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METHYL REORIENTATION IN METHYLPHENANTHRENES—II. SOLID STATE PROTON SPIN-LATTICE RELAXATION IN THE 1-CH₃, 9-CH₃ AND 1-CD₃, 9-CH₃ SYSTEMS

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Abstract—We report proton Zeeman relaxation rates R as a function of temperature T at 8.5 and 53 MHz in polycrystalline 1,9-dimethylphenanthrene (1,9-DMP) and 1-trideuteriomethyl-9-methylphenanthrene (1,9-DMP[1-d₃]). The data are interpreted using a Davidson-Cole spectral density for intramolecular reorientation and the implications of this are discussed. R vs T^{-1} data for 1,9-DMP[1-d₃] are used to determine the parameters that characterize the reorientation of the 9-methyl group. By assuming that the parameters characterizing the dynamics of the 9-methyl group are the same in 1,9-DMP and 1,9-DMP[1-d₃], we subtract out the R vs T^{-1} contribution of the 9-methyl group in 1,9-DMP to determine the parameters that characterize the dynamics of the 1-methyl group. We find that the barrier for reorientation of the 9-methyl group is larger than the barrier for the 1-methyl group and this is discussed in terms of the various contributions to the barrier.

Keywords: Methyl reorientation in solids, methyl phenanthrenes, nuclear Zeeman spin-lattice relaxation.

INTRODUCTION

Nuclear spin relaxation is a useful technique for probing local electrostatic environments in molecular solids. In low temperature solid-state studies of systems like the methyl-substituted phenanthrenes and related molecules [1], methyl group reorientation is the only motion on the nuclear magnetic resonance time scale and the observed proton Zeeman relaxation rate can be related to the activation energy or energies for methyl group reorientation. In 3-methylphenanthrene (3-MP), 9-methylphenanthrene (9-MP) and 3,9-dimethylphenanthrene (3,9-DMP), it was found that the parameters that characterize the dynamics of the 9-methyl group, such as the activation energy for methyl group reorientation E , were very similar in both 9-MP and 3,9-DMP ([1], see Table I). In this paper we present proton Zeeman relaxation rates in 1,9-dimethylphenanthrene (1,9-DMP) and in 1-trideuteriomethyl-9-methylphenanthrene (1,9-DMP[1-d₃]). This study allows us to compare the 1- and 9-positions, which sterically have very similar intramolecular environments as shown in the schematic picture of the molecule in Fig. 1. We find, in agreement with other results [1, 2], that the 9-methyl group has a higher rotational barrier than the 1-methyl group. We discuss this phenomenon in terms of the various steric and electronic contributions to the rotational barrier.

Finally, we show that comparing nuclear spin relaxation measurements in molecular crystals with and without specific deuteration is a good way to test models for intramolecular reorientation.

THE EXPERIMENTS

1,9-Dimethylphenanthrene (1,9-DMP) was prepared by oxidative photocyclization [3] of *o*, α' -dimethylstilbene. Purification by recrystallization from methanol, followed by sublimation [4] at reduced pressure, gave colorless crystals, m.p. 86.8–87.6°C (lit [5] m.p. 87–88°C).

1-Trideuteriomethyl-9-methylphenanthrene (1,9-DMP[1-d₃]), m.p. 87.5–88.0°C (sublimed), was prepared by a Kumada [6] reaction of 1-chloro-9-methylphenanthrene with methyl-d₃-magnesium iodide and 1,3-bis(diphenylphosphino)propane nickel dichloride. The precursor 1-chloro-9-methylphenanthrene was obtained from oxidative photocyclization [3] of *o*-chloro- α' -methylstilbene.

The Zeeman spin-lattice relaxation rates R (the inverses of the spin-lattice relaxation times T_1) were measured using a standard $\pi - t - \pi/2 - t_R$ pulse sequence [7] with the repetition period $t_R > 8.5 T_1$. Two fixed-frequency Spin-Lock CPS-2 Spectrometers operating at 8.50 and 53.0 MHz were used. The free induction decay was time-averaged by an Analogic Data 6000 Waveform Analyser with a Model 630 plug-in. The experimental uncertainty in R is estimated to be typically 5%.

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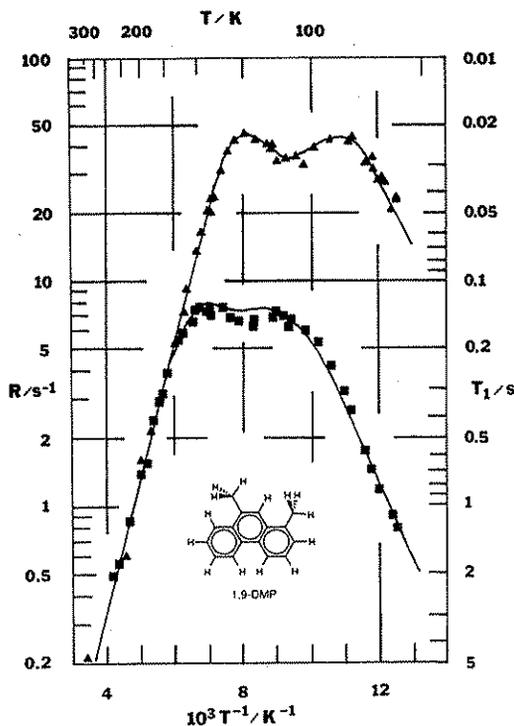


Fig. 1. $\text{Ln}(R)$ vs T^{-1} for 1,9-dimethylphenanthrene (1,9-DMP) at 8.5 (\blacktriangle) and 53 MHz (\blacksquare). The solid lines are the theoretical fits. A schematic picture of the molecule is shown.

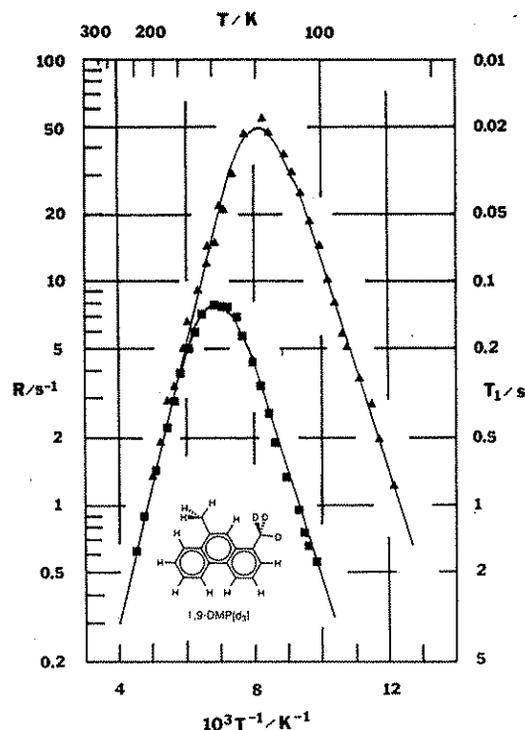


Fig. 2. $\text{Ln}(R)$ vs T^{-1} for 1-trideuteriomethyl-9-methylphenanthrene (1,9-DMP[1- d_3]) at 8.5 (\blacktriangle) and 53 MHz (\blacksquare). The solid lines are the theoretical fits. A schematic picture of the molecule is shown.

Temperature was varied by means of a flow of reheated cold nitrogen gas and temperature was measured with a copper-constantan thermocouple. Absolute temperatures are known to ± 1 K. By using two thermocouples, we have determined that the temperature gradient along that part of the sample inside the NMR coil is less than 0.5 K.

The temperature dependence of the Zeeman relaxation rate at 8.5 and 53 MHz for 1,9-DMP and 1,9-DMP[1- d_3] is shown in Figs 1 and 2, respectively. The temperature dependence of the relaxation rate at 8.5 MHz for both 1,9-DMP and 1,9-DMP[1- d_3] is shown in Fig. 3.

THEORY REVIEW

In many organic molecular solids, proton Zeeman relaxation is caused by the modulation of proton-proton dipole-dipole interactions by methyl group reorientation. The relaxation rate R is given by [8, 9]

$$R = A[J(\omega, \tau) + 4J(2\omega, \tau)], \quad (1)$$

where A is a constant and J is the spectral density. The constant A takes on the theoretical value \tilde{A} if only intramethyl dipole-dipole interactions are considered [1]. In SI units, \tilde{A} is given by

$$\tilde{A} = \frac{9}{40} \frac{n}{N} \left[\frac{\mu_0}{4\pi} \right]^2 \frac{\gamma^4 \hbar^2}{r^6}. \quad (2)$$

The proton-proton separation in a methyl group is r , $\mu_0/(4\pi) = 10^{-7} \text{ m kg}^{-2} \text{ A}$ where μ_0 is the permeability

of free space, the proton magnetogyric ratio is $\gamma = 2.675 \times 10^8 \text{ kg}^{-1} \text{ s A}$, and $\hbar = 1.054 \times 10^{-34} \text{ m}^2 \text{ kg s}^{-1}$. By assuming $r = 1.797 \times 10^{-10} \text{ m}$, the parameter $\tilde{A} = (n/N)(3.80 \times 10^9 \text{ s}^{-2})$. \tilde{A} can be interpreted as the strength of the spin-lattice coupling due to the intramethyl proton dipole-dipole interactions, diluted by n/N , which is the ratio of the number of protons in methyl groups involved in the motion to the number of protons in the molecule. For the reorientation of either the 9-methyl group or the 1-methyl group in 1,9-DMP, $n = 3$, $N = 14$ and \tilde{A} has the theoretical value $\tilde{A} = 8.14 \times 10^8 \text{ s}^{-2}$. For the reorientation of the 9-methyl group in 1,9-DMP[1- d_3], $n = 3$, $n = 11$ and \tilde{A} has the theoretical value $\tilde{A} = 1.04 \times 10^9 \text{ s}^{-2}$. (The ratio of these two \tilde{A} values is just 11/14, the ratio of the numbers of protons in the two molecules.) Dipole-dipole interactions between methyl group protons and other protons will contribute a small amount, typically 0–10%, to the observed relaxation rate, so the theoretical value \tilde{A} gives a lower limit to the value of A that will be determined experimentally.

The spectral density J depends on the model for the methyl group dynamics. A very successful form for molecular solids is [1, 10]

$$J(\omega, \tau) = \frac{2}{\omega} \left\{ \frac{\sin[\epsilon \arctan(\omega\tau)]}{[1 + \omega^2 \tau^2]^{1/2}} \right\}, \quad (3)$$

with the correlation time τ given by

$$\tau = \tau_\infty e^{E/kT}. \quad (4)$$

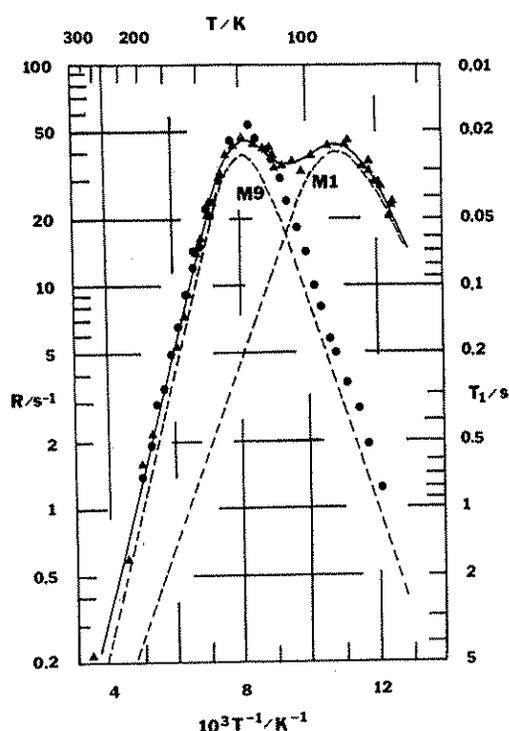


Fig. 3. $\ln(R)$ vs T^{-1} at 8.5 MHz for 1,9-dimethylphenanthrene (1,9-DMP) (\blacktriangle) and 1-trideuteriomethyl-9-methylphenanthrene (1,9-DMP[1- d_3]) (\bullet). The dashed lines labelled M1 and M9 refer to the theoretically predicted relaxation rate due to the reorientation of the 1-methyl and 9-methyl groups, respectively, in 1,9-DMP. The latter is 11/14 of the value of the relaxation rate in 1,9-DMP[1- d_3] as discussed in the text. The indistinguishability of the data in the two molecules at high temperatures is a coincidence as discussed in the text. Schematic pictures of the molecules are shown in Figs 1 and 2.

There are four fitting parameters: the activation energy E , the pre-exponential factor τ_∞ , the constant A and the distribution parameter ϵ .

DATA ANALYSIS

The temperature dependence of the relaxation rate for 1,9-DMP in Fig. 1 shows two maxima in R , one resulting from the reorientation of each methyl group. An observed maximum in R occurs at a temperature where $\tau \sim \omega^{-1}$ and the 1- and 9-methyl groups are characterized by different parameters E

and τ_∞ in eqn (3). Comparing the data for 1,9-DMP (Fig. 1) and 1,9-DMP[1- d_3] (Fig. 2) shows that in 1,9-DMP, the 9-methyl group is responsible for the maximum that occurs at the higher temperature. This is shown for the 8.5 MHz R vs T^{-1} data in Fig. 3. That the data for the two molecules are virtually indistinguishable at higher temperatures (Fig. 3) is a coincidence that will be discussed later.

The 8.5 MHz data for 1,9-DMP[1- d_3] in Fig. 2 are fitted to the Davidson-Cole spectral density in eqn (3) by the technique discussed thoroughly elsewhere [1]. The high temperature linear $\ln(R)$ vs T^{-1} region gives E (the slope) and a relationship between A and τ_∞ (the intercept) and the low temperature linear $\ln(R)$ vs T^{-1} region gives ϵE (the slope) and another relationship between A and τ_∞ (the intercept). The resulting values of the four parameters are $E = 12.1 \pm 0.5$ kJ mol $^{-1}$, $\tau_\infty = (1.1 \pm 0.5) \times 10^{-13}$ s, $A = (1.05 \pm 0.06) \times 10^9$ s $^{-2}$ and $\epsilon = 0.76 \pm 0.03$. Although A and τ_∞ both come from the intercepts, the fit is more sensitive to A because this parameter scales the whole curve [see eqn (1)]. Also, since E appears in the exponential in eqn (4), a relatively small uncertainty in E can lead to a large uncertainty in τ_∞ .

The fit for the 1,9-DMP[1- d_3] data at 8.5 MHz is very good. More importantly, R vs T^{-1} for 1,9-DMP[1- d_3] at 53 MHz can subsequently be predicted with *no adjustable parameters*. This prediction agrees very well with the 53 MHz data in Fig. 2. In Table 1, the experimentally determined values of A are given in units of the theoretically predicted values of A (called \bar{A}) given in the Theory Section and the values of τ_∞ are given in units of values of a calculated τ_∞ , called $\bar{\tau}_\infty$, obtained from a simple model discussed elsewhere [1]. A review of the model leading to $\bar{\tau}_\infty$ is not central or necessary for the present paper, it is simply a convenient scaling parameter. For comparison, the values of these four parameters for the 9-methyl group in 9-MP and 3,9-DMP [1] are also given in Table 1. (The 3-methyl group in 3,9-DMP contributes to R vs T^{-1} at much lower temperatures than does the 9-methyl group and the R vs T^{-1} contribution for the latter is easily extracted from the data.)

It can be concluded that the dynamical model for the reorientation of the 9-methyl group is very good and the parameters that characterize the

Table 1. Fitted relaxation rate parameters for several methylphenanthrenes

Molecule	Methyl group	E (kJ mol $^{-1}$)	A/\bar{A}^\dagger	ϵ	$\tau_\infty/\bar{\tau}_\infty^\ddagger$
9-MP§	9	10.6 ± 0.6	1.0 ± 0.1	0.57 ± 0.04	1.0 ± 0.5
3,9-DMP§	9	12.5 ± 0.9	1.0 ± 0.1	0.68 ± 0.04	1.1 ± 0.5
1,9-DMP¶	9	12.1 ± 0.5	1.01 ± 0.06	0.76 ± 0.03	0.7 ± 0.3
1,9-DMP	1	8 ± 1	1.0 ± 0.2	0.8 ± 0.1	0.1–10

$^\dagger \bar{A}$ is the theoretical value for A given in the text.

$^\ddagger \bar{\tau}_\infty$ is the value based on a model discussed in Ref. 1.

§ Ref. 1.

¶ Values obtained from 1,9-DMP[1- d_3] as described in the text.

|| Values obtained from a comparison of 1,9-DMP and 1,9-DMP[1- d_3] as described in the text.

reorientation are similar in 9-MP, 3,9-DMP and 1,9-DMP[1- d_3]. While this would be compatible with the view that the activation energies for the reorientation of 9-methyl groups originate primarily from intramolecular electrostatic interactions as opposed to intermolecular electrostatic interactions, we have insufficient experimental evidence at present to permit such a conclusion. That is, it might turn out that the crystal structures of 9-MP, 1,9-DMP, and 3,9-DMP, which have not yet been determined, give rise to dominant but fortuitously comparable intermolecular contributions to the electrostatic potential.

The contribution to R vs T^{-1} for the 9-methyl group in the fully protonated 1,9-DMP can now be determined with no adjustable parameters. Only the value of A is different; it is 11/14 of the value of A in 1,9-DMP[1- d_3]. The resulting R vs T^{-1} at 8.5 MHz for the 9-methyl group is shown by the dashed curve labelled M9 in Fig. 3. The difference between this prediction and the observed R vs T^{-1} at 8.5 MHz for 1,9-DMP is assumed to be the R vs T^{-1} due to the reorientation of the 1-methyl group. This difference is fitted using eqns (1)–(4). The resulting R vs T^{-1} at 8.5 MHz for the 1-methyl group in 1,9-DMP is labelled M1 in Fig. 3 and the parameters are $E = 8 \pm 1$ kJ mol $^{-1}$, $\tau_\infty = 3 \times 10^{-13}$ s \pm an order of magnitude, $A = (8.3 \pm 1.7) \times 10^8$ s $^{-2}$ and $\epsilon = 0.8 \pm 0.1$. These values are given in Table 1. This fit is also shown in Fig. 1. Finally, the R vs T^{-1} at 53 MHz for 1,9-DMP can be determined with no adjustable parameters and the theoretical prediction is shown in Fig. 1. The agreement between theory and experiment is very good especially considering that there is a low-temperature linear R vs T^{-1} region at 53 MHz which is not present to such an extent in the 8.5 MHz data.

We note that the data in 1,9-DMP and 1,9-DMP[1- d_3] are indistinguishable at high temperatures at 8.5 MHz as shown in Fig. 3. We attribute this to the coincidental matching of two factors. The component of R at each temperature due to the reorientation of the 9-methyl group is only 11/14 as large in 1,9-DMP as it is in 1,9-DMP[1- d_3]. Evidently this effect is balanced, within experimental uncertainty, by the fact that the observed values of R for 1,9-DMP in the high-temperature region have a small contribution from the 1-methyl group (which is lacking in the 1- CD_3 analog) in addition to the main contribution from the 9-methyl group.

We note that for all the molecules reported in Table 1, the fitted values of A are the same as the theoretical values \bar{A} discussed previously to within experimental uncertainty. This is an important result and shows that intramethyl dipole–dipole interactions dominate the observed spin-lattice relaxation rate. Given the experimental uncertainties, other dipole–dipole interactions are contributing between zero and 10% to the observed relaxation rate for the 9-methyl group and between zero and 20% of the observed relaxation for the 1-methyl group. (The

parameters that describe the reorientation properties of the 1-methyl group are arrived at only indirectly here, i.e. via a subtraction procedure, and will be tested directly in a future study.) Although the crystal structures are not known, this result is consistent with known distances between intramolecular methyl and non-methyl protons and with reasonable estimates for distances between protons on different molecules. These magnetic nuclear spin dipole–dipole interactions which determine the parameter A must not be confused with the electrostatic interactions which determine the parameter E . The latter interactions are discussed in the next section.

DISCUSSION

In general, one can imagine that the barriers for the reorientation of methyl groups in methyl-substituted arenes of the type we are studying can be attributed to the combined influence of three factors: intramolecular electronic effects, intramolecular steric effects, and intermolecular steric effects. We have adopted the tentative working hypothesis that the reorientation barriers for α -methyl groups (defined as methyl groups that are flanked by a *peri* position on one side and an *ortho* position on the other side like the 1- and 9-methyl groups in 1,9-DMP) are largely steric and intramolecular in origin, with the provision that there can also be significant contributions to those barriers from the other two factors in certain cases. The application of this simple hypothesis to the 1,9-DMP system is illustrated in Fig. 4. The reorientation process involves the rotation of a methyl group

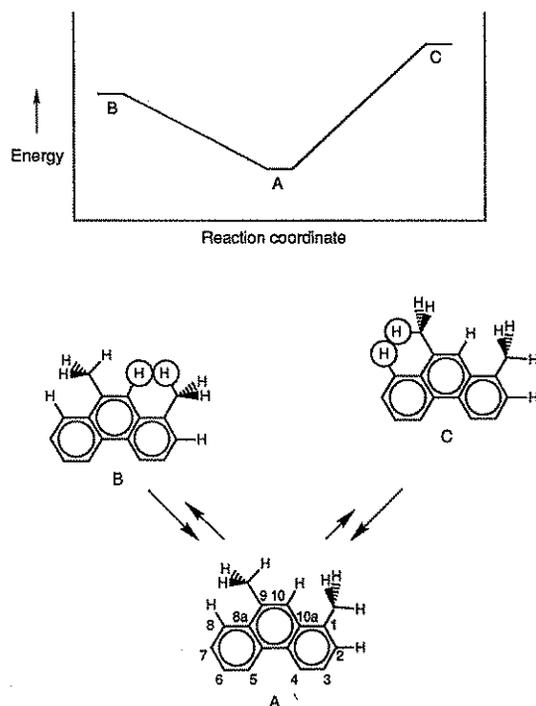


Fig. 4. Energy vs reaction coordinate diagram for the reorientation of the 1-methyl group and the 9-methyl group in 1,9-dimethylphenanthrene (1,9-DMP).

by 120° , passing through a transition structure at the 60° stage. The activation energy for reorientation of the 1-methyl group is thought to be the difference in energy between conformers A and B, and the activation energy for reorientation of the 9-methyl group is thought to be the difference in energy between conformers A and C. Conformer A is essentially free from unfavorable intramolecular steric crowding involving any of the hydrogen atoms of the methyl groups, but conformers B and C are each raised in energy relative to conformer A because they suffer from significant steric crowding between the pairs of hydrogen atoms that are circled in Fig. 4. (In practice these crowdings will lead to distortions in the molecule so as to lessen the extent of the actual interpenetration of van der Waals radii of the two hydrogen atoms by spreading out the destabilization among a number of slightly deformed bond angles and bond distances.)

Our results show that the activation energy for reorientation is slightly larger for the 9-methyl group than for the 1-methyl group in the 1,9-DMP molecule ($12.1 \pm 0.5 \text{ kJ mol}^{-1}$ compared with $8 \pm 1 \text{ kJ mol}^{-1}$). On the basis of the results obtained by ourselves and others that are summarized elsewhere [1], along with some additional unpublished results of our own [2], a pattern has emerged in which the activation energies for the reorientation of α -methyl groups in various methylnaphthalenes, methylanthracenes, and methylphenanthrenes all fall in the range of 8–10 kJ mol^{-1} except for 9-methyl groups in the phenanthrene system, for which anomalously higher values in the range 11–13 kJ mol^{-1} are found. Although the magnitude of this anomaly, approximately 3 kJ mol^{-1} , is too small to be interpreted with confidence, we cautiously offer the following explanation for this phenomenon. The anomaly appears not to originate from intramolecular steric effects. Based on X-ray and neutron diffraction results for the parent phenanthrene system [11], it would appear that the intrinsic steric environment for a methyl substituent would differ only slightly at the 9-position compared with the 1-position. In fact, the small differences in bond distances and bond angles associated with these two positions are such that one might predict that conformer C would be slightly lower in energy than conformer B, not higher as observed. Perhaps a more likely source of the 9-methyl anomaly in phenanthrenes is an electronic effect of the type illustrated in Fig. 5 using propene as a simple example. For propene, conformer D is lower in energy than conformer E by about 8 kJ mol^{-1} [12–15]. Neither conformer experiences any significant steric crowding. The observed conformational preference has been attributed [15, 16] entirely to an electronic effect involving the destabilizing overlap interaction of the filled π orbital of the carbon–carbon double bond with the filled orbital of the methyl group that has the same π symmetry. These two orbitals overlap more in conformer E than they do in conformer D, which

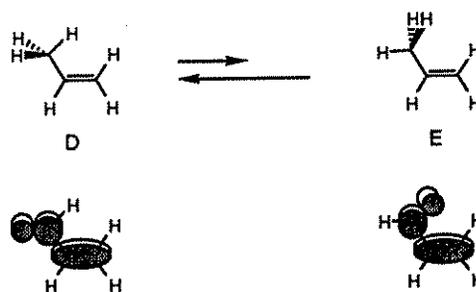


Fig. 5. An illustration of the filled π orbitals of the alkene and the methyl portions of propene whose overlap interactions are responsible for the 8 kJ mol^{-1} conformational preference for conformer D over conformer E in this system.

accounts for the observed higher energy of conformer E. A methyl group attached to an aromatic ring can experience this kind of destabilizing overlap, depending on its conformation, with either of the two flanking carbon–carbon bonds of the ring at the point of attachment. If one of these flanking bonds has appreciably larger double-bond character than the other, this will impose a conformational bias on the methyl group. The extent of this bias will depend on the magnitude of the difference in double-bond character of the two flanking bonds, which can be gauged by the degree of dissimilarity in the two carbon–carbon bond distances as measured by X-ray or neutron diffraction studies. In phenanthrene [11], the 9–10 linkage (1.35 Å) is almost a “pure” double bond ($\sim 1.33 \text{ \AA}$), and the 8a–9 linkage (1.45 Å) is almost a “pure” single bond ($\sim 1.46 \text{ \AA}$). As indicated in Table 2, this difference of about 0.10 Å in the distances of the two flanking bonds at the 9-position in phenanthrene is considerably larger than is found for the 1-naphthyl [17, 18], 1-anthryl [17], or 1-phenanthryl [11] positions (about 0.05, 0.07 and 0.04 Å, respectively). Therefore, a conformer such as C in Fig. 4 is destabilized relative to conformer A not only by the unfavorable steric crowding of the two designated hydrogen atoms, but also by the unfavorable orbital overlap interaction of the type found in conformer E of propene. For the 9-methyl group, this destabilizing interaction is more serious in conformer C, where the interaction involves the electron-rich 9–10 linkage, than it is in conformer A, where the interaction involves the less electron-rich 8a–9 linkage. This orbital effect is less pronounced in conformer B relative to conformer A because there is less of a difference in the π -electron density at the 1–2 linkage compared with that in the 10a–1 linkage.

Table 2. C–C bond distances in selected molecules

System	Flanking C–C bond distances†		Difference (Å)
	(Å)		
1-Naphthyl	1.422 (8a–1)	1.368 (1–2)	0.054
1-Anthryl	1.444 (9a–1)	1.375 (1–2)	0.069
1-Phenanthryl	1.423 (10a–1)	1.386 (1–2)	0.037
9-Phenanthryl	1.453 (8a–9)	1.350 (9–10)	0.103

† Data taken from Refs 9, 15 and 16.

Thus even though the steric contributions to the barriers may be very similar for the 1- and 9-methyl groups, the barrier for rotation of the 9-methyl group has this additional electronic contribution.

SUMMARY

Organic molecular solids provide a convenient molecular laboratory for the study of reorientational properties of intramolecular rotors like methyl groups. In this paper we have compared the proton Zeeman relaxation rate in two dimethyl substituted phenanthrenes; in one, one of the methyl groups is deuterated and as such does not contribute to the observed relaxation rate. A simple model which assumes a distribution of correlation times for intramolecular reorientation fits the data very well. As discussed elsewhere [19], the model has two interpretations: either the correlation function for intramolecular reorientation is non-exponential, or there is a distribution of electrostatic potentials in which the methyl groups reorient. The fitted values of the parameter that characterizes the strength of the proton-proton dipole-dipole interactions are consistent with the assumption that only intramethyl interactions need to be taken into account. Also, the experimentally determined parameter τ_∞ that appears in the Arrhenius relationship agrees very well with simple theories for thermally activated reorientation as discussed elsewhere [1].

From a phenomenological point of view, these kinds of experiments are very good for characterizing rotor sites and distinguishing between sites in molecular solids. The activation energies for the reorientation of 9-methyl groups in several different methylphenanthrene systems cluster around 12 kJ mol⁻¹, which is about 3 kJ mol⁻¹ larger than is found for various other α -methyl groups in polycyclic aromatic systems. We attribute this 3 kJ mol⁻¹ increment to the operation of an intramolecular electronic effect for 9-methylphenanthrenes in addition to

the intramolecular steric effect that we believe provides the dominant part of the energy barrier for reorientation of α -methyl groups.

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