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LETTERS

The reaction of [60]fullerene with 2-diazo-4,5-dicyanoimidazole

Paul G. Rasmussen,[a,*] Taiya S. Fabre,[b] Patricia A. Beck,[b] Marna J. Eissa,[b] Jorge Escobedo[b] and Robert M. Strongin[b,*]

[a]*Department of Chemistry, University of Michigan, Ann Arbor, MI 48109, USA*
[b]*Department of Chemistry, Louisiana State University, Baton Rouge, LA 70803, USA*

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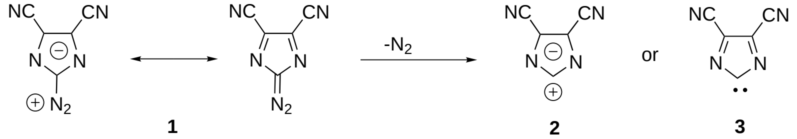
Abstract—The reaction of [60]fullerene with 2-diazo-4,5-dicyanoimidazole affords new compound **4** which contains an electron poor aromatic heterocycle attached to the fullerene sphere. © 2001 Published by Elsevier Science Ltd.

We have previously reported the reaction of [60]fullerene with atomic carbon[1] produced via the thermolytic decomposition of diazotetrazole.[2] We isolated and characterized the dumbbell-shaped dimeric C_{122} from a mixture of several products.[1] Mass spectrometric analysis of semi-purified HPLC fractions of the reaction mixture also showed evidence for the formation of C_{121}[3] and C_{119},[4] as well as solvent-derived (Ph or PhMe, depending on conditions) methanofullerene addends. In order to further our understanding of the interaction of [60]fullerene and azoazole heterocycles, we have begun to examine the reaction of [60]fullerene with 2-diazo-4,5-dicyanoimida-zole (DDI, **1**),[5] a congener of diazotetrazole. In addition, one of us has extensively studied the chemistry of dicyanoimidazoles as substrates towards the fabrication of unique high nitrogen content materials.[6]

A [60]fullerene-**1** reaction product should result in a new electron-poor heterocycle-functionalized fullerene. There is great current interest in tuning the properties of fullerenes via the appendage of electron donor or acceptor groups,[7] thereby relating fullerene chemistry to classical benzene chemistry.[8] The relatively less-studied addition of electron accepting moieties[9] to fullerenes may lead to molecules exhibiting charge and light-induced electron transfer for materials science or biochemical applications.[7]

Although diazo heterocycles are usually known as moderate to weak electron acceptors, the presence of the cyano groups stabilize **1**.[10] Compound **1** undergoes a variety of reactions with olefins, arenes, alcohols, etc.[5] The two possible intermediates (**2** or **3**) formed upon thermolysis of **1** have electrophilic character (Scheme 1).[10] Electrophilic carbon addition to the electron poor 60[fullerene] cage is relatively rare, and has been shown in some cases to afford 1,4-adducts.[11] In contrast, more common diazoalkane reactions with 60[fullerene] typically results in 1,2- (i.e. cyclopropane 6,6 ring junction adducts or homofullerene open 6,5-ring junction annulene) type addition patterns. We thus reasoned that the most viable monoaddition products arising from the thermolysis of **1** in the presence of [60]fullerene could embody one of the structures **4**–**6** (Fig. 1).

We synthesized **1** based on Webster's procedure,[5] which involves addition of a solution of aqueous $NaNO_2$ (0.120 g, 1.739 mmol, 25 equiv., 0.25 mL H_2O) and concentrated HCl (0.9 mL) to a solution of 2-amino-4,5-dicyanoimidazole (0.160 g, 1.20 mmol, 1.4 equiv.) in H_2O (1.8 mL). The solution is diluted with CCl_4 (1



Scheme 1.

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* Corresponding authors. Tel.: 225-578-3238; fax: 225-578-3458; e-mail: rob.strongin@chem.lsu.edu

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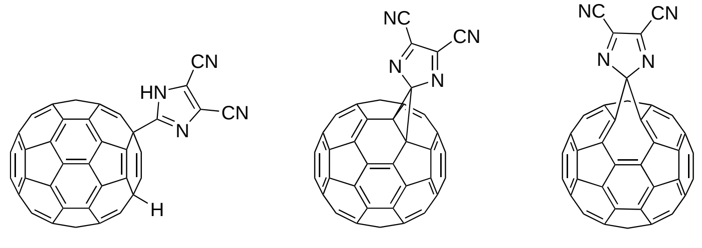

4 **5** **6**

Figure 1.

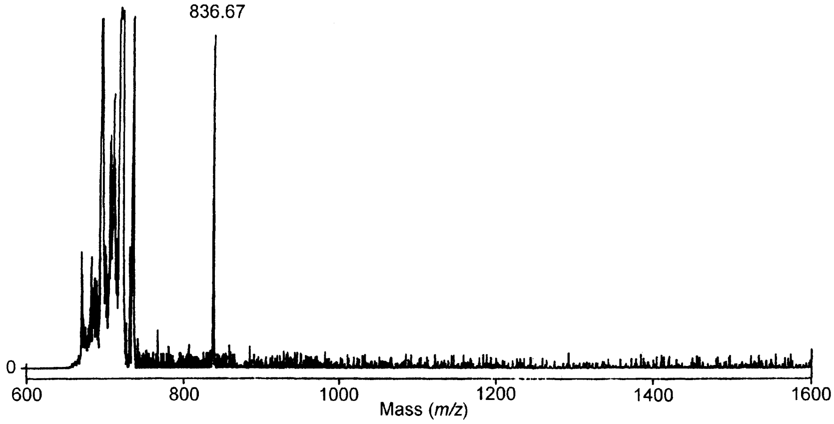

Figure 2. FAB negative ion mass spectrum of the isolated product.

mL). The resultant mixture is added to [60]fullerene (0.050 g, 0.069 mmol, 1 equiv.) in PhH (25 mL). The solution is carefully brought to reflux.[12] A new product is isolated (0.010 g, 20%) via flash column chromatography (TLC $R_f = 0.54$, 4:1 hexane: PhMe) using a gradient elution beginning with 100% hexane and ending with 100% PhMe. It exhibits a well-resolved single HPLC peak at 8.9 min ([60]fullerene elutes at 18.0 min) under reverse-phase (2:3 MeOH:PhMe, 7 mL/min, $\lambda =$ 325 nm, Dynamax 60 Å C_{18} 21.4 mm×25 cm) conditions. Control reactions employing identical conditions as described above but with either (1) no $NaNO_2$ or (2) 4,5-dicyanoimidazole instead of 2-amino-4,5-dicyanoimidazole show no trace of product formation.

The FAB negative ion mass spectrum of the isolated product (Fig. 2) exhibits a very intense peak at 836.67 (M−H), indicating monoaddition of the heterocycle. The UV–vis spectrum is characteristic of 1,4-monoadducts (i.e. **4**), displaying a broad absorption at 440 nm.[13,14] Although spiroannelated adducts of [60]fullerene are well-known,[1,3,8a] a 1,2-adduct (i.e. **5** or **6**) in the present case would embody a non-aromatic heterocycle.

Further evidence for the structure assignment as **4** derives from NMR spectroscopy. The 250 MHz ^{1}H NMR spectrum exhibits a singlet at 4.01 ppm ($C_6D_5CD_3$), which is characteristic of protons attached to the [60]fullerene sphere.[15] An additional resonance appears at 13.4 ppm, which we assigned to the acidic heterocycle proton (this resonance disappears upon addition of D_2O). We acquired a 125 MHz ^{13}C NMR spectrum using a sample prepared from 10–15% randomly ^{13}C enriched C_{60}. It exhibits 49 resolved fullerene resonances (of the expected 58) in the aromatic region. Additionally, we observed two sp^3 resonances at 77.9 and 73.9 ppm, which we assigned to the fullerene carbons bearing the heterocycle and the proton, respectively. The weak unlabeled heterocycle carbon resonances currently elude assignment. We tentatively assign a weak resonance observed at 131.2 ppm to the unlabeled nitrile carbons.[16]

In conclusion, thermolysis of **1** in the presence of [60]fullerene affords new heterocyclic monoadduct **4**. We have presented spectroscopic evidence consistent with a 1,4-addition pattern which preserves the aromaticity of the heterocycle. The method should afford access to other functionalized fullerenes with electron poor heterocycles which could find application as electroactive materials.

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16. Data for **4**: ^{1}H NMR (250 MHz, toluene-d_6) δ 13.4, 4.01; ^{13}C NMR (125 MHz, 4:1 CS_2:$CDCl_3$) δ 153.03, 152.79, 151.42, 151.03, 150.58, 150.47, 150.30, 149.75, 149.70, 149.64, 149.56, 149.48, 149.36, 149.23, 149.04, 140.82, 141.09, 148.86, 148.63, 148.43, 148.24, 148.09, 147.83, 147.55, 147.41, 147.27, 146.90, 146.57, 146.46, 146.23, 146.06, 145.83, 145.75, 145.54, 145.25, 141.45, 144.99, 144.85, 144.73, 144.31, 144.07, 143.86, 143.60, 142.90, 141.45, 141.08, 140.82, 131.2, 77.9, 73.9; FAB MS 836.67 obs. (M−H), (838.03 calcd).