$NaHCO_3$ 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.

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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.

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

F. A. Van-Catledge

Central Research & Development Department, E. I. du Pont de Nemours & Co., Inc., Wilmington, Delaware 19898

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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

† Contribution No. 2750.

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Table II. k_{XY} for the HMO Parameter $\beta_{XY} = k_{XY}\beta_0$

	X												
Y	C	B	N1	N2	O1	O2	F	Si	P1	P2	S1	S2	C1
C	1.00												
B	0.73	0.87											
N1	1.02	0.66	1.09										
N2	0.89	0.53	0.99	0.98									
O1	1.06	0.60	1.14	1.13	1.26								
O2	0.66	0.35	0.80	0.89	1.02	0.95							
F	0.52	0.26	0.65	0.77	0.92	0.94	1.04						
Si	0.75	0.57	0.72	0.43	0.65	0.24	0.17	0.64					
P1	0.77	0.53	0.78	0.55	0.75	0.31	0.21	0.62	0.63				
P2	0.76	0.54	0.81	0.64	0.82	0.39	0.22	0.52	0.58	0.63			
S1	0.81	0.51	0.83	0.68	0.84	0.43	0.28	0.61	0.65	0.65	0.68		
S2	0.69	0.44	0.78	0.73	0.85	0.54	0.32	0.40	0.48	0.60	0.58	0.63	
C1	0.62	0.41	0.77	0.80	0.88	0.70	0.51	0.34	0.35	0.55	0.52	0.59	0.68

element for ethylene. (B) A series of calculations were carried out for all possible C–X pairs with two electrons in the π system. The parameters were calculated as shown in eq 3 and 4. (C) A second series of calculations was

$$h_x = (F_{XX} - F_{CC})/\beta_0 \quad (3)$$

$$k_{C\text{-}X} = F_{C\text{-}X}/\beta_0 \quad (4)$$

carried out for all X–Y pairs (X, Y $\neq$ C). The k_{XY} values were calculated in a manner exactly analogous to eq 4. The quantities $(F_{XX} - F_{YY})/\beta_0$ were within 10% of the expected values based on the results of step B. (D) References values for free-valence calculations were based on HMO results for the neutral species $(CH_2)_nX$. Basing this on carbon binding seems the least ambiguous approach.

The one-center parameters are summarized in Table I. Table II contains the k_{XY} half-matrix. We have compared our parameters for N1, N2, O1, and O2 to those of Hess and Schaad[5] and Streitwieser.[2] Our subset is within $\pm 0.15\beta_0$ of the latter values.

finally, it should be noted that the program[1] is not limited to this parameter set. Provision has been made for easy modification of the matrix elements within a given calculation.

Registry No. C, 7440-44-0; B, 7440-42-8; N, 17778-88-0; O, 17778-80-2; F, 14762-94-8; Si, 7440-21-3; P, 7723-14-0; S, 7704-34-9; Cl, 22537-15-1.

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Rapid Syntheses of Protected 2′-Deoxycytidine Derivatives

Jean Igolen and Christophe Morin*

Unité de Chimie Organique, Département de Biochimie et Génétique Microbienne, Institut Pasteur, 28, rue du Dr. Roux, 75724 Paris Cedex 15, France

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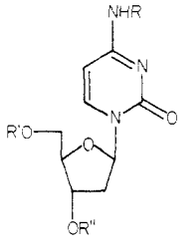
There is still a need for rapid syntheses of protected nucleosides, which are the primary building blocks in oligonucleotide synthesis. We report here a simple method for the rapid preparation of 2′-deoxycytidine protected derivatives, making use of a direct selective protection of the N-4 amino group.

Direct N-4 benzoylation of 2′-deoxycytidine (1) has been previously carried out by means of benzoic anhydride,[1] 2-(chloromethyl)-4-nitrophenyl benzoate,[2] *O*-ethyl *S*-benzoyl dithiocarbonate,[3] or *p*-nitrophenyl benzoate in the presence of 1-hydroxybenzotriazole,[4] thus avoiding use of the two-step classical procedure of Khorana et al.[5] In view of the recent results of Kisfaludy et al.,[6] who used pentafluorophenyl acetate as a selective acylating agent, we reasoned that selective benzoylation might be effected by similar use of pentafluorophenyl benzoate (**2**). This reagent can be prepared from pentafluorophenol by action of benzoyl chloride[7-11] or of benzoic acid[12]—the latter being used here— and yields over 90% can be obtained by using purified dicyclohexylcarbodiimide and anhydrous dimethylformamide under nitrogen.



$C_6F_5OCOC_6H_5$

2

1, R = R′ = R″ = H
3, R = COC_6H_5; R′ = R″ = H
4, R = COC_6H_5; R′ = DMT; R″ = H
5, R = COC_6H_5; R′ = MMT; R″ = H
6, R = R″ = COC_6H_5; R′ = MMT
7, R = R″ = COC_6H_5; R′ = H
8, R = COC_6H_5; R′ = TBDMS; R″ = H
9, R = COC_6H_5; R′ = R″ = TBDMS

MMT = p-$CH_3OC_6H_4(C_6H_5)_2C$; DMT = $(p$-$CH_3OC_6H_4)_2$-$C(C_6H_5)$; TBDMS = $(CH_3)_3CSi(CH_3)_2$

Preliminary experiments showed that **2** reacts with 2′-deoxycytidine (**1**) to give the N-4 protected derivative **3**, the reaction being complete under any one of the following conditions, as determined by TLC: (i) room temperature, 5 h, 3 equiv of **2** in pyridine, (ii) room temperature, 1 day,

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