Tetrahedron Letters No. 52, pp 4627 - 4630, 1977. Pergamon Press. Printed in Great Britain.

THE SEMIEMPIRICAL METHOD HAM/3, APPLIED TO URACIL

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(Received in UK 20 October 1977; accepted for publication 3 November 1977)

The new semiempirical method HAM/3 [1] is based upon a complex description of the atoms from which a molecule is composed. The total energies of these atoms are calculated using shielding constants which were introduced by Slater in 1930 [2]. It is possible to determine these "constants" so that very good agreement with spectroscopic atomic energies is obtained.

From this description and using these shielding constants a molecular orbital SCF method has been constructed.

It has been shown [1] that these shielding constants give very good agreement with experiment, not only for atoms in their ground and ionized states but also for molecules. Therefore it is reasonable to assume that the HAM/3 calculation gives results where errors due to correlation energies or self-repulsion are small or essentially non-existent.

Since correlation energies are supposed to be negligible, Koopman′s theorem cannot be used. Instead, the ionization energies are calculated using a transition state method.

Since in Slater′s work [2] no self-repulsion was introduced, the unoccupied orbitals from the HAM/3 calculation are "excited" and not "virtual". Excitation energies are therefore obtained as the difference of the eigenvalues of the occupied and the unoccupied orbitals. The singlet-triplet splitting can then be easily calculated using PPP-methods.

Electron affinities can easily be calculated using a transition state.

Results obtained with the HAM/3 method have already been presented for ethylene, butadiene, benzene, pyridine, ozone, cyclopropane [1], N_2, CO, HCN, HCCH, CO_2, N_2O, C_2N_2 [3], formic acid [4], TCNQ and p-quinodimethane [5]. In this paper the results of a study of uracil will be presented.

The x-ray crystallographic geometry [6] was used in the calculations although with lengthened C-H and N-H bonds [7]. Only with this correction could correct ordering of the orbitals be obtained.

The result of the HAM/3 calculation is shown in the Table on next page. The calculation is performed for a transition state in which $\frac{1}{2}$ electron has been ionized in order to obtain the ionization energies (not orbital energies!). The orbitals 1-21 are occupied. The higher orbitals are "excited".

URACIL

ONE HALF ELECTRON DIFFUSELY REMOVED. FILLED ORBITALS GIVE IONIZATION ENERGIES

	13	14	15	16	17	18	19	20	21	22	23	24	25
	-14.955	-14.443	-13.739	-13.628	-12.760	-10.742	-10.554	-9.881	-9.791	-5.531	-4.370	-1.713	6.301
N 1	0.044	0.025	0.034	0.0	0.0	-0.097	0.0	-0.018	0.0	0.0	0.0	0.0	-0.557
N 1	0.036	0.067	-0.001	0.0	0.0	0.038	0.0	-0.013	0.0	0.0	0.0	0.0	-0.079
N 1	-0.020	-0.205	-0.072	0.0	0.0	-0.183	0.0	0.011	0.0	0.0	0.0	0.0	-0.145
N 1	0.0	0.0	0.0	-0.350	0.461	0.0	-0.118	0.0	-0.491	0.306	0.318	-0.276	0.0
C 2	-0.114	0.042	0.009	0.0	0.0	0.002	0.0	0.013	0.0	0.0	0.0	0.0	0.579
C 2	0.178	-0.119	0.067	0.0	0.0	-0.039	0.0	0.008	0.0	0.0	0.0	0.0	0.183
C 2	-0.050	0.147	0.072	0.0	0.0	-0.046	0.0	0.0	0.0	0.0	0.0	0.0	-0.088
C 2	0.0	0.0	0.0	-0.222	-0.278	0.0	0.026	0.0	-0.040	0.108	-0.742	0.336	0.0
N 3	0.074	0.017	-0.024	0.0	0.0	0.113	0.0	-0.110	0.0	0.0	0.0	0.0	-0.483
N 3	0.018	0.163	-0.069	0.0	0.0	-0.154	0.0	-0.174	0.0	0.0	0.0	0.0	0.130
N 3	-0.237	-0.166	-0.060	0.0	0.0	-0.061	0.0	0.068	0.0	0.0	0.0	0.0	0.146
N 3	0.0	0.0	0.0	0.300	-0.282	0.0	-0.658	0.0	0.108	-0.320	0.202	-0.355	0.0
C 4	-0.140	-0.113	0.049	0.0	0.0	-0.022	0.0	0.030	0.0	0.0	0.0	0.0	0.124
C 4	-0.115	-0.172	0.151	0.0	0.0	0.025	0.0	-0.041	0.0	0.0	0.0	0.0	-0.152
C 4	0.144	0.207	0.280	0.0	0.0	0.006	0.0	-0.013	0.0	0.0	0.0	0.0	0.216
C 4	0.0	0.0	0.0	0.540	0.053	0.0	0.099	0.0	-0.017	0.441	0.333	0.630	0.0
C 5	0.029	0.058	-0.009	0.0	0.0	0.002	0.0	0.096	0.0	0.0	0.0	0.0	0.041
C 5	0.154	0.140	0.006	0.0	0.0	-0.006	0.0	0.027	0.0	0.0	0.0	0.0	0.018
C 5	-0.236	-0.258	-0.270	0.0	0.0	-0.029	0.0	0.200	0.0	0.0	0.0	0.0	0.017
C 5	0.0	0.0	0.0	0.169	0.283	0.0	0.141	0.0	0.549	0.384	-0.323	-0.621	0.0
C 6	-0.059	-0.040	-0.005	0.0	0.0	0.007	0.0	-0.002	0.0	0.0	0.0	0.0	0.158
C 6	0.004	-0.048	0.057	0.0	0.0	-0.013	0.0	-0.033	0.0	0.0	0.0	0.0	-0.263
C 6	0.092	0.216	0.141	0.0	0.0	0.050	0.0	-0.045	0.0	0.0	0.0	0.0	0.166
C 6	0.0	0.0	0.0	-0.090	0.494	0.0	0.037	0.0	0.322	-0.686	0.065	0.439	0.0
O 7	0.355	-0.251	0.020	0.0	0.0	-0.011	0.0	-0.006	0.0	0.0	0.0	0.0	-0.109
O 7	-0.503	0.469	0.009	0.0	0.0	-0.472	0.0	-0.061	0.0	0.0	0.0	0.0	-0.193
O 7	0.304	-0.226	0.086	0.0	0.0	-0.824	0.0	-0.030	0.0	0.0	0.0	0.0	0.115
O 7	0.0	0.0	0.0	-0.237	-0.415	0.0	0.566	0.0	0.251	-0.091	0.521	-0.172	0.0
O 8	0.149	0.133	-0.354	0.0	0.0	-0.004	0.0	0.011	0.0	0.0	0.0	0.0	-0.052
O 8	0.149	0.119	-0.653	0.0	0.0	-0.019	0.0	-0.502	0.0	0.0	0.0	0.0	0.120
O 8	0.180	0.235	-0.306	0.0	0.0	-0.072	0.0	0.804	0.0	0.0	0.0	0.0	-0.033
O 8	0.0	0.0	0.0	0.463	0.066	0.0	0.452	0.0	-0.501	-0.409	-0.239	-0.316	0.0
H 9	0.208	0.219	0.076	0.0	0.0	0.008	0.0	-0.018	0.0	0.0	0.0	0.0	0.062
H10	-0.087	-0.171	-0.104	0.0	0.0	-0.046	0.0	0.034	0.0	0.0	0.0	0.0	-0.025
H11	0.023	0.023	0.038	0.0	0.0	0.018	0.0	-0.002	0.0	0.0	0.0	0.0	0.253
H12	-0.104	-0.110	-0.069	0.0	0.0	-0.019	0.0	0.027	0.0	0.0	0.0	0.0	0.170

The photoelectron spectrum of uracil [8] is shown in Fig. 1 together with the ionization energies given in the Table. In the lower part of the figure the five highest orbitals of uracil have been denoted as π, n, π, n, π. This order has been determined from studies of the vibrational structure in the photoelectron spectrum and from comparisons with substituted uracils [8, 9, 10] and also by a study of substituted ureas and other fragments of uracil [11].

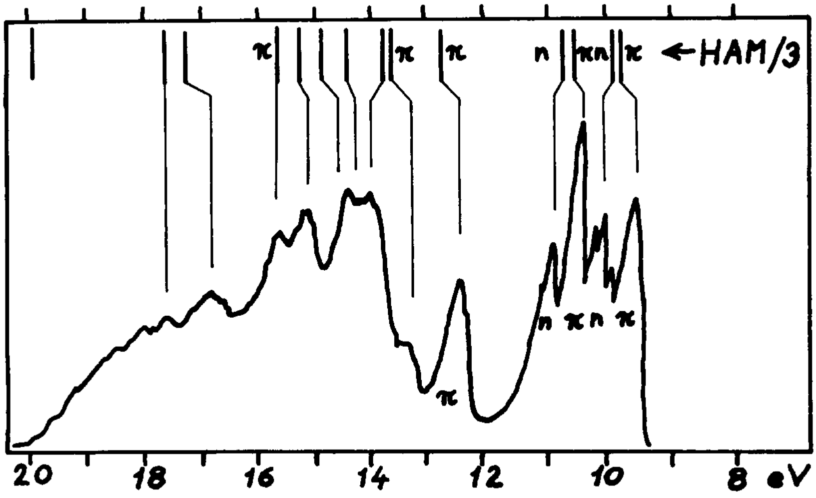
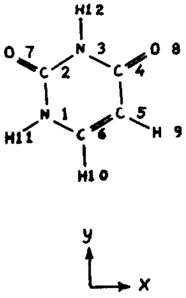


Fig. 1. Photoelectron spectrum of uracil [8].



The photoelectron spectrum in Fig. 1 exhibits very satisfactory agreement with the HAM/3 ionization energies, and the ordering of the orbitals is also in good agreement. No empirical adjustments of the calculated energies are necessary to achieve this agreement.

Usually, however, calculations of the ab initio and semiempirical types give results which differ from the photoelectron-spectroscopic ionization energies, often by large amounts. It is then necessary to introduce empirical corrections. In a recent ab initio study [12] (see also [7]) the correction is performed using the following empirical formula:

Ionization energy = 7.52 eV - 0.551 · (calculated energy)

It is obviously not easy to judge the quality or physical meaning of such a calculation. It has recently been stated that "existing computational methods are not adequate to the task of generating good MO energies for these molecules and hence, relative donor-acceptor (base-acid) characteristics" [13].

Excitation energies are obtained directly from the Table above. For example, the transition 21→22 has an excitation energy of 9.791 - 5.531 = 4.240 eV. The singlet energy of 5.34 eV is then obtained by adding the exchange integral K (= 1.080 eV) which can easily be calculated. (A simple configuration interaction calculation changes this to 5.10 eV). All possible valence transitions are calculated but only few (of ππ* type) have high intensity and are plotted in Fig. 2.

The UV absorption of uracil has been studied in the gas [14], the liquid [15] and the solid [16] phase. The electron impact energy loss in a solid film [17] has also been studied. It is seen from Fig. 2 that there is good agreement between the HAM/3 calculations and experiment. In earlier work (e.g. [18]) it was difficult to explain the high intensities above 6.5 eV and to calculate the nπ* energies.

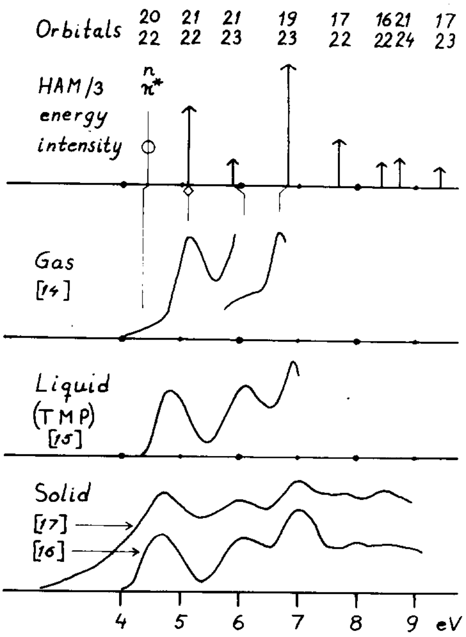


Fig.2. Excitation of uracil.

The computer time used for the calculations presented in this paper was 21 seconds.

Conclusions: The HAM/3 semiempirical method simultaneously gives good agreement with experimental ionization energies and excitation energies. The method may therefore be useful for the calculation of the energies of HOMO and LUMO which often are of interest in organic chemistry.

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