low endothermicity explains why alkyl nitrates are such potent nitrating reagents in acid media.

In our recent study of heterosubstituted diazonium ions, we reported a protonation energy $\Delta E_{1,\mathrm{corr}}$ = 181.6 kcal/mol for the formation of aminodiazonium ion from HN_3 that was determined at the MP4(fc,sdtq)/6-311G**//MP2-(full)/6-31G*+ΔVZPE(MP2/6-31G*) level. The series of CI calculations presented here indicate that the agreement of the theoretical value reported by Cacace et al. with their experimental value is fortuitous. At our highest level, CISD(fc,ssc)/6-311G(df,p)//MP2/6-31G*+ΔVZPE-(MP2/6-31G*) we find a proton affinity of 186.4 kcal/mol for HN_3. Inclusion of core electrons in the active space of the CI calculation, addition of f-type functions, and structural effects were shown to affect this value only modestly. The theoretical estimate for the proton affinity is thus significantly higher (>10 kcal/mol) than the one reported by Cacace et al.

In good agreement with experiment, the reaction energy of ΔE_3 = 2.9 kcal/mol was calculated for the proton-transfer reaction $CH_3ONO_2 + H_2N_3^+ \rightleftharpoons CH_3ONO_2)H^+ + HN_3$ at CISD/6-311G**//RHF/6-31G*+ΔVZPE. These theoretical results suggest that the reported experimental proton affinity of HN_3 (176.6 kcal/mol) might be too low *as a consequence of evaluating the proton-transfer equilibrium with an underestimated proton affinity of* CH_3ONO_2.

With the CI energies of aminodiazonium ion **2a**, we have reconsidered the reaction energy for its dediazotization. Confirming the results obtained at full fourth-order Møller–Plesset levels and in sharp contrast to prior semiempirical results, the dediazotization of **2a** is predicted to be endothermic by 73.6 kcal/mol at the CISD/6-311G-(df,p)//RHF/6-31G*+ΔVZPE level.

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Registry No. 1, 7782-79-8; **2a**, 85990-23-4; **3**, 598-58-3; **4.1**, 99573-80-5; NO_2^+, 14522-82-8; NH_2^+, 15194-15-7.

Supplementary Material Available: Optimized structures determined at the semiempirical levels (19 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

Carbon Acidity. 82. Equilibrium Cesium Ion Pair Acidities of Some Substituted 1,3-Dithianes

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The equilibrium cesium ion pair acidities in tetrahydrofuran have been determined at 25 °C for 2-*p*-biphenylyl-1,3-dithiane (29.1), 2-phenyl-1,3-dithiane (30.5), 4-methyl-2,6,7-trithiabicyclo[2.2.2]octane (30.2), 1,3-dithiane (36.5), and 2-methyl-1,3-dithiane (38.2). Studies of their acidities over a wide range of concentrations indicate that these dithianylcesium salts exist as monomeric ion pairs in solutions with concentrations ranging from 10^{-3} to 10^{-5} M. The corresponding ion pair acidities in cyclohexylamine have been reinvestigated, and the corrected pK_a values are 28.7, 30.0, 29.7, 37.5, and 37.8, respectively. Comparisons of these pK_a values with those in dimethyl sulfoxide show remarkable agreement despite the difference in the nature of the solvents.

Introduction

There is abundant evidence of the abilities of sulfur to markedly enhance both thermodynamic and kinetic acidities of protons on adjacent carbons.[2,3] Of the derived reagents useful in organic synthesis, 1,3-dithianes have been particularly valuable due to their abilities as masked nucleophilic acylating reagents.[4,5] Accordingly, a thorough understanding is desirable of the relative stabilities of dithianyl anions and the nature of their ion pairs in solutions such as that obtained by studying their equilibrium acidities. The pK_a values for several 1,3-dithianes have been previously reported for cesium salts in cyclohexylamine (CHA)[6,7] and lithium salts in tetrahydrofuran

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(THF).[8] Bordwell et al. have also reported the pK_a values for a number of dithiane compounds in dimethyl sulfoxide (DMSO).[9] For the indicator hydrocarbons used to establish the acidity scales in CHA,[10] THF,[11] DMSO[12] and dimethoxyethane (DME),[13] which form highly delocalized anions, the relative pK_a values are nearly equivalent in all four solvents. However, this equivalence does not necessarily hold for compounds that form localized carbanions. A major goal of this study is to examine more thoroughly the effects of solvents on the acidities of carbon acids with localized anions and the nature of these anions in solution compared to delocalized anions. Equilibrium ion pair acidities are defined by eq 1, where RH stands for the carbon acid whose pK_a is to be measured and InH is an appropriate indicator whose pK is on the acidity scale.[11]

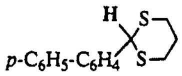
$$\mathrm{RH} + \mathrm{In}^- \mathrm{M}^+ \overset{K}{\rightleftharpoons} \mathrm{InH} + \mathrm{R}^- \mathrm{M}^+ \qquad (1)$$

$$\Delta \mathrm{p}K = \mathrm{p}K_{\mathrm{RH}} - \mathrm{p}K_{\mathrm{InH}} = -\log K$$

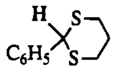
This approach applies to those salts of RH that form monomeric ion pairs. If the ion pairs from RH form aggregates, as shown by eq 2, the equilibrium (1) is displaced toward the right, resulting in a lower measured pK value for RH.

$$n(\mathrm{R}^- \mathrm{M}^+) \rightleftharpoons (\mathrm{R}^- \mathrm{M}^+)_n \qquad (2)$$

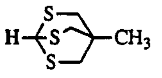
A simple relationship has been shown previously[14] relating the average aggregation number to the measured pK_a values and the ion pair concentrations. This relationship allows us to measure the degree of ion pair aggregation in these systems. The following dithianes were selected for study in THF and CHA with cesium as counterion: 2-*p*-biphenylyl-1,3-dithiane (BPDT), 2-phenyl-1,3-dithiane (PDT), 4-methyl-2,6,7-trithiabicyclo[2.2.2]octane (TRI), 1,3-dithiane (DT), and 2-methyl-1,3-dithiane (MDT). Cesium salts should form only contact ion pairs in these solvents, thus simplifying the interpretation of ion pairing.



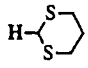
BPDT



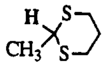
PDT



TRI



DT



MDT

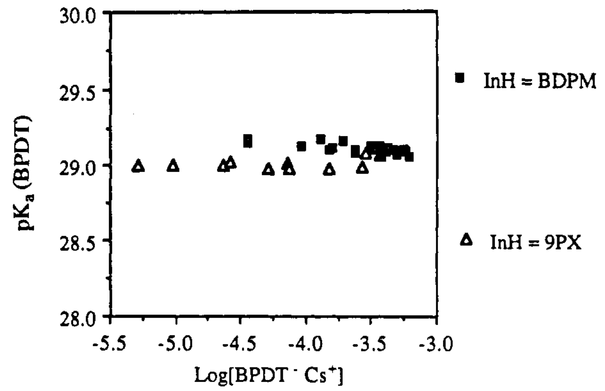


Figure 1. Cesium ion pair acidity of 2-*p*-biphenylyl-1,3-dithiane in THF as a function of anion concentrations at 25 °C.

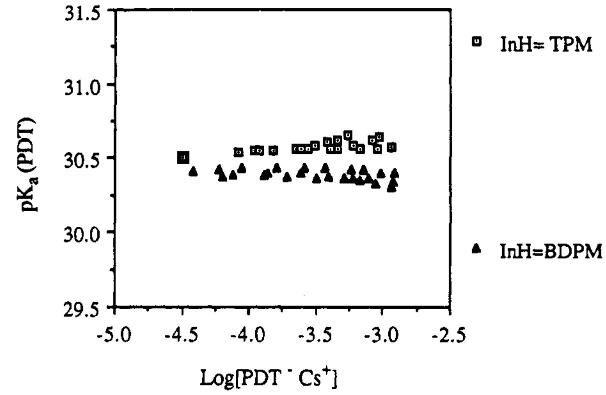


Figure 2. Cesium ion pair acidity of 2-phenyl-1,3-dithiane in THF as a function of anion concentrations at 25 °C.

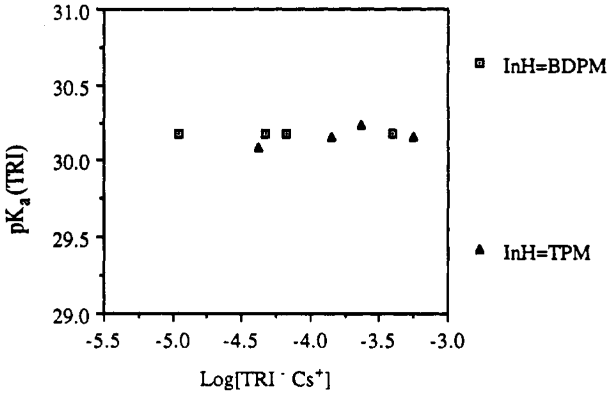


Figure 3. Cesium ion pair acidity of 2,6,7-trithiabicyclo[2.2.2]-octane in THF as a function of anion concentrations at 25 °C.

Results and Discussion

Ion-Pairing Aggregation. Of the five carbon acids studied, the conjugate anions range from highly localized (TRI, DT, and MDT) to somewhat delocalized (BPDT and PDT).[15] The cesium salts of BPDT and PDT have absorbance maxima in the visible region that adhere to Beer's law over the concentration range studied. The anion of BPDT has its absorbance maximum at 456 nm (ϵ = 35 439) in THF and 448 nm (ϵ = 31 400) in CHA. These pK values were conveniently measured by the double indicator method (see Experimental Section). The cesium salt of PDT has an absorbance maximum at 365 nm (ϵ = 14 590) in THF; the pK_a of PDT was also measured by the double indicator method. On the other hand, the cesium salts of

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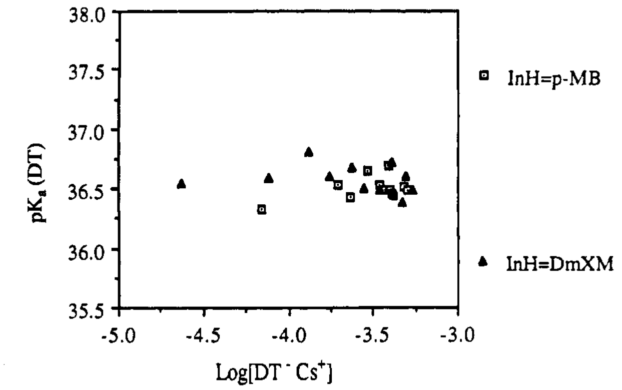

Figure 4. Cesium ion pair acidity of 1,3-dithiane in THF as a function of anion concentrations at 25 °C.

TRI, DT, and MDT have no absorbance in the usable range (Pyrex cells absorb strongly <330 nm) and were consequently measured by the single indicator method (see Experimental Section). Consistency was established by measuring each compound against two indicators. The acidities were also measured over a range of anion concentrations to determine the extent of ion pair aggregation. The average aggregation number, $\bar{n}$, was obtained from eq 3,[14] where pK_a is the experimentally measured acidity, $\bar{n}$

$$pK_a = \frac{(1 - \bar{n})}{\bar{n}} \log [R^- M^+]_t + b \qquad (3)$$

is the average aggregation number, $[R^- M^+]_t$ is the total ion pair concentration, and b is a constant for a specific set of RH and InH. If a given anion is aggregated in solution (i.e., $\bar{n} > 1$), the apparent pK_a varies with the concentration of the cesium salt and the average degree of aggregation is determined by the slope of a plot of pK_a vs log $[R^- M^+]_t$. Such plots for compounds BPDT, PDT, TRI, and DT at 25°C in THF are presented in Figures 1–4, respectively.

The pK_a values for BPDT (Figure 1), PDT (Figure 2), and TRI (Figure 3) are, within experimental error, constant throughout the whole range of concentrations studied (10^{-3}–10^{-5} M), indicating the absence of ion pair aggregation of their cesium salts in THF. Although more scatter can be seen in the plot of DT (Figure 4), there is no obvious indication of ion pair aggregation. Experimental errors are greater in the latter case because the transmetalation equilibria are established more slowly at the high pK end of the acidity scale.

Table I. Equilibrium Data for Some Dithianes in THF at 25 °C

RH[a]	InH[b]	ΔpK[c]	N[d]	anion concns (10^4 M)
BPDT	9-PX	0.29 ± 0.04	11	0.05–3.6
BPDT	BDPM	−0.96 ± 0.03	22	0.4–6.1
BDPM	9-PX	−1.25 (−1.34)[e]		
PDT	BDPM	0.32 ± 0.03	25	0.4–12.2
PDT	TPM	−0.68 ± 0.04	20	0.3–11.4
BDPM	TPM	−1.00 (−1.09)[e]		
TRI	BDPM	0.11 ± 0.01	4	0.1–4.0
TRI	TPM	−1.10 ± 0.06	4	0.4–5.6
BDPM	TPM	−1.21 (−1.09)[e]		
DT	DmXM	0.58 ± 0.10	12	0.2–5.4
DT	*p*-MB	−2.23 ± 0.10	12	0.7–5.0
DmXM	*p*-MB	−2.81 (−2.77)[e]		
MDT	PTS	0.51 ± 0.16	4	0.4–1.0
MDT	*p*-MB	−0.55 ± 0.13	3	0.9–2.3
PTS	*p*-MB	−1.06 (−1.04)[e]		

[a] Abbreviations for RH: BPDT, 2-*p*-biphenylyl-1,3-dithiane; PDT, 2-phenyl-1,3-dithiane; TRI, 4-methyl-2,6,7-trithiabicyclo[2.2.2]octane (trithiane); MDT, 2-methyl-1,3-dithiane; DT, dithiane. [b] See ref 29 for abbreviations. [c] $\Delta pK = pK_{RH} - pK_{InH}$. [d] Number of measurements. [e] Values in parentheses are the ΔpK's for the two indicators by direct measurements (see ref 11d).

Table II. Equilibrium Data for Some Dithianes in CHA at 25 °C

RH[a]	InH[a]	ΔpK	N	anion concns (10^4 M)
BPDT	9-PX	0.18 ± 0.02	3	0.7–2.0
BPDT	BDPM	−1.44 ± 0.01	3	1.7–1.9
9-PX	BDPM	−1.62 (−1.68)[b]		
PDT	9-PX	1.44 ± 0.06	2	2.0–2.2
PDT	BDPM	−0.12 ± 0.06	2	1.2–2.3
9-PX	BDPM	−1.56 (−1.68)[b]		
TRI	9-PX	1.15 ± 0.01	2	2.9–6.1
TRI	BDPM	−0.43 ± 0.05	3	1.0–2.1
9-PX	BDPM	−1.58 (−1.68)[b]		
DT	DmXM	1.26 ± 0.20	2	1.8–2.1
DT	*p*-MB	−1.52 ± 0.13	3	0.7–1.5
DmXM	*p*-MB	−2.78 (−2.7)[b]		

[a] See Table I for abbreviations. [b] Values in parentheses are the ΔpK's for the two indicators by direct measurements (see ref 10).

Table III. Comparisons of Equilibrium Cesium Ion Pair p*K*a's in THF and CHA with p*K*a's in DMSO

dithiane substrate	pK_{CsTHF}[a]	pK_{CsCHA}[b]	pK_{DMSO}[c]
2-*p*-biphenylyl-1,3-dithiane (BPDT)	29.1	28.7	29.1
2-phenyl-1,3-dithiane (PDT)	30.5	30.0	30.7
4-methyl-2,6,7-trithiabicyclo[2.2.2]-octane (TRI)	30.2	29.7	30.5
1,3-dithiane (DT)	36.5[d]	37.5[d]	(39)[e]
2-methyl-1,3-dithiane (MDT)	38.2	37.8[f]	

[a] Reference 11. [b] Reference 10. [c] Reference 9. [d] No statistical correction. [e] Extrapolated value (ref 9). [f] Reference 7.

It is not surprising that cesium salts of BPDT and PDT are monomeric in THF, since their anions are benzylic and extensively delocalized.[16] Our results in solution are in accord with the findings of Amstutz, Dunitz, and Seebach[17] that the lithium salt of PDT exists as a monomer in the solid state. Our results also indicate that the cesium salt of BPDT is monomeric in CHA. Seebach et al. reported that the lithium salt of MDT is dimeric in the solid state,[18] but monomeric in THF by low-temperature NMR techniques[19] and slightly aggregated by freezing-point depression techniques.[20] Our results indicate the existence of monomeric ion pairs in THF solution for the cesium salts of both TRI and DT. Because of the structural similarity of DT and MDT, MDT is presumed to be monomeric as well.

Lithium salts as contact ion pairs involve a much smaller cation than cesium salts and may therefore be more prone to aggregate. Moreover, the concentrations at which our measurements were carried out are rather dilute (normally

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lower than 10^{-3} M) compared to the more concentrated solutions of Seebach; thus, we expect to find the cesium salt of MDT in THF to be less aggregated than Seebach's lithium salt of MDT in THF.

Effects of Solvent on Acidity. Because of the absence of ion pair aggregation in both THF and CHA solution, our measured pK_a values reflect the true ion pair acidities of the compounds studied. Tables I and II list the equilibrium data for these dithiane compounds with appropriate indicators in THF and CHA, respectively. The averaged pK_a values for these dithianes are summarized in Table III, along with the values in DMSO from Bordwell's work.[9] CsCHA values agree reasonably well with those reported some years ago with the singular exception of DT itself;[6] the present value is 6 pK units higher. Application of the single indicator technique is subject to possible error, especially at the high end of the indicator scale when equilibria are established slowly. Since the concentration of the substrate anion is deduced from the decrease in absorbance of the indicator salt when a known amount of substrate is added, any acidic impurity (or moisture) added with the substrate will cause its own reduction of the indicator absorbance and result in a false result. This error is always in the direction to make the substrate appear more acidic than it is. The best check for accuracy is careful repeated experiments, preferably with more than one indicator. Thus, the surprisingly large methyl substituent effect of 5.9 pK units remarked on earlier[6] is an artifact; the effect of 2-methyl substitution in dithiane is actually rather small.

The pK_a values for indicator hydrocarbons that form delocalized carbanions are nearly equivalent in THF, CHA, DMSO, and DME. Table III shows that the acidities in THF, CHA, and DMSO are almost identical for both BPDT and PDT, as expected for compounds with delocalized carbanions where the ion pair interactions are comparable in substrate and indicator; that is, for these systems the ion pair dissociation constants to free ions do not differ much so that the relative ion pair acidities are comparable to ionic acidities.[21] More surprisingly, the pK_a values for TRI, which is expected to form an essentially localized carbanion, also show remarkable consistency in the solvents compared. This result means that the ion pair dissociation constant of this localized cesium salt is comparable to that of the delocalized salts. The carbanion from TRI is undoubtedly stabilized by the polarizability of sulfur and of the bonds to sulfur;[22] this polarization in the carbanion is equivalent to having an induced dipole adjacent to the carbanion carbon. The present results indicate therefore that the electrostatic interaction within an ion pair of a carbanion of the TRI type with its induced dipoles is comparable to that of a more delocalized carbanion. Thus, ion pair interactions do not necessarily provide an operational distinction between delocalization and polarization as stabilizing mechanisms for carbanions. Note that the stabilization of the carbanion by sulfur in TRI is almost the same as the stabilization by a phenyl group in PDT. The situation may be different for DT and MDT. A direct experimental pK_a for DT is unavailable in DMSO because its acidity is lower than that of the solvent, but Bordwell has used the acidities of derivatives to extrapolate a pK_a of 39.[9] This value is unlikely to be in error by much more than 1 unit and is substantially higher than the ion pair pK_a of 36.5 in THF. Figure 4 indicates that the latter value is unlikely to be in error by more than a few tenths of a pK_a unit. Thus, the electrostatic attractions within this ion pair are now significantly higher than in the reference indicators; that is, these results suggest that the ion pair dissociation constant of the cesium salt of DI is about 10^2 less than that of the indicator salts.[21]

Note in Table III that a statistical correction was not applied to DT. It has been shown that the rate of equatorial deprotonation is about 10 times faster than that of axial deprotonation,[23] so that there is only one proton which is "effectively" acidic.

The present results may be used to estimate the ion pair pK_a of methane. The cesium ion pair pK_a of toluene in THF has been evaluated as 40.9.[11d] Addition of two sulfurs in PDT reduces the pK_a to 30.5, a change of 10.4 units. Applying this change to DT provides an estimate of the pK_a of methane of 47. The actual difference between methane and DT is probably somewhat greater—by perhaps 1–2 pK_a units—because benzylcesium is a more delocalized carbanion than the cesium salt of PDT; for example, a *p*-phenyl substituent decreases the pK_a of toluene by 2.2 units[11b] but the difference between PDT and BPDT is only 1.4 units (Table III). The estimated pK_a of methane as its monomeric cesium salt in THF is thus about 48–49, about 5–6 units greater than the pK_a of benzene, estimated to be about 43 (as phenylcesium in cyclohexylamine).[24] This difference may be compared to the kinetic acidity difference with CsCHA of about 10^6.[25]

Of the anions in this study, only the cesium salt of TRI showed decomposition at room temperature. Following addition of TRI to a solution containing anions of an appropriate indicator, an initial drop in the indicator anion absorbance was followed by a slow decrease in the absorbance. This suggests either the decomposition of the anion of TRI or a slow transmetalation equilibrium between the indicator and TRI. Evidence suggesting decomposition rather than a slow equilibrium is found in an experiment in which an neutral indicator was added to a solution of TRI anion. The absorbance of the indicator anion reached a maximum value quickly and then decreased slowly, an observation consistent with the decomposition of TRI anion. These reactions were all carried out in the dark, and control experiments with the light beams of the UV–vis instrument blocked did not decelerate the decomposition. This result indicates that the decomposition does not occur by a photochemical mechanism but the exact mechanism of the decomposition is unknown.

Conclusions

We report here quantitative ion pair equilibrium acidities for five sulfur-containing carbon acids with cesium as counterion. The study shows that these ion pairs exist as monomers in THF solution at dilute concentrations.

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Quantitative data in THF, CHA, and DMSO allow direct comparisons of the effects of solvent on the carbanion stabilities. For 2-*p*-biphenylyl-1,3-dithiane, 2-phenyl-1,3-dithiane, and 4-methyl-2,6,7-trithiabicyclo[2.2.2]octane, the ion pair interactions of the cesium salts are comparable to those of the indicators used and the relative ion pair pK_a's are comparable to the relative ionic pK_a's in DMSO. Ion pair interactions are greater for the weaker acids 1,3-dithiane and 2-methyl-1,3-dithiane, and their ion pair pK_as in THF and CHA are lower than the extrapolated ionic values in DMSO.

Experimental Section

General. Starting materials for syntheses were obtained from commercial suppliers and were purified by recrystallization or distillation prior to use. Melting points (Pyrex capillary) were determined on a Buchi melting point apparatus and are uncorrected. Proton nuclear magnetic resonance (^{1}H NMR) spectra were determined on UCB-250 (a superconducting 250-MHz instrument), Bruker AM-400, and Bruker AM-500 (FT NMR) spectrometers operating in the FT mode. Gas–liquid chromatography (GLC) was performed on a Hewlett-Packard 5880 gas chromatograph using a 6-ft × 18-in. OV-101 column. The sample compartment of an IBM 9431 UV-vis spectrophotometer was contained with a Vacuum Atmospheres glovebox and fitted with a thermostated cell holder for 0.1-cm path length cells. Thus, sample were prepared and measured without removing them from the glovebox. Constant temperatures were maintained by a Neslab RTE-8DD temperature controller with a recirculating bath.

Materials. The hydrocarbon indicators and their extinction coefficients have been described in our previous studies in THF.[11] When warranted, they were multirecrystallized from alcohols and further purified by sublimation under vacuum and their extinction coefficients were checked and compared with previous data for reproducibility. 1,3-Dithianes were synthesized according to literature procedures: 1,3-dithiane (DT);[4d] 2-methyl-1,3-dithiane (MDT);[26] 2-*p*-biphenylyl-1,3-dithiane (BPDT);[27] 2-phenyl-1,3-dithiane (PDT);[27] and 4-methyl-2,6,7-trithiabicyclo[2.2.2]octane (TRI).[27] The purity of the compounds was monitored bv combinations of the following techniques: mp, ^{1}H NMR, GLC, and elemental analysis.

Cumylcesium. The solution of cumylcesium was prepared according to the procedure described previously.[11b]

Acidity Measurements. Double Indicator Method. The method used is a simple modification of the double indicator method which has previously been described in detail.[28] A known amount of both an appropriate hydrocarbon indicator and a substrate dithiane (BPDT or PDT) was transferred into a thermostated 0.1-cm cell (with an attached side arm for mixing) containing a known amount of THF. A stable absorbance base line was obtained and stored for spectra correction. A small amount of cumylcesium solution (in THF) was then added until appropriate absorbance readings (about 0.1–0.2 absorbance units) were obtained for both the indicator anion and the dithiane anion. The spectrum was then recorded and transferred to an IBM 9000 computer for analysis. The successive addition of cumylcesium base and the recording of the spectrum were repeated until the absorbance reached ~2.0 absorbance units. The equilibrium constant and hence the pK_a of the dithiane was calculated by methods described previously.[11b,29]

Single Indicator Method. A known amount of an appropriate hydrocarbon indicator in a prebaked microbeaker was added into a thermostated 0.1-cm cell containing a known amount of THF. The base line reading at the maximum absorption wavelength of the indicator anion was recorded for correction. Cumylcesium was added until the absorbance at the maximum absorption wavelength was 1–2 absorbance units. A small amount (sufficient to decrease the indicator anion absorbance by 0.2–0.3 absorbance units) of dithiane (DT or MDT) was weighed into a microbeaker, and the beaker was dropped into the cell. The mixture was well shaken, and the reading of the absorbance was recorded again. The addition of the dithiane was repeated until the absorbance of the indicator anion reached 0.2–0.3 units. The equilibrium constants and the pK_a values were thus calculated based on the amount of dithiane added and incremental decrease in the absorbance of the indicator anion. Control experiments were conducted to obtain the absorbance decrease caused by the microbeakers, and the correction was incorporated into the calculation. Because of the decomposition of the anion of TRI, a one cell–one microbeaker method was used for the acidity measurement of TRI. After preparing an indicator anion solution with 1–2 absorbance units, a small amount (sufficient to decrease the indicator anion absorbance by 0.2–0.3 absorbance units) of TRI was weighed into the microbeaker and dropped into the cell. The solution was shaken, and the absorbance reading was recorded immediately and used to calculate the pK_a. Then another cell of the indicator anion solution with 1–2 absorbance units was prepared, and a different amount of TRI was added and the absorbance reading was recorded. This procedure was repeated for several cells so that the dependence of pK_a values on the concentrations of dithiane anions could be examined. The procedure in CHA was somewhat different and the results are expected to be somewhat less accurate.

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[29] Abbreviations (and pK_a per hydrogen) for indicator compounds: BDPM, *p*-biphenylyldiphenylmethane (30.07); TPM, triphenylmethane (31.26); 9PX, 9-phenylxanthene (28.73); DmXM, di-*m*-xylylmethane (35.96); PTS, phenyl *p*-tolyl sulfide (37.96); *p*-MB, *p*-methylbiphenyl (38.73).