Theoret. chim. Acta (Berl.) 12, 360—372 (1968)

Valence-Shell Calculations on Polyatomic Molecules

III. The Calculation of Dipole Moments and the Structure of Sydnone*

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Received July 26, 1968

Calculations using the CNDO/2, the Extended Hückel (EH) method, and an iterative Extended Hückel (IEH) method are reported for HF, H_2O, NH_3, CO, H_2CO, $HCONH_2$, HCOOH, HCOF and sydnone. For the IEH method, it is shown that if the dipole moment is calculated by including the atomic dipole moment and the overlap moment (homopolar dipole) as well as the term from the Mulliken populations, then, except for carbon monoxide, the IEH method gives results in good agreement with experiment. The non-iterative EH method predicts dipole moments that are much too high. For molecules with dipole moments smaller than 3 Debyes, the IEH and CNDO/2 methods give similar results, but for molecules with higher dipole moments (formamide and sydnone), the CNDO/2 method gives better agreement with experiment. Comparison of the calculations on sydnone with those on other carbonyl compounds suggests that sydnone is best represented as a resonance stabilized azo-methine imine rather than as a "meso-ionic" or betaine type compound.

Rechnungen mittels des CNDO/2- und des erweiterten Hückelverfahrens (iterativ und nichtiterativ) werden für HF, H_2O, NH_3, CO, H_2CO, $HCONH_2$, HCOOH, HCOF und Sydnon vorgelegt. Im Fall des iterativen Hückelverfahrens zeigt sich, daß die Dipolmomente (außer für CO) gut mit dem Experiment übereinstimmen, wenn man die atomaren Dipol- und die Überlappungsmomente sowie die Terme der Mulliken-Population berücksichtigt. Dagegen sind die entsprechenden Werte des nichtiterativen Verfahrens viel zu groß. Für Moleküle mit Dipolmomenten kleiner als 3 Debye liefert das CNDO/2-Verfahren ähnliche Werte wie die iterative Hückelmethode, für Moleküle mit größeren Dipolmomenten dagegen bessere Resultate. Vergleicht man die Rechnungen für Sydnon mit denen für andere Carbonylverbindungen, so scheint es, daß man es besser als resonanzstabilisiertes Azomethinimin und nicht als Betain auffassen sollte.

HF, H_2O, NH_3, CO, H_2CO, $HCONH_2$, HCOOH, HCOF et la Sydnone on été calculées en utilisant les méthodes CNDO/2, Hückel étendu (EH) et Hückel étendu itératif (IEH). On montre que, pour la méthode IEH, si l'on calcule le moment dipolaire en incluant le moment dipolaire atomique et le moment de recouvrement (dipôle homopolaire) ainsi que le terme provenant des populations de Mulliken, les résultats obtenus sont en bon accord avec l'expérience sauf pour l'oxyde de carbone. La méthode EH non itérative donne des moments dipolaires trop élevés. Pour les molécules de moment inférieur à 3 Debyes, IEH et CNDO/2 donnent des résultats similaires, mais pour les molécules à moments plus élevés (formamide et sydnone) la méthode CNDO/2 donne un meilleur accord avec l'expérience. La comparaison des calculs sur la sydnone avec ceux sur les autres composés carbonylés suggère que la sydnone est mieux représentée comme une azo-méthine imine stabilisée par résonance que comme un composé de type «méso-ionique» ou bétaïnique.

Introduction

It is now generally recognized that in order to calculate realistic dipole moments by semi-empirical methods, it is necessary to include all the valence-shell electrons [1–5].

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* This work was supported by Grant No. MH-12951-02 from the National Institutes of Health, Bethesda, Maryland, USA.

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The great majority of calculations to date have been carried out by one of two types of methods: 1. the Extended Hückel (EH) method which includes overlap but neglects electron-repulsion integrals completely [3–6] and 2. the CNDO/2 SCF MO method [7] which uses the approximation of zero differential overlap, but includes the electron-repulsion integrals. A number of systematic studies using method 2 have now been carried out on a wide variety of compounds [1, 2, 7] and these demonstrate its utility in predicting dipole moments which are in extremely good agreement with experimental results. In the case of EH methods, however, only in the work of Lipscomb *et al.* [6] have the dipole moments been calculated correctly. In other studies [3–5] approximate expressions which omit important contributions to the total dipole moment have been used. It has therefore not been previously possible to evaluate the success of the several versions of the EH method in calculating dipole moments.

In order to show the importance of including the previously neglected terms in the dipole moment expression, and to provide results for evaluating the relative merits of EH methods and the CNDO/2 method, we have carried out calculations using a) the CNDO/2 method, b) the standard EH method, and c) an iterative EH (IEH) method in which the matrix elements of the secular determinant are allowed to depend on the charge densities until selfconsistency between output charge densities and input charge densities has been reached.

The molecules chosen as examples have been chosen both from the point of view of their structural interest (eg. sydnone and formamide) and also from the point of view of demonstrating that in different types of molecules, the relative importance of the different contributions to the total dipole moment is extremely variable and that agreement (or disagreement) between theory and experiment obtained when using approximate expressions [3, 4] has been due to a fortuitous cancelling out of opposing effects (eg. as found in water, pyridine and ammonia).

Method

As previously mentioned, three methods of calculation were utilized in this study: a) the CNDO/2 method, which was used exactly as described previously [2], b) the Extended Hückel (EH) method [9], and c) an iterative type of Extended Hückel (IEH) method.

We chose the same IEH method as that used by Pullman *et al.* [4], which is also very similar to that described by Rein *et al.* [3]. In this method, the diagonal parameters, H_{ii}, are allowed to be charge dependent as given by Eq. (1).

$$H_{ii}^{n} = -I_i - A_r q_r^{\text{input}} \qquad (1)$$

where,

q_r = total charge on atom r,

I_i = valence-state ionization potential of orbital i,

A_r = constant,

n = iteration number.

At the beginning of each iteration, new input charges are calculated from the output charges of the previous iteration by Eq. (2).

$$q_r^{\text{input},n} = q_r^{\text{output},n-1} + \delta(q_r^{\text{input},n-1} - q_r^{\text{output},n-1}) \tag{2}$$

where δ is a convergence parameter, usually given the value 0.85. The iterations are continued until the difference between the input and the output charges of the nth iteration is less than 0.01. Values of I_i and A_r for hydrogen, nitrogen, oxygen and carbon were taken from Ref. [4] and for fluorine from Ref. [10].

For the off-diagonal elements, H_{ij}, we used Cusachs' formula [11], as given by Eq. (3).

$$H_{ij} = (2 - |S_{ij}|) \frac{H_{ii} + H_{jj}}{2} S_{ij} \tag{3}$$

where S_{ij} is the overlap integral between the ith and jth atomic orbitals. In its original form [11] this formula failed to meet the requirement of rotational invariance of the molecular coordinate system. We corrected this by calculating all the H_{ij} values between two atoms A and B over a localized coordinate system, and then the H_{ij} values on the molecular coordinate system were written as linear combinations of the values calculated on the localized system.

The overlap integrals were calculated from Slater atomic orbitals with the single-ζ exponent values given by Clementi and Raimondi [12].

For the non-iterative EH method, the diagonal elements were calculated using Eq. (1) with A_r equal to zero, and the I_i values and the orbital exponents taken from Ref. [13]. Equation (3) was then used to calculate the off-diagonal elements.

The dipole moment of a molecule may be written as a sum of three contributions [14]: a) μ^{Mull}, due to the Mulliken overlap population, b) μ_r^{At}, due to the atomic dipole resulting from asymmetry of the atomic orbitals on atom r (the μ_{sp} of the CNDO/2 method), and c) μ^{rs}, the overlap moment, also known as the homopolar dipole contribution [15].

These components were calculated for each the x, y and z directions. The equations for the x direction are

$$\mu^{\text{Mull}}(x) = \sum_r^{\text{Atoms}} (Z_r - q_r)\, x_r \tag{4}$$

where

Z_r = number of valence electrons contributed by atom r

$$q_r = 2 \sum_m^{\text{occ.MOs}} \sum_i^{r} \sum_j^{\text{AOs}} c_{mi} c_{mj} S_{ij}\,,$$

$$\mu_r^{\text{At}}(x) = \sum_m^{\text{occ.MOs}} \sum_j^{r} \sum_k^{\text{AOs}} c_{mj} c_{mk} \mu_{jk}\,, \tag{5}$$

$$\mu^{rs}(x) = 2 \sum_m^{\text{occ.MOs}} \sum_i^{r} \sum_j^{s} c_{mj} c_{mi} \mu_{ij}\,, \tag{6}$$

$$\mu_{ij} = \int \psi_i \vec{r} \psi_j \, d\tau\,. \tag{7}$$

The calculation of μ_{ij}, the two center dipole moment integrals was carried out using Slater atomic orbitals for ψ_i with the same orbital exponents as we used in calculating the overlap integrals. Similar equations were used for the y and z directions.

In the CNDO/2 method, of course, there is no overlap moment, and instead of Mulliken orbital populations, bond orders were used.

The geometries of all the molecules were taken from experimental results in the literature. For formamide, there were several experimental geometries available. We chose to use that reported in Ref. [16].

Dipole Moment Calculations

The total dipole moments and the three constituents, μ^{Mull}, μ_r^{At}, and μ^{rs} are summarized in Table 1 for all three methods of calculation. It is immediately apparent that non-iterative EH calculations grossly exaggerate the dipole moments. On the other hand, both the CNDO/2 and the IEH method give results for the total dipole moment in good agreement with experiment except for carbon monoxide. There is also a tendency for the IEH method to give high results for the more polar compounds. Examination of the individual components of the dipole moments reveals the reason for the uneven agreement between experiment and theory found by Rein *et al.* [3] in their IEH calculations, in which they compared only one component of the dipole moment, namely μ^{Mull}, directly with experiment. This gives very satisfactory results for formaldehyde, formic acid, formamide, formyl fluoride, and pyridine, but only because of a rough cancelling out of the other two components, μ_r^{At} and μ^{rs}. However, for hydrogen fluoride, hydrogen cyanide, water and ammonia, the value of μ^{Mull} is much smaller than the observed dipole moment because now μ_r^{At} is larger than μ^{rs} and makes a considerable contribution to the total moment. When these terms are both included, the agreement between experiment and theory is restored (Table 1). These results show clearly that an agreement between experimental and calculated dipole moments using only the Mulliken population term, or as has been recently suggested [4], using just μ^{Mull} and μ_r^{At}, is fortuitous and that, except in special cases, it is necessary to include the overlap term as well. The importance of this term has been previously stressed by Coulson [15, 17], and by Mulliken [18], but with the exception of the work of Lipscomb *et al.* [6], these warnings have been ignored by workers using EH theory.

A much stronger criterion for evaluating wave functions than the total dipole moment is the criterion that a calculation should calculate the individual components correctly as well as the resultant and the direction of the total dipole moment of an unsymmetrical molecule. Our calculations for formyl fluoride and formamide show that this criterion is met extremely well by the CNDO/2 method and reasonably well by the IEH method[1].

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[1] Professor L. C. Cusachs (private communication) has obtained substantially improved results by the IEH method for carbon monoxide and some very polar diatomics such as lithium fluoride by including charge-dependent neighbor terms.

Table 1. *Dipole moment comparisons*[a]

		CNDO/2		IEH		EH		Experimental[b]	
		x	y	x	y	x	y	x	y
NH_3	μ^{Mull}	0.42		0.53		2.40			
	μ_r^{At}	1.67		2.64		1.56			
	μ^{rs}	—		−1.52		−0.98			
	μ_{Tot}	2.09		1.58		2.99		1.47	
	Resultant	2.09		1.58		2.99		1.47	
H_2O	μ^{Mull}	0.49	0.64	0.56	0.72	2.48	3.20		
	μ_r^{At}	0.83	1.06	1.38	1.78	0.49	0.63		
	μ^{rs}	—	—	−0.86	−1.11	−0.36	−0.46		
	μ_{Tot}	1.32	1.70	1.08	1.40	2.61	3.27		
	Resultant	2.15		1.77		4.26		1.84	
HCN	μ^{Mull}	−0.87		−1.61		−6.67			
	μ_r^{At}	−1.55		−2.07		−1.10			
	μ^{rs}	—		1.24		1.13			
	μ_{Tot}	−2.42		−2.45		−6.64		−2.95	
	Resultant	2.42		2.45		6.64		2.95	
CO	μ^{Mull}	−0.18		−0.54		−6.02			
	μ_r^{At}	1.18		2.05		2.72			
	μ^{rs}	—		−0.35		−0.17			
	μ_{Tot}	1.00		1.16		3.47		0.13	
	Resultant	1.00		1.16		3.47		0.13	
HF	μ^{Mull}	−1.02		−1.24		−3.64			
	μ_r^{At}	−0.83		−1.38		−0.51			
	μ^{rs}	—		0.96		0.39			
	μ_{Tot}	−1.85		−1.66		−3.74		−1.82	
	Resultant	1.85		1.66		3.74		1.82[c]	
H_2CO	μ^{Mull}	−0.99		−2.09		−8.58			
	μ_r^{At}	−0.93		−1.14		0.21			
	μ^{rs}	—		1.39		1.22			
	μ_{Tot}	−1.92		−1.85		−7.15		−2.17	
	Resultant	1.92		1.85		7.15		2.17	
HCOOH	μ^{Mull}	−1.10	0.48	−1.60	0.53	−5.11	−0.12		
	μ_r^{At}	−0.05	0.20	0.152	0.48	0.41	0.68		
	μ^{rs}	—	—	0.09	0.32	0.39	0.43		
	μ_{Tot}	−1.15	0.68	−1.36	1.33	−4.31	0.99		
	Resultant	1.34		1.90		4.42		1.53	
		149° 29′		135° 33′		167° 03′			
$HCONH_2$	μ^{Mull}	−1.68	1.33	−3.42	2.43	−7.81	7.90		
	μ_r^{At}	−1.00	1.15	−1.68	1.22	−0.42	−0.13		
	μ^{rs}	—	—	0.67	−1.13	−0.48	−1.09		
	μ_{Tot}	−2.68	2.48	−4.42	2.43	−7.75	6.67	−2.88	2.34
	Resultant	3.65		5.05		10.23		3.71[d]	
		137° 13′		151° 13′		139° 16′		140° 50′	
HCOF	μ^{Mull}	−0.64	1.02	−1.01	2.00	−6.24	4.66		
	μ_r^{At}	−0.84	0.31	−0.92	0.40	0.00	−0.53		
	μ^{rs}	—	—	0.80	−1.04	0.88	−0.71		
	μ_{Tot}	−1.48	1.33	−1.13	1.36	−5.36	3.36	−1.67	1.15
	Resultant	1.98		1.78		6.32		2.02[e]	
		138° 00′		140° 12′		147° 56′		145° 20′	

Table 1 (continued)

		CNDO/2		IEH		EH		Experimental[b]	
		x	y	x	y	x	y	x	y
Pyridine	μ^{Mull}	−0.65		−1.91		−4.70			
	μ_r^{At}	−1.54		−1.91		−1.07			
	μ^{rs}	—		1.67		1.45			
	μ_{Tot}	−2.19		−2.16		−4.32		−2.20	
	Resultant	2.19		2.16		4.32		2.20	
Sydnone	μ^{Mull}	2.69	3.63	2.33	5.98	6.26	14.01		
	μ_r^{At}	0.40	2.45	−0.27	2.75	−1.11	0.57		
	μ^{rs}	—	—	0.58	−2.46	0.51	−1.39		
	μ_{Tot}	3.09	6.08	2.64	6.25	5.66	13.19		
	Resultant	6.82		6.78		14.35		7.31[f]	
		53° 19′		86° 40′		65° 56′			

[a] All values in Debyes.
[b] Experimental values from McClellan [35] unless otherwise indicated.
[c] Ref. [15]. — [d] Ref. [36]. — [e] Ref. [37]. — [f] Value given is for 3-Methyl-sydnone [34].

Comparison with Non-Empirical Calculations

The criterion we have applied in the present work for a satisfactory semi-empirical method is the calculation of a dipole moment in agreement with experiment. An alternative criterion, which is gaining in popularity as more accurate non-empirical (NE) calculations become available, is to demand a similarity between the semi-empirical and the NE wavefunctions and eigenvalues [6, 19]. It would of course be ideal if these two criteria would be compatible, but unfortunately this is not so since NE calculations are very sensitive to the type and size of the basis set of atomic orbitals used in the calculation. They are also sensitive to whether or not configuration interaction has been included [20]. The dipole moment is particularly sensitive to changes in the type of atomic orbitals used. For example, in minimum-basis-set calculations on hydrogen fluoride [21], it was found that the dipole moment could be changed from the very low value of 0.87 *D* using orbital exponents calculated from Slater's rules, to a quite reasonable value of 1.49 *D* by adjusting the fluorine exponents slightly and raising the hydrogen exponent from 1.0 to 1.30. The situation is even worse for polyatomic molecules. For example, in formyl fluoride, a minimum-basis-set (Gaussian) calculation [22] gave a quite unrealistic charge distribution and a dipole moment which, although reasonable in magnitude, was in a direction 100° away from the experimental value. Agreement was at least partially restored by increasing the number of Gaussian orbitals in the basis set. In view of the sensitivity of NE calculations, it seems unreasonable to reject a semi-empirical calculation simply because the wave functions obtained do not agree closely with a NE calculation, especially if the latter has been carried out with a small or unbalanced basis set [23]. Nevertheless, in cases where the magnitude and direction of the calculated dipole moments are, in both cases, reasonable, there should be at least a qualitative agreement between the overlap populations and net charges obtained from the NE and semi-empirical type calculations. In Table 2 we have compared values obtained for

Table 2. *Mulliken gross orbital populations*

HF	EH	IEH	NE[a]
F 2s	1.979	1.902	1.944
F 2$p_x(\pi)$	2.000	2.000	2.000
F 2p_y	1.846	1.381	1.308
F 2$p_z(\pi)$	2.000	2.000	2.000
H 1s	0.175	0.717	0.747
μ_{Total}	3.74 D	1.65 D	1.49 D

H_2O	EH	IEH	NE[b]
O 2s	1.957	1.722	1.850
O 2p_x	1.709	1.257	1.590
O 2p_y	1.769	1.346	0.920
O 2$p_z(\pi)$	2.000	2.000	2.000
H 1s	0.282	0.837	0.820
μ_{Total}	4.26 D	1.77 D	1.51 D

NH_3	EH	IEH	NE[c]
N 2s	1.740	1.496	1.598
N 2p_x	1.857	1.717	1.760
N 2p_y	1.358	1.038	1.056
N 2p_z	1.358	1.038	1.056
H 1s	0.562	0.904	0.845
μ_{Total}	2.99 D	1.58 D	1.72 D

HCN	EH	IEH	NE[d]
C 2s	1.260	1.249	1.090
C 2p_x	0.807	0.801	1.014
C 2$p_y(\pi)$	0.639	0.956	1.019
C 2$p_z(\pi)$	0.639	0.956	1.019
N 2s	1.690	1.603	1.764
N 2p_x	1.528	1.479	1.351
N 2$p_y(\pi)$	1.361	1.044	0.981
N 2$p_z(\pi)$	1.361	1.044	0.981
H 1s	0.714	0.869	0.784
μ_{Total}	6.64 D	2.45 D	2.11 D

[a] Ref. [21]. — [b] Ref. [37]. — [c] Ref. [38]. — [d] Ref. [39].

these quantities by our IEH and EH calculations with those available from NE calculations for water, ammonia, hydrogen cyanide, and hydrogen fluoride. There is good agreement between the IEH and the NE calculations for the first three molecules. The EH method, as expected, is grossly different and will not be discussed further. In the case of hydrogen cyanide, the results are qualitatively similar, but the IEH method predicts only about half as much electron transfer from the hydrogen to the carbon as does the minimal-basis-set NE calculation. Also, the polarity of the π-orbital is in the direction C^+–N^- in the IEH method, but is in the opposite direction in the NE method. Improving the basis set actually does change the polarity [24], but the actual charge transferred is very small so that the π-electron bonds in hydrogen cyanide are predicted to be essentually nonpolar.

Two sets of NE calculations have recently been reported for formamide [25, 26]. We have compared our net atomic charges with those of Ref. [26] in Table 3. At a quantitative level, the results are quite different between the two methods, but the qualitative trends are similar. All calculations predict the total charge on the amino nitrogen and the carbonyl oxygen to be strongly negative. The CNDO/2 and the NE calculations predict the negative charge on the nitrogen to be compensated for by positive charges on the adjacent hydrogens, whereas the IEH method predicts a smaller negative charge on the nitrogen and correspondingly smaller positive charge on the carbonyl carbon. The π charges in the IEH calculation are also quite different from the other two calculations.

Table 3. *Net atomic charges for carbonyl compounds*[a]

		CNDO/2	IEH	NE
Formaldehyde	1	0.222	0.079	−0.163[b]
	2	−0.187	−0.269	−0.079
	3	−0.018	0.095	0.121
	4	−0.018	0.095	0.121
Formamide	1	0.370	0.093	0.295[c]
	2	−0.325	−0.397	−0.429
	3	−0.247	−0.126	−0.745
	4	−0.048	0.084	0.134
	5	0.121	0.170	0.362
	6	0.130	0.176	0.383
Formic acid	1	0.385	0.158	
	2	−0.310	−0.311	
	3	−0.238	−0.201	
	4	0.184	0.239	
	5	−0.021	0.115	
Formyl fluoride	1	0.421	0.253	−0.265[d]
	2	−0.228	−0.214	0.225
	3	−0.189	−0.208	0.405
	4	−0.004	0.171	−0.365

[a] For numbering systems see Fig. 1.

[b] Ref. [39]. — [c] Ref. [25].

[d] Ref. [22]. These are the only non-empirical net charges available and are recognized as being unsatisfactory by the author because of the small basis set used.

For pyridine, it has been shown that a CNDO calculation [27] (but with different parameters than CNDO/2) produces a substantially different set of orbital populations than the NE calculation of Clementi [28]. We have found similar results for the standard CNDO/2 and IEH methods. The chief discrepancy is in the amount of charge transfer from the hydrogens to the carbon atoms (a total of −0.04 of an electron for the CNDO/2 method, +0.264 of an electron for the IEH method, and 0.698 of an electron for the NE method). This large difference renders it impossible to carry out a worthwhile comparison of the populations. In general it is becoming apparent that one of the main differences between semi-empirical calculations and NE ones is the amount of charge transfer predicted between carbon and hydrogen.

Eigenvalues

One of the key items of information one hopes to obtain from MO calculations is the energy and type (n, σ or π) of the occupied molecular orbitals. We have tabulated the results of our EH and IEH calculations, along with the results of NE calculations and experimental ionization potentials, in Table 4. In general, the non-iterative EH calculations give values much too negative, but agreement between the IEH results, the NE results and experimental ionization potentials

Table 4. *Energies of* HOMO's *and ionization potential (eV)*

	IEH	EH	NE	Experimental[a]
H_2O	−11.558 (π)	−17.76 (π)	−12.8 (π)[b]	12.7
NH_3	−11.303 (n)	−13.4912 (n)	− 9.9615 (n)[c]	10.52
HCN	−13.754 (σ)	−14.2092 (σ)	−12.963 (π)[d]	13.9
	−14.0026 (π)	−14.58432 (π)	−14.3858 (σ)	
H_2CO	−11.63 (n)	−13.075 (σ)	−10.84 (n)[e]	10.8
Formic acid	−11.468 (n)	−14.343 (σ)		
Formamide	−10.144 (n)	−13.201 (n)	−11.537 (π)[f]	10.20 (n)
	−11.153 (π)	−14.108 (σ)	−11.918 (σ)	
Pyridine	−10.723 (σ)	−11.5847 (σ)	−12.170 (π)[g]	9.8 (π)
	−11.919 (σ)	−12.135 (σ)	−12.477 (π)	
	−12.551 (π)	−12.638 (π)	−12.664 (σ)	
	−12.627 (π)	−13.444 (π)	−15.768 (π)	
Formyl fluoride	−12.7885 (n)	−14.870 (σ)	−13.485 (σ)[h]	
	−14.021 (σ)	−17.846 (n)	−14.916 (π)	
	−14.086 (π)	−18.131 (π)	−17.110 (σ)	

[a] Experimental Values Taken from Ref. [40].

[b] Ref. [37]. — [c] Ref. [38]. — [d] Ref. [38]. — [e] Ref. [41]. — [f] Ref. [25]. — [g] Ref. [28]. — [h] Ref. [22].

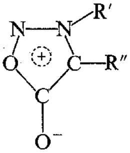
is fairly good. However, there are some differences in the symmetry of the predicted highest occupied MO. For example, both of the semi-empirical methods (IEH and CNDO/2) predict the highest occupied MO to be sigma type in both hydrogen cyanide and pyridine, while the NE calculations predict a π-type to be the highest occupied in both cases.

In formaldehyde, formamide and formyl fluoride, the IEH method predicts the lone-pair orbital on the carbonyl oxygen to be the highest occupied MO in all three cases, whereas the NE calculations predict the highest occupied MO to be of π-type in formamide and formyl fluoride. Only for formaldehyde and pyridine have the assignments been made experimentally. The lone pair is indeed responsible for the first ionization potential of formaldehyde, in agreement with all the calculations. In the case of pyridine, the first ionization potential has been shown to be π-type, in agreement with the NE result and contrary to the IEH result.

These results show that the IEH method, as well as the CNDO/2 method [2], is somewhat unreliable in predicting the symmetry of highest occupied MOs. It seems likely that this situation may be improved by changing the parametrization [29].

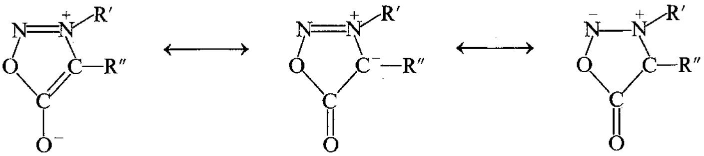
The Structure of Sydnone

As we have already discussed, calculations on sydnone were carried out as test case for an example of a molecule with a high dipole moment. Sydnone, however, is also of interest because of difficulties in writing a suitable structure for it. These difficulties lead Baker and Ollis [30] to write the structure as in I, which they referred to as a "meso-ionic" structure. This structure implies a sextet of π-electrons in the ring, and an ionic carbonyl group with a very small amount of double bond character [30].



I

On the other hand, Katritzky [31] favored the betaine structure, II. More recently, Stewart [8] has suggested that the sydnones should be considered more as resonance stabilized azo-methine imines with structures III and IV being the main canonical forms.



II III IV

A comparison of the population matrices for sydnone with the results on other carbonyl compounds has enabled us to throw some light on this controversy. Since the CNDO/2 calculation gives a dipole moment somewhat closer to the experimental value, we have used the bond orders and charge densities from this method in the following discussion, with comments included wherever the corresponding IEH results differ.

The π-electron charge densities[2] (Fig. 2) show that it is possible to divide the atoms into two groups with little charge transfer between them. The first group contains atoms 2, 3 and 4, and the second group contains atoms 1, 5 and 6. (For numbering system see Fig. 1.) There is only a charge transfer of 0.11 of an electron from the first group of atoms to the second group of atoms, whereas within the first group, there is a transfer of 0.76 of an electron from the amino nitrogen to the two adjacent atoms (3 and 4). Thus, carbon atom 4 is given a negative charge of one-third of an electron, which offers an explanation of a) the shielding of the attached proton as shown by the NMR spectra, b) the low infrared frequency of the C–H stretch, and c) the ease of attack of this position by electrophilic reagents such as mercuric chloride [33].

In the second group, the CNDO/2 method predicts a very high negative charge on the carbonyl oxygen, which is largely balanced out by positive charges on the carbonyl carbon and the adjacent oxygen (Position 1). The charge density pattern for the atoms and also the bond orders are very similar to those we have calculated in formic acid and formamide as shown in Fig. 2 and Table 3. Because of this similarity, and because it is usually accepted that amides are satisfactorily represented by a normal nonpolar structure, we prefer to use a similar nonpolar structure

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[2] The π-electron charge densities are very similar to those reported by Sundaram and Purcell [32], using the π-electron-only Pariser-Parr-Pople method. We have found this correspondence in other heterocyclic molecules [42].

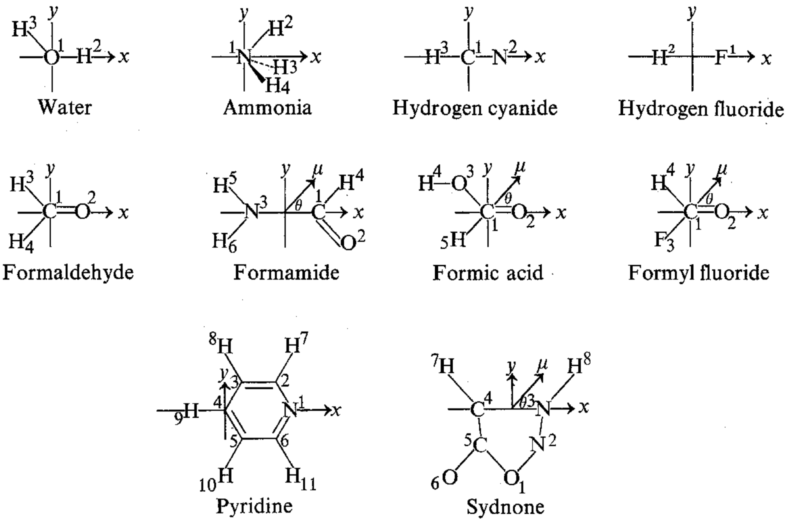

Fig. 1. Numbering systems of the molecules

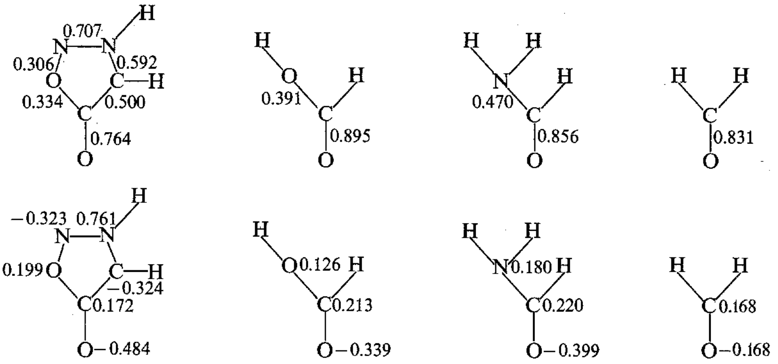

Fig. 2. Comparison of π bond orders and charge densities for sydnone, formic acid, formamide and formaldehyde

for the carbonyl part of sydnone, rather than writing a polar type structure as in the betaine [31] or the "meso-ionic" formulation [30].

Even though the carbonyl bond is very polar, the π-electron bond order is also high so that there is no incompatability in having high intensities for the carbonyl stretch and also a stretching frequency which is slightly higher (1718 to 1770 cm^{-1}) than that found in many amides, i.e., at about the same region where simple carboxylic acids absorb. A much lower frequency would be expected for a "meso-ionic" or betaine type of structure.

Both the CNDO/2 and the IEH calculations also predict a higher overall positive charge on the carbonyl carbon atom than on the amino nitrogen (Table 5), in agreement with experimental findings that the attack by nucleophilic reagents such as hydroxide ion and piperidine takes place at this carbon atom [34].

The results of our sydnone calculations in comparison with similar calculations on formic acid and formamide (Tables 3 and 5 and Fig. 2) lead us to prefer writing the sydnones as resonance hybrids between III and IV rather than as betaines (II) or as true "meso-ionic" compounds, although, of course, it is recognized that this is only an approximate representation since the bond orders show that there is considerable delocalization over the whole system. Our main objection to the "meso-ionic" formulation is its failure to show the negative charge on carbon atom 2, and also, the existence of almost as much double bond character in the sydnone carbonyl group as there is in the amide carbonyl group.

Table 5. *Net atomic charges of sydnone*

Atom No.	CNDO/2	IEH	EH
1	−0.171	−0.181	−0.862
2	−0.049	−0.086	−0.119
3	0.152	0.022	0.337
4	−0.165	0.093	0.071
5	0.405	0.171	1.510
6	−0.366	−0.353	−1.350
7 (H)	0.056	0.116	0.124
8 (H)	0.137	0.218	0.292

Conclusions

The main conclusions of this study may be summarized:

1. In carrying out EH calculations with overlap, it is necessary to include the overlap moment and the atomic dipole moment as well as the contribution from the Mulliken population in order to calculate reasonable dipole moments.

2. The non-iterative EH method grossly overestimates the charge densities and consequently predicts dipole moments which are usually much too high. On the other hand, the IEH method used here produces dipole moments in good agreement with experiment. The agreement with experiment for dipole moments of less than 3 Debyes is about as good as is obtained by the CNDO/2 method, but for more polar compounds, the CNDO/2 method is better.

3. The agreement between the energy of the highest occupied MO calculated by the IEH method and the experimental ionization potential is fairly good for small molecules, but for conjugated systems such as pyridine, the method, as well as the CNDO/2 method, gives unreliable results.

4. Comparison of the calculations on carbonyl compounds with those on sydnone suggests that the best "paper" formulation of this compound is as a resonance-stabilized azomethine imine rather than a betaine or "meso-ionic" type of compound.

Acknowledgement. All calculations were carried out on a Burroughs B 5500 computer using programs written in the ALGOL language. We thank Professor R. Sundberg for a discussion on the chemistry of the sydnones, and Dr. W. N. Lipscomb for a copy of the FORTRAN program by M. D. Newton and F. P. Boer, used to calculate the dipole moments in Ref. [20], and which was used as a basis for our present ALGOL program.

References

1. Pople, J. A., and M. Gordon: J. Amer. chem. Soc. **89**, 4253 (1967).
2. Bloor, J. E., and D. L. Breen: J. Amer. chem. Soc. **89**, 6835 (1967); — J. physical Chem. **72**, 716 (1968).
3. Rein, R., N. Fukuda, H. Win, G. A. Clarke, and F. E. Harris: J. chem. Physics **45**, 4743 (1966).
4. Pullman, A., E. Kochanski, M. Gilbert, and A. Denis: Theoret. chim. Acta (Berl.) **10**, 231 (1968).
5. Adam, W., and A. Grimison: Theoret. chim. Acta (Berl.) **7**, 342 (1967).
6. Newton, M. D., F. P. Boer, and W. N. Lipscomb: J. Amer. chem. Soc. **88**, 2353 (1966).
7. Pople, J. A., D. P. Santry, and G. A. Segal: J. chem. Physics **43**, S 129 (1965).
8. Stewart, F. H. C.: Chem. Reviews **64**, 129 (1964).
9. Hoffmann, R.: J. chem. Physics **39**, 1397 (1963).
10. Cusachs, L. C., and J. W. Reynolds: J. chem. Physics **43**, S 160 (1965).
11. — J. chem. Physics **43**, S 157 (1965).
12. Clementi, E., and D. L. Raimondi: J. chem. Physics **38**, 2686 (1963).
13. Kier, L. B.: Molecular Pharmacology **3**, 487 (1967).
14. Ruedenberg, K.: Rev. mod. Physics **34**, 326 (1962).
15. Rogers, M. T., and C. A. Coulson: J. chem. Physics **35**, 593 (1961).
16. Kurland, R. J., and E. B. Wilson: J. chem. Physics **27**, 585 (1957).
17. Coulson, C. A.: Trans. Faraday Soc. **38**, 433 (1942); — Valence, New York: Oxford University Press 1957.
18. Mulliken, R. S.: J. chem. Physics **3**, 543 (1935).
19. Duke, B. J.: Theoret. chim. Acta (Berl.) **9**, 261 (1968).
20. Grimaldi, F., A. Lecourt, and C. Moser: Internat. J. Quantum Chem. **1**, S 153 (1967).
21. Ballinger, R. A.: Molecular Physics **2**, 139 (1959).
22. Csizmadia, I. G., M. C. Harrison, and B. T. Sutcliffe: Theoret. chim. Acta (Berl.) **6**, 217 (1966).
23. Kaldor, U., and I. Shavitt: J. chem. Physics **45**, 888 (1966).
24. Pan, D. C., and L. C. Allen: J. chem. Physics **46**, 1797 (1967).
25. Robb, M. A., and I. G. Csizmadia: Theoret. chim. Acta (Berl.) **10**, 269 (1968).
26. Basch, H., M. B. Robin, and N. A. Kuebler: J. chem. Physics **47**, 1201 (1967).
27. Emsley, J. W.: J. chem. Soc. (London) (A) 1968, 1387.
28. Clementi, E.: J. chem. Physics **46**, 4731 (1967).
29. Armstrong, A. T., B. Bertus, and S. P. McGlynn: Spectroscopy Letters **1**, 43 (1968).
30. Baker, W., and W. D. Ollis: Quart. Rev. (London) **11**, 15 (1957).
31. Katritzky, A. R.: Chem. and Ind. (London) **391**, 521 (1951).
32. Sundaram, K., and W. P. Purcell: Internat. J. Quantum Chem. **2**, 145 (1968).
33. Tier, J. M., and M. Hunisberger: J. Amer. chem. Soc. **83**, 178 (1961).
34. Roche, E. B., and L. B. Kier: Tetrahedron **24**, 1673 (1968); — J. Pharm. Sci. **55**, 807 (1966).
35. McClellan, A. L.: Tables of experimental dipole moments. San Francisco: W. H. Freeman 1963.
36. LeBlanc, O. H., Jr., V. W. Laurie, and W. D. Gwinn: J. chem. Physics **33**, 598 (1960).
37. Ellison, F. O., and H. Shull: J. chem. Physics **23**, 2348 (1955).
38. Palke, W. E., and W. N. Lipscomb: J. Amer. chem. Soc. **88**, 2384 (1966).
39. Newton, M. D., F. P. Boer, and W. N. Lipscomb: J. Amer. chem. Soc. **88**, 2367 (1966).
40. Field, F. H., and J. S. Franklin: Electron Impact Phenomena. New York: Academic Press 1957.
41. Aung, S., R. M. Pitzer, and S. I. Chan: J. chem. Physics **45**, 3457 (1966).
42. Billingsley, F. P., II, and J. E. Bloor: Theoret. chim. Acta (Berl.) **11**, 325 (1968).

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