Supporting Information

Predicting the thermal behavior in the design of type V deep eutectic solvents: the combined role of polarity and steric asymmetry

Giorgia Mannucci[†], Gabriel Teixeira[‡], Filipe Hobi Bordon Sosa[‡], Matteo Palluzzi[†], Matteo Busato[†], João A.P. Coutinho[‡]*, and Paola D'Angelo[†]*

[†]Department of Chemistry, University of Rome "La Sapienza", P.le A. Moro 5, 00185 Rome, Italy

[‡]CICECO, Aveiro Institute of Materials, Complexo de Laboratórios Tecnológicos, University of Aveiro, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal

Corresponding Author

*Email: p.dangelo@uniroma1.it; jcoutinho@ua.pt

Pages: S1 -S7

Tables: S1 -S8

Figures: S1 -S7

Table S1. Prepared samples for the 4-Met/MEN mixture. The composition is reported as molar fraction of the 4-Met component ($x_{\text{4-Met}}$) and correspondent MEN molar fraction (x_{MEN}).

$x_{\text{4-Met}}$	x_{MEN}	T_m (K)
0.12	0.88	305.8 [a]
0.22	0.78	297.8 [b]
0.30	0.70	290.3 [b]
0.41	0.59	278.0 [b]
0.50	0.50	274.9 [b]
0.59	0.41	298.7 [b]
0.70	0.30	306.6 [b]
0.79	0.21	308.2 [b]
0.90	0.10	316.8 [b]

[a] Visual Method; [b] DSC (Hitachi DSC7000X)

Table S2. Prepared samples for the BHA/MEN mixture. The composition is reported as molar fraction of the BHA component (x_{BHA}) and correspondent x_{MEN}.

x_{BHA}	x_{MEN}	T_m (K)
0.10	0.90	310.6 [a]
0.23	0.77	293.6 [b]
0.29	0.71	287.2 [b]
0.38	0.62	277.3 [b]
0.46	0.54	278.8 [b]
0.51	0.49	281.5 [b]
0.59	0.41	297.9 [b]
0.69	0.31	306.9 [b]
0.80	0.20	315.8 [b]
0.90	0.10	322.9 [a]

[a] Visual Method; [b] DSC (Hitachi DSC7000X)

Table S3. Prepared samples for the TBEP/MEN mixture. The composition is reported as molar fraction of the TBEP component (x_{TBEP}) and correspondent x_{MEN}.

x_{TBEP}	x_{MEN}	T_m (K)
0.12	0.88	301.8 [a]
0.21	0.79	291.1 [a]
0.81	0.19	288.3 [a]
0.90	0.10	294.5 [a]

[a] DSC (Hitachi DSC7000X)

Table S4. Prepared samples for the TBHQ/MEN mixture. The composition is reported as molar fraction of the TBHQ component (x_{TBHQ}) and correspondent x_{MEN}.

x_{TBHQ}	x_{MEN}	T_m (K)
0.11	0.89	304.5 [a]
0.29	0.71	340.2 [b]
0.41	0.59	342.4 [b]
0.49	0.51	359.6 [b]
0.59	0.41	371.3 [b]
0.69	0.31	384.2 [c]
0.90	0.10	394.8 [c]

[a] DSC (Hitachi DSC7000X) ; [b] DSC (Mettler-Toledo DSC 821) ; [c] Visual Method

Table S5. Melting point temperature (T_m), enthalpy of fusion (ΔH_i), and molecular weight (**MW**) of the pure components.

Compound	T_m (K)	ΔH_i (kJ mol^{-1})	MW (g/mol)	Ref
4-Met	328.30	18.30	124.14	[1]
BHA	327.18	14.58	180.24	Experimental
TBEP	301.89	17.07	178.27	Experimental
TBHQ	400.15	27.74	166.22	[2]
MEN	315.60	13.47	156.27	[3]

[1] Lee, Ming-Jer, et al. "Solid–Liquid Equilibria for 4-Methoxyphenol with Catechol, Ethylenediamine, or Piperazine." Journal of Chemical & Engineering Data 42.2 (**1997**): 349-352.

[2] Verevkin, Sergey P. "Substituent effects on the benzene ring. Prediction of the thermochemical properties of alkyl substituted hydroquinones." Physical Chemistry Chemical Physics 1.1 (**1999**): 127-131.

[3] Štejfa, Vojtěch, et al. "Polymorphism and thermophysical properties of L-and DL-menthol." The Journal of chemical thermodynamics 131 (**2019**): 524-543.

Table S6. Weight factors (*wf*) employed to obtain the conformers percentage yield from the DFTB-MD simulations.

Compound	*wf* (*transoid*)	*wf* (*cisoid*)
BHA	0.4	5.6
TBEP	0.4	5.5
TBHQ	0.4	4.7

Table S7. Number of molecules, box dimensions, densities, and employed temperatures for the density functional tight-binding molecular dynamics (DFTB-MD) simulated systems.

System	Number of molecules	Box edge (Å)	Density (g cm^{-3})	Temperature (K)
BHA	36	22.0314	1.008*	333
TBEP	34	21.9965	0.946*	308
TBHQ	37	22.0919	0.947†	408

*experimental density

† density estimated from classical molecular dynamics (MD) simulations.

Table S8. Melting point temperatures (T_m) at the eutectic composition for the 4-Met/MEN, BHA/MEN, TBEP/MEN, and TBHQ/MEN mixtures for the ideal and COSMO-calculated phase diagrams, and difference between the two values (ΔT_m).

System	$T_{m,\,ideal}$ (K)	$T_{m,\,COSMO}$ (K)	ΔT_m (K)
4-Met/MEN	287.9	283.9	4.0
BHA/MEN	283.7	274.9	8.8
TBEP/MEN	276.1	256.8	19.3
TBHQ/MEN	309.9	301.7	8.2

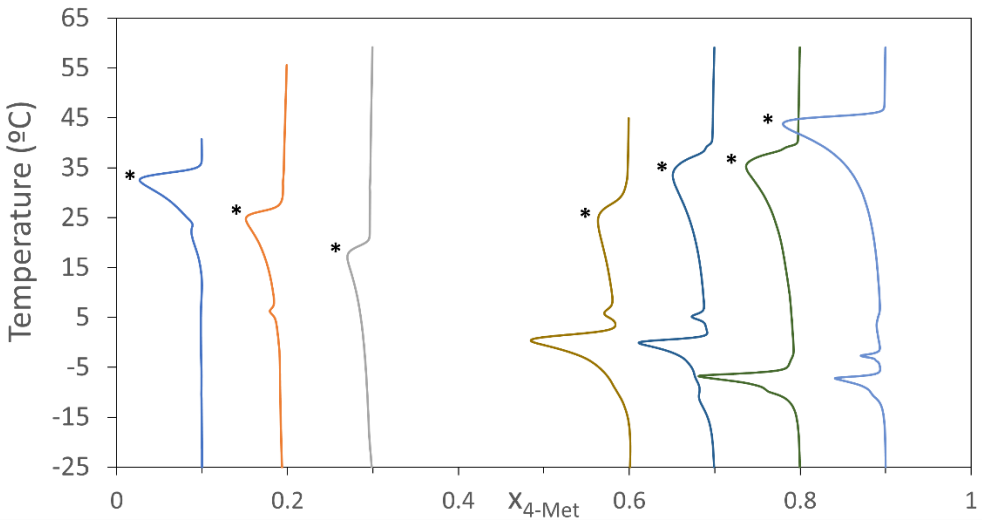

Figure S1. Selected DSC curves for the 4-Met/MEN system. The maximum values of the melting peaks are evidenced (*).

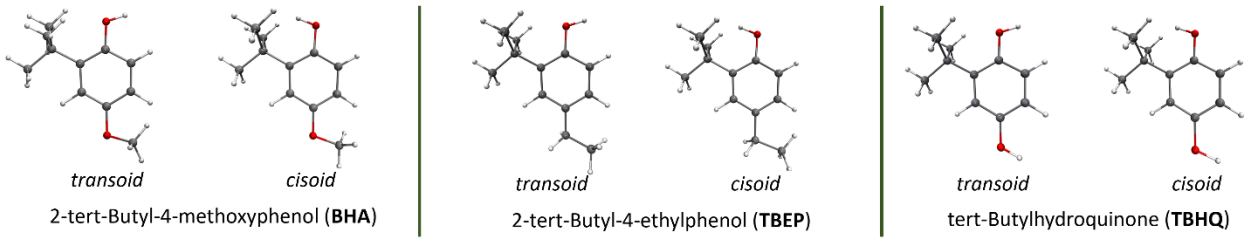

Figure S2. Molecular structures of the BHA, TBEP, and TBHQ rotational conformers.

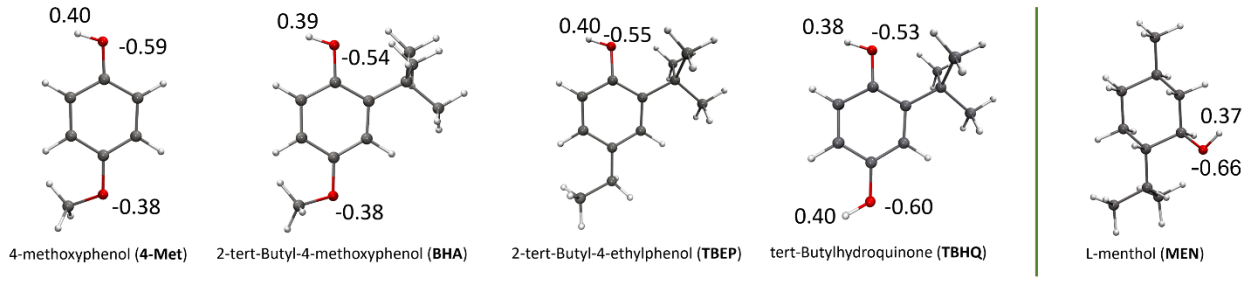

Figure S3. Partial charges calculated with the CHELPG scheme for the hydroxyl and methoxy functional groups of the 4-Met, BHA, TBEP, TBHQ, and MEN molecules from gas phase DFT optimizations at the B3LYP/def2TZVP level of theory.

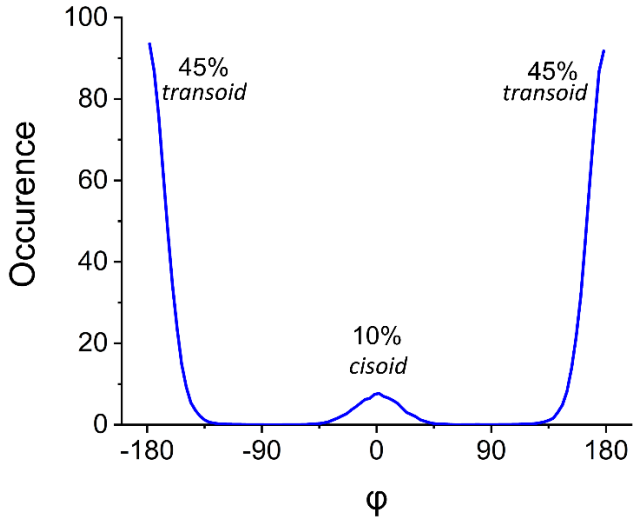

Figure S4. Dihedral distribution function calculated from the DFTB-MD simulations for the pure TBEP system.

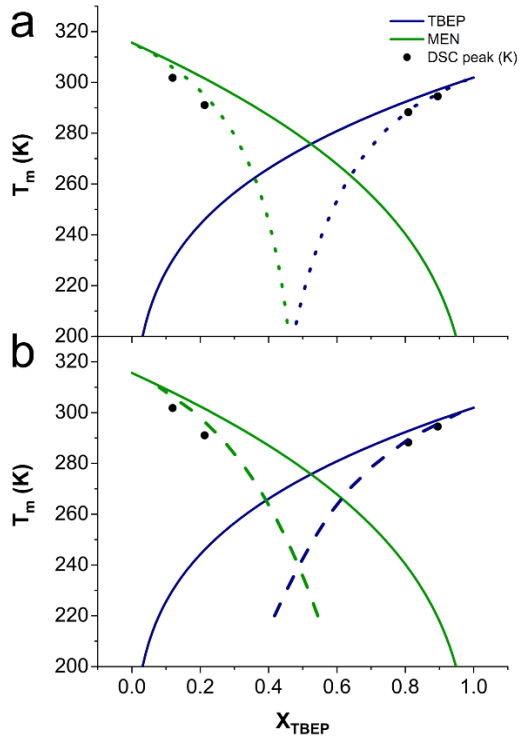

Figure S5. Experimental SLE phase diagram for the TBEP/MEN system measured using the DSC (black circle). Predictions obtained by the ideal liquid phase model (full lines) and COSMO-RS theoretical curves calculated using the BP_TZVP_21 (dot lines) (a) and BP_TZVPD_FINE_21 (dash lines) (b) parametrizations.

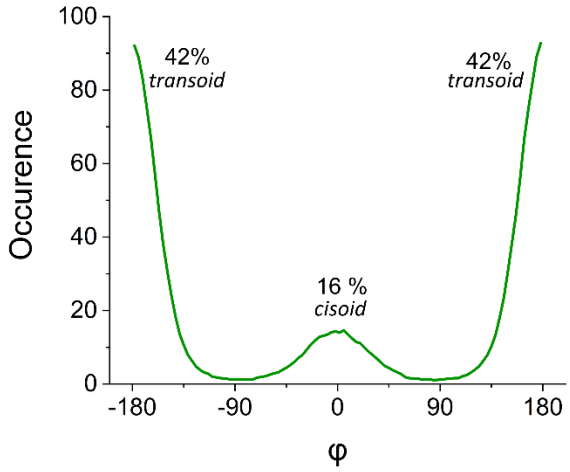

Figure S6. Dihedral distribution function calculated from the DFTB-MD simulations for the pure TBHQ system.

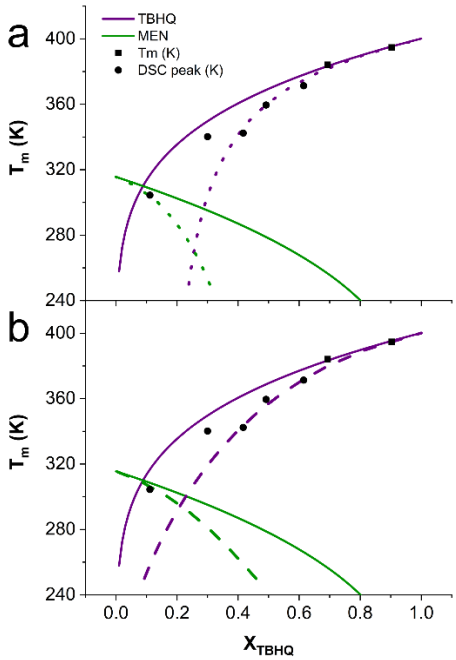

Figure S7. Experimental SLE phase diagram for the TBHQ/MEN system measured using the DSC (black circle) and the visual method. Predictions obtained by the ideal liquid phase model (full lines) and COSMO-RS theoretical curves calculated using the BP_TZVP_21 (dot lines) (a) and BP_TZVPD_FINE_21 (dash lines) (b) parametrizations.