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# THEORETICAL STUDIES ON CHEMICAL SHIFTS OF 3,6- DIIDO-9-ETHYL-9H-CARBAZOLE

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NARODOWA STRATEGIA SPÓJNOŚCI

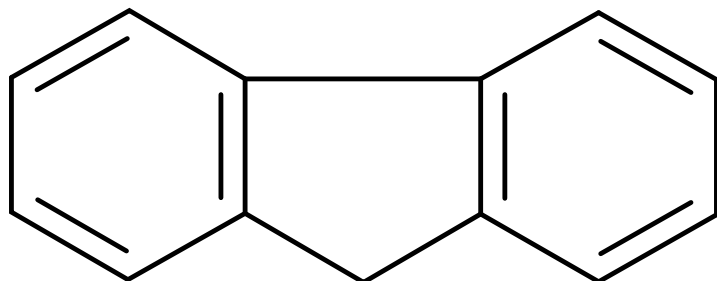
Klaudia Radula-Janik is a recipient of a Ph.D. fellowship from a project funded by the European Social Fund Stypendia doktoranckie-inwestycja w kadre naukową województwa opolskiego. T. Kupka and K. Ejsmont acknowledges financial support from 8/WCh/2012-S and 7/WCh/2012-S projects.

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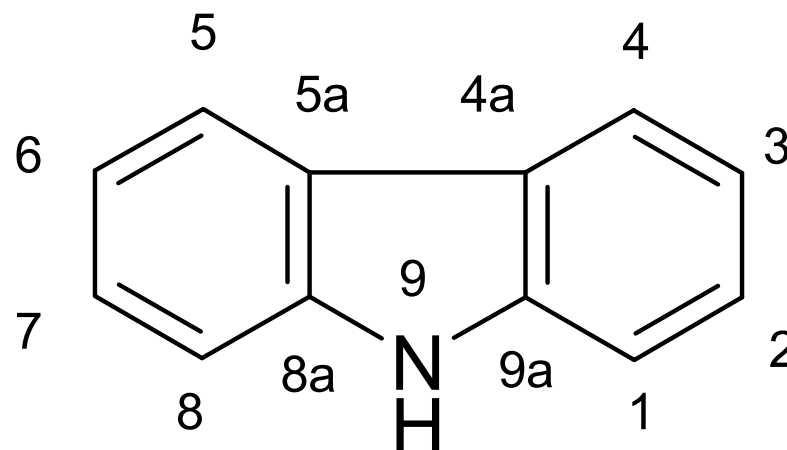




- Carbazole (9-azafluorene, dibenzopyrrole, diphenylenimine, diphenyleneimide)



Fluorene



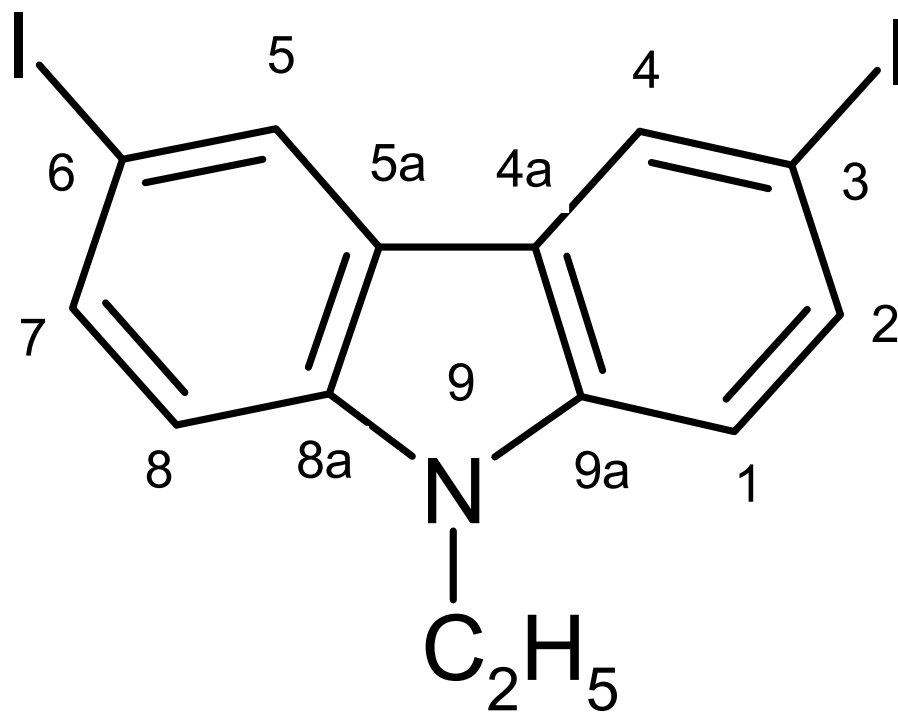
Carbazole



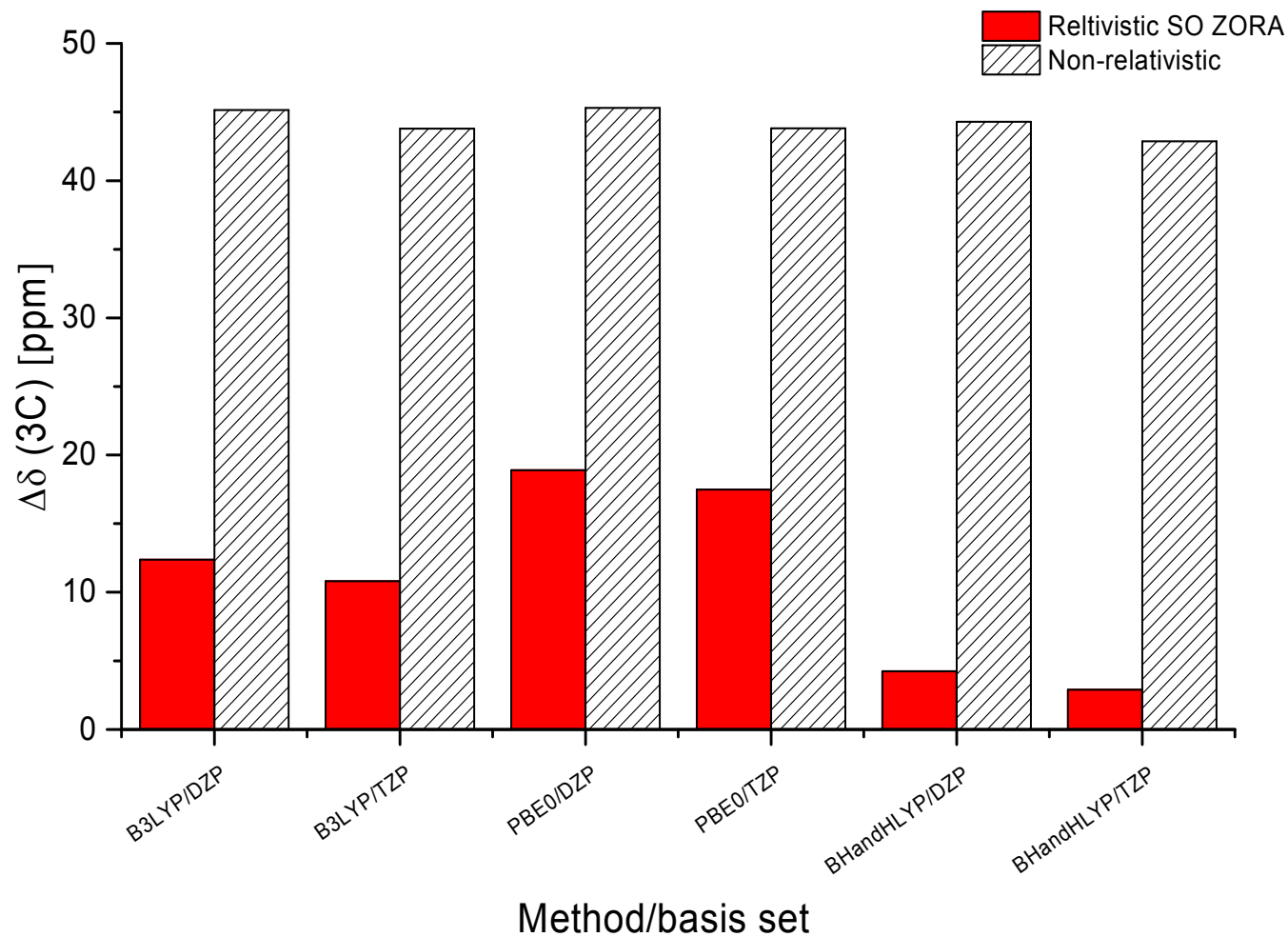
- 9H-carbazole is a very cheap starting material;
- it is a fully aromatic unit providing a better chemical and environmental stability;
- the nitrogen atom can be easily substituted with a wide variety of functional groups to help polymer solubility and to tune the optical and electrical properties;
- it possesses a bridged biphenyl unit resulting in materials with a lower band gap than traditional poly(p-phenylene)s.

Jean-Francois Morin, Mario Leclerc, Dominique Ades, Alain Siove *Macromol. Rapid Commun.* 2005, **26**, 761–778

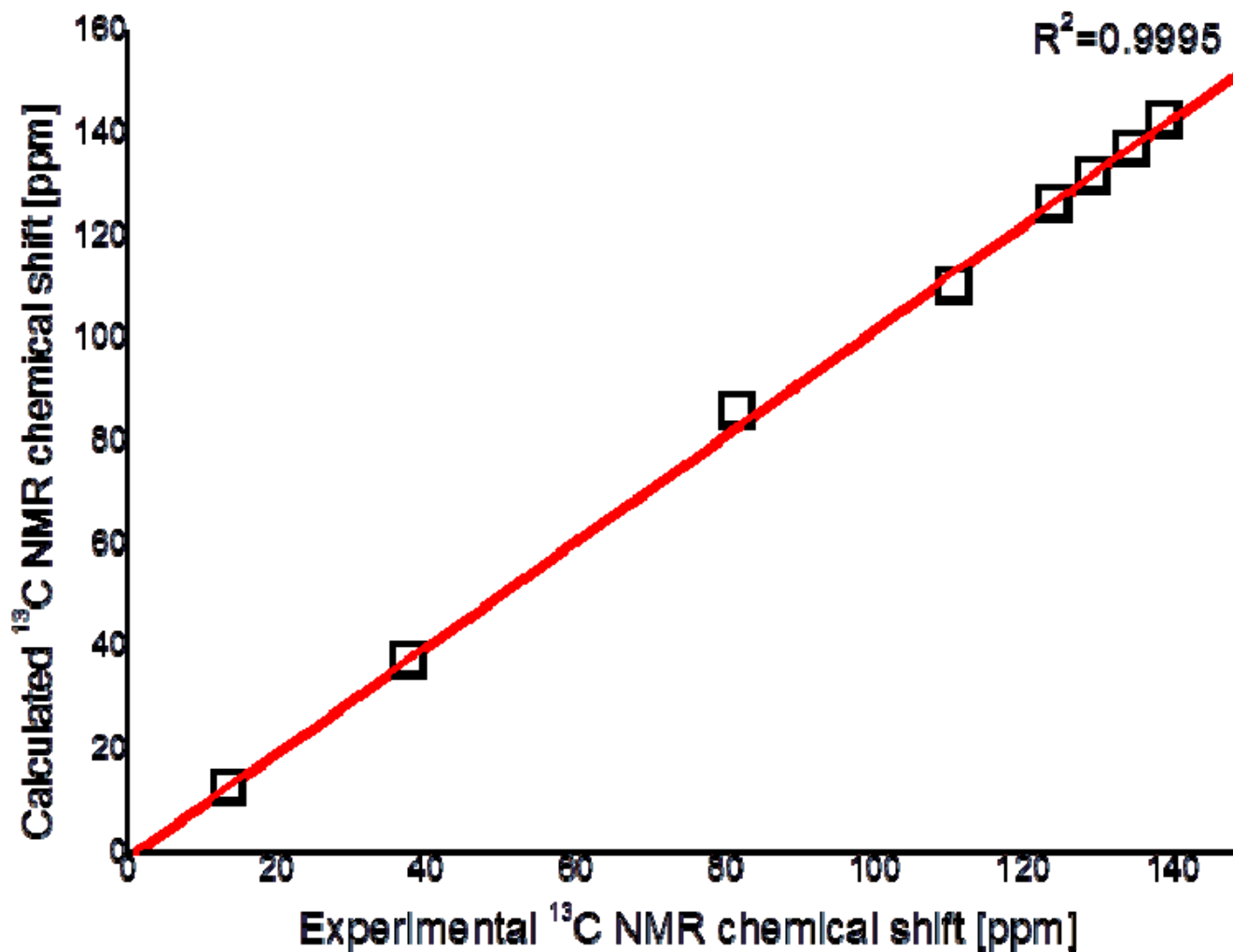
# 3,6-DIIODO-9-ETHYL-9H-CARBAZOLE



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# CONCLUSIONS

- In the case of halogenated carbazoles containing “heavy atoms” (chlorine, bromine and iodine), it is important to employ the SO ZORA approach to accurately assign the observed  $^{13}\text{C}$  NMR spectra;
- deviation from the theoretical (non-relativistic) value and observed experimentally is about 45 ppm;
- dramatic changes for ZORA results (a method accounting for relativistic effect) – deviation from the theoretical value and observed experimentally is about 5 ppm;
- a good linear correlation between theoretically predicted and experimental NMR parameters

# ACKNOWLEDGMENT

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# Thank's for your attention



## THEORETICAL STUDIES ON CHEMICAL SHIFTS OF 3,6-DIODO-9-ETHYL-9H-CARBAZOLE

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Carbazole<sup>1-9</sup> is an important tricyclic aromatic molecule with a central five-membered heteroaromatic ring. Formally, it is considered a derivative of fluorene with one CH<sub>2</sub> group replaced by NH group. Some important modifications of carbazole structure include substitution at nitrogen atom (N9) and at positions 3 and 6 of the carbazoles rings. Carbazole is characterized by high thermal stability and good photophysical properties.<sup>14,15</sup> Despite numerous possible applications of carbazole and its derivatives, these compounds are most extensively studied as materials for electronics and photonics.<sup>16-19</sup> Systematic works on correlation between carbazole structure and its electronic and NMR parameters are lacking in the literature.<sup>110-111</sup>

In this work we report on the prediction of <sup>13</sup>C NMR chemical shifts of 3,6-diiodo-9-ethyl-carbazole (Fig. 1). In most theoretical works, the predicted (nonrelativistic) chemical shifts of atoms adjacent to heavy atom are not accurate because of the heavy atom on light atom (HALA) relativistic effects<sup>21</sup>, so we also employ the SO ZORA approach to account for the HALA effects on carbon nuclear shieldings in the title dihalogenocarbazole derivative.

Fig. 1. Numbering of the title compound.

Fig. 2. The influence of method, basis set and the relativistic effect on the accuracy of theoretically calculated chemical shifts of carbon atom directly connected with iodine.

Fig. 2. Correlation between the theoretical (B3LYP/6-31G(2d,p)) and experimental <sup>13</sup>C chemical shifts in 3,6-diiodo-9-ethyl-9H-carbazole.

In the case of halogenated carbazoles containing “heavy atoms” (chlorine, bromine and iodine), it is important to employ the SO ZORA approach to accurately assign the observed <sup>13</sup>C NMR spectra.

Typical DFT calculations of the chemical shifts of atoms C3 and C6 for 3,6 -diiodo-9-ethyl-9H-carbazole (Fig. 1) lead to a completely meaningless results. In this case, deviation from the theoretical value and observed experimentally is about 45 ppm (Fig. 2). We observe dramatic changes for ZORA results (a method accounting for relativistic effect). Finally, in this work we observed a linear correlation between theoretical and experimental NMR parameters (Fig. 3).

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