BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 52—56 (1970)

Chemical Reactivity of Adamantane and Related Compounds

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(Received June 17, 1969)

The chemical reactivity of hydrogens in adamantane and substituted adamantanes has been calculated. The results of calculation have shown that the bridgehead hydrogens are most reactive toward electrophilic reagents or radicals. The chemical reactivity of hydrogens in diamantane, triamantane, and tetramantane has also been predicted. A discussion has been made of the stable configuration of the 1-adamantyl cation, radical, and anion and of the nature of the back-side conjugation between the two tertiary carbons in these species. A mode of the electrocyclic polymerization of *p*-quinodimethane to form polyamantane has been predicted on the basis of the symmetry properties of the frontier orbitals in the pi and sigma parts of *p*-quinodimethane.

Recently the chemistry of adamantane and its homologues has been developed in connection with the chemical reactivity of the bridgehead hydrogen atoms. Stetter and Wulff have shown that the ionic bromination of adamantane occurred exclusively at the bridgehead.[1] The homolytic abstraction of hydrogen of adamantane and substituted adamantanes has also been reported, demonstrating the occurrence of the predominant removal of the bridgehead hydrogen atoms.[2,3] It has been shown that one of the theoretical reactivity indices, delocalizability, can be a good measure of the reactivity of hydrogens in aliphatic systems.[4,5] Here we will present the results of

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[*1] Present address: Ōe Works, Sumitomo Chemical Co., Ltd., Ehime.

1) H. Stetter and C. Wulff, *Chem. Ber.*, **93**, 1366 (1960).

2) I. Tabushi, J. Hamuro and R. Oda, *J. Amer. Chem. Soc.*, **89**, 7127 (1967).

3) P. H. Owens, G. J. Gleicher and L. M. Smith, Jr., *ibid.*, **90**, 4127 (1968).

4) K. Fukui, "Molecular Orbitals in Chemistry, Physics and Biology," ed. by P.-O. Löwdin and B. Pullman, Academic Press, New York (1964), p. 513, and the references cited therein.

5) K. Fukui, "Modern Quantum Chemistry," Vol. 1, ed. by O. Sinanoglu, Academic Press, New York (1965), p. 49, and the references cited therein.

calculations on adamantane and related compounds undertaken in order to test the validity of the theoretical reactivity indices for such compounds with bridgehead atoms. Calculations have also been carried out on three adamantane homologues, diamantane, triamantane and tetramantane, in an effort to predict the favorable course of the homolytic abstraction of hydrogens. In addition, the potentiality of an ingenious method for the preparation of polyamantane will be suggested.

The Chemical Reactivity of Adamantane and Substituted Adamantanes. It is well known that the quantum-mechanical theory of chemical reactivity has been successfully applied to organic molecules. Of the various chemical reactivity theories thus far presented, the delocalization approach is unique in that this method can be applied to both saturated and unsaturated molecules in a unified manner. The delocalization approach has also achieved a fair success in explaining or predicting the favorable steric course of electrocyclic processes.[6,7] By an application of the molecular orbital (MO) perturbation theory to the chemical reaction, the chemical reactivity indices, superdelocalizability (S_r) and delocalizability (D_r), have been derived.[8,9] Of these, the former is used for unsaturated molecules, and the latter, for saturated molecules. The index D_r is a reliable measure of the reactivity of hydrogens in paraffin hydrocarbons and their derivatives toward abstraction reactions.

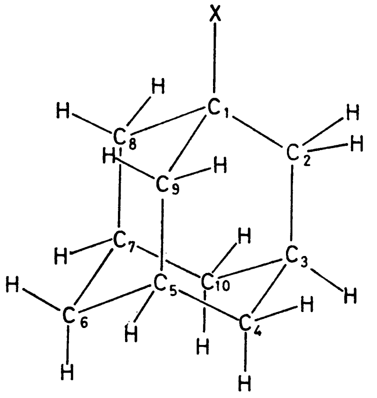
The values of delocalizability for electrophilic attack, $D_r^{(E)}$, are shown in Table 1 with respect to adamantane and several 1-substituted adamantanes. Calculation was made by the simple LCAO MO method for saturated compounds which had previously been employed for paraffin hydrocarbons.[9] We can see that bridgehead hydrogens have the largest chemical reactivity toward attacking electrophiles.

The values of delocalizability for radical attack, $D_r^{(R)}$, are given in Table 2. The experimental findings that the bridgehead hydrogens are most readily removed can be successfully interpreted in terms of $D_r^{(R)}$.[2] Owens *et al.* showed that the relative rate of the homolytic abstraction of bridgehead hydrogen in adamantane and in substituted adamantanes decreased in the order:[3]

$$\text{-CH}_3 > \text{-H} > \text{-OCH}_3 > \text{-COOCH}_3 > \text{-CN}$$

Because of the rough setting of parameters for oxygen hybrids, we can not make a sharp comparison between the results of calculation given in

Table 1. The delocalizability at hydrogen atoms for electrophilic abstraction



X	Position of attack 2	3	4
H	1.0387	1.0407	1.0387
CH_3	1.0388	1.0407	1.0387
OCH_3	1.0383	1.0406	1.0387
$COOCH_3$	1.0380	1.0406	1.0387
CN*	1.0387	1.0406	1.0387

Parameters used are as follows:
Coulomb integrals
$C(sp^3)$: α
$C(sp^2)$: $\alpha+0.1\beta$
H : $\alpha-0.2\beta$
O : $\alpha+0.3\beta$
Resonance integrals
between hybrids belonging to adjacent atoms
$C(sp^3)$–$C(sp^3)$: β
$C(sp^3)$–$C(sp^2)$: β
C–H : 1.1β
C=O : 1.2β
C–O : 0.6β
between hybrids belonging to the same atom
$C(sp^3)$: 0.34β
$C(sp^2)$: 0.40β
O : 0.30β

* The parameters were tentatively put equal to those of carbonyl group.

Table 2. The delocalizability at hydrogen atoms for homolytic abstraction

X	Position of attack 2	3	4
H	1.0195	1.0316	1.0195
CH_3	1.0207	1.0318	1.0195
OCH_3	1.0284	1.0329	1.0195
$COOCH_3$	1.0233	1.0322	1.0197
CN	1.0215	1.0319	1.0196

Numbering is the same as Table 1.

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6) K. Fukui, This Bulletin, **39**, 498 (1966).

7) K. Fukui and H. Fujimoto, *ibid.*, **39**, 2116 (1966).

8) K. Fukui, T. Yonezawa and C. Nagata, *J. Chem. Phys.*, **32**, 1743 (1960).

9) K. Fukui, H. Kato and T. Yonezawa, This Bulletin, **34**, 1111 (1961).

Table 2 and the experimental order of reactivity. However, it should be noted that the calculation gave a correct order with respect to adamantane and 1-methyl adamantane, and also with respect to methoxy, carbomethoxy, and cyano deirvatives.

The $D_T^{(\mathrm{R})}$ values of hydrogens in diamantane, triamantane, and tetramantane are shown in Fig. 1. It can be predicted that, in all of these adamantane homologues, the bridgehead hydrogens can most readily be removed by a radical.

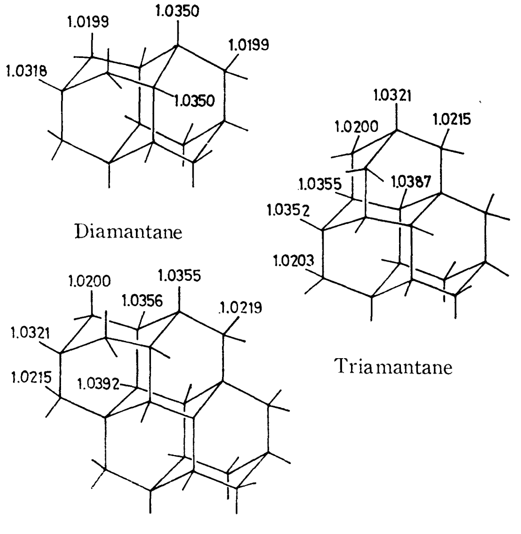

Fig. 1. The delocalizability at hydrogen atoms for homolytic abstraction.

The Electronic Structure of Adamantane, the Adamantyl Radical and Ions. The atom populations and atom-bond populations of adamantane and 1-chloroadamantane, as calculated by the extended Hückel MO method,[10] are shown in Fig. 2. The underlined values indicate the atom populations, while those in parenthesis are those obtained by a SCF MO method for valence electrons with an approximation of the zero-differential overlaps.[11] It can be seen that bridgehead hydrogen have larger electron populations than as secondary hydrogens. The effect of the substituent at the bridgehead carbon, namely, the change in populations, is transmitted in opposite fashions to the adjacent secondary carbons and to the other bridgehead carbons. A similar relation also holds with respect to hydrogens attached to the secondary and tertiary carbons.

The results of the calculations by the extended Hückel MO method on the stable configurations of the 1-adamantyl cation, radical and anion are shown in Fig. 3. In these calculations, only the position of the carbon atom 1 was changed upwards or downwards along the C_3 symmetry axis from its normal position; the positions of the other atoms were unchanged. Here, it should be noted that the most stable position of the carbon 1 in the radical is found to be almost the same as in the parent

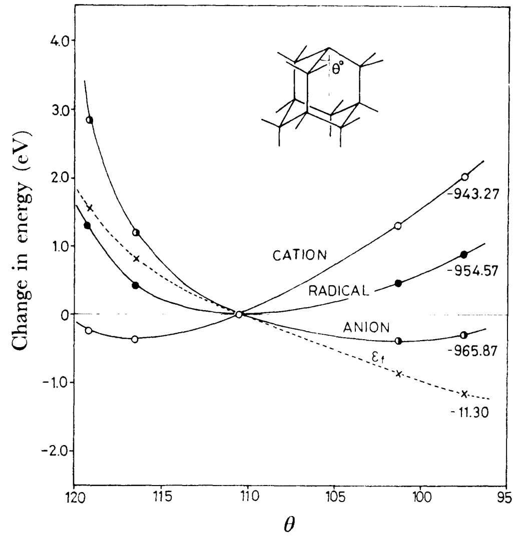

Fig. 3. Energy diagram of 1-adamantyl cation, radical and anion.

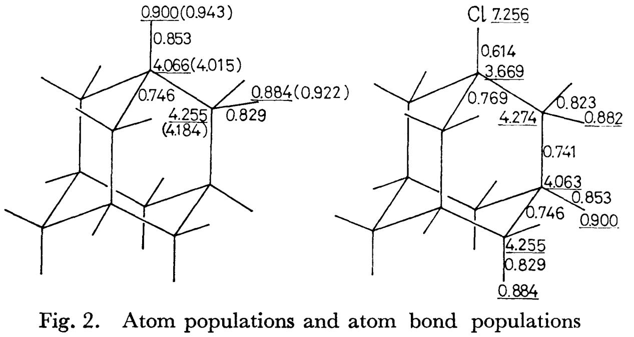

Fig. 2. Atom populations and atom bond populations in adamantane and 1-chloroadamantane.

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[10] R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963); **40**, 2047, 2474, 2480, 2745 (1964).

[11] H. Fujimoto and K. Fukui, unpublished.

compound. The cation becomes more stable as the angle θ increases up to about 117°, while the anion is most stable at about $\theta=101°$. The broken line in Fig. 3 indicates the change in the energy of the orbital, ε_f, housing an electron in radical; this we may term the "frontier orbital." As we employ a one-electron approximation in the extended Hückel MO method, we can see that the stable configuration of the radical and the anion largely depends on the change in the energy of this particular orbital along with the configuration change.

It has been pointed out that the back-side interaction between the hybrids at the carbons 1 and 3 has a significant influence upon the physical properties of the adamantly cation.[12] Here, let us discuss the nature of the stabilization and unstabilization due to the back-side conjugation in the 1-adamantyl cation, radical and anion. The conjugation energy between the two hybrids, χ_1 and χ_3 (see the figure in Table 3), at the carbons 1 and 3 is given by:

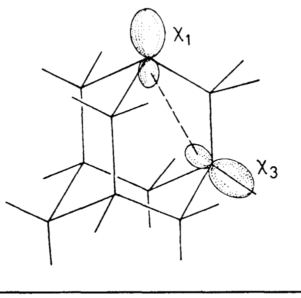
$$E_{\chi_1\chi_3} = 2\sum_i \nu_i C^{(i)}_{\chi_1} C^{(i)}_{\chi_3} h_{\chi_1\chi_3}$$

where ν_i is the occupation number of the ith MO (0, 1 or 2), $C^{(i)}_{\chi_1}$ is the coefficient of χ_1 in the ith MO, $h_{\chi_1\chi_3}$ is the resonance integral between the hybrids χ_1 and χ_3, and $\sum$ implies the summation over all the MO's. We tentatively take the sp^3 hybrid as χ_3, while the hybrid χ_1 is determined by the relation between the hybridized state and the bond angle,[13] corresponding to the most stable configuration of each species shown in Fig. 3. The results of calculation are given in Table 3. It may be seen that the stabilization due to the back-side conjugation between the hybrids χ_1 and χ_3 is larger in the cation than in the radical or anion. The partial conjugation energy arising from the frontier orbital,

$$E^{(f)}_{\chi_1\chi_3} = 2C^{(f)}_{\chi_1} C^{(f)}_{\chi_3} h_{\chi_1\chi_3},$$

is +0.0124 eV (contributing to unstabilization) with regard to the most stable configuration of the radical.

Table 3. Conjugation stabilization due to a pair of hybrids in 1-adamantyl radical, cation and anion



Species	$E_{\chi_1\chi_3}$ (eV)
Radical	−0.0057
Cation	−0.0541
Anion	−0.0010

The partial valence-inactive population[14] of the hybrid, χ_1, in the half-occupied MO is found to be 0.7154, which is important in the event of chemical interaction with other chemical systems. This result makes us suppose that the unpaired electron in the half-occupied level might be somewhat delocalized over the other constituent atoms. The sum of the one-electron energies of the 2-adamantyl radical with the sp^2 hybridized state at the carbon 2 was found in the extended Hückel MO calculation to be lower than that of 2-adamantyl with the sp^3 state at the carbon 2 by the amount of ~0.6 eV.

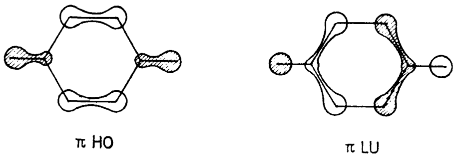


Fig. 4. The nodal property of HO and LU in the pi-electronic part of *p*-quinodimethane.
The shaded and unshaded areas correspond to the positive and negative regions of the wave functions, respectively

A Potential Route to Polyamantane. Now let us present a proposition regarding the potentiality of the preparative method of polyamantane. When we concentrate on the larger homologues of adamantane, we can find that an elemental unit of the repeated sequence has the same constituents as *p*-quinodimethane. Therefore, polyamantane might be produced by the electrocyclic polymerization of *p*-quinodimethane, as long as the methods of the initiation and termination are successfully devised in order to arrange that both chain-end rings have the normal valency. The nodal properties of the highest occuped (HO) MO and one of the lowest unoccupied (LU) MO in the pi-electronic part are shown in Fig. 4. The charge-transfer interaction due to the transfer of one electron from the HO of one molecule into the LU of another molecule favors such an eight-centric cyclic interaction as is shown in Fig. 5, leading to the formation of a polyamantane chain with the adamantane sequence of the form I.

We must here make a reservation that the consideration of sigma-pi interaction[7] predicts the

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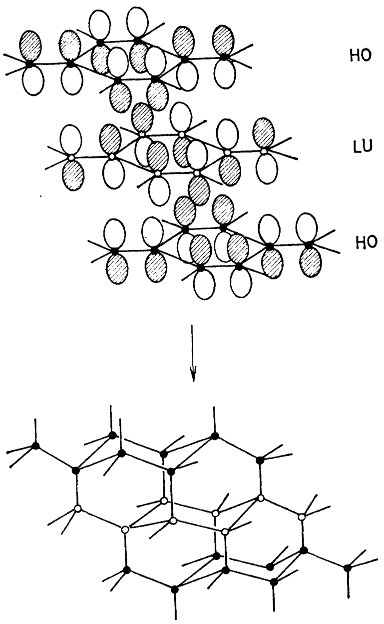
[12] P. von R. Schleyer, R. C. Fort, Jr., W. E. Watts, M. B. Comisarow and G. A. Olah, *J. Amer. Chem. Soc.*, **86**, 4195 (1964).

[13] C. A. Coulson, "Valence," Clarendon Press, Oxford (1953), p. 193.

[14] K. Ruedenberg, *Rev. Mod. Phys.*, **34**, 326 (1962).



I

Fig. 5. A schematic representation of the mode of the intermolecular pi-pi overlap interaction in *p*-quinodimethane.

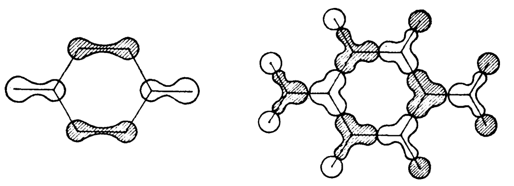
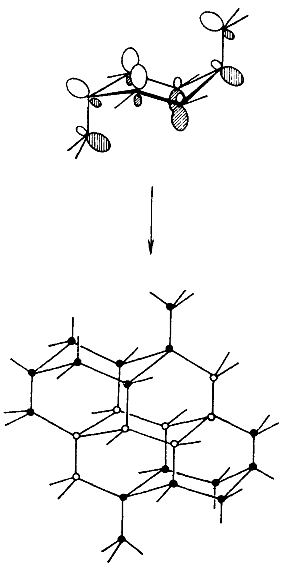


Fig. 6. The nodal property of pi-HO and sigma-LU of *p*-quinodimethane.



II

Fig. 7. A schematic representation of the mode of the intramolecular sigma-pi overlap interaction in *p*-quinodimethane.

formation of a somewhat different sequence. In the chemical interaction of planar conjugated systems in which hybridization change takes place, it has been pointed out,[7] the interaction between the pi part and the sigma part can not be neglected. The interaction between the HO of the pi-electronic part and the LU of the sigma part is usually most important. The nodal properties of these MO's are given in Fig. 6. Therefore, the sigma-pi interaction favors such configuration change a way as is shown in Fig. 7; this may cause the predominant formation of polyamantane of the form II. However, in usual multi-centric interaction between two conjugated molecules, the stereo-controlling effect due to the intramolecular sigma-pi interaction is rather weak and is overcome by that due to the intermolecular pi-pi interaction between two reactants. This point would be clarified if the preparation of polyamantane by the thermally-induced polymerization of *p*-quinodimethane should be achieved.

The calculations were carried out partly on the HITAC 5020E computer at the Computer Center of the University of Tokyo and partly on the FACOM 230.60 at the Computer Center of Kyoto University.