

alcohols) that need the $l_{4b}N_{KL}$ term to be correlated. When we observe that the difference in the N_{KL} parameter between 100% methanol and water (both correlated without N_{KL}) is actually larger than the difference in N_{KL} between water and any of acetic acid, formic acid, 50, 70, or 97% TFE, which all require N_{KL} to be correlated, the idea of solvent nucleophilicity playing a role in the solvolysis of *tert*-butyl chloride (**4b**) loses all strength.⁵² The lN term becomes then simply an adjustable correction needed to bring a certain set of solvents on the mY correlation. The "cruel trick"^{53a} is that normally the decrease in nucleophilicity (expressed by a negative N) is paralleled by an increase in electrophilicity, which is incorporated in Y .^{24,33,34g,35} Since the Y values are obtained from rates of adamantyl substrates (**1**), the *tert*-butyl substrates (**4**), less susceptible to electrophilic assistance, fall off the mY line. The effect of increased electrophilic solvent assistance in **1** is then taken for an effect of nucleophilic assistance in **4**.

C. Nucleophilic solvent participation has been claimed for the solvolysis of *tert*-butyldimethylsulfonium salts (**5**).^{53,54} (Inter-

estingly, electrophilic solvent assistance is considered in that work to be the dominant factor for *tert*-butyl chloride solvolysis.^{53a}) It must be noted, however, that the sulfonium cation can undergo nucleophilic attack not only at the *tert*-butyl group but also at a methyl group. Indeed, not only is the attack at methyl statistically favored by a factor of 2 but the reactivity of methyl group toward attack by a nucleophile is very much higher than that of a *tert*-butyl group.⁵⁵ Therefore, nucleophilic solvent attack at the methyl group should (a) be visible in the reaction kinetics and (b) lead to a significant amount of methyl *tert*-butyl sulfide as a product. If a sizable amount of the latter compound is not formed,⁵⁶ the idea of nucleophilic assistance in the solvolysis of **5** cannot be sustained.

Acknowledgment. We are indebted to Dennis N. Kevill, T. William Bentley, and John S. Lomas for helpful comments. Helpful discussions with Hans-Dieter Beckhaus concerning the molecular mechanics calculations are also acknowledged.

Registry No. **1a**, 97645-21-1; **1e**, 768-95-6; **1f**, 6221-75-6; **2a**, 97645-22-2; **2e**, 31061-64-0; **3a**, 97654-82-5; **3a**, 14504-80-4; **4a**, 1559-07-5; **4e**, 75-65-0; **5**, 52956-50-0; **6**, 31083-61-1; **7**, 5511-18-2; **8**, 17768-41-1; MeLi, 917-54-4; $CF_3(CF_2)_2C(O)Cl$, 375-16-6; 1-homoadamantane-carboxylic acid, 31061-65-1; 1-adamantanecarboxylic acid, 828-51-3.

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(56) Kevill, D. N., personal communication.

(52) A sound physical model involving nucleophilic assistance would require that rates in nonnucleophilic solvents be correlated by the two-parameter equation $\log(k/k_0) = m_{4b}Y$, while for the nucleophilic solvents the deviation be measured by the $l_{4b}N$ term. This approach can be followed intuitively better if HFIP is taken as the reference solvent ($Y = 0, N = 0$), thus moving the origin along the coordinate axes without otherwise affecting the correlation. Inapplicability of this approach casts doubts on the mechanism involving nucleophilic solvent participation for **4b**.

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2-Azapyrylium Salts from Aluminum Halide σ Complexes of Cyclobutadienes and NOCl. On the Possible Intermediacy of a Heteroatom-Substituted Pyramidal Cation

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Abstract: Di-, tri-, and tetraalkyl-2-azapyrylium salts have been obtained in high yield from the reaction of dialuminum hexahalide σ complexes of di-, tri-, and tetraalkylcyclobutadienes with NOCl. The structure of 3,4,5,6-tetramethyl-2-azapyrylium tetrachloroaluminate (**19**) has been studied in the crystalline phase by X-ray crystallography. On the basis of the ¹H and ¹³C NMR, UV, and X-ray data, it is concluded that the 2-azapyrylium ion is a flat, aromatic ring system. From a consideration of bond energies and from the crystallographically determined structure, it follows that **20A** is the most important canonical form contributing to the actual structure of the 2-azapyrylium moiety. The reaction of complexes **6** (Al_2Br_6) and **7** (Al_2Br_6) with NOCl yields in both cases two isomeric 2-azapyrylium salts: **15r/15u** and **16r/16u**, respectively. The substitution pattern of the alkyl groups in **15r** and **16r** is not the same as in the precursor cyclobutadiene Al_2Br_6 σ complexes. A reaction mechanism is proposed to account for the formation of rearranged and unrearranged 2-azapyrylium salts. Finally, the possible intermediacy of the heteroatom-substituted pyramidal cation **28** in this reaction is discussed. On the basis of a comparison of the relevant orbital energies and the principle of isolobality, it is argued that the heteroatom-substituted pyramidal cation **28**, with NO⁺ in the apex and cyclobutadiene as the base of the pyramid, is more likely to exist than the long-sought pyramidal cyclobutadiene-CO complex.

Alkyl-substituted σ -aluminum halide cyclobutadiene complexes react with carbon-carbon and carbon-nitrogen triple-bond-containing reagents¹ to yield benzene² and pyridine³ derivatives (exemplified in Scheme I⁴). We thought it feasible to extend the scope of the reaction scheme by using (positively charged)

heteroatom-heteroatom triple-bond-containing reagents. Use of either of these reagents or of compounds which can be regarded

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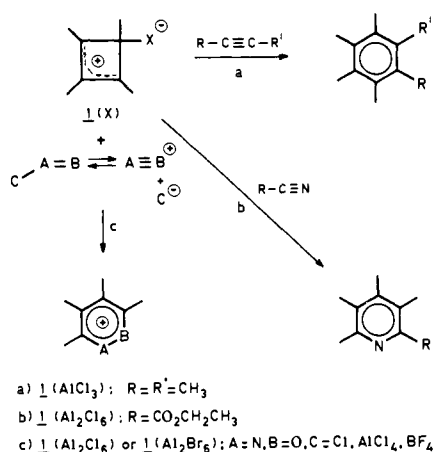
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Scheme I



as "triple bond equivalents"—i.e., covalent compounds $\text{C}-\text{A}\equiv\text{B}$ in equilibrium with their ionic form $\text{A}\equiv\text{B}^+\text{C}^-$ —may lead to existing or new (positively charged) heteroaromatic compounds. In this paper, we describe the results obtained with NO^+ as the heteroatom-heteroatom triple-bond-containing species, yielding 2-azapyrylium ions (Scheme I, path c).

The 2-azapyrylium ion, being heteroanalogous to both the pyrylium and the pyridinium ion, can be considered as one of the fundamental heterocyclic six-membered ring cations. Surprisingly, no systematic study has been made of this species, and few reports dealing with this heterocycle have appeared in the literature.⁵⁻⁷ Lloyd et al.⁵ proposed the 2-azapyrylium structure for the product obtained from the reaction of 1,4-diphenylcyclopent[*d*][1,2]oxazine with diphenylcyclopropanone in an acidic medium. Shelyapin et al.^{6,7} proposed the 2-azapyrylium structure for the products obtained from the protonation of 6*H*-6-hydroxy-3,5,6-triaryl-1,2-oxazines⁶ and from the *O*-alkylation of 6*H*-3,5-diphenyl-1,2-oxazin-6-ones.⁷ Both groups characterized the polyarylated 2-azapyrylium salts obtained rather poorly, the structural evidence being based only on incomplete elemental analyses and UV spectral data.

Results

We have chosen to use Al_2X_6 ($\text{X} = \text{Cl}$ or Br) σ -cyclobutadiene complexes as it is known¹ that in many cases Al_2X_6 σ complexes react faster and cleaner than the corresponding AlX_3 σ complexes. Three NO -containing reagents have been used: NOBF_4 , NO-AlCl_4 , and NOCl . The first two compounds do not dissolve in CH_2Cl_2 , the solvent of choice for the σ -aluminum halide cyclobutadiene complexes. However, the heterogeneous reaction of these reagents with the σ complexes results—according to ^1H NMR spectroscopy—in the same products as the homogeneous reaction using NOCl . The latter reaction is quick and clean, and we have restricted ourselves therefore to the use of NOCl . The σ -aluminum halide cyclobutadiene complexes used and the 2-azapyrylium salts obtained are depicted in Scheme II.

The crude reaction products obtained in CH_2Cl_2 were used as such for the NMR analysis. This was possible because for the tetraalkyl derivatives **10**, **11**, **12**, **17a/17b**, and **18**, the isolated products (yield at least 85%) were almost NMR pure (see Figure 1 for the ^1H NMR spectrum of crude **10**). For the trimethyl and

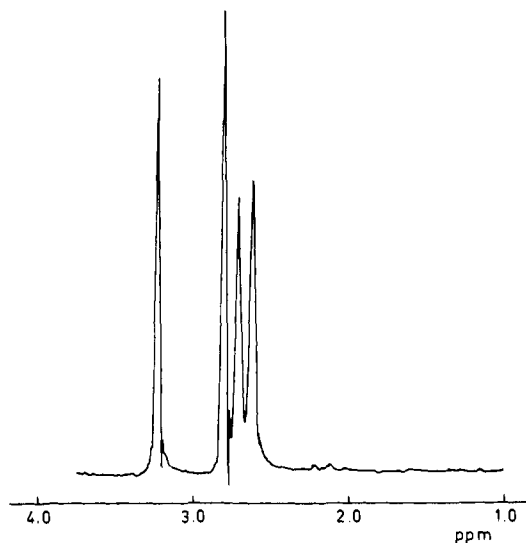
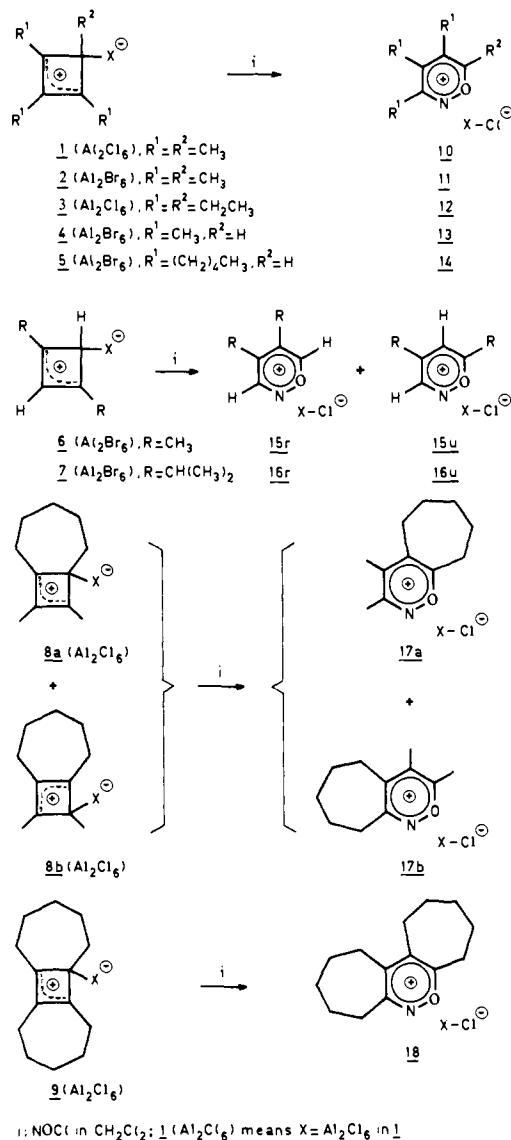


Figure 1. ^1H NMR spectrum of crude **10** in CH_2Cl_2 .

Scheme II



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(4) The aluminum halide between parentheses indicates the group which is attached to the cyclobutadiene moiety. In this paper, the methyl group will be represented by a line like in terpene chemistry.

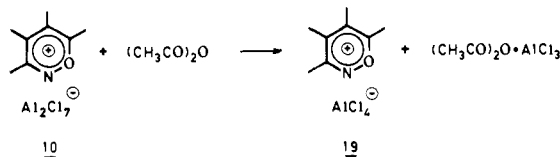
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dimethyl derivatives, the yield is estimated to be at least 60% (based on the ^1H NMR spectra), the other part being unidentified material, which did not disturb the NMR analysis. The reaction of aluminum halide σ complexes of 1,3-dialkylcyclobutadienes

Scheme III



(6 (Al_2Br_6) and 7 (Al_2Br_6), respectively) with NOCl yields two isomeric 2-azapyrylium salts (**15r/15u** and **16r/16u**, respectively). The ratios **15r/15u** and **16r/16u** strongly vary from one experiment to another. A number of factors may contribute to this: the rate of addition of the NOCl , the reaction time at -70°C , and the rate of warming up the solution to room temperature.

The best purification method for labile organic salts is crystallization. Unfortunately, we were not able to obtain compound **10** in the crystalline form; the reaction of **10** however, with 1 equiv of acetic acid anhydride acting as Lewis base leads to the crystalline AlCl_4^- salt **19** (Scheme III). This salt has been used for the elemental analysis, the UV spectrum, and the crystal structure determination.

Experimental Section

The UV spectra were recorded on a Beckman Model 24. The single-crystal X-ray analysis was performed by using an Enraf-Nonius CAD4 diffractometer, interfaced to a PDP-11/23 computer, and graphite-monochromated $\text{Mo K}\alpha$ radiation ($\mu(\text{Mo K}\alpha) = 9.2 \text{ cm}^{-1}$, $\lambda(\text{Mo K}\alpha) = 0.7107 \text{ \AA}$) at -110°C . The ^1H NMR spectra were recorded on a Jeol C-60HL (60 MHz) and a Nicolet NT200 (200 MHz). The ^{13}C NMR spectra were recorded on a Varian XL100 (25 MHz) and a Nicolet NT200 (50 MHz). All NMR spectra were recorded by using CD_2Cl_2 as solvent. The chemical shifts were measured relative to CD_2Cl_2 and were converted to the TMS scale by using $\delta_{\text{CD}_2\text{Cl}_2}$ 5.30 for the ^1H NMR spectra and $\delta_{\text{CD}_2\text{Cl}_2}$ 53.16 for the ^{13}C NMR spectra. ^{13}C NMR spectra were recorded proton-noise-decoupled and proton-coupled; the proton-coupled ^{13}C NMR spectra were recorded in the gyrogate mode. Splitting patterns are designated as follows: s, singlet; d, doublet; t, triplet; q, quartet; qt, quintet; h, heptet; m, multiplet; br, broad; l-r, long-range. The elemental analysis was performed in the Analytical Section of the department.

2,9-Undecadiyne and 6-dodecyne were prepared by using literature procedures.⁸ Other acetylenes, NOBF_4 , AlBr_3 , and CD_2Cl_2 were commercially available and used as received. AlCl_3 was sublimed twice before use. NOAlCl_2 ⁹ and NOCl ¹⁰ were prepared according to the literature. The synthesis of the σ -aluminum halide cyclobutadiene complexes used is described elsewhere.^{11,12} All reactions were carried out in an atmosphere of dry nitrogen.

NOCl. The NOCl was distilled twice before use. An approximately 1 M solution of NOCl in CH_2Cl_2 was prepared and used as stock solution; when stored at 5°C , it is stable for months. The NOCl concentration of the stock solution was determined at appropriate intervals by quenching an aliquot in 1 M aqueous NaOH , followed by acidification to pH 3 and titration with AgNO_3 .

General Procedure for the Reaction of σ -Aluminum Halide Cyclobutadiene Complexes with NOCl . A slight excess of a solution of NOCl in CH_2Cl_2 (1.05 equiv with respect to the σ complex) was added dropwise to a cooled (-70°C) and magnetically stirred 0.5 M solution of σ -aluminum halide cyclobutadiene complex in CH_2Cl_2 . After the addition was completed, the reaction mixture was allowed to warm slowly to room temperature. The reaction mixture was filtered, and the solvent was evaporated. A dark colored oil was obtained and used as such for the NMR measurements. The use of AlBr_3 as Lewis acid always led to the formation of CH_2ClBr , which probably had been formed as a result of a halogen exchange of $\text{Al}_2\text{Br}_6\text{Cl}^-$ with CH_2Cl_2 . In these cases, the crude product was stirred for an additional 4 h at room temperature, in order to remove readily exchangeable Br, before the ^{13}C NMR spectra were run.

Compound 10. Compound **10** was prepared from **1** (Al_2Cl_6) in 95% (isolated) yield: ^1H NMR δ 3.22 (s, 3 H), 2.80 (s, 3 H), 2.71 (s, 3 H),

2.61 (s, 3 H); ^{13}C NMR (-10°C) δ 197.5 (s), 165.1 (s), 157.3 (s), 139.7 (s), 23.3 (q), 18.6 (2 times) (q), 14.9 (q).

Compound 11. Compound **11** was prepared from **2** (Al_2Br_6): ^1H NMR δ 3.25 (s, 3 H), 2.83 (s, 3 H), 2.73 (s, 3 H), 2.63 (s, 3 H); ^{13}C NMR (-10°C) δ 196.7 (s), 165.0 (s), 157.8 (s), 140.2 (s), 23.5 (q), 18.8 (q), 18.5 (q), 14.9 (q).

Compound 12. Compound **12** was prepared from **3** (Al_2Cl_6) in 91% (isolated) yield: ^1H NMR δ 3.59 (q, $J = 7.1$ Hz, 2 H), 3.19 (q, $J = 7.1$ Hz, 2 H), 3.00 (2q, $J = 7.8$ Hz, 4 H), 1.62 (t, $J = 7.1$ Hz, 3 H), 1.49 (t, $J = 7.1$ Hz, 3 H), 1.37 (t, $J = 7.8$ Hz, 3 H), 1.36 (t, $J = 7.8$ Hz, 3 H); ^{13}C NMR (-10°C) δ 199.9 (s), 166.9 (s), 158.9 (s), 142.2 (s), 29.3 (t), 24.7 (t), 22.8 (t), 20.4 (t), 12.4 (q), 12.2 (q), 9.5 (q), 8.0 (q).

Compound 13. Compound **13** was prepared from **4** (Al_2Br_6): ^1H NMR δ 10.3 (br s, 1 H), 2.87 (s, 3 H), 2.72 (s, 3 H), 2.68 (s, 3 H); ^{13}C NMR (-10°C) 181.9 (d $J = 208$ Hz) of q ($J = 6$ Hz), 166.0 (s), 161.6 (s), 139.7 (s), 18.7 (q), 18.1 (q), 15.8 (q).

Compound 14. Compound **14** was prepared from **5** (Al_2Br_6) in 91% (isolated) yield: ^1H NMR δ 10.33 (br s, 1 H), 3.25–2.90 (br, 6 H), 1.90–1.20 (br, 18 H), 0.90 (t, $J = 6.9$ Hz, 9 H) (broad singlets were observed at δ 3.19, 3.05, and 3.00 in a double-resonance experiment (irradiation of region δ 1.90–1.20)); ^{13}C NMR (-10°C) δ 181.9 (d ($J = 207$ Hz) of t ($J = 5$ Hz)), 167.9 (s), 162.8 (s), 142.6 (s), 31.8 (t), 30.9 (t), 30.4 (t), 28.3 (t). An example of line-broadening phenomena is discussed in text: line width at half-height, $\Delta\nu_{1/2}$, of signal at δ 181.9, $J = 12$ Hz at -10°C , $J = 21$ Hz at -65°C , completely broadened at -80°C .

Compounds 15r/15u. The mixture of **15r/15u** was prepared from **6** (Al_2Br_6). NMR spectra were recorded of samples from two different experiments in which the ratio **15r/15u** was 3:1 and 1:3: ^1H NMR of **15r** δ 10.36 (d, $J = 1.6$ Hz, 1 H), 9.72 (d, $J = 1.6$ Hz, 1 H), 2.86 (s, 3 H), 2.68 (s, 3 H); ^{13}C NMR of **15r** (-10°C) δ 182.3 (d ($J = 210$ Hz) of q ($J = 6$ Hz)), 160.9 (s, 1-r m not resolved), 156.2 (d ($J = 192$ Hz) of q ($J = 5$ Hz)), 141.6 (s, 1-r m not resolved), 20.9 (q), 15.6 (q); ^1H NMR of **15u** δ 9.59 (d, $J = 1.9$ Hz, 1 H), 8.26 (distorted d, 1 H), 3.29 (s, 3 H), 2.86 (s, 3 H); ^{13}C NMR of **15u** (-10°C) δ 198.2 (s, 1-r qt, $J \sim 6$ Hz), 159.2 (s, 1-r m not resolved), 155.4 (d ($J = 194$ Hz) of qt ($J \sim 5$ Hz)), 129.7 (d $J = 185$ Hz) of m, 1-r m not resolved), 24.6 (q), 22.2 (q).

Compounds 16r/16u. The mixture of **16r/16u** was prepared from **7** (Al_2Br_6). NMR spectra were recorded of samples from four different experiments in which the ratio **16r/16u** varied from $>10:1$, 7:3, 1:1 to 1:3. Isomer **16u** is the only 2-azapyrylium salt prepared so far which is not stable: it decomposes at room temperature in a few hours: ^1H NMR of **16r** δ 10.52 (d, $J = 1.6$ Hz, 1 H), 9.83 (d, $J = 1.6$ Hz, 1 H), 3.70 (h, $J = 7$ Hz, 1 H), 3.60 (h, $J = 7$ Hz, 1 H), 1.51 (d, $J = 7$ Hz, 12 H); ^{13}C NMR of **16r** (-10°C) δ 182.2 (d ($J = 207$ Hz) of d ($J = 7$ Hz)), 167.1 (s, 1-r m not resolved), 153.5 (d ($J = 192$ Hz) of d ($J = 7$ Hz)), 148.1 (s, 1-r m not resolved), 30.1 (d), 27.2 (d), 20.9 (q), 20.8 (q); ^1H NMR of **16u** δ 9.67 (d, $J = 1.9$ Hz, 1 H), 8.29 (distorted d, 1 H), 3.84 (h, $J = 7$ Hz, 1 H), 3.45 (h, $J = 7$ Hz, 1 H), 1.63 (d, $J = 7$ Hz, 3 H), 1.51 (d, $J = 7$ Hz, 3 H); ^{13}C NMR of **16u** (-10°C) δ 205.4 (s, 1-r m not resolved), 168.2 (s, 1-r m not resolved), 154.4 (d ($J = 192$ Hz) of t ($J \sim 5$ Hz)), 125.9 (d $J = 182$ Hz) of m, 1-r m not resolved), 38.2 (d), 34.7 (d), 20.1 (q), 19.1 (q).

Compounds 17a/17b. The mixture of **17a/17b** was prepared from the mixture of **8a** (Al_2Cl_6)/**8b** (Al_2Cl_6)¹¹ in 96% (isolated) yield. ^1H NMR of the mixture of **17a/17b** δ 3.6, 3.2 (br, CH_2 's adjacent to heterocycle), 3.23, 2.81, 2.72, 2.62 (CH_3 groups), 2.02, 1.96 (br, CH_2 's not adjacent to heterocycle). (singlets appeared at δ 3.59, 3.30, 3.18, 3.14 in a double-resonance experiment (irradiation of $(\text{CH}_2)_3$ region)); ^{13}C NMR of mixture of **17a/17b** (-10°C) δ 201.1 (s), 197.4 (s), 168.8 (s), 165.0 (s), 161.5 (s), 155.5 (s), 144.6 (s), 138.5 (s), alkyl signals at δ 37.1, 32.2, 31.4, 29.8 (2 times); 28.0, 25.3, 25.1, 24.5, (2 times), 23.2, 18.4, 17.8, 14.3.

Compound 18. Compound **18** was prepared from **9** (Al_2Cl_6) in 83% (isolated) yield: ^1H NMR δ 3.57, 3.2, 2.0, 1.9 (all four signals br) (singlets appeared at δ 3.57, 3.25, 3.17, 3.13 (CH_2 's adjacent to heterocycle) in a double-resonance experiment (irradiation of the region δ 2.0–1.9; the $(\text{CH}_2)_3$ groups not adjacent to heterocycle)); ^{13}C NMR (-10°C) δ 201.2 (s), 168.2 (s), 158.8 (s), 142.5 (s), alkyl signals at δ 36.8, 31.9, 30.4, 29.8 (2 times), 27.3, 25.4, 24.8, 24.7, 24.1.

Preparation of 19 from 10. A solution of 30 mmol of **10** in 80 mL of CH_2Cl_2 was prepared from **1** (Al_2Cl_6) as described above. This solution was cooled to -40°C , and 3.06 g of acetic acid anhydride (30.0 mmol) in 20 mL of CH_2Cl_2 was added dropwise to the stirred solution. The solution was allowed to warm to room temperature, it was filtered, and the solvent was removed. The resulting red-brown oil was crystallized from CH_2Cl_2 (~ 30 mL of CH_2Cl_2 ; -50°C). The solvent was removed from the dark-brown crystals with the aid of nitrogen pressure. The crystals were kept at -50°C and were carefully washed with CH_2Cl_2 (4 \times 5 mL of CH_2Cl_2). The resulting red-purple crystals were dried at 0

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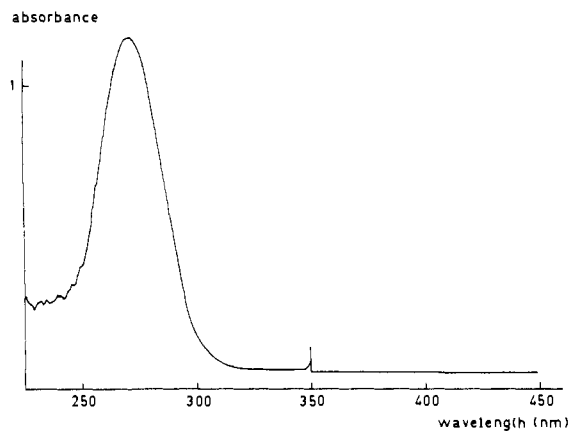


Figure 2. UV spectrum of **19** in 0.1 M acetic acid anhydride-AlCl₃ complex in CH₂Cl₂.

°C under vacuum ($p = 0.1$ mmHg). The crystalline mass was transferred quickly to a clean flask and again washed at -50 °C (2×5 mL of CH₂Cl₂). By then the washing liquid was colorless, and the resulting light-pink, almost colorless crystals were dried at 0 °C under vacuum ($p = 0.1$ mmHg) and stored in sealed ampules (at -30 °C): isolated yield 3.26 g of **19** (33%), mp dec before melting. This material was used for the elemental analysis, the UV spectrum, and the X-ray study. Anal. Calcd for C₈H₁₂NOAlCl₄: C, 31.30; H, 3.94; N, 4.56; Al, 8.79; Cl, 46.20. Found: C, 31.27; H, 4.05; N, 4.66; Al, 8.61; Cl, 45.55.

UV Spectrum of 19 in 0.1 M Acetic Acid Anhydride-AlCl₃ in CH₂Cl₂. For unknown reasons, compound **19** does not redissolve in CH₂Cl₂ after crystallization from CH₂Cl₂. Compound **19** could be dissolved in a 0.1 M solution of acetic acid anhydride-AlCl₃ complex in CH₂Cl₂. This solution was used for recording the UV spectrum of **19**; 2.04 g of acetic acid anhydride (20 mmol) in 50 mL of CH₂Cl₂ was added dropwise to a stirred suspension of 2.667 g of AlCl₃ (20 mmol) in 150 mL of CH₂Cl₂ at 0 °C. The solution was stirred until a colorless homogeneous solution was obtained. A stock solution of **19** was prepared by dissolving 0.153 g of **19** in 25 mL of freshly prepared solvent system: UV $\log \epsilon$ 3.92 at λ_{\max} 270 nm. This solvent does not allow measurements at wavelengths below 254 nm because of its own strong absorbance.

Crystal Structure Determination of 19. A light-pink, almost colorless crystal of **19** (crystal dimensions $0.5 \times 0.4 \times 0.25$ mm) was sealed under a dry-nitrogen atmosphere in a thin-walled capillary. Due to the lability of **19** the X-ray analysis was performed at -110 °C. Compound **19** crystallized in the orthorhombic space group *Pnma* with $a = 17.871$ (6) Å, $b = 14.243$ (2) Å, $c = 10.648$ (2) Å, $V = 2710.3$ Å³, $Z = 8$, $D_{\text{calcd}} = 1.505$ g cm⁻³, $\mu(\text{Mo K}\alpha) = 9.2$ cm⁻¹, $\lambda(\text{Mo K}\alpha) = 0.7107$ Å, by using the $\omega - 2\theta$ scan mode for $1^\circ \leq \theta \leq 25^\circ$. The structure was solved by direct methods (MULTAN 82); 23 reflections with $10^\circ \leq \theta \leq 14^\circ$ were used to refine the unit cell parameters. No absorption corrections were applied. Full-matrix least-squares refinement on F converged to a final $R = 0.054$ and $R_w = 0.071$ ($w = 1$)¹³ for 1830 reflections with $I \geq 3\sigma(I)$, using anisotropic temperature factors. No attempts were made to locate the H atoms.

Discussion

The question whether 2-azapyrylium ions are aromatic species or not can be answered by various (experimental) methods. We have applied UV and NMR spectroscopy as well as X-ray crystallography to address this question.

UV Spectrum. The UV spectrum of **19** in a solution of 0.1 M acetic acid anhydride-AlCl₃ complex in CH₂Cl₂ was recorded: λ_{\max} 270 nm with $\log \epsilon$ 3.92 (Figure 2). Comparison of this spectrum with those of alkyl-substituted pyridinium and pyrylium ions, which are known to be aromatic compounds, shows a strong resemblance. 1,2,4,6-Tetramethylpyridinium and 2,4,6-trimethylpyrylium perchlorate both show two absorptions between 200 and 300 nm:¹⁴ λ_{\max} 268 nm ($\log \epsilon$ 3.87), λ_{\max} 221 nm ($\log \epsilon$ 3.71), and λ_{\max} 285 nm ($\log \epsilon$ 4.08), λ_{\max} 230 nm ($\log \epsilon$ 3.66), respectively. The absorption expected for **19** at about 230 nm was not detected because measurements below 254 nm were impossible due to the solvent system used. It is however quite

Table I. Bond Distances (Å) and Angles (deg) for **19**^a

O-N	1.404 (4)	C(5)-C(9)	1.515 (5)
O-C(6)	1.371 (4)	C(6)-C(10)	1.505 (5)
N-C(3)	1.305 (5)	Cl(1)-Al(1)	2.141 (2)
C(3)-C(4)	1.437 (5)	Cl(2)-Al(1)	2.127 (1)
C(3)-C(7)	1.480 (5)	Cl(3)-Al(1)	2.137 (2)
C(4)-C(5)	1.377 (5)	Cl(4)-Al(2)	2.140 (2)
C(4)-C(8)	1.494 (5)	Cl(5)-Al(2)	2.138 (1)
C(5)-C(6)	1.406 (5)	Cl(6)-Al(2)	2.117 (2)
O-N-C(3)	117.3 (3)	C(6)-C(5)-C(9)	118.9 (3)
N-O-C(6)	121.8 (3)	C(5)-C(6)-O	122.6 (3)
N-C(3)-C(4)	123.1 (4)	C(5)-C(6)-C(10)	124.6 (3)
N-C(3)-C(7)	113.7 (3)	O-C(6)-C(10)	112.8 (3)
C(4)-C(3)-C(7)	123.2 (4)	Cl(1)-Al(1)-Cl(2)	109.32 (6)
C(3)-C(4)-C(5)	118.7 (3)	Cl(1)-Al(1)-Cl(3)	108.74 (9)
C(3)-C(4)-C(8)	119.3 (3)	Cl(2)-Al(1)-Cl(3)	108.46 (6)
C(5)-C(4)-C(8)	122.0 (3)	Cl(4)-Al(2)-Cl(5)	109.19 (8)
C(4)-C(5)-C(6)	116.6 (3)	Cl(4)-Al(2)-Cl(6)	108.92 (8)
C(4)-C(5)-C(9)	124.5 (3)	Cl(5)-Al(2)-Cl(6)	109.63 (6)

^a Estimated standard deviations in parentheses.

Table II. Nonbonded Interatomic Distances (Å) of Interest in Crystalline **19**^a

Al(1)-C(3)	4.521 (14)	Al(2)-C(3)	4.652 (21)
Al(1)-C(4)	4.232 (14)	Al(2)-C(4)	4.409 (21)
Al(1)-C(5)	4.202 (17)	Al(2)-C(5)	4.188 (17)
Al(1)-C(6)	4.489 (21)	Al(2)-C(6)	4.171 (4)
Al(1)-O	4.735 (20)	Al(2)-O	4.434 (13)
Al(1)-N	4.760 (17)	Al(2)-N	4.703 (18)

^a Estimated standard deviations in parentheses.

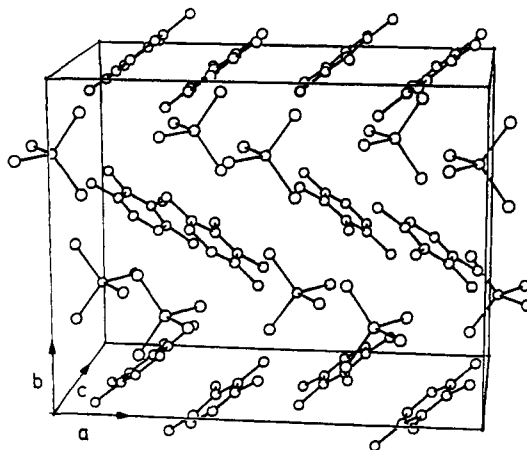


Figure 3. Drawing of the packing in the unit cell for **19**.

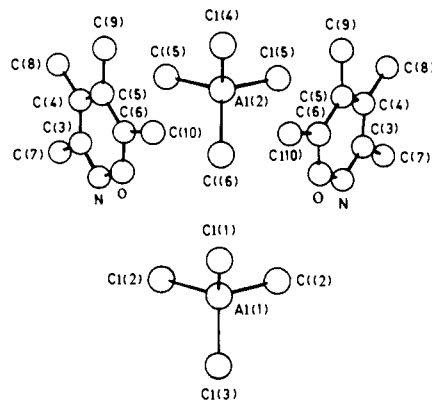


Figure 4. Relation between the two crystallographically independent AlCl₄⁻ anions and the 2-azapyrylium cation. Note the symmetry plane through Cl(3)-Al(1)-Cl(1) and Cl(6)-Al(2)-Cl(4). Spheres are drawn at the 60% probability level.

clear that the absorption at 270 nm is the π - π^* band expected for a normal aromatic compound. Therefore, it is concluded that the 2-azapyrylium moiety is an aromatic system.

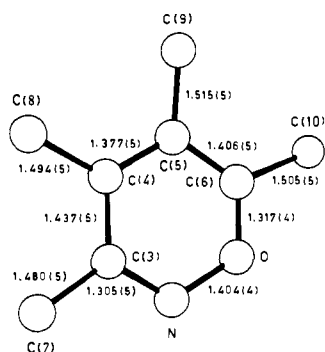
(13) $R = \sum ||F_o| - |F_c|| / \sum |F_o|$, $R_w = \{ \sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2 \}^{1/2}$

(14) Balaban, A. T.; Sahini, V. E.; Keplinger, E. *Tetrahedron* 1960, 9, 163.

Table III. Weighted Least-Squares Planes According to $Ax + By + Cz - D = 0$ through the 2-Azapyrylium Moiety. Distances^b from Atoms to Planes in Å^a

distance		distance	
plane 1		plane 2	
C(3)	0.009 (7)	C(3)	0.005 (7)
C(4)	0.006 (6)	C(4)	0.010 (6)
C(5)	-0.016 (7)	C(5)	-0.010 (7)
C(6)	0.011 (6)	C(6)	0.009 (6)
O	0.001 (5)	C(7)	0.012 (8)
N	-0.010 (6)	C(8)	0.021 (7)
other atoms		C(9)	-0.043 (8)
C(7)	0.017 (8)	C(10)	0.049 (7)
C(8)	0.009 (7)	N	-0.021 (6)
C(9)	-0.057 (8)	O	-0.008 (5)
C(10)	0.051 (7)	other atoms	
A	0.6031	A	0.6046
B	-0.7975	B	-0.7962
C	-0.0169	C	-0.0230
D	-1.9259	D	-1.9564

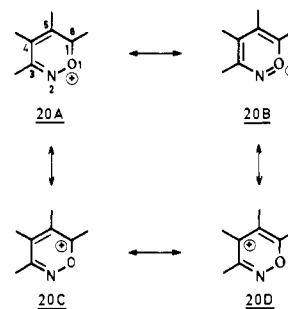
^aPlane 1 through C(3)–C(6), O, and N; plane 2 through C(3)–C(10), N, and O, with an angle of 0.4 deg between both planes.
^bEstimated standard deviations between parentheses.

**Figure 5.** Bond lengths (Å) in the 3,4,5,6-tetramethyl-2-azapyrylium cation. Spheres are drawn at the 60% probability level.

Crystal Structure Determination of 19. The final atomic parameters and the thermal parameters of **19** are supplementary material. Distances and angles of interest are given in the Tables I and II. The unit cell contains two crystallographically independent tetrachloroaluminate anions as shown in Figures 3 and 4. The results presented in Table II show that neither Al(1) nor Al(2) occupies a position straight above the center of the six-membered ring. The shortest distance both from Al(1) and Al(2) to the six-membered ring is about 4.2 Å. Besides the UV absorption, the extent of flatness of the six-membered ring also is a criterion for normal aromatic compounds. This aspect has been investigated for the 2-azapyrylium ion by drawing two weighted least-squares planes through the organic fragment of **19**: one plane through the atoms of the six-membered ring, and one plane through all the non-hydrogen atoms present in the organic fragment. The results of this analysis are collected in Table III. We conclude from this table that the 2-azapyrylium moiety is indeed flat: the largest deviation from planarity is found for C(9) (|0.06 Å| from plane 1).

Four different canonical structures can be drawn for the 2-azapyrylium moiety: **20A–D** (Figures 5 and 6). It is of interest to determine which resonance structure has the lowest energy and therefore contributes most to the actual 2-azapyrylium structure. In a naive first-order approach, it is expected that either **20A** or **20B**, both containing three double bonds in contrast to **20C** or **20D**, has the lowest energy. Using bond enthalpies from the literature,¹⁵ the energy contents of **20A** are estimated to be -673 kcal mol⁻¹; for **20B**, however, it is calculated to be -635 kcal mol⁻¹.

(15) Bond enthalpies from: Wall, F. T. "Chemical Thermodynamics"; Freeman: San Francisco, 1958; p 63. The bond enthalpy of N=O is estimated to be 105 kcal mol⁻¹ by comparison of the tables of bond enthalpies of Wall with the tables of bond dissociation energies from ref 16.

**Figure 6.** Canonical structures of the 2-azapyrylium moiety.**Table IV.**^a ¹³C Resonances and Splitting Patterns^{b,c} Observed for the Aromatic Ring Carbons of 2-Azapyrylium Ions

compd	C(3)	C(4)	C(5)	C(6)
10	165.1	157.3	139.7	197.5
11	165.0	157.8	140.2	196.7
12	166.9	158.9	142.2	199.9
17a	165.0	155.5	144.6	201.1
17b	168.8	161.5	138.5	197.4
18	168.2	158.8	142.5	201.2
13	166.0	161.6	139.7	181.9
14	167.9	162.8	142.6	d, q (208, 6 Hz) 181.9 d, t (207, 5 Hz)
15r	156.2	160.9	141.6	182.3
16r	d, q (192, 5 Hz) 153.5	s* 167.1	s* 148.1	d, q (210, 6 Hz) 182.2
15u	d, d (192, 7 Hz) 155.4	s* 159.2	s* 129.7	d, d (207, 7 Hz) 198.2
16u	d, qt (194, 5 Hz) 154.4	s* 168.2	d* (185 Hz) 125.9	s* 205.4
	d, t (192, 5 Hz)	s*	d* (182 Hz)	s*

^aAssignment of the chemical shifts (in ppm) and relevant coupling patterns discussed in the text. ^bSee Experimental Section for the designation of the splitting patterns. ^cA starred symbol means that the coupling pattern due to the long-range ¹³C–¹H couplings has not been resolved.

Thus, canonical structure **20A** will be energetically favored over **20B** by an amount of 38 kcal mol⁻¹. This expectation is nicely borne out by the crystal structure of **19**. Bond lengths in the six-membered ring of **19** are depicted in Figure 5. From a comparison of these experimentally determined bond lengths with reference molecular fragments from the literature, we conclude, with the necessary precaution, that **20A** indeed contributes most to the actual structure. O–C(6), N–C(3), and C(4)–C(5) are the shortest bonds; N–O, C(5)–C(6), and C(3)–C(4) are the longest bonds. The N–O single bond length in the fragment C=N–O⁺=C is not known in the literature, the structural element C=N–O–R being the closest approximation available. The N–O bond length in **19** is almost the same as in the reference fragment (1.40 and 1.41–1.42 Å,¹⁷ respectively). The C–N bond length in **19** is almost the same as in oximes and imines (1.30 and 1.28 Å,¹⁸ respectively), and it is shorter than the C–N bond in 1-methylpyridinium iodide¹⁹ (about 1.35 Å). The C–O bond length in **19** is also slightly shorter than the C–O bond length in the 2,4,6-triphenylpyrylium ion²⁰ (1.32 and 1.35 Å, respectively). Finally, it is noticed that C(4)–C(5) is shorter and C(3)–C(4) is longer than in benzene¹⁸ (about 1.40 Å).

(16) Gordien, A. J.; Ford, R. A. "The Chemist's Companion"; Wiley-Interscience, New York, 1972; pp 112–113.

(17) (a) Larsen, K. I. *Acta Chem. Scand.* **1971**, *25*, 2409. (b) Kerr, K. A.; Robertson, J. M.; Sim, G. A. *J. Chem. Soc. B* **1967**, 1305. (c) Bachechi, F.; Zambonelli, L. *Acta Crystallogr., Sect. B* **1973**, *B29*, 2598. (d) Hall, D. *Acta Crystallogr.* **1965**, *18*, 955.

(18) March, J. "Advanced Organic Chemistry", International Student Edition, 2nd ed.; McGraw-Hill: Kogakusha, Tokyo, 1977; p 24.

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(20) (a) Tamamura, T.; Yamare, T.; Yasuoka, N.; Kasai, N. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 832. (b) Bokii, N. G.; Vedrinskii, R. V.; Kitaev, V. V.; Lopatina, N. A. *Koord. Khim.* **1976**, *2*, 103.

Analysis of ^{13}C and ^1H NMR Spectra. The assignment of the ^{13}C NMR resonances to the various sp^2 -carbon atoms of the 2-azapyrylium ions is of utmost importance for a structural determination of the different isomers obtained, when not all four substituents are identical. Comparison of the resonances with those of pyrylium and pyridinium ions is obvious. The carbon atom with the absorption at lowest field in 2,4,6-trimethylpyrylium perchlorate is the ring carbon atom next to oxygen²¹ (180.15 ppm). This absorption is at much lower field than that of the ring carbon atom next to nitrogen in 1,2,4,6-tetramethylpyridinium perchlorate²¹ (156.67 ppm). It seems logical that a similar effect can be found in the 2-azapyrylium ion: C(6) is bearing a partial positive charge (20C) and is adjacent to the most electronegative element in the ion, i.e., oxygen which itself carries a positive charge (20A). Thus, the resonances at lowest field in the various 2-azapyrylium ions are assigned to C(6) (Table IV). The assignment for C(5) is also straightforward: C(5) is not adjacent to a heteroatom and does not bear a positive charge in any of the four resonance structures. Thus, it will absorb at highest field. The difference between C(3) and C(4) is not immediately clear: C(4) bears a partial positive charge (20D); on the other hand, C(3) is next to a heteroatom and oxime-like in character. C(3) is certainly expected to resonate downfield of dialkyl oximes, which fall in the region δ 155–160.²² However, from the discussion (presented below) of the ^{13}C - ^1H coupling patterns and the chemical shift changes due to replacement of alkyl groups by hydrogen atoms, we conclude that C(3) absorbs at lower field than C(4). The assignment of the signals in the ^{13}C NMR spectra of the tetraalkyl-substituted 2-azapyrylium salts **10**, **11**, **12**, and **18** is now clear. The ^{13}C NMR spectrum of the mixture **17a/17b** appears as a superposition of the spectra of **10** and **18**. Therefore, **17a** and **17b** must have the structures shown.

Aluminum halide σ complexes of trialkylcyclobutadienes (**4** (Al_2Br_6) and **5** (Al_2Br_6)) give on reaction with NOCl 2-azapyrylium salts with the hydrogen atom attached to the ring carbon C(6) (**13** and **14**). The argument for this assignment is twofold. First, it is generally observed that replacement of an alkyl group by hydrogen atom leads to an upfield shift for ^{13}C resonances of organic compounds. This effect is even more pronounced in cations, the upfield shift for C(6) in the 2-azapyrylium ion being about 15 ppm. Second, the splitting pattern in the proton-coupled ^{13}C NMR spectrum of **13** (respectively, **14**) is revealing. The absorption of C(6) in **13** at 181.9 ppm is a doublet ($^1J_{\text{CH}} = 208$ Hz) of quartets ($^3J_{\text{CH}} = 6$ Hz); the C(6) resonance in **14** at 181.9 ppm is a doublet ($^1J_{\text{CH}} = 207$ Hz) of triplets ($^3J_{\text{CH}} = 5$ Hz). This doublet splitting of 207–208 Hz is very similar to the doublet-splitting of C(2) in the parent pyrylium perchlorate:²³ 216.28 Hz. These values are extremely large for sp^2 -carbon atoms and can be regarded, in the series of six-membered ring heteroaromatic cations, as characteristic for oxygen in the ring. The quartet splitting of 6 Hz of C(6) in **13** (respectively, the triplet splitting of 5 Hz of C(6) in **14**) is caused by a long-range coupling ($^3J_{\text{CH}}$) with one methyl group (respectively, one methylene group).

The ^{13}C NMR spectra of the mixtures **15r/15u** and **16r/16u**, obtained from the Al_2Br_6 σ complexes of 1,3-dialkylcyclobutadienes, are very interesting and have been studied in detail (see Table IV). Crude reaction mixtures in which the ratio **15r/15u**, according to ^1H NMR, was 3:1 and 1:3 (for **16r/16u** the ratios were > 10:1, 7:3, 1:1, and 1:3) were used to unambiguously assign a set of signals to each isomer. The quality of the spectra used for the structural assignment is exemplified for the mixture **16r/16u** (Figure 7). It is clear from Table IV that there is no methyl group on C(6) of **15r** (respectively, no isopropyl group on C(6) of **16r**). The symmetrical long-range splitting pattern observed rules out that the other ring carbon atom without methyl group (respectively, isopropyl group) is C(4) or C(5). Thus, the methyl groups in isomer **15r** reside at C(4) and C(5)

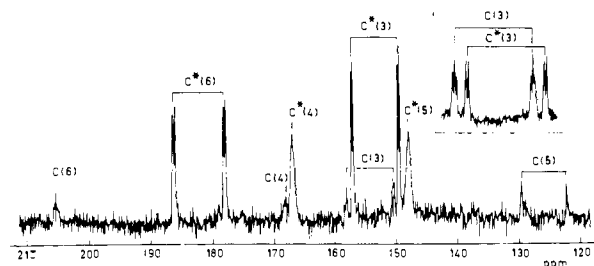


Figure 7. ^1H -coupled ^{13}C NMR spectrum of the mixture **16r** (starred C atoms) and **16u** (ratio 7:3) at 25.16 MHz. Insert: completely resolved ^{13}C - ^1H coupling patterns for C(3) (**16u**) and C*(3) (**16r**) at 50.31 MHz (ratio **16r/16u** is 1:1).

(and the isopropyl groups in isomer **16r** at C(4) and C(5)). Isomer **15u** has, in contrast with **15r**, a methyl group at C(6) (respectively, an isopropyl group on C(6) of **16u**). The doublet ($^1J_{\text{CH}} = 185$ Hz) at 129.7 ppm proves the presence of a hydrogen atom at C(5) of **15u** (C(5) of **16u** also has a large doublet splitting ($^1J_{\text{CH}} = 182$ Hz)). The nonsymmetrical long-range coupling pattern observed for **15u** (and **16u**) rules out a hydrogen atom at C(4) and a methyl group (respectively, an isopropyl group) at C(3), but rather points to the reverse: a methyl group (respectively, isopropyl group) at C(4) and a hydrogen atom at C(3). The upfield shift of C(5) when replacing a methyl group by a hydrogen atom is about 10 ppm (compare **10** and **13** with **15u**). An upfield shift of 10–15 ppm is also expected for C(3) or C(4) on replacing an alkyl group by a hydrogen atom. If the signal at 166.0 ppm in the ^{13}C NMR spectrum of **13** is due to C(3), then it can be seen from the ^{13}C NMR spectrum of **15r** that the expected upfield shift is indeed estimated correctly (166.0 ppm (**13**) – 156.2 ppm (**15r**) \sim 10 ppm). The signal due to C(4) remains at about the same position, going from **13** to **15r** (161.6 ppm for **13**, 160.9 ppm for **15r**). This is a consistent picture of the chemical shift changes due to the replacement of alkyl groups by hydrogen atoms. The picture is not consistent, if the assignment for the signals due to C(4) and C(3) is reversed.

The assignment presented above is in agreement with the ^1H NMR spectra of the 2-azapyrylium ions. The methyl group at C(6) absorbs at lowest field, i.e., 3.22 ppm in **10**. This signal is absent in the ^1H NMR spectrum of **13**; instead a singlet at 10.3 ppm is observed. The aromatic hydrogen atoms in **15r** (respectively, **16r**) resonate at 10.36 and 9.72 ppm (respectively, 10.52 and 9.83 ppm). The hydrogen atoms adjacent to the aromatic nucleus of **15u** (respectively, **16u**) resonate at 9.59 and 8.26 ppm (respectively, 9.67 and 8.29 ppm); the methyl group bonded to C(6) in **15u** again absorbs at \sim 3.2 ppm. Thus, signals at \sim 10.4 ppm are due to C(6)-hydrogen atoms, signals at \sim 9.7 ppm are due to C(3)-hydrogen atoms, and signals at \sim 8.3 ppm are due to C(5)-hydrogen atoms.

Finally, a special effect observed in the ^{13}C NMR spectra of **13**, **14**, **15r/15u**, and **16r/16u** deserves comment. The signals due to the aromatic carbon atoms show reversible temperature-dependent line broadening. Especially the signals due to ring carbon atoms without alkyl substituents broaden markedly below \sim -50 $^\circ\text{C}$. We have not investigated this effect in detail. In our opinion the line broadening is in essence a counterion effect. It has been checked that the line broadening is not caused by merely changing the Lewis acid from Al_2Cl_6 to Al_2Br_6 (Al_2Br_6 is the Lewis acid in the σ -aluminum halide cyclobutadiene complexes used for the synthesis of **13**, **14**, **15r/15u**, and **16r/16u**): 2-azapyrylium salt **11** shows no line broadening between 0 and -75 $^\circ\text{C}$ (line width at half-height $\Delta\nu_{1/2} \sim$ 4 Hz for all aromatic carbon atoms, independent of temperature). Furthermore, we have checked that the chemical shifts of the signals of all the carbon atoms of **11**, **13**, **14**, **15r/15u**, and **16r/16u** are temperature-independent (\pm 0.5 ppm) between room temperature and -75 $^\circ\text{C}$. Thus, this line-broadening effect does not, in our opinion, influence the assignment presented.

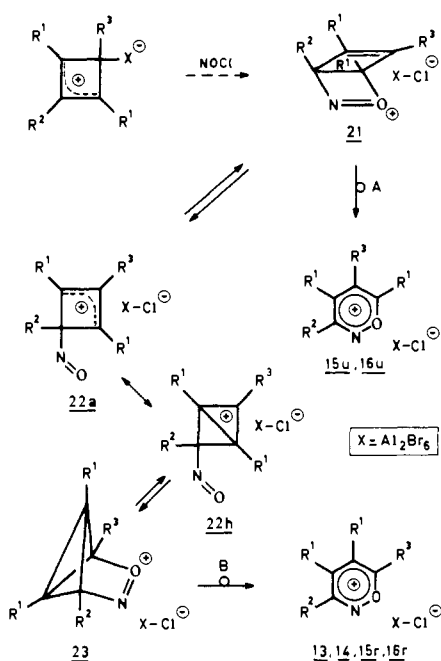
From the fact that the aromatic ring carbon atoms of the 2-azapyrylium ions absorb at extremely low field, it is concluded

(21) Balaban, A. T.; Wray, V. *Org. Magn. Reson.* **1977**, *9*, 16.

(22) Johnson, L. F.; Jankowski, W. C. "Carbon-13 NMR Spectra"; Wiley-Interscience: New York, 1972.

(23) Sandor, P.; Radics, L. *Org. Magn. Reson.* **1981**, *16*, 148.

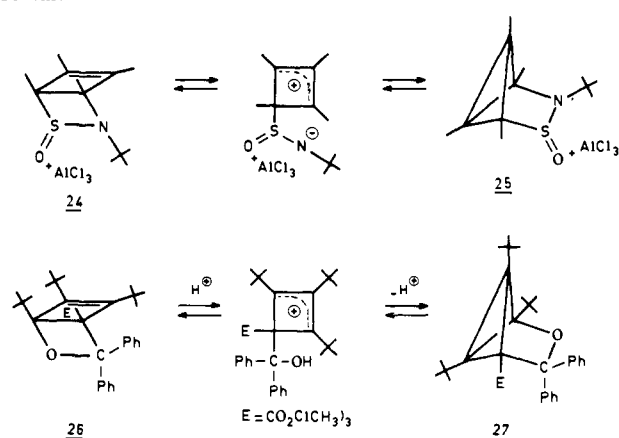
Scheme IV



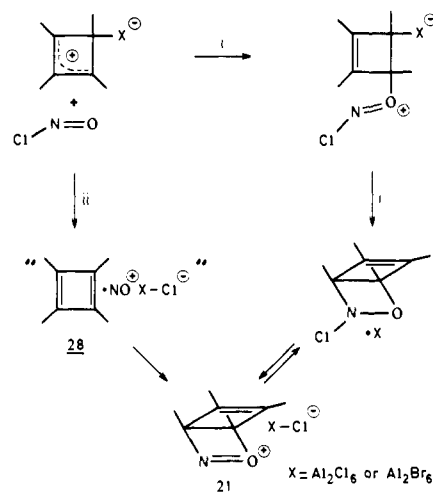
that the 2-azapyrylium moiety is indeed aromatic and that the resonance structures **20C** and **20D** contribute to the actual structure: only carbon atoms with a partially positive charge are expected to absorb at such low field as actually observed.

Mechanistic Considerations. 1. Structure of the Products. The substitution pattern in the products **15r** and **16r** is not the same as in the precursors **6** (Al_2Br_6) and **7** (Al_2Br_6) in the sense that the alkyl groups are 1,2-positioned in the products and 1,3-positioned in the starting materials. A 1,3-position of the substituents is observed in the isomeric products **15u** and **16u**. There is a recent precedent for this type of substituent shuffle.^{3c} The reaction of the AlCl_3 σ complex of 1,3-di-*tert*-butylcyclobutadiene yields on reaction with ethylethanoformate two isomeric pyridines: ethyl 4,5-di-*tert*-butyl-2-picolinate and ethyl 3,6-di-*tert*-butyl-2-picolinate.^{3c} We propose a reaction mechanism for the formation of **13**, **14**, **15r/15u**, and **16r/16u** identical with the one proposed in the case of the isomeric pyridines. This reaction mechanism is depicted in Scheme IV. The Dewar benzene-type intermediate **21** is formed after the initial reaction step(s) of NOCl with a σ -aluminum halide cyclobutadiene complex. Intermediate **21** can either undergo an aromatization reaction (path A, Scheme IV) or undergo a ring opening toward the cyclobutenyl cation **22a**. By now it is soundly established that cyclobutenyl cations have some homocyclopropenium ion character²⁴ (**22a** \leftrightarrow **22h**). Ring closure can lead to the benzvalene-type structure **23**, which on aromatization will give the rearranged 2-azapyrylium ions **13**, **14**, **15r**, and **16r** (path B, Scheme IV). The changes in the ratios **15r/15u** and **16r/16u**, from one experiment to another, might reflect a delicate balance between the difference equilibria shown in Scheme IV. It must be noted, however, that mixtures **15r/15u** and **16r/16u** do not equilibrate at room temperature. Finally, structures analogous to the Dewar benzene-type intermediate **21** and the benzvalene-type intermediate **23** have, in some comparable cases, been measured by NMR spectroscopy and even been isolated.²⁵⁻²⁷ The bicyclic sulfonamide **24**– AlCl_3 and the tricyclic sulfonamide **25**– AlCl_3 complex have both been detected

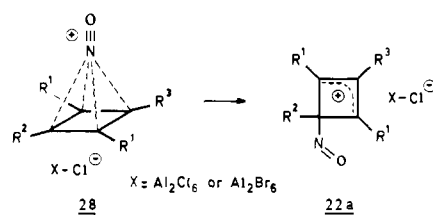
Scheme V



Scheme VI



Scheme VII



by ^{13}C NMR spectroscopy (Scheme V); after quenching with dimethyl sulfoxide, the free bicyclic and tricyclic sulfonamides have both been isolated.²⁵ The bicyclic compound **26** and the tricyclic compound **27** (Scheme V) have also been isolated;²⁶ they have been brought into equilibrium by H^+ instead of a Lewis acid.

2. On the Possible Intermediacy of a Heteroatom-Substituted Pyramidal Cation. We speculate here about the details of the first reaction step of Scheme IV. One possibility is a nucleophilic attack of the oxygen atom of NOCl at the 1-position of the cyclobutenyl part of the precursor σ complex followed by ring closure and a Lewis acid–Lewis base reaction yielding intermediate **21** (route i, Scheme VI). However, NOCl is not expected to act as a nucleophile. Another plausible possibility is a Lewis acid–Lewis base reaction between Cl^{\ominus} of NOCl and aluminum halide of the cyclobutadiene σ complex²⁸ (route ii, Scheme VI). The result of this reaction step would be the “cyclobutadiene- $\text{NO}^+\text{X-Cl}^-$ ” complex **28**, which is redefined in Scheme VII as the NO^+ -

(24) For NMR evidence, see: Olah, G. A.; Staral, J. S.; Liang, G. *J. Am. Chem. Soc.* **1974**, *96*, 6233. For X-ray diffraction evidence, see: Kruger, C.; Roberts, P. J.; Isay, Y. H.; Koster, J. B. *J. Organomet. Chem.* **1974**, *78*, 69.

(25) Fongers, K. S.; Hogeveen, H.; Kingma, R. F. *J. Org. Chem.* **1983**, *48*, 4275.

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(28) For instance, it has been established that both tetra-*n*-butylammonium chloride and tetra-*n*-butylammonium tetrachloroaluminate are capable of removing 1 mol of AlCl_3 from **1** (Al_2Cl_6). Tetra-*n*-butylammonium chloride is also capable of removing AlCl_3 from **1** (AlCl_3): Broxterman, Q. B., unpublished results.

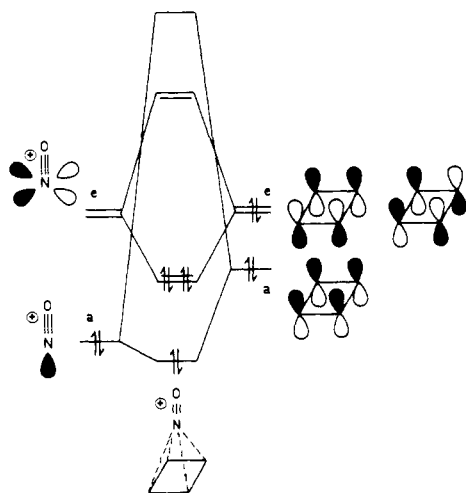


Figure 8. Interaction diagram of NO^+ with cyclobutadiene.

cyclobutadiene pyramidal cation **28**. It is shown in Scheme VII that the intermediacy of the pyramidal carbocation **28** fits into the reaction mechanism of Scheme IV: **28** can collapse to **22a** when R^3 or R^3 and R^2 are hydrogen atoms. Note that these hydrogen atoms (R^2 and R^3 in Scheme VII) do not become attached to the 1,3-positions of the cyclobutenyl cation **22a**, in accord with literature data.²⁹

Regardless of the actual intermediacy of **28** in the reaction of σ -aluminum halide cyclobutadiene complexes, it is of interest to speculate about the capacity of NO^+ and cyclobutadiene to form a stable, i.e., experimentally observable, pyramidal heteroatom-substituted carbocation.³⁰ Pyramidal cations can formally be considered as being the result of the interaction of a positive fragment as the apex and a 4e system (e.g., cyclobutadiene) as the base of the pyramid. The idea was originally developed by using CH^+ ³¹ as the apex fragment. When the concept of isolobality³² was used, CH^+ has been replaced by other fragments such as CO ,^{31b} BH , $\text{Fe}(\text{CO})_3$, and $\text{Os}(\text{CO})_3$.^{30b} The complex of CO with cyclobutadiene has been studied extensively,^{31b,33} though without any experimental proof as yet that the CO -cyclobutadiene complex has a pyramidal structure. Because NO^+ is isoelectronic with CO , it might also be isolobal. At our request, Dr. F. Visser has calculated the energies of the relevant orbitals of NO^+ and CO by ab initio methods by using the same quality basis set: HOMO NO^+ , -1.1397 au; LUMO NO^+ , -0.2805 au; HOMO CO , -0.5553 au; LUMO CO , $+0.1143$ au. Both the HOMO and the LUMO of NO^+ are polarized toward the nitrogen end of the molecule: the HOMO and the LUMO of CO are both polarized toward the carbon end of the molecule.³⁴ The relevant orbital energies of cyclobutadiene are estimated to be³⁵ HOMO -0.30

au and lowest occupied π orbital -0.46 au. The interaction diagram of NO^+ with cyclobutadiene, which is not to be taken as a correlation diagram for the approach of NO^+ to C_4H_4 ,³⁴ is shown in Figure 8. It must be kept in mind that the meaning of this interaction diagram is essentially of topological nature. It can however be seen that the stabilizing interaction for the pyramidal structure, i.e., the interaction between the LUMO of NO^+ (that is, the π^* orbital) and the HOMO of cyclobutadiene, is stronger than for CO with cyclobutadiene because the orbital energies are closer in the former case (NO^+ -cyclobutadiene, -0.28 and -0.30 au, vs. CO -cyclobutadiene, $+0.11$ and -0.30 au). The cyclobutadiene- CO π complex is, according to MNDO and MNDO/3 calculations, not a true minimum on the C_4H_4 CO potential energy surface.^{33a} It can, however, according to the MNDO calculation, be regarded as a charge-transfer complex with a transfer of -0.138 formal charge, mainly from the degenerate π MO's of cyclobutadiene to the π^* MO of CO .^{33a} For these reasons, we think that NO^+ will interact more strongly with cyclobutadiene than CO ; NO^+ is positively charged, and its LUMO level matches perfectly with the HOMO energy level of cyclobutadiene.

Conclusion

The reaction of σ -aluminum halide cyclobutadiene complexes with NOCl yields 2-azapyrylium salts. From UV spectroscopy and X-ray crystallography, it is concluded that the 2-azapyrylium moiety is a flat, aromatic six-membered ring system, with one major resonance structure: **20A**. ¹³C and ¹H NMR spectroscopy corroborate the view that 2-azapyrylium ions are aromatic compounds. From an analysis of the long-range ¹³C-¹H coupling patterns, we conclude that the reaction of σ -aluminum halide complexes of 1,3-dialkylcyclobutadienes with NOCl gives rise to rearranged and unrearranged 2-azapyrylium salts. A reaction mechanism, based on comparable reactions known from the literature, is proposed in order to account for the different isomeric 2-azapyrylium salts obtained. It is discussed whether the heteroatom-substituted pyramidal carbocation **28** may be an intermediate in this reaction. Furthermore, it is argued, on the basis of the relevant orbital energies, that the cyclobutadiene- NO^+ pyramidal complex is more likely to exist than the corresponding cyclobutadiene- CO complex.

The work described in this paper opens up three promising lines for further research: (i) the reaction of the aluminum halide σ complexes of cyclobutadienes with other heteroatom-heteroatom triple-bond-containing reagents, analogously to NO^+ , yielding heteroaromatic systems, (ii) exploration of the synthetic potential of the 2-azapyrylium salts analogously to pyrylium salts,³⁶ and (iii) both experimental and theoretical investigations on the possible existence of the heteroatom-substituted cation **28**.

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Supplementary Material Available: Thermal and final atomic parameters for **19** (2 pages). Ordering information is given on any current masthead page.

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(34) We thank Dr. F. Visser, Institute of Theoretical Chemistry, University of Nijmegen, The Netherlands, for performing these calculations. The orbital energies of NO^+ and CO were taken from an ab initio Hartree-Fock calculation of near Hartree-Fock limit accuracy, using 124 GTO's for each molecule. Technical details of the calculations can be found in: Visser, F.; Wormer, P. E. S. *Chem. Phys.* **1985**, *92*, 129.