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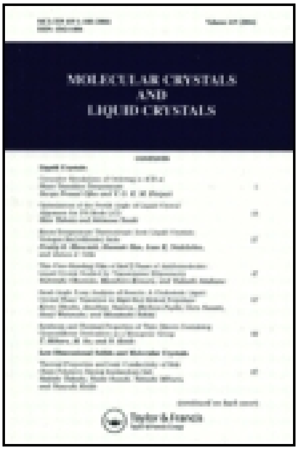

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl18

Erratum

Version of record first published: 24 Sep 2006.

To cite this article: (1991): Erratum, Molecular Crystals and Liquid Crystals, 195:1, 307-308

To link to this article: http://dx.doi.org/10.1080/00268949108030909

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Mol. Cryst. Liq. Cryst., 1991, Vol. 195, pp. 307–308
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Printed in the United States of America

Erratum

"Sudden Conduction at the solid to mesophase transition of octa-*n*-alkoxy substituted phthalocyanines," Johan F. van der Pol†, Matthijs P. de Haas‡, John M. Warman‡ and Wiendelt Drenth†, †Department of Organic Chemistry, Utrecht University, Padualaan 8, 3584 CH UTRECHT, The Netherlands, ‡Radiation Chemistry Department, IRI, Delft University of Technology, Mekelweg 15, 2629 JB DELFT, The Netherlands. *Mol. Cryst. Liq. Cryst.* **183**, pp. 411–420.

In Reference 1 the possibility that the microwave conductivity of approximately 0.1 S/m found for the liquid crystalline phase of octa-*n*-alkoxy substituted phthalocyanines was due to dipole relaxation was dismissed on the basis of an estimate of the maximum possible dipolar contribution to the dielectric loss at the frequencies used, 28 to 38 GHz. Due to a mistake in concentration units this potential contribution was however grossly underestimated. We present a corrected calculation and, as a result, a revised conclusion below.

The dipolar contribution to the high-frequency conductivity (dielectric loss) is given by

$$\sigma(\omega) = N_D(\varepsilon + 2)^2 p^2 F(\omega\tau_D)/27k_BT\tau_D \tag{1}$$

with N_D the dipole concentration (per m^3), ε the relative dielectric constant of the medium, p (Cm) the dipole moment, k_BT (J) the characteristic thermal energy, τ_D (s) the dipole relaxation time, ω (s^{-1}) the radian microwave frequency ($\omega = 2\pi f$ with f in cycles per second), and $F(\omega\tau_D)$ the frequency dispersion term which for a Debye type relaxation is given by

$$F(\omega\tau_D) = (\omega\tau_D)^2/[1 + (\omega\tau_D)^2] \tag{2}$$

From equation (1), $\sigma(\omega)$ is seen to have a maximum possible value, corresponding to the condition $\tau_D = \omega^{-1}$,

$$\sigma(\omega)_{max} = N_D(\varepsilon + 2)^2 p^2 \omega/54k_BT \tag{3}$$

For the conditions of the measurements, carried out at room temperature with $\varepsilon \approx 3$ and a frequency of 30 GHz, equation (3) becomes

$$\sigma(\omega)_{max} = 0.15[M_D]D^2 \tag{4}$$

for the dipole concentration, $[M_D]$, in moles per litre and the dipole moment, D, in debye.

Because of the symmetry of the phthalocyanine unit and the non-polar nature of the alkyl chains, any dipolar contribution to the dielectric loss must be assumed to arise from motional freedom of the alkoxy bridging units in the liquid crystalline phase. Since the concentration of these units in the solid is approximately 5 M and the dipole moments of alkoxybenzenes are typically 1.2 debye[2] the maximum possible dielectric loss from this source would be approximately 1 S/m rather than the 10^{-3} S/m estimated previously. Clearly therefore a dipolar contribution to the measured conductivity is within the realms of possibility.

The condition of maximum $\sigma(\omega)$, $\tau_D = \omega^{-1}$, however corresponds to a dipolar relaxation time of only approximately 5 ps which would seem to be unrealistically short for the present molecular structures since even for simple low viscosity alcohols dipolar relaxation times of tens of picoseconds are found.[3]

Using Equation (2) to estimate the actual relaxation time required to give the experimentally observed conductivity of approximately 0.1 Sm^{-1} we find a value of approximately 100 ps. While this is still rather short, considering the bulky units attached to the bridging oxygen atom, it can not be completely ruled out as a possible timescale for at least partial reorientation or flexing of the Pc-O-R units, particularly if the alkoxy chains are fully "melted" in the liquid crystalline phase as is often taken to be the case.

While the dipolar relaxation explanation of the microwave conductivity observed in the mesophase of octa-*n*-alkoxy substituted phthalocyanines may possibly be judged less likely than that based on the thermal generation of mobile, intra-core charge carriers, it clearly can not be completely ruled out. Additional conductivity measurements at lower microwave frequencies, in the region of a few GHz, and/or electron spin resonance measurements might help to resolve this ambiguity of interpretation.

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2. A. L. McClellan, *Tables of Experimental Dipole Moments, Volume 2*, (Rahara Enterprises, 1974).
3. S. K. Garg and C. P. Smyth, *J. Phys. Chem.*, **69**, 1294 (1965).