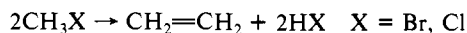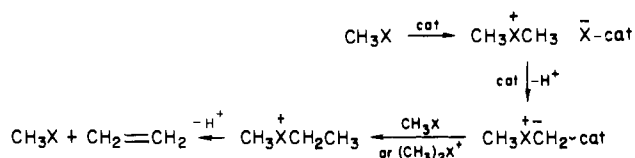of the corresponding methylhalonium methylide. Methylhalonium methylides, as shown in our preceding work, play a key role in the bifunctional acid–base-catalyzed condensation of methyl halides to ethylene

$$2CH_3X \rightarrow CH_2{=}CH_2 + 2HX \quad X = Br, Cl$$

involving the following pathway[16]

Experimental Section

a. Reaction of Methylene with Alkyl Halides. Gaseous diazomethane was prepared by treating *N*-nitrosomethylurea with 80% potassium hydroxide solution under exclusion of light at 0 °C.[10] The diazomethane was then passed through potassium hydroxide pellets under an argon stream and transferred into the cooled methyl or ethyl halide (generally −78 °C). Diazomethane-d_2 was prepared by the reaction of sodium deuteriooxide with *N*-nitrosomethylurea in dimethoxyethane/D_2O[11] and transferred by a stream of argon directly into the corresponding ethyl halide.

A solution of diazomethane or dideuterated diazomethane (prepared from 0.3 g of *N*-nitrosomethylurea) in the corresponding alkyl halide (1 mL) in a reaction tube equipped with a reflux condenser (cooled to −78 °C) was irradiated with a 275-W Sylvania Sunlamp. The apparatus was covered with aluminum foil to ensure that only the liquid phase was exposed to light. After the run was complete (indicated by the disappearance of the yellow color, usually 30 to 60 min), the reaction mixture was cooled to −78 °C in order to condense the low-boiling products and then analyzed by GC and GC/MS. A solution of diazomethane (prepared from 0.3 g of *N*-nitrosomethylurea) in ethyl chloride (1 mL) and

0.05 g of diphenylamine was illuminated as above. Analysis of the reaction mixture indicated a product distribution for the reaction of methylene with ethyl halide comparable to that shown in Table I.

b. Reaction of Dimethyliodonium Hexafluoroantimonate with Sodium Hydride. $(CH_3)_2I^+SbF_6^-$ was prepared by reacting methyl halide in SO_2 with CH_3F/SbF_5 in SO_2 at −78 °C.[17] Removal of SO_2 gave the dimethyliodonium salt in high purity. Sodium hydride (Alfa, 61% mineral oil dispersion) was washed 3 times with pentane followed by heating under vacuum till all traces of hydrocarbons were removed.

One millimole of the dimethyliodonium salt and 10 mmol of sodium hydride were thoroughly mixed under argon atmosphere in a flask cooled to −78 °C. The flask was then connected to a cold trap (−78 °C) and closed with a rubber balloon in order to prevent any gaseous products from escaping. The salt mixture was then mildly heated in order to initiate the reaction. Samples of condensed and gaseous products were analyzed by GC and GC/MS.

c. Preparation of Methyl[(trimethylsilyl)methyl]halonium Hexafluoroantimonates and Their Attempted Reaction with CsF. The corresponding halomethyltrimethylsilane in SO_2ClF was mixed with an equimolar amount of SbF_5/CH_3F in SO_2 at −78 °C. Attempted isolation of the halonium salts lead to disproportionation as indicated by NMR analysis. Reaction with CsF gave only fluoride alkylation products.

d. Analysis. GC analysis of the reaction mixture was conducted on the following instruments: (a) Varian 3700 with an OV 101 glass capillary column (50 m); (b) Hewlet-Packard 5130A with a Poropak Q column (12 ft by $^1/_8$ in.). All percentage numbers are corrected for FID response factors and are given in mol %.

MS data of gas samples were obtained by using a Hewlett-Packard 5985Aa GC/MS system equipped with a Poropak column.

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Long Bonds in Cation Radicals of Vicinally Difunctional Molecules

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Abstract: Ab initio theoretical studies suggest a unique stabilizing effect of vicinal electron donor substituents on long bond cation radical structures. Although cation radicals of amines appear to be of the aminium salt type, with the cation radical character largely localized on nitrogen, the calculated structural minimum of the 1,2-ethanediamine cation radical is a long bond structure which lies 11 kcal below the best localized (aminium salt) type structure. Despite powerful stabilization of the dissociated aminomethyl cation and radical, the long bond maintains substantial bond strength ($D = 23$ kcal).

Theoretically predicted structures of alkane cation radicals are characterized by a unique valence, the elongated, one-electron bond (long bond).[1-5] The optimum length calculated for the carbon/carbon bond of the ethane cation radical, for example, is 1.920 Å,[3] and the dissociation energy is 43 kcal mol^{-1}.[4,5] More complex alkane cation radicals appear to have one such long bond in which the SOMO (single occupied MO) and the "cation radical character" are rather highly localized.[4,5] Recognition of such long

bond structures has already proved fruitful in both vapor phase (e.g., mass spectrometric[6]) and solution (e.g., cycloaddition[7]) chemistry of cation radicals. Recent theoretical research has further suggested that ground state long bond structures may be found for cation radicals of such functionalized organic molecules as alcohols, ethers, and halocarbons.[4] However, cation radicals of molecules containing relatively more ionizable functional groups, such as alkenes, arenes, aldehydes, ketones, amines, and sulfides were predicted generally to have their cation radical sites essentially localized on the ionizable functionality (n or π type cation

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Table I. Bond Lengths and Dissociation Energies of (Long Bond) Vicinally Disubstituted Cation Radicals

Structural Minimum	R_{CC} (MNDO)	R_{CC} (6-31G*)[a]	$D(\overset{+}{C\cdot\cdot C})$ kcal mol⁻¹ (6-31G*)[b]
CH₃⸱⸱⸱CH₃	1.908	1.983	38
HOCH₂⸱⸱⸱CH₂OH	2.086	2.048	23.6
H₂NCH₂⸱⸱⸱CH₂NH₂	1.739	2.030	22.6
HOCH₂⸱⸱⸱CHO	1.768	c	c
H₂NCH₂⸱⸱⸱COOH	1.608	c	c
H—CNHCH₂⸱⸱⸱CNH₂ (diamide)	1.660	c	c
CH₂—CH₂ / HOCH⸱⸱⸱CHOH	2.266	c	c

[a] Optimized at the 4-31G level, with further optimizations of the CC bond at 6-31G*. [b] Calculated by using energies of the dissociation fragments (6-31G*//4-31G). [c] Not computed.

radicals).[4] Theoretical studies of the structures of di- and polyfunctional molecules have not previously been carried out, but they are of relevance to biological chemistry. The present theoretical study suggests that cation radicals of even molecules containing easily ionizable functionality can adopt ground state long bond structures when these functional groups are situated vicinally.

The vicinal disubstitution pattern (1) was chosen for emphasis, in part, because it was apparent that this relative disposition allows both substituents (−Ẍ) simultaneously to stabilize the long bond structure (3), whereas in the absence of neighboring group effects only one of them could presumably contribute major stabilization to the n type structure (2). In addition, this pattern appeared

1 2 (n type) 3 (σ/n type; "long bond")
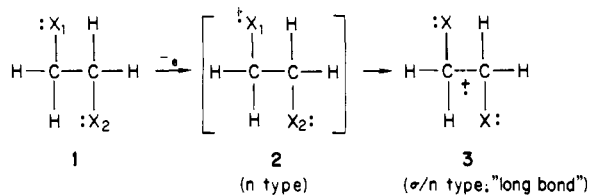
relevant to biologically important molecules such as proteins and carbohydrates. Previous theoretical studies from this laboratory have validated the reliability of MNDO for calculating cation radical structures, by comparing the MNDO structures to those obtained from extended basis set ab initio SCF MO calculations (4-31G and 6-31G*).[4] This efficient calculational approach was retained in the present research, where MNDO was used as the primary calculational method, with extensive checking via extended basis set ab initio calculations.

With cation radicals of simple alcohols (except methanol), both MNDO and 6-31G* ab initio SCF MO calculations reveal energy minima for both long bond and n type structures.[4] For all of these except, possibly, ethanol the long bond structure ($R = 2.015$ Å) is predicted to represent the ground state.[4] In the case of the cation radical of ethylene glycol (1, $X_1 = X_2 = OH$; Table I), no minimum exists at any geometry corresponding to an n type cation radical, the sole energy minimum corresponding to a long bond structure. The SOMO reveals concentration in the CC bond but with extensive delocalization to both hydroxyl substituents (the MNDO coefficients are $a_C^{SOMO} = 0.54$, $a_O^{SOMO} = 0.38$). The hydroxyl protons are virtually perpendicular to the CCO plane (98°) as required for overlap of an oxygen p_x lone pair with the appropriate long bond orbitals (primarily the carbon $2p_x$ orbitals). Such cation radical structures have been referred to as σ/n structures. The fact that dissociation of 3 would yield a highly stabilized carbocation (hydroxymethyl) elicits the concern that the long bond strength in 3 might become negligibly small. Actually the dissociation energy ($D = 23.6$ kcal mol⁻¹; 6-31G*)

is only modestly less than that in the ethane cation, once again confirming the unique ability of the long bond to optimally utilize vicinal substituent stabilization.

The highly ionizable amine function normally generates only n type cation radical structural minima.[4] In contrast, 1,2-ethanediamine (1, $X_1 = X_2 = NH_2$; Table I) has only a long bond minimum. Again the dissociation energy $D = 22.6$ kcal·mol⁻¹ (6-31G*) is impressive in comparison with the value for the ethane cation radical and especially so when it is recalled that the amino substituent stabilizes the aminomethyl carbocation fragment by 93 kcal![7] The n type structure (2) was also explored by setting the CC bond length at 1.54 Å and optimizing all other parameters (4-31G). The 6-31G* energy corresponding to this structure is 11.2 kcal higher than that of the long bond structure. It should be emphasized that no symmetry constraints were imposed in any of these calculations. Nevertheless, the optimum long bond structures of both the glycol and diamine cation radicals are essentially symmetrical. The optimum localized structures, constraining only the C−C bond length, were, of course, highly unsymmetrical and had the cation radical character essentially localized on a single heteroatom. Calculations were performed only on the anti conformers of the glycol and diamine cation radicals and, although the structures were optimized with respect to torsional angle, calculations on the gauche conformers, where neighboring group effects might become involved, have not yet been specifically investigated. Although it is conceded that the present single configuration description of the cation radical long bond is less satisfactory than a MCSCF or CI description, the qualitative principle of specific stabilization of long bond structures by vicinal electron donors undoubtedly should remain valid. Further, the implementation of MP2 and MP3 (CI) descriptions to alkane cation radicals does not invert the predicted preference for the long bond structure in these instances.[5]

In similar fashion to amine cation radicals, the cation radicals of aldehydes and ketones normally exhibit only n type structural minima, but hydroxyacetaldehyde (4) has only a long bond minimum (though not so elongated as in the earlier cases). Glycine, too, appears to prefer a somewhat elongated structure (Table I). Finally, a simplified, model peptide structure was investigated and found to have a long bond minimum. This result suggests a novel mode of cleavage for at least some peptide cation radicals, viz., carbon/carbon bond cleavage at the amide carbonyl.

Vicinally difunctional cation radicals are also of special importance in cation radical olefin cyclodimerizations and cycloadditions.[8] The cyclobutane cation radical formed from cycloaddition of ethene cation radical to ethene has been predicted to have a long bond structure with sufficient bond strength to prevent the rotations which would engender a loss of stereospecificity.[9] Recent calculations including correlation energy estimates, however, place the long band structure (trapezoid) slightly above the rhomboid structure of the cyclobutane cation radical.[5] In practice, virtually all such cation radical cyclodimerizations generate cyclobutane cation radical systems which have vicinal electron donor substituents. In view of the present results, the proposed long bond cyclobutane structures should still be valid for these systems. Indeed, MNDO calculations (Table I) suggest a long bond structural minimum for the 1,2-dihydroxycyclobutane cation radical. In significant contrast, the hydroxycyclobutane cation radical has it sole minimum at a structure which is essentially open ($R = 2.785$).

Registry No. 3 (X = H), 34488-65-8; **3** (X = OH), 83957-60-2; **3** (X = NH₂), 97011-21-7; hydroxyacetaldehyde radical cation, 88034-33-7; aminoacetic acid radical cation, 35492-82-1; 2-(formylamino)acetamide radical cation, 96999-42-7; cyclobutane-1,2-diol radical cation, 97059-11-5.

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