

# Stable photoinduced charge separation in heptacene†‡

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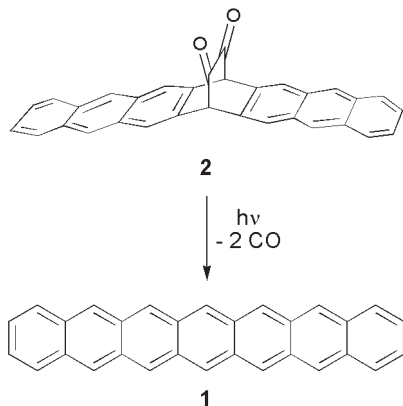
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Heptacene, generated in inert gas matrices by photobisdecarbonylation of a bridged  $\alpha$ -diketone precursor, undergoes ionization into radical anion and radical cation upon UV irradiation.

Acenes are important organic materials for utilization in field effect transistors and in organic light emitting diodes.<sup>1</sup> The potential of acenes longer than pentacene has not yet been tapped in such applications due to their instability. The reactivity of acenes increases rapidly with size,<sup>2</sup> and heptacene (**1**) proved to be too reactive to be isolated in substance.<sup>3</sup> Only in 2005 did Anthony and co-workers succeed in the first synthesis of a true heptacene derivative!<sup>4</sup> But in spite of kinetic stabilization of the acene  $\pi$  system by bulky substituents, the heptacene derivative decomposed within weeks in solution. More recently, Neckers and co-workers<sup>5</sup> used the Strating–Zwanenburg<sup>6</sup> photobisdecarbonylation of a bridged  $\alpha$ -diketone **2** in a poly(methyl methacrylate) (PMMA) matrix at room temperature to generate **1**, which could be characterized by its electronic absorption spectrum in the visible.

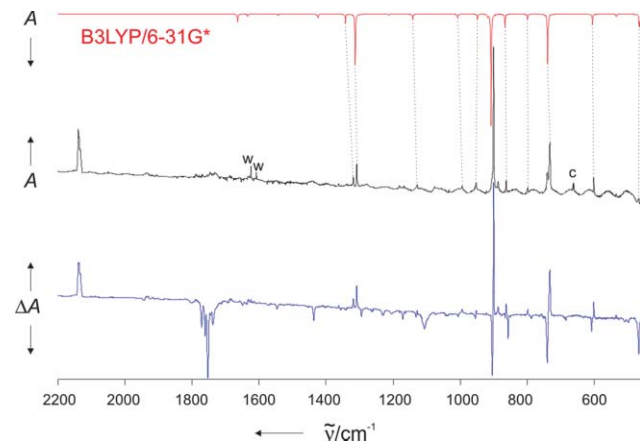


Properties of acenes related to electronic structure appear to converge to a limit with increasing size.<sup>2,3</sup> As the largest known linear acene, **1** is thus of great interest for an improved understanding of the electronic structure of its unknown higher congeners, which are still receiving theoretical scrutiny.<sup>7</sup> The electronic structure, which is predicted to converge to a semimetal

in the infinite limit,<sup>8</sup> suggests that the higher members of the acene series may show very unusual behavior for a hydrocarbon. For example, the low ionization potential of **1**, around 6 eV based on extrapolating from data up to hexacene,<sup>2</sup> is similar to that of metal atoms (e.g., 6.0 eV for Ga).<sup>9</sup>

This suggests unusual photochemical properties for **1**, and we here report that heptacene can undergo stable charge separation in inert gas matrices upon photoexcitation. Isolation of the  $\alpha$ -diketone precursor **2** in inert gas matrices is achieved by heating a sample to approximately 225 °C at a pressure of approximately  $10^{-5}$  mbar. Upon irradiation with a high-pressure mercury lamp ( $385 < \lambda < 450$  nm), all the mid-IR bands of **2** decrease; prolonged photolysis results in complete disappearance of **2**. Concomitantly, a set of new bands (Table 1, see ESI†) as well as a broad feature at 2138  $\text{cm}^{-1}$ , 2137  $\text{cm}^{-1}$ , and 2133  $\text{cm}^{-1}$  due to monomeric and aggregated CO are growing in (Fig. 1).<sup>10</sup> The only organic photoproduct formed in this reaction is assigned to **1** based on comparison of the measured IR spectrum with the one computed at the RB3LYP/6-31G\* level.

Following the photochemical decomposition of **2** by UV/vis spectroscopy at 10 K reveals six isosbestic points at 225 nm, 295 nm, 359 nm, 408 nm, 450 nm, and 504 nm (Fig. 2), confirming that the photodecarbonylation proceeds without any detectable intermediate. The concerted photodecarbonylation of **2** is in agreement with earlier observations for bridged  $\alpha$ -diketones in solution<sup>6,11</sup> and in cryogenic matrices.<sup>12</sup> The electronic absorption spectrum of green heptacene (Fig. 2) is characterized by the very



**Fig. 1** Mid-IR spectra (Ar, 15 K) of the photochemical decomposition of **2**. Bottom: Difference spectrum after 18 h of irradiation ( $385 < \lambda < 450$  nm); bands pointing downwards decrease during irradiation, those pointing upwards increase. Middle: IR spectrum obtained after 18 h of irradiation. w: water, c:  $\text{CO}_2$ . Top: IR spectrum computed for heptacene at the RB3LYP/6-31G\* level scaled by 0.985.

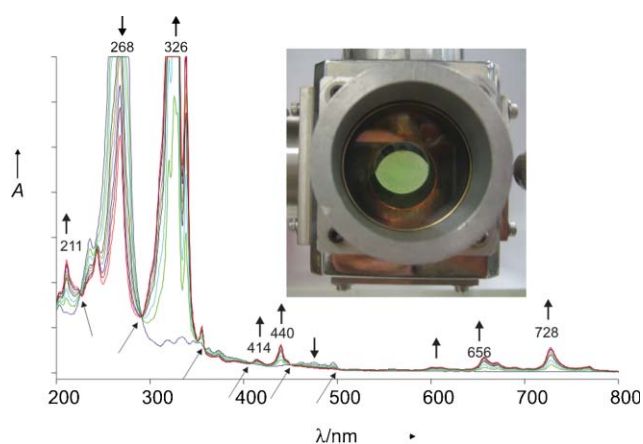
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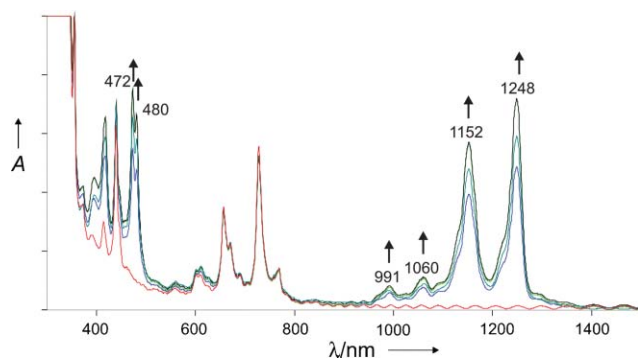


**Fig. 2** UV/vis spectra obtained after deposition of **2** and subsequent irradiation ( $385 < \lambda < 450$  nm) after successively doubled time intervals. Arrows pointing up and down indicate bands which increase and decrease during irradiation. Isosbestic points are marked with small-headed arrows. The photograph shows **1** isolated in Ar.

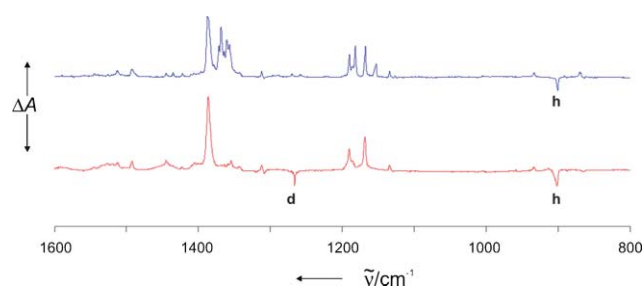
prominent  $\beta$ -band ( $2^1B_{2u} \leftarrow X^1A_{1g}$ ) with its most intense feature at 326 nm and its origin at 338 nm. The weak  $p$ -band ( $1^1B_{1u} \leftarrow X^1A_{1g}$ ) extends from 769 to 559 nm and is characterized by three groups of signals having their strongest absorptions at 728 nm, 656 nm and 601 nm. This is shifted to shorter wavelengths by roughly 30–40 nm compared to the data obtained earlier in PMMA,<sup>5</sup> reflecting the lower degree of interaction between **1** and the argon host. Hypsochromic shifts in matrices of low polarizability and the splitting of the  $p$ -band into features with pronounced fine structure were also observed earlier for pentacene isolated in noble gases.<sup>13</sup>

It is noteworthy that the photochemistry of **2** does not show wavelength dependence down to 254 nm. Likewise, heptacene isolated in Ar is photostable under irradiation with light of wavelength  $\lambda \geq 254$  nm. However, treatment of **1** with the output of a conventional low pressure Hg lamp, which includes a line at 185 nm, results in a number of new bands in the visible, near-IR and mid-IR ( $1350\text{--}1400\text{ cm}^{-1}$  and  $1100\text{--}1200\text{ cm}^{-1}$ ), while those of heptacene only decrease slightly in intensity (Figs. 3 and 4).

The carriers of these new bands are assigned to the radical cation and radical anion of heptacene based on the following spectroscopic observations. (i) Once formed, the corresponding



**Fig. 3** Electronic absorption spectra obtained after irradiation ( $\lambda < 225$  nm) of heptacene in Ar. Red trace: before irradiation.



**Fig. 4** Mid-IR difference spectra obtained after irradiation ( $\lambda < 225$  nm, 15 K) of **1** in Ar. Bands pointing downwards decrease (**h** neutral hexacene, **d**  $\text{CH}_2\text{Cl}_2$ ), those pointing upwards increase during irradiation. Top: Pure Ar. Bottom: Ar doped with 1.5%  $\text{CH}_2\text{Cl}_2$ .

mid-IR and vis/near-IR bands hardly increase upon irradiation, and disappear after long wavelength ( $\lambda > 350$  nm) irradiation. (ii) Compared to the features of **1**, the bands are very intense in the mid-IR and the near-IR region, indicating that the carriers are very polar entities. (iii) While heptacene is ESR silent at 10 K in Ar, a highly structured transition, which could not be further analyzed due to its complexity, occurs upon short wave irradiation. The  $g$  factors of the two radical ions were determined to be 2.0028, similar to those reported for the hexacene radical ions ( $2.0026 \pm 0.0001$ ).<sup>14</sup> (iv) Doping the matrix with 1.5% dichloromethane, an excellent electron trap,<sup>15</sup> suppresses the set of signals ascribable to the radical anion and results in a significantly increased yield of the radical cation of **1**. The latter shows prominent transitions at 480 nm, 971 nm, 1060 nm, 1248 nm, and a weak low-energy band at 2134 nm in agreement with theory (see ESI†). The signals at 472 nm and 1152 nm in Fig. 3 are thus due to heptacene radical anion. As expected, the observed NIR features of heptacene radical anion are red shifted compared to those in hexacene anion.<sup>14</sup>

In summary, we confirm that the photobisdecarbonylation of **2** is a suitable approach toward heptacene **1** and that this reaction proceeds without any detectable intermediates even at temperatures as low as 10 K. The observed photoinitiated charge transfer of heptacene in an Ar matrix suggests that the higher acenes might be interesting for photoelectronic applications.

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## Notes and references

- For recent reviews on acene chemistry, see: J. E. Anthony, *Chem. Rev.*, 2006, **106**, 5028; M. Bendikov, F. Wudl and D. F. Perepichka, *Chem. Rev.*, 2004, **104**, 4891; F. Würthner and R. Schmidt, *ChemPhysChem*, 2006, **7**, 793.
- D. Biermann and W. Schmidt, *J. Am. Chem. Soc.*, 1980, **102**, 3163.
- E. Clar, *Polycyclic Hydrocarbons*, Academic Press, London, 1964.
- M. M. Payne, S. R. Parkin and J. E. Anthony, *J. Am. Chem. Soc.*, 2005, **127**, 8028.
- R. Mondal, B. K. Shah and D. C. Neckers, *J. Am. Chem. Soc.*, 2006, **128**, 9612.
- J. Strating, B. Zwanenburg, A. Wagenaar and A. C. Udding, *Tetrahedron Lett.*, 1969, 125.

- 7 K. N. Houk, P. S. Lee and M. Nendel, *J. Org. Chem.*, 2001, **66**, 5517; M. Bendikov, H. M. Duong, K. Starkey, K. N. Houk, E. A. Carter and F. Wudl, *J. Am. Chem. Soc.*, 2004, **126**, 7416; M. Bendikov, H. M. Duong, K. Starkey, K. N. Houk, E. A. Carter and F. Wudl, *J. Am. Chem. Soc.*, 2004, **126**, 10493 (erratum).
- 8 S. Kivelson and O. L. Chapman, *Phys. Rev. B*, 1983, **28**, 7236; T. Kato and T. Yamabe, *J. Chem. Phys.*, 2001, **115**, 8592; B. Srinivasan and S. Ramasesha, *Phys. Rev. B*, 1998, **57**, 8927.
- 9 *Handbook of Chemistry and Physics*, CRC Press, London, UK, 2007.
- 10 A. Givan, A. Loewenschuss and C. J. Nielsen, *J. Chem. Soc., Faraday Trans.*, 1996, **92**, 4927.
- 11 H. Yamada, Y. Yamashita, M. Kikuchi, H. Watanabe, T. Okujima, H. Uno, T. Ogawa, K. Ohara and N. Ono, *Chem.–Eur. J.*, 2005, **11**, 6212.
- 12 M. B. Rubin, A. Patyk and W. Sander, *Tetrahedron Lett.*, 1988, **29**, 6641.
- 13 T. M. Halasinski, D. M. Hudgins, F. Salama, L. J. Allamandola and T. Bally, *J. Phys. Chem. A*, 2000, **104**, 7484.
- 14 H. Angliker, F. Gerson, J. Lopez and J. Wirz, *Chem. Phys. Lett.*, 1981, **81**, 242.
- 15 T. Bally, in *Reactive Intermediates Chemistry*, ed. R. A. Moss, M. S. Platz, and M. Jones, John Wiley & Sons, Hoboken, 2004.

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