J. Phys. Chem. **1983**, *87*, 895–898

Relative Thermodynamic Stabilities of 1,6-Methano[10]annulene, Dinorcaradiene, and the 1,6-Methano[10]annulene Anion Radical

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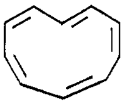
The enthalpies of reaction of both the solvated and solid salts of the potassium 1,6-methano[10]annulene (M10) anion radical were measured with calorimetric techniques. These measurements show that the anion radical of M10 has a surprising degree of thermodynamic stability. The heat of formation of $K^+M10^{-}\cdot_{(s)}$ from gas-phase potassium and gas-phase hydrocarbon (–61.9 kcal/mol) is about 16 kcal/mol more negative than that for the solid potassium salt of the naphthalene anion radical. Combustion experiments were used to show that the open form of M10 is about 5.7 kcal/mol lower in energy than dinorcaradiene.

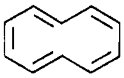
Introduction

Soon after the structure of benzene was proposed by Kekule[1] in 1865, chemists began to suspect that this hydrocarbon might not be unique in its properties, but rather the first member in a series of cyclic, conjugated polyenes similarly endowed with enhanced stability. The simplest vinylogue of benzene, which is predicted to be aromatic by the Hückel rule, contains 10 π electrons and is cyclodecapentaene ([10]annulene). Although HMO theory predicts that [10]annulene should exhibit aromatic stabilization, synthetic attempts to isolate [10]annulene have failed until recently.

Masamune successfully isolated isomers I and II of


I


II


III

[10]annulene at –80 °C and thus ended the long search for these elusive compounds.[2] Both of these isomers undergo ring closure upon warming. So that the planarity necessary to allow π electron delocalization can be achieved, I suffers from severe bond angle (144°) strain, while II and III suffer from nonbonded steric respulsion of the internal protons. After the work of Masamuni, it remained clear that both I and II are highly reactive, nonplanar, olefinic systems with no aromatic stabilization.

The supposition that nonbonded interactions must negate any gain in energy attained by π electron delocalization has been supported by the synthesis of the aromatic 1,6-methano[10]annulene (M10) by Vogel and Roth in 1964.[3] The problem of steric nonbonded interactions was eliminated by the introduction of a methylene bridge across the 1,6 positions. X-ray diffraction work has revealed the near planar geometry of M10.[4] The C–C bond lengths in the periphery of the ring exhibit no significant alternation and lie in the range of 1.40 Å.[5] The ^1H NMR resonances at 7.2 ppm for the ring protons and –0.5 ppm for the methylene protons are very indicative of a diatropic ring current.[3]

The HMO treatment of M10 is very similar to the treatment of [10]annulene, the only difference being the slight perturbation introduced by the bridging methylene group in M10.[6] The methylene bridge is electron releasing and should have no effect upon ψ_-, while ψ_+ should be significantly destabilized (eq 1 and 2).[6]

$$\psi_+ = 0.447(\phi_1 - \phi_6) - 0.138(\phi_2 - \phi_5 - \phi_7 + \phi_{10}) - 0.362(\phi_3 - \phi_4 - \phi_8 + \phi_9) \quad (1)$$

$$\psi_- = 0.425(\phi_2 + \phi_5 - \phi_7 - \phi_{10}) + 0.236(\phi_8 + \phi_9 - \phi_3 - \phi_4) \quad (2)$$

These predictions are well substantiated by the ESR spectra of $M10^{-}\cdot$ and its deuterated derivatives,[7] which indicate that the unpaired electron in the anion radical predominately occupies ψ_-.

In the sense that M10 represents the next higher stable vinylogue of benzene, the anion radical of M10 represents the next higher vinylogue of the benzene anion radical. The anion radical of benzene persists only at low temperatures, however, that for M10 remains intact at room temperature.[7] The stability of $M10^{-}\cdot$ appears to be high despite the destabilizing effect of the electron-releasing methylene bridge. The anion radical of toluene is less stable than that of benzene by about 1.6 kcal/mol, in a thermodynamic sense.[8]

Not only should the methylene group decrease the thermodynamic stability of the M10 anion radical due to the inductive effect but any nonplanarity of the π system would tend to decrease the stability of $M10^{-}\cdot$. There is good evidence that the anion radical of M10 is, indeed, not planar, since the total ESR spectral width is only 13 G[7] (that for the naphthalene anion radical is 26 G[9]). The nonplanarity of the π system breaks the complete orthogonality between the π electron system and the C–H σ bonds, which allows a direct leakage of the π spin population from the p_z orbitals into the 1s orbitals of the ring protons. The sign of the 1s spin density from this effect is opposite to that which results from spin polarization causing a net reduction in the observed coupling constants ($|A_H|$).

It appears that our understanding of the M10 anion radical is quite extensive from a quantum mechanical point

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[1] Kekulé, A. *Bull. Soc. Chim. Fr.* **1865**, *3*, 98.

[2] Masamune, S.; Hojo, K.; Bigam, G.; Rabenstein, D. L. *J. Am. Chem. Soc.* **1971**, *93*, 4966.

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[7] Gerson, F.; Heilbronner, E.; Boll, W. A.; Vogel, E. *Helv. Chim. Acta* **1965**, *48*, 1494.

[8] Lawler, R. G.; Tabit, C. T. *J. Am. Chem. Soc.* **1969**, *91*, 5671.

[9] Carrington, A.; McLachlan, A. D. "Introduction to Magnetic Resonance"; Harper and Row: New York, 1967.

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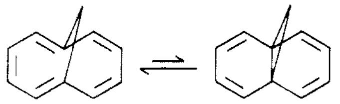
of view. However, the way in which these forces affect the thermodynamic stability of the anion radical is unclear. The presence of $4n + 1$ π electrons appears to be important in increasing the thermodynamic stability of anion radicals generated from the reduction of $4n$ π electron annulenes.[10] The special stability of $4n + 1$ π electron annulenes is evidenced by the very stable anion radicals of [8]annulene and [16]annulene.[10,11] On the other hand, the addition of an extra electron to [6]annulene (a $4n + 2$ π electron system) to yield the $4n - 1$ π electron benzene anion radical is much more difficult than is the addition of the extra electron to the nonaromatic annulenes. The low thermodynamic stability of the benzene anion radical relative to that of the cyclooctatetraene anion radical may be indicative of a general principle concerning $4n + 1$ and $4n - 1$ π electron systems. This can only be confirmed via thermodynamic studies on the higher vinylogues of the benzene anion radical.

As mentioned above, X-ray data on the neutral molecule of M10 confirms the fact that the 1,6 σ bond is not intact and that the equilibrium constant for the tautomerization to dinorcaradiene, eq 3, must be very small. Here we wish to report some thermochemical studies upon M10 and hydrogenated M10 to yield the equilibrium constant for reaction 3. This reaction is analogous to the cycloheptatriene–norcaradiene tautomerization, which is shifted far to the cycloheptatriene side. In fact, norcaradiene has only very recently been observed.[12]



(3)

Experimental Section

M10 was prepared in the manner described by Vogel.[3] Tricyclo[4.4.1.0]undeca-3,8-diene ($M10H_4$) was obtained as one of the precursors in the synthesis of M10.[3] Samples of $M10H_4$ were distilled at 35 °C and 1.0 mmHg and used immediately in the combustion experiments.

The combustion experiments were carried out in a twin-valve (Parr Instrument Co.) adiabatic bomb calorimeter. The liquid $M10H_4$ was placed directly into the steel pan for firing. The pan was kept covered until it was sealed into the bomb to avoid evaporation of the $M10H_4$. For liquids of low vapor pressure, this technique produces less error than does the use of gelatin capsules. After the bomb was charged with 30 atm of oxygen, the samples were fired at about 25 °C. The measured energy of combustion was corrected with the $(\Delta n)RT$ term to give the heat of combustion of the $M10H_4$, which refers to the enthalpy for $C_{11}H_{14} + (29/2)O_2 \rightleftharpoons 11CO_2 + 7H_2O_{(l)}$.

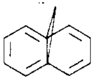
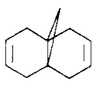
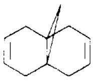
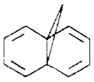
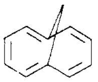
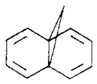
The anion radical of M10 was generated by the reduction of the neutral molecule in tetrahydrofuran (THF) on a freshly distilled alkali metal mirror as previously described.[14,15] After removal of the THF, samples of the solid anion radical were sealed into glass bulbs. The glass bulbs were broken under 100 mL of water in a modified Parr solution calorimeter.[14] The output of the calorimeter was fed into a MINC II 64K computer by Digital as described previously.[17] The heat capacity of the calorimeter is 119.3 cal/deg or 0.03007 cal/byte. After completion of the reaction the contents of the calorimeter were titrated with standardized HCl to yield the millimoles of anion radical in the glass bulbs.

EPR spectra were recorded for each preparation of the M10 anion radical, and the spectra were identical with those previously recorded.[7]

TABLE I: Combustion Data for $M10H_4$

sample, g	ΔT, °C	$\Delta H°_{comb}$, kcal/mol
0.5968	2.606	−1524.8
0.7538	3.292	−1525.5
0.5379	2.353	−1527.3

TABLE II: Heats of Reaction in kcal/mol

reaction	$\Delta H°$	ref
 $+ 27/2O_2 \rightarrow 11CO_2 + 5H_2O$	−1436.9	13
$11CO_2 + 7H_2O \rightarrow 29/2O_2 +$ 	+1525.9	this work
$2H_2 + O_2 \rightarrow 2H_2O$	−136.6	
 $\rightarrow 2H_2 +$ 	+53.3	see text
 $\rightarrow$ 	5.7	

Results and Discussion

The results of the combustion experiments are tabulated in Table I. These data yield an enthalpy of combustion of −1525.9 ± 1.3 kcal/mol for $M10H_4$. This enthalpy of combustion of $M10H_4$ can be coupled with that for M10 to yield the enthalpy of reaction 3. However, the necessary thermochemical cycle requires the heat of hydrogenation of dinorcaradiene. The heat of hydrogenation of cyclohexadiene to yield cyclohexene is −26.65 kcal/mol, and the addition of two hydrogens to dinorcaradiene must have an enthalpy that is very close to twice this value, Table II.

From Table II the enthalpy for the M10 $\rightleftharpoons$ dinorcaradiene tautomerism is about +5.7 kcal/mol, which corresponds to an equilibrium constant of about 10^{-4} for reaction 3. It should be noted that the error in the enthalpy of reaction 3 could be as large as 2 kcal/mol.

Crushing the thin-walled evacuated bulbs containing the solid potassium salt of the M10 anion radical resulted in a rise in the temperature of the calorimeter due to reaction 4, where s indicates a solid. A plot of the change in the temperature of the calorimeter vs. the millimoles of anion radical salt in the bulbs is linear (Figure 1) and corresponds to an enthalpy of reaction 4 of −29.1 ± 1.5 kcal/mol.

$$K^+M10^{-\cdot}{}_{(s)} + H_2O_{(l)} \rightarrow {}^1/_2M10H_{2(l)} + KOH_{(aq)} + {}^1/_2M10_{(l)} \quad (4)$$

Similar calorimetry experiments carried out upon the solid potassium salt of the naphthalene anion radical show that reaction 5 is more exothermic ($\Delta H°$ = −39.1 ± 1.1

$$K^+NP^{-\cdot}{}_{(s)} + H_2O_{(l)} \rightarrow {}^1/_2NPH_{2(s)} + KOH_{(aq)} + {}^1/_2NP_{(s)} \quad (5)$$

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(10) (a) Thielen, D. R.; Anderson, L. B. *J. Am. Chem. Soc.* **1972**, *94*, 2521. (B) Oth, J. F.; Baumann, H.; Gilles, J. M.; Schroder, G. *Ibid.* **1972**, *94*, 3498.

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(17) Stevenson, G. R.; Zigler S. S.; Reiter, R. C. *J. Am. Chem. Soc.* **1981**, *103*, 6057.

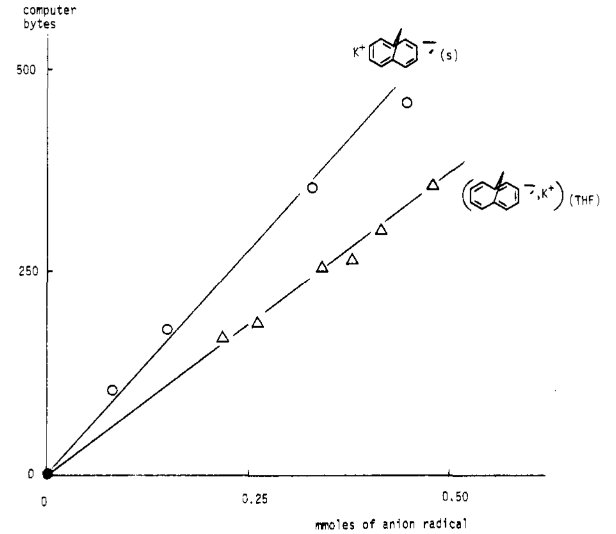
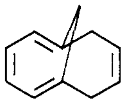


Figure 1. Plots of the change in the temperature of the calorimeter in computer bytes vs. the number of millimoles of solid and solvated M10 anion radical in the glass bulbs.

kcal/mol) than the analogous reaction with M10⁻· (Figure 2). These data indicate that the M10 anion radical is considerably more stable than is the naphthalene (NP) anion radical. This conclusion is, however, not necessarily true, since several factors including the hydrocarbon heats of hydrogenation and vaporization affect the heat of reaction of the anion radical with water. For a meaningful comparison, these enthalpies must be placed into a thermochemical cycle that yields the heat of formation of the anion radical salt from the gas-phase hydrocarbon and potassium metal. The heat of hydrogenation of naphthalene (NP) and the structure of NPH_2 is well-known, but neither of these is known for the M10 system.

In order to ascertain the structure of $M10H_2$ that is generated in reaction 4, we extracted the products of the reaction form the water with hexane. The hexane was then evaporated from the mixture under vacuum, and the remaining mixture of M10 and $M10H_2$ was distilled under reduced pressure (58 °C, at 1 torr). This first fraction is enriched in the $M10H_2$ component, and the ^1H NMR spectrum of the mixture is shown in Figure 3.

The singlet at −0.5 ppm and the multiplet centered at 7.2 ppm are due to the M10 produced in reaction 4. The remaining peaks result from $M10H_2$ that is produced in reaction 4. From the spectrum of $M10H_2$ it is clear that this compound is in the open form described by structure IV. The most convincing evidence for the open structure is the fact that the methylene proton extending over the homoaromatic portion of the molecule appears in a highly shielded region at 0.2 ppm (doublet, integration = 1.0).



IV

Mixtures of M10 and $M10H_2$ obtained from reaction 4 were fired in the oxygen bomb calorimeter as described in the Experimental Section for $M10H_4$. From the composition of the mixtures (taken from NMR integrations) and the known heat of combustion of M10,[13] the heat of combustion of the $M10H_2$ was found to be −1489 ± 8 kcal/mol. The relatively large experimental error in the heat of combustion of IV is due to the fact that mixtures of $M10H_2$ and M10 had to be fired, as opposed to pure $M10H_2$. When this enthalpy of combustion of IV ($M10H_2$) is subtracted from that for M10 (−1436.9 kcal/mol) and the heat of formation of liquid water (−68.3 kcal/mol) is added, one obtains the heat of hydrogenation of M10, eq 6. This heat of hydrogenation can now be placed into a thermochemical cycle with the enthalpy for reaction 4 to yield the heat of formation of $K^+M10^{-}\cdot_{(s)}$ from gas-phase M10 and gas-phase potassium metal (Table III).

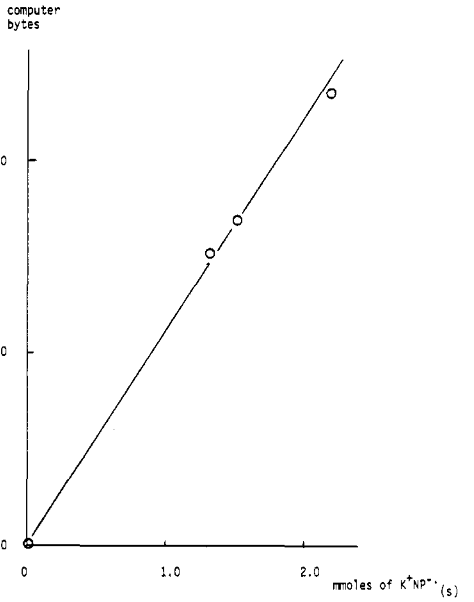


Figure 2. Plot of the computer response to the calorimeter vs. millimoles of $K^+NP^{-}\cdot_{(s)}$ in the glass bulbs.

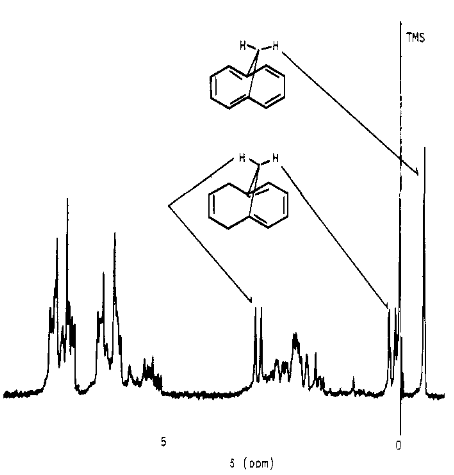
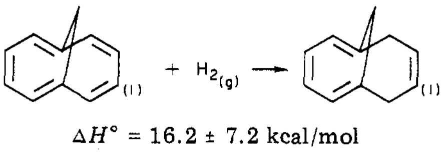


Figure 3. 60-MHz ^1H NMR spectrum of a mixture of 40% M10 and 60% $M10H_2$.



(6)

$$\Delta H^\circ = 16.2 \pm 7.2 \text{ kcal/mol}$$

The thermodynamic stability of the solid anion radical of M10 is much larger than that of naphthalene and, remarkably, almost as large as that for the anthracene system. To make certain that this surprising relative stability of $K^+M10^-\cdot$ is not simply an artifact of the relative crystal lattice energies, we reacted samples of the tetrahydrofuran (THF) solvated $M10^-\cdot,K^+$ ion pair with water in the solution calorimeter:

$$M10^-\cdot,K^+_{(THF)} + H_2O_{(l)} \rightarrow {}^1/_2M10_{(l)} + {}^1/_2M10H_{2(l)} + KOH_{(aq)} \quad (7)$$

TABLE III: Heats of Reaction

	$\Delta H°$, kcal/mol for A =		
reaction[a]	M10	anthracene[b]	naphthalene
$^1/_2AH_2 + {}^1/_2A + KOH_{(aq)} \rightarrow K^+A^{-\cdot}{}_{(s)} + H_2O_{(l)}$	+29.1	+31.0	+39.0
$^1/_2AH_2 + {}^1/_2A + KOH_{(aq)} \rightarrow A^{-\cdot},K^+{}_{(THF)} + H_2O_{(l)}$	+22.0	+21.2	
$K_{(s)} + H_2O_{(l)} \rightarrow KOH_{(aq)} + {}^1/_2H_{2(g)}$	-47.0	-47.0	-47.0
$^1/_2A + {}^1/_2H_{2(g)} \rightarrow {}^1/_2AH_2$	-8.1	-8.5	-1.6
$A_{(g)} \rightarrow A$	-14.5[c]	-23.5	-17.4
$K_{(g)} \rightarrow K_{(s)}$	-21.4	-21.4	-21.4
$K_{(g)} + A_{(g)} \rightarrow K^+A^{-\cdot}{}_{(s)}$	-61.9 ± 5[c]	-69.4 ± 3	-48.4 ± 3
$K_{(g)} + A_{(g)} \rightarrow A^{-\cdot}, K^+{}_{(THF)}$	-69.0 ± 5	-79.2 ± 3	

[a] Both M10 and $M10H_2$ are liquids, and both anthracene and dihydroanthracene are solids. [b] The data for anthracene were taken from ref 14 and 15. [c] The relative larger errors in the final enthalpies for the M10 systems are due to the error in the heat of hydrogenation.

The temperature rise in the calorimeter upon crushing the bulbs containing the THF solution of the M10 anion radical is due to the reaction depicted in eq 7 plus the aquation of the THF. However, the heat due to the aquation of the THF can be subtracted out as described earlier.[14,15] A plot of the change in the temperature of the calorimeter due to the reaction of the anion radical with water (eq 7) vs. the amount of anion radical in the bulbs is linear (Figure 1) and leads to an enthalpy of reaction 7 of -22.0 ± 1.1 kcal/mol. From Table III it is clear that this leads to about the same relative heats of formation of the solvated M10 and anthracene anion radical as exists in the solid phase.

This conclusion concerning the relative stabilities of the solvated anthracene and M10 anion radicals was proven to be the case, as the addition of anthracene to a THF solution of the M10 anion radical leads to the replacement of the EPR signal for M10 with that for the anthracene anion radical. On the other hand, the addition of naphthalene to a THF solution of $M10^{-\cdot},K^+$ does not result in any change in the EPR spectrum from $M10^{-\cdot},K^+$. When neutral M10 was added to the anion radical of naphthalene in THF, the 25-line pattern for the $NP^{-\cdot},K^+$ ion pair was replaced with the spectrum for $M10^{-\cdot},K^+$. The qualitative results of the competition and calorimetry experiments are shown in eq 8-11.

$$AN^{-\cdot},K^+{}_{(THF)} + M10_{(THF)} \rightleftharpoons M10^{-\cdot},K^+ + AN_{(THF)} \quad (8)$$

$$K^+AN^{-\cdot}{}_{(s)} + M10_{(l)} \rightleftharpoons K^+M10^{-\cdot}{}_{(s)} + AN_{(s)} \quad (9)$$

$$NP^{-\cdot},K^+{}_{(THF)} + M10_{(THF)} \rightleftharpoons M10^{-\cdot},K^+{}_{(THF)} + NP_{(s)} \quad (10)$$

$$K^+NP^{-\cdot}{}_{(s)} + M10_{(l)} \rightleftharpoons K^+M10^{-\cdot}{}_{(s)} + NP_{(s)} \quad (11)$$

Conclusions

A summarization of the intramolecular and intermolecular energies controlling the thermodynamic stability of the M10 system is shown in (Figure 4). The thermodynamic stability of the M10 anion radical is much larger than was expected on the basis of the extent of conjugation in the molecule. The total π energy and resonance energy for the planar [10]annulene are 12.9β and 2.9β, respectively,[7] while these numbers for the naphthalene system are 13.6β and 3.6β, respectively.

As mentioned earlier, the neutral M10 molecule is not completely planar. Although the ring current is diatropic, the molecule has been described as weak or intermediate in aromaticity based upon ab initio calculations.[16] The addition of an electron to this system probably results in an increase in planarity and consequently more conjugation in the 11 π electron (4*n* -1) system. The effect is much weaker but reminiscent of the ring flattening observed upon the addition of an electron cyclooctatetraene or [16]annulene. Some of the same forces that come into play for the M10 system produce the inordinate stability of the anion radicals of [8]annulene and [16]annulene relative to their respective neutral molecules. That is, the higher degree of planarity and conjugation in the anion radical increases its stability relative to the gas-phase neutral molecule. Neither benzene, naphthalene, nor anthracene gain such a geometrical advantage upon electron addition.

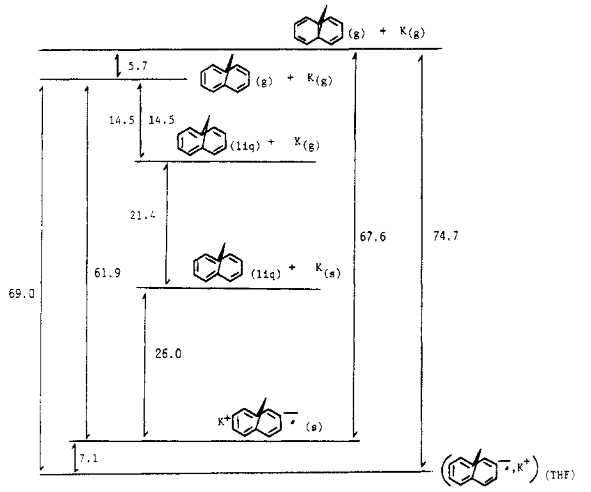


Figure 4. Energy diagram for the 1,6-methano[10]annulene system. The energy differences are in kcal/mol.

On the basis of the combustion experiments, the dinorcaradiene structure of 1,6-methanocyclodecapentaene lies about 5.7 kcal/mol above the open structure.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work. We also thank the National Science Foundation (Grant CDP-8000535) for the purchase of the data acquisition system. We are very grate to Professor E. Vogel for his gift of 1,6-methano[10]annulene.

Registry No. IV, 6074-99-3; M10, 2443-46-1; potassium M10 anion radical, 84175-55-3; dinorcaradiene, 174-23-2; 1,6-methano-1,4,5,8-tetrahydronaphthalene, 27714-83-6.