Linear Polymeric C_{70}^{2-} Ions**

Holger Brumm, Eva Peters, and Martin Jansen*

Dedicated to Professor Hans Georg von Schnering
on the occasion of his 70th birthday

Two of the most obvious characteristics of the fullerenes are their ease of reduction and the large number of negative charges that they can accept. The ions C_{60}^{-} to C_{60}^{12-}[1] and C_{70}^{-} to C_{70}^{9-} have been detected.[2] Naturally such anions are mainly obtained in compounds with electropositive metals and provide a great diversity of structural and electronic phenomena in solid-state chemistry. The fulleride anions may be present as isolated units,[1] as dimers,[3] or as polymers.[4] Fullerides of alkali and alkaline earth metals can be nonconductors, semiconductors, or metallic conductors.[1] Some become superconducting with remarkably high transition temperatures, 40 K, for example.[5] Fullerides derived from C_{60} have received the most attention. Most of the studies of C_{70} have concerned the formation of compounds with alkali metals[2] and preliminary investigations have been carried out with the Ba/C_{70} system.[6] It is disappointing that none of the C_{70}^{n-} phases identified so far become superconducting on cooling.

A logical interpretation of the large range of experimental results obtained to date is restricted by the conspicuous lack of reliable structural information. A complete structure solution with refinement of all the atomic positions has not been possible for any of the linked fullerides reported. Nevertheless, from the experimental data gathered, it appears that the existence of polymeric and oligomeric $(C_{60}^{n-})_x$ ions has been verified. However, doubts still remain concerning the type of linkage. Above all, the available information does not offer a reliable basis for an analysis of the extent of the localization of charges in polymeric fullerides. Only a few structural determinations have been made with single crystals of fullerides that contain completely ordered and isolated C_{60}^{2-} ions,[7] which could be used to verify the theoretically developed models for the expected Jahn–Teller distortion.[1]

In expanding our studies of fullerides to systems including C_{70} we were able to synthesize the first linear polymeric C_{70}^{2-} species (Figure 1) as a barium salt, $[Ba(NH_3)_9]C_{70} \cdot 7NH_3$ (**1**), and to determine its structure by single-crystal X-ray analysis.[8] Compound **1** is obtained from the reduction of C_{70} with barium in liquid ammonia. The product precipitates from liquid ammonia at room temperature in the form of black needles which decompose above −33 °C under normal pressure with loss of ammonia.

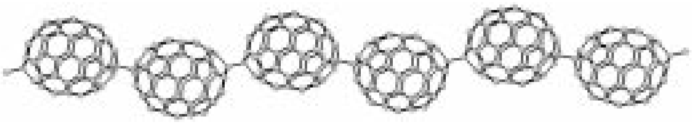


Figure 1. Structure of the linear polymeric $(C_{70}^{2-})_n$ ion. The bond length of each of the bridging C–C single bonds is 1.53(2) Å. The smallest intermolecular distance between the centers of mass of two fullerenes is 10.11 Å, the smallest intramolecular distance is 10.47 Å.

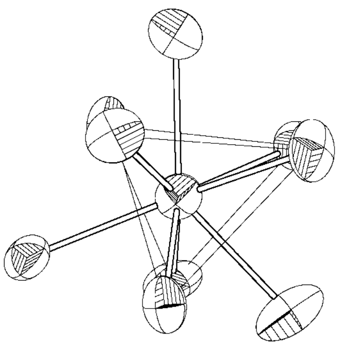


Figure 2. Structure of the cationic unit (anisotropic thermal ellipsoids set at the 50 % probability level). In the first sphere nine NH_3 molecules coordinate the Ba^{2+} ion in a strongly distorted, tricapped trigonal prism geometry.

In **1**, barium is coordinated to nine ammonia molecules and the coordination geometry is a strongly distorted, tricapped trigonal prism (Figure 2). The lengths of the bonds between the barium and the nitrogen atoms vary between 2.89(2) and 3.09(2) Å, which is in agreement with literature values.[7b, 9] Seven of the nine ammonia ligands are each coordinated to a further ammonia solvent molecule that is not bonded to barium (N–N bond lengths of 2.98(5) to 3.69(4) Å).

All the carbon atoms of the fullerene cage could be localized and refined. The fullerene units are linked together in linear chains by bonds between carbon atoms located in each of the two opposing five-membered rings through which the fivefold rotational axis of the neutral C_{70} runs. This type of linkage causes a slight zigzagging in the (001) plane. The angle between the lines connecting the centers of mass of three neighboring fullerene cages is 151°. The length of the bridging bond is 1.53(2) Å, which corresponds to a single C–C bond. This bond length and the bond angle at the bridging carbon atoms show that these atoms have sp^3 hybridization.

Within the chains, the smallest separation between the center of mass of two fullerenes is 10.47 Å. The fulleride chains are ordered along [100] with hexagonal close pack of rods (Figure 3); this is supported by the ratio between the lengths of the b and c axes of approximately $\sqrt{3}$. The smallest intermolecular distance between the centers of mass of a fullerene within a chain and its six neighbors is 10.11 Å. This distance corresponds to van der Waals contact and thus does not indicate any significant bonding interactions.

Because of the one-dimensional linkage and the resulting formation of two sp^3-hybridized carbon atoms, the point symmetry of the C_{70} unit is lowered from D_{5h} for the uncharged fullerene to C_2 (positional symmetry: C_1; Figure 4). This point symmetry, which usually covers only the general topology of one unit of the $(C_{70}^{2-})_n$ polymer with respect to the arrangement of the five- and six-membered rings as well as the two quaternary carbon atoms, also covers, within the limits of error, the variations in bond lengths which result from the localization of charges (Figure 5). Moving away from the bridging sites there is a general tendency for the alternation of the bond lengths to become less pronounced. Thus the five-membered ring and both six-membered rings which include the sp^3-hybridized carbon atom, have "diene

---

[*] Prof. Dr. M. Jansen, Dipl.-Chem. H. Brumm, E. Peters
Max-Planck-Institut für Festkörperforschung
Heisenbergstrasse 1, 70569 Stuttgart (Germany)
Fax: (+49) 711-689-1502
E-mail: martin@jansen.mpi-stuttgart.mpg.de

[**] This work was supported by the Fonds der Chemischen Industrie.

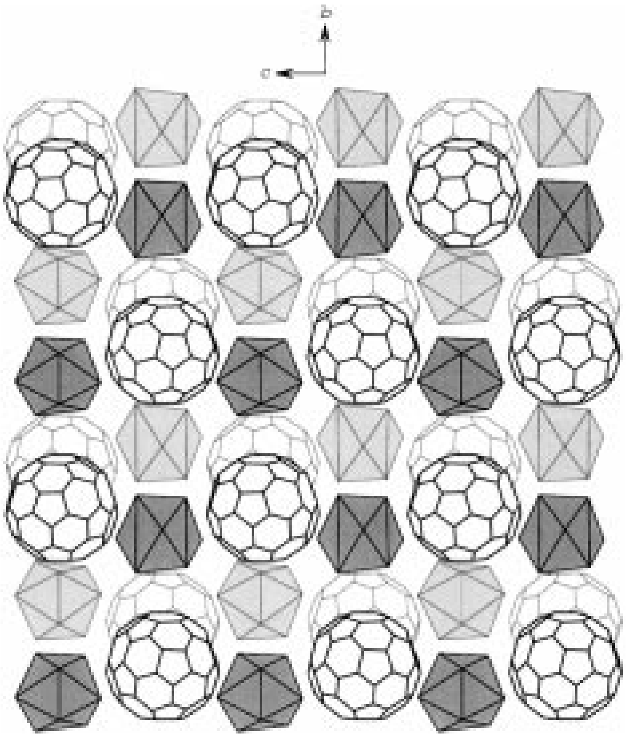


Figure 3. The molecular structure of **1** viewed along the (C_{70}^{2-}) chains which are ordered as a hexagonal close pack of rods.

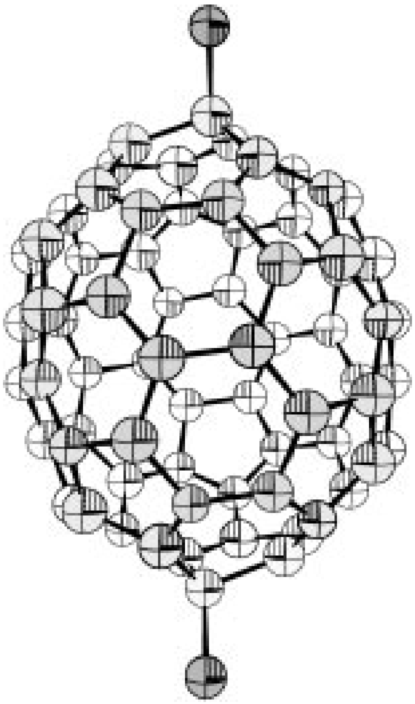


Figure 4. The molecular structure of a C_{70}^{2-} unit viewed along the noncrystallographic twofold rotation axis (isotropic thermal ellipsoids set at the 50 % probability level).

character" while the delocalization of the π electrons increases towards the middle of the fulleride. Therefore, there are no indications of a localization of the negative excess charges on particular carbon atoms.

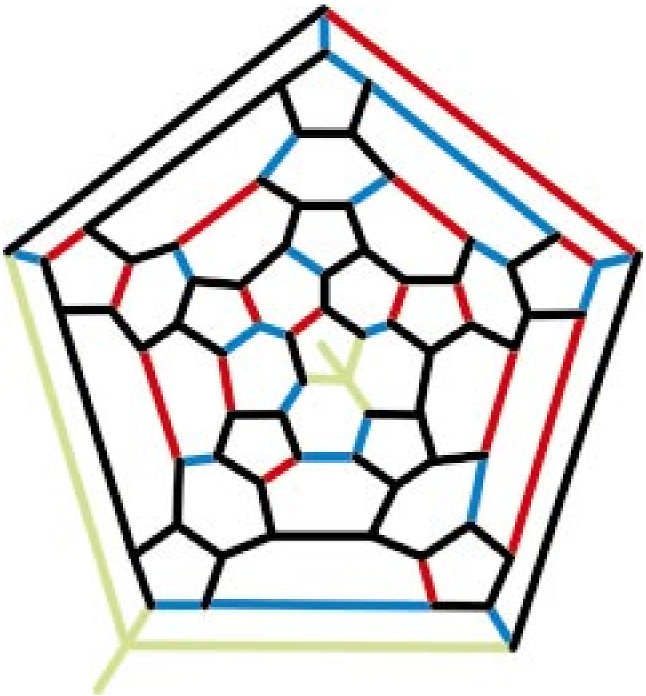


Figure 5. Schlegel diagram of a C_{70}^{2-} unit. Color coding of the bond lengths [Å]: blue <1.39, black 1.39–1.47, red 1.47–1.52 Å, green >1.52. The average standard deviation of the bond lengths is 0.02 Å, the maximum standard deviation is 0.03 Å.

Experimental Section

Under argon, Ba (4.0 mg, 2.91×10^{-5} mol) and C_{70} (25.1 mg, 2.99×10^{-5} mol), previously purified by sublimation, were added to an ampoule (∅ = 8 mm) fused onto the base to a oven dried Schlenk vessel. The Schlenk vessel was subsequently evacuated and ammonia introduced by condensation. This mixture of starting materials was frozen solid with liquid nitrogen and the glass ampoule was sealed. After three weeks at −33 °C, the solution which was initially blue had changed color to red-brown. Subsequently, the ampoule was carefully warmed to room temperature and then stored for ca. 4 months. During this period, shiny black needles formed on the bottom and on the glass walls. The ampoule was refrozen with liquid nitrogen and opened under argon. At −78 °C, the thawed ammonia and the crystals were transferred under inert gas into degassed and cooled perfluoropolyether oil (Galden HT230). A crystal suitable for single-crystal X-ray analysis was removed from the oil with a glass capillary attached to a preadjusted goniometer head. The crystal was immediately cooled with liquid nitrogen and placed in the diffractometer.

Received: December 22, 2000 [Z16318]

---

[1] C. A. Reed, R. Bolskar, *Chem. Rev.* **2000**, *100*, 1075–1119.

[2] M. Kobayashi, Y. Akahara, H. Kawamura, H. Sato, H. Shinohara, Y. Saito, *Phys. Rev. B* **1993**, *48*, 16877–16880.

[3] G. Oszlanyi, G. Bortel, G. Faigel, L. Granasy, G. M. Bendele, P. Stephens, L. Forro, *Phys. Rev. B* **1996**, *54*, 11849–11852.

[4] P. Stephens, G. Bortel, G. Faigel, M. Tegze, A. Janossy, S. Pekker, G. Oszlanyi, L. Forro, *Nature* **1994**, *370*, 636–639; G. Oszlanyi, G. Baumgartner, G. Faigel, L. Forro, *Phys. Rev. Lett.* **1997**, *78*, 4438–4441.

[5] T. T. M. Palstra, O. Zhou, Y. Iwasa, P. E. Sulewski, R. M. Fleming, B. R. Zegarski, *Solid State Commun.* **1995**, *93*, 327–330.

[6] X. H. Chen, D. H. Chi, Z. Sun, T. Takenobu, Z. S. Liu, Y. Iwasa, *J. Am. Chem. Soc.* **2000**, *122*, 5729–5732; T. Takenobu, X. Chen, Y. Iwasa, T. Mitani, *Mol. Cryst. Liq. Cryst.* **2000**, *340*, 617–622.

[7] a) P. Paul, Z. Xie, R. Bau, P. D. W. Boyd, C. A. Reed, *J. Am. Chem. Soc.* **1994**, *116*, 4145–4146; T. F. Fässler, A. Spiekermann, M. E. Spahr, R. Nesper, *Angew. Chem.* **1997**, *109*, 502–504; *Angew. Chem.*

Int. Ed. Engl. **1997**, *36*, 486–488; K. Himmel, M. Jansen, *Chem. Commun.* **1998**, 1205–1206; K. Himmel, M. Jansen, *Eur. J. Inorg. Chem.* **1998**, 1183–1186; b) K. Himmel, M. Jansen, *Inorg. Chem.* **1998**, *37*, 3437–3439.

[8] X-ray structural analysis of **1**: black needles, crystal dimensions $0.4 \times 0.1 \times 0.1$ mm^3, orthorhombic, space group $Pna2_1$ (no. 33), $a = 20.289(4)$, $b = 20.357(4)$, $c = 12.870(3)$ Å, $V = 5315(2)$ Å^3, $\rho_{calcd} = 1.563$ g cm^{-3}, $Z = 4$, $F(000) = 2544$, $\lambda = 71.073$ pm, $T = 143$ K, SMART-CCD (Bruker-AXS), 26738 measured reflections, 6954 symmetry independent reflections, empirical absorption correction (SADABS[10]), $R_{int} = 0.2677$. The R_{int} value given includes all data measured up to an angle of $2\theta = 45.4°$. This large value is caused by a high proportion of reflections of very low intensity in the high-angle range. If, for example, only the reflections up to an angle of $2\theta = 30°$are taken into consideration, then R_{int} decreases to a value of 0.1606. The determination and refinement of the position of all the atoms is, however, only possible when all the measured reflections are taken into consideration. The determination of the positions of the heavy atoms was carried out by direct methods,[11] the positions of the light atoms were determined with difference Fourier transformation.[12] The best fit with anisotropic temperature factors was obtained with the assumption of a noncrystallographic twofold rotation axis for the C_{70}^{2-} unit, as shown in Figure 4, in combination with the correlating bond lengths. The anisotropic temperature factors were positively defined, although in some cases they led to deflection parameters which were not physically meaningful. No indication of twinning was found during the refinement. The absolute configuration found is validated with a Flack parameter of 0.052. Refined parameters = 750, $R_1 = 0.1188$, wR_2(all data) = 0.2846, GOF = 0.894. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-157752. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[9] J. Daniels, N. Korber, *Z. Anorg. Allg. Chem.* **1996**, *622*, 1833–1838.

[10] G. M. Sheldrick, SADABS, Göttingen, **1998**.

[11] G. M. Sheldrick, SHELXS97, Programs for Crystal Structure Determination and Refinement of Structures, Göttingen, **1997**.

[12] G. M. Sheldrick, SHELXL97, Programs for Refinement of Crystal Structures, Göttingen, **1997**.

Orthogonal Photolysis of Protecting Groups**

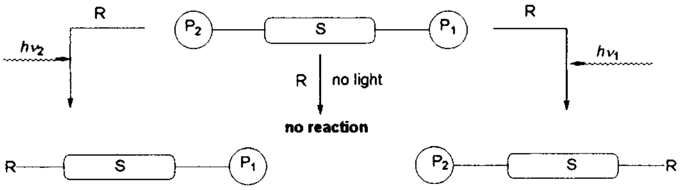
Christian G. Bochet*

Dedicated to Professor Barry M. Trost
on the occasion of his 60th birthday

One of the major challenges in the chemistry of protecting groups is orthogonality, that is, the possibility of selectively removing one group in the presence of others in any chronological sequence.[1] Photolabile protecting groups form an attractive subclass of these groups, since they are essentially cleaved without the need for any reagent, which thus increases compatibility with other functionalities.[2, 3] However, orthogonality between such protecting groups has never been observed. We recently published our preliminary results on the possible use of monochromatic light to differentiate photolabile groups,[4] and we wish to disclose here the first orthogonal photochemical protection/deprotection of polyfunctional molecules.

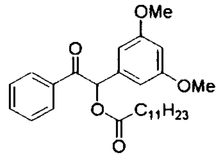
Before considering applying a strategy such as that shown in Scheme 1, several critical issues have to be addressed:

a) The intrinsic stability of each protecting group should be very different at various wavelengths.
b) The energy transfer between an excited chromophore and its ground-state neighbor should be suppressed.
c) The cleavage at high energy (for example, at 254 nm) should be very fast, to avoid photodegradation of otherwise sensitive groups.

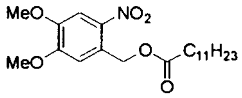


Scheme 1. General strategy for photochemical orthogonal deprotection of functional groups. S = substrate; P_1, P_2 = groups which are photoactivatable at ν_1 or ν_2; R = reacting species (for example, H).

Among the known photolabile protecting groups, the 3′,5′-dimethoxybenzoin esters attracted our attention since they were found to be equally reactive in nonabsorbent solvents and in neat piperylene (1,3-pentadiene).[5] This suggested the absence of quenching by the solvent and a very short-lived excited state. This feature, combined with the very high quantum yield ($\phi = 0.64$) makes this ester an ideal candidate for an orthogonal protecting group. On the other hand, the nitrobenzyl derivatives are known to be less reactive, but with sensitivity to much longer wavelengths (up to 420 nm).[3] These differences in wavelength sensitivity are clearly illustrated by the UV spectra of **1** and **2** (Figure 1).



1



2

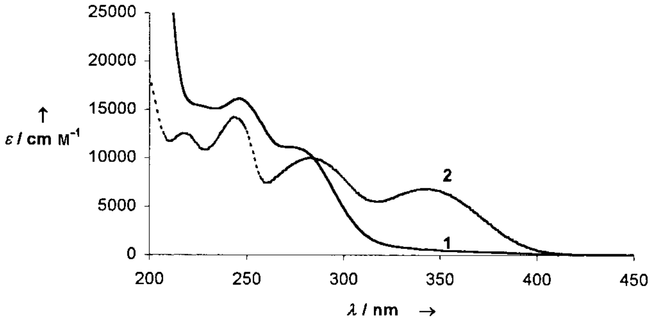


Figure 1. UV spectra of benzoin ester **1** and benzyl ester **2**.

---

[*] Dr. C. G. Bochet
Department of Organic Chemistry, University of Geneva
30 quai Ernest Ansermet, 1211 Geneva 4 (Switzerland)
Fax: (+41)22-328-7396
E-mail: Christian.Bochet@chiorg.unige.ch

[**] Financial support from the Swiss National Science Foundation (grant no.: 21-57044.99) and the Fonds Frédéric Firmenich et Philippe Chuit is gratefully acknowledged.