

The effect of nature and number of alkyl groups in tetraalkyl ammonium cations acting as templates during the synthesis of ZSM-5

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Abstract

Computer simulation studies have been applied to investigate the effect of alkyl groups in the structure directing property of the tetraalkyl ammonium cations (TAA) acting as templates during the synthesis of ZSM-5. The interaction between the model compounds has been studied to mimic the alkyl groups of the template molecule and the ZSM-5 framework as the nature and number of alkyl groups vary. Different cluster models were considered to study the extent of interaction with model compounds. The results of MNDO calculations show that the efficiency of TAA as template is dependent on the number and nature of alkyl groups present in them. The procedures used can successfully identify optimum templates for a given host and have applications in the synthesis of new microporous materials.

Keywords: Alkyl groups in TAA; ZSM-5 zeolite synthesis; Quantum chemical calculations; Template–zeolite interactions

1. Introduction

The main applications of ZSM-5 zeolites in the fields of fuel processing and synthesis of chemicals are based on the shape-selective catalytic properties introduced by their structure [1,2]. The structure is believed to be directed by the templating organic molecules (TOM), during the synthesis. To understand the role of organic templates in the synthesis of zeolites, the location and dynamic states have been probed by many techniques, e.g. IR spectroscopy [3,4], Raman spectroscopy [5,6], NMR spectroscopy [7,8], thermal analysis [9,10] and

quantum chemical calculations [11–13]. The semiempirical quantum chemical method has proved useful as an aid in interpreting chemical behavior of templates during the crystallization process of zeolite ZSM-5 [14].

There have been attempts to calculate the electronic properties of templates and to model their templating role [11,15]. There are also simulation studies using model compounds [14] or modeling the as-synthesized structure, where the template molecules are incorporated in pores [16]. The crystallization rate in the presence of different templates has been correlated with calculated interaction energies of the template with the framework [17]. There is a recent work based on a combined molecular dynamics,

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Monte Carlo and energy minimization technique to probe the nonbonded interactions between guest molecules and zeolite frameworks [18]. Indeed, the van der Waals interactions can be used to determine the efficacy of the template at forming a particular framework [18] — a quantification of the ‘good fit’ noted empirically [19] — although there are other properties of the organic species — especially the charge [20], the hydrophobicity, the flexibility and the rotational dynamics — which will be vital for the successful synthesis of a material, particularly in the case of three-dimensional channel systems. In our earlier study [12,13] we emphasize the electronic interaction of templating molecules with host framework to find the most effective template for the ZSM-5 synthesis out of odd 50 different TOMS. It was shown that TPA (tetra propylammonium cation) is the best possible template in the synthesis of ZSM-5. The present communication is directed to showing the importance of the nature and number of alkyl groups in deciding the electronic properties of the TAA type of template molecule and consequently probe their structure directing role during the synthesis of ZSM-5. Propane and butane are chosen as representative molecules to mimic the alkyl groups of TAA (with a special emphasis on TPA and tetrabutylammonium cation (TBA)) to study the effect of alkyl groups in the structure directing property of TAA. The interactions of these guest molecules with different cluster models of host framework have been performed and it is observed that the pentameric cluster model is the best possible model to study the host–guest interaction. The energetics of host framework and template interactions are calculated by semi-empirical quantum chemical MNDO calculations.

2. Calculation methods and cluster models

Modified neglect of differential overlap (MNDO) calculations have been performed on typical cluster models of the ZSM-5 framework,

on the TAA containing different and varying numbers of alkyl groups and on the adsorption complexes formed between the framework cluster and organic molecules. The calculations were carried out using AMPAC (QCPE program No. 506) and the calculation procedure was described by Dewar and Thiel [21]. Although non-empirical calculations would be desired, the MNDO technique was adopted, because this semiempirical method has been shown to be well-parameterised. The computational advantages in using this semi-empirical procedure for performing a multitude of calculations on large cluster models of zeolite framework [22], as well as the reliability of these results for the description of electronic interactions [14], are reported in the literature. All the calculations were carried out in a Silicon Graphics, IRIS workstation.

The atomic positions in the cluster model representing the ZSM-5 framework are as reported by X-ray crystal structure studies of van Koningsveld et al. [23]. We have adopted a localized cluster model approach to represent the zeolite framework, as introduced by Derouane et al. [24] in their pioneering work. Calculations have been performed on monomer ($\text{T}(\text{OH})_4$), and pentamer ($\text{T}-\text{O}_4[\text{T}(\text{OH})_3]_4$) cluster models whose geometries were described in our earlier work [13]. In all the cluster models the peripheral oxygen atoms are saturated by hydrogen atoms. The position of these hydrogen atoms are the same as those of the adjacent T sites. Conformation of pentameric cluster model is discussed in details in our earlier study [12,13].

3. Results and discussion

The selection of a suitable template has not evolved to a ‘rule based’ situation even for the well studied ZSM-5 system. More than 50 TOM have been reported for the synthesis of ZSM-5 [12]. Among these, tetraalkyl ammonium cations (TAA) are reported to be the most efficient. We

attempt to compare and contrast the electronic interactions of alkanes and alkylammonium ions with the ZSM-5 framework in order to study the influence of alkyl groups present in TAA, in deciding its efficiency as templates.

3.1. Electronic properties of framework cluster

The electronic properties calculated for the framework clusters are given in Table 1. All the clusters are generated taking site 1 as center. In the monomer cluster models the adjacent T sites are approximated by H atoms only (T-(OH)₄). The pentamer cluster model consists of five TO₄ groups, (T₃-T₂-T₁-T₄-T₅) in which the valency of peripheral oxygen atoms are saturated by H atoms. Monomer and pentamer clusters are chosen as representative of possible cluster models. The interaction of mono-, di-, tri- and tetra-methyl ammonium cations are studied only using pentamer cluster model. The calculations are performed for all silicon clusters as well as for one-aluminum-substituted clusters. The total energies for all the free cluster models are given in Table 1. The net charges on various atoms of the clusters calculated by the Mulliken population analysis are also included in Table 1. The charge polarizations are well depicted in larger clusters while going from smaller to larger clusters. The pentamer cluster indicates the lattice to be 50% ionic, as derived from the net charges calculated on various atoms; such results match experimental reports.

3.2. Nature of alkyl groups

Our earlier paper [12,13] explains that all the template molecules except TPA can diffuse to the outer surface from the pores of ZSM-5. Therefore, it may be understood that the molecules larger than the diameter of the pore have less dynamic freedom, thus leading to better nucleation and further crystallization. The electronic interaction of the alkyl group was studied by the interaction of the molecules with the host framework cluster models. The polarization in the alkyl group was also studied from Mulliken population analysis.

While the positions of atoms in the framework are kept fixed, as reported in X-ray crystallographic studies [23], the locations of the interacting molecules are varied. Our attempt is to find the common factor present in quaternary ammonium cations containing different alkyl groups become the most efficient template molecule. First, propane has been chosen as the interacting molecule, keeping in mind that TPA is the best template [12] for the synthesis of ZSM-5. The propane molecule has been oriented in such a way that the central -CH₂ is pointing towards the framework oxygen as observed in the case of as synthesized TPA-ZSM-5 X-ray structure; the terminal methyl groups of TPA are oriented pointing towards the framework oxygen and are at a distance of 2.50 Å from the framework. The propane molecule is interacting with the framework oxygen through

Table 1
The electronic properties of framework cluster models

Property	Monomer	Dimer	Pentamer
Total energy (eV)	-1433.93 ^a	-2519.97 ^a	-5779.78 ^a
	-1389.52 ^b	-2475.44 ^b	-5690.06 ^b
Net charge on T site at site 1	1.83 ^a	1.81 ^a	1.97 ^a
	0.96 ^b	0.91 ^b	0.96 ^b
Average charge on terminal oxygens	-0.71 ^a	-0.68 ^a	-0.84 ^a
	-0.47 ^b	-0.54 ^b	-0.76 ^b
Average charge on bridging oxygens	— ^a	-0.93 ^a	-0.95 ^a
	— ^b	-0.76 ^b	-0.79 ^b

^a All Si cluster.

^b Cluster containing one Al at site 1.

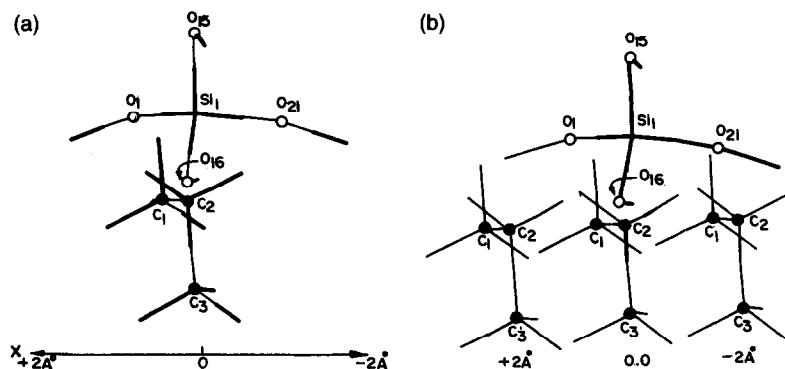


Fig. 1. (a) The location of the propane molecule with respect to the monomer cluster, keeping a distance of 2.50 Å between the T₁ site and C₂ of the propane molecule. The axis of displacement of propane molecule is also shown. (b) Typical locations of the propane molecule with respect to fixed monomer cluster along X-axis.

its methylene hydrogens. The propane molecule has been located at a distance of 2.50 Å from the framework T₁ site (i.e. the distance between framework T₁ site and C₂ of the interacting molecule is 2.50 Å) in a perpendicular orientation with respect to the framework, as shown in Fig. 1(a). The hydrogens of the interacting molecule are kept at a distance greater than 1.5 Å from the framework. The location of propane with respect to the monomer cluster, as shown in Fig. 1(a), is the position at zero displacement point; this specific location is considered as the starting point for all the cases. The interacting molecule is then shifted along the X-axis in the +ve and -ve direction with respect to zero

displacement point, as shown in Fig. 1(a). The interacting molecule and the framework cluster are in the same plane of interaction. So the molecule is not shifted in either Y or in Z direction as in those cases the molecule will be away from the plane of the framework which will violate the X-ray crystallographic structure report [21].

In these calculations, the absolute values of energy do not carry much chemical meaning due to the semiempirical parameterization involved in the MNDO method and due to cluster model approximation used for ZSM-5 framework. Hence, only qualitative trends of the interaction energy are discussed. Due to repeating

Table 2

The effect of displacement on the interaction of the propane molecule along the X-axis (as shown in Fig. 1(a)) with monomer clusters

Property	Displacement (Å)				
	+ 2.0	+ 1.0	+ 0.0	- 1.0	- 2.0
Total energy of complex (eV)	-1923.79 ^a -1880.83 ^b	-1919.10 ^a -1877.25 ^b	-1922.03 ^a -1881.25 ^b	-1925.22 ^a -1882.32 ^b	-1925.82 ^a -1884.23 ^b
Interaction energy (eV)	8.17 ^a 6.73 ^b	12.86 ^a 10.30 ^b	9.93 ^a 6.31 ^b	6.74 ^a 5.24 ^b	6.14 ^a 3.32 ^b
Charge on central -CH ₂ of propane ^c	-0.08 ^a 0.11 ^b	0.11 ^a 0.20 ^b	0.24 ^a 0.12 ^b	0.02 ^a 0.13 ^b	-0.13 ^a 0.12 ^b
Charge on T site at site 1	1.76 ^a 0.89 ^b	1.76 ^a 0.90 ^b	1.82 ^a 0.94 ^b	1.84 ^a 0.94 ^b	1.79 ^a 0.90 ^b

^a All Si cluster.

^b Cluster containing one Al at site 1.

^c Total energy of propane molecule = -498.03 eV.

Table 3
The effect of displacement on the interaction of the propane molecule along the X-axis with pentamer clusters

Property	Displacement (Å)				
	+ 2.0	+ 1.0	+ 0.0	- 1.0	- 2.0
Total energy of complex (eV)	-6223.25 ^a	-6241.31 ^a	-6266.52 ^a	-6248.96 ^a	-6225.56 ^a
	-6138.65 ^b	-6156.31 ^b	-6178.91 ^b	-6162.04 ^b	-6141.52 ^b
Interaction energy (eV)	54.56 ^a	36.50 ^a	11.29 ^a	28.85 ^a	52.25 ^a
	49.44 ^b	31.78 ^b	9.18 ^b	26.05 ^b	46.57 ^b
Charge on central -CH ₂ of propane ^c	-0.58 ^a	-0.32 ^a	-0.27 ^a	-0.30 ^a	-0.54 ^a
	-0.39 ^b	-0.19 ^b	-0.15 ^b	-0.18 ^b	-0.33 ^b
Charge on T site at site 1	1.781 ^a	1.79 ^a	1.81 ^a	1.80 ^a	1.77 ^a
	0.86 ^b	0.87 ^b	0.90 ^b	0.88 ^b	0.87 ^b

^a All Si cluster.

^b Cluster containing one Al at site 1.

^c Total energy of propane molecule = -498.03 eV.

symmetry in ZSM-5 framework, we assume that the interactions from the rest of the framework will have a qualitative correlation for all the molecules for a uniform Si/Al ratio.

The interaction energies of propane for Si and Al monomer clusters have been calculated and are reported in Table 2. The interaction energy for the adsorption complex of propane with framework cluster was studied for different locations. The propane molecule has been moved along the X-axis (shown in Fig. 1(a)) in both the +ve and -ve direction to locate the favorable position. A typical position of the propane molecule with a fixed monomer cluster is shown in Fig. 1(b). The results shown in Table 2 indicate that the interaction is unfavorable at the perpendicular position or at the zero distance conformation of propane in comparison to the values obtained by moving the molecule in the negative direction. As we move in the +ve direction of the X-axis starting from the zero position, the interaction energy is unfavorable at 1.0 Å, while at 2.0 Å the interaction is favorable, as the molecule is going away from the framework. When the molecule is moved along the -ve direction of the X-axis, the interaction is favorable as the molecule is going away from the framework. This means that propane is interacting with framework oxygen through its methylene hydrogen and the bond polarization is understood from the charge density values,

which shows that the interaction is more unfavorable at acid sites due to the distribution of charges.

To establish the polarization of methylene hydrogen and also to see the effect of host on the interacting molecule we have repeated the calculation with a pentamer cluster. The interactions of the propane molecule with pentamer clusters are shown in Table 3. For a pentamer, the propane molecule is interacting with the bridging oxygen between three T sites depending on its positions. The pentamer cluster is centered on T₁ and is as T₃-T₂-T₁-T₄-T₅ i.e. the molecule at zero displacement position will interact with the bridging oxygens of T₂, T₁ and T₄ sites. The results in Table 3 show that the interaction energy is most favorable at the zero displacement position, as in both the cases i.e.

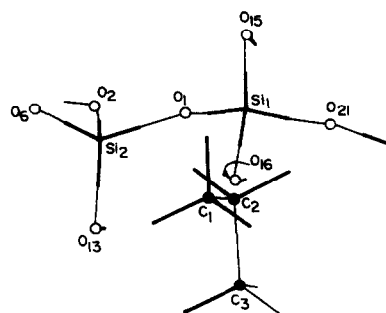


Fig. 2. The location of the butane molecule with respect to the monomer cluster at a distance of 2.50 Å between T₁ site and C₂ of butane.

Table 4

The effect of displacement on the interaction of the butane molecule along the *X*-axis (as shown in Fig. 1(a)) with monomer clusters

Property	Displacement (Å)				
	+ 2.0	+ 1.0	+ 0.0	- 1.0	- 2.0
Total energy of complex (eV)	-2077.22 ^a -2034.17 ^b	-2070.90 ^a -2028.85 ^b	-2072.24 ^a -2031.22 ^b	-2078.20 ^a -2035.27 ^b	-2079.89 ^a -2038.24 ^b
Interaction energy (eV)	7.97 ^a 6.61 ^b	14.29 ^a 11.93 ^b	12.75 ^a 9.56 ^b	6.99 ^a 5.52 ^b	5.30 ^a 2.54 ^b
Charge on central -CH ₂ of butane ^c	0.06 ^a 0.03 ^b	0.01 ^a -0.02 ^b	0.02 ^a -0.01 ^b	0.01 ^a -0.02 ^b	0.03 ^a -0.01 ^b
Charge on T site at site 1	1.76 ^a 0.89 ^b	1.75 ^a 0.90 ^b	1.81 ^a 0.94 ^b	1.84 ^a 0.95 ^b	1.79 ^a 0.90 ^b

^a All Si cluster.^b Cluster containing one Al at site 1.^c Total energy of butane molecule = -651.265 eV.

when the molecule is moved either in the +ve or -ve direction of the *X*-axis the molecule comes closer to the other T site and obviously undergoes strong interaction with the bridging oxygens which makes the energy more unfavorable. The charge on the central -CH₂ shows that at zero position the charge is more in comparison to other positions, which confirms the polarization of the methylene hydrogen during interaction with the framework. The charge on the bridging oxygen follows the same trend as that of the interaction energy, this means that the bridging oxygen actively takes part in the interaction with propane. The results of the interaction of propane with pentamer clusters

show the role of the additional TO₄ unit in the framework.

Now the interaction of butane with framework clusters has been performed to rationalize the ineffectiveness of TBA molecule as template in comparison to TPA. Now, in propane the conformation is chosen in such a way that the central -CH₂ is connected with two methyl groups, one on each side, as shown in Fig. 1(a). In case of butane the central -CH₂ is connected with two dissimilar alkyl groups, i.e. on one side of the central -CH₂ is methyl and on the other side it is ethyl. This orientation of butane molecule is chosen to compare with the experimental location of TBA molecule. In our earlier

Table 5

The effect of displacement on the interaction of the butane molecule along the *X*-axis with pentamer clusters

Property	Displacement (Å)				
	+ 2.0	+ 1.0	+ 0.0	- 1.0	- 2.0
Total energy of complex (eV)	-6389.56 ^a -6301.72 ^b	-6405.12 ^a -6318.36 ^b	-6419.34 ^a -6332.01 ^b	-6403.79 ^a -6317.87 ^b	-6391.42 ^a -6303.22 ^b
Interaction energy (eV)	41.48 ^a 39.60 ^b	25.92 ^a 22.96 ^b	11.70 ^a 9.31 ^b	27.25 ^a 23.45 ^b	39.62 ^a 38.10 ^b
Charge on central -CH ₂ of butane ^c	-0.62 ^a -0.48 ^b	-0.34 ^a -0.26 ^b	-0.30 ^a -0.24 ^b	-0.32 ^a -0.25 ^b	-0.59 ^a -0.46 ^b
Charge on T site at site 1	1.76 ^a 0.85 ^b	1.78 ^a 0.87 ^b	1.80 ^a 0.89 ^b	1.80 ^a 0.88 ^b	1.77 ^a 0.86 ^b

^a All Si cluster.^b Cluster containing one Al at site 1.^c Total energy of butane molecule = -651.265 eV.

study [13] we have shown that TPA is more effective than TBA due to the typical orientation of the TBA molecule inside the framework. The location of butane molecule with respect to the monomer cluster is shown in Fig. 2. It is observed that when the alkyl chain length is less or the number of carbon atoms attached is less, the interaction energy is favorable, as shown in Table 2. With C_2H_5 in one side the interaction of butane is unfavorable as shown in Table 4. The butane molecule is interacting with both the terminal oxygens of the monomer cluster, resulting in an increase in unfavorable interaction. The interaction of pentamer cluster with butane molecule follows the same trend as with the propane molecule. The results of this interaction are shown in Table 5. The charge on the bridging oxygen of the pentamer cluster also follows the same trend as that of the propane interaction, as shown in Table 3. In the case of butane, the interaction is unfavorable due to the location of the molecule inside the framework. So it is observed from the energetics of butane interaction with framework monomer and pentamer clusters that the extra methyl group and the uniqueness of the orientation of the butane molecule while interacting with the framework result in unfavorable interaction energy.

The interaction energy trend is different in the case of the pentamer cluster in comparison to the monomer cluster, this is due to the additional TO_4 unit and also the different orientation of the propane and butane molecules inside the

framework. The interaction of propane and butane with the framework cluster model shows that the structure directing role of TAA depends largely on the interaction of methylene hydrogen with framework oxygen, by which the methylene hydrogens get polarized during the process of crystallization. Here we have shown emphatically the change in the interaction energy depending on the environment of the terminal methyl group which undergoes interaction with framework. It is observed that in case of TPA or TBA the active site is the terminal methyl group which affects the nucleation of ZSM-5. At this stage we cannot conclusively say that TPA is better template than TBA, to justify that we need to see the effect of number of alkyl groups on framework interaction.

3.3. Number of alkyl groups

The electronic properties of mono-, di-, tri- and tetra-methyl ammonium ions as well as their interaction energy values with the pentamer framework are given in Table 6. The positions of molecules such as $[NH_3(CH_3)]^+$, $[NH_2(CH_3)_2]^+$, $[NH(CH_3)_3]^+$ and $[N(CH_3)_4]^+$ are chosen in such a way that their terminal methyl group position is same as the position of the terminal methyl group of TPA according to the X-ray crystallographic structure report [21]. The locations of tetramethyl ammonium cation molecules with respect to the pentameric framework cluster are shown in Fig. 3. The results in

Table 6

The electronic properties of mono-, di-, tri- and tetra-methyl ammonium cations; their interaction with pentamer framework clusters

Property	$[NH_3(CH_3)]^+$	$[NH_2(CH_3)_2]^+$	$[NH(CH_3)_3]^+$	$[N(CH_3)_4]^+$
Total energy of the molecule (eV)	-409.87	-564.99	-719.62	-873.30
Total energy of framework cluster ^a with interacting molecule (eV)	-6191.39	-6343.04	-6494.81	-6648.43
Interaction energy (eV)	-1.73	1.74	4.59	4.65
Net charge on N in				
(i) Free molecule	-0.13	-0.14	-0.15	-0.16
(ii) Interacting molecule	-0.12	-0.13	-0.14	-0.15
Net charge on one alkyl chain				
(i) Free molecule	0.34	0.32	0.31	0.30
(ii) Interacting molecule	0.36	0.34	0.31	0.32

^a Total energy of the framework cluster model = -5779.78 eV.

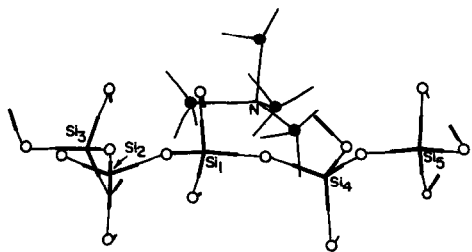


Fig. 3. The orientation of the tetramethyl ammonium ion with respect to pentamer cluster.

Table 6 show that the interaction energy increases with increase in the number of alkyl groups; this is due to the fact that here the number of methyl group is changing which affects the negative charge on the central nitrogen, as well as with increase in number of methyl groups the interaction with framework also increases. Whereas if it increases in the order methyl, ethyl, propyl and butyl, i.e. from tetramethyl to tetrabutyl then it is observed that upto TPA with increase in alkyl chain length the distance between central nitrogen and framework increases. In the case of TBA the same rule holds good with an additional effect of the conformation of the molecule adds up, which results in the unfavorable interaction with the framework in comparison to TPA as reported in our earlier study [12]. So the dimension of the molecule and its location inside the framework are also important factors for determining the efficiency of TOM in synthesizing zeolites. This study shows very clearly the role of the alkyl group in the effectiveness of TAA as templating molecule during the synthesis of ZSM-5. The electron transfer is expected to occur from the HOMO of the zeolite, which are contributed from framework oxygen atoms. The geometric fitting as well as electronic interaction with the framework decide the efficiency of template.

4. Conclusions

The results of computational studies on the structure-directing role of alkyl groups present

in TAA during the synthesis of ZSM-5 are reported. To report the extent of interaction, different cluster models have been chosen. Propane and butane have been chosen to interact with the framework clusters to understand the role of alkyl groups in TPA and TBA, which are used in the synthesis of ZSM-5 as template. It is observed that the location of the molecule inside the framework plays a decisive role in predicting the efficiency of template. This is due to the typical location of the additional methyl group of the butane molecule inside the framework, which results in a stronger interaction with the framework. The additional methyl group of butane plays a crucial role in the polarization of the methylene hydrogen of C_2 of the interacting butane molecule.

The efficiency of template depends on the variation in the number of alkyl groups in ammonium cations containing different alkyl groups. This study indicates that tetra-methyl ammonium cation gives a more unfavorable interaction than mono-, di- and tri-methyl ammonium cations do. These results indicate the trend that higher numbers of alkyl groups in the template produce more unfavorable interactions with the framework at a particular orientation of the molecule i.e. keeping the position of the terminal methyl group fixed.

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