

Supporting information: Photo- and Collision-Induced Isomerization of a Charge-Tagged Norbornadiene–Quadricyclane System

Ugo Jacovella,[†] Eduardo Carrascosa,^{†,§} Jack T. Buntine,[†] Nicolai Ree,[‡] Kurt V.
Mikkelsen,[‡] Martyn Jevric,[¶] Kasper Moth-Poulsen,[¶] and Evan J. Bieske*,[†]

[†]*School of Chemistry, The University of Melbourne, Victoria 3010, Australia*

[‡]*Department of Chemistry, University of Copenhagen, Universitetsparken 5, 2100
Copenhagen Ø, Denmark*

[¶]*Department of Chemistry and Chemical Engineering, Chalmers University of Technology,
41296 Gothenburg, Sweden*

[§]*Current address: Laboratoire de Chimie Physique Moléculaire, École Polytechnique
Fédérale de Lausanne, EPFL SB ISIC LCPM, Station 6, CH-1015 Lausanne, Switzerland*

E-mail: evanjb@unimelb.edu.au

Computational Methods

The photochromic properties of the NBD–QC carboxylate system were theoretically studied using density functional theory (DFT) and its time-dependent analogue (TD-DFT). All calculations were performed using Gaussian16.¹ Structures resulting from geometry optimizations were confirmed as energy minima or transition states through harmonic frequency analyses (having zero or a single imaginary frequency, respectively). The Gibbs free energy calculations include the zero-point vibrational energy and thermal contributions evaluated at a temperature of 298.15 K and a pressure of 1.00 atm.

The geometries of the NBD and QC carboxylate were optimized in vacuum using the range-separated hybrid functional CAM-B3LYP² and the Pople style 6-311+G(d) basis set³⁻⁵ with a negative charge and a spin multiplicity of one. This method has previously provided spectroscopic properties of similar systems that are in good agreement with experimental results.⁶⁻¹⁰ The adiabatic electron detachment energies were obtained using the same method and basis set.

Conformational samplings of the two structures were performed by employing the Confab algorithm implemented in Open Babel 2.4.1¹¹ with an energy cutoff of 50.0 kcal/mol and a RMSD cutoff of 0.3 Å. This resulted in 5-6 conformers, which were reduced to 1-2 distinct conformers after geometry optimizations in both vacuum and methanol followed by RMSD calculations using the Kabsch algorithm^{12,13} with a tolerance of 0.3 Å. The solvent was treated as a dielectric medium through a static and an optical dielectric constant ($\epsilon_{st} = 32.61$ and $\epsilon_{op} = 1.766$, respectively) using the IEF-PCM continuum solvation model.^{14,15} Subsequently, TD-DFT calculations for the lowest-energy conformers were performed in order to simulate the UV-Vis spectra shown in Figure S2. For the transition state (TS), calculations were also performed in both vacuum and methanol and the imaginary frequencies were confirmed to correspond to the breaking/forming of the π -bonds in the NBD isomer and the forming/breaking of the σ -bonds in the QC isomer. Intrinsic reaction coordinate (IRC) calculations confirmed the connection of the TS to the NBD and QC isomers. The energy

of the TS allowed us to calculate the energy barrier of the thermal back-reaction going from the QC isomer to the NBD isomer ($\Delta H_{\text{QC} \rightarrow \text{NBD}}^\ddagger$ and $\Delta G_{\text{QC} \rightarrow \text{NBD}}^\ddagger$). It should be mentioned, that we have performed calculations with both unrestricted DFT (UDFT) and restricted DFT (RDFT), due to previous studies on similar systems^{6,8} reporting spin contamination of about 1 in the area of the TS, as the S_0 and T_1 states become degenerate. However, for this system we observed no spin contamination and obtained similar results for the two methods. Furthermore, the IRC calculations resulted in an energy landscape with a proper saddle point having a finite curvature, which further indicates that the S_0 and T_1 states of this specific system are not degenerate.

Molecular geometries

In this section, we present the geometries and energies of the lowest-energy conformers calculated at the CAM-B3LYP/6-311+G(d) level of theory with and without the IEF-PCM solvation model to mimic the polarization effects of methanol. Energies are reported in units of Hartree and Cartesian coordinates (XYZ) in units of Ångström. Intrinsic reaction coordinate (IRC) calculations connecting the NBD carboxylate and the QC carboxylate are also presented. Table S1 summarizes the energy barrier of the thermal back-reaction going from the QC carboxylate isomer to the NBD carboxylate isomer and the corresponding storage energy.

NBD in vacuum

Electronic energy: -782.619904035

Gibbs free energy: -782.449536

Atom	X	Y	Z
C	2.16091	-1.45237	0.44984
C	2.30821	0.81471	0.07420
C	2.92023	-1.75416	-0.84676
C	3.33121	-0.88806	1.28972
H	1.58692	-2.26921	0.87803
C	3.69362	0.14424	0.20092
C	2.17777	2.17950	-0.25351
C	3.83658	-0.80368	-0.99583
H	2.67023	-2.55290	-1.53245
H	4.11624	-1.62534	1.46953
H	3.01086	-0.43101	2.22732
H	4.52159	0.82525	0.38780
N	2.15176	3.30246	-0.51461
H	4.50682	-0.65040	-1.83143
C	-0.08462	-0.10369	0.14772
C	-0.81143	-1.28149	-0.08108
C	-0.80348	1.09142	0.30215
C	-2.19324	-1.26191	-0.16108
H	-0.28804	-2.22232	-0.21562
C	-2.18541	1.09727	0.23360
H	-0.27469	2.01829	0.49291
C	-2.90197	-0.07571	0.00199
H	-2.76546	-2.16353	-0.34578
H	-2.75319	2.01122	0.36252
C	1.36703	-0.14542	0.21868
C	-4.44908	-0.06608	-0.06466
O	-4.97195	-1.17598	-0.28429
O	-4.97700	1.04792	0.11105

QC in vacuum

Electronic energy: -782.575905401

Gibbs free energy: -782.408368

Atom	X	Y	Z
C	2.17710	-1.61181	0.55160
C	2.51232	0.66969	-0.12790
C	2.29851	-1.32511	-0.92910
C	3.41211	-1.15112	1.28850
H	1.59560	-2.46471	0.87660
C	3.77941	0.02458	0.41520
C	2.33802	2.07529	-0.22740
C	3.37011	-0.22472	-1.00770
H	2.01000	-2.00321	-1.71940
H	4.20140	-1.90912	1.30300
H	3.19511	-0.85052	2.31710
H	4.62721	0.66518	0.62380
N	2.24243	3.21849	-0.31380
H	3.93931	0.07748	-1.87520
C	1.42271	-0.45211	-0.06250
C	-0.04819	-0.28110	-0.04730
C	-0.81279	-0.52120	-1.18670
C	-0.70209	0.10050	1.12570
C	-2.19659	-0.40359	-1.14810
H	-0.31699	-0.81050	-2.10930
C	-2.08289	0.22301	1.15560
H	-0.11989	0.29300	2.02360
C	-2.85019	-0.03619	0.02230
H	-2.80809	-0.59669	-2.02190
H	-2.60888	0.51151	2.05830
C	-4.39409	0.06872	0.06900
O	-4.97489	-0.18828	-1.00380
O	-4.86919	0.39192	1.17540

TS in vacuum

Electronic energy: -782.511020739

Gibbs free energy: -782.345270

Atom	X	Y	Z
C	-3.22334	-0.26982	1.13738
C	-3.73567	-0.02761	-0.22064
C	-2.13641	-1.64962	-0.35077
C	-2.28626	-1.33018	1.13007
C	-3.49400	-1.33502	-0.96990
H	-3.44041	-1.17871	-2.04812
H	-4.23123	-2.10758	-0.73680
C	-2.42819	0.75376	-0.38647
C	-1.41751	-0.36942	-0.19424
H	-4.65682	0.52711	-0.35621
H	-1.59250	-2.53507	-0.65084
H	-1.60458	-1.60000	1.91733
H	-3.45143	0.37076	1.97902
C	-2.33621	2.09512	-0.04812
N	-2.33223	3.23269	0.19800
C	0.01849	-0.25081	-0.10229
C	0.64371	1.00286	-0.18051
C	0.83548	-1.39313	0.02248
C	2.02643	1.10179	-0.15446
H	0.04611	1.90024	-0.26971
C	2.20659	-1.27881	0.06310
H	0.38676	-2.37771	0.10114
C	2.82573	-0.02859	-0.02947
H	2.52350	2.06182	-0.22426
H	2.85019	-2.14469	0.16309
C	4.37101	0.08100	0.01030
O	4.81815	1.23777	-0.08389
O	4.96645	-1.00705	0.13147

NBD in methanol

Electronic energy: -782.715129331

Gibbs free energy: -782.544555

Atom	X	Y	Z
C	-2.20736	-1.42132	-0.51677
C	-2.29281	0.83041	-0.04343
C	-2.95085	-1.75522	0.78461
C	-3.37979	-0.79079	-1.30879
H	-1.65988	-2.23460	-0.98518
C	-3.69759	0.20545	-0.16983
C	-2.07774	2.16483	0.35769
C	-3.83807	-0.78836	0.99072
H	-2.72235	-2.60224	1.41741
H	-4.18738	-1.49747	-1.50006
H	-3.06995	-0.30553	-2.23549
H	-4.51101	0.91246	-0.31091
N	-1.94932	3.26185	0.68884
H	-4.50604	-0.66026	1.83184
C	0.07282	-0.11575	-0.18680
C	0.77994	-1.27544	0.14913
C	0.80145	1.04969	-0.45286
C	2.16274	-1.26114	0.24061
H	0.24369	-2.19425	0.35688
C	2.18380	1.05225	-0.37069
H	0.28544	1.95559	-0.74706
C	2.88460	-0.09941	-0.01817
H	2.70237	-2.15951	0.51226
H	2.74222	1.95448	-0.58591
C	-1.38608	-0.14549	-0.25082
C	4.41068	-0.08922	0.07471
O	4.96030	-1.16611	0.40338
O	4.98141	0.99554	-0.18481

QC in methanol

Electronic energy: -782.677131373

Gibbs free energy: -782.507844

Atom	X	Y	Z
C	-2.22717	-1.50727	-0.78697
C	-2.48512	0.65883	0.22815
C	-2.35671	-1.44641	0.71447
C	-3.42760	-0.88266	-1.45789
H	-1.67382	-2.32258	-1.23463
C	-3.77206	0.15052	-0.41236
C	-2.22876	2.00953	0.56371
C	-3.39050	-0.33198	0.95254
H	-2.10887	-2.24777	1.39543
H	-4.24211	-1.59720	-1.60132
H	-3.18174	-0.43210	-2.42203
H	-4.59663	0.84236	-0.52288
N	-2.01751	3.10687	0.84221
H	-3.95298	-0.14395	1.85505
C	-1.44246	-0.47514	0.00515
C	0.02663	-0.32503	0.01381
C	0.84032	-1.19829	0.73372
C	0.63472	0.69144	-0.72570
C	2.22227	-1.06903	0.70043
H	0.38849	-1.98482	1.32865
C	2.01513	0.82254	-0.74662
H	0.02259	1.38409	-1.29445
C	2.83021	-0.05807	-0.03846
H	2.84827	-1.75328	1.25968
H	2.48027	1.61356	-1.32176
C	4.35029	0.08329	-0.07208
O	5.01101	-0.75972	0.58003
O	4.81449	1.02972	-0.75111

TS in methanol

Electronic energy: -782.613376919

Gibbs free energy: -782.446750

Atom	X	Y	Z
C	-3.23168	-0.02204	1.26281
C	-3.73959	0.02709	-0.12915
C	-2.20949	-1.67225	-0.03223
C	-2.22436	-0.98659	1.34742
C	-3.59382	-1.42068	-0.61748
H	-3.60727	-1.48217	-1.70551
H	-4.34230	-2.09461	-0.19778
C	-2.42290	0.67635	-0.58482
C	-1.46729	-0.40728	-0.08288
H	-4.65854	0.56896	-0.31883
H	-1.70942	-2.62774	-0.10751
H	-1.60166	-1.21940	2.19388
H	-3.48648	0.69699	2.03273
C	-2.19323	2.03078	-0.61638
N	-2.01955	3.18465	-0.71002
C	-0.00219	-0.29581	-0.04328
C	0.61239	0.87159	0.42021
C	0.80508	-1.34688	-0.48640
C	1.99302	0.97581	0.44649
H	0.00528	1.69579	0.77379
C	2.18601	-1.22905	-0.46888
H	0.35416	-2.25541	-0.86702
C	2.79819	-0.07075	0.00100
H	2.46725	1.87685	0.81456
H	2.80930	-2.04008	-0.82327
C	4.32345	0.05006	0.02455
O	4.79397	1.11170	0.49323
O	4.96917	-0.92343	-0.42709

Table S1: Energy barriers for the thermal back-reaction and the corresponding storage energy calculated at the CAM-B3LYP/6-311+G(d) level of theory in vacuum and in methanol solution.

	Vacuum	Solution
$\Delta H_{\text{QC} \rightarrow \text{NBD, gas}}^{\ddagger}$ [kcal/mol]	39.1	38.2
$\Delta G_{\text{QC} \rightarrow \text{NBD, gas}}^{\ddagger}$ [kcal/mol]	39.6	38.3
$\Delta H^{\text{storage}}$ [MJ/kg]	0.48	0.41
$\Delta G^{\text{storage}}$ [MJ/kg]	0.46	0.41

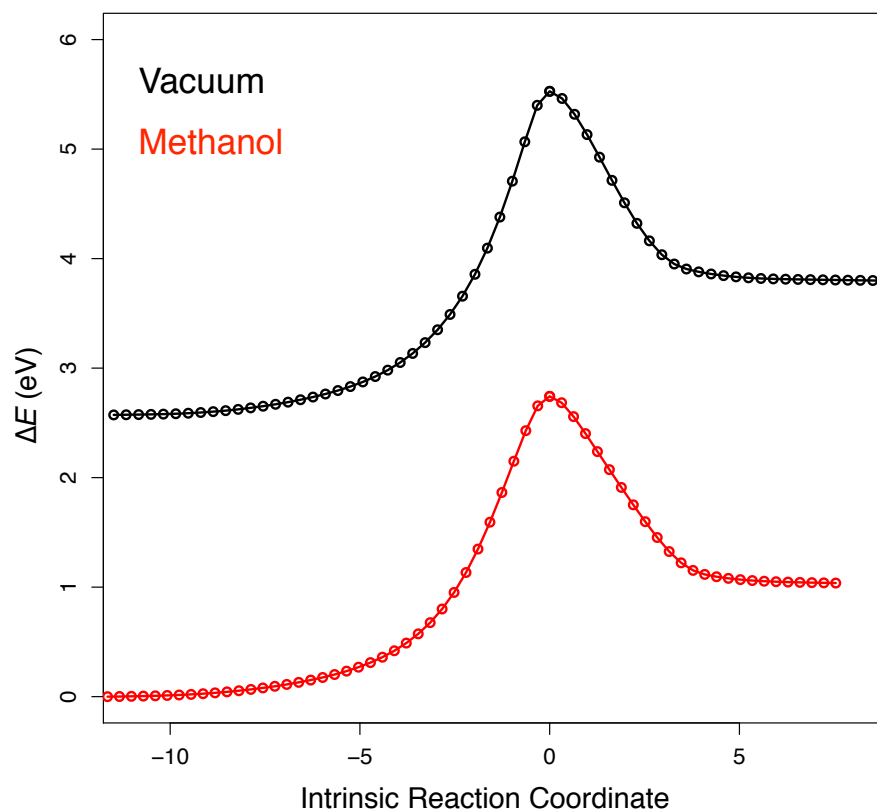


Figure S1: IRC calculations at the CAM-B3LYP/6-311+G(d) level of theory for conversion of NBD carboxylate (left) to QC carboxylate (right). Energies are relative to the NBD carboxylate isomer in methanol.

Simulating UV-Vis Spectra

In this section, we describe the methods used to simulate the UV-Vis spectra of NBD carboxylate. The spectrum is simulated assuming the bands can be represented by Gaussian functions with intensities proportional to the oscillator strengths. Thus, the UV-Vis spectra can be plotted as the extinction coefficient, ϵ , versus the wavelength, λ , using the following equation¹⁶

$$\epsilon(\lambda) = \sum_{i=1}^n \epsilon_i(\lambda) = \sum_{i=1}^n k \cdot \frac{f_i}{\Delta\tilde{\nu}_{1/2}} \cdot \exp \left[-4 \cdot \ln(2) \cdot \left(\frac{\frac{1}{\lambda} - \frac{1}{\lambda_i}}{\Delta\tilde{\nu}_{1/2} \cdot 10^{-7}} \right)^2 \right], \quad (1)$$

where f_i is the calculated oscillator strength, λ_i is the corresponding wavelength in nm, and $\Delta\tilde{\nu}_{1/2}$ is the full width at half maximum of the Gaussian band (in these simulations $\Delta\tilde{\nu}_{1/2} = 0.4 \text{ eV} = 0.4 \cdot 8065.54 \text{ cm}^{-1} = 3226.22 \text{ cm}^{-1}$). Furthermore, the constant k is given by

$$k = \frac{N_A \cdot e^2}{2 \cdot m_e \cdot c^2 \cdot \epsilon_0 \cdot \ln(10)} \cdot \sqrt{\frac{\ln(2)}{\pi}} = 2.1751 \cdot 10^8 \frac{L}{\text{mol} \cdot \text{cm}^2} \quad (2)$$

where N_A is Avogadro's constant, c is the speed of light, e is the elementary charge, m_e is the mass of an electron, and ϵ_0 is the vacuum permittivity.

Figure S2 shows the calculated UV-Vis spectra of the NBD-QC carboxylate system using TD-DFT at the CAM-B3LYP/6-311+G(d) level of theory in both vacuum and a dielectric medium of methanol. The black solid line shows that a fairly strong low-energy transition of NBD carboxylate in vacuum occurs at $\lambda=317 \text{ nm}$, while this transition is blue-shifted by 14 nm in methanol (red dashed line). For the QC carboxylate in vacuum (blue solid line), the first strong electronic transition occurs at $\lambda=220 \text{ nm}$, whereas the first strong electronic transition of QC carboxylate in methanol (green dashed line) is red-shifted by 12 nm.

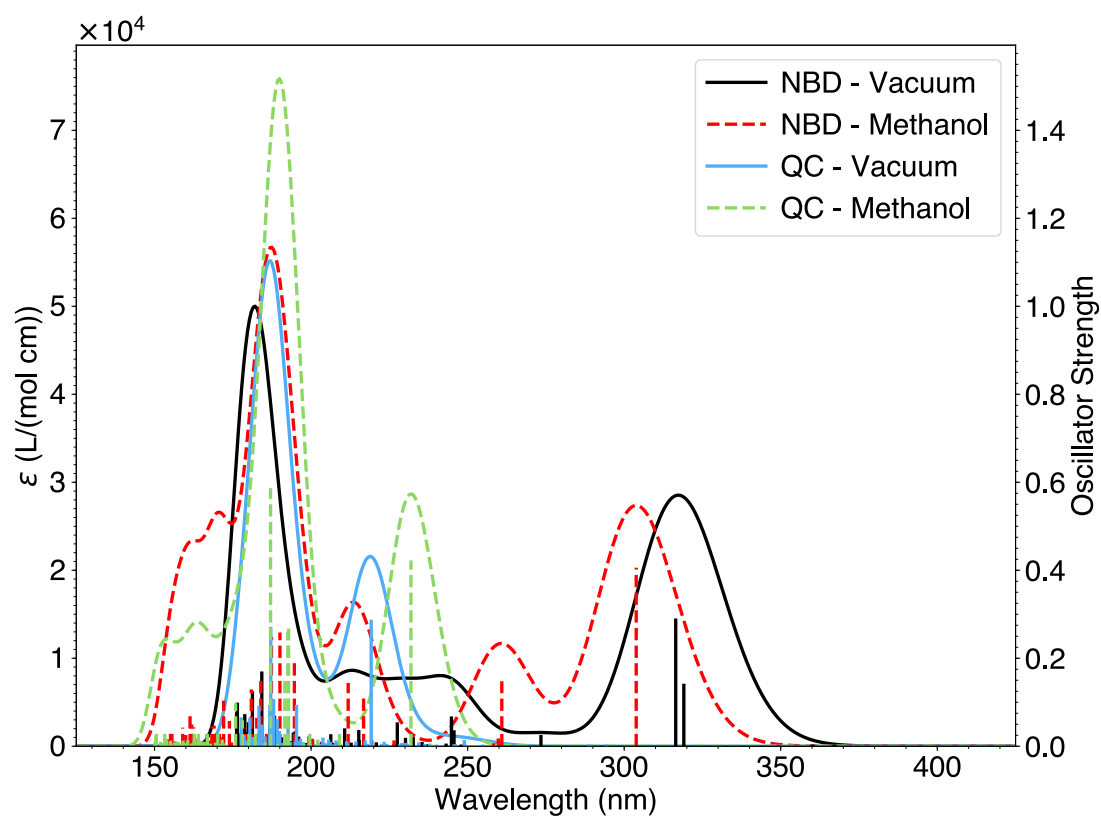


Figure S2: Calculated UV-Vis spectra of the NBD and QC carboxylate using TD-DFT at the CAM-B3LYP/6-311+G(d) level of theory in vacuum and in a methanol dielectric medium.

References

- (1) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H. et al. Gaussian 16 Revision A.03. 2016; Gaussian Inc. Wallingford CT.
- (2) Yanai, T.; Tew, D. P.; Handy, N. C. A new hybrid exchange–correlation functional using the Coulomb-attenuating method (CAM-B3LYP). *Chem. Phys. Lett.* **2004**, *393*, 51–57.
- (3) Hehre, W. J.; Ditchfield, R.; Pople, J. A. Self-consistent molecular orbital methods. XII. Further extensions of Gaussian-type basis sets for use in molecular orbital studies of organic molecules. *J. Chem. Phys.* **1972**, *56*, 2257–2261.
- (4) Binkley, J. S.; Pople, J. A.; Hehre, W. J. Self-consistent molecular orbital methods. 21. Small split-valence basis sets for first-row elements. *J. Am. Chem. Soc.* **1980**, *102*, 939–947.
- (5) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. Self-consistent molecular orbital methods. XX. A basis set for correlated wave functions. *J. Chem. Phys.* **1980**, *72*, 650–654.
- (6) Kuisma, M. J.; Lundin, A. M.; Moth-Poulsen, K.; Hyldgaard, P.; Erhart, P. Comparative ab-initio study of substituted norbornadiene-quadracyclane compounds for solar thermal storage. *J. Phys. Chem. C* **2016**, *120*, 3635–3645.
- (7) Quant, M.; Lennartson, A.; Dreos, A.; Kuisma, M.; Erhart, P.; Börjesson, K.; Moth-Poulsen, K. Low molecular weight norbornadiene derivatives for molecular solar-thermal energy storage. *Chem. Eur. J.* **2016**, *22*, 13265–13274.
- (8) Jorner, K.; Dreos, A.; Emanuelsson, R.; Bakouri, O. E.; Galván, I. F.; Börjesson, K.; Feixas, F.; Lindh, R.; Zietz, B.; Moth-Poulsen, K. et al. Unraveling factors leading to

- efficient norbornadiene–quadricyclane molecular solar-thermal energy storage systems. *J. Mater. Chem. A* **2017**, *5*, 12369–12378.
- (9) Jevric, M.; Petersen, A. U.; Mansø, M.; Kumar Singh, S.; Wang, Z.; Dreos, A.; Sumby, C.; Nielsen, M. B.; Börjesson, K.; Erhart, P. et al. Norbornadiene-based photo-switches with exceptional combination of solar spectrum match and long-term energy storage. *Chem. Eur. J.* **2018**, *24*, 12767–12772.
- (10) Mansø, M.; Kilde, M. D.; Singh, S. K.; Erhart, P.; Moth-Poulsen, K.; Nielsen, M. B. Dithiafulvene derivatized donor–acceptor norbornadienes with redshifted absorption. *Phys. Chem. Chem. Phys.* **2019**, *21*, 3092–3097.
- (11) O'Boyle, N. M.; Banck, M.; James, C. A.; Morley, C.; Vandermeersch, T.; Hutchison, G. R. Open Babel: An open chemical toolbox. *J. Cheminformatics* **2011**, *3*, 33–47.
- (12) Kabsch, W. A solution for the best rotation to relate two sets of vectors. *Acta Cryst. A* **1976**, *32*, 922–923.
- (13) Kromann, J. C.; Bratholm, L. Calculate root-mean-square deviation (RMSD) of two molecules using rotation. <http://github.com/charnley/rmsd>, 2013.
- (14) Miertuš, S.; Scrocco, E.; Tomasi, J. Electrostatic interaction of a solute with a continuum. A direct utilization of ab initio molecular potentials for the prevision of solvent effects. *Chem. Phys.* **1981**, *55*, 117–129.
- (15) Cancès, E.; Mennucci, B.; Tomasi, J. A new integral equation formalism for the polarizable continuum model: Theoretical background and applications to isotropic and anisotropic dielectrics. *J. Chem. Phys.* **1997**, *107*, 3032–3041.
- (16) Serr, A.; O'Boyle, N. M. Convoluting UV-Vis spectra using oscillator strengths. http://gausssum.sourceforge.net/GaussSum_UVVis_Convolution.pdf, 2009.