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Uthrene, a *radically* new molecule?†

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We have studied uthrene with a large range of quantum chemical models. Uthrene is predicted to be naturally twisted and to possess a triplet ground state, making it the smallest non-planar polycyclic biradical that can be derived from graphene.

The experimental isolation of graphene in 2005 and its remarkable physical properties sparked the imagination of physicists and chemists alike.[1–3] Graphene is nothing more than a sheet of benzene rings fused together or, in other words, a gigantic Polycyclic Hydrocarbon (PH). PHs with an even number of carbon atoms are typically closed-shell, *i.e.* all their electrons are paired, but may, in special cases, have open-shell character resulting in unique electronic, optical and magnetic properties that make them potential candidates for spintronics[4–6] and energy storage.[7]

We report the computational characterization of the smallest non-planar biradical PH species that can be "cut" from graphene: dibenzo[*de*,*hi*]tetracene or uthrene.‡ Uthrene is a non-Kekulé molecule composed by six fused benzenoid rings, Fig. 1. We will study computationally a representative set of molecules with six fused benzenoid rings, namely: fulminene, hexacene, zethrene, uthrene and triangulene, Fig. 1. Fulminene and hexacene are isomers of $C_{26}H_{16}$, hexacene is very reactive due to its small HOMO–LUMO gap and, in contrast, fulminene is one of the hexabenzenoids with larger HOMO–LUMO gap. Zethrene is very similar to uthrene, with which it shares its chemical formula, $C_{24}H_{14}$. Triangulene is, like uthrene, a non-Kekulé molecule and the smallest graphene fragment with a high spin multiplicity.[8] Theoretical models have predicted remarkable magnetic properties in triangular graphene fragments due to high spin multiplicity.[9,10] A tri-*t*-butylated triangulene derivative was synthesized[11] and characterized 60 years after Clar's original proposal.[12] Uthrene does not occur naturally and has yet to be synthesized, but its biradical open-shell character has been noted, if briefly, in systematic computational studies of PHs[13,14]

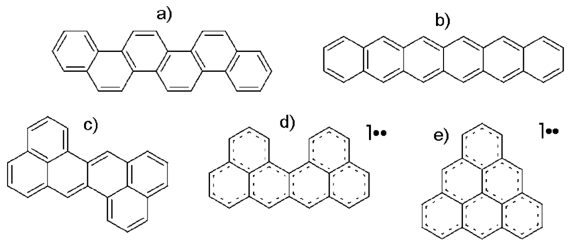

Fig. 1 (a) Fulminene/[6]phenacene ($C_{26}H_{16}$); (b) hexacene ($C_{26}H_{16}$); (c) zethrene ($C_{24}H_{14}$); (d) uthrene/dibenzo[*de*,*hi*]tetracene ($C_{24}H_{14}$) and (e) triangulene ($C_{22}H_{12}$).

We have applied different quantum chemical models to the chosen hexa-benzenoid molecule set.§ The results are qualitatively similar: fulminene shows a large HOMO–LUMO gap, 3.6 eV, while zethrene and hexacene present much smaller values, 1.8 and 1.4 eV, respectively. Triangulene and uthrene have an open-shell double degenerate ground state at the tight-binding level. In fact, uthrene and triangulene are non-Kekulé biradicals: it is not possible to assign alternating single and double bonds in these molecules without leaving two unpaired, radical, electrons. Interestingly uthrene is very similar to zethrene, both molecules are derivatives of the phenalenyl radical.[8] Phenalenyl and uthrene are non-Kekulé while zethrene is a Kekulé molecule,¶ see Fig. 2.

Table 1 shows the results of different DFT models in our set of hexa-benzenoids.‖ All models yielded spin contamination in open-shell singlet calculations for hexacene, uthrene and

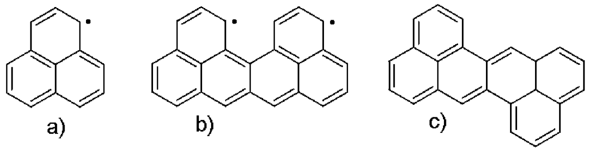

Fig. 2 (a) Phenalenyl radical; (b) uthrene and (c) zethrene.

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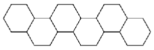
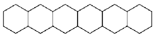
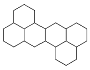
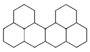
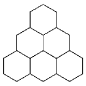
† Electronic supplementary information (ESI) available: Total energies for all the DFT models presented in Table 1 and rendering and Cartesian coordinates of all the DFT optimized structures for singlet and triplet ground states at the CAM-B3LYP/6-31g(d,p) level. See DOI: 10.1039/c5cc01276g

Table 1 Energy differences (kcal mol^{-1}) for the triplet and unrestricted singlet (S_U) open-shell ground states. Spin contamination for the singlet unrestricted calculations ($\langle S^2 \rangle$). Energy differences between closed-shell restricted (CS_R) and unrestricted singlet (S_U) and triplet (T_U). All energies refer to optimized geometries

Name	Structure	ΔE^a (T_{RO}–S_U)	ΔE^b (T_U–S_U)	$\langle S^2 \rangle$	ΔE^c (S_U–CS_R)	ΔE^d (T_U–CS_R)	Model
Fulminene/[6]napthacene		67.9	62.8	0.0	0.0	62.8	CAM-B3LYP/6-31g(d,p)
Hexacene		18.4	13.4	0.9	−2.7	10.7	CAM-B3LYP/6-31g(d,p)
Zethrene		23.4	16.5	0.0	0.0	16.5	CAM-B3LYP/6-31g(d,p)
Uthrene/dibenzo[*de*,*hi*]tetracene		2.2	−7.7	1.1	−23.9	−31.6	CAM-B3LYP/6-31g(d,p)
		−0.1	−4.9	1.1	−14.8	−19.7	B3LYP/6-31g(d,p)
		−6.3	0.5	1.1	N.C.	N.C.	HSE06/6-31(d,p)
Triangulene		−0.7	−11.2	1.1	−23.2	−34.4	CAM-B3LYP/6-31g(d,p)
		−2.0	−7.0	1.1	N.C.	N.C.	B3LYP/6-31g(d,p)
		−6.6	−1.5	1.1	N.C.	N.C.	HSE06/6-31(d,p)

[a] Restricted open triplet (T_{RO}) energy minus singlet energy (S_U). [b] Unrestricted open triplet (T_U) energy minus singlet energy (S_U). [c] Unrestricted singlet energy minus restricted closed-shell energies (CS_R). [d] Unrestricted triplet energy minus restricted closed-shell energies. Negative values indicate open-shell ground states. N.C.: calculations not converged. $\langle S^2 \rangle$ values for triplet calculations range between 2 and 2.25.

triangulene. Unrestricted calculations in the closed-shell molecules, fulminene and zethrene, gave, as expected, the same energies as restricted calculations. Hexacene is predicted to have an open-shell ground state coherently with its high reactivity.[15,16] DFT models confirmed tight-binding results for uthrene and triangulene yielding open-shell ground states. For triangulene a triplet ground state was predicted by all models as observed experimentally.[11] For uthrene, B3LYP and CAM-B3LYP Hamiltonians predict a triplet ground state, while the HSE06 functional predicts a biradical singlet state.

The spin density for both triplet and singlet open-shell ground states is depicted in Fig. 3. For the singlet ground state the two radicals are localized in different sides of the molecules. In contrast, for the triplet ground state the spin density is delocalized through the molecule conserving molecular symmetry. In both cases there is larger spin density at the molecular edges.

We performed calculations at the CASSCF(14,14)/6-31g(d,p) level for singlet and triplet multiplicities for the chosen hexabenzenoid molecule set. The natural orbital (NO) populations of the frontier orbitals for the singlet CASSCF calculations are plotted in Fig. 4. NO populations for fulminene and zethrene are very near to either two (double occupied) or zero (unoccupied) and consequently these molecules are closed-shell. Hexacene has more fractional populations occupancies and larger open shell character as observed before.[17] In contrast, uthrene and triangulene singlets are biradicals (two single occupied orbitals). At the CASSCF level fulminene, hexacene and zethrene are confirmed to be singlets, while uthrene and trianguelene are found to be triplets with ΔE(Triplet-Singlet) of −10.9 and −11.7 kcal mol^{-1}, respectively.

Twisting the aromatic moiety of PHs is a good strategy to enhance solubility and to modulate electronic properties.[18–21] Twisting is typically achieved by attaching bulky functional groups. Uthrene, however, is naturally twisted by an angle** of $\sim 20^\circ$ to minimize steric repulsion between two neighbouring hydrogen atoms.

In order to estimate the thermodynamic feasibility of uthrene we have also calculated formation energies with respect to graphene

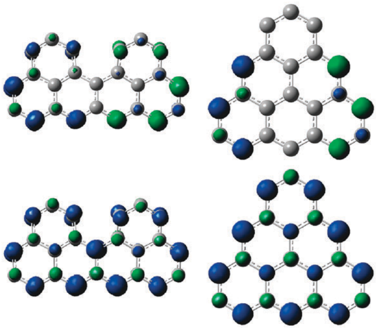


Fig. 3 Uthrene (left) and triangulene (right) spin density for singlet open-shell ground state (top) and triplet open-shell ground state (bottom) at the CAM-B3LYP/6-31g(d,p) level. Blue and green colours show up and down spin densities (surface value = 0.01).

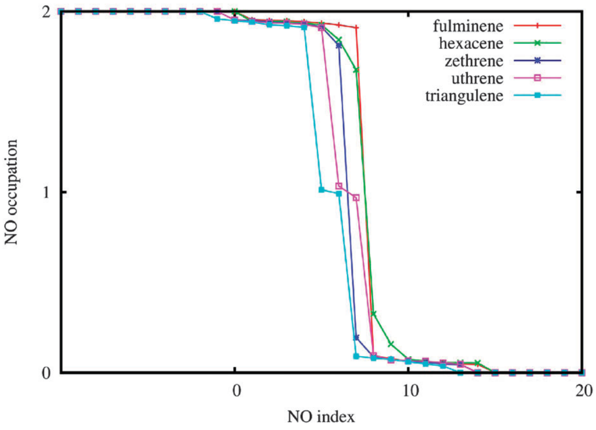


Fig. 4 Natural orbital (NO) population for singlet CASSCF(14,14)/6-31(g,d) calculations. Populations range from two (double occupied) to zero (unoccupied).

and molecular hydrogen. The formation energies so calculated are (in kcal mol^{-1}): fulminene = 10, hexacene = 34, zethrene = 24, uthrene = 39 and triangulene = 30. Uthrene is predicted to be thermodynamically more costly, but only 5 kcal mol^{-1} more than hexacene. In addition, a biradical zethrene derivative with a similar, yet larger, steric hindrance has been synthesized: 1,2:9-10-dibenzoheptazethrenze.[22] Both facts indicate that uthrene might be synthetically possible.

Summing up, we have computationally characterized the biradical uthrene. Uthrene is non-planar, presents a twisting angle of 20° and has a triplet ground state which makes it potentially suitable for a number of technological applications. We hope the present study helps draw more attention to this neglected fascinating molecule.

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Notes and references

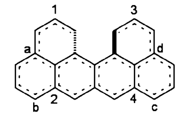
‡ Named by analogy with zethrene, whose name is due to its Z-like molecular shape.

§ Computer models: different levels of theory were applied through this study, namely: molecular mechanics, tight-binding and *ab initio* spin-polarized DFT and CASSCF(14,14). The 6-31g(d,p) basis set was used throughout this study. Three DFT hybrid Hamiltonians were used: B3LYP,[8,23,24] CAM-B3LYP[22,25] and HSE.[5] Geometries of all models but CASSCF were fully optimized. Starting geometries for *ab initio* models were obtained with a DFTB Hamiltonian that allows for fractional electron occupancies. In order to explicitly allow for relaxation through the Jan-Teller effect and study lower symmetry conformations, two different sets of geometries were considered with and without symmetrisation. In addition, in open-shell calculations, homo and lumo orbitals were initially swapped to destroy α-β spatial symmetry. Geometry optimization for high and low symmetries gave virtually the same energies and only high symmetries results are presented: fulminene: C_{2H}; hexacene: D_{2H}; zethrene: C_{2H}; uthrene: C_2; triangulene: D_{3H}. HOMO–LUMO gaps and formation energies were calculated with the HSE06 functional without thermal and vibrational corrections. In addition to the molecules in this study, a complete set containing all benzenoid molecules derived from graphene with an even number of number atoms with 2, 4, 5, and 6 hexagonal rings were systematically optimized with Brenner, DFTB and HSE06 Hamiltonians. Triangulene and uthrene were found to be the two smallest biradical PH that can be cut from graphene. Modelling software: different software packages were used for different Hamiltonians: molecular models (home version of TINKER[26–28]), tight-binding (home software[29–31]), DFTB (DFTB+[32]) and DFT and CASSCF (Gaussian 09[33]). Graphics were generated by the programs Gaussview[34] and Jmol.[35] Computational details: DFT calculations were quite inexpensive, with wall times inferior to 87 and 47 minutes for the singlet and triplet ground states respectively for the UHSE functional. UB3LYP and UCAM-B3LYP calculations used UHSE molecular geometries and ran in less time. These computations were run with 8 parallel threads using 7 GB of memory in Intel Xeon X5650/E5649 dual socket computers. CASSCF(14,14) calculations, in contrast, took much more time with up to 76 hours wall time when run with 24 parallel threads using 60 GB of memory in Intel Xeon E5-2695v2 dual socket computers.

¶ Note that the two double bonds of the central part of zethrene possess a strong diene character as the two resonance structures (not shown) keep the same central double bonds.

‖ Experimentally, the open-shell nature and low HOMO–LUMO gap of some PHs make them consistently difficult to synthesize and characterize. Higher order acenes (> pentacene[15,16]) and, in general, low gap PHs[37] are difficult to isolate as they polymerize and oxidize quickly. Theoretically, acenes can be qualitatively understood in terms of Clar sextets.[36,38] In contrast, quantitative work in acenes is more subtle, from the DFT work of Bendikov[23] to the multiconfigurational work of Plasser,[17] and has been the subject of controversy as reported by Hajgató.[39–41] Single determinant DFT calculations agree with available experimental data on magnetic, open-shell, PHs.[8,22] In addition, a systematic study on *m*-xylylene, another non-Kekulé structure, found that B3LYP and full π valence CASSCF yield comparable results.[42]

** Twist angles of 18–20° and 21–24° for the tetracene backbone (dihedral of *abcd* atoms) and the full molecule (dihedral of 1234 atoms), respectively, were measured on DFT geometries.



1 K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva and A. A. Firsov, *Science*, 2004, **306**, 666–669.
2 A. K. Geim and K. S. Novoselov, *Nat. Mater.*, 2007, **6**, 183–191.
3 A. H. Castro Neto, F. Guinea, N. M. R. Peres, K. S. Novoselov and A. K. Geim, *Rev. Mod. Phys.*, 2009, **81**, 109.
4 Y.-W. Son, M. L. Cohen and S. G. Louie, *Nature*, 2006, **444**, 347–349.
5 V. Barone, O. Hod, J. E. Peralta and G. E. Scuseria, *Acc. Chem. Res.*, 2011, **44**, 269–279.
6 C. Tao, L. Jiao, O. V. Yazyev, Y.-C. Chen, J. Feng, X. Zhang, R. B. Capaz, J. M. Tour, A. Zettl, S. G. Louie, H. Dai and M. F. Crommie, *Nat. Phys.*, 2011, **7**, 616–620.
7 Y. Morita, S. Nishida, T. Murata, M. Moriguchi, A. Ueda, M. Satoh, K. Arifuku, K. Sato and T. Takui, *Nat. Mater.*, 2011, **10**, 947–951.
8 Y. Morita, S. Suzuki, K. Sato and T. Takui, *Nat. Chem.*, 2011, **3**, 197–204.
9 J. Fernández-Rossier and J. J. Palacios, *Phys. Rev. Lett.*, 2007, **99**, 177204.
10 W. L. Wang, O. V. Yazyev, S. Meng and E. Kaxiras, *Phys. Rev. Lett.*, 2009, **102**, 157201.
11 J. Inoue, K. Fukui, T. Kubo, S. Nakazawa, K. Sato, D. Shiomi, Y. Morita, K. Yamamoto, T. Takui and K. Nakasuji, *J. Am. Chem. Soc.*, 2001, **123**, 12702–12703.
12 E. Clar, *Polycyclic hydrocarbons*, Academic Press, 1964.
13 J. C. Fetzer, *Large (C = 24) polycyclic aromatic hydrocarbons: chemistry and analysis*, John Wiley & Sons, 2000.
14 J. R. Dias, *Polycyclic Aromat. Compd.*, 2014, **34**, 177–190.
15 J. E. Anthony, *Angew. Chem., Int. Ed.*, 2008, **47**, 452–483.
16 R. Mondal, C. Tönshoff, D. Khon, D. C. Neckers and H. F. Bettinger, *J. Am. Chem. Soc.*, 2009, **131**, 14281–14289.
17 F. Plasser, H. Pašalić, M. H. Gerzabek, F. Libisch, R. Reiter, J. Burgdörfer, T. Müller, R. Shepard and H. Lischka, *Angew. Chem., Int. Ed.*, 2013, **52**, 2581–2584.
18 J. Lu, D. M. Ho, N. J. Vogelaar, C. M. Kraml and R. A. Pascal, *J. Am. Chem. Soc.*, 2004, **126**, 11168–11169.
19 J. E. Norton and K. N. Houk, *J. Am. Chem. Soc.*, 2005, **127**, 4162–4163.
20 S. Choudhary, C. Gozalvez, A. Higelin, I. Krossing, M. Melle-Franco and A. Mateo-Alonso, *Chem. – Eur. J.*, 2014, **20**, 1525–1528.
21 S. More, S. Choudhary, A. Higelin, I. Krossing, M. Melle-Franco and A. Mateo-Alonso, *Chem. Commun.*, 2014, **50**, 1976–1979.
22 Z. Sun, S. Lee, K. H. Park, X. Zhu, W. Zhang, B. Zheng, P. Hu, Z. Zeng, S. Das, Y. Li, C. Chi, R.-W. Li, K.-W. Huang, J. Ding, D. Kim and J. Wu, *J. Am. Chem. Soc.*, 2013, **135**, 18229–18236.
23 M. Bendikov, H. M. Duong, K. Starkey, K. N. Houk, E. A. Carter and F. Wudl, *J. Am. Chem. Soc.*, 2004, **126**, 7416–7417.
24 D. Jiang and S. Dai, *J. Phys. Chem. A*, 2008, **112**, 332–335.
25 J. L. Zafra, R. C. G. Cano, M. C. R. Delgado, Z. Sun, Y. Li, J. T. L. Navarrete, J. Wu and J. Casado, *J. Chem. Phys.*, 2014, **140**, 054706.
26 M. Melle-Franco, M. Prato and F. Zerbetto, *J. Phys. Chem. A*, 2002, **106**, 4795–4797.

27 A. Catheline, L. Ortolani, V. Morandi, M. Melle-Franco, C. Drummond, C. Zakri and A. Pénicaud, *Soft Matter*, 2012, **8**, 7882–7887.

28 K. Strutyński, J. A. N. F. Gomes and M. Melle-Franco, *J. Phys. Chem. A*, 2014, **118**, 9561–9567.

29 P. Ruffieux, M. Melle-Franco, O. Gröning, M. Bielmann, F. Zerbetto and P. Gröning, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2006, **71**, 153403.

30 M. Melle-Franco, M. Marcaccio, D. Paolucci, F. Paolucci, V. Georgakilas, D. M. Guldi, M. Prato and F. Zerbetto, *J. Am. Chem. Soc.*, 2004, **126**, 1646–1647.

31 C. T. Cioffi, A. Palkar, F. Melin, A. Kumbhar, L. Echegoyen, M. Melle-Franco, F. Zerbetto, G. M. A. Rahman, C. Ehli, V. Sgobba, D. M. Guldi and M. Prato, *Chem. – Eur. J.*, 2009, **15**, 4419–4427.

32 B. Aradi, B. Hourahine and T. Frauenheim, *J. Phys. Chem. A*, 2007, **111**, 5678–5684.

33 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, 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. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, *Gaussian 09 revision A.01*.

34 R. Dennington, T. Keith and J. Millam, *Gauss view version 5.0.3*.

35 A. Herraez, *How to use Jmol to study and present molecular structures*, Lulu.com, Morrisville, NC, 2008.

36 E. Clar, *The aromatic sextet*, J. Wiley, 1972.

37 Z. Sun, Q. Ye, C. Chi and J. Wu, *Chem. Soc. Rev.*, 2012, **41**, 7857–7889.

38 M. Solà, *Front. Chem.*, 2013, **1**, 22, DOI: 10.3389/fchem.2013.00022.

39 B. Hajgató, M. S. Deleuze, D. J. Tozer and F. D. Proft, *J. Chem. Phys.*, 2008, **129**, 084308.

40 B. Hajgató, D. Szieberth, P. Geerlings, F. De Proft and M. S. Deleuze, *J. Chem. Phys.*, 2009, **131**, 224321.

41 M. Huzak, M. S. Deleuze and B. Hajgató, *J. Chem. Phys.*, 2011, **135**, 104704.

42 D. Reta Mañeru, A. K. Pal, I. de P. R. Moreira, S. N. Datta and F. Illas, *J. Chem. Theory Comput.*, 2014, **10**, 335–345.