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lished by high-resolution mass spectroscopy; *m/e* 294.2345 obsd, 294.2347 calcd. ^{1}H NMR ($CDCl_3$): δ 5.80 (dd, *J* = 8.8, 1.6 Hz, 2 H), 2.26 (m, 4 H), 2.09 (m, 4 H), 1.75 (m, 20 H). ^{13}C NMR ($CDCl_3$): δ 153.4 (s), 129.9 (d), 36.8 (t), 34.6 (d), 34.5 (t), 34.1 (t), 31.9 (d), 29.6 (d). UV (C_6H_{12}): 244 (log ε 3.852), 200 (3.795) nm.

4,4′-Bihomoadamantenyl Peroxide (16). A solution of 58.9 mg (0.2 mmol) of **11** in 10 mL of CH_2Cl_2 was cooled to −78 °C with a stream of oxygen bubbling through it, 0.5 mL each of trifluoroacetic acid and trifluoroacetic anhydride were added, and 0.4 mL of a solution of 20 mg of $\mathbf{15}^+SbCl_6^-$ in 2 mL of CH_2Cl_2 was added dropwise, until the solution remained green (3.8 μmol, 1.9 mol %). The reaction mixture was quenched with ether, warmed to room temperature, and evaporated to give 70 mg of residue, which was recrystallized from methanol to give 55 mg of **16** (84%), mp 196.5–197.5 °C. The empirical formula of $C_{22}H_{30}O_2$ was established by high-resolution mass spectroscopy; *m/e* 326.2238 obsd, 326.2246 calcd. ^{1}H NMR ($CDCl_3$): δ 4.53 (s, 2 H), 3.15 (m, 2 H), 2.26 (br s, 2 H), 2.0–1.5 (m, 24 H). ^{13}C NMR ($CDCl_3$): δ 137.3 (s), 86.1 (d), 39.5 (t), 38.5 (t), 36.6 (d), 36.5 (t), 33.5 (t), 32.0 (d), 30.6 (t), 27.1 (d), 27.0 (d).

Ascaridole (18). A solution of 0.68 g (5 mmol) of α-terpinene (**17**) in 10 mL of CH_2Cl_2 was cooled to −78 °C under oxygen, 0.5 mL each of trifluoroacetic acid and trifluoroacetic anhydride were added, and a solution of 20.0 mg (0.019 mmol, 0.38 mol %) of $\mathbf{15}^+SbCl_6^-$ in 1 mL of CH_2Cl_2 was added dropwise. After the addition was complete, the initial green color faded and was replaced by an orange color, but addition of a small amount of additional oxidant did not make the solution turn green again. After quenching with 1.5 mL of triethylamine, the solution was poured into water, extracted with ether, dried with K_2CO_3, and concentrated to give 1.0 g of oil. This material was filtered through a plug of alumina in pentane solution and Kugelrohr distilled (60–80 °C, 0.1 torr), giving 0.81 g of **18** (96%).

1,1′-Bicyclohexenyl Peroxide (20). A mixture of 90 mL of CH_2Cl_2, 0.1 mL of trifluoroacetic acid, and 0.1 mL of trifluoroacetic anhydride was cooled to −95 °C in an ethanol slush bath and saturated with oxygen. **19** (160 mg, 1.00 mmol) in 10 mL of CH_2Cl_2 was added via syringe (10 mM initial concentration of **19**), followed by slow addition of 40 mg (0.038 mmole, 3.8 mol %) $\mathbf{15}^+SbCl_6^-$ in 2 mL of CH_2Cl_2. After quenching with 10 mL of 1 M Na_2CO_3, warming to 0 °C, extraction with more carbonate solution, drying, and concentration, 200 mg of an oil was obtained, which analyzed as a 10:1.5:1 mixture of **20**:**19**:**15** by NMR. TLC mesh column chromatography (30 g of SiO_2, 95:5 hexane:ethyl acetate) gave 75 mg of **20** (39%). ^{1}H NMR ($CDCl_3$): δ 4.29 (m, 2 H), 2.71 (m, 2 H), 2.1–1.0 (m, 14 H).

Acknowledgment. We thank the Petroleum Research Fund, administered by the American Chemical Society, for partial financial support of this work, and the Amoco Oil Co. for a fellowship to M.F.T. We thank Prof. Marshall Wilson (University of Cincinnati) for the singlet oxygen experiment on **11**, Prof. Robert West (University of Wisconsin) and his group for their assistance with the low-temperature visible spectroscopy, and Scott Hewitt and Tom Knickelbine for initial synthetic studies on **11**. We thank Prof. Squillacote for helpful discussions and preprints.

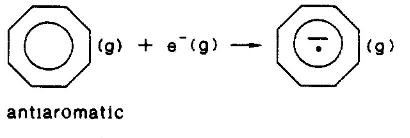
Heats of Generation of Substituted [8]Annulene Dianions

Gerald R. Stevenson* and Mark A. Nebgen

Contribution from the Department of Chemistry, Illinois State University, Normal, Illinois 61761. *Received November 12, 1985*

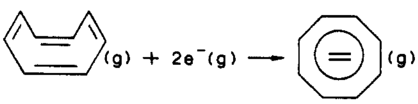
Abstract: Calorimetric studies have shown that either a phenyl or *tert*-butoxy substituent on [8]annulene ([8]) increases the heat of generation ($\Delta H_{gen}°$) of the respective dianion {$\Delta H°$ for R-[8](HMPA) + 2Na(s) → $R\text{-}[8]^{2-}$ + $2Na^+$(HMPA)} in hexamethylphosphoramide relative to that of [8]. The values for $\Delta H_{gen}°$ are −51, −38, and −42 kcal/mol respectively for R = H, C_4H_9, and C_6H_5. The destabilization of the dianion relative to the neutral molecule due to the presence of a phenyl group is accounted for by the fact that the phenyl group is nearly orthogonal to the charged eight-member ring system. This is supported by the NMR spectrum of $Ph\text{-}[8]^{2-}$. ^{1}H NMR studies carried out upon the solvent (HMPA) in the presence of $[8]^{\bullet -}$ show that the Knight shift is very close to that predicted from changes in bulk paramagnetic susceptibility. This confirms the facts that $[8]^{\bullet -}$(HMPA) is free of ion association and that ion association must be present to provide a mechanism of spin transfer from the anion radical to the solvent. The previously reported dissociation enthalpy of $[8]^{2-},K^+$ in HMPA has been combined with several calorimetrically determined values and an extra thermodynamic parameter to obtain a value of −195 kcal/mol for the single ion heat of solvation of the dianion of [8]annulene in HMPA.

The gas-phase electron affinity of [6]annulene (benzene) is −26.6 kcal/mol while that of [8]annulene ([8]) is +13 kcal/mol.[1,2] The opposite signs of these EA's are due to the fact that [6] diverges from aromatic character while nonaromatic [8] approaches aromatic character upon electron addition. The EA of [8] is positive despite the 15 kcal/mol needed to flatten the tub conformation into the fully conjugated antiaromatic system[3] to generate the planar anion radical;[4] see reaction 1. The addition of the second electron to [8] is not so facile due to the very strong electron–electron repulsion energy of 106 kcal/mol.[5] Thus, it would take 106 − 28 − 13 = 65 kcal/mol to add two electrons to [8] in the gas phase (reaction 2). For this reason the aromatic gas phase dianion is unknown.



(1)

$\Delta H°$ = −13−15 = −28 kcal/mol



(2)

$\Delta H°$ = +65 kcal/mol

In contrast to the case in the gas phase, the dianion of [8] can be generated exothermically in solution. For example [8] will react exothermically with potassium metal in tetrahydrofuran to form the dianion ion pair (reaction 3).[6] The exothermicity of reaction

$$[8](THF) + 2K(s) \rightarrow [8]^{2-},2K^+(THF) \qquad (3)$$

$$\Delta H° = -90 \text{ kcal/mol}$$

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3 is accounted for by interactions of the dianion with the solvent and gegenions. It has been pointed out that the Coulombic relaxation from the association of a dicarbanion with two cation centers can more than compensate for the electron–electron repulsion energy.[7]

The addition of a phenyl group to the anion radical of COT results in a splitting of the degeneracy of the two nonbonding molecular orbitals in the manner expected for an electron-withdrawing group; that is, the energy of ψ_s is lowered relative to that of ψ_A.[8] Thus, it is expected that the addition of two electrons to phenyl-[8] would be more exothermic than their addition to [8]. Indeed, Anderson and co-workers[9] have recently observed that this extension of the conjugation of the π system does decrease the free energy of the two-electron reduction as evidenced by the fact that the formal potential for the two-electron transfer reaction in hexamethylphosphoramide (HMPA) with 0.1 M TBAP is 88 mV/e less negative for phenyl-[8] than it is for [8]. This 88 mV corresponds to a difference of 4.0 kcal/mol of dianion (reaction 4).

$$[8]^{2-}(\text{HMPA}) + \text{R-}[8](\text{HMPA}) \rightarrow \text{R-}[8]^{2-}(\text{HMPA}) + [8](\text{HMPA}) \quad (4)$$

$$\text{when R} = \text{Ph} \; \Delta G^\circ_4 = -4.0 \text{ kcal/mol}$$

In contrast to reaction 4, the analogous electron transfer (reaction 5) involving a single electron is just slightly endothermic.[10] Anderson and co-workers[9] have confirmed this observation as evidence by the fact that the reduction potential of Ph-[8] is 0.007 V more negative than that for [8]. Their 7-mV difference corresponds to a free energy of reaction 5 of 0.16 kcal/mol, which

$$[8]^{\bullet-}(\text{HMPA}) + \text{R-}[8](\text{HMPA}) \rightarrow \text{R-}[8]^{\bullet-}(\text{HMPA}) + [8](\text{HMPA}) \quad (5)$$

$$\text{when R} = \text{Ph} \; \Delta G^\circ_5 = +0.15 \text{ kcal/mol}, \; \Delta H^\circ_5 = -2.4 \text{ kcal/mol, and } \Delta S^\circ_5 = -12.8 \text{ eu}$$

is in excellent agreement with our value[10] of 0.14 ± 0.02 kcal/mol taken from ESR measurements of the relative concentrations of $[8]^{\bullet-}$ and Ph-$[8]^{\bullet-}$ obtained from the reduction of a mixture of [8] and Ph-[8] with a very deficient amount of Na metal.

The ESR measurements show that the positive value for ΔG_5° is due to the entropy term, which is mostly due to differences in the solvation of the two anion radicals. The entropy of reaction 5 is close to zero in the gas phase due to the fact that the partition functions of the reactants and products are nearly identical. In Ph-[8] the rotation of the phenyl group may well be hindered more with a planar COT ring than with a neutral ring. However, molecular rotation and translation are the major contributers to the partition functions. For the analogous reaction involving substituted [6]annulenes, the partition functions of the products and reactants are nearly identical.[11] The endoenergetic nature of reaction 5 must be due to the fact that Ph-$[8]^{\bullet-}$ is more solvated than is $[8]^{\bullet-}$.[10]

We have developed an experimental technique for measuring the sum of the first and second solution electron affinities of π-conjugated systems and have applied this procedure to [8], Ph-[8], and *tert*-butoxy-[8] to gain insight into the nature of electron-withdrawing and electron-releasing substituents upon the thermodynamic stabilities of the resulting dianions. We were very surprised to find that, in terms of the second solution electron affinity, both the *tert*-butoxy and phenyl groups act as electron-releasing substituents.

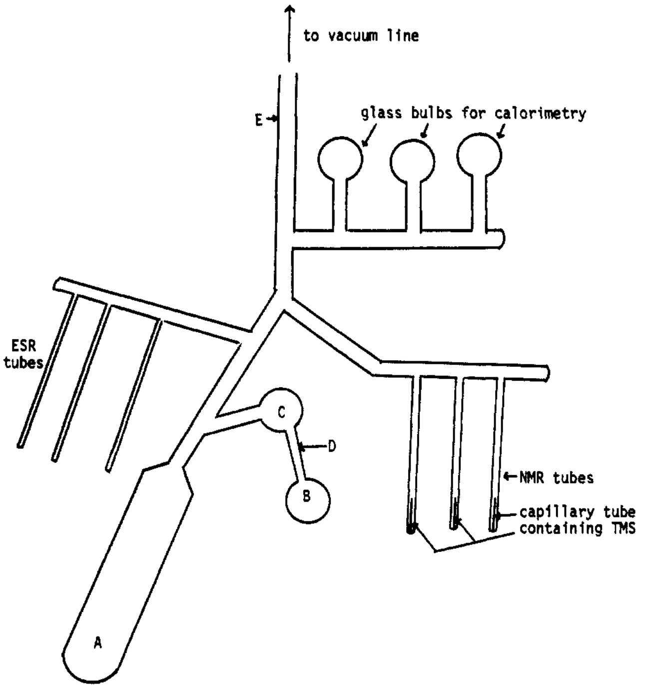

Figure 1. Apparatus used for the generation of the dianions of [8], Ph-[8], and C_4H_9O-[8]. Bulb B was charged with sodium metal. The apparatus was then evacuated, and the substituted [8]annulene was distilled into tube A. With tube A immersed in liquid nitrogen, the alkali metal was distilled into bulb C, and bulb B was sealed from the apparatus at point D. HMPA was then distilled into bulb A from the vacuum line. The apparatus was then sealed from the vacuum line at point E, and the HMPA solution was allowed to pass into bulb C where the reduction took place. During the reduction, both ESR and NMR samples could be sealed from the apparatus for analysis. After the reduction was complete, samples of the dianion solution were poured into the glass bulbs, which were in turn sealed from the apparatus. These glass bulbs were then placed into the calorimeter.

From the discussion above it is clear that dianion solvation plays a major role in controlling the thermodynamic stabilities of the substituted [8]annulene dianions. This new experimental technique allows a direct measure of the heats of generation (from the metal and HMPA solvated hydrocarbon) of these dianions, and since the dianions have been shown to be free of ion association with Na^+ in HMPA,[10b] we are afforded the solvation enthalpy of the dianion of [8]. All of this is very helpful in our unraveling the relative importance of solvation, aromaticity (the benzene dianion is unknown), and the effects of substituents upon the generation of the smallest annulene dianion known.

Experimental Section

The reductions of *tert*-butoxy-[8], Ph-[8], and [8] were carried out, using 2 mol of freshly distilled sodium metal per mol of annulene under high vacuum in an all-glass apparatus fitted with several glass bulbs, NMR tubes, and ESR samples tubes (Figure 1). During the reduction of the annulene, NMR and ESR samples were sealed from the apparatus. The well-known ESR spectra[8] for the anion radicals of [8]annulene and of the substituted [8]annulenes were recorded during the reduction. Completion of the reduction was indicated by the disappearance of the ESR signal and the appearance of sharp NMR spectra for the dianions (Figure 2). After completion of the reduction, samples of the HMPA–dianion solutions were poured into the glass bulbs, which were in turn sealed from the apparatus. NMR spectra were recorded on a CW Perkin-Elmer R-24B 60 MHz NMR spectrometer, and the chemical shifts were measured from a Me_4Si signal that originated from sealed capillary tubes containing the Me_4Si placed directly in the NMR tubes. The ESR spectra were recorded on a Brucker (IBM) E-200 spectrometer.

The glass bulbs containing 0.5 to 3.5 mL of the HMPA–dianion solutions (0.05–0.6 M) were placed in a modified Parr solution calorimeter that has been previously described.[12] The calorimeter was charged

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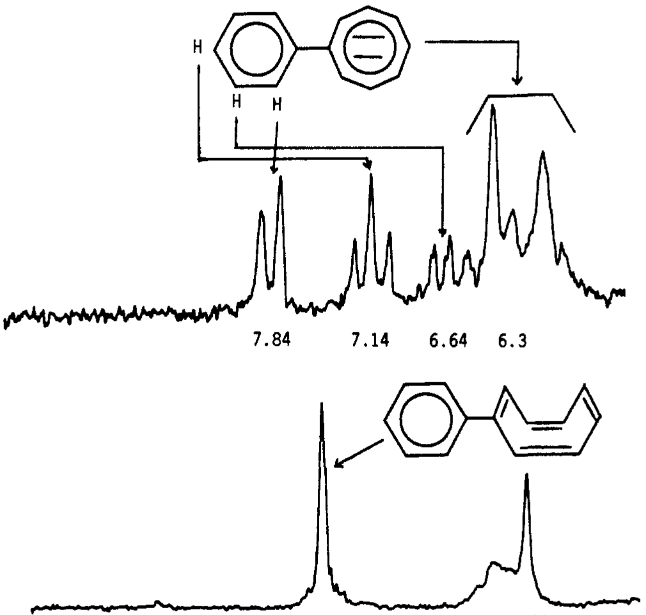

Figure 2. ^{1}H NMR spectra of Ph-[8] (lower) and of Ph-[8]$^{2-}$ (upper) in HMPA at 35 °C.

Table I. Heats of Solution in HMPA (in kcal/mol)

substance	$\Delta H_{soln}°$
[8]annulene	−0.43 ± 0.05
iodine	−15.1 ± 1.4
NaI	−7.0 ± 0.3
KI	−3.8 ± 0.4
H_2O	−2.0 ± 0.1

with 100 mL of dry HMPA containing 0.6 g of dissolved iodine. When the bulbs were crushed under this HMPA–I_2 solution, an increase in the temperature of the calorimeter due to reaction 6 was recorded. The

$$\text{R-[8]}^{2-}\text{(HMPA)} + I_2\text{(HMPA)} \rightarrow \text{R-[8](HMPA)} + 2I^-\text{(HMPA)} \quad (6)$$

output of the calorimeter was fed directly into a data collection system previously described,[12] and plots of this output vs. the millimoles of salt in the bulbs were generated. For each experiment carried out in a separate apparatus, one of the sample bulbs containing the dianion solution was weighed and broken under water. Titration of the water solutions with HCl was used to obtain the amount of dianion in the sample. Weighing of the bulb and of the remaining glass yielded the amount of solvent and the concentration of the dianion. The dianion concentration in this bulb is necessarily the same as that in the bulbs used to obtain the calorimetric data.

Any protic material, as water, contaminating the HMPA in the calorimeter would result in the presence of dihydroannulene after the reaction with I_2. When freshly distilled HMPA (from CaH_2) is used and the calorimeter is maintained under a N_2 atmosphere prior to and during the reaction, only the annulene itself could be recovered from the calorimeter solution.

The heat capacity of our calorimeter system charged with 100 mL of water is 124.22 cal/deg. The heat capacity of the system charged with 100 mL of HMPA as opposed to water was determined by simply subtracting the heat capacity of the water (99.43 cal/deg) and adding the heat capacity of the 100 mL of HMPA (44.01 cal/deg).[13] Thus, the heat capacity of the calorimeter system charged with 100 mL of HMPA is 68.80 cal/deg.

Carefully weighed portions of [8]annulene, I_2, NaI, and KI sealed in glass bulbs were placed in the calorimeter to obtain their heats of solution in HMPA. All four of these materials have small heats of solution in HMPA (Figure 3, Table I). Our values for the heats of solution of KI and NaI differ considerably from those reported by Noroselov et al. (−15.0 and −7.8 kcal/mol, respectively, for NaI and KI).[14] Their values are, however, suspect in that −15.0 kcal/mol is about half of the heat of reaction of potassium with water, and a vigorous exothermic dissolution of KI in HMPA is not evident. To be certain that our system was operating correctly when small temperature changes are involved, we measured the heats of solution of water in HMPA and the heat of solution of NaI in water. In both of these experiments we were able to reproduce the literature values, which are −2.1 and −1.80 kcal/mol, respectively.[15,16]

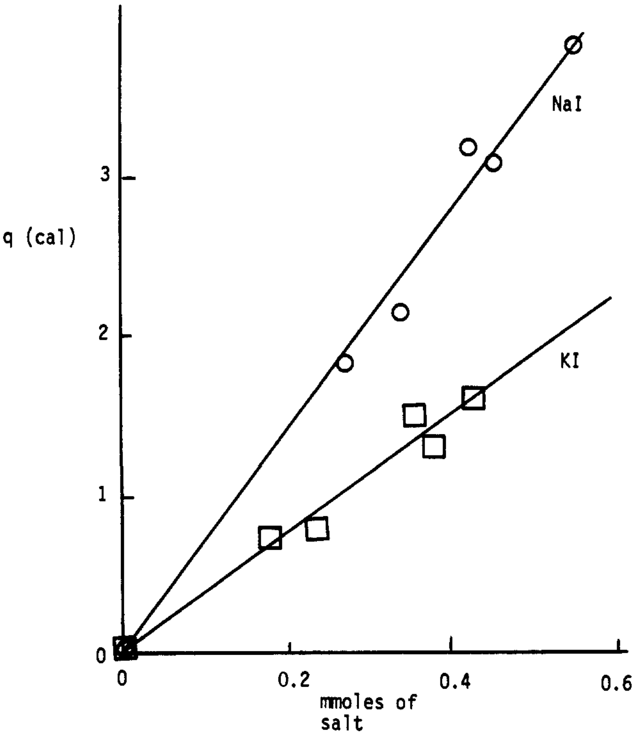

Figure 3. Plots of the heat change in the calorimetric upon dissolution of the salt in HMPA vs. the millimoles of KI (squares) and NaI (circles). The slopes of these lines represent the heats of solution of these two salts in HMPA. These salts were dried under high vacuum for 24 h prior to the calorimetric studies.

Anion radical spin concentrations were measured using the dual-cavity technique.[17] A spin standard (DPPH) was placed in one of the cavities of our dual-cavity ESR system, and an HMPA solution containing [8]$^{2-}$ and [8]$^{\cdot-}$ (sealed from the apparatus shown in Figure 1) was placed in the remaining cavity. With the spectrometer critically tuned, the overmodulated ESR signals were sent to the data collection system and doubly integrated. For a typical experiment, the anion radical concentration first increases as the reduction proceeds. It then reaches a maximum and falls to zero as the [8] is completely reduced to dianion.

The *tert*-butoxycyclooctatetraene was synthesized from bromocyclooctatetrene as described by Krebs.[18] The phenylcyclooctatetraene was prepared and purified as described by Cope and Kinter.[8a,19] Both compounds were purified via vacuum distillation, and both compounds did yield NMR spectra identical with those described in the literature.

Results and Discussion

As the sodium reduction of [8] in HMPA proceeds, the NMR signal of the HMPA at first broadens and shifts downfield. Then, as the reduction nears completion (2 mol of metal/mol of annulene), the signal again sharpens and moves back upfield. A plot of this Knight shift vs. the concentration of [8]annulene anion radical is linear and has a slope that is within experimental error of the theoretical value of 2.6 ppm/M[20] (Figure 4) that is predicted for changes in the paramagnetic bulk magnetic susceptibility. In the presence of anion radicals, the solvent protons are shifted upfield due to the bulk paramagnetic effect, but this is attenuated by the transfer of some spin density to the solvent molecules in the first solvation shell.[20,21] It is clear from Figure 3 that there

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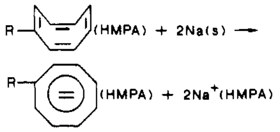
Table II. Enthalpies of Reaction (in kcal/mol)

reaction	$\Delta H°$ for R = H	$\Delta H°$ for R = C_4H_9O	$\Delta H°$ for R = Ph
$2I^-(HMPA) + R\text{-}[8](HMPA) \rightarrow I_2(HMPA) + R\text{-}[8]^{2-}(HMPA)$	+86.5 ± 2.1	+99.6 ± 3.0	+95.3 ± 3.2
$I_2(HMPA) \rightarrow I_2(s)$	+15.1	+15.1	+15.1
$2NaI(s) \rightarrow 2Na^+(HMPA) + 2I^-(HMPA)$	-14.0	-14.0	-14.0
$2Na(s) + I_2(s) \rightarrow 2NaI(s)$	-138.6[a]	-138.6	-138.6
 R (HMPA) + 2Na(s) → R (HMPA) + 2Na⁺(HMPA)	-51.0 ± 3.2	-37.9 ± 3.9	-42.2 ± 3.7

[a] Reference 23.

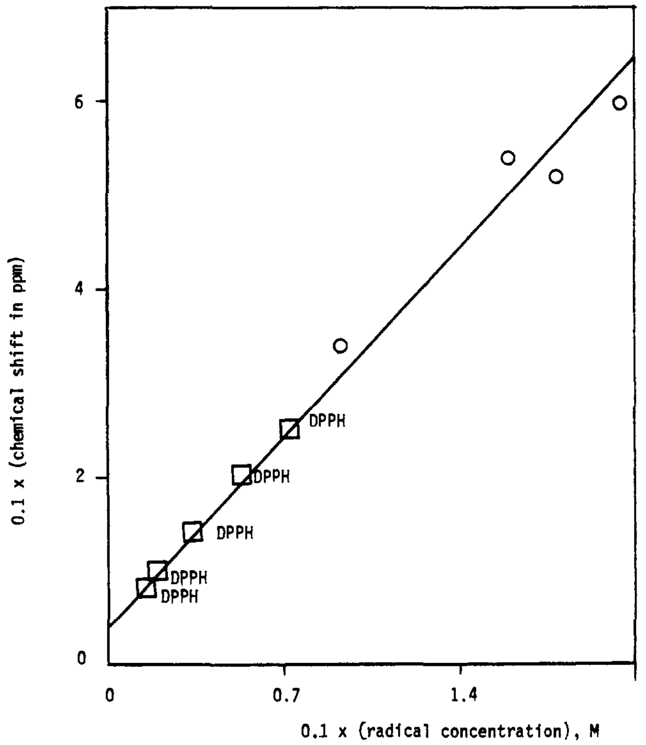


Figure 4. Plot of the chemical shift of the HMPA protons vs. concentration of [8]annulene anion radical or 2,2-diphenyl-1-picrylhydrazyl (DPPH), a stable free radical. Note that the line generated for $[8]^{\bullet-}$ is collinear with that generated for DPPH.

is no such transfer of spin density from $[8]^{\bullet-}$ to the HMPA. This means that either the interaction between HMPA and $[8]^{\bullet-}$ is very weak or that there is no mechanism for transfer of spin to the solvent. It will be shown that the solvation of $[8]^{\bullet-}$ by HMPA is very exothermic, which leaves only the latter explanation.

Screttas and co-workers[21] have proposed a mechanism of spin transfer from an anion radical to the solvent which includes a transfer of spin from the anion to the metal and then a transfer from the metal to the solvent.[21] This mechanism would preclude a spin transfer from $[8]^{\bullet-}$ to HMPA in the absence of ion association, and it is known that there is no ion association between Na^+ and either the dianion or anion radical of [8] in HMPA.[10b,22] Thus, Figure 4 confirms the conclusions of Screttas and co-workers.

When the evacuated glass bulbs containing HMPA solutions of Na^+ plus $[8]^{2-}$, Ph-$[8]^{2-}$, or C_4H_9O-$[8]^{2-}$ were broken under 100 mL of the HMPA–I_2 solution in the calorimeter, the resulting temperature increase was due to reaction 6. Plots of the heat change in the calorimeter vs. the millimoles of dianion in the bulbs are linear (Figure 5), and their slopes (Table II) are equal to the enthalpies of reaction 6 ($\Delta H_{rxn}°$). When the $\Delta H_{rxn}°$ values are treated as shown in Table II, the heats of generation ($\Delta H_{gen}°$) of the dianions from the HMPA-solvated hydrocarbon and the solid sodium metal are obtained.

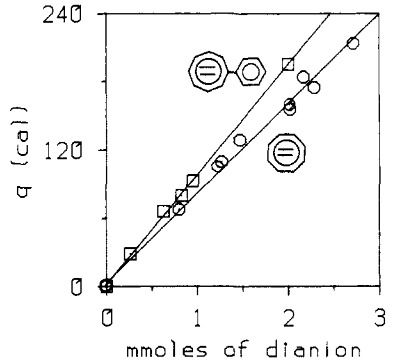


Figure 5. Plots of the heat change in the heat content of the calorimeter vs. the millimoles of dianion in the bulbs. For the sodium systems the heat generated is due to reaction 6. The line with the larger slope represents data taken from the Ph-$[8]^{2-}$(HMPA) + Na^+(HMPA) system reacting with I_2 in HMPA. For the lower line, some of the data were taken from the $[8]^{2-}$(HMPA) + Na^+(HMPA) system and some from the $[8]^{2-},K^+$(HMPA) system. The data taken from the later system were corrected for ion association prior to plotting. The upper line has a slope of -95.3 kcal/mol and the lower line has a slope of -86.5 kcal/mol (see Table II).

In view of the facts that the phenyl group should act as an extension of the conjugation (electron-withdrawing group) and increases (makes less negative) the reduction potential of [8] in HMPA,[9] it is very surprising that Table II reveals that the heat of generation of Ph-$[8]^{2-}$ is less negative than it is for [8].

ESR measured spin densities in Ph-$[8]^{\bullet-}$ show that the dihedral angle between the phenyl and cyclooctatetraene ring systems is large but is smaller than 90°.[8a] However, for the phenyl group to act so strongly as an electron donor as to destabilize the dianion of [8] by more than 10 kcal/mol, it must be twisted very nearly to 90° relative to the eight-member ring system. A look at the ^1H NMR spectrum of this dianion (Figure 2) helps support this conclusion. The neutral molecule of Ph-[8] shows only a singlet for the phenyl protons. However, the dianion exhibits a doublet for the ortho protons at 7.84 ppm, a multiplet for the meta protons at 6.64, and a triplet for the para protons at 7.14. The center of mass for the phenyl protons is 7.22 ppm. Charge drain into the phenyl group would result in a dramatic upfield shift of the phenyl protons due to electron shielding and loss of aromatic character. Since only a very small upfield shift is observed, it would appear that very little electron density is diffusing into the phenyl ring. The chemical shift center of mass for the COT ring system is not expected to vary from Ph-[8] to Ph-$[8]^{2-}$ due to the canceling effects of the diamagnetic ring current and shielding due to the added electrons. In agreement with this, very little spin density is found in the phenyl ring in the radical anion.[8a]

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[22] (a) Wiedrich, C. R.; Catlett, D. L.; Sedgwick, J. B.; Stevenson, G. R. *J. Phys. Chem.* **1983**, *87*, 578. (b) The dissociation enthalpy for $[8]^{2-},K^+$ in HMPA (1.2 ± 0.4 kcal/mol) was obtained by measuring the anion radical disproportionation equilibrium constant and algebraically relating it to the ion pair dissociation constant.

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Table III. Enthalpies of Reaction (in kcal/mol)

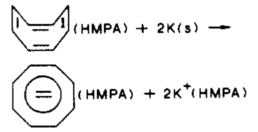
reaction	$\Delta H°$	ref
$2I^-(HMPA) + [8](HMPA) \rightarrow I_2(HMPA) + [8]^{2-}(HMPA)$	+86.5 ± 2.1	this work
$I_2(HMPA) \rightarrow I_2(s)$	+15.1	this work
$2KI(s) \rightarrow 2K^+(HMPA) + 2I^-(HMPA)$	-7.6	this work
$2K(s) + I_2(s) \rightarrow 2KI(s)$	-157.7	23
	-63.7 ± 3.6	

Table IV. Enthalpies of Reaction (in kcal/mol)

reaction	$\Delta H°$	ref
$[8](HMPA) + 2K(s) \rightarrow [8]^{2-}(HMPA) + 2K^+(HMPA)$	-63.7	this work
$2K(g) \rightarrow 2K(s)$	-42.8	24
$2K^+(g) + 2e^-(g) \rightarrow 2K(g)$	-200.0	25
$2K^+(HMPA) \rightarrow 2K^+(g)$	+187.1	26[a]
$[8](l) \rightarrow [8](HMPA)$	-0.43	this work
$[8](g) \rightarrow [8](l)$	-10.3	27
$[8]^{2-}(g) \rightarrow [8](g) + 2e^-(g)$	-65	28
$[8]^{2-}(g) \rightarrow [8]^{2-}(HMPA)$	-195	

[a] This number was obtained using the TATB assumption and represents an extrathermodynamic value.

Comparison of the potentials reported by Anderson et al.[9] which show that the free energy of reduction of Ph-[8] to Ph-$[8]^{2-}$ is less negative than the free energy of reduction of [8] to $[8]^{2-}$ with the fact that the heat of generation of $[8]^{2-}$ is more negative than that of Ph-$[8]^{2-}$ probably means that the entropy change for the reduction of [8] to its dianion is more negative than that for the reduction of Ph-[8] to Ph-$[8]^{2-}$ in HMPA. If the more concentrated charge in the dianion of [8] requires greater solvation, then this greater solvation will contribute a more negative heat but at an entropy cost. The more delocalized Ph-$[8]^{2-}$ imposes a smaller negative entropy change upon its formation. This argument neglects any contribution due to the presence of ion association with Bu_4N^+ in the electrochemical study. Anderson and coworkers[9] do mention the possibility of such ion pairing in their paper. Further, it is known that the alkali metal cations that are larger than Na^+ do form ion pairs with $[8]^{2-}$.[10b,22] From Table II we would predict that the enthalpy of reaction 4 is 8.8 kcal/mol. When this is combined with the free energy of reaction 4 reported by Anderson,[9] an unrealistic entropy change for the reaction of +43 eu is predicted. The presence of ion association in Anderson's experiments would help account for this. We also must keep in mind the fact that the value for the enthalpy of reaction 4 (8.8 kcal/mol) was obtained as a small difference between two large numbers. Thus, the error in this value could be as large as 6.9 kcal/mol. The unrealistic value for the entropy mentioned above most probably results from a combination of our large error in the enthalpy change and ion association of $[8]^{2-}$ with Bu_4N^+.

The calorimetry experiments with the *tert*-butoxy[8]annulene dianion confirm the fact that an electron-releasing substituent on [8] increases the enthalpy of generation of the dianion. However, it is interesting to note that sodium metal reacts with C_4H_9O-[8] as exothermically as it does with water. The NMR of C_4H_9O-$[8]^{2-}$ reveals that the chemical shift of the methyl protons (1.67 ppm) is identical with that of the neutral molecule, while the cyclooctatetraene ring protons in C_4H_9O-[8] shift from 6.16 ppm to 5.90 ppm upon reduction to the dianion.

When evacuated bulbs containing the potassium salt of $[8]^{2-}$ in HMPA were broken under 100 mL of the HMPA–I_2 solution in the calorimeter, the resulting temperature increase was due to reaction 7. By simply subtracting the heat of dissociation of the

$$[8]^{2-},K^+(HMPA) + I_2(HMPA) \rightarrow [8](HMPA) + K^+(HMPA) + 2I^-(HMPA) \quad (7)$$

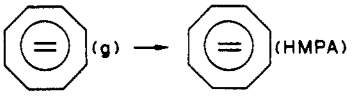
charged ion pair reaction 8,[22] we should obtain the enthalpy of

$$[8]^{2-},K^+(HMPA) \rightarrow [8]^{2-}(HMPA) + K^+(HMPA) \quad (8)$$

$$\Delta H° = 1.2 \text{ kcal/mol}$$

reaction 6. This proved to be the case. The experimental points obtained from reaction 7 were corrected for ion association by simply subtracting the product of 1.2 and the moles of dianion in the bulbs from the heat change in the calorimeter. The corrected data proved to be collinear with that obtained from the sodium reduced solutions of [8] (Figure 5).

The enthalpy for reaction 6, which was obtained from Figure 5, can be combined with two heats of solution and the heat of formation of KI to obtain the heat of generation of the potassium salt of $[8]^{2-}$ in HMPA that is free of ion association (Table III). This heat of generation can be used to estimate the solvation enthalpy of the [8]annulene dianion. Parker and co-workers[26] have used the TATB assumption (an extra thermodynamic assumption) to estimate the single-ion solvation enthalpy of the K^+ ion in HMPA. We can now combined Parker's value with our heat of generation and some other constants to estimate the solvation enthalpy of $[8]^{2-}$ (Table IV, reaction 9).

 (9)

$\Delta H° = -195$ kcal/mol

Almost a decade ago, the heat of reaction of two gas-phase electrons with [8](g) to yield the HMPA solvated $[8]^{2-}$ (-125 kcal/mol) was estimated by measuring the heat of reaction of the solid potassium dianion salt with water and using this enthalpy in a thermochemical cycle that contained a number of constants including Parker's[26] value and the heat of solution of the dianion salt in HMPA.[29] Since that time, it has been demonstrated that the heat of solution of $K^+{}_2[8]^{2-}$ (s) in HMPA, which was obtained via the thermal dependence upon solubility, is not strictly valid.[30] This is the case because the nature of the solid salt in contact with the solvent is not known.[30] Despite these considerations, the single-ion solvation enthalpy estimated from the older measurements, -125 - 65 = -190 kcal/mol, is remarkably similar to the one reported here.

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Registry No. HMPA, 680-31-9; $[8]^{2-}$, 34510-09-3; Ph-$[8]^{2-}$, 50277-25-3; *t*-BuO-$[8]^{2-}$, 103423-18-3; $[8]\bullet^-$, 34510-85-5.

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