Electronic Supplementary Material (ESI) for CrystEngComm.

Halogen bonding in multi-connected 1,2,2-triiodo-alkene involving geminal and/or vicinal iodines: A crystallographic and DFT study

G. Berger,[a,b] K. Robeyns,[c] J. Soubhye,[a] R. Wintjens,[d] and F. Meyer[d*]

[a] *Chimie Pharmaceutique Organique, Faculty of pharmacy, Université Libre de Bruxelles (ULB), Boulevard du Triomphe, 1050 Bruxelles, Belgium*

[b] *Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139, United States*

[c] *Institute of Condensed Matter and Nanosciences (IMCN), Université Catholique de Louvain (UCL), Bâtiment Lavoisier - Place Louis Pasteur 1, 1348 Louvain-la-Neuve, Belgium.*

[d] *Laboratory of Biopolymers and Supramolecular Nanomaterials, Faculty of pharmacy, Université Libre de Bruxelles (ULB), Boulevard du Triomphe, 1050 Bruxelles, Belgium*

Correspondence e-mail: franck.meyer@ulb.ac.be

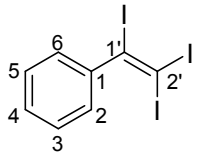
Contents

1. Experimental details

1.1. Materials

Phenylacetylene was purchased from Aldrich, potassium hydroxide, iodine and methanol were used as received.

1.2. (1,2,2-triiodovinyl)benzene



To a solution of phenylacetylene (0.5 g, 4.9 mmol) in 50 mL of methanol was slowly added an aqueous solution of KOH (840 mg, 15 mmol) in 10 mL of water. Then, iodine (2.54 g, 10 mmol) was slowly added within a period of 10-15 min at room temperature. After stirring overnight, the mixture was diluted with water and extracted three times with hexane. The combined organic layers were washed with a saturated solution of sodium thiosulfate and dried over sodium sulphate. After evaporation, a yellowish oil was recovered, consisting of a mixture (iodoethynyl)benzene/(1,2,2-triiodovinyl)benzene. After 3 months at 4 °C, colourless crystals of (1,2,2-triiodovinyl)benzene were grown and separated from the oily residue. Yield ~ 5%; Mp = 110 °C.

To a solution of the resulting mixture in 20 mL of dioxane was slowly added iodine (5 g, 20 mmol) within 3-5 min at rt and the reaction mixture was stirred for 48 h. After evaporation of the solvent, the residue was dissolved in CH_2Cl_2 and washed with a saturated solution of $Na_2S_2O_3$ until the color disappears. Then, the organic layer was dried over sodium sulphate, the solvent was evaporated to give the desired compound as a white powder (2 g, 85 % yield).

^{1}H NMR ($CDCl_3$) δ 7.37-7.32 (m, 2H, H 2 and 6), 7.24-7.16 (m, 3H, H 3, 4 and 5);

^{13}C NMR ($CDCl_3$) δ 147.8 (C1), 128.9 (C4), 128.7 (C3 and 5), 127.5 (C2 and 6), 112.6 (C1'), 22.6 (C2').

1.3. X-ray crystallography

The crystal structure of the reported compound was determined by single crystal X-ray diffraction. Data were recorded on a MAR345 image plate detector, using MoKα radiation generated by a Rigaku Ultra18S rotation anode generator, Xenocs fox3D mirrors. The pale-yellow, plate-like crystal was measured at room temperature. The data-reduction program

CrysalisPRO was used to treat the data and the implemented absorption correction was applied. Structure was solved by SHELXS and refined (SHELXL) by full-matrix least squares on $|F^2|$.[1] Non-hydrogen atoms were anisotropically refined and the hydrogen atoms were placed on calculated positions in riding mode with temperature factors fixed at 1.2 times U_{eq} of the parent atoms. The asymmetric unit of X consists of 2 molecules and pack in the monoclinic space group *C*c (Z=8), both molecules showed disorder. CrysalisPRO: Rigaku Oxford Diffraction, (2014), CrysAlisPro Software system, version 1.171.37.31, Rigaku Corporation, Oxford, UK.

CCDC number 1435564

Crystal data and structure refinement details

Identification code	ulb_fm_mef
Empirical formula	C8 H5 I3
Formula weight	481.82
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	Cc
Unit cell dimensions	a = 10.5124(3) Å b = 10.5580(3) Å c = 20.3568(7) Å β = 97.390(3)°
Volume	2240.63(12) $Å^3$
Z	8
Density (calculated)	2.857 Mg/m^3
Absorption coefficient	8.314 mm^{-1}
F(000)	1696
Crystal size	0.30 x 0.30 x 0.10 mm^3
Theta range for data collection	2.837 to 25.327°.
Index ranges	-12<=h<=12, -11<=k<=12, -24<=l<=24
Reflections collected	3638
Independent reflections	3638 [$R_{(int)}$ = /] †
Completeness to theta = 25.242°	99.4 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.07516
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3638 / 262 / 353

[1] G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, **64**, 112–122.

Goodness-of-fit on F^2	1.056
Final R indices [I>2sigma(I)]	R_1 = 0.0726, wR_2 = 0.2182
R indices (all data)	R_1 = 0.0777, wR_2 = 0.2233
Largest diff. peak and hole	1.355 and -1.407 e.Å^{-3}

† [$R_{(int)}$ = ?], twinned data, HKLF5 format

2. DFT methods

Triiodostyrene was first DFT-optimized and the pyridines were then added to obtain the desired complexes. N-I distances were set at typical halogen-bonded N-I distances (around 3 Å). The system was energy-minimized without any constraint, allowing the N-I contacts to reach their equilibrium values.

All quantum chemical computations were performed using Gaussian09 revision D.01. Geometries were fully optimized using the ωB97x-D exchange-correlation functional[2] together with the balanced polarized triple-zeta basis set from Ahlrichs and co-workers, def2-TZVP.[3,4] The Stuttgart/Dresden effective core potential was used for the iodine atom.

Optimized geometries were verified by frequency calculations as minima (i.e. zero imaginary frequencies) and free energies were corrected to account for the zero-point energy.

Total DFT energy, root mean square (RMS) gradient norm at the end of the geometry optimization, number of imaginary frequencies, dipole moment and Cartesian coordinates are given for all the calculated structures.

2.1. Gaussian full reference

Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G.

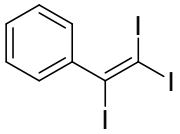
[2] Chai, J.-D.; Head-Gordon, M. *Phys. Chem. Chem. Phys.* **2008**, *10*, 6615-6620

[3] Weigend, F.; Ahlrichs, R. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297-3305.

[4] Weigend, F. *Phys. Chem. Chem. Phys.* **2006**, *8*, 1057-1065.

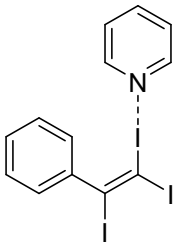
Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowskiand, D. J. Fox, Gaussian, Inc., Wallingford CT, 2010.

2.2. Geometries and optimization data



Level of theory: ωB97x-D/def2TZVP
Total Energy = -342.09476184 au
RMS Gradient Norm = 0.00001725 au
Imaginary Frequencies = 0
Dipole Moment = 1.6987 Debye

Symbol	X	Y	Z
C	2.57615	0.118389	-1.20265
H	2.039383	0.219123	-2.13768
C	3.937233	-0.136	-1.2001
H	4.465508	-0.23485	-2.13961
C	4.61902	-0.26457	0.000562
H	5.683454	-0.46157	0.000757
C	3.936592	-0.13689	1.200923
H	4.46431	-0.23644	2.140663
C	2.575476	0.117505	1.202882
H	2.038233	0.217552	2.137705
C	1.889492	0.239902	-2.1E-05
C	0.43356	0.509718	-0.00016
C	-0.50652	-0.42432	-0.00018
I	-0.00643	2.586855	-0.00012
I	0.036427	-2.47586	-0.0003
I	-2.58578	-0.10432	0.000237

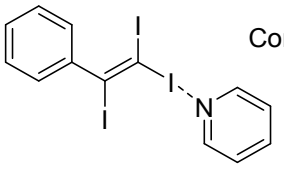


Complex **A**

Level of theory: ωB97x-D/def2TZVP
Total Energy = -590.38820294 au
RMS Gradient Norm = 0.00000200 au
Imaginary Frequencies = 0
Dipole Moment = 5.2465 Debye

Symbol	X	Y	Z
C	-0.53666	2.536449	-1.20198
H	-0.78281	2.047309	-2.13615
C	0.094705	3.768824	-1.20032
H	0.339306	4.247756	-2.13982

C	0.412729	4.386579	0.000098
H	0.904891	5.350876	0.000128
C	0.09473	3.768736	1.200485
H	0.33935	4.247604	2.140013
C	-0.53663	2.536364	1.202063
H	-0.78276	2.047148	2.136202
C	-0.8488	1.911347	0.00002
C	-1.50527	0.582768	-4E-06
C	-0.84854	-0.56862	0.000027
I	-3.62585	0.727517	-0.00009
I	1.27479	-0.5975	0.000067
I	-1.73161	-2.48232	0.000026
N	4.295909	-0.40695	0.000041
C	5.168538	-1.40926	-5.1E-05
C	4.770519	0.834705	0.000029
C	6.541053	-1.21876	-0.00017
H	4.748376	-2.40924	-2.8E-05
C	6.12477	1.127745	-7.2E-05
H	4.030413	1.62846	0.000095
C	7.027688	0.07775	-0.00017
H	7.208286	-2.07009	-0.00025
H	6.458678	2.156581	-7.2E-05
H	8.093789	0.266764	-0.00026

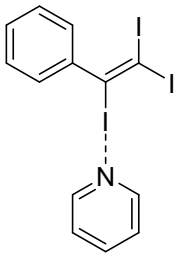


Complex **B**

Level of theory: ωB97x-D/def2TZVP
Total Energy = -590.38806918 au
RMS Gradient Norm = 0.00000108 au
Imaginary Frequencies = 0
Dipole Moment = 2.8601 Debye

Symbol	**X**	**Y**	**Z**
C	3.732572	0.299995	-1.18998
H	3.19401	0.363241	-2.12727
C	5.108006	0.141101	-1.18028
H	5.648021	0.081349	-2.11653
C	5.790697	0.057144	0.02398
H	6.866026	-0.06729	0.030103
C	5.093556	0.134463	1.220375
H	5.622244	0.069502	2.162718
C	3.718107	0.293341	1.214346
H	3.16827	0.351369	2.14541
C	3.030718	0.369896	0.008204

C	1.558996	0.528527	-8E-06
C	0.674507	-0.45817	-0.00687
I	0.969061	2.573321	0.000654
I	1.377783	-2.46682	-0.00718
I	-1.42686	-0.29884	-0.01726
N	-4.44728	-0.08027	-0.00775
C	-5.11372	-0.05799	1.142028
C	-5.14578	0.003837	-1.13542
C	-6.4932	0.047839	1.216678
H	-4.5141	-0.12809	2.043353
C	-6.52676	0.112596	-1.1652
H	-4.5719	-0.01684	-2.05574
C	-7.21347	0.134862	0.037146
H	-6.98635	0.061305	2.179265
H	-7.04688	0.177989	-2.11132
H	-8.29279	0.218709	0.054619

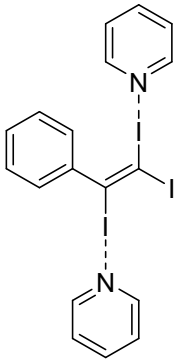


Complex **C**

Level of theory: ωB97x-D/def2TZVP
Total Energy = -590.38716187 au
RMS Gradient Norm = 0.00000083 au
Imaginary Frequencies = 0
Dipole Moment = 4.1706 Debye

Symbol	X	Y	Z
C	-1.44223	2.541285	1.201951
H	-1.25877	2.025658	2.136376
C	-1.91112	3.844236	1.20012
H	-2.09386	4.349928	2.13967
C	-2.14742	4.497899	0.000038
H	-2.51464	5.516239	0.000051
C	-1.91103	3.844298	-1.20006
H	-2.0937	4.350036	-2.1396
C	-1.44214	2.541346	-1.20192
H	-1.2586	2.02577	-2.13636
C	-1.21224	1.881335	0.000008
C	-0.71422	0.485513	-8E-06
C	-1.50681	-0.5765	0.000011
I	1.406451	0.366808	-0.00007
I	-3.61835	-0.35231	0.000036
I	-0.88138	-2.58726	-2.4E-05

N	4.481494	0.218218	-0.00005
C	5.058546	-0.97908	0.000071
C	5.268446	1.289165	-7.8E-05
C	6.432503	-1.15901	0.000175
H	4.388244	-1.83217	0.000094
C	6.652184	1.213736	0.000015
H	4.766514	2.250903	-0.00018
C	7.245146	-0.03774	0.000146
H	6.850577	-2.15661	0.000279
H	7.246373	2.117613	-1.1E-05
H	8.323268	-0.13753	0.00022

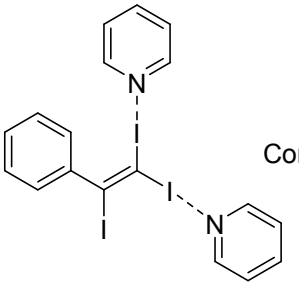


Complex **D**

Level of theory: ωB97x-D/def2TZVP
Total Energy = -838.67715234 au
RMS Gradient Norm = 0.00000517 au
Imaginary Frequencies = 0
Dipole Moment = 3.0363 Debye

Symbol	**X**	**Y**	**Z**
C	0.498471	2.273039	-1.28309
H	0.269303	1.768361	-2.21334
C	1.074713	3.532375	-1.2928
H	1.289465	4.016673	-2.23697
C	1.373804	4.170714	-0.09834
H	1.823967	5.155352	-0.10677
C	1.091257	3.545398	1.106926
H	1.320183	4.039265	2.042758
C	0.514733	2.286308	1.118992
H	0.299636	1.791275	2.057726
C	0.223257	1.639341	-0.0766
C	-0.37228	0.281109	-0.06576
C	0.357205	-0.82584	-0.05322
I	-2.49595	0.31067	-0.06831
I	2.478116	-0.73414	-0.03702
I	-0.41214	-2.79137	-0.04039
N	-5.60713	0.505814	0.035036
C	-6.39443	0.509956	-1.03553
C	-6.17631	0.65955	1.22619
C	-7.7698	0.667103	-0.96582
H	-5.90032	0.381742	-1.9927

C	-7.54115	0.8234	1.400595
H	-5.50596	0.651658	2.07938
C	-8.35384	0.827524	0.279244
H	-8.3639	0.663627	-1.86991
H	-7.95337	0.94552	2.393219
H	-9.42476	0.954797	0.375291
N	5.485541	-0.04687	0.022242
C	6.578742	-0.75141	0.295103
C	5.6161	1.265444	-0.14732
C	7.837961	-0.18427	0.411069
H	6.438586	-1.81847	0.429771
C	6.831589	1.924139	-0.05502
H	4.702848	1.811378	-0.36306
C	7.965546	1.182762	0.231495
H	8.695052	-0.80407	0.638139
H	6.883046	2.994497	-0.20295
H	8.932531	1.66256	0.315451

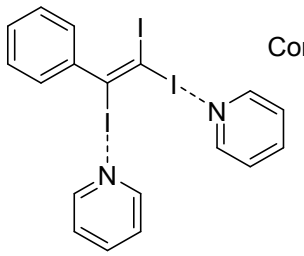


Complex **E**

Level of theory: ωB97x-D/def2TZVP
Total Energy = -838.67774538 au
RMS Gradient Norm = 0.00000312 au
Imaginary Frequencies = 0
Dipole Moment = 3.5367 Debye

Symbol	X	Y	Z
C	1.957915	2.799577	-1.25208
H	1.50198	2.429264	-2.16173
C	3.155489	3.492908	-1.29822
H	3.637244	3.669303	-2.25151
C	3.736439	3.956676	-0.12767
H	4.673902	4.496956	-0.16465
C	3.114359	3.726811	1.090322
H	3.564225	4.087554	2.006503
C	1.916626	3.03362	1.139285
H	1.427943	2.849826	2.087913
C	1.335733	2.560613	-0.03178
C	0.063168	1.804979	0.014217
C	-0.04459	0.485055	0.061783
I	-1.63499	3.096763	-0.01942
I	1.717498	-0.71244	0.098786
I	-1.83615	-0.62819	0.089111

N	-4.53455	-2.09811	0.050487
C	-5.61115	-1.31915	0.079729
C	-4.7149	-3.40419	-0.11613
C	-6.90232	-1.80451	-0.05477
H	-5.42901	-0.25835	0.216576
C	-5.96455	-3.98524	-0.25987
H	-3.81623	-4.0116	-0.13651
C	-7.08115	-3.16636	-0.22901
H	-7.74365	-1.12519	-0.02494
H	-6.05616	-5.05455	-0.39472
H	-8.07393	-3.58401	-0.34014
N	4.296666	-2.41393	0.050484
C	4.902411	-2.56723	-1.12236
C	4.871448	-2.94881	1.122497
C	6.096613	-3.25318	-1.2762
H	4.408505	-2.11735	-1.97727
C	6.06367	-3.65368	1.072564
H	4.353588	-2.80483	2.064765
C	6.688143	-3.80791	-0.15373
H	6.548453	-3.3485	-2.25436
H	6.488893	-4.06936	1.97617
H	7.622234	-4.34971	-0.23345



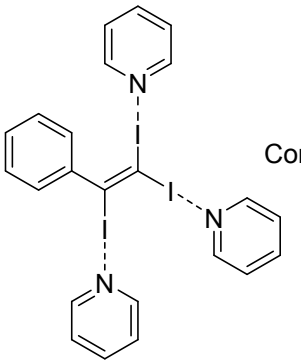
Complex **F**

Level of theory: ωB97x-D/def2TZVP
Total Energy = -838.67696888 au
RMS Gradient Norm = 0.00015255 au
Imaginary Frequencies = 2*
Dipole Moment = 5.5501 Debye

* The calculation was difficult to converge to a true minimum, but the two negative frequencies were examined. These correspond to very low vibration modes and none of them imply vibrations along the XB axis, thus affording reliable N-I distances.

Symbol	**X**	**Y**	**Z**
C	3.804869	0.380607	-1.16456
H	3.273322	0.295438	-2.10418
C	5.171014	0.607196	-1.15079
H	5.707914	0.702134	-2.08608
C	5.84784	0.710924	0.054957
H	6.916059	0.886836	0.06473
C	5.152203	0.58895	1.248341

H	5.67476	0.669732	2.193044
C	3.786023	0.362797	1.237386
H	3.240036	0.264941	2.167429
C	3.105722	0.249522	0.030101
C	1.644839	0.003184	0.016758
C	1.081186	-1.19582	-0.00869
I	0.514657	1.807662	0.043698
I	2.311893	-2.93492	-0.02788
I	-0.98525	-1.62873	-0.03229
N	-1.06609	4.506196	0.030948
C	-1.24158	5.13274	-1.1275
C	-1.59068	5.053947	1.121677
C	-1.94007	6.323603	-1.24788
H	-0.80181	4.659045	-1.99889
C	-2.30617	6.240697	1.105963
H	-1.42971	4.517898	2.051013
C	-2.48351	6.887838	-0.10566
H	-2.05433	6.793608	-2.21543
H	-2.71303	6.643747	2.023664
H	-3.03597	7.817518	-0.15949
N	-3.98648	-2.25625	-0.03002
C	-4.63391	-2.32709	1.128513
C	-4.6808	-2.4637	-1.14404
C	-5.98726	-2.60744	1.226401
H	-4.04021	-2.15062	2.019236
C	-6.03667	-2.75135	-1.15137
H	-4.12483	-2.39738	-2.07321
C	-6.70211	-2.82489	0.060486
H	-6.46512	-2.65367	2.19566
H	-6.55256	-2.91374	-2.08814
H	-7.76101	-3.04822	0.096695



Complex **G**

Level of theory: ωB97x-D/def2TZVP
Total Energy = -1086.96641739 au
RMS Gradient Norm = 0.00000514 au
Imaginary Frequencies = 0
Dipole Moment = 2.3331 Debye

Symbol	X	Y	Z
C	-1.11662	-3.19307	-1.26494
H	-0.90224	-2.67093	-2.18911
C	-1.79098	-4.40257	-1.28369
H	-2.10243	-4.82951	-2.22865
C	-2.06777	-5.06447	-0.09702
H	-2.59444	-6.01027	-0.11279
C	-1.66562	-4.51195	1.109659
H	-1.87828	-5.02355	2.039877
C	-0.99142	-3.30278	1.130559
H	-0.67843	-2.86509	2.070331
C	-0.71896	-2.63216	-0.05665
C	-0.00512	-1.33347	-0.03151
C	-0.60514	-0.15328	0.036463
I	2.110285	-1.5726	-0.10543
I	-2.73093	-0.03658	0.115537
I	0.35467	1.727633	0.084347
N	5.261137	-2.00081	-0.0851
C	6.047223	-2.00594	-1.15626
C	5.830939	-2.16292	1.104382
C	7.421823	-2.17257	-1.0892
H	5.552829	-1.87006	-2.11226
C	7.195074	-2.33678	1.276695
H	5.161618	-2.15297	1.958423
C	8.006472	-2.34173	0.154446
H	8.014859	-2.16922	-1.99406
H	7.607664	-2.46544	2.268401
H	9.076738	-2.47615	0.248631
N	1.746711	4.506659	0.054686
C	2.257063	5.103679	1.12638
C	1.88209	5.113949	-1.11942
C	2.918042	6.320807	1.074915
H	2.129806	4.583119	2.069592
C	2.524401	6.332155	-1.27498
H	1.45448	4.600705	-1.97437
C	3.05367	6.946876	-0.15272
H	3.315642	6.763141	1.978495
H	2.606587	6.78401	-2.25436
H	3.562346	7.89929	-0.23394
N	-5.85536	0.163849	0.090509
C	-6.64044	0.151256	1.162353
C	-6.42879	0.314348	-1.0988

C	-8.01825	0.288465	1.095911
H	-6.14243	0.025826	2.117865
C	-7.79633	0.459033	-1.2701
H	-5.75944	0.319825	-1.95285
C	-8.60691	0.446424	-0.14731
H	-8.61056	0.272288	2.001087
H	-8.2121	0.580111	-2.26141
H	-9.67972	0.559194	-0.24076