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SOME CYCLIC C_9H_6 ISOMERS AND THEIR POTENTIAL TREFOIL AROMATICITY

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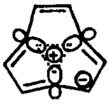
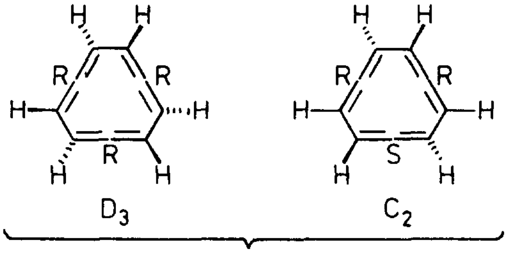
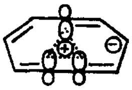
Summary: Cyclonona-1,2,4,5,7,8-hexaene (2) and cyclonona-1,2,4,8-tetraen-6-yne (4) are relatively strain-free according to MINDO/3 and MNDO calculations. The valence isomeric structures (1) and (3) with trefoil aromaticity are less stable by ∿100 and 37 kcal mol^{-1} respectively.

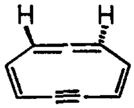
Fukunaga et al.[1] recently advanced the imaginative idea of trefoil aromaticity where a three-centre two electron bond is embedded in the plane of an annulene perimeter containing 4n+2 out-of-plane π-electrons. The principal example cited was [5.5.5]trefoilene (1), a valence isomer of the tris-allene (2). The three-centre two-electron bonding in (1)


(1)

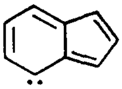


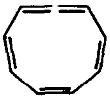
D3
C2
(2)

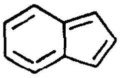

(3)



(4)


(5)


(6)


(7)

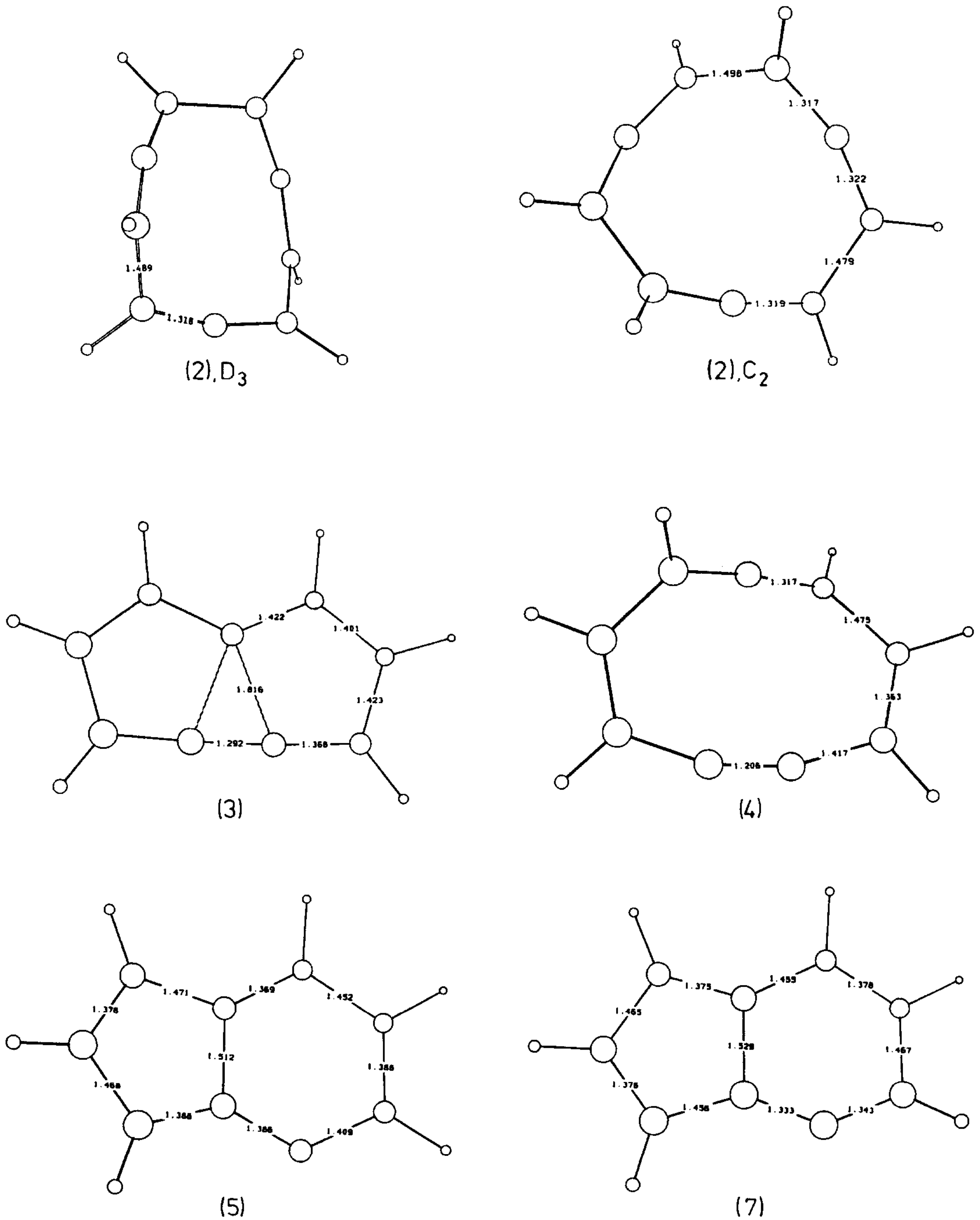

(8)


(9)

resembles that in the trishomocyclopropenyl cation[2] or in Coates cation.[3] Three-centre, two-electron bonding in which two of the centres are also directly σ-bonded is also well-known, e.g. in the 7-norbornenyl cation.[4] It occurred to us that this type of bonding might also be embedded in an annulene perimeter, e.g. (3) which in trefoil nomenclature would be [3.6.6]-trefoilene. The related classical structure is cyclonona-1,2,4,8-tetraen-6-yne (4). Although this structure looks exotic, it, or (3), might be the product of generation of carbene (5). Carbene (5) might, in turn, be reasonably accessible from indene precursors such as the interesting 4-diazoindene (4-diazoniumindenide). We now report MNDO calculations on (1)-(5) and some related species. Contrary to the impression given by Fukunaga et al.,[1] (1) is enormously less stable than (2), and the gap between classical and trefoil structures is much less for (3) and (4).

Fukunaga et al.[1] describe (2) as "non-planar and considerably strained" and later report a heat of formation for a species, drawn as (2), of 259 kcal mol^{-1} by MINDO/3. We were puzzled by this figure since MINDO/3 normally overestimates the stability of molecules containing sp carbons and a group additivity calculation for (2) gave ΔH_f 143 kcal mol^{-1}, ignoring ring strain. Two diastereosomers of (2) of D_3 and C_2 symmetry are possible and the D_3 isomer in particular appeared relatively strain-free from models. This was confirmed by MINDO/3 calculations which give ΔH_f 136.6 (152.5) and 150.3 (165.4) kcal mol^{-1} for the D_3 and C_2 isomers respectively after full geometry optimisation (MNDO figures are in brackets). The 259 kcal mol^{-1} figure reported by Fukunaga et al.[1] is for a planar structure (D_{3h} symmetry) with formal bonding as in (2); MNDO calculations on singlet D_{3h} (2) give a heat of formation of 260.2 kcal mol^{-1}, but also indicate a dipole moment of 2.5 Debye. The electronic configuration given by this calculation has 10 π electrons, leaving a total of 20 electrons for the carbon-carbon sigma orbitals and the in-plane lone pairs. The highest of these occupied sigma orbitals is, however, one of a degenerate (E') set, so that (2) in D_{3h} symmetry is an unusual sigma Jahn-Teller system. This is confirmed by a single point calculation for triplet (2) at the geometry found for the D_{3h} singlet. This gives a zero dipole moment and a heat of formation of 221 kcal mol^{-1} using the half-electron method. [5.5.5]Trefoilene (1), to which similar considerations may apply, is calculated to have D_{3h} symmetry by MNDO, with a heat of formation of 245.7 kcal mol^{-1}. The ordering of the sigma orbitals is, however, different to that in (2) so that (1) is not a Jahn-Teller system. Diagonalization of the force constant matrix of (1) at MNDO gives three negative frequencies, indicating that [5.5.5]trefoilene is neither a minimum nor a transition state. The negative vibrations lead to the D_3 and C_2 isomers of (2). We therefore conclude that (1) is not a real structure on the C_9H_6 energy surface.

Cyclonona-1,2,4,8-tetraen-6-yne (4) is a surprisingly strain-free molecule from molecular models. A group additivity calculation, without ring strain, gives ΔH_f 133 kcal mol^{-1}, while MNDO with full geometry optimisation gives ΔH_f 130.9 kcal mol^{-1}. MNDO may overestimate the stability of (4), but it is clearly almost strainless. The C_2 structure for (4) permits a substantial amount of conjugation of the two orthogonal π-bonds of the allene through the twisted dienyne unit. The chemical and spectroscopic consequences of this interesting structural feature are not obvious. As far as we are aware the only other species which has



(2),D_3 (2),C_2

(3) (4)

(5) (7)

Figure 1. MNDO structures for (2), D_3 isomer ΔH_f 152.5; (2), C_2 isomer ΔH_f 165.4; (3) ΔH_f 167.8; (4) ΔH_f 130.9; (5), ΔH_f 150.8 and (7) ΔH_f 144.6 kcal mol^{-1}.

been generated which could possess this feature is (6), but this underwent such rapid electrocyclic ring closure to 3aH-indene (and then conversion to indene), that it could not be directly observed.[5]

MNDO calculations have located three other minima related to (4) which may be described in terms of structures (3), (5), and the bicyclic allene (7). The trefoil aromatic (3) is very nearly planar but (5) and (7) are twisted (see Figure 1). Structures (5) and (7) might be described as bond-shift isomers. They are reminiscent of cycloheptatrienylidene (8) and cycloheptatetraene (9). A recent MNDO study[6] found (9) to be 23 kcal mol^{-1} more stable than (8), and indeed that (8) only represented the transition state for racemisation of (9).

MNDO calculations on the reaction path from (5) to (4) pass through (3) as a reaction intermediate, protected by very low barriers (<2 kcal mol^{-1}). Thus the chances of observation of (3) look remote, although it might be an intermediate in the racemisation of (4).

We conclude that trefoil aromaticity in hydrocarbons will be very difficult to substantiate. On a more positive note, our calculations suggest that some surprisingly strain-free highly unsaturated structures are possible within medium rings; in particular the preparation of (4) is an interesting challenge.

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