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MINDO/3 STUDY OF 1,2-DIDEHYDROCYCLOOCTATETRAENE AND RELATED PLANAR CONJUGATED EIGHT-MEMBERED CARBOCYCLES[1]

Nai Zheng Huang[2]
Shanghai Institute of Organic Chemistry
Academia Sinica
345 Linglin Lu, Shanghai, China

Thomas C.W. Mak and Wai-Kee Li*
Department of Chemistry
The Chinese University of Hong Kong
Shatin, N.T., Hong Kong

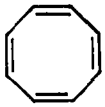
Abstract: MINDO/3 calculations indicate the 1,2-didehydrocyclooctatetraene (**2**) and 1,2,5,6-tetradehydrocyclooctatetraene (**10**) and their benzo derivatives have planar skeletons. In addition, in the cases of **2** and its benzo derivatives, the acetylenic structure is found to be thermodynamically more stable than the cumulenic one.

Cyclooctatetraene, **1**, is notoriously nonplanar[3]. Its observed tub conformation is not merely due to the severe angular strain inherent in the idealized symmetric planar configuration but, more importantly, arises in consequence of pseudo Jahn-Teller distortions[4]. Thus, in order to make **1** planar, it is imperative to eliminate, or at least significantly reduce, these two effects.

We considered that the introduction of one or two acetylenic bonds in a hypothetical planar cyclooctatetraene would reduce its tendency to undergo out-of-plane distortion caused by the pseudo Jahn-Teller effect. Furthermore, with the triple bond(s) absorbing most of the angular strain, the ethylenic bond angles would approach closer to the idealized sp^2 value of 120°. Fully conjugated eight-membered carbocycles containing one or two acetylenic linkages thus stand an excellent chance of being planar.

The elegant work of Krebs[5] pioneered the study of planar cyclooctatetraenes; he reported the fugitive existence of 1,2-didehydrocyclooctatetraene, **2**, in 1965. Unfortunately, the presence of **2** could only be confirmed by trapping reactions. Also, **2** could exist in acetylenic (**2a**) and cumulenic (**2b**) forms, which cannot be easily distinguished. Subsequently, Wong and Sondheimer prepared a series of benzannelated conjugated eight-membered ring compounds incorporating acetylene and possibly cumulene features. In particular, 5,6,11,12-tetradehydrodibenzo[a,e]cyclooctene[6], **3**, and 5,6-didehydrodibenzo[a,e]cyclooctene[6], **4**, have been shown to be planar by X-ray crystallography[7,8], while 5,6,9,10-tetradehydrobenzocyclooctene[9], **5**, has been demonstrated to possess a planar skeleton by examination of its electronic and NMR spectra[9]. On the hand, 6,7-didehydrobenzocyclooctene[10], **6**, 10-methyl-5,6-didehydrobenzocyclooctene[11], **7a**, 5,6-

didehydrodibenzo[a,c]cyclooctene[12], 8, as well as 13,14-didehydrotribenzo[a,c,e]cyclooctene[13], 9, were found to be so unstable that their independent isolation proved impossible. The existence of these transient species could only be inferred from their respective trapping products The syntheses of 1,2,5,6-tetradehydrocyclooctatetraene, 10 and 7,8-didehydrobenzocyclooctene, 11, are currently under investigation in our laboratories.



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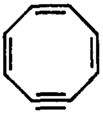

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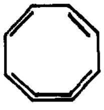

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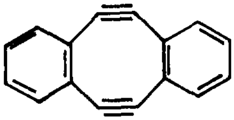

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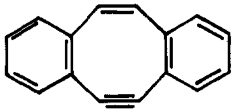

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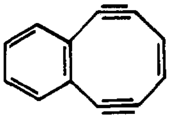

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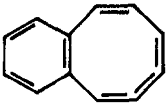

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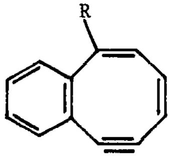
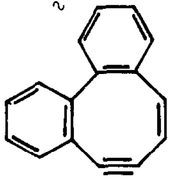


7 a, R=Me
b, R=H



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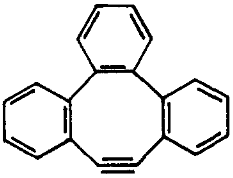

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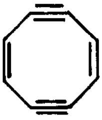

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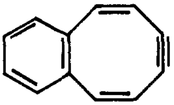
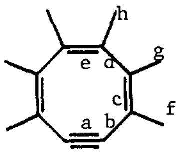


11

In this note, we report the results of MINDO/3[14] calculations on compounds 2, 6, 7b, 10 and 11. The structure of each species is optimized with respect to all relevant geometrical variables. The results (bond lengths in Å and bond angles in degrees) are summarized below.*

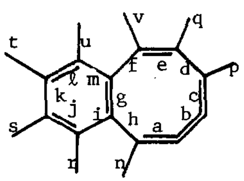


2 (C_{2v}), ΔH_f=107.6 kcal/mol.

a=1.22, b=1.42, c=1.35, d=1.49, e=1.36, f=1.11, g=1.11, h=1.12,

ab=150, bc=120, cd=129, de=141, fc=120, gc=118, he=111°.

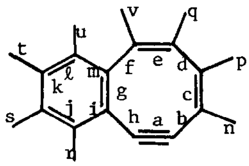
6 (C_s), ΔH_f=148.4 kcal/mol.



a=1.32, b=1.32, c=1.33, d=1.46, e=1.35, f=1.50, g=1.46, h=1.52, i=1.43, j=1.41, k=1.39, ℓ=1.41, m=1.41, n=1.11, p=1.11, q=1.12, r=1.11, s=1.10, t=1.11, u=1.11, v=1.12.

ab=168, bc=125, cd=128, de=135, ef=143, fg=134, gh=124, ha=123, ij=124, jk=118, kℓ=119, ℓm=125, mg=115, gi=119, nh=115, pd=113, qe=114, ri=118, sk=121, tk=121, um=119, vf=108.

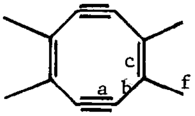
[*] It is of interest to note that MINDO/3 ΔH_f values for acetylene and allene are 57.8 and 42.0 kcal/mol, respectively. The experimental values are 54.3 and 45.6 kcal/mol, respectively.



7b (C_s), ΔH_f=126.5 kcal/mol.

a=1.22, b=1.42, c=1.35, d=1.49, e=1.36, f=1.51, g=1.46, h=1.44, i=1.41, j=1.41, k=1.40, ℓ=1.41, m=1.42, n=1.10, p=1.11, q=1.12, r=1.11, s=1.10, t=1.10, u=1.11, v=1.12.

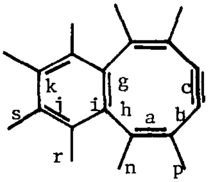
ab=149, bc=119, cd=128, de=141, ef=146, fg=125, gh=115, ha=157, ij=121, jk=120, kℓ=120, ℓm=121, mg=118, gi=119, nc=121, pc=118, qd=107, ri=120, sj=120, tℓ=120, um=120, ve=108.



10 (D_{2h}), ΔH_f=150.7 kcal/mol.

a=1.23, b=1.45, c=1.36, f=1.10.

ab=153, bc=117, fc=122.



11 (C_{2v}), ΔH_f=138.4 kcal/mol.

a=1.35, b=1.42, c=1.22, g=1.47, h=1.51, i=1.43, j=1.40, k=1.40, n=1.12, p=1.11, r=1.11, s=1.11.

ab=118, bc=149, gh=133, ha=139, gi=116, ij=126, jk=118, na=111, pa=121, ri=118, sj=120.

From the MINDO/3 results, the following points may be noted:

(i) All species were found to be planar. This is in agreement with the aforementioned speculation that the conversion of one or two ethylenic bonds into acetylenic bonds would make the eight-membered ring planar.

(ii) Judging from the results for 2, the structure of this compound should be described as acetylenic (2a) rather than cumulenic (2b). Indeed, no minimum corresponding to structure 2b could be located in the potential energy surface.

(iii) Whereas structures 2a and 2b have identical molecular topologies (i.e., the same arrangement of hydrogen atoms) and could conceivably interconvert through readjustment of the C-C bond lengths, this is not so for the pair of benzo derivatives 6 and 7b. The cyclic acetylene 7b was found to be thermodynamically more stable than the cumulenic isomer 6 by about 22 kcal/mol. Compound 11, with its acetylenic bond farthest away from the benzene ring, is also thermodynamically favored over 6, whose relative instability can be ascribed to severe bending of its cumulenic system from linearity. It may be concluded, then, that when two neighboring hydrogen atoms are removed from a cyclooctatetraene, the resulting planar eight-membered ring preferentially adopts the acetylenic structure.

(iv) In each of the benzo derivatives 6, 7b and 11, the common bond shared by the two rings is significantly lengthened in comparison with other bonds in the benzene moiety. Angular strain in the larger ring is somewhat reduced, and benzannelation thus enhances the stability of planar conjugated eight-membered carbocycles.

(v) The acetylenic bond angles in 2 and 11 are both very close to 150°. In compound 7b, the corresponding angles (ha=157° and ab=149°) differ as a result of unsymmetrical benannelation. Their mean value, however, is in good agreement with X-ray values of 152-156° found for the symmetrical dibenzannelated compound 4[8]. The acetylenic bond angle (153°) in 10 is slightly smaller than the corresponding angle (155.8°) in **3** as determined by crystal-structure analysis[7], and this is consistent with the notion of angular strain relief through benzannelation.

References and Notes

1. Dedicated to the memory of the late Prof. Franz Sondheimer, F.R.S.
2. Formerly spelled as H.N.C. Wong.
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