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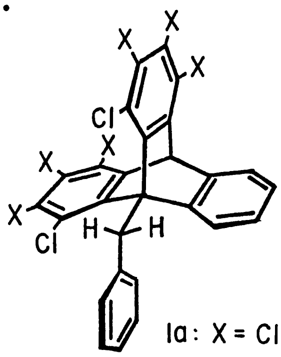
BUTTRESSING EFFECT IN OPPOSITE DIRECTION(1)

Gaku YAMAMOTO, Masahiko SUZUKI, and Michinori ŌKI*
Department of Chemistry, Faculty of Science,
The University of Tokyo, Bunkyo-ku, Tokyo 113

Rotational barrier in 1,2,3,4-tetrachloro-9-(1,1-dimethyl-2-phenylethyl)triptycene was 1.8 kcal/mol lower than that in the corresponding 1,4-dichloro derivative. This apparently anomalous "reverse" buttressing effect may be originated from the tilting of the 9-substituent away from the peri-chloro group in this highly congested system.

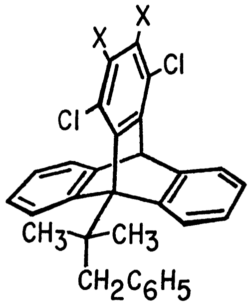
Steric effects on barriers to rotation about a single bond exerted by groups remote from the bond in question have been documented as buttressing effects, the most typical example being suppression of the racemization rates of optically active 2'-methoxy-6-nitrobiphenyl-2-carboxylic acid by 3'-substituents.(2) The phenomena are interpreted on the basis that the 3'-substituents prevent the in-plane bond-angle deformation of the 2'-methoxyl group which is one of the ways to avoid a strong steric interaction in the transition state for rotation.

Examples reported so far are always accompanied by increase in barriers to rotation if the buttressing effect is present. Our recent finding that 1,2,3,4,5,6,7,8-octachloro-9-benzyltriptycene (1a) showed a higher barrier to rotation than that of a 1,8-dichloro derivative 1b falls in the same line.(3) We have come across an example that shows a lower barrier to rotation if a buttressing substituent is present in the 2-position of the triptycyl skeleton. This paper reports such a finding and discusses the possible causes.



1a: X = Cl
1b: X = H

Reaction of 9-(1,1-dimethyl-2-phenylethyl)anthracene (3) with tetrachlorobenzyne gave stereoselectively the ap rotamer of 1,2,3,4-tetrachloro-9-(1,1-dimethyl-2-phenylethyl)triptycene (2a), mp 283-285°C.(4,5) Similar reaction of 3 with 3,6-dichlorobenzyne gave the ap rotamer of the corresponding 1,4-dichloro derivative 2b, mp 297-299°C.(5)



2a: X = Cl
2b: X = H

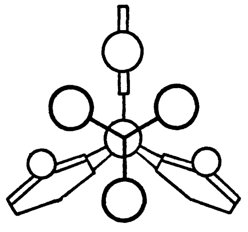
Isomerization of the ap rotamers was effected at 162-225°C range as 1-chloronaphthalene solutions and the intensity change of the methyl proton signals due to the ap and the forming ±sc rotamers was followed to give the kinetic data. The results are shown in Table 1.

Interesting is the fact that the tetrachloro derivative 2a has a lower barrier to rotation than the dichloro derivative 2b, manifesting the buttressing effect in opposite direction. This result may be apparently anomalous but is consistent with our previous findings that highly congested 9-t-alkyltriptycenes

Table 1. Thermodynamic and Kinetic Parameters ap $\underset{k_{-1}}{\overset{2k_1}{\rightleftharpoons}}$ ±sc : $K=2k_1/k_{-1}$

2a				2b			
Temp. °C	K	k_1 $10^{-6}s^{-1}$	$\Delta G^{\ddagger}$ kcal/mol	Temp. °C	K	k_1 $10^{-6}s^{-1}$	$\Delta G^{\ddagger}$ kcal/mol
208	0.49	48.0	38.1_2	225	0.57	31.6	39.9_2
196	0.47	20.1	37.96	212	0.55	12.1	39.7_8
184.5	0.45	7.62	37.8_9	189	0.52	1.71	39.6_4
162	0.42	1.20	37.5_8	175	0.50	0.55	39.4_2
$\Delta H^{\ddagger}$ =32.6 kcal/mol, $\Delta S^{\ddagger}$ =−12 eu				$\Delta H^{\ddagger}$ =35.3 kcal/mol, $\Delta S^{\ddagger}$ =−9 eu			

carrying a peri-chloro or a methyl group had lower barriers to rotation than the peri-unsubstituted derivatives.[4,6]



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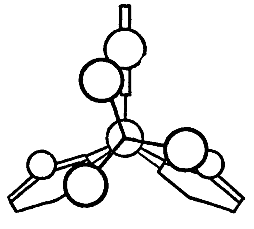

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Tilting of the substituents at peri- and 9-positions away from each other, as is typically shown in the crystal structure of 1,2,3,4-tetrachloro-9-t-butyltriptycene,[7] may be the key to understand these phenomena. A bulkier peri-substituent causes greater tilting and a buttressing substituent in the 2-position can also increase the tilting of the 9-substituent. On one hand, the tilting should affect the ground state. The larger the tilting is, the less stable becomes the ground state due to the steric interaction and the deformation. Newman projection 3 along the bond axis in question shows the situation. On the other hand, the tilting should also affect the transition state for rotation. During the rotational itinerary the maximal eclipsings between the peri-groups and the side chains of the 9-substituent do not occur simultaneously at the three sites but successively as is shown by the projection 4. The greater the tilting is, the larger become the timing gaps of the maximal eclipsings at the three sites to result in less destabilization of the transition state. Both of these factors may cause decrease in barriers to rotation, although the extent of the contribution of the two factors is not known. The observed "reverse" buttressing effect is regarded as a compilation of these and other minor factors which are not mentioned in this paper.

References

1) Restricted rotation involving the tetrahedral carbon. Part 37. Part 36: G. Yamamoto and M. Ōki, Bull. Chem. Soc. Jpn., in press.
2) S. L. Chien and R. Adams, J. Am. Chem. Soc., 56, 1787 (1934).
3) G. Yamamoto and M. Ōki, Bull. Chem. Soc. Jpn., in press.
4) G. Yamamoto, M. Suzuki, and M. Ōki, Angew. Chem., in press.
5) New compounds were satisfactorily analyzed.
6) S. Otsuka, T. Mitsuhashi, and M. Ōki, Bull. Chem. Soc. Jpn., 52, 3663 (1979); S. Otsuka, G. Yamamoto, T. Mitsuhashi, and M. Ōki, ibid., 53, 2095 (1980).
7) M. Mikami, K. Toriumi, M. Konno, and Y. Saito, Acta Cryst., B31, 2474 (1975).

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