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Heats of Formation of the [16]Annulene Dianion and Neutral Molecule

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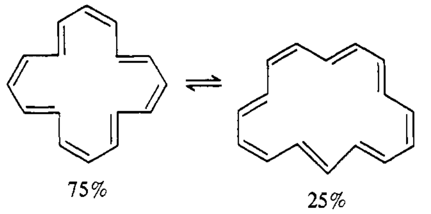
Abstract: The enthalpy of reaction of the disodium salt of [16]annulene with water and the heat of combustion of neutral [16]annulene were both measured calorimetrically. These measurements were utilized in a thermochemical cycle to yield the heat of reaction of sodium metal with [16]annulene to give the solid dianion salt. The enthalpy of reaction of the dianion with water (−10.9 kcal/mol) is much less exothermic than that for the dianion of [8]annulene. The results indicate that the [16]annulene dianion is greatly stabilized via aromatization. Further, its relative thermodynamic stability over that of the [8]annulene dianion has been attributed to a reduced electron–electron repulsion force in the larger annulene dianion. The combustion measurements indicate that the neutral [16]annulene does not possess any conjugative stability. The heat of combustion of [16]annulene (−2182.2 kcal/mol) is more exothermic by 9 kcal/mol than that for two [8]annulenes.

Introduction

Since the Reppe synthesis of cyclooctatetraene in 1948,[1] the first annulene containing $4n$ π electrons to be synthesized is [16]annulene.[2] Unlike [8]annulene which exists in a tube conformation,[3] [16]annulene has been shown to exist as a dynamic equilibrium between two interconverting configurations (see eq 1), each having double and single bond alternation.[4]



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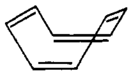
[8]Annulene (structure I) lacks conjugative stabilization that



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planar aromatic molecules possess. Since [8]annulene consists simply of a benzene ring expanded by one ethylene group with elimination of the aromaticity, the resonance energy of benzene can be estimated by comparing the heat of combustion of [8]-annulene minus one ethylene with that of benzene ([6]annulene).

$$C_6H_6 + {}^{15}/_2O_2 \rightarrow 6CO_2 + 3H_2O \quad \Delta H_1^\circ = -780.9 \text{ kcal/mol} \quad (2)$$

$$C_8H_8 + 10O_2 \rightarrow 8CO_2 + 4H_2O \quad \Delta H_2^\circ = 1086 \text{ kcal/mol} \quad (3)$$

Since [8]annulene is effectively unconjugated and contains four ethylene groups, the enthalpy of combustion of three ethylene functions would be $\Delta H_3^\circ = {}^3/_4\Delta H_2^\circ$.

$$C_6H_6 \text{ (unconjugated)} + {}^{15}/_2O_2 \rightarrow 6CO_2 + 3H_2O \quad \Delta H_3^\circ = -814.5 \text{ kcal/mol} \quad (4)$$

The difference between ΔH_1° and ΔH_3° represents the resonance energy of the benzene ring, assuming a zero-resonance energy for the cyclooctatetraene ring. Actually, the cyclooctatetraene ring system has about 4 kcal/mol of resonance energy.[5] Thus, our value is too low by $^3/_4 \times 4$ kcal/mol. This comparison of benzene to [8]annulene yields a resonance energy for benzene of 814.5 − 780.9 + 3 = 36.6 kcal/mol, which is in excellent agreement with the accepted value.[6]

In the Hückel sense both [8]annulene and [16]annulene are antiaromatic. However, both of these neutral annulenes will react with alkali metals to form the corresponding aromatic dianion, each containing $(4n + 2)$ π electrons.[7,8] The heats of formation of neither [16]annulene nor its dianion are known. Here, we wish to report both of these heats of formation and the insight that these measurements have yielded into the aromatic nature of these 16- and 18-π-electron systems. The comparison of the thermodynamic stabilities of the [16]annulene neutral molecule and dianion to those for [8]annulene has been carried out in a manner analogous to that described above for [8]annulene and [6]annulene.

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(1) Reppe, W.; Schlichting, O.; Klager, K.; Toepel, T. *Annalen* **1948**, 560.

(2) Sondheimer, F.; Gaoni, Y. *J. Am. Chem. Soc.* **1961**, *83*, 4883.

(3) Katz, T. J.; Strauss, H. L. *J. Chem. Phys.* **1960**, *32*, 1873.

(4) Oth, J. F. M.; Gille, J. M. *Tetrahedron Lett.* **1968**, 6259.

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(7) Strauss, H. L; Katz, T. J.; Fraenkel, G. K. *J. Am. Chem. Soc.* **1963**, *85*, 2360.

(8) Oth, J. F. M.; Bauman, H.; Gilles, J. M.; Schroder, G. *J. Am. Chem. Soc.* **1972**, *94*, 3498.

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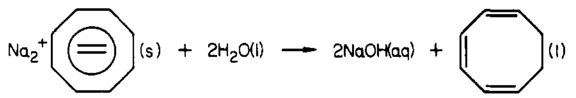
The most common method of obtaining the heat of formation of any compound involves the measurement of the heat of combustion. Here we report the heat of combustion of [16]annulene. However, heats of combustion are not often practical to measure for organometallic compounds,[9] especially those that are air sensitive as is the [16]annulene dianion. The heat of formation of the [8]annulene dianion was measured indirectly through its heat of reaction with water (eq 5).[10] We have applied this technique to the dianion of [16]annulene (eq 6).



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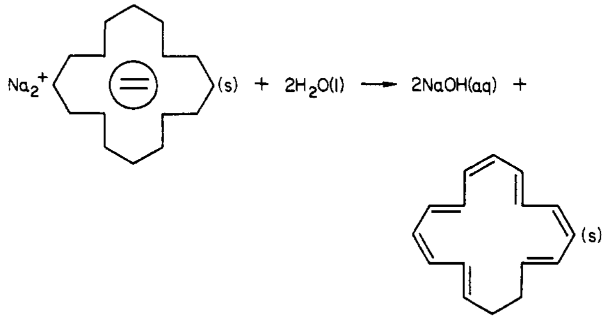

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Experimental Section

[16]Annulene was prepared by the photolysis of the 2 + 2 dimer of cyclooctatetraene (COT) as described by Sondheimer and Gaoni.[11] The product was recrystalized from an ethanol–ether mixture to yield deep purple crystals. These crystals were then kept under high vacuum for several hours to remove any traces of solvent. They were then stored at liquid-nitrogen temperatures until use.

An NMR was taken for each batch of [16]annulene just prior to submitting it to a calorimetry experiment, and only the NMR line at 6.73 ppm for the [16]annulene could be observed for each sample fired in the calorimeter. Even with the [16]annulene NMR line magnified by a factor of 10 off scale, no impurity resonances could be observed.

The combustions were carried out in a twin-valve bomb (Parr Instrument Co.). The solid [16]annulene was sealed into gelatin capsules (Parr Instrument Co.) for firing. After the bomb was charged with the capsule containing the annulene, 7 mL of water, and 30 atm of oxygen, the sample was fired in the adiabatic calorimeter at 25 °C. The measured ΔE of combustion was corrected with the $(\Delta n)RT$ term to give the heat of combustion of [16]annulene, which refers to the enthalpy for eq 7.

$$C_{16}H_{16}(s) + 20O_2(g) \rightarrow 16CO_2(g) + 8H_2O(l) \qquad (7)$$

Tetrahydrofuran (THF) solutions of the [16]annulene dianion were generated under vacuum via sodium reduction of the neutral annulene in the apparatus shown in Figure 1. The ESR spectrum of the solution was monitered during the reduction, which was identical with that previously reported.[8] After complete reduction to the dianion the sample would not yield an ESR spectrum. At this point an NMR sample was sealed from the apparatus. Even though the dianion solutions in THF were quite dilute, it was demonstrated that the annulene dianion NMR spectra were identical with those reported by Oth et al.[8] prior to taking a calorimetery sample. The THF was then removed from the dianion by freezing blub A in liquid nitrogen after passing the completely reduced solution into bulb B. The solid dianion was then sealed into the thin-walled evacuated glass bulbs, which were subsequently crushed under 100 mL of deoxygenated water in the solution calorimeter as previously described.[12] Samples of the dianion salt were also broken under D_2O from which NMR samples were taken. These D_2O solutions did not exhibit the presence of THF. The amount of dianion that reacted in the calorimeter or with the D_2O was determined by titrating the resulting water solutions with standardized HCl. The number of moles of dianion that had reacted was taken as half of the number of moles of HCl used in the titration.

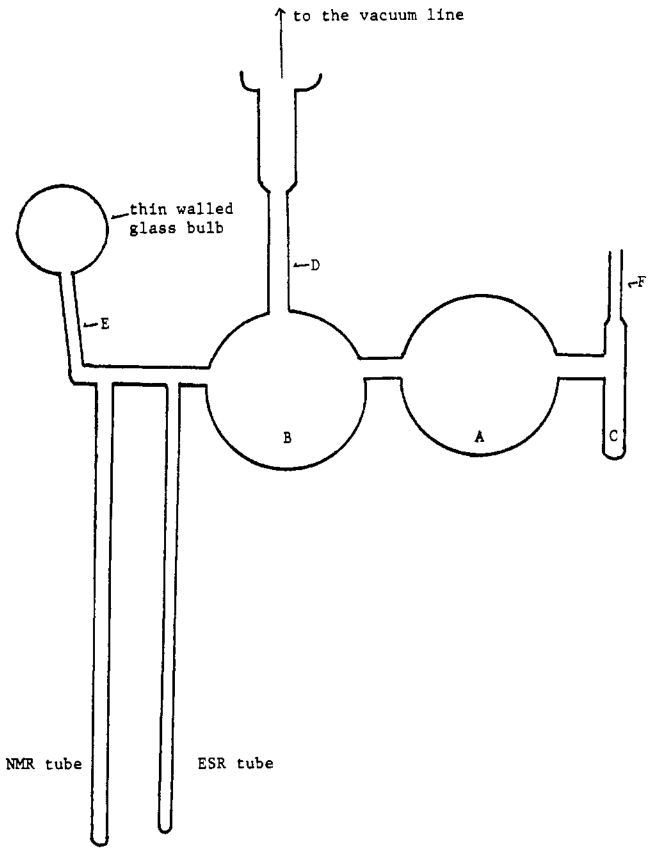

Figure 1. Apparatus used for the reduction of [16]annulene. The sodium metal was distilled from tube C into bulb A after sealing at point F under high vacuum. The apparatus was removed from the vacuum line by sealing at point D. Calorimetry samples were taken by sealing a sample of the solid dianion in the thin walled glass bulbs, which were sealed off at point E. The THF was not removed from the dianion salt until the dianion was completely formed as evidenced by the disappearance of the ESR signal and the appearance of the NMR signal for the dianion.

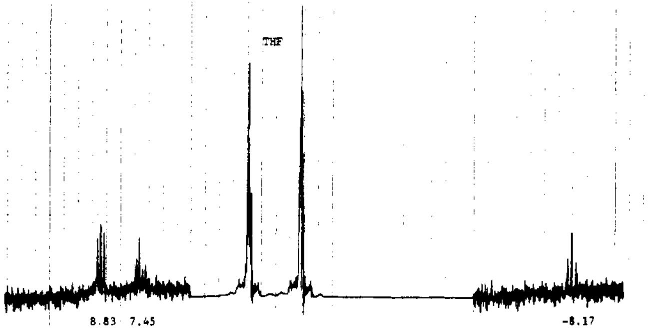

Figure 2. NMR spectrum of a dilute solution of the [16]annulene dianion in THF. The sample was prepared in the apparatus shown in Figure 1. It took about 3 days to generate these solutions, which were recorded at 35 °C. The chemical shifts are listed in parts per million. The spectrum amplitude was reduced to record the THF lines.

NMR spectra were recorded on a Perkin-Elmer 90 MHz spectrometer, and the ESR spectra were recorded on a Varian E-4 ESR spectrometer.

The experimental errors reported for the enthalpies of reaction of the dianions with water are propagated from the standard deviation of the error in the slope of the line generated from a plot of the change in the temperature of the calorimeter vs. the millimoles of dianion salt.[8] The error reported in the heat of combustion of [16]annulene simply represents the standard deviation in the four measurements.

Results and Discussion

The [16]annulene dianion reacts with water to give the dihydro annulene (possibly a mixture of isomers) that appears as a yellow solid. The yellow dihydro annulene can be isolated from the

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[9] Good, W. D.; Scott, D. W.; Waddington, G. *J. Phys. Chem.* **1956**, *60*, 1080.

[10] (a) Stevenson, G. R.; Ocasio, I.; Bonilla, A. *J. Am. Chem. Soc.* **1976**, *98*, 5469. (b) Stevenson, G. R.; Ocasio, I. *Tetrahedron Lett.* **1976**, 427.

[11] Stevenson, G. R.; Valentin, J.; Williams E.; Caldewell, G.; Alegria, A. E. *J. Am. Chem. Soc.* **1979**, 101, 515.

[12] Stevenson, G. R.; Williams, E.; Caldwell, G. *J. Am. Chem. Soc.* **1979**, *101*, 520.

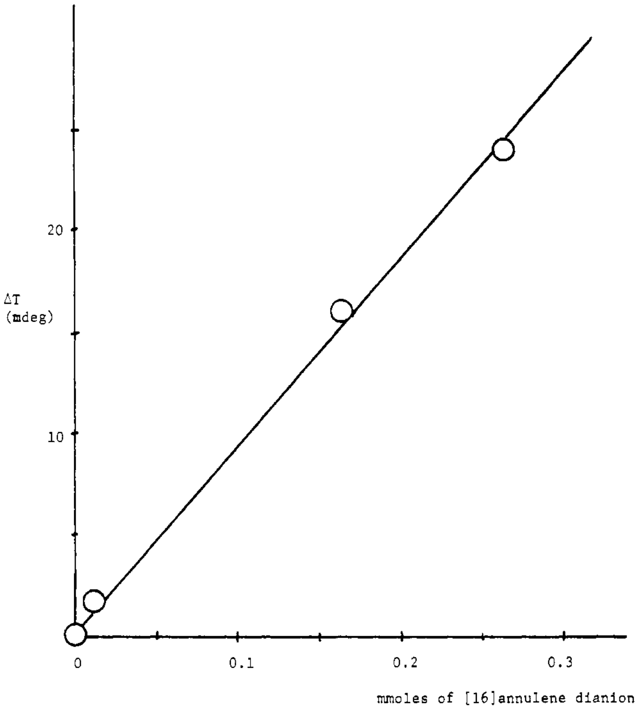

Figure 3. Plot of the change in the temperature of the calorimeter vs. the millimoles of solid sodium [16]annulene dianion salt in the glass bulbs. The slope of this line is proportional to the enthalpy of reaction of the salt with water. The proportionality constant is 119.3 cal/deg. The standard deviation in the slope of this line is 0.002, and the slope is 0.09114 deg/mmol. Propagating this error into the enthalpy yields 10.9 ± 0.3 kcal/mol for the enthalpy of the reaction of the salt with water (eq 6).

reaction mixture taken from the calorimeter by ether extraction.

When a plot of the change in temperature of the calorimeter vs. the quantity of dianion salt in the evacuated glass bulbs is compared to a similar plot for the disodium [8]annulene dianion,[11] *it is found that the [16]annulene dianion reacts less than one-third as exothermically with water as does the [8]annulene dianion* (Figure 3). The enthalpy of the reaction depicted in eq 6 is −10.9 ± 0.2 kcal/mol.

These calorimetry data indicate that the COT dianion is much less thermodynamically stable than is the [16]annulene dianion. This fact was confirmed via a simple NMR experiment. We generated the dianion of COT in hexamethylphosphoramide (HMPA) with sodium metal. An NMR sample of this dianion solution exhibited the single resonance for the dianion at 5.68 ppm. An equal molar portion of [16]annulene was then added to the COT dianion solution via a break-seal. After the addition of the [16]annulene, a large signal appeared for the COT neutral molecule. The presence of this neutral [8]annulene NMR line is necessarily due to the oxidation of the [8]annulene dianion by neutral [16]annulene to yield the [16]annulene dianion and neutral COT. The NMR signal for the [16]annulene dianion could not be observed due to rapid electron transfer with small amounts of the anion radical. This NMR experiment shows that the reaction depicted in eq 8 is shifted far to the right in agreement with the calorimetry results.

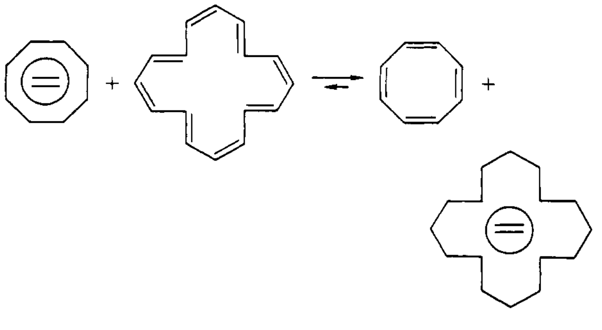

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Table I. Experimental Heats of Combustion of [16]Annulene

wt of sample, g	ΔT,[a] deg	$\Delta H_c°$,[b] kcal/mol	ΔE_c,[c] cal
0.0553	0.473	−2184.3	−540.804
0.1388	0.835	−2181.5	−540.804
0.2670	1.401	−2178.4	−540.804
0.3230	1.645	−2184.4	−540.804

[a] In converting these temperature changes in the calorimeter to the enthalpies of combustion, a correction for the unused fuse wire had to be made. [b] The average heat of combustion is −2182.2 ± 2.8 kcal/mol; for eq 7. [c] For the gelatin capsule.

Table II. Heats of Combustion ($\Delta H_c°$) and Heats of Hydrogenation ($\Delta H_{H_2}°$)

compd	$\Delta H_c°$, kcal/mol	$\Delta H_{H_2}°$,[b] kcal/mol	ref
[6]annulene	−780.97	+5.6	14
[8]annulene	−1086.5	−25.6	5
[16]annulene	−2182	≃−28[a]	this work
[18]annulene	−2347		15
cyclooctane	−1258.4		14
cyclohexadecane	−2501.4		14
cyclooctene		−23.5	14

[a] See discussion. [b] These are the enthalpies of hydrogenation of the first double bond only and represent solution values.

Scheme I

	$\Delta H°$, kcal/mol
$C_8H_8 + 10O_2 \rightarrow 8CO_2 + 4H_2O$	−1086.5
$8CO_2 + 8H_2O \rightarrow C_8H_{16} + 12O_2$	+1258.4
$4H_2 + 2O_2 \rightarrow 4H_2O$	−273.26
$[8]\text{annulene} + 4H_2 \rightarrow C_8H_{16}$	−101.4

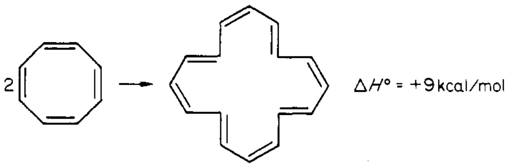
Shortage of sample allowed only four successful combustions to be carried out. This difficulty resulted in our experimental error being a little larger than 0.1%, whereas errors less than 0.1% should be strived for in combustion calorimetry.[13] The results of these four combustions are listed in Table I.

Table II shows the heats of combustion ($\Delta H_c°$) and heats of hydrogenation for the compounds needed for the comparison of the [16]annulene data.

Conclusions

For annulenes that are antiaromatic in the Hückel sense and exhibit very poor delocalization of π electrons, the heat of hydrogenation of a single double bond can be simply calculated from the heat of combustion of the annulene and the completely hydrogenated compound. For example, the heat of hydrogenation of [8]annulene to yield cyclooctatriene (C_8H_{10}) can be calculated from the thermochemical cycle given in Scheme I and the data given in Table II. Considering the lack of conjugation in [8]-annulene, the heat of hydrogenation of a single double bond must be −101.4/4 = −25.3 kcal/mol. Note, this is very close to that measured directly (Table II).

It is apparent from the heat of combustion data in Table II that [16]annulene does not possess any extra stabilization due to π-electron delocalization. In fact its heat of combustion is 9 kcal/mol more exothermic than that for two cyclooctatetraenes (eq 9). We



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are assumming that there are no energy changes except for those of conjugation. In reality, the heats of vaporization and any strain

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[13] Wilberg, K. B. In "Determination of Organic Structures by Physical Methods"; Nachod, F. C., Zuckerman, J. J., Ed.; Academic Press: New York, 1971; Chapter 4.

Scheme II

	$\Delta H°$, kcal/mol
$H_2[16](s) + 2NaOH(aq) \rightarrow Na^+{}_2[16]^{2-}(s) + 2H_2O(l)$	$+10.9 \pm 0.3$
$[16](s) + H_2(g) \rightarrow [16]H_2$	-28
$2Na°(s) + 2H_2O(l) \rightarrow 2NaOH(aq) + H_2(g)$	-88.2
$2Na°(s) + [16](s) \rightarrow Na^+{}_2[16]^{2-}(s)$	-105 ± 4 (estimated error)

energies are incorporated into this enthalpy. However, both annulenes are distorted from planarity and have little strain energy. Further, both are hydrocarbons and the heat of vaporization of COT should be very close to half of that for [16]annulene. See the examples in ref 14. It is interesting to note that [18]annulene burns just 4 kcal/mol more exothermically than does three benzenes, indicating that it is indeed stabilized by aromatization.[15]

A similar procedure is used to yield the heat of hydrogenation of [16]annulene as shown above for the [8]annulene system. With use of the enthalpy of combustion of cyclohexadecane, the heat of hydrogenation of [16]annulene turns out to be −28 kcal/mol.

From the heat of hydrogenation of [16]annulene and the heat of reaction of its dianion with water, the thermochemical cycle given in Scheme II can be constructed to yield the enthalpy of reaction of Na^0 with [16]annulene ([16]) to form the sodium dianion salt ($Na^+{}_2[16]^{2-}$).

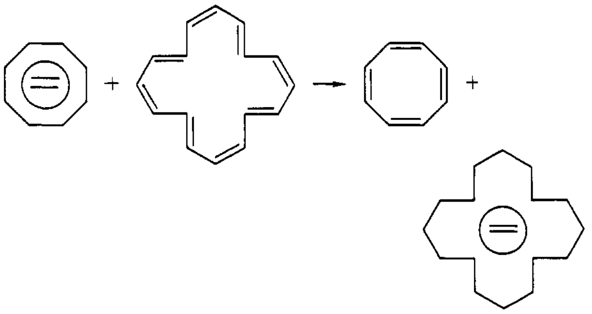
Only two other dianion salts have been studied in this manner, that of COT and that of anthracene.[11] A comparison of the enthalpies is shown in Table III.

Table III. Enthalpies of Reaction

reaction[a]	$\Delta H°$,[b] kcal/mol anthracene	 COT	 [16]-annulene
$Na^+{}_2X^{2-}(s) + 2H_2O(l) \rightarrow XH_2 + 2NaOH(aq)$	−79.1	−33.3	−10.9
$2Na^0(s) + X \rightarrow Na^+{}_2X^{2-}(s)$	−26.1	−81.1	−105

[a] XH_2 represents a solid when X = anthracene or [16]annulene and a liquid when X = COT. [b] The standard errors in the enthalpies are 0.9, 0.8, and 0.3 for X = anthracene, COT, and [16]annulene, respectively, for the reaction with water.

In agreement with the theory expounding the extra thermodynamic stability of $4n + 2$ π-electron systems, both the COT and [16]annulene dianions react much less exothermically with water than does the anthracene dianion and both annulene dianions form much more exothermically from their neutral molecules via sodium reduction. The fact that the dianion of [16]annulene forms more exothermically than does the dianion of [8]annulene by 24 kcal/mol (eq 10) is probably accounted for by the much weaker electron–electron repulsion forces in the larger dianion. Of course the crystal lattice energies of the two dianions are of considerable importance in controlling the enthalpy of the reaction depicted in eq 10, but it is expected that the smaller dianion would have the larger crystal lattice energy. Thus, the intermolecular factor would tend to make the enthalpy of the reaction (eq 10) positive.


(10)

In conclusion, the dianion of [16]annulene clearly exhibits a strong stabilization due to its aromatic character (18 π electrons), this stabilization is aided by the relatively weak electron–electron repulsion forces, and the neutral molecule does not show any extra thermodynamic stability over that of other nonconjugated olefins such as COT. The actual heats of formation of the [16]annulene dianion and neutral molecule are 26 ± 5 and 131.3 ± 3.0 kcal/mol, respectively.

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(14) Cox, J. D.; Pilcher, G. "Thermochemistry of Organic and Organometallic Compounds"; Academic Press: New York, 1970.

(15) Beezer, A. E.; Mortimer, C. T.; Springall, H. D.; Sondheimer, F.; Wolovsky, R. *J. Chem. Soc.* **1965**, 6970.