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# SHORT COMMUNICATION

# HOMOAROMATICITY OF DECAMETHYL [5] PERICYCLYNE

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**It is shown that a theoretical computation of the Dewar resonance energy of decamethyl [5] pericyclyne should give the same value for the homoaromaticity of this compound as that calculated earlier from heat of hydrogenation measurements. Both methods show this quantity to be small, but the accuracy of the methods appears insufficient for more exact agreement.**

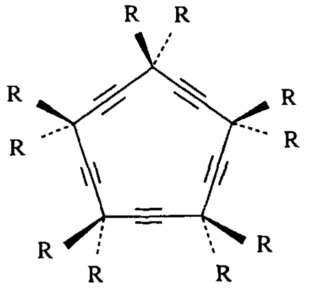
In 1988 Scott *et al.*[1] found that the heat of hydrogenation in the series of acyclic alkynes (**1**, $R = CH_3$) decreases linearly with $n$ from $n = 2$ to 5 with a least-squares slope of $-69 \cdot 8$ kcal mol$^{-1}$ (1 kcal = 4·184 kJ) per triple bond. The difference between five times this quantity ($-349 \cdot 0$ kcal mol$^{-1}$) and the heat of hydrogenation ($-340 \cdot 7$ kcal mol$^{-1}$) of decamethyl [5] pericyclyne (**2**, $R = CH_3$) was corrected for 2 kcal mol$^{-1}$ of extra strain in the cyclic hydrogenation product to give a remainder of 6 kcal mol$^{-1}$, which was taken to be the homoaromatic stabilization of **2** ($R = CH_3$). However, changes in heats of hydrogenation did vary in the series **1** ($R = CH_3$) and using, for example, $-68$ kcal mol$^{-1}$, the change from $n = 4$ to 5, instead of the average slope would make **2** ($R = CH_3$) *anti*-homoaromatic by 3 kcal mol$^{-1}$.

This uncertainty and recent discussions of homoaromaticity in triquinacene[2–6] led us to a theoretical reinvestigation of the homoaromaticity of **2**. To shorten computations by avoiding an extreme number of rotomers, R in **1** and **2** was made hydrogen. This is assumed to have no significant effect on the energy differences calculated. We computed the resonance energy of **2** ($R = H$) using a Dewar energy reference.[7–9]

The program CADPAC 4.0[10] was used to optimize the structures of **1** ($R = H$) in RHF/3–21G calculations

$$CR_3 \left( C \equiv C - CR_2 \right)_n R$$

**1**



**2**

on the completely antiperiplanar conformations for $n = 2$ to 5. Optimum structures have $C_{2v}$ symmetry for even $n$ and $C_{2h}$ for odd $n$. The cyclic alkyne **2** ($R = H$) was optimized in $D_{5h}$ symmetry. Harmonic frequencies were calculated for this best $D_{5h}$ structure, and all were found to be real. This shows two things. First, CADPAC, like most such programs, does not search directly for a structure of minimum energy but rather for a structure of zero-energy derivative with respect to all geometry parameters. Transition structures and maxima and also minima all have this property, but only for minima are all eigenvalues of the force constant positive and hence all frequencies real. Second, the force constant matrix tests distortions that destroy in addition to those that preserve the symmetry assumed in the optimization. Since all frequencies are

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real, the minimum energy $D_{5h}$ structure is minimum even relative to non-$D_{5h}$ structures. All optimum (i.e. zero-gradient) structures reported below were similarly tested. The frequencies and geometries of the optimum structures were then used to calculate partition functions and gas-phase enthalpies at 298 K relative to separated electrons and nuclei at rest in the rigid-rotor, harmonic-oscillator approximation. These are collected in Table 1.

The homoaromaticity of **2** will be seen to depend on fairly small energy differences. Because of this, it would be desirable to use a basis larger than 3–21G and also to test the accuracy of our assumption that these energy differences are not affected by the replacement of hydrogen by methyl. Unfortunately, even with these simplifications the SCS 40 computer whose vector speed is 35–40 MFLOPs required about 72 h of running time for the computation of the frequencies of **2**, so that more complete computations are not possible.

The Dewar model for aromaticity is applied by first making a least-squares fit to the enthalpies of the open-chain compounds in Table 1. This gives a slope of $-114{\cdot}028733$ a.u. per —C ≡ C—CH$_2$— unit and a standard deviation of the points of $2{\cdot}1\times10^{-5}$ a.u. $=0{\cdot}01$ kcal mol$^{-1}$ (the current value[11] of 1 a.u. of energy $=627{\cdot}50955$ kcal mol$^{-1}$ is used). Compound **2** (R = H), [5]pericyclyne, consists of five such units and, in the absence of special stability, should have an enthalpy of $5(-114{\cdot}028733) = -570{\cdot}143665$ a.u. The actual enthalpy is computed to be higher by $1{\cdot}472\times10^{-3}$ a.u. = 1 kcal mol$^{-1}$. Hence these RHF/3–21G calculations predict [5]pericyclyne to be antihomoaromatic by 1 kcal mol$^{-1}$ (the use instead of the uncorrected potential energy minima predicts an antiaromaticity of $2{\cdot}3$ kcal mol$^{-1}$).

Table 1. RHF/3–21G energies of the conjugated alkynes **1** and **2** (R = H)

| Compound | $E$ (a.u.)[a] | $H_{298}$ (a.u.)[b] |
|---|---|---|
| Heptadiyne (**1**, $n=2$) | $-268{\cdot}127856$ | $-267{\cdot}984662$ |
| Decatriyne (**1**, $n=3$) | $-382{\cdot}202043$ | $-382{\cdot}013432$ |
| Tridecatetrayne (**1**, $n=4$) | $-496{\cdot}276176$ | $-496{\cdot}042149$ |
| Hexadecapentayne (**1**, $n=5$) | $-610{\cdot}350308$ | $-610{\cdot}070865$ |
| [5]Pericyclyne | $-570{\cdot}367116$ | $-570{\cdot}142193$ |

[a] Energy of minimum on potential energy surface.
[b] Gas-phase enthalpies relative to separated electrons and nuclei at rest.

To see that the homoaromaticity calculated in this way should agree with that determined by Scott *et al.*[1] from heats of hydrogenation, consider Figure 1. Let $H_i$ be the enthalpy of the alkyne **1** ($n=i$) and $\mathscr{H}_i$ the enthalpy of the corresponding alkane. These depend on R, but it will be assumed that the enthalpy differences in Figure 1 are independent of whether R is H or CH$_3$. The data in Table 1 show that $\Delta H_i \equiv (H_{i+1}-H_i)$ is independent of $i$. Call this difference $\Delta H$. Experiment[1] shows that $(\Delta H_{i+1}^{\text{hyd}} - \Delta H_i^{\text{hyd}}) \equiv \Delta(\Delta H^{\text{hyd}})$ is constant. It follows that $\Delta\mathscr{H}_i \equiv (\mathscr{H}_{i+1}-\mathscr{H}_i) = \Delta H + \Delta(\Delta H^{\text{hyd}})$ is also constant. Call this $\Delta\mathscr{H}$. Scott *et al.*[1] define the homoaromatic stabilization energy of **2**, $\Delta H_1^{\text{res}}$, a positive quantity, by

$$\Delta H_1^{\text{res}} = \Delta H_c^{\text{hyd}} - 5\,\Delta(\Delta H^{\text{hyd}}) - 2 \qquad (1)$$

where $\Delta H_c^{\text{hyd}}$ is the heat of hydrogenation of **2**. With a Dewar reference homoaromatic stabilization $\Delta H_2^{\text{res}}$ is defined instead:

$$\Delta H_2^{\text{res}} = 5\,\Delta H - H(\text{cyclic alkyne } \mathbf{2}) \qquad (2)$$

However, $\Delta H = \Delta\mathscr{H} - \Delta(\Delta H^{\text{hyd}})$, and the quantity $5\,\Delta\mathscr{H}$ is the enthalpy of the unstrained hydrogenation product of **2**, which is taken to be 2 kcal mol$^{-1}$ lower than the actual strained product, so that

$$\Delta H_2^{\text{res}} = H(\text{cyclic alkane}) - H(\text{cyclic alkyne}) - 5\,\Delta(\Delta H^{\text{hyd}}) - 2 \qquad (3)$$

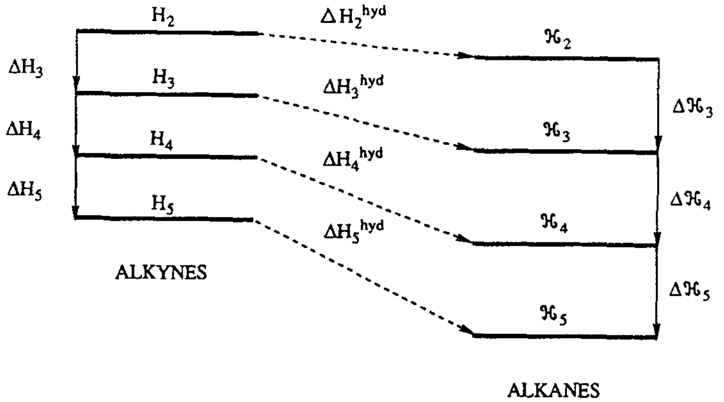

Figure 1. Relative enthalpies. $H_i$ is the enthalpy of **1** ($n=i$) and $\mathscr{H}_i$ is that of the corresponding product of hydrogenation

The first two terms in equation (3) are just the heat of hydrogenation of **2** so that $\Delta H_2^{\rm res} = \Delta H_1^{\rm res}$ and equations (1) and (2) are equivalent.

The disagreement between the 6 kcal mol$^{-1}$ experimental value and the $-1$ kcal mol$^{-1}$ theoretical value for the homoaromaticity of **2** moves us to conclude that the magnitude of the homoaromaticity, whether positive or negative, is probably not large, and that the accuracy of the methods used, either theoretical or experimental or both, is insufficient to fix the quantity more accurately.

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