2-Aryl-1,3-dithianes and -dithiolanes: A Nearly Ideal Series for Relating the Energies for Bond Breaking to Electron Transfer

Daniel T. Stoelting, Richard T. Ludwig, and Edward M. Arnett*

Department of Chemistry, Duke University, Box 90346, Durham, NC 27708-0346

Received 13 May 1996; revised 19 June 1996

ABSTRACT

By virtue of the stabilizing effect of the 1,3-sulfur atoms on the carbocations, radicals, and carbanions generated from the title compounds, it has been possible to measure a variety of bond-making and bond-breaking processes in the two very similar solvents, DMSO and sulfolane, and relate them to electron-transfer energies obtained by electrochemical techniques. Important properties reported from this and previously published work are as follows: heats of hydride transfer to the cations from cyanoborohydride ion, pK_R, in aqueous acid, heats of deprotonation by $K^+DMSYL/DMSO$, pK_{HA}, redox potentials for the cations, and carbanions, which relate their energies to their conjugate radicals and to each other. The results support our previous assertion that the electron-transfer energy between the three trivalent oxidation states of carbon and the Parr–Pearson absolute hardness, η, derived from it are the fundamental properties that determine energies for making and breaking two-electron bonds and thus determine most of organic chemistry.

Excellent correlations are found for the substituent effects on energy changes associated with the various processes for making and breaking bonds to the cations, radicals, and carbanions and the electron-transfer energies for interconverting them. Many comparisons can be made with the corresponding 2-aryl-

1,3-dioxo systems. Careful "bookkeeping" of these energies through appropriate thermochemical cycles shows excellent consistency despite a small solvent effect for transferring the ions from sulfolane to DMSO.

Direct reaction of the carbocation with the carbanion of 2-phenyl-1,3-dithiane produced a clean formation of the dimer from which the heat of heterolysis (40.6 kcal/mol) and homolysis (19.1 kcal/mol) could be calculated.

AM1 structures and heats of formation of two neutral species and two cations, a radical and an anion, have been computed and are generally consistent with stabilizing interactions of the gem sulfurs with the reactive center.

The present study is the first, to our knowledge, to provide a coordinated view of the energies for generating the carbocations, radicals, and carbanions from a series of heterocycles. These energies are related to each other and to the electron-transfer energies for interconverting these reactive trivalent forms of carbon. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

General Background.

The energies (pK_{R^+}s, BDEs, pK_{HA}s) for converting neutral compounds (ROH, RX, RH) into carbocations, radicals, or carbanions (henceforth $R^{+/\cdot/-}$) provide some of the most valuable fundamental information undergirding contemporary organic
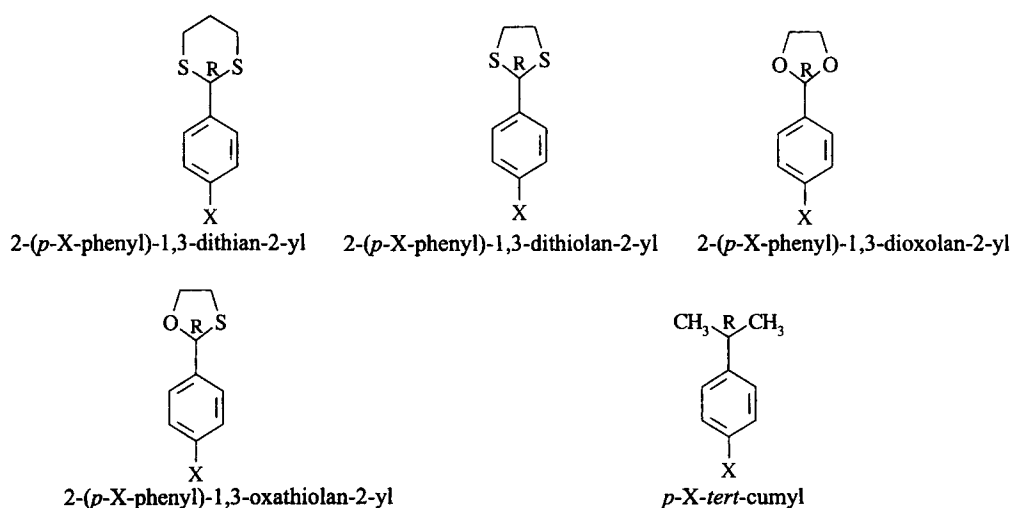
chemistry. However, there are very few types of tetra-covalent compounds for which all three of these conjugate trivalent oxidation states of carbon are stable under similar conditions in the same or equivalent solvents. We have applied the term *amphihydric* to such compounds [1,2] to emphasize the facile cleavage or formation of their C–H bonds by removal of a hydride ion, hydrogen atom, or proton.

Triarylmethanes are the best-known examples, and trityl $R^{+/\cdot/-}$ have been studied extensively since the early 1900s [2,3]. Recently [2], we have reported the effects of changing *p*-substituents on the stabilities of a series of trityl- and 9-phenylxanthyl-$R^{+/\cdot/-}$. The present article applies the same methods to a series of *p*-substituted 2-phenyl-1,3-dithianes, which provide carbocations and carbanions that are stabler, respectively, in DMSO and sulfolane than those of the trityl series and so allow a more rigorous thermodynamic analysis of the formally related bond-breaking energies required to produce the substituted 1,3-dithyl $R^{+/\cdot/-}$ and their redox potentials. Some of the corresponding properties for dithiolanes, dioxolanes, and related substituted arylmethyl systems allow comparison of the effects of substitution and other structural changes on these compounds and their conjugate $R^{+/\cdot/-}$, relative to each other, and to other criteria of stability such as Hammett parameters. Figure 1 presents the structures to be discussed. Of particular interest are the abilities of S, O, and C to stabilize negative charge, electron

deficiency, or an unpaired electron on an adjacent carbon. The present study is the first, to our knowledge, to provide a complete roster of such data obtained under the same conditions in a single laboratory.

As before [1b,2,4], stabilities of R^+s have been compared in terms of their hydride affinities, $\Delta H_{H^-}(R^+)$, i.e., their heats of reaction with cyano-borohydride ion in sulfolane, and by other relevant published data. Stabilities of R^-s relative to RHs have been compared through their pK_{HA}s and heats of deprotonation, ΔH_{dep}s, in DMSO. The stabilities of $R^{+/\cdot/-}$ relative to each other have been compared through redox potentials of solutions of stable R^+s and R^-s. Radical stabilities are expressed as homolytic bond-dissociation energies (BDEs) [5,6] derivable in solution by combining pK_{HA}s or ΔH_{dep}s with free energies of oxidation of the R^-s to their conjugate $R\cdot$s [7]. The relationships between these properties are shown in Figure 2. All measurements reported here have been made at 25°C in DMSO or sulfolane.

Although most of the relevant properties of these solvents are virtually interchangeable [2], the relatively high Lewis basicity of DMSO limits its use for the study of R^+, and the insolubility of the K^+ salt of sulfolane rules it out as a superbase system comparable to K^+DMSYL/DMSO for generating and studying R^-. Therefore, we have not been able to do the *ideal* study of the aryldithianyl $R^{+/\cdot/-}$ system in a sin-

2-(*p*-X-phenyl)-1,3-dithian-2-yl   2-(*p*-X-phenyl)-1,3-dithiolan-2-yl   2-(*p*-X-phenyl)-1,3-dioxolan-2-yl

2-(*p*-X-phenyl)-1,3-oxathiolan-2-yl   *p*-X-*tert*-cumyl

$$R = \text{"+" } or \text{ "•" } or \text{ "–" } or \text{ "—H"}$$

$$\text{Typically, } X = NO_2, CF_3, F, Cl, H, Me, \text{ or OMe}$$

FIGURE 1 Structures of the heterocyclic amphihydric precursors and their carbocations, radicals, and carbanions discussed in this article.
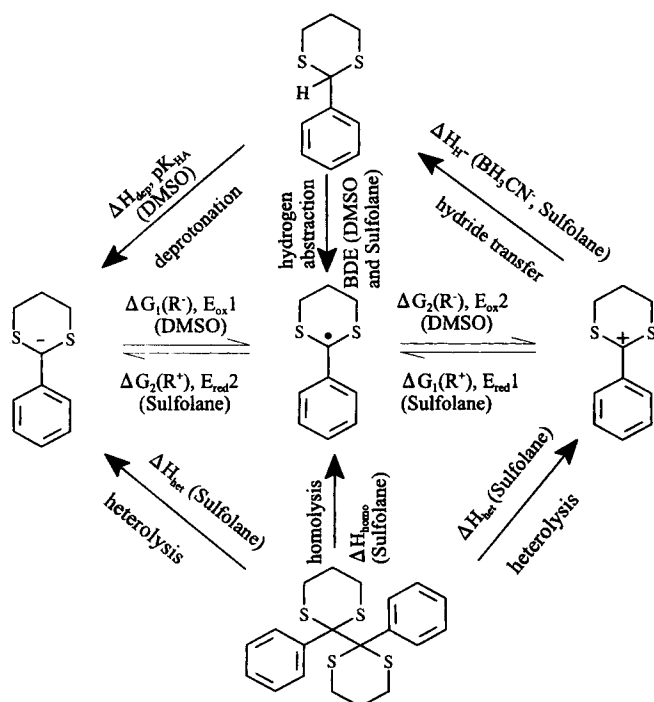
FIGURE 2 Formal relationships between bond-making and bond-breaking processes and electron transfer.

gle solvent. As will be seen below, a small solvation energy difference of about 2 kcal between sulfolane and DMSO is carried into all of the redox-free energies in Figure 2 and the values derived from them.

Like all thermodynamic properties, the stabilities of R^+ and R^- are scaled to arbitrary, but convenient reactions for bond breaking as represented, for example, by pK_{R^+}s [8] or pK_{HA}s [9] obtained from indicator equilibria. Reaction calorimetry can also be used to establish the relative stabilities of R^+s in sulfolane by their hydride affinities, $\Delta H_{H^-}(R^+)$s, from reaction with cyanoborohydride ion, which correlate well with pK_{R^+}s [2]. The stabilities of R^-s, by their heats of deprotonation, ΔH_{dep}s, in DMSO, correlate well with their pK_{HA}s [10]. The triphenylmethanes and 2-aryl-1,3-dithianes fall fortuitously within the window where some representatives of both types of their ionizations (to R^+ and R^-) are amenable to study on these energy scales. In contrast, the 2-aryl-1,3-dioxolanes have R^+s that are quite stable in dilute aqueous acid, DMSO, or sulfolane. Although they are much too weakly acidic to be deprotonated by $K^+DMSYL^-/DMSO$, their R^-s have a transient existence in sulfolane by two-electron reduction of the dioxolenium cations using cyclic voltammetry [4a].

The Redox-Free Energies; ΔG_1 (R^+), ΔG_2 (R^+),

$\Delta G_1(R^-)$, ΔG_2 (R^-). These terms are the key to all the energy interelations between $R^{+/-}$s and the bond-making and bond-breaking processes depicted in Figure 2. They are derived by multiplying the four corresponding reversible electrode potentials (obtained in sulfolane for the cation and DMSO for the anion) by the usual conversion factor, -23.06 kcal/mol V. By convention, the electrode potentials are taken as reduction potentials and are referred to the normal hydrogen electrode (NHE). Although the observed potential is the same whether one is considering the oxidation or the reduction process in equilibrium at the electrode, the sign of the derived ΔG term depends, of course, on which direction the process is taken.

It is crucially important that the electrode processes be reversible, and there is considerable precedent for this assumption here. If all four of the redox-free energies were obtained in the same solvent, $\Delta G_1(R^+)$ should exactly equal $-\Delta G_2(R^-)$, and $\Delta G_1(R^-)$ should equal $-\Delta G_2(R^+)$ if the electrode potentials being compared truely refer to reversible processes, since it should not matter whether the intermediate radical is approached from a solution of R^+ or R^-. This is a powerful operational test for reversibility and has been applied successfully to other similar systems [2,12,13]. As will be seen below, the consistency of a number of values derived from the four redox-free energies supports the consistency of the total thermodynamic analysis presented here.

ΔG_3, The Energy Gap between R^+ and R^-: The reversible two-electron oxidation potential for converting R^- to R^+, or the corresponding potential for reduction of R^+ to R^-, is of great significance to physical organic chemistry since they can be converted into the free-energy changes $\Delta G_3(R^-)$ or $\Delta G_3(R^+)$ that separate the Bronsted base species R^- from its conjugate Lewis acid R^+.

$$\Delta G_3(R^+) = \Delta G_1(R^+) + \Delta G_2(R^+) \qquad (1a)$$

$$\Delta G_3(R^-) = \Delta G_1(R^-) + \Delta G_2(R^-) \qquad (1b)$$

Breslow [14] recognized that if either of these species were stable enough to provide a reliable pK by the usual indicator methods, then the normally inaccessible pK for its conjugate could be estimated by using cyclic voltammetry to obtain the necessary ΔG_3. Thus, pK_{R^+}s of some very unstable carbocations were derived from the pK_{HA}s of their stable carbanions and vice versa. This pioneering combination of electrochemistry with indicator free energies, or subsequently with calorimetric heats of reaction [15], has opened the way to determining a wide range of formerly inaccessible thermodynamic values for bond-making and bond-breaking processes.

484 Stoelting, Ludwig, and Arnett

Clearly, if all electrode processes are reversible, and measured under the same conditions, $\Delta G_3(R^+) = -\Delta G_3(R^-)$. In the present study, a small solvent effect is revealed since the reduction of R^+ occurs in sulfolane, but the oxidation of R^-, in DMSO.

ΔG_{ET}; The Electron-Transfer Energy between R· and its Conjugate Ions; The Bridge between Homolysis and Heterolysis Energies. The formation or rupture of bonds takes place by the reorganization of two-electron bonds. Correspondingly, oxidation and reduction of radicals to give cations or anions occurs through electron transfer and reorganization between the three trivalent states of carbon. The free energy of electron transfer is related to the reversible redox potentials of the two ions if they are obtained in the same solvent, as shown in Equation 2a. If, as in the present case, reduction of R^+ and oxidation of R^- occur in different solvents, Equations 2b and 2c apply.

$$\Delta G_{ET} = \Delta G_1(R^+) + \Delta G_1(R^-) \qquad (2a)$$

$$\Delta G_{ET}(R^+) = \Delta G_1(R^+) - \Delta G_2(R^+) \qquad (2b)$$

$$\Delta G_{ET}(R^-) = \Delta G_1(R^-) - \Delta G_2(R^-) \qquad (2c)$$

Since ΔG_{ET} is the free-energy difference between the two conjugate ions and their related radical, this property is the bridge between homolytic and heterolytic bond energies, as shown in the cycles of Figure 2. Thus, $\Delta G_1(R^-)$ has been used extensively to interrelate $pK_{HA}s$ and BDEs [7]; the heterolytic and homolytic modes of C–H bond rupture for carbon acids. Correspondingly, we have used $\Delta G_{ET}s$ to convert heterolytic bond energies $\Delta H_{het}s$ for a variety of C–C [16], C–O [17], C–S [18], and C–N [19] bonds into their homolytic bond energies, $\Delta H_{homo}s$, and Parker has used $\Delta G_1 R^+$ to calculate $\Delta G_{H^-}(R^+)$ from BDEs [12].

Parr–Pearson Absolute Hardness. ΔG_{ET} also represents the energy difference between the highest occupied orbital, which is filled in the R^-, and the corresponding lowest unoccupied orbital, which is empty in the R^+. This HOMO/LUMO gap and ΔG_{ET} have been related by Parr and his students [20] and Pearson [21] to the absolute hardness η of the radical. This property can be regarded as the resistance of this species to electron reorganization to form its conjugate cation and anion and is defined by Equation 3:

$$\eta = (I - A)/2 = -\Delta G_{ET}/2 \qquad (3)$$

where I is the ionization potential of the radical and A is its electron affinity. This is obviously closely related to the Mullikan electronegativity,

$$\chi = (I + A)/2 \qquad (4)$$

Here, I and A are gas phase properties so that solvation energies must be considered when relating them to redox energies in solution [20f,21f]. Since solvation terms for large, stable ions will usually be constant or proportional to other energy terms, such as those considered here, they are not apt to compromise the conclusions drawn from the following discussions.

Pearson and Parr have demonstrated the fundamental importance of η to a wide variety of chemical processes [20,21]. We have drawn attention to its direct relation to bond-making and bond-breaking processes [22] and thus its importance as a *fundamental property that underlies and determines most of organic chemistry.* η provides a measurable value, if the radical is accessible, which immediately puts the well-known hard and soft generalizations of Pearson on a quantitative basis. The softness, σ, of the radical, atom, or molecule under discussion is simply the reciprocal of η.

It is observed very generally [7,16–18,23] that, for a series of structurally related R^-s, a close correlation is found between their heats or free energies of deprotonation of their conjugate RH's in basic solution and the free energies for their oxidation to their conjugate R·s. Equivalent correlations [2,4,24] are found for the formation of related R^+s by heterolytic cleavage of RH, ROH, or RX vs. the free energies of reduction of their conjugate R^+s. The oxidation and reduction potentials of a series of R·s are therefore a potent guide to the energies for making and breaking the bonds from their conjugate R^+ or R^- to leaving groups. Since the making and breaking of bonds is generally considered to lie at the heart of organic chemistry, the electron-transfer energy and absolute hardness are key indicators that unify an enormous range of seemingly unrelated carbocation, radical, and carbanion chemistry.

Apparent Stabilities of R^+ R·, R^-, and Ground-State Effects in RH

Now, it should be emphasized that if a pair of trivalent species are being compared in terms of their energies of formation (e.g., BDEs, $pK_{HA}s$, $pK_{R^+}s$) from tetrahedral precursors erroneous interpretations will result if some special effect stabilizes or destabilizes one of their precursors but not the other. Such *ground-state effects* are a familiar driving force for the reactions of highly strained molecules and are being appreciated increasingly in other contexts [25–27].

Of particular relevance to the present study is the

large anomeric effect that geminal heteroatoms may have on the heat of formation of a molecule [25,26,28]. The dramatic difference of 8 kcal/mol between the heats of formation for 1,3-dioxane and 1,4-dioxane could lead to corresponding errors in comparing the stabilities of their radicals or ions as deduced from the heats or free energies of homolytic or heterolytic C–H bond cleavage of the dioxane precursors. Corresponding ground-state effects in the dithio and dioxo compounds considered here will lead to false conclusions regarding the inherent stabilities of R^+, $R\cdot$, or R^- as inferred from ΔH_H-s, ΔH_{dep}s, pKs, or BDEs. Moreover, as shown by Figure 3, any stabilizing or destabilizing effect in their common ground-state RH compared to that of another compound RH′ may contribute equally to the energies for conversion to R'^+, $R'\cdot$, R'^-.

No wonder that subtle structural contributions, such as the anomeric effect, may be sources of controversy when used to interpret reactivity data! Without complete sets of heats of formation for the reacting tetrahedral precursors to the trivalent species being compared, it is not possible to evaluate completely the roles of ground-state effects by comparing the stabilities of $R^{+/\cdot/-}$s from relative energies for bond-making and bond-breaking or redox processes. This places a limitation on the interpretations of the stability data given here, as it also does (less explicitly) for many other published accounts.

As may be gathered from the above background on heteroatom stabilized $R^{+/\cdot/-}$, there is significant literature about the carbocations and carbanions from 1,3-dithianyl systems; voluminous literature
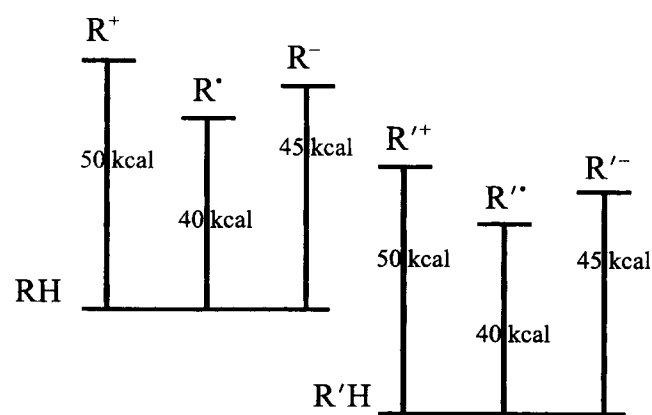
FIGURE 3 Demonstration that ground-state energy differences between similar compounds RH and RH′ are carried equally to their respective trivalent species and so cannot be quantified directly (or even detected) from bond-breaking or redox energies. Units are arbitrary and need not be the same for the two systems.

for dioxolenium cations but comparatively little about their conjugate R^- or $R\cdot$. A few discussions of 1,3-oxythio systems are also relevant to the abilities of adjacent sulfur atoms to stabilize $R^{+/\cdot/-}$ compared to oxygen. Since we are concerned here with the stabilities of all three of these types of trivalent species, both with respect to each other and to their tetracovalent precursors, it is important to review briefly the current state of evidence and opinion as background for the results of the present study.

Stabilization of Carbocations by Adjacent O or S. A very recent review by Richards includes a summary of the relative abilities of adjacent sulfur vs. oxygen atoms to stabilize R^+s and transition states for their reactions with nucleophiles [25,28,29] and ground-state effects. Another review by Satchell Satchell [30] elaborates the mechanistic problems of the acid-catalyzed hydrolysis of O–C–O, O–C–S, and S–C–S acetals and ketals. The kinetic results are sometimes confusing, and the interpretations are correspondingly complicated and often unconvincing because the hydrolysis of the O–C–O and O–C–S compounds are often too fast to permit convenient study of the R^+ intermediates.

Caserio's classic gas phase study [31] probed the oxygen vs. sulfur stabilization question with several compounds and concluded that sulfur was superior at stabilizing adjacent carbenium ion centers so that some of the confusing condensed phase results must be due to differential solvation. Her results are supported by theoretical studies with appropriate warnings of solvation effects [28d]. A slight superiority of the p-OMe group compared to -SMe is suggested by their respective sigma$^+$ values of -0.78 and -0.60 [32]. A careful analysis of the rates of formation and reaction of alpha-oxygen and -sulfur stabilized 4-methoxybenzyl R^+ in trifluoroethanol/H_2O shows a slight thermodynamic preference for sulfur, although the oxygen-stabilized cation is formed faster [29].

A review by Okuyama on dithio R^+ [33] describes methods of preparation and thermodynamic as well as kinetic data for a variety of 2-substituted 1,3-dithiocarbocations. Of direct relevance is the reported $p^KR^+ = 2.5$ of 2-phenyl-1,3-dithiolanium ion compared to -6.6 for the trityl cation. Accordingly, these dithiocarbocations should be made easily from their 2-H precursors by hydride transfer to trityl cation, and they should be capable of generating tropylium ion, $p^KR^+ = 4.7$ [3b] by abstracting hydride ion from cycloheptatriene.

A very recent comparison [34] of the stabilities of $tris$(chalcogenato) carbenium ions $[C(XR_3)]^+$ for

X = O, S, Se, Te shows a small superiority (1.03 kcal/mol) for S over O in CH_2X^+, but O is dramatically superior (15.6 kcal/mol) over S in $CH(XH)_2^+$ and even more so (35 kcal/mol) in $C(XH)_3^+$.

In contrast to our results (discussed later), effects of ring size are claimed [33] to be small on the p^KR^+ values for 2-*t*-butyl-1,3-dithianylium (six-membered ring) vs. dithiolanium (five-membered) cations. The carbocation of the 2-anisyl-1,3-dithio five-membered ring is reported to be [33] more stable (pK_{R^+} = 4.1) than the corresponding 1,3-oxythio cation (pK_{R^+} = 1.8) or the 1,3-dioxolenium ion (pK_{R^+} = 1.1). Unfortunately, none of the extensive data for 1,3-dihetero-2-ylium cations in the classic review of Pittman et al. [35] are directly relevant to the present study.

$\Delta H_{H^-}(R^+)$s are reported here for a series of 2-(*p*-substituted phenyl)-1,3-dioxolenium ions and corresponding dithianylium and dithiolenium ions as a contribution to the question of oxygen vs. sulfur stabilization of carbocationic centers.

Cabanions. The thermodynamic stabilities of dithianyl R⁻ are in relatively good shape. Bordwell's group determined pK_{HA}s for a number of sulfur-containing hydrocarbons, including the parent 2-phenyldithiane, in DMSO/K⁺DMSYL⁻ [9,36]. This compound has a pK_{HA} = 30.65, within experimental error of that (30.62) of triphenylmethane. Unsubstituted dithiane is too weakly acidic (pK_{HA} = ca. 39 extrapolated) for accurate study in the K⁺DMSYL⁻/DMSO system. Since diphenylmethane is only slightly less acidic (pK_{HA} = 32.2) than triphenylmethane, addition of a phenyl group to dithiane has a comparatively large effect (39 − 31 = 8 pK unit). The 2-phenyl-1,3-dioxolanes are far too weakly acidic to be deprotonated by K⁺DMSYL⁻/DMSO, but Eliel [37] has used the Lochmann–Schlosser superbase (BuLi/KO-*t*-Bu) successfully to generate (Li⁺/K⁺)R⁻ ion pairs of 2-phenyl-1,3-dioxanes in THF at −40°.

There are no good gas-phase comparisons between acidities of 1,3-dithio vs. 1,3-dioxo compounds. However, the effect of one heteroatom on an R⁻ is shown by the differences in gas-phase acidities (ΔG_{acid}) between propane (411 kcal/mol) dimethyl ether (398 kcal/mol) and dimethyl sulfide (386 kcal/mol) [38]. Thus, oxygen has a modest ability to stabilize adjacent negative charge and sulfur considerably more so. The corresponding ΔG_{acid} for 5,5-dimethyl-1,3-dithiane is 369 kcal/mol, reflecting the potent stabilizing effect of two adjacent sulfurs in a six-membered ring modulated perhaps by the two methyls. There are no comparable data for its dioxoanalog.

Other studies of ion-paired acidities in THF [39,41] are more directly relevant to the wide synthetic applications of dithianyl alkali reagents. The superior ability of neighboring sulfur over oxygen to stabilize R⁻ has been the subject of many theoretical discussions [41–45], one of the more recent ones [46] citing most of the significant literature and examining the matter through high-level *ab initio* geometry and energy calculations. Eliel [40] has investigated conformational factors, such as the anomeric effect, as they influence the stereochemistry of dithio and dioxo anions.

Radicals. Radical stabilization energies RSEs are scaled in terms of the differences between BDEs of the relevant C–H bonds in RHs and that for H_3C–H, 105 kcal [5,6]. The rather small catalog of BDEs determined by classical gas-phase thermochemical methods has been expanded enormously in the past decade by combining free energies [2,7] or heats [17] of ionization with redox energies of the relevant ions in solution or by computation [49,50]. The upshot of such comparisons is that, for the most part, the stabilizing effects of C, O, or S on adjacent carbon radicals are trifling compared to their effects on their conjugate R⁺ or R⁻. Leroy's summary [49] of the measured and calculated BDEs of the precursor RHs, which are most relevant to the case in hand, gives the following (in kcal/mol): CH_2CH_3 (100.2), ·CH_2OH (95.1), ·CH_2SH (96.0), ·$CH(CH_3)_2$(96.13), ·$CH(OH)_2$ (91.9), ·$CH(OCH_3)_2$(91.2), ·$CH(SH)_2$ (91.1). Bordwell has summarized a variety of published data [47b] and determined the RSEs of a variety of R, O, S, and N functionalities on 9-fluorenyl and several other families of radicals compared to their effects on the pK_{HA}s of their conjugate R⁻s.

In the following discussion, we will present our results for calorimetric ΔH_{dep}s for a series of 2-aryl-1,3-dithio heterocycles; the $\Delta H_{H^-}(R^+)$s and free energies of reduction of their 2-carbocations free energies of oxidation of their 2-carbanions, the correlations of these properties with each other and with corresponding ones, where available, for dioxolane systems, and appropriate substituent constants.

Results and Discussion

General: We shall follow the same order for presentation and discussion of data that was used in organizing the Introduction. Under each catagory–carbocations, carbanions, and radicals), the calorimetric and electrochemical results determined here will be compared and correlated with each other and with other structure and/or stability criteria (e.g., Hammett substituent parameters).

In order to minimize confusion in making comparisons between our data for free energies enthalpies, pKs, and sigma parameters and those from other laboratories, the following conventions will be followed. Calorimetric data will be expressed in kcal/mol at 25°, electrode potentials will be referred to the NHE (see Experimental) and converted into free energies by multiplying by -23.06 kcal/mol V. Hammett sigma parameters will be cited from the 1991 review by Hansch et al. [51]. To make correlations of our enthalpy and electrochemical free-energy data comparable to other Hammett correlations where pKs or log ks have been plotted vs. sigma parameters, we divide both ΔG and ΔH values by 1.364 (i.e., 2.303 RT) kcal to give unitless rho values [52].

There is justification for treating most of our differential free energy and enthalpy data on a common basis, as though the corresponding entropy terms were insignificant or directly proportional to ΔG and ΔH. This has been demonstrated repeatedly for redox free energies of resonance-stabilized cations and anions in sulfolane and DMSO [16,53]. It has also been shown [10] that good linear plots of nearly unit slope result from correlation of ΔG_{HA} vs. ΔH_{dep} for the ionization of a wide variety of weak acids in DMSO, as shown below for dithianes.

There is no free-energy scale of carbocation stabilities in nonhydroxylic media with which we can compare ΔH_{H^-} values and thus estimate entropy terms for hydride ion transfer in sulfolane. However, in the absence of specific interactions, the electrostatic solvation of a dithianylium cation in sulfolane should be nearly equivalent to that of its conjugate anion and therefore have similar electrostatic entropies of solvation [8d, 22b]. Ion pairing has been removed by the addition of crown ether to the sodium cyanoborohydride solution, and hydrogen bonding should not make a significant contribution to the solvation by sulfolane to the resonance-stabilized ions considered here. It is, therefore, reasonable that differential entropy factors for hydride transfer to resonance-stabilized cations should be negligible [20f], as they are for deprotonation to produce the corresponding carbanions in sulfolane or DMSO.

The Redox Free Energies. As stated earlier, if all redox processes were reversible and in the same solvent, $\Delta G_1(R^+)$ = $-\Delta G_2(R^-)$ and $-\Delta G_2(R^+)$ = $\Delta G_1(R^-)$. Comparison of these properties in Tables 1 and 2 for the three 2-[p-X-phenyl]-1,3-dithianyl species (X = NO_2, Cl, H), for which there are complete data, shows an average difference of 2.5 kcal/mol between these properties.

We take this to be the difference in solvation energies for the electrode processes on going from DMSO to sulfolane and to be a rough confirmation of reversibility. Corresponding differences between $\Delta G_2(R^+)$ and $\Delta G_1(R^-)$ for six p-substituted trityl systems [2] average to 1.7 kcal/mol with no obvious var-

iation due to size or polarity of the p-group. In all cases, $\Delta G_1(R^+)$ is exergonic, as seems reasonable for the transfer of an electron to a carbocation, and the magnitude is inversely proportional to the stability of the ion. As expected, the redox free energies correlate well with other stability properties for the ions. The corresponding process in DMSO, $-\Delta G_2(R^-)$, is also exergonic but less so by 2.6 kcal/mol. Thus, R^+s are more stable (solvated better) in DMSO.

The free energies of reduction of R· to R^- in sulfolane, $\Delta G_2(R^+)$, are endergonic, and their magnitudes are inversely proportional to the stabilities of the ions. The corresponding process in DMSO, $-\Delta G_1(R^-)$ is more endergonic by 2.5 kcal/mol than $\Delta G_2(R^+)$ in sulfolane. Thus, if we make the usual assumption that solvent effects on radicals are negligible compared to those on ions, it is clear that DMSO is relatively a better solvent for R^+ than is sulfolane, but the latter is relatively better for R^-. The dielectric constant [54] of DMSO is 46.7 compared to sulfolane, 43.3, so a small electrostatic factor favors DMSO for ions of both charge. The observed solvent effect specifically favoring DMSO for R^+ is consistent with the higher basicity of DMSO [2] against Lewis acids. The reason why sulfolane is preferred by R^- remains obscure.

In order to provide perspective on the redox measurements reported here and the properties derived from them, selected values from published studies are also tabulated.

ΔG_3: This property is the key to Breslow's [14] method of estimating pKs for very unstable ions. It defines the free-energy gap between R^+ and R^- (Equations 1a and 1b) and varies enormously with structure. It is dominated by the wide variations in stability of R^-. Comparison of Table 1 with Table 2 shows a high value of ΔG_3 = 54.5 kcal/mol for conversion of the 4,4,5,5-tetramethyl-2-phenyl-1,3-dioxolenium ion to its carbanion and a low of 2.3 kcal/mol for oxidizing the fluorenyl anion to its cation. A photomodulation redox study of benzyl, cumyl, and benzhydryl radicals [13] shows the very high instability of these carbanions relative to their cations compared to those of trityl xanthyl, or dithio anions. Two geminal oxygens produce the largest ΔG_3 gap between R^+ and R^- in Table 1. On this broad scale, the 2-aryl-1,3-dithianyl and substituted trityl systems have relatively modest gaps separating their carbocations from conjugate carbanions. This, of course, is a major reason why they are readily studied as amphihydric systems.

Comparison of $\Delta G_3(R^+)$ with $\Delta G_3(R^-)$ shows the

TABLE 1 Stability Data for 2-Substituted 1,3-Dithi-2-yl, 1,3-Diox-2-yl Cations and Some Other Representative Carbocations

Series	Substituent	$\Delta H_H{}^{-a}$	$\Delta G_1(R^+)^b$	$E_{red}1^c$	$\Delta G_2(R+)^b$	$E_{red}2^c$	pK_{R+}	$\Delta G_{ET}(R^+)^d$	$\Delta G_3(R^+)^e$	BDE^{+f}
1,3-Dithian-2-ylium	2-(p-NO₂)Ph	−48.9	−9.4	408	−1.0	42		−8.4	−10.4	79.5
1,3-Dithian-2-ylium	2-(p-Cl)Ph	−47.3	−4.7	202	15.1	−655		−19.8	10.4	82.6
1,3-Dithian-2-ylium	2-Ph	−47.2	−3.9	168	17.7	−766		−21.5	13.8	83.3
1,3-Dithian-2-ylium	2-(p-Me)Ph	−46.6	−2.2	94	19.0	−826		−21.2	16.9	84.4
1,3-Dithian-2-ylium	2-(p-OMe)Ph	−45.6	−1.2	54	20.8	−902		−22.0	19.6	84.4
1,3-Dithian-2-ylium	None	−47.3								
1,3-Dithiolan-2-ylium	2-(p-CF₃)Ph	−45.21	−7.8	340						77.4
1,3-Dithiolan-2-ylium	2-(p-Cl)Ph	−40.9	−5.6	243					75.3	
1,3-Dithiolan-2-ylium	2-Ph	−40.2	−4.2	183			2.5			76.0
1,3-Dithiolan-2-ylium	2-(p-Me)Ph	−38.2	−2.9	126						75.3
1,3-Dithiolan-2-ylium	2-(p-OMe)Ph						4.1			
1,3-Dioxolan-2-ylium	2-(p-Cl)Ph	−43.5								
1,3-Dioxolan-2-ylium	2-(p-F)Ph						−0.5			
1,3-Dioxolan-2-ylium	2-Ph	−42.1					−0.6			
1,3-Dioxolan-2-ylium	2-(p-Me)Ph	−40.8					0.0			
1,3-Dioxolan-2-ylium	2-(p-OMe)Ph	−37.2					1.1			
Me₄-1,3-Dioxolan-2-ylium^g	2-Ph	−31.4	11.7	−509	42.8	−1856	1.4	−31.1	54.5	83.1
Xanthenyl^h	None	−46.1	−10.5	454	15.3	−664	−0.84	−25.8	4.8	75.6
Xanthenyl^h	2-Ph	−45.1	−8.6	372	17.8	−773	0.81	−26.4	9.2	76.5
Thioxanthenyl^h	2-Ph	−45.3	−8.7	377	16.6	−718		−25.3	7.9	76.6
Benzyl^i	None		−16.8	730					49.9	
Cumyl^i	None		−3.7	160					43.7	
Benzhydryl^i	None		−8.1	350					34.4	
Triphenylmethyl^h	None	−52.7	−12.5	542	16.7	−722	−6.6	−29.1	4.2	80.2
Tropylium^h	None	−43.4	1.4	−60	32.5	−1410	4.7	−31.1	33.9	84.8
Cyclopropenyl^h	1,2,3-triphenyl	−38	4.1	−176	29.7	−1290	3.1	−25.7	33.8	82.1

aUnits in kcal/mol relative to 0.1 M sodium cyanoborohydride in sulfolane at 25°C.
bUnits in kcal/mol relative to the normal hydrogen electrode (NHE).
cUnits in mV relative to the NHE by adding 750 mV to the values relative to ferrocene.
d$\Delta G_{ET}(R^+) = \Delta G_1(R^+) - \Delta G_2(R^+)$.
e$\Delta G_3(R^+) = \Delta G_1(R^+) + \Delta G_2(R^+)$.
f$BDE^+ = -\Delta H_{H^-} + \Delta G_1(R^+) + 40.0$.
gData from Ref. [4a].
hData from Ref. [1].
iData from Ref. [13].

ΔG_{ET}, the Electron-Transfer Energy and Absolute Hardness. This term (Equation 2) is the free-energy difference between a given R· and its conjugate R^+ and R^-, or for transferring one electron from the carbanion to the carbocation. As shown in Figure 2, it provides the important link between ΔH_{het}s and ΔH_{homo}s; pK_{HA}s or ΔH_{dep}s to BDEs; ΔH_H-s or pK_{R+}s to BDEs. It is also related directly to the absolute hardness (Equation 3). Comparison of ΔG_{ET} in three 2-aryl-1,3-dithyl systems (p-NO₂, p-Cl, and H) shows good agreement between the values obtained in sulfolane, from the reduction potentials of R^+, and those from R^- in DMSO (average difference of 0.9 kcal/mol). This agreement stands in contrast to the large solvent effects on ΔG_3 (about 5 kcal/mol), described earlier, that probably reflect the additive er-

rors in ΔG_3, as a sum of solvent effects on electrode potentials, whereas there is cancellation in ΔG_{ET} as a difference in potentials.

Comparison of ΔG_{ET} for the various systems listed in Tables 1 and 2 also shows a much narrower range of values than for ΔG_3. ΔG_{ET}s for the 1,3-dithio systems fall in the same range as those found for benzyl, benzhydryl, trityl, and xanthyl systems [2] with cumyl and 1,3-dioxolanyl much higher. It is also seen that ΔG_{ET}s are relatively insensitive to substituent effects because, in general, groups that stabilize R^+ destabilize R^-, although the NO₂ group in the present context is much more effective at stabilizing the R^- through resonance than destabilizing its conjugate R^+ inductively.

Carbocations. Table 1 presents the important thermodynamic data for the stabilities of relevant carbocations both by bond making and breaking and

TABLE 2 Stability Data for 2-Substituted 1,3-Dithan-2-ylides and Some Other Representative Carbanions

Series	Substituent	$\Delta H_{dep}{}^a$	$\Delta G_f(R^-)^b$	$E_{ox}1^c$	$\Delta G_2(R^-)^b$	$E_{oc}2^c$	$pK_{HA}{}^d$	$\Delta G_3(R^-)^e$	$\Delta G_{ET}(R^-)^f$	BDE^g	BDE^{-h}
1,3-Dithian-2-ylide	2-(p-OMe)Ph	−4.0	−21.4	−926	—	—	—	—	—	—	81.7
1,3-Dithian-2-ylide	2-(p-Me)Ph	−7.4	−20.6	−894	—	—	—	—	—	—	79.1
1,3-Dithian-2-ylide	2-(p-F)Ph	−8.2	−19.7	−854	2.5	108	31.1	−17.2	−22.2	78.7	79.2
1,3-Dithian-2-ylide	2-Ph	−8.7	−19.5	−844	1.0	42	30.7	−18.5	−20.4	78.4	78.9
1,3-Dithian-2-ylide	2-(p-Cl)Ph	−11.4	−17.3	−752	3.8	166	29.3	−13.5	−21.2	78.6	78.4
1,3-Dithian-2-ylide	2-(p-NO₂)Ph	−28.0	−2.5	−110	5.5	238	16.9	3.0	−8.0	76.5	76.6
Benzyl[i]	None		−33.0	−1430					−49.9	−16.0	
Cumyl[i]	None		−39.9	−1730					−43.7	−36.3	
Benzhydryl[i]	None		−26.3	−1140					−34.4	−18.2	
Trityl[j]	None	−9.0	−19.1	−830	13.9	604	30.6	−19.1	−33.1	78.6	79.0
Xanthenyl[j]	None	−10.3	−21.6	−938			30.0			75.3	75.2
Xanthenyl[j]	9-Ph	−13.3	−19.3	−835	8.6	372	27.9	−19.3	−27.8	74.8	74.6
Thioxanthenyl[k]	9-Ph	−13.9	−16.7	−723			27.4			76.6	76.5
Fluorenyl[k]	9-Ph	−53.7	−11.3	−491	13.6	590	17.9	2.3	−24.9	69.1	42.1

[a]Units in kcal/mol relative to 0.1 M K⁺DMSYL⁻ in DMSO at 25°C.
[b]Units in kcal/mol relative to the normal hydrogen electrode (NHE).
[c]Units in mV relative to the NHE by adding 750 mV to the values relative to ferrocene.
[d]Experimental pK_{HA} determined by NMR except 2-phenyl-1,3-dithiane [36].
[e]$\Delta G_3(R^-) = \Delta G_1(R^-) + \Delta G_2(R^-)$.
[f]$\Delta G_{ET}(R^-) = \Delta G_1(R^-) - \Delta G_2(R^-)$.
[g]C–H bond dissociation enthalpy calculated according to Bordwell's Equation [36]: BDE = $1.364 pK_{HA} + \Delta G_1(R^-) + 56$.
[h]BDE = $\Delta H_{dep} + \Delta G_1(R^-) + 107.1$.
[i]Data from Ref. [13].
[j]Data from Ref. [2].
[k]Data from Ref. [16].

electrochemical criteria. Perspective can be gained from the following order of decreasing ΔH_{H^-} (with bracketed numbers in kcal/mol): trityl (−52.7) < 1,3-dithianylium (−47.3) < 2-phenyl-1,3-dithianylium (−47.2) < xanthylium (−46.7) < thioxanthylium (−45.26) < 9-phenyl xanthylium (−45.08) < tropylium (−43.4) < 2-phenyl dioxolenium (−42.1) > 2-phenyl dithiolanium (−40.2) < < 1,2,3-triphenylcyclopropenium (−38) < 2-phenyl-4,4,5,5,tetramethyl-1,3-dioxolenium (−30.22).

In terms of ΔH_{H^-}, the 2-phenyl-1,3-dithiocarbocations are stabilized considerably relative to trityl cations and are enormously more stable than the equivalent, benzyl, cumyl, or benzhydryl cations. The relative stabilizing effect of sulfur over oxygen, from comparison of the unsubstituted 2-phenyl-1,3-dithiolanyl vs. the corresponding dioxolanyl cations, is a modest 1.9 kcal/mol in favor of sulfur with similar differences seen for the p-methyl and chloro cations.

Of obvious interest is the surprisingly large increase in stability (8.7 kcal/mol) that results from placing four methyl groups at the 4- and 5 positions of the 2-phenyl-1,3-dioxolenium ions. The X-ray structures of 2-phenyl-1,3-dioxolenium ion and its 4,4,5,5-tetramethyl derivative have been studied carefully and shown to be strictly planar [4b]. Very long O(1)–C(5) and O(3)–C(4) bonds in the tetra-

methylated ion indicate considerable charge delocalization to C(4) and C(5) and to the attached methyl groups consistent with the large observed stabilizing effect on ΔH_{H^-}. Unfortunately, no equivalent published data are available for the dithiocations.

A further comparison in terms of ring size shows the five-membered dithiolanyl carbocations to be 6–8 kcal more stable than their six-membered dithianyl analogs. Lacking structural data, this large difference must be attributable to differences in conformation or ring strain between the two cations or their corresponding neutrals. No directly applicable comparison has been possible for the five- and six-membered dioxocations because of the instability of the six-membered cations under reaction conditions.

Comparisons of ΔH_{H^-} with Other Criteria of R^+ Stability. The superiority of sulfur over oxygen in stabilizing cyclic carbocations, as measured by ΔH_{H^-}, accords with many of the data bearing on the O vs. S matter that were cited in the Introduction. The most familiar thermodynamic property for comparing relatively stable carbocations in solution is the pK_{R^+} for equilibration with their carbinols in aqueous acid [8]. The stabilities derived from ΔH_{H^-}, values correlate well with ΔG_{R^+} (i.e., 1.364 pK_{R^+});

slope $= -0.888$, R $= 0.989$ for trityl ions [2]. A few such data are listed in Table 1. Since the dithiocations discussed here and their cyanoborohydride reduction products can be studied at leisure by NMR in sulfolane and DMSO, we have confidence in their structures and thus of the corresponding ΔH_{H^-} values.

Also appropriate are correlations of ΔH_{H^-} vs. $\Delta G_i(R^+)$, which are all determined in sulfolane under similar conditions in the same laboratory listed in Table 3.

This correlation [like that for ΔH_{dep} or pK_{HA} vs. $\Delta G_i(R^-)$] compares the energy of the carbocation with that of a conjugate neutral species. However, there may be significant steric factors that differentiate the energy for converting a tetrahedral neutral RH to R^+ or R^- from that for forming the ions by reduction of a neutral trigonal radical. Electrode processes also involve surface and diffusion phenomena in addition to the presence of supporting electrolyte that may contribute to difference between the electrochemical processes and the bond-breaking reactions.

For comparison [2], the slope of $\Delta H_{H^-}(R^+)$ vs. $\Delta G_i(R^+)$ for 40 widely different cations is 1.04 ($r = 9.23$) and for 11 trityl cations is 0.932 ($r = 0.982$). However, a range of slopes is seen for the dithio and dioxocations listed in Table 3, implying differential steric energies in the cations, radicals, or both. Table 4 correlates ΔH_{H^-} for different series of carbocations against each other, thereby removing the question of radicals.

Clearly, different steric factors contribute to the stabilities of the different groups of ions or to their neutrals. Correlations of $\Delta G_i(R^+)$ in Table 5 for the same series of cations and their radicals against each other shows smaller differences in terms of their slopes than those in Table 4, suggesting that the steric differences are in the tetrahedral neutrals.

However, AM1 calculations, presented later, indicate a rather weak overlap interaction between the cationic centers of both the five- and six-membered dithio systems and the phenyl group compared to that for the radical and anion.

Correlation with Hammett Parameters. Table 6 compares correlations of the various types of carbocation properties against Hammett substituent constants σ^+ and σ. ΔH and ΔG values were divided by 1.364 to normalize them to the pK scales from which the Hammett parameters were derived [52].

Although the generally excellent correlations may reflect the small number of points, the slopes are significant, especially when compared with similar correlations for five monosubstituted trityl cations, $\rho^+ = -3.93$, for $\Delta H_{H^-}(R^+)$ [2], -5.6 for oxidation of benzhydryl radicals in acetonitrile [13], -6.8 for oxidation of cumyl radicals in acetonitrile [13], or -4.5 for the standard hydrolysis of cumyl chlorides in 80% aqueous acetone. Cationic properties for the 2-(p-phenyl)-4,4,5,5-tetramethyl-1,3-

TABLE 4 Correlations of ΔH_{H^-} for 2-(p-X-phenyl)-1,3-dithian-2-ylium between Various Cation Classes

Cation Class (y axis)	Slope[a]	n[b]	r[c]
2-(p-X-phenyl)-1,3-dithiolan-2-ylium	3.7 ± 0.4	3	0.99
2-(p-X-phenyl)-4,4,5,5-tetramethyl-1,3-dioxolanylium[d]	3.1 ± 0.8	4	0.94
2-(p-X-phenyl)-1,3-dioxolan-2-ylium	3.4 ± 0.4	4	0.99
4-X-trityl[e]	2.9 ± 0.3	3	0.99

[a]Slope is from the correlation of ΔH_{H^-} for another cation (y axis) with ΔH_{H^-} for 2-(p-X-phenyl)-1,3-dithian-2-ylium (x axis).[b]n is the number of observations.
[c]r is the correlation coefficient.
[d]Data for correlation from Ref. [4a].
[e]Data for correlation from Ref. [2].

TABLE 3 Correlations of ΔH_{H^-} vs. $\Delta G_i(R^+)$ for Various Carbocations

Carbocation	Slope[a]	n[b]	r[c]
2-(p-X-phenyl)-1,3-dithian-2-ylium	2.6 ± 0.3	5	0.97
2-(p-X-phenyl)-1,3-dithiolan-2-ylium	0.7 ± 0.1	4	0.98
2-(p-X-phenyl)-4,4,5,5-tetramethyl-1,3-dioxolanylium[d]	1.22 ± 0.09	7	0.99
4-X-trityl[e]	0.93 ± 0.06	11	0.98

[a]Slope is from the correlation of $\Delta G_i(R^+)$ (y axis) with ΔH_{H^-} (x axis).
[b]n is the number of observations.
[c]r is the correlation coefficient.
[d]Data for correlation from Ref. [4a].
[e]Data for correlation from Ref. [2].

TABLE 5 Correlations of $\Delta G_i(R^+)$ 2-(p-X-phenyl)-1,3-dithian-2-ylium between Various Cation Classes

Cation Class (y axis)	Slope[a]	n[b]	r[c]
2-(p-X-phenyl)-1,3-dithiolan-2-ylium	1.0 ± 0.2	3	0.97
2-(p-X-phenyl)-4,4,5,5-tetramethyl-1,3-dioxolanylium[d]	1.6 ± 0.5	4	0.91
4-X-trityl[e]	0.4 ± 0.5	3	0.63

[a]Slope is from the correlation of $\Delta G_i(R^+)$ for another cation (y axis) with $\Delta G_i(R^+)$ for 2-(p-X-phenyl)-1,3-dithian-2-ylium (x axis).
[b]n is the number of observations.
[c]r is the correlation coefficient.
[d]Data for correlation from Ref. [4a].
[e]Data for correlation from Ref. [2].

dioxolanium ions correlate better with σ parameters than with σ^+, as do those for 9-aryl-xanthylium ions [2]. In terms of ΔH_{H^-}, the order of sensitivity to substitution on an attached phenyl group is dithiolanium (-5.6) > dioxolanium (-4.9) > trityl (-3.9) > dithianylium (-1.52). Presumably, this order reflects the demand on the attached phenyl group for stabilizing electron deficiency at the point of attachment and, by implication, the inability of the heterocyclic system to delocalize it. This view is completely at odds with the observed order in Table 1 of ΔH_{H^-} for the unsubstituted phenyl compounds, which is (in kcal/mol) trityl (-52.7) > dithianyl, (-47.2) > dioxolanyl, (-42.1) > dithiolanyl, (-40.2), from least to most stable. Clearly, these systems involve enough complicating factors to preclude a simple interpretation.

Carbanion and Radical Properties. Measured and derived electrochemical properties for carbanions shown in Table 2 have mostly been discussed earlier; it remains to consider the bond-breaking properties ΔG_{HA} (1.364 pK_{HA}) and ΔH_{dep}. As reported for many other systems in K$^+$DMSYL$^-$ [10], these properties listed in Table 2 correlate well ($\rho = 1.01$, $r = 1.00$), as shown in Table 7. Also in Table 7 is seen the excellent correlation of ΔH_{dep} vs. ΔG_1 (R$^-$) for which ($\rho = -0.829, r = 0.994$).

Table 8 compares correlations of various carbanion properties with σ, all of which show excellent correlation coefficients for reasonable numbers of points. By comparison, Sim *et al.* [13] obtain for reduction of nine p-substituted benzyl radicals ($\rho = 13.5, r = 0.97$) and for eight cumyl radicals ($\rho = 11.0, r = 0.98$); for trityl radicals [2] ($\rho = -6.17, r = 0.942$).

Tables 1 and 2 list BDEs calculated by several routes: from pK_{HA}s and ΔG_1(R$^-$)s [7], ΔH_{dep}s and ΔG_1(R$^-$)s, and ΔH_{H^-}(R$^+$)s and ΔG_1(R$^+$)s [2]. All three methods require empirical constants in order to scale them to the gas-phase standard state [2]. The generally good agreement between the three independent routes reflects good agreement between the componant properties used to derive them.

Structures. The significant influence of 1,3-dihetero-substitution on the conformational equilibria of six-membered rings, i.e., the anomeric effect, has been a lively field for research over the past 41 years, since the seminal observations of Edwards [53] and Lemieux [54]. Most of the subsequent deluge of re-

TABLE 7 Correlations of ΔH_{dep} vs. ΔG_1(R$^-$) or pK_{HA} for Two Carbanions

Carbanion	Correlation	Slope[a]	n[b]	r[c]
2-(p-X-phenyl)-1,3-dithian-2-ylide	vs. ΔG_1(R$^-$)	-0.83 ± 0.05	6	0.99
	vs. 1.364pK_{HA}	1.01 ± 0.03	4	0.99
4-X-trityl	vs. ΔG_1(R$^-$)	-0.5 ± 0.2	9	0.66
	vs. 1.364pK_{HA}	0.70 ± 0.04	4	1.00

[a]Slope is from the correlation of ΔG_1(R$^-$) for another carbanion (y axis) with ΔH_{dep} for 2-(p-X-phenyl)-1,3-dithian-2-ylide (x axis).
[b]n is the number of observations.
[c]r is the correlation coefficient.
[d]Data for correlation from Ref. [2].

TABLE 6 Hammett ρ^+ Values for Reactions of 2-Phenyl-1,3-dithian-2-ylium, 2-Phenyl-1,3-dithiolan-2-ylium, 2-Phenyl-1,3-dioxolan-2-ylium, and 2-Phenyl-4,4,5,5-tetramethyl-1,3-dioxolan-2-ylium[a]

Measured Reaction Property	ρ^+	r	n
ΔH_{H^-} of 2-(p-phenyl)-1,3-dithian-2-ylium	-1.52	1.00	5
ΔG_1(R$^+$) of 2-(p-phenyl)-1,3-dithian-2-ylium	-3.9	0.97	5
ΔH_{H^-} of 2-(p-phenyl)-1,3-dithiolan-2-ylium	-5.6	1.00	4
ΔG_1(R$^+$) of 2-(p-phenyl)-1,3-dithiolan-2-ylium	-4.0	0.99	4
pK_{R^+} of 2-phenyl-1,3-dithiolan-2-ylium[b]	-2.1	—	2
pK_{R^+} of 2-phenyl-1,3-dioxolan-2-ylium[c]	-2.21	1.00	4
ΔH_{H^-} of 2-(p-phenyl)-1,3-dioxolan-2-ylium	-4.9	0.99	4
ΔH_{H^-} of 2-(p-phenyl)-4,4,5,5-1,3-dioxolan-2-ylium[d]	-7.6[e]	0.99	7
ΔG_1(R$^+$) of 2-(p-phenyl)-4,4,5,5-1,3-dioxolan-2-ylium-2-ylium[d]	-9.4[e]	0.99	7

[a]r is the correlation coefficient, and n is the number of points.
[b]pK_{R^+} data from Ref. [33].
[c]pK_{R^+} data from Ref. [28h].
[d]Data from Ref. [4a].
[e]Plotted vs. σ not σ^+ since a better fit is obtained.

TABLE 8 Hammett ρ^- Values for Deprotonation of 2-Phenyl-1,3-dithiane, Reduction of 2-Phenyl-1,3-dithian-2-yl and 2-Phenyl-4,4,5,5-tetramethyl-1,3-dioxolan-2-yl radicals, and Oxidation of 2-Phenyl-1,3-dithian-2-ylide[a]

Measured Reaction Property	ρ^-	r	n
ΔH_{dep} of 2-(p-phenyl)-1,3-dithiane	11.1	1.00	6
ΔG_1(R$^-$) of 2-(p-phenyl)-1,3-dithian-2-ylide	9.3	1.00	6
ΔG_2(R$^+$) of 2-(p-phenyl)-1,3-dithian-2-yl radical	10.4	1.00	5
ΔG_2(R$^+$) of 2-Phenyl-4,4,5,5-tetramethyl-1,3-dioxolan-2-yl radical[b]	9.3	0.98	6

[a]r is the correlation coefficient, and n is the number of points.
[b]Data from Ref. [4a].

ports have been reviewed recently by Juaristi and Cuevas [55]. The modulation of the conformational phenomena is mostly a rather subtle ground-state effect despite the 8 kcal/mol difference in 1,3- vs. 1,4-dioxanes already referred to [26]. Thus, an enthalpic preference of 2.01 kcal/mol for equatorial phenyl in 2-phenyl-2,6-dimethyl-1,3-dioxanes [56] and 0.16 kcal/mol difference for cis- and trans-2-carboethoxy-4,6-dimethyl-1,3-dithianes [27e] accords with other miniscule enthalpic contributions reported for anomeric systems, thereby leaving special entropy assignments, by default, as the driving force for observed conformational equilibria for these cases. Pure entropy arguments are of course inconsistent with many spectroscopic and computational results or a recent crystallographic study [57] of 2-substituted-1,3-dithianes. The origin of the effect has been identified closely with "negative hyperconjugation" [27d].

The synthetic importance of 1,3-dithianyllithiums has elicited many studies of conformational studies of these carbanions including crystal structures, most of which have been reviewed fairly recently [58], and give no unequivocal statement on conformations of the anions in the somewhat complicated organolithium crystals. Eliel's NMR [40b] and trapping [40a] experiments support the conclusions of the original X-ray study [59], showing the phenyl of the 2-phenyl-1,3-dithiyl anion to be axial to the ring.

Electron spin resonance (ESR) studies of 1,3-dioxo and dithio radicals show significant delocalization of spin onto the heteroatoms and evidence of some bending of the rings [60]. 2-Benzoyl-1,3-dithiane and the corresponding dithiolane are of almost equal acidity in DMSO [61], but the BDE of the latter is 3.8 kcal/mol higher, implying a somewhat stabler radical for the five-membered 1,3-dithio system.

Against these diverse reports, we report AM1 computations (Figures 4–8) of 2-phenyl-1,3-dithiane, the 2-phenyl-dithianyl, and 2-phenyl-dithiolanyl cations and the corresponding dithianyl carbanion and radical.

Of particular interest is the fact that the two cations are found with their phenyl rings skewed to the planar part of the dithio rings, while the carbanion and radical are coplanar. Figures 9 and 10 examine the relationship between the dihedral angle and energy.

A wealth of published data and the new results presented here indicate stabilization of the dithio cations, carbanions, and radicals relative to the corresponding phenylcyclohexyl species. It is reasonable that coplanarity of the p-orbital containing elec-

trons in the radical and carbanions with both rings would give maximum stability. The same may be said for coplanarity of the open orbital of the carbenium ion. Figures 5, 6, and 9 indicate the significantly different positions of lowest energy for the skewed phenyls in the two cations, although there are no apparent steric obstacles from the 4,6- or 4,5-hydrogens.

The Coupling Product; Bis-(2-Phenyl-1,3-Dithiane). In view of our success in determining ΔH_{het}s for a variety of compounds by reacting stable R^+s with stable R^-s [15–19], one of the goals of the present study was to form the coupling product shown at the bottom of Figure 2 by direct reaction of the 2-phenyl-1,3-dithianylium cation with its conjugate carbanion. If this could be accomplished cleanly in a calorimeter, it would yield the ΔH_{het} for the coupling product, which could then be converted into the corresponding ΔH_{homo} by combination with ΔG_{ET} [16]. Since such symmetrical coupled products normally arise from radical coupling, only the bond energies for homolysis have previously been available. The opportunity to relate the energies for the two different types of bond cleavage directly by experiment in solution was attractive. Although such coupling might take place through radicals formed by electron transfer from R^+ to R^-, it would not affect the measured ΔH_{het} provided the initial state of the reaction was the ions and the product was pure R–R. We have reported recently [20f] on the calculation of ΔH_{het} and ΔH_{homo} for cleavage of the central bond of bibenzyl, bi-t-butyl (i.e., 2,2,3,3-tetramethylbutane), and ethane based on measured bond dissociation energies and redox potentials of the radicals [13]. We had also claimed such a determination [1a] for the reaction of xanthyl cation and anion to give dixanthyl. However, subsequent repetitions of the experiment [1a] indicated that the calorimetric reaction was not clean, which casts a shadow on the reported heat of reaction. The question of structure is also at issue in such coupled products in view of the now recognized [62] unsymmetrical cyclohexadienyl system that results from the coupling of trityl radicals.

Addition of a sulfolane solution of 2-phenyl-1,3-dithianylium tetrafluoroborate to the potassium salt of its conjugate carbanion gave a clean reaction that evolved 40.6 ± 0.45 kcal/mol of heat. We were unable to obtain a suitable crystal for X-ray structure determination. However, the product was shown to be the symmetrical dimer by demonstrating that its properties were identical to those of the product obtained by condensing two equivalents of 1,3-propane
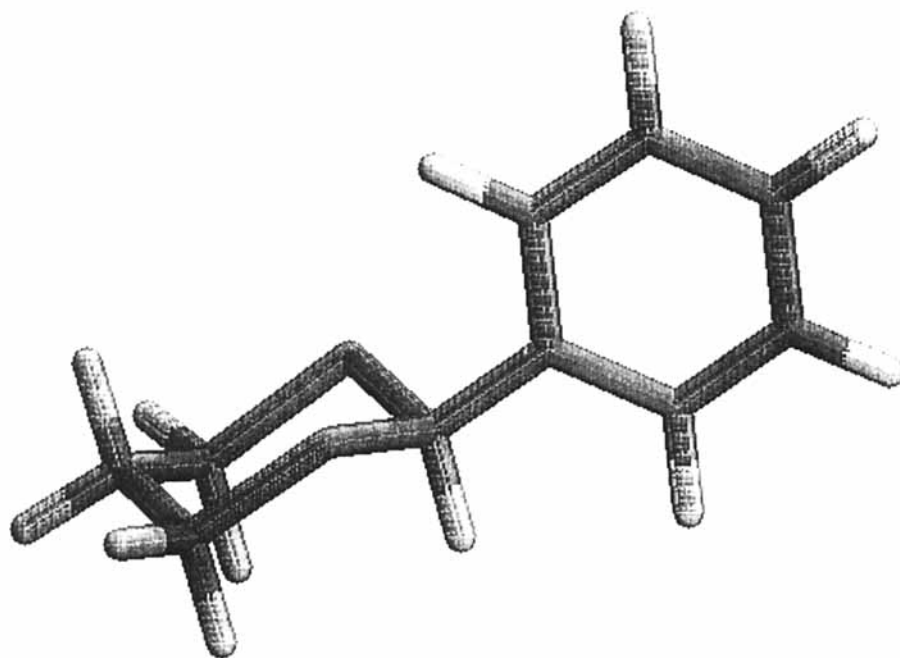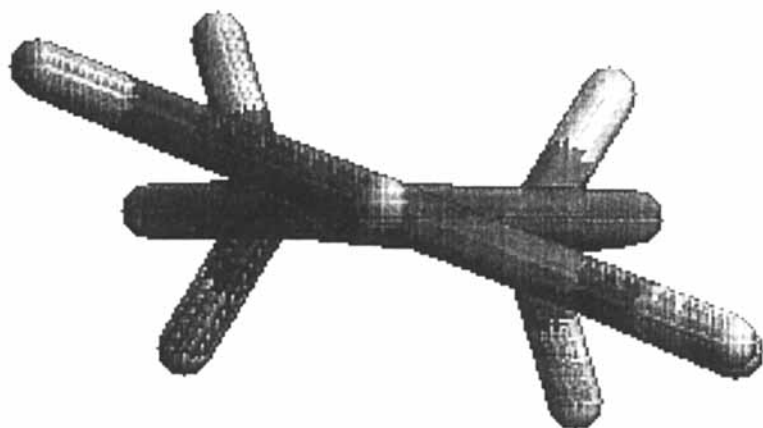
FIGURE 4 AM1 structure for 2-phenyl-1,3-dithiane.
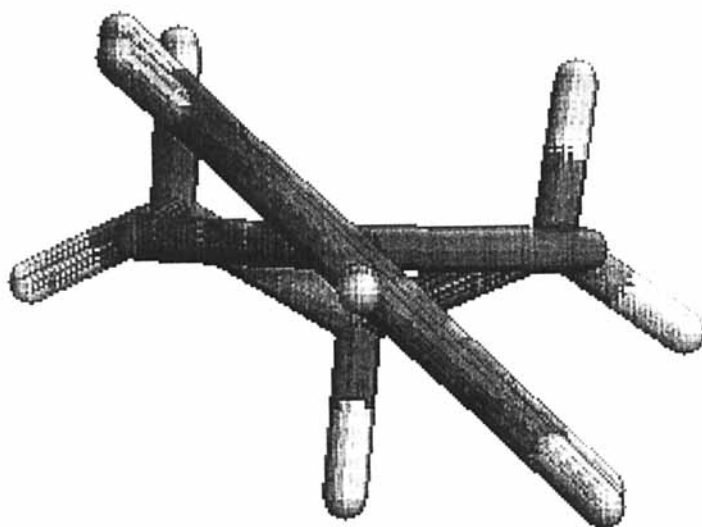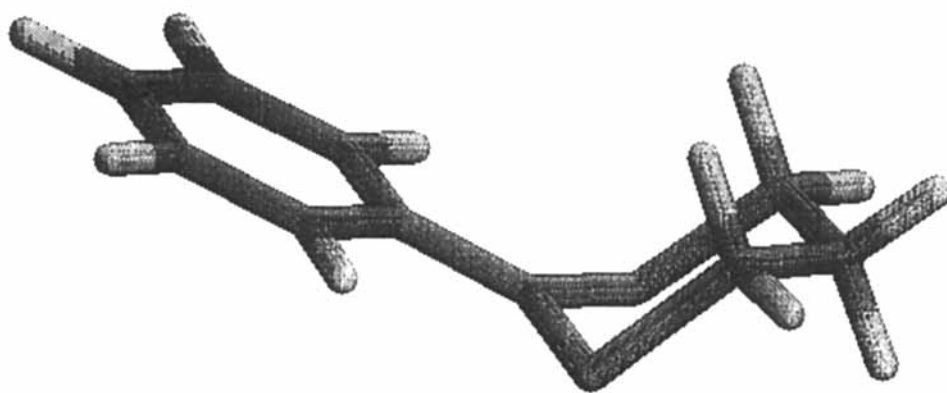

FIGURE 5 AM1 structure for 2-phenyl-1,3-dithian-2-yl cation. Note lack of coplanarity of rings.

dithiol with benzil. Addition of ΔG_{ET} (-21.5 kcal/mol) for the 2-phenyl-1,3-dithiyl system yields $\Delta H_{homo} = 19.1$ kcal/mol. These values for ΔH_{homo} and ΔH_{het} provide the first bona fide example for a symmetrical coupling product in solution and fall in the normal range that we have reported [16] for cleavage of the C–C bonds of a variety of compounds formed by reaction of resonance-stabilized carbocations and carbanions.

Figure 11 portrays the AM1-computed structure of the dimer. A check on the consistency of ΔH_{homo} of the dimer from calorimetry and electrochemistry is found as follows. Combining the AM1-computed energies for 2-phenyl-1,3-dithiane (21.93 kcal/mol) and its radical (34.23 kcal/mol) with the heat of formation of the hydrogen atom (52.10 kcal/mol), one obtains 64.39 kcal/mol as the BDE of the dithiane, which is 14 kcal/mol below the experimental value

FIGURE 7 AM1 structure for 2-phenyl-1,3-dithian-2-yl carbanion.
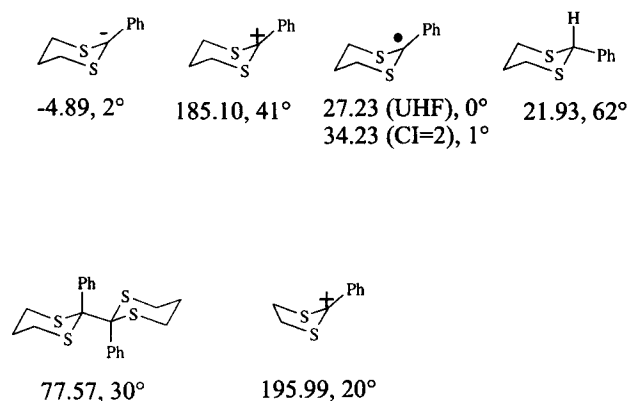

FIGURE 8 AM1 structure for 2-phenyl-1,3-dithian-2-yl radical.

of 78.4 kcal/mol given in Table 2. A corresponding difference obtained from the computed ΔH_{homo} of the dimer is -9.1 kcal/mol, which is too low by 28.2 kcal/mol or 2×14 kcal/mol. The source of the discrepancy is unknown but is at least consistent.

CONCLUSIONS

The dithio title compounds are nearly ideal amphihydric heterocyclic compounds for providing an un-

precedented complete accounting of the energy relationships between bond making and breaking of the neutral tetrahedral precursors and the electron-transfer energies between their conjugate trivalent oxidation states: $R^{+}/\cdot/^{-}$. Accordingly, the six 1,3-dithian-2-ylium and five 1,3-dithiolan-2-ylium tetrafluoroborates listed in Table 1 were prepared in sulfolane and their heats of reaction with sodium cyanoborohydride determined calorimetrically at 25°. The resulting hydride affinities, $\Delta H_{H^{-}}$, could

-4.89, 2°   185.10, 41°   27.23 (UHF), 0°   21.93, 62°
                            34.23 (CI=2), 1°

77.57, 30°   195.99, 20°

FIGURE 9 AM1 structure species shown in Figures 4–8 and 11 with heats of formation in kcal/mol and dihedral angles.

then be compared with those of a number of other carbocations, including five 1,3-dioxolanyl-2-ylium cations, both directly and through a variety of extrathermodynamic correlations. First and second reduction potentials of the cations were determined and converted to standard free energies of reduction; first to the radical and then to the carbanion. These free energies could be combined to give the electron-transfer free energies, ΔG_{ET}, for converting the ions into their conjugate free radicals and also to ΔG_3, the free energy for converting the cation into the anion.

A series of six conjugate 1,3-dithian-2-ylide carbanions was prepared in DMSO by deprotonation with the conjugate base of the solvent, $K^+ DMSYL^-$. The heat of this reaction, ΔH_{dep}, was determined calorimetrically and also several new pK_{HA} values using NMR spectroscopy as the analytical tool for measuring differential ionization constants. First and second oxidation potentials of the carbanions were determined in DMSO from which ΔG_{ET} and ΔG_3 could be estimated taking the opposite route from that described above for the cations. Except for a small consistent solvation difference between sulfolane and DMSO, the results derived from the carbanions were in good agreement with those from the carbocations. Self-consistent bond dissociation energies (BDEs) for homolytic cleavage of the C–H bonds could also be derived independently from the cation and anion data.

A solution of the 2-phenyl-1,3-dithian-2-ylium tetrafluoroborate in sulfolane was reacted with an equivalent amount of the potassium salt of its conjugate carbanion to yield a single product. This was shown to be bis-2-phenyl-1,3-dithiane both by its spectra and by its identity to the product obtained from reacting two equivalents of 1,3-propanedithiol with benzil. The heat of reaction of the cation with the anion is the negative of the heat of heterolysis,

ΔH_{het}, of the central bond of the bis compound and was converted to the corresponding heat of homolysis by combination of ΔH_{het} with ΔG_{ET} of the ions.

AM1 calculations of the structures and energies of 2-phenyl-1,3-dithiane, its carbocation, carbanion, and radical and the bis coupling product allow comparison of conformational and overlap effects.

The excellent correlations between bond-making and bond-breaking energies for generating the carbocations and carbanions from their R–H precursors by heterolysis of their C–H bonds and the corresponding redox energies for interconverting the trivalent state support the claim that the HOMO-LUMO gap between the radical and its conjugate ions, or the Parr–Pearson hardness of the radical, η, is a fundamental property that lies behind the observed reactivity of organic compounds.

EXPERIMENTAL

Materials. All materials were available commercially and were generally checked for purity before use.

General Instrumentation

Varian XL-300 NMR spectrometer, Vacuum Atmospheres HE-63-P PEDATROL dry box, Mettler DL18 Karl Fischer Titrator.

Reaction Solvent Preparation

DMSO. DMSO was vacuum distilled from CaH_2 using triphenylmethane/n-butyllithium as an indicator and stored in the dry box. DMSO with a water content of 40 ppm or less as checked by Karl Fisher was used for electrochemistry and calorimetry.

95% Sulfolane/5% 3-Methyl Sulfolane. Sulfolane was distilled from CaH_2 in a manner analogous to DMSO, except that no indicator was used, and Karl Fisher titration was not employed. As before [16], 3-methylsulfolane was added to lower the freezing point (28.9°C) and was purified by vacuum distillation from CaH_2 through a short-path distillation head. Sulfolane and 3-methylsulfolane were mixed in the dry box in a 19:1 ratio, by volume, and were left stirring overnight over chunks of CaH_2 and then filtered to remove the solids.

Preparation of 2-(p-X-Phenyl)-1,3-dithianes

Procedure. Formation of the dithianes was effected by acid-catalyzed (TsOH) reaction of the dithiol and aldehyde in refluxing benzene with re

-△- 2-phenyl-1,3-dithian-2-ylium   -●- 2-phenyl-1,3-dithiolan-2-ylium

-⊟- 2-phenyl-1,3-dithian-2-ylide   -✖- 2-phenyl-1,3-dithian-2-yl radical
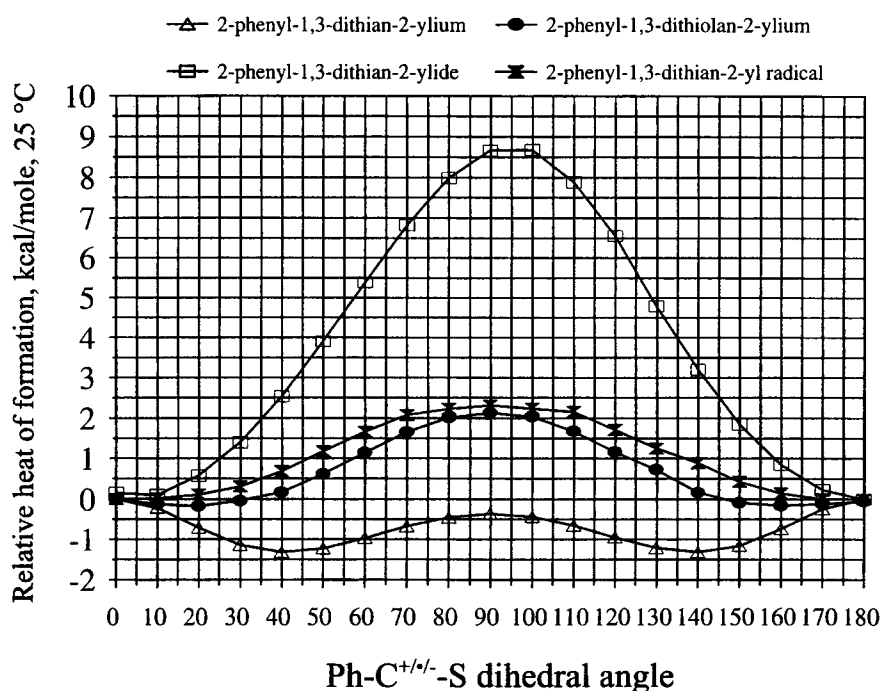
FIGURE 10 Relation of AM1 energies to dihedral angle during rotation of the phenyl ring.

Ph-C$^{+/\cdot/-}$-S dihedral angle
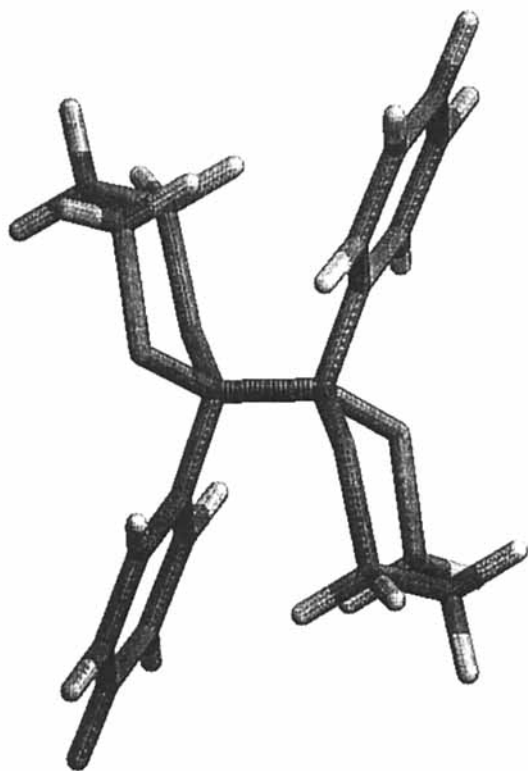
FIGURE 11 AM1 structure for dimer resulting from reaction of 2-phenyl-1,3-dithian-1,3-yl carbocation with its conjugate carbanion in sulfolane at 25°C.

moval of water to a Dean–Stark trap [4,35]. The cooled reaction mixture was extracted once with saturated aqueous sodium bicarbonate and twice with water. The *para*-nitro derivative was insoluble in benzene during workup, so methylene chloride was added to dissolve the product. The solution was dried over MgSO$_4$ and vacuum filtered. After evaporation of the solvent, the dithiane was recrystallized for calorimetric experiments.

$X = OCH_3$. ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.82–2.00 (m, 1H, D part of the AA'BB'CD spin system of the SCH$_2$CH$_2$CH$_2$S group), 2.10–2.22 (m, 1H, C part of the AA'BB'CD spin system of the SCH$_2$CH$_2$CH$_2$S group), 2.84–2.95 (m, 2H, BB' part of the AA'BB'CD spin system of the SCH$_2$CH$_2$CH$_2$S group), 2.98–3.12 (m, 2H, AA' part of the AA'BB'CD spin system of the SCH$_2$CH$_2$CH$_2$S group), 3.791 (s, 3H, OCH$_3$), 5.135 (s, 1H), 6.82–6.9 (m, 2H, BB' part of the AA'BB' spin system of the phenyl group), 7.35–7.45 (m, 2H, AA' part of the AA'BB' spin system of the phenyl group); ^{13}C NMR (75.43 MHz, decoupled, CDCl$_3$) δ 25.095 (CH$_2$), 32.214 (CH$_2$), 50.751 (CH), 55.311 (CH$_3$), 114.095 (CH), 128.936 (CH), 131.317 (C), 159.575 (C).

$X = CH_3$. ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.84–2.12 (m, 1H, D part of the AA'BB'CD spin system of the SCH$_2$CH$_2$CH$_2$S group), 2.11–2.23 (m, 1H, C part of the AA'BB'CD spin system of the SCH$_2$CH$_2$CH$_2$S group), 2.85–2.95 (m, 2H, BB' part of the AA'BB'CD

spin system of the $SCH_2CH_2CH_2S$ group), 3.00–3.12 (m, 2H, AA' part of the AA'BB'CD spin system of the $SCH_2CH_2CH_2S$ group), 5.150 (s, 1H), 7.12–7.22 (m, 2H, BB' part of the AA'BB' spin system of the phenyl group), 7.32–7.42 (m, 2H, AA' part of the AA'BB' spin system of the phenyl group); ^{13}C NMR (75.43 MHz, decoupled, $CDCl_3$) δ 21.214 (CH_3), 25.147 (CH_2), 32.171 (CH_2), 51.218 (CH), 127.622 (CH), 129.422 (CH), 136.197 (C), 138.275 (C).

X = *F.* ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.83–2.0 (m, 1H, D part of the AA'BB'CD spin system of the $SCH_2CH_2CH_2S$ group), 2.11–2.23 (m, 1H, C part of the AA'BB'CD spin system of the $SCH_2CH_2CH_2S$ group), 2.85–2.95 (m, 2H, BB' part of the AA'BB'CD spin system of the $SCH_2CH_2CH_2S$ group), 2.98–3.12 (m, 2H, AA' part of the AA'BB'CD spin system of the $SCH_2CH_2CH_2S$ group), 5.147 (s, 1H), 6.97–7.09 (m, 2H, BB' part of the AA'BB'X spin system of the phenyl group, J_{HF} = 8.4 Hz), 7.4–7.5 (m, 2H, AA' part of the AA'BB'X spin system of the phenyl group, J_{HF} = 5.4 Hz); ^{13}C NMR (75.43 MHz, decoupled, $CDCl_3$) δ 24.996 (CH_2), 32.086 (CH_2), 50.504 (CH), 115.659 (d, J_{CF} = 21.5 Hz, CH), 129.542 (d, J_{CF} = 4.2 Hz, CH), 135.029 (d, J_{CF} = 3.2 Hz, C), 162.533 (d, J_{CF} = 247.0 Hz, CF). ^{1}H NMR (300 MHz, DMSO) δ 1.63–1.8 (m, 1H, D part of the AA'BB'CD spin system of the $SCH_2CH_2CH_2S$ group), 2.07–2.19 (m, 1H, C part of the AA'BB'CD spin system of the $SCH_2CH_2CH_2S$ group), 2.84–2.95 (m, 2H, BB' part of the AA'BB'CD spin system of the $SCH_2CH_2CH_2S$ group), 3.02–3.15 (m, 2H, AA' part of the AA'BB'CD spin system of the $SCH_2CH_2CH_2S$ group), 5.424 (s, 1H), 7.15–7.25 (m, 2H, BB' part of the AA'BB'X spin system of the phenyl group, J_{HF} = 8.7 Hz), 7.42–7.52 (m, 2H, AA' part of the AA'BB'X spin system of the phenyl group, J_{HF} = 5.4 Hz); ^{13}C NMR (75.43 MHz, decoupled, DMSO) δ 24.596 (CH_2), 30.965 (CH_2), 48.881 (CH), 115.517 (d, J_{CF} = 21.3 Hz, CH), 129.563 (d, J_{CF} = 8.30 Hz, CH), 135.835 (d, J_{CF} = 2.87 Hz, C), 161.632 (d, J_{CF} = 244.4 Hz, CF).

X = *H.* ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.85–2.06 (m, 1H, D part of the AA'BB'CD spin system of the $SCH_2CH_2CH_2S$ group), 2.12–2.26 (m, 1H, C part of the AA'BB'CD spin system of the $SCH_2CH_2CH_2S$ group), 2.86–2.98 (m, 2H, BB' part of the AA'BB'CD spin system of the $SCH_2CH_2CH_2S$ group), 3.0–3.16 (m, 2H, AA' part of the AA'BB'CD spin system of the $SCH_2CH_2CH_2S$ group), 5.177 (s, 1H), 7.28–7.4 (m, 3H, BB'C part of the AA'BB'C spin system of the phenyl group), 7.45–7.53 (m, 2H, AA' part of the AA'BB'C spin system of the phenyl group); ^{13}C NMR (75.43 MHz, decoupled, $CDCl_3$) δ 25.140 (CH_2), 32.131 (CH_2), 51.508 (CH), 127.774 (CH), 128.463

(CH), 128.753 (CH), 139.134 (C). ^{1}H NMR (300 MHz, DMSO) δ 1.65–1.82 (m, 1H, D part of the AA'BB'CD spin system of the $SCH_2CH_2CH_2S$ group), 2.08–2.19 (m, 1H, C part of the AA'BB'CD spin system of the $SCH_2CH_2CH_2S$ group), 2.84–2.95 (m, 2H, BB' part of the AA'BB'CD spin system of the $SCH_2CH_2CH_2S$ group), 3.03–3.16 (m, 2H, AA' part of the AA'BB'CD spin system of the $SCH_2CH_2CH_2S$ group), 5.399 (s, 1H), 7.285–7.47 (m, 5H, AA'BB'C spin system of the phenyl group); ^{13}C NMR (75.43 MHz, decoupled, DMSO) δ 24.714 (CH_2), 30.994 (CH_2), 49.975 (CH), 127.485 (CH), 128.213 (CH), 128.636 (CH), 139.526 (C).

X = *CL.* ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.6–2.0 (m, 1H, D part of the AA'BB'CD spin system of the $SCH_2CH_2CH_2S$ group), 2.1–2.22 (m, 1H, C part of the AA'BB'CD spin system of the $SCH_2CH_2CH_2S$ group), 2.84–2.95 (m, 2H, BB' part of the AA'BB'CD spin system of the $SCH_2CH_2CH_2S$ group), 2.98–3.12 (m, 2H, AA' part of the AA'BB'CD spin system of the $SCH_2CH_2CH_2S$ group), 5.117 (s, 1H), 7.25–7.45 (m, 4H, AA'BB' spin system of the phenyl group); ^{1}H NMR (300 MHz, DMSO) δ 1.63–1.84 (m, 1H), 2.06–2.20 (m, 1H), 2.83–3.0 (m, 2H), 3.0–3.18 (m, 2H), 5.429 (s, 1H), 7.44 (almost a singlet, 4H, AA'BB' spin system of the phenyl group); ^{13}C NMR (75.43 MHz, decoupled, DMSO) δ 24.597 (CH_2), 30.882 (CH_2), 48.930 (CH), 128.713 (CH), 129.359 (CH), 132.680 (C), 139.503 (C).

X = *NO₂.* ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.85–2.02 (m, 1H, D part of the AA'BB'CD spin system of the $SCH_2CH_2CH_2S$ group), 2.1–2.22 (m, 1H, C part of the AA'BB'CD spin system of the $SCH_2CH_2CH_2S$ group), 2.87–3.0 (m, 2H, BB' part of the AA'BB'CD spin system of the $SCH_2CH_2CH_2S$ group), 3.0–3.14 (m, 2H, AA' part of the AA'BB'CD spin system of the $SCH_2CH_2CH_2S$ group), 5.222 (s, 1H), 7.6–7.7 (m, 2H, BB' part of the AA'BB' spin system of the phenyl group), 8.15–8.25 (m, 2H, AA' part of the AA'BB' spin system); ^{13}C NMR (75.43 MHz, decoupled, $CDCl_3$) δ 24.818 (CH_2), 31.781 (CH_2), 50.409 (CH), 124.016 (CH), 128.954 (CH), 146.191 (C), 147.662 (C).

Preparation of 2-(*p-X-Phenyl*)-1,3-dithian-2-ylium Fluoroborates

Procedure. The procedure of Klaveness and Undheim [64] was followed for the synthesis of all five 2-aryl-1,3-dithian-2-ylium fluoroborates. An oven-dried round-bottom flask and addition funnel were assembled while hot and attached to an argon inlet. To the cooled flask a solution of acid chloride (25

mmol) and 1,3-propanedithiol (25 mmol) in anhydrous diethyl ether (125 mL) was added via syringe. The latter solution was stirred magnetically and cooled to 0°C under an argon atmosphere. Next, HBF₄· Et₂O (85% in ether, 42.5 mmol) was added to the ether solution in a dropwise manner via the addition funnel. Following addition of the fluoroboric acid solution, the reaction mixture was stirred for ca. 10 minutes warmed to room temperature, and then refluxed for ~ 20 minutes. The methoxy-substituted (X = OCH₃) and unsubstituted (X = H) salts precipitated during heating under reflux. If the salt did not precipitate, most of the ether was removed by distillation and the oil transferred to the dry box. For the chloro-substituted (X = Cl) salt, trituration with ether induced precipitation of a pure salt. For the methyl- (X = CH₃) and nitro- (X = NO₂) substituted salts, an extended pumping for several hours on the oil under high vacuum to remove all volatile material was necessary. The dried oil could then be triturated with diethyl ether to precipitate the salt that was purified in the dry box by dissolution in dry acetonitrile, filtration, and then precipitation of the salt by addition of ether. Salts purified in this way were found to contain ca. 1 mol% of both diethyl ether and acetonitrile by ¹H NMR. All salts were isolated by vacuum filtration through a fritted funnel, rinsed with dry ether, and dried by suction.

X = OCH₃. ¹H NMR (300 MHz, CD₃CN) δ 2.41–2.61 (m, 2H, CD part of the AA′BB′CD spin system of the SCH₂CH₂CH₂S group), 3.62–3.70 (m, 4H, AA′BB′ part of the AA′BB′CD spin system of the SCH₂CH₂CH₂S group), 3.943 (s, 3H), 7.1–7.2 (m, 2H, BB′ part of the AA′BB′ spin system of the phenyl group), 7.9–8.05 (m, 2H, AA′ part of the AA′BB′ spin system of the phenyl group); ¹³C NMR (75.43 MHz, decoupled, CD₃CN) δ 19.473 (CH₂), 33.879 (CH₂), 57.185 (CH₃), 116.702 (CH), 130.642 (C), 131.158 (CH), 169.686 (C), 218.402 (C).

X = CH₃. ¹H NMR (300 MHz, CD₃CN) δ 2.449 (s, 3H), 2.41–2.55 (m, 2H, CD part of the AA′BB′CD spin system of the SCH₂CH₂CH₂S group), 3.65–3.75 (m, 4H, AA′BB′ part of the AA′BB′CD spin system of the SCH₂CH₂CH₂S group), 7.4–7.5 (m, 2H, BB′ part of the AA′BB′ spin system of the phenyl group), 7.75–7.85 (m, 2H, AA′ part of the AA′BB′ spin system of the phenyl group); ¹³C NMR (75.43 MHz, decoupled, CD₃CN) δ 18.543 (CH₂), 22.073 (CH₃), 34.209 (CH₂), 128.371 (CH), 131.883 (CH), 135.572 (C), 151.434 (C), 221.602 (C).

X = H. ¹H NMR (300 MHz, CD₃CN) δ 2.42–2.55 (m, 2H, CD part of the AA′BB′CD spin system of the

SCH₂CH₂CH₂S group), 3.7–3.8 (m, 4H, AA′BB′ part of the AA′BB′CD spin system of the SCH₂CH₂CH₂S group), 7.6–7.7 (m, 2H, CC′ part of the ABB′CC′ spin system), 7.82–7.95 (m, 3H, ABB′ part of the ABB′CC′ spin system of the phenyl group); ¹³C NMR (75.43 MHz, decoupled, CD₃CN) δ 18.102 (CH₂), 34.409 (CH₂), 128.355 (CH), 131.247 (CH), 138.041 (C), 138.431 (CH), 222.673 (C).

X = Cl. ¹H NMR (300 MHz, CD₃CN) δ 2.4–2.55 (m, 2H, CD part of the AA′BB′CD spin system of the SCH₂CH₂CH₂S group), 3.67–3.79 (m, 4H, AA′BB′ part of the AA′BB′CD spin system of the SCH₂CH₂CH₂S group), 7.6–7.7 (m, 2H, BB′ part of the AA′BB′ spin system of the phenyl group), 7.75–7.85 (m, 2H, AA′ pat of the AA′BB′ spin system of the phenyl group); ¹³C NMR (75.43 MHz, decoupled, CD₃CN) δ 18.004 (CH₂), 34.517 (CH₂), 129.874 (CH), 131.395 (CH), 136.489 (C), 144.314 (C), 221.107 (C).

X = NO₂. ¹H NMR (300 MHz, CD₃CN) δ 2.45–2.55 (m, 2H, CD part of the AA′BB′CD spin system of the SCH₂CH₂CH₂S group), 3.75–3.85 (m, 4H, AA′BB′ part of the AA′BB′CD spin system of the SCH₂CH₂CH₂S group), 7.95–8.05 (m, 2H, BB′ part of the AA′BB′ spin system of the phenyl group), 8.35–8.45 (m, 2H, AA′ part of the AA′BB′ spin system of the phenyl group); ¹³C NMR (75.43 MHz, decoupled, CD₃CN) δ 17.327 (CH₂), 34.935 (CH₂), 125.975 (CH), 129.986 (CH), 142.367 (C), 153.234 (C), 221.152 (C).

NMR Characterization of Potassium 2-(p-X-Phenyl)-1,3-dithian-2-ylides

General. These anions were prepared in a dry box by reaction of a 2-aryl-1,3-dithiane with one equivalent of potassium dimsyl in DMSO. Also in the dry box, the anion solution was added to the NMR tube and capped and removed from the dry box for NMR analysis.

X = CH₃. This anion was unstable over the time span of the ¹H-NMR experiments. Initially, the ¹H-NMR spectrum showed aromatic resonances for the anion, which, when integrated relative to the resonance for DMSO-d₅, suggested either that only 19% conversion to the anion had occurred or that the initially formed anion had already decomposed to the extent of 81%. Possible decomposition products of the anion have chemical shifts similar to those of 2-(p-tolyl)-1,3-dithiane; in addition, other unassignable resonances are apparent. A subsequent proton spectrum showed the nearly complete disappearance of the peaks assigned to the anion. ¹H NMR (300 MHz, DMSO) δ 2.1 (broad m, AA′BB′CD spin

system of the SCH₂CH;2CH₂S group), 6.3–6.45 (broad m, 2H, BB' part of the AA'BB' spin system of the phenyl group), 6.65–6.78 (broad m, 2H, AA' part of the AA'BB' spin system of the phenyl group).

$X = F.$ ¹H NMR (300 MHz, DMSO) δ 2.095 (broad m, 6H, AA'BB'CD spin system of the SCH₂CH₂CH₂S group), 6.28–6.44 (br t, 2H, AA' part of the AA'BB'X spin system of the phenyl group, $J_{HF} = 9.3$ Hz), 6.61–6.74 (br d of d, 2H, AA' part of the AA'BB'X spin system of the phenyl group, $J_{HF} = 5.1$ Hz); ¹³C NMR (75.43 MHz, decoupled, DMSO) δ 29.359 (CH₂), 29.821 (CH₂), 43.254 (C, probably the C-2 of the dithio ring, but this peak is similar in size to the noise in the spectrum), (CH), 113.248 (CH, $J_{CF} = 19.4$ Hz), 115.641 (CH, $J_{CF} = 6.2$ Hz); ipso ¹³C and ¹³C–F are uncertain due to noise.

$X = H.$ ¹H NMR (300 MHz, DMSO) δ 2.104 (broad singlet, 6H, AA'BB'CD spin system of the SCH₂CH₂CH₂S group), 5.45–5.55 (br t, 1H, C part of the AA'BB'C spin system of the phenyl group), 6.42–6.54 (br t, 2H, BB' part of the AA'BB'C spin system of the phenyl group), 6.64–6.76 (br d, 2H, AA' part of the AA'BB'C spin system of the phenyl group); ¹³C NMR (75.43 MHz, decoupled, DMSO) δ 29.787 (CH₂), 30.316 (CH₂), 46.583 (C), 103.910 (CH), 115.908 (CH), 127.016 (CH), 153.704 (C).

$X = Cl.$ ¹H NMR (300 MHz, DMSO) δ 2.126 (broad m, 6H, AA'BB'CD spin system of the SCH₂CH₂CH₂S group), 6.25–6.75 (m, 4H, AA'BB' spin system of the phenyl group); ¹³C NMR (75.43 MHz, decoupled, DMSO) δ 29.471 (CH₂), 30.624 (CH₂), 48.324 (C), 105.2 (CH), 116.334 (CH), 126.410 (CH), 151.763 (C).

$X = NO_2.$ ¹H NMR (300 MHz, DMSO) δ 1.96–2.05 (m, 2H, CD part of the AA'BB'CD spin system of the SCH₂CH₂CH₂S group), 2.7–2.9 (m, 4H, AA'BB' part of the AA'BB'CD spin system of the SCH₂CH₂CH₂S group), 6.45–6.6 (d, 2H, BB' part of the AA'BB' spin system of the phenyl group), 7.0–7.15 (d, 2H, AA' part of the AA'BB' spin system of the phenyl group); ¹³C NMR (75.43 MHz, decoupled, DMSO) δ 25.572 (CH₂), 30.595 (CH₂), 102.205 (C), 116.678 (CH), 122.342 (CH), 124.656 (C), 139.639 (C).

Estimated pK_a Values for 2-(p-Chlorophenyl)-1,3-dithiane, 2-(p-Nitrophenyl)-1,3-dithiane and 2-(p-Fluorophenyl)-1,3-dithiane in DMSO-d₆ by ¹H NMR Spectroscopy

A preliminary experiment showed that 2-(p-chlorophenyl)-1,3-dithiane is converted completely to the conjugate base by potassium 2-phenyl-1,3-dithian-2-ylide. This conclusion was consistent with both the ¹H- and the ¹³C-NMR spectra. Since 2-phenyl-1,3-dithiane was not acidic enough to serve as an indicator, 9-tolylxanthene was tried, which has a pK_a of 28.5 [9a]. Integration of the appropriate proton resonances gave a pK_a of 29.3.

The pK_a for 2-(p-nitrophenyl)-1,3-dithiane was estimated using nitroethane ($pK_a = 16.727$ [9c]) as an indicator. Integration of the appropriate proton resonances gave a pK_a for 2-(p-nitrophenyl)-1,3-dithiane of 16.9.

The pK_a for 2-(p-fluorophenyl)-1,3-dithiane was determined using 2-phenyl-1,3-dithiane ($pK_a = 30.7$ [36]) as the indicator acid. Integration of the appropriate proton resonances gave a pK_a for 2-(p-nitrophenyl)-1,3-dithiane of 31.1.

Reaction Calorimetry

Basic Instrumentation and Setup. Tronac isoperibol titration calorimeters (models 458 and 450) were employed. The temperature of the model 458 water bath was controlled at 25°C by a Tronac temperature controller (models PTC-40 or PTC-41) with a precision of approximately 0.001°C. Titration and calibration thermograms were recorded for each run on a Sargent–Welch strip-chart recorder, and times of heating were found from a digital stopwatch accurate to a hundredth of a second. Temperature changes were obtained in units of millimeters from the thermogram using a ruler. For treatment of data, see Ref. [65].

Procedure

Hydride Affinities (ΔH_{H-}) of Cations in 95% Sulfolane/5% 3-Methylsulfolane. Procedures described previously [2,4] were followed. Preparation for the experiment took place in a dry box. Solutions of 18-crown-6 (0.11 M) and NaBH₃CN (0.1 M) in 95/5 sulfolane/3-methylsulfolane were prepared. The NaBH₃CN solution was poured into the glass (ca. 20 mL) dewar calorimeter vessel while the cation solution was taken up into a precision titration syringe. The reaction vessel and syringe were removed from the dry box and connected quickly to the calorimeter insert assembly. Determination of ΔH_{H-} values involved recording a calibration thermogram, using electrical heating, and a titration thermogram. Typically, 7–10 ΔH_{H-} values were found from a single syringe full of cation, and the average was calculated for the experiment as a whole. For the 2-aryl-1,3-dithian-2-yliums, at least three experiments were repeated and averaged to get the number reported in this work.

Heats of Deprotonation (ΔH_{dep}) *of Weak Acids by* $K^+DMSYL/DMSO$. The heat of reaction between a weak base and DMSYL⁻ solution followed procedures previously described [2,10]. For the 2-aryl-1,3-dithianes, at least three experiments were repeated and averaged, except for 2-(*p*-nitrophenyl)-1,3-dithiane for which only one value was found.

Electrochemistry

Instrument, Techniques, and Materials. The BAS-100A Electrochemical Analyzer from Bioanalytical Systems, Inc., was used to find redox potentials for all anions and cations employing standard procedure [2] with a three-electrode arrangement consisting of a platinum-disk working electrode, a silver-wire auxiliary electrode, and a Ag/AgI (sat.) reference electrode. The reference electrodes were assembled in a dry box and were constructed of a tapered glass tube capped on the tapered bottom end with a Vycor tip using shrink wrap and on top with a plastic cap. The Vycor tip, shrink wrap, and caps were purchased from Bioanalytical Systems, Inc. Silver wire was inserted through the plastic top so that it reached to the bottom. The electrode was filled with either DMSO or 95% sulfolane/5% 3-methylsulfolane that were 0.1 M in tetrabutylammonium iodide and saturated with AgI.

Preparation of Analyte Solutions. Solutions (~10 mL) of cations and anions that were 0.1 M in tetrabutylammonium tetrafluoroborate (TBABF₄) supporting electrolyte were prepared in a dry box just prior to electrochemical analysis. Reduction potentials for cations (<100 mg) were determined in 95% sulfolane/5% 3-methylsulfolane (v/v). The anions were prepared from DMSO solutions of the weak acid (<50 mg) by reaction with an equivalent of a potassium dimsyl (K⁺CH₃SOCH₂⁻). K⁺ DMSYL⁻ was prepared as needed in the dry box by interaction of potassium hydride and DMSO. TBABF₄ was added either along with the weak base or immediately following the preparation of the anion.

Electrochemical Methods. To obtain redox potentials for the cations and anions, both cyclic voltammetric (CV) and Osteryoung squarewave voltammetric (OSWV) methods with IR compensation were employed. Typically, the cation or anion was analyzed by both methods over a wide range of scan rates. For CV, the scan rate was usually varied from 100 to 500 mV/s in 100 mV/s steps. For OSWV, the peak potentials were found at 15 Hz and from 100 to 500 Hz in 100 Hz steps with an A.C. amplitude of 25 mV and a step size of 4 mV. OSWV gave results

that were quite similar to CV, except in one case where $E_{red}2$ for the reduction of 2-(*p*-tolyl)-1,3-dithian-2-ylium fluoroborate was observable using OSWV but not observable using CV. Final values for peak potentials were determined relative to the peak potential for external ferrocene found using the same solvent, electrolyte reference, auxiliary, and working electrodes. Measured values were corrected to the normal hydrogen electrode by adding 750 mV.

AM1 Semiempirical Computations. Initial geometries for the 2-phenyl-1,3-dithian-2-yl anion and cation and the 2-phenyl-1,3-dithiolan-2-yl cation were obtained from PCMODEL 4.0 [66]. We thank Dr. James L. Fry for the use of PCMODEL for DOS. The structures were obtained using MOPAC 6.0 (MOPAC, Version 6.0; Frank Seiler Research Laboratory: U.S. Air Force Academy, Colorado Springs) using the AM1 Hamiltonian and the PRECISE option. For the radical, the UHF option was used to obtain the energies of the 2-phenyl-1,3-dithian-2-yl radical as a function of phenyl-group conformation. To obtain the heats of formation as a function of phenyl-group rotation, one Ph–C–S dihedral angle was flagged as the reaction coordinate, and all other variables were optimized. As recommended by Beckwith and Zavitsas [67], the heat of formation of the radical using the C.I = 2 rather than the UHF option was employed at the minimum of the latter plot. The BDE for 2-phenyl-1,3-dithiane was calculated using the known heat of formation (52.10 kcal/mol) of the hydrogen atom at 25°C taken from Ref. [68]. RasWin Molecular Graphics for Windows Version 2.4 by R. Sayle was used to produce the stick representations of the molecules by reading in the MOPAC Z matrix after translation to the Alchemy structure format using the Babel program Version 1.06 by Pat Walters and Matt Stahl.

Coupling Products for 2-Phenyl-1,3-dithiane. Calorimetric determination of the heat of coordination could be determined for bis-2-phenyl-1,3-dithiane by titrating a 0.1 M solution of 2-phenyl-1,3-dithian-2-ylium tetrafluoroborate to a 0.1 M solution of the potassium salt of 2-phenyl-1,3-dithiane in sulfolane. The heat of coordination was determined to be 40.6 ± 0.45 kcal/mol. Only one reaction product was seen from the coupling reaction by TLC and ¹H-NMR spectra. The ¹³C and ¹H NMR and mass spectra (MS) confirmed the structure. In addition, the bis thioacetal resulted from condensation of two equivalents of 1,3-propanedithiol with benzil following described for the synthesis of the 2-aryl-1,3-dithianes. The bis thioacetal's proton and ¹³C NMR spec-

tra presented were identical to the coupling product's spectra. MS m/e 380 M + NH_4^+ (100%), 363 MH^+ (24%), 181 (18%). 300 MHz ^1H NMR δ 7.26 (4H, d, l = 6.3 Hz), 7.36-7.30 (6H, m), 2.81-2.64 (8H, m), 2.06-2.00 (1H, m), 1.90-1.80 (1H, m). 75 MHz ^{13}C NMR δ 133.36, 131.15, 127.65, 125.54, 70.15, 28.39, 26.57, 24.08.

Attempts to prepare unsymmetrical coupled products in the same manner led to formation of mixtures of the desired product as well as 2-aryl-1,3-dithianes. Dithianes can form by electron transfer between the ions followed by hydrogen abstraction from the solvent. For this reason, heats of coordination could not be determined for the remainder of the cation–anion combinations.

ACKNOWLEDGMENTS

REFERENCES

[1] (a) E. M. Arnett, R. A. Flowers II, A. E. Meekhof, L. Miller, *J. Am. Chem. Soc., 115,* 1993, 12603–12604. (b) E. M. Arnett, R. A. Flowers II, R. T. Ludwig, A. E. Meekoff, S. A. Walek, *Pure Appl. Chem., 67,* 1995, 729–734.

[2] E. M. Arnett, R. A. Flowers II, R. T. Ludwig, A. E. Meekhof, S. Walek, (submitted).

[3] (a) G. A. Olah, P. von R. Schleyer: *Carbonium Ions* (4 vols.), Wiley-Interscience, New York, London, Sydney, Toronto (1970). (b) D. Bethell, V. Gold: *Carbonium Ions, An Introduction,* Academic Press, London, New York (1967). (c) C. D. Nenitzescu: in G. A. Olah, P. von R. Schleyer (eds): *Carbonium Ions,* Vol. 1, Interscience Publishers, New York (1968).

[4] (a) E. M. Arnett, R. A. Flowers II, A. E. Meekoff, A. Pourjavadi, S. A. Walek, *J. Phys. Org. Chem., 7,* 1994, 663–671. (b) R. F. Childs, R. M. Orgias, C. J. L. Lock, M. Mahendran, *Can. J. Chem., 71,* 1993, 836.

[5] D. F. McMillen, D. M. Golden, *Ann. Rev. Phys. Chem., 33,* 1982, 493–532.

[6] S. W. Benson: *Thermochemical Kinetics,* 2nd Ed., Wiley-Interscience Publication, New York (1976).

[7] (a) F. G. Bordwell, X.-M. Zhang, *Acc. Chem. Res., 26,* 1993, 510–517. (b) F. G. Bordwell, A. V. Satish, S. Zhang, X.-M. Zhang, *Pure Appl. Chem.,* 735–740.

[8] (a) N. C. Deno, J. J. Jaruzelski, A. Schriesheim, *J. Am. Chem. Soc., 77,* 1955, 304 (b) N. C. Deno, A. Schriesheim, *J. Am. Chem. Soc., 77,* 1955, 3051. (c) N. C. Deno, W. L. Evans, *J. Am. Chem. Soc., 79,* 1957, 5804. (d) E. M. Arnett, R. D. Bushick, *J. Am. Chem. Soc., 86,* 1964, 1564.

[9] (a) W. S. Matthews, J. E. Bares, J. E. Bartmess, F. G. Bordwell, F. J. Cornforth, Z. Margolin, R. J. McCallum, G. J. McCollum, N. R. Vanier, *J. Am. Soc., 97,* 1975, 7006. (b) F. G. Bordwell, *Acc. Chem. Res., 21,* 1988, 456–463. (c) Cumulative printout of pK_{HA} values as of February 1992 graciously provided by Prof. F. G. Bordwell.

[10] (a) E. M. Arnett, T. C. Moriarity, L. E. Small, J. P. Rudolph, R. P. Quirk, *J. Am. Chem. Soc., 95,* 1973, 1492. (b) E. M. Arnett, D. E. Johnston, L. E. Small, *J. Am. Chem. Soc., 97,* 1975, 5598. (c) E. M. Arnett, K. G. Venkatasubramanian, *J. Org. Chem., 48,* 1983, 1569.

[11] Since the pK_{HA} of sulfolane is about 31 (18 b) (DMSO, 35), it would be reasonable that this medium would be deprotonated rapidly by the very basic dioxolenyl anions formed at the electrode. This remains a moot point since the $E_{red}2$s of the dioxolenium cations appear to be reversible.

[12] (a) V. D. Parker, *Acta Chem. Scand., 46,* 1992, 1133–1134. (b) J.-P. Cheng, K. L. Handoo, V. D. Parker, *J. Am. Chem. Soc., 115,* 1993, 2655–2660.

[13] B. A. Sim, P. H. Milne, D. Griller, D. D. M. Wayner, *J. Am. Chem. Soc., 112,* 1990, 6635–6638.

[14] R. Breslow, *Pure Appl. Chem., 40,* 1974, 493–509.

[15] (a) E. M. Arnett, N. G. Harvey, K. Amarnath, J.-P. Cheng, *J. Am. Chem. Soc., 111,* 4143. (b) E. M. Arnett, K. Amarnath, N. G. Harvey, J.-P. Cheng, *Science, 247,* 1990, 42. (c) E. M. Arnett, R. A. Flowers II, *Chem. Soc. Rev., 22,* 1993, 9–15.

[16] E. M. Arnett, K. Amarnath, N. G. Harvey, J.-P. Cheng, *J. Am. Chem. Soc., 112,* 344.

[17] E. M. Arnett, K. Amarnath, N. G. Harvey, S. Venimadhavan, *J. Am. Chem. Soc., 112* 1990, 7346.

[18] S. Venimadhavan, K. Amarnath, N. G. Harvey, E. M. Arnett, *J. Am. Chem. Soc., 114,* 1992, 221.

[19] E. M. Arnett, S. Venimadhavan, K. Amarnath, *J. Am. Chem. Soc., 11,* 1992, 5.

[20] (a) R. G. Parr, R. G. Pearson, *J. Am. Chem. Soc., 105,* 1983, 7512. (b) R. G. Parr, W. Yang: *Density Functional Theory of Atoms and Molecules* Oxford University Press, New York (1989). (c) P. K. Chattaraj, H. Lee, R. G. Parr, *J. Am. Chem. Soc., 113,* 1991, 1855. (d) P. K. Chattaraj, R. G. Parr: *Structure and Bonding,* Vol. 80, Springer-Verlag, Heidelberg, pp. 11–26 (1993). (e) R. G. Parr, Z. Zhou, *Acc. Chem. Res.,* 1993, 26. (f) P. K. Chattaraj, A. Cedillo, R. A. Parr, E. M. Arnett, *J. Org. Chem., 60,* 1995, 4707.

[21] (a) R. G. Pearson, *J. Org. Chem., 52,* 1987, 2131–2136. (b) R. G. Pearson, *J. Org. Chem., 54,* 1989, 1423. (c) R. G. Pearson, *J. Am. Chem. Soc., 110,* 1988, 7684. (d) R. G. Pearson, *J. Mol. Struct. (Theochem), 255,* 261–270. (e) R. G. Pearson, *Acc. Chem. Res., 26,* 1993, 250–255. (f) R. G. Pearson, *J. Am. Chem. Soc., 108,* 1986, 6109. (g) R. G. Pearson, *Inorg. Chim. Acta, 240,* 1995, 93. (h) R. G. Pearson, *Int. J. Quant. Chem., 56(4),* 1995, 211.

[22] E. M. Arnett, R. T. Ludwig, *J. Am. Chem. Soc., 117,* 1995, 6627–6628.

[23] (a) See for example: R. E. Dessy, W. Kitching, T. Psarras, R. Salinger, A. Chen, T. Chivers, *J. Am. Chem. Soc., 88,* 1966, 460. (b) M. R. Feldman, W. C. Flythe, *J. Org. Chem., 43,* 1978, 596. (c) Y. Okamoto, *J. Org. Chem., 39,* 1983, 40. (d) D. D. M. Wayner, *J. Am. Chem. Soc., 112,* 1990, 6635. (e) E. M. Arnett, J. A. Harrelson, *Gazzetta Chem. Ital., 117,* 1987, 237. (f) V. D. Parker, *J. Org. Chem., 58,* 1993, 5811–5815.

[24] E. M. Arnett, S. Venimadhavan, *J. Am. Chem. Soc.*, *113*, 1991, 6967.

[25] J. P. Richard, *Tetrahedron*, *51*, 1995, 1535–1573.

[26] S. W. Benson, *Angewandte Chem.*, *17*, 1978, 812–819.

[27] (a) F. G. Bordwell, X.-M. Zhang, A. V. Satish, I.-P. Cheng, *J. Am. Chem. Soc.*, *116*, 1994 6605–6610. (b) K. B. Clark, D. D. M. Wayner, *J. Am. Chem. Soc.*, *113*, 1991, 9363–9365. (c) J. M. White, *Aust. J. Chem.*, *48*, 1995, 1227–1251. (d) P. von R. Schleyer, A. J. Kos, *Tetrahedron*, *39*, 1983, 1141–1150. (e) L. A. Torres, A. Rojas, G. Cuevas, E. Juaristi, *J. Phys. Org. Chem.*, *7*, 1994, 561–5.

[28] (a) P. von R. Schleyer, E. D. Jemmis, G. W. Spitznagel, *J. Am. Chem. Soc.*, *107*, 1985, 6393–6394. (b) Y.-D. Wu, W. Kirmse, K. N. Houk, *J. Am. Chem. Soc.*, *112*, 1990, 4557–4559. (c) A. J. Kresge, M. Leibovitch, *Can. J. Chem.*, *68*, 1990, 1786–1790. (d) Y. Apeloig, M. Karni, *J. Chem. Soc. Perkin Trans. II*, 1988, 625–636. (e) E. Juaristi, J. Tapia, R. Mendez, *Tetrahedron*, *42*, 1986, 1253–1264. (f) E. Juaristi, G. Cuevas, A. Vela, *J. Am. Chem. Soc.*, *116*, 1994, 5796–5804. (g) E. Juaristi, L. Valle, B. A. Valenzuela, M. A. Aguilar, *J. Am. Chem. Soc.*, 1986, 2000–2005. (h) M. Ahmad, R. G. Bergstrom, M. J. Cashen, Y. Chiang, A. J. Kresge, Mc Clelland, M. F. Powell, *J. Am. Chem. Soc.*, *101*, 1979, 2669–2677. (i) A. E. Reed, P. von R. Schleyer, *Inorg. Chem.*, *27*, 1988, 3969–3987. (j) P. P. Graczyk, M. Mikolajczsk, *J. Org. Chem.*, *61*, 1996, 2995–3002.

[29] V. Jagannadham, T. L. Amyes, J. P. Richard, *J. Am. Chem. Soc.*, *115*, 1993, 8465.

[30] D. P. N. Satchell, R. S. Satchell, *Chem. Soc. Rev.*, *19*, 1990, 55–81.

[31] J. K. Pau, M. B. Ruggera, J. K. Kim, M. C. Caserio, *J. Am. Chem. Soc.*, *100*, 1978, 4242–4248.

[32] O. Exner: in N. B. Chapman, J. Shorter (eds): *Advances in Linear Free Energy Relationships*, Plenum Press, London, New York, p. 32 (1972).

[33] Okuyama, T. in S. Oae (ed): *Reviews on Heteroatom Chemistry*, Vol. 1, MYU, Tokyo.

[34] D. Ohlmann, C. M. Marchand, H. Grützmacher, G. S. Chen, D. Farmer, A. Glase Currao, R. Nesper, H. Pritzkow, *Angewandte Chemie*, *35*, 1996, 300–303.

[35] C. U. Pittmann, Jr., S. P. McManus, J. W. Larsen, *Chem. Rev.*, *72*, 1972, 357–438.

[36] (a) F. G. Bordwell, G. E. Drucker, N. H. Andersen, A. D. Denniston, *J. Am. Chem. Soc.*, *108*, 1986, 7310–7313. (b) F. G. Bordwell, J. E. Bares, J. E. Bartmess, G. E. Drucker, J. Gerhold, McCollum, M. Van Der Puy, N. R. Vanier, W. S. Matthews, *J. Org. Chem.*, *42*, 1977, 326–332.

[37] M. T. Jernigan, E. L. Eliel, *J. Am. Chem. Soc.*, *117*, 1995, 9638–9644.

[38] J. E. Bartmess: *Gas Phase Acidity Scale as of October*, Vol. 25 (1994).

[39] H. J. Reich, J. P. Borst, R. R. Dykstra, *Tetrahedron*, *50*, 1994, 5869–5880.

[40] (a) A. G. Abatjoglou, E. L. Eliel, L. F. Kuyper, *J. Am. Chem. Soc.*, *99*, 1977, 8262–8269. (b) E. L. Eliel, A. A. Hartmann, A. G. Abatjoglou, *J. Am. Chem. Soc.*, *96*, 1974, 1807–1816. (c) O. Hofer, E. L. Eliel, *J. Am. Chem. Soc.*, *95*, 1973, 8045–8050. (d) E. L. Eliel, A. Abatjoglou, A. A. Hartmann, *J. Am. Chem. Soc.*, *94*, 1972, 478. (e) A. A. Hartmann, E. L. Eliel, *J. Am. Chem. Soc.*, *93*, 1971, 2572–2573.

[41] (a) L. Xie, A. Streitwieser, *J. Org. Chem.*, *60*, 1995, 1339–1346. (b) P. Speers, K. E. Laidig, A. Streitwieser, *J. Am. Chem. Soc.*, *116*, 1994, 9257–9261. (c) L. Xie, D. A. Bors, A. Streitwieser, *J. Org. Chem.*, *57*, 1992, 4986–4990.

[42] P. von R. Schleyer, T. Clark, A. J. Kos, G. W. Spitznagel, C. Rohde, D. Arad, K. N. Houk, N. G. Rondan, *J. Am. Chem. Soc.*, *106*, 1984, 6467–6475.

[43] W. T. Borden, E. R. Davidson, N. H. Andersen, A. D. Denniston, N. D. Epiotis, *J. Am. Chem. Soc.*, *100*, 1978, 1604–1605.

[44] I.-M. Lehn, G. Wipff, *J. Am. Chem. Soc.*, *98*, 1976, 7498–7505.

[45] F. Bernardi, A. Mangini, G. Tonachini, P. Vivarelli, *J. Chem. Soc. Perkin Trans. II*, 1985, 111–114.

[46] K. B. Wiberg, H. Castejon, *J. Am. Chem. Soc.*, *116*, 1994, 10489–10497.

[47] (a) M. S. Alnajjar, X.-M. Zhang, J. A. Franz, F. G. Bordwell, *J. Org. Chem.*, *60*, 1995, 4976–4977. (b) F. G. Bordwell, X.-M. Zhang, *J. Am. Chem. Soc.*, *116*, 1994, 973–976. (c) F. G. Bordwell, X.-M. Zhang, M. S. Alnajjar, *J. Am. Chem. Soc.*, *114*, 1992, 7623–7629.

[48] P. Arya, C. Samson, M. Lesage, D. Griller, *J. Org. Chem.*, *55*, 1990, 6248–6250.

[49] G. Leroy, M. Sana, C. Wilante, *J. Mol. Struct. (Theochem.)*, *234*, 1991, 303–328.

[50] J. L. Ginsburg, J. C. Baum, R. F. Langler, *J. Phys. Chem.*, *94*, 1990, 1750–1755.

[51] C. Hansch, A. Leo, R. W. Taft, *Chem. Rev.*, *91*, 1991, 165.

[52] C. D. Johnson: *The Hammett Equation*, Cambridge University Press, Cambridge (1973).

[53] J. T. Edward, *Chem. Ind. (London)*, 1955, 110L.

[54] R. U. Lemieux, *Pure Appl. Chem.*, *25*, 1971, 527.

[55] (a) E. Juaristi, G. Cuevas, *Tetrahedron*, *48*, 1992, 5019–5087. (b) See P. A. Kollman, et al, *J. Org. Chem.*, *61*, 1996, 3662–3668, for a very recent discussion.

[56] W. F. Bailey, H. Common, E. L. Eliel, K. B. Wiberg, *J. Am. Chem. Soc.*, *100*, 1978, 2209.

[57] M. Mikolajczyk, P. P. Graczyk, M. W. Wieczorek, *J. Org. Chem.*, *59*, 1994, 1672–.

[58] G. Boche, *Angewandt Chemie, I. Ed. Eng.*, *28*, 1989, 277–297.

[59] R. Amstutz, J. D. Dunitz, D. Seebach, *Angewandt Chemie*, *20*, 1981, 465–466.

[60] (a) C. Gaze, B. C. Gilbert, *J. Chem. Soc., Perkins Trans. II*, 1979, 763–769. (b) A. L. J. Beckwith, S. Brumby, *J. Chem. Soc., Perkin Trans. II*, 1987, 1801–1807.

[61] M. S. Alnajjar, X.-M. Zhang, J. A. Franz, F. G. Bordwell, *J. Org. Chem.*, *60*, 1995, 4977.

[62] (a) H. Lankamp, W. T. Nauta, C. MacLean, *Tetrahedron Lett.*, *2*, 1968, 249–254. (b) J. M. McBride, *Tetrahedron*, *30*, 1974, 2009–2022.

[63] Compare with T. Gade, M. Streek, J. Voss, *Chem. Ber.*, *121*, 1988, 2245.

[64] J. Klaveness, K. Undheim, *Acta Chim. Scand. B*, *37*, 1983, 687–690.

[65] J. K. Grime (ed): *Analytical Solution Calorimetry*, John Wiley and Sons, New York (1985).

[66] J. J. Gajewski, K. E. Gilbert, J. McKelvey: in D. L. (ed): *Advances in Molecular Modeling*, JAI Press, Greenwich, CT (1990).

[67] A. L. J. Beckwith, A. A. Zavitsas, *J. Am. Chem. Soc.* *117*, 1995, 607–614.

[68] John A. Dean: *Lange's Handbook of Chemistry*, 14th Ed., McGraw-Hill, Inc., New York (199?).