

TOWARDS PERSISTENT CYCLOBUTADIENE RADICAL CATIONS?  
 THE TETRA-1-ADAMANTYL-, AND TETRANEOPENTYLCYCLOBUTADIENE RADICAL CATIONS.

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Summary: The persistence of alkyl substituted cyclobutadiene radical cations strongly depends on the method of generation and the size of the alkyl substituents used. Hindered rotation, the consequence of bulky substituents, is observed in the title compounds.

Cyclobutadiene radical cations are transient species amenable to study by ESR<sup>1-3</sup> or mass spectroscopy.<sup>4</sup> In order to study these species with other, less sensitive techniques higher concentrations are needed, and thus more persistent examples than those already published are essential.<sup>1-3</sup> In the present communication results are presented which indicate that the persistence (kinetic stability<sup>5</sup>) is strongly influenced by two factors: the bulk of the alkyl groups attached to the four-membered ring and the method of generation of the radical cations.

We have compared two methods<sup>2,3</sup> used for the generation of cyclobutadiene radical cations: method A, involving photolysis of a separately prepared  $\sigma$ -aluminum halide cyclobutadiene complex,<sup>2</sup> and method B, involving photolysis of a mixture of alkyne and Lewis acid<sup>3</sup> (Figure 1). Our results show that the radical cation 1 generated by method A is considerably more persistent than that generated by method B. The decay rates of the tetraethylcyclobutadiene

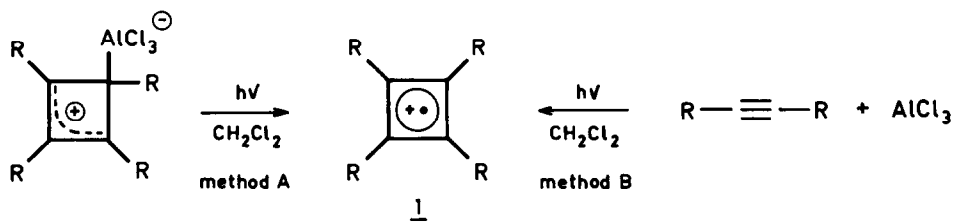


Figure 1. Methods A and B. R=CH<sub>2</sub>CH<sub>3</sub>.

radical cation 1<sup>2b</sup> (Figure 1), generated by both methods,<sup>6</sup> have been compared at -55°C: for 1 (method A)  $t_{\frac{1}{2}}$ <sup>7</sup> at -55°C is larger than 14 min, whereas for 1 (method B)  $t_{\frac{1}{2}}$ <sup>7</sup> at -55°C is  $\approx$  15 sec. Method A is clearly the method of choice with regard to persistence.

An alternative approach to enhance the persistence of cyclobutadiene radical cations is to increase the bulk of the alkyl substituent. With this in mind we have studied the tetra-neopentyl- and tetra-1-adamantylcyclobutadiene radical cations 2 and 3 (Figure 2). In the case of the tetra-neopentylcyclobutadiene radical cation 2 it was hoped that the neopentyl groups would "block" the top and bottom side of the radical moiety by pointing alternately up and down (Figure 2).

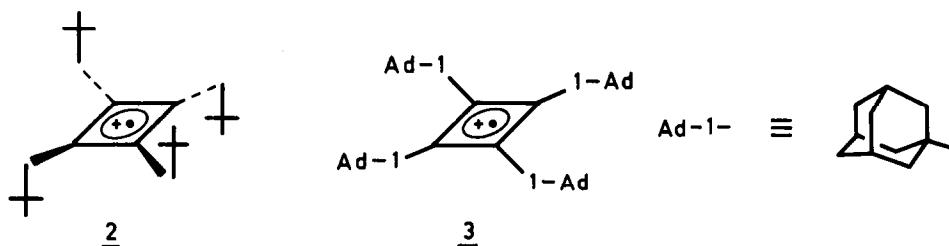


Figure 2.

Unfortunately, radical cations 2 and 3 cannot be prepared using method A,<sup>6</sup> because the corresponding  $\sigma$ -aluminum halide cyclobutadiene complexes of dineopentyl- or di-1-adamantyl-acetylene could not be obtained in any detectable amounts. The radical cations 2 and 3 can be prepared by method B;<sup>6</sup> small transient amounts of the  $\sigma$ -aluminum halide cyclobutadiene complexes are probably formed while shaking the ESR tubes cautiously at low temperatures. The decay of 2 at  $-55^\circ\text{C}$  is slow ( $t_{1/2} > 15$  min). Radical cation 2 has indeed the expected conformation (Figure 2), which can be concluded<sup>8,9</sup> from the value of  $a_{\beta}^{\text{H}}$  (8H):  $4.32 \pm 0.05$  G ( $g = 2.0026 \pm 0.0002$ ), constant in the temperature range  $-90^\circ\text{C}$  to  $-40^\circ\text{C}$ .

The decay of 3 at  $-55^\circ\text{C}$  has a  $t_{1/2}$  of  $\approx 3$  min. The best interpretation of the ESR spectrum of 3 (based on numerous computer simulations) is the following<sup>8</sup>:  $a_{\gamma}^{\text{H}}$  (16H) = 0.288 G,  $a_{\gamma}^{\text{H}}$  (8H) = 0.144 G,  $a_{\beta}^{13\text{C}}$  ( $8^{13\text{C}}$ ) = 3.456 G,  $a_{\beta}^{13\text{C}}$  ( $4^{13\text{C}}$ ) = 10.9 G<sup>11</sup> ( $g = 2.0026 \pm 0.0002$ ), invariant in the range  $-85^\circ\text{C}$  to  $-30^\circ\text{C}$  (Figure 3). The 24  $\gamma$ -H's are clearly not equivalent; 3 is frozen out in a conformation which is presumed to be 3a (Figure 3). The argument for assigning conformation 3a to 3 is twofold. The dihedral angle ( $\theta$ ) of 16  $\gamma$ -H's with the orbital containing the unpaired electron is  $30^\circ$ , for the other 8  $\gamma$ -H's however it is  $90^\circ$ . Although the Heller-McConnell equation<sup>9,10</sup> cannot be used for  $\gamma$ -H's, a small  $\theta$  still remains vital for a large coupling constant.<sup>12</sup> Secondly, conformation 3a contains 8  $\beta$ - $^{13}\text{C}$ 's with  $\theta = 30^\circ$  and 4  $\beta$ - $^{13}\text{C}$ 's with  $\theta = 90^\circ$ . Again, a small  $\theta$  will result in a large coupling constant ( $a_{\beta}^{13\text{C}}$  ( $8^{13\text{C}}$ ) = 3.456 G) and a large  $\theta$  will result in a small coupling constant ( $a_{\beta}^{13\text{C}}$  ( $4^{13\text{C}}$ ) not observed).

It is of interest to compare our results on 3 with those obtained recently for the tetra-*t*-butylcyclobutadiene radical cation (4).<sup>1,3</sup> First, hindered rotation is not observed for the *t*-butyl groups in 4. The reason for this discrepancy between the neopentyl- and 1-adamantyl groups on one hand and the *t*-butyl group on the other hand is not clear to us. Second, a  $^{13}\text{C}$ -satellite spectrum with  $a_{\beta}^{13\text{C}}$  ( $4^{13\text{C}}$ ) = 10.0 G has been observed for 4.<sup>1</sup> This  $^{13}\text{C}$ -coupling constant has been assigned to the four ring carbons in 4. The authors<sup>1</sup> interpret this large value of  $a_{\beta}^{13\text{C}}$  as an indication for a deviation of the four-membered ring in 4 from planarity. If this

interpretation is correct, this would imply that in case of 3, for which a larger  $^{13}\text{C}$ -coupling constant ( $10.9\text{ G}$ )<sup>11</sup> has been observed, the deviation from planarity is even more pronounced.

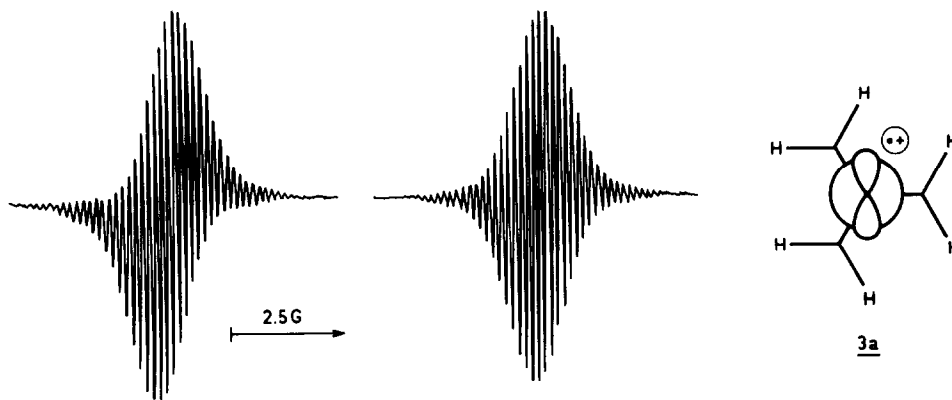


Figure 3.11 Left: exp. spectrum of 3 at  $-41^\circ\text{C}$ . Middle: computer-simulation. Right: projection of rotamer 3a.

In summary, two conclusions can be drawn from the foregoing. Firstly, 2 and 3 are much more persistent than 1 when generated under the same conditions. Secondly, the expected concomitant effect of vicinal bulky groups, i.e. hindered rotation, is indeed observed. The next step towards more persistent cyclobutadiene radical cations would be an attempt to prepare 2 and 3 via a route more conducive to persistence than the method used.

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#### References and Notes:

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6. Method A: an ESR tube filled with 0.15 mmol intensely red coloured  $\sigma$ - $\text{Al}_2\text{Cl}_6$  complex of tetraethylcyclobutadiene<sup>2b</sup> in 0.5 ml  $\text{CH}_2\text{Cl}_2$  is used.  
 Method B: an ESR tube filled with 0.3 mmol 3-hexyn, 0.3 mmol  $\text{AlCl}_3$  and 0.5 ml  $\text{CH}_2\text{Cl}_2$  is used. Both samples are deoxygenated by several freeze-thaw cycles (pressure below  $10^{-4}$  Torr, thaw cycles at  $-95^\circ\text{C}$ ). If the sample of method B is prepared and thawed carefully enough, it remains almost colourless. Both samples are sealed and stored at  $-196^\circ\text{C}$  until used.
7. The decay is followed by monitoring the height of a peak of the first derivative ESR spectrum, after switching off the lamp.
8. The designation used for the position of H's and  $^{13}\text{C}$ 's is the following: C(ring)-CoH $\beta$ -C $\beta$ H $\gamma$ .
9.  $a_{\beta}^{\text{H}}$  (12H) = 8.75 G for the tetramethyl derivative.<sup>2a</sup> Choosing  $a \cong 0$  G in the Heller-McConnell equation<sup>10</sup> ( $a_{\beta}^{\text{H}} = \rho^{\text{H}} (a + b < \cos^2\theta >)$ ) results in  $b \cong 70$  G. This leads to  $\theta = 60^\circ \pm 1^\circ$  for 2.
10. C. Heller and H.J. McConnell, J. Chem. Phys., 32, 1535 (1960).
11. The position of the  $^{13}\text{C}$ -atoms (C(ring) or C $_{\alpha}$ ?) responsible for the satellite spectrum with  $a^{13}\text{C}$  ( $X^{13}\text{C}$ ) = 10.9 G is not yet clear. The number (X) of  $^{13}\text{C}$ -atoms involved should reasonably be 4 (3,6 actually being measured). The hyperfine structure of this satellite spectrum cannot be resolved due to the low S/N ratio in the satellite spectrum. The  $^{13}\text{C}$  coupling constant of 10.9 G has, for this reason, not been included in the experimental and computer simulated spectrum shown in Figure 3.
12. For the effect of  $\theta$  on  $a_{\gamma}^{\text{H}}$  see: K.U. Ingold and J.C. Walton, J. Am. Chem. Soc., 104, 616, (1982).

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