A Hydrocarbon Existing Uniquely in Solution: a Heterolytically dissociative Hydrocarbon that produces the Corresponding Hydrocarbon Salt by Crystallization

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A covalent hydrocarbon (R_4–R_1), formed in chloroform or the other aprotic solvents by cation–anion co-ordination of the tricyclopropylcyclopropenylium ion (R_4^+) and the tris(7*H*-dibenzo[c,g]fluorenylidenemethyl)methide ion (R_1^-), can not be isolated in the solid state, but is converted into the corresponding hydrocarbon salt ($R_4^+R_1^-$) at the moment of crystallization by evaporation or refrigeration of the solutions.

In our search for the genuine hydrocarbons with novel physical and chemical characteristics, we reported previously the first example of a hydrocarbon salt ($R_2^+R_1^-$)[1] containing only hydrocarbon ions, *i.e.*, Agranat's cation, the tris-1-(5-isopropyl-3,8-dimethylazulenyl)cyclopropenylium ion (R_2^+),[2] and Kuhn's anion, the tris(7*H*-dibenzo[c,g]fluorenylidenemethyl)methide ion (R_1^-).[3] We have also reported the first heterolytically dissociative hydrocarbon (R_3–R_1) which partially gives the tropylium ion (R_3^+) and Kuhn's anion (R_1^-) in dimethyl sulphoxide (DMSO).[1‡] Herein we report another

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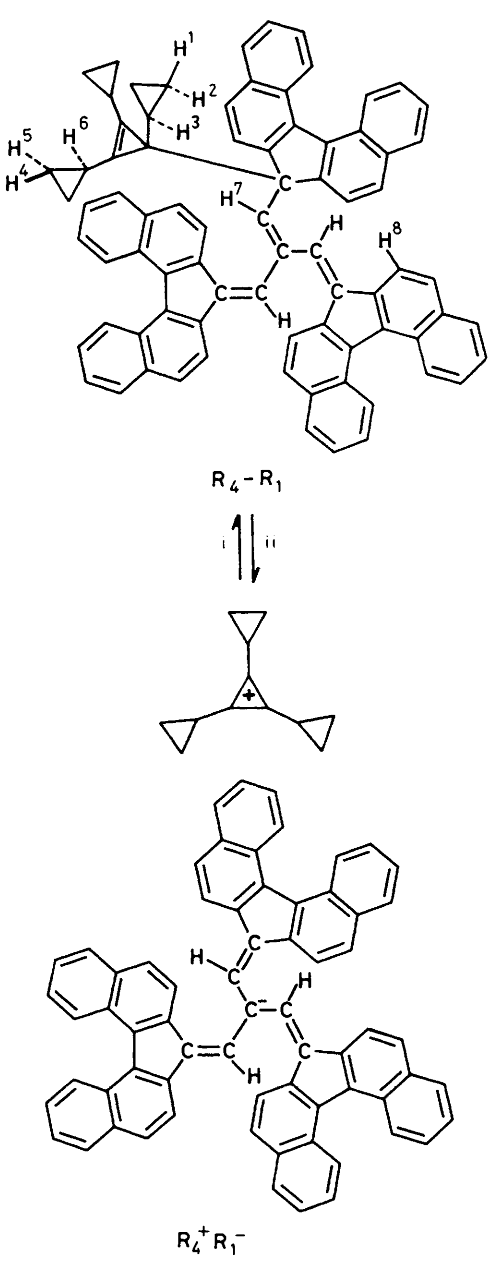
[‡] Equilibria for the heterolysis of the C–C bond were first reported on systems containing hetero-atom groups, such as cyano and nitro.[4]



Scheme 1. Reversible conversion of R_4–R_1 into $R_4^+R_1^-$. *Reagents and conditions:* i, evaporation or refrigeration; ii, dissolution in $CHCl_3$.

hydrocarbon that exists only 'in solution' and is 'heterolytically' converted into the corresponding hydrocarbon salt at the moment of crystallization from the solution.

To prepare the new hydrocarbon salt ($R_4^+R_1^-$) tricyclopropylcyclopropenylium fluoroborate ($R_4^+BF_4^-$)[5] in tetrahydrofuran (THF)-acetonitrile (8:1, v/v) was mixed with an equivalent amount of the potassium salt of Kuhn's anion ($K^+R_1^-$)[3] in THF solution; the resulting green solution left a green mixture of $R_4^+R_1^-$ and KBF_4 after removal of the solvent *in vacuo*. The pure hydrocarbon salt was obtained in 60% yield by successive treatments of the mxiture to remove KBF_4 ($CHCl_3$ extraction, evaporation *in vacuo*, THF extraction, and precipitation with acetonitrile).

When $CHCl_3$ extraction was employed, the green salt $R_4^+R_1^-$ underwent co-ordination to give a red-brown solution of the hydrocarbon (R_4–R_1). Unexpectedly, but fortunately, evaporation (*in vacuo*) gave the green salt again, instead of the expected covalent hydrocarbon (R_4–R_1). Refrigeration of the $CHCl_3$ solution at −60 °C also gave the green precipitates of the salt.

The structure of the salt was confirmed by satisfactory microanalytical data, the i.r. spectrum (KBr disc),§ its complete dissociation in DMSO, evidenced by the u.v.–visible spectrum§ and its equivalent conductivity.¶

Proof of the covalent structure in solution rests on the n.m.r. spectroscopy. Thus, the green salt was first dissolved in $CDCl_3$, exhibiting the complete colour change from green to red-brown. The brown $CDCl_3$ solution is stable for a period sufficient to allow the measurement of ^1H n.m.r. spectra (>3 h). As expected from the change in colour, 400 MHz ^1H n.m.r. spectra of the $CDCl_3$ solution (*ca.* 0.5 wt%) did not indicate the presence of the salt $R_4^+R_1^-$, but that of the hydrocarbon R_4–R_1, alone,†† in agreement with the structure shown in Scheme 1.

Besides the complete co-ordination (in $CDCl_3$) and the complete dissociation (in DMSO), $R_4^+R_1^-$ undergoes partial co-ordination to give the hydrocarbon R_4–R_1 in acetone, acetonitrile, 1,2-dichloroethane, THF, and CH_2Cl_2, and in each case the co-ordination is reversed by evaporation of the solvent. Logarithms of dissociation constants (measured spectrophotometrically) of R_4–R_1 correlate linearly with the reciprocals of the dielectric constants of these aprotic solvents.

As a corollary, the heterolytically dissociative hydrocrabon R_4–R_1 exists *only* in solution. Ionization to the 'hydrocarbon salt' ($R_4^+R_1^-$) at the moment of crystallization is most probably due to great steric congestion in any hypothetical solid state of the hydrocarbon (R_4–R_1), and such conversion can be seen, in some sense, as a mechanochemical phenomenon at the molecular level.

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§ Consisted of the i.r. spectra or u.v.–visible spectra of R_4^+ and R_1^- superimposed.

¶ Measured at ac 100 V and equal to the sum of the equivalent conductivities of R_4^+ and R_1^-.

†† *Selected ^1H n.m.r. data* for R_4–R_1: ($CDCl_3$, 400 MHz) δ −0.46 (dddd, 2H, H-1), −0.33 (dddd, 2H, H-2), 0.43 (tt, 1H, *J* 8.4 and 5.2 Hz, H-3), 0.53 (dddd, 4H, H-4), 0.87 (dddd, 4H, *J* 11.7, 8.7, 8.7, and 4.2 Hz, H-5), 1.69 (tt, 2H, *J* 8.2 and 4.9 Hz, H-6), 6.47 (br. s, 1H, H-7), and 6.55 (d, 1H, *J* 8.5 Hz, H-8). The assignments are based on spin–spin decoupled spectra.