ORIGINAL PAPER

Bis-dibenzo[a.i]fluorenylidene, does it exist as stable 1,2-diradical?

**Basem Kanawati · Alexander Genest ·
Philippe Schmitt-Kopplin · Dieter Lenoir**

Abstract The geometries, energies, and electronic properties of the two possible configurations of bis-[dibenzo[a.i]-fluorenylidene] were investigated theoretically by density functional theory DFT B3LYP at the UB3LYP/6-311+G (2d,p) // UB3LYP/6-31+G(d,p) level of theory. According to the performed calculations, it was found that the singlet is 3.4 kcal mol^{-1} lower in energy compared to triplet state at room temperature. This gap is compared with those of other alkenes like ethylene, (61.9 kcal mol^{-1}) tetra-*tert*-butyethylene, (6.4 kcal mol^{-1}) and bis-fluorenylidene (19.5 kcal mol^{-1}). These results confirm the experimental findings of the paramagnetic properties determined by Franzen and Joschek. The low singlet-triplet gap in the case of bis-[dibenzo[a.i]fluorenylidene] is the result of a steric destabilization of the singlet due to strain and stabilization of the triplet electronic state by delocalization of each free electron within each aromatic moiety. This correlates with the special electronic structure of the triplet state of this compound, where facial interaction of two hydrogen atoms lying close to the lobes of each p-orbital occupied with a single electron at the distorted double bond in the triplet electronic state.

Introduction

Steric strain at the ethylenic double bond results in torsion and in twisting of this bond, which prefers a planar structure due to sp^2 hybridization [1–5]. Tetra-*tert*-butylethylene (**1**) (Fig. 1) has not been prepared until now [6], but it was expected according to previous calculations that **1** is a stable alkene. A central dihedral angle of 45° around the C=C double bond has been calculated for this elusive hydrocarbon using DFT calculations with BLYP/DZd level [7] and 47.1° with B3LYP/6-31+G(d,p) level of theory [8] and this work. The most distorted double bond is found in the perchloroderivative of bis-9,9'-fluorenylidene **2,** a torsion angle of 66° has been deduced by single x-ray structure analysis of this compound [9]. Hydrindanylidene-hindrindane is another highly strained alkene, it has a torsion angle of 49°, found at the central double bond [10]. Bis-[dibenzo[a.i]fluorenyli-dene] (**3**) (IUPAC name: 13-H-dibenzo[a,i]fluorene) is a compound, which also contains a highly strained double bond. It was prepared and characterized already in 1925 by Magidson [11] and in 1953 by the group of Bergmann [12, 13] , using oxidative coupling reactions at the CH$_2$ group of the dibenzofluorenylidene unit.

In 1961 Franzen and Joschek postulated the radical character for the deeply green colored compound **3** by measuring its paramagnetic properties [14]. They measured the molar paramagnetic susceptibility in toluene at room

B. Kanawati (✉) · P. Schmitt-Kopplin · D. Lenoir (✉)
Research Unit Analytical Biogeochemistry,
Helmholtz Zentrum München, Ingolstädter Landstr.1,
85758 Neuherberg, Germany
e-mail: Basem.Kanawati@helmholtz-muenchen.de
e-mail: Lenoir@helmholtz-muenchen.de

A. Genest
Department Chemie and Catalysis Research Center,
Technische Universität München,
85747 Garching, Germany

P. Schmitt-Kopplin
Technische Universität München,
Lehrstuhl für Analytische Lebensmittelchemie/Chair
of Analytical Food Chemistry,
Alte Akademie 10,
85354 Freising, Germany
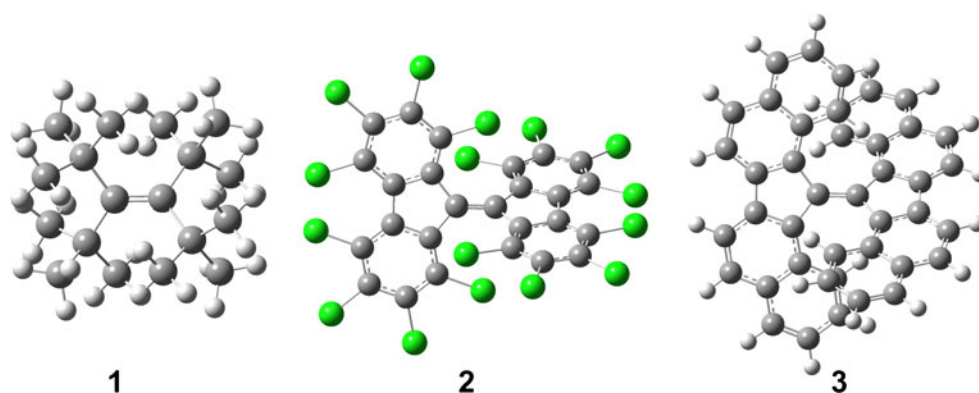
temperature and estimated that about 4 % of the bulk chemical should exist as a paramagnetic species, which is in equilibrium with its diamagnetic configuration. In addition, they obtained the ESR spectrum of this compound and calculated a value of 6 % for the paramagnetic contribution. By cooling the sample the ESR signal disappears at -196 °C, but it is retained at room temperature, showing a reversible equilibrium between paramagnetic and diamagnetic forms of compound **3**. The biradical character of hydrocarbon **3** was also deduced from its chemical reactivity; the autooxidation of benzaldehyde and the polymerization of styrene is prohibited in the presence of this compound, so that compound **3** behaves as a radical scavenger [14].

These authors suggested that the paramagnetic configuration is in accordance with the 90° distorted geometry which describes the triplet electronic state and represents a stable form of this alkene as a 1,2-biradical. However, these interesting results were not followed up later since that time, neither by Franzen himself nor by the chemical community. It should be mentioned that Schlenk identified another hydrocarbon which represents another example of a stable biradical but it is 1,5 biradical [15]. Other long range biradicals have been reported [16–18]. A value of 4 kcal mol^{-1} can be deduced for the singlet-triplet gap from the experimental results of Franzen and Joschek. This value is unusually low for an alkene; ethylene itself has a gap in the range of 60-65 kcal mol^{-1} [19]. It is in the same order of magnitude with the inherent *cis-trans* isomerization barrier of ethylene, extrapolated starting from a series of polyalkyl-ethylenes [20]. Alkenes with conjugated aryl groups have singlet-triplet gaps in the range of 30-50 kcal mol^{-1} [21].

The crowded alkene, tetra-*tert*-butyethylene (**1**) has a low singlet-triplet gap of 12.6 kcal mol^{-1} calculated by BLYP/DZd method [7]. This was explained by a possible stabilization of the triplet electronic state by hyperconjugation of the alkyl groups. Our recent calculations done by the implementation of B3LYP/6-311+G(2d,p) level of theory gives even a lower gap of 6.4 kcal mol^{-1} . Because of our interest of distorted alkenes we tried to perform x-ray analysis of

crystalline compound **3** in the past, but we failed due to the significant disorder of the crystals. In 1993 Beck succeeded to perform the x-ray analysis of compound **3** described in his thesis, the compound was co-crystallized with other aromatic hydrocarbons like pyrene in toluene [10]. Since new theoretical tools are now available to solve the unusual behavior of alkene **3**, we applied DFT calculations to solve the open questions and to confirm or disprove the results of Franzen. For comparison purposes we included ethylene and bis-fluorenylidene in our calculations.

It should be mentioned that 1,2-biradicals have been investigated intensively in organic chemistry [21] but the investigated 1,2-biradicals are highly reactive intermediates, produced either photochemically or by catalytic processes from their precursors. We address a possibly stable 1,2-biradical which can exist in equilibrium with its singlet electronic ground state. We want to mention that 1,2-biradical character was observed recently by ESR measurements of substituted 1,2-disilenes investigated by Apeloig [22].

Computational methods

The electronic structure calculations were performed by using density functional theory (DFT), incorporated in Gaussian 03 W program [23]. The hybrid DFT method B3LYP was employed with 2d polarization functions for each heavy atom and 1p for each hydrogen atom in all single point energy calculations to obtain accurate electronic energy values. All geometry optimizations were performed using 6-31+G(d,p) basis set. Frequency calculations were also done for each optimized geometry using the same basis set 6-31+G(d,p) to obtain the zero point vibrational energy (ZPVE). This value is multiplied by the scaling factor 0.9877 to correct for vibrational anharmonicities [24]. Single point energy (SPE) calculations were done using 6-311+ G(2d,p) level of theory. Unrestricted calculations were performed for all geometry optimizations and single point energetics related to the triplet electronic state. Stability tests were performed on all calculated structures to ensure that the used wave function does represent the

lowest energy solution of the self consistent field (SCF) equations. Markovic et al. have shown that the functional B3LYP with the basis set 6-311+G(d,p) was excellently capable to describe the triplet electronic state of several aromatic hydrocarbons [25].

For geometry optimization, the analytical gradient optimization routines were used in combination with the GDIIS algorithm. The requested convergence in the density matrix was 10^{-8}, the threshold value for maximum displacement was 0.0018 Å, and that for the maximum force was 0.00045 Hartree/Bohr. The nature of the stationary points was established by calculating and diagonalizing the Hessian matrix (force constant matrix) to ensure no negative eigenvalues are present. The data derived from the DFT results was used to calculate the Gibbs free energy change of the difference between singlet and triplet form of the molecule using standard textbook thermodynamic formulas [26].

Results and discussion

Beck published the single crystal x-ray structure of compound **3** in his PhD thesis. He solved the problem of the general disorder in the crystal of the problematic highly crowded alkenes by co-crystallization with pyrene and toluene as solvents [27]. This enabled scientists to approach more accurate experimental geometric parameters at the central double bond of highly crowded alkenes [28]. Figure 2 shows a comparison between the experimentally obtained single crystal x-ray structure of **3** with the calculated optimized geometry according to B3LYP/6-31+G(d,p) level of theory. The x-ray structure could achieve an R-value of 8.5 % which indicates that the geometry parameters around the central C=C bond of compound **3** are reliable. The experimental structure has a C=C bond length of 1.41 Å and is in excellent agreement with the C=C bond length in the calculated DFT structure. However, the single crystal x-ray structure shows two values of the characteristic dihedral angle
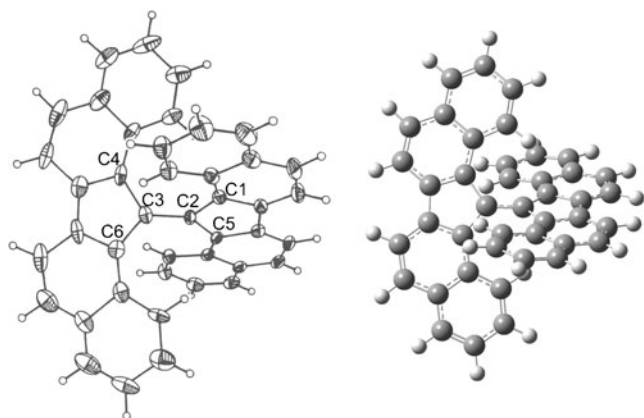
Table 1 Geometry parameters at the double bond C2=C3 for the experimental and calculated structures of compound **3**. Bond lengths are given in Å and angles in degrees. Values inside parenthesis indicate absolute standard deviation for the experimentally determined structure (see ref. [27])

Geometry parameter	Experimental	Calculated
C2=C3	1.41 (0.10)	1.41
C1C2C3C4	53.1 (0.09)	53.2
C5C2C3C6	50.3 (0.09)	53.2
C1C2	1.46 (0.09)	1.48
C2C5	1.47 (0.09)	1.48
C3C4	1.49 (0.10)	1.48
C3C6	1.44 (0.11)	1.48

around the central C=C bond: C1C2C3C4 dihedral angle is 53.1° whereas the C5C2C3C6 is 50.3°. This is due to experimental uncertainty due to disorder in crystal packing. Our optimized DFT structure shows no difference between C1C2C3C4 and C5C2C3C6 dihedral angles which represents a consistantly calculated geometry due to the planarity of the ligands connected to the central C=C atoms. The calculated dihedral angle equals to 53.2° and is in very good agreement with the experimental value for this highly distorted double bond. In the crystal the vinylic four bonds (C1C2, C2C5, C3C4 and C3C6) are slightly different (Table 1). This is an additional indicator for the slight experimental uncertainty of the structure of compound **3** caused by minor crystal packing disorder. The DFT calculation shows a unique bond length for all the four mentioned vinylic bonds which is in agreement with the high symmetry of this structure.

We conclude that the performed DFT calculation can reproduce the experimentally obtained geometry quite well. Consequently, the performed calculations on this level of theory are valid for highly crowded structures like compound **3**.
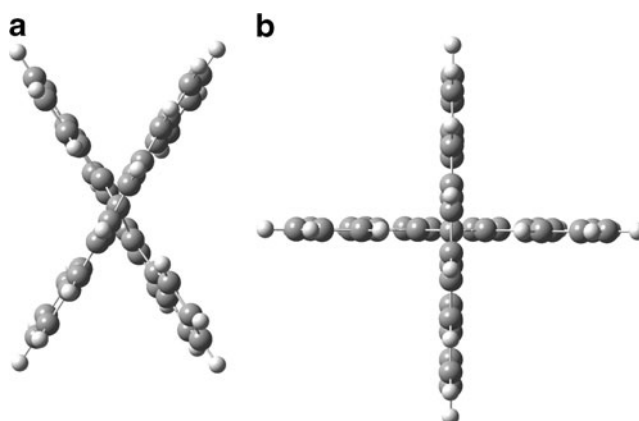

Fig. 2 Experimental versus calculated structure of compound **3**

Fig. 3 (**a**) Calculated structure of compound **3** in the singlet electronic state. (**b**) Calculated structure of compound **3** in the triplet electronic state

Table 2 Singlet-triplet gap ΔH[T-S] for ethylene (1-7 calculated by seven different methods compared with the experimental value 8) in kcal mol^{-1}

Number	Method	ΔH[T-S]
1	UMP2/6-311-+G*, 1992 [34]	68.5
2	BLYP/DZd, 1996, [7]	64.8
3	CSSD(T)/aVQZ, 2008, [31]	65.2
4	CSSD(T)/CBS(2), 2008, [31]	65.6
5	TAE, 2008, [19]	65.8
6	DCM (diffusion Monte Carlo),2003, [35]	66.4
7	B3LYP/6-311+G(2dp), 2011 (This work)	61.3
8	Recent experimental [33]	58±3

In regard to the triplet electronic state of compound **3**, no experimental data exist. However, we performed DFT calculations on the triplet electronic state on the same level of theory to investigate the changes in important geometry parameters while going from singlet to triplet. Figure 3 shows a clear difference in the central dihedral angle between the singlet and the triplet electronic states of compound **3**. The central dihedral angle changes from 53.2° in the singlet electronic state to 90.0° in the triplet electronic state, as expected. This indicates a clear 1,2-biradical character of compound **3** in the triplet electronic state. Triplet alkenes has been studied intensively in the recent decades but most of these studies concerned normal non-distorted alkenes [29–31]. The idea goes back to the theoretical concept of Mulliken, who first suggested a 90° distorted C=C double bond in the triplet ethylene [32].

In order to test and answer the question about how reliable are the implemented DFT method for describing the triplet electronic state of ethylene as a simple model of a C=C bond, we calculated the singlet-triplet gap for ethylene and compared the result with other theoretical methods. Table 2 shows that the calculated gap for ethylene by DFT B3LYP/6-311+G(2d,p) (61.3 kcal mol^{-1}) comes very close
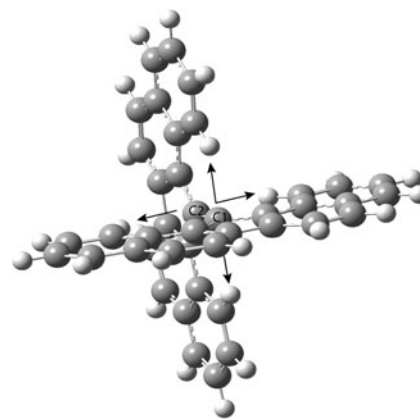
Fig. 4 Another view of compound **3** in its triplet electronic state. The double bond was between C1 and C2 before the structure is further distorted while going from the singlet to the triplet electronic state

to the most reliable and recently experimentally determined value by Qi et al. which equals to 58±3 kcal mol^{-1} [33].

Table 3 shows the differences in the C=C bond length as well as in the torsion angle around the C=C bond in three crowded alkenes compared to ethylene in both singlet and triplet electronic states. The C=C bond elongation of all three crowded alkenes listed in Table 3 occurs to the same extent, no matter whether the structure is aliphatic or aromatic and regardless to the extent of torsion around the C=C bond. When going from the singlet to the triplet electronic state, a significant C=C bond elongation occurs and the torsion angle changes to around 90°. The C=C bond elongation in the triplet state indicates the destruction of the C=C bond and the formation of a biradical with partial single C-C bond character.

We return back to discuss the singlet-triplet gap of compound **3**. The calculated gap according to our work at the B3LYP/6-311+G(2dp) level equals to 3.4 kcal mol^{-1} at 300 K. This value represents the lowest known value for all investigated crowded alkenes so far. This result suggests that both singlet and triplet states of compound **3** exist in

Table 3 Effect of steric crowding on the C=C bond length (Å) and the central dihedral angle (degree) of both singlet and triplet structures as well as the singlet-triplet gap ΔH [T-S] (kcal mol^{-1})

Alkene	C=C bond length [S] in Å	C=C torsion angle [S] in degree	C=C bond length [T] in Å	C=C torsion angle [T] in degree	ΔH [T-S] in kcal/mol
Ethylene	1.334	0.0	1.451	90.0	61.3 [58±3] exp.[a]
Tetra-*tert*-butylethylene (**1**)	1.390	45.1	1.512	82.2°, 94.1° *	6.4**
Bis-fluorenylidene	1.381 ***	34.3 ***	1.464	90.0	19.5
Bis-dibenzo[a.i] fluorenylidene (**3**)	1.408	53.2	1.470	90.0	3.4

* Two dihedral angles were identified for compound **1** in the triplet electronic state. This is an indication of a slight pyramidalization of the compound **1** in the triplet electronic state.

** The singlet-triplet splitting of compound **1** was found earlier to be 12.6 kcal mol^{-1} on the BLYP/DZd level of theory [7].

*** These values are in agreement with the experimental C=C bond length and torsion angle found in the x-ray structure of bis-fluorenylidene which was obtained by co-crystallization with pyrene [36].
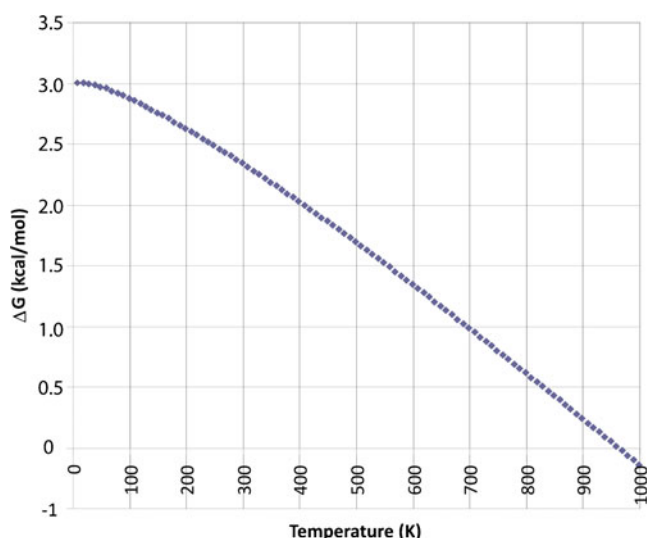
Fig. 5 Temperature dependency of ΔG (singlet-triplet gap) of compound **3**, calculated by B3LYP/6-311+G(d,p) level of theory

Fig. 7 SOMO and SOMO-1 molecular orbitals for compound **3** in its triplet electronic state

thermal equilibrium. This means that the structure of the triplet state of compound **3** is relatively stable. This interesting result induces the following question: If the triplet structure of compound **3** is stable, what are the stabilizing factors for this compound?

There exists a significant electron delocalization possibility for each free electron in the biradical along its own aromatic moiety so that 24 different canonical forms can be written for this structure. Evidence for this aromatic stabilization effect is discussed below. Moreover, we also observe an important steric consequence shown in Fig. 4, which correlates with the special stabilization of the triplet electronic state of compound **3**. On each carbon atom C1 and C2, there are two facial interactions between the p-orbital of the free single electron and the two available hydrogen

atoms located above and below the plane of each aromatic moiety. The distance between C1 and either hydrogen atoms is only 2.46 Å. The same is true for the distance between C2 and any of the two circumferential hydrogen atoms. There is no difference in the C-H bond lengths of the mentioned hydrogen atoms between the singlet and the triplet structure. The absence of any C-H elongation when going from the singlet to the triplet electronic state can be understood by the fact that the odd electron on C1 or C2 atoms is not fixed inside the unhybridized p-orbital of C1 or C2. Each of these two odd electrons is actually delocalized over the whole corresponding aromatic moiety (further evidence for this delocalization is given below where SOMO, SOMO-1 and Mulliken atomic spin density distribution for compound **3** in its triplet electronic state is provided below). We wanted to indicate according to Fig. 4 that no noticeable interaction between the unhybridized p-orbital and any of the two facial hydrogen atoms can be expected and this is due to the mentioned delocalization of each odd electron over its corresponding large aromatic moiety.

Fig. 6 Mulliken atomic spin density distribution of compound **3** in its triplet electronic state. Two views are presented for the same compound **3** to show details on each large aromatic moiety. The hydrogen atoms are not visible to simplify the view
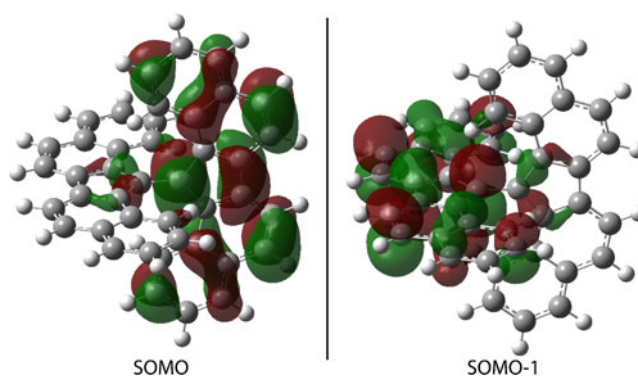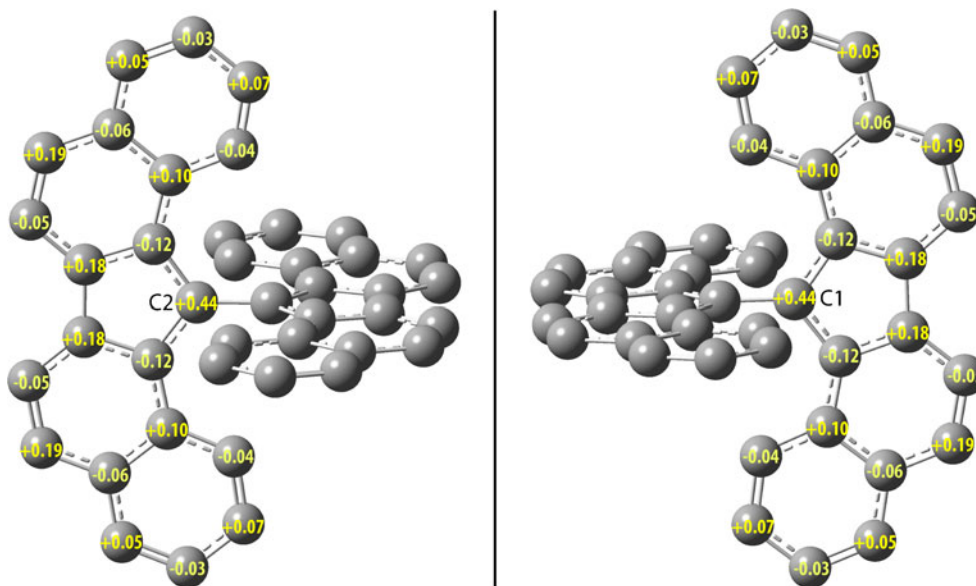
Figure 5 shows the temperature dependency of ΔG (singlet-triplet gap) taking into consideration also the possible entropy dependence of temperature. When the difference in ΔG for the triplet and singlet state of **3** is extrapolated from 0 K (3.2 kcal mol^{-1}) to its values at 100 K (2.9 kcal mol^{-1}) as well as 300 K (2.3 kcal mol^{-1}), one notices a lowering of the differences. These differences translate, assuming the barrier is overcome and spin flips are accessible, into a thermodynamic equilibrium at 0 %, 10^{-5} %, and 2 % at near 0 K, 100 K, and 300 K, respectively. This explains why at room temperature the experiment could track the signal of the radical, while at 100 K it was not traceable by Franzen and Joschek [14].

Figure 6 shows two views for compound **3** to facilitate providing details on the Mulliken atomic spin density distribution. Figure 6 indicates that the odd electron on each side of the C=C double bond has the ability to delocalize over almost the entire large aromatic substituent in general and over the 5-membered rings in the bis-dibenzo[a.i]fluorenylidene in particular. Figure 7 provides the shapes of the SOMO and SOMO-1 molecular orbitals for compound **3** in its triplet electronic state. Figure 7 is in agreement with the Mulliken atomic spin density distribution of compound **3** in its triplet electronic state (as shown in Fig. 6). The mentioned delocalization of each odd electron over each large available aromatic moiety contributes to the stability of the triplet electronic state of compound **3**.

We are also convinced that another reason for the interesting small singlet-triplet gap of compound **3** is the destabilization of its singlet electronic state, due to its large torsion angle at the double bond. The total energy difference between the closed shell singlet ethylene and the closed shell twisted ethylene equals to 11.9 kcal mol^{-1}, if the dihedral angle around the C=C double bond in singlet ethylene is made 53.2° (the same as the characteristic dihedral angle around the double bond in the singlet state of compound **3**). Therefore, we conclude that the amount of this destabilization of the singlet electronic state of compound **3** equals to 11.9 kcal mol^{-1}. Further studies of compound **3** in regard to its consequent paramagnetic properties are in progress.

Conclusions

Stable biradicals are very rare in organic chemistry, while compound **3** may be the only stable 1,2-biradical to our knowledge. The singlet-triplet gap of compound **3** was calculated and is found to be very small (ΔH = 3.4 kcal mol^{-1}) at room temperature. This can explain the experimental ESR spectrum and the molar susceptibility measurement of the synthesized compound **3** which was investigated by Franzen and Joschek in the past. The calculated temperature dependence of the gap is also in agreement with the former experimental results. This DFT study sheds light on the optimized structures of a couple of highly crowded alkenes including compound **3** in their singlet and triplet electronic states and could reveal the structural differences and give the reason for the noticeably very low singlet-triplet gap in case of compound **3**.

References

1. Liebman JF, Greenberg A (1976) A survey of strained organic molecules. Chem Rev 76:311–365
2. Lenoir D (1979) Force field calculations: e.g. strained alkenes. Nachr Chem Techn Lab 27:762–765
3. Sandström J (1983) Static and Dynamic Stereochemistry of Push-Pull and Strained. Ethylenes. Top Stereochem 14:83–181
4. Luef W, Keese R (1991) Strained Olefins: Structure and Reactivity of Nonplanar Carbon-Carbon Double Bonds. Top Stereochem 20:231–318
5. Lenoir D, Smith PJ, Liebman JF (2009) In: Dodziuk H (ed) Distorted Alkenes in Strained Hydrocarbons, Beyond the van't Hoff and Le Bel Hypothesis. Wiley-VCH, Weinheim, pp 103–145
6. Lenoir D, Wattenbach C, Liebman JF (2006) Tetra-*tert*-butylethylene, fantasy, fake, or reality. Struct Chem 17:419–422
7. Sulzbach HM, Bolton E, Lenoir D, Schleyer PvR, Schaefer III HF (1996) Tetra-*tert*-butylethylene: An elusive molecule. J Am Soc 118:9908–9914
8. Kanawati B, Lenoir D, Schmitt-Kopplin P (2011) Can Tetra-*tert*-butylethylene be formed by ion–ion recombination or ion–molecule reaction of two di-tert-butylcarbene units?—a DFT study. J Phys Org Chem 24:83–91
9. Molins E, Miravitlles C, Espinosa BM (2002) 1,1',3,3',6,6',8,8'-octachloro-9,9'-bisfluorenylidene and Perchloro-9,9'-bifluorenyldene. Two exceedingly Twisted Ethylenes. J Org Chem 67:7175–7178
10. Beck AH, Gompper R, Polborn K, Wagner HU (1993) Bi[1,3-bis(dicyanomethylene)indan-2-ylidene]—an ethylene derivative with extremely pronounced, twisting of the C=C bond. Angew Chem Int Ed Eng 32:1352–1354, See also ref. 27
11. Magidson OI (1925) Schliessung des Fluoren-Ringes in der Di-α-naphthyl-methan-Reihe. Ber Dtsch Chem Ges 58B:433–442
12. Bergmann ED, Fischer E, Hirshberg Y, Lavie D, Sprinzak Y, Szmuszkovicz J (1953) Fulvenes et ethylenes thermochromes. 26. Partie, Naphthofulvenes. Bull Soc Chim Fr 789-809
13. Bergman ED, Fischer E, Jaffe JH (1953) Exalted distortion polarization of some colored hydrocarbons. J Am Chem Soc 75:3230–3233
14. Franzen V, Joschek HI (1961) Zum Radikalcharakter des Bis-dibenzo[a.i]fluorenylidens. Liebigs Ann Chem 648:63–68
15. Schlenk W, Weichselfelder TH (1915) Zur Kenntnis des Hydrazins. Ber Dtsch Chem Ges 48:669–676
16. Montgomery LK, Huffman JC, Jurczak EA, Grendze MP (1986) The molecular structures of Thiele's and Chichibabin's hydrocarbons. J Am Chem Soc 108:6004–6011
17. McMasters DR, Wirz J (2001) Spectroscopy and reactivity of Kekulé hydrocarbons with very small singlet−triplet gaps. J Am Chem Soc 123:238–246
18. Wiberg KB, Hadad CM, Foresman JB, Chupka WA (1992) Electronically excited states of ethylene. J Phys Chem 96:10756–10768

19. Unett DJ, Caldwell RA (1995) The triplet state of alkenes: structure, dynamics, energetics and chemistry. Res Chem Intermed 21:665–709

20. Doering WvE, Roth WR, Bauer F, Breuckmann R, Ebbrecht T, Herbold M, Schmidt R, Lennartz HW, Lenoir D, Boese R (1989) Rotational barriers of strained olefines. Chem Ber 112:1263–1275

21. Sebastien V, Henrik O (2009) Aromaticity Changes along the Lowest-Triplet-State Path for C=C Bond Rotation of Annulenyl-Substituted Olefins Probed by the Electron Localization Function. J Phys Chem A 113:12304–12310

22. Apeloig Y (2011) Low-Coordination Silicon Compounds-Mechanistic Implications. The 13th European symposium of organic reactivity. Tartu, Estonia

23. Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Montgomery JA Jr, Vreven T, Kudin KN, Burant JC, Millam JM, Iyengar SS, Tomasi J, Barone V, Mennucci B, Cossi M, Scalmani G, Rega N, Petersson GA, Nakatsuji H, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Klene M, Li X, Knox JE, Hratchian HP, Cross JB, Bakken V, Adamo C, Jaramillo J, Gomperts R, Stratmann RE, Yazyev O, Austin AJ, Cammi R, Pomelli C, Ochterski JW, Ayala PY, Morokuma K, Voth GA, Salvador P, Dannenberg JJ, Zakrzewski VG, Dapprich S, Daniels AD, Strain MC, Farkas O, Malick DK, Rabuck AD, Raghavachari K, Foresman JB, Ortiz JV, Cui Q, Baboul AG, Clifford S, Cioslowski J, Stefanov BB, Liu G, Liashenko A, Piskorz P, Komaromi I, Martin RL, Fox DJ, Keith T, Al-Laham MA, Peng CY, Nanayakkara A, Challacombe M, Gill PMW, Johnson B, Chen W, Wong MW, Gonzalez C, Pople JA (2004) Gaussian 03, Revision C02. Gaussian Inc, Wallingford, CT

24. Foresman JB, Frisch A (1996) Exploring chemistry with electronic structure methods, 2nd edn. Gaussian Inc, Pittsburgh, PA

25. Marković S, Đurđević J, Jeremić S, Gutman I (2011) Triplet fluoranthenes: aromaticity versus unpaired electrons. J Mol Model 17:805–810

26. http://www.gaussian.com/g_whitepap/thermo.htm.

27. Beck AH (1993) Sterisch gehinderte Doppelbindungssysteme. Dissertation, Ludwig Maximilians Universität München

28. Polborn K, Private communication to Dieter Lenoir (2011)

29. Caldwell RA, Carlacci L, Doubleday CE, Furlani TR, King HF, McIver JW (1988) Viable geometries for T1-S0ISC in alkene triplets. J Am Chem Soc 110:6901–6903

30. Brink M, Möllerstedt H, Ottoson CH (2001) Characteristics of the electronic structures of diabatically and adiabatically Z/E-isomerizing olefins in the T1 state. J Phys Chem A 105:4071–4083

31. Nguyen MT, Matus MH, Lester WA, Dixon DA (2008) Heats of formation of triplet ethylene, ethylidene, and acetylene. J Phys Chem A 112:2082–2087

32. Mulliken RS, Roothaan CCJ (1947) The twisting frequency and the barrier height for free rotation in ethylene. Chem Rev 219–231

33. Qi F, Sorkhabi O, Suits AG, Chien SH, Li WK (2001) Photodissociation of ethylene sulfide at 193 nm: a photofragment translational spectroscopy study with VUV synchrotron radiation and ab initio calculations. J Am Chem Soc 123:148–161

34. Klein O, Hopf H, Grunenberg J (2009) The Ever-Elusive Tetra-tert-butylethene (TTBE, 3,4-Di-tert-butyl- 2,2,5,5-tetramethylhex-3-ene): Further Insight on Its Preparation. Eur J Org Chem 13:2141–2148

35. Akramine OE et al. (2003) Quantum Monte Carlo study of singlet-triplet transition in ethylene. J Chem Phys 3:1483–1488

36. Lee JS, Nyburg SC (1985) Refinement of the α-modification of 9,9-bifluorenylidene, $C_{26}H_{16}$. Acta Cryst C 41:560–567