Commentationes

Valence Shell Calculations on Polyatomic Molecules

IV. The Effect of Deorthogonalization on CNDO/2 Dipole Moments and Charge Distributions

D. D. SHILLADY* and F. P. BILLINGSLEY, II**

Department of Chemistry, University of Virginia, Charlottesville, Virginia 22901

J. E. BLOOR***

Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37916

Dipole moments and charge distributions for twenty molecules of widely different types have been calculated using (a) the CNDO/2 method and (b) a CNDO/2D method in which the orbitals from the CNDO/2 method are deorthogonalized by a Löwdin transformation and are then used to calculate the dipole moments in a rigorous manner. A statistical analysis of the results for the dipole moments calculated by the CNDO/2D method shows that they are in very slightly better agreement with experiment than those from the CNDO/2 method. The net charge distributions from the CNDO/2D method follow more closely the trends of *ab initio* calculations than do the CNDO/2 net charges.

Dipolmomente und Ladungsdichten von Molekülen unterschiedlichen Typs wurden mittels des CNDO/2- und CNDO/2D-Verfahrens (d. i. mit delokalisierten Löwdin-Orbitalen als AO's) berechnet. Eine statistische Analyse zeigt, daß die Resultate der zweiten Methode etwas besser als die der ersten den experimentellen Ergebnissen folgen. Das Analoge gilt für die Nettoladungsverteilungen in bezug auf die Trends bei *ab initio*-Rechnungen.

Les moments dipolaires et les distributions de charge pour vingt molécules de types divers ont été calculés par: a) la méthode CNDO/2; b) une méthode CNDO/2D où les orbitales de CNDO/2 sont déorthogonalisées par une transformation de Löwdin. Une analyse statistique montre que les moments dipolaires calculés par CNDO/2D sont légèrement en meilleur accord avec l'expérience que ceux calculés par CNDO/2. Les distributions de charge de CNDO/2D sont plus ressemblantes à celles de calculs *ab-initio* que ne le sont les distributions de CNDO/2.

The CNDO/2 method developed by Pople and colleagues [1] has been particularly successful in the calculation of dipole moments [3—5]. However, in our work we have encountered two serious failures in applying the CNDO/2 method, namely the failure to predict the effect of replacing hydrogen atoms attached to nitrogen and oxygen by methyl groups, and also we have found [6] that the charge distribution in boron coordination complexes, such as borazane, was very different from that found in recent *ab initio* calculations [7—9]. We

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** NASA Research Trainee.
*** To whom any correspondence concerning this paper should be addressed.

intend to show in this paper that the simple additional procedure of deortho-gonalizing the CNDO/2 orbitals as recently discussed by Giessner-Prettre and Pullman [10] (CNDO/2D method) results in the removal, to a large extent, of the above mentioned deficiencies. Also, we have found that for twenty molecules of widely different structures (Fig. 1) the dipole moments calculated by the more rigorous CNDO/2D method are at least as good, on a statistical basis, as those calculated by the CNDO/2 method. A conclusion which differs from that given in Ref. [10].

Procedure

The MOs resulting from a CNDO/2 calculation may be interpreted [1] as linear combinations of orthogonal (delocalized) AOs χ which can be transformed back to Slater AOs χ' with coeffcients C' by the transformation (1)

$$S^{-1/2}C\chi S^{1/2} = C'\chi' . \tag{1}$$

The matrix $S^{-1/2}$ is easily obtained by diagonalizing S followed by replacement of the diagonal elements with the square roots of their reciprocals and retrans-formation back to the original representation. Thus one can easily transform the CNDO/2 eigenvectors C over orthogonal orbitals into vectors C' over a deortho-gonalized atomic orbital basis using Eq. (2). This procedure, which we will refer to as the CNDO/2D method, was carried out on a series of CNDO/2 calculations and the

$$C' = S^{-1/2}C \tag{2}$$

resulting functions were used to compute the valence shell dipole moments using the rigorous dipole moment program we have described previously [5]. The molecules chosen are shown in Fig. 1 where net charges calculated both by the CNDO/2 and the CNDO/2D methods are given for comparison. Although we have not separated charges due to σ and π orbitals as was done in Ref. [10], we agree with the findings reported therein that deorthogonalization has very little effect on π electronic systems. Thus, the differences in net charges displayed in Fig. 1 can be understood to be almost entirely due to changes in the σ bond structure. Our understanding of this effect is that, while deorthogonalization does have some effect on all the orbitals, the overlap between π orbitals is usually less than that between nearest neighbor σ orbitals. While the π orbitals are changed somewhat, the $S^{-1/2}$ transformation in (2) couples the σ orbitals more strongly upon deorthogonalization.

Discussion

The results for the net charges (Fig. 1) and dipole moments (Table 1) for twenty molecules of widely different structure lead us to propose that the CNDO/2D method is to be preferred, at least for these two quantities, over the CNDO/2 method which has been almost exclusively used previously. Certainly we believe that the slight extra effort to convert the CNDO/2 basis set to an atomic orbital basis set is well worth it both in agreement of the results with experiment and the extra rigor obtained in the method used to calculate molecular properties. Our reasons for these conclusions may be summarized as follows:

Table 1. *Comparison of dipole moments (in debyes)*

Molecule	CNDO/2	CNDO/2D	*Ab initio*[a]	Experimental	Ref.	Weight[b]
NH_3	2.09	1.50	1.66	1.47	14	3
CH_3NH_2	1.82	1.34	1.41	1.34	14	3
Aniline	1.53	1.27		1.53	14	2
$(CH_3)_2NH$	1.69	1.25	1.19	1.01	15	3
Pyrrole[c]	1.99	1.0		1.84	14	3
$(CH_3)_3N$	1.71	1.14	0.95	0.612	16	3
Pyridine[c]	2.15	1.44		2.20	14	3
$HCONH_2$	3.65	3.10	3.34	3.71	17	3
H_2CO[c]	1.89	1.63	1.53	2.17	14	3
HCN	2.42	2.15	2.43	2.95	14	3
H_2O	2.15	1.76	1.78	1.84	14	3
CH_3OH	1.95	1.55	1.51	1.71	14, 18	3
$(CH_3)_2O$	1.73	1.23	1.18	1.31	19	3
BH	2.06	1.16		1.784[d]	20	1
BH_3NH_3	6.46	6.22		4.92	21	2
CO	1.0	0.25		0.112	22	3
BH_3CO	3.01	2.26		1.795	23	3
BF	2.22	1.28		1.13[d]	24	1
HBF_2	0.42	0.33		0.971	25	3
CH_3F	1.72	1.43	0.96	1.855	26	3

[a] Results of minimal STO-3G calculations using energy optimized exponents, from Ref. [13].
[b] See text for explanation of weighting.
[c] Denotes previous calculation, Ref. [10].
[d] *Ab initio* values for the dipole moments used in lieu of experimental values.

1. The CNDO/2 method, in which the dipole moment is calculated by the approximate method of Pople and Segal [11] predicts too small a change in the dipole moment when a hydrogen attached to an electronegative atom such as nitrogen or oxygen is replaced by a methyl group. If, however, we use the deortho-gonalized AOs in the rigorous expression for the dipole moment, then the results (Table 1) are in much better agreement with experiment. The results also agree better with the results of recent minimal basis set *ab initio* calculations [12, 13] (Table 1). The only exception is the failure to predict the observed large drop in dipole moment on replacing the final nitrogen proton in dimethyl amine, by methyl. However, the *ab initio* calculations also fail to make this prediction [12, 13].

2. Although in Ref. [10] it was claimed that the dipole moments calculated by the CNDO/2D method were in poorer agreement with experiment than the results from the CNDO/2 method, this conclusion was based on the results of only three compounds (formaldehyde, pyrrole and pyridine). In order to provide a more definitive answer to the question of whether one method is to be preferred over the other we have carried out a statistical analysis of the relationship between dipole moments calculated by the two different methods and the experimental results, where available. For certain of our compounds experimental dipole moments were not available and the results of *ab initio* calculations were used, points for these molecules were then given a weight only one third of that given to the points for molecules for which experimental values were available. In other
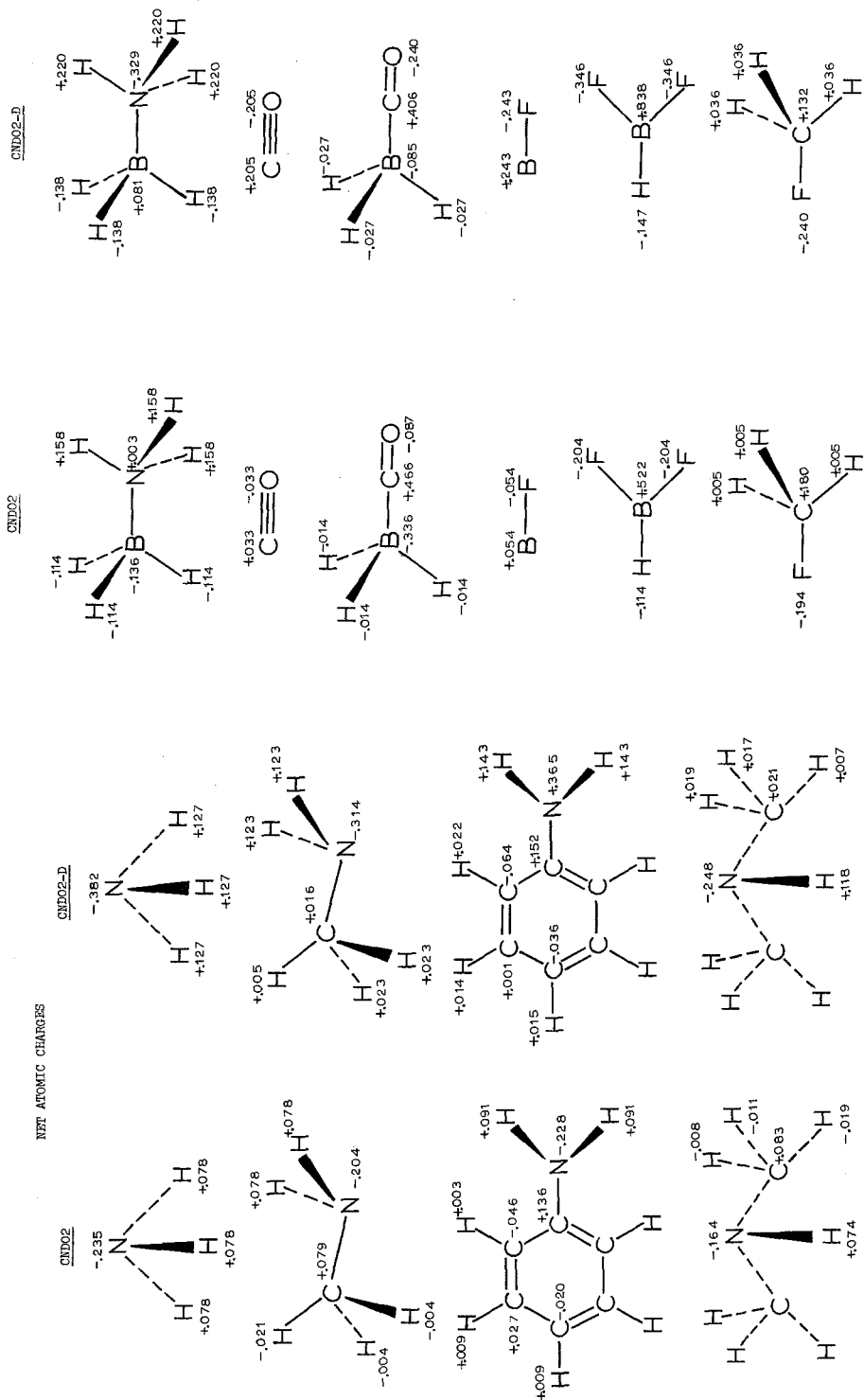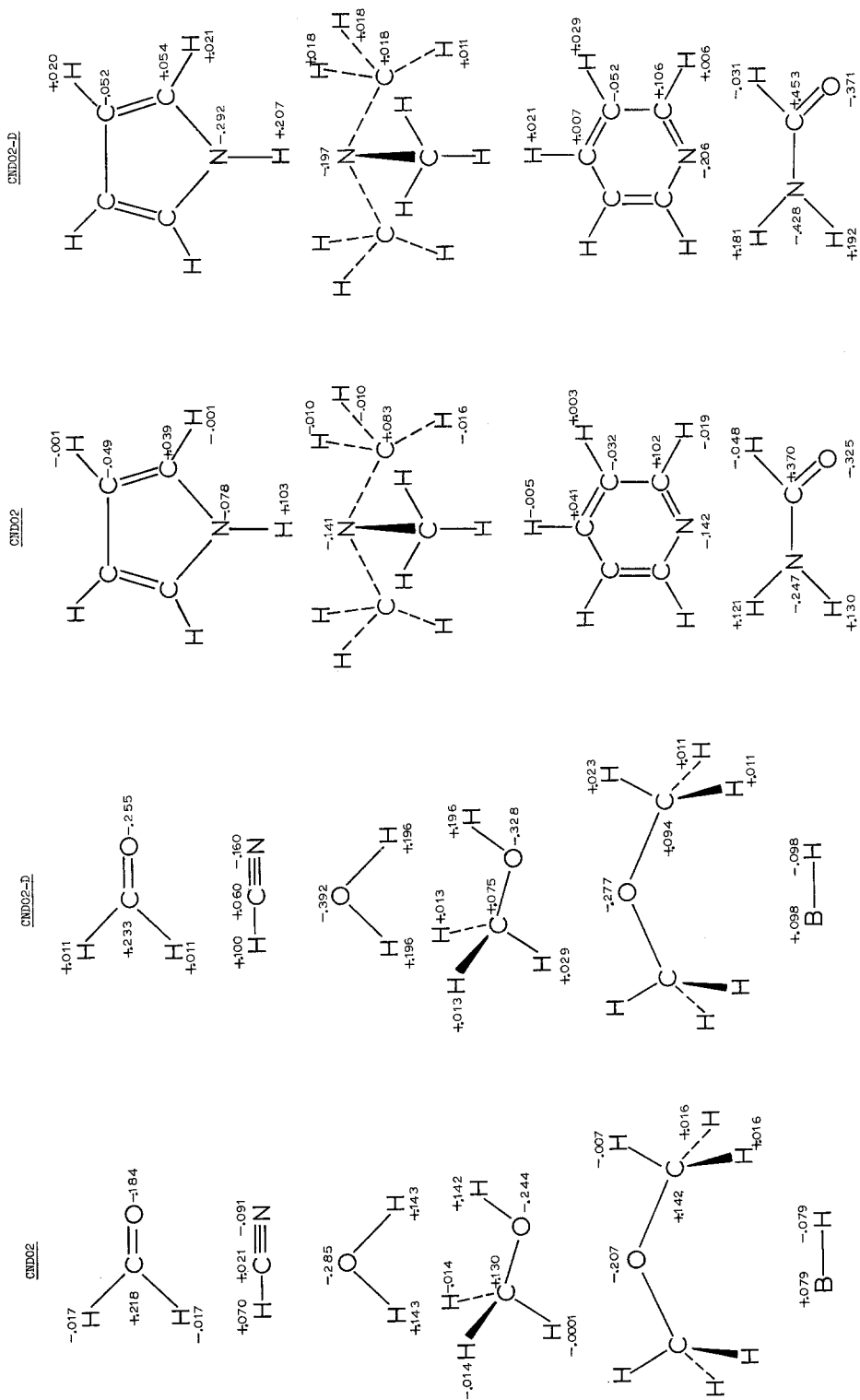
Fig. 1

NET ATOMIC CHARGES

Fig. 1

cases, noted in Table 1, idealized rather than experimental geometry was used. For these compounds a statistical weighing of two thirds was used. The correlation coefficients were then calculated using Eqs. (3)–(5).

$$r = \sum_i \left[(Y_i - Y_{av})(X_i - X_{av}) \right] / n\sigma_x\sigma_y , \tag{3}$$

$$\sigma_x = \left[\sum_i (X_i - X_{av})^2 / n \right]^{1/2} , \tag{4}$$

$$X_{av} = \left(\sum_i X_i \right) / n . \tag{5}$$

The correlation coefficient for the CNDO/2D method came out *very* slightly better than the CNDO/2 value (0.89 compared to 0.86) thus showing that the methods are of very similar reliability. A visual plot of the results is given in Figs. 2 and 3. These plots illustrate the wide range in the dipole moments of the compounds we have.

3. In general the trends in the net charges, calculated using the Mulliken populations from the CNDO/2D method, follow the same trends as *ab initio* calculations much better than do the net charges calculated from CNDO/2 charge densities (Fig. 1). In Ref. [10] it was found that the net charges calculated by the CNDO/2D method were in closer agreement with those obtained by other semi-empirical methods than were those calculated by the CNDO/2 method.

We have not presented a quantitative comparison because of the great sensitivity of net charges, particularly for hydrogen atoms, to the size of the basis set and to the orbital exponent used. One particular case where the CNDO/2 method gives, what can be considered, a completely unrealistic net charge distribution is
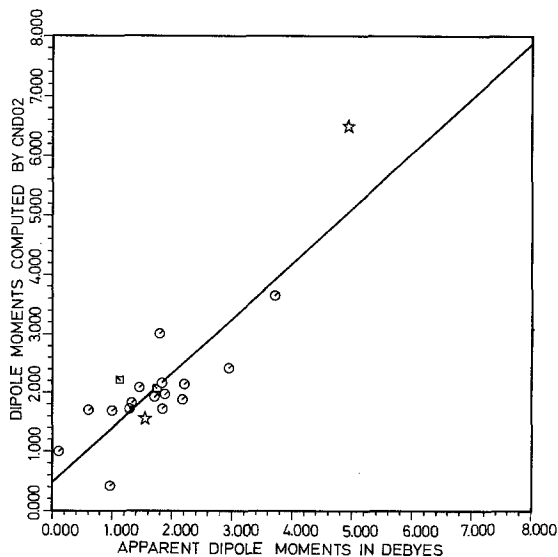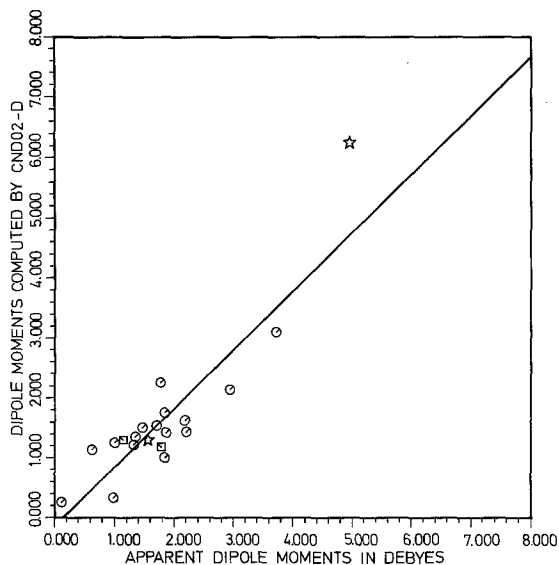

Fig. 2

Fig. 3

for borazane H_3BNH_3. Several *ab initio* calculations are now available [7–9] for this molecule and, despite quite large differences in the individual populations in the different calculations, they all agree in predicting that the main change, on forming a covalent B–N bond, is a loss of electronic charge from the amine hydrogens with an almost equivalent gain in charge of the boron hydrogens, there being very little change in the net charges on the boron and nitrogen atoms. These features are fairly well produced by the CNDO/2D calculation but the CNDO/2 calculation predicts a loss of charge of 0.23 e from the nitrogen (relative to NH_3) and a gain on the boron of 0.33 e (relative to BH_3) in contradiction to any of the *ab initio* results. A fuller discussion of the charge redistributions on coordination complexes of boron will be given elsewhere [6].

In conclusion we reiterate our findings that the simple process of deorthogonalizing CNDO/2 orbitals (Eq. (3)) statistically yields slightly improved dipole moments which are invariably smaller in magnitude than the corresponding CNDO/2 values. Deorthogonalization has the greatest effect on directed bonds with large overlap in the nonorthogonal basis; hence, the σ structure is affected much more than the π structure. Also, deorthogonalization tends to give net charges which are often chemically more reasonable than the CNDO/2 values, especially for protons. Since it is an easy matter to incorporate deorthogonalization into a CNDO/2-type program, we recommend this procedure as an easy means of obtaining additional information about bonding and net charges with improved moments. We also believe it is better to calculate the dipole moment rigorously using the CNDO/2D MOs. Thus we believe deorthogonalization can provide a useful improvement to the semiempirical CNDO/2 valence shell calculational method.

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Professor J. E. Bloor
Department of Chemistry
University of Tennessee
Knoxville, Tennessee 37916, USA