Does Chair Cyclo-octatetraene Exist?

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MINDO/3 and MNDO calculations are reported for chair cyclo-octatetraene (*cis*-1,5-*trans*-3,7-cyclo-octatetraene) and for its conversions into the normal tub (all *cis*) isomer and into bicyclo[4.2.0]octa-2,4,7-triene.

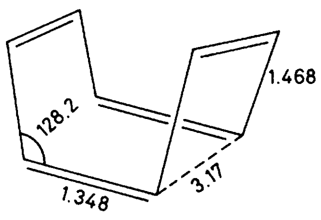
Studies of the normal tub isomer (**1**) of cyclo-octatetraene led us to speculate on the possible existence of its chair isomer (**2**).[1] Examination of models suggested that this should not be impossibly strained and that the barrier to its rearrangement to (**1**) could be quite large. The main threat to its existence seemed to be the possibility of cyclisation to bicyclo-[4.2.0]octa-2,4,7-triene, (**3**). We therefore carried out calculations for (**2**) and for its conversions into (**1**) and (**3**).

The calculations were carried out using the MINDO/3[2] and MNDO[3] SCF MO models as implemented in the MOPAC[4] package of programs. These have proved effective in numerous studies of reactions of hydrocarbons, giving results comparable with those from good *ab initio* methods. Use of any comparable *ab initio* procedure would in any case have been impracticable. Stationary points were characterised by calculating force constants[5] and all geometries were fully optimised, using the procedures included in MOPAC. The heats of formation calculated by both procedures for (**1**) and (**3**) are shown in Table 1 and the corresponding MNDO geometries in Figure 1. The MINDO/3 geometries are not reported because they differed minimally from the MNDO ones. Our calculations predict (**2**) to be less stable than (**1**) by *ca.* 240 kJ/mol (MINDO/3, *ca.* 245; MNDO, *ca.* 230 kJ/mol). This is no greater than the corresponding differences in energy between benzene and its valence isomers.†

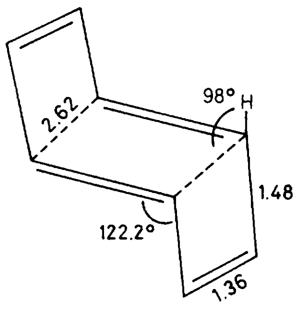
The conversion of (**2**) into (**1**) involves rotation about C=C bonds and must therefore involve a biradical like interme-

Table 1. MNDO and MINDO/3 heats of formation (kJ/mol) for (**1**)—(**5**).

	(1)	(2)	(3)	(4)	(5)
MNDO	236.15	467.35	269.03	721.74	531.37
MINDO/3	236.81	484.93	320.91	773.20	539.32



(1)



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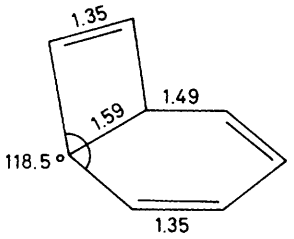

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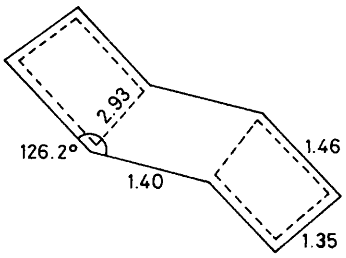

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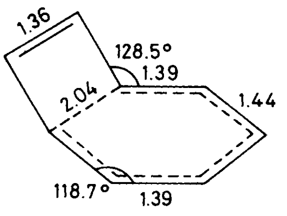

(5)

Figure 1. MNDO Geometries for structures (**1**)—(**5**) (bond lengths in Å, bond angles in degrees).

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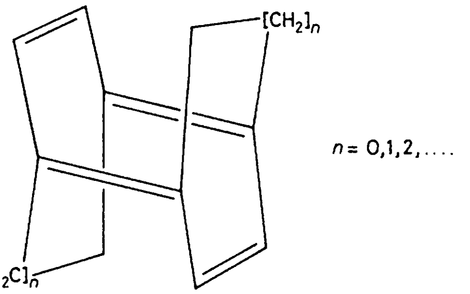
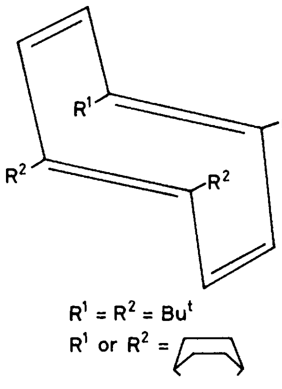
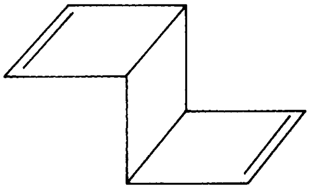
† The conversions of hexamethylDewar benzene and hexamethylprismane into hexamethylbenzene are exothermic by 235 and >375 kJ/mol, respectively. See L. T. Scott and M. Jones, Jr., *Chem. Rev.*, 1972, **72**, 181.



(**6**)



(**7**)



(**8**)

diate. However, the RHF versions of MINDO/3 and MNDO have been found[2,3] to give good estimates of the barriers to rotation about double bonds and therefore were used here. The transition state [TS; (**4**)] for (**2**) → (**1**) was located by a new procedure[6] recently developed here and included in MOPAC. The heats of formation calculated for (**4**) are shown in Table 1 and the MNDO geometry in Figure 1. The calculated barrier for conversion of (**2**) into (**1**) is therefore *ca.* 270 kJ/mol (MINDO/3, 288; MNDO, 255 kJ/mol). With respect to isomerization to (**1**), (**2**) should therefore be stable.

Next we studied the rearrangements of (**1**) and (**2**) to (**3**). Both reactions are effectively 'allowed', the TS in each case containing one aromatic ring and one antiaromatic one.[7] No problems arose in finding the TS for either reaction. Their calculated heats of formation (Table 1) correspond to activation energies of *ca.* 59 (MINDO/3, 54; MNDO, 64) kJ/mol for the rearrangement of (**2**) to (**3**) and *ca.* 194 (MINDO/3, 179; MNDO, 209) kJ/mol for that of (**1**) to (**3**).

The rearrangement of (**3**) to (**1**) is well known and its activation energy has been determined[8] experimentally (78 kJ/mol) and calculated[9] by MINDO/3 (95 kJ/mol). Our MNDO calculations led to a value (176 kJ/mol) which is much too large, presumably because of the known[3] tendency of MNDO to overestimate the stabilities of compounds containing four-membered rings. The heat of formation calculated for (**3**) by MNDO is clearly much too negative.

Our calculations therefore indicate that (**2**) itself will be a rather unstable species, surviving rearrangement to (**3**) only at low temperatures. Since (**3**) rearranges easily and exothermically to (**1**), the final product from (**2**) will be (**1**).

Figure 1 shows the geometry calculated for the TS (**5**) for conversion of (**2**) into (**3**). If the cyclisation to (**3**) can be hindered sufficiently by substituents [*e.g.* (**6**) or (**7**)], the corresponding derivative of (**2**) should be stable. A suitable precursor for the synthesis of (**6**) has appeared in the literature[10] and has also pointed to the possible 2 + 2 cyclisation of (**2**) to (**8**). While MINDO/3 predicts[9] the analogous cyclisation of (**1**) to have a very high activation energy, cyclisation of (**2**) would be assisted by relief of strain. Since (**8**) rearranges fairly readily to (**1**), apparently *via* the triplet state, this would provide a third route from (**2**) to (**1**).

Table 2. MNDO Vibrational frequencies for (**1**) and (**2**)[a] (in cm^{-1}).

(**2**)[b]	Symmetry	(**1**)[c]	Symmetry	Type
1693	A_g	1791	B_2	Stretch/compression/ motion
1710	B_u	1852	E	Asymmetric stretch
1768	A_u	1853	E	Asymmetric stretch
1783	A_g	1910	A_1	Symmetric stretch

[a] MNDO Vibrational frequencies are in error by *ca.* 10%. See reference 11. [b] C_{2h} Point group. [c] D_{2h} Point group.

We have also calculated the vibration frequencies of (**1**) and (**2**) as an aid to identification of the latter from its i.r.–Raman spectra. Since it gives better results, MNDO was used rather than MINDO/3 for C=C vibrational modes.[11] Table 2 shows the results. The most striking differences appear in the C=C stretching modes, the frequencies for (**2**) being much less. This of course reflects the weakening of the *trans* C=C bonds in (**1**), because of their nonplanarity.

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