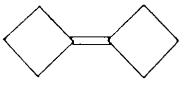
The Radical Cation of Bicyclobutylidene

Kenji Morihashi,* Hiroyuki Kometani, Ohgi Takahashi, Hideo Togo, and Osamu Kikuchi*

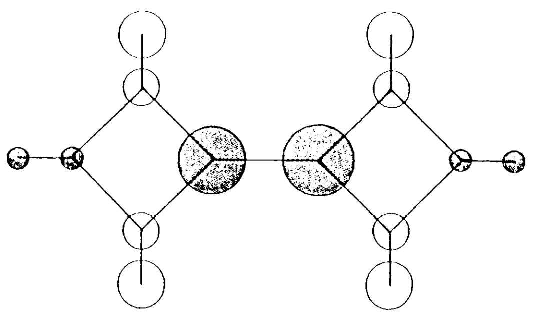
Department of Chemistry, The University of Tsukuba, Tsukuba 305, Japan

The radical cation generated from bicyclobutylidene in the $CFCl_3$ solution γ-irradiated at 77 K exhibits a 26.2 G nonet (1 G = 10^{-4} T) of 2.7 G quintets in its e.s.r. spectrum; this experimental result and INDO and MINDO/3-UHF calculations predict a planar structure for the bicyclobutylidene radical cation.

The question of twisting of alkene cation radicals is an interesting subject in the theoretical and structural chemistry of organic radical cations.[1] Recently, the effects of alkyl-group substitution on the twisting angle of alkene cation radicals were investigated experimentally[2—4] and theoretically.[5,6] For methylsubstituted alkene radical cations such as trimethylethylene and propylene cations, however, the structures suggested from the e.s.r. analysis[2] do not correspond to those predicted by the recent AM1 calculations.[6] One cause of the disagreements is the rotational flexibility of the substituted methyl-groups, which makes the e.s.r. spectra complex. Simple e.s.r. spectra of the alkene radical cations may be obtained when small-membered alkane rings are substituted on both sides of the ethylene double bond. Bicyclobutylidene (**1**) has a more rigid structure than methyl-substituted alkenes, and the e.s.r. spectra of the radical cation ($\mathbf{1}^{+\bullet}$) may give clear information about double-bond twisting. This communication reports the first e.s.r. spectrum of bicyclobutylidene radical cation ($\mathbf{1}^{+\bullet}$) generated by the solid-state Freon γ-radiolysis technique[1,7] and considers its structure.



(1)

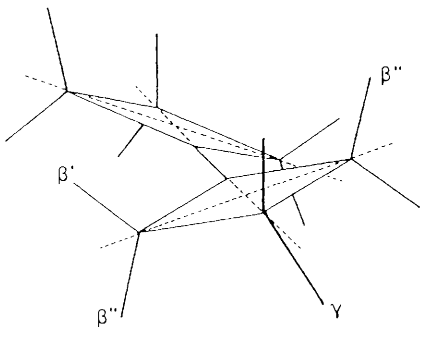


SOMO (b_{3u})

Compound (**1**) was obtained according to the literature procedure.[8] $CFCl_3$ solutions (1 mol.%) of (**1**) were γ-irradiated at 77 K, with a dose of about 0.5 Mrad. The ^{60}Co γ-irradiation and the e.s.r. measurements were performed at Tokai Establishment, Japan Atomic Energy Research Institute. The e.s.r. spectra of ($\mathbf{1}^{+\bullet}$) were observed between 108 and 133 K; the spectra were almost unchanged over this temperature range. The spectrum of ($\mathbf{1}^{+\bullet}$) at 110 K is shown in Figure 1. It consists of nine lines with a splitting constant of 26.2 G, each line being further split into five lines by 2.7 G (1 G = 10^{-4} T). The *g*-value is 2.0037. Obviously the nine and five lines arise from the eight β-protons and four γ-protons of ($\mathbf{1}^{+\bullet}$), respectively. The spectrum suggests that the unpaired π-electron on the central double bond interacts hyperconjugatively with the β- and γ-protons.

The structure of ($\mathbf{1}^{+\bullet}$) can be estimated by the comparison of the β-proton splitting with that of the tetramethylethylene cation radical ($\mathbf{2}^{+\bullet}$) generated in the same Freon matrix.[9] The splitting constant of the methyl protons (12H) for ($\mathbf{2}^{+\bullet}$) is reported to be 17.2 G, and corresponds well with that from INDO calculations assuming a planar structure.[9] The planar structure of ($\mathbf{2}^{+\bullet}$) is also predicted from recent AM1 calculations.[6] The ratio of the β-proton splitting for ($\mathbf{1}^{+\bullet}$) to that of the methyl groups for ($\mathbf{2}^{+\bullet}$) is 1.52, which agrees with the expected ratio of 1.5 (0.75 : 0.5) for the $\cos^2\theta$ dependence of the β-proton splitting in the two cations. This good agreement suggests that ($\mathbf{1}^{+\bullet}$) is a planar π-species.

With the D_{2h} planar structure optimized by MINDO/3-UHF calculations, the splitting constants for the β- and γ-protons of ($\mathbf{1}^{+\bullet}$) were calculated by the INDO-UHF method. The calculated values, 27.9 G for the β-protons and



D_2 twisted form

Figure 1. First derivative e.s.r. spectrum of ($\mathbf{1}^{+\bullet}$) in $CFCl_3$ irradiated at 77 K and measured at 110 K.

-0.3 G for the γ-protons, correspond well with the present experimental values, and this supports the planar structure of (**1**+$^{\bullet}$). The favourable planar structure is also predicted from the singly occupied MO(SOMO). The b_{3u} SOMO of planar (**1**$^{+\bullet}$) is the ethylenic π orbital. It has bonding character between the central carbon atoms and more than 70% of the unpaired electron is localized at these carbon atoms. The strong bonding character of the central ethylene unit in the SOMO is effective in preventing the double bond from twisting. Thus the planarity of (**1**$^{+\bullet}$) makes the SOMO stable. The hyperconjugative stabilization of the SOMO with the cyclobutylidene rings is also important in keeping the planar structure.

The probable twisted structure of (**1**$^{+\bullet}$) may have D_2 symmetry. In the twisted structure, the eight β-protons of (**1**$^{+\bullet}$) are not equivalent, and they split into two sets of four protons, *i.e.*, $4H_{\beta'}$ and $4H_{\beta''}$. As the twisting angle of the double bond becomes larger, the difference between the splitting constants for $4H_{\beta'}$ and $4H_{\beta''}$ becomes more marked. In fact, with the MINDO/3 optimized D_2 structure, where the twisting angle is 36.8°, the splitting constants calculated by INDO are 37.5 ($4H_{\beta'}$), 3.1 ($4H_{\beta''}$), and -1.0 G ($4H_{\gamma}$). In the MINDO/3 calculations, the total energy of the twisted form of (**1**$^{+\bullet}$) is 2.1 kcal/mol (1 cal = 4.184 J) lower than that of the planar form. If the MINDO/3 result for the energy difference is correct, the planar structure is the transition state between rapidly interconverting twisted structures, such that an average splitting is observed from the eight β-protons. However, no alternating linewidth effect was observed in the temperature range of the present e.s.r. measurements. This MINDO/3 result for the total energies of the two forms is rather unexpected and may arise from a defect of MINDO/3 calculations in underestimating stabilities of conjugate systems. It is difficult to explain the nine-line e.s.r. spectrum of (**1**$^{+\bullet}$) with assumption of a twisted structure. Although bent forms of the cyclobutylidene rings, the C_{2v} *syn*- and C_{2h} *anti*-forms, may also be considered as alternative structures for (**1**$^{+\bullet}$), the equivalence of the eight β-protons is lost as is shown in the D_2 twisted form. The present nine-line e.s.r. spectrum and MO calculations support the planar D_{2h} structure for (**1**$^{+\bullet}$).

Received, 14th April 1989; Com. 9/01539F

References

1 M. C. R. Symons, *Chem. Soc. Rev.*, 1984, **12**, 393.

2 K. Toriyama, K. Nunome, and M. Iwasaki, *Chem. Phys. Lett.*, 1984, **107**, 86.

3 M. Shiotani, Y. Nagata, and J. Sohma, *J. Phys. Chem.*, 1984, **88**, 4078.

4 J. Fujisawa, S. Sato, K. Shimokoshi, and T. Shida, *J. Phys. Chem.*, 1985, **89**, 5481.

5 D. J. Bellville and N. L. Bauld, *J. Am. Chem. Soc.*, 1982, **104**, 294.

6 T. Clark and S. F. Nelsen, *J. Am. Chem. Soc.*, 1988, **110**, 868.

7 T. Shida, E. Haselbach, and T. Bally, *Acc. Chem. Res.*, 1984, **17**, 180.

8 L. K. Bee, J. Beeby, J. W. Everett, and P. J. Garratt, *J. Org. Chem.*, 1975, **40**, 2212.

9 T. Shida, Y. Egawa, H. Kubodera, and T. Kato, *J. Chem. Phys.*, 1980, **73**, 5963.