

Fluorescence kinetics study of rhodamine B lactone in polar aprotic solvents – a global analysis approach

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Abstract. Dual fluorescence of the lactone form of rhodamine B (LRB) in polar aprotic solvents has been ascribed to two forms of the dye: lactone and zwitterion, which is built up after the dissociation of the lactonic bond in the excited state. We have studied the kinetics of fluorescence in both bands in several aprotic solvents as a function of temperature by the SPC technique using global analysis of the decay curves. It has been found that under certain conditions (solvent, temperature) the decay kinetics of the zwitterion fluorescence cannot be described by monoexponential function. The two-exponential fits of zwitterionic fluorescence decays are discussed in terms of a quenching effect of the surroundings on the excited molecule. The possibility of diabatic (back-) closure of the lactone ring as a deactivation channel is also considered.

Keywords. Electron transfer; fluorescence kinetics; global analysis; rhodamine B.

1. Introduction

Photophysics and spectroscopy of rhodamine dyes have been extensively studied over the last two decades (Drexhage 1977; Vogel *et al* 1988; Lopez Arbeloa *et al* 1989). Especially much attention has been paid to rhodamine B (RB), a dye which has wide application as the active medium in dye lasers. This research has also been stimulated by some controversies and discussions connected with clarifying the influence of factors affecting absorption and fluorescence spectra of this dye (Ferguson and Mau 1973; Sadkowski and Fleming 1978; Snare *et al* 1982). Recently there also arose a problem concerning the mode of the radiationless deactivation of rhodamines (Baumann *et al* 1985; Vogel *et al* 1988; Lopez Arbeloa *et al* 1989) linked with discussion about the role of TICT ("twisted" intramolecular charge transfer (Grabowski *et al* 1979)) states in these compounds (Vogel *et al* 1988).

Most of these studies on RB have used the dye as its salt (in the cationic monoprotonated form) and concentrated on investigations in protic solvents, primarily in alcohols. The rhodamine B base, however, can also exist as a solid after converting the dye into the lactone form and this substance – when protected from humidity – may be stored for years. In solution rhodamine B can occur in the form of lactone, zwitterion

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or cation, depending on proticity and polarity of the solvent, pH of the solution, temperature and concentration and also on the nature of the dissolved substance i.e. salt or lactone (Ramette and Sandell 1956; Rosenthal *et al* 1979; Hinckley *et al* 1986; Hinckley and Seybold 1988). Equilibria between these different forms in the ground state and factors affecting these equilibria have been recently investigated in detail (Hinckley and Seybold 1988) by measuring absorption spectra under different conditions. It was concluded that in aprotic solvents the zwitterion form is absent, being the dominating one in protic solvents where it occurs in equilibrium with lactone (LRB). The cation (CRB) form of RB appears in both protic and aprotic solvents under acidic conditions.

Photophysics of RB has been the subject of a large number of studies. They have focused their attention, however, on the ZRB form of the dye and much less interest has been directed towards investigating the lactone and equilibria between the lactone and the zwitterion in the excited state. This is not justified because, as has been claimed recently (Hinckley *et al* 1986), even in such a protic (and frequently used) solvent like ethanol, due to equilibrium between ZRB and LRB only 71% of the dye occurs as ZRB and the rest is in the LRB form.

The first extensive report on the luminescence of the lactone form was that by Klein and Hafner (1976) who found the excited state of LRB very highly polar (which has been considered as an analogy to the TICT states). This was followed by almost parallelly published papers by Grigorieva *et al* (1977, 1978). These two papers reported on the dual luminescence of LRB in some medium-polarity aprotic solvents and ascribed the short-wave fluorescence to the relaxed state of the lactone, and the long-wave one to the zwitterion built up after dissociation of the lactonic C–O bond in the excited state. More recently Vlaskin *et al* (1988) investigated this dissociation by measuring the picosecond transient absorption measurement and limited the time in which the dissociation occurs to $t \leq 1$ ps.

The present work was undertaken to study the photophysics of the lactone of rhodamine B in aprotic media in greater detail and – in particular – to investigate processes occurring in the excited state of the molecule after the C–O bond cleavage in polar aprotic solvents by measuring fluorescence decays by means of time-correlated Single Photon Counting (SPC). This technique has been shown to have a large dynamic range with high signal-to-noise ratio (Demas 1983; O'Connor and Philips 1984). As we have found that the decays of the zwitterionic fluorescence in some solvents and at certain temperatures could not be analyzed by single exponential decays we decided to apply a global (simultaneous) analysis to test the multiexponential models. In this type of analysis of fluorescence decays one is analyzing several decay curves taken at slightly different – but in a controlled manner related to each other – conditions of experiment (e.g. at different wavelengths) with a common global χ^2 . The technique of analysis of the data collected in SPC experiments has been found to be a powerful tool for testing kinetic models involving multiexponential decay functions (Knutson *et al* 1983; Janssen *et al* 1990).

2. Experimental

Rhodamine B has been converted into lactone form by the method described by Klein and Hafner (1976). The product was recrystallized from cyclohexane several times

and then dried under vacuum over CaCl_2 . The absorption spectrum of the cyclohexane solution agreed with that reported (Klein and Hafner 1976). Spectroscopic grade benzonitrile (BZ) (Janssen) and acetonitrile (AN) (Rathburn) as well 1,2-dimethoxyethane (DME) (Fluka, for HPLC) were used as received. Butyronitrile (BN) (Merck, for synthesis) was distilled twice over KMnO_4 and K_2CO_3 , followed by a distillation over P_2O_5 . All solvents were carefully checked for traces of luminescence and none of them showed any under conditions of both stationary and SPC experiments. Only perfectly colorless solutions were used in order to avoid any contamination by ionic forms which strongly absorb in the visible. Details concerning the sensitivity of the lactone to protic additions and also the possibility of use of the lactone for the proticity test of a given solvent will be published elsewhere (Karpiuk and Grabowski, to be published).

Absorption spectra have been measured with Zeiss Specord M40 and Perkin Elmer Lambda 6 spectrophotometers. Fluorescence spectra were measured with a Jasný spectrofluorimeter (Jasný 1978) and with SPEX Fluorolog 212. The quantum yields reported here are those corrected for (very small) differences in absorbance at different temperatures. The quantum yields were measured using quinine sulphate in 0.1 N H_2SO_4 as a standard.

Decay measurements were performed on the SPC apparatus based on synchronously pumped, cavity dumped, frequency doubled DCM dye laser (320 nm). The detection system was essentially the same as already described (Boens *et al* 1987). The fluorescence was observed through a polarizer set at the magic angle. Repetition of the excitation pulses was at 800 kHz. The response function of the detection system was measured by using reference compounds at the same wavelength as the measured fluorescence that allowed the avoiding of a wavelength effect on the photomultiplier (Boens *et al* 1988). The references used were 1,2-dimethyl-POPOP in methylcyclohexane ($\tau = 1.13$ ns) when measured in a lactone band and erythrosine in methanol or in water ($\tau = 95$ ps or 460 ps, respectively) (Boens *et al* 1990) in the 550–600 nm range. The prevailing condition in the data collection was that the number of counts in the peak channel exceeded 10^4 . The temperature of the sample was maintained within $\pm 1^\circ\text{C}$. The samples were not degassed as we have not found any influence of the dissolved oxygen on the decay curves.

Measurements were performed in a concentration range of $10^{-6} - 10^{-4}$ M to check a possible influence of concentration on the observed results. As no such influence was observed, the concentration typically used was 2×10^{-5} M.

Fluorescence decays were first analyzed in single curve analysis with a DECAN deconvolution program using a reference convolution method and based on the Marquardt algorithm (Marquardt 1963). The software for global analysis calculation was essentially the same as used by Janssen *et al* (1990). The criterion for the fit in global analysis was $|Z(\chi^2)| < 3$.

3. Results

Fluorescence of LRB is very strongly solvent dependent. Already in cyclohexane there is a large Stokes shift ($\approx 7000\text{ cm}^{-1}$) which can be further increased by 5000 cm^{-1} on increasing solvent polarity.

In more polar solvents, starting from dichloromethane ($\epsilon = 8.9$) a dual fluorescence

Table 1. Results of temperature measurements.

Solvent	Temperature (°C)	Φ_T	Φ_L	Φ_Z	τ_L (ns)	k_L^F ($\times 10^6 \text{ s}^{-1}$)
DME	20	0.043			10.49	4.1
	30	0.041			10.30	4.0
	50	0.037			9.90	3.7
	70	0.037			10.20	3.6
BN	20	0.039	0.013	0.026	5.75	2.3
	30	0.031	0.013	0.018	5.84	2.2
	50	0.022	0.013	0.009	6.02	2.2
	70	0.020	0.014	0.005	6.30	2.2
BZ	20	0.085	0.017	0.068	9.31	1.8
	50	0.059	0.018	0.040	9.67	1.9
	70	0.043	0.019	0.023	9.67	2.0
	80	0.038	0.019	0.019	9.58	2.0
AN	20	0.127	0.001	0.126	1.72	0.6
	30	0.105		0.104		
	50	0.067		0.066		
	70	0.041	0.0015	0.040	2.15	0.7

appears. In very polar media like AN or DMSO, LRB also displays dual fluorescence, although the lactonic band is very weak. Table 1 reports for the given solvent the quantum yields of the total luminescence Φ_T , quantum yields of the lactonic and zwitterionic fluorescence, Φ_L and Φ_Z , lifetimes of the lactone fluorescence τ_L and fluorescence rate constants (Φ_L/τ_L) in solvents under investigation as a function of temperature. The Φ_L and Φ_Z have been evaluated by resolving the overlapping bands with the use of known band shapes of both. Noticeable is a difference in Φ_Z in AN when compared with a value reported by Klein and Hafner (1976) (0.22). As fluorescence spectrum in AN consists almost exclusively of one band the discrepancy cannot be related to the manner of separation of *L* and *Z* bands. We therefore believe the reason could be related to direct excitation of the cations of RB present in a small amount in the lactone solution due to the presence of traces of proton-donating impurities.

The temperature range of the measurements was 20–70°C. In DME ($\epsilon = 7.2$) the spectrum in this range is broad and consists of one band which shifts towards shorter waves as the temperature increases. The FWHM of the spectrum changes slightly from 5300 cm^{-1} at 20°C to 5500 cm^{-1} at 70°C. The quantum yields change also in narrow limits. Changes in Φ_L in three other solvents are also small with a slight trend to increase with elevation of the temperature. Fluorescence rate constants for lactone fluorescence k_L^F seem to be more informative and they remain practically constant. Much more dramatic changes occur in the zwitterion band. Figure 1 shows – as an example – the fluorescence spectra of LRB in BZ as a function of temperature. The spectra in BN change with temperature in a very similar manner and an isoemissive point was also observed in this solvent. The very low quantum yield of lactone fluorescence in AN compared with that of zwitterion prevents any observation of such eventual isoemissive point.

The excitation spectra of both zwitterionic and lactonic fluorescences have been found to be identical with each other and to agree with the absorption spectrum of

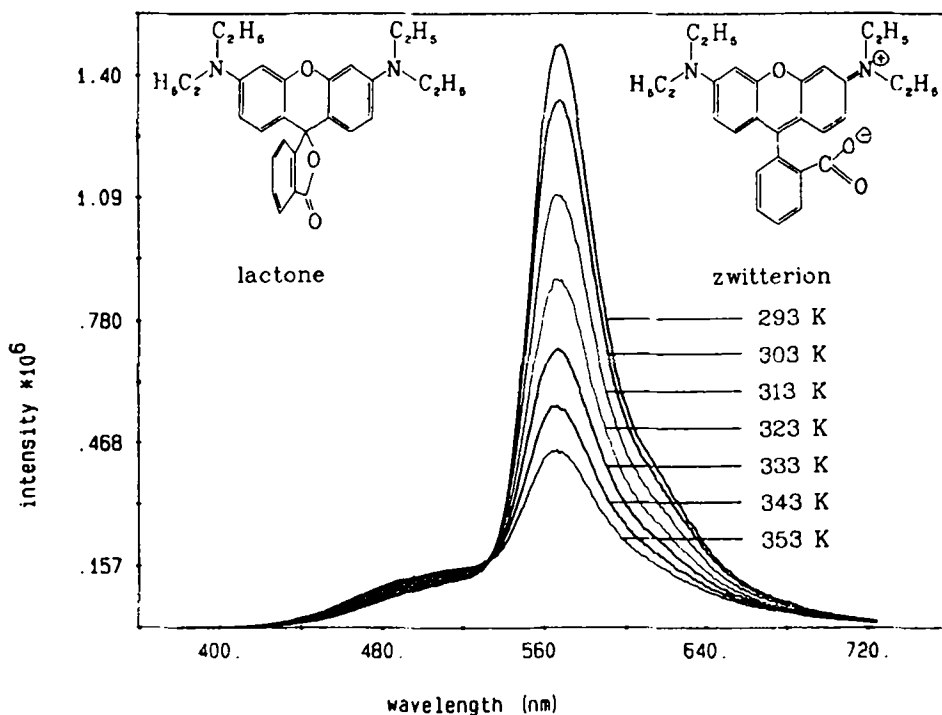


Figure 1. Fluorescence spectra of rhodamine B lactone in benzonitrile as a function of temperature.

the lactone. The ratio of intensity of both bands was constant and did not depend on the excitation wavelength.

Decays of LRB in DME at room temperature were measured at 460, 500 and 540 nm. All of them could be fitted by a monoexponential function with essentially the same lifetimes giving an average of 10.4 ns. Increase of temperature did not significantly change the lifetime.

Decays of LRB in the lactone bands in BN, BZ and AN were measured at 490 nm. All these decays measured at all temperatures applied in this study could be fitted by monoexponential decay functions.

A completely different situation occurs when decays in the zwitterionic band in these three solvents are considered. They are generally not monoexponential and are very sensitive to the temperature. In BN and BZ the decays were measured every 10 nm between 550 and 600 nm and in the temperature range +20°C to +70°C (figure 2).

In order to investigate possible reasons of this kinetic picture we have checked whether it is caused by a trivial overlap of two fluorescence bands each of them decaying with its own characteristic lifetime and tried to fit them with two-exponential functions. While this model could be successfully applied in the case of LRB in BZ at room temperature, two-exponential functions gave rather unacceptable fits for the decays of LRB/BN system at all temperatures as well as for decays of LRB/BZ at elevated temperatures. By this we mean not only the χ^2 values > 1.2, regularities in residuals and in autocorrelation function but, first of all, the fact that the recovered

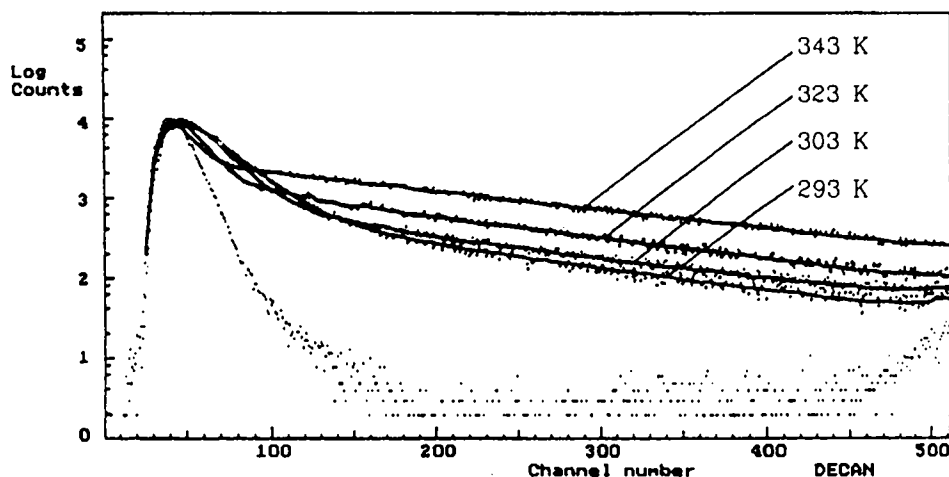


Figure 2. Decays of LRB in BN measured at 560 nm at different temperatures. The channel width used was 34 ps.

Table 2. Results of global analysis calculations for LRB in BN at room temperature.

λ (nm)	490	550	560	570	580
$A_1(\tau_1 = 0.66 \text{ ns})$	—	0.208	0.217	0.232	0.241
$A_2(\tau_2 = 1.52 \text{ ns})$	—	0.017	0.014	0.013	0.009
$A_3(\tau_3 = 5.76 \text{ ns})$	0.69	0.013	0.008	0.007	0.008

longer lifetimes differed – out of the error limits – from those measured in the lactone band, and were significantly different among themselves along the zwitterionic band. This suggested that the nonexponentiality can not be due only to the overlap of two monoexponential decays. The significant overlap of two fluorescences could not, however, be neglected and therefore we have decided to analyze the decays with triexponential functions with certain constrains both in single and in global analysis. The constrain in single analysis was that one of the lifetimes was held to be constant and equal to that of the lactone fluorescence measured under the same conditions. Global analysis was performed using one decay curve collected in the lactone band together with several (typically 4 to 6) decay curves taken in zwitterion band between 550 and 600 nm.

During global calculations the decay at 490 nm was fitted by a monoexponential function and the zwitterionic decays were fitted by triexponential functions with one of the lifetimes linked to that of lactonic fluorescence. Results of global analysis calculations for LRB in BN are presented in table 2.

These results show that zwitterionic fluorescence itself after the overlapping component with long lifetime (τ_L) was accounted for, cannot be regarded as a monoexponential one. The component with decay time τ_2 – although with a minor contribution – was necessary to obtain acceptable fits both in single curve and in global analysis. The same qualitative conclusion could be drawn from measurements

Table 3. Decays of LRB in Z band as a function of temperature*.

Solvent	Temperature (°C)	τ_1 [ns]	τ_2 [ns]	A_1	A_2
BN	20	0.66	1.52	0.22	0.014
	30	0.48	1.61	0.27	0.008
	50	0.21	1.01	0.43	0.008
	70	0.08	0.67	0.98	0.007
BZ	20	2.74	—	0.37	—
	50	1.79	0.75	0.13	0.054
	70	0.59	1.38	0.17	0.077
	80	0.36	1.00	0.21	0.080

* Measured at 560 nm, after the overlapping component with long lifetime (τ_L) was accounted for; channel width was 34 ps.

in BN at higher temperatures. Elevation of temperature causes, however, relevant shortening of τ_1 (table 3). Although decay of zwitterion in BZ at room temperature could be fitted by single decay time (table 3), the same was impossible at higher temperatures and two-exponential fittings were necessary: The values of τ_2 and A_2 changed more than respective values of the first component, the presence of the second component was however necessary to obtain proper fits.

Degassing of the sample by freeze-pump-thaw technique did not change significantly the observed decays. For instance, for solution in BN at 20°C a triexponential fitting in the zwitterion band was also necessary yielding τ_1 and τ_2 values of 0.6 and 1.6 ns, respectively. τ_3 both in Z as well in L band (monoexponential fit) was 7.2 ns.

4. Discussion

The molecule of LRB can be considered as being composed of two mutually perpendicular π -electronic subsystems which are approximately non-interacting in the ground state: the xanthene part and the phthalide part. Very large Stokes shifts and the high sensitivity of the fluorescence spectra to the solvent polarity imply that electron transfer in the excited state should be involved. The free energy of the electron transfer reaction in the excited state from xanthene to phthalide part, ΔG_0 , may be estimated by means of Weller's equation (Rehm and Weller 1970). When we use a reduction potential for phthalide -2.11 eV (Leedy and Muck 1971), assume the oxidation potential for the xanthene part as 0.8 eV and take the usual form for the Coulomb term then for BN ($\epsilon = 20.3$), $d = 5 \text{ \AA}$ (distance between the donor and acceptor) the resulting free energy change will be $\Delta G_0 = -0.8$ eV. If we modify the influence of the solvent as a dielectric medium in the sense proposed by Suppan ($e^2/4d$) (Suppan 1988) then the Coulomb term changes to -0.7 eV giving $\Delta G_0 = -1.3$ eV. These values (and also correspondingly the values for BZ and AN) would cause the electron transfer from the xanthene to the phthalide part to occur within a very short (several picoseconds) range of time after excitation. After this first step a non-relaxed, charge transfer state will be populated. We postulate this state or a crossing point at its potential hypersurface and not that achieved directly upon excitation is a starting point for the subsequent steps. In the case where only lactonic fluorescence occurs

the subsequent step will be the vibrational relaxation to the emitting lactonic state. When double fluorescence is observed this hot, non-relaxed state will deactivate via at least two channels i.e. through a relaxation to the thermalized emitting state and via dissociation of the lactonic bond to the zwitterion excited state. If the dissociation occurs after electron transfer has occurred this would explain the identity of the excitation spectra of both lactonic and zwitterion fluorescences.

The existence of the isoemissive point could suggest certain kinetical coupling of the two emitting states. The monoexponential decays in the lactone band in all cases observed limit such coupling to a population of the zwitterion from the lactone. This, however, could not be confirmed within the performed kinetical analysis because the type of the analysis applied to the zwitterion decays (separation of the overlap of two bands) made impossible any elucidation of a component with the rise time being equal to the decay time of the lactone. Further experiments are needed to explain mutual connection of these excited states.

The large Stokes shift and the high sensitivity of the position of the lactone band to the solvent polarity indicated a big change in dipole moment of the molecule upon excitation, estimated to be 25 D (Klein and Hafner 1976). This would suggest that lactonic fluorescence is directly connected with a back electron transfer from the phthalide to the xanthene moiety. The main component of the transition moment of this fluorescence would be polarized along the principal axis of the molecule and the transition should be forbidden due to a negligible overlap. The transition moment of the zwitterion fluorescence is, on the other hand, directed along the xanthene π -subsystem and thus perpendicular to the principal axis (Drexhage 1977). The difference in dipole moment between the ground and the excited state of the zwitterion is much smaller than that of the lactone and – using charge distributions calculated by Bergamasco *et al* (1990) – can be estimated to less than 10 D. When we assume for the ground state of the zwitterion $M \approx 5.5$ D (Desai and Pandhare 1963) and neglect the dipole moment of the ground state of lactone, there would still remain considerable difference in dipole moments of these two fluorescent states. This allows us to conclude that the charge distributions in the lactone and the zwitterion excited states should significantly differ. In particular the carbon atom in position 9 must have different hybridizations – sp^3 and sp^2 , respectively – in both excited states. This implies also a marked structural difference between these states. The presence of a considerable barrier connected with the reorganizational energy for transition from lactone to zwitterion cannot be therefore excluded. Such a proposal weakens further the possibility of the direct equilibrium between the two emitting states.

The temperature dependence of quantum yields and of the decay curves of the zwitterion fluorescence indicates an efficient quenching mechanism of this excited state. In contrast to Vogel *et al* (1988) we refute in this case the temperature activated transition to the non-emissive TICT state because of observation of very similar behaviour for the lactone of rhodamine 101 (with the rigidly fixed amino groups), although in solvents of lower polarity. On the basis of present experimental data we cannot conclude whether the influence of temperature is connected with occurrence of any energetic barrier or it is a simple manifestation of the changes in solvent polarity as a function of temperature. More polar solvents (like BZ or AN at room temperature) stabilize the zwitterion which has the longer lifetime and higher quantum yield.

The relevant shortening of the lifetime being the main contribution in the decay

of zwitterion fluorescence in BN at room temperature (0.66 ns) may be connected with the accessibility of the deactivation channel being diabatic (back-) closure of the lactone ring. Operation of the mechanism could be linked to the polarity of the surrounding medium in such a way that the molecule with an open lactonic bond would require an electrostatic stabilization by the reorientation of the solvent molecules to prevent the quenching. Apparent lack of quenching of zwitterion in BZ ($\epsilon = 25.2$) as compared with BN ($\epsilon = 20.3$) would confirm this supposition.

Very interesting is the manifestation of this quenching by a non-exponential behaviour of zwitterion fluorescence. Rettig *et al* (1986) while investigating dynamics of some photoreactions involving electron transfer have observed such non-exponentiality for primary luminescence of dimethylaminobenzonitrile and some other compounds. They tried to test two kinetic models: (i) "multiphasic decay" model (Cremers and Windsor 1980) and (ii) "barrierless sink" model (Bagchi *et al* 1983), both of them can be well fitted by biexponential functions. We think the "multiphasic decay" model would be a natural extension of the postulated mechanism of quenching. A very rapid photodissociation followed by structural rearrangements generates a distribution of molecules with slightly different conformations of the former "phthalide" part in relationship to the xanthene part (e.g. different angles, different surroundings etc.). Additionally there is a barrier which is related to the solvent polarity and connected with structural and geometrical changes on the way of closing the lactone ring. These differences in "initial conditions" should result in a distribution of lifetimes characteristic for given conformations. Further work devoted to these questions is in progress.

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