Novel approach for synthesis of a carbyne film by electrochemical reduction of hexachlorobuta-1,3-diene

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Electrochemical reduction of hexachlorobuta-1,3-diene with a Pt cathode leads to a semiconductive carbon deposit in the form of a thin film consisting of a carbyne analogue doped and stabilized with the electrolyte.

Carbyne, defined as an infinite linear polyyne, or cumulenic-type carbons,[1] is an attractive target in development of new quasi-one-dimensional electroconducting materials. Several attempts to synthesise carbyne have led only to ill-defined materials.[2] Spectrometric characteristics suggest the transformation of reactive carbon chains to graphite-like carbon by inter- or intra-chain reactions during reaction. At present, long carbyne chains are reported to exist either in polymer matrices[3] or as end-capped species.[4]

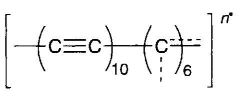
Here, we present a novel electrochemical synthesis of a carbyne analogue by electrochemical reduction of hexachlorobuta-1,3-diene (HCBD). HCBD (50 mmol dm^{-3}) was cathodically electrolysed at a Pt plate (at −2.0 V *vs.* saturated calomel electrode) in DMF containing 0.1 mol dm^{-3} tetrabutylammonium perchlorate (TBAP) at 0 °C in a two-compartment cell. A black film deposit grew at the Pt surface and upon decreasing the current, the reaction was stopped. The film was washed several times with DMF and acetonitrile, removed from the electrode, dried under vacuum at room temperature, and stored in a freezer under an argon atmosphere.

The product was a fragile lustrous black film of thickness *ca.* 50–100 μm depending on the electrolytic conditions. SEM observations showed that the solution-side surface had a cauliflower-like morphology. Powder X-ray analysis showed a broad peak at $2\theta = 20.8°$ indicating the product to be amorphous.

The IR spectrum was similar to the product obtained from diiodoacetylene[5] but with stronger characteristic broad absorptions in the range 2195–1705 cm^{-1} with the peak maximum at 1979 cm^{-1} shifted to lower wavenumber; exposure to air of this sample led to a decrease in the intensity of this band. The Raman spectrum also showed a peak at 1950 cm^{-1} and such IR and Raman peaks around 2000 cm^{-1} are considered as diagnostic of the stretching mode of conjugated carbon–carbon triple bonds.[2,3,5] The extent of conjugation was estimated as *ca.* 10 according to the Raman data using an equation recently proposed by Kuzmany and coworkers.[6] However, the Raman peaks around 2000 cm^{-1} might also be due to a stretching mode of cumulenic carbons.[7]† Solid-state NMR (^{13}C CP MAS) data suggested the presence of TBA^+ (δ 14.6, 20.3, 24.4, 58.3)‡ and acetylenic sp carbons (δ 70–90)[4,8] along with some unidentified carbons that may be cumulenic sp[9]† or aromatic sp^2 [8,10] (δ 90–170). The product appears to consist of polyyne chains in contrast to results reported by Nishihara *et al.*[11]

The as-grown sample showed an EPR signal at $g = 2.0036$ with a linewidth (ΔH_{pp}) of 2.53 G. The number of spins (1×10^{19} g^{-1}) is similar to that found for conductive polymers.[12] Upon I_2 doping, the spin density increased and ΔH_{pp} was reduced to 2.11 G, suggesting the formation of mobile spins generated by p-type doping. The as-grown film sample showed a negative thermoelectric power, whereas the I_2-doped sample showed a positive value, suggesting that the as-grown product was electrochemically n-doped by TBA^+ during the cathodic process. The electrical conductivity of the pristine film was 5×10^{-8} S cm^{-1}, and it increased to 5×10^{-5} S cm^{-1} upon I_2 doping; the low conductivity may be due to incorporation of the bulky counter cation.

A schematic structure of the repeating unit may be postulated from the structural analyses, electronic and electrical characteristics, and elemental analysis.§ The product would appear to consist of a decaacetylenic chain with two acetylenic units doped by TBA^+, and incorporated TBAP. The doped moiety, an acetylenic radical anion, may cause cross-coupling of the linear chains or cumulene formation by combination. The remaining radicals in the polymeric matrix, amounting to one spin per *ca.* 1500 carbynoid carbons, can be detected by EPR spectroscopy. The dopant (TBA^+) and the incorporated TBAP are assumed to play a key role in the stabilization of the carbyne chains as found in composites of carbyne metal fluorides.[13] In conclusion, this is the first report of the synthesis of a carbyne analogue consisting of long polyyne chains *via* monomeric compounds. The product can be classified as a third category of stabilized carbynes in addition to carbynes in polymer matrices[3] and end-capped carbynes.[4]



$$\left[-\!\left(C\equiv C\right)_{10}\!-\!\left(C\right)_{6} \right]^{n^{\bullet}-} \bullet n\, TBA^{\bullet +} \bullet m\, TBAP$$

$n = 1.5$
$m = 1.0$

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Footnotes

† Two model compounds containing cumulenic bonds were prepared for spectral data comparison. 1,1,4,4-Tetraphenylbutatriene: UV–VIS, $\lambda_{max} = 420$ nm; Raman, 2030 cm^{-1} ($\nu_{C\equiv C}$); ^{13}C NMR δ($CDCl_3$), 122.7 (=C=C=), 151.9 (Ph_2C=). 1,1,6,6-Tetraphenylhexapentaene: UV–VIS, $\lambda_{max} = 485$ nm; Raman, 1970 cm^{-1} ($\nu_{C\equiv C}$); ^{13}C NMR δ ($CDCl_3$), 127.3, 124.7 (=C=C=), 149.4 (Ph_2C=).

‡ ^{13}C NMR data for tetrabutylammonium perchlorate; δ ($CDCl_3$), 13.47, 19.50, 23.76, and 58.51.

§ Elemental analysis. Found: C, 78.0; H, 8.8; N, 3.8; Cl, 3.2. Calc. for $C_{25}\cdot 1.6NBu_4^+\cdot 1.0NBu_4ClO_4$: C, 77.9; H, 9.05; N, 3.5; Cl, 3.4%.

References

1 A. M. Sladkov, *Sov. Sci. Rev., Sect. B*, 1981, **3**, 75.

2 V. V. Korshak, V. I. Kasatochkin, A. M. Sladkov, Y. P. Kudryavtsev and K. Usenbaev, *Dokl. Akad. Nauk SSSR*, 1961, **136**, 1342; A. M. Sladkov, V. V. Korshak and V. P. Nepochatykh, *Izv. Akad. Nauk SSR, Ser. Khim.*, 1968, 196; A. S. Hay, *J. Polym. Sci. Part A-1*, 1969, **7**, 1625; H. Matsuda, H. Nakanishi and M. Kato, *J. Polym. Sci., Polym. Lett. Ed.*, 1984, **22**, 107.

3 V. V. Korshak, Y. P. Kudryavtsev, Y. V. Korshak, S. E. Evsyukov, V. V. Khvostov, V. G. Babaev and M. B. Guseva, *Mokromol. Chem., Rapid Commun.*, 1988, **9**, 135; H. Kise and H. Ogata, *J. Polym. Sci.*,

Polym. Chem. Ed., 1983, **21**, 3443; K. Akagi, M. Nishiguchi and H. Shirakawa, *Synth. Met.*, 1987, **17**, 557; L. Kavan and F. P. Dousek, *Synth. Met.*, 1993, **58**, 63.

4 R. Eastmond, T. R. Johnson and D. R. M. Walton, *Tetrahedron*, 1972, **28**, 4601; R. Kuhn, H. Fischer and H. Fischer, *Ber.*, 1964, **97**, 1760; R. J. Lagow, J. J. Kamp, H. Wei, S. L. Battle, J. W. Genge, D. A. Laude, C. J. Harper, R. Bau, R. C. Stevens, J. F. Haw and E. Munson, *Science*, 1995, **267**, 362; T. Bartik, B. Bartik, M. Brady, R. Dembinski and J. A. Gladysz, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 414.

5 M. Kijima, Y. Sakai and H. Shirakawa, *Chem. Lett.*, 1994, 2011; M. Kijima, Y. Sakai and H. Shirakawa, *Synth. Met.*, 1995, **71**, 1837.

6 J. Kastner, H. Kuzmany, L. Kavan, F. P. Dousek and J. Kürti, *Macromolecules*, 1995, **28**, 344.

7 F. A. Miller, W. F. Elbert and W. Pingtore, *J. Mol. Struct.*, 1977, **40**, 25; J. Kürti, C. Magyar, A. Balázs and P. Rajczy, *Synth. Met.*, 1995, **71**, 1865.

8 C. A. Costello and T. J. McCarthy, *Macromolecules*, 1987, **20**, 2819; D. L. Trumbo and C. S. Marvel, *J. Polym. Sci., Part A*, 1986, **24**, 2311.

9 G. Roth and H. Fischer, *Organometallics*, 1996, **15**, 1139; R. W. Lass, P. Steinnert, J. Wolf and H. Werner, *Chem. Eur. J.*, 1996, **2**, 19.

10 Y. Kojima, M. Tsuji, T. Matsuoka and H. Takahashi, *J. Polym. Sci., Part A, Polym. Chem.*, 1994, **32**, 1371.

11 H. Nishihara, H. Harada, M. Tateishi, K. Ohashi and K. Aramaki, *J. Chem. Soc., Faraday Trans.*, 1991, **87**, 1187.

12 H. Shirakawa, T. Ito and S. Ikeda, *Makromol. Chem.*, 1978, **179**, 1965; K. Tanaka, K. Yoshizawa, T. Takeuchi, T. Yamabe and J. Yamauchi, *Synth. Met.*, 1990, **38**, 107.

13 L. Kavan, J. Hlavatý, J. Kastner and H. Kuzmany, *Carbon*, 1995, **33**, 1321.

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