Preparation and Properties of a Huge, Crystalline, and Water-Soluble Compound ($C_{72}H_{132}N_{12}Br_6S_{12}$) That Possesses Six Carbenium Salt Units

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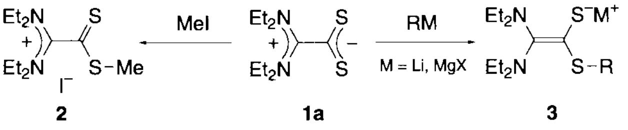
The reaction of hexakis(bromomethyl)benzene with six molar amounts of 2,2-bis(diethylamino)-2-ethylium-1-dithiocarboxylate furnished a huge, crystalline, and water-soluble compound ($C_{72}H_{132}N_{12}Br_6S_{12,}$ MW = 2030) that possesses six carbenium bromide units.

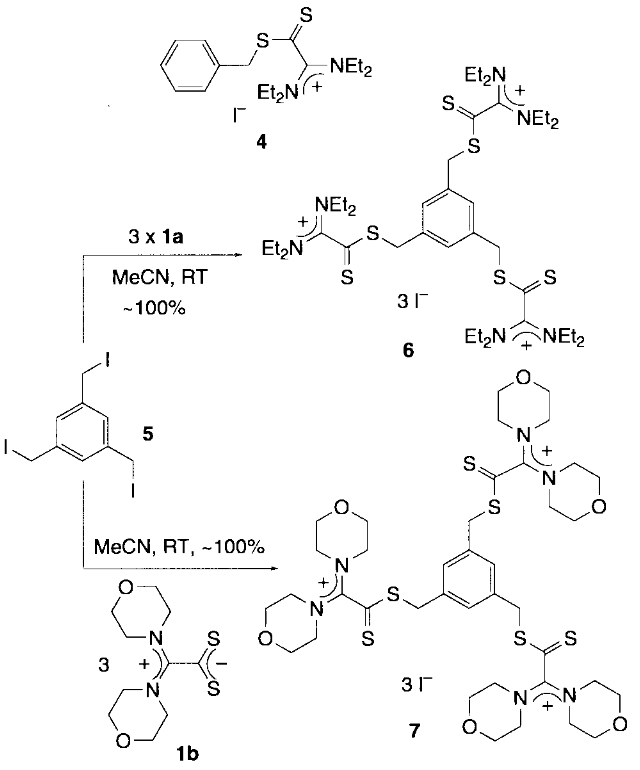
We have been investigating the synthesis, structure, and reactivities of 2,2-bis(diethylamino)-2-ethylium-1-dithiocarboxylate (**1a**) and the related inner salts.[1,2] The structure and reactivities of **1a** are of particular interest. The quasi-planes of the carbenium and dithiocarboxylate moieties of **1a** are nearly perpendicular to each other.[1b,k] Its sulfur atom reacts not only with MeI to give the carbenium iodide **2**[1a,b] but also with RM (M = Li, MgX) to provide the thiolates **3** in high yields,[1e] thus revealing a unique ability to serve both as a nucleophile and as an electrophile. This paper reports that the nucleophilicity of **1a** was now satisfactorily applied to the preparation of a huge, orange-crystalline, and water-soluble compound that possesses six carbenium bromide units.



2 **1a** **3**

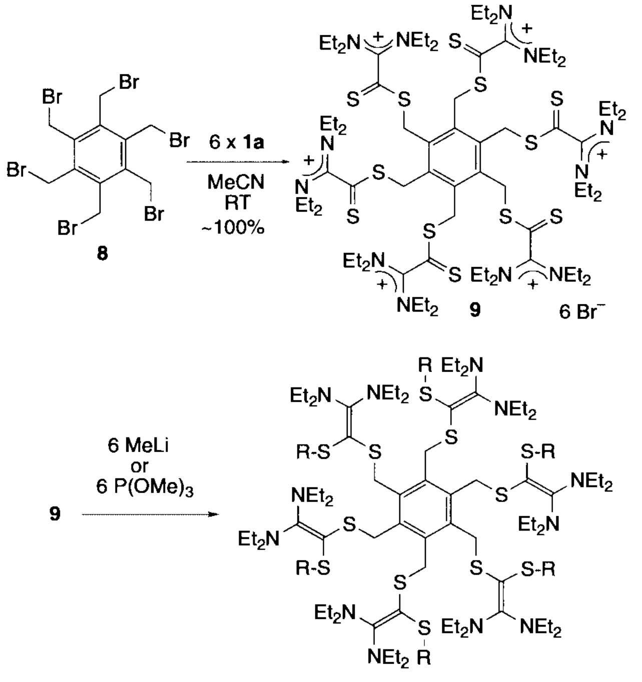
Thus, for the purpose of obtaining a series of molecular systems bearing a regularly increasing number of carbenium salt units, reactions of **1a** with benzyl iodide, 1,3,5-tris(iodomethyl)benzene (**5**), and hexakis(bromomethyl)benzene (**8**)[3] were examined. The reaction of equimolar amounts of **1a** and benzyl iodide took place cleanly to furnish the carbenium iodide **4**[4] quantitatively in MeCN at room temperature. The reaction of three molar amounts of **1a** with **5** gave the carbenium iodide **6**[4] quantitatively under similar conditions. Three molar amounts of the inner salt **1b**[1d] also reacted with **5** to give the carbenium iodide **7**[4] quantitatively. The ^{13}C NMR spectra of **4**, **6**, and **7** showed the carbenium carbon peaks at δ 163, 164, and 164, respectively, and the thiocarbonyl carbon peaks at δ 213, 214, and 212, respectively.[4]

Encouraged by these results, the reaction of **8**[3] with six molar amounts of **1a** was examined in MeCN at room temperature. The reaction proceeded smoothly to give the expected huge molecule **9** nearly quantitatively, which is composed of six carbenium bromide units with a molecular formula of $C_{72}H_{132}N_{12}Br_6S_{12}$ and a molecular weight of 2030.[5] Compound **9**, which was obtained as orange fine needles[6] on crystallization from a mixed solvent of MeCN and Et_2O, is soluble in organic solvents such as CH_2Cl_2, $CHCl_3$, MeCN, and MeOH, but is hardly soluble in nonpolar solvents such as hexane, benzene, and CCl_4. It is also easily soluble in water because of the presence of six hydrophilic carbenium salts units and is recovered from its aqueous solution without any decomposition on evaporation of the water.[7] The carbenium and thiocarbonyl carbon peaks of **9** resonated at δ 163 and 214,[5] respectively, comparable positions with those of **4**, **6**, and **7**. Interestingly, in the ^{1}H NMR spectrum of **9** in $CDCl_3$, the ethyl signals appeared as broad singlet-like multiplets, and the signal due to the CH_2, attached to the ring, is too broad to determine its chemical shift value.[5] The observed peak-widening is probably due to the decreased relaxation time of the hydrogen nuclei as is often observed with polymeric compounds. These signals turned sharp gradually on changing the solvent to CD_3CN and then to D_2O; thus, in D_2O, the CH_3, CH_2 (of CH_2CH_3), and CH_2 (attached to the ring) signals appeared as triplet-like multiplet, ill-defined multiplet, and broad singlet each centered at δ 1.36, 3.73, and 4.71, respectively.[5]



4 **6** **5** **1b** **7**

Previously, we reported that **2** reacts with negatively charged species such as RM (M = Li, MgX) at the thiocarbonyl sulfur atom exclusively, despite the presence of the positively charged carbenium carbon, to give a series of enediamines.[1c] Compound **9** also reacted in such a manner with six molar amounts of MeLi to provide a 61% yield of **10**[8] that has six enediamine moieties. Treatment of **9** with six molar amounts of MeMgI also gave the same compound **10** in 37% yield.



10: R = Me; 61%
11: R = P(O)(OMe)$_2$; 92%

Similarly, the Arbuzov-type reaction of **9** with six molar amounts of $(MeO)_3P$ took place at the sulfur atom exclusively to furnish compound **11**[8] in 92% yield.

Further study on the properties and reactions of **9** is under way with particular emphasis being placed on its functionality.[9]

References and Notes

1 a) J. Nakayama and I. Akiyama, *J. Chem. Soc., Chem. Commun.*, **1992**, 1522. b) A. Nagasawa, I. Akiyama, S. Mashima, and J. Nakayama, *Heteroatom Chem.*, **6**, 45 (1995). c) J. Nakayama, T. Otani, Y. Sugihara, and A. Ishii, *Tetrahedron Lett.*, **38**, 5013 (1997). d) K. Akimoto and J. Nakayama, *Heteroatom Chem.*, **8**, 505 (1997). e) J. Nakayama, T. Otani, Y. Sugihara, and A. Ishii, *Chem. Lett.*, **1998**, 321. f) J. Nakayama, K. Akimoto, and Y. Sugihara, *Tetrahedron Lett.*, **39**, 5587 (1998). g) J. Nakayama, T. Kitahara, Y. Sugihara, T. Otani, and A. Ishii, *Chem. Lett.*, **1998**, 887. h) T. Otani, Y. Sugihara, A. Ishii, and J. Nakayama, *Heteroatom Chem.*, **9**, 703 (1998). i) J. Nakayama, I. Akiyama, Y. Sugihara, and T. Nishio, *J. Am. Chem. Soc.*, **120**, 10027 (1998). j) J. Nakayama, T. Kitahara, Y. Sugihara, and A. Ishii, *Chem. Lett.*, **1999**, 187. k) J. Nakayama, T. Kitahara, Y. Sugihara, A. Sakamoto, and A. Ishii, *J. Am. Chem. Soc.*, **122**, 9120 (2000). l) J. Nakayama, L. Zhao, T. Otani, Y. Sugihara, and A. Ishii, *Chem. Lett.*, **2000**, 1248.

2 For other works related to this type of inner salts, see J. Nakayama, *Sulfur Lett.*, **15**, 239 (1993) and references cited therein; N. Kuhn, H. Bohmen, and G. Henkel, *Z. Naturforsch.*, **49b**, 1473 (1994); N. Kuhn, G. Weyers, S. Dümmling, and B. Speiser, *Phosphorus, Sulfur, Silicon*, **128**, 45 (1997); N. Kuhn, G. Weyers, and G. Henkel, *Chem. Commun.*, **1997**, 627; S. Dümmling, B. Speiser, N. Kuhn, and G. Weyers, *Acta Chem. Scand.*, **53**, 876 (1999).

3 Commercially available from Aldrich.

4 **4**: mp 105–112 °C (dec); orange-red needles; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.33 (12H, t, J = 7.0 Hz), 3.70 (8H, q, J = 7.0 Hz), 4.77 (2H, s), 7.33–7.40 (5H, m); ^{13}C NMR (50 MHz, $CDCl_3$) δ 13.5, 41.6, 48.5, 128.5, 128.9, 129.4, 132.4, 163.3, 213.4. Anal. Calcd for $C_{17}H_{27}IN_2S_2$: C, 45.33; H, 6.04; N, 6.22%. Found: C, 45.22; H, 6.00; N, 6.14%. **6**: mp 47–62 °C (dec); reddish brown powder; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.35 (36H, t, J = 7.2 Hz), 3.71 (24H, q, J = 7.2 Hz), 4.88 (6H, s), 7.90 (3H, s); ^{13}C NMR (100.6 MHz, CD_3CN) δ 13.7, 41.5, 48.9, 131.8, 135.5, 163.9, 214.3. Anal. Calcd for $C_{39}H_{69}I_3N_6S_6$: C, 39.19; H, 5.82; N, 7.03%. Found: C, 39.35; H, 5.89; N, 6.89%. **7**: mp 183.5–185.0 °C (dec); dark red powder; ^{1}H NMR (400 MHz, CD_3CN) δ 3.58–3.77 (48H, m), 3.74 (6H, s), 7.61 (3H, s); ^{13}C NMR (100.6 MHz, CD_3CN) δ 42.0, 52.4, 67.4, 131.9, 135.7, 163.6, 212.4. Anal. Calcd for $C_{39}H_{57}I_3N_6O_6S_6$: C, 36.62; H, 4.49; N, 6.57%. Found: C, 36.66; H, 4.56; N, 6.75%.

5 **9**: mp 172–173 °C (dec); orange fine needles; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.41 (72H, broad singlet-like m), 3.85 (48H, broad singlet-like m) (peak width of CH_2, attached to the ring, is too broad to determine the chemical shift value); ^{1}H NMR (400 MHz, CD_3CN) δ 1.29 (72H, ill-defined t, J = 7.0 Hz), 3.66–3.81 (48H, ill-defined m), 5.02 (12H, broad s); ^{1}H NMR (400 MHz, D_2O) δ 1.36 (72H, t, J = 7.0 Hz), 3.73 (48H, m), 4.71 (12H, broad s); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 13.6, 38.4, 48.5, 136.3, 163.0, 212.2; ^{13}C NMR (100.6 MHz, CD_3CN) δ 14.0, 39.6, 49.3, 137.2, 163.7, 214.2; IR (KBr) 1596, 1106 cm^{-1} (very intense). Although satisfactory elemental analyses of **9** could not be obtained despite many attempts, derivation of **11** in a high yield, in addition to the spectroscopic data, will guarantee the purity of the compound. The following is one of the results. Anal. Calcd for $C_{72}H_{132}Br_6N_{12}S_{12}$: C, 42.60; H, 6.55; N, 8.28%. Found: C, 41.64; H, 6.60; N, 7.82%.

6 Attempts to prepare single crystals suitable for X-ray crystallographic analysis are not successful.

7 **9** is more soluble in water than are **6** and **7**.

8 **10**: mp 152–154 °C (dec); pale yellow needles; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.92 (36H, t, J = 7.1 Hz), 1.00 (36H, t, J = 7.1 Hz), 2.19 (18H, s), 3.00 (24H, q, J = 7.1 Hz), 3.07 (24H, q, J = 7.1 Hz), 4.32 (12H, s); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 13.1 (overlapping of two peaks), 18.0, 33.6, 43.3, 43.4, 84.4, 136.0, 160.4. Anal. Calcd for $C_{78}H_{150}N_{12}S_{12}$: C, 57.09; H, 9.21; N, 10.24%. Found: C, 57.36; H, 9.44; N, 10.01%. **11**: mp 133–136 °C (dec); colorless cubes; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.99–1.10 (36H, ill-defined m), 1.15 (36H, t, J = 7.0 Hz), 3.06–3.20 (48H, ill-defined m), 3.73 (36H, d, $^3J_{(H,P)}$ = 12.2 Hz), 4.11 (12H, broad s); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 12.4, 13.1, 36.7, 43.4 (overlapping of two peaks), 53.0 (d, $^2J_{(C,P)}$ = 5.4 Hz), 61.5, 134.4, 171.4. Anal. Calcd for $C_{84}H_{168}N_{12}O_{18}P_6S_{12}$: C, 45.76; H, 7.68; N, 7.62%. Found: C, 45.56; H, 7.67; N, 7.41%.

9 Synthesis and properties of the hexasubstituted benzene octopus $[C_6(CH_2SC_2H_2N_3S)_6$: $C_2H_2N_3S$ = 5-amino-1,3,4-thiadiazole-2-yl] and the sulfoxide derivative were reported: C. Yang, X.-M. Chen, X.-Q. Lu, Q.-H. Zhou, and Y.-S. Yang, *Chem. Commun.*, **1997**, 2041.