primarily from the O(2p) levels. The present calculations only add to the confusion, since they lead to another different ordering. Nevertheless, the situation is not as bad as it seems, since all of these states cluster in a 1-3-eV band. The experimental XPS spectrum of UO_2CO_3 by Veal et al.[17] shows a strong 2-eV wide band which corresponds to the states arising from the O(2p) levels. Therefore, experiment cannot resolve the discrepancies among the theoretical calculations. On the other hand, there is reasonable agreement among all the calculations and experiment as to the position and nature of the higher states, namely, those arising from the U(6p) and O(2s). All the calculations show a strong mixing between the U(6p) and O(2s) because of their proximity as well as the significant effect of spin-orbit coupling on the U(6p). An extensive discussion of this problem is given by Wood et al.[16]

The situation for ThO_2 is very similar, namely, a broad band corresponding to the cluster of states arising from the O(2p), followed by the states arising from the Th(6p) and O(2s), which again are strongly mixed. This prediction is borne out by the XPS spectra of ThO_2.[18]

Conclusions

Relativistic effective core potential (RECP) calculations using double-zeta-plus-polarization quality basis sets correctly predict that UO_2^{2+} possesses a linear geometry while isoelectronic ThO_2 is strongly bent with a bond angle of 118° (experiment[1] gives 122 ± 2°). The calculated Th–O bond length of 1.91 Å is the most reliable value for this experimentally undetermined quantity. Moreover, the theoretical value differs considerably from recent estimates (1.80 Å)[19] used in calculating thermodynamic data.

Analysis of the results shows that the 6p levels do not play a key role in determining the linear geometry of UO_2^{2+} as proposed by Tatsumi and Hoffmann.[3] Instead we find that the difference in geometries for UO_2^{2+} and ThO_2 has its origin in the relative ordering of the 5f and 6d levels. For uranium the 5f levels are lower and dominate the back-bonding from the oxygen in UO_2^{2+}, while for thorium the 6d levels are lower and dominate the back-bonding in ThO_2. Finally, the 5f levels prefer linear geometries, while the 6d prefer bent geometries; hence, the difference which exists between UO_2^{2+} and ThO_2. So it is clear that relative ordering of the 5f and 6d levels has a profound effect. This unique feature of two valence levels possessing different principal quantum numbers makes the electronic structure and chemistry of the early actinides a fascinating subject.

Acknowledgment. I enjoyed stimulating discussions with Jeff Hay and Mike Boring. This work was performed under the auspices of the U.S. Department of Energy.

---

(15) C. Y. Yang, K. H. Johnson, and J. A. Horsley, *J. Chem. Phys.*, **68**, 1001 (1978).

(16) J. H. Wood, M. Boring, and S. B. Woodruff, *J. Chem. Phys.*, **75**, 5225 (1981).

(17) B. W. Veal, D. J. Lam, W. T. Carnall, and H. R. Hoekstra, *Phys. Rev. B*, **12**, 5651 (1975).

(18) B. W. Veal and D. J. Lam, *Phys. Rev. B*, **10**, 4902 (1974).

(19) D. W. Green, *J. Nucl. Mater.* **88**, 51 (1980).

Polyacene Dianion Crystal Lattice Energies and Thermodynamic Stabilities: The Quantitative Effect of Aromaticity

Gerald R. Stevenson,* Steven S. Zigler, and Richard C. Reiter

Contribution from the Illinois State University, Department of Chemistry, Normal, Illinois 61761. *Received March 30, 1981*

Abstract: A calorimeter interfaced with a data acquisition system has been used to measure the heats evolved from the reactions of solid sodium polyacene dianion salts with water. These heats were utilized in a thermochemical cycle to obtain the thermodynamic stabilities (heats of formation) of the salts. For all of the polyacene dianion salts including those from anthracene, tetracene, pentacene, etc., the heats of formation from the polyacene and sodium metal were found to be negative. Electron-electron repulsion energies ($E_{(rep)}$) were calculated for each of the dianions. The calculated results could then be used with the experimental heats of formation to obtain the actual crystal lattice energies for the salts. For all of the systems studied the crystal lattice energies were found to be between 400 and 440 kcal/mol. Assuming a similar crystal lattice energy for the sodium benzene dianion ($Na^+{}_2Bz^{2-}$), its heat of formation from benzene and sodium metal was found to be very endothermic (+96 kcal/mol). Much of this endothermicity is due to the antiaromatic nature of the benzene dianion. The enthalpy of transferring two electrons from the benzene dianion to the antiaromatic (planar) cyclooctatetraene neutral molecule to form benzene and the cyclooctatetraene dianion is about −177 kcal/mol.

Chemists have known for some time that it is easier to add extra electrons to 4n π-electron annulenes than to aromatic systems. The dianions of both [8]annulene[1] and [16]annulene[2] are readily generated via alkali metal reduction of the neutral molecular systems. However, the dianion of benzene (a 4n + 2 π-electron annulene) is still unknown. The dianions of fused polyaromatic systems can be generated but with more difficulty than those for the 4n π-electron annulenes.[3] The reason for the less negative reduction potentials of the 4n π-electron annulenes than of the aromatic system is the fact that the addition of two electrons leads to an aromatic annulene in the 4n π-electron systems and to a divergence from aromatic character in the aromatic systems.

In a previous communication we reported that the solid sodium salts of both [8]annulene and anthracene are stable while main-

---

(1) Allendoerfer, R. D.; Rieger, P. H. *J. Am. Chem. Soc.* **1965**, *87*, 2336.

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

(3) Sommerdijk, J. L.; De Boer, E. In "Ions and Ion Pairs in Organic Reactions", Szwarc, M., Ed.; Intersciences Publishers: New York, 1972; Vol. 1, pp 363-374.

0002-7863/81/1503-6057$01.25/0

tained under vacuum.[4] While the thermodynamic stability of the anthracene salt was shown to be less than that of the cyclooctatetraene (COT) dianion, both could be stored for days at room temperature. The thermodynamic stability of the sodium salt of [8]annulene is due, in part, to its aromatic character but that for the anthracene dianion must be due to the large contribution from the crystal lattice energy. This must be the case, since no π-electron dianion can be generated in the gas phase.[5]

Here we wish to report the thermodynamic stabilities (heats of formation) for a series of polyaromatic dianions and compare them to those of [8]annulene and [16]annulene. This will yield the thermodynamic significance of aromatic character. This is true, since our comparisons will be between 4n and 4n + 2 systems, and the number of π-electrons is what the Hückel model is all about. However, aromatic character is not the only factor controlling the thermodynamic stabilities of these salts. The very large crystal lattice energies are of considerable importance, and there have not been any reports of crystal lattice energies for π-electron dianion salts. Thus, we would also like to report the first dianion crystal lattice energies and show how these lattice energies contribute along with the aromatic properties to the overall thermodynamic stability of the salts.

Although crystal lattice energies of organic dianion salts have not been reported, we have recently developed a technique to determine those for organic anion radical salts.[6] For a series of solid sodium anion radical salts, including those of anthracene, tetracene, pyrene, and perylene, the crystal lattice energies were found to be the same (about 167 kcal/mol).[6,7] This value is typically about a factor of 10 greater than the electron affinity of the hydrocarbon, thus it accounts for the majority of the thermodynamic stability of the solid anion radical salts. Here we will show that this is also the case for the dianion salts, especially since the second electron affinities (electron affinity of the anion radical) are all very negative. These negative values for the second EA's are due to the electron–electron repulsion energies in the dianions.[8] The second EA's cannot be measured, but the electron–electron repulsion energies can be calculated via the method of Hush and Blackledge.[8,9]

Experimental Section

Solvent free dianion salts were prepared as previously described[4] and placed into thin-walled evacuated glass bulbs. In order to ensure that no tetrahydrofuran (THF) was left incorporated into the crystal lattice of the solid salts, D_2O was added and the solution submitted to NMR analysis. No THF was observed in the D_2O. However, it would often take several days with the salt left exposed to high vacuum (10^{-6} torr) to remove all of the solvent.

The glass bulbs containing the sodium salts were placed into a modified cell of a Parr solution calorimeter, and the bulbs were broken under 100 mL of water in the calorimeter.[4] The output from the calorimeter was fed directly into a MINC II 64K computer by Digital. The change in the temperature of the calorimeter, monitored in units of computer bytes, was due to the reaction of the dianion salts with the water. After the reaction, the contents of the calorimeter were titrated with standardized HCl to obtain the amount of salt in the bulbs. The millimoles of salt in a given bulb was half the number of millimoles of HCl required to neutralize the contents of the calorimeter. The apparatus used is shown in Figure 1.

Using the technique described previously, we did analyze for the production of hydrogen gas from the reactions between the dianions and water.[7] None was found.

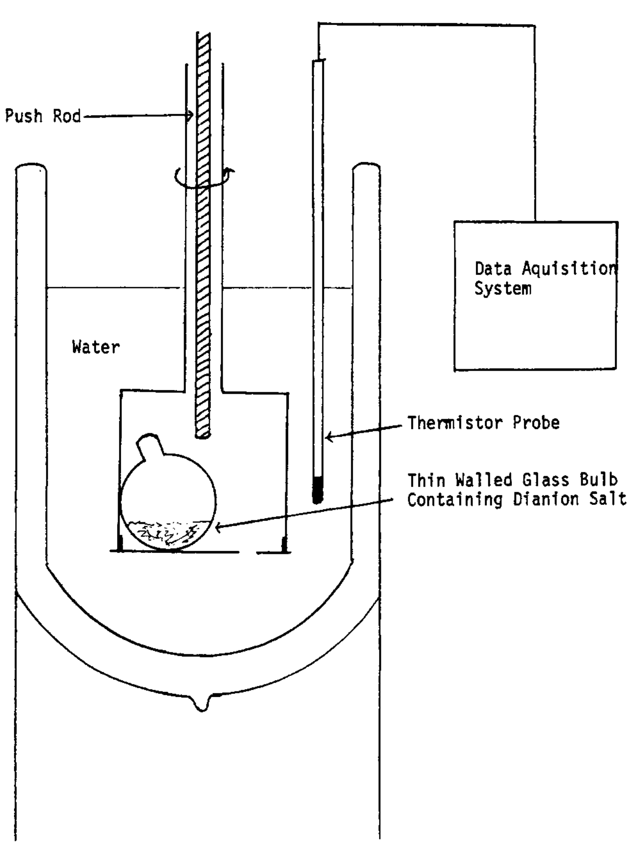


Figure 1. Calorimeter interfaced to the data acquisition system used to measure the enthalpy of reaction of the dianion salt with water.

Table I. Enthalpies of Reaction of Solid Dianion Salts with Water

reaction no.	salt	$\Delta H°$, kcal/mol	ref
1	$Na^+{}_2AN^{2-}$	−79.1 ± 0.9	4
2	$Na^+{}_2TE^{2-}$	−75.6 ± 1.8	11, this work
3	$Na^+{}_2PT^{2-}$	−68.7 ± 1.4	this work
4	$Na^+{}_2PY^{2-}$	−43.2 ± 1.3	11, this work
5	$Na^+{}_2PE^{2-}$	−66.8 ± 1.3	11, this work
6	$Na^+{}_2BPY^{2-}$	−70.9 ± 1.7	this work
7	$Na^+{}_2COT^{2-}$	−33.3 ± 0.8	12
8	$Na^+{}_2[16]^{2-}$	−10.9 ± 0.3	13

The electron–electron repulsion energies in the dianions were calculated by the method of Hush and Blackledge.[9] For the interatomic distances less than 2.78 Å, the Pariser–Parr ξ_{uv} and r values given in ref 9 were fit by a nonlinear-least-squares method to the equation $\xi_{uv} = 10.8642e^{-0.285923r}$ with a correlation coefficient greater than 0.9999. This equation was then utilized to generate ξ_{uv} values as a function of the interatomic distances in the molecules treated. Following Hush and Blackledge,[9] for r greater than 2.78 Å, these atomic interaction integrals were calculated by using the classical point charge treatment. The reactions taking place in the calorimeter and the dianions for which these calculations were carried out are shown below in Scheme I. For the polyaromatics and annulenes involved in the reactions shown in eq 1–8 the following abbreviations are used for the remainder of the paper: AN, TE, PT, PY, PE, BPY, COT, [16], respectively.

Calibration of the calorimeter yielded a heat capacity of 119.3 cal/deg which corresponds to a response from the computer of 0.02997 cal/byte. Thus, the slopes of the lines generated by plotting the computer response vs. the number of millimoles of dianion in the bulbs can be multiplied by 0.02997 cal/byte to yield the enthalpy of the reaction in kilocalories per mole.

Results and Discussion

Plots of the change in the temperature of the calorimeter vs. the millimoles of dianion salt in the glass bulbs did yield linear graphs, Figures 2 and 3. In order to be sure that the computer response to the calorimeter was calibrated correctly, samples of lithium metal were placed in the glass bulbs and reacted with water in the calorimeter. Using 0.02997 cal/byte, we obtained an enthalpy of reaction of Li with water of −52.6 kcal/mol. This is within experimental error of the −53.1 kcal/mol reported in the literature.[10] The enthalpies of reaction of the dianion salts

---

(4) Stevenson, G. R.; Valentin, J.; Williams, E.; Caldwell, G.; Alegria, A. E. *J. Am. Chem. Soc.* **1979**, *101*, 515.

(5) Bowie, J. H.; Stapelton, B. J. *J. Am. Chem. Soc.* **1976**, *98*, 6480.

(6) Stevenson, G. R.; Wiedrich, C. R. *J. Am. Chem. Soc.* **1979**, *101*, 5092.

(7) Stevenson, G. R.; Wiedrich, C. R.; Clark, G. *J. Phys. Chem.* **1981**, *85*, 374.

(8) Szwarc, M.; Jagur-Grodzinski, J. In "Ions and Ion Pairs in Organic Reactions", Szwarc, M., Ed.; Intersciences Publishers: New York, 1974; Vol. 2, p 91.

(9) Hush, N. S.; Blackledge, J. *J. Chem. Phys.* **1955**, *23*, 514.

Table II. Enthalpies of Reaction

reaction[a]	$\Delta H°$, kcal/mol, for π =							ref
	AN	TE	PT	PY	PE	BPY	COT	
$\pi H_2 + 2NaOH\ (aq) \rightarrow Na^+{}_2\pi^{2-} + 2H_2O$	79.1	75.6	68.7	43.2	66.8	70.9	33.3	
$2Na + 2H_2O \rightarrow 2NaOH\ (aq) + H_2$	−88.2	−88.2	−88.2	−88.2	−88.2	−88.2	−88.2	10
$\pi + H_2 \rightarrow \pi H_2$	−17.0	−12.5	−15	−2.7	−15.0	−15	−25.6	15–17
$2Na + \pi \rightarrow Na^+{}_2\pi^{2-}$	−26.1[b]	−25.1	−34.5	−47.7	−36.4	−32.3	−80.5	

[a] Unless otherwise indicated all of the substances are in their standard state at 25 °C and 1 atm. Of all the hydrocarbons studied, only COT and $COTH_2$ are liquids. [b] The errors in these final enthalpies are all less than 2 kcal/mol.

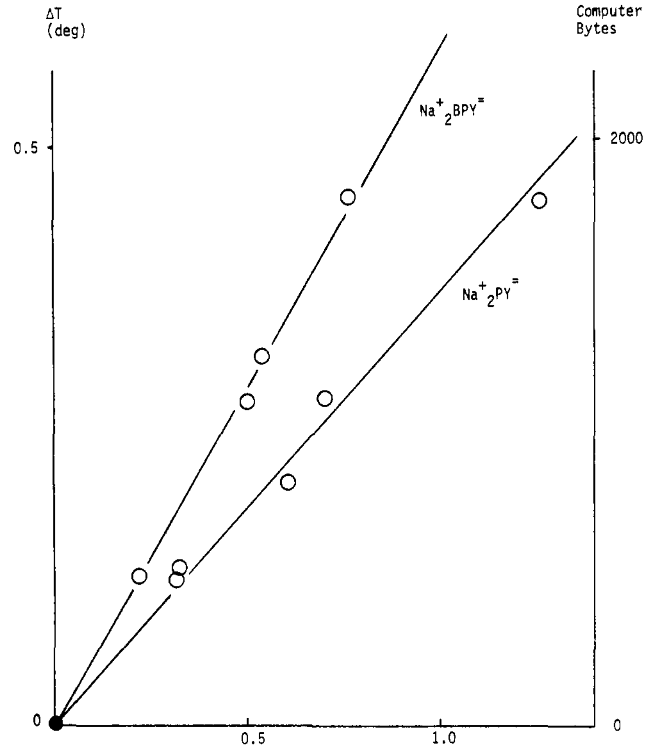


Figure 2. Plot of the change in the temperature of the calorimeter and computer response vs. the number of millimoles of sodium dianion salt in the glass bulbs.

measured in this way along with some that have been previously measured are listed in Table I.

Many effects (including enthalpies of hydrogenation) must be considered in the interpretation of these enthalpies, but the expected result of the aromatic dianions reacting less exothermically was born out. It is also interesting to note that the polyacene dianions react with water much more exothermically than does sodium metal. Of much more significance are the enthalpies of formation of the solid salts from the neutral hydrocarbons and sodium metal in their standard states. These enthalpies are calculated via the thermochemical cycle shown in Table II, which shows that all of the heats of formation of the dianion salts from the hydrocarbons and sodium metal are negative. Further, the heats of formation of the aromatic dianions are as much as 50 kcal/mol more exothermic than those of the polyacene dianions.

The electron–electron repulsion energies are identical with the gas phase disproportionation enthalpies for the anion radicals ($\Delta H°$ for the reaction depicted in eq 9).[14] The calculations of the

$$2\pi^{-}\cdot\ (g) \rightarrow \pi^{2-}\ (g) + \pi\ (g) \qquad (9)$$

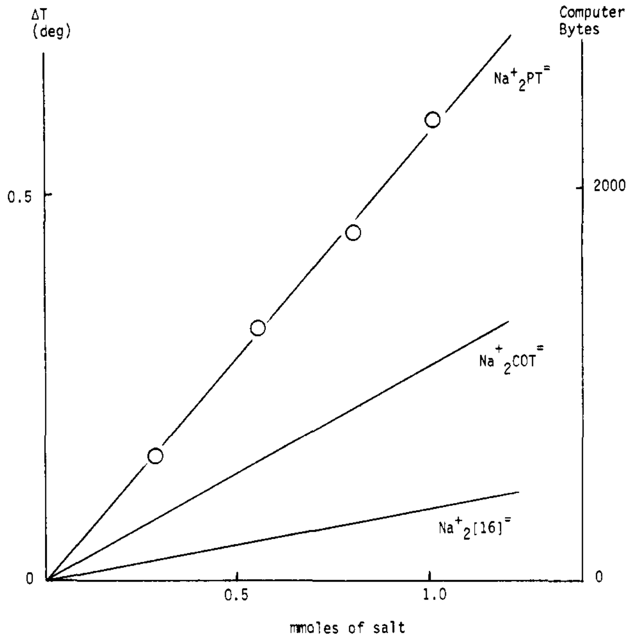


Figure 3. Plot of the change in the temperature of the calorimeter and computer response vs. the number of millimoles of dianion in the glass bulbs. The lines for $Na^+{}_2[16]^{2-}$ and $Na^+{}_2COT^{2-}$ were reported earlier.[4,13]

Table III. Electron–Electron Repulsion Energies for the Dianion and Electron Affinities for the Neutral Molecule, kcal/mol

hydrocarbon	$E_{(rep)}$	electron affinity[18]
AN	117	12.7
TE	107	26.5
PT	99	29.3
PY	108	13.3
PE	100	24.4
BPY	101	19.1
COT	106	28 (for planar COT)

electron–electron repulsion energies ($E_{(rep)}$) were carried out as described in the Experimental Section for all of the polyacene dianions used in this study, Table III. A calculation was also carried out for the naphthalene dianion. The results of this calculation were compared to those of Dewar.[14] Our value of −127 kcal/mol agrees quite well with the MINDO II value of −121.3 kcal/mol.[14]

The electron affinity for COT reported in Table III is that for the planar symmetrical form of COT. It was calculated by simply adding the EA of tub COT (13 kcal/mol) to the 15 kcal/mol necessary to flatten COT into the planar symmetrical form.[19,20]

---

(10) Gunn, S. R. *J. Phys. Chem.* **1967**, *71*, 1386.

(11) Stevenson, G. R.; Zigler, S. S. *J. Am. Chem. Soc.* **1981**, *103*, 2513.

(12) Stevenson, G. R.; Ocasio, I.; Bonilla, A. *J. Am. Chem. Soc.* **1976**, *98*, 5469.

(13) Stevenson, G. R.; Forch, B. E. *J. Am. Chem. Soc.* **1980**, *102*, 5985.

(14) Dewar, M. J. S.; Harget, A.; Haselbach, E. *J. Am. Chem. Soc.* **1969**, *91*, 7521.

(15) Shaw, R.; Golden, D. M.; Bensen, S. W. *J. Phys. Chem.* **1977**, *81*, 1716.

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

(17) The enthalpies of hydrogenation for PE and BPY are unreported, and these numbers are estimations based upon the other hydrocarbons.

(18) Becker, R. S.; Chen, E. *J. Chem. Phys.* **1966**, *45*, 2403.

(19) Anet, F. A. L.; Bourn, A. J. R.; Lin, Y. S. *J. Am. Chem. Soc.* **1964**, *86*, 3576.

(20) Wentworth, W. E.; Ristau, W. *J. Phys. Chem.* **1969**, *73*, 2126.

Scheme I

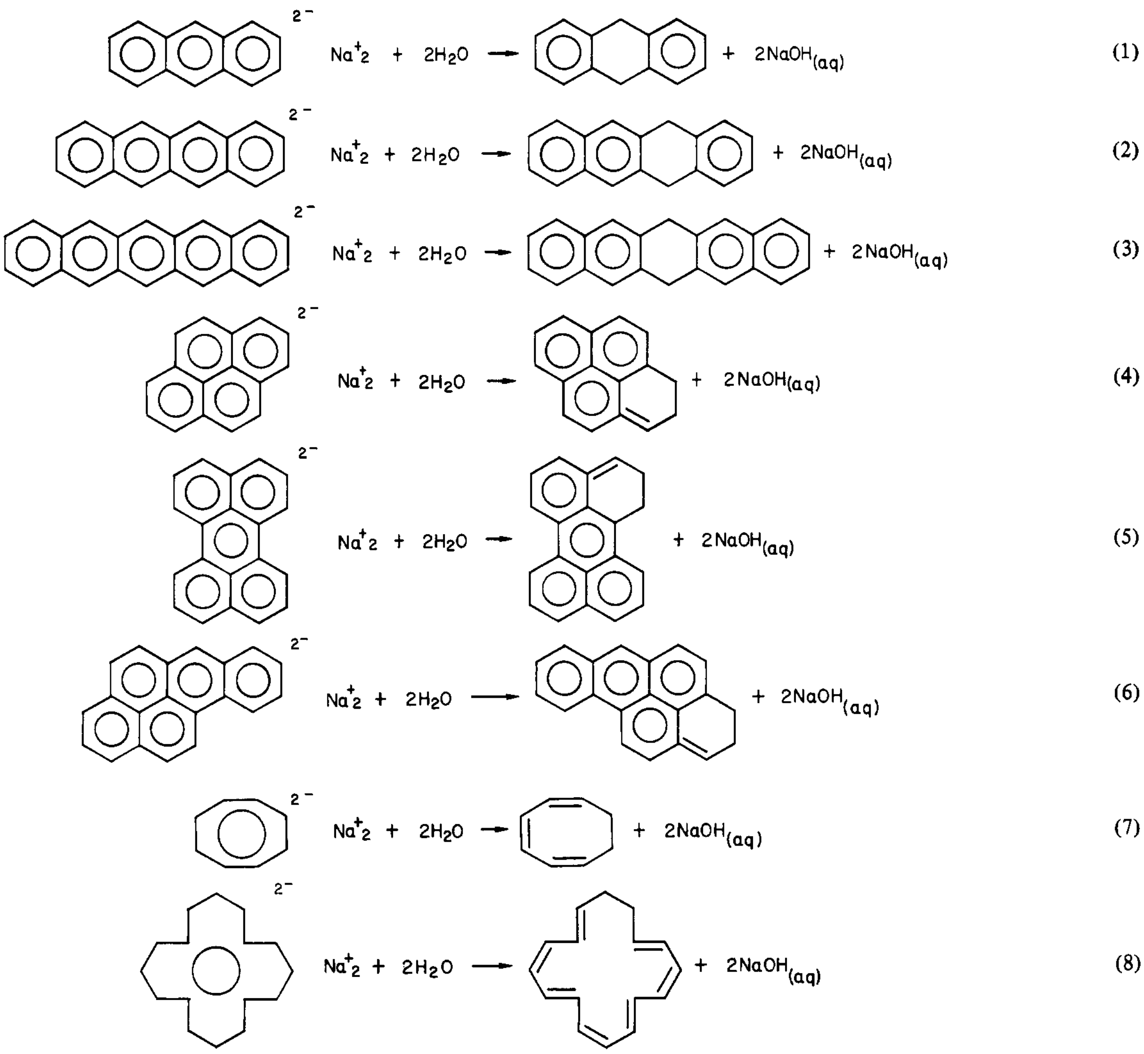
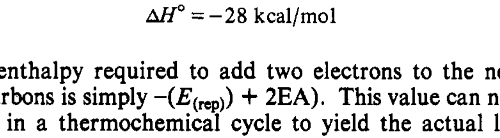


Table IV. Enthalpies of Reaction, kcal/mol

reaction[a]	AN	TE	PT	PY	PE	BPY	COT	ref
	$\Delta H°$ for π =							
$2Na + \pi \rightarrow Na^+{}_2\pi^{2-}$	−26.1	−25.1	−34.5	−47.7	−36.4	−20.3	−80.5	
π (g) $\rightarrow \pi$	−23.5	−29.8	−35	−22.2	−30.0	−28.3	−10.3	21, 16
2Na (g) $\rightarrow$ 2Na	−51.8	−51.8	−51.8	−51.8	−51.8	−51.8	−51.8	22
$2Na^+$ (g) + $2e^-$ (g) $\rightarrow$ 2Na (g)	−236.8	−236.8	−236.8	−236.8	−236.8	−236.8	−236.8	23
π^{2-} (g) $\rightarrow \pi$ (g) + $2e^-$ (g)	−92	−54	−40	−81	−51	−63	−50	
$2Na^+$ (g) + π^{2-} (g) $\rightarrow Na^+{}_2\pi^{2-}$	−430	−398	−398	−440	−406	−412	−429	

[a] All substances are in their standard states unless otherwise indicated.

Thus, this electron affinity is the negative of the enthalpy of reaction 10.



$\Delta H° = -28$ kcal/mol

The enthalpy required to add two electrons to the neutral hydrocarbons is simply $-(E_{(\mathrm{rep})}) + 2\mathrm{EA})$. This value can now be utilized in a thermochemical cycle to yield the actual lattice energies for the dianion salts, Table IV.

Conclusions

From Table IV, we can see that the dianion salts have crystal lattice energies that are more than 200 kcal/mol greater than those for the anion radicals. All of the sodium anion radical salts have about the same crystal lattice energy,[7] and this also appears to be the case for the sodium dianion salts, which vary less than 5% from the average of the seven systems studied. The average and standard deviation of this crystal lattice energy is 417 ± 16 kcal/mol. This average value has a very small standard deviation considering that calculated values for $E_{(\mathrm{rep})}$ were used in its determination.

It is impossible to measure the heat of reaction between the benzene dianion salt ($Na^+{}_2BZ^{2-}$) and water, since the dianion of benzene cannot be generated. However, the lattice energy for

---

(21) For BPY see: Murray, J. J.; Pottie, R. F.; Pupp, C. *Can. J. Chem.* **1974**, *52*, 557.

(22) Hicks, W. T. *J. Chem. Phys.* **1963**, *38*, 1873.

(23) Lotz, W. *J. Opt. Soc. Am.* **1967**, *57*, 873.

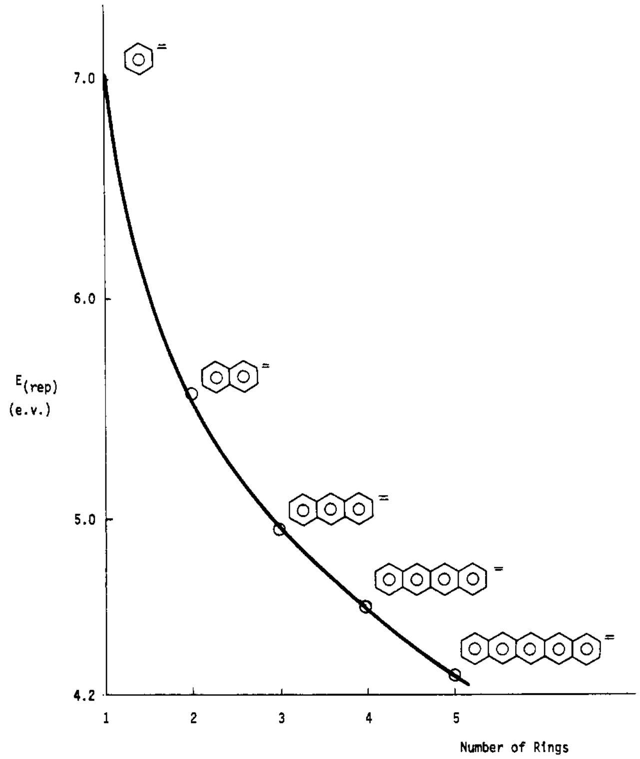


Figure 4. Plot of $E_{(\mathrm{rep})}$ vs. the number of ring systems (N) for the linear polyacenes.

the sodium dianion salt of benzene must be about 417 kcal/mol. Using this value, we can now back calculate with the same thermochemical cycles shown in Tables II and IV to obtain a rough approximation of the enthalpy for reaction 11.

$$\mathrm{Na^+{}_2BZ^{2-} + 2H_2O \rightarrow 2NaOH\ (aq) + BZH_2} \qquad (11)$$

$$\Delta H^\circ \simeq -179\ \mathrm{kcal/mol}$$

The value calculated for $E_{(\mathrm{rep})}$ is 162 kcal/mol.[9] The $E_{(\mathrm{rep})}$ values for pentacene, tetracene, anthracene, and naphthalene plotted against the number of rings (5, 4, 3, and 2, respectively) yield a smooth curve, Figure 4, represented by the equation $E_{(\mathrm{rep})} = 7.036N^{-0.3036}$ when fitted by a nonlinear-least-squares method. N represents the number of rings, and the correlation coefficient is 0.999. This equation predicts a value of $E_{(\mathrm{rep})}$ of 7.036 eV or 162 kcal/mol. This is in perfect agreement with the calculated value.

With use of the appropriate thermodynamic values for the benzene system (EA = −26.6 kcal/mol,[24] heat of vaporization = −8.9 kcal/mol,[16] heat of hydrogenation = 5.6 kcal/mol), the enthalpy of reaction of $\mathrm{Na^+{}_2BZ^{2-}}$ with water is found to be −179 kcal/mol, eq 11. From this, the heat of formation of $\mathrm{Na^+{}_2BZ^{2-}}$ from liquid benzene and solid sodium metal is simply 179 − 88.2 + 5.6 = 96.4 kcal/mol, eq 12. This value is very endothermic,

$$\mathrm{2Na + BZ \rightarrow Na^+{}_2BZ^{2-}} \qquad (12)$$

$$\Delta H^\circ = +96.4\ \mathrm{kcal/mol}$$

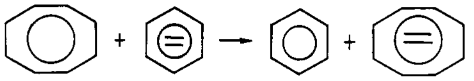
which explains the failure of all attempts to prepare this dianion.

By subtracting the heat for the reaction depicted in eq 12 from the corresponding enthalpy for $\mathrm{Na^+{}_2COT^{2-}}$ the enthalpy for the reaction shown below is obtained. Since both crystal lattice

$$\mathrm{Na^+{}_2BZ^{2-} + COT(planar\ symmetrical\ form) \rightarrow Na^+{}_2COT^{2-} + BZ} \qquad (13)$$

$$\Delta H^\circ \simeq -177\ \mathrm{kcal/mol}$$

energies are about the same and the heats of vaporization are about the same, this value of −177 kcal/mol is correct also for the gas phase reaction, eq 14.



(14)

The enthalpy for the reaction depicted in eq 14 represents a transfer of electrons from an antiaromatic dianion to an antiaromatic annulene to form an aromatic dianion and an aromatic annulene. But, aromaticity is not the only driving force for this electron transfer, as the electron–electron repulsion energies are not identical for $\mathrm{COT^{2-}}$ and $\mathrm{BZ^{2-}}$. In fact, the value for $E_{(\mathrm{rep})}$ is 56 kcal/mol larger for the benzene dianion. *This means that the concept of aromaticity accounts for −167 + 56 or about −121 kcal/mol of the enthalpy of generation of two aromatic systems from two antiaromatic systems via electron transfer.* Although there could be considerable error in this number (perhaps 20 kcal/mol), it is so large and negative that the force exerted by aromaticity upon the electron transfer must be quite large.

Since the reaction depicted in eq 14 represents a change from two antiaromatic systems to two aromatic systems, the driving force from one antiaromatic to one aromatic system must be about half of this or about −61 kcal/mol. Incidentally, if one assumes that the destabilization due to antiaromaticity is the same in magnitude but opposite in sign as the stabilization due to aromatic character, then half of 61 (30 kcal/mol) should be close to the value for a change from a nonaromatic system to an aromatic one. This is fairly close to the accepted value of 36 kcal/mol.

---

(24) Jordan, K. D.; Michejda, J. A.; Burrow, P. D. *J. Am. Chem. Soc.* **1976**, *98*, 1295.