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Mellitic Triimides: C_3-Symmetric, Three-Electron Acceptors for Supramolecular Chemistry

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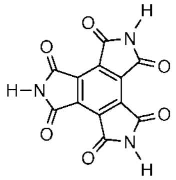
Supramolecular systems containing electroactive components, i.e. units that are readily oxidized or reduced, have tended to favor a limited range of building blocks.[1] This observation highlights the fact that these popular units may be confidently incorporated in a supramolecular design, and synthetic scheme, since their properties are well-known and synthetic utility well documented. A number of more exotic electron donors and acceptors have been prepared but, principally due to their synthetic inaccessibility, these units tend not to appear in complex assemblies.[2] We report here a general route to systems containing a surprisingly simple C_3-symmetric core via elaboration of mellitic triimide **1** by simple substitution processes. These system possess the capacity to accept up to *three* electrons, each at a distinct and well separated potential—an unusual ability, especially for a simple organic system.[3]

1



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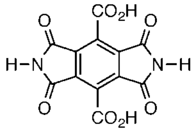


The literature relating to **1** is scant, dated, and inextricably linked to that of euchroic acid, **2**: only three reports have been made in the past 160 years.[4] Chaigneau describes, in passing, the formation of material designated as mellitic triimide **1** from the thermal decomposition of ammonium mellate ($C_6(CO_2NH_4)_6$), but this assignment was made solely on the basis of elemental data. We examined this work with the aim of isolating useful amounts of mellitic triimide **1**.

Scheme 1. Thermal Decomposition of Ammonium Mellate[4]

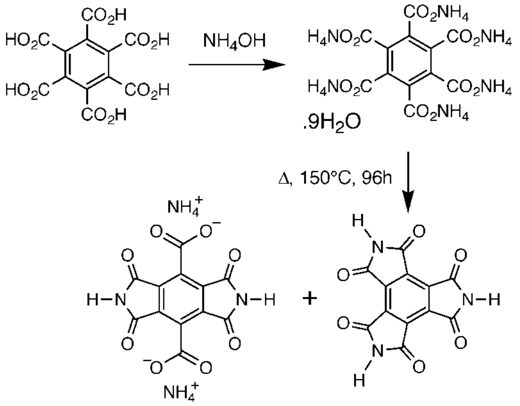
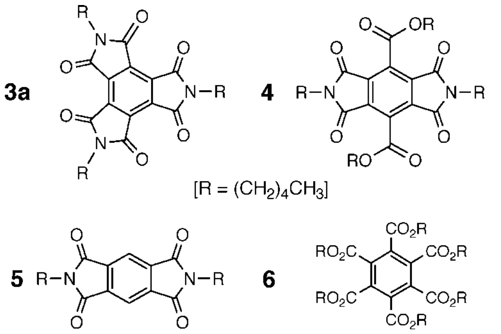


Chart 1. Isolated Products from Mitsunobu Alkylation of the Residue Obtained from Decomposition of Ammonium Mellate



Mellitic acid was converted to ammonium mellate by dissolution in hot aqueous ammonia solution: the crystalline hydrate is obtained on cooling. This salt was then dehydrated in a lyophilizer, spread on a watch glass, and baked in a standard drying oven at 150 °C for 4 days (Scheme 1).

In our first experiments the gruesomely insoluble postbaking residues were alkylated directly with *n*-pentanol under Mitsunobu conditions (Ph_3P/DIAD/THF). From these reactions the predominant isolable product was dialkyl euchroate **4** ($\approx$20%), though with careful chromatographic separation target triimide **3a** ($<$10%) could also be isolated.[5] These materials are accompanied by a significant number of side products, among which diimide **5** and hexa-ester **6** have been identified. Chaigneau reported that above 165 °C decomposition of ammonium mellate is complicated by a variety of side reactions. It seems clear that these reactions also occur to an appreciable extent at 150 °C, i.e. the situation is more complex than that shown in Scheme 1, and that one of these reactions is decarboxylation of ammonium euchroate to pyromellitic diimide (the precursor to **5**).[6] Additionally, it would appear that thermal decomposition of ammonium mellate is a rather delicate process: the isolation of both **5**, from *over*-reaction in the baking process, and **6**, presumably derived from *unchanged* ammonium mellate, suggests that a bake temperature of 150 °C represents an unavoidable compromise between inertness and decarboxylation. The array of products obtained from the alkylation reaction prompted attempts to purify the post baking residue prior to further use. We eventually found that Soxhlet extraction

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(1) In this context ubiquitous electron acceptors are bipyridinium salts and aromatic diimides, see: (a) Wiederrecht, G. P.; Niemczyk, M. P.; Svec, W. A.; Wasielewski, M. R. *J. Am. Chem. Soc.* **1996**, *118*, 81−88. (b) Lokey, R. S.; Kwok, Y.; Guelev, V.; Pursell, C. J.; Hurley, L. H.; Iverson, B. L. *J. Am. Chem. Soc.* **1997**, *119*, 7202−7210. (c) Hamilton, D. G.; Montalti, M.; Prodi, L.; Fontani, M.; Zanello, P.; Sanders, J. K. M. *Chem. Eur. J.* **2000**, *6*, 608−617. (d) Buchwalter, S. L.; Iyengar, R.; Viehbeck, A.; O'Toole, T. R. *J. Am. Chem. Soc.* **1991**, *113*, 376−377. (e) Amabilino, D. B.; Ashton, P. R.; Balzani, V.; Boyd, S. E.; Credi, A.; Lee, J. Y.; Menzer, S.; Stoddart, J. F.; Venturi, M.; Williams, D. J. *J. Am. Chem. Soc.* **1998**, *120*, 4295−4307. (f) Miller, L. L.; Mann, K. R. *Acc. Chem. Res.* **1996**, *29*, 417−423.

(2) For examples of C_3-symmetric electron *donors* that conform to this general description see: (a) Gonzalez, A.; Segura, J. L.; Martin, N. *Tetrahedron Lett.* **2000**, *41*, 3083−3086. (b) Fouormigué, M.; Johannese, I.; Boubekeur, K.; Nelson, C.; Batail, P. *J. Am. Chem. Soc.* **1993**, *115*, 3752−3759. The electron donating units in these systems are not electronically coupled, they are simply arrayed with C_3 symmetry.

(3) Benzophenone and perylene diimides share this distinction though both possess, from a supramolecular perspective, rather unwieldy structures, see: Viehbeck, A.; Goldberg, M. J.; Kovac, C. A. *J. Electrochem. Soc.* **1990**, *137*, 1460−1466.

(4) Chaigneau, M. *C. R. Hebd. Seances Acad. Sci.* **1955**, *240*, 2324−2326. This work describes the isolation and structural characterization of euchroic acid **2**, a molecule first reported and named by Wöhler over 100 years previously (Wöhler, F. *Ann. Der Ch. Und Ph.* **1841**, *37*, 268. Schwarz, H. *Ann. Der Ch. Und Ph.* **1848**, *66*, 52). To the best of our knowledge these are, to date, the only published reports relating to the chemistry of euchroic acid or mellitic triimide.

(5) **3a**: mp 141.5−143 °C; ^{13}C (63 MHz, $CDCl_3$) δ 162.62 (0), 133.52 (0), 39.54 (2), 29.10 (2), 28.05 (2), 22.42 (2) 14.11 (3) ppm; ^1H (270 MHz, $CDCl_3$) δ 3.80 (t, $J = 7$ Hz, 6H), 1.72 (quintet, $J = 7$ Hz, 6H), 1.34 (multiplet, 12 H), 0.88 (t, $J = 7$ Hz, 9H) ppm; ESI-MS (positive ion) 496.3 ($[M + H]^+$, 5%), 518.3 ($[M + Na]^+$, 100%).

(6) The complex nature of the product mixtures is only apparent once *soluble* and relatively *nonpolar* derivatives are generated.

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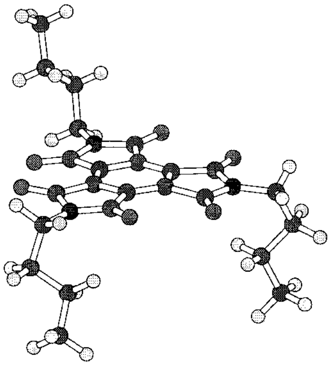
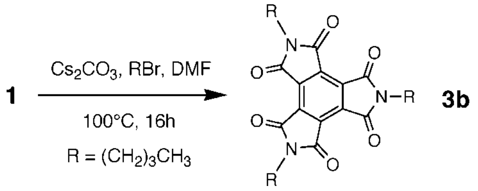


Figure 1. X-ray structure of triimide **3b** (disorder in two of the three butyl side chains has been omitted for purposes of clarity).

Scheme 2. Cs_2CO_3 Mediated Alkylation of Mellitic Triimide



with water (to remove carboxylate based materials) followed by suspension in, and filtration from, warm DMF gave refined "mellitic triimide" **1**.[7] Alkylation of this material with *n*-pentanol under Mitsunobu conditions gave 30−35% yields of **3a** after separation and recrystallization. Comparable yields of **3b** could be obtained by alkylation with 1-bromobutane in the presence of cesium carbonate (Scheme 2), expanding the synthetic options available from the core **1**.[8]

Crystals of triimide **3b** (from DMF/H_2O) proved suitable for X-ray analysis (Figure 1).[9] The structure reveals the triimide framework to be essentially planar, thereby confirming a recent prediction, based on analysis of the related trianhydride, that no substantial nonbonded contacts exist between the carbonyl functions.[10] The structure otherwise holds no surprises,[11] other than the observation that despite the *N*-butyl substituents the triimide packs in perfect C_3 symmetry.

The well documented electrochemical profiles of benzene and naphthalene diimides prompted the use of cyclic voltammetry to probe the electron accepting potential of the triimide framework. Aromatic diimides typically undergo two sequential *one* electron reductions, yielding first radical anions, then dianions.[3] A simple arrow pushing sketch indicated that it was theoretically possible to introduce three electrons into the triimide framework presented here. Theory is borne out by experiment: triimide **3a** undergoes three sequential, well separated, one electron reductions (Figure 2).[12] Thus, the triimide has *four* accessible electronic states: neutral, radical anion, dianion, and radical trianion.

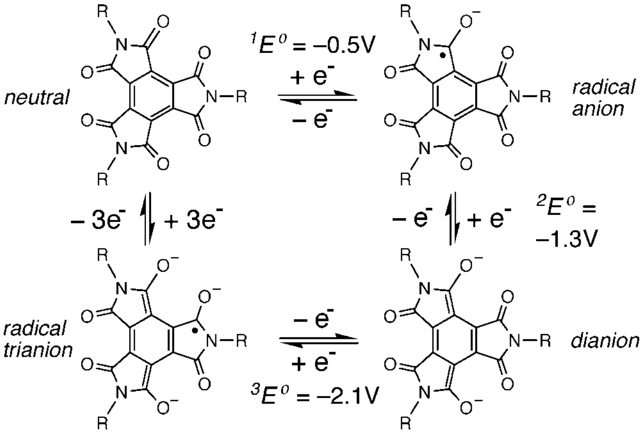


Figure 2. Possible forms, with their reduction potentials, for the radical anion, dianion, and radical trianion obtained on reduction of triimide **3a** (drawn to preserve a quinoidal substructure for the latter two species).[13]

We anticipate that the electron accepting ability of these systems, coupled with their symmetry and synthetic accessibility, will lead to numerous applications. Macrobicyclic cryptands from 3-fold linking of two triimides represent an attractive initial target which we are exploring: in the solid state, replacing a C_2-symmetric diimide with a C_3-symmetric triimide could prompt the formation of networks. Trisubstitution also potentially surrounds the core with a high level of insulation from its environment. A unit functionalized with three dendrimeric wedges would provide an isolated electron sink,[14] and substitution with perfluorinated alkyl chains could yield suitable derivatives for electronic device manufacture.[15]

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Supporting Information Available: Procedures for the conversion of mellitic acid to mellitic triimide **1**, isolation and characterization of **3a**, **3b**, **4**, **5**, and **6**, CV trace for **3a**, and crystal data for **3b** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(7) The efficiency of conversion of mellitic acid to mellitic triimide is low, a not unexpected result given the plethora of materials formed in the baking step. We are currently exploring alternative routes to **1** and its derivatives, and other methods for refining the postbaking residue.

(8) The yields for both reactions are rather lower than we would wish. Under the same conditions pyromellitic diimide affords around 60% yields of *N*-substituted derivatives, indicating that even our "refined" residue probably contains less than half mellitic triimide **1**.

(9) Crystal data for **3b**: $C_{24}H_{27}N_3O_6$, $M_r = 453.49$, $T = 293(2)$ K, $\lambda = 0.71073$ Å, trigonal, $a = 27.6903(4)$ Å, and $c = 10.8284(2)$ Å, $V = 7190.4(2)$ Å^3, space group R^3, colorless crystal ($0.75 \times 0.40 \times 0.35$ mm^3), $Z = 12$, $\rho_{calcd} = 1.257$ g cm^{-3}. The crystal contains 1.333 molecules per asymmetric unit and has two disordered alkyl chains that were treated using split-site refinements. The final R_1 value was 4.9% ($S = 1.060$).

(10) The trianhydride deviates substantially from planarity in the solid state, adopting a chiral propeller form induced by anhydride oxygen lone pair−carbonyl LUMO interactions, see: Ermer, O.; Neudörfl, J. *Helv. Chim. Acta* **2000**, *83*, 300−309.

(11) No bond localization effect within the aromatic ring resulting from the presence of the fused 5-membered imide rings is found for **3b**. The emergence of such a property, the Mills−Nixon effect, remains a goal in aromatic structural chemistry, see: Frank, N. L.; Baldridge, K. K.; Siegel, J. S. *J. Am. Chem. Soc.* **1995**, *117*, 2102−2103.

(12) Recorded as a 2 mM solution in anhydrous THF (0.1 M $^nBu_4NPF_6$ supporting electrolyte) versus an Ag/AgCl reference electrode at a sweep rate of 200 mV s^{-1}. Under these conditions the reductions are *electrochemically quasi*-reversible, though *chemically* fully reversible.

(13) For comparison, typical first and second reduction potentials for benzene diimides (e.g. **5**) are −0.9 and −1.5 V, for naphthalene diimides −0.7 and −1.1 V (all ±0.1 V depending on *N*-substitution, ref 1c).

(14) Liwporncharoenvong, T.; Luck, R. L. *J. Am. Chem. Soc.* **2001**, *123*, 3615−3616 and references therein.

(15) Katz, H. E.; Johnson, J.; Lovinger, A. J.; Li, W. *J. Am. Chem. Soc.* **2000**, *122*, 7787−7792. The first reduction potential of the systems reported here, close to those of C_{60} and naphthalene diimides, suggests they may be useful molecular electronic components, see: Würthner, F. *Angew. Chem., Int. Ed.* **2001**, *40*, 1037−1039.