of water (15 mL) and ammonia (25 mL) with stirring. The solution was adjusted to ca. pH 10 by adding ammonia, and the solution was then extracted with CHCl₃ (2 × 100 mL). The CHCl₃ extract after treating with anhydrous Na₂SO₄ was evaporated to dryness on a rotavap. The white residue was extracted with boiling petroleum ether (80–100 °C), which on slow evaporation deposited colorless cubic crystals, yield 2.3 g (38%).

Method II. To a boiling MeOH solution (50 mL) of 4-methyl-2,6-diformylphenol (4.9 g, 30 mmol) were added a mixture of Pb(OAc)₂·3H₂O (5.7 g, 15 mmol) and Pb(NO₃)₂ (5 g, 15 mmol) dissolved in hot DMF (20 mL) and 1,3-diaminopropane (2.2 g, 30 mmol) diluted with MeOH (20 mL) at one time. The resulting mixture was refluxed for 8 h during which an orange-yellow crystalline product deposited. This was collected by filtration, washed with MeOH and CHCl₃, and finally air-dried. [Pb₂L(N-O₃)₂]·4H₂O thus obtained (9 g) was pulverized and slurried with MeOH (120 mL). NaBH₄ (3.5 g) dissolved in water (10 mL) was added to this stirred suspension over a period of 30 min. Stirring was continued for 2 h, after which the solution was filtered to remove any undissolved material. The filtrate was diluted with water (350 mL) and acidified with cold dilute H₂SO₄ (8 M). PbSO₄ precipitated, was removed by filtration, and was washed several times with cold water. The combined filtrate was treated with ammonia in an ice bath until the solution reached ca. pH 10. This was then extracted with CHCl₃ (2 × 100 mL). The CHCl₃ layer was treated as described above: yield 2.1 g (35%); mp 125 °C dec; IR (Nujol) 3540 [m, ν(OH)], 3260 [m, ν(NH)], 1605 [m, δ(NH)], 1250 cm⁻¹ [m, ν(CO)]; ¹H NMR (CDCl₃) δ 1.86 (quint, 4 H, CH₂CH₂CH₂), 2.18 (s, 6 H, Me), 2.58 (t, 8 H, CH₂CH₂CH₂), 3.83 (s, 8 H, ArCH₂), 5.1 (br, 6 H, NH, OH), 6.74 (s, 4 H, Ph); ¹³C NMR (CDCl₃) δ 20.14 (q, Me), 29.79 (t, CH₂CH₂CH₂), 46.54 (t, CH₂CH₂CH₂), 51.15 (t, ArCH₂), 123.95 (s, 4-Ph), 127.20 (s, 2,6-Ph), 128.82 (d, 3,5-Ph), 154.37 (s, 1-Ph); MS, m/e 412.16 (M⁺, 2.3%), 268.05 (M⁺ − 2 C₃H₈N₂, 2.8%), 266.02 (268.05 − 2 H due to OH coupling, 2.2%). Anal. Calcd for C₂₄H₃₆N₄O₂: C, 69.90; H, 8.74; N, 13.59. Found: C, 69.75; H, 8.68; N, 13.47.

Macrocycle 2. This compound was prepared according to method I. The product obtained after evaporation of CHCl₃ was recrystallized three times from MeOH: yield 20%; mp 210–211 °C; IR (Nujol) 3520 [m, ν(OH)], 3250 [m, ν(NH)], 1605 [m, δ(NH)], 1250 cm⁻¹ [m, ν(CO)]; ¹H NMR (CDCl₃) δ 2.20 (s, 6 H, Me), 2.80 (s, 8 H, CH₂CH₂), 3.76 (s, 8 H, ArCH₂), 4.06 (br s, 6 H, NH, OH), 6.73 (s, 4 H, Ph). Anal. Calcd for C₂₂H₃₂N₄O₂: C, 68.75; H, 8.33; N, 14.58. Found: C, 69.02; H, 8.28; N, 14.70.

Macrocycle 4. Method I was followed to prepare this compound, recrystallized three times from MeOH: yield 15%; mp 178–179 °C; IR (KBr) 3450 [br, ν(OH)], 3310 (w), 3270 [m, ν(NH)], 1610 [m, δ(NH)], 1260 cm⁻¹ [m, ν(CO)]; ¹H NMR (CDCl₃) δ 1.56 (m, 8 H, CH₂CH₂CH₂CH₂), 2.21 (s, 6 H, Me), 2.61 (t, 8 H, CH₂CH₂CH₂CH₂), 3.81 (s, 8 H, ArCH₂), 4.71 (br s, 6 H, NH, OH), 6.73 (s, 4 H, Ph). Anal. Calcd for C₂₆H₄₀N₄O₂: C, 70.91; H, 9.09; N, 12.72. Found: C, 70.72; H, 9.0; N, 12.60.

Macrocycle 5. To a boiling MeOH solution (50 mL) of 4-methyl-2,6-diformylphenol (4.9 g, 30 mmol) were added triethylamine (3 g, 30 mmol), Pb(NO₃)₂ (9.9 g, 30 mmol) dissolved in hot DMF (20 mL), and 1,2-diaminoethane (0.9 g, 15 mmol) mixed with MeOH (15 mL). The resulting mixture was heated under reflux for 9 h, and the product formed was collected by filtration that was then washed with MeOH. Compound 6 thus obtained (9.2 g) was finely powdered and suspended in MeOH (50 mL), and under vigorously stirred conditions to 0.74 g of 1,3-diaminopropane diluted with MeOH was added. The mixture was stirred and refluxed for 10 h after which it was filtered. The lead complex formed was reduced according to the procedure described in method II. The overall yield of 5 was 9%; mp 148–149 °C; IR (KBr) 3440 [br, ν(OH)], 3260 [m, ν(NH)], 1610 [m, δ(NH)], 1240 cm⁻¹ [ν(CO)]; ¹H NMR (CDCl₃) δ 1.71 (quint, 2 H, CH₂CH₂CH₂), 2.20 (s, 6 H, Me), 2.58–2.82 (m, 8 H, CH₂CH₂CH₂CH₂CH₂), 3.77 (s) and 3.81 (s) (8 H, ArCH₂), 4.5 (br, NH, OH), 6.77 (s, 4 H, Ph). Anal. Calcd for C₂₃H₃₄N₄O₂: C, 69.34; H, 8.54; N, 14.07. Found: C, 69.56; H, 8.60; N, 13.97.

The Stability of Footballene

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Haymet[1] has reported a theoretical study of the intriguing C₆₀ "alkene", footballene (1), an approximately spherical, fully conjugated compound which contains 12 five- and 20 six-membered rings. By comparing the Hückel delocalization energy (DE) per carbon of 1 with those of benzene and a related molecule, [5.6.1]corannulene (2), he concluded that 1 might be stable.

However, there is a very little correlation between Hückel DE and the chemical behavior of cyclic conjugated hydrocarbons. An early paper by Roberts, Streitwieser, and Regan[2] reported calculated DE's for a large number of interesting systems, many of which were predicted to be aromatic and therefore stable. Subsequent efforts by synthetic chemists showed most of these predictions to be incorrect. In 1969 Dewar and De Llano[3] proposed a change in the reference structure for computing resonance energies, and when this new reference structure was applied[4] to the Hückel method a quite good qualitative correlation was found between theory and experiment for a wide range of conjugated systems.[5,6] A simple demonstration of this can be seen by examining the series of linearly annelated polyacenes: benzene, naphthalene, anthracene, tetracene, and pentacene. Table I lists the computed DE/Carbon or π electron (DEPE) and Hückel resonance energies per π electron (REPE). It is seen that as the number of rings increases, DEPE also increases, but REPE decreases. Thus REPE predicts decreasing stability with increasing size, in agreement with the known chemical behavior of this series,[8] while DEPE predicts increasing stability. Hence a high DEPE should not be used to support potential stability.

Both DEPE and REPE were developed as indices for the prediction of "aromaticity", a vague concept, but one that most would agree implies extra stability (though again in some poorly defined sense). It turns out that DEPE fails so badly that REPE can be seen to be a better index (see especially Fig. 1 of ref 9) in spite of these ambiguities.

We have computed REPE's for 1 (0.031 β),[10] the corannulene 2 (0.049 β),[11] and also for the other C₆₀ system,

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(2) Roberts, J. D.; Streitwieser, A., Jr.; Regan, C. M. *J. Am. Chem. Soc.* **1952**, *74*, 4579.
(3) Dewar, M. J. S.; de Llano, C. R. *J. Am. Chem. Soc.* **1969**, *91*, 789.
(4) Hess, B. A., Jr.; Schaad, L. J. *J. Am. Chem. Soc.* **1971**, *93*, 905.
(5) Hess, B. A., Jr.; Schaad, L. J. *J. Am. Chem. Soc.* **1971**, *93*, 2413.
(6) Hess, B. A., Jr.; Schaad, L. J. *J. Org. Chem.* **1971**, *22*, 3418.
(7) Herndon, W. C.; Ellzey, M. L. Jr. *J. Am. Chem. Soc.* **1974**, *96*, 6631.
(8) Badger, G. M. *Aromatic Character and Aromaticity*; Cambride University Press: London, 1969; p 19.
(9) Schaad, L. J.; Hess, B. A., Jr.; *J. Am. Chem. Soc.* **1972**, *94*, 3068.
(10) The computation of the reference energy of footballene is surprisingly easy in spite of the 12 500 Kekulé structures since each has the same number of all bond types and hence each has the same additive energy.
(11) Agranat, I.; Hess, B. A., Jr.; Schaad, L. J. *Pure Appl. Chem.* **1980**, *52*, 1399.

Table I. Computed Stabilization Energies of the
Polyacenes

compound	DEPE[a]	REPE[a]
benzene	0.333	0.065
naphthalene	0.368	0.055
anthracene	0.380	0.047
tetracene	0.385	0.042
pentacene	0.388	0.038
infinite polyacene[b]	0.403	0.022

[a] In units of β. [b] Reference 7.

graphitene (0.020 β), mentioned by Haymet. For comparison, REPE = 0.053β for graphite. Thus the isolation[12] of 2 which has a considerably higher REPE than 1 does not have a strong bearing on the potential isolation of 1. The computed REPE of 1 is higher than that of azulene (0.023 β); but in the benzenoid series, where there are usually many possibilities for rearrangement to more stable systems, an REPE of this size does not guarantee stability.[5]

Registry No. Footballene, 99685-96-8.

(12) Barth, W. E.; Lawton, R. C. *J. Am. Chem. Soc.* 1971, *93*, 1730.

A Unique Application of the Sulfide Reduction Useful for the Preparation of Isomerically Pure Aromatic Nitro Compounds and Anilines

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The preparation of isomerically pure substituted aromatic nitro compounds and anilines continues to be an important aspect of agricultural and pharmaceutical chemistry.[1] Since nitration, which is usually the most expeditious manner to prepare such chemicals, invariably gives mixtures of isomers that are often difficult to separate, a practical laboratory method to obtain pure isomers would be of general interest and utility. Recently, we encountered a need to prepare pure 2. To achieve this, a chemical method was discovered whereby the separation could be effected through a simple laboratory procedure. Reported here is a unique application of a sulfide (Zinin) reduction of a mixture of nitration isomers useful to obtain both 3 and 2 isomerically pure.

The *m*-xylene derivative 1, which could be obtained in good yield by a published method,[2] was nitrated to afford a complicated mixture of nitro compounds[3] (cf. Scheme I). Interestingly, the most hindered isomer, 3, was the major product (42%). It is known, however, that nitration of *m*-toluic acid and *m*-tolualdehyde gives the analogous isomer as >50% of their product mixture.[4]

Separation of the mixture was effected by a unique application of the Zinin reduction.[5] While sulfide salts are known to reduce pure nitration isomers,[6] they are also sensitive to the steric environment of the nitro group.[5]

(1) *The Chemistry of the Nitro and Nitroso Groups*; Feuer, H. Ed., Interscience: New York, 1970; Part 2.
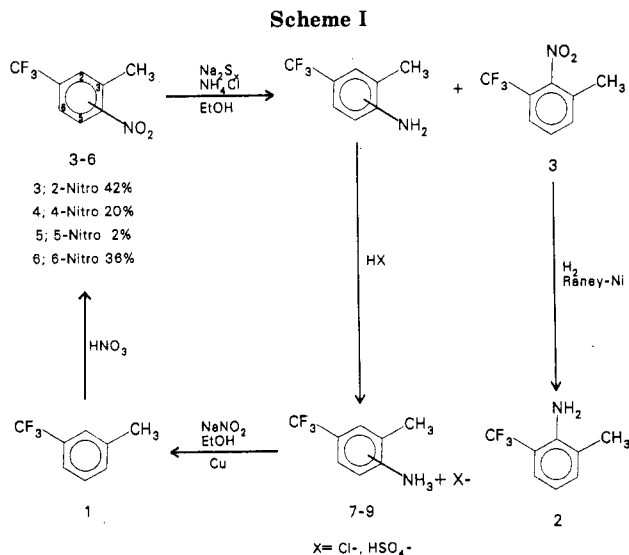(2) Matsui, K.; Tobita, E.; Ando, M.; Kondo, K. *Chem. Lett.* 1981, 1719-1720.
(3) Chupp, J. P.; Alt, G. H. U.S. Patent 4,467,125; 1984.
(4) Mayer, F., *Ber. Dtsch. Chem. Ger.* 1914, *47*, 406.
(5) Porter, H. K., *Org. React.* (N.Y.) 1973, *20*, 455-481.
(6) Groggins, P. H. *Unit Processes in Organic Synthesis*; McGraw-Hill: New York, 1958; pp 186-190.

Scheme I

Thus, we expected to see some kinetic differentiation among the isomers 3-6. This turned out to be true since we saw a clean conversion of isomers 4-6 to their respective anilines (7-9) without any observable alteration of 3 (cf. Scheme I). In fact, the anilines 7-9 were precipitated from dichloromethane by gaseous HCl in 88% yield while 3 was isolated in 95% yield.

The rate of reduction was pH sensitive and required that caustic be added to maintain pH >10.5. It was also important to keep the pH <12 to mitigate the loss of aniline products which were prone to decomposition in the presence of strong hydroxide. We found that the polysulfide reagents were milder and preferable to the monosulfide salts. Ultimately a buffered system was developed using sodium disulfide and ammonium chloride to lower the pH into the 11-12 range. Pure ammonium disulfide could not be used since its pH was <10.5. Other buffers and conditions were studied, and none showed any improvement over those given here. Eventually, this procedure was optimized so that the reduction could be run with a pH meter to monitor the caustic concentration. After complete reaction (GLC), the crude product was worked up with the anilines either being extracted into acid or the entire mixture being dissolved in dichloromethane and the anilines precipitated with HCl gas in 88% yield (Scheme I). Crude 3, obtained in 95% yield (40% from 1), was either crystallized or reduced directly to 2 with Raney Ni under H₂ atmosphere. The reduction to 2 proceeded in 95% yield (cf. Scheme I).

The overall process was made extremely efficient when anilines 7-9 as their H₂SO₄ salts were reductively deaminated to recover 1 in 83% yield (cf. Scheme I).

We investigated several other approaches to perform this unique method of separating the nitration isomers without success. Efforts to find a selective catalyst for hydrogenation failed while examination of the literature did not reveal any simple alternatives to the Zinin reduction.

Other examples were run to test the general nature of this reaction. In one example *m*-xylene was nitrated to get the usual 85:15 ratio of isomers. Reaction of this mixture with sodium sulfide proceeded at a much slower rate due to the lack of an additional electron-withdrawing group. However the 2-nitro isomer could be cleanly separated, albeit in a poor yield.

Experimental Section

All NMR spectra were recorded on a Varian EM-390 NMR spectrometer at 90 MHz. All chemical shifts are reported in parts