

for 3 hr. during which time water distilled from the reaction vessel. Water (10 ml.) was added to the combined distillate and residue and the mixture was extracted with ether. The extracts were washed with dilute hydrochloric acid and water, dried, and the solvent was removed. The residue was distilled through a short-path still yielding 0.085 g. (76%) of the diether 9. An analytical sample was collected by gas chromatography. The diether had $[\alpha]^{21}_{578} + 52.4^\circ$, $[\alpha]^{21}_{546} + 58.9^\circ$, $[\alpha]^{21}_{510}$ calculated from the preceding rotations $+50.3^\circ$ (c 4.63, chloroform).

Anal. Calcd. for $C_{10}H_{20}O_2$: C, 69.72; H, 11.70. Found: C, 69.55; H, 11.83.

(b).—To a stirred, ice-cooled solution of 0.067 g. of (+)-*trans*-1,2-cyclooctanediol (10) in 10 ml. of methylene chloride was added 0.18 ml. of fluoroboric acid solution (prepared by addition of 0.133 ml. of 50% fluoroboric acid to 25 ml. of 3:1 ether-methylene chloride). A solution of diazomethane in ether was added until the yellow color of diazomethane persisted. More of the catalyst solution (0.05 ml.) was added whereupon the yellow color disappeared, and more diazomethane was added as before.²¹ A few drops of the catalyst solution was added to decompose the excess diazomethane. Four pellets of potassium hydroxide were added, the solution was filtered through magnesium sulfate, and the solvent was removed. The residue was distilled through a short-path still.²² The pure diether 9 was ob-

(21) The alkylation is not instantaneous and to ensure complete alkylation it was essential to add diazomethane until the yellow color persisted for about 5–10 min. The alkylation could be followed by gas chromatography (silicone rubber, 90°); a peak corresponding to monoalkylated product was seen when there was incomplete alkylation (or if the alkylation was carried out at -20°).

(22) A sample of optically inactive *trans*-1,2-dimethoxycyclooctane prepared by methylation of *trans*-1,2-cyclooctanediol²³ had b.p. 97–100° (18

tained from the distillate by collection from gas chromatography (silicone rubber, 90°) as a colorless oil (0.040 g., 50%). It had $[\alpha]^{21}_{578} + 51.4^\circ$, $[\alpha]^{21}_{546} + 57.1^\circ$, $[\alpha]^{21}_{510}$ calculated from the preceding rotations $+49.5^\circ$ (c 4.337, chloroform).

Anal. Calcd. for $C_{10}H_{20}O_2$: C, 69.72; H, 11.70. Found: C, 69.81; H, 11.70.

The infrared spectra and retention times of the (+)-*trans*-1,2-dimethoxycyclooctane (9) prepared by the two methods were identical and very different from those of *cis*-1,2-dimethoxycyclooctane.

cis-1,2-Dimethoxycyclooctane was prepared by treatment of *cis*-1,2-cyclooctanediol²⁴ with diazomethane-fluoroboric acid in the manner described for the *trans* isomer. It displayed the following n.m.r. spectrum ($CDCl_3$): 6.63 (8H, singlet superimposed on broad peak), 8.4 τ (12H, broad multiplet).

Anal. Calcd. for $C_{10}H_{20}O_2$: C, 69.72; H, 11.70. Found: C, 69.84; H, 11.67.

(+)-*trans*-1,2-Cyclooctanediol (10) was prepared^{6,25} by osmylation of (–)-*trans*-cyclooctene⁵ [$[\alpha]^{28}_{578} - 432^\circ$, $[\alpha]^{28}_{546} - 500^\circ$, $[\alpha]^{28}_{510}$ calculated from the preceding rotations -412° (c 1.110, methylene chloride)] and decomposition of the osmate ester with sodium sulfite. The glycol was obtained in 64% yield and had $[\alpha]^{21}_{578} + 17.21^\circ$, $[\alpha]^{21}_{546} + 19.46^\circ$, $[\alpha]^{21}_{510}$ calculated from the preceding rotations $+16.51^\circ$ (c 3.34, absolute ethanol).

Anal. Calcd. for $C_{10}H_{20}O_2$: C, 69.72; H, 11.70. Found: C, 69.64; H, 11.70.

(23) A. C. Cope, S. W. Fenton, and C. F. Spencer, *J. Am. Chem. Soc.*, **74**, 5884 (1952).

(24) *cis*-1,2-Cyclooctanediol was prepared from *cis*-cyclooctene, sodium chlorate, and osmium tetroxide.²³

(25) This reaction on the optically active olefin was first performed by Dr. T. V. Van Auken.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF TEXAS, AUSTIN 12, TEXAS]

The Stabilities of Heteroaromatic Sulfur-Containing Cations

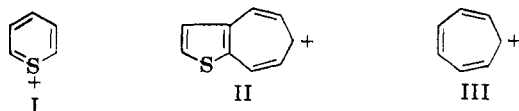
BY R. G. TURNBO, D. L. SULLIVAN, AND R. PETTIT

RECEIVED AUGUST 20, 1964

The pK_R^+ determinations have been made for several aromatic sulfur-containing cations and a comparison of these systems with their isoelectronic homonuclear carbon cations is given. Replacement of a double bond by a sulfur atom is found to enhance considerably the stability (as measured by the electrophilicity) of the cation. A satisfactory linear relationship is found to exist between the pK_R^+ values and the π -electron localization energies for the cations. Hückel molecular orbital calculations suggest that the reason for the increased stability of the sulfur-containing cations is the conjugate bases of these systems possess a much lower π -electron bonding energy than the carbon systems.

Introduction

Previous investigations in these laboratories into the chemistry of aromatic sulfur-containing cations have shown that the thiapyrylium (I) and thienotropylium (II) cations are more stable (less electrophilic) than the tropylium cation (III).^{1,2} This order of stability is indicated by the relative



pK_R^+ values associated with the three species and also by the fact that the tropylium cation will abstract a hydride ion from the heterocyclic compounds obtained upon treatment of the cations I and II with sodium borohydride to regenerate these cations.

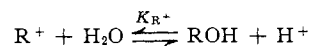
That the thienotropylium cation is more stable in this sense than the tropylium ion is especially interesting as the benzotropylium cation, which is iso-

electronic with II, is considerably less stable than the tropylium cation.³

These results have then prompted the present investigation into the stability of several other aromatic sulfur-containing cations and a comparison of these with their corresponding carbocyclic analogs.

Results and Discussion

A measure of the relative electrophilicities of a series of carbonium ions is afforded by the various equilibrium constants (K_R^+) involved in the following reaction



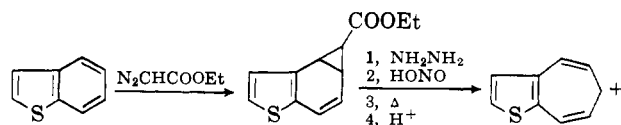
The pK_R^+ values for several thienyl cations isoelectronic with the diphenylmethyl and the triphenylmethyl carbonium ions have now been measured and are listed in Table I together with those for the thiapyrylium and thienotropylium cations. The values associated with the diphenylmethyl, triphenylmethyl, and tropylium cations are also listed for comparison.

(1) R. Pettit, *Tetrahedron Letters*, No. 23, 11 (1960).

(2) D. Sullivan and R. Pettit, *ibid.*, No. 6, 401 (1963).

(3) G. Naville, H. Strauss, and E. Heilbronner, *Helv. Chim. Acta*, **43**, 1221 (1960).

The carbinols were all prepared by previously published procedures except for β -thienyldiphenylcarbinol which was made by reaction of β -thienyllithium with benzophenone. The perchlorate salt of the thienotropylium cation was prepared by reaction of diazoacetic ester with thianaphthalene followed by the conversions indicated in the reaction scheme below. A



preliminary account of this synthesis has recently been given²; the full details are described in the Experimental section.

The pK_{R^+} values associated with the various substituted methyl cations (no. 1-7) were determined spectrometrically using solutions of the corresponding carbinols in sulfuric acid as in the procedure outlined by Deno and co-workers,⁴ while those of the thiapyrylium, thienotropylium, and tropylium cations (no. 8-10) were obtained from hydrolysis data of the perchlorate salts in water.⁵

TABLE I

No.	Cation	pK_{R^+}	Total π -energy of the cation, $E_{\pi}(R^+)$	Total π -energy of the conjugate base, $E_{\pi}(ROH)$
1	Ph_2CH^+	-13.1	$12\alpha + 17.03\beta$	$12\alpha + 16.00\beta$
2	$\text{Ph}-\text{CH}^+-\text{S}$	-9.9	$12\alpha + 15.20\beta$	$12\alpha + 13.96\beta$
3	$\text{S}-\text{CH}^+-\text{S}$	-4.1	$12\alpha + 13.31\beta$	$12\alpha + 11.92\beta$
4	Ph_3C^+	-6.6 ^a	$18\alpha + 25.44\beta$	$18\alpha + 24.00\beta$
5	$\text{Ph}_2-\text{C}^+-\text{S}$	-3.4	$18\alpha + 23.58\beta$	$18\alpha + 21.96\beta$
6	$\text{Ph}_2-\text{C}^+-\text{S}$	-5.0	$18\alpha + 23.56\beta$	$18\alpha + 21.96\beta$
7	$\text{Ph}-\text{C}^+(\text{S})_2$	-1.2	$18\alpha + 21.68\beta$	$18\alpha + 19.93\beta$
8	C_6H_6^+	+4.7 ^b	$6\alpha + 9.99\beta$	$6\alpha + 6.99\beta$
9	$\text{C}_6\text{H}_5\text{S}^+$	+8.7	$6\alpha + 7.47\beta$	$6\alpha + 5.16\beta$
10	$\text{C}_8\text{H}_6\text{S}^+$	+6.0	$10\alpha + 12.87\beta$	$10\alpha + 10.94\beta$

^a Previously reported by N. C. Deno and co-workers (ref. 4).

^b Previously reported by W. von E. Doering and L. H. Knox (ref. 5).

It is readily evident from the data in Table I that replacement of a phenyl group by an α -thienyl group in a conjugated carbonium ion system produces a very pronounced increase in the stability of the cation. A comparison of the α - and β -thienyldiphenylmethyl cations (no. 5 and 6) indicates that attachment through the α -position of the thiophene ring is slightly more effective in stabilizing the cation than through the β -position. The pK_{R^+} values given in Table I then suggest that in general an aromatic cationic system

(4) N. C. Deno, J. J. Jaruzelski, and A. Schriesheim, *J. Am. Chem. Soc.*, **77**, 3044 (1955).

(5) The degree of hydrolysis of tropylium salts in water has been previously determined by W. von E. Doering and L. H. Knox, *ibid.*, **76**, 3203 (1954).

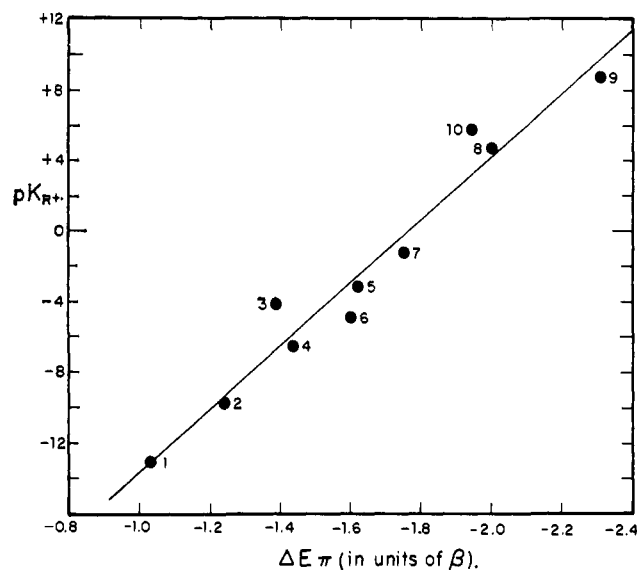


Fig. 1.—Plot of pK_{R^+} vs. ΔE_{π} as determined from the total π -energies in Table I for a series of aromatic cationic systems.

containing a sulfur atom is more stable than the analogous isoelectronic cation having a carbon-carbon double bond in place of sulfur.

In an attempt to understand further these results, we have performed Hückel molecular orbital calculations for the cations listed in Table I together with those for the corresponding conjugate bases. Assuming that differences in the pK_{R^+} values are primarily dependent on the differences in the change in π -electron bonding energy in going from the cation to the carbinol in each system, then one expects there to exist a linear relationship between pK_{R^+} and ΔE_{π} where $\Delta E_{\pi} = E_{\pi}(ROH) - E_{\pi}(R^+)$. In these calculations the parameters $\alpha_S = \alpha_C$ and $\beta_{C-S} = 0.8\beta_{C-C}$ were used for sulfur and $\beta_{C-aryl} = 0.87\beta_{C-C}$ for the bonds involving attachment of an aryl group to the noncyclic carbon atom in the cation. These parameters for sulfur have previously been used by other workers⁷ while the reduced value of β_{C-aryl} is to allow for deviations from coplanarity in the diaryl and triaryl cations. The total calculated π -energies for the cations and their conjugate bases are listed in Table I.

The correlation between pK_{R^+} and ΔE_{π} is shown in Fig. 1 from which it can be seen that the expected linear relationship is satisfactorily attained. Insofar as this reflects a satisfactory choice of parameters used in the calculations, the origin of the higher stability shown by the sulfur cations can be readily seen from the total π -electron energies given in the table. From these data the very plausible deduction is made that the sulfur cations have the greater stability not because they have a higher π -electron energy than the corresponding carbocyclic systems; in fact it is less; rather it is because the conjugate bases of the sulfur cations have a much lower total π -electron energy than the corresponding carbon cations, so that the gain in π -energy in going from the conjugate base to the cation is larger for the sulfur-containing systems.

These results then raise the question as to whether other heteroatomic cations such as selenapyrylium and tellurapyrylium might not also prove to be more

(6) See A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, Chapter 12.

(7) J. Koutecky, *Collection Czech. Chem. Commun.*, **24**, 1608 (1959).

stable than the tropylium cation despite the fact that they should be less "aromatic" owing to the nature of the heteroatomic orbitals which would be involved in the conjugation.

Experimental

(a) **Preparation of the Carbinols Materials.**—Diphenyl- and triphenylcarbinol were obtained in a pure state through recrystallization of samples obtained commercially.

Diphenyl-2-thienylcarbinol was prepared according to the method of Gomberg and Jichling.⁸ The material formed white prisms from petroleum ether; m.p. 131–132°.

Phenyl-2,2'-dithienylcarbinol was obtained by the method described by Minnis⁹; the substance crystallized from petroleum ether in white prisms, m.p. 91–92.5°.

Phenylthienylcarbinol was prepared from 2-thienylmagnesium bromide and benzaldehyde in the usual manner. Recrystallization from petroleum ether gave white prisms, m.p. 59–60°, in agreement with that reported by Minnis.⁹

Dithienylcarbinol was prepared following the method of Gol'dfarb and Kirmalova.¹⁰

Diphenyl-3-thienylcarbinol was prepared from β -thienyllithium and benzophenone in the following manner. An equivalent amount of *n*-butyllithium in ether (30 ml.) was added to 3-iodothiophene (14.6 g.) in ether (50 ml.) maintained at –60°. After stirring for 10 min. an ethereal solution of benzophenone (12.9 g.) was added dropwise, during which time the temperature was maintained between –20 and –60°. After the addition, the reaction mixture was brought to room temperature and poured into saturated aqueous ammonium chloride (200 ml.). Evaporation of the ether gave 10.2 g. of crude product. The material crystallized from petroleum ether in white prisms, m.p. 151–152°.

Anal. Calcd. for C₁₇H₁₄OS: C, 76.66; H, 5.30; S, 12.04. Found: C, 76.81; H, 5.21; S, 12.20.

(b) **Preparation of Thienotropylium Perchlorate.**—Diazoacetic ester (200 g.) was slowly added with stirring to 700 g. of thianaphthene, the temperature being maintained at 150°. This addition was carried out over a 5-hr. period, and heating was continued for 30 min. following the addition to bring about complete reaction. Excess thianaphthene was removed from the mixture by distillation and, upon redistillation of the crude material, 70 g. of product (b.p. 118–128°, 0.3 mm., reflux ratio 20/1), believed to be a mixture of isomeric esters, was obtained.

The product (20 g.) obtained in the above manner was heated with 60 ml. of 95% hydrazine hydrate and 100 ml. of alcohol for 2 hr. The solution was slowly poured into 800 ml. of water with stirring, and the acid hydrazide which separated from solution was filtered, washed with 300 ml. of water, and dried. This crude acid hydrazide (14.0 g., m.p. 199°) was recrystallized once from chloroform yielding 8.0 g. of a product (m.p. 201°) which

showed a consistent increase in melting point with each successive recrystallization. *Anal.* Calcd. for C₁₀H₁₀N₂OS: C, 58.25; H, 4.85; N, 13.60; S, 15.53. Found: C, 58.05; H, 4.65; N, 13.4; S, 15.31.

To a solution, at 0°, of 2 g. of the acid hydrazide (m.p. 201°) in 10 ml. of benzene, 10 ml. of water, and 25 ml. of acetic acid, was added 1 g. of sodium nitrite with stirring. The solution was stirred for 45 min. following the addition, then added to 200 ml of water and extracted with benzene (2 × 75 ml.). The benzene solution was washed successively with 25 ml. of water and 25 ml. of sodium carbonate solution and dried over sodium sulfate. After heating the benzene solution at reflux for 1 hr., the solvent was removed (25°, 30 mm.) from the isocyanate obtained. The isocyanate was dissolved in 20 ml. of nitromethane, cooled to 0°, and the solution then saturated with hydrogen bromide. Precipitation of the yellow bromide salt which formed was completed by the addition of 250 ml. of anhydrous ether. The salt was collected, dissolved in 15 ml. of water, and treated with 5 ml. of 35% perchloric acid. The thienotropylium perchlorate (0.3 g.) which precipitated was collected; it recrystallized from water in pale yellow plates. *Anal.* Calcd. for C₉H₇ClO₄S: C, 43.81; H, 2.86; Cl, 14.37; S, 13.00. Found: C, 43.79; H, 2.93; Cl, 14.21; S, 12.68.

Determination of the pK_R - Values.—The pK_R⁺ values were obtained from the acidity function $C_0 = pK_{R^+} - \log [R^+]/[ROH]$ as outlined by Deno and co-workers.⁴ For the diaryl- and triarylcarbinols the ratios [R⁺]/[ROH] in various concentrations of sulfuric acid were determined spectrophotometrically in the manner described by these workers except that the samples for the ultraviolet absorption measurements were prepared by pipetting 0.05 ml. of an ethanol solution of the carbinols into a 10-ml. volumetric flask followed by the required volume of aqueous H₂SO₄.

The solutions of the phenylthienylcarbinol and dithienylcarbinol underwent fairly rapid decomposition in strong H₂SO₄ solutions. In these two cases the ultraviolet absorption at several wave lengths was obtained by extrapolating back the set of values taken at short intervals on a freshly prepared solution to zero time. The triarylmethyl cations were stable in concentrated sulfuric acid solutions; such solutions regenerated the carbinol in good yield upon dilution with water.

The pK_R⁺ values for the tropylium cation were estimated from a determination of the pH of aqueous solutions of the perchlorate salts. The value thus obtained for the tropylium cation agreed well with that previously reported by Doering and Knox. The pK_R⁺ value for the thiapyrylium and thienopyrylium cations were also determined by measurement of the pH of aqueous solutions of the perchlorate salts; the values determined in this manner were reproducible over a range of concentrations. The pK_R⁺ values of these three cations were also determined by potentiometric titration with essentially the same results.

Acknowledgment.—We thank the Petroleum Research Fund administered by the American Chemical Society and the Robert A. Welch Foundation for financial support.

(8) M. Gomberg and R. L. Jichling, *J. Am. Chem. Soc.*, **35**, 446 (1913).

(9) W. Minnis, *ibid.*, **51**, 2144 (1929).

(10) Y. L. Gol'dfarb and M. L. Kirmalova, *Invest. Akad. Nauk, S.S.R. Otdel. Khim. Nauk*, 746 (1956); *Chem. Abstr.*, **51**, 1935 (1957).