(28) (a) Judging from the line widths at 23 °C, the asymmetric conformer does not interconvert with itself or with the C_3-symmetric conformer a rate ≥ 1 s^{-1}. At 40 °C the lines of the asymmetric conformer but not those of the C_3-symmetric conformer begin to broaden. This indicates that the rate of *intra*molecular conversion is faster than that of *inter*molecular conversion. (b) See, e.g., Pople, J. A.; Schneider, W. G.; Bernstein, H. J. "High-Resolution Nuclear Magnetic Resonance", McGraw-Hill: New York, 1959; Chapter 10.

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(34) Since k_d (the dissociation rate constant) $\sim \tau^{-1}$ (the average lifetime of the complex) $\ll T_2^{-1} = 2\pi\Delta\nu_{1/2}$ (the natural line width) no line broadening due to dissociation can be observed. See ref 28b.

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Barriers to Rotation of Methyl Groups in 9-Methyltriptycene and 9-Methyl-9,10-dihydro-9,10-ethenoanthracene

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Abstract: Rotational barriers of methyl groups in solid 9-methyltriptycene (**1**) and 9-methyl-9,10-dihydro-9,10-ethenoanthracene (**2**) are determined to be 5.16 ± 0.10 and 3.35 ± 0.04 kcal/mol for **1** and **2**, respectively, by the temperature dependence of the ^1H spin-lattice relaxation times. Calculations of the rotational barriers by the molecular mechanics (MM1) method give too large values, while those by the molecular orbital (CNDO/2) method yield reasonable values. The diminution of the rotational barriers by the CNDO/2 method can be interpreted by nonbonded attractive interactions between the unoccupied σ^*_{CH} orbitals of the methyl group and the occupied σ_{CH} orbitals of the peri CH bonds in the rotational transition state.

Since 9-methyltriptycenes are considered to have intramolecularly large steric hindrances about the methyl groups due to substituents at peri positions and consequently to have large barriers to methyl rotation, DNMR studies in solutions have been carried out by Ōki et al.[1,2] on several peri-substituted 9-methyltriptycenes to investigate their rotational barriers. However, the barrier of the most interesting and fundamental compound, 9-methyltriptycene (**1**) itself, cannot be measured by the DNMR method because of its molecular symmetry.

In this article the authors have measured the ^1H spin-lattice relaxation times (T_1) in the solid state of **1** and 9-methyl-9,10-dihydro-9,10-ethenoanthracene (**2**) (Figure 1) having less steric hindrance due to fewer peri hydrogens, and have determined the barriers to rotation of the methyl groups of **1** and **2** from the temperature dependence of T_1 values. Relaxation mechanisms for **1** and **2** seem to be much simpler in solids than in solutions, because in solids the molecular motion efficient for the relaxation is expected to be only the methyl rotation whereas molecular tumbling and molecular diffusion are also important relaxation mechanisms in solutions.[3]

Further, the origin of the rotational barriers for **1** and **2** is considered on the basis of molecular mechanical calculations (the MM1 method[4]) and molecular orbital calculations (the CNDO/2 method[5]), and an interesting result is found that in addition to the "steric effects" nonbonded attractive interactions[6] between the methyl group and the peri group notably influence the rotational barrier.

Experimental Section

Materials. Melting points were uncorrected. Mass, infrared, and NMR spectra were recorded on Hitachi RMU-6C mass, JASCO IRA-1 diffraction grating infrared, and Varian HA-100 spectrometers, respectively.

A. 9-Methyltriptycene (1). **1** was prepared by treating 9-methylanthracene with benzyne in the manner similar to the preparation of 1,4,9-trimethyltriptycene.[2] Purifications through a silica gel column and by repeated recrystallizations gave **1** as colorless prisms, mp 270 °C (lit. 253–254,[7] 258–259 °C[8]).

B. 9-Methyl-9,10-dihydro-9,10-ethenoanthracene (2). In a sealed glass tube a mixture of 0.8 g of 9-methylanthracene and 4.2 g of *trans*-dichloroethylene was heated for 24 h at 200 °C. After cooling, the sealed tube was opened and the reaction mixture was chromatographed on a silica gel column eluted with CCl_4. The eluate was concentrated, and the residue was refluxed with a mixture of 5 g of Zn, 150 mg of $CuSO_4$, 1 mL of water, and 20 mL of ethanol for 4 h. After cooling, the whole was extracted with ether and the extract was washed with aqueous NaCl and dried over anhydrous Na_2SO_4. The solvent was evaporated, and the residual white solids were chromatographed on a silica gel column. The fraction eluted with benzene-hexane (2:1) was concentrated, and the residual crystals were recrystallized with petroleum ether to give 670 mg (74%) of **2** as colorless prisms: mp 98.0–98.5 °C; NMR δ (CCl_4) 2.12 (3 H, s, methyl), 4.97 (1 H, dd, J = 6.0, 1.5 Hz, bridgehead), 6.50 (1 H, dd, J = 7.0, 6.0 Hz, olefinic), 6.80–6.92 (4 H, m, aromatic), 6.95 (1 H, dd, J = 7.0, 1.5 Hz, olefinic), 7.08–7.26 (4 H, m, aromatic); IR (cm^{-1}) 1445, 1330, 1020, 760, 740, 680; mass spectrum *m/e* (rel intensity) 218 (M^+, 57), 203 (100), 202 (42). Anal. ($C_{17}H_{14}$) C, H.

Measurements. Samples for NMR measurements were degassed by several freeze-pump-thaw cycles. Measurements of T_1 were performed using a homemade pulsed spectrometer operated at 59.5 MHz. T_1 values were determined by the saturation-recovery method: ten 90° pulses at 1.2-ms intervals were applied for saturation,[9] and the solid-echo method[10] was used in order to detect full FID amplitudes hidden by the dead time. A least-squares analysis of the data points enabled T_1 to be determined within an error of ±5%. Tem-

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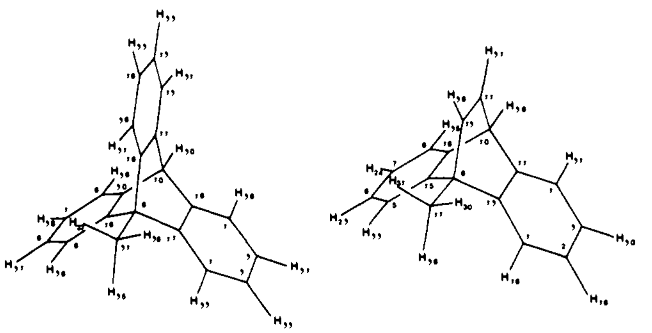


1 **2**

abbreviation	1	2
methyl C	C_{21}	C_{17}
methyl H	H_{11}, H_{36}, H_{37}	H_{29}, H_{30}, H_{11}
bonded C	C_9	C_9
torsional C	C_{16}, C_{17}, C_{19}	C_{12}, C_{13}, C_{11}
peri C	C_1, C_5, C_{11}	C_1, C_9
peri H	H_{22}, H_{26}, H_{34}	H_{18}, H_{22}
peri' H	-	H_{28}

Figure 1. The position numbers of the atoms in 9-methyltriptycene (**1**) and 9-methyl-9,10-dihydro-9,10-ethenoanthracene (**2**) together with their abbreviations.

peratures of the samples were controlled within ±0.2 K by the gas-flow method using a homemade temperature controller.

All calculations were carried out on the FACOM M-190 computer at the Data Processing Center of Kyoto University.

Results and Discussion

Determination of Rotational Barriers. Results of T_1 measurements at various temperatures for **1** and **2** are shown in Figure 2. Each T_1 curve indicates a sharp minimum and the slopes of the linear parts above and below the minimum are practically equal for **1** and **2**, respectively, suggesting that only a single relaxation mechanism, that is, the reorientation of the methyl group, should be efficient. Taking into account only the intramethyl contribution to the relaxation process, one can write the observed initial relaxation rate as[9,11,12]

$$\frac{1}{T_1} = \frac{N_{\mathrm{CH_3}}}{N_{\mathrm{all}}} K \left[\frac{\tau}{1 + \omega^2\tau^2} + \frac{4\tau}{1 + 4\omega^2\tau^2} \right] \quad (1)$$

where N_{all} is the total number of protons in the molecule, $N_{\mathrm{CH_3}}$ is the number of protons in the methyl group, $\omega/2\pi$ is the proton Larmor frequency, τ is the correlation time for the reorientation of the methyl group, and $K = 9\gamma^4\hbar^2/20r^6$, r being the intramethyl proton-proton distance. The correlation time, τ, is assumed to have an Arrhenius dependence on temperature:

$$\tau = \tau_0 \exp(E_a/RT) \quad (2)$$

where E_a is the activation energy and τ_0 is the correlation time at infinite temperature.

Treating K in eq 1 and E_a and τ_0 in eq 2 as adjustable parameters,[13] the experimental data in Figure 2 are satisfactorily fitted to the BPP expression, eq 1, by application of a nonlinear least-squares computer program, and the "best fit" lines are shown as solid curves in Figure 2. The resulting "best fit" values of these parameters are given in Table I.

The "best fit" values of T_1(min) for **1** and **2** are only ca. 20% larger than those predicted using the interproton distance in the methyl group calculated by the MM1 method which will be described later. The ratio of T_1(min) for **1** to that for **2** comes to be 1.16, which is very close to the ratio (1.14) of the total proton number in **1** to that in **2**. Therefore, the same molecular motion, rotation of the methyl group, is effective to the relaxation mechanisms for **1** and **2**, and E_a in eq 2 can be regarded as the rotational barrier of each methyl group.

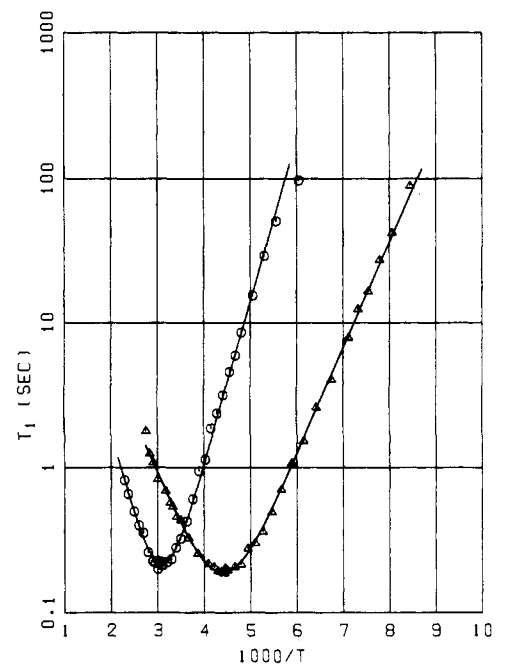


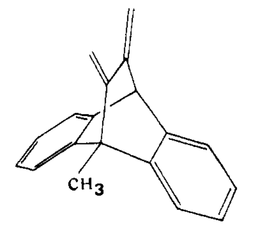
Figure 2. The temperature dependence of the ¹H spin-lattice relaxation times (T_1) for 9-methyltriptycene (**1**, ◐) and 9-methyl-9,10-dihydro-9,10-ethenoanthracene (**2**, △). The solid curves through the data points are "best fits" described by the parameters of Table I.

Table I. "Best Fit" Parameters to the T_1 Data and the T_1(min) Values for 9-Methyltriptycene (**1**) and 9-Methyl-9,10-dihydro-9,10-ethenoanthracene (**2**)[a]

	K, s^{-2}	E_a, kcal/mol	τ_0, s	T_1(min), s
1	(1.19 ± 0.04) × 10^9	5.16 ± 0.10	(5.4 ± 1.1) × 10^{-13}	0.220
2	(1.39 ± 0.03) × 10^9	3.35 ± 0.04	(9.9 ± 1.2) × 10^{-13}	0.189

[a] Error is 2.5σ.

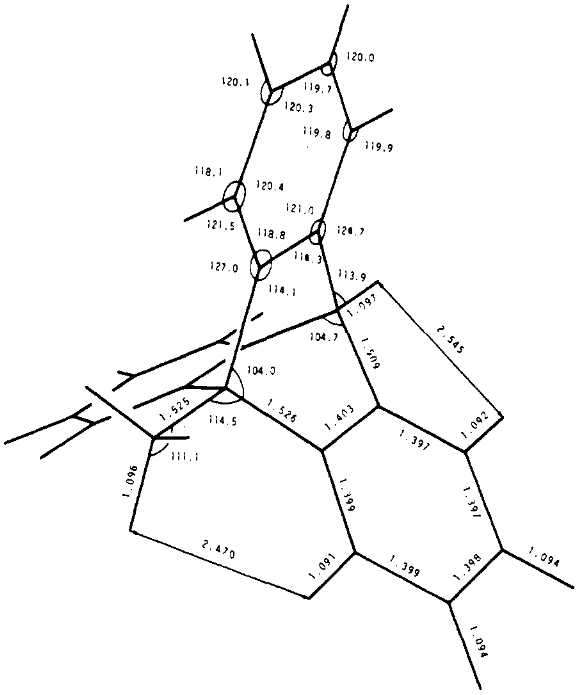
The present value, 5.16 ± 0.10 kcal/mol, for **1** is in line with values which are expected to be much smaller than 8 kcal/mol from the DNMR results for peri-substituted 9-methyltriptycenes.[1,2,14] A recent T_1 study on the compound **3** in solution shows that the rotational barrier for **3** is estimated to be 4.5 kcal/mol,[3a] which interestingly lies between the barriers for **1** and **2**.



3

In view of a barrier of 2.93 kcal/mol in ethane[15] and a barrier as large as 5.40 kcal/mol in 1,1,1-trichloroethane,[16] however, rather small barriers for **1** and **2** appear incomprehensible. Further, a methyl barrier of 2.20 kcal/mol in solid 1-methylnaphthalene[17] may suggest that the rotational barrier for **1** should be 6.6 kcal/mol or even larger on account of the presence of larger torsional energy change for **1**. In the following sections, the origin of the rotational barriers for **1** and **2** is discussed on the basis of two different types of calculations.

MM1 Calculations for Rotational Barriers. The most stable



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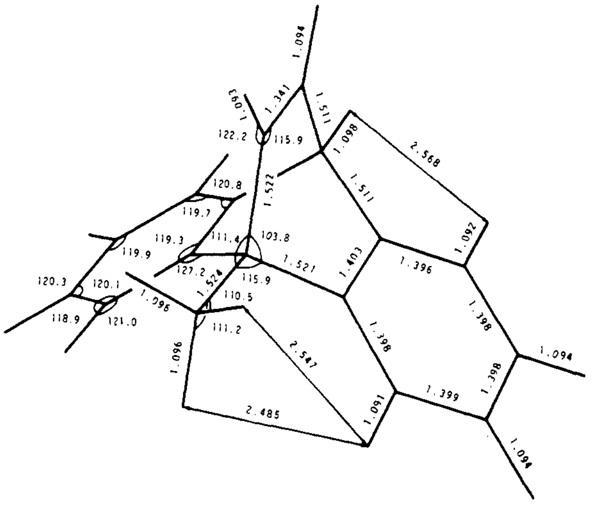

2

Figure 3. The most stable conformations for 9-methyltriptycene (**1**) and 9-methyl-9,10-dihydro-9,10-ethenoanthracene (**2**) calculated by the MM1 method. (Bond lengths and nonbonded distances in angstroms, bond angles in degrees.)

conformations of **1** and **2** have been calculated by the molecular mechanics method proposed by Allinger in 1973 (the MM1 method[4]). Calculated bond lengths and bond angles are shown in Figure 3, where **1** and **2** belong to the symmetry point groups C_{3v} and C_s, respectively. The conformation of **1** seems reasonable for the triptycene system;[18] standard deviations of C-C bond lengths and C-C-C bond angles of **1** from the corresponding experimental values of 9-(β-chloroethyl)triptycene determined by an X-ray study[18b] are 0.011 Å and 0.7°, respectively. As for the conformation of **2**, the C_{17}–C_9 bond is slightly inclined (by 4.2°) from the C_9–C_{10} axis toward the C_{12}–C_9 bond.

Since the methyl groups of **1** and **2** can be considered to take a local C_{3v} symmetry, only the C-C-C-H torsional angles are varied without changing this local C_{3v} symmetry in evaluating the rotational barriers. As expected, the rotational transition states thus obtained are eclipsed conformations where methyl H (abbreviations for atoms are given in Figure 1) eclipse torsional C.[19] The calculated energy barriers, which are equal to the sum of steric energy differences between the transition and the ground states, are collected in Table II. The major contributions to the barriers are seen to be the van der Waals and the bending energies. The former is ca. 40% and the latter is ca. 30% of the total barriers for **1** and **2**. The enhancement of the van der Waals energy in the transition state is mainly attributable to repulsions between methyl H and peri H (including peri′ H for **2**), which amount to 3.89 and 2.69 kcal/mol for **1** and **2**, respectively. The increase of the bending energy is due to changes in the bond angles about methyl C and bonded C. Barriers in terms of these two kinds of steric energies are nearly twice as large as the experimental values, suggesting the presence of particular electronic effects in these systems.

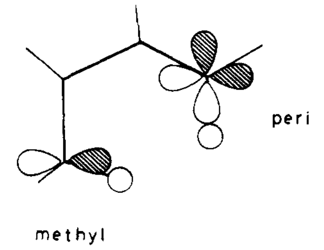

Figure 4. The valence atomic orbitals responsible for the large resonance energy change in the methyl rotation of 9-methyltriptycene (**1**).

Table II. Steric Energy Differences between the Transition and the Ground States in the Methyl Rotation of 9-Methyltriptycene (**1**) and 9-Methyl-9,10-dihydro-9,10-ethenoanthracene (**2**) Calculated by the MM1 Method

steric energy[a]	1	2
bond stretching	1.58	0.78
angle bending	4.02	2.59
torsion	1.60	1.62
van der Waals	4.90	3.44
others[b]	−0.03	−0.04
total steric energy	12.07	8.39

[a] Energies are given in units of kcal/mol. [b] Sum of stretch-bend, torsion-bend, and dipole energies.

CNDO/2 Calculations for Rotational Barriers. In the present CNDO/2 calculations, the most stable conformations generated by the MM1 method are adopted as the ground-state geometries for **1** and **2**. The methyl group is treated as a rigid rotor, bond lengths and bond angles being fixed as the dihedral angle is varied.[20,21] The transition-state geometries thus obtained are similar to those by the MM1 method; methyl H eclipse torsional C. From these calculations the barriers to rotation are found to be 4.89 and 3.94 kcal/mol for **1** and **2**, respectively, in good agreement with the experimental values.[22]

In order to trace the origin of the barriers by the CNDO/2 method, the energy difference between the rotational transition state and the ground state is divided into one-center and two-center energy terms.[23] The two center terms turn out to be 5.67 and 4.89 kcal/mol, respectively, and the important terms are tabulated in Tables III and IV. In these tables the terms participating in the direct bonding, ΔE^{b}, are 1.01 and 0.49 kcal/mol, whereas the nonbonded terms, ΔE^{nb}, are 4.82 and 4.07 kcal/mol for **1** and **2**, respectively. Evidently ΔE^{nb} is the main contribution to the rotational barrier.[24] In ΔE^{nb}, interaction terms between methyl C, H and peri C, H (including peri′ H for **2**), $\Delta E_1{}^{nb}$, and those between methyl C, H and torsional C, $\Delta E_2{}^{nb}$, amount to 1.17 and 3.68 kcal/mol for **1**

Table III. Two-Center Energy Differences between the Transition and the Ground States in the Methyl Rotation of 9-Methyltriptycene (**1**) Calculated by the CNDO/2 Method[a]

	methyl C	methyl H	bonded C	torsional C	peri C	peri H
methyl C		1.83	−1.32	0.57	4.99	3.65
methyl H	1.83	−0.28	0.97	2.14	−2.67	−4.80
bonded C	−1.32	0.97		0.59	0.00	0.10
torsional C	0.57	2.14	0.59	0.35	−2.00	−0.20
peri C	4.99	−2.67	0.00	−2.00	0.01	1.91
peri H	3.65	−4.80	0.10	−0.20	1.91	−0.01

[a] Energies are given in units of kcal/mol. See Figure 1 for abbreviations.

Table IV. Two-Center Energy Differences between the Transition and the Ground States in the Methyl Rotation of 9-Methyl-9,10-dihydro-9,10-ethenoanthracene (**2**) Calculated by the CNDO/2 Method[a]

	methyl C	methyl H	bonded C	torsional C	peri C	peri′ H	peri H
methyl C		0.99	−0.44	1.03	2.94	0.55	2.17
methyl H	0.99	−0.23	0.84	1.73	−1.67	−0.23	−3.06
bonded C	−0.44	0.84		0.19	0.00	0.03	0.07
torsional C	1.03	1.73	0.19	0.02	−1.19	−0.20[b]	−0.14
peri C	2.94	−1.67	0.00	−1.19	0.00	0.00	1.18
peri′ H	0.55	−0.23	0.03	−0.20[b]	0.00		0.00
peri H	2.17	−3.06	0.07	−0.14	1.18	0.00	0.00

[a] Energies are given in units of kcal/mol. See Figure 1 for abbreviations. [b] Energy difference in bonded CH(C_{12}–H_{28}) is −0.24 kcal/mol.

and 0.70 and 3.60 kcal/mol for **2**, respectively. $\Delta E_2{}^{\mathrm{nb}}$ may be regarded as the torsional energy difference by the MM1 method, and it is of interest to note that there is little difference either between $\Delta E_2{}^{\mathrm{nb}}$ or between the torsional energy change of **1** and **2**. On the other hand, $\Delta E_1{}^{\mathrm{nb}}$ may represent the van der Waals energy difference by the MM1 method. $\Delta E_1{}^{\mathrm{nb}}$ of **1** and **2** is, however, very small compared with the corresponding van der Waals energy difference. Therefore, these nonbonded interactions deserve more detailed examination.

In view of the above-mentioned discrepancy, there should be electronic stabilization partly to compensate the "steric effects" or the nuclear repulsions in the transition state. Let us consider the two-center resonance term,[5,23] which can be written

$$E^{\mathrm{R}}{}_{\mathrm{AB}} = 2 \sum_{\mu} \sum_{\nu} P_{\mu\nu} S_{\mu\nu} \beta^0{}_{\mathrm{AB}} \tag{3}$$

where $P_{\mu\nu}$ is the bond order and $S_{\mu\nu}$ is the overlap integral between a pair of atomic orbitals χ_μ (on atom A) and χ_ν (on atom B), and $\beta^0{}_{\mathrm{AB}}$ is the bonding parameter. The differences in these terms for methyl C, H and peri C, H in **1** are presented in Table V. It is again seen that the resonance interactions between methyl H and peri C, H lead to appreciable energetic stabilization (−11.88 kcal/mol), while those between methyl C and peri C, H lead to destabilization (8.73 kcal/mol). The valence atomic orbitals which are mainly responsible for the energy change in the resonance terms are schematically represented in Figure 4. It can be readily recognized that these energy changes should be mainly ascribed to the nonbonded attractive interactions between the occupied σ_{CH} orbitals of the peri CH bonds and the unoccupied $\sigma^*{}_{\mathrm{CH}}$ orbitals of the methyl CH bonds. This consideration also explains the destabilization of the peri and the methyl CH bonds given in Table V, because charge depletion occurs in the bonding orbitals of the peri CH bonds and charge accumulation occurs in the antibonding orbitals of the methyl CH bonds.

Table V. Differences in the Two-Center Resonance Terms in 9-Methyltriptycene (**1**)[a]

	methyl C	methyl H	peri C	peri H
methyl C		1.32	5.11	3.62
methyl H	1.32	−0.29	−4.05	−7.83
peri C	5.11	−4.05	0.00	1.22
peri H	3.62	−7.83	1.22	0.00

[a] Energies are given in units of kcal/mol.

Other interactions between the occupied and the unoccupied orbitals in the methyl and the triptyl fragments are likely to make little contribution to the resonance energy difference.[25] That is, the interactions between the methyl σ_{CH} and the peri $\sigma^*{}_{\mathrm{CH}}$ orbitals are smaller than the interactions described above, because the methyl σ_{CH} levels lie far below the peri σ_{CH} levels though the peri $\sigma^*{}_{\mathrm{CH}}$ lie slightly below the methyl $\sigma^*{}_{\mathrm{CH}}$ levels. The interactions between the methyl σ_{CH} or $\sigma^*{}_{\mathrm{CH}}$ orbitals and the π^* and π orbitals of the benzene rings in the triptyl fragment are also small. The π and π^* orbitals are split into a_2 and e types by the C_{3v} structure of **1**, while the methyl σ_{CH} and $\sigma^*{}_{\mathrm{CH}}$ orbitals are split into a_1 and e types. Thus, only each e-type orbital can interact mutually. Moreover, each 1s atomic orbital of methyl H is located just on the nodal plane of the nearest π orbitals of the benzene rings in the transition state. Therefore, the interactions involving the π and π^* orbitals are expected to be small.

In conclusion, the observed relatively small barriers to rotation of the methyl groups in **1** and **2** can be understood by recognition that the large nuclear repulsions between the methyl and the peri hydrogens are greatly reduced by the electronic nonbonded attractive interactions between the methyl $\sigma^*{}_{\mathrm{CH}}$ and the peri σ_{CH} orbitals.

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Internal Rotation in Biacetyl. A Theoretical Study

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Abstract: The internal rotation about the central C–C bond in biacetyl has been investigated using both semiempirical and ab initio molecular orbital techniques. The results indicate that, while both trans and cis conformers can exist, the latter is present to less than 1% at room temperature. This result is in agreement with experimental studies in which only the trans conformer was observed. The highest occupied molecular orbitals are the n_a, π_b, n_b, and π_a orbitals in order of increasing Koopmans' theorem ionization potentials.

Introduction

The 1,2-dicarbonyls (OXCCXO) have been the subject of extensive experimental and theoretical study. These investigations have concentrated on determining the barrier to internal rotation about the central C–C bond and on the ordering of the highest occupied molecular orbitals. Glyoxal (OHCCHO) has been shown to exist predominantly in the trans form[1,2] but there is also experimental evidence for the existence of a cis planar structure.[3,4] The existence of both planar trans and cis conformers for glyoxal was confirmed by the ab initio calculations of Dykstra and Schaefer,[5] who found a trans-cis energy separation of 5.9 kcal/mol and a barrier to internal rotation of 7.5 kcal/mol with respect to the trans structure. They also determined the ordering of the highest occupied molecular orbitals to be n_a, π_b, n_b, π_a in order of increasing ionization potential (Koopmans' theorem). Kanev and Tyutyulkov[6] used a semiempirical PPP(CI) procedure on *trans*-glyoxal to show that the antibonding ^1A_g and ^1B_g levels crossed when singly or polyexcited configurations were considered and on this basis changed the assignment of the 43 000-cm^{-1} band of glyoxal from a charge transfer to a symmetry-forbidden ^1A_g transition. Oxalyl fluoride (OFCCFO) has also been shown spectroscopically[7] to exist in the trans and cis planar forms and this has been confirmed theoretically[8] with the trans structure again being the dominant form. The ordering of the highest occupied molecular orbitals in oxalyl fluoride was found to be identical with that in glyoxal, though the n_b and π_a orbitals are nearly degenerate in energy. Spectroscopically[9] oxalyl chlorofluoride (OClCCFO) has been identified only in the planar trans form, but ab initio calculations[8] suggest that a planar cis form should also exist and again indicate an orbital ordering of n, π, n, π. The experimental evidence on oxalyl chloride (OClCCClO) is somewhat contradictory suggesting either dominant trans and less stable cis forms[10] or a dominant trans and a less abundant gauche form.[11] Ab initio calculations[8] support the latter result but give an orbital ordering, in the trans form, of n_a, n_b, π_b, π_a, though the latter three orbitals are nearly degenerate.

Biacetyl or 2,3-butanedione (OCH_3CCCH_3O) was investigated by Hagen and Hedberg[12] using electron-diffraction methods and no evidence was found for anything other than the trans conformer. Their conclusion was that, if any other forms were present, they must be in amounts less than 10%. They obtained a value of $V^* = V_1 + 4V_2 + 9V_3 = 11.4$ kcal/mol. These results were in good agreement with earlier spectroscopic investigations.[13] Henderson and Meyer[14] carried out dipole-moment measurements on biacetyl in solution, pure liquid, and vapor phases and their results again show the presence of only the trans conformer. Their value for $V^* = 7.60$ kcal/mol was somewhat lower than that obtained by Hagen and Hedberg.[12] Sidman and McClure[15] investigated the electronic spectra of biacetyl and concluded that the ordering of the highest occupied molecular orbitals was n_a, n_b, π_b, π_a with the n orbitals being degenerate.

The purpose of this study is to investigate the ground-state structure of biacetyl with particular attention being paid to the internal rotation potential and to determine whether more than

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