squares plane of the carbon atoms except t-butyl groups. These skeletal carbon atoms are coplanar within the maximum deviation of 0.05 Å. Two hydrogen atoms, H(4) and H(9'), deviate away the opposite sides of the molecular plane to reduce the short atomic contact. The conformation of t-butyl groups is fixed in the manner to have the molecular plane as the mirror plane even including the hydrogen atoms of methyl groups. Good coincidence of the bond distances and angles is observed between the chemically equivalent parts of the molecule. The molecule has an approximate mmm symmetry. Assuming this symmetry, the molecular structure was averaged and shown in Fig.2.

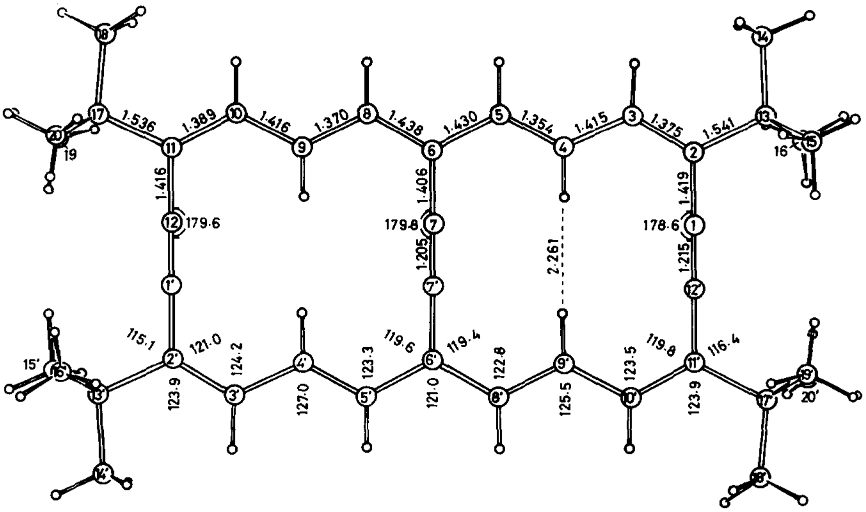
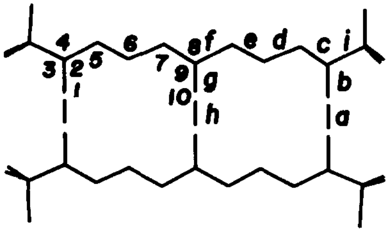


Fig. 1. Selected bond distances and angles

The estimated standard deviations being 0.005 - 0.006 Å and 0.3°, respectively.



a	1.215 Å	*1*	178.6°
b	1.418	*2*	120.4
c	1.382	*3*	115.8
d	1.416	*4*	123.9
e	1.362	*5*	123.9
f	1.434	*6*	126.3
g	1.406	*7*	123.1
h	1.205	*8*	121.0
i	1.539	*9*	119.5
		10	179.8

Fig. 2. Averaged molecular structure
assuming the mmm symmetry

The remarkable features in the averaged molecular structure are; (1) the bond alternation is observed in the bonds through *b* to *g*, (2) these bonds lie between the single (1.541 Å)[6] and double (1.337 Å)[6] bond distances, (3) bond *a* is slightly longer than bond *h*, which is identical with triple bond distance (1.204 Å)[6], (4) bond *g* is much shorter than the C-C single bond distance in $H_3C-C\equiv CH$ (1.460 Å)[6]. These structural evidences verify that the π-electrons in a trisdehydro[10.10.2][14]annuleno[14]annulene delocalize within two separate 14-carbon ring system rather than within a 22-carbon ring system.

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