nylalanine peptides extended structures are preferentially stabilized over folded structures owing to the intramolecular NH⋯phenyl ring interactions.[22]

It should be noted that in previous studies of the folding process of natural amino acids as a function of temperature a decrease of the equilibrium constant $K = f_F/f_S$ was observed, resulting in a negative enthalpy change[23,24] and a negative entropy change.[24] However, those measurements were performed on amino acids with an aliphatic side chain (unable to interact with the peptide function) and in carbon tetrachloride or chloroform as solvent.

Conclusion

In this study, it has been shown that the molecular dynamics of the peptide chain can be probed by the excimer formation between chromophores that are covalently bound to the amino acid side chain. Both configurational and conformational effects have to be taken into account when analyzing the fluorescence decay of BPA. Two sets of ground-state conformations are im-

portant in BPA: an extended C_5 conformation which has to fold to a C_7 conformation to form the excimer and the C_7 conformation itself.

Both the ϕ_{exc}/ϕ_{py} ratio and the values of f_F/f_S, calculated from the transient measurements, indicate the ground-state conformational equilibrium shift when changing from a solvent, unable to form hydrogen bonds with the peptide function, to a solvent which destroys the intramolecular hydrogen bond of the folded conformation.

Since the enthalpy change of folding is about zero for e- and slightly positive for t-BPA, it can be concluded that the folding process is entropy driven, due to the NH⋯π interactions in C_5 between the chromophores and the peptide function. The diastereomeric difference, however, is due to enthalpic effects, because of the steric hindrance in t-C_7.

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Molecular Structure of 1,4,5,8-Tetramethylnaphthalene and In-Plane Molecular Rotation of Some Methyl-Substituted Naphthalenes in Solids

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Abstract: The crystal structure of 1,4,5,8-tetramethylnaphthalene (I) was determined by X-ray crystallography. Least-squares refinement of 904 independent reflections reduces to $R = 0.0609$ and $R_w = 0.0548$ ($w = 1.0$). Crystals of **1** are monoclinic, space group $P2_1/n$, $Z = 2$, $a = 7.948$ (2) Å, $b = 5.190$ (3) Å, $c = 12.887$ (2) Å, $\beta = 104.95$ (2)°. The carbon framework is nearly planar, and the adjacent peri-methyl groups take a clashed-gear conformation. The observed bond lengths and bond angles are well reproduced by molecular mechanics (MMPI) calculations on the assumption of D_{2h} symmetry for the molecular structure. Potential energy calculations for the in-plane molecular rotation of **1** in the crystalline state indicate the molecular motion in the high-temperature region is in-plane 180° flipping. The calculated barrier height (16.9 kcal mol^{-1}) compares favorably with the experimental value. In-plane molecular rotation in the solid state is also investigated for related compounds: naphthalene and 1,5- and 1,8-dimethylnaphthalenes.

How and to what extent aromatic rings keep their planarity with an increase of numbers and/or bulkiness of substituents have been of continuous interest. Recently, we deduced the planarity of methyl-substituted aromatic molecules possessing three fused rings from the barriers to rotation of their methyl groups and their ^{13}C cross-polarization–magic angle sample spinning (CPMAS) NMR spectra.[2] Several X-ray and/or neutron diffraction studies have been performed for dimethylnaphthalenes; carbon frameworks of 1,5-dimethylnaphthalene (**3**),[3] 2,6-dimethylnaphthalene,[4]

and 1,8-dimethylnaphthalene (**4**)[5] are planar, whereas the carbon atoms in 3-bromo-1,8-dimethylnaphthalene (**5**)[6] are not coplanar, and further the aromatic and methyl carbon atoms in 1,8-dimethyl-2-naphthyl acetate (**6**)[7] take a "chair-like" conformation: the C1 and C5 carbons are located above the average molecular plane and the C4 and C8 carbons are located below the plane. Octamethylnaphthalene (**7**)[8,9] has a definite "chair-like" conformation; the displacement of the peri-methyl carbons is as large as 0.73 Å. "Chair-like" conformations are also observed for fully peri-halogenated naphthalenes such as 1,4,5,8-tetrachloro-

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Table I. Final Least-Squares Fractional Coordinates and Thermal Parameters with Estimated Standard Deviations in Parentheses[a]

atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C9	0.4529 (2)	0.5982 (3)	0.4642 (1)	0.0121	0.0274	0.0044	-0.0009	0.0018	-0.0027
C1	0.5240 (2)	0.6954 (4)	0.3793 (1)	0.0151	0.0331	0.0048	-0.0013	0.0023	-0.0009
C2	0.6776 (2)	0.5950 (4)	0.3691 (1)	0.0176	0.0483	0.0062	0.0001	0.0049	0.0009
C3	0.7668 (2)	0.4050 (4)	0.4364 (2)	0.0142	0.0492	0.0073	0.0032	0.0045	-0.0004
C4	0.7097 (2)	0.3081 (4)	0.5199 (1)	0.0130	0.0335	0.0055	0.0016	0.0018	-0.0025
C11	0.4476 (3)	0.9069 (4)	0.3017 (1)	0.0209	0.0451	0.0064	0.0014	0.0031	0.0044
C12	0.8247 (3)	0.1045 (4)	0.5869 (2)	0.0192	0.0493	0.0073	0.0117	0.0032	0.0008

atom	x	y	z	$B_i/Å^2$	atom	x	y	z	$B_i/Å^2$
H2	0.901	0.661	0.300	4.0	H11C	0.856	1.000	0.250	4.0
H3	0.330	0.370	0.442	4.0	H12A	0.772	0.145	0.655	4.0
H11A	0.433	0.868	0.250	4.0	H12B	0.916	-0.079	0.582	4.0
H11B	0.523	1.082	0.337	4.0	H12C	0.453	0.093	0.550	4.0

[a] The anisotropic temperature factor expression for the carbon atom is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. For the hydrogen atoms a temperature factor of the form $\exp(-B_i \sin^2 \theta/\lambda^2)$ was used.

Table II. Bond Lengths, Bond Angles, and Dihedral Angles Involving the Carbon Atoms with Estimated Standard Deviations in Parentheses

atoms	bond lengths/Å	atoms	bond angles/deg	atoms	dihedral angles/deg
C1-C2	1.365 (2)	C2-C1-C9	118.3 (2)	C9-C1-C2-C3	0.1
C1-C9	1.446 (2)	C2-C1-C11	115.6 (2)	C1-C2-C3-C4	-1.6
C1-C11	1.503 (3)	C9-C1-C11	126.1 (2)	C2-C3-C4-C10	2.1
C2-C3	1.382 (3)	C1-C2-C3	122.6 (2)	C3-C4-C10-C9	-1.2
C3-C4	1.366 (2)	C2-C3-C4	122.4 (2)	C4-C10-C9-C1	-0.2
C4-C10	1.445 (2)	C3-C4-C10	118.7 (2)	C10-C9-C1-C2	0.8
C4-C12	1.514 (3)	C3-C4-C12	115.6 (2)	C11-C1-C9-C8	2.9
C9-C10	1.447 (2)	C10-C4-C12	125.7 (2)	C5-C10-C4-C12	0.3
		C1-C9-C8	122.0 (1)		
		C1-C9-C10	119.3 (1)		
		C8-C9C10	118.7 (1)		

naphthalene,[10] 1,4,5,8-tetrabromonaphthalene,[11] and octachloronaphthalene,[12,13] whereas "boat-like" conformations, where the C1 and C4 carbons are located above the molecular plane and the C5 and C8 carbons are located below the plane, are found for 1,4,5,8-tetrasubstituted naphthalenes with larger substituents such as phenyl[15] and nitro[16] groups. Since two proximate methyl groups prefer to take a clashed-gear conformation in the ground state, it is appropriate to adopt Charton's minimum size (1.72 Å)[17] for the van der Waals radius of the peri-methyl groups in 1,8-dimethylnaphthalenes. This value is slightly smaller than that of chlorine (1.75 Å)[18] and significantly smaller than that of bromine (1.85 Å);[18] therefore, the planarity of the molecular structure of 1 and the conformation of its methyl groups are quite interesting in connection with intra- and intermolecular steric interactions.

From the temperature dependence of the ^1H spin–lattice relaxation times (T_1) in the solid state[19] we found a molecular motion other than the reorientation of the methyl groups for 1 at high temperatures. The high activation energy (17.4 ± 1.6 kcal mol^{-1}) with a notably long T_1 minimum (0.258 s) for this molecular motion and the non-axially symmetric powder pattern of the ^{13}C NMR spectra at room temperature lead us to conclude that the molecular motion is in-plane molecular rotation. Although no molecular motion except for reorientation of the methyl groups

was detected for 3 and 4 by proton T_1 measurements up to their melting points, in-plane molecular rotation with an activation energy of 16 kcal mol^{-1} was reported for 3 by von Schütz and Weithase[20] on the basis of proton $T_{1\rho}$ (spin–lattice relaxation times in the rotating frame) measurements. Notably rapid molecular motion, the barrier for which is comparable with those for the reorientation of the methyl groups, was observed for 1-methyl-8-bromonaphthalene (9) and 1-methyl-8-chloronaphthalene (10).[19] We considered that this molecular motion is in-plane rotational diffusion on the basis of their ^{13}C powder-pattern NMR spectra and ^1H second moments at room temperature. Von Schütz and Wolf[21] found that naphthalene (2) molecules undergo an in-plane molecular rotation just below the melting point with a high activation energy (25 ± 2 kcal mol^{-1}).

If the crystal structure is known and the type of molecular motion in the crystalline state is properly assumed known, the geometrical factor C in the Bloembergen–Purcell–Pound (BPP) equation,[2,19] which describes the proton T_1 values, can be calculated and the activation energy for the molecular motion can also be estimated from the change in intermolecular interactions during the molecular motion. Therefore, we have determined the crystal structure of 1 by X-ray crystallography and carried out empirical force field calculations for planar and nonplanar molecular structures of 1 by using the MMPI method[22] (a molecular mechanics method for compounds containing delocalized electronic systems) to interpret the characteristic features in the molecular structure of 1. Further, in order to confirm the molecular motion of 1 in the high-temperature region, we have investigated the potential energy profile for the in-plane molecular rotation, taking into account intermolecular van der Waals interactions. Similar studies have been made of the potential energy profiles for 2, 3, and 4 to elucidate the characteristic features of molecular motion in the solid state.

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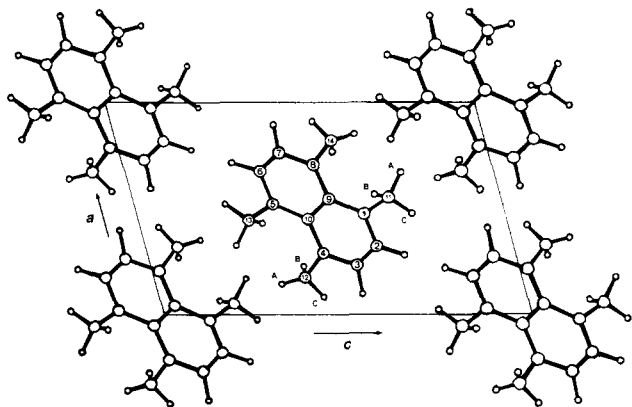
Molecular Structure of Substituted Naphthalenes

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Figure 1. Projection of the molecular structure of 1,4,5,8-tetramethyl-naphthalene (**1**) viewed down the *b* axis.

Table III. Values of Potential Energy Parameters for the Function $[-Ar^{-6} + B \exp(-\alpha r)]^{24}$

atom pair	A/kcal mol^{-1} Å^6	B/kcal mol^{-1}	α/Å^{-1}
C···C	512.69	71782.0	3.60
C···H	111.82	8503.0	3.67
H···H	24.39	2171.0	3.74

Experimental Section

X-ray Structure Determination. Crystals of **1** were obtained from ethanol and are monoclinic, space group $P2_1/n$, $Z = 2$, $a = 7.948$ (2) Å, $b = 5.190$ (3) Å, $c = 12.887$ (2) Å, $\beta = 104.95$ (2)°, $V = 513.58$ (35) Å^3, and $D_c = 1.192$ g cm^{-3} (C$_{14}$H$_{16}$, mol wt 184.28). Intensity data were obtained on a Rigaku four-circle diffractometer (Mo Kα radiation, $2\theta/\omega$ scanning mode, scan speed 2 deg min^{-1}). A total of 904 reflections ($F > 3\sigma(F)$) were measured for $2\theta < 60°$. The structure was solved by Patterson–Fourier techniques and refined by block-diagonal least-squares with the X-STANP program.[23] The 16 hydrogen atoms were fixed on a D-map for least-squares cycles. In the final refinement anisotropic thermal parameters were used for the carbon atoms, but isotropic temperature factors were used for the hydrogen atoms. The hydrogen atoms were included in the structure-factor calculations without refining their parameters. The final discrepancy was $R = 0.0609$ and $R_w = 0.0548$ ($w = 1.0$). The final atomic parameters are listed in Table I. Bond lengths, bond angles, and dihedral angles involving the carbon atoms are collected in Table II. The projection of the structure along the *b* axis is shown in Figure 1.

Potential Energy Calculations. In the calculations for in-plane molecular rotation we assume that the energy of interaction between the two adjacent molecules in a crystal is given by the sum over atom–atom pair interactions and that each atom–atom interaction is a function only of the distance between the two atoms, written in the well-known "exp(-6)" form

$$V = -Ar^{-6} + B \exp(-\alpha r) \qquad (1)$$

where r is the interatomic distance. The empirical parameters A, B, and α in eq 1 for each pair of atoms, which are proposed by Williams,[24] are listed in Table III. The potential energy U is defined as the sum of the nonbonding pairwise interactions between all the atoms in the molecule A, which is rotated, and all the atoms in its neighboring molecules B, which are fixed during rotation of the molecule A

$$U = \sum_i^A \sum_j^B V_{ij} \qquad (2)$$

where the atoms i and j belong to the molecules A and B, respectively.

The atomic coordinates of the molecules in a crystal were adopted from the X-ray analyses. Since the positions of the hydrogen atoms are somewhat ambiguous in X-ray crystallography, we carried out MMPI calculations for the isolated molecule to obtain adequate coordinates for the hydrogen atoms. The positions of the carbon atoms were fixed to the X-ray structure during optimization of the positions of the hydrogen atoms. The fractional coordinates of the hydrogen atoms thus determined for **1** are listed in Table IV. To calculate the interaction energy V by eq 1, however, the positions of the hydrogen atoms were shifted to the

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Table IV. Fractional Coordinates of the Hydrogen Atoms in 1,4,5,8-Tetramethylnaphthalene (**1**) for Potential Energy Calculations

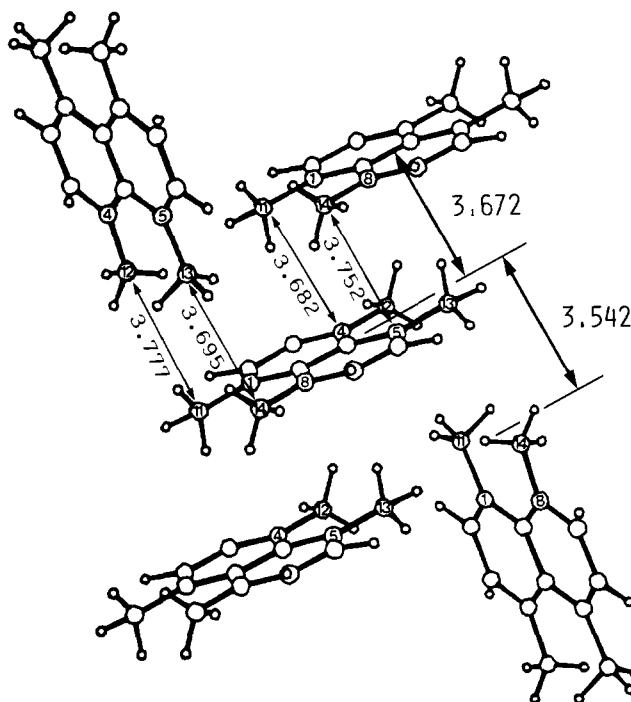| atom	x	y	z
H2	0.7285	0.6492	0.3000
H3	0.9038	0.3637	0.4420
H11A	0.3250	0.8470	0.2465
H11B	0.4536	1.0908	0.3439
H11C	0.5232	0.9561	0.2444
H12A	0.8819	0.1779	0.6678
H12B	0.7593	-0.0824	0.5771
H12C	0.9421	0.0510	0.5624

Figure 2. Molecular packing of 1,4,5,8-tetramethylnaphthalene (**1**). Values are given in units of Å and stand for the distances between the average molecular plane and another plane along the *b* axis and those between the former plane and the average position of the two adjacent peri-methyl carbon atoms. The closest intermolecular distances involving the methyl carbon atoms are also shown.

bonding carbon atoms by 0.07 Å, because the center of electron density of a bonded hydrogen atom shifts into the bonding region.[24,25] Thus, all the coordinates of the atoms in 7 × 7 × 7 unit cells were obtained from the newly established fractional coordinates. The average planes and the axes of the in-plane rotation for the central molecules were determined from the coordinates of the aromatic carbon atoms for **1**, **2**, and **3**, while from those of all the carbon atoms for **4**.

U was calculated by eq 2 as a function of the rotation angle φ, graduated counterclockwise from the C1 to C8 carbons: $\varphi = 0°$ was defined as the original position of the central molecule. Rotation of the methyl groups was not taken into consideration. All the interatomic distances up to 10 Å were included in the calculations.

Results and Discussion

Planarity of Molecular Structures for 1. The molecular packing for **1** is illustrated in Figure 2. The carbon atoms in the molecule are nearly coplanar,[26] and the two adjacent peri-methyl groups take a clashed-gear conformation. The molecules are stacked like stairs along the *b* axis with a distance of 3.672 Å between the stacked molecules.. The distance of the average position of the C11 and C14 carbons from the plane spanned by the adjacent naphthalene ring is 3.542 Å. The closest contacts for the carbon atoms are also given in Figure 2.

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(26) The root-mean-square distance of the carbon atoms from the least-squares plane through all the carbon atoms ($0.3838X + 0.7725Y + 0.6807Z = 7.130$ Å) is 0.022 Å.
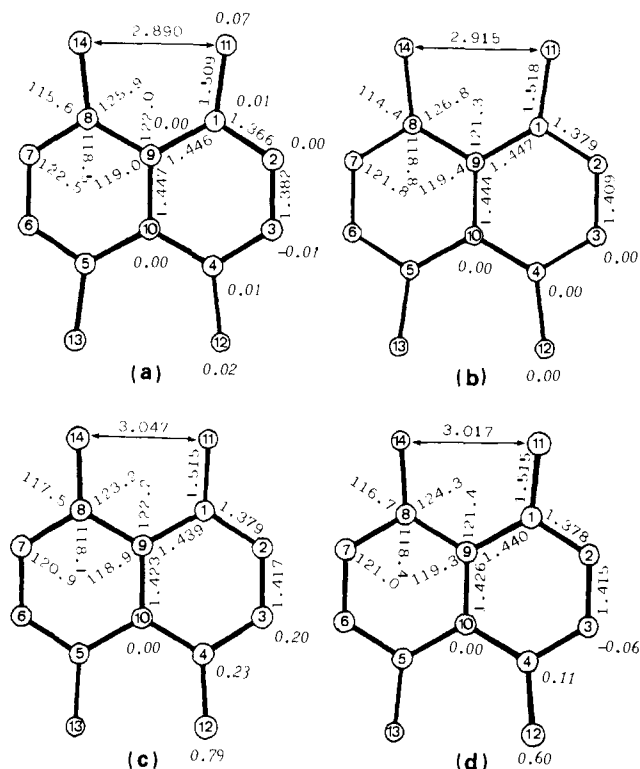
Figure 3. Nonbonding distances (Å) between peri-methyl carbon atoms, bond lengths (Å), bond angles (deg), and distances (Å) of the carbon atoms above the molecular planes in the molecular structure for 1,4,5,8-tetramethylnaphthalene (**1**). (a) Averaged experimental values. The distances of the carbon atoms from the molecular plane are not averaged. (b) Calculated values for the planar D_{2h} conformation. (c) Calculated values for the "chair-like" D_2 conformation. (d) Calculated values for the "boat-like" C_{2h} conformation.

The best plane through the aromatic carbon atoms is determined with respect to the orthogonal crystal axes

$$0.3891X + 0.7803Y + 0.6755Z = 7.130 \text{ Å} \qquad (3)$$

where X and Y coincide with the unit cell x and y axes and Z is normal to x and y. The root-mean-square distances of the aromatic and the whole carbon atoms in the molecule to the best plane are 0.08 and 0.027 Å, respectively. The distances of the individual carbon atoms from the best plane, the average bond lengths, and the average bond angles obtained by X-ray crystallography are shown in Figure 3a. The two methyl carbons (C11 and C13), which are related by the C_i symmetry, deviate distinctly from the best plane, and the other two methyl carbons (C12 and C14) deviate slightly from the best plane. Departures of the C11 and C12 (C13 and C14) carbons in the same direction suggest that **1** tends to take a "boat-like" conformation in the crystalline state.

The molecular structure of **1** in the isolated state is investigated by MMPI calculations. Here we assume three different symmetries for the molecular structure of **1**: planar D_{2h}, nonplanar "chair-like" D_2, and nonplanar "boat-like" C_{2h} conformations. The calculated bond lengths, bond angles, nonbonding distances between the peri-carbon atoms, and distances of the carbon atoms to the respective best planes through the naphthalene ring carbon atoms are shown in Figure 3b–d. The calculated most stable structure for the isolated state of **1** is a "chair-like" conformation; the steric energies for "boat-like" and planar conformations are 2.02 and 5.51 kcal mol⁻¹, respectively, with reference to the steric energy for the "chair-like" conformation. The MMPI calculations for biphenyl by Carter and Liljefors[27] indicated that the steric energy for the planar structure is higher than that for the twisted one by 3.4 kcal mol⁻¹. The present MMPI calculations for **1** also favor a nonplanar structure in the isolated state, but the naph-

thalene ring carbon atoms of **1** are essentially planar in the crystalline state (Figure 3a). It is, therefore, of particular interest how the molecules of **1** are packed in the crystalline state to compensate the large steric energy for the planar structure.

As shown in Figure 2, the C11 and C14 methyl carbons of the central molecule are simultaneously compressed by the C12 and C13 methyl carbons of a second molecule, respectively, from one side with an average distance of 3.732 Å and by the C4 and C5 ring carbons of a third molecule, respectively, from the other side with an average distance of 3.717 Å. A similar situation exists for the C12 and C13 methyl carbons of the central molecule. Although these C···C intermolecular contacts are not unusually close, the former distance is much shorter than twice the usual van der Waals radius for the methyl group (2.0 Å),[28] and the latter is shorter than the sum of the van der Waals radius for the methyl group and that for the carbon atoms in benzene (1.77 Å).[18] The distance between the stacked molecules (3.672 Å) is longer than the sum of Charton's minimum size for the methyl group (1.72 Å)[17] and the van der Waals radius for the carbon atoms in benzene but shorter than the sum of either Charton's maximum size (2.23 Å)[17] or the usual van der Waals radius for the methyl group and the latter value. Thus, the intermolecular compression may force the central molecule to be planar.

Then, we examined crystal packing effects by MMPI calculations. To simplify the calculations the two molecules located in parallel above and below the central molecule and the four methyl groups in the other two molecules surrounding the central molecule shown in Figure 2 were replaced by two 1,8-dimethylnaphthalene and four methane molecules, respectively. Under fixation of all the coordinates of the carbon atoms in the replaced molecules the calculations yield a "boat-like" conformation for the central molecule. The steric energy in this conformation is 0.97 kcal mol⁻¹ higher than that in the stable "boat-like" conformation shown in Figure 3d, because the former conformation is flatter than the latter. Clearly, the intermolecular compression forces the central molecule to take a flatter structure, which is favorable for "boat-like" conformations. The present calculations do not reproduce the planar conformation for the central molecule, since MMPI calculations give sometimes too large steric energies because of a "hard" hydrogen atom in the parametrization.[29]

Molecular Dimensions of 1. In this section, we will discuss characteristic features in the molecular dimensions of **1** in terms of the (average) bond lengths and bond angles shown in Figure 3a. Two characteristic features are found for the bond lengths in **1** compared with those in the related compounds. One is the lengthening of the C9–C10 bond (1.447 Å); the C9–C10 bond lengths in the related compounds are 1.405,[30] 1.380 or 1.444,[3] 1.431,[5] and 1.423[9] Å for **2**, **3**, **4**, and **7**, respectively. The other is the shortening of the C2–C3 bond (1.382 Å); the lengths of the corresponding bonds are 1.416,[30] 1.425 or 1.419,[3] 1.391,[5] and 1.411[9] Å for **2**, **3**, **4**, and **7**, respectively. The bond angles about the C1 carbon in **1** are similar to the corresponding bond angles in **4**, whereas the C1–C9–C8 bond angle in **1** (122.0°) is significantly smaller than that in **4** (125.2°).

The molecular structure for the planar conformation of **1** obtained by the MMPI calculations (Figure 3b) is in good agreement with the X-ray structure: standard deviations are 0.013 Å for all the C–C bond lengths and 0.8° for all the C–C–C bond angles. This indicates that these features are inherent properties of 1,4,5,8-tetrasubstituted naphthalene molecules in the planar conformation. On the other hand, the molecular structures for the two nonplanar, "chair-like" (Figure 3c) and "boat-like" (Figure 3d) conformations of **1** have notably different lengths for the C9–C10 and C2–C3 bonds.

The nonbonding distance between the adjacent peri-methyl carbons is a measure of peri interactions. The distance observed

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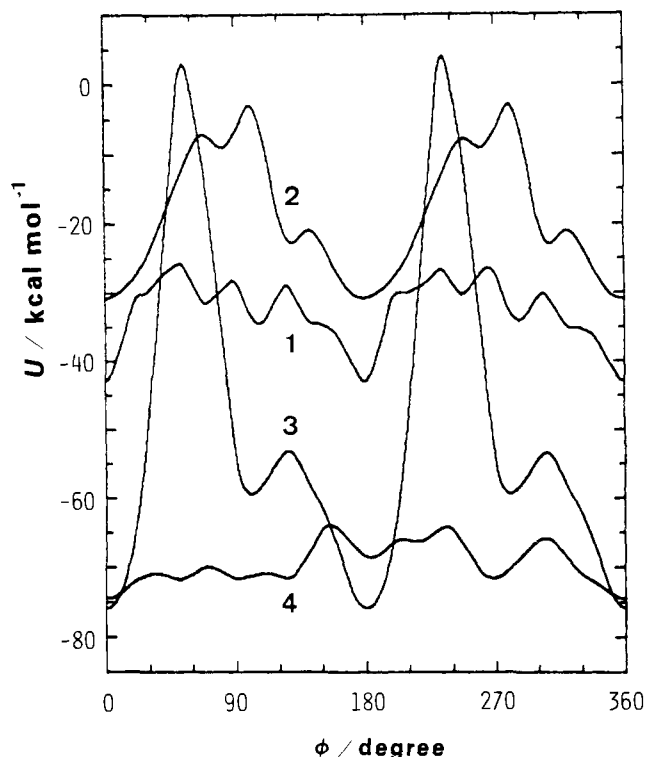
Figure 4. Potential energy profiles for the in-plane molecular rotation of 1,4,5,8-tetramethylnaphthalene (**1**), naphthalene (**2**), 1,5-dimethyl-naphthalene (**3**), and 1,8-dimethylnaphthalene (**4**). The potential energies U are plotted against the rotation angle φ, and those of **3** and **4** are lowered by 40 kcal mol^{-1}.

for **1** (2.890 Å) is slightly shorter than that in octamethyl-naphthalene (**7**, 2.90 Å)[9] but much shorter than those in 1,8-dimethylnaphthalenes (**4**, 2.932 Å;[5] **5**, 2.92 Å;[6] and **6**, 2.965 Å[7]). The peri-methyl groups in **5–7** are effectively separated by the out-of-plane deformation of the molecular structures. However, both **1** and **4** possess planar molecular conformations. The decrease of the nonbonding distance between the C11 and C14 carbons in **1** compared with that between the C11 and C12 carbons in **4** is ascribable to the buttressing effect due to the steric interactions between the opposite peri-methyl groups, as supported by the smaller C1–C9–C8 bond angle in **1**.

Finally, it is to be noted that the adjacent peri-methyl groups in **1** take a clashed-gear conformation. This conformation is predicted by the MMPI calculations and observed for the peri-methyl groups in **4**[6] and **6**,[7] the bridgehead- and peri-methyl groups in 1,4,9,10-tetramethyltriptycene,[31] and the two methyl groups in 4,5-dimethylphenanthrene.[32] Blount et al.[33] have pointed out that 1,8-bis(trimethylelement)naphthalenes prefer taking a clashed-gear conformation, when the substituents are relatively small in bulkiness. This consideration holds for 1,8-dimethyl-naphthalenes.

Potential Energy Profiles for In-Plane Molecular Rotation in Solids. The calculated potential energy profiles for the in-plane molecular rotations of **1–4** are plotted against the rotation angle φ in Figure 4. The activation energy for rotation is equated to the difference in energies between the lowest potential minimum (usually at $\varphi = 0°$) and the highest potential maximum.

a. 1,4,5,8-Tetramethylnaphthalene (1). The calculated potential curve for **1** shows a pair of three maxima with nearly equal height and two large minima at 179 and 359°. Since the three maxima are separated by relatively shallow minima, the in-plane molecular

rotation for **1** is 180° flipping. The highest potential maximum is −25.8 kcal mol^{-1} at 52° and the second highest one is −26.5 kcal mol^{-1} at 266°, whereas the two lowest potential minima are −43.1 and −43.0 kcal mol^{-1} at 179 and 359°, respectively. Consequently, the average activation energy for the in-plane 180° flipping of **1** is 16.9 kcal mol^{-1}. This value is in good agreement with the experimental value of 17.4 ± 1.6 kcal mol^{-1}.[19]

If one assumes that only one molecule undergoes 180° flipping as is considered here, one can evaluate the geometrical factor C appearing in the BPP equation for the proton relaxation times by the equation[34]

$$C = \frac{3}{640}\gamma^4\hbar^2 \sum_i \left(\frac{1}{r_{i1}{}^6} + \frac{1}{r_{i2}{}^6} + \frac{1 - 3\cos^2\theta_{i12}}{r_{i1}{}^3 r_{i2}{}^3} \right) \quad (4)$$

where r_{i1} denotes the distance between the protons of the ith intermolecular pair before the in-plane 180° flipping, r_{i2} represents that between the same proton pair after the flipping, and θ_{i12} is the angle between the proton-pair directions in the two states. We calculated C using the fractional coordinates of the hydrogen atoms in Table IV, regarding the protons in the methyl groups as condensed nuclei owing to their rapid reorientation: $C = 1.00 \times 10^9$ s^{-2}. This value is in excellent agreement with the experimental value of $(1.02 \pm 0.08) \times 10^9$ s^{-2}.[19] These results strongly support the conclusion that the molecular motion detected by the proton T_1 measurements for **1** in the high-temperature region is in-plane 180° flipping.[35] Molecular rotations other than the in-plane rotation are not considered because of the too close contact between the stacked molecules in the crystalline state.

b. Naphthalene (2). For the molecular motion of **2** associated with the high activation energy (25 ± 2 kcal mol^{-1}) Ostertag[36] calculated the potential energy and found the potential maximum of 30 kcal mol^{-1} and two submaxima of 18 and 27 kcal mol^{-1} relative to the potential energy at 0°. Boyd et al.[37] also examined the potential energy profile and stated the molecular motion to be in-plane 180° flipping.[38] As shown in Figure 4, our calculations also indicate that the in-plane rotation for **2** is 180° flipping; the highest potential energy is −3.0 kcal mol^{-1} at 100 and 280° and the lowest one is −30.9 kcal mol^{-1} at 179 and 359°. Thus, the activation energy for the in-plane 180° flipping of **2** amounts to 27.9 kcal mol^{-1}. This value is nearly equal to the value reported by Ostertag but slightly higher than the experimental one.

c. 1,5-Dimethylnaphthalene (3). The in-plane molecular rotation for **3** is also 180° flipping as expected, but two potential maxima with 42.9 and 43.9 kcal mol^{-1} appearing at 54 and 234°, respectively, are significantly high. The average activation energy (79.4 kcal mol^{-1}) calculated from the lowest potential energy (−36.0 kcal mol^{-1}) is too large in comparison with the experimental one (16 kcal mol^{-1}). Therefore, we considered tilting[37] of the molecular plane of **3** during the in-plane rotation. At $\varphi = 54°$, the decrease of the potential energy amounts to 44.0 kcal mol^{-1} with a tilting (θ) of 17° about the axis making a counterclockwise angle (φ') of 50° with the long axis of the naphthalene ring: the activation energy is reduced to about 35 kcal mol^{-1}.[39] This value is still higher than the experimental one. The potential energy of the second maximum at $\varphi = 126°$ (−13.3 kcal mol^{-1}) is decreased by 4.7 kcal mol^{-1} after tilting of the molecular plane (θ

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(38) Their calculated values are incorrect, since they had an erroneous factor of 1/2 in front of the right-hand side of eq 2 to evaluate the barrier height. See: Polak, M. *J. Chem. Phys.* **1977**, *67*, 5572–5576.
(39) The decrease of the potential energy by tilting of the molecular plane is not significant for **1**: 1.3 kcal mol^{-1} with $\theta = -8°$ and $\varphi' = -67°$ for the potential maximum at $\varphi = 52°$. However, the decrease of the potential maximum at $\varphi = 100°$ for **2** is somewhat large (4.7 kcal mol^{-1} with $\theta = -6°$ and $\varphi' = 73°$), bringing the barrier height closer to the experimental value.

= 13° and φ' = 70°). The activation energy for this barrier is, therefore, 18.0 kcal mol⁻¹, which is fairly close to the observed value. The decrease of the potential minimum at φ = 100° (−19.6 kcal mol⁻¹) is only 6.3 kcal mol⁻¹ by the tilting (θ = −4° and φ' = −65°), keeping the potential energy of the second minimum still higher (by 10.1 kcal mol⁻¹) than the lowest potential energy. The results suggest a two-site jumping between the unequal potential depths for the molecular motion of **3**. However, this model is not confirmed at present, because the high-temperature region of the $T_{1\rho}$ curve for **3** has not been measured.[20] Thus, the molecular motion for **3** is not fully appreciated yet.

d. 1,8-Dimethylnaphthalene (4). The potential energy profile for the in-plane rotation of **4** around the axis through the average position of all the carbon atoms is of much interest. Since the molecule has no C_2 axis perpendicular to the molecular plane, the in-plane rotation is not 180° flipping (see Figure 4). Three maxima of the potential energy appear at 155, 236, and 305°, but their values are not so high (−24.2, −24.4, and −26.0 kcal mol⁻¹, respectively) compared with the minimum value at 0° (−34.7 kcal mol⁻¹). In this energy profile, there are several metastable states with the potential energies higher by ca. 3 kcal mol⁻¹ than the

most stable state. The reason for observation of no molecular motion for **4** by T_1 measurements may be ascribable to its relatively low melting point (337 K) and the expected long T_1 minimum. If **9** and **10** have crystal structures similar to the crystal structure of **4** and the potential minima increase for one reason or another, the molecular motion for **9** and **10** is explained by the in-plane molecular reorientation or rotational diffusion among many sites. The latter model was adopted to interpret the temperature dependence of their proton T_1 values.[19] We tried to determine the crystal structure of **9** by X-ray crystallography, but unfortunately high-angle reflections were not detected effectively because of rapid molecular motion even at room temperature.

Laser–Ion Beam Photodissociation Studies of $C_6H_6^+$ Radical Cations: The 2,4-Hexadiyne System

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Abstract: The results of a laser–ion beam study of the photodissociation of $C_6H_6^+$ ions are presented. In the visible wavelength range of the argon ion laser, $C_6H_6^+$ ions from 2,4-hexadiyne were the only $C_6H_6^+$ ions for which photodissociation was observed. The observed products were $C_6H_5^+$, $C_6H_4^+$, $C_4H_4^+$, and $C_3H_3^+$. The absorption was assigned to a $\tilde{A}^2E_u \leftarrow \tilde{X}^2E_g$ transition in the 2,4-hexadiyne cation. The photodissociation spectrum, photofragment branching ratios, information on the product relative kinetic energies, and photofragment angular distributions are presented and discussed along with the results of statistical theory model calculations. We conclude that dissociation of 2,4-hexadiyne cation $\tilde{A}^2E_u$ proceeds by internal conversion to the ground state followed by vibrational predissociation. The relatively large anisotropy of the photofragment angular distributions indicates that isomerization to a benzene structure does not precede dissociation.

I. Introduction

The benzene ion and other $C_6H_6^+$ radical cations have been studied since the earliest days[1] of mass spectrometry and gas-phase ion chemistry. One motivation for this interest is that the benzene ion is one of the simplest hydrocarbon ions, so understanding this system is important from a fundamental point of view. The size of the research effort directed toward understanding the $C_6H_6^+$ system is demonstrated by a recent review[2] devoted entirely to this problem.

In recent years two key issues have emerged. First, for non-dissociating $C_6H_6^+$ ions, which of the possible structural isomers are stable and what are the barriers to isomerization? Second, for $C_6H_6^+$ ions with sufficient internal energy to dissociate, does relaxation from excited states to the ground state and/or isomerization precede dissociation?

Determining the structures of gas-phase ions has always been difficult. The application of conventional spectroscopic techniques is usually not possible owing to the low ion densities. In addition, the low-energy requirements for hydrogen and carbon skeleton rearrangements make structural assignment of hydrocarbon ions

particularly challenging. Collision-induced dissociation (CID), probably the most widely used technique for probing ion structures, does not generally yield distinguishable "fingerprint" spectra for hydrocarbon ions.[3] For $C_6H_6^+$ CID is of little utility since the CID spectra of $C_6H_6^+$ isomers (benzene and acyclic) are very similar.[4] Bimolecular reactivity studies[5] have identified three distinct cyclic $C_6H_6^+$ isomers—benzene, fulvene (5-methylene-1,3-cyclopentadiene), and 3,4-dimethylenecyclobutene—which are distinguishable from the linear isomers 1,3-hexadien-5-yne, 1,5-hexadiyne, and 2,4-hexadiyne. However, the linear isomers of $C_6H_6^+$ could not be differentiated. Which of the ground-state linear isomers of $C_6H_6^+$ are stable (i.e., have a minimum on the

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