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Theoretical Barrier to Rotation in Substituted Triptycenes: A Semi-empirical and Ab Initio Study

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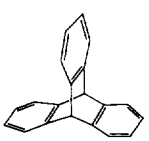
Abstract: The semi-empirical molecular orbital method AM1 has been found to accurately reproduce both the structure and barrier to rotation in a wide variety of 9-substituted triptycenes. Additionally, the general trends observed for derivatives which display the "negative buttressing effect" are also reproduced well.

INTRODUCTION

Atropisomerism has been defined as the phenomenon in which rotational isomers of a compound can be isolated by the freezing of internal rotation about a single bond in that compound.[1] Among the many systems which are capable of displaying atropisomerism, one which has been extensively studied is the triptycene system **1**.[2] With suitably substituted derivatives, *viz.* **2**, it is possible to differentiate



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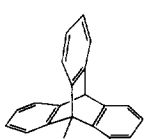

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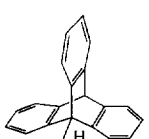

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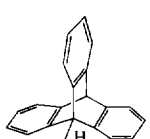

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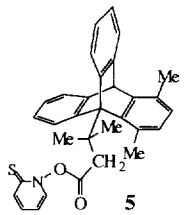
between two possible isomeric forms: the *sc* isomer **3**, in which the 9-substituent is directed between the substituted and unsubstituted rings, and the *ap* isomer **4**, in which the 9-substituent is directed between the two unsubstituted rings. Oki[3] has found that when there is a possibility of electronic interaction between the 9-substituent and a substituent at the 1-position, the *sc* form can be favoured, contrary to that which one would expect on steric grounds. With a symmetrical 9-substituent, such as *t*-butyl, the possibility of individual isomers existing is removed.

Estimates of the barrier to rotation of a substituent at the 9-position have been provided by NMR spectrometry, and these suggest that a barrier of 25 kcalmol^{-1} is required for isolation of the individual isomers at room temperature.[4] It has been shown that the different isomers can possess markedly different reactivities, for example the Barton ester **5** (*sc* form), when thermolysed in toluene solution produces

mainly the combination product **7**, unlike the corresponding *ap* form **6**, which gives predominantly the cyclised product **8** under the same conditions.[5]



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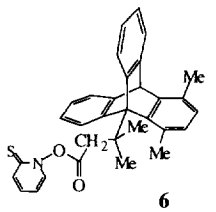

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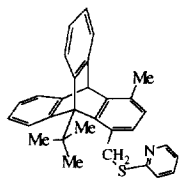

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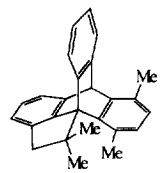

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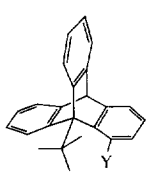
Because synthesis of these systems is a far from trivial matter, we felt that the application of MO techniques was desirable. Although semi-empirical methods are inherently less accurate than *ab initio* methods, the sheer size of these systems precludes their study by the latter, apart from a few model calculations. Oki[6] using the MM2 forcefield, and more recently Sakakibara and Allinger[7] employing the MM3 forcefield, have had some success in determining the relative energies of isomers, but, surprisingly no work has been done to date using the more rigorous molecular orbital techniques.

RESULTS AND DISCUSSION

Calculational Methods:

All calculations were performed on Silicon Graphics INDY workstations, using the SPARTAN suite of programs.[8] All optimisations were conducted without symmetry constraints. The barriers to rotation of the 9-*t*-butyl and 9-methyltriptycenes were calculated as the difference between the two forms (**9**, staggered) and (**10**, eclipsed).



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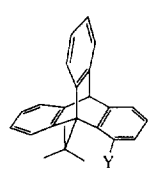

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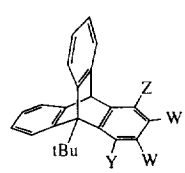


11, Y=W=Z=Cl

Structure:

To establish the efficacy of the AM1 method[9] in the study of triptycene derivatives, we decided to compare the calculated structural parameters with those published by Mikami and co-workers on the tetrachloro derivative **11**.[10] The calculated bond-lengths are displayed in Figure 1a, and show that, as in the crystal structure, the bicyclo[2.2.2]octyl moiety is tapered: the bonds joining C_9 with the three rings are some 0.05-0.06Å longer than those joining C_{10} with the three rings, presumably as a response to the highly crowded steric environment prevailing at that site. In fact, the three latter bonds are all substantially shorter than a "normal" carbon-carbon bond, ranging from 1.499-1.511Å. These are slightly shorter than those determined by Mikami *et al*, as are the distances joining C_9 with its three rings, but the trend is identical in both cases. It is interesting to note that AM1 calculates identical geometries for the two unsubstituted rings,

unlike the crystal structure where very slight differences are observed, probably due to the effect of the packing forces.

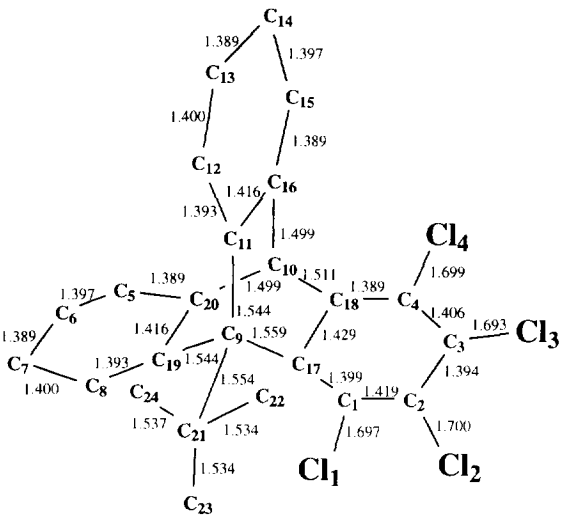


Figure 1a: AM1 calculated bond-lengths for tetrachloro triptycene derivative **11.**

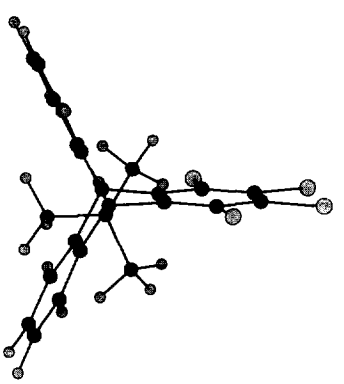


Figure 1b: AM1 optimised structure of tetrachloro triptycene derivative **11.**

Figure 1b shows the AM1 optimised geometry for **11**: from this it is clear that both the *t*-butyl substituent and the 1-chloro substituent are aligned away from each other, precisely as seen in the crystal structure. Selected AM1 calculated bond angles are displayed in Table 1, and further illustrate the rather dramatic effect of placing two large substituents (Cl and *t*-Bu) in such close proximity. The angle between the *t*-butyl substituent and the chlorinated ring, 119.8°, is much larger than the angle between the substituent and the unhalogenated rings, 111.8°; furthermore, the angle $C_9C_{17}C_1$, 132.2°, is significantly larger than that calculated for the unchlorinated derivative (**9**, Y = H), 128.6° at 3-21G level of theory. The corresponding angles between C_9 and the unsubstituted rings in **11**, 129.0°, indicate that the main steric interaction is, as expected, between the substituents at C_9 and C_1.

Table 1: Selected angle parameters for AM1 optimised structure (**11**), and comparison with the experimentally determined angle parameters.

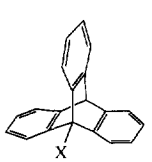
Atoms	$Ø_{expt}$[a]	$Ø_{calc}$[b]	Atoms	$Ø_{expt}$[a]	$Ø_{calc}$[b]
$C_1C_2Cl_2$	120.5	120.3	$C_{10}C_{16}C_{15}$	123.8	123.6
$C_2C_3Cl_3$	120.2	120.9	$C_{10}C_{20}C_{19}$	113.7	113.5
$C_3C_4Cl_4$	118.8	119.3	$C_{11}C_9C_{21}$	113.0	111.8
$C_9C_{11}C_{12}$	128.9	129.0	$C_{12}C_{11}C_{16}$	116.8	116.8
$C_9C_{11}C_{16}$	114.3	114.1	$C_{17}C_1Cl_1$	125.4	125.0
$C_9C_{17}C_1$	133.3	132.2	$C_{17}C_9C_{21}$	118.9	119.8
$C_9C_{17}C_{18}$	111.5	111.6	$C_{17}C_{18}C_{10}$	114.8	115.2
$C_9C_{19}C_8$	128.7	129.0	$C_{18}C_{10}C_{16}$	106.0	105.2
$C_9C_{19}C_{20}$	114.5	114.1	$C_{18}C_{10}C_{20}$	105.2	105.2
$C_9C_{21}C_{22}$	112.0	111.9	$C_{19}C_9C_{21}$	113.2	111.8
$C_9C_{21}C_{23}$	110.9	111.8	$C_{20}C_{10}C_{16}$	107.7	106.7
$C_9C_{21}C_{24}$	110.2	110.4	$C_{20}C_{19}C_8$	116.8	116.9
$C_{10}C_{16}C_{11}$	113.7	113.5			

a) angles in degrees; b) taken from reference 10.

In summary, AM1 reproduces the structure of **11** well, particularly bond angles and trends in the bond lengths, although absolute bond lengths are generally slightly shorter, in the order of 0.01-0.02Å.

Barriers to Rotation:

We took as our first objective to verify that the AM1 method handled the energetics of these systems well; to do so we calculated the barrier to rotation for the methyl substituted triptycene (**12**, X = Me) and the *t*-butyl substituted triptycene (**12**, X = *t*-Bu) at various levels of theory. The results are contained in Table 2, and show that, in the case of the latter compound, AM1 gives a value very close to that obtained by full optimisation at the *ab initio* level 3-21G. The value obtained (40.30 kcalmol^{-1}) is very close to that obtained experimentally (40.4 kcalmol^{-1})[11] or theoretically (40.45 kcalmol^{-1}) for compound **14**. It is not possible to determine experimentally the barrier for (**12**, X = *t*-Bu) because of the inability to differentiate between the different isomers in this highly symmetrical species. It has been demonstrated that the phenyl component of the 9-substituent in **14** is directed upright, away from the triptycene skeleton, and should have little or no effect on the barrier to rotation.[12] This reasoning is supported by our observations as the rotational barrier for **14** is essentially identical to that for (**12**, X = *t*-Bu). The calculated value for the methyl-substituted triptycene (5.39 kcalmol^{-1}) is significantly smaller than the *ab initio* value; however no comparison can be made with experiment as no value exists for a 9-methyltriptycene with no substituents at the *peri*-positions (**13**, X = Me, W = Y = Z = H).



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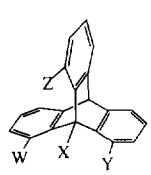

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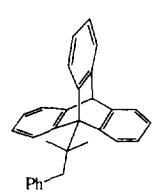

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Table 2: Comparison of rotational barriers[a] at semi-empirical and ab initio levels of theory for compounds **12.**

X	AM1	STO-3G//AM1	3-21G//AM1	3-21G//3-21G
Me	5.39	8.50	9.14	8.14
t-Bu	40.30	--	44.56	39.72
$(Me)_2CCH_2Ph$	40.45	--	--	--

a) All barrier energies given in $kcalmol^{-1}$.

Table 3: Rotational barriers[a] for substituted triptycenes **13** at semi-empirical level of theory.

X	W	Y	Z	Barrier[a](calc)	Barrier[a,b](expt)
Me	H	H	H	5.39	--
Me	Br	H	H	7.12	--
Me	Br	Br	H	8.41	--
Me	Br	Br	Br	9.30	--
Me	Cl	H	H	7.74	--
Me	Cl	Cl	H	9.92	10.9
Me	Cl	Cl	Cl	12.06	--
Me	F	Cl	Cl	11.63	--
Me	F	Cl	OMe	13.10	11.2
Me	F	Cl	Me	13.57	12.1
Me	F	H	H	6.76	--
Me	F	F	H	8.29	--
Me	F	F	F	10.02	--
Me	I	H	H	7.06	--
Me	I	I	H	8.33	--
Me	I	I	I	9.32	--
Me	OMe	H	H	7.02	--
Me	*t*-Bu	H	H	6.44	--
Et	H	H	H	11.34	--
i-Pr	H	H	H	21.10	--
$SiMe_3$	H	H	H	19.83	--
$SiMe_3$	Me	H	H	21.25[d]	--
CH_2Cl	H	H	H	11.19	c.13
t-Bu	H	H	H	40.81	40.4
t-Bu	Me	H	H	39.28	38.4[c]
t-Bu	I	H	H	39.93	--
t-Bu	Br	H	H	40.71	39.2
t-Bu	OMe	H	H	43.55	42.5[c]
t-Bu	Cl	H	H	41.95	40.4
t-Bu	F	H	H	41.99	43.2

a) All barrier energies given in $kcalmol^{-1}$; b) tabulated in reference 2;
c) the experimental values in these cases refer to 1,4-disubstituted isomers of **14**;
d) value for the 1,4-dimethyl analogue.

Substitution at the 9-position:

Table 3 lists the calculated energy barriers for triptycenes **13**, along with comparison with experiment, where appropriate; in the case of the *t*-butyl species, comparison is made with the experimental barriers measured for **14**. It can be seen that, on the whole, the agreement with experiment is excellent for both the *t*-butyl and methyl substituted triptycenes. It was found experimentally that the rotational barrier increases directly with the size of the substituent in the 1-position, the only exception being *t*-butyl.[13] In the present study, this trend is reproduced, with the rotational barrier increasing with steric size as expected :

X = *t*-Bu > *i*-Pr > Et > Me > H. Of particular interest is the calculated barrier for the trimethylsilyl substituent which contains a carbon-to-heteroatom bond instead of the usual carbon-carbon bond. Based on steric arguments alone it would have been predicted that the barrier should be significantly higher than 19.83 kcalmol^{-1} as it has a steric size at least as large as the *t*-Bu substituent. The observed reduction is in line with experimental observations and can be attributed to two factors which decrease steric strain.[14] The first is the increase in the C-Si bond length over a C-C bond length. The second is the easier bond angle deformation of C-Si-C. The magnitudes of each factor are yet to be defined. The 1,4-dimethyl-9-trimethylsilyltriptycene derivative also behaves similarly with a calculated barrier of 21.25 kcalmol^{-1}.

Substitution at the peri-positions:

In the methyl triptycene series the rotational barrier for fluoro is smaller than the barrier for chloro. Bromo, on the other hand, gives a barrier smaller than chloro, and comparable with fluoro while the calculated rotational barrier for the iodo substituent was equal in magnitude to the bromo substituent. Furthermore, the same trend is reproduced for the *t*-butyl substituted triptycenes although the overall changes were smaller. The fluoro and chloro substituents lead to an initial increase in barrier of approximately 1 kcalmol^{-1} while the bromo and iodo cases have barriers approximately the same as the unsubstituted derivative. Introduction of these substituents in all likelihood will result in slight increases in bond lengths presumably as a result of steric crowding and hence lead to the unusual results found within this study It is particularly pleasing that AM1 reproduces all the experimental trends; the placement of *t*-butyl in the 1-position results in the smallest barrier (6.44 kcalmol^{-1}), in keeping with the experimental behaviour of this substituent.

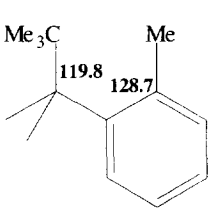
One interesting feature of the calculations on the 9-methyl triptycenes is the apparent additivity of the substituent effects when the substituent is relatively small; placement of one chlorine raises the barrier by 2.35 kcal, placement of a second raises the barrier by a further 2.18 kcal, and a third raises the barrier by a further 2.14 kcalmol^{-1}. The same trend is observed for the fluoro substituted 9-methyltriptycenes while the bromo and iodo series lead to an increase in barrier with increasing substitution although the overall additivity is somewhat decreased. This is entirely in keeping with the observations mentioned above.

Effects of substitution at positions 1, 2, 3 and 4 in 9-t-butyl-triptycene:

Experimentally, it has been observed that the rotational barrier for various 1, 2, 3 and 4-substituted 9-(2-phenyl-1,1-dimethylethyl)triptycenes are high when there is a small substituent in the 1-position and decrease as the size of the substituent is increased. This unusual phenomenon has been termed the "negative buttressing effect".[15] Essentially, substitution in the 1-position by a small substituent gives rise to a relaxed ground state, relative to a large substituent. In both cases, the transition state will be (necessarily) of a high energy, and it is the higher ground state energy of a large substituent which results in the general trend of a lowering in the rotational barrier. In the case of the 9-(2-phenyl-1,1-dimethylethyl)triptycene series it was found that the 1-fluoro derivative had the highest barrier (43.2 kcalmol^{-1}) while increasing the size of the 1-substituent to chloro (40.4 kcalmol^{-1}) and then methyl (38.4 kcalmol^{-1}) gave rise to a reduction in the barrier.[15] Additionally, it was found that further substitution in the 2-position enhances this effect. In order to examine the proposed "negative buttressing effect" it was decided to determine the rotational barriers for a series of 9-*t*-Bu-triptycenes substituted in positions 1, 2, 3 and 4. The derivatives studied were the fluoro, chloro and methyl analogues and the data are collated in Table 4.

Table 4: Rotational barriers for various 9-*t*-Bu-triptycenes substituted in positions 1, 2, 3 and 4.

Position of substitution.				Barrier
1	2	3	4	(kcalmol^{-1})
F	H	H	H	41.99
H	F	H	H	40.30
H	H	F	H	40.35
H	H	H	F	40.52
F	F	H	H	41.98
F	H	F	H	42.03
F	H	H	F	42.15
H	F	F	H	40.34
H	F	H	F	40.54
F	F	F	H	42.00
F	H	F	F	42.20
F	F	H	F	42.15
F	F	F	F	42.19
Cl	H	H	H	41.95
H	Cl	H	H	40.38
H	H	Cl	H	40.30
H	H	H	Cl	40.73
Cl	Cl	H	H	41.68
Cl	H	Cl	H	41.89
Cl	H	H	Cl	42.06
H	Cl	Cl	H	40.34
H	Cl	H	Cl	40.82
Cl	Cl	Cl	H	41.61
Cl	H	Cl	Cl	42.10
Cl	Cl	H	Cl	41.71
Cl	Cl	Cl	Cl	41.67
Me	H	H	H	39.28
H	Me	H	H	40.32
H	H	Me	H	40.24
H	H	H	Me	40.66
Me	Me	H	H	37.75
Me	H	Me	H	39.31
Me	H	H	Me	39.19
H	Me	Me	H	42.17
H	Me	H	Me	40.68
Me	Me	Me	H	37.31
Me	H	Me	Me	39.23
Me	Me	H	Me	37.53
Me	Me	Me	Me	35.44



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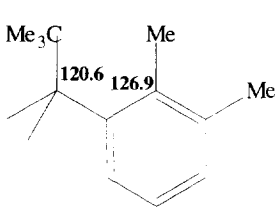

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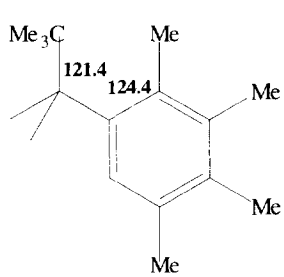

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Structures **15-17** are partial representations of the methyl substituted series. Inspection of these structures reveals that the placement of a second methyl group reduces the C1-Me bond angle; placement of further methyl groups enhances this reduction. Thus, the placement of extra substituents "pushes" the *peri* substituent towards the *t*-butyl substituent, causing an effective increase in its size, and a lowering of the barrier, in keeping with the negative buttressing trends outlined above.

It is noticeable that within the fluoro and chloro substitution series the calculated rotational barriers are remarkably stable and range approximately from 40.3 to 42.2 kcalmol^{-1}. The methyl substituted series on the other hand afforded quite a diverse range of rotational barriers. Once again the AM1 level of theory accurately predicts the "negative buttressing effect" trends discussed above. For example, fluoro-substitution in the 1-position yielded the highest barrier (41.99 kcalmol^{-1}) while the "bulkier" methyl substituent yielded the lowest barrier (39.28 kcalmol^{-1}). Substitution in the 2 and/or 3-positions by all substituents studied does not lead to an increase in the rotational barrier over that for the unsubstituted derivative (40.30 kcalmol^{-1}), attributable to the lack of steric interactions between the *t*-butyl group and the substituents. However, as predicted from experiment, introduction of a second substituent in the 2-position of the 1-substituted derivatives should lead to a further lowering of the rotational barrier. This trend is observed here; the effect being greatest for the "bulkier" methyl substituent.

In summary, the semi-empirical method AM1 reproduces well both the structure of substituted triptycenes, and the barrier to rotation of substituents in the 9-position. The trends for the experimentally observed phenomenon of the "negative buttressing effect" are also well accounted for by the AM1 level of theory when substituents are placed in the 1, 2, 3 and 4-positions. The electronic interactions between substituents will be the subject of further investigation.

ACKNOWLEDGEMENTS

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