

Supporting Information

Photoisomerization of a 4-dicyanomethylene-2-methyl-6-(*p*-dimethylaminostyryl)-4*H*-pyran analog dye: a combined photophysical and theoretical investigation

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1. Crystallographic data collection, structure determination and refinement

The compound (*E*)-2-(2-(4-((2-azidoethyl)(methyl)amino)styryl)-6-(tert-butyl)-4H-pyran-4-ylidene) malononitrile was obtained in similar red solid forms suitable to Single Crystal X-ray Diffraction analyses. Both crystal forms could be mounted upon a nylon loop with a drop of paratone oil to be irradiated at room temperature using a RIGAKU XtaLabPro diffractometer equipped with a Mo microfocus sealed tube generator coupled to a double-bounce confocal Max-Flux® multilayer optic and a HPAD PILATUS3 R 200K detector. Data collections were carried out using the software *CrysAlisPro 1.171.41.96a*¹. SCALE3 ABSPACK scaling algorithm implemented within *CrysAlisPro* was applied to the processed data for the empirical absorption correction using spherical harmonics. The two structures were readily solved by intrinsic phasing methods (*SHELXT* program)² and refined by full-matrix least-squares methods on F^2 using *SHELXL*.³ One form was refined in the centrosymmetric triclinic space group (**form I**) while the second one crystallized in an orthorhombic unit cell (**form II**). Although the normalized structure factor distribution was in favor of a centrosymmetric structure, the non-centrosymmetric $Pna2_1$ space group, which is consistent with the systematic absences, was first tested to deal with the azido disorder in the course of the structure refinement. The ethyl azido atoms were therefore refined over two sites whose occupancy factors converged to a value close to 0.5 and were thus fixed to half occupancy. However, to ensure satisfactory refinement of that disorder and avoid chemically unreasonable ellipsoids, rigid-body restraints (*SHELXL* commands DELU and SIMU with esd 0.005 and 0.01 Å² respectively) were applied to atoms of the ethylazido group with resort to displacement parameters constrained to be identical (command EADP upon the following pair of atoms C21-C21B, and C22-C22B), as well as similar distance restraints (DFIX, DANG and SADI with esd ranging from 0.001 to 0.01 Å²). If the *checkCIF* implementation of *PLATON*⁴ ADDSYM could not fail to detect the mirror plane instead of 2₁ axis, the refinement of the model after *b-c* axes permutation in the higher symmetry space group *Pnma* with ADDYM-exact worsened the model statistics (see Table S1), the weighting scheme refinement and the electron residuals on both side of the mirror with or without application of ADP or bond length restraints. Nevertheless, the refined model was kept in the holohedral group *Pnma* -whose $Pna2_1$ is an hemihedral subgroup- in link with the molecular geometry, which does not eventually affect the packing structure interaction type analyses. In both cases, anisotropic refinement improved all parameters of non-hydrogen atoms of the molecule of interest. If most of the H atoms were identified in difference maps, methyl H atoms were idealized and included as rigid groups allowed to rotate but not tip and refined with U_{iso} set to 1.5 $U_{eq}(C)$ of the parent carbon atom. All other H atoms bound to carbon atoms were positioned geometrically and refined with U_{iso} set to 1.2 $U_{eq}(C)$ of the parent carbon atom. Both polymorphic crystal structures are shown in Ortep⁵ representation in Figure S1. It has to be noticed that in both crystal forms the *s-trans*-(*E*) configuration was unveiled. The triclinic structure appears slightly the most accurate one with no static disorder. It is made of one conformer in the asymmetric unit, featuring regular geometry parameters except a short terminal triple bond distance of 1.131(2) Å leading to a |Z-score| value of 4.681 after a Mogul⁶ check. Unsurprisingly for such (*E*)-2-(2-styryl-4H-pyran-4-ylidene) malononitrile core as observed in 15 previous hits found in the Cambridge Structural Database⁷ (CSD version 5.42, updated Sep 2021), the DCM platform is indeed quasi-planar in the triclinic form and would be constrained to be lying within the mirror plane

¹ Rigaku OD (2015). *CrysAlis PRO*. Rigaku Oxford Diffraction, Yarnton, Oxfordshire, England.

² Sheldrick, G. M. (2015). *Acta Crystallogr.*, **A71**, 3-8.

³ Sheldrick, G. M. (2015). *Acta Crystallogr.*, **C71**, 3-8.

⁴ Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.

⁵ Burnett, M. N. & Johnson, C. K. (1996). *ORTEP/III*. Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.

⁶ Bruno, I. J., Cole, J. C., Kessler, M., Luo, J., Motherwell, W. D. S., Purkis, L. H., Smith, B. R., Taylor, R., Cooper, R. I., Harris, S. E. & Orpen, A. G. (2004). *J. Chem. Inf. Comput. Sci.* **44**, 2133-2144.

⁷ Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* **B72**, 171–179.

perpendicular to [0 1 0] in the putative *Pnma* orthorhombic space group. This putative mirror bisects the tert-butyl group and the two sites between which the azido-ethyl chain is allowed to swing. In the triclinic form the mean plane is allowed to slightly wave (rmsd of 0.094 Å for 22 atoms and C21 out of the mean plane by 0.62 Å) and the dihedral angle between the two central six-membered rings is 9.6°. More striking structural differences between the two polymorphs are the relative switch of the azidoethyl chain with respect to the pyran-4-ylidene substituents and its conformation which points almost perpendicular to the molecule mean plane in the triclinic form. An overlay of both conformers is shown in Figure S2 to underscore these crystal structure differences. As expected, the molecules are in each form assembled in layers parallel to the (2 1 1) or (1 0 1) plane respectively for the triclinic case and the orthorhombic one. The interplanar distance is slightly longer in the triclinic form (3.6 Å vs 3.54 Å) probably due to the anchorage of azidoethyl chains in-between the layers. Furthermore, in the triclinic packing all the molecules aligned along the [0 1 -1] direction in an anti-parallel manner, both on the top of each other and within the same plane making pairwise non-conventional H-bonds between C4-H4 ... N1 to develop infinite 1D ribbons bordered in the 2D-sheets by van der Waals interactions through tert-butyl groups and adjacent aromatic H atoms, and stacking interactions in the third dimension. In the orthorhombic form, the molecules viewed down the *b* axis pack in a herringbone arrangement, which is staggered from one layer to another one. The relevance of different intermolecular interactions describing the polymorphism can be established *via* Hirshfeld surface (HS) analysis.⁸ These surfaces, along with the two-dimensional fingerprint (FP) plots,⁹ were evaluated using *Crystal Explorer 17.5*.¹⁰ The red spots, corresponding to contacts that are shorter than the van der Waals radii sum of the closest atoms, are observed in few spots in the triclinic HS: two weak ones at the opposite long side of the molecule, the N2 atom and C22-H22B atom whose successive N/H interactions link the molecules in 1D-chain along the [0 1 -1] direction, and two intense ones at C5-H5 and N1 as pairwise interaction location to propagate the 2D network. They are more numerous in the orthorhombic HS (Figure S3) regularly scattered at the periphery of the molecule, involving in particular the nitrogen atoms of the disordered azido group and the acetonitrile groups. The surfaces mapped with curvedness, a function of the root-mean-square curvature of the surface show the large green flat region of the molecule core separated by dark blue edges (large positive curvature). In the triclinic CS, these surfaces are on the top of each other in adjacent asu but the shorter centroid to centroid distance is not below 4.0 Å. In the second form, it is even longer (5 Å) due to shifted overlaps with adjacent molecules in the *b* direction.

The fingerprint plots (Figure S5) depict the various interactions (*All*) in the two polymorphs and the individual contributions of the different interactions, the grey shadow being an outline of the complete fingerprint plot. The upper spike corresponds to the donor, spike with the lower spike representing the acceptor. Significant differences between the molecular interactions in the two polymorphs are reflected in the distribution of scattered points in the fingerprint plots which appeared more condensed in the orthorhombic form region of 1.0 Å-2.4 Å (d_e+d_i) vs 1.0 Å-2.8 Å (d_e+d_i) for the triclinic one. It is observed that the relative contributions of H/H and N/H are comparable in both forms and account for 2/3 of the interactions. It is followed by a significant number of C-H \cdots π or π - π interactions whose proportions differ noticeably between the two forms (13.7 % vs 16.1 % and 9% vs 5%). Another contribution specific to the form II is C/N contacts (3%). Structure refinement statistics are reported in Table S1.

⁸ Spackman, M. A. & Jayatilaka, D. (2009). *CrystEngComm*, **11**, 19–32.

⁹ McKinnon, J. J., Jayatilaka, D. & Spackman, M. A. (2007). *Chem. Commun.* pp. 3814–3816.

¹⁰ Turner, M. J., McKinnon, J. J., Wolff, S. K., Grimwood, D. J., Spackman, P. R., Jayatilaka, D. & Spackman, M. A. (2017). *CrystalExplorer17*. University of Western Australia. <http://hirshfeldsurface.net>.

CCDC 2120494 and 2121293 (**triclinic** form and **orthorhombic** form respectively) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

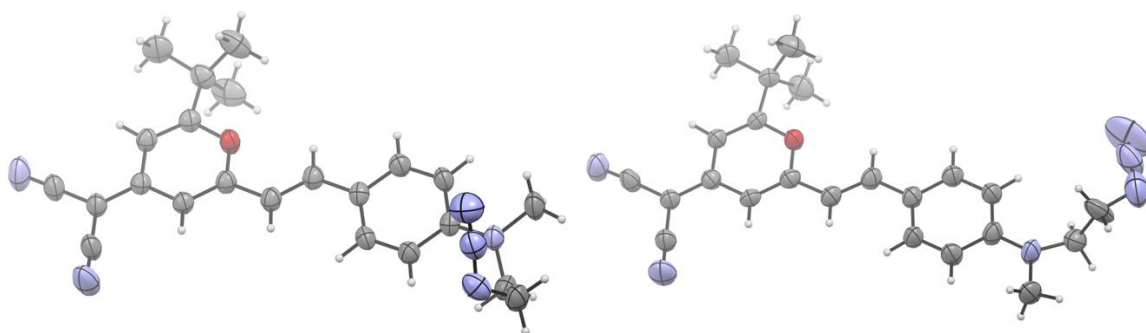


Figure S1 Ortep plot of one conformer (the disorder of the azido moiety is not shown for clarity) of the **triclinic form** (form I, left), and crystal structure of the **orthorhombic form** (form II, right). Ellipsoids are drawn at 50% of probability and hydrogen atoms, with sphere radius of arbitrary size.

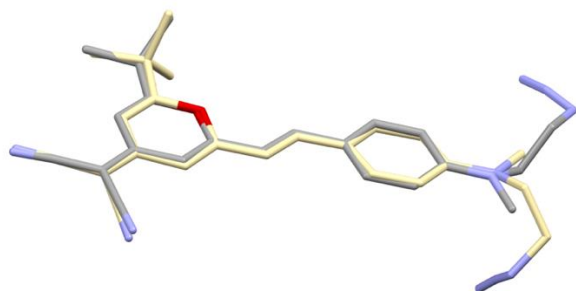


Figure S2 (Left) Overlay plot of the two forms (carbon atoms in yellow belong to the triclinic structure, grey ones are those of the orthorhombic structure).

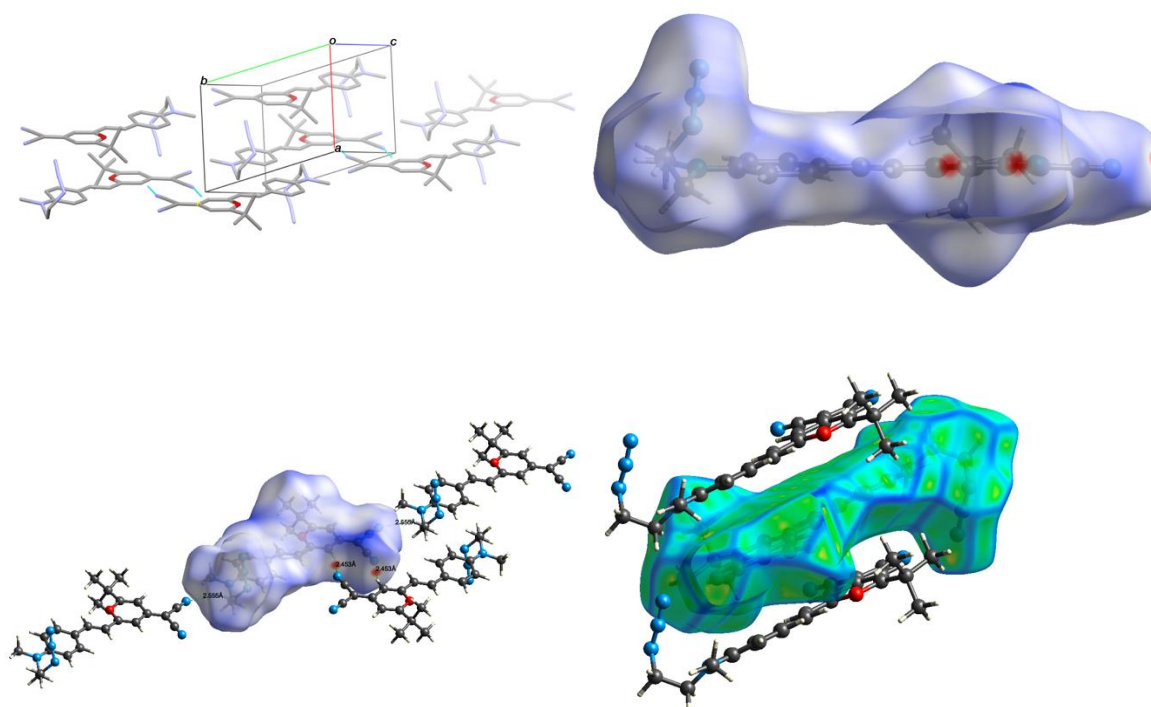


Figure S3 (a) Partial view of the triclinic crystal showing the molecular association in linear ribbon along the [0 1 -1] direction (b) Hirshfeld surface for form I mapped with d_{norm} over the range -0.13 to 2.08. (c) Neighboring molecules associated with close contacts are shown along with distances between the atoms involved (d)

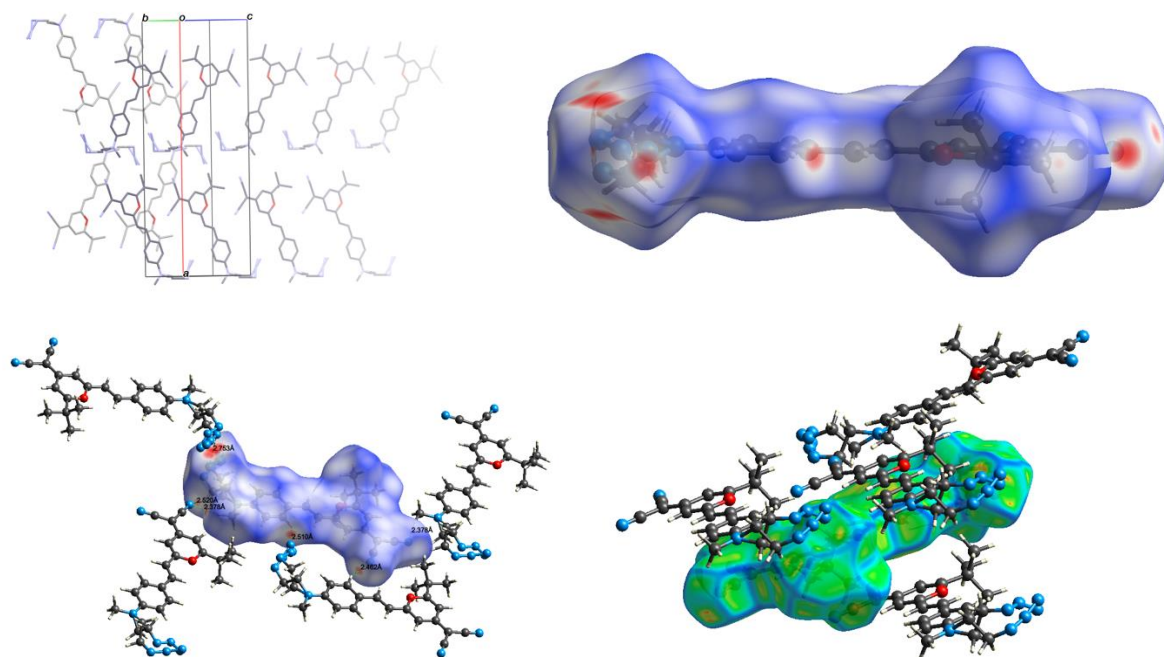


Figure S4 (a) Partial view down the b axis of the orthorhombic crystal showing the herringbone pattern waving along the a direction. (b) Hirshfeld surface for form II mapped with d_{norm} over the range -0.22 to 1.20. (c) Neighbouring molecules associated with close contacts are shown along with distances between the atoms involved and (d) the map with curvedness

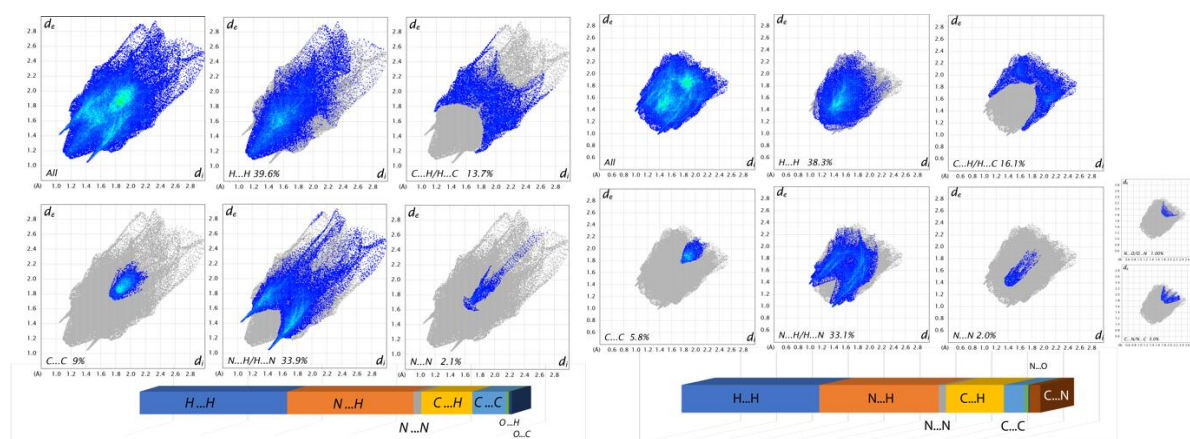
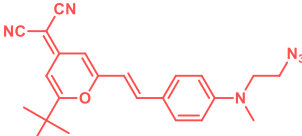


Figure S5 Fingerprint plots for the molecule in form I (triclinic, left) and in form II (orthorhombic, right), broken down into contributions from specific pairs of atom-types. For each plot the grey shadow is an outline of the complete fingerprint plot (upper left plot). Below the histograms for the major atom-type/atom-type contacts represent the percentage contributions to the Hirshfeld surface area for the various close intermolecular contacts for molecules in forms I and II.

Table S1 Crystal data and structure refinement of *s-trans-(E)* conformer of DCM-azide obtained in **Form I** (triclinic) and **Form II** (orthorhombic).

CRYSTAL DATA				
Identification code		Form I		Form II
Name		<i>(E)</i> -2-(2-(4-((2-azidoethyl)(methyl)amino)styryl)-6-(tert-butyl)-4H-pyran-4-ylidene)malononitrile		
Structure				
Empirical formula		C ₂₃ H ₂₄ N ₆ O		
Formula weight		400.48		
Crystal system, Space group		Triclinic, P -1		Orthorhombic, Pna21
Unit cell dimensions (Å, °)		a Å	b	c
		α °	β	γ
Volume (Å ³)		1098.48(10)		1537.41(16)
Z, Calculated density (Mg/m ³)		2, 1.211		4, 1.246
Absorption coefficient (mm ⁻¹)		0.078		0.081
F(000)		424		848
Crystal size (mm)		0.32 x 0.16 x 0.03		0.35 x 0.22 x 0.05
DATA COLLECTION				
Diffractometer		Rigaku XtaLabPro mm003 diffractometer with Pilatus 200K Hybrid pixel array detector (HPAD)		
Wavelength (Å)		0.71073		
Temperature (K)		293(2)		
θ range for data collection (°)		2.483 to 26.022		2.881 to 26.019
Limiting indices		-9 ≤ h ≤ 9, -11 ≤ k ≤ 11, -19 ≤ l ≤ 19		-31 ≤ h ≤ 36, -12 ≤ k ≤ 12, -7 ≤ l ≤ 8
Reflections collected / unique R(int)		22812 / 4312 0.0294		13702 / 3751 0.0192
Completeness to θ _{full} (%)		99.8		99.6
Absorption correction		Semi-empirical from equivalents		
Max. and min. transmission		1.000 and 0.270		1.000 and 0.686
REFINEMENT				
Refinement method		Full-matrix least-squares on F ²		
		IAM	HAR	IAM
Data / restraints / parameters		4310 / 0 / 275	4310 / 0 / 487	3745 / 52 / 308
Goodness-of-fit on F ²		1.021	1.1751	1.114
Final R indices [I > 2σ(I)]		0.0454, 0.1262	0.294, 0.0709	0.0543, 0.1537
R indices (all data)		0.0527, 0.1314	0.0367, 0.0736	0.0626, 0.1631
Largest diff. peak and hole (e. Å ³)		0.168 and -0.187		0.185 and -0.112
CCDC deposit number		2120494		2121293

2. DFT calculations

Optimized Cartesian coordinates of four stable isomers and conformers of DCM-azide at PBE0/6-311G++(d,p) level with IEFPCM model of THF solvent.

Table S2. *s-trans-(E)* (most stable form)

C	-4.947723	0.057511	0.15126	N	7.712552	1.773028	0.104317
C	-4.11564	-1.004332	0.23043	N	8.149488	2.415586	1.045255
O	-2.780855	-0.850768	0.084059	N	8.60965	3.079201	1.837116
C	-2.236153	0.364733	-0.144102	H	-6.011285	-0.093864	0.272526
C	-3.029965	1.475348	-0.234036	H	-2.557655	2.432335	-0.41783
C	-4.433456	1.371799	-0.089661	H	-0.383969	1.362671	-0.454061
C	-5.280329	2.485738	-0.175496	H	-6.232062	-3.651739	0.81559
C	-4.488504	-2.443792	0.479503	H	-6.379982	-2.027256	1.490703
C	-0.809914	0.380945	-0.276519	H	-6.53791	-2.286138	-0.260684
C	-5.999886	-2.598426	0.638937	H	-4.26476	-4.338109	-0.535927
C	-4.011208	-3.289087	-0.712768	H	-2.929625	-3.21681	-0.847058
C	-3.787388	-2.916072	1.763885	H	-4.497994	-2.972109	-1.63962
C	-0.030887	-0.723436	-0.192355	H	-2.701195	-2.838218	1.678273
C	1.403604	-0.792565	-0.310723	H	-4.11048	-2.327665	2.627552
C	2.042084	-2.038985	-0.210091	H	-4.041842	-3.963191	1.950195
C	3.411537	-2.175489	-0.31349	H	-0.527522	-1.675387	-0.017107
C	4.236998	-1.050042	-0.531594	H	1.43935	-2.928066	-0.045805
C	3.597666	0.211438	-0.621934	H	3.845423	-3.163203	-0.228688
C	2.230094	0.326859	-0.518165	H	4.178643	1.113367	-0.767008
N	5.591283	-1.186774	-0.652311	H	1.79468	1.318003	-0.593686
C	6.457616	-0.048746	-0.863579	H	7.358883	-0.390475	-1.377785
C	6.209451	-2.484286	-0.464335	H	5.981512	0.675042	-1.529616
C	6.850696	0.631349	0.442609	H	5.99974	-2.89638	0.529258
C	-4.766116	3.777629	-0.413813	H	5.868421	-3.20359	-1.217325
N	-4.328447	4.83324	-0.610108	H	7.288904	-2.37857	-0.564977
C	-6.677263	2.358701	-0.026792	H	5.957413	0.97393	0.977576
N	-7.824327	2.242106	0.097404	H	7.386884	-0.073905	1.088286

Table S3. *s-cis-(E)* ($\Delta E = 0.0027$ eV compared to *s-trans-(E)*)

c	-4.958722	0.429697	0.096962	N	7.670186	1.669825	0.154393
C	-4.119842	1.466543	-0.119852	N	8.112276	2.292464	1.106219
O	-2.787001	1.268631	-0.208161	N	8.573628	2.941758	1.909182
C	-2.243946	0.033677	-0.084462	H	-6.022065	0.613173	0.16398
C	-3.048166	-1.050456	0.137682	H	-2.597658	-2.02944	0.236567
C	-4.449701	-0.900517	0.238463	H	-0.404873	1.064337	-0.374267
C	-5.304676	-1.990403	0.466064	H	-6.218557	4.184335	-0.312169
C	-4.482735	2.920167	-0.290123	H	-6.532549	2.572711	-0.960872
C	-0.814139	0.071661	-0.215741	H	-6.377288	2.8165	0.792897
C	-5.993123	3.122517	-0.184363	H	-4.025954	4.792198	0.688107
C	-3.778989	3.733679	0.808233	H	-2.693456	3.627483	0.750434
C	-3.999537	3.388022	-1.672608	H	-4.107008	3.417675	1.802795
C	-0.008123	-1.014085	-0.158015	H	-2.918107	3.275572	-1.777019
C	1.426506	-1.043115	-0.282163	H	-4.486932	2.821857	-2.471674
C	2.095431	-2.276284	-0.218592	H	-4.248019	4.444985	-1.803325
C	3.466845	-2.376172	-0.332015	H	-0.465277	-1.989988	-0.004759
C	4.263479	-1.225195	-0.523119	H	1.515345	-3.184015	-0.076818
C	3.593209	0.022813	-0.575237	H	3.92487	-3.354974	-0.276844
C	2.224199	0.101981	-0.462038	H	4.151487	0.942295	-0.697617
N	5.619314	-1.325302	-0.654026	H	1.764426	1.083863	-0.507664
C	6.456056	-0.161799	-0.845236	H	7.360689	-0.469487	-1.374626
C	6.270185	-2.612556	-0.50861	H	5.956868	0.565684	-1.489974
C	6.844029	0.496702	0.473442	H	6.075712	-3.059159	0.47292
C	-4.796734	-3.298417	0.605786	H	5.942654	-3.316699	-1.281608
N	-4.361972	-4.3677	0.718446	H	7.346134	-2.477059	-0.610875
C	-6.700849	-1.819887	0.564313	H	5.947393	0.801623	1.025366
N	-7.847953	-1.66748	0.643396	H	7.405868	-0.208903	1.09644

Table S4. *s-trans*-(Z) ($\Delta E = 0.0127$ eV compared to *s-trans*-(E))

C	-3.588794	-0.97489	0.446582	N	5.754888	-2.197641	-1.05191
C	-2.314873	-0.68066	0.791639	N	6.310045	-2.483008	-2.100424
O	-1.70949	0.437834	0.328009	N	6.82279	-2.860054	-3.035407
C	-2.381228	1.3223	-0.441909	H	-4.045865	-1.874224	0.834966
C	-3.668035	1.067823	-0.828789	H	-4.173628	1.80135	-1.444354
C	-4.331408	-0.112796	-0.417761	H	-2.437267	3.296929	-1.142213
C	-5.641454	-0.413466	-0.812671	H	-1.541149	-3.113853	3.094302
C	-1.4115	-1.509349	1.673077	H	-2.992198	-2.103212	3.059814
C	-1.732889	2.571272	-0.746847	H	-2.687958	-3.286052	1.768511
C	-2.217544	-2.560488	2.437808	H	0.285329	-2.822159	1.406608
C	-0.380512	-2.220855	0.780641	H	0.23006	-1.504468	0.22895
C	-0.691869	-0.594077	2.674548	H	-0.872906	-2.886528	0.066261
C	-0.47076	3.024979	-0.546323	H	-0.06676	0.143836	2.168065
C	0.770692	2.3791	-0.175898	H	-1.408527	-0.066209	3.310807
C	1.771767	3.146119	0.4427	H	-0.051211	-1.203091	3.318174
C	2.995142	2.613685	0.795331	H	-0.363725	4.095871	-0.715925
C	3.308365	1.265949	0.509785	H	1.575051	4.191262	0.665378
C	2.328201	0.510812	-0.175576	H	3.718605	3.250983	1.286966
C	1.099977	1.052421	-0.492298	H	2.534246	-0.506845	-0.482734
N	4.515106	0.733771	0.87409	H	0.391247	0.443542	-1.041253
C	4.870774	-0.630762	0.55858	H	5.60094	-0.977362	1.29377
C	5.527038	1.576542	1.478924	H	4.000252	-1.283812	0.660051
C	5.461159	-0.77284	-0.83971	H	5.827113	2.398275	0.818071
C	-6.366898	0.451105	-1.659506	H	5.177494	2.003508	2.425391
N	-6.951026	1.170893	-2.355767	H	6.408859	0.972429	1.689223
C	-6.285033	-1.591964	-0.379804	H	4.749052	-0.416019	-1.592808
N	-6.803243	-2.563959	-0.017737	H	6.377034	-0.176601	-0.925155

Table S5. *s-cis*-(Z) ($\Delta E = 0.0121$ eV compared to *s-trans*-(E))

C	3.336382	1.159432	0.130299	N	-4.960518	2.246765	-1.162243
C	4.039371	0.043045	-0.167512	N	-4.828768	3.355124	-0.668926
O	3.465787	-1.175629	-0.087464	N	-4.743106	4.427185	-0.318794
C	2.174774	-1.326898	0.298781	H	3.817559	2.124553	0.053271
C	1.428528	-0.23651	0.634412	H	0.412497	-0.387026	0.973695
C	1.973366	1.068423	0.551429	H	2.682975	-3.372839	0.498372
C	1.220747	2.208109	0.868553	H	7.145724	1.246559	-1.022853
C	5.477985	-0.042044	-0.611455	H	5.592594	1.981913	-1.426396
C	1.818074	-2.724594	0.387427	H	6.108743	1.855403	0.269768
C	6.106772	1.347411	-0.698839	H	7.298838	-0.971394	0.089342
C	6.255174	-0.892947	0.406385	H	5.843912	-1.902137	0.479946
C	5.526443	-0.713621	-1.993579	H	6.234213	-0.43512	1.399626
C	0.599282	-3.313336	0.419375	H	5.103938	-1.720366	-1.963592
C	-0.733051	-2.791336	0.181643	H	4.976332	-0.127131	-2.735238
C	-1.826765	-3.40143	0.814449	H	6.566805	-0.788473	-2.322063
C	-3.117643	-2.934638	0.662093	H	0.620947	-4.374075	0.666139
C	-3.396803	-1.834584	-0.17843	H	-1.65368	-4.253274	1.466423
C	-2.303985	-1.262005	-0.871912	H	-3.916392	-3.428659	1.199762
C	-1.021076	-1.729549	-0.690948	H	-2.456724	-0.439986	-1.559586
N	-4.674263	-1.366992	-0.32585	H	-0.22052	-1.265796	-1.25684
C	-4.954787	-0.165223	-1.08022	H	-4.373885	-0.150402	-2.005825
C	-5.745698	-1.933388	0.468771	H	-6.004763	-0.184992	-1.38029
C	-4.680788	1.103585	-0.280197	H	-5.572481	-1.809681	1.544791
C	-0.132484	2.105696	1.255199	H	-6.677038	-1.429251	0.213924
N	-1.245859	2.004866	1.563325	H	-5.873533	-3.000616	0.259418
C	1.782549	3.500219	0.798539	H	-5.328091	1.138183	0.604008
N	2.256235	4.55683	0.736855	H	-3.638521	1.130291	0.057764

Table S6. Absorption and emission transition energies of *s-trans-(E)* form of DCM-azide, calculated by TDDFT with the 6-311G++(d,p) basis set in THF (IEFPCM), using the default Linear Response equilibrium (LR), corrected Linear-Response (cLR) and State-Specific (SS) solvation models, together with experimental data recorded for the *E*-form in THF solution.

	Calc. values						Exp. data	
	PBE0		CAM-B3LYP		ω B97-XD		(ev)	(nm)
	(eV)	(nm)	(eV)	(nm)	(eV)	(nm)		
Abs LR	2.68	463	3.06	405	3.15	394		
Abs cLR	2.71	457	3.11	402	3.31	386	2.70	459
Abs SS	2.42	512	2.85	436	2.98	416		
Em LR	2.38	521	2.44	509	2.45	507		
Em cLR	2.60	478	2.71	457	2.74	452	2.15	576
Em SS	2.42	528	2.56	485	2.56	482		
Stokes shift LR	2404 cm ⁻¹		5045 cm ⁻¹		5657 cm ⁻¹			
Stokes shift cLR	947 cm ⁻¹		3236 cm ⁻¹		4609 cm ⁻¹		4425 cm ⁻¹	
Stokes shift SS	607 cm ⁻¹		2350 cm ⁻¹		3336 cm ⁻¹			

Figure S6. Molecular orbitals involved in the main excited states of the 4 conformations *s-trans*-(*E*), *s-cis*-(*E*), *s-trans*-(*Z*), *s-cis*-(*Z*) at the PBE0/6-311G++(d,p) level with IEFPCM model of THF solvent.

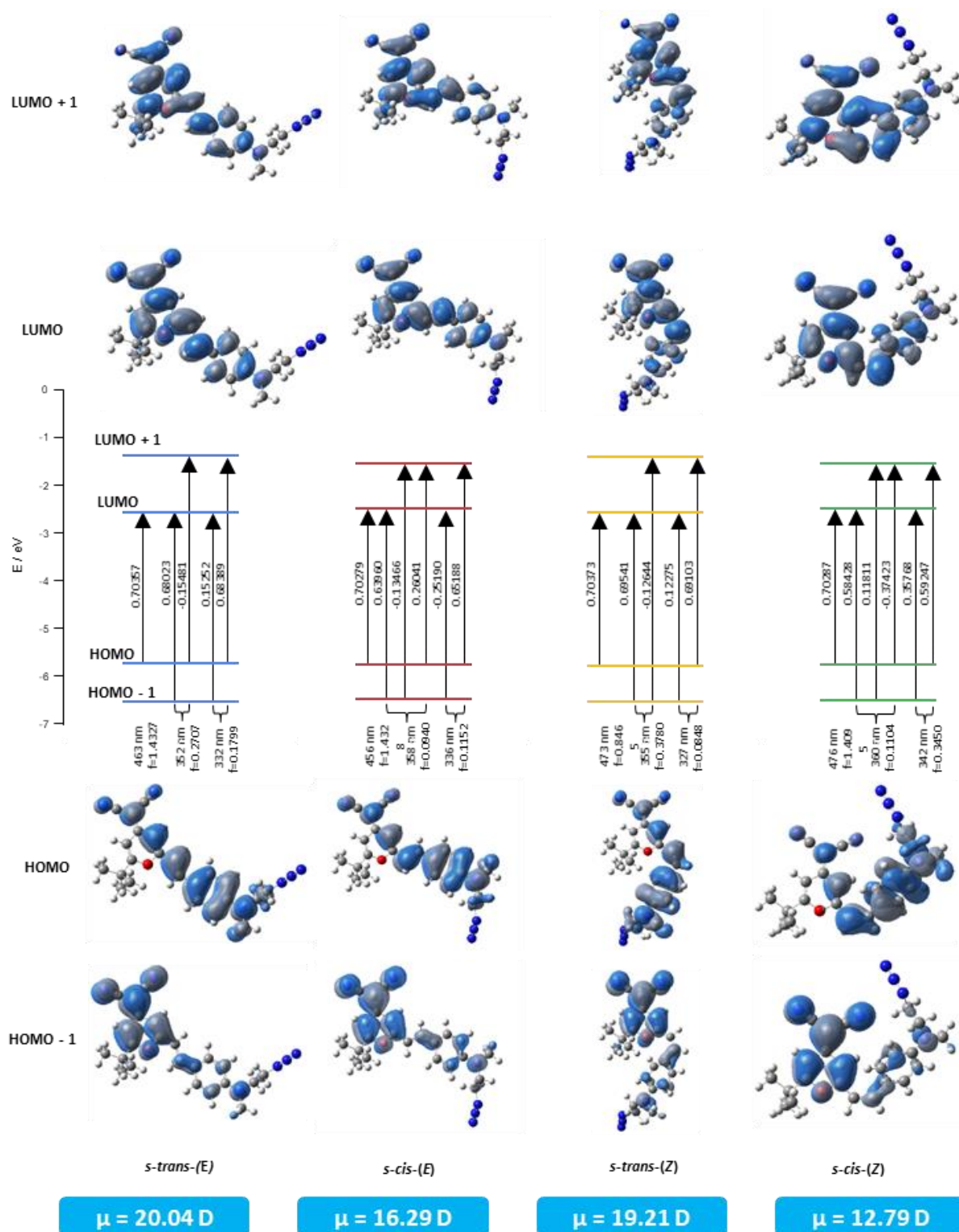


Figure S7. Molecular orbitals involved in the main excited states of the 4 conformations *s-trans*-(*E*), *s-cis*-(*E*), *s-trans*-(*Z*), *s-cis*-(*Z*) at the CAM-B3LYP/6-311G++(d,p) level with IEFPCM model of THF solvent.

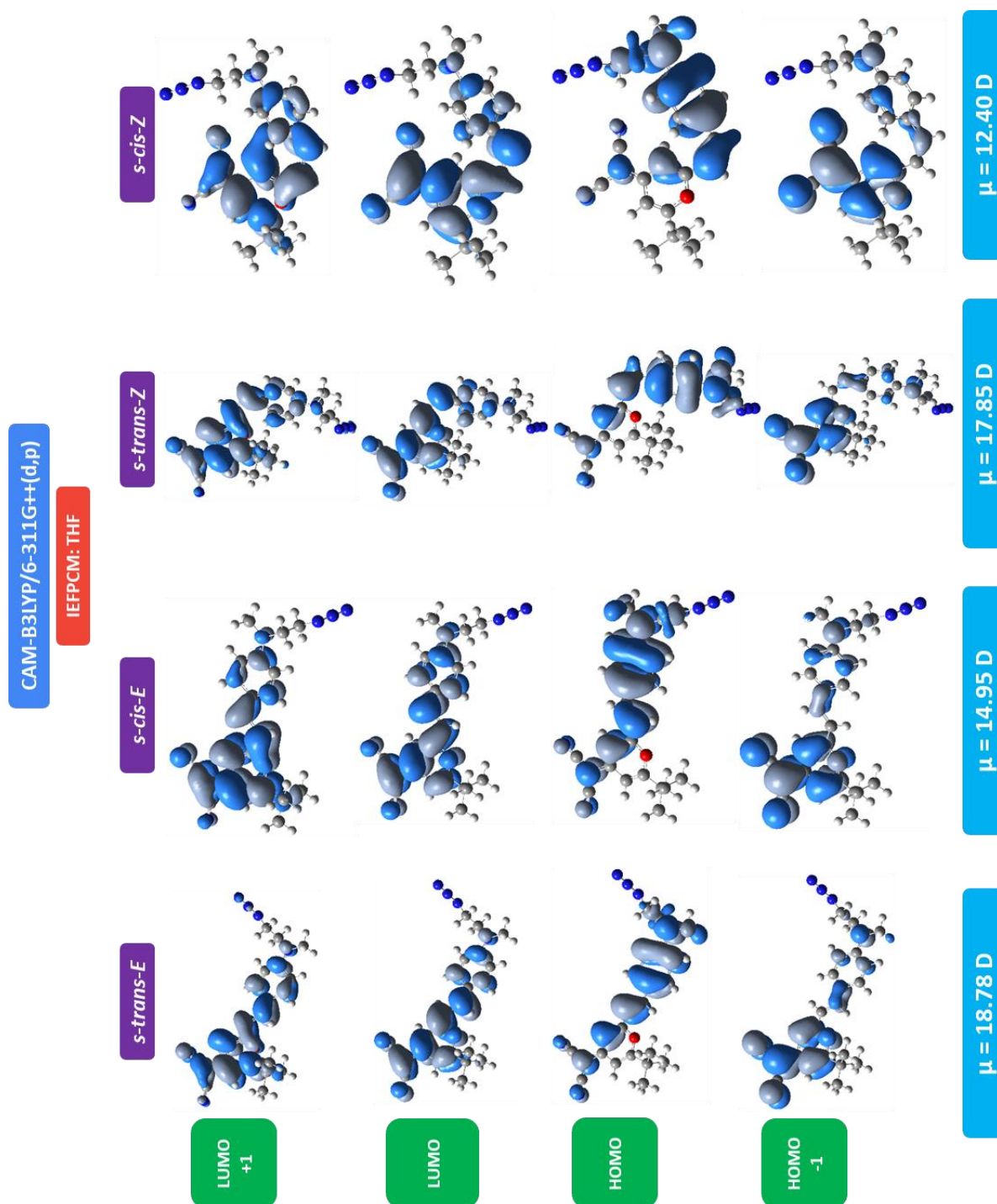


Figure S8. Molecular orbitals involved in the main excited states of the 4 conformations *s-trans*-(E), *s-cis*-(E), *s-trans*-(Z), *s-cis*-(Z) at the ω B97X-D/6-311G++(d,p) level with IEFPCM model of THF solvent.

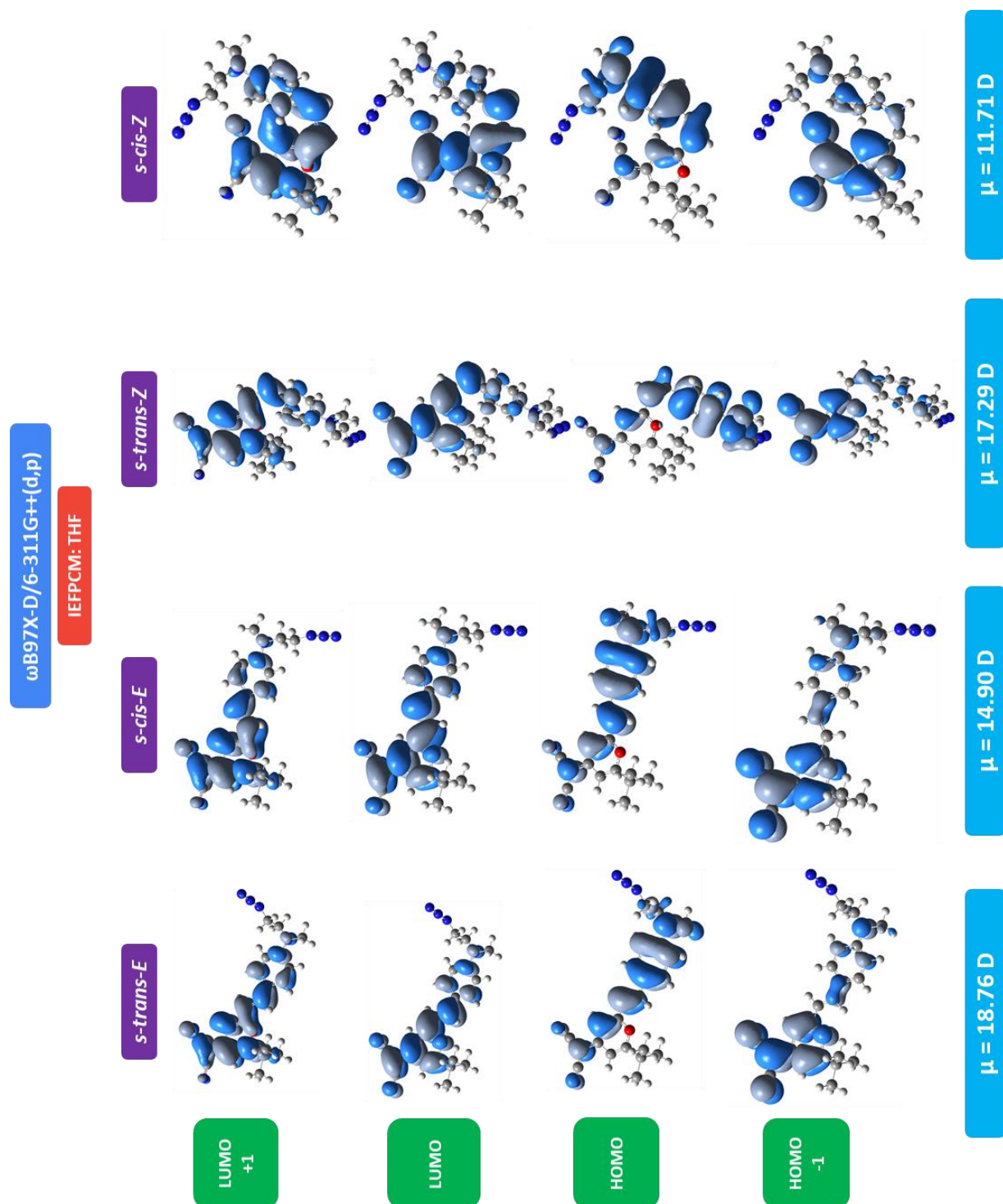


Figure S9. Molecular orbitals involved in the main excited states of DCM-azide *E*-forms calculated by DFT at the PBE0/6-311G++(d,p) level with IEFPCM model of DMSO, acetonitrile and THF solvent.



Figure S10. Molecular orbitals involved in the main excited states of DCM-azide Z-forms calculated by DFT at the PBE0/6-311G++(d,p) level with IEFPCM model of DMSO, acetonitrile and THF solvent.

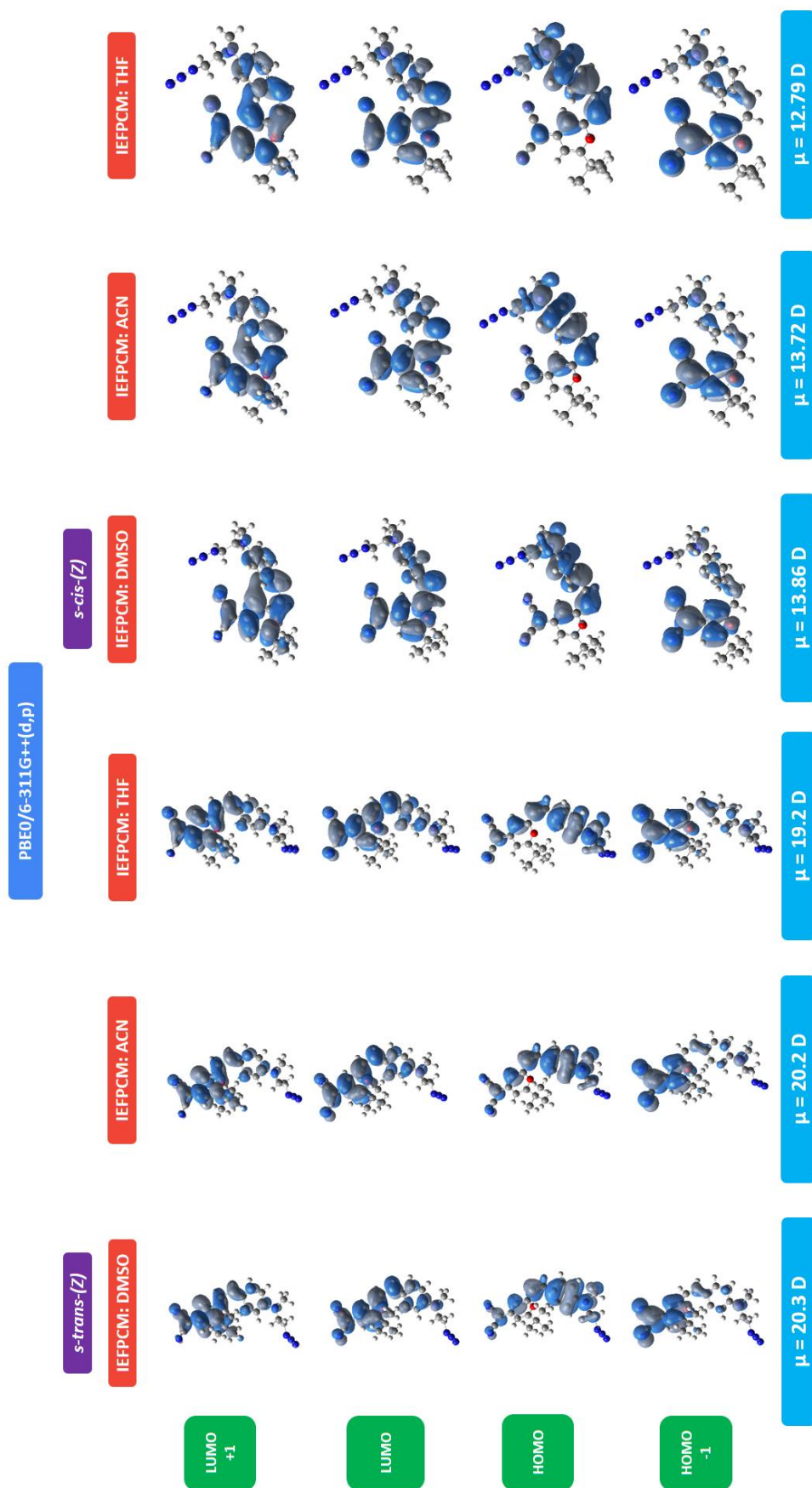


Figure S11. The bond lengths C_4-C_9 and $C_9=C_{13}$ vs. scan coordinates D1 and D2 (dihedral angles, see main text, Figure 1) for DCM-azide calculated at the PBE0/6-311G+(d,p) level with IEFPCM model of THF solvent.

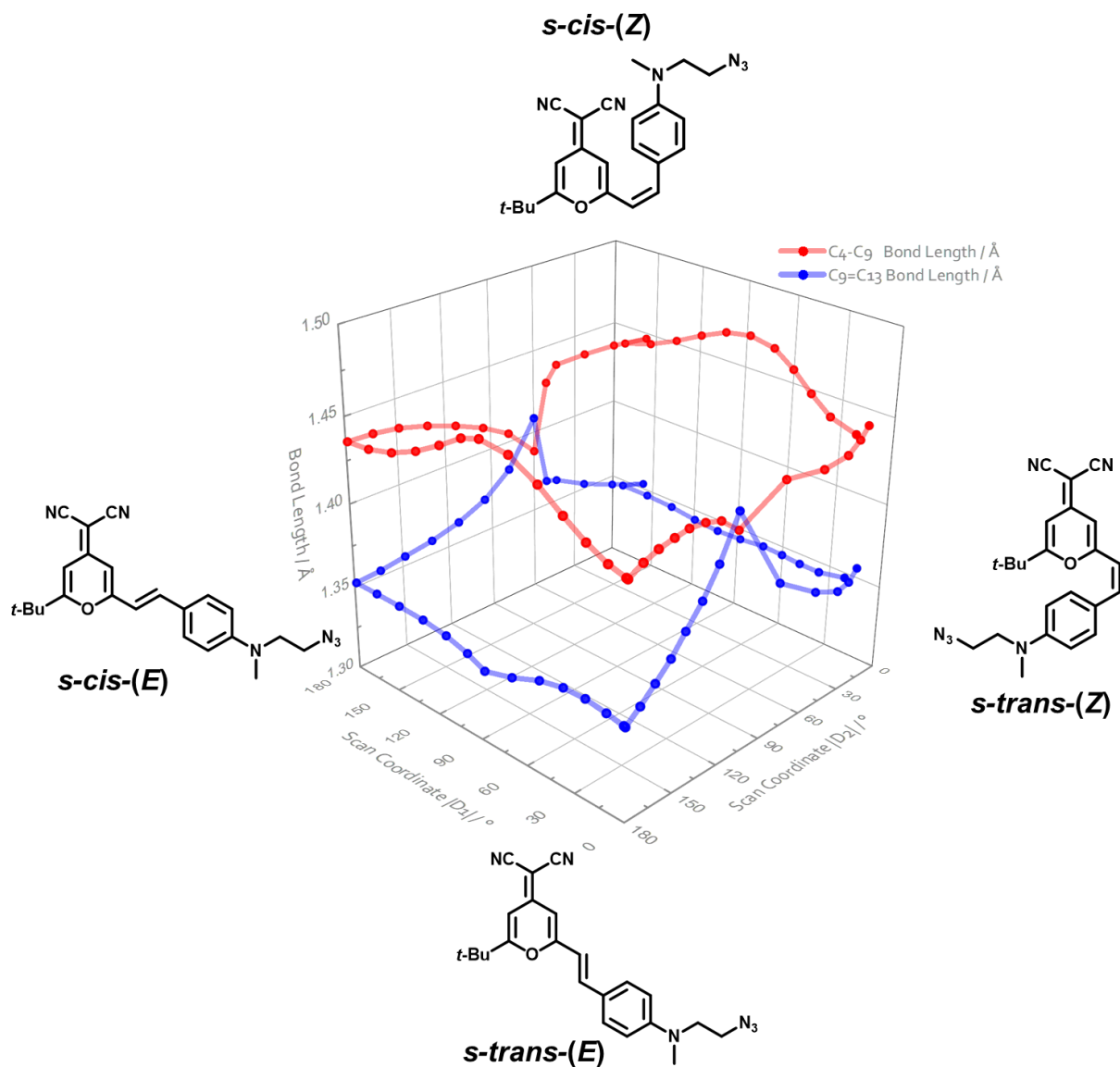
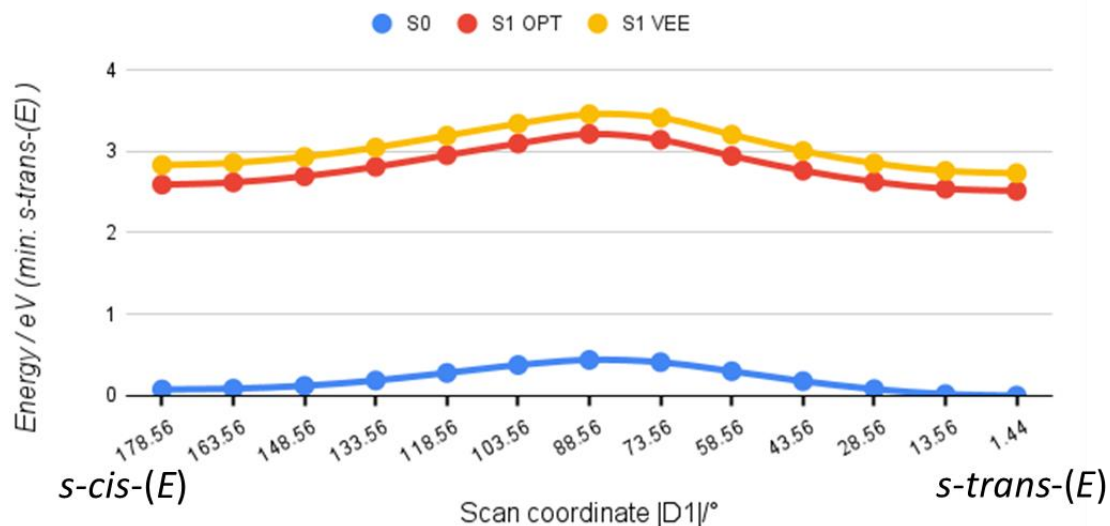


Figure S12. C₄-C₉ single bond dihedral D1 scan between *s-cis* and *s-trans* conformers of the ground states energy (S_0), relaxed excited state energy (S_1 opt), and $S_0 \rightarrow S_1$ vertical excitation energies (S_1 VEE) calculated at the PBE0/def2-SVP level with IEFPCM model of THF solvent.

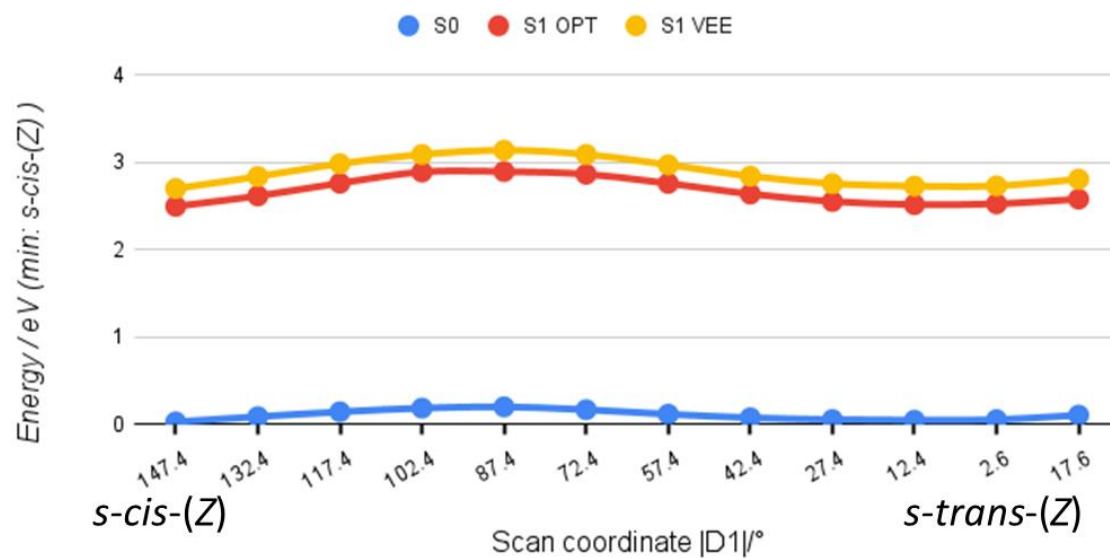
Dihedral D1 scan optimization from optimized *s-cis*-(E)

PBE0/def2-SVP DFT/TDDFT



Dihedral D1 scan optimization from optimized *s-cis*-(Z)

PBE0/def2SVP DFT/TDDFT



3. Cartesian coordinates of conical intersections

Table S7. CI-1 *s-cis* type

Optimized Geometry: $D_1 = 171.664780^\circ$ $D_2 = -78.582787^\circ$

$D_{C-C} = 1.39874 \text{ \AA}$

$D_{C-C} = 1.46450 \text{ \AA}$

$E(S_0) = -1292.8949705457$ a. u. $\langle S^2 \rangle = 0.1986$

$E(S_1) = -1292.8934745913$ a. u. $\langle S^2 \rangle = 0.1421$

$E_{\text{gap}}(S_0/S_1) = 0.0014959544$ a. u. 0.04 eV

C	0.6356678	-0.63559532	1.38684916	N	8.13875484	4.07203007	3.95549035
C	1.5110631	-1.32766545	0.61327189	N	7.5050621	5.09260321	3.71603775
O	2.49175406	-2.07581162	1.16255069	N	7.008986	6.07331991	3.41495252
C	2.69305801	-2.05970097	2.51205945	H	-0.15129089	-0.06150969	0.91506886
C	1.85937834	-1.35196066	3.35392952	H	2.10031819	-1.37013066	4.4126277
C	0.73869061	-0.64821392	2.81805658	H	4.16499615	-3.48904395	2.2010119
C	-0.16259339	-0.01503781	3.66069436	H	0.50027561	-0.58298916	-2.59410954
C	1.55536652	-1.36884046	-0.89383656	H	-0.55646545	-0.88451159	-1.21146715
C	3.72581482	-2.86723757	2.99994588	H	0.52359593	0.53167152	-1.22520137
C	0.43604133	-0.52423352	-1.50342929	H	2.97394371	-0.82899398	-2.43484116
C	2.92008257	-0.81174511	-1.34169018	H	3.74753737	-1.40964985	-0.94972014
C	1.41410768	-2.82848811	-1.35784602	H	3.05344939	0.22418962	-1.01193523
C	4.24257803	-2.89080691	4.37034512	H	2.21000743	-3.45905018	-0.95145822
C	5.13421631	-1.86414552	4.78188896	H	0.44813445	-3.25051212	-1.05981529
C	5.49331284	-1.68174076	6.14194059	H	1.47643638	-2.86496592	-2.45015645
C	6.42494535	-0.74331927	6.55448437	H	3.64500928	-3.4476223	5.0849967
C	7.09105778	0.10008202	5.65066433	H	5.02619886	-2.31342578	6.89483738
C	6.72638702	-0.04094121	4.30386019	H	6.63830519	-0.68119425	7.61716938
C	5.79007339	-0.97608489	3.88899326	H	7.18358755	0.58164227	3.53964806
N	8.10451317	0.99321198	6.07851028	H	5.58619022	-1.02395046	2.81898975
C	8.55032635	2.02411342	5.17979002	H	9.47557545	2.45527339	5.5791173
C	8.15621948	1.30978549	7.48473024	H	8.82013226	1.58381271	4.21317101
C	7.54743624	3.1530962	4.94420242	H	7.20717382	1.70284355	7.88930845
C	-0.04333416	-0.07192465	5.07628202	H	8.42442799	0.42417338	8.07434654
N	0.04491945	-0.13354023	6.23319054	H	8.93602943	2.05845857	7.65229511
C	-1.26465833	0.69754976	3.11557174	H	6.5996809	2.74496675	4.57041311
N	-2.15173411	1.26643169	2.62456322	H	7.33984041	3.68294597	5.88402367

Table S8. CI-2 *s-trans* typeOptimized Geometry: $D_1 = 18.876789^\circ$ $D_2 = -87.396843^\circ$ $D_{C-C} = 1.39486 \text{ \AA}$ $D_{C=C} = 1.45635 \text{ \AA}$ $E(S_0) = -1292.8945194677$ a. u. $\langle S^2 \rangle = 0.1771$ $E(S_1) = -1292.8934989218$ a. u. $\langle S^2 \rangle = 0.1360$ $E_{\text{gap}}(S_0/S_1) = 0.0010205459$ a. u. 0.03 eV

C	0.27079824	-1.07720625	1.48285675	N	8.59030533	2.13576984	1.51913226
C	1.41102612	-0.48953256	1.92357552	N	7.98227072	3.00523686	0.90496492
O	2.08921957	-0.98115432	2.98199463	N	7.49088478	3.79010344	0.2418187
C	1.74327576	-2.17015195	3.53505325	H	-0.27489105	-0.63631231	0.65815347
C	0.64282352	-2.87386179	3.062433	H	0.40417621	-3.83337879	3.510952
C	-0.20275667	-2.2979219	2.07621527	H	2.31094575	-3.61578417	4.93746233
C	-1.40452898	-2.90780687	1.71869969	H	1.80862224	2.24382114	-0.13729842
C	2.12672377	0.69320363	1.3197962	H	1.03777027	0.72000873	-0.58087397
C	2.47670507	-2.568748	4.65166903	H	0.32219145	1.74837995	0.6829654
C	1.26498902	1.38190007	0.26206341	H	3.07331586	2.5166924	1.9782306
C	2.50470781	1.69408822	2.42416668	H	3.12324142	1.22500229	3.19401169
C	3.41457915	0.14895043	0.66771805	H	1.61388314	2.11715937	2.9011066
C	3.27135658	-1.66042411	5.46741056	H	4.06445599	-0.32759866	1.40873349
C	4.59626198	-1.25424242	5.3086915	H	3.18510532	-0.57901883	-0.11880878
C	5.13921165	-0.25795725	6.17418337	H	3.9663341	0.97766995	0.21136408
C	6.40694332	0.25811893	6.01025724	H	2.63830709	-1.08449721	6.14547062
C	7.25814056	-0.18993704	4.98526812	H	4.51454306	0.12002107	6.98023653
C	6.76493835	-1.21712744	4.15531731	H	6.73737049	1.03709304	6.69038868
C	5.49314356	-1.73029149	4.3025732	H	7.40565634	-1.6293081	3.37992883
N	8.55726624	0.33176693	4.79600668	H	5.16651964	-2.51854467	3.62693238
C	8.92586994	0.69990146	3.44377327	H	9.98933983	0.96437818	3.43146873
C	9.06684208	1.21447086	5.81912613	H	8.81460381	-0.15798298	2.77343917
C	8.110075	1.86390889	2.88298178	H	8.53916359	2.18212914	5.89703465
C	-1.82292283	-4.11933708	2.32747531	H	9.0029583	0.72123504	6.79418802
N	-2.13437867	-5.10978937	2.85320354	H	10.12159634	1.42292976	5.61528158
C	-2.25490522	-2.30861688	0.75415939	H	7.04563189	1.59372842	2.87457037
N	-2.927001	-1.78035545	-0.03549787	H	8.2278738	2.75683379	3.51234365