for 12–20 h. After a dilute acid wash, vacuum distillation afforded the products. GC analysis (5-ft 3% SE-30, 70–100 °C) indicated a purity of 95% for *n*-butoxy-*tert*-butyldimethylsilane and ≥98% for the other silyl ethers purified by distillation. For TBDPS derivatives, the presence of dichlorodiphenylsilane in the sample of TBDPS-Cl led to mixtures, and the desired ethers were isolated by preparative GC (10-ft 20% SE-30, 200–220 °C).

Cyclohexoxy-*tert*-butyldimethylsilane: bp 78 °C (5 mm); IR and NMR data were consistent with literature values.[3]

***n*-Butoxy-*tert*-butyldimethylsilane**:[9] bp 38–42 °C (4 mm); IR 2960 (s), 2930 (s), 2860 (s), 1480 (m), 1470 (m), 1395 (w), 1370 (w), 1260 (s), 1130 (m), 1105 (s), 1045 (m), 1010 (w), 985 (m), 945 (w), 895 (m), 840 (s) cm^{-1}; ^1H NMR δ 3.44 (m, 2 H), 1.29 (m, 4 H), 0.85 (m, 3 H), 0.72 (s, 9 H), −0.15 (s, 6 H). Anal. Calcd for $C_{10}H_{24}OSi$: C, 63.76; H, 12.84. Found: C, 63.82; H, 12.89.

Cyclohexoxytriisopropylsilane: bp 88–95 °C (1 mm); IR 2940 (s), 2870 (s), 1470 (m), 1455 (m), 1390 (w), 1375 (m), 1260 (w), 1140 (m), 1110 (s), 1075 (m), 1060 (m), 1020 (m), 1000 (m), 920 (w), 885 (s), 860 (m), 815 (m), 780 (m) cm^{-1}; ^1H NMR δ 3.8 (m, 1 H), 1.2–2.0 (m, 10 H), 1.04 (s, 21 H). Anal. Calcd for $C_{15}H_{32}OSi$: C, 70.24; H, 12.58. Found: C, 70.04; H, 12.27.

***n*-Butoxytriisopropylsilane**: bp 90 °C (5 mm); IR 2960 (s), 2940 (s), 2900 (s), 2870 (s), 1470 (s), 1390 (m), 1370 (w), 1250 (w), 1130 (s), 1110 (s), 1070 (m), 1045 (m), 1015 (m), 1000 (m), 985 (m), 920 (w), 885 (s), 775 (m), 720 (m) cm^{-1}; ^1H NMR δ 3.53 (m, 2 H), 1.1–1.5 (m, 4 H), 0.90 (s, 21 H), 0.76 (m, 3 H). Anal. Calcd for $C_{13}H_{30}OSi$: C, 67.76; H, 13.12. Found: C, 67.80; H, 13.28.

Cyclohexoxy-*tert*-butyldiphenylsilane: IR 3070 (m), 3050 (m), 2930 (s), 2860 (s), 1960 (w), 1900 (w), 1830 (w), 1660 (w), 1590 (w), 1480 (m), 1465 (m), 1450 (m), 1430 (s), 1395 (m), 1380 (m), 1365 (m), 1260 (w), 1190 (w), 1115 (s), 1095 (s), 1055 (m), 1030 (m), 1020 (m), 1010 (m), 1000 (m), 940 (w), 890 (w), 860 (m), 825 (m), 785 (w), 740 (m), 705 (s) cm^{-1}; ^1H NMR δ 7.61 (m, 4 H), 7.29 (m, 6 H), 3.62 (m, 1 H) 1.1–1.9 (m, 10 H), 0.99 (s, 9 H). Anal. Calcd for $C_{22}H_{30}OSi$: C, 78.05; H, 8.93. Found: C, 78.15; H, 8.98.

***n*-Butoxy-*tert*-butyldiphenylsilane**: IR 3080 (m), 3060 (m), 2960 (s), 2940 (s), 2870 (s), 1960 (w), 1900 (w), 1830 (w), 1660 (w), 1595 (w), 1480 (m), 1465 (m), 1435 (s), 1395 (m), 1370 (m), 1310 (w), 1270 (w), 1240 (w), 1195 (w), 1115 (s), 1045 (m), 1010 (m), 1000 (m), 990 (m), 945 (w), 890 (m), 825 (m), 780 (m), 740 (m), 700 (s) cm^{-1}; ^1H NMR δ 7.52 (m, 4 H), 7.15 (m, 6 H), 3.52 (m, 2 H), 1.0–1.6 (m, 4 H), 0.91 (s, 9 H), 0.68 (m, 3 H). Anal. Calcd for $C_{20}H_{28}OSi$: C, 76.87; H, 9.03. Found: C, 76.66; H, 8.99.

Half-Life Determinations. Conditions reported by Barton and Tully were empolyed.[3] Acid cleavage was effected by using a stock solution of 1% HCl in aqueous ethanol prepared by mixing 2.9 g of concentrated (37%) hydrochloric acid and 97.1 g of 95% ethanol. A mixture of the silyl ether (50 μL) in 0.90 mL of the stock solution was thermostatted at 22.5 °C and aliquots were withdrawn periodically for GC determination of the remaining silyl ether. Base cleavage employed a stock solution of 5 g of NaOH in 95 g of 95% ethanol. A mixture of the silyl ether (50 μL) in 0.90 mL of the stock solution was stirred for 10 min at room temperature and 50-μL portions were transferred to melting-point tubes. These were sealed, thermostatted at 90 °C, and opened sequentially for GC determination of the amount of silyl ether remaining.

Tetra-*n*-butylammonium fluoride cleavages were carried out by thermostatting a mixture of 2.5 mmol of the silyl ether, 5.0 mmol of the fluoride reagent, 0.2–0.3 g of decane or undecane (internal standard) and sufficient THF to make 5.0 mL at 22.5 °C. Aliquots were periodically withdrawn, and the yield of cyclohexanol was determined by GC.

Registry No. Cyclohexoxy-*tert*-butyldimethylsilane, 67124-67-8; *n*-butoxy-*tert*-butyldimethylsilane, 37170-50-6; cyclohexoxytriisopropylsilane, 75031-66-2; *n*-butoxytriisopropylsilane, 75031-67-3; cyclohexoxy-*tert*-butyldiphenylsilane, 75031-68-4; *n*-butoxy-*tert*-butyldiphenylsilane, 75031-69-5; cyclohexanol, 108-93-0; butanol, 71-36-3; chloro(1,1-dimethylethyl)dimethylsilane, 18162-48-6; chlorotris(1-methylethyl)silane, 13154-24-0; chloro(1,1-dimethylethyl)diphenylsilane, 58479-61-1.

(9) Hudrlik, P. F.; Feasley, R. *Tetrahedron Lett.* **1972**, 1781.

Ortho Functionalization of *N*-(*tert*-Butoxycarbonyl)aniline[1]

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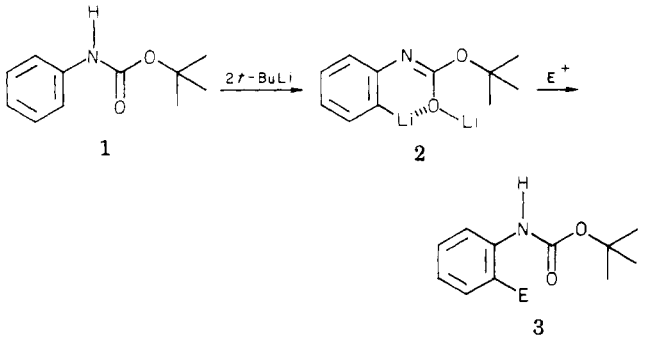
The direct ortho functionalization of aniline and derivatives thereof has been the subject of several recent publications.[2] Of particular note are those which describe the utilization of anilinodichloroboranes for the ortho acylation and ortho hydroxyalkylation of anilines and N-substituted anilines[3] and the specific ortho substitution of *N*-pivaloylanilines via the corresponding dilithio species.[4] The latter process is especially attractive because of the wide range of functional groups which can be incorporated but has the disadvantage that the pivaloyl group must be removed if the substituted aniline is required. Although it is reported[4,5] that this protecting group can be excised hydrolytically (HCl or Et_3OBF_4/H_2O), it was apparent to us that a more readily removable moiety would be advantageous. As a consequence, a study of the ortho lithiation of *N*-(*tert*-butoxycarbonyl)aniline (**1**) was undertaken.

When **1** was reacted with excess (2.5 equiv) *n*-butyllithium (with or without added tetramethylethylenediamine) or *sec*-butyllithium, in tetrahydrofuran-hexane solution, dilithiation did not occur, even after several hours at room temperature. Ortho metalation did, however, take place relatively rapidly with *tert*-butyllithium at low temperatures, as demonstrated by the isolation of *N*-(*tert*-butoxycarbonyl)-*o*-toluidine (**4**) from the mixture obtained when the reaction was quenched with 1 equiv of methyl iodide. Optimization of the reaction conditions for the formation of this product showed that the best yield thereof (59%; 92% based on recovered starting material) was obtained when metalation was effected with 2.4 equiv of *tert*-butyllithium at −20 °C for 2–2.5 h. No *N*-methyl-*N*-(*tert*-butoxycarbonyl)-*o*-toluidine (**5**) was formed, although this substance could be prepared in high



1 2 3

(1) Contribution No. 552 from the Syntex Institute of Organic Chemistry.

(2) For a summary of recent publications in this area see citations in ref 3 and 4.

(3) Sugasawa, T.; Toyada, T.; Adachi, M.; Sasakura, K. *J. Am. Chem. Soc.* **1978**, *100*, 4842. Sugasawa, T.; Adachi, M.; Sasakura, K. *J. Org. Chem.* **1979**, *44*, 578. Sugasawa, T.; Hamana, H.; Toyoda, T.; Adachi, M. *Synthesis* **1979**, 99.

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(5) Similar observations have been made by others: Gschwend, H. W., unpublished data; Ho, P. T. *Can. J. Chem.* **1980**, *58*, 861.

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(7) Gabriel, S.; Stelzner, R. *Chem. Ber.* **1896**, *29*, 1300.

(8) Kunckell, F. *Chem. Ber.* **1910**, *43*, 1234.

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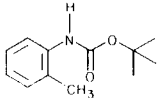
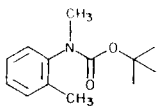
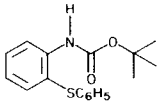
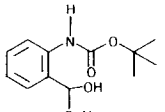
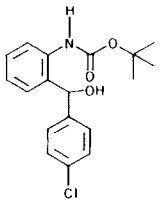
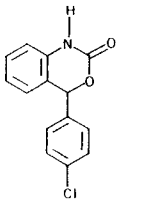
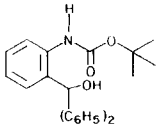
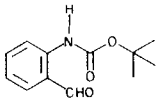
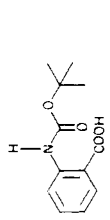
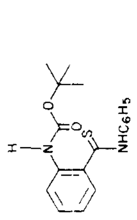
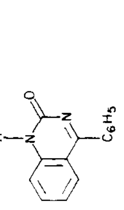
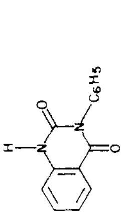
Table I. Ortho Functionalization of *N*-(*tert*-Butoxycarbonyl)aniline

electrophile	product	reaction time, h (temp, °C)	yield, %	mp, °C (solvent)	anal., found (calcd)	IR,[a] cm^{-1}	NMR,[b] δ
CH_3I (1 equiv)	 **4**	0.5 (−20)	59	82–83 (hexane)	C, 69.53 (69.36) H, 8.26 (8.45) N, 6.75 (6.80)	3240 1675 1585	1.50 (s, 9 H), 2.17 (s, 3 H), 6.37 (s, 1 H, w_H = 8 Hz), 7.05–7.30 (m, 3 H), 7.62–7.84 (m, 1 H)
CH_3I (4 equiv)	 **5**	0.25 (−20) 2 (room temp)	82	oil, bp 70 (0.5 mm)	C, 69.70 (70.55)[c] H, 8.37 (8.65) N, 6.25 (6.33)	1680[d] 1595 1570	1.38 (s, 9 H), 2.23 (s, 3 H), 3.18 (s, 3 H), 7.01–7.54 (m, 4 H)
$(C_6H_5S)_2$	 **6**	2 (−20)	91	61–62 (hexane)	C, 67.52 (67.84) H, 6.37 (6.36) N, 4.75 (4.65)	3300 1710 1580	1.45 (s, 9 H), 7.05–7.72 (m, 9 H), 8.35 (q, 1 H, J = 1.5, 8.0 Hz)
C_6H_5CHO	 **7**	2.5 (−20)	67	141–142 (ether–hexane)	C, 72.26 (72.21) H, 7.17 (7.07) N, 4.67 (4.67)	3490 3185 1725 1595	1.42 (s, 9 H), 3.28 (s, 1 H, w_H = 10 Hz),[e] 5.86 (s, 1 H), 7.00–7.46 (m, 8 H), 7.70 (s, 1 H), 7.85 (d, 1 H, J = 8 Hz)
4-ClC_6H_4CHO	 **8**	2.5 (−20)	72	148–150 (ether–hexane)	C, 64.84 (64.76) H, 5.86 (6.03) N, 4.55 (4.19)	3390 3170 1720 1590	1.42 (s, 9 H), 3.50 (d, 1 H, J = 3.6 Hz),[e] 5.83 (d, 1 H, J = 3.6 Hz), 7.00–7.60 (m, 8 H), 7.80 (d, 1 H, J = 7.6 Hz)
4-ClC_6H_4CHO	 **9**	2.5 (−20) 16 (room temp)	35	172–173 (ether)	C, 64.72 (64.75) H, 3.88 (3.88) N, 5.49 (5.39)	3100 1710 1600	6.42 (s, 1 H), 6.78–7.54 (m, 8 H), 9.67 (s, 1 H, w_H = 5 Hz)
$(C_6H_5)_2CO$	 **10**	2 (−20)	78	183–184 (ether–hexane)	C, 76.82 (76.77) H, 6.81 (6.71) N, 3.65 (3.73)	3350 3280 1680 1600 1580	1.27 (s, 9 H), 6.56 (s, 1 H),[e] 6.69–7.23 (m, 3 H), 7.40 (s, 10 H), 7.90 (q, 1 H, J = 1.2, 8.0 Hz), 8.60 (s, 1 H, w_H = 3 Hz)
$(CH_3)_2NCHO$	 **11**	1 (20) 2 (room temp)	65 53[f]	54–55 (ether–petroleum ether)	C, 65.29 (65.14) H, 6.84 (6.83) N, 6.34 (6.33)	3280[d] 2730 1720 1660 1580	1.57 (s, 9 H), 7.05–7.80 (m, 3 H), 8.60 (q, 1 H, J = 1.4, 8.0 Hz), 10.01 (s, 1 H), 10.50 (s, 1 H, w_H = 10 Hz)

CO_2	 **12**	2 (room temp)[g]	73	156-157 (ether-hexane) (lit.[6] 155.5-157)	C, 60.85 (60.75) H, 6.43 (6.37) N, 6.07 (5.90)		
C_6H_5NCS	 **13**	2 (−20) 1 (room temp)	69	156-158 (ether-hexane)	C, 65.79 (65.82) H, 6.16 (6.13) N, 8.73 (8.52)	3400 3250 1690 1605 1580	1.50 (s, 9 H), 6.90-8.13 (m, 9 H), 8.84 (s, 1 H, w_H = 6 Hz), 9.88 (s, 1 H, w_H = 8 Hz)
C_6H_5CN	 **14**	2 (−20) 1 (room temp)	83	251-252 (ethyl acetate-hexane) (lit.[7] 250-251)			
C_6H_5NCO	 **15**	2 (−20) 1 (room temp)	57	283-284 (ethyl acetate-hexane) (lit.[8] 278-280)	C, 70.53 (70.58) H, 4.23 (4.33) N, 11.75 (11.57)		

[a] Measured as a dispersion in KBr unless specified otherwise. [b] Measured in $CDCl_3$ with internal Me_4Si. [c] Mol wt 221.142 33 (calcd for $C_{13}H_{19}NO_2$ 221.141 57). [d] Liquid film. [e] Exchanged with D_2O. [f] Yield when carried out on 0.1-mol scale. [g] Dianion added to a slurry of solid CO_2 (excess) in THF and then left at room temperature.

yield (see Table I) when excess methyl iodide was used. The dianion **2** also reacted, to give the expected ortho-substituted products, with sundry other electrophilic reagents which included diphenyl disulfide, aromatic aldehydes, benzophenone, dimethylformamide, carbon dioxide, and phenyl isothiocyanate (see Table I). When the dianion was quenched with benzonitrile or phenyl isocyanate, cyclization of the primary product occurred spontaneously in the reaction medium to give the quinazolinone and quinazolinedione derivatives **14** and **15**, respectively. Furthermore, if the adduct derived from *p*-chlorobenzaldehyde was left in the reaction mixture overnight, the benzoxazinone derivative **9** was formed, albeit only in 35% yield.

In summary, these results demonstrate that the ortho functionalization of *N*-(*tert*-butoxycarbonyl)aniline, and presumably derivatives thereof, via the corresponding dilithio species provides a rapid, facile, and practical means of synthesis of a broad spectrum of ortho-substituted anilines and compounds derived therefrom. The accessibility of the starting materials (see Experimental Section) and the facility with which the protecting group can be removed, as exemplified by the synthesis of 2-amino-4′-chlorobenzhydrol (**16**) from **8**, make this process even more attractive.

Experimental Section

The melting points were taken on a Fischer-Johns hot stage and are not corrected. The NMR spectra were recorded with a Varian EM-360 spectrometer. The IR spectra were measured with a Perkin-Elmer Model 237 grating infrared spectrometer.

N-(*tert*-Butoxycarbonyl)aniline [**1**, mp 137 °C (lit.[9] mp 136 °C)] could be prepared in high yield in the manner described below for *N*-(*tert*-butoxycarbonyl)-*o*-toluidine (**4**) or by heating phenyl isocyanate in *tert*-butyl alcohol.[9] Di-*tert*-butyl dicarbonate was purchased from Fluka, A.G.

***N*-(*tert*-Butoxycarbonyl)-*o*-toluidine (4).** A solution of *o*-toluidine (2.7 mL, 25 mmol) in tetrahydrofuran (25 mL) containing di-*tert*-butyl dicarbonate (6.0 g, 27.5 mmol) was heated at reflux temperature for 2 h. The solvent was removed in vacuo, the residue was dissolved in ethyl acetate, and this solution was washed successively with 1 M citric acid solution and saturated salt solution. The organic phase was dried over sodium sulfate and evaporated in vacuo. The residue was crystallized from hexane to give a solid (4.0 g, 77%), mp 82–83 °C, identical in all respects with a sample prepared by alkylation of the dianion **2**.

Dilithiation of *N*-(*tert*-Butoxycarbonyl)aniline. A 2.0 M solution of *tert*-butyllithium in pentane (12.0 mL, 24 mmol) was added in a dropwise manner to a solution of **1** (1.93 g, 10 mmol) in anhydrous tetrahydrofuran (25 mL, N_2 atmosphere) maintained at −78 °C. Addition of the first equivalent of the lithium reagent gave a colorless solution; additional reagent produced a yellow colored solution. After 15 min at −78 °C, the solution was allowed to warm to −20 °C where it was maintained for 2–2.5 h. This solution of **2** was then ready for use in subsequent reactions.

Reaction of Dianion 2 with Electrophiles. Except in those cases noted below, a solution of the appropriate electrophilic reagent (12.5 mmol) in anhydrous THF (7–8 mL) was added to a stirred THF solution (N_2 atmosphere) of the dianion (10 mmol, prepared as described above) at −20 °C. [For the synthesis of compounds **4**, **5**, and **11**, the reagent (12.5, 40, and 67 mmol) was added next to the dianion. For preparation of the anthranilic acid derivative **12**, the dianion solution was added to a slurry of solid carbon dioxide in THF.] The reaction mixture was stirred for the times and at the temperatures indicated in Table I and then it was partitioned between ether and water. (1 M NaOH was used for **6**; 5% HCl was used for **11**.) The organic phase was washed with saturated salt solution, dried over sodium sulfate, and evaporated in vacuo. For the synthesis of the carboxylic acid **12**, the reaction mixture was partitioned between ether and 5%

(9) Knoevenagel, E. *Justus Liebigs Ann. Chem.* 1897, *297*, 113.

$NaHCO_3$ solution. The aqueous phase was made acidic with solid citric acid and the product was extracted into ether and then processed as described above.

In some cases, the crude products obtained on removal of the solvent required purification by column chromatography on silica gel [e.g., compounds **7** and **9** (CH_2Cl_2–EtOAc, 9:1) and **6** and **11** (CH_2Cl_2)] before crystallization or distillation was effected.

2-Amino-4′-chlorobenzhydrol (16). To a solution of compound **8** (0.334 g, 1.0 mmol) in 50% aqueous THF (10 mL) was added concentrated hydrochloric acid (5 mL) and the resultant mixture was stirred at room temperature for 3 h. The THF was removed in vacuo and the aqueous solution was made basic by the addition of 2 M sodium hydroxide. After the mixture cooled, the solid product was collected by filtration and dried in vacuo to give the amino alcohol **16** (0.220 g, 94%), mp 98–9 °C, identical in all respects with an authentic specimen[10] prepared by the sodium borohydride reduction of 2-amino-4′-chlorobenzophenone. Attempted deprotection of **8** under anhydrous conditions (trifluoroacetic acid/CH_2Cl_2) gave cyclic urethane **9** in near quantitative yield.

Acknowledgment. We thank Dr. A. F. Kluge for much helpful discussion on various aspects of this work.

Registry No. 1, 3422-01-3; 2, 74965-30-3; 4, 74965-31-4; 5, 74965-32-5; 6, 74965-33-6; 7, 74965-34-7; 8, 74965-35-8; 9, 74965-36-9; 10, 74965-37-0; 11, 74965-38-1; 12, 68790-38-5; 13, 74965-39-2; 14, 23441-75-0; 15, 603-23-6; 16, 34999-56-9; iodomethane, 74-88-4; diphenyl disulfide, 882-33-7; benzaldehyde, 100-52-7; 4-chlorobenzaldehyde, 104-88-1; diphenylmethanone, 119-61-9; *N,N*-dimethylformamide, 68-12-2; carbon dioxide, 124-38-9; isothiocyanatoethane, 542-85-8; benzonitrile, 100-47-0; isocyanatobenzene, 103-71-9.

(10) Lednicer, D.; Emmert, D. E. *J. Heterocycl. Chem.* **1971**, *8*, 903.

A Pariser–Parr–Pople-Based Set of Huckel Molecular Orbital Parameters†

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Despite its admitted limitations, Huckel molecular orbital (HMO) theory continues to be a useful methodology. The usually computed quantities, e.g., charge density and bond order, are usually good estimates for a given compound when compared to more sophisticated methods. Moreover *trends within a class of compounds* are generally well-accounted for. Further, comparisons may be made *among* classes. Thus it is worthwhile to maintain the capacity for performing HMO calculations, even in this era of high-speed computers and packaged ab initio programs. The semiquantitative information available in this fashion is thereby rapidly and easily accessible to the synthetic organic chemist.

We have recently made available a HMO computer program designed for interactive operation.[1] In developing this program difficulty was encountered with regard to finding a relatively complete data base for heteroatoms. A partial set was reported by Streitwieser[2] some time ago. Subsequent to that, Purcell and Singer[3] prepared a compendium of all parameters available at that time. More recently Hess and Schaad[4] have developed an HMO-based analysis of aromaticity which shows promise. The methodology has since been extended to include selected heteroatoms, namely O, N, and S.[5] None of these sets is "complete". The vast majority of possible two-center terms β_{xy} are not available where x and y are both heteroatoms. Further, selected terms often have several proposed values.[3] One possible resolution of this would be to extend the studies of Hess, Schaad, et al.,[4,5] basing the parameter set on thermodynamic properties. This approach is not without its problems, particularly with regard to the existence of mutliple solutions.[5a] More critical is the lack of sufficient experimental data for generation of a set of parameters as extensive as we required.

Table I. One-Center HMO Parameter Based on PPP Calculations

atom type	no. of π electrons	h_X for $\alpha_X = \alpha_0 + h_X\delta_0$	free valence ref F_X^0
C	1	0.00	1.732
B	0	−0.45	1.705
N1	1	0.51	1.393
N2	2	1.37	1.583
O1	1	0.97	0.909
O2	2	2.09	0.942
F	2	2.71	0.179
Si	1	0.00	1.732
P1	1	0.19	1.409
P2	2	0.75	1.666
S1	1	0.46	0.962
S2	2	1.11	1.229
Cl	2	1.48	0.321

Given the current state of affairs as outlined above we have chosen to extract our parameter set from Pariser–Parr–Pople (PPP) calculations.[6] It may be argued that we are using a semiempirical method to derive parameters for an empirical one. While this is true, we must counterbalance this with the fact that we are thus to determine in an unambiguous fashion the *complete* set of parameters desired. We have chosen the Beveridge–Hinze[7] parameterization for the PPP method. This particular set represents an internally consistent approach and could be readily extended to include the second-row elements Si, P, S, and Cl. Further, it appears to be the closest to a general purpose PPP parameterization in the following sense. While the PPP formalism focuses primarily on spectral predictions, the Beveridge–Hinze parameterization also does well for predictions of spin-densities, implying good descriptions of ground-state charge distributions. On the other hand, since configuration interaction is a prominent feature of the PPP formalism we cannot expect the HMO method to be especially useful for spectral predictions.

The usual HMO definitions are employed.

$$\alpha_C = \alpha_0 \qquad \alpha_X = \alpha_0 + h_X\beta_0 \tag{1}$$

$$\beta_{C\text{-}C} = \beta_0 \qquad \beta_{X\text{-}Y} = k_{X\text{-}Y}\beta_0 \tag{2}$$

The parameter set was developed by the following sequence. (A) β_0 was equated to the two-center Fock matrix

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(7) D. L. Beveridge and J. Hinze, *J. Am. Chem. Soc.*, **93**, 3107 (1971). We have used the value 0.56 instead of 0.545 in the equation for β.

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