Tetrahedron Vol 36, pp 2945 to 2953
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ALKYLATED TROPYLIUM IONS—IV[1]

STATISTICAL ANALYSIS OF ^{13}C NMR CHEMICAL SHIFTS OF METHYLATED TROPYLIUM IONS BY THE USE OF CONFORMATIONAL MODEL. POSSIBLE OUT-OF-PLANE DISTORTION OF HIGHLY CONGESTED METHYL GROUPS

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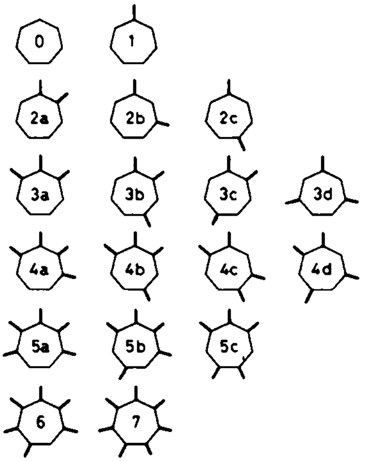
(*Received in Japan 7 December* 1979)

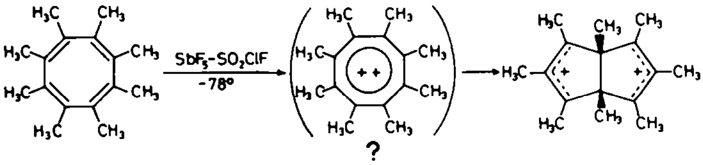
Abstract The Me and the ring ^{13}C chemical shifts for all members of methylated tropylium ions have been statistically analyzed by the application of Grant's conformational model for methylated benzenes, and the additive substituent parameters (δ_k) determined. The predicted Me ^{13}C chemical shifts of highly congested Me groups in 1,2,3,4,5-pentamethyl-, hexamethyl-, and heptamethyl-tropylium ions considerably deviate from experimental Me ^{13}C chemical shifts, whereas the predicted values for other 33 Me groups are fairly well correlated (multiple R = 0.9910) with experimental values. On the other hand, all the predicted 72 ring ^{13}C chemical shifts are linearly correlated with experimental values with high precision (multiple R = 0.9991). The results suggest out-of-plane distortion of highly congested Me groups in the above mentioned methylated tropylium ions, with the 7-membered ring being kept planar. Grant's valence bond (VB) approach has been applied to the interpretation of conformational dependence of the ^{13}C chemical shifts of these adjacent Me groups, giving a linear correlation of the substituent parameters reflecting conformational features with the nonbonded H–H repulsive force acting along the C–H bond axis. Smaller sensitivity of the substituent parameters to the steric force than the case of methylated benzenes has been interpreted to suggest leakage of sterically-induced charge polarization to the positively charged tropylium ring.

Methyl substituent effects on the ^{13}C NMR chemical shifts of various compounds have been thoroughly studied.[2] Especially Grant *et al.* carried out scrutinized study on the ^{13}C chemical shifts of all methylated benzenes and succeeded in explaining all ^{13}C shift data in terms of additive parameters which reflect conformational features existing between adjacent Me groups.[3,4] The excellent agreement of the calculated shifts for hexamethylbenzene in particular, with experimental data, were interpreted to show that significant ring puckering due to steric strain is unlikely even in hexamethylbenzene.[3]

Previously we succeeded in preparing all members of the methylated tropylium ions (Scheme 1) in the form of perchlorates[5] and obtained their ^{13}C NMR spectral data in acetonitrile-d_3,[1] and were interested in examining if Grant's treatment on methylated benzenes could be applied to the interpretation of their ^{13}C chemical shifts. We further hoped to obtain information on the structural feature of the heptamethyltropylium ion in which Me groups are more congested than in hexamethylbenzene because of the smaller dihedral angle between the Me groups. Furthermore, such information appeared of significance since the next higher, entirely methylated 6 π-electron Huckeloid aromatic system, octamethylcyclooctatetraene dication, has been reported *not* to be formed from octamethylcyclooctatetraene by the 2 π-electron oxidation with SbF_5 in SO_2ClF solution at low temperatures, whereas 1,3,5,7-tetramethylcyclooctatetraene dication is produced from the respective cyclooctatetraene under similar conditions.[6–8] The octamethylcyclooctatetraene dication was presumed to be thermodynamically unstable and to isomerize to octamethyldihydropentalene dication.[8]



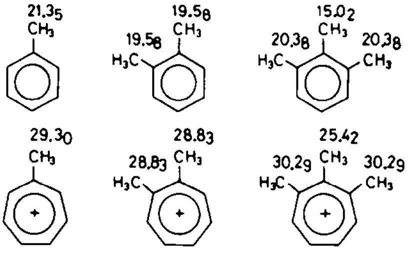
Scheme 1.



In this paper we present determination of additive parameters for the Me and the ring ^{13}C chemical shifts for methylated tropylium ions on the basis of Grant's conformational model,[3,4] and discuss the possible out-of-plane distortion of congested Me groups in these ions. The nonbonded H–H interactions between adjacent Me groups are also discussed in comparison with the case of methylated benzenes.

RESULTS AND DISCUSSION

Preferred methyl conformations. Before applying Grant's treatment on methylated benzenes[3,4] to the methylated tropylium system, we first examined qualitatively if similarity be present between the two systems regarding the effect of introducing one Me group on the ^{13}C chemical shifts of other Me groups. As shown in Scheme 2 the effects of introduction of adjacent Me groups on the Me ^{13}C shift of the monomethyl systems are qualitatively similar between the two systems:† Especially it should be noted that the central Me groups are much more shielded than the other two Me groups in both systems. Therefore, we adopted Grant's empirical rules[3] only by changing the "benzene ring" to the "tropylium ring" as follows.

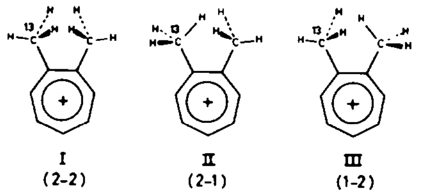


Scheme 2.

(1) Only the three conformational structures (I, II, and III) shown in Scheme 3 are considered as important in the molecular structure whenever two or more Me groups occupy adjacent tropylium ring positions.

(2) The 2-2 conformation (I) is assumed to be the most stable of the three structures allowed by rule 1, and therefore it will always exist between at least one pair of adjacent Me groups except in the case of the completely substituted heptamethyltropylium ion where the molecular structure does not favor this geometrical orientation.‡

(3) All possible 2-2 conformations (I) allowed by the molecular geometry for a series of adjacent Me groups are equally probable.



Scheme 3.

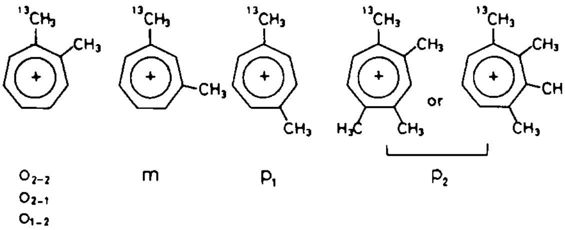
Grant and Woolfenden showed on the basis of semitheoretical calculation that it is unnecessary to take into account the repulsion energy between a single Me proton and one of the *ortho*-ring proton in the methylated benzene system.[3] Although such interaction is expected to be greater in the methylated tropylium system than in the methylated benzene system for geometrical reason, we employed their conformational postulates on the basis of the similarities in the above-mentioned features of Me ^{13}C chemical shifts (Scheme 2).

Methyl ^{13}C *chemical shifts.* Following Grant's method,[3] six parameters denoting conformational and geometrical features (three *ortho*, one *meta*, and two *para* parameters),§ o_{2-2}, o_{2-1}, o_{1-2}, m, p_1, and p_2, were used as shown in Scheme 4 and their populational factors determined (Table 1). Details of the meaning of these parameters and the method for calculating populational factors are explained in Grant's paper,[3] and will not be repeated here.

The chemical shifts of the *i*th Me carbons were correlated by eqn (1)

$$\delta(i) = \delta(\text{Me of } \mathbf{1}) + \sum_k p_{ik}\delta_k \qquad (1)$$

where the substituent parameter, δ_k, denotes induced chemical shift by the Me substituent possessing the *k*th structural feature and the populational factor, p_{ik}. [The sum of p_{ik} $\left(\sum_k p_{ik}\right)$ is equal to $n - 1$, where n is the total



Scheme 4

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† The chemical shifts from TMS for methylated benzenes were calculated by using the data in Ref 3 and $\delta_{C_6H_6}$ of 128.7 ppm.[2]

‡ As described in a later section the hydrogen-hydrogen interaction in the 2-2 conformation (I) was shown to be smaller than in the 2–1 (II) or 1–2 (III) conformation (Table 3).

§ In this paper we use *ortho*, *meta*, and *para* to indicate the positions in the ring for convenience.

Table 1. Populational factors of the important conformational and geometrical features, and methyl ^{13}C chemical shifts for the methylated tropylium ions

Item	Tropylium ion[e]	Methyl position	o_{2-2}	o_{2-1}	o_{1-2}	m	p_1	p_2	δ^a exptl	calcd[b]	calcd[c]
1	**1**	1							29.3_0	29.2_4	29.2_8
2	**2a**	1,2	1						28.8_3	29.1_6	29.0_6
3	**2b**	1,3				1			29.3_6	29.5_1	29.4_4
4	**2c**	1,4					1		28.7_1	28.4_0	28.5_0
5	**3a**	1,3	1/2		1/2	1			30.2_9	30.2_0	30.1_6
6	**3a**	2	1	1					25.4_2	25.8_3	25.6_5
7	**3b**	1	1				1		28.3_0	28.3_2	28.2_9
8	**3b**	2	1			1			28.7_7	29.4_3	29.2_2
9	**3b**	4				1	1		28.7_7	28.6_6	28.6_6
10	**3c**	1,2	1				1		28.1_2	28.3_2	28.2_9
11	**3c**	5					2		27.6_5	27.5_6	27.7_3
12	**3d**	1,5				1	1		28.7_7	28.6_6	28.6_6
13	**3d**	3				2			29.4_7	29.7_7	29.6_0
14	**4a**	1,4	1/3		2/3	1		1	29.6_5	29.3_6	29.5_0
15	**4a**	2,3	2/3	1	1/3	1			26.5_4	26.6_1	26.4_4
16	**4b**	1	1/2		1/2	1	1		29.6_5	29.3_6	29.3_8
17	**4b**	2	1	1			1		24.8_3	24.9_8	24.8_8
18	**4b**	3	1/2		1/2	2			30.3_5	30.4_7	30.3_2
19	**4b**	5				1	2		27.7_7	27.8_2	27.8_9
20	**4c**	1,5	1					2	27.3_0	26.9_7	27.1_1
21	**4c**	2,4	1			1		1	28.3_0	28.3_3	28.2_4
22	**4d**	1,2	1			1	1		28.3_7	28.5_9	28.4_5
23	**4d**	4,6				2	1		29.0_0	28.9_3	28.8_2
24	**5a**	1,5	1/4		3/4	1		2	28.4_7	28.3_9	28.6_7
25	**5a**	2,4	1/2	1	1/2	1		1	25.7_7	25.7_7	25.7_7
26	**5a**	3	1/2	1	1/2	2			28.0_0	27.1_3	$(26.9_1)^d$
27	**5b**	1,4	1/3		2/3	2		1	29.8_2	29.6_3	29.6_5
28	**5b**	2,3	2/3	1	1/3	1	1		25.8_9	25.7_6	25.6_7
29	**5b**	6				2	2		27.8_3	28.0_9	28.0_5
30	**5c**	1,3	1/2		1/2	2		1	29.8_2	29.3_7	29.3_4
31	**5c**	2	1	1				2	24.0_7	23.6_3	23.6_9
32	**5c**	5,6	1			1		2	27.3_6	27.2_3	27.2_6
33	**6**	1,6	1/5		4/5	2		2	28.4_7	28.7_4	28.9_3
34	**6**	2,5	2/5	1	3/5	1		2	24.5_4	24.8_2	24.9_8
35	**6**	3,4	2/5	1	3/5	2		1	26.8_9	26.1_9	$(26.1_2)^d$
36	**7**	1 - 7		1	1	2		2	24.4_8	25.7_1	$(25.8_9)^d$

[a] The ^{13}C chemical shift (ppm) from TMS in CD_3CN. [b] Calculated from 36 data. [c] Calculated from 33 data by excluding items 26, 35, and 36. [d] Calculated from the data of Table 2 obtained by the use of 33 data. [e] Perchlorates; for the notation, see Scheme 1.

number of the Me groups.] The δ_k values and statistical data were calculated by the linear regressional analysis on eqn 1 for experimental $\delta(i)$ values and populational factors, p_{ik}.

As the first trial the δ_k values were calculated by the use of all 36 data and the results are tabulated in Table 2 along with the reported values for methylated benzenes for comparison. The calculated $\delta(i)$ values are given in Table 1. The plot of the predicted vs experimental values are shown in Fig. 1; but the correlation is considerably worse than the case of methylated benzenes. Especially the points for 3-Me of

Table 2. Regressional analysis of methyl ^{13}C chemical-shift parameters in the methylated tropylium ions and methylated benzenes

	Methylated tropylium ions (CD_3CN)				Methylated	
	36 data[a]		33 data[b]		benzenes[c]	
Multiple R	0.9764		0.9910		0.9996	
F ratio	593		1436		——	
Standard error in predicted shift	0.37 ppm		0.22 ppm		0.08 ppm	
Constant term[d]	29.24 ppm		29.28 ppm		21.35 ppm	
Parameter	δ_k (ppm)	F-test	δ_k (ppm)	F-test	δ_k (ppm)	F-test
o_{2-2}	-0.08±0.22	0.1	-0.22±0.08	2.7	-1.87±0.05	1225
o_{2-1}	-3.34±0.27	400	-3.41±0.09	864	-4.43±0.04	9904
o_{1-2}	+1.47±0.14	19.1	+1.66±0.05	63.2	+0.14±0.09	2.2
m	+0.27±0.38	4.9	+0.16±0.13	4.2	-0.05±0.03	2.5
p_1	-0.84±0.34	39.2	-0.78±0.12	88.2	-0.38±0.05	62
p_2	-1.10±0.43	107	-0.98±0.15	210	-0.14±0.06	6.8

[a] Calculated from all data. [b] Calculated from 33 data excluding items 26, 35, and 36 in Table 1. [c] Ref. 3. [d] The chemical shift from TMS.

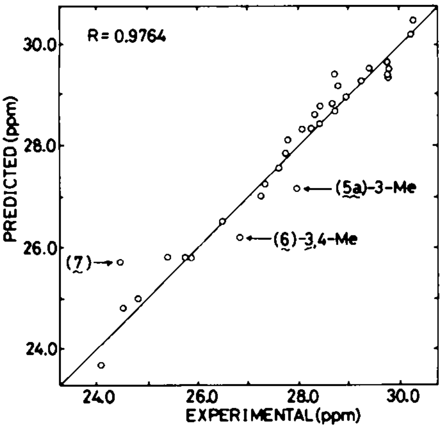


Fig. 1. Plot of the methyl ^{13}C chemical shifts predicted by the use of the substituent parameters calculated from 36 data against experimental chemical shifts for methylated tropylium ions in CD_3CN at 25°.

5a, 3- and 4-Me's of **6**, and Me's of **7** deviate appreciably from the theoretical line, with the multiple correlation coefficient (R) of 0.9764. When the three deviated data are precluded, the correlation is much improved to give R = 0.9910 (Fig. 2), the δ_k and the calculated $\delta(i)$ values being given in Table 2 and Table 1, respectively. The worse correlation in the present system than in the methylated benzene system may be ascribed to (a) stronger solute-solvent interaction due to positive charge of the methylated tropylium ions, and (b) possibility of contribution of other conformations of adjacent Me groups. However, it would be concluded for the first approximation that the considerable deviation of the three data as compared with others, strongly suggests the need for assuming other conformations or out-of-plane distortion of these Me groups. Mere steric effect on the solute-solvent interaction would result in scattering of the points for these sterically crowded ions on either one side of the theoretical line. This aspect will be discussed in a later section.

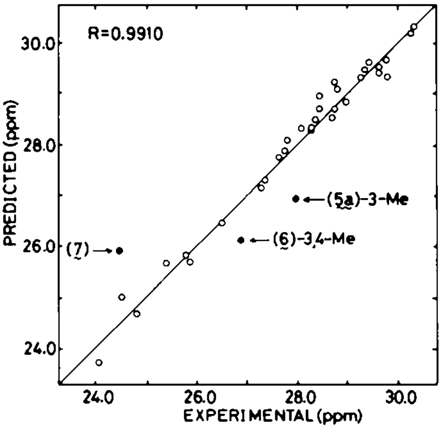
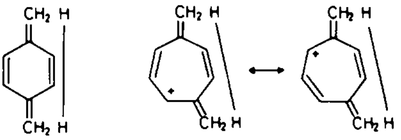


Fig. 2. Plot of the methyl ^{13}C chemical shifts predicted by the use of the substituent parameters calculated from 33 data against experimental chemical shifts for methylated tropylium ions in CD_3CN at 25°. (Closed circles represent the values predicted from the substituent parameters obtained from other 33 data.)

Regarding the substituent parameters, δ_k, two features are characteristic. One is concerned with the greater shielding effect of p_1 and p_2, and the other is related to the smaller shielding effect of o_{2-2}, o_{2-1}, and o_{1-2} parameters for the methylated tropylium ions as compared with the methylated benzenes. The former effect may be understood by assuming greater *para* interaction for the methylated tropylium system due to higher electron delocalization within the ring.† As Scheme 5 shows one can write two canonical sets for hyperconjugative *para* interaction for 1,4-dimethyltropylium ion, instead of one canonical set for *p*-xylene which was proposed by Grant *et al.*[3] In contrast to the methylated benzene system the δ_{p_1} and δ_{p_2} values are similar to each other; therefore, it would be of no considerable importance to distinguish the two kinds of effect of the *para* Me substituents.



Scheme 5.

Nonbonded hydrogen-hydrogen interactions between adjacent methyl groups. Steric perturbation on ^{13}C nuclear shielding appears to have been accepted as one of important factors which determine ^{13}C chemical shifts.[2,9] Grant and Cheney[10] derived an expression for the nonbonded repulsive H–H interaction by means of the simple valence bond (VB) approach;

$$F(r) = 1.297 \times 10^{-2} \exp(-2.671r) \text{ dynes} \quad (2)$$

where r is the proton–proton distance in Å.‡ Based on the assumption that the sterically induced ^{13}C chemical shifts are caused by the sterically induced polarization of charge along the H–^{13}C bond, they succeeded in linearly correlating the ^{13}C substituent parameters, $\delta_{o_{2-2}}$, $\delta_{o_{2-1}}$, and $\delta_{o_{1-2}}$ for methylated benzenes,[3] with the component of the force along the H–^{13}C bond axis, $F(r)\cos\theta$ [$= F_l(r)$], where θ is the angle between the H–^{13}C bond axis and a line drawn between the interacting H atoms.[10]

In order to examine the propriety of their approach by the use of the methylated tropylium system on the one hand, and to compare the steric perturbation of the Me ^{13}C chemical shift by the *ortho* Me group between the two systems on the other, we calculated $F_l(r)$ values by assuming 1.095 Å[11] for carbon–hydrogen bond distance in the Me substituent, 1.501 Å[12] for the Me-carbon–ring-carbon distance, and 1.431 Å[12] for the carbon–carbon distance in the tropylium ring;§ the results of the calculation are summarized in Table 3. As Fig. 3 shows

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†The latter effect will be discussed in the next section.

‡Although more rigorous equation has been proposed by Schneider and Weigand on the basis of the consistent force field theory,[9] we follow the VB approach in order to make the comparison with the methylated benzene system feasible.

§The C_1–C_2 bond length (1.431 Å) calculated for methyltropylium ion[12] was taken, and a regular heptagon was assumed

Table 3. Structural parameters and ^{13}C substituent shifts for various conformations of adjacent methyl groups

Conformation^{a}	r Å	F(r)x10^{5} dyne	cos θ	$F_l(r)$x10^{5} dyne	δ_k^{b} ppm
I (2 - 2)	2.120	4.504	0.2801	1.26	-0.22
II (2 - 1)	1.894	8.239	0.5318	4.38	-3.41
III (1 - 2)	1.894	8.239	-0.0811	-0.668	+1.66

^{a}See Scheme 3. ^{b}See Table 2.

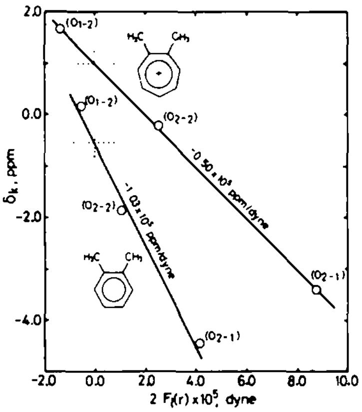


Fig. 3. Plot of the substituent parameters for various ortho conformations against 2 × $F_l(r)$, the steric force directed along the H ^{13}C bond.

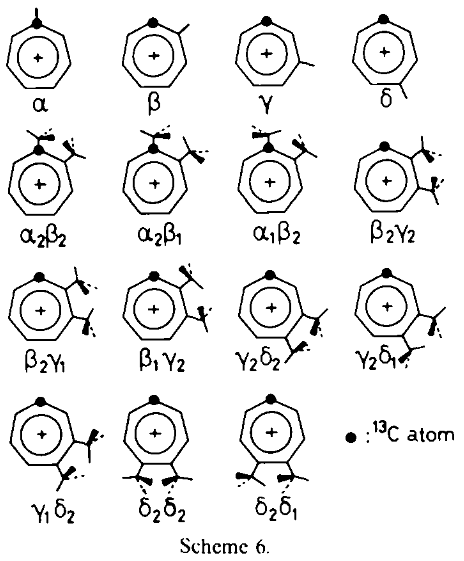
the plot of δ_{o_2-2}, δ_{o_2-1}, and δ_{o_1-2}, which were calculated from 33 data, against 2 × $F_l(r)$ values for the methylated tropylium system gives a straight line, supporting the simple VB approach, but the slope (-0.50×10^5 ppm/dyne) is about a half as small as that for the methylated benzene system (-1.03×10^5 ppm/dyne),[†] which is also illustrated in Fig. 3. The smaller sensitivity of the δ_k values toward $F_l(r)$ values in the methylated tropylium system may be ascribed to the presence of positive charge on the ring. Sterically induced polarization of the valence electrons along the H ^{13}C bond would partially leak to the tropylium ring due to the positive charge, resulting in the smaller sensitivity of δ_k values to $F_l(r)$ than in the methylated benzene system.

The intercept (+1.0 ppm) for the methylated tropylium system is considerably larger than that (−0.5 ppm) for the methylated benzene system. This would mean that when steric perturbation is absent between adjacent *ortho* Me groups, each Me group behaves as an electron-withdrawing substituent in the methylated tropylium system, whereas it acts as a weakly electron-donating substituent in the methylated benzene system. This may be qualitatively explained on the basis that Me hyperconjugation can place full negative charge on the *ortho* and *para* ring-carbons in methylated benzenes, whereas it results in mere neutralization of the positive charge on the ring in methylated tropylium ions. Thus, positive intercept for the methylated tropylium system would be ascribable to the negative inductive effect of the Me group.[14]

Ring ^{13}*C chemical shifts.* Statistical analysis of ring ^{13}C chemical shifts of methylated benzenes were carried out by Grant *et al.*[4] Therefore, we applied their method of using conformational model to the methylated tropylium system, and the chemical shifts of the *i*th ring carbons were calculated by eqn (3)

$$\delta(i) = \delta(\text{tropylium ion}) + \sum_k p_{ik}\delta_k \qquad (3)$$

where p_{ik} and δ_k are the populational factor and the substituent parameter, respectively.[‡] As the substituent parameters, four positional parameters, α, β, γ, and δ, and eleven correction parameters which reflect conformational features of the Me substituents were used as shown in Scheme 6. Following Grant *et al.*,[4] the Greek letters refer to the Me position relative to the carbon of interest, and the subscripted numeral describes the number of hydrogens which that Me group has oriented toward its vicinal Me neighbour in a particular minimum energy conformation. Table 4 shows the populational factors determined for these



Scheme 6.

[†] Grant and Cheney obtained a slope of -1.30×10^5 ppm/dyne[10] for a plot including the effect of an axial Me group on the ^{13}C shift of a cyclohexane ring-carbon.[13]

[‡] Grant *et al.* used conformational and dynamic models However, we prefer the conformational model because of consistency with the statistical analysis of Me ^{13}C chemical shifts

Table 4 Populational factors of the important conformational and geometrical features, and ring ^{13}C chemical shifts for the methylated tropylium ions

Item	Tropylium ion[b]	Position	α	β	γ	δ	$\alpha_2\beta_2$	$\alpha_2\beta_1$	$\alpha_1\beta_2$	$\beta_2\gamma_2$	$\beta_2\gamma_1$	$\beta_1\gamma_2$	$\gamma_2\delta_2$	$\gamma_2\delta_1$	$\gamma_1\delta_2$	$\delta_2\delta_2$	$\delta_2\delta_1$	δ[a]	
																		exptl	calcd
1	**0**[c]	1 - 7																156.2_5	156.4_7
2	**1a**	1	1															174.1_3	173.2_2
3	**1a**	2,7		1														156.6_4	157.0_0
4	**1a**	3,6			1													153.5_9	154.0_0
5	**1a**	4,5				1												153.9_9	154.0_1
6	**2a**	1,2	1	1			1											171.9_0	171.5_4
7	**2a**	3,7		1	1					1								155.0_0	155.6_4
8	**2a**	4,6			1	1							1					151.5_9	151.7_2
9	**2a**	5				2										1		151.5_9	151.4_3
10	**2b**	1,3	1		1													170.9_0	170.7_5
11	**2b**	2		2														157.1_7	157.5_4
12	**2b**	4,7		1		1												154.7_6	154.5_4
13	**2b**	5,6			1	1												151.3_0	151.5_4
14	**2c**	1,4	1			1												171.2_6	170.7_6
15	**2c**	2,3		1	1													154.1_7	154.5_3
16	**2c**	5,7		1		1												154.4_0	154.5_4
17	**2c**	6			2													151.5_3	151.5_3
18	**3a**	1,3	1	1	1		1/2	1/2		1/2		1/2						168.9_6	168.9_2
19	**3a**	2	1	2			1		1									170.7_3	170.3_2
20	**3a**	4,7		1	1	1				1/2	1/2		1/2		1/2			153.4_7	153.6_6
21	**3a**	5,6			1	2							1/2	1/2		1/2	1/2	149.4_0	148.8_8
22	**3b**	1	1	1		1	1											169.3_2	169.0_8
23	**3b**	2	1	1	1		1											169.0_9	169.0_7
24	**3b**	3		2	1					1								155.9_4	156.1_7
25	**3b**	4	1		1	1							1					168.3_2	168.4_6
26	**3b**	5		1		2										1		152.0_0	151.9_6
27	**3b**	6			2	1							1					149.4_2	149.2_5
28	**3b**	7		1	1	1				1								152.4_7	153.1_8
29	**3c**	1,2	1	1		1	1											168.9_6	169.0_8
30	**3c**	3,7		1	2					1								153.1_7	153.1_7
31	**3c**	4,6		1	1	1							1					152.1_8	152.2_5
32	**3c**	5	1			2										1		168.0_8	168.1_8
33	**3d**	1,5	1		1	1												168.0_3	168.2_9
34	**3d**	2,4		2		1												155.0_0	155.0_8
35	**3d**	3	1		2													168.4_4	168.2_7
36	**3d**	6,7		1	1	1												152.4_7	152.0_7

[a] The chemical shift (ppm) from TMS in CD_3CN. [b] Perchlorates; for the notation and methyl positions, see Scheme 1.

[c] Unsubstituted tropylium ion.

Table 4, continued

Item	Tropylium ion[b]	Position	α	β	γ	δ	$\alpha_2\beta_2$	$\alpha_2\beta_1$	$\alpha_1\beta_2$	$\beta_2\gamma_2$	$\beta_2\gamma_1$	$\beta_1\gamma_2$	$\gamma_2\delta_2$	$\gamma_2\delta_1$	$\gamma_1\delta_2$	$\delta_2\delta_2$	$\delta_2\delta_1$	δ[a] expt1	calcd
37	**4a**	1,4	1	1	1	1	1/3	2/3		1/3	1/3	1/3	1/3		2/3			165.9$_7$	165.9$_9$
38	**4a**	2,3	1	2	1		2/3	1/3	1	1/3		2/3						168.6$_7$	168.4$_8$
39	**4a**	5,7		1	1	2				1/3	2/3		1/3	1/3	1/3	1/3	2/3	150.9$_4$	151.0$_3$
40	**4a**	6			2	2							2/3	4/3		1/3	2/3	146.7$_2$	146.3$_0$
41	**4b**	1	1	1	1	1	1/2	1/2		1/2		1/2						166.7$_9$	166.4$_9$
42	**4b**	2	1	2	1		1		1									168.0$_8$	167.8$_5$
43	**4b**	3	1	1	2		1/2	1/2		1/2		1/2						166.0$_3$	166.4$_5$
44	**4b**	4		2	1	1				1/2	1/2		1/2		1/2			154.2$_3$	154.2$_0$
45	**4b**	5	1		1	2							1/2	1/2		1/2	1/2	165.4$_4$	165.6$_3$
46	**4b**	6		1	1	2							1/2	1/2		1/2	1/2	150.1$_2$	149.4$_1$
47	**4b**	7		1	2	1				1/2	1/2		1/2		1/2			151.6$_5$	151.1$_9$
48	**4c**	1,5	1	1		2	1									1		166.2$_0$	166.5$_0$
49	**4c**	2,4	1	1	1	1	1						1					166.5$_0$	166.7$_9$
50	**4c**	3		2	2					2								155.0$_0$	154.8$_1$
51	**4c**	6,7		1	2	1				1			1					151.0$_0$	150.8$_9$
52	**4d**	1,2	1	1	1	1	1											166.5$_0$	166.6$_1$
53	**4d**	3,7		2	1	1				1								153.8$_2$	153.7$_1$
54	**4d**	4,6	1		2	1							1					165.7$_3$	165.9$_9$
55	**4d**	5		2		2										1		152.6$_5$	152.5$_0$
56	**5a**	1,5	1	1	1	2	1/4	3/4		1/4	1/2	1/4	1/4	1/4	1/2	1/4	3/4	162.8$_6$	162.9$_7$
57	**5a**	2,4	1	2	1	1	1/2	1/2	1	1/4	1/4	1/2	1/4		3/4			165.3$_3$	165.4$_6$
58	**5a**	3	1	2	2		1/2	1/2	1	1/2		3/2						167.7$_9$	167.4$_1$
59	**5a**	6,7		1	2	2				1/4	3/4		1/2	5/4	1/4	1/4	3/4	148.7$_1$	148.5$_3$
60	**5b**	1,4	1	1	2	1	1/3	2/3		1/3	1/3	1/3	1/3		2/3			163.8$_5$	163.5$_2$
61	**5b**	2,3	1	2	1	1	2/3	1/3	1	1/3		2/3						165.9$_7$	166.0$_2$
62	**5b**	5,7		2	1	2				1/3	2/3		1/3	1/3	1/3	1/3	2/3	151.8$_8$	151.5$_6$
63	**5b**	6	1		2	2							2/3	4/3		1/3	2/3	162.2$_8$	163.0$_5$
64	**5c**	1,3	1	1	2	1	1/2	1/2		1/2		1/2	1					164.0$_9$	164.1$_7$
65	**5c**	2	1	2		2	1		1							1		164.9$_7$	165.2$_8$
66	**5c**	4,7		2	2	1				3/2	1/2		1/2		1/2			153.2$_9$	152.8$_3$
67	**5c**	5,6	1	1	1	2	1						1/2	1/2		1/2	1/2	163.7$_4$	163.9$_5$
68	**6**	1,6	1	1	2	2	1/5	4/5		1/5	3/5	1/5	2/5	6/5	2/5	1/5	4/5	160.6$_3$	160.2$_6$
69	**6**	2,5	1	2	1	2	2/5	3/5	1	1/5	2/5	2/5	1/5	1/5	3/5	1/5	4/5	162.1$_0$	162.3$_5$
70	**6**	3,4	1	2	2	1	2/5	3/5	1	2/5	1/5	7/5	1/5		4/5			164.3$_9$	164.6$_4$
71	**6**	7		2	2	2				2/5	8/5		2/5	6/5	2/5	1/5	4/5	150.5$_3$	150.8$_7$
72	**7**	1 - 7	1	2	2	2		1	1		1	1		1	1		1	160.2$_8$	160.5$_0$

[a] The chemical shift (ppm) from TMS in CD_3CN. [b] Perchlorates; for the notation and methyl positions, see Scheme 1.

Table 5. Regressional analysis of ring ^{13}C chemical-shift parameters in the methylated tropylium ions and methylated benzenes

	Methylated tropylium ions (CD_3CN)		Methylated benzenes[a]	
Multiple R	0.9991		0.9997	
F ratio	31180		2920	
Standard error in predicted shift	0.31 ppm		0.12 ppm	
Constant term[b]	156.47 ppm		128.5 ppm	
Parameter	δ_k (ppm)	F-test	δ_k (ppm)	F-test
α	+16.75±0.21	12398	+9.0±0.07	19300
β	+0.53±0.30	25.8	+0.8±0.05	284
γ	-2.47±0.30	568	-0.1±0.05	7.1
δ	-2.46±0.25	371	-3.0±0.07	2110
$\alpha_2\beta_2$	-2.21±0.16	134	-2.1±0.09	576
$\alpha_2\beta_1$	-5.79±0.08	231	-3.5±0.20	277
$\alpha_1\beta_2$	-1.76±0.15	68.1	-2.5±0.10	638
$\beta_2\gamma_2$	+1.11±0.19	45.2	+0.6±0.07	75.0
$\beta_2\gamma_1$	+1.96±0.10	40.2	+1.3±0.15	73.6
$\beta_1\gamma_2$	+2.18±0.11	56.5	+0.6±0.15	15.4
$\gamma_2\delta_2$	+0.18±0.18	1.0	+0.5±0.09	38.4
$\gamma_2\delta_1$	-0.12±0.11	0.04	-0.5±0.10	27.4
$\gamma_1\delta_2$	-0.06±0.08	0.04	+0.9±0.20	19.6
$\delta_2\delta_2$	-0.12±0.13	0.26	——	——
$\delta_2\delta_1$	-0.33±0.08	0.74	——	——

[a] Ref. 4. [b] The chemical shift from TMS.

substituent parameters. The δ_k values were calculated by the linear regressional analysis on eqn 3 for populational factors, p_{ik}, and summarized in Table 5 along with various statistical data and the relevant values for methylated benzenes for comparison. Although we utilized fifteen parameters, only ten parameters from α to $\beta_1\gamma_2$ in Table 5 are essentially important, as evident from the F-values.

When the predicted $\delta(i)$ values (Table 4) were plotted against the experimental data, an excellent linear relation (R = 0.9991) was obtained as shown in Fig. 4. It should be noted that the data for **5a**, **6**, and **7** fall on the theoretical line, although the data for the Me groups in these ions exhibit significant deviations (Figs 1 and 2). The results are reasonably interpreted by assuming that the ring puckering due to steric strain among the congested Me groups is unlikely even in **5a**, **6**, and **7**, whereas the congested Me groups in these ions assume conformations other than those presumed as in Scheme 3, or more possibly suffer out-of-plane distortion.

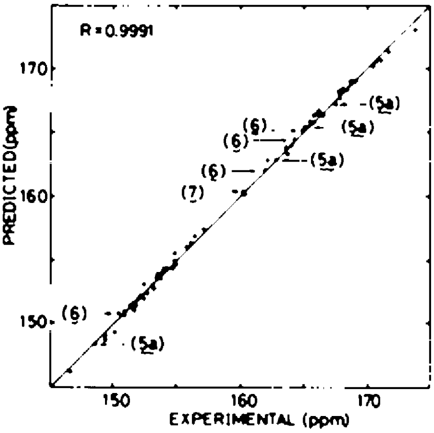


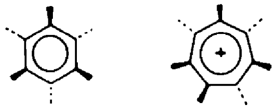
Fig. 4. Plot of the predicted vs the experimental ring ^{13}C chemical shifts for the methylated tropylium ions in CD_3CN at 25°.

When the δ_k values for the methylated tropylium system are compared with those for the methylated benzenes (Table 5), the trend of variation of their sign and magnitude is similar between the two systems. However, it is to be noted that the α parameter for the former system is much more positive than the corresponding value for the latter system. This would suggest smaller electron-donating hyperconjugative effect of Me groups to the *ipso* carbon in the tropylium system than in the methylated benzene system because of spread-out of electron donation to entire ring carbons in the former system. Similar interpretation has been made by Olah and Forsyth in explaining exceptionally low α-Me substituent-induced chemical shift for the isopropyl cation compared with cations with more extended π systems.[14b]

Possible out-of-plane distortion of congested methyl groups. From the analysis of the Me and the ring ^{13}C chemical shifts we suggested that the structures of the methylated tropylium ions whose Me substituents are highly congested are the ones in which the Me groups are most probably distorted out of plane, whereas the 7-membered ring is still planar. Grant *et al.* interpreted their results of the ^{13}C chemical shifts of methylated benzenes as indicating that significant ring puckering due to steric strain is unlikely even in hexamethylbenzene;[3] however, nothing was mentioned on distortion of Me groups. On the other hand, Wang *et al.* studied the structure of hexamethylbenzene by electron diffraction and concluded that the benzene ring is planar, whereas the Me carbons are not coplanar with the ring, alternately deviating by ± 9.9 from the plane of the inner ring.[15] It may be plausible that such a small distortion was hardly reflected to Me ^{13}C chemical shifts.

The possibility of departure from planarity of aromatic rings by the introduction of various substituents has been examined for the benzene and the naphthalene systems.[16] However, many data suggest that the benzene ring of 1,2-*di-t*-butylbenzene is planar.[3] Even 1,2,4,5-*tetra-t*-butylbenzene was found to be planar by means of X-ray analysis.[18] Consequently, it appears reasonable to interpret the results of the ^{13}C chemical shifts for the methylated tropylium ions **5a**, **6**, and **7** as indicating out-of-plane distortion of the Me groups, with the planarity of the tropylium ring being kept.†

In hexamethylbenzene all the Me groups are equivalent to NMR even if they undergo out-of-plane distortion. On the contrary, the heptamethyltropylium ion (**7**) is expected to exhibit four kinds of Me group as the result of their out-of-plane distortion. Unfortunately, however, both the ^{1}H (220 MHz) and the ^{13}C (25.00 MHz) NMR spectra for the Me groups of **7** in dichloromethane-d_2 at − 50 failed to show any splitting of the signals.‡ It is strongly hoped that the structure of this ion (**7**) will be clarified by means of X-ray analysis.



EXPERIMENTAL

^{1}H NMR spectra of **7** in CD_2Cl_2 at − 50 were recorded on a Varian HR-220. ^{13}C NMR spectra of the same soln at − 50 were recorded on a JNM FX100 (25.00 MHz) operating in the Fourier transform mode. No splitting of signals were observed in either case.

The linear regressional analysis of ^{13}C NMR chemical shift data was conducted by utilizing our own software and the FACOM M-200 computer at Kyoto University.

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†An examination of molecular models suggests that out-of-plane distortion of 3-Me of **5a** and 3- and 4-Me's of **6** results in some departure of the 2-2 conformation (I, Scheme 3) toward the 1-2 conformation (III, Scheme 3) regarding these Me groups. This would explain the more-downfield shifts for these Me groups (Fig. 2). A similar examination on **7** suggests that departure from 2-1 (II) and 1-2 (III) conformations makes the δ_{o} value more negative than that statistically obtained, whilst keeping the δ_{o} value unaffected significantly. This may explain the significant upfield shift of the Me groups of **7** as compared with the predicted value.

‡The rates of one-electron reduction of **5a**, **6**, and **7** with the Cr(II) ion are anomalously fast. This may be ascribed to steric strain among congested Me groups, and the results will be reported shortly.