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Molecular Structure of 9-Chloromethyl-1,4-dimethoxytriptycene and Its Implications for the Presence of O···CH$_2$Cl Interactions

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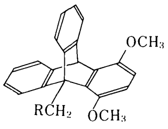
Changing the substituent at the 4-position of 9-chloromethyl-1-methoxytriptycene shows that the nitro group increases the *sc* conformation whereas the methoxyl group favors the *ap* conformation in a relative sense, as judged from the ^{1}H NMR spectra at low temperatures. Examination of rotational barriers, solvent effects, and thermodynamic parameters has not been able to distinguish three possibilities, O···CH$_2$Cl interactions, head-to-tail arrangement of two dipoles, and van der Waals repulsions as a main cause for the observed population change. X-Ray crystallographic analyses of the title compound and related ones suggest that in the crystalline state the 1-methoxyl group in the title compound takes an anomalous conformation in which the group is nonplanar with the benzeno bridge. This feature was not observed in 1,4-dimethoxy-9-methyltriptycene. This structural feature is attibuted to the presence of O···CH$_2$Cl interactions in the title compound and eliminates the van der Waals repulsion and the head-to-tail arrangement of two dipoles from being the main cause that favors the *ap* form.

The *ap* conformation of 9-chloromethyl-1, 4-dimethoxytriptycene (**1**) is known to be lop-sidedly favored over the *sc* conformation: the ^{1}H NMR signal due to the methylene protons of the chloromethyl group, which is a sharp singlet at room temperature, becomes broad at about 0 °C, and is again sharp at low temperature, the explanations being that the *sc* conformer is too unstable to be observed at low temperature relative to the *ap* form.[1)] This population ratio was used as standard in detecting molecular interactions between the methoxyl group and π^*-systems: the population of the *sc* form of 9-benzyl-1,4-dimethoxytriptycene (**2**) was more than the statistical value.



1 : R=Cl
2 : R=C$_6$H$_5$
3 : R=CH=CH$_2$
4 : R=CH$_3$
5 : R=CH$_2$OCOR′

However, as the population study on rotamers of triptycene derivatives develops, examples that show substantial amount of *sc* conformers are increasing. Both 9-allyl-(**3**) and 9-ethyl-1,4-dimethoxytriptycene (**4**) show the population ratios *sc*/*ap* of ca. 0.7.[2,3)] Since the methyl group is bulkier than the chloro substituent, if the steric repulsion is the main factor in controlling the populations of the rotamers, compound **4** should show smaller populations of the *sc* form than compound **1** to the first approximation, although in the former there must be a contribution of the CH$_3$···O hydrogen bond.[4)]

In the mean time, we have been able to show that there is an attractive interaction between the acyloxymethyl group and the methoxy-oxygen in 9-(2-acyloxyethyl)-1, 4-dimethoxytriptycenes (**5**).[5)] Since both distances between the 1-substituent and a group at the alpha position and that at the beta position of 9-substituent in triptycene derivatives are close to 3 Å,[6)] the results naturally suggest that there can be attractive interactions between the chloromethyl group and the methoxy-oxygen in compound **1**. This idea prompted us to reexamine the case of compound **1** and this paper is to report the results.

Substituent Effect

The first step we took was to change the electron density of the 1-methoxyl group by changing the 4-substituent in 4-substituted 9-chloromethyl-1-methoxytriptycenes in a hope that the low electron density would disfavor the O···CH$_2$Cl interactions. 9-Chloromethyl-1-methoxytriptycene (**7**) was prepared by addition of 3-methoxybenzyne to 9-chloromethylanthracene (**6**) to form a mixture of the desired product and 9-chloromethyl-4-methoxytriptycene (**8**). The mixture was separated by chromatography. The assignment of structures was performed by taking advantage of the chemical shift of the 10-H of the triptycenes in ^{1}H NMR spectra. As our experiences reveal, if there is a substituent present in the 4-position, the chemical shift of the 10-H is lower than that which has no substituent in the 4-position. Compound **7** was nitrated by nitronium tetrafluoroborate and the obtained mixture of 4-nitro and 2-nitro compounds (**9** and **10**) were separated by chromatog-

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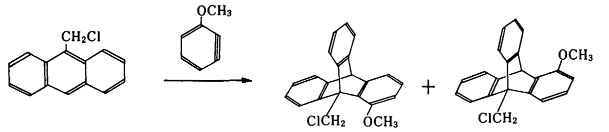

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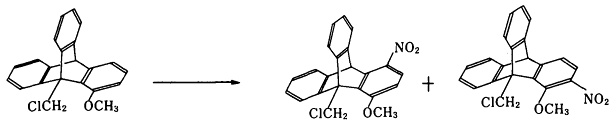

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raphy. Assignment of the structures of the nitrated products was easy by comparing the chemical shifts of the 10-H signal in ^{1}H NMR spectra.

The populations of the rotational isomers were determined by ^{1}H NMR spectroscopy at 400 MHz at low temperatures. The methylene protons in the *ap* conformation give a singlet signal because they are enantiotopic and those in the *sc* give an AB quartet signal due to their diastereotopic nature when the internal rotation is frozen. Actually however, the separation of the AB and C_2 signals due to the methylene protons are not necessarily good, thus preventing quantitative treatment. Thus the best-separated signals for the pair were used for the determination of populations. The results are shown in Table 1.

The results in Table 1 indicate that, although compounds **1** and **7** give slmost the same population ratios, compound **9** gives a large *sc*/*ap* ratio. This may be taken as indicative of the presence of charge-transfer interactions between the CH_2Cl group and the methoxy-oxygen, but there are other factors to be taken into account. One is a case in which one conformation is destabilized by structural deformation, while another is not. Another is a case in which various molecular interactions favor or disfavor a patricular conformation. The main contributers for this effect are Coulombic interactions, both stabilization and destabilization, and van der Waals interactions, both attractive and repulsive.

Diagnosis whether a given conformation is destabilized by structural deformation is possible if one compares the rotational barrier, because the transition state energy of the unsubstituted compound can be assumed to be practically the same with that of the substituted. The rotational barriers were determined by the dynamic NMR technique. For compound **1**, the aromatic 2, 3-proton signals of the benzeno bridge which carries the two methoxyl groups were used. The barriers to rotation in compounds **7** and **9** were determined with the use of methoxy-methyl signals. The results are shown in Table 2 and the kinetic parameters are shown in Table 3. Due to the fact that the *sc* rotamer populations are sparse, the barriers may contain large errors. Therefore, we should like to refer only to the free energy of activation here. As is seen in Table 3, the free energies of activation, both for *ap*→*sc* and *sc*→*ap* processes, especially the former, do not change significantly when the substituent in the 4-position is changed. The results confirm that no abrupt destabilization of any conformer is actually taking place.

The thermodynamic parameters were calculated by the van't Hoff plots with the use of the equilibrium constants thus obtained. The results are shown in Table 4. The large errors derived by the fact that one isomer sparsely populates preclude again detailed discussions. However, it is evident that the *ap* form of the 4-methoxy compound (**1**) is most stabilized among the compounds examined in the relative sense.

Coulombic interactions in the *ap* conformation are considered to be bigger than in the *sc* conformation because the C–O–C group dipole of the 1-methoxyl

Table 1. Populations and Population Ratios of Rotamers in 4-Substituted 9-Chloromethyl-1-methoxytriptycenes in $CDCl_3$

Substituent	*sc*/%	*sc*/*ap*[a)]	Temperature/°C	σ value[b)]
CH_3O	4.6±0.2	0.024	−10.0	−2.7
H	4.2±0.3	0.022	−9.6	0.0
NO_2	8.8±0.4	0.048	−9.6	0.78

a) The population of the *sc* form was divided by 2 to accommodate the fact that the *sc* form has two degenerate positions. b) From Ref. 7.

Table 2. Rate Constants for the Isomerization (*sc*→*ap*) in 4-Substituted 9-Chloromethyl-1-methoxytriptycenes in $CDCl_3$

Substituent	k/s^{-1} (Temperature/°C)
CH_3O	0.0 (−39.6), 2.0 (−20.3), 6.0 (−10.0), 10.0 (−5.0), 17.0 (−0.1), 28.0 (5.3), 45.0 (10.4), 66.0 (15.1), 100.0 (20.1), 155.0 (25.0)
H	2.0 (−14.6), 4.0 (−9.6), 7.5 (−4.7), 13.0 (0.3), 54.0 (15.3), 94.0 (20.3)
NO_2	0.0 (−19.7), 0.9 (−9.8), 4.0 (0.1), 7.0 (5.1), 13.0 (10.2), 20.0 (15.0), 38.0 (20.0)

Table 3. Activation Parameters for the Isomerization in 4-Substituted 9-Chloromethyl-1-methoxytriptycenes in $CDCl_3$[a)]

Subst	Process	$\Delta H^{\neq}$	$\Delta S^{\neq}$	$\Delta G^{\neq}_{298}$	r[b)]
		kcal mol^{-1}	cal mol^{-1} K^{-1}	kcal mol^{-1}	
CH_3O	*sc* → *ap*	13.8±0.1	−2.2±0.5	14.4	0.999
	ap → *sc*	15.8±0.2	−2.3±0.6	16.5	0.999
H	*sc* → *ap*	15.7±0.8	4.0±2.8	14.5	0.998
	ap → *sc*	17.5±0.6	3.3±2.4	16.5	0.999
NO_2	*sc* → *ap*	18.3±1.1	11.3±4.1	15.0	0.998
	ap → *sc*	21.7±0.8	17.7±4.1	16.4	0.999

a) 1 cal=4.184 J. b) r factor in the statistical treatment.

Table 4. Thermodynamic Parameters for the Equilibrium between Rotational Isomers of 4-Substituted 9-Chloromethyl-1-methoxytriptycenes in $CDCl_3$

Substituent	ΔH°/kcal mol^{-1}	ΔS°/cal mol^{-1} K^{-1}	r[a)]
CH_3O	2.0±0.7	1.4±0.3	0.986
H	1.0±0.3	−2.5±1.1	0.988
NO_2	0.9±0.1	−1.2±0.2	0.999

a) r factor in statistical treatment.

group directs toward the bisecting line of the angle and the negative end directs toward the C–Cl bond, which has a large dipole moment, in the *ap* conformation. By contrast, in the *sc* conformation, the C–Cl bond and the methoxyl dipoles make an angle of ca. 60 °. Thus the *ap* conformation is much more polar than the *sc*. In the normal cases, this kind of arrangement of two dipoles render a molecule rather unstable in nonpolar solvents, but there is one point which should not be overlooked in this particular case. That is, the two dipoles, in this *ap* case, are close to the head-to-tail arrangement rather than the pararell arrangement. This should stabilize the system and the *ap* conformation should be favored over the *sc*.

When we introduce a nitro group in the 4-position, due to the strong dipolar nature of the nitro group, the group dipole of the 1-methoxyl group will be reduced and the effects should result in relatively favoring the *sc* conformation on the stand point of the head-to-tail arrangement of dipoles. This agrees with the experimental results. When a methoxyl group is introduced into the 4-position, the dipolar nature of the 1-methoxyl group will be enhanced. In addition, the 4-methoxyl group is adding another dipolar fragment into the molecule to make the molecule more polar than that without the 4-substituent. It is not simple to say how these factors affect the populations of the rotamers, but the experimental results suggest that these, if operative as main factors, cancel out. The result of the 4-nitro compound suggests that the head-to-tail arrangement of the two dipoles may be important in favoring the *ap* conformation.

It is evident that the steric effects favor the *ap* conformation in all the molecules because the *sc* conformation is disfavored due to the repulsive interaction between the chloro substituent and the methoxyl group. However, when we compare the population in the series of compounds, we may have to take the followings into consideration. Firstly, as the electron density on the 1-methoxyl group decreases, the effective bulkiness of the oxygen atom will decrease. Secondly, when the nitro group is introduced to the 4-position, the C_1–O bond which connects the 1-methoxyl group and the C_1 of the triptycene skeleton will become short due to the resonance effect. These two factors all contribute to relatively favor the *sc* conformation by easing the steric repulsions.

Dispersion forces are expected to be stronger in the *sc* conformation than in the *ap* because of the distances between the groups concerned. Then it is difficult to explain why low electron density on the methoxy-oxygen should favor the *sc* form: the low electron density enlarges the distance. Dispersion forces may not be the main factor which controls the populations of the rotamers here, probably because electron density affects polarizability and ionization potential in opposite directions.

Charge-transfer interactions may be another likely factor that stabilizes the *ap* form. The n-electrons of the ether-oxygen atom is known to be easily used for forming change-transfer complexes,[8)] and the σ^*-orbital of the C–Cl bond should be electron-accepting.[9)] It is especially tempting to consider this possibility because of the successful finding of attractive interactions in compound **5**:[6)] the geometric arrangement of the two groups is ideal for the interactions.

Chloroform is known to be a special solvent in that

Table 5. Solvent Effects on the Populations (%) of *sc* Forms in 4-Substituted 9-Chloromethyl-1-methoxytriptycene at −9.6 °C

Solv	Substituent			Dielectric constant[a]
	CH_3O	H	NO_2	
$CDCl_3$	4.6±0.2[b]	4.2±0.3	8.8±0.4	4.81
THF-d_8	3.2±0.3	7.7±0.7[c]	8.2±0.2	7.58
Toluene-d_8	5.4±0.3	5.5±1.3	12.9±1.5	2.38

a) From Ref. 11. b) At −10.0 °C. c) At −9.7 °C.

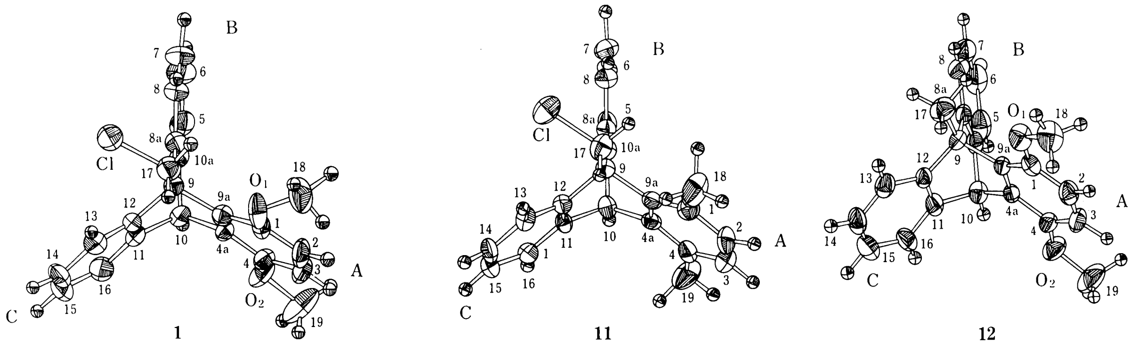

Fig. 1. ORTEP diagrams of compounds **1**, **11**, and **12** with numberings of atoms and designation of benzene rings.

it can form hydrogen bond with electron donors.[10] This ability of chloroform may enhance the charge-tansfer interactions or the head-to-tail arrangement of dipoles in the solute. Therefore, it will be of interest to see the solvent effects on the population ratios of the compounds examined here. As typical solvents, we have selected tetrahydrofuran-d_8 and toluene-d_8. The former acts as a solvent that is a little more polar than chloroform but incapable of forming hydrogen bond with electron donors and the latter is nonpolar. The results are shown in Table 5. Those data with the THF-d_8 solutions may contain some errors because the spectral lines which are used for the analyses of the rotamers overlap to some extent.

In toluene-d_8, the populations of the *sc* forms increase, as expected from the polarities of the *ap* and *sc* conformers. In THF-d_8, the general tendency is that the populations of the *sc* forms are lower than those in chloroform-*d* and will mean that the effect of hydrogen bonding, $Cl_3CD\cdots ClCH_2$, which stabilizes the charge-transferred form or the head-to-tail arrangement of the two dipoles, is significant. However, the effect is small and there is an exception (compound **7**). Thus we defer to draw a concrete conclusion until some more convincing data become available.

X-Ray Structures

Summarizing the above discussions, we point out that the charge-transfer interactions and/or the interactions due to the head-to-tail arrangement of two dipoles are most likely the stabilizing factors for the *ap* forms in compounds **1**, **7**, and **9**, but the steric effect cannot be completely ruled out from being the main factor for the stability control. Thus the X-ray study of **1** and related compounds were carried out. They are 9-chloromethyl-1,4-dimethyltriptycene (**11**) and 1,4-dimethoxy-9-methyltriptycene (**12**). Atomic coordinates, selected bond lengths, selected bond angles, selected torsion angles, and selected nonbonding distances in these compounds are given in Tables 6—10, respectively. ORTEP diagrams of compounds **1**, **11**, and **12** are given in Fig. 1 with numberings of atoms and designations of the benzeno bridges.

Although there are distinctly anomalous points in the structure of compound **1** from others, they contain various common features as well. The bond lengths of those which connect C_9 with benzeno bridges are all long relative to a normal C_{sp^2}–C_{sp^3} bond. It is also true that the bond angles involving the C_9 are small, if the two bonds direct toward the benzene rings. These are commonly observed for substituted triptycenes and are interpreted to mean that the steric strain is relieved by the deformation. The effect of this strain seems to be divided to other parts of the molecule and can be seen in the bond angles in Table 8.

The C–Cl bonds in compounds **1** and **11** take conformations which are very close to 180° to the benzene ring which bears the 1, 4-substituents, and almost bisects the torsion angle made by rings B and C. Torsion angles made by benzene rings are widened to a considerable extent when a nonhydrogen atom is placed between the planes.

Table 6-1. Atomic Coordinates (×10⁴) of Non-hydrogen Atoms in 9-Chloromethyl-1,4-dimethoxytriptycene with Standard Deviations in Parentheses and Thermal Factors

Atom	x	y	z	B_{eq} a)
C(1)	3240(1)	−4831(2)	−2444(1)	3.37
C(2)	3516(1)	−5645(2)	−3208(1)	4.21
C(3)	2962(1)	−5975(2)	−4064(1)	4.15
C(4)	2110(1)	−5450(2)	−4194(1)	3.43
C(4a)	1832(1)	−4600(2)	−3443(1)	2.92
C(5)	746(1)	−899(2)	−3877(1)	3.78
C(6)	975(1)	653(2)	−3591(2)	4.55
C(7)	1519(1)	940(2)	−2720(2)	4.53
C(8)	1838(1)	−314(2)	−2109(1)	3.47
C(8a)	1603(1)	−1869(2)	−2380(1)	2.75
C(9)	1921(1)	−3393(2)	−1821(1)	2.59
C(9a)	2381(1)	−4310(2)	−2562(1)	2.82
C(10)	923(1)	−3908(2)	−3505(1)	2.98
C(10a)	1063(1)	−2153(2)	−3274(1)	2.88
C(11)	578(1)	−4654(2)	−2654(1)	3.04
C(12)	1115(1)	−4417(2)	−1759(1)	2.76
C(13)	921(1)	−5156(2)	−931(1)	3.53
C(14)	162(1)	−6064(2)	−1006(1)	4.62
C(15)	−383(1)	−6235(3)	−1882(2)	4.91
C(16)	−171(1)	−5561(2)	−2720(1)	4.05
C(17)	2484(1)	−3077(2)	−838(1)	3.24
C(18)	4647(1)	−4228(4)	−1553(2)	6.66
C(19)	1761(2)	−6650(3)	−5772(2)	6.99
O(1)	3771(1)	−4566(2)	−1564(1)	4.85
O(2)	1506(1)	−5700(2)	−5021(1)	4.54
Cl	1897(0)	−2085(1)	4(0)	4.06

a) Equivalent isotropic temperature factor defined by Hamilton.[12]

Table 6-2. Atomic Coordinates (×10⁴) of Non-hydrogen Atoms in 9-Chloromethyl-1,4-dimethyltriptycene with Standard Deviations in Parentheses and Thermal Factors

Atom	x	y	z	B_{eq}
C(1)	−485(3)	7535(2)	7087(4)	3.10
C(2)	−1151(3)	7915(2)	6614(5)	3.65
C(3)	−1876(3)	7730(2)	5896(5)	3.66
C(4)	−2000(3)	7144(2)	5613(4)	2.71
C(4a)	−1362(2)	6756(2)	6085(4)	2.10
C(5)	−545(3)	5630(2)	3922(5)	2.59
C(6)	279(3)	5527(2)	3322(4)	3.20
C(7)	1038(3)	5733(2)	3932(5)	3.26
C(8)	995(3)	6024(2)	5171(5)	2.91
C(8a)	192(3)	6116(2)	5792(4)	2.45
C(9)	10(2)	6415(2)	7169(4)	2.41
C(9a)	−606(2)	6943(2)	6802(4)	2.46
C(10)	−1418(2)	6101(2)	5871(4)	2.29
C(10a)	−578(2)	5929(2)	5143(4)	2.21
C(11)	−1350(2)	5831(2)	7278(4)	2.37
C(12)	−593(2)	6004(2)	7989(4)	2.48
C(13)	−467(3)	5802(2)	9315(5)	3.26
C(14)	−1080(3)	5422(2)	9874(5)	3.69
C(15)	−1812(3)	5245(2)	9149(5)	3.44
C(16)	−1954(3)	5450(2)	7840(4)	2.78
C(17)	855(3)	6585(2)	7916(5)	3.29
C(18)	276(4)	7804(2)	7869(6)	5.28
C(19)	−2797(3)	6944(2)	4802(5)	4.82
Cl	1545(1)	5959(1)	8317(2)	4.80

Table 6-3. Atomic Coordinates of Non-hydrogen Atoms in 1,4-Dimethoxy-9-methyltriptycene with Standard Deviations in Parentheses with Thermal Factors

Atom	x	y	z	B_{eq}
C(1)	4334(2)	3144(1)	2628(3)	2.87
C(2)	4597(2)	2650(1)	3803(3)	3.55
C(3)	3944(2)	2608(1)	5093(3)	3.73
C(4)	3006(2)	3061(1)	5214(3)	3.09
C(4a)	2719(2)	3549(1)	4022(3)	2.58
C(5)	2504(2)	5172(1)	5361(3)	4.04
C(6)	3255(3)	5720(1)	5325(3)	4.64
C(7)	3942(2)	5792(1)	4090(3)	4.24
C(8)	3894(2)	5323(1)	2859(3)	3.61
C(8a)	3132(2)	4775(1)	2878(3)	2.92
C(9)	2960(2)	4208(1)	1617(3)	2.80
C(9a)	3384(2)	3606(1)	2738(2)	2.54
C(10)	1694(2)	4075(1)	4018(3)	2.95
C(10a)	2453(2)	4702(1)	4134(3)	3.06
C(11)	803(2)	4058(1)	2260(3)	3.15
C(12)	1469(2)	4132(1)	986(3)	3.10
C(13)	780(2)	4128(1)	−679(3)	4.23
C(14)	−577(3)	4052(1)	−1039(4)	5.42
C(15)	−1219(2)	3980(1)	223(4)	5.26
C(16)	−540(2)	3980(1)	1891(3)	4.22
C(17)	3636(3)	4329(1)	212(3)	4.44
C(18)	5964(3)	2757(1)	1258(4)	5.67
C(19)	2583(3)	2592(2)	7710(4)	6.59
O(1)	4980(2)	3215(1)	1361(2)	4.18
O(2)	2313(2)	3072(1)	6450(2)	4.45

Table 7. Selected Bond Lengths (Å) in Compounds **1**, **11**, and **12** with Standard Deviations in Parentheses

Bond	Compound		
	1	**11**	**12**
C(9)–C(8a)	1.539(2)	1.546(6)	1.546(3)
C(9)–C(9a)	1.560(2)	1.570(5)	1.553(3)
C(9)–C(12)	1.543(2)	1.540(6)	1.542(3)
C(9)–C(17)	1.520(2)	1.524(6)	1.504(4)
C(10)–C(4a)	1.528(2)	1.521(5)	1.531(3)
C(10)–C(10a)	1.520(2)	1.510(5)	1.516(3)
C(10)–C(11)	1.519(2)	1.521(6)	1.526(3)
O(1)–C(1)	1.378(2)	—	1.372(3)
O(2)–C(4)	1.376(2)	—	1.377(3)
C(17)–Cl	1.813(2)	1.819(4)	—

The distinct features in the structure of compound **1** are that it has a long C–Cl distance and that the 1-methoxyl group is out of plane of the benzene ring to which it is attached.

Although it seemd that the C–Cl bond in compound **1** was abnormally long,[13] it became clear that the C–Cl bond length is rather normal in this series of compounds when one examines the structure of compound **11**. Compound **11**, which possesses a methyl group instead of a methoxyl and in which no O···CH$_2$Cl interaction is possible, has about the same C–Cl bond length with compound **1**. It seems that, due to the steric effect of the triptycene skeleton, the C–Cl bond is stretched.

Table 8. Selected Bond Angles (Å) in Compounds **1**, **11**, and **12** with Standard Deviations in Parentheses

Atoms A-B-C	Compound		
	1	**11**	**12**
C(8a)-C(9)-C(9a)	102.9(1)	104.3(3)	104.0(2)
C(8a)-C(9)-C(12)	107.3(1)	107.0(3)	104.7(2)
C(8a)-C(9)-C(17)	113.5(1)	112.8(3)	112.4(2)
C(9a)-C(9)-C(12)	103.6(1)	104.1(3)	104.3(2)
C(9a)-C(9)-C(17)	114.8(1)	114.3(3)	117.6(2)
C(12)-C(9)-C(17)	113.7(1)	113.6(3)	112.6(2)
C(4a)-C(10)-C(10a)	105.0(1)	106.1(3)	104.4(2)
C(4a)-C(10)-C(11)	104.5(1)	105.8(3)	105.4(2)
C(10a)-C(10)-C(11)	107.2(1)	105.6(3)	106.2(2)
C(9)-C(8a)-C(10a)	113.7(1)	112.9(3)	114.3(2)
C(4a)-C(9a)-C(9)	112.5(1)	111.1(3)	112.8(2)
C(9)-C(12)-C(11)	113.9(1)	113.4(3)	114.1(2)
C(9a)-C(4a)-C(10)	114.4(1)	114.6(3)	114.4(2)
C(8a)-C(10a)-C(10)	113.4(1)	113.8(3)	113.6(2)
C(10)-C(11)-C(12)	113.4(1)	113.3(3)	113.5(2)
X(1)-C(1)-C(9a)[a]	118.5(2)	126.6(4)	117.4(2)
X(2)-C(4)-C(4a)[b]	116.6(2)	122.1(4)	115.9(2)
C(1)-O(1)-C(18)	119.1(2)	—	117.9(2)
C(4)-O(2)-C(19)	117.4(2)	—	118.2(2)
C(9)-C(17)-Cl	112.5(1)	112.5(3)	—

a) X(1) and X(2) are O(1) and O(2) atoms, respectively, for compounds **1** and **12**, and are carbon atoms 18 and 19, respectively, for compounds **11**.

Table 9. Selected Torsion Angles (°) in Compounds **1**, **11**, and **12** with Standard Deviations in Parentheses

Atoms 1-2-3-4	Compound		
	1	**11**	**12**
C(18)-O(1)-C(1)-C(9a)	144.9(2)	—	178.7(2)
C(19)-O(2)-C(4)-C(4a)	176.2(2)	—	179.0(2)
X-C(1)-C(9a)-C(9)[a]	1.8(2)	1.9(7)	1.0(3)
C(1)-C(9a)-C(9)-C(17)	1.8(2)	1.1(6)	0.0(3)
C(9a)-C(9)-C(17)-Cl	177.5(1)	180.0(3)	—
A-B[b]	114.7(1)	118.3(2)	117.6(1)
B-C[b]	128.6(1)	122.5(1)	121.4(1)
A-C[b]	116.6(1)	119.1(2)	120.9(1)

a) X's are O(1), C(18), and O(1) for compounds **1**, **11**, and **12**, respectively. b) Dihedral angles formed by benzeno bridges. For designation of benzeno bridges, see Fig. 1.

Table 10. Selected Nonbonding Distances within the Molecules of **1**, **11**, and **12** with Standard Deviations in Parentheses

Atoms 1-2	Compound		
	1	**11**	**12**
X-C(17)[a]	2.711(2)	2.935(6)	2.756(3)
Cl-C(8)	3.284(2)	3.211(5)	—
Cl-C(13)	3.168(2)	3.214(5)	—
C(1)-C(17)	3.079(3)	3.088(6)	3.131(3)
C(8)-C(17)	2.992(2)	3.002(6)	2.955(4)
C(13)-C(17)	2.995(2)	3.019(6)	2.952(4)

a) X's are O(1), C(18), and O(1) for compounds **1**, **11**, and **12**, respectively.

The nonplanarity of the methoxyl group in the anisole moiety is interesting because the methoxyl group is usually planar with the benzene ring,[14] and indeed the 4-methoxyl group is planar with the benzene ring. This anomalous structure may be caused by two possibilities, one being intramolecular and the other intermolecular.

The intermolecular factor is attributed to the effect of packing the molecules in the crystal lattice. By a special intermolecular interaction that has to be unavoidable because of the crystal packing which is of higher priority than the deformation of the molecule, the molecule could take otherwise unfavorable structure. To exclude this possibility, intermolecular distances may be examined. We have examined the distances between the 1-methoxyl group and atoms of the closest neighbor.

It was found that the oxygen atom of the 1-methoxyl group was close to the hydrogen attached to C_{15} and to the chlorine atom of another molecule, the distance being 3.102 and 3.328 Å, respectively. The methyl group of the methoxyl had the following close contacts with another molecule: C_{10a} 3.718, C_8 3.665, C_{8a} 3.574, HC_{15} 3.432, HC_{18} 3.731, HC_{14} 3.535, HC_{19} 3.660 Å. The distances do not exceed the sum of the van der Waals radii of the atoms (or the groups) concerned, to a significant extent. The situation is by and large the same for the 4-methoxyl group. Thus we conclude that the crystal packing cannot be the cause for the distortion of the 1-methoxyl group.

We have reported one example of twisting a methoxyl group from the coplanar position in an anisole derivative. In that case, the methoxyl group takes such a conformation to make $CH_3\cdots O$ hydrogen bond facile.[4b] The same explanation may be applied here. By rotating from the benzene plane, the ionization potential of the 1-methoxy-oxygen lowers, rendering the charge-transfer interaction easier. This conformation is neither favorable for the head-to-tail arrangement of dipoles nor explainable on the steric ground. Thus, $ClCH_2\cdots O$ charge-transfer interactions are the most probable cause for the present case, both for populations of rotamers and the unusual conformation of the 1-methoxyl group.

We have reported that the coupling constant between a hydrogen in the methyl group and the 1-fluorine atom in 8,13-dichloro-1,2,3,4-tetrafluoro-9-methyltriptycene in ^{1}H NMR spectra is the largest when the C–H bond is *ap* to the 1-fluorine atom.[15] The cause for this phenomenon was attributed to the overlap between the back lobe of the C–H bond and the lone-pair orbitals of the fluorine atom. This interaction is on the same line with the interactions discussed in this paper. We also believe that the formation of a 5-membered cyclic ether on diazotization of 9-aminomethyl-1,4-dimethoxytriptycene[16] is an extreme case of the interaction in a similar geometry.

The nonbonding distances listed in Table 10 give also interesting information. That is, though the C_{17} is located almost equally distant from the peri-carbons in compound **1** and compound **11**, the chlorine atom is significantly dislocated toward C_{13} in compound **1**. This feature is probably caused by the requirement of the best overlap of the orbitals for the charge-transfer interactions. The short distance between 1-methoxy-oxygen and the C_{17} makes this interaction possible.

Experimental

^{1}H NMR Spectra. These were recorded with a Varian EM390 instrument which operated at 90 MHz or with a JEOL GX400 which operated at 400 MHz. The data described in this experimental section are those obtained at 90 MHz at room temperature unless otherwise mentioned.

Determination of Population Ratios of Rotamers. The ^{1}H NMR spectra at low temperatures were determined with the use of the 400 MHz machine. The temperatures were read by a thermocouple. The NMR data at low temperatures are summarized in Table 11. The assignment of the 1- and 4-methoxy-protons in **1** was not possible because the temperature change did not appreciably change the line shape of the methoxy-protons in coalescing. For the determination of populations, the integrated intensities of the signals due to 2,3-protons of the aromatic nucleus were used for **1**, whereas those due to methoxy-protons were used for compounds **7** and **9**. The scanned chart papers were cut and weighed. The populations were obtained by measuring the weight of the papers for several times. The measurements were carried out at several temperatures and the equilibrium constants thus obtained are compiled in Table 12. The observed equilibrium constants did not give a good straight line when treated by the van't Hoff equation in the case of compound **9**. Thus the calculated populations obtained by the simulations of the line shapes (see below) were used to calculate the thermodynamic parameters for **9** in Table 4.

Table 11. ^{1}H NMR Data of 4-Substituted 9-Chloromethyl-1-methoxytriptycenes in $CDCl_3$ at −39.5 °C (δ)

Substituent	Form	CH_2	CH_3O
CH_3O	*ap*	5.52	3.72, 3.78
	sc	4.97, 5.62 (J=14.2)	3.82, 3.83
H[a]	*ap*	5.52	3.76
	sc	4.96, 5.60 (J=14.3)	3.85
NO_2	*ap*	5.51	3.88
	sc	4.98, 5.62 (J=12.1)	3.95

a) At −14.6 °C.

Table 12. Population Ratios of Rotamers in 4-Substituted 9-Chloromethyl-1-methoxytriptycenes in $CDCl_3$ at Various Temperatures

Subst	*sc/ap* (temp/°C)
CH_3O	0.029 (−39.6), 0.042 (−20.3), 0.048 (−10.0), 0.048 (−5.0)
H	0.043 (−14.6), 0.044 (−9.6), 0.047 (−4.7), 0.048 (0.3)
NO_2	0.075 (−39.4), 0.081 (−29.7), 0.088 (−19.7), 0.094 (−9.8)

Dynamic NMR Study. The berriers to rotation were obtained by the NMR spectral change at various temperatures and similation of the spectra with the use of DNMR3 program.[17] The spectrometer used for the measurement was the JEOL GX400. The peaks used for the analyses were those due to 2, 3-protons for compound **1** and the methoxy-protons for **7** and **9**. Chemical shift differences, coupling constants, populations, and T_2 were determined at several temperatures at the slow exchange limit and were extrapolated to the temperatures where line shapes changed. Small modifications of these parameters were necessary to obtain the best fit of the calculated spectra with those observed.

9-Chloromethyl-1-methoxytriptycene (7). To a refluxing solution of 0.70 g (3.1 mmol) of 9-chloromethylanthracene (**6**)[18] in 15 mL of 1,2-dimethoxyethane (DME), were added 2.07 g (12.4 mmol) of 6-methoxyanthranilic acid[19] in 30 mL of DME and 4.09 g (41.8 mmol) of isopentyl nitrite in 40 mL of DME, the two solutions being added from respective funnels, in 7 h and the whole mixture was refluxed for further 30 min. The solvent was evaporated off and the residue was submitted to chromatography on silica gel (4:1 hexane–dichloromethane eluent). The desired compound was eluted more easily than the 4-methoxy isomer (**8**). Compound **7** was recrystallized from THF–hexane to give 0.14 g (14%) of the pure compound, mp 221—222 °C. Found: C, 79.23; H, 4.98; Cl, 10.42%. Calcd for $C_{22}H_{17}ClO$: C, 79.39; H, 5.15; Cl, 10.65%. ^{1}H NMR ($CDCl_3$) δ=3.73 (3H, s), 5.26 (1H, s), 5.44 (2H, br s), 6.47 (1H, dd, J=7.3 and 2.3 Hz), 6.7—8.0 (10H, m).

The 4-methoxy compound (**8**), mp 224—225 °C, was obtained in 0.07 g yield, after recrystallization from THF–hexane. Found: C, 79.11; H, 5.14; Cl, 10.65%. Calcd for $C_{22}H_{17}ClO$: C, 79.39; H, 5.15; Cl, 10.65%. ^{1}H NMR ($CDCl_3$) δ=3.84 (3H, s), 5.09 (2H, s), 5.87 (1H, s), 6.5—7.9 (11H, m).

Nitration of 9-Chloromethyl-1-methoxytriptycene (7). To a solution of 118 mg (0.35 mmol) of 9-chloromethyl-1-methoxytriptycene in 20 mL of acetonitrile, was added a saturated solution (ca. 10%) of 440 mg (ca. 0.33 mmol) of nitronium tetrafluoroborate, which was available from Aldrich, in acetonitrile at −10 °C. The nitration was completed by adding further few drops of the saturated solution of nitronium tetrafluoroborate, the completion being checked by TLC. The mixture was poured into water and the precipitate was collected. The product was separated by chromatography on alumina (4:1 hexane–dichloromethane eluent), when the 4-nitro compound (**9**) was eluted earlier than the 2-nitro compound (**10**). The para and the ortho nitro compounds were purified by recrystallization from THF–hexane and dichloromethane–hexane, respectively.

4-Nitro compound (**9**): Yield 0.07 g (53%), mp 283—285 °C. Found: C, 69.94; H, 4.16; N, 3.60%. Calcd for $C_{22}H_{16}ClNO_3$: C, 69.94; H, 4.27; N, 3.71%. ^{1}H NMR ($CDCl_3$) δ=3.86 (3H, s), 5.45 (2H, br s), 6.55 (1H, s), 6.57 and 7.65 (2H,

Table 13. Crystallographic Data

Compound	**1**	**11**	**12**
Observed reflections	3836	1072	2930
Measured reflections	5784	3621	5535
Formula	$C_{23}H_{19}ClO_2$	$C_{23}H_{19}Cl$	$C_{23}H_{20}O_2$
Formula weight	362.83	330.83	328.39
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_1/a$	Pcab	$P2_1/a$
a/Å	15.668(2)	15.108(3)	10.516(1)
b/Å	8.416(1)	22.962(4)	20.717(2)
c/Å	13.920(2)	9.845(2)	8.184(1)
β/°	99.80(1)	90.00	103.30(1)
V/Å^3	1808.6(4)	3415.3(11)	1735.1(4)
Z	4	8	4
D_c/g cm^{-3}	1.33	1.29	1.26
R_w/%	6.21	4.48	7.13
R/%	4.57	3.65	5.61
μ/cm^{-1}	2.30	2.27	0.853

ABq, J=8.3 Hz), 6.8—8.1 (8H, m).

2-Nitro compound (**10**): Yield 0.05 g (38%), mp 239—239.5 °C. Found: C, 69.69; H, 4.32; N, 3.76; Cl, 9.38%. Calcd for $C_{22}H_{16}ClNO_3$: C, 69.94; H, 4.27; N, 3.71; Cl, 9.38%. ^{1}H NMR ($CDCl_3$) δ=3.77 (3H, s), 5.41 (1H, s), 5.41 (2H, s), 6.9—8.0 (10H, m).

9-Chloromethyl-1,4-dimethyltriptycene (11). To a boiling solution of 0.33 g (1.5 mmol) of 9-chloromethylanthracene (**6**) in 10 mL of dichloromethane, were added simultaneously a solution of 1.54 g (9.3 mmol) of 3,6-dimethylanthranilic acid[20] in 40 mL of acetone and that of 1.41 g (12.0 mmol) of isopentyl nitrite in 40 mL of dichloromethane in 2 h. The mixture was refluxed for further 30 min and then the solvent was evaporated. The residue was submitted to chromatography on silica gel with a hexane–dichloromethane eluent. The product was recrystallized from dichloromethane–hexane to afford 0.21 g (44%) of the desired product, mp 257—258 °C. Found: C, 83.32; H, 5.54; Cl, 11.17%. Calcd for $C_{23}H_{19}Cl$: C, 83.49; H, 5.79; Cl, 10.72%. ^{1}H NMR ($CDCl_3$) δ=2.40 (3H, s), 2.50 (3H, s), 5.39 (2H, s), 5.58 (1H, s), 6.54 and 6.63 (2H, ABq, J=7.8 Hz), 6.8—8.0 (8H, m).

9-Chloromethyl-1,4-dimethoxytriptycene (**1**)[1] and 1,4-dimethoxy-9-methyltriptycene (**12**)[21] were prepared by the procedure already published. Their physical constants agreed with those reported.

X-Ray Crystallography. Crystals of compound **1** and **11** were grown from dichloromethane-hexane and those of compound **12** from tetrahydrofuran-pentane.

A colorless crystal of **1** (0.4×0.3×0.3 mm) was mounted on a Rigaku AFC-5R automated four-circle diffractometer and the intensity data were collected using Mo $K\alpha$ radiation (λ=0.71073 Å). The collection of the intensity data of **11** and **12** was carried out with colorless crystals of dimensions 0.6×0.3×0.3 mm and 0.5×0.3×0.3 mm, respectively, using a Rigaku AFC-5 diffractometer. The ω–2θ scan technique was employed at a scan rate of 4° min^{-1} in ω for **1**, and 3° min^{-1} for **11** and **12**. The scan range was calculated by 1.2°+0.5° tan θ. The measurement ranges were $2\theta<60°$ for all the compounds. The numbers of measured reflections and those judged as observed with $|F_o|>3\sigma|F_o|$ are given in Table 13 with the crystal data.

The structure was solved by direct methods (MULTAN 78) and refined by the block-diagonal least-squares technique with anisotropic thermal parameters for non-hydrogen atoms and isotropic for hydrogens. All the hydrogen atoms were located on a difference map and their positional parameters were refined. The atomic scattering factors were taken from International Tables for X-Ray Crystallography.[22] The weighting scheme $w=[\sigma_c^2+(0.02|F_o|^2)]^{-1}$ was employed for compounds **1** and **11** and it was $w=[\sigma_c^2+(0.03|F_o|^2)]^{-1}$ for compound **12**. The final R and R_W values together with relevant data are listed also in Table 13.

All the caluclations were carried out on a HITAC M-200H computer with crystallographic computation program system, MULTAN and UNICS III, filed at the Computer Center of the Institute for Molecular Science. The complete F_o–F_c data are deposited as Document No. 8937 at the Office of the Editor of Bull. Chem. Soc. Jpn.

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