1 Force Field Parameters for 9AB9

The force field description of the perfluoroalkylated azobenzene derivative 9AB9 (F_3C-$(CF_2)_6$-CH_2-O-CO-AB-CO-O-CH_2-$(CF_2)_6$-CF_3) is based on the azobenzene (AB) parameters published recently [1]. Following the procedure given there, the ester linkage is parametrised based on the GROMOS force field [2] using benzoic acid methyl ester ($H_3C-O-CO-C_6H_5$) as the model system for the ab initio calculations, and the resulting additional parameters are listed in Table 1. The additional parameters for the perfluorinated hydrocarbon chain have been derived using pentafluor-propane ($F_3C-CF_2-CH_3$) as the model system for single point ab initio calculations and are collected in Table 2.

Table 1: Extension of azobenzene force field to include ester linkage $C_{alk}-O-CO-C_{ar}$

	entity	force constant	ref. value
bonds:	$C-C_{ar}$	8.66×10^2 kJ/(mol Å^4)	1.501 Å
	$C=O$	1.66×10^3 kJ/(mol Å^4)	1.230 Å
	$C-O$	1.02×10^3 kJ/(mol Å^4)	1.380 Å
	$C_{alk}-O$	6.10×10^2 kJ/(mol Å^4)	1.463 Å
angles:	$C_{alk}-O-C$	620.0 kJ/mol	114.5°
	$O-C=O$	730.0 kJ/mol	123.5°
	$O-C-C_{ar}$	610.0 kJ/mol	115.5°
	$O=C-C_{ar}$	685.0 kJ/mol	124.5°
	$C-C_{ar}-C_{ar}$	560.0 kJ/mol	120.0°
dihedrals:	$O-C-C_{ar}-C_{ar}$	1.20 kJ/mol	180.0°
	$C_{alk}-O-C-C_{ar}$	8.35 kJ/mol	180.0°
point charges:	C_{ar}		0.038 e
	C		0.503 e
	$O=$		-0.404 e
	$O-$		-0.298 e
	C_{alk} †		0.161 e

† united atom approach

Table 2: Extension of azobenzene force field to include perfluorinated hydrocarbon chain

	entity	force constant	ref. value
bond:	$C-F$	8.00×10^2 kJ/(mol Å^4)	1.370 Å
angles:	$F-C-F$	380.0 kJ/mol	106.5°
	$F-C-C$	425.0 kJ/mol	109.5°
	$C-C-C$	530.0 kJ/mol	111.0°
dihedrals:	$X-C-C-X$	0.60 kJ/mol	0.0°
point charges:†	F		-0.200 e
	C		0.400 e

† terminal F_3C group: F = -0.15 e, C = 0.45 e

References

[1] M. Böckmann, C. Peter, L. D. Site, N. L. Doltsinis, K. Kremer, and D. Marx, J. Chem. Theory Comput. **3**, 1789 (2007).

[2] W. F. van Gunsteren, S. R. Billeter, A. A. Eising, P. H. Hüneneberger, P. Krüger, A. E. Mark, W. R. P. Scott, and I. G. Tironi, *Biomolecular Simulation: The GROMOS96 Manual and User Guide* (vdf Hochschulverlag AG, ETH Züerich, 1996).