COMPARISON OF THE CALCULATED QUANTUM-CHEMICAL CHARACTERISTICS OF SYDNONES AND SYDNONIMINES WITH THE EXPERIMENTALLY OBSERVED MOLECULAR PARAMETERS

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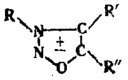
UDC 547.793.1+541.6

Approximate correlations of the interatomic distances, dipole moments, IR spectral frequencies, and polarographic reduction potentials of sydnones and sydnonimines with the quantum-chemical characteristics of these molecules, calculated by the Hückel method with four variants of parameters obtained from the Pariser–Parr–Pople method, were found.

In [1], the electronic structure indexes of 23 substituted sydnones (I) and sydnonimines (II) were calculated by the Hückel method with two variants of parameters obtained from the Pariser–Parr–Pople method (PPP). In this paper, we present a comparison of these indexes with experimental data on the interatomic distances, dipole moments, polarographic reduction potentials, and IR spectra.



I $R'' = O$
II $R'' = NR'''$

Interatomic Distances. The following expressions were obtained in [2] on the basis of Badger's rule, which relates the bond lengths with the force constants:

$$l_{C-C} = 1.510 - 0.198\ p_{C-C}. \tag{1}$$

$$l_{C-N} = 1.458 - 0.175\ p_{C-N}. \tag{2}$$

$$l_{C-O} = 1.394 - 0.174\ p_{C-O}. \tag{3}$$

$$l_{N-N} = 1.414 - 0.181\ p_{N-N}. \tag{4}$$

$$l_{N-O} = 1.318 - 0.138\ p_{N-O}. \tag{5}$$

where l is the interatomic distance in angstroms, and P is the π-bond order.

The most accurate data on the interatomic distances in the sydnone ring are known for 4,4'-dichloro-3,3'-ethylenebissydnone [3]. In Table 1 they are compared with the values calculated by means of Eqs. (1)-(5) from the sydnone ring bond orders computed by the Hückel method with various parameter variants.

It is apparent that all of the variants for calculation of the π-electron shell of unsubstituted sydnone by the Hückel method lead to interatomic distances whose mean-square deviation from the experimental values is approximately constant and appreciably exceeds the experimental error of 0.005 Å. Moreover, satisfactory correlation between the calculated and experimental values is observed for the $N_{(2)}-N_{(3)}$,

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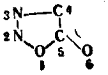
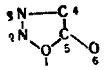
Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 10, pp. 1407-1412, October, 1971. Original article submitted December 30, 1970.

TABLE 1. Lengths (l_{rs}, Å) and Orders (p_{rs}) of Sydnone Ring Bonds



Computational method		Bonds						Mean-sq. deviation, Å
		1—2	2—3	3—4	4—5	5—6	1—5	
Exptl. interatomic distances in 4,4'-dichloro-3,3'-diethylenebissydnone	l_{rs}	1,389	1,313	1,344	1,395	1,215	1,407	
Hückel method, Orgel parameters [4]	p_{rs}	0,258	0,532	0,696	0,469	0,589	0,483	
	l_{rs}	1,282	1,318	1,336	1,417	1,292	1,314	0,064
Hückel method, Pullman parameters [5]	p_{rs}	0,360	0,749	0,507	0,532	0,733	0,331	
	l_{rs}	1,186	1,279	1,369	1,405	1,267	1,337	0,063
ω Method [6]	p_{rs}	0,222	0,569	0,503	0,660	0,635	0,231	
	l_{rs}	1,287	1,311	1,370	1,379	1,284	1,354	0,055
Hückel method, variant A [1]	p_{rs}	0,185	0,560	0,648	0,418	0,806	0,225	
	l_{rs}	1,293	1,313	1,345	1,427	1,254	1,355	0,048
Hückel method, variant B [1]	p_{rs}	0,173	0,640	0,672	0,405	0,778	0,280	
	l_{rs}	1,294	1,298	1,340	1,430	1,259	1,345	0,051

TABLE 2. Atomic Charges and Dipole Moment of the Sydnone Ring



μ_{exp} = 7.3 D (for 3-methylsydnone)

Computational method	Effective atomic charges, (q^i_π)						μ_πD*
	1	2	3	4	5	6	
Huckel method:							
Orgel parameters [4]	0,217	—0,430	0,566	0,113	0,243	—0,709	7,4
Pullman parameters [5]	0,200	—0,105	0,660	---0,382	0,160	—0,533	7,9
ω Method [6].	0,080	—0,119	0,421	0,044	0,100	—0,530	6,8
Variant A [1]	0,087	—0,389	0,549	—0,065	0,261	—0,449	4,9
Variant B [1]	0,092	—0,420	0,739	—0,238	0,347	—0,529	6,0
	q_σ						μ_σ
Del Re method [7]	0,140	0,317	—0,478	0,181	0,347	—0,501	3,3
	$q_{\pi+\sigma}$						$\vec{\mu}_\pi + \vec{\mu}_\sigma$
Variant A [1], Del Re method [7]	0,227	—0,072	0,071	0,116	0,608	—0,950	6,7
Variant B [1], Del Re method [7]	0,232	—0,103	0,261	—0,057	0,694	—1,030	8,1
ZDO/2 [8]	—0,171	—0,049	0,152	—0,165	0,405	—0,366	6,8

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*The interatomic distances and angles between the bonds in the 4,4'-dichloro-3,3'-ethylenebissydnone molecule [3] were used in the calculations of the dipole moment.

$N_{(3)}-C_{(4)}$, and $C_{(4)}-C_{(5)}$ bonds. There is considerably poorer correlation for the $C_{(5)}-O_{(6)}$, $C_{(5)}-O_{(1)}$, and, especially, the $O_{(1)}-N_{(2)}$ bonds.

Dipole Moments. The π-electron charges of the ring atoms, calculated under the approximation indicated above, are presented in Table 2. In order to somehow take into account the effect of the σ skeleton, in calculating the dipole moment within the framework of the Hückel method we used the σ charges of the sydnone ring atoms that were calculated in [7] by the Del Re method. The dipole moment of the σ skeleton calculated using this approximation is of considerable magnitude. It is apparent from Table 2 that calculations made with the parameters from the PPP method [1] predict the lowest value of the dipole moment of the π charges. The overall dipole moments (π + σ) of the charges in both variants A and B are in complete-

TABLE 3. Calculated and Experimentally Observed Characteristics of Sydnones and Sydnonimines

	Compound			$-E_{1/2}$, V[a]	ν_{CO}[b], cm^{-1}	Computational model			$-m_{m+1}$		p_{CO}	
	R	R′	R″			R	R′	R″	A	B	A	B
1	CH_3	H	O	1,50	1722	CH_3	—	O	0,288	0,349	0,806	0,778
2	C_6H_5	H	O	1,21	1752	C_6H_5	—	O	0,260	0,304	0,804	0,776
3	β-Py	H	O	—	1725	β-Py	—	O	0,259	0,303	0,804	0,776
4	C_6H_5	CHO	O	—	1774 1641 c	C_6H_5	CHO	O	0,070	0,130	0,827 0,701 c	0,797 0,719 c
5	C_6H_5	C_2H_5	O	1,35	1732	C_6H_5	CH_3	O	0,267	0,308	0,810	0,780
6	C_6H_5	Br	O	—	1780	C_6H_5	Br	O	0,278	0,315	0,807	0,777
7	CH_3	C_6H_5	O	1,27	1730	CH_3	C_6H_5	O	0,239	0,298	0,822	0,790
8	C_6H_5	$COOCH_3$	O	—	1790 1710 c	C_6H_5	COOH	O	0,097	0,157	0,823 0,660 c	0,794 0,670 c
9	C_6H_5	$CONH_2$	O	—	1762 1680 c	C_6H_5	$CONH_2$	O	0,104	0,164	0,822 0,644 c	0,793 0,653 c
10	C_6H_5	C_6H_5	O	1,14	1756	C_6H_5	C_6H_5	O	0,218	0,262	0,821	0,789
11	C_4H_9	H	$NCOC_6H_5$	1,20	1629	CH_3	—	$NCOC_6H_5$	0,206	0,268	0,684	0,688
12	C_4H_9	H	$NCOOCH_3$	1,26	1642	CH_3	—	NCOOH	0,241	0,316	0,708	0,719
13	C_6H_5	H	$NCOOCH_3$	—	1669	C_6H_5	—	NCOOH	0,219	0,281	0,707	0,709
14	C_4H_9	H	$NCOCH_3$	1,19	1638	CH_3	—	NCHO	0,221	0,295	0,767	0,771
15	C_4H_9	H	$+NH_2$	0,89d	—	—	—	$+NH_2$	—0,872	—	—	—

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[a] With a borate buffer (pH 9.3-10.8), results from [13, 14].

[b] Suspensions in mineral oil, results from [15-22].

[c] For the carbonyl group in the substituent.

[d] In water at pH 7.4 [19].

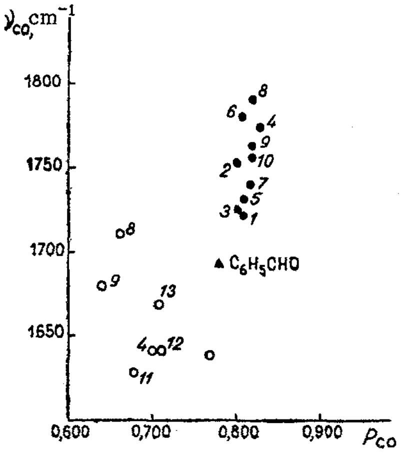

Fig. 1. Dependence of the ν_{CO} frequencies of the exocyclic carbonyl group of sydnones (●) and the carbonyl groups of substituents in substituted sydnones and sydnonimines (○) on the calculated C = O bond orders for computational variant A (the picture is similar for variant B). The symbols correspond to those in Table 3.

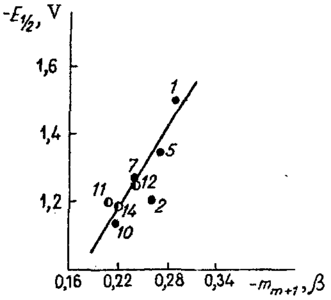

Fig. 2. Dependence of the polarographic reduction potentials of substituted sydnones (●) and sydnonimines (◐) on the calculated LVMO energies for variant A. (The picture is similar for variant B.) The symbols correspond to those in Table 3.

ly satisfactory agreement with the experimental value. For comparison, Table 2 also contains data from the calculation of the sydnone molecule by the ZDO/2 (zero differential overlap) method, in which all of the valence electrons are considered within the approximation of zero differential overlap, allowing for the atomic dipoles, which include the moments of the p electron pairs.

It follows from Table 2 that the distributions of the total ($\pi + \sigma$) charges in the sydnone ring, calculated by the simple method and the ZDO/2 method, are close, and the greatest overall ($\pi + \sigma$) positive charge in the sydnone ring is localized on the $C_{(5)}$ atom, and the greatest total negative charge is localized on the $O_{(6)}$ atom. The charges of the $O_{(1)}$, $N_{(2)}$, $N_{(3)}$, and $C_{(4)}$ atoms are lower in absolute value than the charges of the $C_{(5)}$ and $O_{(6)}$ atoms, and a positive charge is found on the $N_{(3)}$ atom. A negative charge is found on the $N_{(2)}$ atom, while the signs of the ($\pi + \sigma$) charges of the $O_{(1)}$ and $C_{(4)}$ atoms change as a function of the computational method and parameters. We note that in [9] the values of the total ($\pi + \sigma$) charges on adjacent carbon atoms, calculated by the Hofman method, were contrasted with the chemical shifts of the hydrogen atoms of a large number of five-membered heterocycles. A small (~0.1) total positive charge on $C_{(4)}$ corresponded to the point for $H_{(4)}$ of sydnone that lies satisfactorily on the general correlation line.

IR Spectra. In [12], in a comparison of the ν_{CO} frequencies with the C = O bond orders, calculated by the Hückel method with Pullman parameters, it was noted that the points for sydnones deviate considerably from the general dependence toward the higher-frequency side. A sufficiently distinct correlation between the ν_{CO} frequencies and the p_{CO} bond orders was found directly for five sydnones.

The p_{CO} bond orders for a number of sydnones and N-acylsydnonimines, calculated in [1] with the parameters obtained from the PPP method (Table 3, variant A), are contrasted in Fig. 1. The point for benzaldehyde is presented also for comparison. We could not use the data for heterocycles with an exocyclic carbonyl group because of the absence of data calculated with the system of parameters adopted in [1]. It follows from Fig. 1 that the ν_{CO} frequencies for the exocyclic carbonyl group of sydnones vary considerably, while the orders of this bond change only slightly, and these values do not intercorrelate. A similar result was obtained in [1], in which it was shown that sydnones and sydnonimines are weak conductors of π-electron effects from the 3 and 4 positions to the 5 and 6 positions; i.e., the calculated charges of the $C_{(5)}$ and $O_{(6)}$ atoms and the orders of the exocyclic $C_{(5)}-O_{(6)}$ bond of sydnones I are almost independent of the R and R' substituents. This is in good agreement with the fact that the effect of substituents in the 3 and 4 positions on the ν_{CO} frequency and intensity (A_{CO}) of the carbonyl band is satisfactorily described by the σ_1 constants of R and R' [11]. According to the calculated data [1], the exocyclic carbonyl group has larger p_{CO} values than those for the carbonyl groups in the substituents, which is in agreement with the fact that the higher ν_{CO} values correspond to the former in the IR spectra (Fig. 1).

Polarographic Reduction. In [12], the polarographic reduction potentials ($E_{1/2}$) of sydnones, sydnonimines, and sydnonimine cations ($R'' = \overset{+}{N}HR'''$) were compared with the energies of the lower vacant molecular orbitals (LVMO) calculated with the Pullman parameters.* The mechanisms of the polarographic reduction of the indicated compounds have much in common, and we therefore had a right to expect that the $E_{1/2}$ potentials of the latter can be described in the form of a single correlation scheme. However, it was found that in calculations with the Pullman parameters the points for the sydnonimines and particularly the sydnonimine cations deviate appreciably from the straight line for sydnones toward the lower $E_{1/2}$ side. In this study, the LVMO energies calculated in [1] were contrasted with the latter. The points for the sydnones and sydnonimines lie on the general correlation line (Fig. 2), the slope of which corresponds to $\beta_{\text{eff}} = 4.1$ eV (variant A in [1]) and 5.1 eV (variant B). Let us recall that in [1], $\beta = 4.17$ eV corresponded to variant A, and $\beta = 4.90$ eV corresponded to variant B. The point for the sydnonimine cation diverges, since computation with the parameters from the PPP method predicts an LVMO energy for it that is too low.

Thus we have shown in this paper that the calculations of sydnones and sydnonimines by the Hückel method with parameters obtained from the PPP method make it possible to correctly describe the changes as a function of the structure and polarographic reduction potential of sydnones and sydnonimines, as well as the dipole moment of sydnone (with allowance for the σ-skeleton charges calculated by the Del Re method). It was shown that the C and O atoms of the exocyclic carbonyl group of sydnones are carriers of large positive and negative $(\pi + \sigma)$ charges at high orders of the exocyclic C=O bond in sydnones, which is in good agreement with concepts regarding the high degree of double bond character and polarity of this bond [15, 23, 24].

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*The Streitwieser parameters [10] were used in [1] for benzaldehyde and for the substituent atoms in substituted sydnones and sydnonimine.