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CYCLIC DELOCALIZED 3 π-ELECTRON SYSTEMS. AN ESR SPECTROSCOPIC INVESTIGATION OF SOME TETRA ALKYL-SUBSTITUTED CYCLOBUTADIENE RADICAL CATIONS.

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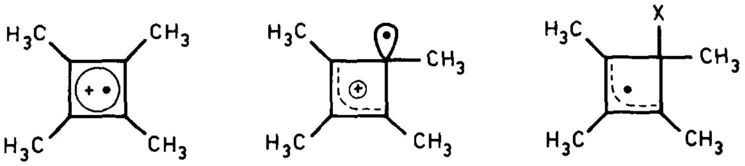
Summary: Tetra alkyl-substituted cyclobutadiene radical cations are π- and not σ-radicals. This can be concluded from the ESR spectra of the tetramethylcyclobutadiene radical cation at low temperatures, and from the ^{13}C hyperfine splitting constants of the tetraethylcyclobutadiene radical cation.

Alkyl-substituted cyclopropenyl radicals have been shown by ESR spectroscopy to be σ-radicals.[1-3] For the tri-t-butyl-cyclopropenyl radical this conclusion came from the large ^{13}C hyperfine splitting (hfs) of the ring carbons.[1] Very recently, two research groups have shown that at temperatures below -138°C the trimethylcyclopropenyl radical can be frozen out as a localized σ-radical.[2,3] The ESR spectra of the tetra-t-butyl-[4] and the tetramethylcyclobutadiene[5] radical cations have been reported. In the present communication results are presented that indicate that, in contrast to the corresponding cyclopropenyl radicals, alkyl-substituted cyclobutadiene radical cations are π-radicals.[6]

A priori one can conceive of three reasonable structures for the radical species generated by photolysis of the aluminum halide σ-complex of tetramethylcyclobutadiene[5] (Fig 1):



1a 1b 1c

Figure 1

the π-radical 1a, the σ-radical 1b, and the β-X substituted cyclic allyl radical 1c (X being unknown). The symmetry of the spectra for 1b or 1c will be the same as that of 1a, provided that a rapid equilibration process renders all methyl carbons equivalent on the ESR time scale (exemplified for 1c in Fig. 2)

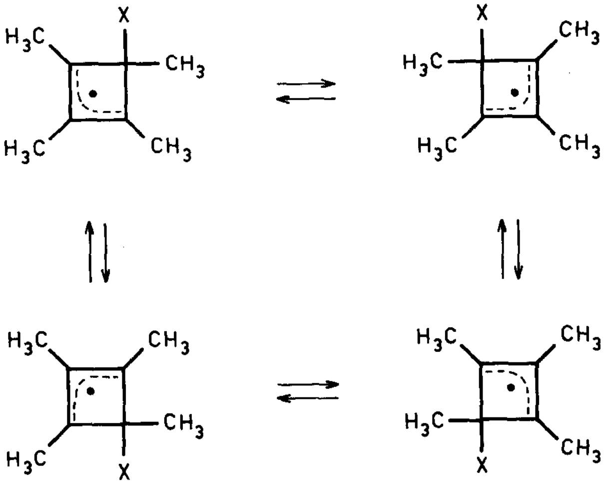


Figure 2

We have excluded possibility 1c by recording the ESR spectrum of the tetramethylcyclobutadiene radical cation at -80°C, -132°C and -196°C. Although the solid-phase spectra are somewhat broadened, it is clear that the hfs ($a_{\beta}^{H}(12H)=8{,}75 \pm 0{,}05G$) and the symmetry of the ESR spectrum remain unchanged in this temperature range. It is not possible to freeze out an equilibration process, and therefore it is concluded that the species involved is intrinsically symmetrical. It is very unlikely that the equilibration process for 1c is rapid on the ESR time scale at -196°C. For 1b the argument is the same, but it is not completely impossible (although improbable) that the potential barrier for interconversion is very low in this case.

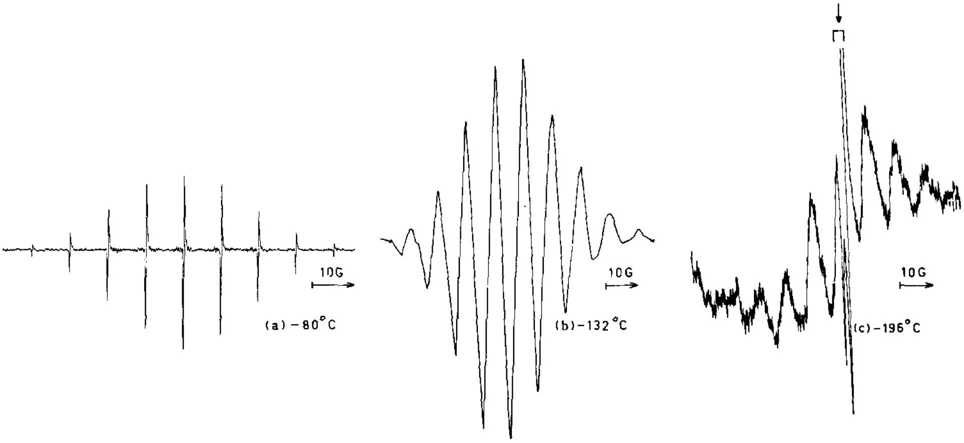


Figure 3. ESR spectra of 1a or 1b.[7] The arrow points to a paramagnetic impurity in the Dewar.

However, the structure 1b can be excluded rigorously by another method. The ESR spectrum of the tetraethylcyclobutadiene radical cation[8] shows, apart from the hydrogen hfs, three different ^{13}C hfs's (-40^{o}C:g=2,0029; a^{H}_{β}(8H)=7,69G; a^{H}_{γ}(12H) $\leq$ 0,02G; $a\ ^{13}C_{1,2,3}$ =3,7; 4,4; 5,0G; ΔHpp=0,14G). At the moment we are not able to assign the different hfs's to the appropriate carbon atoms, but this is not essential because all three hfs's have approximately the same value (~4,5G).

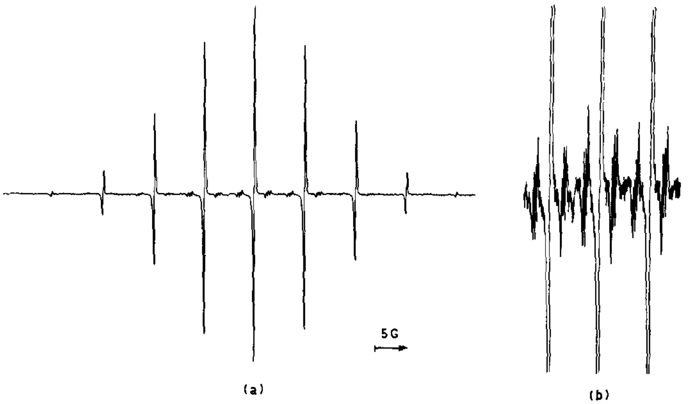


Figure 4. The ESR spectrum of the tetraethylcyclobutadiene radical cation at -40^{o}C under normal conditions (a), under conditions of optimal resolution of of the ^{13}C satellites (b).

This low approximate value of ~4,5G leads to the conclusion that the unpaired electron resides in an orbital of p-character. For a radical of type 1b the ^{13}C hfs for the ring carbons are expected to be much larger.[9] The value of ~4,5G can be compared with that found for the pentamethylcyclopentadienyl radical[10] (a^{13C}=3,5G; π-radical) and with the value found for the tri-t-butylcyclopropenyl radical[1] (a^{13C}=30G; σ-radical). The conclusion is therefore that the tetraethylcyclobutadiene radical cation is a π-radical Of course the same must be true for 1a, and thus 1b can be excluded.

We have also prepared two other novel cyclobutadiene radical cations: the tetra-n-propyl- and tetra-n-pentylcyclobutadiene radical cations.[8,11] There is only one ^{13}C hfs visible in the ESR spectra of these species. This is due to considerable overlapping of several different ^{13}C satellites. However, the observed average value of ~4,5G for the ^{13}C hfs's is in good agreement with the value mentioned for the tetraethylcyclobutadiene radical cation.[11]

Our investigations in this field will be continued.

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References and Notes

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4. H. Bock, B. Roth and G. Maier, Angew.Chem., 92, 213 (1980).
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6. A part of this work has been presented orally at the meeting of the Netherlands Foundation for Chemical Research (SON) at Lunteren, 9-10 November 1981.
7. The ESR spectrum at -80°C results from an irradiation of a 0.5 molar solution of Al_2Cl_6 σ-complex of tetramethylcyclobutadiene. The solid-phase spectra (-132°C and -196°C) result from an irradiation of a 0,06 molar solution of the same precursor in a 80/20 (v/v) mixture of CH_2Cl_2 and $CHCl_3$. The equipment used has been described earlier.[5]
8. All cyclobutadiene radical cations reported in this communication are generated from a 0,5 molar solution of the Al_2Cl_6 σ-complexes of the corresponding cyclobutadienes in CH_2Cl_2.
9. The expected ^{13}C hfs will be in the range of 22-30G, when the argumentation of Schreiner and Berndt is applied to 1b.[1]
10. A.G. Davies and J. Lustzyk, J.C.S. Chem. Comm., 554 (1980).
11. The β-proton hfs's and ΔHpp's show a curious temperature-dependency. For the tetraethylcyclobutadiene radical cation: a_β^H(8H)=7,90G at -82°C drops to a_β^H(8H)=7,58G at +10°C, no great variation in ΔHpp (0,200 + 0,075G). For the tetra-n-propylcyclobutadiene radical cation (g=2,0028; a_γ^H(8H) $\leq \sim$0,1G): a_β^H(8H)=7,10G; ΔHpp=0,98G at -82°C drops to a_β^H(8H)=6,96G and ΔHpp=0,70G at +10°C. For the tetra-n-pentylcyclobutadiene radical cation (g=2,0030; a_γ^H (8H) $\leq \sim$0,15G): a_β^H(8H)=7,10G; ΔHpp=1,45G at -82°C drops to a_β^H(8H)=6,98G and ΔHpp=0,95G at +10°C. The ESR spectra of these three radical cations have been recorded on a Varian E-4[5] and on a Varian E-12 apparatus (at the Philipps-Universität, Marburg, West-Germany).

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