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CRYSTAL AND MOLECULAR STRUCTURE OF 9,10-DIPHENYLBICYCLO[6.2.0]DECAPENTAENE A 10π AROMATIC COMPOUND

Chizuko Kabuto and Masaji Oda*
Department of Chemistry, Faculty of Science, Tohoku University
Sendai 980, Japan

Summary: X-ray analysis of 9,10-diphenylbicyclo[6.2.0]decapentaene 2b has revealed good planarity of the decapentaene nucleus, remarkably long bond length of the central bond, and appreciably small alternation of the peripheral bonds. It is thus concluded that 2b is a pericyclic 10π aromatic compound.

A considarable attention has been paid whether the conjugated fused-ring system with two 4nπ electron rings, thus having overall 4n+2π electrons, shows aromaticity or not, and a number of studies on such systems have been reported.[1] Among them, butalene 1[1b] and octalene 3[1k] were concluded to be non-aromatic, whereas heptalene dianion 4 to be aromatic.[1j] As to bicyclo[6.2.0]decapentaene 2, the syntheses and properties of derivatives have given some controversies on the aromaticity.[1e-i] Thus, the structural informations have been expected to provide an important clue to the question. We wish here to report the results of X-ray analysis of 2b[1h] which lead us to a conclusion that this system is aromatic to fair extent.

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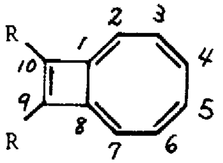
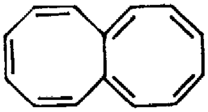


2a: R=H
2b: R=Ph



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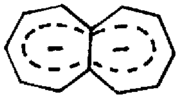

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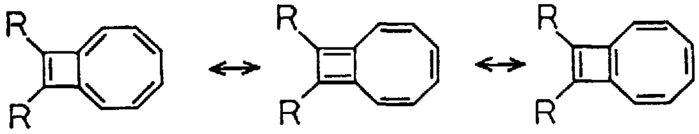
Crystal Data: $C_{22}H_{16}$, MW=280.4, Triclinic Space Group $P\bar{1}$, F(000)=592, Z=4; a=11.340(1), b=11.961(1), c=14.308(1)Å, α=63.73(1), β=68.40(1), γ=66.67(1)°, V=1553.6 Å^3, Dx=1.20g/cm^3. Intensity data were collected at 15°C room temperature by the θ-2θ scan method on a Rigaku automated four circle diffractometer with graphite monochromatized CuKα radiation The structure was solved by the direct method making use of a new potential technique involving quartet invariants,[2] and refined by the block-diagonal least-squares method. After several cycles of refinement with all hydrogen atoms, the R-value reached 0.09 for 4300 reflections.

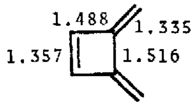
There are two independent molecules in the crystal with a slight difference in the planarity but with no significant difference in the bond lengths and angles. The bond lengths and angles are shown in an ORTEP diagram (Fig. 1) and the planarities are shown in Fig. 2. Fig. 3 summarizes the bond lengths and angles averaged over the molecules assuming mirror symmetry.

Of the two independent molecules, one's decapentaene nucleus is almost planar and the other's is a shallow tub form in the eight-membered ring. The latter's distortion from the planarity may be due to the packing force, suggesting that energetic compromize of the molecule is considerably sensitive to the environment.

Importantly, the length of the central C1-C8 bond (av. 1.535Å) is remarkably long for a bond between trigonally hybridized carbon atoms, being longer than the corresponding ones of known 10π aromatic system such as azulenes (1.490-1.507Å)4) and N,N-dimethylaminotroponeimine(1.490Å).5) This fact should mean that the anti-aromatic resonance contribution of the particular canonical form C to the structure is negligible. On the other hand, the alternation of the peripheral bonds is significantly small, except the relatively short C1-C2 and C7-C8 bonds, in comparison with those of 3,4-dimethylenecyclobutene 56) and cyclooctatetraene 6.7) Particularly, the length of C3-C4-C5-C6 bonds are close to those of C7-C8-C9-C10 bonds of 1,6-methano[10]annulene-2-carboxylic acid.8) The relatively short length of C1-C2 and C7-C8 bonds may be due to some change of hybridization on these carbons from the rest.



A B C



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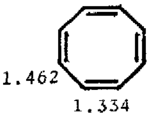

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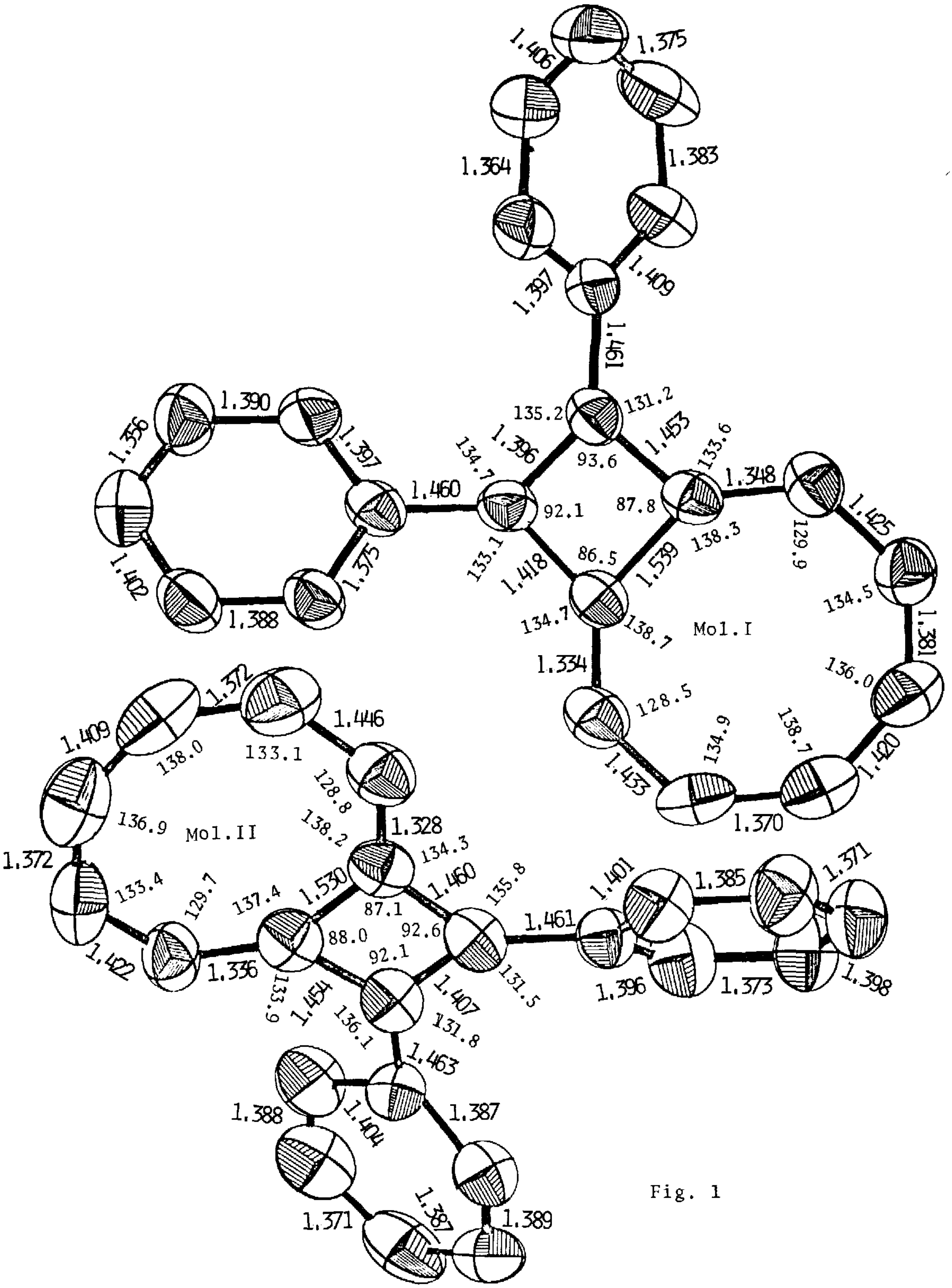
The results indicate that although the most important resonance contributor to the structure of 2b is the canonical form A, the contribution of B is so appreciable as to give sufficient delocalization energy to compensate the strain energy in the planar conformation. Since the parent compound 2a shows similar spectroscopic properties with 2b,9) it can be concluded that bicyclo[6.2.0]decapentaene 2 is a 10π aromatic compound like azulene and methano[10]annulenes,10) although its aromaticity seems weaker.

Our view as a general conclusion for the opening question is that the conjugated fused-ring systems with two 4nπ rings can be in principle aromatic, and their actual property, aromatic or non-aromatic, would largely depend on the counteraction of delocalization energy and strain energy in their planar conformations. The non-aromatic character of butalene 1 and octalene 3 may be ascribed to the greater strain energy in the planar conformation compared to 2.


1.406
1.375
1.364
1.383
1.397
1.409
1.461
135.2
131.2
1.396
1.453
133.6
134.7
93.6
1.348
1.390
1.356
1.397
1.460
92.1
87.8
138.3
1.425
129.9
133.1
1.418
86.5
1.539
1.402
1.375
1.388
134.5
134.7
138.7
Mol.I
1.381
1.334
136.0
128.5
134.9
138.7
1.420
1.433
1.370
1.372
1.409
1.446
138.0
133.1
128.8
138.2
1.328
136.9
Mol.II
1.372
134.3
133.4
129.7
137.4
1.530
1.460
135.8
1.401
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1.371
87.1
88.0
92.6
92.1
1.461
1.422
1.336
133.9
1.454
136.1
1.407
131.5
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1.404
1.387
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1.387
1.389

Fig. 1

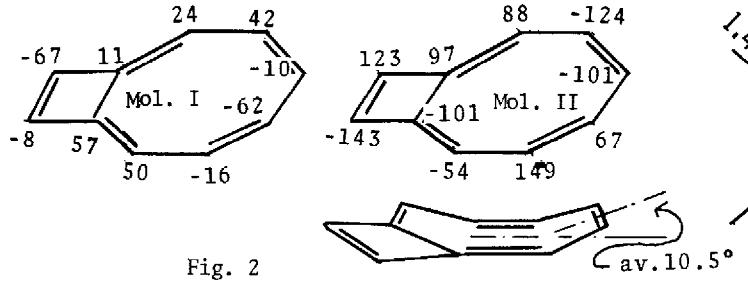

Fig. 2

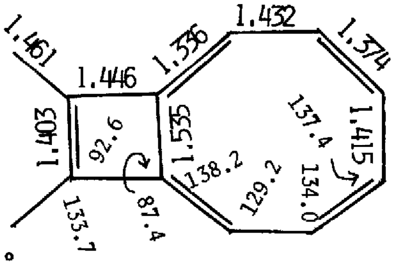

Fig. 3

Fig. 1 An ORTEP diagram of the two independent molecules viewed along b axis. Thermal ellipsoid is drawn at the 50% probability level, the hydrogen atoms being omitted for clarity. The e.s.d.'s for bond lengths and angles lie between 0.009-0.012 A and 0.5-0.8°, respectively.

Fig. 2 Deviations (x 10^3 A) of atoms from the best planes involving ten atoms of the decapentaene nuclei. The shallow tub form of the eight-membered ring in the molecule II is also shown.

Fig. 3 Averaged bond lengths and angles of the decapentaene nucleus.

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