Azonin Anion (1-Azacyclonona-2,4,6,8-tetraenide)

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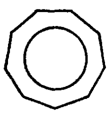
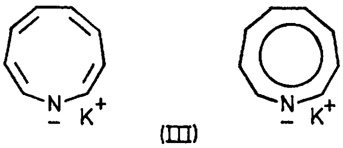
Summary The azonin anion behaves in a manner similar to cyclononatetraenide and exhibits properties characteristic of a coplanar, aromatic 10π-electron system.

In view of the remarkable properties of cyclononatetraenide anion (I) discovered several years ago,[1] one might expect that its nitrogen analogue would behave in a similar manner. We describe the isolation and properties of salts of the title anion.

N-Ethoxycarbonylazonin[2] (II) (1 mmol) in a small amount of tetrahydrofuran (2 ml) was treated with potassium t-butoxide (1 mmol) at 0° for 20 min;[3] cooling the solution to $-15°$ provided needles (III) (*ca.* 60% yield), which were recrystallized from the same solvent under argon. A combustion analysis and volumetric titration [after decomposing (III) with water] show the elemental composition of (III) to be C_8H_8NK. Since treatment of (III) with ethoxycarbonyl chloride *without added base* converted (III) into (II), and hydrogenation of salt (III) over Pt in tetrahydrofuran provided azacyclononane,[1b] the structure of the salt should be represented by (III). Although (III) was air-sensitive, it remained unchanged in crystalline form at 60° for two days *in vacuo*, at 0° for one year under argon, and in solution (THF, degassed) (III) decomposed at a measurable rate only at elevated temperatures (half life, *ca.* 10 min at 100°). In contrast, (II) underwent thermal rearrangement readily at 40°.[2] A u.v. spectrum of (III) (dry THF, manipulated in a dry box) demonstrated maxima at 255 nm (log ϵ 4·5)‡ and 329 (3·6) and is reminiscent of that of (I) [K salt in THF, 249 (5·0), 314 (4·0), and 320 (4·0).].[1a] These results are interpretable in terms of extensive delocalization of π-electrons in both systems (I) and (III) [*cf.* uv. of (II) ref. 2a].



(I)



(III)

An n.m.r. spectrum of (III) ([$^2H_8$]-THF, 100 MHz) showed a multiplet at τ 3·4—3·55(6H) and a multiplet at 1·39 ($W_{1/2}$ 7 Hz, 2H). The former signal is in a region expected for this species,[4] but the latter deserves comment. Chemical shifts of model anions such as pyrrole and indole are slightly different from those of the neutral species (*e.g.*, pyrrole anion, τ 3·30, 3·96; pyrrole, τ 3·35, 3·93)[5] and appear at higher fields than those of the corresponding ethoxycarbonyl derivatives (ethoxycarbonylpyrrole 2·74 and 3·81). The low field signal of (III) is slightly solvent-dependent and largely dependent on counter ions (the corresponding lithium salt showed a signal at τ 2·45) and

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‡ Short path u.v. cells were used to avoid the necessity of dilution of solutions of (III), which might involve unavoidable introduction of moisture.

thus the degree of ionization and aggregation varies with cation and solvent. The α-protons of (III) appear to be responsible to this resonance peak but this assignment is tentative and the significant deshielding effect (rather than shielding effect due to the negative charge) requires further study to establish its true origin.

A crude estimate of the acidity of the conjugate acid (III′) of (III) can be made, using McEwen's classical method.[7] Thus (III) either in THF or Me_2SO was mixed with weak acids of pK_a 15—21 and the decrease of the signals of (III) was measured relative to an internal standard (n.m.r.). While (III) remained unchanged with indene for one day, it appeared to exchange its potassium ion slightly with pyrrole. In contrast, the intensity of the signals substantially decreased in the presence of methanol and cyclopentadiene but the results were not quantitatively reproducible, presumably because of the instability (or air-sensitivity) of the conjugate acid, (III′), which appeared to undergo further reactions under the exchange conditions. We can only estimate that the pK_a of (III′) is 15—16.

Our results show that an analogy exists between the 5-membered 6π-electron system (cyclopentadienide and pyrrole anion) and the 9-membered 10π-electron system, (I) and (III), and as such, the azonin anion is very likely to be a coplanar system in which π-electrons are delocalized to a significant extent.

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