Synthesis and Characterization of the Tetra-aminotriafulvalene Dication

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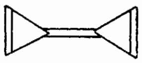
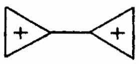
Summary The tetra-aminotriafulvalene dication (**3**), the first dication of the simplest fulvalene, has been synthesized and its spectroscopic characteristics are briefly described.

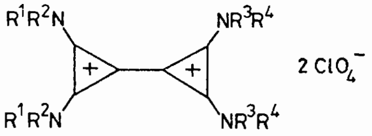
ALTHOUGH a variety of cyclic cross-conjugated hydrocarbons has been synthesized, the simplest member of fulvalenes, bicyclopropenylidene ('triafulvalene') (**1**) has not been prepared so far. Molecular orbital calculations predict that triafulvalene is polyolefinic and has a low ionization potential.[1] Even triafulvalene dication (**2**) consisting of the two cyclopropenium ions has never been isolated, to our knowledge. We now report the synthesis and properties of tetra-aminotriafulvalene dication (**3**), which was obtained during our studies on diaminocyclopropenylidene.[2]



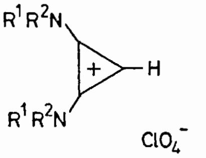
(1)



(2)



(3)



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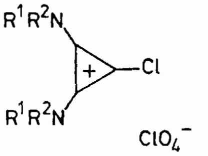

(5)

a; $R^1 = R^2 = R^3 = R^4 = Pr^i$
b; $R^1 = R^4 = Me, R^2 = R^3 = Bu^t$
c; $R^1 = R^2 = Pr^i, R^3 = Bu^t, R^4 = Me$

A suspension of bis(di-isopropylamino)cyclopropenium perchlorate (**4a**) in ether was treated with an excess of butyl-lithium under argon at 30 °C. To the mixture was added an equimolar amount of 1,2-bis(di-isopropylamino)-3-chlorocyclopropenium perchlorate (**5a**) at room temperature. Stirring for 1 h, followed by treatment with dil. $HClO_4$, gave (**3a**) as colourless crystals, m.p. 296 °C, in 69% yield.† Similarly, the symmetrical dication (**3b**) and the asymmetrical dication (**3c**) were prepared from (**4b**) and (**5b**), and (**4a**) and (**5b**), respectively. These dications were isolated as perchlorate salts which are stable in air and also stable in acidic and neutral solutions. However, treatment of (**3a**) with 0·1 N NaOH gave yellow crystals formulated as $C_{30}H_{57}ClN_4O_5$ from combustion analyses. Spectral data indicate the cleavage of a cyclopropenium ring.[2] The ^1H n.m.r. spectrum of (**3a**) reflects the strong electron-withdrawing nature of the cyclopropenium ring. The methine protons of isopropyl groups of (**3a**) in $(CD_3)_2CO$ show signals at δ 4·40 and 4·21 (a pair of septets). These peaks appear at lower magnetic field (by 0·3—0·4 p.p.m.) than those of the corresponding protons of (**4a**) or (**5a**). The ^{13}C n.m.r. spectrum of (**3a**) measured in $(CD_3)_2SO$ showed the following signals: δ (p.p.m. from Me_4Si) 134·2 (s, C-2 and C-3), 89·6 (s, C-1), 55·0 (d), 50·5 (d, *C*H), and 21·4 (q, *C*H_3). The carbons (C-1) of the 'pivot' bond in (**3a**) are less deshielded than the corresponding carbons of 1-substituted-2,3-bis(di-isopropylamino)cyclopropenium perchlorate (where the 1-substituent is H, Cl, Me, Ph, *etc.*).[3] This remarkable shielding effect of the pivotal carbons (C-1) is partly due to the repulsion of two positive charges. The u.v. spectrum of (**3a**) (MeCN) exhibits an absorption maximum at 250 nm (logϵ 4·20). The large bathochromic shift observed in the u.v. spectra of (**3a**) compared with those of (**4**) and (**5**) (λ_{max} below 210 nm) can be ascribed to the increased π-electron delocalization.

The skeletal structure of the dication containing four nitrogen atoms was estimated by i.r. and Raman spectroscopy. The diaminocyclopropenium ion skeleton (C_{2v} geometry) possesses two characteristic vibrations in the region 2000—1500 cm^{-1}.[4] The corresponding vibrations of (**3a**) appear at 1876 and 1571 cm^{-1} in the i.r. and 1950 and 1529 cm^{-1} in the Raman spectrum. These observations are most compatible with a planar geometry (D_{2h}) for (**3**) on the basis of selection rules. Analysis on the assumption of lower symmetry gives more than two i.r. and/or Raman active vibrations.

Attempts to reduce the dication (**3**) to triafulvalene have failed. This trend seems to coincide with the result of HMO calculations; the lowest unoccupied molecular orbital of (**3**) lies in anti-bonding level. The stability of (**3**) is doubtless due to large electron donation from the four peripheral amino-groups.

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† Satisfactory elemental analyses were obtained for this compound.

[1] J. D. Roberts, A. Streitwieser, Jr., and C. M. Regan, *J. Amer. Chem. Soc.*, 1952, **74**, 4579; H. Yamaguchi, T. Nakajima, and T. L. Kunii, *Theor. Chim. Acta*, 1968, **12**, 349; S. Yoneda, Y. Kamitori, and Z. Yoshida, unpublished result.

[2] Z. Yoshida, H. Konishi, Y. Tamaru, K. Nishikawa, and H. Ogoshi, *Tetrahedron Letters*, 1973, 2619.

[3] Unpublished results.

[4] Z. Yoshida, *Topics Current Chem.*, 1973, **40**, 47.