# 1,9-Disubstituted Triptycenes: An Excellent Probe for Weak Molecular Interactions

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1,9-Disubstituted triptycenes (1) are sensitive and convenient probes for the detection of weak yet attractive molecular interactions by virtue of the following structural characteristics of the system.
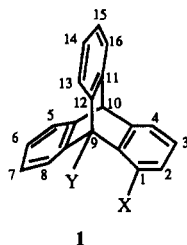

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Firstly, the distance between the two substituents concerned is unusually small as a nonbonded distance. It is ca. 2.7 Å between X and Y.[1-3] If the substituent at position 9 carries a non-hydrogen atom at the α-position, the distance between the β atom of the 9-substituent in the sc position and X is ca. 3.0 Å. Thus the overlap of the orbitals concerned is very efficient to facilitate charge-transfer interactions between an electron donor and an acceptor.

Secondly, the structural feature of the molecules, short distances between the groups concerned, makes it possible to detect a weak molecular interaction as a population ratio of the rotamers, due to a small difference in the repulsive forces between the two rotameric positions: The repulsive forces between the β non-hydrogen atom (plus atoms attached to it) in the 9-substituent are nearly the same on going from one conformation to another. In the present probe, near-cancellation of strong repulsive forces gives an opportunity of finding weak yet attractive interactions.

Thirdly, 9-substituted triptycenes exhibit unusually high barriers to rotation about the C_9-to-substituent bond.[4,5] This makes it possible to measure the population ratios easily by NMR spectroscopy.

For the convenience of the measurements, 1,9-disubstituted triptycenes that bear a primary alkyl group at the 9-position have mainly been used. The rotational circuit in these molecules is shown in the following scheme with the nomenclature of the rotational isomers. Possessing C_{2v} symmetry, the ap form exhibits a singlet signal for the methylene protons in the NMR spectra, while the $\pm sc$ forms show an AB quartet signal due to the diastereotopic nature of the methylene protons.
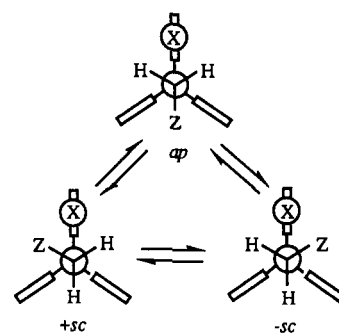
This article is an account of studies on weak molecular interactions using this system. Detection of very weak interactions that have been controversial or have been theoretically possible but experimentally difficult to prove will be described.

(1) Mikami, M.; Toriumi, K.; Konno, M.; Saito, Y. Acta Crystallogr., Sect. B 1975, 31, 2474.
(2) Nogami, N.; Ōki, M.; Sato, S.; Saito, Y. Bull. Chem. Soc. Jpn. 1982, 55, 3580.
(3) Ōki, M.; Takiguchi, N.; Toyota, S.; Yamamoto, G.; Murata, S. Bull. Chem. Soc. Jpn. 1988, 61, 4295.
(4) Ōki, M. Angew. Chem., Int. Ed. Engl. 1976, 15, 87.
(5) Ōki, M. Top. Stereochem. 1983, 14, 1.

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Table I
Population Ratios, ±sc/ap, of Rotamers in 9-Substituted
1,2,3,4-Tetrachlorotriptycenes (13-16) in Chloroform-d

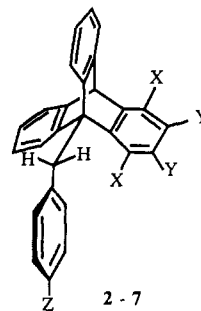| 9-substituent	±sc/ap	obsd temp, °C
CH_2COCH_3	≥10	-20
CH_2COOCH_3	6	-40
CH_2CHO	1.1	-20
CH_2CN	0	-40

n–π* Interactions

If an acceptor is strong enough, such as (polynitro)-benzenes, an n donor can form a strong charge-transfer complex that can be a reaction intermediate. Nitrobenzene can form a charge-transfer complex with aniline[6] because the electron-accepting ability of nitrobenzene is strong enough to form such a complex. However, benzene itself or benzenes that carry an electron-donating substituent are believed to be too weak π-acids to form charge-transfer complexes.

Interactions between an amino nitrogen and a carbonyl carbon are well documented.[7] This work became the starting point for investigating the incipient transition state for the addition of nucleophiles to carbonyl groups both by crystallographic and by theoretical methods.[8,9] Being a much weaker base than the amine, an ether oxygen gives unambiguous results in a similar investigation of cyclic oxa ketones by infrared spectroscopy,[10] though such interactions were found by crystallography.[11]

1,9-Disubstituted triptycenes have been used to demonstrate the presence of charge-transfer interactions involving weak acceptors or weak donors.

Benzene Rings as π Acceptors. 9-Benzyl-1,4-dimethoxytriptycene (2) exhibits anomalous population ratios.[12] The ratio ±sc/ap is 2.8 at -50 °C in CDCl₃–CS₂, over 2.0, which is the statistical value, in contrast to the fact that a bulky substituent tends to occupy the ap position or less bulky substituents tend to occupy the ±sc positions in 1,9-disubstituted triptycenes.[13] The unusual population ratio was attributed to the charge-transfer interaction between the methoxy oxygen and the benzylic benzene ring which favors the ±sc forms. The conclusion is supported by the population change on introduction of a substituent to the para position of the benzylic benzene ring. Introduction of a chloro group (compound 3) increased the ±sc/ap ratio to 3.5, whereas that of a methoxy group (compound 4) decreased it to 2.4.

If the 9-benzyltriptycene carries a chloro substituent at the 1-position (compound 5), the population ratio ±sc/ap is reduced to 1.0 at -23 °C in CS₂, well below the statistical value. This result indicates that electron donation from the chloro substituent is much more difficult than from the methoxy oxygen. The argument
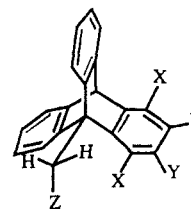
(6) Polle, N. N.; Polle, E. G.; Pushnikova, L. N. *J. Gen. Chem. USSR (Engl. Transl.)* 1972, *42*, 202.

(7) Leonard, N. J. *Rec. Chem. Prog.* 1956, *17*, 243.

(8) Bürgi, H. B.; Dunitz, J. D.; Shefter, E. *J. Am. Chem. Soc.* 1973, *95*, 5056.

(9) Bürgi, H. B.; Dunitz, J. D.; Lehn, J. M.; Wipf, G. *Tetrahedron* 1974, *30*, 1563.

(10) Leonard, N. J.; Milligan, T. W.; Brown, T. L. *J. Am. Chem. Soc.* 1960, *82*, 4075.

(11) Bürgi, H. B.; Dunitz, J. D.; Shefter, E. *Acta Crystallogr., Sect. B* 1974, *30*, 1517. Kaftory, M.; Dunitz, J. D. *Ibid.* 1975, *31*, 2917.

(12) Suzuki, F.; Ōki, M. *Bull. Chem. Soc. Jpn.* 1975, *48*, 596.

(13) Suzuki, F.; Ōki, M.; Nakanishi, H. *Bull. Chem. Soc. Jpn.* 1974, *47*, 3114. Yamamoto, G.; Ōki, M. *Ibid.* 1983, *56*, 2082.

	X	Y	Z
2	CH_3O	H	H
3	CH_3O	H	Cl
4	CH_3O	H	CH_3O
5	Cl	Cl	H
6	Br	Br	H
7	CH_3	H	H

that the result might mainly be attributed to the steric effect of the 1-substituent is ruled out because, if it were the case, the bromo compound (6) should have given a lower ±sc/ap ratio than the chloro compound (5), contrary to the finding that the ±sc/ap ratio is also 1.0 under the same conditions. The lower ionization potential of bromobenzene than of chlorobenzene[14] must be responsible.

9-Benzyl-1,4-dimethyltriptycene (7) exhibits a ±sc/ap ratio of 0.85 in CDCl₃–CS₂ at -50 °C. The result was originally attributed to the high ionization potential of the moiety involving the 1-methylbenzeno bridge, but it should also involve the consequence of the CH–π interactions discussed later in this paper.

Carbonyl Groups as n Acceptors. Examination of the ¹H NMR spectra of 1,4-dimethoxy-9-(substituted carbonylmethyl)triptycenes (8–10) showed exclusively the ±sc form, and no ap form could be detected at -30 to -50 °C in CDCl₃.[15] In similar experiments, 9-(cyanomethyl)-1,4-dimethoxytriptycene (11) was found to give a ±sc/ap ratio of 1.1, whereas sterically similar 9-(2-butynyl)-1,4-dimethoxytriptycene (12) gave a ratio of 0.1. This is consistent with the tendency of cyano groups to show a less electrophilic nature than carbonyl groups,[16] yet it shows that there is an attractive force operating in the systems of compound 11.

8-16

	X	Y	Z
8	CH_3O	H	$COCH_3$
9	CH_3O	H	$COOCH_3$
10	CH_3O	H	CHO
11	CH_3O	H	CN
12	CH_3O	H	$C≡CCH_3$
13	Cl	Cl	$COCH_3$
14	Cl	Cl	$COOCH_3$
15	Cl	Cl	CHO
16	Cl	Cl	CN

(14) Watanabe, K. *J. Chem. Phys.* 1957, *26*, 542.

(15) Ōki, M.; Izumi, G.; Yamamoto, G.; Nakamura, N. *Bull. Chem. Soc. Jpn.* 1982, *55*, 159.

(16) Pearson, R. G. *Inorg. Chem.* 1988, *27*, 734.

It was possible to see the order of the electron-accepting power of the carbonyl groups when a 1-chloro substituent was introduced (13–16) in place of the 1-methoxy group. The sequence shown in Table I is unusual in that the aldehyde is less electron accepting than the ketone. This anomaly is caused by the difference in conformation. According to X-ray crystallographic results,[2,15] the ketone takes an O-inside (17) conformation whereas the aldehyde takes an O-outside (18) conformation due to the steric effect. Being O-outside, the ±*sc* form of the aldehyde is less favored due to the parallel arrangement of two dipoles. The methoxycarbonyl group takes both O-inside and O-outside conformations as shown by infrared spectroscopy; thus the methoxycarbonyl compound (14) gives a lesser amount of ±*sc* conformers than the ketone and more ±*sc* than the aldehyde. Here the nitrile group is too weakly electron accepting to show the presence of the ±*sc* form (compound 16).

17   18
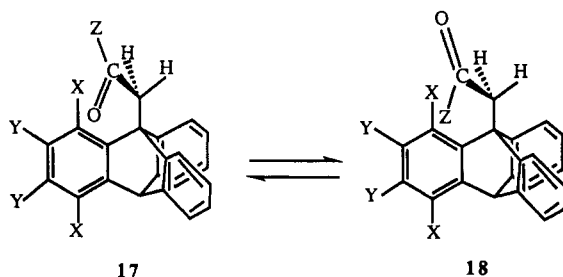
The X-ray structures of ketone 13 are very informative because the crystal contains both *ap* and ±*sc* forms.[2] A number of structural features of the molecules, which are small but indicative of the presence of Cl···O interactions, were cited. However, the carbonyl group is essentially planar, differing from those in the amine–CO case,[8] due to the weak nature of the Cl···O interaction and/or the structural constraint in the system.

n–σ* Interactions

Typical examples of n–σ* interactions are the aggregates that intervene during the process of S_N2 reactions. The aggregates were observed in the gas phase,[17,18] and theoretical calculations are in agreement with the observations.[19] Crystallographic investigations also shows the presence of such interactions in certain cases.[20]

As to the intramolecular interactions of this type, examples are rather sparse except for the phenomena associated with anomeric effects.[21] Therefore, it is worthwhile to look into the intramolecular n–σ* interactions using 1,9-disubstituted triptycenes.

Interactions Forming Six-Membered Rings. Attempted synthesis of 9-(2-chloroethyl)-1,4-dimethoxytriptycene (19) failed due to a facile reaction between the chloroethyl and the methoxy groups,[22] which

suggests that the interaction between the groups concerned is strong enough to cause a reaction. More weakly electron accepting σ* orbitals than the C–Cl moiety can be obtained with the use of acyloxy groups.

Population ratios ±*sc*/*ap* of 9-[2-(acyloxy)ethyl]-1,4-dimethoxytriptycene (20) rotamers were determined by ¹H NMR spectra at ca. –50 °C for chloroform-*d* solutions.[22] The ratio varies from 1.5 for the acetoxy compound to 3.0 for the trichloroacetoxy and trifluoroacetoxy compounds. The change in the population ratios is almost linear with the acidity of the carboxylic acids, from which the 2-(acyloxy)ethyl group is constituted. By contrast, the corresponding 2-methoxyethyl compound (21), which possesses steric size similar to that of the acyloxy comopunds but the high-lying σ* orbital associated with the methoxy group with respect to the acyloxy group, gives a ±*sc*/*ap* ratio of only 0.7.

19-24
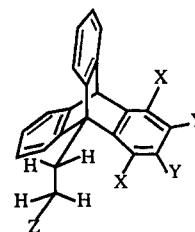
	X	Y	Z
19	CH₃O	H	Cl
20	CH₃O	H	RCOO
21	CH₃O	H	CH₃O
22	CH₃O	H	H
23	Cl	Cl	CH₃COO
24	Cl	Cl	Cl

The results may be interpreted in two ways: (a) stabilization of the ±*sc* form by head-to-tail arrangement of two dipoles and (b) n–σ* charge-transfer interactions. The former cannot be the main factor that gives high ±*sc*/*ap* values for these compounds for the following reasons. Firstly, in solvents of low polarity like chloroform, the stabilization due to such an arrangement of dipoles is unlikely. Secondly, the ±*sc*/*ap* value for the 9-(2-methoxyethyl) compound (21) is almost the same as that of 9-ethyl-1,4-dimethoxytriptycene (22)[23] at ca. 0.7. Thirdly, if the arrangement of the dipoles were important, the 1-chloro derivatives (23 and 24) would more strongly favor the ±*sc* conformation than the 1-methoxy compound due to a larger dipole moment of the C–Cl bond than the methyl ether moiety and a more favorable geometry for the former than the latter.

Interactions Forming Five-Membered Rings. Since the distance between the 1-substituent and the α atom of the 9-substituent in the triptycene system is even smaller than that involving the β atom of the 9-substituent, it is naturally expected that n–σ* interactions should be observed in the former cases. Natural candidates are 9-(chloromethyl)-1-methoxytriptycene (26). Indeed, 9-(chloromethyl)-1,4-dimethoxytriptycene (25) exhibits strong evidence that it exists almost exclusively as *ap* conformers. Detailed examination of the ¹H NMR spectra at 400 MHz reveals that the population of the ±*sc* isomer is ca. 4% at –40 °C in CDCl₃.[24]

(17) Dougherty, R. C.; Dalton, J.; Roberts, J. D. *Org. Mass Spectrom.* 1974, *8*, 77. Dougherty, R. C. *Ibid.* 1974, *8*, 85.

(18) Olmstead, W. M.; Brauman, I. J. *J. Am. Chem. Soc.* 1977, *99*, 4219. Pelerite, M. J.; Brauman, I. J. *Ibid.* 1980, *102*, 5993.

(19) Kozaki, T.; Morihashi, K.; Kikuchi, O. *J. Am. Chem. Soc.* 1989, *111*, 1547 and papers cited therein.

(20) Rosenfield, R. E.; Parthasarathy, R.; Dunitz, J. D. *J. Am. Chem. Soc.* 1977, *99*, 4860.

(21) Kirby, A. J. *The Anomeric Effect and Related Stereoelectronic Effects at Oxygen*; Springer: Berlin, 1983; pp 62–71.

(22) Izumi, G.; Yamamoto, G.; Ōki, M. *Bull. Chem. Soc. Jpn.* 1981, *54*, 3064.

(23) Nakanishi, H.; Yamamoto, O. *Bull. Chem. Soc. Jpn.* 1978, *51*, 1777.
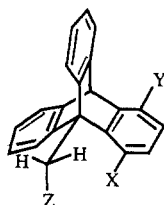
25-34

	X	Y	Z
25	CH$_3$O	CH$_3$O	Cl
26	CH$_3$O	H	Cl
27	CH$_3$O	NO$_2$	Cl
28	CH$_3$	CH$_3$	Cl
29	CH$_3$O	H	CH$_3$
30	CH$_3$O	NO$_2$	CH$_3$
31	CH$_3$	CH$_3$	ArO
32	CH$_3$	CH$_3$	RO
33	CH$_3$O	CH$_3$O	CH(CH$_3$)$_2$
34	CH$_3$O	CH$_3$O	CH$_2$=CH

Introduction of a substituent (**25–27**) into the 4-position of 9-(chloromethyl)-1-methoxytriptycene changes the electron density on the 1-methoxy group and causes the population change. Thus the 4-nitro compound (**27**) shows the existence of the ±*sc* isomer up to 8% in chloroform. When the solvent is changed from chloroform to toluene, the ±*sc* population increases to 12% for compound **27**. These results can be explained by steric effects, a head-to-tail arrangement of two dipoles, and charge-transfer effects.

The X-ray structure of the *ap* form of compound **25** could be obtained because the crystals of the compound contained only the *ap* form. It revealed two structural features of interest. The C–Cl bond distance is long, 1.813 Å. The 1-methoxy group is rotated from the benzene plane to which it is attached, the torsion angle C$_2$–C$_1$–O–C$_{Me}$ being 35°. The long C–Cl distance, however, is due to the steric effects of the triptycene nucleus, because *ap*-9-(chloromethyl)-1,4-dimethyltriptycene (**28**), in which no n–σ* interaction involving the C–Cl moiety is possible, also shows a long C–Cl distance, 1.818 Å.[24]

The nonplanarity of the 1-methoxy group with the benzene ring is unusual because the planar conformation is believed to be the most stable for methoxybenzene and its derivatives unless steric effects demand otherwise,[25,26] and the methoxy group in the other end of the molecule is indeed in the plane of the benzene ring. The structural feature of the 1-methoxy group is best interpreted on the basis that such a structure is favored because the ionization potential of the lone-pair electrons of the oxygen is reduced to facilitate the n–σ* interactions in the nonplanar conformation.

## Interactions Involving Methyl Groups

Hydrogen bonding involving a CH group as an electron acceptor has attracted the interest of many investigators.[27] It is generally believed that the CH groups in hydrogen cyanide, acetylene, and chloroform form hydrogen bonds with atoms bearing nonbonded

electron pairs or π-systems. However, formation of a hydrogen bond by normal CH groups is doubtful. The results of theoretical studies are not in complete agreement. Two papers mention that the CH···π interaction is possible, though weak.[28,29] Other papers mention that hydrogen-bond formation between an ether oxygen and nitromethane or acetonitrile, which should be a strong acceptor among CH compounds, is not possible.[30]

Hirota, Nishio, and co-workers worked extensively in this area.[31] These authors showed various experimental results to postulate the existence of the CH···π bond, but the results could be interpreted in other ways. The existence of the CH···π interaction is doubtful at best.

The 1,9-disubstituted triptycene system should contribute to finding such a weak interaction, because exclusion of the presence of the CH$_3$···O hydrogen bond between nitromethane and an ether oxygen by calculation must be an example that shows the repulsive force is stronger than the attractive one. Indeed, in the literature that reports the population ratios of rotational isomers in the triptycene series, anomalous rotamer populations can be found.

Both 9-ethyl-1,4-dimethoxytriptycene (**22**) and 9-allyl-1,4-dimethoxytriptycene (**34**) exhibit a ±*sc/ap* ratio of ca. 0.7, irrespective of the large steric size of the methyl group with respect to the π-system.[15,23] The ±*sc/ap* ratio of rotamers in 1,4-dimethyl-9-(1-methyl-2-propenyl)triptycene (**35**) is 1.52, whereas that in 1,2,3,4-tetrabromo-9-(1-methyl-2-propenyl)triptycene (**36**) is only 0.8,[32] irrespective of similar sizes of the 1-substituents in these compounds. If there is an attractive interaction between a CH group and an ether oxygen or a π-system, these can be rationalized. Further evidence for the presence of such interactions have been sought on these bases.
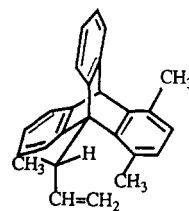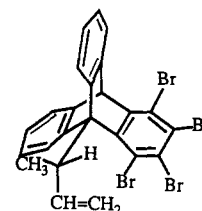
35   **36**

CH$_3$···O Hydrogen Bond. The effect on the ±*sc/ap* ratios of changing the electron density of ether oxygens while maintaining a methyl group constant has been examined for the diagnosis of the presence of the CH···O bond. Compounds that carry hydrogen or a nitro group at the 4-position of 9-ethyl-1-methoxytriptycene (**29** or **30**) were selected. Reduction in the electron density at the 1-methoxy oxygen results in an increase in the ±*sc/ap* ratio.[33] The results are in accordance with the idea that an increase in the steric bulkiness by increasing the electron density enhances the repulsive

(24) Tamura, Y.; Takizawa, H.; Yamamoto, G.; Ōki, M.; Murata, S. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 2555.

(25) Dodziuk, H.; Voitehenberg, H. von; Allinger, N. L. *Tetrahedron* **1982**, *38*, 2811.

(26) Breen, P. J.; Bernstein, E. R.; Secor, H. V.; Seeman, J. I. *J. Am. Chem. Soc.* **1989**, *111*, 1958.

(27) Green, R. D. *Hydrogen Bonding by C-H Groups*; John-Wiley: New York, 1974.

(28) Abe, K.; Hirota, M.; Morokuma, K. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 2713.

(29) Takagi, T.; Tanaka, A.; Matsuno, S.; Maezaki, H.; Tani, M.; Fujiwara, H.; Sasaki, Y. *J. Chem. Soc., Perkin Trans. 2* **1987**, 1015.

(30) Damewood, J. R., Jr.; Kumpf, R. A. *J. Phys. Chem.* **1987**, *91*, 3449. Kumpf, R. A.; Damewood, J. R., Jr. *J. Chem. Soc., Chem. Commun.* **1988**, 621.

(31) Nishio, M.; Hirota, M. *Tetrahedron* **1989**, *45*, 7201.

(32) Kikuchi, H.; Hatakeyama, S.; Yamamoto, G.; Ōki, M. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 3832.

(33) Tamura, Y.; Yamamoto, G.; Ōki, M. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 1781.

Table II
Population Ratios, ±sc/ap, of Rotamers in
9-[(Aryloxy)methyl]-1,4-dimethyltriptycenes (31) in
Chloroform-d at Ca. -50 °C and Substituent Constants of
the Substituents

aryl substituent	substituent constant, σ	±sc/ap
4-(CH$_3$)$_2$N	-0.600	0.289
4-CH$_3$O	-0.268	0.242
H	0.000	0.224
4-NO$_2$	0.778	0.191
3,4-(NO$_2$)$_2$	1.385^a	0.165

^{a} Calculated from the dissociation constant of 3,4-dinitrobenzoic acid.

force. Although this is a negative result from the standpoint of charge-transfer interactions, it helps to establish the presence of the CH$_3$···O hydrogen bond in the other systems.

In order to change the basicity of the ether oxygen and the acidity of the methyl group, 9-(substituted phenoxymethyl)-1,4-dimethyltriptycenes (31) were designed. The results are shown in Table II together with other relevant data.[33] Clearly, the ±sc/ap ratio increases as the electron density on the aryloxy oxygen increases. This tendency is contrary to the steric effect mentioned above and supports the presence of the CH$_3$···O hydrogen bond, though the ±sc conformer has never become the majority. Interesting is the ρ value in the Hammett plot, -0.114. The upward concave nature of the Hammett plot, together with the rather low population of the ±sc conformer with the electron-rich oxygen and the small ρ value, suggests that the population is in a delicate balance of the attractive force with the repulsive.

This delicate balance is again seen when one compares the ±sc/ap ratio of 1,4-dimethyl-9-(methoxymethyl)triptycene (32, R = CH$_3$) with the corresponding 9-phenoxymethyl compound (31, Ar = C$_6$H$_5$). They give almost the same ±sc/ap ratios, irrespective of the fact that the basicity of the methoxy oxygen should be higher than that of the phenoxy oxygen. However, this does not mean to be evidence against the presence of a CH$_3$···O hydrogen bond, because when one changes the basicity of the ether oxygen of compound 32 (R = CH$_3$) by introducing an ethyl (32, R = C$_2$H$_5$) or a 2,2,2-trifluoroethyl (32, R = CF$_3$CH$_2$) group in place of the methyl, again the high electron density on the oxygen atom favors the ±sc conformer.[34]

The rather low population ratios of the ±sc isomers in 9-[(aryloxy)methyl]-1,4-dimethyltriptycene (31) or 9-(alkoxymethyl)-1,4-dimethyltriptycene (32) in spite of the attractive interactions between the CH$_3$ group and the oxygen are due to the presence of very large repulsive forces. If we wish to see the result that the ±sc isomer is a major component, we have to further introduce factors that reduce the difference in the repulsive forces in the two rotamers to the models discussed above.

This type of reduction in the energy difference between the two rotameric forms is accomplished by introducing an extra substituent. Because of the geometry of the triptycene molecules, introduction of two ortho methyl groups to the benzylic phenyl group in 9-benzyltriptycene (e.g., 2-7) necessarily places one of

(34) Tamura, Y.; Yamamoto, G.; Ōki, M. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 3789.

the methyl groups into the triptycene notch. This makes the conformation unstable.[35] Analogously, 9-isobutyl-1,4-dimethoxytriptycene (33) was designed in the expectation that one of the methyl groups in the isobutyl group would be directed inside of the triptycene notch. This makes the repulsive interaction between the inside methyl and the triptycene severe and hopefully masks the small difference in the repulsive forces between the ap and the ±sc forms of the compound that does not carry such substituents.

Both rotamers of compound 33 are observed by ^{1}H NMR spectra at 400 MHz.[3] The majority conformation is ±sc below -85 °C, and at -110 °C both forms exist in the statistical amounts. In addition, the molecular motion with respect to the isopropyl group in the ±sc conformation is much slower than that in the ap, as the line shapes of the NMR spectra suggest. These imply that, in spite of the unfavorable conditions, weak oxygen basicity and weak CH$_3$ acidity, it is possible to observe conformational ratios affected by the CH$_3$···O hydrogen bond.

Compound 33 crystallizes in ±sc conformers. The molecular structure of the compound exhibits two features that deserve mention here. One of the methyl groups of the isobutyl that inserts into the triptycene notch is very closely located to the 1-methoxy oxygen, the distance being only 3.02 Å, while the other methyl has the C-O nonbonding distance of 3.33 Å. The other feature is the out-of-plane structure of the 1-methoxy group, the torsion angle C$_2$-C$_1$-O-C$_{Me}$ being ca. 10°. It is suggested that these two features also support the presence of the CH$_3$···O hydrogen bond.

CH$_3$···π Interactions. 9-Benzyl-8,13-dichloro-1-methyltriptycenes (37-42) were examined to evaluate the possible presence of CH$_3$···π interaction. Triptycenes 37-42 possess substituents of similar size in all the peri positions. This minimizes differences in repulsive forces between the ap and the ±sc positions. Because of the benzyl substituent, the population ratios and kinetic parameters for rotation can be obtained by classical methods in this system.[35] Lastly, the aromatic methyl groups are more acidic than the aliphatic ones,[36] thereby providing a better chance to observe the presence of the interactions.
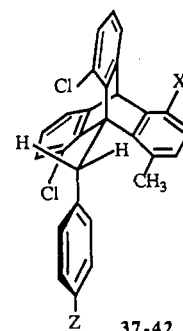
	X	Z
37	CH$_3$	NO$_2$
38	CH$_3$	H
39	CH$_3$	N(CH$_3$)$_2$
40	H	H
41	COOCH$_3$	H
42	CN	H

(35) Yamamoto, G.; Ōki, M. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 481.
(36) Shatenstein, A. I. *Adv. Phys. Org. Chem.* **1963**, *1*, 155. Streitwieser, A.; Hammons, J. H. *Prog. Phys. Org. Chem.* **1965**, *3*, 41.

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Introduction of a substituent into the 4-position of the benzyl group (37–39) affects the population ratios as expected from the presence of the $CH_3 \cdots \pi$ interactions: a higher ±sc/ap value for the compound with a dimethylamino group than that with a nitro group.[37] Although it is likely that the data support the presence of the $CH_3 \cdots \pi$ interactions especially because the ±sc/ap ratio is close to 3 in the dimethylamino compound (39), it is not possible to exclude the possibility that the n–π* charge-transfer interaction between the chloro substituent and the benzene ring of the benzyl favors the ap conformation as the latter becomes electron-accepting.

In order to avoid this complexity, a substituent is introduced to the 4-position of 9-benzyl-8,13-dichloro-1-methyltriptycene (40–42). The substituent is expected to affect the acidity of the 1-methyl group and thus the formation of the CH···π interactions. The results are summarized in Table III together with relevant data.[37]

Although there are some irregularities, the general tendency is that, as the acidity of the 1-methyl group is enhanced, the ±sc/ap ratio increases. This is consistent with the presence of the $CH_3 \cdots \pi$ interactions. The results of MM2 calculations shown in Table III clearly indicate that all the compounds examined here should favor the ap forms by ca. 1.0 kcal mol⁻¹. The observation is contrary to the prediction. MM2 calculations are known to reproduce the structures of triptycenes that are obtained by X-ray methods and in some cases to give the rotamer populations correctly.[38] Therefore, one is forced to consider that factors that are not taken into account in the MM2 calculations are important here. Charge-transfer interactions thus become the most likely interactions that favor the ±sc conformation.

Long-Range Coupling in Nuclear Magnetic Resonance Spectra

The foregoing discussion on n–σ* interactions clearly reveals that there are significant interactions between

lone-pair electrons belonging to the 1-substituent and σ* orbitals belonging to a bond ap to the 1-substituent in the triptycene system. The orbital interactions will also apply to the occupied ones. Then the interactions should affect the spin–spin coupling in NMR spectra, if two nuclei are properly located. Therefore, the triptycene system should contribute further to understanding the mechanism of the long-range coupling.

The H–F coupling constant between the 1-fluorine nucleus and the proton in the 9-methyl group in 8,13-dichloro-1,2,3,4-tetrafluoro-9-methyltriptycene (43) is 8.7 Hz for the ap proton and 6.1 Hz for the ±sc proton.[39] Since the C-9 does not show coupling with the 1-fluorine whereas the methyl C does show coupling with 1-F, it is clearly the through-space coupling. It is interesting that the proton in the remote position gives a larger coupling constant than those in proximity with respect to the 1-fluorine. This clearly shows that the overlap of the orbitals extending toward the fluorine atom with those belonging to the fluorine is important.
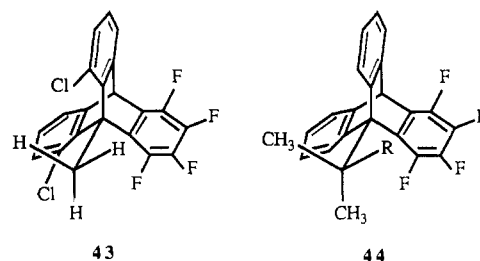
When the 9-substituent is a *tert*-butyl group instead of the methyl, e.g., 44 (R = CH_3), the ap-methyl protons fail to show observable coupling with the 1-fluorine, whereas the coupling with the ap-methyl protons is observed, though the coupling constant is small (ca. 1 Hz), in 1,2,3,4-tetrafluoro-9-isopropyltriptycene (44, R = H).[40] The failure to observe the coupling in the *tert*-butyl case is attributed to tilting of the *tert*-butyl group[1] away from the 1-fluoro substituent owing to the steric effect that makes the overlaps of the orbitals concerned less effective than in the isopropyl case.

Conclusion

The 1,9-disubstituted triptycene system is shown to be a convenient and sensitive probe for the detection of weak molecular interactions as population ratios of the rotamers. It can detect weak n–σ* and n–π* charge-transfer interactions as well as interactions involving a methyl group that could not be found in other systems. This system will serve to detect further weak interactions in the future. The principle discussed in this Account, cancellation of the difference in repulsive forces among rotational isomers, is a useful concept for manifesting weak interactions as populations of the rotamers. It will serve as a direction for designing suitable molecules for detection of weak interactions in systems other than triptycenes.

(37) Nakai, Y.; Inoue, K.; Yamamoto, G.; Ōki, M. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 2923.

(38) Abe, K.; Hirota, M.; Yamamoto, G.; Ōki, M. *Chem. Lett.* **1984**, 665.

(39) Yamamoto, G.; Ōki, M. *Tetrahedron Lett.* **1985**, *26*, 457.

(40) Yamamoto, G.; Ōki, M. *J. Org. Chem.* **1984**, *49*, 1913.