somewhat broad, hydroxyl stretch at ν ($CHCl_3$) 3440 cm^{-1} which is unaffected by dilution (no free $-OH$ from 15–1%). Clearly, **2** is exclusively internally hydrogen bonded and must have the assigned *cis* structure. The strength of the hydrogen bond is such that it resists rapid proton exchange in $CDCl_3$, so that J_{HCOH} is observable (12.5 cps). This value is also obtained in CCl_4 and is unaffected by dilution (15–5% $CDCl_3$) or temperature (−60° to ambient). Even DMSO only slightly disrupts the bond. In this solvent J_{HCOH} = 10.7 cps. The addition of several drops of water still does not affect the hydroxyl doublet, but addition of a few drops of acid does eliminate it.

The coupling constants obtained here are more than twice as large as any we have noted in the literature (3.5–5.7 cps[3–6]). It is therefore suggested, and models support this suggestion, that the internal hydrogen bond of **2** effectively locks the O–H bond into a conformation *trans* (ϕ = 180°) to the carbinol methine C–H bond and that, accordingly, $J_{\mathrm{HCOH}}^{trans}$ = 12–13 cps.

In contrast to **2**, **1** has J_{HCOH} (DMSO) = 4 cps (no splitting observed in $CDCl_3$). This is a typical HCOH splitting and indicates that the large splitting found for **2** is unrelated to the electronegativity of the adjacent phenyl rings.

The value of $J_{\mathrm{HCOH}}^{trans}$ found here is in the range observed for $J_{\mathrm{HCCH}}^{trans}$ (sp^3 carbon) (10.5–12.4 cps[10]). The "free rotation" value of J_{HCOH} (3.5–5.7 cps) is apparently a little smaller than that of J_{HCCH} (6–8 cps). It therefore appears that J_{HCOH} (ϕ) and J_{HCCH} (ϕ) are quantitatively comparable.

Registry No.—**1**, 15591-50-1; **2**, 15591-51-2.

Acknowledgment.—We thank the National Science Foundation and the Welch Foundation for support of this work.

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(10) A. A. Bothner-by, "Advances in Magnetic Resonances," Vol. I, Academic Press Inc., New York, N. Y., 1965, p 203.

The Preparation and Reactions of Some Stable Dibenzotropylium and Dihydrodibenzotropylium Ions

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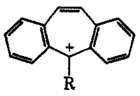
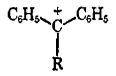
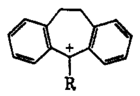
The stability of the dibenzotropylium and some 5-aryldibenzotropylium ions has been determined by measurement of their pK_{R^+} values[1–3] (Table I). These results are noteworthy because the phenyl- and *p*-methoxyphenyl-substituted compounds were less stable than the unsubstituted one. Examination of the pK_{R^+} values of the di- and triphenylmethyl series (Table I) would have predicted the order of stability to be *p*-methoxyphenyl > phenyl > unsubstituted in the dibenzotropylium series. These unexpected results were attributed to steric inhibition of resonance. The dihydrodibenzotropylium ions exhibited the expected order of stability (Table I), the only discrepancy being the large difference in pK_{R^+} between the unsubstituted ion and the diphenylmethyl ion. The values reported in Table I for the dibenzo- and dihydrodibenzotropylium ions have been confirmed in our work.

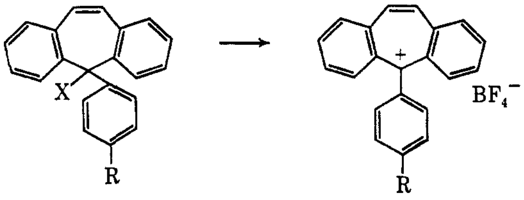
Table I[a]

pK_{A^+} Values

R			
H	−3.7	−13.3	−8.0
C_6H_5	−5.8	−6.6	−7.0
	−5.7[b]		−6.7[b]
p-$MeOC_6H_4$	−6.1	−3.4	−4.5

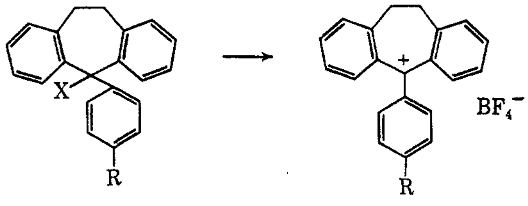
[a] See ref 1. [b] See ref 3.

The purpose of this investigation was to examine the possibility of preparing stable ions of the dibenzotropylium (**2**) and dihydrodibenzotropylium (**4**) types, and study their chemical properties. The ions chosen for examination were those having the *p*-methoxyphenyl (**2a** and **4a**) and *p*-dialkylaminophenyl group (**2b**, **2c**, and **4b**).



1a, R = OMe; X = OH
b, R = NMe_2; X = OH
c, R = OMe; X = H
d, R = OH; X = H
e, R = NMe_2; X = H

2a, R = OMe
b, R = NMe_2
c, R = NEt_2



3a, R = OMe; X = OH
b, R = NMe_2; X = OH
c, R = OMe; X = H
d, R = OH; X = H
e, R = NMe_2; X = H

4a, R = OMe
b, R = NMe_2

The *p*-methoxyphenyldibenzotropylium ion **2a** was isolated as the black fluoroborate in good yield from the corresponding alcohol **1a**, upon treatment with fluoroboric acid. Although it can be stored unchanged in the cold, it is rapidly converted back into the alcohol by atomospheric moisture. Sodium borohydride reduction of **2a** gave ether **1c**, which was identical with material prepared from the *p*-hydroxy compound **1d**. When treated with cycloheptatriene, compound **2a** abstracted a hydride ion and gave the tropylium ion (86%), as would be predicted from the pK_{R^+} values (Table I) of the two ions (tropylium ion pK_{R^+} = +9.9).[4]

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(1) G. Berti and A. DaSettimo, *Ann. Chim.*, **49**, 1237 (1959).

(2) G. Berti, *J. Org. Chem.*, **22**, 230 (1957).

(3) P. Rumpf and R. Reynaud, *Bull. Soc. Chim. Fr.*, **1964**, 558.

(4) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, p 365.

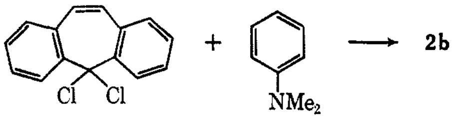
TABLE II

EXPERIMENTAL DATA FOR NEW COMPOUNDS

Compd	Mp, °C	Yield, %	Recrystn solvent	Molecular formula	Calcd %			Found %		
					C	H	N	C	H	N
1b	169–170	28	Ethanol	$C_{23}H_{21}NO$	84.5	6.4	4.3	84.2	6.3	4.3
3b	149–150	79	Ethanol	$C_{23}H_{23}NO$	84.0	7.1	4.3	84.3	7.1	4.3
2a	206 dec	90	None	$C_{22}H_{17}BF_4O$	68.8	4.5		68.4	4.7	
2b	241–242	95	Ethyl acetate–nitromethane	$C_{23}H_{20}BF_4N$	69.5	5.1	3.5	69.4	4.9	3.3
2c	241–243	12	Ethyl acetate–acetonitrile	$C_{25}H_{24}BF_4N$	70.5	5.7	3.3	70.5	5.9	3.6
4a	172–173	90	None	$C_{22}H_{19}BF_4O$	68.4	5.0		68.1	5.1	
4b	255–257	95	Ethyl acetate–nitromethane	$C_{23}H_{22}BF_4N$	69.1	5.6	3.5	69.3	5.7	3.4
1c	138–139	71	Ethanol	$C_{22}H_{18}O$	88.6	6.1		88.3	6.1	
1e	141–142	55	Ethanol	$C_{23}H_{21}N$	88.6	6.8	4.5	88.4	6.7	4.5
3c	103–104	80	Ethanol	$C_{22}H_{20}O$	88.0	6.7		88.3	6.9	
3e	101–102	32	Ethanol	$C_{23}H_{23}N$	88.2	7.4	4.5	87.9	7.3	4.5
3d	154–155	44	Methylcyclohexane	$C_{21}H_{18}O$	88.0	6.3		87.8	6.4	

The yellow dihydro ion **4a** was obtained as the fluoroborate in an analogous manner from alcohol **3a**. It is slowly converted by moisture or aqueous acetonitrile back into the alcohol, and is reduced to ether **3c** by sodium borohydride. This ether was identical with material prepared by methylation of phenol **3d**. Dihydro ion **4a** also afforded the tropylium ion (86%) when treated with cycloheptatriene.

Attention was next turned to the more electron-donating dialkylamino substituent, in the hope of obtaining more stable compounds. A variety of methods were examined for the preparation of the dimethylamino compound **2b**. Treatment of alcohol **1b** with fluoroboric acid gave the expected product in good yield. A second successful method of preparation was condensation of N,N-dimethylaniline with dichloride **5**. The observation that the methoxyl group of compound **2a** can be displaced by dimethylamine afforded still a third method, although the yield was low. When diethylamine was used in this procedure, the diethylamino compound **2c** was obtained. The structure of **2b** was established by reduction to amine **1e**, which was prepared independently by condensation of 5-chloro-5H-dibenzo[*a,d*]cycloheptene with N,N-dimethylaniline.



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The stability of the *p*-alkylaminophenyl compounds **2b** and **2c** is noteworthy, and unexpected from the trend found in Table I. They are quite stable to atmospheric moisture, and the orange color of the ions in acetonitrile persists for days. Since they do not abstract a hydride ion from cycloheptatriene, their pK_{R^+} values must be greater than that of the tropylium ion (+9.9). This stability must mean that the 5-phenyl group can be forced to be nearly coplanar with the dibenzotropylium system by a sufficiently strong electron-donating group, thus overcoming the proposed[1] steric hindrance.

The dihydro system is also markedly stabilized by a *p*-dimethylaminophenyl group. Treatment of alcohol **3b** with fluoroboric acid gave compound **4b**, which is stable to moisture and unreactive toward cycloheptatriene. Its pK_{R^+} value is thus greater than +9.9. Reduction of **4b** with sodium borohydride gave amine **3e**, prepared independently from 5-chloro-10,11-dihydro-5H-dibenzo[*a,d*]cycloheptene and N,N-dimethylaniline.

Experimental Section[5]

Preparation of Alcohols.—Compounds **1a** and **3a** were prepared as described,[1] and new alcohols **1b** and **3b** (Table II) were prepared in a similar manner.

Preparation of Carbonium Ion Salts.—The procedure used was that of Dauben, *et al.*,[6] on 0.01 mol of the alcohol (**1a**, **1b**, **3a**, and **3b**). The product was precipitated from solution with ether.

A second method of preparation was by alkylation with dichloride **5**.[7] A mixture of 13 g (0.050 mol) of dichloride **5**, 12 g (0.10 mol) of N,N-dimethylaniline, and 50 ml of 1,2-dimethoxyethane was allowed to stand for 1 hr. The solvent was removed and the residue dissolved in 3% hydrochloric acid. Addition of excess 48% fluoroboric acid caused an oil to separate, which was dissolved in a minimum of propionic anhydride. Addition of ether gave red solid **2b** which was recrystallized from ethyl acetate–nitromethane (8.0 g, 42%).

A third method was displacement of a methoxyl group. A solution of 3.8 g (0.010 mol) of compound **2a** in 10 ml of acetonitrile was treated with diethylamine dropwise until the color disappeared. A 100-ml portion of ether was added and, upon cooling, 1.4 g of solid separated. After recrystallization from acetonitrile–ethyl acetate, 0.5 g (12%) of **2c** was obtained, mp 241–243°.

The use of dimethylamine gave 0.22 g (5%) of compound **2b**.

Reduction of Carbonium Ion Salts.—A 1.0-g portion of the salt was added to a solution of 0.5 g of sodium borohydride in 10 ml of diglyme. The color of the ion disappeared, water was added in excess, and the precipitate was recrystallized from ethanol. Mixture melting points with the materials prepared as described below were not depressed.

Alternate Preparation of Ethers 1c and 3c.—Phenol **1d** was prepared as described,[8] and phenol **3d**, mp 154–155°, was prepared in a similar manner with 5-chloro-10,11-dihydro-5H-dibenzo[*a,d*]cycloheptene[9] (44%). Methylation of phenol **1d** with sodium hydride and dimethylsulfate gave ether **1c** (53%), and similar treatment of phenol **3d** gave ether **3c** (73%).

Alternate Preparation of Amines 1e and 3e.—A solution of 1 g of 5-chloro-5H-dibenzo[*a,d*]cycloheptene[8] and 2 g of N,N-dimethylaniline in 30 ml of benzene was heated at reflux for 30 min. The solvent was removed and the residue was washed with dilute sodium hydroxide solution before extraction into methylene chloride. The solid obtained upon removal of the solvent was recrystallized from ethanol to give amine **1e** (66%).

Amine **3e** was prepared similarly (53%) from 5-chloro-10,11-dihydro-5H-dibenzo[*a,d*]cycloheptene.[9]

Nmr Spectra.—The spectra of compounds **1a–e** contained singlet peaks for the vinyl protons at δ 6.65–6.72 ppm; the tertiary CH peak appeared at 5.25 and 5.30, respectively, in **1c** and

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[5] All melting points are uncorrected. The nmr spectra were measured on a Varian Model A-60 instrument in deuteriochloroform.

[6] H. J. Dauben, Jr., L. R. Honnen, and K. M. Harmon, *J. Org. Chem.*, **25**, 1442 (1960).

[7] J. J. Looker, *ibid.*, **31**, 3599 (1966).

[8] G. Berti, *Gazz. Chim. Ital.*, **87**, 293 (1957).

[9] Aldrich Chemical Co., Milwaukee, Wis.

1e. In the tropylium salts **2a–c**, the vinyl proton peaks were merged with the aryl protons. In the dihydro alcohols **3a–b**, the $-CH_2CH_2-$ protons were present as multiplets at δ 2.75 and 2.87, respectively; this peak appeared at 2.8–2.9 in **3c–e**, and as a singlet at 3.15–3.20 in **4a–b**. Signals for aryl protons and alkyl substituents appeared at the expected positions.

Registry No.—**1b**, 5371-47-1; **1c**, 15735-61-2; **1e**, 15856-55-0; **2a**, 15722-31-3; **2b**, 15722-32-4; **2c**, 15722-33-5; **3b**, 5371-46-0; **3c**, 15735-63-4; **3d**, 15735-64-5; **3e**, 4821-67-4; **4a**, 15722-34-6; **4b**, 15722-35-7.

Indolothiapyrylium Compounds. IV. Indolo[3,2-*c*]thiapyrylium Perchlorate[1,2]

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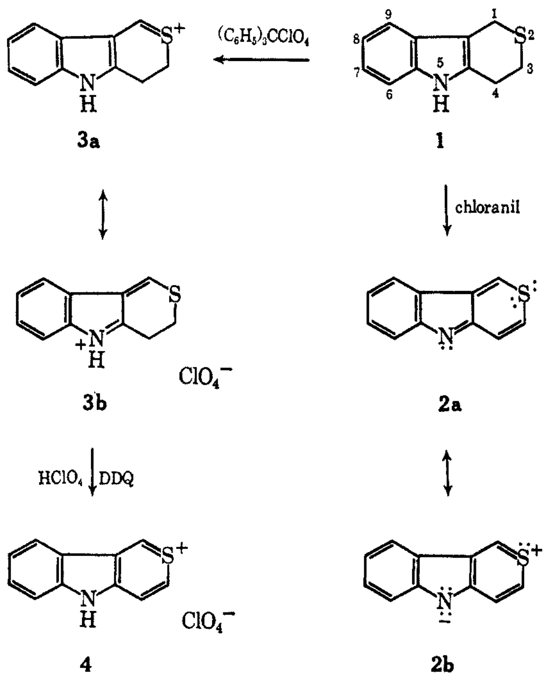
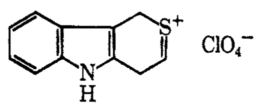
Received October 4, 1967

In a recent article,[2] we reported that 1,3,4,5-tetrahydrothiapyrano[4,3-*b*]indole (**1**) and several of its substituted analogs were readily dehydrogenated with chloranil or dicyanodichloroquinone (DDQ) to yield the corresponding thiapyrano[4,3-*b*]indoles (*e.g.*, **2** from **1**), which represent a new class of pseudoazulenes having pronounced thiapyrylium-like character of the sulfur-containing ring (*cf.* canonical form **2b**). Although the parent thiapyranoindole (**2**), at 10^{-4} *M* concentration in 95% ethanol, could be titrated spectrophotometrically with ethanolic hydrogen chloride to give the conjugate cation, repeated attempts to prepare indolothiapyrylium salts (**4**) by direct interaction of **2** with acids gave tars which were exceedingly difficult to purify. We now wish to report the isolation of indolo[3,2-*c*]thiapyrylium perchlorate (**4**),[4] prepared by the alternative route shown in formulas **1** → **3** → **4**.



1,3,4,5-Tetrahydrothiapyrano[4,3-*b*]indole (**1**)[2,5] reacted with an equimolar portion of trityl perchlorate[6] in refluxing glacial acetic acid to give a 94% yield of 3,4-dihydroindolo[3,2-*c*]thiapyrylium perchlorate (**3**), and the same product was obtained in only slightly reduced yield (84%) when a 100% excess of trityl perchlorate was used. This orange crystalline compound (**3**) exhibited an intense visible absorption at 414 mμ (log ε 4.20) attributable to the chromophore $-\overset{+}{N}H{=}C{-}C{=}C{-}S- \longleftrightarrow -NH{-}C{=}C{-}C{=}\overset{+}{S}-$ (*cf.* **3a** ⟷ **3b**), and lying in the same range (400–420 mμ) as the long wavelength absorption of the thiapyrano[4,3-*b*]indoles (**2**)[2] and the benz[*b*]indolo[2,3-*d*]thiapyrylium perchlorates.[7]

The nmr spectrum of **3** (*cf.* Experimental Section) was also consistent with the assigned structure in which H-1 appeared as a singlet resonance band at very low field (δ 9.48) as expected[7,8] for a proton adjacent to a thionium sulfur. The observation that both the low-field proton of the $-CH{=}\overset{+}{S}-$ group and the four methylene protons (δ 3.65) appeared as singlets ruled out the possibility of the alternate structure (**5**) in which the $-\overset{+}{S}{=}CH{-}CH_2-$ group should exhibit an AX_2 splitting pattern.[9]



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Dehydrogenation of **3** with dicyanodichloroquinone in acetic acid containing perchloric acid afforded a 33% yield of indolo[3,2-*c*]thiapyrylium perchlorate (**4**), a stable green-yellow salt, which was also stable in glacial acetic acid solution and recrystallized well from this solvent. In acetonitrile, containing excess perchloric acid to suppress dissociation[10] of the cation, this salt (**4**) exhibited an ultraviolet-visible spectrum essentially identical with that previously illustrated[2] for the same cation produced from **2** with ethanolic hydrogen chloride at spectrophotometric concentration.

The nmr spectrum of **4** (*cf.* Experimental Section) showed well-defined absorptions of three unusually deshielded protons assignable to H-1, -3, and -4. As in the case of other polynuclear thiapyrylium compounds[8] the two most deshielded protons (H-1 and -3) are associated with positions of unusually low electron density and exhibit characteristic splitting[8] (J_{13} = 3.0 cps) through the thionium sulfur. The HMO electron density pat-

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[1] Abstracted in part from the Ph.D. Thesis of C. J. Ohnmacht, Lehigh University, 1966.

[2] Part III: T. E. Young, C. J. Ohnmacht, and C. R. Hamel, *J. Org. Chem.*, **32**, 3622 (1967).

[3] Warner-Lambert Research Fellow, 1965–1966.

[4] For consistency with the recommended name of the free base (**2**) *viz.*, thiapyrano[4,3-*b*]indole, the name of the cation (**4**) should be thiapyrano-[4,3-*b*]indolium. However, the alternate name indolo[3,2-*c*]thiapyrylium appears to be more accurately descriptive of the structure of cation **4**, and is therefore preferred.

[5] G. M. Bennet and W. B. Waddington, *J. Chem. Soc.*, 2829 (1929).

[6] K. A. Hoffman and H. Kirmreuther, *Ber.*, **42**, 4865 (1909).

[7] T. E. Young and P. H. Scott, *J. Org. Chem.*, **30**, 3613 (1965).

[8] T. E. Young and C. J. Ohnmacht, *ibid.*, **32**, 1558 (1967).

[9] J. D. Roberts, "An Introduction to the Analysis of Spin-Spin Splitting in High Resolution Nuclear Magnetic Resonance Spectra," W. A. Benjamin, Inc., New York, N. Y., 1962, p 64.

[10] As previously discussed in detail[8] the cation of **4** dissociates to the free base (**2**) in nonacidic solvents, and in 95% ethanol solution exhibits an apparent pK_a = 5.2 at 25°.