Electronic Structure of Sydnones. An Investigation by Means of ESCA and Molecular Orbital Calculations

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The core electron binding energies of 3-methyl- and 3-phenyl-sydnone are reported together with *ab initio* and semiempirical molecular orbital calculations of the electronic structure of these molecules. The *ab initio* calculation of 3-methylsydnone yields intramolecular chemical shifts in good agreement with experiment and also provides a new description of the bonding in this molecule. A point-charge potential model is unsatisfactory in interpreting the ESCA spectrum.

THE bonding and charge distribution in mesoionic compounds,[1] for which valence structures cannot be written without formal positive and negative charges being placed on atoms of the molecule, are not well understood at present.[2] The most commonly written formula for the sydnones[3] (Figure 1,A) implies aromaticity and this would account both for the weak basicity of these compounds[4] and their benzenoid electronic spectra;[5] at the same time, such a representation is unable to accommodate very readily the high frequency and intensity of the carbonyl stretching vibration in the i.r. spectra of 3-alkylsydnones.[6] A more recent formulation (Figure 1,B) postulates a normal σ-framework extending through the sequence O–N–N–C–C, a weak ring C–O σ-bond, and delocalisation of the π-electrons over the ring atoms.[7]

The lack of a more definite description of the bonding in such molecules as these reflects both the lack of experimental data which yields direct information on the molecular charge distribution and the differing descriptions of the electronic structure which are obtained from various semiempirical molecular orbital treatments of these systems.[8] However, the measured binding energies of core electrons (ESCA) are known to be sensitive to molecular environment and, in many cases, may be interpreted in terms of the formal molecular charge

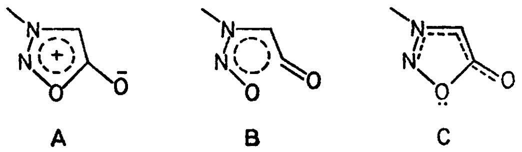

FIGURE 1 Formal representations of 3-alkylsydnone: A, Baker and Ollis (ref. 1); B, Hope and Thiessen (ref. 12); and C, this work

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distribution.[9] Accurate molecular orbital calculations of quite large molecules can now be performed which allow a discussion of the mode of bonding and which provide direct theoretical estimates of the measured core electron binding energies. In this paper we describe the application of these experimental and theoretical methods to the interpretation of the bonding in 3-methyl- and 3-phenyl-sydnones.

EXPERIMENTAL

The compounds were prepared by the method of Hammick and Voaden.[10] Binding energies of the carbon, nitrogen, and oxygen 1*s* electrons were measured with an AEI ES100 spectrometer. In the case of 3-methylsydnone the effects of sample charging on binding-energy measurements were allowed for by co-condensing an internal standard, nitromethane. The nitrogen 1*s* binding energy in the latter is known (406·0 eV),[11] so that all the ionisation potentials of the sydnone could be calibrated by reference to this line in the photoelectron spectrum. The core ionisation potentials shown in Table 1 were obtained in this way. This calibration procedure was not possible for the 3-phenylsydnone owing to its involatile nature. The core ionisation potentials of this molecule quoted in Table 1 were obtained by assigning that of the main carbon 1*s* peak, due to the phenyl ring-carbon core electron ionisations, a value of 285·0 eV and measuring the other values relative to this in the usual manner.

TABLE 1

Experimental and calculated core binding energies (eV)

	3-Methylsydnone		3-Phenylsydnone
	Found	Calc.	Found [a]
C 1*s*	285·6, 287·9	307·8, 308·0, 311·2	
N 1*s*	401·2, 402·6 [b]	427·7, 429·8	400·8, 402·2
O 1*s*	531·0, 533·9	558·9, 563·0	531·4, 533·8

[a] Obtained by taking the main carbon 1*s* peak to correspond to an ionisation potential of 285·0 eV. [b] There is also a satellite peak at 405·8 eV; see text.

Computational Details.—An all-electron *ab initio* self-consistent field molecular orbital (SCF–MO) calculation of the electronic structure of 3-methylsydnone was performed for the molecular geometry of Table 2 which is taken from that of 3,3′-ethylenebis-sydnone [12] and assumes a N–CH_3 bond length of 1·47 Å. The molecular orbitals (ψ) are represented as linear combinations (1) of atomic orbitals (χ), the coefficients (C) being obtained as described by

$$\psi_i = \sum_j C_{ij}\chi_j \qquad (1)$$

Roothaan. In this calculation the atomic orbitals are represented by Slater type orbitals (STO), one STO for each core (1*s*) and 2*s* atomic orbital and two for each valence 2*p* and hydrogen 1*s* orbital, the exponents of the STOs being given in Table 2. Such a double-zeta description of the valence orbitals allows the atomic orbitals to adjust their size on bond formation and, of particular importance in aromatic molecules, allows for the π- and σ-orbitals to be of different size. Owing to the difficulty in evaluating multicentre integrals over STOs, each STO was expanded in Gaussian type functions (GTF) by the least-squares method, the carbon, nitrogen, and oxygen 1*s* and 2*s* STOs being expanded in six and three GTFs respectively,[13] and the remaining STOs in two such functions.[14] The calculation was thus performed in a basis of 163 GTFs contracted to 64 Gaussian type orbitals (GTO) and took *ca.* 6 h on an ICL 1906A computer with use of the ATMOL system of programmes.

TABLE 2

Atomic co-ordinates * (a.u.) and orbital exponents of 3-methylsydnone

	Co-ordinates		
Atom *	*x*	*y*	*z*
C(1)	−2·781715	0	0
C(2)	1·517229	2·006120	0
C(3)	3·994007	1·091859	0
H(1)	0·764205	3·635825	0
H(2)	−3·371753	1·675505	0
H(3)	−3·371753	−0·837752	1·451038
H(4)	−3·371753	−0·837752	−1·451038
N(1)	0	0	0
N(2)	1·159547	−2·180803	0
O(1)	3·679643	−1·544578	0
O(2)	6·104041	1·987517	0

	Orbital exponents				
Atom	1*s*		2*s*	2*p*	
Carbon	5·7		1·6083	1·25572	2·72625
Nitrogen	6·7		1·9237	1·50585	3·26741
Oxygen	7·7		2·2458	1·65372	3·68127
Hydrogen	0·9	1·4			

* The numbering of the atoms is shown in Figure 3.

From the calculated molecular orbitals (ψ), atomic electron populations can be defined following Mulliken.[15] The population of atom *a* (P_a), being given by the relation (2)

$$P_a = \sum_j N_j \sum_{l\varepsilon a} (C^2_{jl} + \sum_{m\neq} C_{jl}C_{jm}S_{lm}) \qquad (2)$$

where N_j is the number of electrons in molecular orbital j, and the labels l and m run over the basis atomic orbitals. The first term represents a ' net atomic population ' and the second an ' overlap population,' S_{lm} being the overlap integral between orbitals l and m. By this method, the total electron population on a particular atom (a) can be broken down into contributions from the atomic orbitals (l) on the atom. The bond overlap population between two atoms (a, b) can be similarly defined as (3). This quantity is

$$P_{ab} = 2\sum_j N_j \sum_{l\varepsilon a} \sum_{m\varepsilon b} C_{jl}C_{jm}S_{lm} \qquad (3)$$

analogous to the bond order of semiempirical π-molecular orbital calculations and gives an estimate of the relative bond strength and of the atomic orbital contributions to the bond. An *ab initio* SCF–MO calculation of acetone was also carried out in order to compare the bonding in the carbonyl group of the sydnone with that in a normal carbonyl compound. As 3-phenylsydnone is too large a molecule to investigate by means of an *ab initio* SCF–MO calculation in a reasonable amount of computer time, an all valence electron semiempirical SCF–MO calculation by the

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intermediate neglect of differential overlap (INDO) method [16] was performed both on 3-phenyl- and on 3-methylsydnone to compare the charge distributions in these molecules. The molecular geometry of 3-phenylsydnone was taken from that of *p*-bromophenylsydnone.[17]

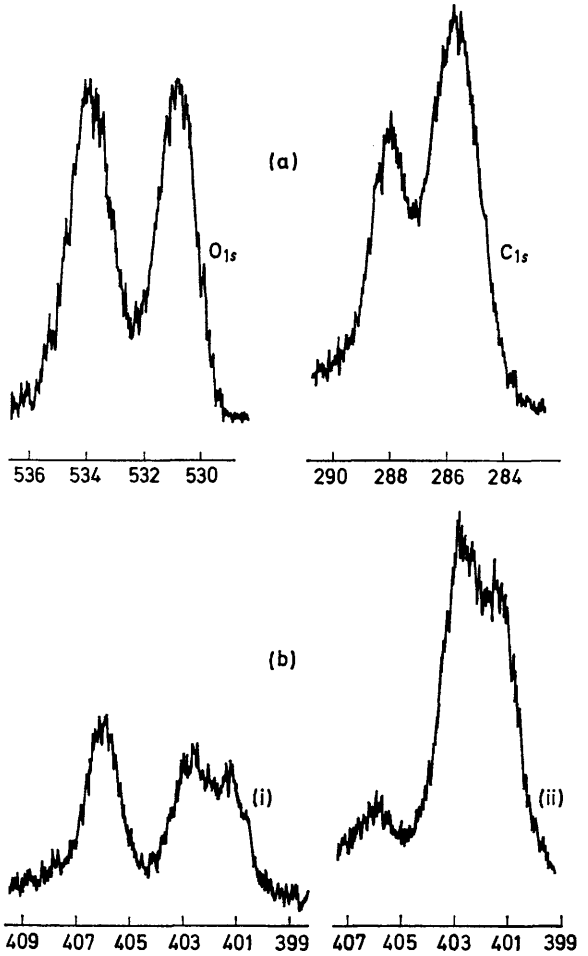

FIGURE 2 *X*-Ray photoelectron spectra of 3-methylsydnone: (a) O 1*s* and C 1*s* ionisation; (b) N 1*s* ionisation showing (i) the calibration relative to MeNO$_2$ (binding energy 406·0 eV) and (ii) the presence of a satellite (binding energy 405·8 eV)

RESULTS AND DISCUSSION

The relevant regions of the *X*-ray photoelectron spectrum of 3-methylsydnone are shown in Figure 2. There are two carbon 1*s* peaks with intensity ratio 2 : 1 (within the error inherent in the necessary deconvolution) which are separated by 2·3 eV. Two oxygen 1*s* peaks of equal intensity are separated by 2·9 eV. Two nitrogen 1*s* peaks of near-equal intensity (1·1 : 1·0) are separated by 1·4 eV. There is also a weak peak in the nitrogen 1*s* region of the spectrum whose intensity relative to the lower binding energy peak of the main ionisation is *ca.* 0·1. The binding energy of this weak peak is 405·8 eV (Figure 2).

The measured ionisation potentials can be equated directly to the negative of the calculated orbital energies by the use of Koopmans' theorem [18] (Table 1). Although the core ionisation potentials calculated in this way are always greater than the experimental values owing to neglect of orbital relaxation upon ionisation, the change in core binding energy on change of chemical environment (chemical shift) is usually given quite well by a medium basis calculation such as we have performed.[9] Although 3-methylsydnone contains three carbon atoms, our calculation does predict that there should be only two carbon 1*s* peaks resolved in the photoelectron spectrum as the calculated difference in the 1*s* ionisation potentials of the methyl carbon [C(1), Figure 3] and C(2) (Figure 3) is less than 0·2 eV. The less intense peak at higher binding energy corresponds to ionisation from the carbonyl carbon, C(3). The calculation indicates that the oxygen atom with the larger core ionisation potential is that in the ring [O(1)], that of the carbonyl oxygen, O(2), being smaller. The nitrogen attached to the methyl group [N(1)] has a larger core ionisation potential than N(2) (Figure 3). The values in Table 1 show that the calculation predicts the trend in the magnitude of the intramolecular shifts (O > C > N), although the calculated values of the shifts are rather greater than the experimental values. We are unable to assess the origin of this discrepancy which may originate from the use of Koopmans' theorem, from the difficulty of describing the bonding in mesoionic compounds

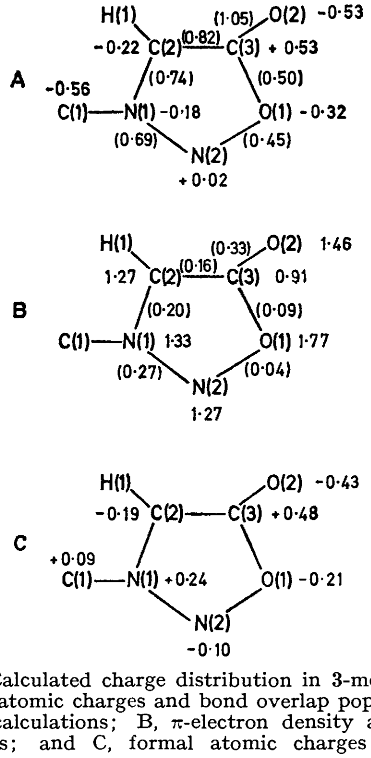

FIGURE 3 Calculated charge distribution in 3-methylsydnone: A, formal atomic charges and bond overlap populations from *ab initio* calculations; B, π-electron density and π-overlap populations; and C, formal atomic charges from INDO calculations

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by means of a molecular orbital scheme, or from the use of an insufficiently large basis set in the calculations.

The formal atomic charges and bond overlap populations obtained by the use of equations (2) and (3) are shown in Figure 3,A, while the atomic π-electron density and the contribution of the π-electrons to the bond overlap populations are shown in Figure 3,B. The calculation reveals a large degree of charge asymmetry in the molecule, the carbon atom charges ranging from $-0{\cdot}56$ to $+0{\cdot}53$, both oxygen atoms having large negative charges and the nitrogen atoms showing the smallest deviations from charge neutrality. There are considerable overlap populations between all bonded atoms, although those between O(1) and N(2) and C(3) are smaller than those in the rest of the molecule. The π-electron contribution to the bond overlap populations (Figure 3,B) shows that there is little π-bonding between O(1) and its adjacent atoms. The considerable π-density (1·8 e) on O(1) can therefore be assessed as predominantly non-bonding, whilst the larger π-overlap populations between the sequence of atoms N(2)–N(1)–C(2)–C(3)–O(2) allows π-delocalisation among these atoms to be inferred. It is noteworthy that the total π-electron density associated with these five atoms is very near to six electrons (6·2 e). When compared with the carbonyl group in acetone, which has formal calculated charges of C($+0{\cdot}30$)–O($-0{\cdot}44$), that in the sydnone is calculated to be considerably more polar. Thus, although the σ-electron density on O(2) in 3-methylsydnone (7·1 e) is less than that on the oxygen atom of acetone (7·2 e), its greater π-electron density (1·5 e compared with 1·2 e in acetone), arising from the conjugation of the π-system, results in an increased polarity. The greater electron density of the carbonyl oxygen of the sydnone than of acetone is reflected in the greater O 1*s* binding energy of acetone (534·6 eV) than of O(2) in 3-methylsydnone (531·0 eV). Although the assignment of the core binding energies by means of the SCF–MO calculations follows the formal atomic charges of the carbon and oxygen atoms $\{1s[\mathrm{C}(3)] > 1s[\mathrm{C}(1),\mathrm{C}(2)];\ 1s[\mathrm{O}(1)] > 1s[\mathrm{O}(2)]\}$ the larger of the two nitrogen 1*s* binding energies corresponds to that of N(1) which has a greater electron density than N(2).

In an attempt to obtain a more quantitative correlation between the calculated charge distribution and the measured core level shifts we have investigated the use of the semiempirical relation (4) between the binding energy of a core electron on atom *i* (E_i) and the formal atomic charge, *q*, which has been suggested by Gelius *et al.*[19] In this expression, *A* is an atomic constant

$$E_i = Aq_i + V_i + l \qquad (4)$$

which may be interpreted as the average repulsion between an atomic core and valence electron, V_i is the point-charge potential at atom *i* given by equation (5)

$$V_i = \sum_{j\neq i}\frac{q_j}{R_{ij}} \qquad (5)$$

where R_{ij} is the separation of atom *i* and *j*. In equation (4), *l* is a constant determined by the choice of reference level. Values of the parameter *A* have been obtained from a study of the core binding energies of a series of simple pseudohalides.[20] When used in conjunction with the calculated atomic charges from the *ab initio* calculation (Figure 3), equation (4) does not provide a satisfactory assignment of the experimental photoelectron spectrum. Thus, three lines are predicted in the carbon 1*s* spectrum, each separated from the next by 1·5—2·0 eV, the assignment of the nitrogen 1*s* spectrum is the reverse of that given by the use of Koopmans' theorem, and only in the case of the oxygen 1*s* ionisation potentials is the separation (2·1 eV) and assignment of the spectrum in reasonable accord with the calculated orbital energies.

Semiempirical molecular orbital calculations, which do not yield binding energies of the core electrons directly, can be used to estimate chemical shifts by means of equation (4), together with the calculated atomic charges. The calculated charge distribution of 3-methylsydnone obtained by the INDO method is shown in Figure 3,C. The use of equation (4) with values of *A* obtained previously [20] does not provide an interpretation of the carbon 1*s* photoelectron spectrum. Although 1*s* electrons of carbon atom C(2) are calculated by this method to be the most weakly bound by *ca.* 3 eV, those of the methyl, C(1), and carbonyl, C(3), carbon atoms are calculated to have binding energies differing by only 0·6 eV, leading to the photoelectron peak at higher binding energy being the more intense, in conflict with the observed spectrum (Figure 2). This model does however lead to the same assignment of the nitrogen and oxygen 1*s* spectra with calculated intramolecular shifts of 3·8 and 2·7 eV respectively. The INDO calculation of 3-phenylsydnone leads to a charge distribution on the sydnone ring and derived chemical shifts essentially unaltered from those calculated for 3-methylsydnone by the same method. This is in agreement with the essentially unchanged core binding energies which we observe (Table 1).

We now discuss the origin of the weak peak to high binding energy of the main peaks in the nitrogen 1*s* photoelectron spectrum of 3-methylsydnone (Figure 2). Such satellite peaks have been observed in the ESCA spectrum of a number of molecules such as carbon suboxide [21] and a series of transition-metal carbonyls.[22] Although the origin of these satellite peaks is not completely understood at present, they are generally attributed to transitions to ionic states which not only have a core level hole, but in which excitation of a valence electron has also taken place. Transitions to such states may be observed as a result of intensity borrowing from

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the usual core level hole states, and in this regard we note that the photoelectron peak (Figure 2) which we assign to be due to ionisation from nitrogen atom N(2) (Figure 3) is of significantly lower intensity than the peak at higher binding energy. Examination of the atomic orbital composition of the *ab initio* SCF molecular orbitals shows that both the highest filled and lowest unfilled molecular orbitals are of π-type. The $2p$ π-atomic orbitals on N(2) contribute 28 and 35% to these molecular orbitals, respectively. It is thus consistent with the calculation that the satellite peak is due to a transition to an ionic state described by ionisation of a $1s$ electron from N(2), and electron excitation from the highest filled to the first virtual π-orbital.

Conclusions.—The experimental high-energy photoelectron spectra of the sydnones yield chemical shifts of sufficient magnitude for this technique to be potentially valuable in providing information on the charge distribution in such molecules (*cf.* ref. 23). The chemical shifts calculated in a double-zeta basis are in satisfactory agreement with experiment, indicating that such a calculation gives a reliable picture of the bonding. The use of the point-charge potential model when used in conjunction with formal atomic charges from either the *ab initio* or semiempirical (INDO) molecular orbital calculations is found to be unsatisfactory for the interpretation of the experimental spectra. The conjunction of experiment and calculation leads to a revised formal representation of the 3-alkylsydnones (Figure 1,C), which is clearly related to that of Hope and Thiessen [12] (Figure 1,B).

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