The Radical Cation of Bicyclopropylidene: ESR Spectrum, Structure, and Reaction Products

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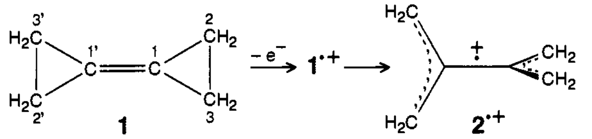
Abstract: Whereas the radical cation of bicyclopropylidene (**1**) in a CF_3CCl_3 matrix rearranges to that of tetramethyleneethane (**2**) already at 77 K, it persists in $CFCl_3$ and $CF_2ClCFCl_2$ matrices up to ca. 100 K, giving rise to a well-defined ESR spectrum. On going from **1** to $\mathbf{1}^{\bullet+}$, the set of eight equivalent β-protons splits into two sets of four, as the two protons in each CH_2 group have greatly differing coupling constants, 2.24 and 0.27 mT. This striking inequivalence is due to considerable changes in geometry upon ionization of **1**, such as a twist about the central C(1)−C(1′) bond and some unusual features of the electronic structure of $\mathbf{1}^{\bullet+}$. Above 100 K, the spectrum of a secondary paramagnetic species appears which in the $CFCl_3$ matrix is also $\mathbf{2}^{\bullet+}$. In the $CF_2ClCFCl_2$ matrix, on the other hand, an allyl-type radical $\mathbf{4}^{\bullet}$ is formed by the loss of a proton from $\mathbf{1}^{\bullet+}$, without opening of the three-membered rings.

Several years ago, it was reported in a preliminary communication[1] that the radical cation of bicyclopropylidene (**1**), generated from the neutral compound by γ-irradiation in a CF_3CCl_3 matrix at 77 K, rapidly rearranges to the radical cation of tetramethyleneethane (**2**).



Recently, we have found that the propensity of $\mathbf{1}^{\bullet+}$ to undergo such a rearrangement depends on the Freon matrix used and that the primary radical cation $\mathbf{1}^{\bullet+}$ can also be detected. Here, we describe its ESR spectrum and discuss its rather unusual structure. The nature of the secondary paramagnetic species, to which $\mathbf{1}^{\bullet+}$ converts at higher temperatures, is also matrix-dependent.

Results

In $CFCl_3$ and $CF_2ClCFCl_2$ matrices, contrary to CF_3CCl_3, the primary radical cation $\mathbf{1}^{\bullet+}$ persists up to ca. 100 K. Its ESR spectrum, taken with a $CFCl_3$ matrix at 90 K, is reproduced in Figure 1 ($g = 2.0028 \pm 0.0002$). The hyperfine pattern consists essentially of a quintet spaced by 2.24 ± 0.02 mT and split into another quintet with a separation of 0.27 ± 0.01 mT. Computer simulation, which uses these values for isotropic coupling constants, each of four equivalent protons, is also shown in Figure 1; it reproduces well the major features of the ESR spectrum. Differences between experimental and calculated derivative curves appear as deviations of the peak amplitudes from the binomial intensity distribution and as some underlying unidentified signals which distort the shape of several components (marked by asterisks). These differences were more or less pronounced for all samples studied, and they essentially remain, even when the temperature is lowered from 90 to 30 K. Attempts to account for them by hyperfine and/or g anisotropy and/or by formation of secondary paramagnetic products did not prove conclusive. Moreover, ENDOR spectra which might have provided additional information, as has often been the case with radical cations in Freon matrices,[2] were rather poor and unreliable for $\mathbf{1}^{\bullet+}$.

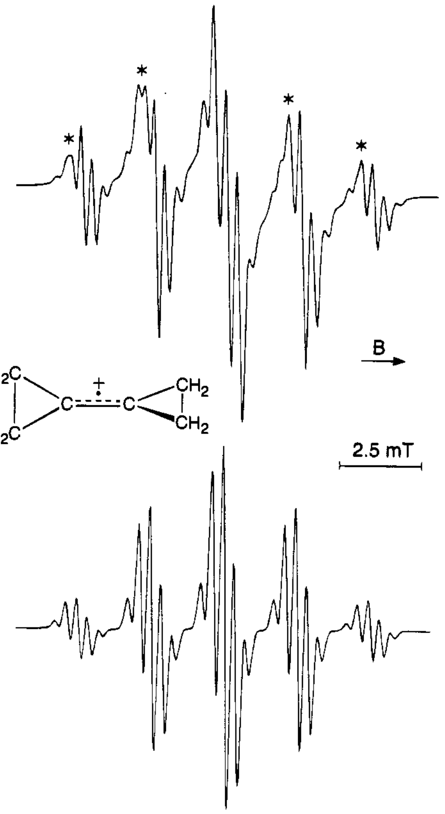


Figure 1. (top) ESR spectrum of $\mathbf{1}^{\bullet+}$ in a $CFCl_3$ matrix at 90 K. (bottom) Computer simulation with the use of the coupling constants, 2.24 and 0.27 mT, each for four protons: line shape, Gaussian; line width, 0.25 mT.

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[1] Gerson, F.; de Meijere, A.; Qin, X.-Z. *J. Am. Chem. Soc.* **1989**, *111*, 1135–1136.

[2] Gerson, F. *Acc. Chem. Res.* **1994**, *27*, 63–69.

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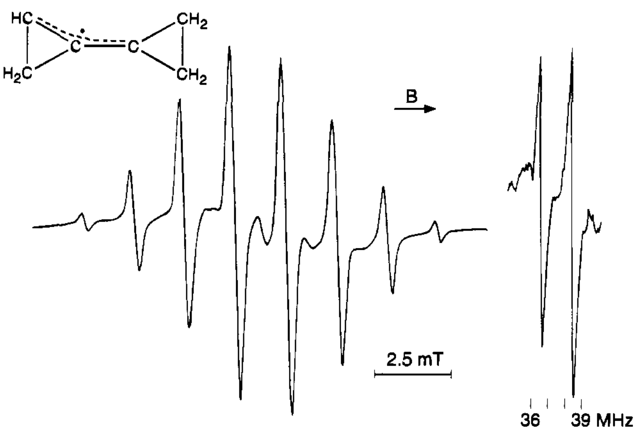
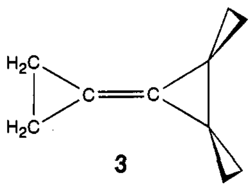


Figure 2. (left) ESR spectrum of **4**$^\bullet$ in a $CF_2ClCFCl_2$ matrix at 120 K. (right) Corresponding proton-ENDOR signals.

The ESR spectrum of $\mathbf{1}^{\bullet+}$ clearly establishes that, on passing from the neutral compound **1** (symmetry D_{2h})[3,4] to its radical cation, the set of eight equivalent protons separates into two sets of four. Theoretical calculations, specified in the Discussion, indicate that $\mathbf{1}^{\bullet+}$ is not planar and that the two β-protons[5] in each of the four CH_2 groups are not equivalent. This statement is consistent with the ESR spectrum of the radical cation generated under the same conditions from 7-cyclopropylidenedispiro[2.0.2.1]heptane (**3**). The hyperfine pattern



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of $\mathbf{3}^{\bullet+}$ is a triplet spaced by 2.5 ± 0.1 mT, arising from two equivalent protons in that cyclopropylidene moiety which has not been modified by the cyclopropanation at the other end. The splittings from the remaining protons in $\mathbf{3}^{\bullet+}$ are masked by the large line width (0.5 mT) of the triplet components.

Upon raising the temperature above 100 K, the ESR spectrum of $\mathbf{1}^{\bullet+}$ in $CFCl_3$ and $CF_2ClCFCl_2$ matrices is gradually replaced by that of a secondary paramagnetic product. With $CFCl_3$, the new species is the same as that previously observed with CF_3CCl_3,[1] i.e. the radical cation $\mathbf{2}^{\bullet+}$, whereas an allyl-type radical forms in $CF_2ClCFCl_2$ by the loss of a proton from a CH_2 group of $\mathbf{1}^{\bullet+}$, without opening of the three-membered rings. The ESR spectrum of this radical ($\mathbf{4}^\bullet$) presented in Figure 2 (g = 2.0032 ± 0.0002) is an octet spaced by 1.64 ± 0.02 mT, arising from seven equivalent or nearly equivalent protons. Two coupling constants of 44.0 ± 0.2 MHz or 1.57 ± 0.01 mT and 47.8 ± 0.2 MHz or 1.71 ± 0.01 mT are derived from the corresponding ENDOR signals at 36.5 and 38.4 MHz (Figure 2) with 14.5 MHz as the frequency of the free proton. The similar intensities of these signals of "isotropic" shape point to a comparable number of protons giving rise to them, and the average of the two coupling constants is equal to the value observed in the ESR spectrum. According to MO calculations for $\mathbf{4}^\bullet$ (see below), the larger coupling constant should be assigned to the single α-proton and the two CH_2 β-protons at the three-membered ring, from which the proton is abstracted, thus leaving the smaller value for the four β-protons at the unaffected ring.[5]

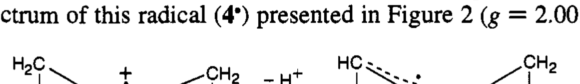

Table 1. Structural Data for **1** and $\mathbf{1}^{\bullet+}$

			1		$\mathbf{1}^{\bullet+}$	
	el diff	X-ray	AM1	6-31G**	AM1	6-31G**
C(1)−C(1′)[a]	131.4	131.4	129.1	129.6	132.2	134.2
C(1)−C(2)	146.8	146.9	146.7	146.2	147.8	147.1
C(2)−C(3)	155.4	154.4	151.4	152.7	150.1	150.1
C−H			110.6	107.8	111.3	107.7
C(2)C(1)C(3)[b]	63.8	63.4	62.1	63.0	61.0	61.4
HCH			111.8	114.3	111.4	115.3
ω[c]	0	0	0	0	43.0	32.8

[a] Bond lengths in pm. [b] Angles in degrees. [c] Angle of twist about the C(1)−C(1′) bond.

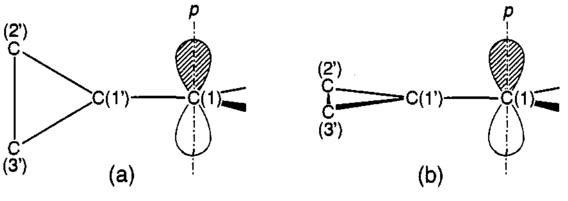

Figure 3. Three-membered ring and the (positively charged) exocyclic π-center in $\mathbf{1}^{\bullet+}$. (a) parallel and (b) perpendicular conformations.

Discussion

Table 1 lists the structure parameters computed for **1** and $\mathbf{1}^{\bullet+}$ by a semiempirical (AM1)[6] and an *ab initio* (6-31G**)[7] procedure, along with corresponding data determined for **1** by electron diffraction (el diff)[3] and X-ray crystallography.[4] The excellent agreement between the experimental and theoretical values for **1** assures that those calculated for $\mathbf{1}^{\bullet+}$ by the same MO methods can be trusted with a considerable degree of accuracy. Surprisingly, on going from **1** to $\mathbf{1}^{\bullet+}$, the bond lengths and the bond angles are predicted to change only slightly; in particular, the C(1)−C(1′) bond is not markedly lengthened, despite the removal of an electron from it. As the most striking consequence of the ionization, the calculations predict a twist about this central C(1)−C(1′) bond by an angle ω of about 40° (Table 1), whereby the symmetry of the molecular framework is reduced from D_{2h} to D_2 and the two β-protons, H_I and H_{II}, in each CH_2 group become inequivalent. Both structural features of $\mathbf{1}^{\bullet+}$, the relative shortness of the now essentially one-electron C(1)−C(1′) π-bond and the twist about it, can be considered as being due to the conjugation between the Walsh orbitals of the three-membered rings and the positively charged, exocyclic π-centers.[8] Such a stabilizing interaction between the C(1′)C(2′)C(3′) ring and the C(1) atom (Figure 3), on one side, and between the C(1)C(2)C(3) ring and the C(1′) atom, on the other, would strengthen the C(1)−C(1′) bond. The twist about this bond can be interpreted as the tendency of three-membered rings to adopt a conformation parallel to the p-axes at the respective exocyclic π-centers, in which conformation (Figure 3a) the

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(3) Traetteberg, M.; Simon, A.; Peters, E. M.; de Meijere, A. *J. Mol. Struct.* **1984**, *118*, 333−343.

(4) Boese, R.; Haumann, T.; de Meijere, A.; Kozhushkov, S. *Acta Crystallogr.*, submitted for publication.

(5) In ESR spectroscopy, protons separated by 0, 1, 2 ... sp^3-hybridized carbon atoms from a π-center are denoted α, β, γ, ...

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(7) *Spartan*, Version 3.1.5., Wavefunction Inc., Irvine, CA, 1993. See also: Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory;* Wiley: New York, 1986; pp 10−62.

(8) Deno, N. C.; Richey, H. G., Jr.; Liu, J. S.; Lincoln, D. N.; Turner, J. O. *J. Am. Chem. Soc.* **1965**, *87*, 4533−4538. Pittman, C. U., Jr.; Olah, G. A. *Ibid.* **1965**, *87*, 5123−5132.

interaction is more effective than in the perpendicular one (Figure 3b).[8]

The proton-coupling constants can be directly obtained from the AM1 s-spin populations at the H atoms by means of a conversion factor $K_\beta = +117.7$mT which was derived from correlation of such populations with experimental data for a number of radical ions;[9] these values are $a(\mathrm{H_I}) = +3.18$ and $a(\mathrm{H_{II}}) = -0.06$ mT. It is interesting to note that use of the same factor K_β with the s-spin populations calculated by the semiempirical MNDO procedure,[10] a forerunner of AM1, yields $a(\mathrm{H_I}) = +2.49$ and $a(\mathrm{H_{II}}) = -0.22$ mT, in even better agreement with the observed $|a(\mathrm{H})|$ values of 2.24 and 0.27 mT. The coupling constants computed by the INDO method[11] for the 6-31 G^{**}-optimized geometry come to $a(\mathrm{H_I}) = +2.47$ and $a(\mathrm{H_{II}}) = -0.14$ mT. These results corroborate both the assignment of the observed ESR spectrum (Figure 1) to $\mathbf{1}^{\bullet+}$ and the reliability of the applied MO procedures. The predicted negative sign of $a(\mathrm{H_{II}})$ is rather unexpected because opposite signs of the coupling constants of β-protons in the same CH_2 groups are unprecedented.[12] Unfortunately, this sign of $a(\mathrm{H_{II}})$, which may be an artifact of the calculation, could not be verified experimentally.[14]

It is tempting to rationalize the greatly differing $a(\mathrm{H_I})$ and $a(\mathrm{H_{II}})$ values in terms of the conventional equation for β-proton coupling constants[17]

$$a(\mathrm{H}) = (B_0 + B\cos^2\theta)\varrho_\mu \tag{1}$$

where B_0 and B are parameters involving π,σ-spin polarization and π,σ-spin delocalization (hyperconjugation), respectively; ϱ_μ stands for the π-spin population at the carbon center μ bearing the CH_2 group, while θ is the dihedral angle between the p-axis at this center and the C−H bond. In $\mathbf{1}^{\bullet+}$, the angles θ are those between the p-axis at the π-centers C(1) or C(1′) and the C−H bonds of that three-membered ring, in which the pertinent carbon atom participates, i.e. C(2)−H and C(3)−H for C(1) (Figure 4) or C(2′)−H and C(3′)−H for C(1′). As $|B_0|$ is much smaller than $|B|$, it is, in general, neglected so that eq 1 simplifies to

$$a(\mathrm{H}) = B\cos^2\theta\,\varrho_\mu \tag{2}$$

Accordingly, the β-protons in the same CH_2 group should have coupling constants $a(\mathrm{H})$ of the same sign.

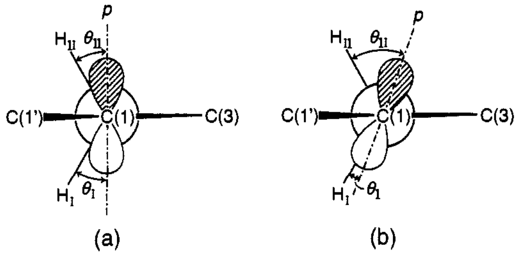
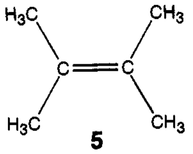


Figure 4. Newman projections at C(1) in $\mathbf{1}^{\bullet+}$ viewed in the direction of the C(1)−C(2) bond: (a) $\theta_I = \theta_{II} \approx 30°$ and (b) $\theta_I \approx 10°$, $\theta_{II} \approx 50°$.



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An appropriate reference species for $\mathbf{1}^{\bullet+}$ is the radical cation of 2,3-dimethylbut-2-ene (tetramethylethene, **5**) which, like $\mathbf{1}^{\bullet+}$, has a formal π-spin population ϱ_μ of 0.5 at each of its two carbon centers μ. The coupling constant, $a(\mathrm{H})$, of the 12 equivalent CH_3 β-protons in $\mathbf{5}^{\bullet+}$ is 1.72 mT,[18] and its positive sign can be taken for granted. Setting this value in eq 2 with $\langle\cos^2\theta\rangle = 0.5$ for the freely rotating methyl substituents leads to a parameter $B = +6.9$ mT, which in turn may be used for $\mathbf{1}^{\bullet+}$ to calculate $a(\mathrm{H_I})$ and $a(\mathrm{H_{II}})$ by means of the same relation. Such a procedure would yield $a(\mathrm{H_I}) = a(\mathrm{H_{II}}) = +2.6$ mT if the dihedral angles θ_I and θ_{II} for C−H_I and C−H_{II} were equal and both amounted to ca. 30° (Figure 4a). The coupling constant thus calculated resembles the observed one for $|a(\mathrm{H_I})| = 2.24$ mT, but it is in sharp variance with experiment for $|a(\mathrm{H_{II}})| = 0.27$ mT. In order to account for this discrepancy, the following arguments can be put forward.

The dihedral angles θ_I and θ_{II} are not equal because MO calculations suggest that the p-axes at the spin-bearing π-centers C(1) and C(1′) in $\mathbf{1}^{\bullet+}$ deviate by ca. 20° from orthogonality to the plane of the adjacent three-membered ring (Figure 4b). This structure contrasts with that of $\mathbf{5}^{\bullet+}$ which, according to calculations of the same kind, should have the p-axes at the π-centers strictly orthogonal to the molecular plane. If the deviations of the p-axes in $\mathbf{1}^{\bullet+}$ are taken at face value, the angles θ_I and θ_{II} turn ca. 10 and 50°, respectively, and eq 2 would give $a(\mathrm{H_I}) = +3.3$ and $a(\mathrm{H_{II}}) = +1.4$ mT. These results are still quite far from the experimental findings. Use of eq 1 instead of eq 2, to match the observed coupling constants, requires a parameter B_0 of such a magnitude (−2 mT) that a straightforward applicability of the eqs 1 and 2 to the β-protons in $\mathbf{1}^{\bullet+}$ must seriously be doubted.

On the other hand, when the conjugation of the Walsh orbitals at the three-membered rings with the respective exocyclic π-centers bearing charge and spin populations of ca. 0.5 is invoked, the protons in $\mathbf{1}^{\bullet+}$ are no longer exclusively β but additionally acquire "γ-character" [5] (Figure 5). The contributions by hyperfine γ-splitting to $a(\mathrm{H_I})$ and $a(\mathrm{H_{II}})$ should be very different because one of the C−H bonds in a CH_2 group is aligned with the p-axis at the corresponding exocyclic π-center and the other is not. Even when originating from positive spin populations at the π-centers, these contributions can be negative[13,19] and, thus, cancel the positive ones from the "conventional" hyperfine β-coupling.

Calculations, analogous to those carried out for the radical cation $\mathbf{1}^{\bullet+}$, bear out the expectation that the neutral radical $\mathbf{4}^{\bullet}$ formed therefrom should be planar. The coupling constants

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(12) Such findings have been reported for the γ-protons.[13]

(13) Gaze, C.; Gilbert, B. C. *J. Chem. Soc., Perkin Trans. 2* **1977**, 116−121, 754−759. Ess, C. H.; Gerson, F.; Adam, W. *Helv. Chim. Acta* **1991**, *74*, 2078−2093.

(14) When the ESR spectrum of a radical cation in a Freon matrix is observed, the relative signs of proton-coupling constants can, in principle, be derived therefrom by a general-TRIPLE-resonance experiment.[15] Also, it is often possible to determine the absolute signs of these values, if the residual hyperfine anisotropy is resolved in the ENDOR spectrum.[2,16] Unfortunately, information of either kind was not available for $\mathbf{1}^{\bullet+}$.

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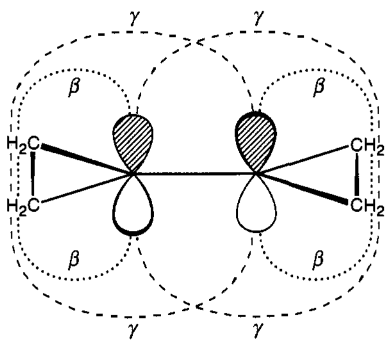
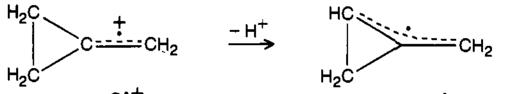


Figure 5. β- and γ-hyperfine interactions in **1**$^{\bullet+}$.

predicted for the seven protons in **4**$^{\bullet}$ are in fair agreement with the experimental values and thus allow a tentative assignment to individual positions (see Results).

Concluding Remarks

Bicyclopropylidene (**1**), in which each of the two central carbon atoms forming the double bond is part of a three-membered ring, provides, in a 3-fold way, a paradigm for oxidation of a small organic molecule. Firstly, the striking structural change on going from **1** to **1**$^{\bullet+}$ is in common with that of other related hydrocarbons upon ionization.[2,20,21] This statement holds, in particular, for molecules containing three-membered rings such as cyclopropane,[20,22] bicyclo[1.1.0]butane,[2,23] bicyclo[2.1.0]pentane,[24] and their methyl derivatives,[2,16,25,26] as well as spiro[2.2]pentane.[27] However, in the radical cations of the quoted molecules, there is a marked weakening of a C−C σ-bond in a three-membered ring, whereas in **1**$^{\bullet+}$, the π-bond becomes twisted without substantial changes of the bond lengths. Secondly, rearrangement of **1**$^{\bullet+}$ to **2**$^{\bullet+}$ by ring openings is characteristic of strained rings in radical cations undergoing thermally or photolytically induced isomerization.[2,16,20,21,24-30] Thirdly, conversion of **1**$^{\bullet+}$ into **4**$^{\bullet}$ is a well-documented bimolecular reaction of radical cations having alkyl protons adjacent to a double bond, so that an allyl-type neutral radical is easily formed therefrom by the loss of a proton; this reaction occurs preferably in the "mobile" $CF_2ClCFCl_2$ matrix upon raising the temperature.[20,21,31,32] Most relevant in respect to the formation of **4**$^{\bullet}$ from **1**$^{\bullet+}$ is the finding that the radical cation of methylenecyclopropane (**6**) yields the neutral radical **7**$^{\bullet}$ under the same conditions.[33]



6$^{\bullet+}$ **7**$^{\bullet}$

Experimental Section

Bicyclopropylidene (**1**)[34] and 7-cyclopropylidenedispiro[2.0.2.1]heptane (**3**)[35] were prepared according to the recently published new procedures.[36]

A ^{60}Co source was used for γ-irradiation (dose of ca. 0.5 Mrad; concentration of substrates $10^{-1}-10^{-2}$ mol dm^{-3}). The ESR spectra were taken on a Varian-E9 instrument and a Bruker ESP-300-system equipped with an ENDOR unit and an ESR-900 continuous-flow cryostat (Oxford-Instruments Ltd.).

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