Rotamer Populations and Molecular Structure of 9-Isobutyl-1,4-dimethoxytriptycene: Further Evidence for the Presence of CH_3···O Hydrogen Bond

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^{1}H NMR spectra of the title compound at low temperatures show the presence of the *sc* conformer as a major constituent: ΔH°=0.9±0.3 kcal mol^{-1}, ΔS°=5±2 cal mol^{-1} for the $sc \rightleftarrows ap$ equilibrium. The line shape analysis of the spectra at various temperatures afforded the following activation parameters for the internal rotation about the C_9-$C_{i\text{-}Bu}$ bond: ΔH^*=8.8±0.3 kcal mol^{-1}, ΔS^*=−5.0±1.2 cal mol^{-1} K^{-1} for the $ap \rightarrow sc$ process. X-Ray crystallography of the compound revealed that the molecule exists as *sc* conformers in the crystal. One of the methyl groups of the isobutyl group that directs inward relative to the triptycene skeleton, is placed very closely to the 1-methoxy-oxygen to indicate the presence of the CH_3···O hydrogen bond. Implications of other structural parameters are also discussed.

While we have reported that the presence of CH_3 ··· O hydrogen bond can be detected as the population ratios of rotamers in appropriately substituted triptycenes, the population of the *sc* isomer has never overwhelmed that of the *ap* isomer, although the former is stabilized by the presence of the hydrogen bond.[1,2] The results have been attributed to the weakness of the hydrogen bond that competes with other repulsive forces like van der Waals repulsion in determining the population ratios. Indeed, it has been pointed out that the ρ value in the Hammett plot of the population ratios against the substituent constants for the series of 9-(aryloxymethyl)-1,4-dimethyltriptycenes is unusually small, −0.114,[1] for the interaction involving an atom that is directly attached to the aromatic ring.[3]

This reluctance of showing the electronic effect of the substituent on the rotamer populations is attributed to the steric effect that destabilizes the *sc* form of 1,9-disubstituted triptycenes, although that form is stabilized by the hydrogen bond. Although the β atom in the 9-substituent is close enough to the unsubstituted peri-positions of the triptycene skeleton, when it takes the *ap* position relative to the 1-substituent, the distance is still larger than that between the 1-substituent and the β atom of the 9-substituent when it takes the *sc* position. The situation is clear when one considers the cases in which no strong interactions between the 1- and 9-substituents are expected. 1-Substituted 9-isopropyltriptycenes are known to exist exclusively as the *sc* isomer except for the 1-fluoro derivative.[4] So are 9-allyl-1,4-dimethyltriptycene,[5] 9-(formylmethyl)-1,4-dimethyltriptycene,[5] and 9-(2-acetoxyethyl)-1,2,3,4-tetrachlorotriptycene.[6]

We have been interested in manifesting the overwhelming population of *sc* isomers due to the weak interactions. To this end, it is necessary to lessen the difference in the steric situations of the *sc* and *ap* conformers of the 1,9-disubstituted triptycenes relative to the cases cited. This must be accomplished by destabilizing the *ap* form, while the ground state of the *sc* form is destabilized little, by a modification of the molecule. As one of the candidates of this technique, introduction of a substituent in the β position of the 9-substituent has been tried for the following reasons. Introduction of a methyl group to an *o*-position of the benzyl-phenyl group in 9-benzyltriptycenes raises the ground state energy, if the methyl group directs inward, and the molecule resides in the conformation only for a short time.[7] This idea led to the finding that the molecular gears with two- and three-toothed wheels[8] and two three-toothed wheels[9] could be made. Although the β-carbon in the substituent in the former is sp^2-hybridized, that in the latter is sp^3-hybridized. There is a good reason to expect that the introduction of a substituent there manifests the desired effect.

Following these considerations, we decided to prepare 9-isobutyl-1,4-dimethoxytriptycene (**1**). There are two rotational axes in the 9-substituent of this molecule: C_9-C_α and C_α-C_β. Although there is limited freedom of rotation in the C_9-C_α bond if we consider only stable conformations, namely *ap* and ±*sc* only, there are varieties of conformations we must take into account about the C_α-C_β axis.

If the molecule takes the *ap* conformation about the C_α-C_β axis (Fig. 1a), the steric interactions between the peri-CH groups and the isopropyl-methyl groups are too severe to allow the conformation to exist. If the molecule takes the *sc* conformation about the same axis (Fig. 1b), one of the isopropyl-methyl groups is still too close to the peri-CH group to be stable. If this conformation is to exist, it may be necessary to rotate this part slightly so that the repulsive interactions concerned become smaller.

If the molecule has to take a conformation twisted slightly from the normal staggerred form, it will also be possible to take a conformation that is twisted

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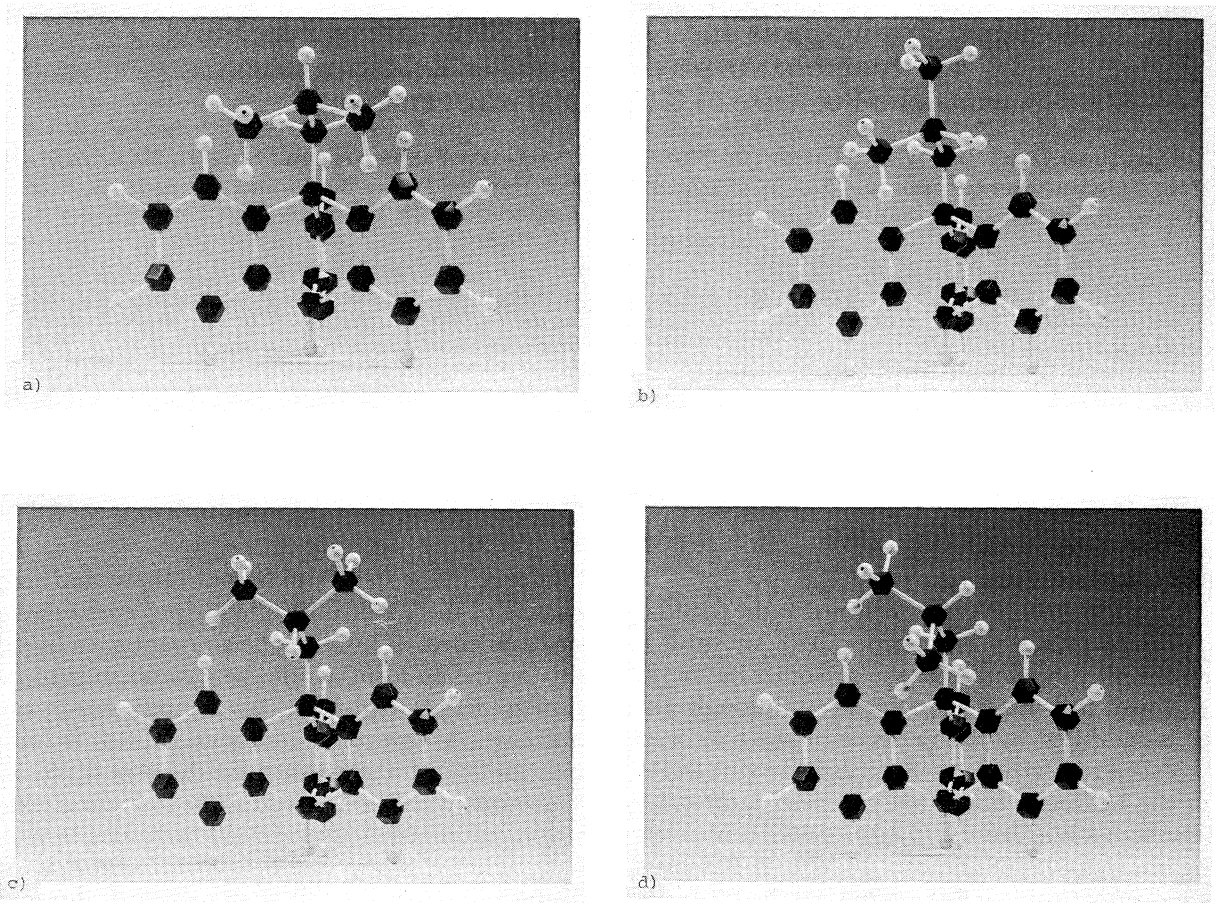


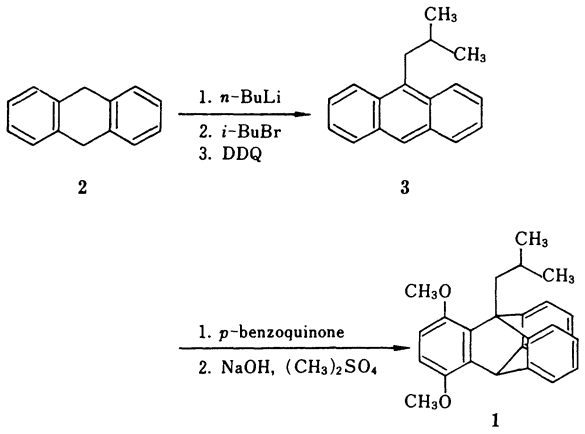
Fig 1. Some extreme conformations of 9-isobutyltriptycene: for clarity, two methoxyl groups at 1 and 4 positions are removed. a) *ap* conformation, b) $+sc$ conformation, c) *sp* conformation, d) $+ac$ conformation.

slightly from the eclipsed conformations. The *sp* conformation (Fig. 1c) may be stabilized by rotating the isopropyl group to some extent about the C_α-C_β bond, because the strain due to eclipsing is eased by doing so. However, this twisting causes another strain between the isopropyl-methyl group and the peri-CH group. It is unlikely that the molecule takes a conformation that is close to the *sp*. In the $\pm 120°$ conformations (Fig. 1d), the repulsive interactions between the two benzeno bridges and the isopropyl-methyl group, which is directing inward relative to the triptycene skeleton, will be minimal. However, the molecule has to avoid the eclipsing interactions of the groups concerned. Although this twisting about the isopropyl-to-methylene bond in the isobutyl group necessarily increases the steric repulsions between the benzeno bridge and the inside-methyl group, these interactions might not be so severe as are expected from the molecular models, because, in the molecular structures of 9-(prim. alkyl)triptycenes, it is known that the dihedral angles made by the two benzeno bridges which flank the β-atom of the substituent is larger than the normal one.[5,10]

In the conformation which is $\pm sc$ about the C_9-C_α bond and is a little twisted from the $\pm 120°$ form about the C_α-C_β bond in 9-isobutyl-1,4-dimethoxytriptycene, the $CH_3 \cdots O$ hydrogen bond is possible, while the $CH \cdots O$ hydrogen bond may have to be between the β-CH and the methoxy-oxygen in the conformation which is $\pm sc$ about the C_9-C_α and is a little twisted from the $\mp 120°$ form about the C_α-C_β bond, if one considers the steric effects caused by the methyl groups by proximating one of them to the 1-methoxy-oxygen. Therefore, if the molecule takes this type of conformation, at the equilibrium between the rotamers, the *sc* conformation may be favored relative to the *ap* owing to the presence of the $CH_3 \cdots O$ hydrogen bond, because the steric effect given by the inward-methyl group will be severe not only in the *sc* conformation but also in the *ap*.

It is not possible to decide which of the two possible conformations discussed above, nearly $\pm sc$ and nearly $\pm ac$ conformations about the C_α-C_β bond, is more stable from the molecular models. In order to find the experimental results, the synthesis of 9-isobutyl-1,4-dimethoxytriptycene (**1**) was undertaken in the following way. Deprotonation of 9,10-dihydroanthracene (**2**) with butyllithium followed by alkylation with iso-

butyl bromide afforded 9-isobutyl-9,10-dihydroanthracene, of which dehydrogenation with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone afforded 9-isobutylanthracene (**3**). The reaction of **3** with *p*-benzoquinone in the presence of boron trifluoride afforded a Diels-Alder adduct which was treated with aqueous sodium hydroxide and dimethyl sulfate to give the desired compound (**1**).



In accordance with the expectation, the barrier to rotation in compound **1** about the C_9-C_α bond is lowered considerably, as evidenced by the fact that the ^{1}H NMR spectrum of the compound in chloroform-*d* did not show decoalescence of any signals, although broadened, at the lowest temperature attainable for the solvent at 270 MHz: The barrier to rotation about the C_9-C_α bond in 1-substituted 9-(prim. alkyl)triptycenes is normally 12—16 kcal mol^{-1} (1 cal=4.184 J) and decoalescence of various signals is complete at about −20 °C.[11-13]

We thus measured the ^{1}H NMR spectra of compound **1** in CD_2Cl_2-CS_2 at 400 MHz. At this magnetic field, the rotation about the C_9-C_α bond was negligibly slow at or below −90 °C. The population ratios were determined at these temperatures and the differences in standard enthalpy and entropy were obtained. The results are shown in Table 1.

Assignment of the signals to *ap* and *sc* conformers was accomplished by finding that, in the 400 MHz ^{1}H NMR spectra at low temperatures, an AB quartet and a singlet,[14] each of which showed further coupling with the methine proton, were separated. In those spectra, the two-proton signals due to the aromatic protons of the dimethoxybenzeno bridge appeared as AB quartets; one at the lower field showed a larger chemical shift difference than that at the higher magnetic field, indicating that the signals at the lower field should be ascribed to the *sc* isomer. The intensity ratios of the proton signals due to the aromatic ring and the α-methylene of the 9-substitutent agreed satisfactorily. Due to the overlaps, however, the determination of the populations was made with the use of the isopropyl-methyl signals.

Table 1. Population Ratios of Rotameric 9-Isobutyl-1,4-dimethoxytriptycene and Differences in Standard Enthalpy and Entropy of the Rotamers in 1 : 1 CD_2Cl_2-CS_2 for the *sc* ⇄ *ap* Equilibrium

Temp/°C	−110.6	−100.5	−95.5	−90.5	−85.4
ap/*sc*	0.33	0.37	0.41	0.43	0.48

$\Delta H°$=0.87±0.28 kcal mol^{-1}
$\Delta S°$=4.5±1.6 cal mol^{-1} K^{-1}

Clearly the majority is the *sc* conformation at or below −85 °C. The population of the *sc* form is more than the statistical one and suggests the presence of a kind of stabilizing effects in that form, because no apparent destabilization of the *ap* form is expected. According to the discussion (vide supra), this effect is very likely to be the CH_3···O hydrogen bond. Of another interest is that the preference of the *sc* form over the *ap* diminishes when the temperature is raised: although the low correlation coefficient, 0.984, in the statistical treatment of the equilibrium constants precludes the detailed discussion of the difference in standard entropy, it is tempting to consider that the entropy increases in the process *sc*-**1**→*ap*-**1**, as it appears in the numerical value. This is consistent with the idea that the CH_3···O hydrogen bond reduces the freedom of rotation of the methyl group concerned.

The chemical shift differences between the protons due to isopropyl-methyls are interesting. Whereas that due to the *ap* form gives a simple doublet, the chemical shift differences for the diastereotopic methyl groups in the *sc* form is very large. As is already discussed, there are two conformations of the isobutyl in each rotamer about the C_α-C_β bond. If the rotation of the isopropyl group is slow on the NMR time scale, the chemical shift differences between the two methyl-protons should be large even in the *ap* form because of the anisotropy effect of the benzene ring. The simple doublet signal for these two methyls in the *ap* means that the rotation is fast on the NMR time scale. It is tempting to consider that the large chemical shift difference between the methyl-protons in the *sc* form means that one of the conformers is stabilized relative to the other to make the life-time long, because otherwise the chemical shift differences may be reduced due to the fact that the inside-methyl group in one form is outside in another.

Total line shape analysis of the isopropyl-methyl proton signals was performed with the use of DNMR3 program.[15] Here the rotation of the isobutyl group, in which the isopropyl group passes over the 1-methoxyl group, is assumed not taking place because of the large chemical shift difference between the two methyl signals of the *sc* form: if this rotation takes place, the inside methyl group exchanges the site with the outer methyl even in the absence of rotation about the C_α-C_β bond. The results are shown in Table 2. The low barrier to rotation in compound **1** is clearly derived by

Table 2. Rates of Isomerization ($ap \rightarrow sc$) of Rotameric 9-Isobutyl-1,4-dimethoxytriptycene and Kinetic Parameters for the Isomerization in 1 : 1 CD_2Cl_2-CS_2

Temp/°C	−85.4	−80.4	−75.4	−70.4	−65.4	−60.3	−49.8
k/s^{-1}	20.0	37.5	65	116	205	370	980

$\Delta H^{\ddagger}$=8.8±0.3 kcal mol
$\Delta S^{\ddagger}$=−5.0±1.2 cal mol^{-1} K^{-1}
$\Delta G^{\ddagger}_{200}$=9.8 kcal mol^{-1}

Table 3. Atomic Positional Parameters (×10^4) with Estimated Deviations in Parentheses and Equivalent Isotropic Thermal Parameters of 9-Isobutyl-1,4-dimethoxytriptycene

Atom	x	y	z	B_{eq}[a]
C(1)	3284(1)	5019(2)	7197(1)	2.78
C(2)	3515(1)	4121(2)	6532(1)	3.28
C(3)	2919(1)	3682(2)	5806(1)	3.29
C(4)	2075(1)	4207(2)	5714(1)	2.71
C(4a)	1835(1)	5079(2)	6392(1)	2.37
C(5)	−203(1)	4564(2)	7063(1)	3.54
C(6)	−493(1)	4223(3)	7822(2)	4.53
C(7)	16(1)	4598(3)	8606(2)	4.61
C(8)	832(1)	5274(3)	8654(1)	3.59
C(8a)	1140(1)	5582(2)	7898(1)	2.60
C(9)	2006(1)	6402(2)	7828(1)	2.38
C(9a)	2413(1)	5419(2)	7158(1)	2.36
C(10)	956(1)	5869(2)	6334(1)	2.49
C(10a)	599(1)	5264(2)	7104(1)	2.65
C(11)	1153(1)	7658(2)	6510(1)	2.53
C(12)	1708(1)	7953(2)	7302(1)	2.50
C(13)	1947(1)	9528(2)	7543(1)	3.34
C(14)	1625(1)	10791(2)	6984(1)	4.15
C(15)	1081(1)	10501(2)	6209(1)	4.05
C(16)	835(1)	8917(2)	5963(1)	3.23
C(17)	2584(1)	6771(2)	8706(1)	3.13
C(18)	2873(1)	5408(3)	9387(1)	4.00
C(19)	2921(1)	3690(3)	9049(1)	5.03
C(20)	3717(2)	5904(4)	9968(2)	6.25
C(21)	4759(1)	5482(3)	7872(2)	5.31
C(22)	1681(2)	3060(3)	4304(1)	5.28
O(1)	3875(1)	5584(2)	7889(1)	4.25
O(2)	1440(1)	3953(2)	4996(1)	3.57

a) Equivalent isotropic temperature factor defined by Hamilton.[16]

Table 4. Selected Bond Distances in 9-Isobutyl-1,4-dimethoxytritpycene with Standard Deviations in Parentheses

Atom(1)-Atom(2)	Distance/Å
C(1)-O(1)	1.371(2)
C(21)-O(1)	1.405(3)
C(4)-O(2)	1.375(2)
C(22)-O(2)	1.426(3)
C(4a)-C(10)	1.523(2)
C(10)-C(11)	1.528(2)
C(10)-C(10a)	1.513(3)
C(9)-C(9a)	1.564(2)
C(9)-C(8a)	1.550(2)
C(9)-C(12)	1.551(2)
C(9)-C(17)	1.533(2)
C(17)-C(18)	1.561(3)
C(18)-C(19)	1.524(3)
C(18)-C(20)	1.521(3)

Table 5. Selected Bond Angles in 9-Isobutyl-1,4-dimethoxytriptycene with Standard Deviations in Parentheses

Atom(1)-Atom(2)-Atom(3)	θ/°
C(9a)-C(1)-O(1)	117.8(2)
C(2)-C(1)-O(1)	122.9(2)
C(1)-O(1)-C(21)	119.6(2)
C(3)-C(4)-O(2)	125.1(2)
C(4a)-C(4)-O(2)	116.3(2)
C(4)-O(2)-C(22)	116.5(2)
C(4a)-C(10)-C(10a)	106.6(1)
C(4a)-C(10)-C(11)	104.6(1)
C(10a)-C(10)-C(11)	105.7(1)
C(8a)-C(9)-C(9a)	107.6(1)
C(8a)-C(9)-C(12)	102.6(1)
C(8a)-C(9)-C(17)	114.0(1)
C(9a)-C(9)-C(17)	117.3(1)
C(12)-C(9)-C(17)	112.5(1)
C(9)-C(17)-C(18)	121.2(2)
C(17)-C(18)-C(19)	117.6(2)
C(17)-C(18)-C(20)	108.9(2)
C(19)-C(18)-C(20)	111.4(2)

the relatively unstable ground state. The same reason may apply for the lower barrier to rotation in 9-benzyl-1,4-dimethoxytriptycene[11] than those in 9-ethyl-1,4-dimethoxytriptycene[12] and 9,10-bis(chloromethyl)-triptycene.[13]

The results presented here are all in accordance with the presence of the $CH_3 \cdots O$ hydrogen bond in the *sc* form of compound **1**. However, the results do neither guarantee that the real conformation about the isobutyl group is nearly 120°, nor tell which of the two isopropyl-methyl groups forms the $CH_3 \cdots O$ hydrogen bond with the 1-methoxy-oxygen atom. In order to get further into insight, we decided to perform X-ray crystallographic study of the molecular structure of **1**.

The atomic coordinates, selected bond distances, selected bond angles, selected torsion angles, selected nonbonding distances, and deviations of carbon atoms comprising three benzene rings from the mean plane of the rings are compiled in Tables 3—8, respectively. An ORTEP diagram is shown in Fig. 2 together with numbering of atoms and designation of rings.

The crystallography clearly shows that the molecules are packed in the crystals as *sc* forms. This is quite fortunate, because the molecular structural parameters give information about the $CH_3 \cdots O$ hydrogen bond, but is quite unusual. We have shown that a compound which exhibits the presence of *ap* conformation only gives crystals of *ap* conformation,[5]

Table 6. Selected Torsion Angles in 9-Isobutyl-1,4-dimethoxytriptycene with Standard Deviations in Parentheses

Atom(1)-Atom(2)-Atom(3)-Atom(4)	ϕ/°
C(2)-C(1)-O(1)-C(21)	10.2(3)
C(3)-C(4)-O(2)-C(22)	0.8(3)
C(8)-C(8a)-C(9)-C(9a)	136.6(2)
C(8a)-C(9)-C(9a)-C(1)	140.4(2)
C(12)-C(9)-C(9a)-C(1)	112.4(2)
C(9a)-C(9)-C(12)-C(13)	123.0(2)
C(8)-C(8a)-C(9)-C(12)	117.2(2)
C(8a)-C(9)-C(12)-C(13)	125.8(2)
C(4)-C(4a)-C(10)-C(11)	121.7(2)
C(4a)-C(10)-C(11)-C(16)	123.3(2)
C(11)-C(10)-C(10a)-C(5)	121.6(2)
C(10a)-C(10)-C(11)-C(16)	124.4(2)
C(4)-C(4a)-C(10)-C(10a)	126,7(2)
C(4a)-C(10)-C(10a)-C(5)	127,5(2)
C(10)-C(4a)-C(9a)-C(1)	167.6(1)
C(8)-C(8a)-C(10a)-C(10)	171.8(2)
C(10)-C(11)-C(12)-C(13)	179.5(2)
C(4)-C(4a)-C(9a)-C(9)	179.7(1)
C(9)-C(8a)-C(10a)-C(5)	178.7(2)
C(16)-C(11)-C(12)-C(9)	179.6(2)
C(8a)-C(9)-C(17)-C(18)	56.7(2)
C(9a)-C(9)-C(17)-C(18)	70.3(2)
C(9)-C(17)-C(18)-C(19)	26.5(3)
C(9)-C(17)-C(18)-C(20)	154.4(2)

Table 7. Selected Nonbonding Distances in 9-Isobutyl-1,4-dimethoxytriptycene with Standard Deviations in Parentheses

Atom(1)-Atom(2)	Distance/Å
O(1)-C(17)	2.788(2)
O(1)-C(18)	3.080(3)
O(1)-C(19)	3.017(3)
O(1)-C(20)	3.334(3)
C(1)-C(19)	3.262(3)
C(1)-C(20)	4.337(3)
C(8)-C(18)	3.213(3)
C(8)-C(19)	3.495(3)

Table 8. Atomic Shifts from the Least-Squares Planes in the Benzene Rings of 9-Isobutyl-1,4-dimethoxytriptycene

Ring A		Ring B		Ring C	
Carbon	d/Å	Carbon	d/Å	Carbon	d/Å
C(1)	0.041	C(5)	−0.006	C(11)	−0.001
C(2)	0.004	C(6)	−0.015	C(12)	0.000
C(3)	−0.038	C(7)	0.012	C(13)	0.001
C(4)	0.017	C(8)	0.009	C(14)	−0.001
C(4a)	0.022	C(8a)	−0.018	C(15)	−0.001
C(9a)	−0.044	C(10a)	0.017	C(16)	0.002

and that even a compound which exists solely as *sc* conformation in solution gives crystals which contain both *ap* and *sc* conformations.[10] We believe the reasons for this phenomenon that compound **1** crystallizes in the *sc* form should include the factor that the *sc* form is more stable than the *ap*.

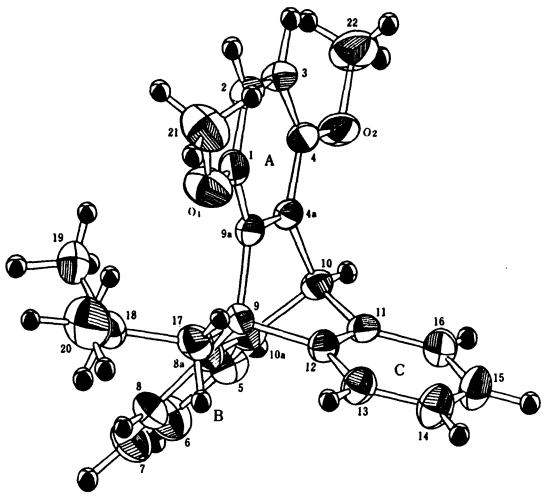


Fig. 2. An ORTEP diagram of 9-isobutyl-1,4-dimethoxytriptycene with numberings of atoms and designation of rings.

As all the data suggest, the structure around the C(10), that is the opposite side of the 9-substituent in the triptycene skeleton, is nearly normal, whereas abnormal are the atomic positions comprising the 9-substituent and the peri-positions which are close to the 9-substituent. We can point out some of the common features of 9-substituted triptycenes[5,10] which are also seen in this compound. The bonds connecting the C(9) and the benzene rings are long, especially long being that between C(9) and the aromatic ring which carries two methoxyl groups. The pyramid made by C(8a), C(9a), C(12), and C(9) has very small C-C-C apex angles at C(9) and correspondingly the angles C(17)-C(9)-C(n), where C(n) is the carbon atom of the aromatic rings, are large. These features are derived to relieve the steric strain formed by the 1- and 9-substituents.

One of the methyl groups in the 9-substituent directs inward relative to the triptycene skeleton, as was expected from the model study, and the eclipsing strain is relieved by rotating 26.5° from the eclipsing position. To accommodate the inward-directing methyl group, the C(8a)-C(9)-C(9a) angle is widened considerably relative to other apex angles and the torsion angles consisting this notch, i.e. C(8)-C(8a)-C(9)-C(9a) and C(8a)-C(9)-C(9a)-C(1), are very large. These are reflected in the dihedral angles made by two average planes of the benzene rings: A and B 132.7°, A and C 112.3°, B and C 114.9°. The difference in the torsion angles involving the same notch is due to the twisting of the benzene rings at the peri-carbons: the peri-carbons flanking the 9-substituent are dislocated from the average plane of the benzene rings away from the substituent, whereas another peri-carbon, C(13), is closely in the average plane of the benzene ring. This situation is clearly seen by the torsion angles involving the axes of bridge carbons of the benzeno moiety.

Whereas the torsion angle, C(10)-C(11)-C(12)-C(13), is very close to 180°, those that involve the peri-carbons flanking the 9-substituent, C(10)-C(4a)-C(9a)-C(1) and C(8)-C(8a)-C(10a)-C(10), are much smaller than 180°. The corresponding torsion angles about the bridge carbon-carbon axis involving the C(9) and the peri-carbon that is in the opposite side of the triptycene skeleton relative to the 9-substituent are again very close to 180°.

Deformation of the benzene rings in the molecule deserves special mention. As are shown in Table 8, while ring C is practically planar and ring B is slightly distorted, deviations of atoms comprising ring A from the average plane are rather large. The situation of ring A is more distinct if one takes deviations of atoms from the mean plane formed by atoms C(3), C(4), C(4a), and C(9a): these atoms comprise a fairly good plane, the atomic shifts being less than 0.003 Å, though that does not mean that these atoms are located normally because, whereas C(9) is in this plane, C(10) is out of this plane by 0.142 Å. C(1) is out of this plane away from the 9-substituent by 0.144 Å and so is C(2) by 0.106 Å. These deformations must be due to the severe steric interactions of the methyl group in the 9-substituent and the atoms of the ring concerned.

The torsion angle at the C_α-C_β axis of the 9-substituent indicates that the substituent is tilted toward the benzene ring which does not carry the methoxyl groups. This is considered to avoid the steric interactions between the 1-methoxyl group and the 9-substituent. The C_α-C_β bond in the substituent is unusually long as an sp^3-sp^3 carbon bond and the bond angle C(9)-C(17)-C(18) is very large. These should be the results of relieving the strain caused by the inside-methyl group and the benzeno bridges that form the notch.

The inside-methyl group is very close to the 1-methoxy-oxygen, the distance being 3.017 Å, well within the sum of the van der Waals radii of the groups concerned. Of course, this distance alone cannot be taken as evidence for the presence of the $CH_3 \cdots O$ hydrogen bond, because the intramolecular nonbonding distance can be very small,[17] especially in congested molecules. However, if one compares the distances, C(19)-O(1) and C(20)-O(1), there is a significant difference between them. This may well support the presence of the $CH_3 \cdots O$ hydrogen bond.

There is another interesting feature in the molecular structure of **1**. That is the 1-methoxyl group is twisted to make the methoxy-methyl group out of the plane of the average benzene ring. Since anisole and related compounds are believed to be stable at a planar structure[18] and the 4-methoxyl group in **1** is indeed in the plane of the benzene ring, there must be a reason for this nonplanar conformation of the 1-methoxyl group. We should tentatively like to attribute this structure to being favorable for forming the $CH_3 \cdots O$ hydrogen bond. If the 1-methoxy-oxygen is sp^2-hybridized, both the direction of the orbital of the oxygen lone pair, of which ionization potential is minimum, and the high ionization potential of the electrons in the orbital, of which axis is parallel to the p-orbitals of the benzene ring, are not favorable for the hydrogen bond. Thus although energetically unfavorable from the view point of conjugation with the benzene ring, the 1-methoxyl group rotates to a small extent about the C(1)-O(1) bond to make the $CH_3 \cdots O$ interaction favorable.

The structure around the methoxy-oxygen is of interest in another point. That is, the C(1)-O(1) bond is bent out of the average plane of ring A and the O(1) atom is shifted from the C(3)-C(4)-C(4a)-C(9a) plane by 0.359 Å away from the 9-substituent. The reason for this deformation is not clear at present, but we believe both the steric and $CH_3 \cdots O$ hydrogen-bond effects are responsible for this unusual structure.

In conclusion, all the data presented in this paper suggest that there is $CH_3 \cdots O$ hydrogen bond in compound **1** both in solution and in the solid state. The technique of introducing a substituent to the β-position of the 9-substituent to lessen the steric energy gap between the *sc* and the *ap* forms may find other uses in manifestation of weak molecular interactions.

Experimental

Material. The sythesis of the compound was carried out as follows.

9-Isobutylanthracene (3). To a solution of 5.4 g (30 mmol) of 9,10-dihydroanthracene (**2**) in 75 mL of tetrahydrofuran, was slowly added 13.5 mL (32 mmol) of butyllithium in hexane at ca. −45 °C under a nitrogen atmosphere. Stirring was continued for further 30 min and then the solution was added to 3.6 mL (33 mmol) of isobutyl bromide in 10 mL of tetrahydrofuran at −30 °C under a nitrogen atmosphere. The mixture was allowed to warm up and then stirred overnight at room temperature. The mixture was treated with water and extracted with benzene. After evaporation of the solvent, the residue was taken up in 30 mL of benzene and heated at 40—60 °C for 1 h with 6.81 g (30 mmol) of 2,3-dichloro-5,6-dicyano-*p*-benzoquinone. The precipitate was filtered off and the solvent was evaporated from the filtrate. The residue was submitted to chromatography on silica gel (hexane eluent) to afford 2.79 g (40%) of the desired product, mp 66—67 °C (lit,[19] mp 57 °C). ^{1}H NMR ($CDCl_3$) δ=0.98 (6H, d, J=6.3 Hz), 2.19 (1H, nonet, J=6.3 Hz), 3.47 (2H, J=6.3 Hz), 7.3—7.8 (9H, m).

9-Isopropyl-1,4-dimethoxytriptycene (1). A solution of 980 mg (4.2 mmol) of 9-isobutylanthracene and 710 mg (6.6 mmol) of *p*-benzoquinone in 7.5 mL of ether was mixed with 1.1 mL of boron trifluoride-etherate and the mixture was stirred for 1 h under a nitrogen atmosphere at room temperature. The produced precipitate was collected by filtration to yield 970 mg of a Diels-Alder adduct. The adduct (670 mg or 2.0 mmol) was dissolved in 22 mL of dioxane and treated with aqueous sodium hydroxide and dimethyl sulfate by adding them alternatively in small portions. In total, 2.0 g of sodium hydroxide (500 mmol) in 20 mL of water and 7.0 mL (75 mmol) of dimethyl sulfate were used. The precipi-

tate was collected and submitted to chromatography on silica gel (5:1 hexane–dichloromethane eluent) to afford 260 mg (36%) of **1**, mp 188.5—189.5 °C. Found: C, 84.30; H, 7.08%. Calcd for $C_{26}H_{26}O_2$: C, 84.29; H, 7.07%. ^{1}H NMR ($CDCl_3$, 270 MHz, room temperature): δ=1.19 (6H, d, J=6.6 Hz), 2.76 (1H, m), 3.31 (2H, d, J=7.7 Hz), 3.70 (3H, s), 3.78 (3H, s), 5.83 (1H, s), 6.45 and 6.49 (2H, ABq, J=9.0 Hz), 6.98 (4H, m), 7.38 (2H, m), 7.59 (2H, m). ^{1}H NMR (CD_2Cl_2–CS_2, δ, 400 MHz, −100 °C): *ap*-form 1.20 (6H, d, J=6.6 Hz), 2.49 (1H, m), 3.36 (2H, d, J=6.6 Hz), 3.68 (3H, s), 3.75 (3H, s), 5.77 (1H, s), 6.41 (2H, br s), 6.87 (2H, t, J=7.1 Hz), 6.97 (2H, t, J=7.5 Hz), 7.25 (2H, d, J=7.3 Hz), 7.60 (2H, m); *sc*-form 0.80 (3H, d, J=6.6 Hz), 1.28 (3H, d, J=6.6 Hz), 2.87 (1H, m), 3.00 and 3.32 (2H, AB of ABX, J=14.3 and 8.8 Hz), 3.70 (3H, s), 3.80 (3H, s), 5.79 (1H, s), 6.52 and 6.57 (2H, ABq, J=9.2 Hz), 7.06 (4H, m), 7.33 (1H, d, J=7.3 Hz), 7.41 (2H, m), 7.73 (1H, d, J=7.0 Hz).

NMR Spectroscopy at Low Temperatures. Compound **1** was dissolved in 1:1 (v/v) carbon disulfide and dichloromethane-d_2 to make up a 19 mmol L^{-1} solution. The spectra at various temperatures were obtained with a JEOL GX400 spectrometer, the temperature being calibrated with a thermocouple. The populations, chemical shift differences, and the coupling constants were checked at 4 temperatures in the slow exchange limit. For the determination of the populations of rotamers, the signals due to the isopropyl-methyl protons were used for the following reasons. Although there was an overlap of the signal due to the α-methylene protons of the 9-substituent in the *ap* form with the lower signal of the two due to the α-CH_2 (AB) protons of the *sc* form, clearly the signals due to the *sc* form were more intense than that due to the *ap* at −100 °C and the assignment of the signals due to the isopropyl-methyl protons was possible by comparing the intensities of the two. The signals due to the isopropyl-methyl protons were found to give more accurate populations than those due to the α-CH_2 protons. The spectra were simulated with the use of the signals due to the isopropyl-methyl protons by the DNMR3 program.[15]

Logarithms of the popultaiton ratios shown in Table 1, when plotted gainst $1/T$(K), afforded the difference in standard enthalpy and entropy, which were used to estimate the populations of the rotamers at temperatures where the change in the line shapes was observed. The coupling constants were constant in the temperature range examined, whereas the chemical shift differences changed linearly with temperature. A straight line was drawn by the least squares method to correlate the chemical shift difference ($\Delta\nu$/Hz) with temperature (t/°C). The following equations were obtained, where A is the chemical shift at a lower magnetic field than the counterpart B of the AB protons and C denotes the chemical shift of the protons due to the *ap* form: $\Delta\nu_{AC}$=−0.21110 t+13.63 Hz, $\Delta\nu_{AB}$=−8.287 t+109.70 Hz. These lines were used for the calculation of the chemical shift differences at a given temperature. The chemical shift of the X proton was used as observed at low temperatures. T_2 was estimated as 0.10 s from the line width due to other protons and this value was used throughout the line shape simulation. It was assumed that the observed process was $A_3B_3X \rightleftarrows C_6X \rightleftarrows B_3A_3X$, the direct exchange $A_3B_3X \rightleftarrows B_3A_3X$ being negligibly slow, and could be approximated by $ABX \rightleftarrows C_2X \rightleftarrows BAX$.

X-Ray Crystallography. Crystals were grown from a tetrahydrofuran–hexane solution. The colorless crystal with dimensions 0.6×0.6×0.2 mm was mounted on a Rigaku AFC-5R four-circle diffractometer and the intensity data were collected using Mo $K\alpha$ radiation (λ=0.71073 Å). The ω-2θ scan technique was employed at a scan rate of 4° min^{-1} in ω, and the scan range was calculated by 1.2°+0.5° tanθ. A total of 6644 independent reflections within the 2θ<60° were measured, and 3364 reflections with $|F_o| \geq 3\sigma|F_o|$ were regarded as observed reflections and used for the structure determination and refinement.

The crystal data are as follows: $C_{26}H_{26}O_2$, F.W.=370.47, monoclinic, space group $P2_1/a$, a=15.803(3), b=8.276(1), c=15.706(3) Å, β=101.02(2)°, V=2016.2 Å^3, Z=4, D_c=1.22 g cm^{-3}, μ=0.816 cm^{-1}. 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 but their positional parameters were not refined. The atomic scattering factors were taken from International Tables for X-Ray Crystallography.[20] The weighting scheme $w=[\sigma_c^2+(0.03 F_o^2)]^{-1}$ was employed. The final R and R_w values were 4.93 and 6.08%, respectively.

All the calculations were carried out on a HITAC M-200H computer with crystallographic computation program systems, 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. 8838 at the Office of the Editor of the Bulletin of the Chemical Society of Japan.

The ^{1}H NMR spectra at 400 MHz were obtained at the JEOL laboratory. We wish to thank for the assistance and the permission of the use of the spectrometer.

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