nature chemistry

SUPPLEMENTARY INFORMATION

DOI: 10.1038/NCHEM.2438

Reversible Bergman cyclization by atomic manipuation

Bruno Schuler,[1] Shadi Fatayer,[1] Fabian Mohn,[1,*] Nikolaj Moll,[1] Niko Pavliček,[1] Gerhard Meyer,[1] Diego Peña,[2] and Leo Gross[1,†]

[1] *IBM Research – Zurich, 8803 Rüschlikon, Switzerland*

[2] *CIQUS, Universidade de Santiago de Compostela, E-15782 Santiago de Compostela, Spain*

(Dated: 20th November 2015)

This supplemental information presents complementary information about the reaction products from the debromination of 9,10-dibromoanthracene (DBA **6**) on Cu(111). Further, the bond orders of 9,10-didehydroanthracene (diradical **5**) and 3,4-benzocyclodeca-3,7,9-triene-1,5-diyne (diyne **4**) are discussed and the triplet state spin-density analyzed.

CONTENTS

I. SUPPLEMENTARY AFM MEASUREMENTS

A. DBA: Reactions on Cu(111)

Unlike on the passive NaCl(2ML)/Cu(111) thin film, diyne creation was not possible on Cu(111). However, the radical and diradical could be created also on the Cu substrate. DBA on Cu was always found next to another adsorbate (usually CO in our case). By applying a voltage pulse of 1.8 V, the first Br atom could be dissociated from DBA. A CO tip AFM image of the resulting radical is shown in Fig. 1a. Similar to the I dissociation from diiodonaphthoperylene[1], the radical appears significantly bent downwards at the missing Br site, indicative of a strong interaction with the substrate[2]. The Br atom itself exhibits a fainter Δf contrast than on NaCl(2ML)/Cu(111). A further voltage pulse of about 3.3 V also removed the second Br atom and a diradical was created. The diradical on Cu is substantially bent downwards at its center, again indicating strong chemical bonding to the metal. The above findings support that the insulating substrate is crucial to maintain the radical character of the diradical (without forming a bond to the substrate), to facilitate the retro-Bergman cyclization to diyne.

* Permanent address: ABB Corporate Research, 5405 Baden-Dättwil, Switzerland.
† lgr@zurich.ibm.com

II. SUPPLEMENTARY DFT CALCULATIONS

A. Bond-order analysis of diradical and diyne

The bond order b is approximated by using an exponential relationship with the bond length l in Ångström[3]:

$$b = -\frac{1}{p_1} \ln\left(\frac{l - p_2}{p_3}\right) \qquad (1)$$

$$\text{with} \quad p_1 = 0.6852, p_2 = 1.0979, p_3 = 0.4397$$

The parameters p_1, p_2 and p_3 were obtained by fitting the length of 1.54 Å of a single bond of ethane ($H_3C{-}CH_3$), the length of 1.33 Å of the double bond of ethylene ($H_2C{=}CH_2$), and the length of 1.21 Å of the triple bond of acetylene (HC≡CH) to the equation (1).

In Fig. 2 bond lengths and bond orders of the free diradical singlet and triplet as well as the diyne singlet are shown. The central ring of the diradical triplet is slightly contracted along the short molecular axis and widened along the long molecular axis compared to the diradical singlet (cf. also values reported in Ref. 4). For the diyne structure, the short bonds in the molecule center are the most noticeable features. Having a calculated bond order of about 1.73 they show a strong triple bond character, suggesting the resonance structure depicted in Fig. 2d as the major contribution. The characteristic triple bond contrast was also recognized in the measurements (see Fig. 3).

Including the surface (2 NaCl and 4 Cu slabs), the bond lengths and bond orders are calculated as shown in Fig. 3. First of all, the structure of the diyne singlet is almost unaffected by the surface. For the singlet and triplet diradical there arises small differences in the central ring upon adsorption. In general, on the surface both singlet and triplet adopt an almost identical geometry, probably in response to the substrate registry.

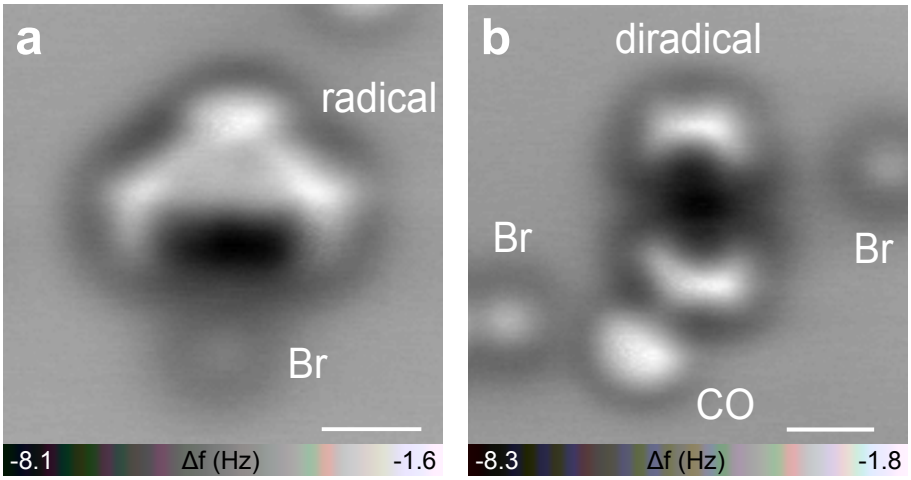

Figure 1. **DBA reactions on Cu(111) a** AFM image of the radical on Cu(111), after dissociating a Br from DBA with 1.8 V. The contrast reveals a strongly tilted adsorption geometry, indicative of a strong binding of the debrominated side with the substrate. The dissociated Br appears less pronounced. **b** When removing the second Br by 3.3 V, the diradical is always formed. Unlike on NaCl, the diradical is strongly pulled to the substrate at the molecule center. Scale bars: 5 Å.

B. Diradical triplet state spin-density

As shown in Fig. 4e in the manuscript, on the surface the triplet state is clearly favored over the singlet state in the diradical conformation, with a singlet-triplet spacing of about 0.15 eV. The triplet state emerges from two half-filled lone pairs. In Fig. 4 the resulting spin-density isosurface of the diradical triplet is plotted (in this case for the free molecule). Clearly, the uncompensated spin is concentrated at the anticipated radical sites and to a minor extent at the bonds of the central ring in general.

[1] Pavlicek, N. *et al.* On-surface generation and imaging of arynes by atomic force microscopy. *Nature Chem.* **7**, 623–628 (2015).
[2] Schuler, B. *et al.* Adsorption geometry determination of single molecules by atomic force microscopy. *Phys. Rev. Lett.* **111**, 106103 (2013).
[3] Pauling, L., Brockway, L. O. & Beach, J. Y. The dependence of interatomic distance on single-double bond resonance. *J. Am. Chem. Soc.* **57**, 2705 (1935).
[4] Kötting, C., Sander, W., Kammermeier, S. & Herges, R. Matrix isolation of 3,4-benzocyclodeca-3,7,9-triene-1,5-diyne. *Eur. J. Org. Chem.* **1998**, 799–803 (1998).

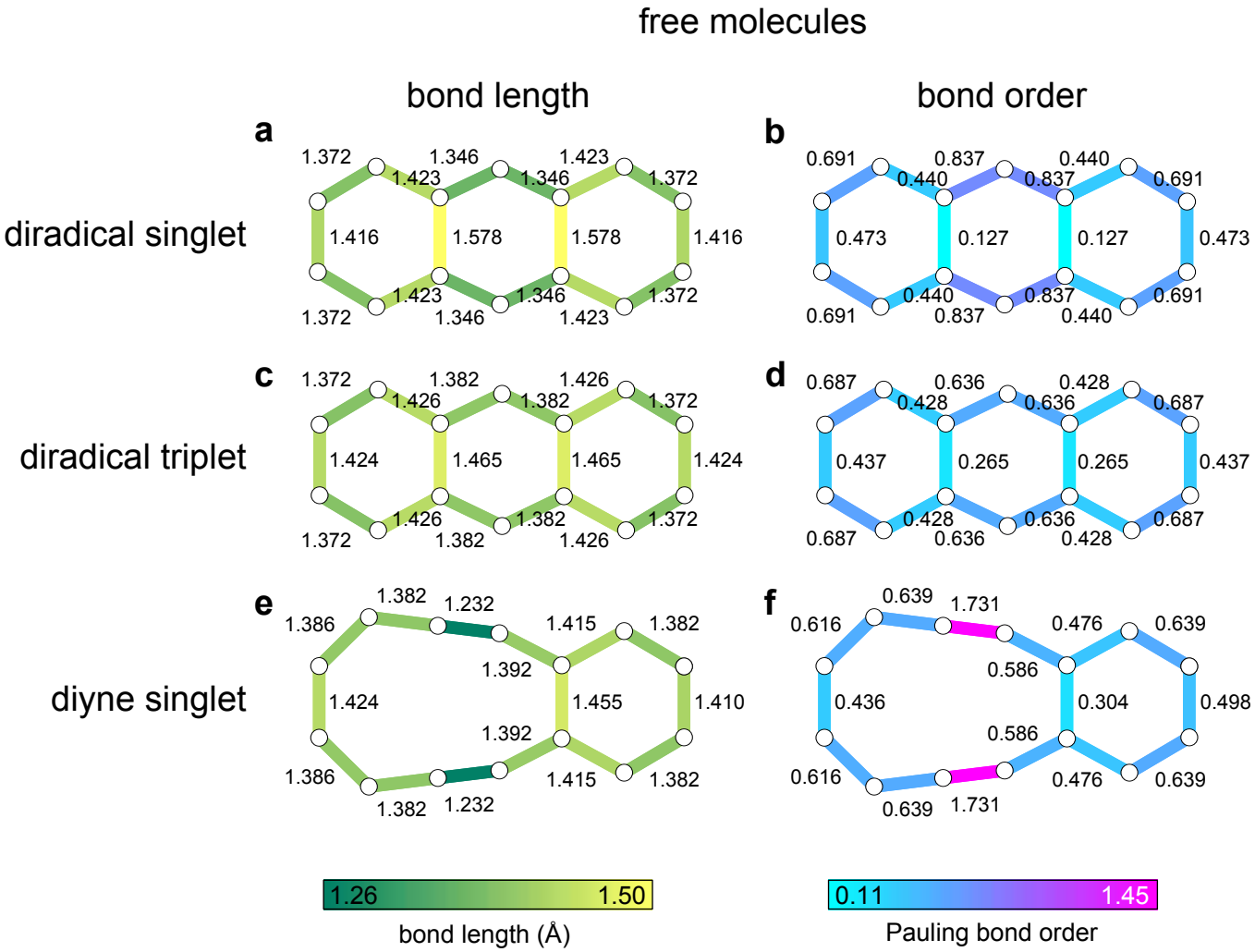

Figure 2. **Bond-order analysis of the free molecules.** Calculated bond lengths and derived bond orders of diradical singlet (**a,b**), diradical triplet (**c,d**) and diyne singlet (**e,f**) in vacuum.

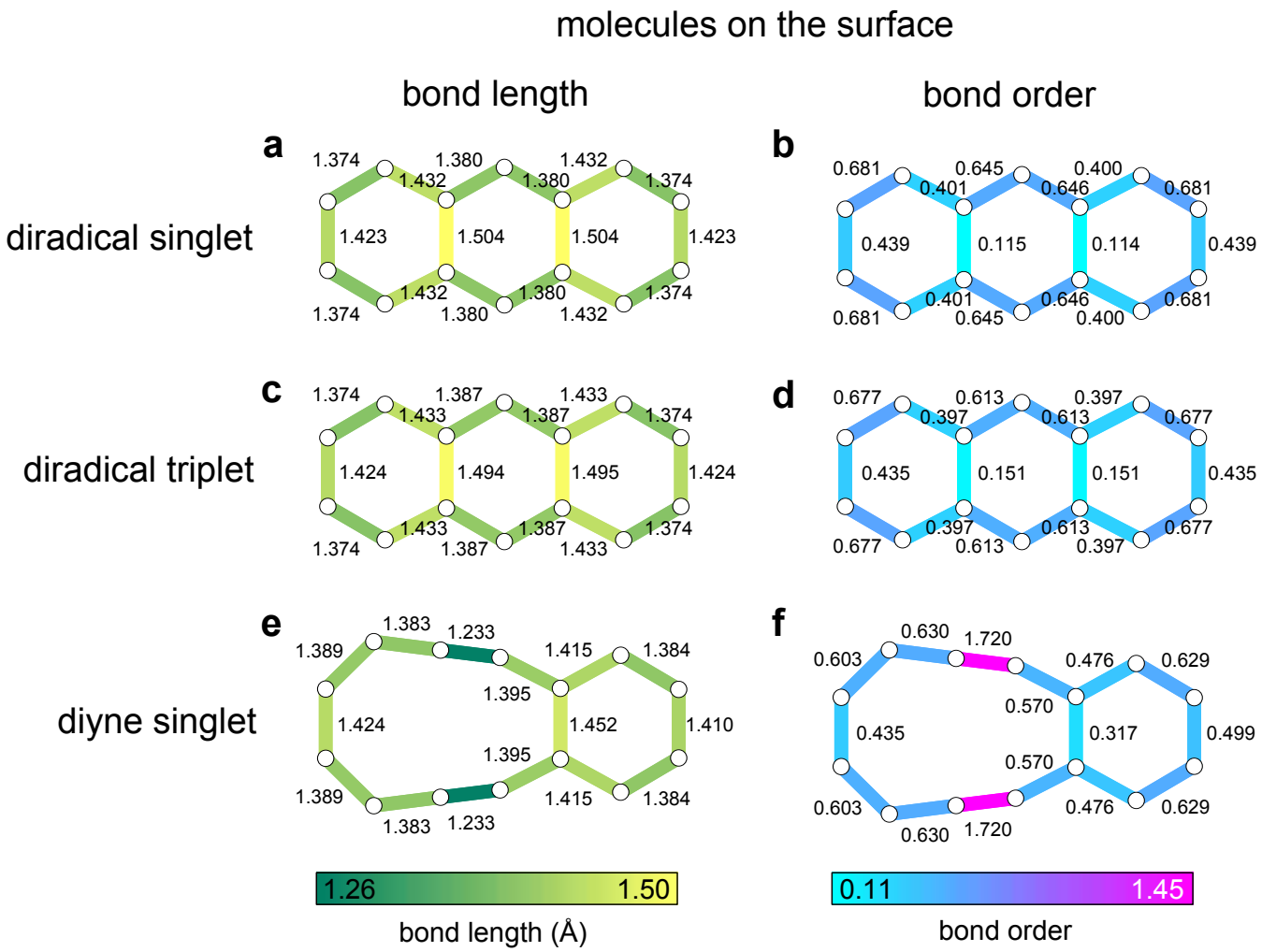

Figure 3. **Bond-order analysis with molecules on the surface.** Calculated bond lengths and derived bond orders of diradical singlet (**a**,**b**), diradical triplet (**c**,**d**) and diyne singlet (**e**,**f**) on the surface.

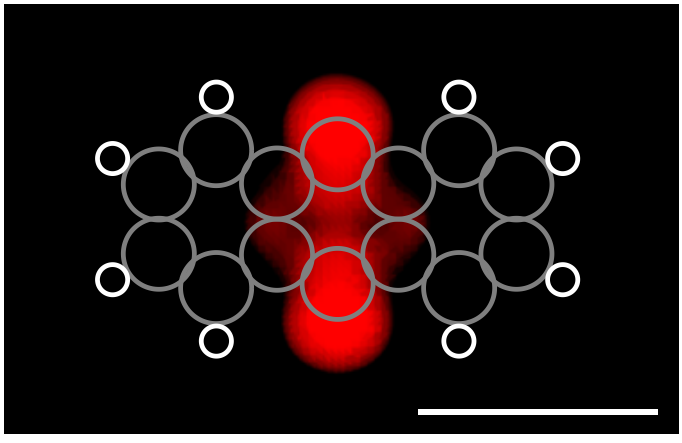

Figure 4. **Spin density of the diradical triplet.** Spin density isosurface at 0.2 e of the diradical triplet state calculated from the free molecule with the molecular structure overlaid as a guide to the eye. Scale bar: 5 Å.