observed. The voltages are independent of the ratio of ferro to ferriheme and of the total heme concentration for the values explored, namely, $^1/_4 < [Fe^{II}P]_{tot}/[Fe^{III}P]_{tot} < 10$ and 0.2 mM $< [FeP]_{tot} < 0.5$ mM. The observed photoeffect does *not* require a semiconductor electrode. Comparable voltages are observed when a Pt foil electrode is illuminated. Moreover, no voltage occurs when a solution without CO was illuminated. Thus, the photovoltage in fact arises from a light-induced perturbation of the CO-binding equilibrium of Scheme I. The photovoltage decreases with [Im] and increases with P(CO) and with the light intensity (decreasing filter absorbance; Figure 2). For $P(CO) = 0.01$ atm, approach to the saturating value of $\Delta V_P \sim 100$ mV is clearly seen by $I \sim I_0/10$, whereas at full available light intensity the photovoltage of the cell with $P(CO) = 1$ atm is much larger, $\Delta V_P \sim 200$ mV, and is well below light saturation.

Experiments were also performed on the iron porphyrin coated SnO_2 OTE. Illumination of an electrode whose film had been quantitatively reduced to $Fe^{II}TPP(Im)(CO)$ gave unstable photovoltages. If the film contained finite proportions of the Fe^{III} TPP, a stable photovoltage was obtained having light dependence and limited $\Delta V_P \sim 100$ mV such as that in Figure 2.

Discussion

The results presented here show that a photoinduced alteration in the ligand equilibrium of a ferroporphyrin gives rise to an appreciable photovoltage. The following model is consistent with these results. Since the oxidation of $Fe^{II}P(Im)(CO)$ is highly irreversible and occurs at a very positive potential, the half-cell potential of the dark electrode is set by the dark concentration ratio $([Fe^{III}P(Im)_2]/[Fe^{II}P(Im)_2])_{dark}$, and that of the illuminated electrode by the concentration ratio $([Fe^{III}P(Im)_2]/[Fe^{II}P(Im)_2])_{light}$, at the electrode surface. As a consequence, an illuminated cell under open-circuit conditions should generate a photovoltage that depends parametrically on the light intensity through the equation

$$\Delta V_P = -0.059 \log \frac{[(Fe^{II}P(Im)_2)]_{light}}{[(Fe^{II}P(Im)_2)]_{dark}} \qquad (2)$$

which is independent of $[Fe^{III}P(Im)_2]$. For high [Im] and [CO], where Scheme I applies, this can be rewritten in terms of the ligation equilibrium parameters

$$\Delta V_P{}^L = -0.059 \log \frac{1 + L_0[CO]/K_2[Im]}{1 + L(I)[CO]/K_2[Im]} \qquad (3)$$

In particular eq 3 shows that ΔV_P should reach a limiting value with increasing light intensity:

$$\Delta V_P = -0.059 \log \frac{[Fe^{II}P]_{total}}{[Fe^{II}P(Im)_2]_{dark}} = -0.059 \log \frac{L_0[CO]}{K_2[Im]} \qquad (4)$$

The analysis is in qualitative agreement with the overall behavior of ΔV_P as $P(CO)$, light intensity (Figure 2), and [Im] vary. Also, the peak currents of the cyclic voltammogram from an illuminated cell qualitatively correspond with the observed ΔV_P. However, a rigorous, quantitative treatment of the cyclic voltammogram under illumination is not yet available, and we therefore defer attempts to apply 2 directly.

The observations of photovoltages from a carbonylferroporphyrin photogalvanic cell clearly validate our initial premise. Of course, other complexes must be examined and photocurrent measurements performed.

Acknowledgment. We thank Dr. William Euler for helpful discussions. Dr. T. E. Phillips and J. Martinsen performed early measurements on this system. This work has been supported by National Science Grant DMR 77-26409 and has benefited from the facilities supported under the NSF-MRL program through the Material Research Center of Northwestern University (Grant DMR 79-23573).

Thermodynamics of Homoantiaromaticity and Homoaromaticity: Homo[8]annulene and Its Dianion

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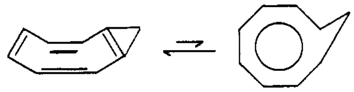
Abstract: Calorimetric techniques were used to find that the heat of formation of the homoaromatic homo[8]annulene dianion potassium salt from potassium metal and *cis*-bicyclo[6.1.0]nona-2,4,6-triene (CBN) is very close to zero. The very low thermodynamic stability of this homoaromatic system relative to that for the aromatic cyclooctatetraene dianion was found to be due to the large electron–electron repulsion in the homoaromatic dianion, the low electron affinity of CBN, and the fact that the protruding methylene group perturbs the crystal lattice. The equilibrium constant controlling the electron transfer from the anthracene anion radical to CNB in dimethoxyethane to yield the homo[8]annulene anion radical and anthracene was studied as a function of temperature by using ESR techniques. The enthalpy of this electron-transfer reaction was used in a thermochemical cycle to obtain the electron affinity of CBN. Further, the heat of tautomerization of CBN to the homoantiaromatic open structure has been estimated to be about 32 kcal/mol.



The concept of aromaticity accounts for the extraordinary thermodynamic stability of a number of charged and neutral cyclic π-conjugated organic systems. Equally, antiaromaticity has accounted for the instability of a number of these systems with 4*n* π electrons. The concept of aromatic character was extended to include homoaromaticity in order to account for the high stability of molecules in which conjugation is interrupted in one or more places by aliphatic groups.[1] This concept of homoaromaticity

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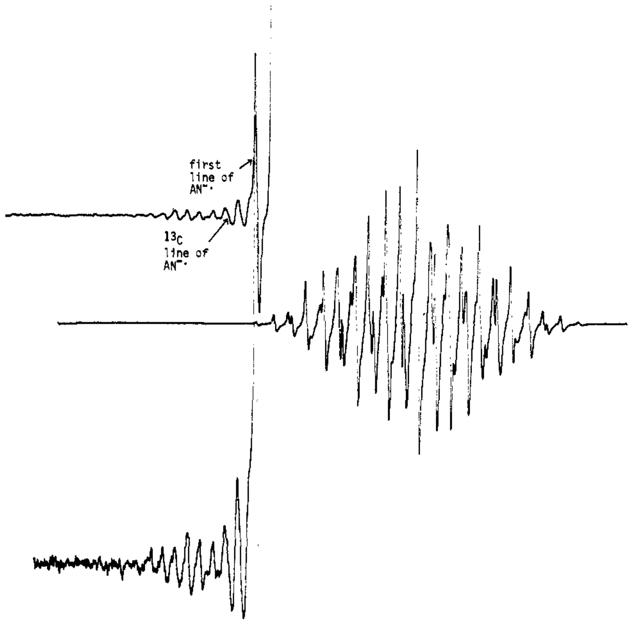
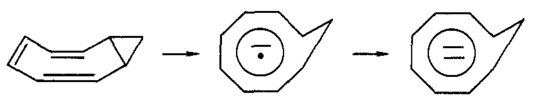


Figure 1. ESR spectrum of the anion radicals formed by the potassium reduction of a 1.5:1 mixture of AN and CBN in DME at -70 °C. When the spectrum is recorded with the $AN^{-}\cdot$ signal on scale, the signal for $HCOT^{-}\cdot$ cannot be observed. However, amplification of the spectrum by 10-fold (upper) or 50-fold (lower) results in the appearance of the signal for $HCOT^{-}\cdot$ outside of the spectral lines for $AN^{-}\cdot$. The computer simulations were carried out by keeping only the first lines of the AN anion radical on scale. Spectra were also obtained for solutions containing as much as 25:1 CBN:AN. For these solutions the $HCOT^{-}\cdot$ signal is much more intense compared to that for $AN^{-}\cdot$, but the calculated value for K_{eq} is the same. The spectrum for $HCOT^{-}\cdot$ is identical with that previously reported.[3a]

is now over 20 years old, but its antithesis (homoantiaromaticity) has yet to be studied.

The first suggestion of homoaromaticity was advanced by Thiele to explain the decreased acidity of the methylene protons of cycloheptatriene relative to those of cyclopentadiene.[2] This explanation is, of course, incorrect; but homoaromaticity has turned out to be very important in controlling the chemistry of a number of charged organic systems.[3] One of the most notable is the homo[8]annulene dianion ($HCOT^{2-}$).[4] The chemical reduction of *cis*-bicyclo[6.1.0]nona-2,4,6-triene (CBN) proceeds through



CBN HCOT⁻· HCOT²⁻ (1)

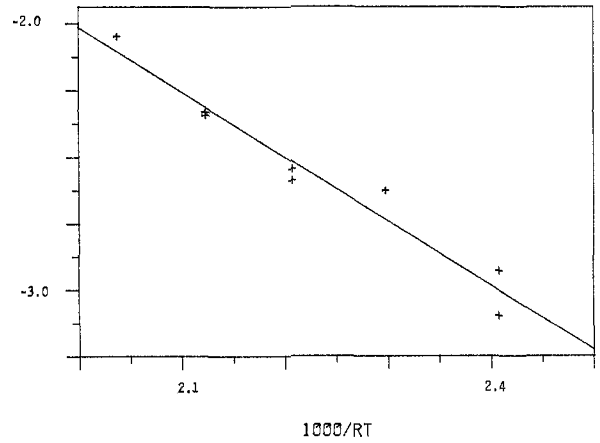
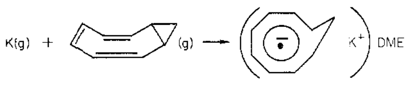


Figure 2. Plot of ln K_{eq} vs. $10^3/RT$ for the electron transfer between $AN^{-}\cdot$ and CBN (eq 2). The slope of the line is 3.9 kcal/mol, and the standard deviation is 0.3. Points were taken from several different solutions with different AN:CBN ratios.

Table I. Enthalpies of Reaction

reaction	ΔH, kcal/mol	reference
$(AN^{-}\cdot, K^{+})_{DME} + (CBN)_{DME} \rightarrow (AN)_{DME} + (HCOT^{-}\cdot, K^{+})_{DME}$	+3.9	this work
$K^{+}(g) + AN^{-}\cdot(g) \rightarrow (AN^{-}\cdot, K^{+})_{DME}$	−168	5
$CBN(g) \rightarrow CBN(l)$	−7.5	this work[6,7]
$CBN(l) \rightarrow (CBN)_{DME}$	+0.3	this work[8]
$(AN)_{DME} \rightarrow AN(s)$	−4.6	this work[9]
$AN(s) \rightarrow AN(g)$	+24.3	
$AN(g) + e^{-}(g) \rightarrow AN^{-}\cdot(g)$	−12.7	
$K(g) \rightarrow K^{+}(g) + e(g)$	+100.1	
	−64.2	

the nine-electron homoconjugated anion radical ($HCOT^{-}\cdot$) to the delocalized (homoaromatic) monohomocyclooctatetraene dianion.[4c] Here we would like to report the first thermodynamic stability of a homoantiaromatic system (homo[8]annulene) and the thermodynamic stabilities of $HCOT^{-}\cdot$ and $HCOT^{2-}$.

In contrast to the dianion of cyclooctatetraene (COT^{2-}), which can be stored at room temperature in tetrahydrofuran (THF) for years, $HCOT^{2-}$ is not stable in this solvent except at lower temperatures.[4a] Indeed, it has been shown that $HCOT^{2-}$ is a much stronger base than is COT^{2-}, due to the former's inability to delocalize charge as efficiently as does the planar p π analogue.[4c] The instability of $HCOT^{2-}$ is due to its ability to deprotonate the solvent.[4c] By measuring the thermodynamic stability of $HCOT^{2-}$, we were intent upon a determination of the thermodynamic criterion for homoaromaticity.

Results and Discussion

Calorimetric studies of the HCOT anion radical could not be carried out due to the fact that this anion radical disproportionates to such an extent that the concentration of dianion is much greater than the concentration of $HCOT^{-}\cdot$. However, the heat of formation of $HCOT^{-}\cdot$ can be obtained from the enthalpy of electron transfer from an anion radical with a known heat of formation to CBN.

The reduction of a 1:15 mixture of anthracene (AN) and CBN with a very deficient amount of potassium metal in dimethoxyethane (DME) at -70 °C yields a solution that exhibits the ESR spectrum of $HCOT^{-}\cdot$ superimposed with that of $AN^{-}\cdot$ (Figure 1). Computer simulations of the spectra using various relative concentrations of $AN^{-}\cdot$ and $HCOT^{-}\cdot$ yield the equilibrium constant for the reaction in eq 2. From the dependence of K_{eq} upon the

$$(AN^{-}\cdot, K^{+})_{DME} + CBN \rightarrow (HCOT^{-}\cdot, K^{+})_{DME} + AN \quad (2)$$

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(1) Winstein, S.; Adam, R. *J. Am. Chem. Soc.* **1948**, *70*, 838.

(2) Garratt, P. J. "Aromaticity"; McGraw Hill: London, 1971; p 159.

(3) (a) Grutzner, J. B.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1981**, *103*, 1372. (b) Applequist, D. E.; Roberts, J. D. *Ibid.* **1956**, *78*, 4012. (c) Paquette, L. A.; Kukla, M. J.; Ley, S. V.; Traynor, S. G. *Ibid.* **1977**, *99*, 4756. (d) Haddon, R. C. *J. Org. Chem.* **1979**, *44*, 3608.

(4) (a) Smentowski, F. J.; Owens, R. M.; Faubion, B. D. *J. Am. Chem. Soc.* **1968**, *90*, 1537. (b) Katz, T. J.; Talcott, C. *Ibid.* **1966**, *88*, 4732. (c) Ley, S. V.; Paquette, L. A. *Ibid.* **1974**, *96*, 6670.

(5) Stevenson, G. R.; Chang, Y. *J. Phys. Chem.* **1980**, *84*, 2265.

(6) The vapor pressure of CBN was measured as a function of temperature. The experimental procedure has already been described in ref 7.

(7) Stevenson, G. R.; Kokosinski, J. D.; Chang, Y. *J. Am. Chem. Soc.* **1981**, *103*, 6558.

(8) The heat of solution of CBN was measured in a Parr Solution Calorimeter as described in ref 7.

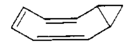
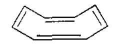
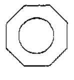
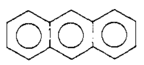
(9) This enthalpy was obtained from the solubility of AN in DME as a function of temperature. The concentration of AN in saturated DME was monitored via UV spectroscopy.

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

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

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

Table II. Electron-Electron Repulsion Energies (E_{rep}) for the Corresponding Dianions and Electron Affinities (EA) for the Neutral Molecules in kcal/mol

hydrocarbon	EA	$E_{\text{rep}}^{\text{calcd}}$	reference
	−3.7	+139	this work
	+13	+106	14, 15
 (antiaromatic)	+28	+106	14
	12.7	+117	14, 11
 (homoantiaromatic)	EA_{open}	+139	this work

temperature (Figure 2), the enthalpy of reaction 2 was found to be +3.9 ± 0.3 kcal/mol. This enthalpy can be utilized in a thermochemical cycle (Table I) to obtain the heat of formation of the solvated homoconjugated anion radical from the gas-phase CBN plus the gas-phase potassium metal, $\Delta H° = -64.2$ kcal/mol. The analogous heat of formation of $AN^{-}\cdot$, K^+ in DME is more exothermic by 16.4 kcal/mol.

It has been shown that the enthalpy of solvation of gas-phase anion radicals plus the gas-phase cation in solvents like tetrahydrofuran (THF) and DME is independent of the anion radical.[13] This solvation enthalpy turns out to be −168 kcal/mol when DME and K^+ serve as the solvent and cation, respectively.[5]

By adding 168 kcal/mol and subtracting 100.1 kcal/mol (the ionization potential of potassium) to −64.2 kcal/mol, we obtain the electron affinity of CBN (Table II). The more endothermic addition of an electron to CBN relative to the addition of an electron to COT is presumably accounted for by the fact that, relative to CBN, only minor conformational readjustments are necessary to allow the COT ring system to attain planarity and allow for p π overlap. This is the same argument that was used to explain the more negative reduction potential of CBN relative to COT.[16] The electron affinity (EA) is about 17 kcal/mol less than that for COT (see Table II). This difference is in excellent agreement with the previously reported reduction potentials of the two compounds. The $E_{1/2}$'s of COT and CBN in THF with 0.2 M tetra-*n*-butylammonium perchlorate are −1.96 and −2.55 V, respectively.[16] The difference between these two corresponds to 13.5 kcal/mol, and we have to keep in mind that this value is affected by ion association with the tetra-*n*-butylammonium ion and by entropy effects.

It should be pointed out that the authors in ref 16 mentioned that the half-wave potential of the first wave for CBN suggests that direct conversion to open $HCOT^{-}\cdot$ may not operate. In view of the similarity between their electrolytic results and ours, where the open form of $HCOT^{-}\cdot$ is in equilibrium with $AN^{-}\cdot$, the direct conversion of CBN to $HCOT^{-}\cdot$ probably was in effect.

The dianion of HCOT is very basic and unstable in THF at room temperature. This required the thermodynamic studies on $HCOT^{2-}$ to be carried out on the solid salt. After the formation of the dianion in THF via potassium reduction, the solvent was distilled off under high vacuum while the dianion was maintained below −20 °C. Once the solvent was removed, the solid green crystals of $K^+_2(HCOT)^{2-}$ could be kept at room temperature for days without noticable decomposition.

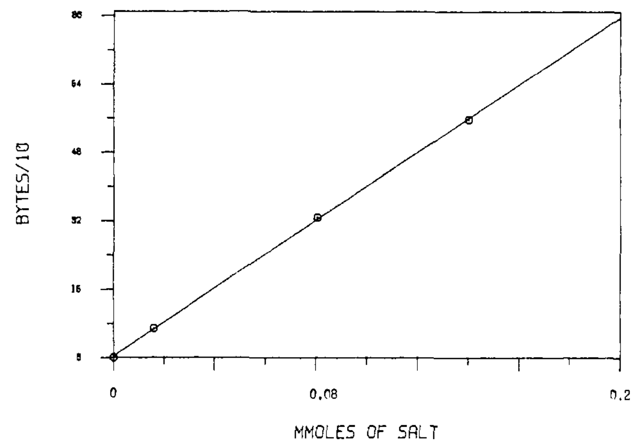


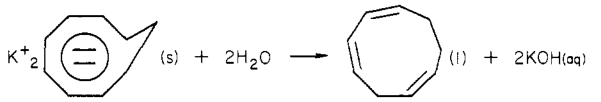
Figure 3. Plot of the computer response to the change in the temperature of the calorimeter vs. the number of millimoles of $K^+_2(HCOT)^{2-}$ salt in the glass bulbs. The heat capacity of the calorimeter in terms of the computer response is 0.030 07 cal/byte.

Table III. Enthalpies of Reaction

reaction	ΔH, kcal/mol for X =	
	HCOT	COT
$XH_2(l) + 2KOH(aq) \rightarrow (K^+)_2X^{2-}(s) + 2H_2O(l)$	+119.1	+40.4[a]
$X(l) + H_2(g) \rightarrow XH_2$	−25[b]	−25.6[a]
$2K(s) + 2H_2O(l) \rightarrow 2KOH(aq) + H_2(g)$	−94.0[c]	−94.0
$2K(s) + X(l) \rightarrow (K^+)_2X^{2-}(s)$	+0.1[d]	−79.2

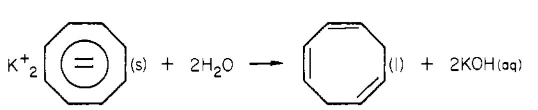
[a] Data taken from ref 17. [b] See Appendix. [c] This value was taken from ref 18. [d] The error in these final enthalpies is close to 2 kcal/mol; thus this value is within experimental error of zero.

Samples of the crystalline potassium HCOT dianion salt were sealed into evacuated thin-walled glass bulbs. The glass bulbs were broken under 100 mL of water in a modified solution calorimeter as previously described.[13,14] The products of the reaction between the HCOT dianion and water have been determined,[4c] and the reaction that takes place in the calorimeter is shown below.



(3)

A plot of the change in the temperature of the calorimeter vs. the mmoles of dianion in the glass bulbs is linear (Figure 3). Multiplying the slope of this line by 0.0301 cal/byte yields an enthalpy for reaction 3 of −119.1 ± 1.1 kcal/mol. This reaction is extremely exothermic relative to the analogous reaction for the COT dianion, eq 4 ($\Delta H° = 40.4 \pm 1.5$ kcal/mol).[17]



(4)

A number of factors must be taken into account in order to interpret the very exothermic nature of reaction 3. But it is interesting to note that this HCOT dianion, which is basic enough to pull protons from ammonia,[4c] reacts with water more than 12 kcal/mol per electron more exothermically than does potassium metal. The heat of formation of $K^+_2(HCOT)^{2-}$ from the neutral hydrocarbon and potassium metal is calculated and compared to that for $K^+_2(HCOT)^{2-}$ in Table III. It appears from Table III that the solid dianion of HCOT is close to thermoneutral. This means that the enthalpy for the electron exchange shown below is 79 kcal/mol.

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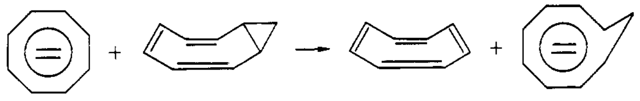
(13) Stevenson, G. R.; Williams, E. *J. Am. Chem. Soc.* **1979**, *101*, 5910.

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

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

(16) Anderson, L. B.; Broadhurst, M. J.; Paquette, L. A. *J. Am. Chem. Soc.* **1973**, *95*, 2198.

(17) (a) Stevenson, G. R.; Ocasio, I.; Bonilla, A. *J. Am. Chem. Soc.* **1976**, *98*, 5469. (b) The enthalpy for reaction 4 reported in ref 17a has been corrected by using our new computerized calorimeter system.[24]

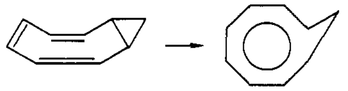


(5)

The energy necessary to add two electrons to CBN to form the dianion in the gas phase is equal to the difference between the electron–electron repulsion energy in the dianion (E_{rep}) and the sum of the first EA and the EA of the open antiaromatic form (EA_{open}) (see Scheme I). Similarly, the enthalpy for the addition of two electrons to COT is equal to minus the first EA plus the difference between the electron–electron repulsion energy and the EA of the planar antiaromatic form (Scheme II).

Conclusion

The fully conjugated (homoantiaromatic) homo[8]annulene (HCOT) logically could have an electron affinity (EA_{open}) that is similar to the EA for planar symmetrical COT (28 kcal/mol), since the incoming electron will be delocalized in eight p orbitals occupying the same relative positions in the molecule. By subtracting this vertical electron affinity of HCOT (EA_{open} = 28 kcal/mol) from the adiabatic EA of CBN (–3.7 kcal/mol), we find the difference in the heats of formation of CBN and HCOT to be about 32 kcal/mol. This represents an approximation of the enthalpy of tautomerization of CBN to its fully homoantiaromatic form (reaction 6). The 32 kcal/mol energy difference between CBN and the homoantiaromatic system means that the equilibrium constant for the reaction depicted in eq 6 is about 10^{-23}. The endothermic nature of the reaction is accounted for by the forces of homoantiaromaticity and steric effects.



(6)

From Schemes I and II it is clear that the enthalpy of reaction 5 in the gas phase must be 143 – EA_{open} – 65, while in the condensed phase the enthalpy of reaction 5 is 79 kcal/mol. The gas-phase enthalpy must be equal to 79 – ΔU_0, where ΔU_0 is the crystal lattice energy of $K^+{}_2(COT)^{2-}$ minus that for $K^+{}_2(HCOT)^{2-}$ (eq 7).

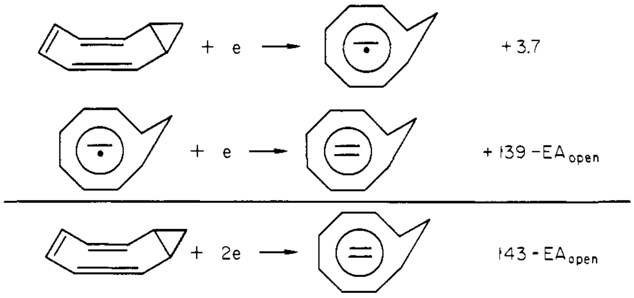
$$143 - EA_{open} - 65 = 79 - \Delta U_0 \qquad (7)$$

If EA_{open} is indeed close to 28 kcal/mol, then ΔU_0 is about 29 kcal/mol. However, regardless of the value of EA_{open} (as long as it is positive), eq 7 will require that ΔU_0 be positive. This positive difference between the crystal lattice energy of $K^+{}_2(COT)^{2-}$ and $K^+{}_2(HCOT)^{2-}$ is consistant with the expected disruption of the crystal lattice in $K^+{}_2(HCOT)^{2-}$ due to the methylene group that protrudes from the plane of the ring, and it is consistant with the data from other hydrocarbon anion radicals and dianions.[14,18] Regardless of whether the estimation of 28 kcal/mol for EA_{open} is correct or not, the extreme reactivity of the homoaromatic HCOT dianion that has been observed by other workers has been found to be due to its very low thermodynamic stability. This low thermodynamic stability is a result of three factors: the negative EA of CBN, the large electron–electron repulsion energy in the HCOT dianion, and the relatively small crystal lattice energy of $K^+{}_2(HCOT)^{2-}$.

Experimental Section

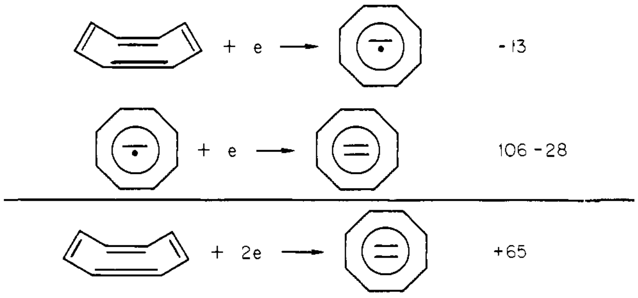
The dianion of HCOT was prepared free of solvent and potassium metal as previously described.[14,17] The CBN was exhaustively reduced with a potassium mirror in THF at –80 °C. The THF was then distilled from the dianion solution into a liquid nitrogen trap while the solution was maintained at –20 °C. The solid salt was then exposed to a high vacuum (10^{-6} torr) for 24 h to remove the last traces of THF. When this solid was redissolved in cold (–80 °C) THF and a small amount of neutral CBN added to the solution, the HCOT anion radical was generated and its EPR spectrum recorded. The anion radical resulted from the electron transfer from the dianion to the CBN.

Scheme I[a]



[a] ΔH° values are in kcal/mol.

Scheme II[a]



[a] ΔH° values are in kcal/mol.

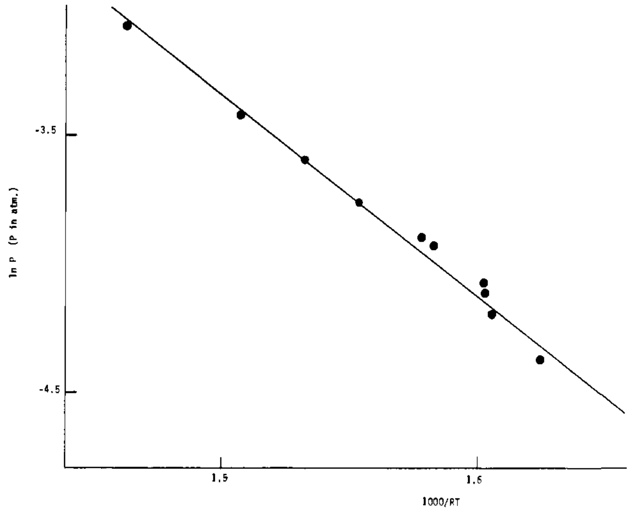


Figure 4. Plot of the vapor pressure of CBN vs. $10^3/RT$. The slope of this line yields an enthalpy of vaporization of 7.5 ± 0.3 kcal/mol.

The glass bulbs containing the $K^+{}_2(HCOT)^{2-}$(s) salt were placed into a modified cell of a Parr solution calorimeter and the bulbs broken under 100 mL of H_2O in the calorimeter.[14] The total number of millimoles of HCl used for the titration of the calorimeter contents and the products of any left over dianion and water was always equal to twice the number of millimoles of CBN that was reduced.

The electron–electron repulsion energy in $HCOT^{2-}$ was calculated by the method of Hush and Blackledge[19] as described earlier.[14] Actual EPR-determined spin densities were utilized in place of the HMO spin densities in the Hush and Blackledge calculation.

Vapor pressure measurements were carried out with a modified isoteniscope in a manner identical with that described earlier by Solsky and Grushka.[20] Our apparatus has been previously tested,[7] and the data for

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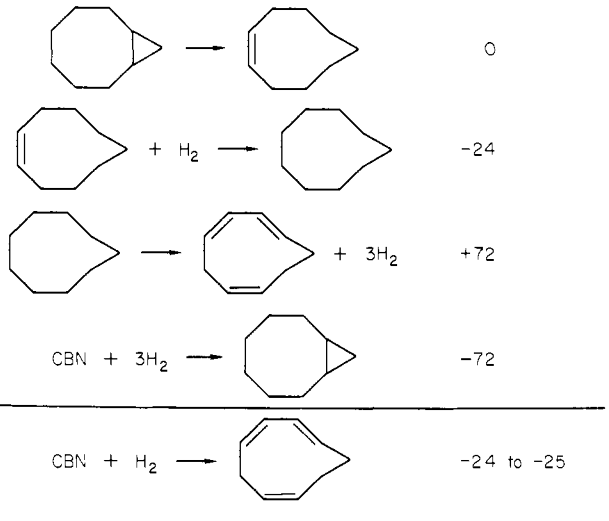
(18) Stevenson, G. R.; Wiedrich, C. R.; Clark, G. *J. Phys. Chem.* **1981**, *85*, 374.

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

(20) Solsky, J. F.; Grushka, E. *J. Phys. Chem.* **1974**, *78*, 275.

Scheme III[a]



[a] ΔH° values are in kcal/mol.

CBN are plotted in Figure 4.

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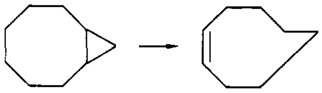
Appendix

The heats of combustion of bicyclo[6.1.0]nonane and cyclononene are identical.[21-23] Thus, the tautomerization shown below has an enthalpy that is within 0.3 kcal/mol of being zero.



$\Delta H = 0 \pm 0.3$ (8)

The heat of hydrogenation of all nonplanar seven to nine member ring systems is between -24 and -25 kcal/mol per double bond.[22-24] This includes cyclononatetraene, cyclononene, cyclooctatetraene, and cycloheptatriene. Thus, the complete hydrogenation of CBN to bicyclo[6.1.0]nonane has an enthalpy of -72 to -75 kcal/mol. From Scheme III it is clear that the heat of hydrogenation of CBN to yield cyclononane is -25 kcal/mol.

Registry No. Anthracene, 120-12-7; *cis*-bicyclo[6.1.0]nona-2,4,6-triene, 26132-66-1; potassium, 7440-09-7; homo[8]annulene anion radical, 34526-28-8; homo[8]annulene dianion·2K, 36523-65-6; homo[8]annulene, 7129-70-6.

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

(22) Nachod, F. C.; Zuckerman, J. J. "Determination of Organic Structures by Physical Methods"; Academic Press: New York, 1971, Vol. 3, pp 214-218.

(23) The heat of hydrogenation of cyclononene to yield cyclononane is -24 kcal/mol. See ref 22.

(24) Schock, L. E.; Stevenson, G. R., unpublished results.

Selective M^+-H^+ Coupled Transport of Cations through a Liquid Membrane by Macrocyclic Calixarene Ligands

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Abstract: Macrocyclic *p-tert*-butylcalix[4]arene, -calix[6]arene, and -calix[8]arene have been studied as cation carriers in H_2O-(organic solvent)-H_2O liquid membranes. When the source water phase is a solution of the metal nitrate salt, no cation transport through the membrane ($CHCl_3$) is observed with these ligands in contrast to measurable transport when the macrocyclic carrier, 18-crown-6, is present. However, if the source phase is a solution of the metal hydroxide, transport of cations is observed with calixarenes but not with 18-crown-6 in the membrane (25% v/v CH_2Cl_2-CCl_4). Transport by the calixarenes is selective for Cs^+ over other alkali metal cations with the selectivity increasing in the order [8] < [6] < [4]. Preliminary work with *p-tert*-pentylcalix[4]arene and -calix[8]arene shows transport behavior to be similar to that of the corresponding *p-tert*-butylcalixarenes. These calixarene ligands offer several features desirable to membrane carriers: (1) low water solubility, (2) formation of neutral complexes with cations through loss of a proton, and (3) the potential for coupling cation transport to the reverse flux of protons.

Introduction

Macrocyclic phenol-formaldehyde condensation products, which have been designated as calixarenes,[1] are similar in structure to certain cyclic polyethers and other macrocyclic ligands which are noted for their size-related selectivity in binding cations[2]. The calixarenes, first reported by Zinke and Ziegler,[3] have received careful synthetic study by Gutsche and his co-workers, who have published methods for the "one-flask" synthesis of *p-tert*-butyl-

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(1) (a) Gutsche, C. D. Muthukrishnan, R. *J. Org. Chem.* **1978**, *43*, 4905-4906. (b) Gutsche, C. D.; Levine, J. A. *J. Am. Chem. Soc.* **1982** *104*, 2652-2653. (c) Ninagawa, A.; Matsuda, H. *Makromol. Chem. Rapid Commun.* **1982**, *3*, 65-67.

(2) (a) Lamb, J. D.; Izatt, R. M.; Christensen, J. J.; Eatough, D. J. In "Coordination Chemistry of Macrocyclic Compounds"; Melson, G. A., Ed.; Plenum Press: New York, 1979; pp 145-217. (b) Lamb, J. D.; Izatt, R. M.; Swain, C. S.; Christensen, J. J. *J. Am. Chem. Soc.* **1980**, *102*, 475-479.

(3) Zinke, A.; Ziegler, E. *Chem. Ber.* **1944**, *77*, 264-272.

0002-7863/83/1505-1782$01.50/0