Heinz Mustroph*

Merocyanine dyes

Abstract: Merocyanine dyes belong to the class of neutral polymethine dyes, where one terminal component is typically found in cyanine dyes and the second obtained from an active methylene compound. The different electron acceptor/donor abilities of the two terminal components have a marked impact on the electronic structure of a merocyanine dye and its equilibrium structure and electronic spectra. Their first technical application was spectral sensitization in silver halide photography. Today they have numerous of applications in textile dyeing and as membrane potential sensitive fluorescent dyes.

Keywords: bond lengths alternation, Brooker's merocyanine, electronic spectroscopy, Franck–Condon principle, isoenergetic point, merocyanine dyes, neutral polymethine dyes, nonlinear optics, Valence Bond theory, silver halide photography

1 Fundamentals

To introduce a concept of importance when considering the influences on the spectra of merocyanine dyes, this chapter will open by examining the case of *N,N*-dimethylformamide (DMF) as a simple model for such colorants. Usually the structural formula that has been used for DMF is **1N**. In the formalism of the *Valence Bond (VB) theory* the electronic structure of molecules can be described by a linear combination of *contributing structures* to the so-called *resonance hybrid*. Linus Pauling postulated that the charge-separated contributing structure **1S** with a nitrogen-carbon double bond instead a single bond contributes significantly to the electronic structure of the ground state [1]. Pauling estimated that the non-charge-separated contributing structure **1N** contributes 60% and **1S** contributes 40% to the electronic ground state. This results in a value of $p_{\text{NC}} = 0.4$ for the VB- π bond order of the NC bond. Pauling's prediction was later experimentally confirmed in the early days of dynamic NMR spectroscopy. In the ¹H NMR spectrum of DMF at room temperature two methyl signals are observed. From this it can be concluded that the two methyl groups are differently shielded. With increasing temperature these two signals broaden and on continuing rise in the temperature further the two peaks become a narrow peak, exactly between the two peaks at room temperature. The reason is that the NC bond has a high proportion of double bond character, which causes a

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hindered internal rotation of the amide group at room temperature. With increasing temperature the rotation barrier is overcome and the rate at which the methyl groups exchange their positions is so high that they can no longer be distinguished on the NMR time scale [2]. The free activation enthalpy of the internal rotation of the amide group is of $\Delta G^\ddagger = 20.4\text{--}22.4 \text{ kcal mol}^{-1}$.

For the *neutral polymethine dyes* [3], where one terminal component is typically found in *cyanine dyes* and the second obtained from an active *methylene compound*, like e.g. **2**, **3**, Frances M. Hamer suggested the term *merocyanine* ($\mu\epsilon\rho\sigma$ = part) dyes [4].

Based on the term *streptocyanine dyes* [3, 5–7] for cyanine dyes with two open-chain R_2N groups ($\text{R} = \text{H}$, alkyl, aryl) like e.g. **4**, the open-chain merocyanines **5** are called *streptomerocyanine dyes* [3, 8], which are the simplest model compounds for merocyanines.

Due to their electronic structure, merocyanine dyes are classified as neutral polymethine dyes [3, 5–9]. As cyanine dyes they are characterised by an odd number $2n + 3$ of π -centres and $2n + 4$ π -electrons (where n is the number of vinylenes groups $-\text{CH}=\text{CH}-$). Therefore, one would expect them to show the characteristic feature of cyanine dyes like narrow absorption bands in the electronic spectrum, increasing molar absorption coefficient with increasing n and each additional vinyl group in the polymethine chain giving a bathochromic shift of the 0–0 vibronic transition of about 100 nm (the so-called vinylenes shift) [5–12].

Table 1: Absorption maxima $\lambda_{\max}$ (nm) and molar absorption coefficients $\epsilon_{\max}$ ($10^{-3} \text{ M}^{-1} \text{ cm}^{-1}$) of the streptocyanines **4** and the streptomerocyanines **5** in dependence on the number of vinylene groups n in dichloromethane [13].

n	4		5	
	$\lambda_{\max}$	$\epsilon_{\max}$	$\lambda_{\max}$	$\epsilon_{\max}$
1	312	64.5	283	37
2	416	119.5	361	51
3	519	207	421	56
4	625	295	462	65
5	734	353	491	68
6	848	(220)	512	72

The streptocyanines **4** confirm these predictions perfectly (Table 1), with exception when $n = 6$. The reason for falling $\epsilon_{\max}$ in this case is the dye's existence as a complex mixture of geometric isomers.

However, the streptomerocyanines **5** in no way meet both predictions (Table 1). There is a much smaller increasing molar absorption coefficient than in the case **4** with increasing n and no vinylene shift of $\lambda_{\max}$.

The probably most well-known merocyanine is *Brooker's Merocyanine 6* with $\lambda_{\max} = 605 \text{ nm}$, $\epsilon_{\max} = 154 \cdot 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ in pyridine and $\lambda_{\max} = 444 \text{ nm}$, $\epsilon_{\max} = 54 \cdot 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ in water [14]. Leslie G. S. Brooker et al. interpreted the electronic spectra of the merocyanines in terms of the VB theory with the assumption that the electronic structure of merocyanines can be described as a *resonance hybrid* between a *non-charge-separated contributing structure 6N* and *charge-separated contributing structure 6S* [15, 16]. Each contributing structure has a special electronic energy $E^{\text{el}}(\mathbf{N})$ and $E^{\text{el}}(\mathbf{S})$, respectively. In the 2×2 matrix representation of the electronic Hamiltonian $E^{\text{el}}(\mathbf{N}) - E$ and $E^{\text{el}}(\mathbf{S}) - E$ represent the diagonal matrix elements and the off-diagonal matrix element β is the electronic interaction matrix element between **N** and **S**. Solving the 2×2 matrix gives two electronic Eigenvalues E [17]. In other words, the linear combination of the two contributing structures causes a splitting between them (Figure 1).

Then it is assumed that the lowest electronic Eigenvalue corresponds to the electronic energy of the ground state $E^{\text{el}}(S_0)$ while the second provides the energy of the first electronic excited state $E^{\text{el}}(S_1)$. The energy difference ΔE from the electronic

Figure 1: VB interaction diagram of the non-charge-separated contributing structure **N** and the charge-separated contributing structure **S** with (a) exact equivalent electronic energies $E^{\text{el}}(\mathbf{S}) = E^{\text{el}}(\mathbf{N})$ and different electronic energies (b) $E^{\text{el}}(\mathbf{S}) > E^{\text{el}}(\mathbf{N})$ and c) $E^{\text{el}}(\mathbf{S}) < E^{\text{el}}(\mathbf{N})$ with the resulting electronic transition energy ΔE from the electronic ground state $E^{\text{el}}(S_0)$ to the first electronic excited state $E^{\text{el}}(S_1)$.

ground state $E^{\text{el}}(S_0)$ to the first electronic excited state $E^{\text{el}}(S_1)$ is the electronic transition energy [16, 17]:

$$\Delta E = E^{\text{el}}(S_1) - E^{\text{el}}(S_0) = \{[(E^{\text{el}}(\mathbf{S}) - E^{\text{el}}(\mathbf{N}))^2 + 4\beta^2]^{1/2} \quad (1)$$

Brooker assumed that β in eq. (1) is a constant. In a symmetrical polymethine dye the two principal contributing structures have the same electronic energy, resulting in $\Delta E = 2\beta$. This provides the lowest possible electronic transition energy. Brooker called the electronic states of a molecule, described by linear combination of two contributing structures of exact equivalent electronic energy the *isoenergetic point* (Figure 1(a)) [16].

In an unsymmetrical dye the two contributing structures have different electronic energies. With increasing difference between $E^{\text{el}}(\mathbf{N})$ and $E^{\text{el}}(\mathbf{S})$ ΔE increases, which shall cause a hypsochromic effect (Figure 1(b) and Figure 1(c)). Furthermore, Brooker assumed, that polar solvents stabilize **S**, whereas **N** remains unaffected and, therefore, $E^{\text{el}}(\mathbf{S})$ is lowered and so polar solvents causes a bathochromic effect in the case $E^{\text{el}}(\mathbf{S}) > E^{\text{el}}(\mathbf{N})$ (Figure 1(b)). Vice versa, in the case $E^{\text{el}}(\mathbf{S}) < E^{\text{el}}(\mathbf{N})$ polar solvents lead to a hypsochromic effect (Figure 1(c)).

Already in 1963 John N. Murrell wrote regarding this model: “This is an elegant explanation but it sounds too simple to be true.” [18] Systematic experimental studies suggested that this model is indeed too simple [17, 19].

Theodor Förster suggested that the Eigenfunctions of the electronic ground state $\psi(S_0)$ [eq. (2)] and first electronic excited state $\psi(S_1)$ [eq. (3)] can be approximated as a linear combination of the wavefunctions of the two contributing structures $\psi_{\mathbf{N}}$ and $\psi_{\mathbf{S}}$ [20]. The degree of mixing of **N** and **S** is determined by c^2 .

$$\psi(S_0) = (1 - c^2)^{1/2} \psi_N + c \psi_S \quad (2)$$

$$\psi(S_1) = c \psi_N - (1 - c^2)^{1/2} \psi_S \quad (3)$$

Seth R. Marder et al. built on this model and called the resonance hybrid where the two contributing structures contribute equally ($c^2 = 0.5$) the *cyanine limit*, in which it is assumed that the equilibrium geometry R_e in the ground electronic state S_0 [$R_e(S_0)$] and R_e in the first excited electronic state S_1 [$R_e(S_1)$] are equal [21, 22].

The region $c^2 < 0.5$ was called „before the cyanine limit“ and $c^2 > 0.5$ „beyond the cyanine limit“ [21, 22]. From this model it follows, as c^2 moves away from $c^2 = 0.5$ the equilibrium geometries in S_0 and in S_1 differ increasingly in dependence on the deviation to $c^2 = 0.5$.

As a simplified measure of $R_e(S_0)$ bond length alternation (BLA) in the electronic ground state was introduced [21, 22]. BLA is estimated as the average of the absolute difference between adjacent carbon-carbon equilibrium bond lengths in a polymethine chain. So, the equilibrium geometry in the ground electronic state of polyatomic molecules is transferred to a simplified parameter in a diatomic molecule. Hence the value is BLA = 0 at the theoretical cyanine limit [$c^2 = 0.5$ in eq. (2)].

Of course, the solution of the 2×2 matrix representation of the electronic Hamiltonian gives the same results like eq. (1). In Brooker's model β in eq. (1) is a constant. Marder et al. set $\beta = -t$ and (different to Brooker's model) it is said the electronic interaction matrix element between **N** and **S** – t depends on c^2 . In the two cases $c^2 = 0$ and $c^2 = 1$ the value of $-t = 0$ and ΔE is given by the difference $E^{\text{el}}(\mathbf{S}) - E^{\text{el}}(\mathbf{N})$.

The wavefunctions of the two contributing structures ψ_N and ψ_S are purely electronic and so the wavefunctions of the two molecular states $\psi(S_0)$ and $\psi(S_1)$, are purely electronic too. Consequently, as in Brooker's model in this model ΔE is the purely electronic transition energy. However, in molecules there are no pure electronic transitions!

Only in single atoms are there pure electronic transitions. Atoms do not rotate and vibrate and therefore, the spectral bandwidth is narrow in atomic absorption spectroscopy. In contrast to atoms molecules rotate, nuclei vibrate and transitions between electronic states are connected with simultaneous transitions between rotational and vibrational states. Therefore, absorption bands in molecular spectroscopy are broader than those encountered in atomic spectroscopy. The shapes of the former are mainly determined by the spacing and intensity distribution of the vibrational sub-bands.

In both models the pure electronic value ΔE is used and correlated with the easily measured absorption maxima λ_{max} as experimental comparative values. However, the λ_{max} value is nothing more than the intensity maximum in an electronic spectrum. It corresponds to the vibronic (vibrational-electronic) transition with the highest Franck-Condon factor [$S_{00,1v}^2$] as illustrated in Figure 2 [12, 23].

Figure 2: Two diagrams providing the effect of different equilibrium geometry in the electronic ground S_0 [$R_e(S_0)$] and first excited state S_1 [$R_e(S_1)$] on the vibronic sub-bands transition intensities of diatomic molecules. The adiabatic potential energy surfaces of S_0 and S_1 are modelled by the quantum harmonic oscillator, its vibrational eigenfunctions assuming equal vibrational frequency in S_0 and S_1 and the relative transition intensities [$S^2_{00,1v}$] in dependence on the differences of $R_e(S_0)$ and $R_e(S_1)$ [12, 23, 24].

The spacing of sub-bands in polymethine dye spectra is primarily determined by a dominant symmetric vibration associated with its polymethine chain and the observed intensities of these sub-bands can be explained in terms of this dominant vibration by the Franck–Condon principle for diatomic molecules [24].

At the cyanine limit, where it is assumed that R_e in S_0 and S_1 are equal [$R_e(S_1) = R_e(S_0)$] the only vibronic transition will obviously be the 0–0 vibronic transition [12, 23–25]. That does not correspond to experimental reality. The $S_0 \rightarrow S_1$ electronic transition in polymethine dyes can be ascribed mainly to an electronic transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). The HOMO has bonding character whereas the LUMO has antibonding character. It therefore follows that $R_e(S_1)$ is basically greater than $R_e(S_0)$. The difference $R_e(S_1) - R_e(S_0)$ depends on the electronic structure in S_1 and S_0 .

If the difference between equilibrium geometries is relatively low [$R_e(S_1) \napprox R_e(S_0)$] as in symmetric cyanine dyes the absorption intensity is largely concentrated in the 0–0 vibronic transition (Figure 2(a)) [10, 12, 23]. Already different terminal heterocyclic groups in unsymmetrical cyanine dyes cause an unsymmetrical electronic

structure in S_1 and S_0 . This leads to increasing differences $R_e(S_1) > R_e(S_0)$ which cause an intensification of higher 0- ν vibronic transitions (Figure 2(b)) [26]. If the change of the equilibrium geometries is much larger in unsymmetrical cyanine dyes [$R_e(S_1)$ $R_e(S_0)$] the absorption curve does not exhibit a vibrational fine structure [26], as it is the case in most spectra of merocyanine dyes. In general, if the spectra do not show a vibrational structure, it is not clear which underlying vibronic transitions is represented by the $\lambda_{\max}$ values. Obviously, neither the effects of structural changes nor solvents on the electronic spectra of merocyanine dyes can be accounted for by the simple pure electronic model with two contributing structures.

It is very important not to consider the pure electronic transitions only, but the effects of the changes in equilibrium geometry S_1 and S_0 on the distribution of the spacing and intensity of the vibrational sub-bands. Therefore, the Förster model with the linear combination of the two wavefunctions ψ_N and ψ_S [20] should be used only in combination with the Franck-Condon principle for diatomic molecules [12, 23, 24].

This shall be illustrated with Figure 3. The spectra of 4,4'-dimethylpyrido-trimethincyanine show a clear vibrational structure in dichloromethane (DCM) and in MeOH and $\lambda_{\max}$ corresponds to the 0-0 vibronic sub-band. The spectrum of the iso- π -electronic Brooker's Merocyanine exhibits in DCM a clear vibrational structure and also here $\lambda_{\max}$ is represented by the 0-0 sub-band (Figure 3(a)). However, in MeOH the vibrational structure disappears and $\lambda_{\max}$ is substantially hypsochromic shifted (Figure 3(b)).

Both contributing structures for 4,4'-dimethylpyrido-trimethincyanine have the same two terminal components with the same electron acceptor/donor abilities and so there is a small solvatochromic effect on the 0-0 transition only. In **6** the two terminal components have different electron acceptor/donor abilities and, therefore, already in DCM there is a change of R_e from S_0 to S_1 [$R_e(S_1) > R_e(S_0)$], so $\lambda_{\max}$ is represented by the 0-0 sub-band, but the intensity of the 0-1 sub-band is substantially higher. Within the Förster model it follows, that the polar solvent MeOH moves c^2 to $c^2 \gg 0.5$ with the result of a big change of R_e from S_0 to S_1 [$R_e(S_1) \gg R_e(S_0)$] the absorption curve does not exhibit a vibrational fine structure and $\lambda_{\max}$ is substantially hypsochromic shifted (Figure 3(b)).

Increasing the electron donor ability of the terminal phenolate component by substitution of two t-Bu groups as in **7**, leads to a more symmetric electronic structure and spectra with a clear vibrational structure in all aprotic solvents and in most alcohols [17, 27, 28].

Figure 3: Normalized absorption spectra of Brooker's Merocyanine and the iso- π -electronic 4,4'-Dimethylpyrido-trimethincyanine (a) in DCM and (b) in MeOH.

A similar effect can be achieved by replacing oxygen in the streptomercyanine **5** with malodinitrile as in **8** (Table 2).

Table 2: Absorption maxima $\lambda_{\max}$ (nm) and molar absorption coefficient $\epsilon_{\max}$ ($10^{-3} \text{ M}^{-1} \text{ cm}^{-1}$) of the streptomerocyanines **8** in dependence on the number of vinylene groups n in EtOH [29].

n	$\lambda_{\max}$	$\epsilon_{\max}$
1	372	93
2	473	260
3	579	470
4	670	520

8

The crystal structures of **5** ($n = 3$) BLA = 5.8 pm and of **8** ($n = 3$) BLA = 0.5 pm provide direct evidence for decreased BLA in **8** in comparison with **5** [21].

NMR investigations and related quantum chemical calculations on a number of cyanines, merocyanines and polyenes have revealed that there is an almost linear correlation between the $^3J(\text{H,H})$ coupling constants for *trans* vicinal protons in the polymethine chain and the carbon–carbon equilibrium bond lengths [28–34]. Accordingly, the degree of bond length alternation in solution can be estimated by the absolute difference ΔJ of the $^3J(\text{H,H})$ coupling constants between adjacent vinylene groups. For illustration, for **5** ($n = 1$) is the value $\Delta J = 4.8 \text{ Hz}$ in CDCl_3 [30], whereas for **8** ($n = 1$) is $\Delta J = 1.0 \text{ Hz}$ in $[\text{D}_6]\text{DMSO}$ [31]. For comparison, for **4** ($n = 2$) is $\Delta J = 0.6 \text{ Hz}$ in CDCl_3 and $\Delta J = 0.8 \text{ Hz}$ in $[\text{D}_6]\text{DMSO}$.

To transfer the structural influence in polyatomic molecules to the Franck-Condon principle for diatomic molecules the BLA (ΔJ) in the electronic ground state can be used. The small BLA and ΔJ in the streptomerocyanines **8** are clear experimental evidence, that the differences between carbon–carbon equilibrium bond lengths in the polymethine chain are small. From eqs. (2) and (3) it follows that the difference $R_e(S_1) - R_e(S_0)$ is small and it is highly likely $\lambda_{\max}$ values represent the 0–0 vibronic transition energy. So, the streptomerocyanines **8** reflect the above discussed structure influences on $\lambda_{\max}$ and $\epsilon_{\max}$ in an excellent manner and all spectra of compounds $n > 0$ exhibit a clear vibrational structure [31].

Vice versa, the great BLA and ΔJ in the streptomerocyanines **5** are clear experimental evidence, that the differences between carbon–carbon equilibrium bond lengths in the polymethine chain are great. With increasing BLA (ΔJ) $R_e(S_0)$ and $R_e(S_1)$ differ increasingly and it is highly likely $\lambda_{\max}$ values represent another 0– ν vibronic transition. In addition, all spectra of series **5** exhibit no fine structure [13].

In summary, merocyanines fall within the polymethine dye class, but whoever discusses their absorption spectra should pay attention to fine structure of the absorption bands.

2 History of the merocyanine dyes

The first merocyanine dye **9** was synthesized by John D. Kendall at the photographic company Ilford by the reaction of rhodanic acid with 3-ethyl-2-methylthio-benzthiazolium [35].

9

As mentioned already Hamer suggested the term merocyanine [4]. Also here, silver halide photography was the driving force to make further developments in the field of merocyanine dyes. A short time later Hamer and Brooker presented a lot of new merocyanines based on components from cyanine dye chemistry and open-chain or cyclic keto-methylene compounds like e.g. acetylacetone, barbituric acids, cyanoacetamides, cyanoacetates, hydantoin, isoxazolones, malodinitrile, malonates, pyrazolones, thiohydantoin, thio-oxazolidinediones and thiazolinones [4–7, 36].

For illustration only, one of the most successful and widely used merocyanines in black and white materials was the green sensitizer **10** (Sto 749).

10

Later merocyanines for textile dyeing and other applications were developed. Since completely different technical requirements were demanded of them, e.g. fastness, they were constructed from new components.

3 General synthetic routes to merocyanine dyes

The first merocyanine dye **9** was prepared from the reaction between rhodanic acid with 3-ethyl-2-methylthio-benzthiazolium [35]. It is the general way to synthesize

R = Cl, Br, I, SR, SO_3^- , ...

Figure 4: Reaction scheme.

zeromethine merocyanines **13** using heterocyclic quaternary salt **11** with a leaving group R and the anions of keto-methylene compounds **12** (Figure 4) [4–7, 36].

To obtain the vinylogues of the zeromethine merocyanines **13** a 2-methyl heterocyclic quaternary salt **14** reacts with diphenylformamidine hydrochloride **15** ($n = 0$), malondialdehyde dianil hydrochloride **15b** ($n = 1$) or glutacondialdehyde dianil hydrochloride **15c** ($n = 2$) to the intermediate **16** with β -acetanilido vinyl groups (sometimes β -anilino vinyl groups). groups. Then the intermediate **16** is condensed with anions of keto-methylene compounds **17** to the merocyanines **18** (Figure 5) [4–7, 36]. Commercially used are only zeromethine **13**, dimethine **18** ($n = 0$) and tetramethine **18** ($n = 1$) merocyanines. Dyes with longer polymethine chain **18** ($n > 1$) are of less technical importance due to their low stability.

Figure 5: Reaction scheme.

Especially for the synthesis of dimethine dyes based on 1-alkyl-2,3,3-trimethylindole-nine the corresponding aldehyde (Fischer's aldehyde) is used. So, e.g. **3** is synthesized by the reaction of 2-(1,3,3-trimethylindolin-2-ylidene)acetaldehyde with 1-phenyl-3-methylpyrazol-5-one.

4 Commercial uses of merocyanine dyes

The first and main technical application of merocyanine dyes was in silver halide photography as spectral sensitizers [37–39].

Zeromethine merocyanines like **9**, **19** and **20** are suitable blue sensitizers in the region 450–500 nm. The carboxyl groups in **19** and **20** increase the water solubility, preventing residual coloration after processing.

Dimethine merocyanine like e.g. **2**, **10** and **21** are used as green sensitizers in the region 500–600 nm.

As red sensitizers in the region 600–700 nm tetramethine and trinuclear merocyanines **22** are used. In all cases the function of the carboxyl groups is to increase the water solubility, preventing residual coloration after processing.

Due to their low light fastness and thermal stability merocyanines like **2**, **6**, **7**, **9**, **10**, **19–22** are not suitable for textile dyeing. To improve these properties derivatives of N-alkyl-1,8-naphtholactam were introduced. By condensation of N-ethyl-1,8-naphtholactam with malodinitrile the yellow dye **23** is obtained. The reaction of the corresponding methylene- ω -aldehyde with ethyl cyanoacetate gives the dimethine merocyanine dye **24**. The extension of the polymethine chain by a vinyl group leads to a red color of **24**.

23 **24**

The dimethinemerocyanine **25** is obtained by condensation of Fischer's aldehyde with ethyl cyanoacetate and gives a stable yellow dye. Substitution with a carboxylate group at the 5-position of the indoline heterocycle produces a very lightfast dye.

25 **26**

Textile dyeing is not the main field of application of merocyanine dyes, however the samples **23–26** illustrate how dyes, developed for use in another technology, provide suggestions for the development of new textile dyes with higher demands on fastness properties.

In the 1990s the field of nonlinear optics (NLO) was inflated with too much hype [21, 22, 40], followed by an abrupt decline. Due to the low light fastness and thermal stability of the functional colorants developed for this field there was no real technical application. Nevertheless, this area of research stimulated many new and interesting dye syntheses [40, 41] like e.g. **27** and **28**.

27 **28**

Merocyanine 540 **29** was among the first fluorescent dyes to determine membrane potentials in eukaryotic cells and prokaryotic bacteria [42].

29

However, its use for this application has declined with the advent of superior probes and its extreme phototoxicity. Irradiation of Merocyanine 540 **29** produces both singlet oxygen and other reactive oxygen species, including oxygen radicals. Therefore, it is now more commonly used as a photosensitizer in photodynamic therapy.

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