

3-Pyrenylacrylates: Synthetic, Photophysical, Theoretical and Electrochemical Investigations

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Supporting Information

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Methods

DPV studies were performed at room temperature in dry DMF under Argon atmosphere in the presence of tetrabutylammonium tetrafluoroborate (0.1 mol L^{-1}) as conducting salt using an Autolab (PGSTAT 302N, Eco Chemie). Working electrode was a platinum disk electrode (Eco Chemie, $d = 2\text{mm}$), the counter electrode a laboratory-made Pt plate electrode. Via 3 M KCl salt bridge the reference electrode Ag/AgCl/3 M KCl (Sensortechnik Meinsberg GmbH) was connected. All in this paper mentioned potentials were measured with regard to this reference system and were checked by using the ferrocen/ferrocenium internal reference system. The CV scans were done three times at a scan rate of 25 mV s^{-1} . The differential pulse voltammograms were performed in oxidative and in reductive direction with a scan rate of 5 mV s^{-1} (step potential 2.5 mV , modulation amplitude 25 mV , modulation time 0.05 s , interval time 0.5 s). Concentrations of 1 mmol L^{-1} analyt were used for the measurements.

Theoretical calculations The optimization of the structures and electrostatic potential surface were calculated with the 6-31g* basis sets and the Becke3LYP density functional method^{1, 2} by using the GAUSSIAN-09 Package.³ For B3LYP method the Becke-3 parameter gradient corrected exchange functional is combined with the gradient-corrected correlation LYP functional by Lee, Yang and Parr. No imaginary frequencies were found indicating that all geometries represent at least local minimum structures on the potential energy surface. The calculation of the 30 electron transition states requires the solutions of the time dependent Schrödinger equations and was carried out by using the time dependent density functional theory (TD-DFT) method with the B3LYP functional. Orbitals and energies, atomic charges, vibrational modes and thermodynamic properties were chosen as output parameters. HOMO and LUMO orbital surfaces and electrostatic potential density maps then obtained from the output. Additionally we calculated the natural atomic charges by applying the NBO program as implemented in Gaussian 09.^{3, 4} All calculations have been carried out on the HPPC-Cluster in Rostock.

Solvatochromic spectra

Definition of the solvatochromic parameters of Kamlet and Taft

The description is made based on the Kamlet-Taft LSE (linear solvation energy) equation (1):

$$XYZ = XYZ_0 + a \alpha + b \beta + s(\pi^* + d \delta) \quad (1)$$

XYZ: band parameter where solvatochromatism takes place

XYZ₀: band parameter where solvatochromatism does not take place

a, b, d, s: solvent-independent coefficients which reflect the susceptibility of the polarity terms upon XYZ

π^* : polarity/polarisability

α : hydrogen bond donor (HBD) ability

β : hydrogen bond acceptor (HBA) ability

δ : polarisability correction term (1.0 for aromatic, 0.5 for polyhalogenated and zero for nonchlorinated aliphatic solvents)

α and β give the opportunity to distinguish between solvent-to-solute and solute-to-solvent hydrogen bonds.

Thus, except for dichloromethane is $\delta = 0$ and the coefficient *d* is mostly zero or finite negative. Hence a simplified equation can be used (2):

$$XYZ = XYZ_0 + a \alpha + b \beta + s \pi^* \quad (2)$$

Selected solvent properties

Table S1. Selected solvent properties.

solvent	Polarity	HBD	HBA	Dielectric constant	Dipole moment
	π^*	α	β	E	D
<i>n</i> -Hexane	-0.08	0.00	0.00	1.89	—
Ethyl acetate	0.55	0.19	0.45	6.02	1.78
Dioxane	0.55	0.00	0.37	2.21	0.45
Tetrahydrofurane	0.58	0.00	0.55	7.50	1.75
Dichloromethane	0.82	(0.30)	0.00	8.93	1.60
Dimethylformamide	0.88	0.00	0.76	36.70	3.82
Acetonitrile	0.75	0.00	0.35	37.50	3.92
Dimethylsulfoxide	1.00	0.00	0.76	46.68	3.96

Theoretical calculations

Table S2. The B3LYP/6-31g* optimized geometries, the Cartesian coordinates are given in Å.

Atom	<i>x</i>	<i>y</i>	<i>z</i>
C	-3.708593	3.02529	-0.215918
C	-2.874864	1.895295	-0.258177
C	-3.427547	0.606548	0.005429
C	-4.822362	0.486853	0.295281
C	-5.616564	1.644279	0.33019
C	-5.06401	2.898949	0.078492
C	-5.368126	-0.818541	0.539142
C	-4.582217	-1.929062	0.492648
C	-3.178334	-1.837943	0.209725
C	-2.594277	-0.554748	-0.025506
C	-1.191078	-0.432184	-0.290293
C	-0.380399	-1.604369	-0.282293
C	-1.003617	-2.855706	-0.108965
C	-2.360286	-2.976592	0.14272
C	-1.483101	1.979898	-0.587911
C	-0.684631	0.875718	-0.606681
C	1.076892	-1.635658	-0.422397
C	1.998914	-0.73419	-0.029535
C	3.434894	-1.022828	-0.227681
O	4.196781	-0.00943	0.254485
C	5.623666	-0.176057	0.121817
C	6.308184	1.081397	0.651874
C	5.917746	2.324542	-0.159083
O	3.899377	-2.021313	-0.746839
C	7.829452	0.871317	0.663303
H	-2.800468	-3.958505	0.296809
H	-0.38638	-3.749861	-0.141067
H	1.480049	-2.55779	-0.841548
H	-5.007292	-2.913531	0.67208
H	0.351628	0.976894	-0.90264
H	-6.429756	-0.902827	0.758294
H	1.752191	0.193953	0.472406
H	-6.675975	1.550596	0.556041
H	-1.070191	2.952921	-0.843225
H	-5.695258	3.782788	0.108797
H	-3.282163	4.004481	-0.419478
H	5.865743	-0.351871	-0.933175
H	5.926975	-1.067394	0.682504
H	5.970484	1.223341	1.688389
H	8.339035	1.751463	1.070618
H	8.21335	0.706794	-0.351745
H	8.114421	0.00629	1.273824

H	6.38157	3.225174	0.259267
H	4.833216	2.468996	-0.163301
H	6.251104	2.230761	-1.201093

Table S3. The 30 electron transition states of product **3d**, calculated on TD B3-LYP / 6-31g* level of theory.

Band	State	λ (nm)	f
1L_a	1	391.43	0.519
	2	348.12	0.029
1B_b	3	303.00	0.028
	4	294.01	0.002
	5	290.15	0.003
	6	285.49	0.328
	7	279.60	0.023
	8	266.10	0.187
1B_a	9	249.21	0.007
	10	241.77	0.023
	11	236.66	0.009
	12	230.97	0.045
	13	228.91	0.123
	14	225.70	0.037
	15	223.26	0.465
	16	220.89	0.049
	17	216.85	0.055
II	18	213.88	0.004
	19	212.20	0.003
	20	210.10	0.013
	21	207.17	0.018
	22	205.00	0.037
	23	203.42	0.116
	24	200.68	0.077
	25	197.79	0.024
	26	197.30	0.004
	27	196.29	0.085
	28	190.16	0.228
	29	189.83	0.016
	30	189.13	0.003

Table S4. Fragment of the NBO donor acceptor interactions, calculated by 2nd order perturbation theory analysis of Fock matrix in NBO basis.

Donor	Acceptor	kcal mol ⁻¹
BD (1) C 17 - C 18	RY*(2) C 12	1.78
BD (1) C 17 - C 18	RY*(1) C 19	2.36
BD (1) C 17 - C 18	BD*(1) C 12 - C 13	1.36
BD (1) C 17 - C 18	BD*(1) C 12 - C 17	2.79
BD (1) C 17 - C 18	BD*(1) C 17 - H 28	1.49
BD (1) C 17 - C 18	BD*(1) C 18 - C 19	1.63
BD (1) C 17 - C 18	BD*(1) C 18 - H 32	1.92
BD (1) C 17 - C 18	BD*(1) C 19 - O 20	1.72
BD (2) C 17 - C 18	RY*(3) C 12	0.72
BD (2) C 17 - C 18	RY*(6) C 19	0.62
BD (2) C 17 - C 18	BD*(1) C 11 - C 12	0.71
BD (2) C 17 - C 18	BD*(2) C 11 - C 12	8.91
BD (2) C 17 - C 18	BD*(1) C 12 - C 13	0.6
BD (2) C 17 - C 18	BD*(1) C 16 - H 30	0.59
BD (2) C 17 - C 18	BD*(2) C 19 - O 24	21.13

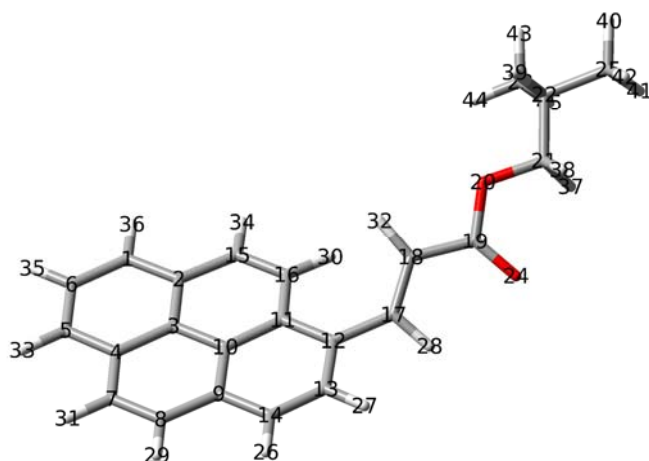


Figure S1. Numeration of the atoms in **3d**.

Literature

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- ⁴ NBO Version 3.1, E. D. Glendening, A. E. Reed, J. E. Carpenter, and F. Weinhold.