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J. W. Emsley[a]
[a] Department of Chemistry, University of Southampton, Southampton, England

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The conformations adopted by α,δ-bis(phenoxy)ethane in isotropic and nematic solutions

by J. W. EMSLEY
Department of Chemistry, University of Southampton,
Southampton SO9 5NH, England

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Errors in the calculations of Cheung and Emsley (*Liquid Crystals*, **13**, 265 (1993)) used to derive the populations of α,δ-bis(phenoxy)ethane dissolved in isotropic and nematic liquid crystalline solvents have been corrected, and the results are compared with those obtained on the same molecule by Abe, Iizumi and Kimura (*Liquid Crystals*, **16**, 655 (1994)). The principal difference between these two calculations is that Abe *et al.*, obtain 0·80 as the population of the $tg\pm t$ conformers, and they find this to be independent of temperature, whereas the present calculations obtain 0·42 to 0·58 depending upon solvent and temperature.

Abe *et al.* [1], have pointed out that the conformational distributions obtained by Cheung and Emsley [2] for α,δ-bis(phenoxy)ethane (PO2OP) dissolved in both isotropic and liquid crystalline solvents are inconsistent with the values reported by Cheung and Emsley for E_{tg}^{CC}, the energy difference between *gauche* ($g\pm$) and *trans* forms (t) generated by rotating about the central C–C bond. A re-examination of the data on the PO2OP samples reveals that there are errors in the calculations reported by Cheung and Emsley, which have been remedied, and the correct results are reported here and compared with those obtained by Abe *et al.*

The first error concerned the data obtained from the 360 MHz spectrum of PO2OP dissolved in acetone, and the correct values are given in table 1. The value of $L=J_{13}-J_{14}$ is related to the fraction, n_t, of the *trans*-conformer by,

$$L=(\tfrac{1}{2}-3n_t/2)(J_t-J_g),$$

which with $(J_t-J_g)=10$ Hz, and L positive gives $E_{tg}=-3\cdot1$ kJ mol^{-1}, which is close to the values obtained by Abe *et al.*, for samples dissolved in deuteriated benzene and dimethyl sulphoxide.

The conformer distributions, and orientational order parameters for PO2OP dissolved in nematic liquid crystalline solvents were obtained by comparing observed deuterium quadrupolar splittings with those calculated by the additive potential (AP) model introduced by Emsley, Luckhurst and Stockley [3]. A mistake in the computer program has been discovered, which affects only those calculations in which E_{tg}^{CC} is negative, and most of the results of Cheung and Emsley are unaffected by this error. The major effect is to change the values derived for E_{tg}^{CC}, and hence of the conformer distributions for PO2OP dissolved in the three liquid crystalline solvents. The results from the corrected calculations are given in tables 1 and 2, which correspond to tables 3 and 5 in Cheung and Emsley. As before, the data for PO2OP are consistent with negative values of E_{tg}^{CC}, in the range $-1\cdot83$ to $-0\cdot75$ kJ mol^{-1}, which are less negative than those obtained for isotropic solutions in acetone, benzene or dimethyl sulphoxide, but are of reasonable magnitude, given the uncertainties in the value of (J_t-J_g) which is

Table 1. Values of E_{tg}^{CC}, $\epsilon_{2,0}^{R}$, λ_R and λ_{CC} obtained for the PONOP molecules.

Molecule	Solvent	T/K	E_{tg}^{CC}/kJ mol^{-1}	$\epsilon_{2,0}^{R}$/kJ mol^{-1}	λ_R	λ_{CC}
PO4OP	EBBA	344	2·5†	1·60	0·06	0·34
		306	2·5†	3·59	0·10	0·32
	Phase 5	342	2·5†	1·49	0·04	0·34
		301	2·5†	3·20	0·07	0·33
	ZLI 1132	339	2·5†	1·97	0·41	0·22
		300	2·5†	3·99	0·54	0·19
PO3OP	EBBA	344	0·00	1·37	0·17	0·34†
		307	0·00†	3·14	0·18	0·29
	Phase 5	342	0·145	1·25	0·15	0·34†
		300	0·145†	3·02	0·17	0·28
	ZLI 1132	340	0·00	1·89	0·48	0·22†
		300	0·00†	4·16	0·56	0·18
PO2OP	EBBA	347	−1·12	1·45	0·19	0·34†
		305	−1·12†	3·49	0·26	0·31
	Phase 5	342	−1·831	1·41	0·21	0·34†
		300	−1·831†	2·93	0·27	0·36
	ZLI 1132	337	−0·754	1·71	0·58	0·22†
		305	−0·754†	3·34	0·68	0·25

† Fixed.

Table 2. Populations p^{iso} and p^{LC} of the conformations adopted by PO2OP when dissolved in ZLI 1132 at T_{NI} together with the values of the local order parameters, $S_{zz}^{R}(n)$ and $S_{xx}^{R}(n) - S_{yy}^{R}(n)$, and the order parameters for the conformations, $S_{z'z'}(n)$ and $S_{x'x'}(n) - S_{y'y'}(n)$ referred to principal axes.

Conformer	G†	p^{iso}	p^{LC}	$S_{zz}^{R}(n)$	$S_{xx}^{R}(n) - S_{yy}^{R}(n)$	$S_{z'z'}(n)$	$S_{x'x'}(n) - S_{y'y'}(n)$
1. ttt	1	0·16	0·17	0·26	0·25	0·27	0·24
2. $ttg\pm$	4	0·10	0·10	0·06	0·18	0·17	0·15
3. $tg\pm t$	2	0·41	0·42	0·27	0·04	0·28	0·10
4. $tg\pm g\pm$	4	0·14	0·12	0·02	0·11	0·09	0·11
5. $tg\pm g\mp$	4	0·14	0·13	0·04	0·25	0·16	0·20
6. $g\pm tg\pm$	2	0·01	0·01	0·06	0·26	0·14	0·24
7. $g\pm tg\mp$	2	0·01	0·01	0·22	0·26	0·23	0·25
8. $g\pm g\pm g\pm$	2	0·01	0·01	0·24	0·05	0·24	0·10
9. $g\pm g\pm g\mp$	4	0·02	0·02	0·07	0·21	0·17	0·19
10. $g\pm g\mp g\pm$	2	0·01	0·01	0·20	0·26	0·22	0·25

† G is the degeneracy of the conformer.

used in the derivation of E_{tg}^{CC} from data on the isotropic solutions, and the sensitivity of this energy difference to the nature of the solvent.

The major change in the new conformer distributions compared to the incorrect values in Cheung and Emsley, lies in the increased populations of the $tg\pm t$ conformers, which from the data in table 2 are now seen clearly to dominate in both isotropic and liquid crystalline solutions.

The only other data in Cheung and Emsley changed by the corrected calculations concerns that for the pure nematogen, CBO2OBC. The calculations for E_{tg}^{CC} positive are unaffected, but those for $E_{tg}^{CC} = -1·76$ kJ mol^{-1} are quite different. Thus, with the

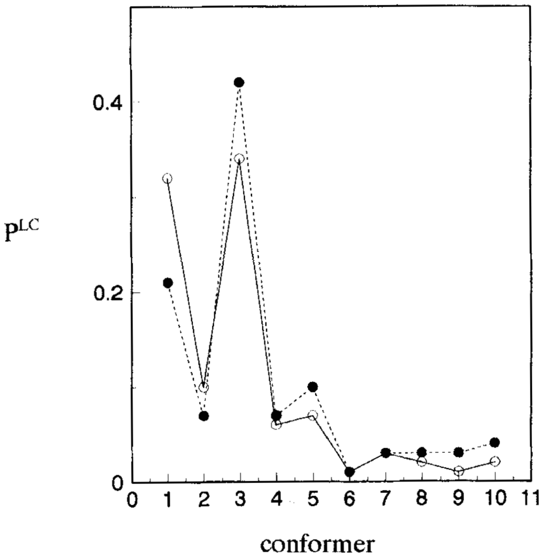

Figure 1. Changes in the populations, p^{LC}, of the conformers of CBO2OBC at T_{NI}, when E_{tg}^{CC} is reduced in value from 1·76 (○) to −1·76 kJ mol^{-1} (●). The conformer labels are those in table 2.

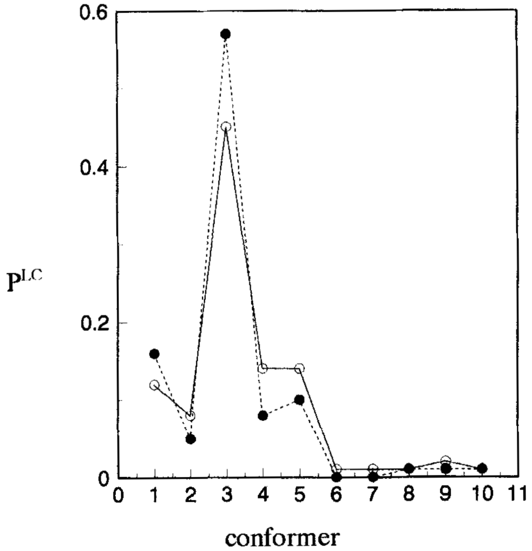

Figure 2. Changes in the populations of the conformers of PO2OP dissolved in Phase 5 when the temperature is reduced from T_{NI} of 342 K (○) to 300 K (●). The conformer labels are those in table 2.

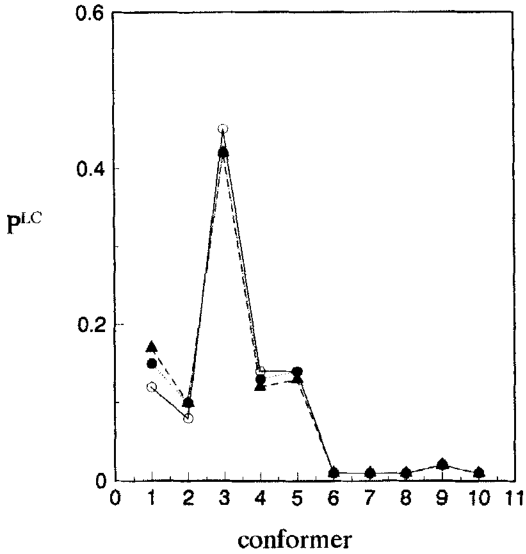

Figure 3. The dependence of the conformer populations of PO2OP on the liquid crystal solvent. Phase 5 (○), EBBA (●) and ZLI 1132 (▲). The conformer labels are those in table 2.

negative value for E_{tg}^{CC}, the population of $tg \pm t$ is considerably enhanced, so that figure 6 in Cheung and Emsley is misleading. A correct representation of the effect on the conformer distribution of changing E_{tg}^{CC} from 1·76 to −1·76 kJ mol^{-1} is shown in figure 1.

The calculations by Abe *et al.*, use a different model to that used here for predicting the conformational dependence of the orientational order parameters of PO2OP, and they fit the observed and calculated data by adjusting the population of the *gauche* forms generated by rotation about the central C–C bond. They obtain a conformational distribution with 80 per cent of the $tg \pm t$ conformers, which is almost double that found by the present calculations. They also conclude that although the conformer distribution changes dramatically on going from the isotropic to the nematic phases, which implies a large contribution of the mean nematic field to the effective conformational energy differences, it does not change with temperature. The present calculations, however, obtain conformer distributions which depend on both temperature and on the solvent, as shown in figures 2 and 3. It should be noted that the measurements reported by Abe *et al.*, extend over a much shorter range of temperature (about 12°) than those of Cheung and Emsley (about 43°). However, their temperatures do cover the range close to T_{NI} where the orientational order is changing most rapidly, so that the absence of a temperature dependence for their derived conformer distribution is significant. Perhaps the only way to decide which of these conformer distributions is correct, that obtained by Abe *et al.*, or that obtained here by the AP method, is to compare these with a simulation which uses a realistic intermolecular potential, rather than models for the mean molecular field.

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