or EM-390 instrument with Me_4Si as an internal standard. A Hitachi 260-10 spectrophotometer was used to obtain IR spectra. Chromatography was performed on 230-400-mesh silica gel.

1-[(Trimethylsilyl)methyl]pyrrole (4a) was prepared from pyrrole in 38% yield according to the procedure of Ashby:[12] bp 88.5-89 °C (37 mm) [lit.[12] bp 84 °C (30 mm)].

1-[(Trimethylsilyl)methyl]imidazole (4c) was prepared from imidazole in 41% yield according to the procedure of Barcza:[13] bp 110-111 °C (7 mm) [lit.[13] bp 65 °C (0.5 mm)].

Preparation of 1-[(Trimethylsilyl)methyl]pyrazole (4b). A suspension of pyrazole (10 g, 147 mmol), (chloromethyl)trimethylsilane (19.8 g, 161 mmol), powdered K_2CO_3 (24.4 g, 177 mmol), and dry Me_2SO (200 mL) was stirred at 25 °C for 62 h. The resulting mixture was poured into ice-water and extracted with Et_2O. The organic layer was washed with water, dried (Na_2SO_4), and evaporated. The residue was distilled under reduced pressure to give 11.5 g of **4b** (51%): bp 118-119 °C (126 mm); ^1H NMR ($CDCl_3$) δ 0.11 (s, 9 H, Me_3), 3.71 (s, 2 H, CH_2), 6.08-6.21 (m, 1 H, 4-position of pyrazole ring), 7.14-7.26 (m, 1 H, 3-position), 7.33-7.46 (m, 1 H, 5-position); IR (neat) 3100, 2950, 2890, 1510, 1440, 1410, 1390, 1245, 1125, 1085, 1045, 960, 915, 850, 745, 700 cm^{-1}. Anal. Calcd for $C_7H_{14}N_2Si$: C, 54.49; H, 9.15; N, 18.16. Found: C, 54.20; H, 9.03; N, 17.95.

1-[(Trimethylsilyl)methyl]-1,2,4-triazole (4d) was prepared in a similar manner. 1,2,4-Triazole (12 g, 174 mmol) was converted into 20.7 g of **4d** (77%): bp 102-103 °C (15 mm); ^1H NMR (CCl_4) δ 0.11 (s, 9 H, Me_3), 3.67 (s, 2 H, CH_2), 7.62 (s, 1 H, 3-position of 1,2,4-triazole ring), 7.76 (s, 1 H, 5-position); IR (neat) 3100, 2950, 2890, 1500, 1410, 1345, 1290, 1270, 1250, 1210, 1140, 1010, 950, 850, 760, 700, 680 cm^{-1}. Anal. Calcd for $C_6H_{13}N_3Si$: C, 46.41; H, 8.44; N, 27.06. Found: C, 46.00; H, 8.47; N, 26.90.

1-[(Trimethylsilyl)methyl]tetrazole (4e) and 2-[(trimethylsilyl)methyl]tetrazole were prepared in a similar manner. Tetrazole (6 g, 86 mmol) gave **4e** (3.35 g, 25%) and 2-[(trimethylsilyl)methyl]tetrazole (1.97 g, 15%), which were separated from each other by flash chromatography using AcOEt-benzene (1:4) as an eluent. **4e**: mp 56-57.5 °C; ^1H NMR ($CDCl_3$) δ 0.17 (s, 9 H, Me_3), 3.94 (s, 2 H, CH_2), 8.50 (s, 1 H, 5-position of tetrazole ring); IR (Nujol) 3090, 1485, 1425, 1270, 1255, 1240, 1180, 1120, 1100, 975, 900, 870, 850, 775, 710 cm^{-1}. Anal. Calcd for $C_5H_{12}N_4Si$: C, 38.43; H, 7.74; N, 35.85. Found: C, 38.16; H, 7.71; N, 35.64. 2-[(Trimethylsilyl)methyl]tetrazole: bp 85-86 °C (17 mm); ^1H NMR ($CDCl_3$) δ 0.18 (s, 9 H, Me_3), 4.22 (s, 2 H, CH_2), 8.43 (s, 1 H, 5-position of tetrazole ring); IR (neat) 3135, 2950, 2895, 1445, 1410, 1350, 1275, 1250, 1170, 1130, 1090, 1020, 1000, 850, 765, 740, 700 cm^{-1}. Anal. Calcd for $C_5H_{12}N_4Si$: C, 38.43; H, 7.74; N, 35.85. Found: C, 37.91; H, 7.58; N, 35.55.

General Procedure for CsF-Catalyzed Reaction of 1-[(Trimethylsilyl)methyl]azole 4 with Carbonyl Compounds. To a solution of carbonyl compound (500 mg, 2.7-5.1 mmol) and **4** (1.2 molar equiv/mol of carbonyl compound) in dry diglyme (1.9 mL/mmol of carbonyl compound) under nitrogen atmosphere at room temperature was added powdered CsF (0.1 molar equiv/mol of carbonyl compound, dried 150 °C under vacuum). The suspension was stirred at 100 °C for the period shown in Table I. After cooling to room temperature, 6 N HCl (2 mL) was added and the mixture was stirred for 6 h. The reaction mixture was poured into 5% NaOH and extracted with CH_2Cl_2. The organic layer was washed with water, dried (Na_2SO_4), and evaporated. The residue was purified by flash chromatography and the results are summarized in Table I (entries 1, 3, 5, 7, 9).

General Procedure for TBAF-Catalyzed Reaction of 4 with Carbonyl Compounds. To a mixture of carbonyl compound (500 mg, 2.7-5.1 mmol) and **4** (1.2 molar equiv/mol of carbonyl compound) in dry THF (1.9 mL/mmol of carbonyl compound) under nitrogen atmosphere at room temperature was added anhydrous TBAF (0.1 molar equiv/mol of carbonyl compound, 1 M in THF). The mixture was refluxed for the period shown in Table I. The reaction mixture was worked up in a similar manner to that described above, and purified by flash chromatography to give **8** with or without **9**, as shown in Table I (entries 2, 4, 6, 8, 10, 13 14).

General Procedure for *t*-BuOK-Induced Reaction of 1-[(Trimethylsilyl)methyl]azole 4 with Benzophenone (5g). *t*-BuOK (148 mg, 1.3 mmol) was added to a solution of **5g** (200 mg, 1.1 mmol) and **4** (1.2 molar equiv/mol of **5g**) in dry THF (2 mL) and the mixture was stirred under the conditions described in Table I. The mixture was poured into ice-water and extracted with CH_2Cl_2. The organic layer was washed with water, dried (Na_2SO_4), and evaporated. The residue was chromatographed on silica gel to give the products listed in Table I (entries 11, 12, 15-18).

TBAF-Catalyzed Reaction of 1-[(Trimethylsilyl)methyl]-1,2,4-triazole (4d) with α-Tetralone (10). To a solution of **10** (470 mg, 3.2 mmol) and **4d** (1 g, 6.4 mmol) in dry THF (10 mL) was added anhydrous TBAF (0.3 mL, 1 M in THF) under nitrogen atmosphere at room temperature, and the mixture was refluxed for 2 h. The reaction mixture was evaporated to remove THF and chromatographed on silica gel. The fractions eluted with benzene-hexane (1:1) gave **11** (257 mg, 37%): ^1H NMR (CCl_4) δ 0.24 (s, 9 H, Me_3), 2.06-2.91 (m, 4 H, -$(CH_2)_2$-), 5.05 (t, 1 H, J = 4.2 Hz, CH=), 6.88-7.54 (m, 4 H, Ar H); IR (neat) 1640 cm^{-1}. The fractions eluted with benzene gave α-tetralone (137 mg, 29%). The fraction eluted with benzene-AcOEt (10:1) afforded a mixture of **12** and **13** (272 mg, 12:13 = 2.5:1 by ^1H NMR spectrum, 25%). **12**: ^1H NMR (CCl_4) δ 0.0 (s, 9 H, Me_3), 1.57-2.95 (m, 6 H, -$(CH_2)_3$-), 3.80 (s, 3 H, Me), 7.02-7.43 (m, 4 H, Ar H), 7.48 (s, 1 H, 3-position of 1,2,4-triazole ring). **13**: ^1H NMR (CCl_4) δ 0.0 (s, 9 H, Me_3), 1.57-2.95 (m, 6 H, -$(CH_2)_3$-), 4.13 (d, 1 H, J = 14.4 Hz, NCH*H*), 4.40 (d, 1 H, J = 14.4 Hz, NC*H*H), 7.02-7.43 (m, 4 H, Ar H), 7.70 (s, 1 H, 3-position of 1,2,4-triazole ring), 8.05 (s, 1 H, 5-position of 1,2,4-triazole ring).

Acknowledgment. We thank Drs. K. Horiki and H. Hamana for helpful discussion in these studies.

Registry No. **4a**, 5833-50-1; **4b**, 92525-04-7; **4c**, 39579-48-1; **4d**, 103817-03-4; **4e**, 103817-04-5; **5f**, 104-88-1; **5g**, 119-61-9; **5h**, 99-91-2; **5i**, 108-94-1; **5j**, 104-53-0; **8f**, 62881-59-8; **8g**, 76674-04-9; **8h**, 79983-74-7; **8i**, 103817-05-6; **8j**, 103817-06-7; **9g**, 103817-08-9; **9h**, 103817-15-8; **9i**, 103817-16-9; **10**, 529-34-0; **11**, 38858-72-9; **12**, 103817-13-6; **13**, 103817-14-7; **18b**, 103817-07-8; **18c**, 24155-45-1; **19a**, 103817-09-0; **19b**, 103817-10-3; **19c**, 65570-68-5; **20e**, 33452-23-2; **21e**, 103817-12-5; CsF, 13400-13-0; TBAF, 429-41-4; *t*-BuOK, 865-47-4; pyrazole, 288-13-1; 1,2,4-triazole, 288-88-0; (chloromethyl)trimethylsilane, 288-94-8; tetrazole, 288-94-8; 2-[(trimethylsilyl)methyl]tetrazole, 103817-11-4.

Synthesis of Some Macrocyclic Compounds Containing 2,6-Bis(*N*-alkylamino)phenol Units

Sanat K. Mandal[1] and Kamalaksha Nag*

Department of Inorganic Chemistry, Indian Association for the Cultivation of Science, Calcutta 700 032, India

Received March 6, 1986

Many macrocyclic compounds showing cation-selective behavior[2,3] are commonly prepared either by metal template condensation reactions[4] or by high-dilution techniques.[5] Structural, magnetic, spectroscopic, and redox

(1) Present address: Chemistry Department, Memorial University of Newfoundland, St. John's, Newfoundland, Canada.

(2) (a) Izatt, R. M., Christensen, J. J., Eds. *Synthetic Multidentate Macrocyclic Compounds*; Associated Press: New York, 1978. (b) Izatt, R. M.; Bradshaw, J. S.; Nielsen, S. A.; Lamb, J. D.; Christensen, J. J.; Sen, D. *Chem. Rev.* **1985**, *85*, 271.

(3) (a) Melson, G. A., Ed. *Coordination Chemistry of Macrocyclic Compounds*; Plenum: New York, 1979. (b) Lehn, J. M. *Pure Appl. Chem.* **1980**, *52*, 2441. (c) Henrick, K.; Tasker, P. A.; Lindoy, L. F. *Prog. Inorg. Chem.* **1985**, *33*, 1. (d) Meade, T. J.; Busch, D. H. *Ibid.* **1985**, *33*, 59.

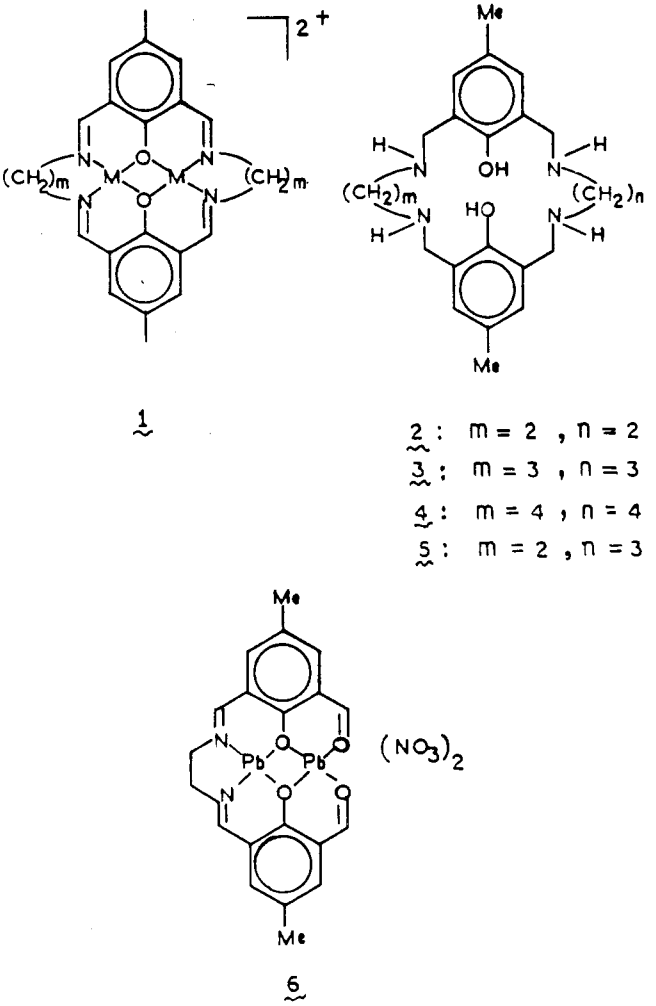
(4) (a) Curtis, N. F. *Coord. Chem. Rev.* **1968**, *3*, 3. (b) Black, D. St. C.; Hartshorn, A. J. *Coord. Chem. Rev.* **1972-1973**, *9*, 219. (c) De Sousa Healy, M.; Rest, A. J. *Adv. Inorg. Radiochem.* **1978**, *21*, 1.

(5) (a) Stetter, H.; Mayer, K.-H. *Chem. Ber.* **1961**, *94*, 1410. (b) Dietrich, B.; Lehn, J. M.; Sauvage, J. P.; Blanzat, J. *Tetrahedron* **1973**, 1629. (c) Atkins, T. J.; Richman, J. E.; Oettle, W. F. *Org. Synth.* **1978**, *58*, 86. (d) Rossa, L.; Vögtle, F. *Top. Curr. Chem.* **1983**, *113*, 1.

0022-3263/86/1951-3900$01.50/0

studies of the binuclear complexes of the type $[M^{II}_2L]^{2+}$ (1),[6,7] obtained by reacting stoichiometric amounts of 4-methyl-2,6-diformylphenol and its analogues with primary diamines in the presence of some bivalent metal salts, have been extremely useful in understanding the properties of coupled metal systems.[8-10] Although the metal-encapsulated compounds are available, the metal-free macrocycles (H_2L) are not. This is because their synthesis via the nontemplate route invariably yields polymeric products, whereas removal of the metal ions from 1 leads to the hydrolytic cleavage of the azomethine linkages. We have been interested to prepare the fully saturated analogues of H_2L for several reasons: (a) The cation-selective behavior of these compounds can be discriminated by determining the formation constants of their metal complexes. (b) The chemistry of their binuclear metal complexes at higher oxidation states can be investigated. (c) The effect of flexibility and hole size in their metal complexes can be investigated. (d) The secondary amino groups of these molecules can be functionalized[11] to generate macrocyclic compounds with modified structure. We report here the preparation of four macrocyclic compounds, **2–5**, by $NaBH_4$ reduction of 1.

The obvious method for preparing compounds **2–5** would be to reduce a suitable precursor complex (1), followed by removal of the metal ions. Cyclic voltammetric studies of the dicopper(II) complexes[8-10] revealed that reduction of the metal centers occurs prior to the reduction of C=N bonds, and the reduction of the latter does not take place at least up to −1.2 V vs. SCE. It also became apparent that although $NaBH_4$ reduces the C=N bonds, undesirable side reactions such as oligomerization of the phenolic groups and hydrolysis of the C=N bonds consequent to the reduction of the Cu^{2+} ions take place. Clearly, it was necessary to use a metal ion for precursor complex formation whose reduction potential should be more negative than that of C=N, and the metal ion should be able to form stable complexes with the reduced macrocyclic rings. Preliminary studies showed that the magnesium complexes $[Mg_2L(NO_3)_2]\cdot 2H_2O$ (1) are suitable starting materials for preparing symmetric macrocyclic compounds **2–4**. Compound **3** can also be obtained in good yield from $[Pb_2L(NO_3)_2]\cdot 4H_2O$. However, an attempt to obtain the precursor Pb complex from 1,2-diaminoethane led to the formation of one-sided condensation product (**6**). The formation of **6** is not unexpected, because the cavity of the macrocyclic ring obtained from 1,2-diaminoethane is too small to accommodate two Pb^{2+} ions whose ionic radius (1.17 Å) is much greater than that of the Mg^{2+} ion (0.78 Å). Compound **6**, in turn, can be condensed with one molecule of 1,3-diaminopropane, from which the asymmetric macrocyclic compound **5** can be obtained after $NaBH_4$ reduction.



1

2 : m = 2 , n = 2
3 : m = 3 , n = 3
4 : m = 4 , n = 4
5 : m = 2 , n = 3

6

Experimental Section

General Comments. All reagents and solvents were purchased from commercial sources and used as such. 4-Methyl-2,6-diformylphenol was prepared by a known procedure.[12]

All melting points were determined in open capillary tubes and are uncorrected. Elemental analyses were performed on a Perkin-Elmer Model 240C elemental analyzer. Infrared spectra were recorded on a Perkin-Elmer Model 783 infrared spectrophotometer. ^1H NMR spectra were obtained in $CDCl_3$ with Me_4Si as the internal standard and recorded on a Bruker WP/80 spectrometer. ^{13}C NMR spectra were also recorded on the same instrument at 20.1 MHz. Mass spectra (MS) were measured on a V.G. Micromass 7070HS mass spectrometer using an ionization energy of 70 eV.

Synthesis of Macrocycle 3. Method I. To a boiling MeOH solution (50 mL) of 4-methyl-2,6-diformylphenol (4.9 g, 30 mmol) were added a hot MeOH solution (20 mL) of $Mg(NO_3)_2\cdot 6H_2O$ (7.7 g, 30 mmol) and 1,3-diaminopropane (2.2 g, 30 mmol). The mixture was refluxed for 8 h during which a yellow crystalline compound deposited. The product was collected by filtration, washed with MeOH, and air-dried. The magnesium complex (8.1 g) was finely ground to powder and suspended in MeOH (150 mL). To this stirred suspension was added an aqueous solution (10 mL) of $NaBH_4$ (5 g) in small portions over a period of 1 h. During this period, all the material went into solution and a colorless solution was obtained. After additional stirring for 1 h, the solution was filtered, diluted with water (400 mL), and acidified with HCl (6 M) to make a clear solution. To this solution was added the disodium salt of EDTA (10 g) dissolved in a mixture

(6) For review, see: (a) Groh, S. E. *Isr. J. Chem.* **1976–1977**, *15*, 277. (b) Casellato, U.; Vigato, P. A.; Fenton, D. E.; Vidali, M. *Chem. Soc. Rev.* **1979**, *8*, 199.

(7) (a) Pilkington, N. H.; Robson, R. *Aust. J. Chem.* **1970**, *23*, 2225. (b) Okawa, H.; Kida, S. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 1759. (c) Addison, A. W. *Inorg. Nucl. Chem. Lett.* **1976**, *12*, 899.

(8) (a) Gagné, R. R.; Koval, C. A.; Smith, T. J.; Cimolino, M. C. *J. Am. Chem. Soc.* **1979**, *101*, 4571. (b) Gagné, R. R.; Spiro, C. L.; Smith, T. J.; Thies, W. R.; Schiemke, A. K. *Ibid.* **1981**, *103*, 4073. (c) Spiro, C. L.; Lambert, S. E.; Smith, T. J.; Duesler, E. N.; Gagné, R. R.; Hendrickson, D. N. *Inorg. Chem.* **1981**, *20*, 1229.

(9) (a) Long, R. C.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1983**, *105*, 1513. (b) Lambert, S. L.; Hendrickson, D. N. *Inorg. Chem.* **1979**, *18*, 2683.

(10) (a) Mandal, S. K.; Nag, K. *J. Chem. Soc., Dalton Trans.* **1983**, 2429. (b) Mandal, S. K.; Nag, K. *Ibid.* **1984**, 2141. (c) Mandal, S. K.; Adhikary, B.; Nag, K. *Ibid.* **1986**, 1175.

(11) For example, see: (a) Murase, I.; Mikuriya, H.; Sonoda, H.; Kida, S. *J. Chem. Soc., Chem. Commun.* **1984**, 692. (b) Barefield, E. K.; Freeman, G. M.; Van der Veer, D. G. *Ibid.* **1983**, 1358 and references cited therein.

(12) Ullman, F.; Brittner, K. *Chem. Ber.* **1909**, *42*, 2539.

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 $CHCl_3$ (2 × 100 mL). The $CHCl_3$ extract after treating with anhydrous Na_2SO_4 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 $Pb(OAc)_2 \cdot 3H_2O$ (5.7 g, 15 mmol) and $Pb(NO_3)_2$ (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 $CHCl_3$, and finally air-dried. $[Pb_2L(NO_3)_2] \cdot 4H_2O$ thus obtained (9 g) was pulverized and slurried with MeOH (120 mL). $NaBH_4$ (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 H_2SO_4 (8 M). $PbSO_4$ 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 $CHCl_3$ (2 × 100 mL). The $CHCl_3$ 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 ($CDCl_3$) δ 1.86 (quint, 4 H, $CH_2CH_2CH_2$), 2.18 (s, 6 H, Me), 2.58 (t, 8 H, $CH_2CH_2CH_2$), 3.83 (s, 8 H, $ArCH_2$), 5.1 (br, 6 H, NH, OH), 6.74 (s, 4 H, Ph); ^{13}C NMR ($CDCl_3$) δ 20.14 (q, Me), 29.79 (t, $CH_2CH_2CH_2$), 46.54 (t, $CH_2CH_2CH_2$), 51.15 (t, $ArCH_2$), 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 ($M^+ - 2\ C_3H_8N_2$, 2.8%), 266.02 (268.05 - 2 H due to OH coupling, 2.2%). Anal. Calcd for $C_{24}H_{36}N_4O_2$: 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 $CHCl_3$ 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 ($CDCl_3$) δ 2.20 (s, 6 H, Me), 2.80 (s, 8 H, CH_2CH_2), 3.76 (s, 8 H, $ArCH_2$), 4.06 (br s, 6 H, NH, OH), 6.73 (s, 4 H, Ph). Anal. Calcd for $C_{22}H_{32}N_4O_2$: 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 ($CDCl_3$) δ 1.56 (m, 8 H, $CH_2CH_2CH_2CH_2$), 2.21 (s, 6 H, Me), 2.61 (t, 8 H, $CH_2CH_2CH_2CH_2$), 3.81 (s, 8 H, $ArCH_2$), 4.71 (br s, 6 H, NH, OH), 6.73 (s, 4 H, Ph). Anal. Calcd for $C_{26}H_{40}N_4O_2$: 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), $Pb(NO_3)_2$ (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 was then 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 ($CDCl_3$) δ 1.71 (quint, 2 H, $CH_2CH_2CH_2$), 2.20 (s, 6 H, Me), 2.58–2.82 (m, 8 H, $CH_2CH_2CH_2CH_2CH_2$), 3.77 (s) and 3.81 (s) (8 H, $ArCH_2$), 4.5 (br, NH, OH), 6.77 (s, 4 H, Ph). Anal. Calcd for $C_{23}H_{34}N_4O_2$: C, 69.34; H, 8.54; N, 14.07. Found: C, 69.56; H, 8.60; N, 13.97.

Acknowledgment. We are grateful to the Chemistry Department of Memorial University of Newfoundland for recording ^{13}C NMR and mass spectra. Financial support received from the Council of Scientific and Industrial Research, India, by K.N. is also gratefully acknowledged.

Registry No. 2, 103776-06-3; **3**, 103776-07-4; **4**, 103776-08-5; **5**, 103793-59-5; **6**, 103776-10-9; $Mg(NO_3)_2$, 10377-60-3; $H_2N(CH_2)_3NH_2$, 109-76-2; $Pb(OAc)_2$, 301-04-2; $Pb(NO_3)_2$, 10099-74-8; $H_2N(CH_2)_2NH_2$, 107-15-3; $H_2N(CH_2)_4NH_2$, 110-60-1; 4-methyl-2,6-diformylphenol, 7310-95-4.

The Stability of Footballene

B. Andes Hess, Jr.,* and L. J. Schaad*

Department of Chemistry, Vanderbilt University, Nashville, Tennessee 37235

Received April 28, 1986

Haymet[1] has reported a theoretical study of the intriguing C_{60} "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 thse ambiguities.

We have computed REPE's for **1** (0.031 β),[10] the corannulene **2** (0.049 β),[11] and also for the other C_{60} system,

(1) Haymet, A. D. J. *J. Am. Chem. Soc.* **1986**, *108*, 319.
(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.

0022-3263/86/1951-3902$01.50/0