

USE OF SEMIEMPIRICAL METHODS FOR THE PREDICTION OF EQUILIBRIUM GEOMETRIES AND IONIZATION POTENTIALS OF 4H-PYRAN-4-ONE AND SULPHUR ANALOGUES

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ABSTRACT

Equilibrium geometries and ionization energies of 4H-pyran-4-one (I), 4H-pyran-4-thione (II), 4H-thiapyran-4-one (III) and 4H-thiapyran-4-thione (IV) are calculated by CNDO/2 and MINDO/3 semiempirical methods. The geometries obtained are compared to the MW data available for I, II and IV. Reliability of geometry optimization and predictions based on semiempirical results are discussed.

For I the vertical ionization energies estimated from ab initio, CNDO/2 and MINDO/3 orbital energies are compared to each other and to those obtained by HAM/3 calculations. The HAM/3 results are in the best agreement with the experimental data. For systematic HAM/3 studies on molecules for which no experimental geometries are available, the use of CNDO/3 or MINDO/3 optimized geometries is suggested.

INTRODUCTION

Molecular geometries are, in addition to thermodynamic data, among the quantities most frequently cited by the everyday chemists. For instance, from relations between geometrical parameters within one molecule or in a series of molecules, characteristic variations in reactivities or relative magnitudes of certain spectroscopic constants can be predicted. A series of different experimental techniques has been developed for the determination of molecular geometries. Although the physical meaning of the geometrical parameters determined by different methods are different [1], the numerical

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values obtained e.g., from diffractational and spectroscopic studies can be compared to each other.

In general, the experimental geometries denoted r_g and r_s , obtained from gas-phase electron-diffraction (ED) and microwave (MW) spectroscopy, respectively, are suggested as the best estimates of r_e values, the hypothetical "equilibrium" arrangement of the nuclei. Empirical determination of r_e geometries is possible only for simple, highly symmetric species, since the different observations result in expectational values averaged over various rotational and vibrational states.

On the other hand, equilibrium geometries can quite easily be determined from quantum chemical calculations where they are defined via the nuclear positions belonging to the absolute minimum of the potential energy surface. For recent reviews on ab initio predictions of geometries see refs. 2 and 3; on semiempirical methods see refs. 4–9. In spite of the fact that there are some molecular systems for which semiempirical methods certainly fail to reproduce the experimental data, it must be accepted that they do well in reproducing trends in geometries. Within a series of congeners the errors are mainly of a systematic character, thus the utility of the semiempirical methods in structure predictions cannot be undermined [9]. In spite of the convincing facts, CNDO and MINDO type methods are frequently regarded as out of date and their results are disregarded (see e.g., ref. 2). Such treatment is surprising, at least, in the light of the huge number of successful applications.

We share the opinion of Dewar [10] that a computer carrying out semiempirical calculations should be regarded as a "device" producing "empirical" results with known, almost systematic errors. Thus, using semiempirical methods one should not attempt the reproduction of results for individual molecules but trends in a family of molecules with similar structure. It should be noted here, that without any a posteriori scaling the ab initio calculations, even after the inclusion of limited CI expansion, may reproduce only trends in certain molecular properties and provide only rough estimates for some observable quantities. The situation with equilibrium geometries, force fields and related quantities has been reviewed recently by Fogarasi and Pulay [11]. It is worthy of note also that the ideas proved to be most fruitful for "the chemists" of recent decades, borne in the frame of very simple semiempirical (or even empirical) results, see e.g., the Woodward–Hoffmann rules [12] or Fukui's frontier orbital theory [13].

In this work we do not intend to interpret the deviations between our semiempirical results, instead, we present two fields of application, where the use of semiempirical r_e geometries could be recommended. The first one is the prediction of "empirical" equilibrium geometries on the basis of the parallel trends in experimental data and semiempirical CNDO/2 or MINDO/3 results. The second one is the calculation of vertical ionization potentials, where the need for acceptable geometry is not very crucial, as long as the Koopman's theorem [14] is used to predict the ionization energies. In the case of the HAM/3 method [15] the dependence of computed ionization potentials on the molecular geometries is studied.

Both fields will be presented after a brief summary of computational details.

COMPUTATIONAL DETAILS

Geometry optimizations have been carried out using a modified version of Rinaldi's GEOMO program system [16] with the corrections suggested in ref. 17. Energy gradients were calculated in both CNDO/2 and MINDO/3 approximations according to Pulay's "force method" [18]. For automatic geometry optimizations the GDIIS method [19] was applied. Starting with the experimental geometries [20] for I, II and IV and an approximate geometry for III, 6–8 full SCF energy and gradient calculations were sufficient to reach the optimum in each case. Optimization was terminated when the predicted changes in the internal coordinates became less than 0.05 pm and 0.05 degrees for the bond stretchings and bendings, respectively.

The ab initio calculations on I with split valence 4-21 basis [21] was realized using the program TEXAS [22]. The ab initio results presented here are the side products of an extensive force-field calculation [23].

The HAM/3 method was used in its original parametrization [15] for the calculation of vertical ionization potentials.

GEOMETRY PARAMETERS

There are several MW studies on the structure of I–IV [20, 24]. The most comprehensive study is that of McDonald et al. [20] reporting the complete MW r_s structures and dipole moments of I, II and IV. Their results confirm the fact that the aromaticity of these compounds is negligible [25]. Delocalization effects increase passing from I to IV, however. The experimentally determined large and almost constant dipole moments [20, 26] support the earlier assumption [27] that these molecules are highly polarized. Compound III has been studied less extensively, MW structural data are not available for it.

Very recently an NMR study on the r_α structure of I was also published [28]. The conclusion of this work is that there are only negligible differences between the gas-phase and nematic-phase structures.

Optimized geometries for compounds I–IV obtained by CNDO/2 and MINDO/3 methods are listed in Table 1 together with the available experimental data [20]. The numbering of atoms is given in Fig. 1. As they were obtained for other types of heterocyclic compounds [7], the exo-ring distances are in better agreement with the experimental values than the extra-ring ones and the C–H bond lengths are overestimated by up to 4 pm by both methods.

The bond angles are reproduced better by the MINDO/3 than by the CNDO/2 method. The average error in the exo-ring angles is 1.7° and 3.1°, respectively.

TABLE I

Experimental and theoretical equilibrium molecular geometries for compounds I-IV

Parameter ^a	I		II ^e		III ^e		IV			
	Exp. ^b	CNDO/2 ^c	MINDO/3 ^c	Exp. ^b	CNDO/2 ^c	Exp. ^d	CNDO/2 ^c	Exp. ^b	CNDO/2 ^c	MINDO/3 ^c
r(X ₁ -C ₁)	135.8	135.7	132.8	135.3	135.5	172	172.4	175.9	175.2	173.8
r(C ₂ =C ₃)	134.4	133.7	135.3	135.7	134.3	133	133.0	134.2	133.7	134.3
r(C ₃ -C ₄)	146.3	144.0	148.8	143.1	142.0	145	144.4	140.6	142.2	146.3
r(C ₁ -H ₇)	107.9	111.8	111.4	108.2	111.8	108	111.3	108.2	111.3	110.1
r(C ₃ -H ₆)	108.2	111.4	110.3	108.2	111.4	108	112.0	108.2	112.1	110.9
r(C ₁ -Y ₁)	122.6	128.0	121.1	166.5	168.1	123	128.0	167.1	167.1	161.6
∠H ₇ C ₂ X ₁	110.9	108.8	109.5	111.4	109.2	113	112.2	- ^f	112.0	112.7
∠H ₆ C ₃ C ₄	119.1	120.0	121.1	120.4	121.2	115	116.0	- ^f	116.7	115.6
∠C ₆ X ₁ C ₂	117.3	113.4	121.5	116.9	114.5	104	108.5	101.4	109.5	106.1
∠X ₁ C ₂ C ₃	123.9	126.3	122.4	123.8	125.6	122	119.4	122.4	118.9	121.1
∠C ₂ C ₃ C ₄	120.9	120.3	120.9	120.3	119.0	129	126.2	128.1	124.1	127.0
∠C ₃ C ₄ C ₅	113.1	113.4	111.9	114.9	116.3	114	120.3	117.5	124.5	117.7

^aBond lengths in pm, bond angles in degrees.^bReference 20.^cThis work.^dNo experimental data are available, the listed values are predicted from the present calculations.^eNo MINDO/3 parameters are available for the O-S bond.^fExperimental data are not reported in ref. 20.

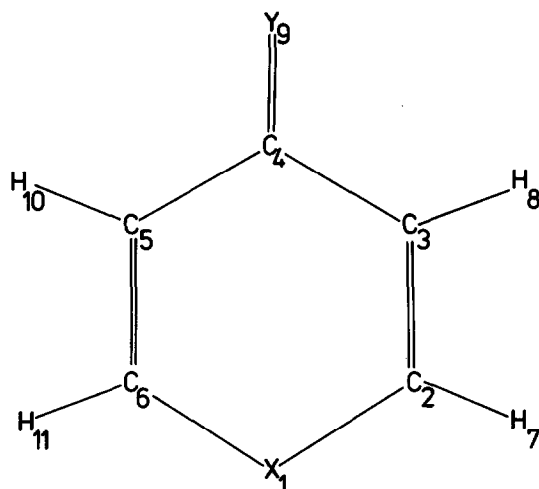


Fig. 1. Numbering of atoms in compounds I–IV (I: X = O, Y = O; II: X = O, Y = S; III: X = S, Y = O; IV: X = S, Y = S).

It is interesting to investigate how the applied methods reproduce the changes of the bond lengths and angles within this series. The changes related to the replacement of the carbonyl group to thiocarbonyl (I–II) are well reproduced by the calculations. The relative magnitudes of the calculated C=C bond lengths in I, II and IV are also in good agreement with the experiments [20].

On the basis of the observed trends it is possible to predict the expected experimental r_s geometry for compound III as given in Table 1. Of course, the validity of this prediction should be approved by experiments.

From the dipole moments given in Table 2 the prospect of an MW struc-

TABLE 2

Calculated and experimental dipole moments^a of compounds I–IV

	I	II	III	IV
CNDO/2 ^b	3.84	3.73	1.93	1.09
MINDO/3 ^b	4.73	— ^c	— ^c	4.63
Ab initio ^d	3.85	—	—	—
Exp. ^e	3.79	3.95	—	3.9
Exp. ^f	3.72	4.08	3.96	4.41

^aIn Debyes = 3.33564×10^{-30} Cm. ^bThis work, at geometries optimized on the same level. ^cNo MINDO/3 parameters are available for the O–S bond. ^dAb initio 4-21 calculation at corrected MW geometry, ref. 23. ^eReference 20. ^fReference 26.

tural study on compound III is not bad. Its computed dipole moment is comparable with that of compound IV.

From inspection of the data of Table 2 it may be seen that CNDO/2 and ab initio calculations resulted in almost the same dipole moment for compound I. For compounds III and IV, by contrast to the available experimental data and MINDO/3 results, CNDO/2 gives a distinct, very low dipole moment. This could be attributed to the inclusion of *d*-functions on the sulphur atoms, leading to overestimated charges on these atoms, reducing the dipole moments considerably.

IONIZATION ENERGIES

According to the Koopman's theorem [14] the ionization potentials obtained from photoelectron spectroscopy (PES) experiments can be related directly to the orbital energies calculated by quantum chemical methods. In spite of its well established limited validity, the Koopmans' theorem is widely used for estimation of the ionization energies and for the assignation of the experimental PE spectra.

The ionization potentials of compounds I–IV have been investigated experimentally by Colonna et al. [29]. In their photoelectron (He(I) and He(II) UPS and XPS) study full assignments are given for the valence orbital and core ionizations of compounds I–IV. In order to facilitate the assignments they have also carried out CNDO/2 and ab initio (for compound I only) calculations at standard geometries. As was expected, the CNDO/2 calculations failed to reproduce the absolute value of ionization energies, and even worse, the order of the MO energies is not acceptable.

The ionization energies of compound I calculated by CNDO/2, MINDO/3, ab initio and HAM/3 methods at the theoretical equilibrium and/or experimental geometries together with the experimental values and assignments of ref. 29 are shown in Table 3. It is seen that the calculated orbital energies are quite independent of the geometry at which the SCF calculations are carried out. Therefore, for the three other compounds the orbital energies are calculated only at the theoretical optimized geometries. The results obtained and those calculated by Colonna et al. [29] are listed in Table 4 together with the experimental values [29]. One can observe that for II, III and IV the differences between our CNDO/2 results and those of ref. 29 are greater than for I. This is because of the very different geometries used by Colonna et al. and by us.

It is seen also from Tables 3 and 4 that the ionization energies obtained by the CNDO/2 method differ considerably from the corresponding experimental values both in the orbital energies and in the order of the orbitals. The agreement with the MINDO/3 orbital energies is somewhat better but also far from satisfactory, mainly in the low energy region.

The ionization energies of I calculated by the HAM/3 method are in excellent agreement with the experimental values. It is seen that HAM/3 results,

TABLE 3

Experimental and calculated vertical ionization potentials (eV) of 4H-pyran-4-one (I)

Assignment ^a	Exp. ^a	HAM/3 ^b		MINDO/3 ^c		Ab initio		MINDO/3 ^b		CNDO/2 ^b	
		CNDO/2 ^c	MWD	MINDO/3 ^c	MWD	4-21 ^e	STO-3G ^a	opt. ^f	MWD	opt. ^f	MWD
6b ₂ (n γ)	9.35	8.99	9.33	9.34	9.33	10.98	8.44	9.31	9.32	12.51	12.36
3b ₁ (π)	9.52	9.63	9.73	9.62	9.73	9.53	6.59	9.39	9.51	11.74	11.91
1a ₂ (π)	10.90	10.91	10.90	10.75	10.90	11.10	9.50	10.38	10.49	15.90	15.78
2b ₁ (π)	12.85	12.97	13.20	13.14	13.20	14.59	12.33	13.61	13.51	19.04	19.25
8a ₁	12.25	13.13	13.47	13.38	13.47	14.66	12.00	10.92	11.01	15.46	15.52
5b ₂		13.55	13.65	13.55	13.65	15.32	13.58	12.45	12.41	16.55	16.97
7a ₁	13.7	14.00	14.07	14.09	14.07	16.40	13.67	12.88	12.98	18.91	18.76

^aReference 29.^bThis work.^cHAM/3 calculations at the CNDO/2 and MINDO/3 optimized geometries, respectively.^dCalculations at the microwave geometry of ref. 20.^eReference 23, at corrected r_s geometry.^fCalculations at the corresponding optimized geometries.

TABLE 4

Experimental and calculated vertical ionization potentials (eV) of compounds II-IV

Assignment ^a	II			III			IV					
	Exp. ^a	CNDO/2 ^a	CNDO/2 ^b	Assignment ^a	Exp. ^a	CNDO/2 ^a	CNDO/2 ^b	Assignment ^a	Exp. ^a	CNDO/2 ^a	CNDO/2 ^b	MINDO/3 ^b
6b ₂ (nγ)	8.10	10.18	10.52	3b ₁ (π)	8.97	11.18	10.91	6b ₂ (nγ)	7.96	10.36	11.18	8.51
3b ₁ (π)	8.44	9.91	9.72	6b ₂ (nγ)	9.25	12.29	12.57	3b ₁ (π)	8.11	9.74	9.57	8.42
1a ₂ (π)	10.66	16.00	15.97	1a ₂ (π)	10.73	15.78	16.73	1a ₂ (π)	10.50	15.79	16.70	10.72
2b ₁ (π)	11.60	17.91	18.24	2b ₁ (π)	11.91	15.94	15.71	2b ₁ (π)	11.9	14.79	14.45	10.96
8a ₁	12.3	13.19	13.22	8a ₁	12.5	14.66	13.79	8a ₁	12.2	13.01	13.36	9.68
5b ₂		15.48	15.48	5b ₂		15.32	15.34	5b ₂		14.04	13.80	10.30
7a ₁	12.7	17.79	17.96	7a ₁	12.8	16.88	16.97	7a ₁	12.55	15.35	14.28	10.67

^aReference 29.^bThis work, calculations at the optimized geometries.

at any appropriate geometry, are in better agreement with the experiments than the ab initio results using 4-21 basis set. It seems that our ab initio results are also examples of the breakdown of the Koopmans' theorem in α, β -unsaturated carbonyl compounds [30].

In spite of the fact that the orbital energies and the order of the orbitals are not very sensitive for the geometry used in HAM/3 calculations (see Table 3) it could be observed that the lone-pair orbital energies, $6b_2(n_Y)$, are dependent on the C=Y bond length. We suggest that this variation may be important when the molecule studied has a π orbital with approximately the same energy as that of a lone-pair orbital. When tendencies in ionization energies are studied, it is desirable to use geometries obtained in the same way: either quantum chemically or experimentally.

Unfortunately, traditional semiempirical methods without further efforts cannot be used for the interpretation of the PE spectra, except for the low-lying ionization energies by MINDO/3. For systematic studies of ionization energies with the HAM/3 method we recommend the use of CNDO/2 and/or MINDO/3 optimized geometries.

CONCLUSIONS

The results presented in this work support the almost generally accepted suggestions that semiempirical quantum chemical methods are useful for geometry predictions within a series of compounds with similar structure. Geometry variations on different substitutions can be well predicted by both the CNDO/2 and MINDO/3 methods.

Our results obtained by the HAM/3 method on the orbital energies of compound I support the use of the HAM/3 method for the interpretation of the photoelectron spectra. Its performance is superior to the ab initio results using basis sets of double-zeta quality. Comparison our theoretical results obtained at different geometries, it is concluded that the orbital energies may vary within 0.2–0.3 eV depending upon the geometry used. Although these differences are practically unimportant, for systematic studies it is desirable to use geometries obtained in a consistent way. We suggest the use of CNDO/2 or MINDO/3 optimized geometries both in HAM/3 studies and for prediction of low-lying ionization energies by MINDO/3.

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