MOLECULAR DYNAMICS—VII

COMPONENT ANALYSIS OF LOCAL MOLECULAR MOTIONS*

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Abstract—The local molecular correlation times obtained from lineshape analysis of —CHD-- proton resonances, have been separated into contributions from *overall* and *internal* molecular motions in a series of compounds I–XIII. The results obtained from I–III are then transferred to compounds IV–XIII, for which overall and internal correlation times are calculated. It is possible to study the *dynamic coupling* of these two types of motions making up local motions. The results allow discussing *structural effects* on molecular overall and internal reorientations. Intermolecular effects have also been observed. *Component analysis* of the local molecular motions obtained from quadrupolar labelling, thus allows a detailed description of the dynamic behaviour of molecules in solution.

Résumé—Les temps de corrélation locaux obtenus par analyse de la forme de raie de signaux de résonance protonique CHD dans les composés I–III, ont été décomposés en deux contributions: celle provenant de la réorientation *globale* de la molécule et celle due aux mouvements *internes*. Ces résultats ont ensuite été utilisés pour l'analyse des réorientations globales et internes dans les composés IV–XIII. Le *couplage dynamique* de ces deux types de mouvement a été étudié. Les résultats de cette analyse permettent de discuter les *effets structuraux* sur les réorientations globales et internes des systèmes I–XIII. Des effets intermoléculaires ont aussi été observés. L'analyse des *composantes* des mouvements moléculaires locaux permet ainsi de décrire en détail les propriétés dynamiques des molécules en solution.

INTRODUCTION

IN THE PRECEDING PAPER[1] we have presented the general tenure of our studies of molecular dynamics in organic molecules using deuterium quadrupolar relaxation and we have discussed the correlation times obtained from the deuterium relaxation times in terms of *local* molecular motions. In non-rigid molecules, such local motions are composite processes resulting from the combination of two or more elementary dynamic processes like overall reorientation, internal rotations, inversions.[2, 3]

In the present paper we analyze local motions in a number of organic molecules. Starting with specifically labelled model systems it is possible to *separate* local motions into their components and then to *transfer* these components to structurally equivalent sites in other molecules (for instance those studied in the preceding paper[1]). This also allows analyzing *structural effects* on dynamic coupling and internal motions.

Local molecular motions have been studied in some relatively simple molecules with internal motion using quadrupolar relaxation data (deuterated acetonitrile[4] methylacetylenes,[5] isobutylenes,[6] N,N-dimethylformamide,[7] methylbenzylcyanides,[8] methylchloroform,[8] trichloroacetonitrile[9] and several deuterated organic liquids [10–15]). However, only in a few cases has the separation of local motions into overall and internal motions been attempted.[6, 7, 12, 14]

* Nuclear Relaxation and Molecular Properties, VII: previous paper in this series: see reference 1.
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METHOD AND RESULTS

Analysis of local correlation times

Lineshape analysis of the resonance of protons coupled to a deuterium nucleus leads to the deuterium quadrupolar relaxation time T_q, which, using a quadrupolar coupling constant of 170 kHz, is related to the local correlation time τ_q by the following equation:

$$T_q^{-1} = 0.43 \, 10^{12} \, \tau_q \tag{1}$$

The method of lineshape analysis and the derivation of (1) are described in detail in the preceding paper. τ_q is the *effective local correlation time* which, in molecules with internal rotation, results from a given superposition of overall and internal motions. The relation between τ_q and the elementary motions has been studied first by Stejskal and Gutowsky[16] and by Woessner;[17] extensions to various cases have been treated by several authors.[3, 12, 18-20] If internal rotation occurs at a rate τ_i^{-1} around an axis whose reorientation is described by a correlation time τ_M, the effective local correlation time τ_q is given by equations (2) or (3) depending on the model used. (i) For a diffusional internal rotation process among a very large number of equilibrium positions, one has:

$$\tau_q = A\tau_M + B\left(\frac{1}{\tau_M} + \frac{1}{\tau_i}\right)^{-1} + C\left(\frac{1}{\tau_M} + \frac{4}{\tau_i}\right)^{-1} \tag{2}$$

(ii) For a three-fold rotation barrier, with random jumps between the three equilibrium positions at an average rate $(3\tau_i)^{-1}$, one has:

$$\tau_q = A\tau_M + (B + C)\left(\frac{1}{\tau_M} + \frac{1}{\tau_i}\right)^{-1} \tag{3}$$

In equations (2) and (3) A, B and C are geometrical parameters:

$$\begin{aligned}
A &= \tfrac{1}{4}(3\cos^2\theta - 1)^2 \\
B &= \tfrac{3}{4}\sin^2 2\theta \\
C &= \tfrac{3}{4}\sin^4\theta
\end{aligned} \tag{4}$$

where θ is the angle between the rotation axis and the main field gradient axis. For a —CHD— group, this axis may be assumed to lie along the C—D bond direction: θ is then nearly equal to the tetrahedral angle ($\theta \sim 109°\,28'$). Equations (2) and (3) become respectively (5) and (6):

$$\tau_q = 0.11\tau_M + 0.30\left(\frac{1}{\tau_M} + \frac{1}{\tau_i}\right)^{-1} + 0.59\left(\frac{1}{\tau_M} + \frac{4}{\tau_i}\right)^{-1} \tag{5}$$

$$\tau_q = 0.11\tau_M + 0.89\left(\frac{1}{\tau_M} + \frac{1}{\tau_i}\right)^{-1} \tag{6}$$

Both elementary processes τ_M and τ_i are assumed to be independent. It is seen that the coupling of τ_M and τ_i leads to the resultant local motions τ_q. The effect of the internal process depends on the relative magnitude of τ_M and τ_i, *i.e.*, on whether internal rotation is fast or slow with respect to the motions of the rotation axis itself;

the coupler is thus the barrier to internal rotation. One may define a *coupling coefficient* ξ^*:

$$\xi = \tau_q/\tau_M \tag{7}$$

which varies from 0·11 to 1 and should be dependent on the barrier of internal rotation.

For $\xi = 0·11$, there is maximum decoupling between overall and local motions and $\tau_i \sim 0$ (extremely fast internal rotation: τ_M, τ_i coupling is minimum). $\xi = 1$ corresponds to maximum coupling: internal rotation is very slow and local motions are the same as overall reorientations. It is seen that internal rotations can only shorten τ_q and increase T_q. If the internal rotation axis is directly attached to the molecular framework and if the motions of the framework are assumed to be isotropic (see preceding paper), τ_M describes the motions of the axis which are the same as the overall molecular reorientations. In addition, the number of equilibrium positions is not always clear in the compounds studied here and may differ from one molecule to the other, but it is certainly not very large,† so that we shall use the three jump model, equation (6), for analyzing local motions. Although these assumptions limit the quantitative accuracy of the analysis, the results obtained are nevertheless a good approximation to the actual molecular motions. When several internal rotation processes are present, the resulting local motions may be derived in analogous fashion. Starting with the largest rigid part of the molecule, the motion of the nth bond axis results from the motion of the $(n - 1)$th axis and from the $(n - 1)$th internal rotation. For instance for two internal rotations with time constants τ_i and τ_j the motion of the deuterium label D is given by:

$$\tau_q^{(D)} = 0·11 \, \tau_{M'} + 0·89 \left(\frac{1}{\tau_{M'}} + \frac{1}{\tau_j}\right)^{-1}$$

$$\tau_{M'} = 0·11 \, \tau_M + 0·89 \left(\frac{1}{\tau_M} + \frac{1}{\tau_i}\right)^{-1} \tag{8}$$

Where τ_M and $\tau_{M'}$ are the motions of the first and second rotation axes. When $\tau_i \ll \tau_M$ and $\tau_j \ll \tau_{M'}$, then $\tau_q(D) \sim 0·01 \, \tau_M$. If several internal rotations are present between the molecular framework and the site of the label, the coupling coefficient ξ may drop below 0·11. Thus, each internal rotation process may have an effect. Such stepwise decoupling of local motions from the motions of the rigid framework is especially important when studying the complexation of labelled small molecules with macromolecules, which have very long τ_M.[18]

Substrates

The preparation of the substrates used for the present work is described in the

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* We prefer the present definition of ξ to the previous one ($\xi = \tau_M/\tau_i)^2$ as it relates the two observed motions and gives to ξ values between 0 and 1 (see also below).

† The rotation barrier is six-fold for the —CH_2D groups in Ia and VIb, c. However, the rotation is so fast (very short τ_i; see below) that only the first term in equations (5) and (6) is important: thus (5) and (6) are equivalent in this case. O—CH_2D (in III–V) and —CO—CH_2D (in VIc) rotations have a three-fold

experimental section (see below) for I–V. Their properties are in agreement with the structures indicated. Compounds VI–XIII have been studied previously.[1]

Local, overall and internal correlation times. Activation parameters

Compounds I–V all display quadrupolar effects on the proton lineshapes of the —CHD— signals. Compounds VI–XIII have already been studied:[1] the data obtained for local motions[1] are used here for further analysis by means of the results gained from the study of I–III. Assuming isotropic overall reorientation, the deuterium atom linked to the molecular framework in I–III describes the motion of the C—CHDX (I), C—CHDOAc (II) or C—OCH$_2$D (III) axes. Lineshape analysis of the proton resonance at C(9) in I, at C(11) in II or at C(4) in III leads to the deuterium T_q from which the correlation time τ_M for overall reorientation is obtained using equation (1). Lineshape analysis of the proton resonance of the —CHDX, —CHDOAc, —CH$_2$D groups in I, II, III, similarly leads to the local correlation times τ_q. Using these τ_M and τ_q values in equation (6), the rates of internal rotation τ_i^{-1} around the C—CHDX (I), C—CHDOAc (II) and C—OCH$_2$D (III) bonds may be obtained.

Assuming *transferability* of these τ_M and τ_i values from the initial systems to *similar frameworks* and to *locally similar sites*, it becomes possible to separate the local motions in compounds IV–XIII into their overall and internal components using only the effective local τ_q in the —CHD— side groups and equation (6). The τ_q values for compounds VI–XIII have been taken from the preceding paper. The Table lists the τ_q, τ_M and τ_i values obtained in this way. In the course of the analysis the following transfer sequences have been followed (assumed values in brackets):*

(a) τ_i (Ic) $\sim$ $[\tau_i$ (VIb)$] \to \tau_M$ (VIb) $\sim$ $[\tau_M$ (VII)$] \to \tau_i$ (VII) $\sim$ $[\tau_i$ (VIII)$] \to \tau_M$ (VIII) $\sim$ $[\tau_M$ (IX)$] \to \tau_i$ (IX);

(b) τ_i (Ic) $\sim$ $[\tau_i$ (XI)$] \to \tau_M$ (XI) $\sim$ $[\tau_M$ (X)$] \to \tau_i$ (X)

(c) τ_i (II) $\sim$ $[\tau_i$(X)$] \to \tau_M$ (X) $\sim$ $[\tau_M$ (XI)$] \to \tau_i$ (XI)

(d) τ_i (II) $\sim$ $[\tau_i$ (XII)$] \to \tau_M$ (XII)

(e) τ_M (XII) $\sim$ $[\tau_M$ (XIII)$] \to \tau_i$ (XIII)

(f) τ_i (Ib) $\sim$ $[\tau_i$ (VIa)$] \to \tau_M$ (VIa)

Sequences (b) and (c) allow cross-checking the results and testing the transferability hypothesis. It is indeed found that τ_i (X) (40·0 psec) from sequence (b) is similar to τ_i (II) (36·0 psec; sequence (c)) and that τ_i (XI) (17·9 psec) from sequence (c) is similar to τ_i (Ic) (18·2 psec: sequence (b)). The activation parameters $\Delta G^{\ddagger}$, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for local, overall and internal motions may be calculated using the equations given in the preceding paper[1] and plots of log $(\tau T)^{-1} = f(1/T)$. The values obtained are also listed in the Table. $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ have not been obtained for all compounds: as $\Delta S^{\ddagger}$ is expected to be very small for an intramolecular process, the $\Delta G^{\ddagger}$ values may be taken as a measure of the barrier hindering the process;[21] however this is not true when intramolecular interactions are present as in alcohols Ib and VIa (see below). In the case of the internal rotations, the plot log $(\tau_i T)^{-1} = f(1/T)$ uses τ_i values calculated from τ_M and τ_q values at the same temperature. Although the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values are not very accurate they nevertheless allow calculating $\Delta G^{\ddagger}$ and τ values for the different processes at any temperature in the range studied. Figures 1

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* The correlation times are given in picoseconds: psec = 10^{-12} sec.

TABLE. DEUTERIUM QUADRUPOLAR RELAXATION TIMES (T_Q), OVERALL (τ_M), LOCAL (τ_q) AND INTERNAL (τ_i) CORRELATION TIMES, COUPLING COEFFICIENTS (ξ) AND ACTIVATION PARAMETERS ($\Delta G^\ddagger$, $\Delta H^\ddagger$, $\Delta S^\ddagger$) OBTAINED FOR COMPOUNDS I–XIII[a]

Compound (1M, CDCl₃)	Group	J_{HD} Hz ± 0.1	Δ^b Hz ± 0.1	T_q msec ± 5%	Correlation time[c] (psec)	ξ	$\Delta G^\ddagger_{306}$ kcal/mole ± 0.1	$\Delta H^\ddagger$ kcal/mole ± 0.5	$\Delta S^\ddagger$ eu ± 2
Ia	—CHD—	3.5	1.9	143	τ_M: 16.3		2.8	2.4	0.0
Ia (−46.5°)	—CHD—	3.5	1.9	27	τ_M: 86.6	0.09	2.7		
	—CH₂D	2.2	1.1	310	τ_q: 7.5		1.6		
					τ_i: ~0		~0		
Ib	—CHD—	3.5	1.9	95	τ_M: 24.6	0.43	3.0	3.5	1.3
	—CHDOH	1.9	0.9	290	τ_q: 10.6		2.5	5.0	8.0
					τ_i: 13.9		2.7	6.6	11.5
Ic	—CHD—	3.5	1.9	100	τ_M: 23.4	0.50	3.0	3.2	0.4
	—CHDOAc	1.9	0.9	200	τ_q: 11.7		2.6	3.0	1.2
					τ_i: 18.2		2.8	2.5	−1.4
Ic (−43.5°)	—CHD—	3.5	1.9	11	τ_M: 212.7	0.28	3.1		
	—CHDOAC	1.9	0.9	40	τ_q: 58.5				
					τ_i: 48.8		2.4		
Id	—CHD—	3.5	2	74	τ_M: 31.6	0.47	3.2		
	—CHDCl	1.9	1	158	τ_q: 14.8		2.7		
					τ_i: 21.2		2.9		
II	—CHD—	3.4	1.6	50	τ_M: 46.8	0.50	3.4	3.2	−0.7
	—CHDOAC	1.9	0.8	100	τ_q: 23.4		3.0	3.1	0.3
					τ_i: 36		3.3	3.0	−0.9
IIIa	—CH=CD—	1.25		102	τ_M: 17.5	0.26	2.8	2.5[d]	−1.1[d]
IIIb	—OCH₂D	1.6		450	τ_q: 4.6		2.0	1.6	−1.4
					τ_i: 3.7		1.9		
IV	—OCH₂D	1.7	0.3	540	τ_q: 4.3		1.8	2.3	1.6
V	—OCH₂D	1.65	0.3	520	τ_q: 4.5		2.1	2.3	0.7
VIa	—CHDOH	1.9	0.9	458	τ_q: 5.1	0.70	2.1		
					τ_i: 13.9		2.7	6.6	11.5
					τ_M: 7.3		2.3	4.0	5.8

TABLE—continued

Compound (1M, CDCl₃)	Group	J_{HD} Hz ± 0.1	Δ^b Hz ± 0.1	T_q msec ± 5%	Correlation time[c] (psec)	ζ	$\Delta G^{\ddagger}_{306}$ kcal/mole ±0.1	$\Delta H^{\ddagger}$ kcal/mole ± 0.5	$\Delta S^{\ddagger}$ eu ± 2
VIb	—CHDOAC	1.9	0.8	390	τ_q: 6		2.2	1.7	−1.8
					τ_i: 18.2		2.8	2.5	−1.4
					τ_M: **8.3**	**0.72**	**2.4**	**1.9**	**−1.9**
VIb (−43.5°)	—CH₂D	2.2	1.0	360	τ_q: 6.5	**0.11**	1.6		
					τ_i: **0.12**		0		
	—CHDOAC	1.9	0.9	78	τ_q: 30	**0.52**	2.2		
					τ_i: 48.8		2.4		
					τ_M: **58.1**		**2.6**		
	-O—COCH₂D	2.2		297	τ_q: 7.8	0.26	1.6		
					τ_i: 0.2		0		
VIc	—CHDOAc	1.9	1.0	700	τ_q: 18.2		2.8		
					τ_i: 3.3		1.8		
					τ_M: 3.9		1.8		
VII	—CHDOAC	1.9	0.7	383	τ_q: 6.1	0.73	2.2		
					τ_i: **20**		**2.9**		
					τ_M: 8.3		2.4		
VIII	—CHDOAC	1.9	0.7	248	τ_q: 9.4	**0.61**	2.4	2.0	
					τ_i: 20.0		2.9		
					τ_M: **15.3**		2.7		
IX	—CHDOAC	1.9	0.7	170	τ_q: 13.7	0.89	2.7	2.3	−1.5
					τ_i: **110**		**3.9**		
					τ_M: 15.3		2.7		

TABLE—*continued*

Compound (1M, CDCl$_3$)	Group	J_{HD} Hz ± 0.1	Δ^b Hz ± 0.1	T_q msec ± 5%	Correlation time^c (psec)	ζ	ΔG‡$_{306}$ kcal/mole ±0.1	ΔH‡ kcal/mole ±0.5	ΔS‡ eu ± 2
X	CHDOAC	1.9	0.7	222	τ_q: 10.5 τ_i: 40 (36) τ_M: 13.7 (**13.9**)	0.76 (**0.75**)	2.5 3.3 (3.3) 2.7 (**2.7**)	2.7	0.6
XI	—CHDOAC	1.9	0.9	275	τ_q: 8.5 τ_i: 18.2 (**17.9**) τ_M: 13.7 (*13.9*)	0.62	2.4 2.8 (**2.8**) 2.7 (*2.7*)	2.5 2.5 2.6	0.6 *-1.4* -0.4
XII	—CHDOAC	1.9	1.0	116	τ_q: 20.1 τ_i: *36* τ_M: **36.6**	0.55	2.9 *3.3* **3.3**		
XIII	—CHDOAC	1.9	0.9	90	τ_q: 26.0 τ_M: *36.6* τ_i: **83.0**	*0.71*		2.8	-0.4

^{a} T_q, τ_q and ΔG‡ values are for 33° ± 2°

^{b} Δ is the "natural" linewidth at half height due to other processes than quadrupolar relaxation. It is obtained by the computer fitting of calculated to experimental curves

^{c} Correlation times in picoseconds. The normal type values are obtained from the experimental T_q values: the values in italics are transferred from another compound: the block type values are calculated from the two other ones using equation (6)
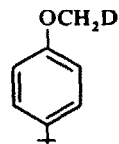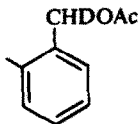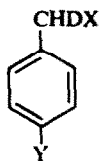
^{d} Decalin solutions, 2M
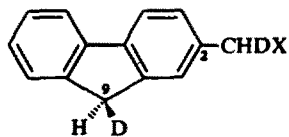
Ia X = H
Ib X = OH
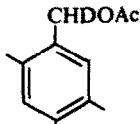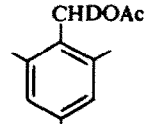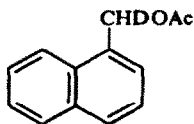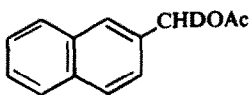Ic X = OAc
Id X = Cl
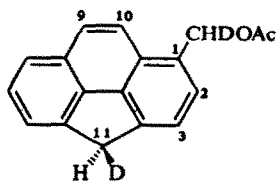
II
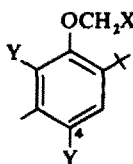
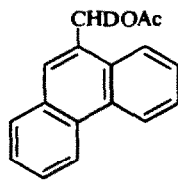IIIa X = H; Y = D
IIIb X = D; Y = H

IV

V
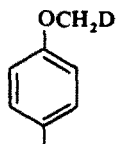
VIa X = OH Y = CH$_2$D
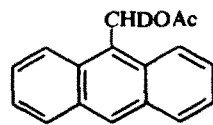VIb X = OCOCH$_2$D Y = CH$_2$D
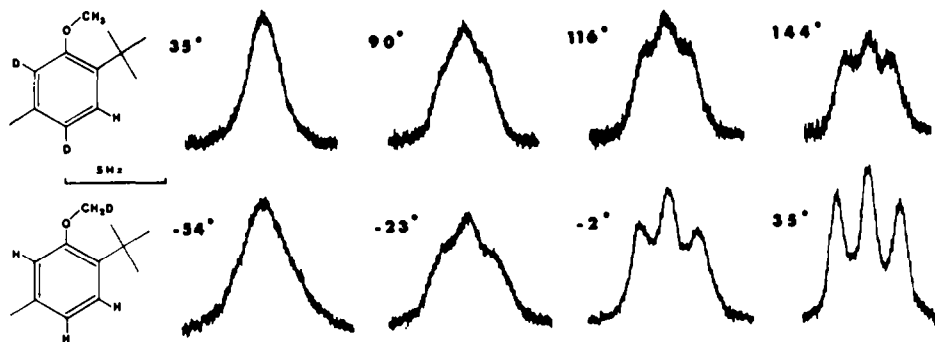VIc X = OAc Y = H

VII

VIII

IX

X

XI

XII

XIII

FIG 1. Temperature dependence of the lineshapes of the —H(3) resonance in compound IIIa (upper curves) and of the —OCH$_2$D resonance in compound IIIb (lower curves) (60 MHz; IIIa: decalin solution; IIIb: CDCl$_3$ solution)

and 2 respectively represent the temperature dependence of the —H(3) and —CH$_2$D proton lineshapes in IIIa and in IIIb, and the activation plots for compounds IIIa, IIIb, IV and V. The temperature dependence of the —CHD— and —CHDX proton lineshapes in Ia and in Ic are shown in Figs 3 and 4 of ref. 2. Fig 3 illustrates the results of the component analysis of the molecular motions in compounds Ia–Id.
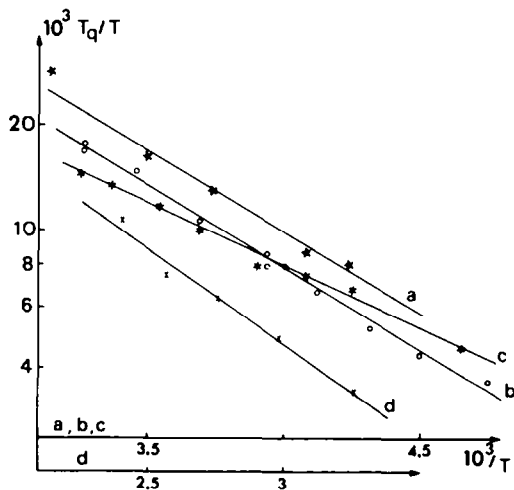

FIG 2. Activation plots of the deuterium quadrupolar relaxation times in compounds IIIa(d), IIIb(c), IV(a) and V(b)
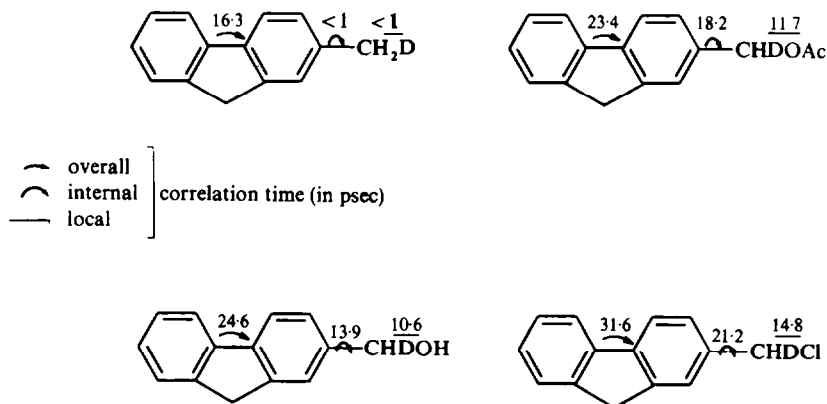
FIG 3. Results of the component analysis of local correlation times (τ_e) into overall (τ_M) and internal (τ_i) correlation times in compounds Ia–Id (see also Table)

DISCUSSION

Physical significance of the results

Before proceeding to the discussion of the results, it is worth trying to assess the relations between the numbers obtained and the molecular dynamical properties they are supposed to describe. A check is provided by the results obtained from other physical methods. The correlation time τ_q obtained from equation (1) is the time constant characterizing the mean time for appreciable changes to occur in the correlation function describing the nature and the rate of the fluctuation of molecular orientation. Further analysis may then be performed in two steps: first a model for molecular motion has to be specified and then the parameters of this model have to be related to molecular structure. The number obtained for τ_q in (1) is independent of such a model. Thus τ_q and τ_M are dynamical parameters characterizing the behaviour of a given molecule in given conditions. Even at this level they may have much value especially when comparing different molecules or as indexes of local flexibility (see previous paper[1]). The analysis of local motions into overall and internal contributions according to equation (6) allows a deeper insight. It suffers however from a number of approximations which in addition to those inherent in the model used[3] include the assumptions of isotropic motions and of a jump process between three equilibrium positions. Furthermore it is not clear how exactly the activation parameters for the internal reorientation τ_i are related to the rotation barriers determined by other methods. Especially τ_i also incorporates librational motions without complete rotation; thus high rotation barriers are probably significantly underestimated. Conversely, this underestimation is in itself instructive, as it points to the presence of such limited local oscillations. The reorientation times τ_r obtained from dielectric studies are related in a different way to the NMR correlation times when reorientation occurs by large angle jumps or through infinitesimal steps. In this last case:[3]

$$\tau_r = 3\tau_q \tag{9}$$

in the former case:

$$\tau_r = \tau_q \tag{10}$$

Because of the basic difficulties in the description of molecular dynamics in liquids even for very simple systems, it seems best using the data as they come out of a comparatively simple description and assessing their information content by comparison with data from other methods and by interpreting them in terms of molecular structure. The results are mainly of qualitative or semiquantitative significance, but the discussion to follow shows that they correctly describe structural effects on internal motions and agree with available data from other methods. They may thus have much chemical significance.

Overall molecular reorientation

The τ_M values listed in the Table have been obtained either directly from D linked to the molecular framework or from the sequential calculations described above. As expected,[1] the τ_M values increase with molecular size. The attachment of a side chain slows down considerably the molecular reorientations, and the effect is larger the bulkier the substituent group (see also ref 1). Thus a —CH_2OAc group raises τ_M from 10·6 and 13·0 psec in fluorene and in methylene-phenanthrene[1] to 23·4 and 46·8 psec in Ic and II respectively. Comparing VII, VIII and X to VIc, one obtains the effect of adding one Me group, three Me groups or a benzo group. II and XII give the effect of adding a methylene group. The largest molecule is II, which is found to have the longest τ_M and the highest $\Delta G^{\ddagger}$ values. Dielectric relaxation data[24] lead to overall relaxation times which are *ca.* 2–3 times larger than the present τ_M values (see equation (9)) for similar (but not the same) compounds.

Internal rotation

The analysis of local motions described above leads to rates and barriers of internal rotation. It should be pointed out that the rates of internal rotation obtained here are *total* rates *i.e.* they include rates for going over the barrier and rates for tunneling through the barrier. Thus the τ_i and $\Delta G^{\ddagger}$ values obtained in the present analysis are *lower limits* of the values for a pure thermally activated process for barrier over-crossing. Tunnel effects are especially important for low symmetrical barriers (see discussion in ref 21), for instance barriers to rotation around X—Me bonds. For —CH_2D groups attached to an aromatic nucleus (Ia, VI and —CH_2D derivatives of several other compounds among I–XIII) only a very slight temperature dependence of the lineshape is observed. The triplet splitting of the —CH_2D proton resonance is too well resolved above *ca.* 0° for performing a meaningful lineshape analysis. The τ_i and $\Delta G^{\ddagger}$ obtained for rotation about the C—CH_2D bond in Ia are zero within experimental accuracy.* Furthermore τ_q/τ_M is near to 0·11 from $-56°$ to $-8°$. These results are in very good agreement with the very low barrier to rotation (*ca.* 14 cal/mole) measured in toluene and in several substituted toluenes by microwave spectroscopy.[22]

The series of —CHDOAC substituted compounds allows studying *steric* effects on barriers to rotation about the C—CHDOAC bond. *Ortho* substitution by one or by two Me groups should markedly slow down the rate of rotation and raise the energy barrier. Indeed τ_i goes from 18·2 psec in Ic to 20 psec in VII and to 110 psec in IX,

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* τ_i for Ia is in fact calculated to be slightly negative. This has of course no sense and arises both from experimental inaccuracy and from the approximations in the treatment.

and the free energy barrier increases by 0·1 and 1·1 kcal/mole. The barrier to rotation in IX is probably higher than the value of 3·9 kcal/mole found here; the accuracy of the present analysis is lowest at both extremes of low and high barriers. The increase of τ_i from XI (18·2 psec) to X (40 psec) may be attributed to the presence of a *peri* interaction between the —CHDOAC groups and the C—H bond at C(8). Two such interactions are present in XIII, decreasing further the rate of internal rotation ($\tau_i = 83.0$ psec).

In compounds III–V two internal rotations, about the (ring) C—O and the O—CH$_2$D bonds, are present. ζ is equal to 0·26. Thus neither of the rotations is a very fast one. If one assumes that the motion around the (ring) C—O bond is much slower than the O—CH$_2$D rotation because of steric hindrance by the bulky ortho ter-butyl group, then the τ_i calculated represents O—CH$_2$D rotation. The corresponding free energy barrier is 1·9 kcal/mole, reasonably close to the barrier to rotation about the O—Me bond in dimethylether (2·72 kcal/mole)[23] measured by microwave spectroscopy. Taking into account the slow rotation about the (ring) C—O bond would slightly increase τ_i and the barrier for O—CH$_2$D rotation. Dielectric relaxation studies[24] of various anisoles have been performed on the pure liquids[25, 26] and on benzene solutions.[27] A barrier of *ca.* 1·5–2·0 kcal/mole has been obtained for rotation around the C—OMe bond in anisole. The group relaxation times in anisole and in chloromethyl benzenes[24] appear to be be too short in comparison to the internal and local correlation times obtained here.

The component analysis of the local motions found in the triply labelled compound VIb[1] illustrates particularly well the objectives of such dynamical studies. τ_i for C—CH$_2$D rotation is obtained from τ_M determined in sequence (a) above. The —CH$_2$D group in the Ac group is four bonds removed from the benzene ring. Taking τ_i for the motion about the C—CHDOAC bond from Ic and assuming O—COCH$_2$D rotation to be slow with respect to $\tau_M{}^*$, a τ_i value of 0·2 psec is obtained using equation (8). This correlation time describes the combined effect of the remaining two motions about the CHD—O and the CO—CH$_2$D bonds.

Intermolecular effects

Intermolecular effects are expected to have a strong influence on molecular motions. This is clearly apparent in the alcohols Ib and VIa which may autoassociate or form hydrogen bonds with the solvent. The effect on τ_q and especially the high activation enthalpy and entropy of τ_q have already been noted.[1] Decomposing τ_q into τ_M and τ_i in Ib now shows that whereas τ_M has activation parameters similar to those found for non-associated systems of same size, τ_i leads to high $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values. Thus, the effect found in local motions τ_q^i, is almost entirely due to the internal rotation process. In addition, as dielectric relaxation studies[24] have shown that association does not seem to affect much the rotation of the —OH group, it appears that the intermolecular interactions perturb principally the rotation about the C—CHDOH bond. This is clear evidence for specific differential medium effects on molecular motions.

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* This is a good approximation as barriers to rotation about the CO—O bond in esters lie around 8 kca/mole.[28]

CONCLUSION

From the results obtained in the present and in the preceding paper it appears that quadrupolar relaxation provides important information about the dynamic structure of relatively complex molecules. The analysis may be performed in three stages: (1) determining local motions, (2) decomposing local motions into their components, (3) devising a physical model which relates dynamical behaviour to molecular structure and intermolecular interactions. Detailed studies of all three points may be performed on simple molecules. In more complex systems the questions of the component analysis and especially of the physical model become much more intricate. However, despite the approximations which one may have to introduce, important information may be gained about ultrafast dynamical processes in molecules as well as about the dynamics of intermolecular interactions and associations.[34] Thus, the results obtained are potentially of much chemical significance in understanding molecular dynamics and reactivity.

EXPERIMENTAL

Spectra and Computations

Spectral measurements, lineshape analysis and calculations of the various parameters have been performed as described in the preceding paper. Component analysis of local motions using equation (6) has been done on an Olivetti Programma 101 electronic desk calculator.

Substrates

2-Substituted-9d-fluorenes, Ia, Ib, Ic, Id. The preparation of these compounds has been achieved by the methods outlined in the preceding paper using deuterated reagents.

Acetate of 1d-*hydroxymethyl*-11d-4.5-*methylene phenantrene*, II. 1-*aldehyde*-11d-4.5-*methylene phenantrene*. The aldehyde is prepared according to the method developed by Rieche:[29] 0·92 ml of $SnCl_4$ was added to 774 mg of 11-*d*-methylene phenantrene (preceding paper) dissolved in 50 ml of CH_2Cl_2 at 0°. 650 mg of *n*-butyl-dichloromethyl ether ($CHCl_2$—O-*n*Bu) was slowly added and the mixture allowed to stand for 15 min at room temp with stirring and poured on ice. After separation and drying, the organic solvent was evaporated and the residue dissolved in ether. The resulting solution was stirred with $NaHSO_3$ aq for 12 hr and the precipitate then destroyed with a 10% solution of K_2CO_3 after being thoroughly washed with water and EtOH. Extraction with ether gave 350 mg of the aldehyde. NMR: CHD: 4·2; Aromatic: 7·4–7·9; CHO: 10·3 ppm. Substitution at position 1 is favoured by the following arguments. The NMR spectrum shows clearly a doublet, part of an AB spectrum, at low field from the aromatic peaks. This doublet arises from an aromatic proton in β position with respect to the carbonyl function and coupled to an *ortho* proton ($J = 9$ Hz). This excludes positions 9 or 10 for the CHO group. On the other hand, the Friedel–Crafts acetylation of 4.5-methylene phenantrene leads to 2 isomers: 1 and 3,[30] and 1 isomer being the major product, while the reaction carried out with succinic anhydride yields only the 1 isomer.[31]

Acetate of 1d-*hydroxymethyl*-11d-4,5-*methylene phenantrene*. This acetate was obtained from the acetylation of the labelled alcohol prepared by reduction of the corresponding aldehyde by LAD. Mp: 80°. (Calc.: C, 82·42%; 1·920 mg H_2O for 4·005 mg of product. Found: C, 82·40%; 1·900 mg H_2O for 4·005 mg of product). *NMR*: CH_3: 2·08; CHD: 4·25; —CHD—O: 5·6, Aromatic: 7·5–7·9 ppm.

2-t-Butyl-5-methyl-4d-anisole (IIIa). The deuterium atom was introduced by basic exchange (NaOD, D_2O, 100°) of the corresponding phenol. The methylation of the phenolic group was easily achieved by reaction with CH_2N_2 in CH_2Cl_2. The mass spectrum shows more than 98% D atom. The anisole was purified by TLC on a silica plate; elution solvent: AcOEt/cyclohexane, 1/4.

2-t-Butyl-5-methyl-αd-anisole (IIIb) 4-*methyl-αd-anisole* (IV) 4-*t-butyl-αd-anisole* (V). α-*chloro-anisoles*. By heating at 220° a mixture of phenol, NaOH and sodium chloromethane sulfonate (CH_2Cl—SO_3 Na) the sodium aryloxy methanesulfonate was obtained. The sodium chloromethane sulfonate was prepared by Demars' method[33] by treating sodium sulfite with chlorobromethane. The chloro-anisole was obtained by treating the corresponding aryloxymethane sulfonate with PCl_5 or $POCl_3$.

αd-*Anisoles* (IIIb), (IV), (V). Reduction of the α-chloro-anisole by LAD in THF gave the corresponding α-*d*-anisole. The anisoles IIIb and V were purified by TLC on silica; elution solvent: AcOEt/cyclohexane, 1/4. Compound IV was purified by gas chromatography using a carbowax column at 115°.

d-*Labelled acetates* (VI–XIII). See preparation in the preceding paper.

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