Electronic Supplementary Information (ESI)

Methods and Computational Procedures

All molecular structures were determined with the B3LYP/6-311G(d,p) method[1] without any symmetry constraints. The solvent or crystalline environments were simulated by the dielectric continuum standard PCM method[2] with chloroform (dielectric constant 4.9) and acetonitrile (dielectric constant 36.64) as the dielectric media.

The NMR isotropic shieldings were calculated with the B3LYP and PBE1[3] functional using the 6-311++g(d,p) basis sets. The chemical shifts were obtained using tetramethylsilane for ^{1}H and ^{13}C, and nitromethane for ^{15}N as references. The molecular structures of these reference molecules were obtained with the method used to obtain the NMR results. The NICS (nucleus-independent chemical shifts) indices were calculated using a ghost nucleus placed at the center of each ring.

The electronic transitions were computed with the INDO/S-CIS method[4] with the transition energies and oscillator strengths being used to fit a Lorentzian line shape (30 nm half height width) to generate the spectra[5]. The INDO/S-CIS calculations employed 800 configurations generated by single replacements within the 20 highest and the 20 lowest energy molecular orbitals. All DFT calculations were performed with the Gaussian 03 program[6] and the INDO/S calculations with the ZINDO program[7].

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[1] A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648; C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785; P. J. Stephens, F. J. Devlin, C. F. Chabalowski and M. J. Frisch, *J. Phys. Chem.*, 1994, **98**, 11623.

[2] S. Miertus, E. Scrocco and J. Tomasi, *Chem. Phys.*, 1981, **55**, 117.

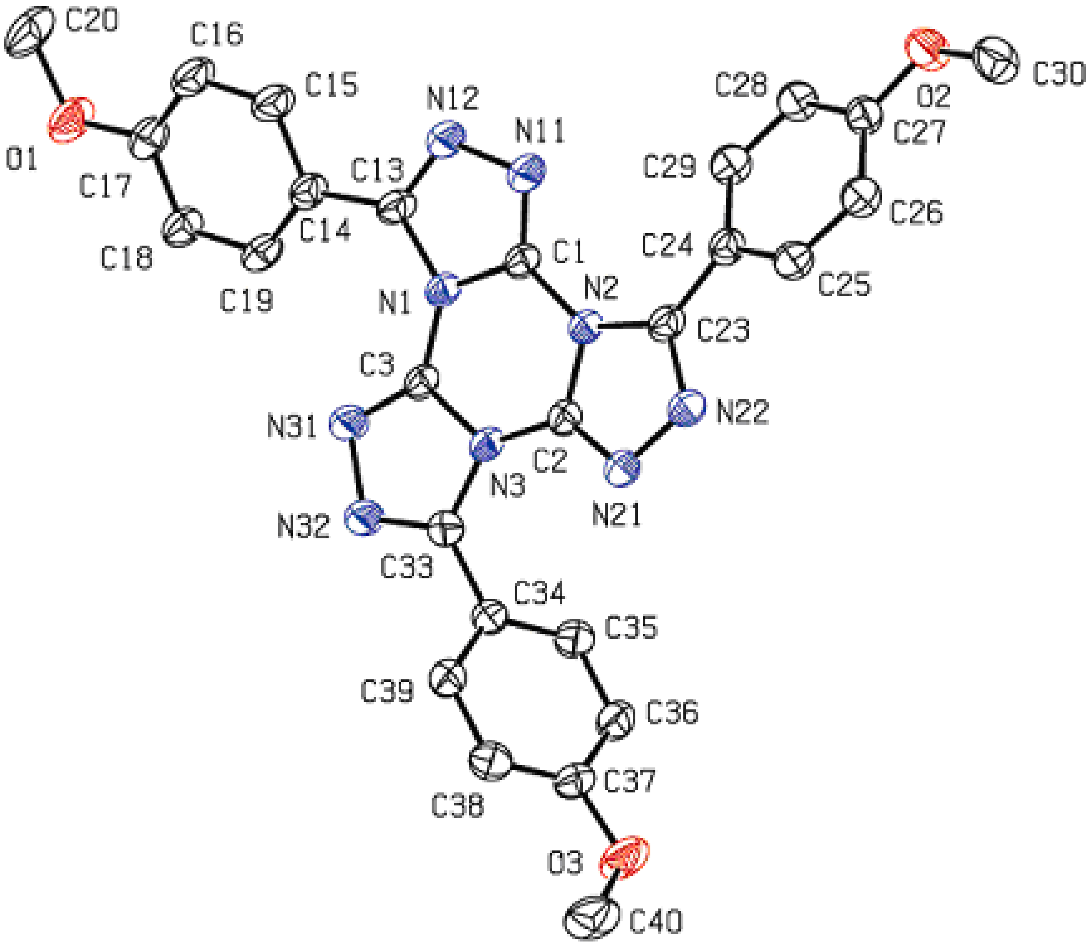
[3] J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1997, **78**, 1396.

[4] J. Ridley, M. C. Zerner, *Theor. Chim. Acta*, 1973, **32**, 111; M. C. Zerner, G. H. Loew, R. F. Kichner, U. T. Mueller-Westerhoff, *J. Am. Chem. Soc.*, 1980, **102**, 589.

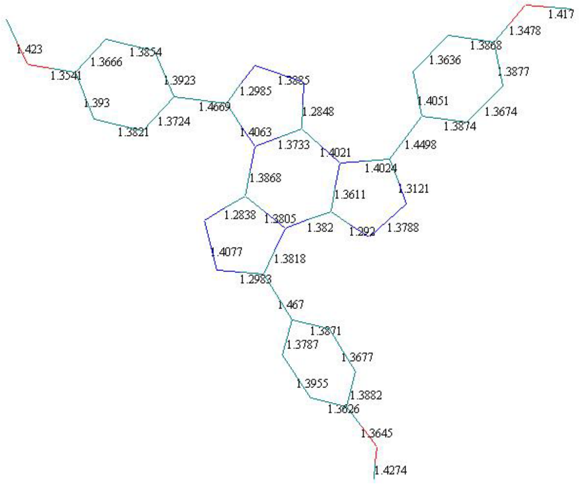
[5] A. V. M. de Andrade, R. L. Longo, A. M. Simas and G. F. de Sá, *J. Chem. Soc., Faraday Trans.*, 1996, **92**, 1835.

[6] Gaussian 03, Revision C.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, Gaussian, Inc., Pittsburgh PA, 2003.

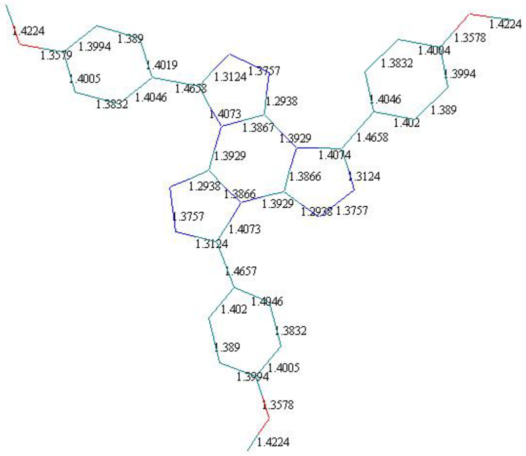
[7] M. C. Zerner, *ZINDO Manual*, Department of Chemistry, Quantum Theory Project, University of Florida, Gainesville, FL, 1990.



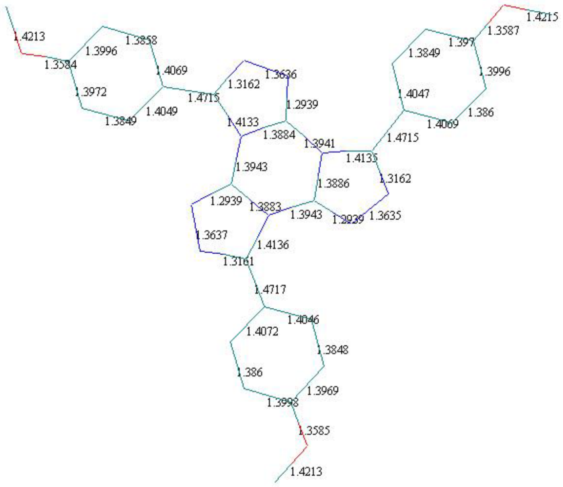
Crystallographic structure and atomic numbering.



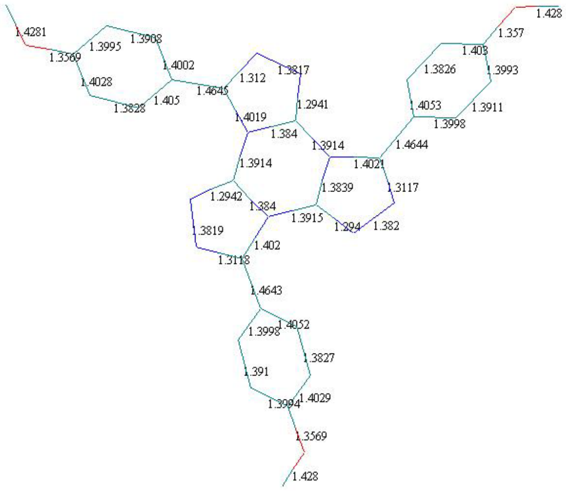
Distances in the crystallographic structure.



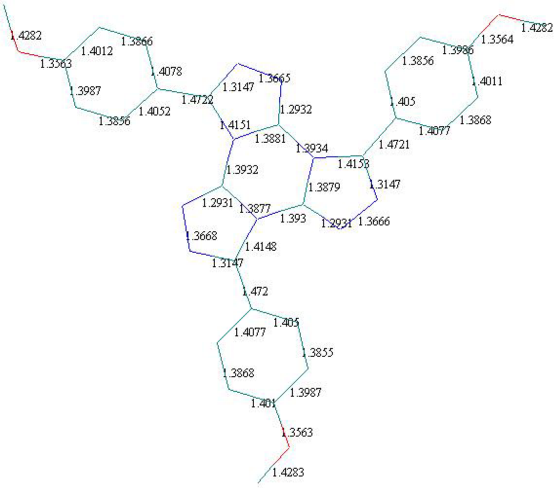
Distances in the isolated optimized structure at the B3LYP/6-311G(d,p) level. In the optimized structure, the dihedral angles are nearly equal, namely, N12-C13-C14-C15 ≈ N22-C23-C24-C25 ≈ N32-C33-C34-C35 ≈ –26.5°.



Distances in the isolated optimized structure at the B3LYP/6-311G(d,p) level. The dihedral angles are nearly planar.



Distances in the optimized structure at the B3LYP/6-311G(d,p) level in chloroform simulated by the PCM method. The dihedral angles are nearly equal, namely, N12-C13-C14-C15 ≈ N22-C23-C24-C25 ≈ N32-C33-C34-C35 ≈ –35°.



Distances in the optimized structure at the B3LYP/6-311G(d,p) level in chloroform simulated by the PCM method. The dihedral angles are nearly planar.

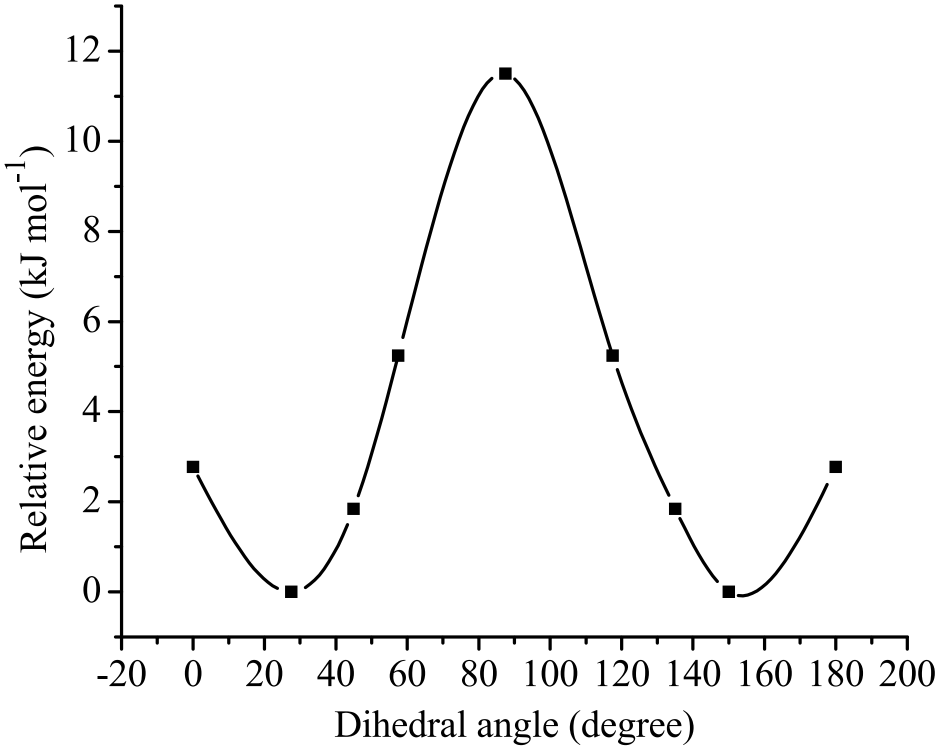
Bond lengths [Å], angles [°] and dihedral angles [°]. Molecular properties: relative energies (ΔE) in kJ mol^{-1} and dipole moments (μ) in D. Calculations at B3LYP/6-311G(d,p) level.

	X-ray	X-ray conformations	Non-planar conformations	Planar conformations
ΔE (isolated)	--	7.1	0.0	6.6
ΔE (chloroform)	--	6.6	0.0	15.5
ΔE (acetonitrile)	--	6.3	0.0	20.3
μ (isolated)	--	2.01	1.84	0.02
C1-N11	1.285(4)	1.293	1.294	1.294
C1-N1	1.373(3)	1.393	1.387	1.388
C1-N2	1.403(3)	1.395	1.393	1.394
N1-C3	1.387(3)	1.396	1.393	1.394
N1-C13	1.406(3)	1.412	1.407	1.413
C2-N21	1.292(3)	1.292	1.294	1.294
C2-N2	1.361(3)	1.385	1.387	1.388
C2-N3	1.382(3)	1.389	1.393	1.394
N2-C23	1.402(3)	1.412	1.407	1.413
C3-N31	1.284(3)	1.297	1.294	1.294
C3-N3	1.381(3)	1.381	1.387	1.388
N3-C33	1.382(4)	1.399	1.407	1.413
N11-N12	1.389(3)	1.370	1.376	1.363
N12-C13	1.298(4)	1.314	1.312	1.316
C13-C14	1.467(4)	1.469	1.466	1.471
C14-C19	1.373(4)	1.405	1.404	1.405
C14-C15	1.393(4)	1.405	1.402	1.406
C15-C16	1.386(4)	1.387	1.389	1.386
C16-C17	1.366(4)	1.400	1.399	1.399
C17-O1	1.354(3)	1.358	1.358	1.358
C17-C18	1.394(4)	1.399	1.400	1.397
C18-C19	1.382(4)	1.385	1.383	1.385
O1-C20	1.422(4)	1.423	1.422	1.421
N21-N22	1.379(3)	1.374	1.376	1.363
N22-C23	1.312(4)	1.314	1.312	1.316
C23-C24	1.450(4)	1.467	1.466	1.471
C24-C25	1.388(4)	1.404	1.402	1.407
C24-C29	1.405(4)	1.405	1.404	1.405
C25-C26	1.368(4)	1.388	1.389	1.386
C26-C27	1.387(4)	1.399	1.399	1.399
C27-O2	1.348(3)	1.358	1.358	1.358
C27-C28	1.387(4)	1.399	1.400	1.397
C28-C29	1.363(4)	1.384	1.383	1.384
O2-C30	1.418(4)	1.423	1.422	1.421
N31-N32	1.408(3)	1.380	1.376	1.363
N32-C33	1.299(4)	1.309	1.312	1.316
C33-C34	1.467(4)	1.468	1.466	1.471
C34-C39	1.378(4)	1.395	1.402	1.407
C34-C35	1.388(4)	1.403	1.404	1.405

C35-C36	1.368(4)	1.382	1.383	1.385
C36-C37	1.388(4)	1.402	1.400	1.397
C37-C38	1.362(4)	1.398	1.399	1.399
C37-O3	1.365(3)	1.358	1.358	1.358
C38-C39	1.396(4)	1.392	1.389	1.385
O3-C40	1.428(4)	1.422	1.422	1.421
N11-C1-N1	113.2(2)	111.5	111.7	111.2
N11-C1-N2	127.9(3)	129.3	129.9	129.5
N1-C1-N2	118.9(2)	119.2	118.4	119.2
C1-N1-C3	121.7(2)	120.9	121.5	120.8
C1-N1-C13	102.8(2)	103.4	103.5	103.7
C3-N1-C13	135.1(2)	135.5	134.7	135.4
N21-C2-N2	113.0(2)	112.4	111.7	111.2
N21-C2-N3	128.6(3)	129.4	129.9	129.5
N2-C2-N3	118.3(2)	118.1	118.4	119.2
C2-N2-C23	104.0(2)	103.1	103.5	103.7
C2-N2-C1	120.5(2)	120.9	121.5	120.8
C23-N2-C1	134.3(2)	135.7	134.7	135.5
N31-C3-N3	111.5(2)	111.2	111.7	111.3
N31-C3-N1	131.4(2)	130.9	129.9	129.5
N3-C3-N1	117.0(2)	117.9	1183	119.2
C3-N3-C33	104.1(2)	104.0	103.5	103.7
C3-N3-C2	122.6(2)	122.8	121.5	120.8
C33-N3-C2	132.2(2)	133.0	134.6	135.4
C1-N11-N12	105.5(2)	107.0	106.7	107.2
C13-N12-N11	109.9(2)	110.2	109.9	110.3
N12-C13-N1	108.6(2)	107.8	108.2	107.4
N12-C13-C14	121.7(2)	121.4	112.6	120.6
N1-C13-C14	129.7(3)	130.7	129.2	131.9
C19-C14-C15	118.9(3)	118.0	118.4	117.7
C19-C14-C13	126.4(2)	125.9	124.6	136.6
C15-C14-C13	114.7(3)	116.1	116.8	115.6
C16-C15-C14	120.6(3)	121.5	121.3	121.7
C17-C16-C15	120.0(3)	119.8	119.6	119.8
O1-C17-C16	124.9(3)	124.7	124.7	124.8
O1-C17-C18	115.4(3)	116.1	115.9	116.1
C16-C17-C18	119.7(3)	119.2	119.4	119.1
C19-C18-C17	120.1(3)	120.8	120.6	120.9
C14-C19-C18	120.6(3)	120.6	120.5	120.7
C17-O1-C20	118.1(3)	118.7	118.7	118.9
C2-N21-N22	105.2(2)	106.2	106.7	107.2
C23-N22-N21	110.5(2)	110.3	109.9	110.3
N22-C23-N2	107.3(2)	107.9	108.1	107.4
N22-C23-C24	122.4(2)	121.9	122.6	102.6
N2-C23-C24	130.0(2)	130.2	129.3	131.9
C25-C24-C29	117.4(3)	118.1	118.4	117.8
C25-C24-C23	116.9(2)	116.3	116.8	115.7
C29-C24-C23	125.2(3)	125.4	124.7	126.5

C26-C25-C24	121.9(3)	121.5	121.4	121.6
C25-C26-C27	120.3(3)	119.7	119.6	119.7
O2-C27-C28	116.4(2)	116.0	115.9	116.1
O2-C27-C26	125.2(3)	124.7	124.7	124.7
C28-C27-C26	118.5(3)	119.2	119.4	119.1
C29-C28-C27	121.4(3)	120.8	120.6	120.9
C28-C29-C24	120.6(3)	120.6	120.5	120.7
C27-O2-C30	118.5(2)	118.7	118.7	118.7
C3-N31-N32	106.5(2)	107.0	106.7	107.2
C33-N32-N31	108.2(2)	109.2	109.9	110.3
N32-C33-N3	109.6(2)	108.5	108.2	107.4
N32-C33-C34	126.4(3)	125.0	122.6	120.6
N3-C33-C34	123.9(2)	126.4	129.2	131.9
C39-C34-C35	119.3(3)	118.9	118.4	117.8
C39-C34-C33	120.5(3)	118.9	116.8	115.5
C35-C34-C33	120.2(3)	122.3	124.6	126.6
C36-C35-C34	120.3(3)	120.5	120.5	120.7
C35-C36-C37	120.1(3)	120.3	120.6	120.9
C38-C37-O3	124.9(3)	124.7	124.7	124.7
C38-C37-C36	120.4(3)	119.7	119.4	119.1
O3-C37-C36	114.7(3)	115.6	115.9	116.1
C37-C38-C39	119.5(3)	119.5	119.6	119.8
C34-C39-C38	120.4(3)	121.0	121.3	121.6
C37-O3-C40	117.9(3)	118.7	118.7	118.6
N12-C13-C14-C15	–14.8	–13.2[a]	–26.4	–0.1
N22-C23-C24-C25	–18.4	–18.3[a]	–26.4	–1.7
N32-C33-C34-C35	122.5	122.8[a]	148.9	179.5
C16-C17-O1-C20	–2.0	0.1	0.1	0.9
C26-C27-O2-C30	–2.3	0.5	0.2	0.9
C36-C37-O3-C40	172.0	179.6	179.9	–179.2

[a] Dihedral angles kept fixed at these values.



Conformational analysis of the N3-C33-C35-C35, with the dihedral angles N12-C13-C14-C15 and N2-C23-C24-C29 kept at near 0°.

NMR spectra.

The ^{1}H-, ^{13}C- and ^{15}N-NMR chemical shifts were calculated with the PBE1/6-311++g(d,p) method for both planar and non-planar conformations and with the B3LYP/6-311++g(d,p) method for the planar conformations. The chemical shifts of the magnetically equivalent nuclei were obtained from the average isotropic shieldings of each nucleus. For the non-planar conformations, the largest difference for the equivalent carbons was 9.6ppm between the C16-C26-C36 and C18-C28-C38 groups. The other carbon nuclei were equivalent within 0.8ppm, the ^{1}H and ^{15}N nuclei were equivalent within 0.5 and 0.9ppm, respectively. PBE1PBE/6-311++G(d,p) NMR calculation[8] yielded chemical shifts in close agreement with the experimental spectra and were employed in the complete spectral assignments, including the very negative chemical shift associated with N1, N2 and N3. Also, the calculated results for the non-planar conformations are in better overall agreement with the experimental spectra than the planar ones. Solvent effects were taken into account via the polarization continuum model (PCM)[9] and, as expected, the stability of the non-planar conformations increased from 6.6 in vacuum to 15.5 and 20.3 kJ mol^{-1} in chloroform and acetonitrile, respectively.

Experimental and calculated ^{1}H-, ^{13}C- and ^{15}N-NMR chemical shifts (ppm). The calculations used the 6-311++g(d,p) basis sets.

		Non-planar	Planar	
Nuclei	Experimental	PBE1	PBE1	B3LYP
C1-C2-C3	142.4	141.0	141.6	142.6
C13-C23-C33	149.7	152.6	153.3	154.4
C14-C24-C34	117.4	118.1	118.8	120.0
C15-C25-C35-C19-C29-C39	132.2	134.3	134.3	134.5
C16-C26-C36-C18-C28-C38	114.6	112.6	113.2	113.4
C17-C27-C37	162.2	163.9	163.9	165.4
C20-C30-C40	56.2	50.8	50.6	51.2
H15-H25-H35-H19-H29-H39	7.96-7.94	8.9	10.2	10.2
H16-H26-H36-H18-H28-H38	7.20-7.18	7.1	7.1	7.1
H20-H30-H40	3.88-3.34	3.7	3.7	3.8
N1-N2-N3	–226.64	–232.2	–232.0	–233.0
N11-N12-N13	–99.76	–88.8	–87.7	–87.7
N12-N22-N32	–69.18	–60.0	–65.1	–63.6

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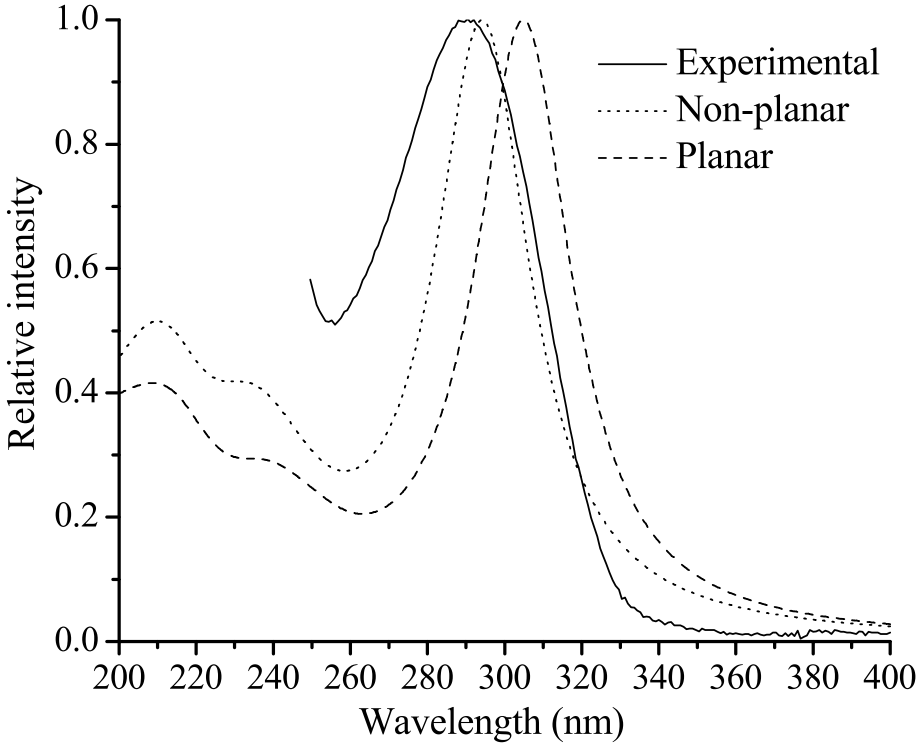
[8] J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1997, **78**, 1396.

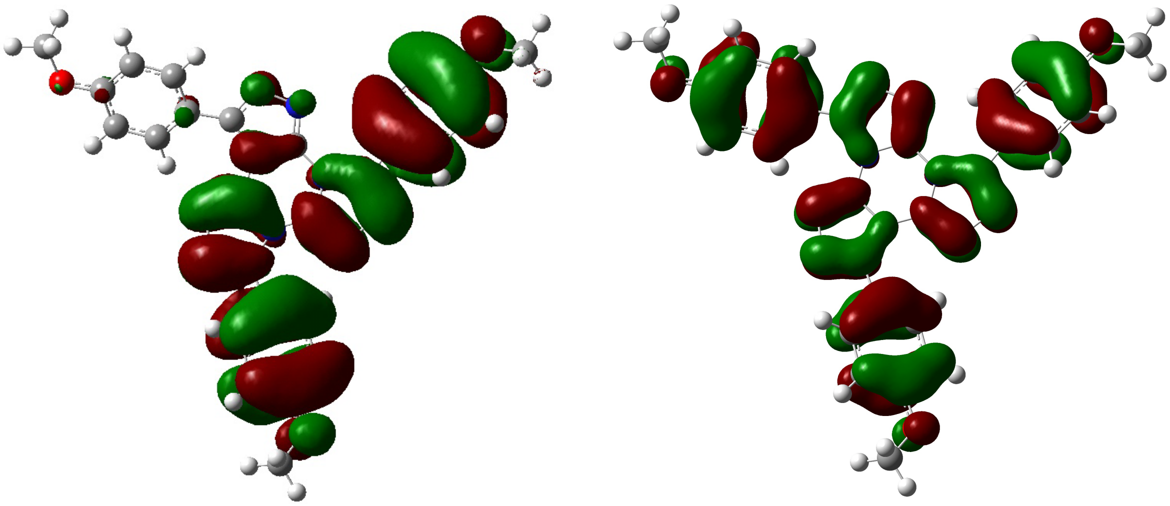
[9] S. Miertus, E. Scrocco and J. Tomasi, *Chem. Phys.*, 1981, **55**, 117.

Electronic spectra.

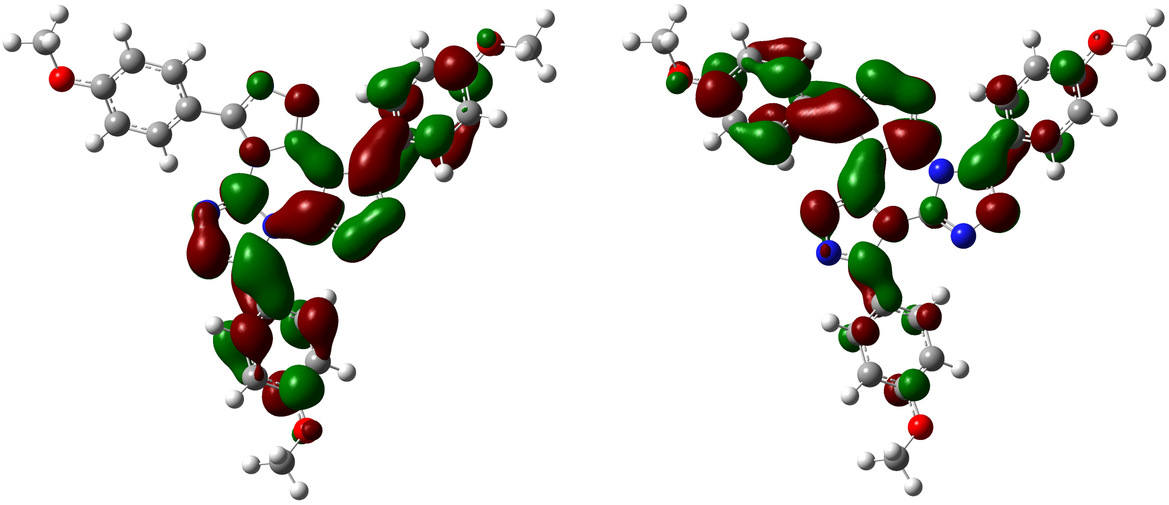
The electronic spectra for the non-planar and planar conformations were calculated with the INDO/S-CIS method with its standard spectroscopic parametrization. For a better comparison with the experimental spectrum the transition energies and oscillator strengths were fitted to a Lorentzian line shape with a 30 nm half height width.



Experimental (line) and calculated (INDO/S-CI) absorption electronic spectra for the non-planar (dotted) and planar (dashed) conformations.


HOMO–1 HOMO

Highest occupied molecular orbitals at the INDO/S level.



LUMO LUMO+1

Lowest unoccupied molecular orbitals at the INDO/S level.