Gas-phase Tautomerism in 2,4-Dihydropyrazol-3-ones: an Ultraviolet Photoelectron Spectroscopic Study and MNDO Molecular Orbital Calculations

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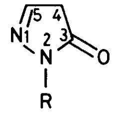
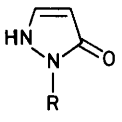
The He^I photoelectron spectra of 2,5-dimethyl-, 5-methyl-2-phenyl-, 4,4,5-trimethyl-2-phenyl-, and 5-amino-2-phenyl-2,4-dihydropyrazol-3-one and 1,5-dimethyl-2-phenyl-1,2-dihydropyrazol-3-one have been recorded. Comparison of the spectra where three tautomeric forms may be present with those of the fixed tautomeric forms and with MNDO calculations indicates that the 2,4-dihydropyrazol-3-one is the predominant tautomeric form in the gas phase. The low ionization energy bands are assigned on the basis of MNDO calculations. The HOMO in 2,5-dimethyl-2,4-dihydropyrazol-3-one has $n_{N\text{-}2}\text{–}\pi_{C=N}$ character and the oxygen lone pair is the second outermost occupied MO. In the 2-phenyl derivatives, these MOs are in reverse order. The calculated relative stability of the tautomeric forms increases in the order 1,2-dihydropyrazol-3-one, 5-hydroxy-1*H*-pyrazole, 2,4-dihydropyrazol-3-one.

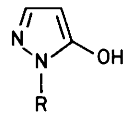
The tautomeric equilibria of 2,4-dihydropyrazol-3-one derivatives have been widely studied in solutions. I.r., u.v., n.m.r., and pK_a measurements revealed that, in non-polar solvents, the CH tautomeric form predominates and, with the increasing polarity of the solvent, the equilibrium shifts towards the NH and OH forms.[1–10]



CH



NH



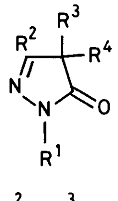
OH

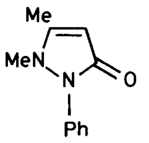
X-Ray diffraction studies show that the OH and NH forms are present in the solid state;[11] however, information on the gas; phase equilibria is scarce. The presence of the 1 740 cm^{-1} band in the i.r. spectra of the gas phase indicates that the gas-phase equilibrium favours the CH and NH form.[12,13] Fragmentation patterns in the mass spectra favour the CH form but possible changes in the relative stability of tautomers on going from neutral forms to the radical cation prevent unambiguous conclusions.[14]

Comparison of ultraviolet photoelectron (PE) spectra of some 2,4-dihydropyrazol-3-ones with the orbital energies calculated by the HAM/3 method also indicates that the CH form predominates in the gas phase.[15] Various semiempirical calculations assuming the planarity of the tautomeric forms and using estimated bond lengths and angles have predicted the highest stability for the CH form,[16,17] and the MNDO method has been succesfully used for investigation of the influence of methyl substituents on the tautomeric equilibria.[18]

Gas-phase ultraviolet PE spectroscopy is a particularly suitable technique for the investigation of tautomeric equilibria. The tautomeric forms differ in the orbitals involved in the π-bonding and consequently different ionization energies (I.E.s) of the outermost molecular orbitals are observed.

The aim of this work is to obtain further information on the gas-phase tautomeric equilibria of 2,4-dihydropyrazol-3-one derivatives and to provide a deeper insight into the electronic structure of tautomeric forms. The comparison of the PE spectra of the tautomerizable derivatives (**2**)—(**4**) with the spectra of species fixed in the CH (**5**) and NH (**6**) form allows a more reliable conclusion to be drawn on the site of the tautomeric equilibria. The MNDO calculations were carried out with the full optimization of the geometry of the pyrazole ring avoiding the uncertainty which stems from the use of estimated internal co-ordinates in previous calculations.[15–18]





(**6**)

(**1**) $R^1 = R^2 = R^3 = R^4 = H$
(**2**) $R^1 = R^2 = Me,\ R^3 = R^4 = H$
(**3**) $R^1 = Ph,\ R^2 = Me,\ R^3 = R^4 = H$
(**4**) $R^1 = Ph,\ R^2 = NH_2,\ R^3 = R^4 = H$
(**5**) $R^1 = Ph,\ R^2 = R^3 = R^4 = Me$

Experimental and Computational Details

The He^I PE spectra were recorded on a VG Scientific UVG 3 instrument at temperatures in the range from 100—200 °C. The Ar–Xe mixture served as the internal calibration standard. The resolution, 30–40 meV measured on the Ar $^2P_{3/2}$ peak, was constant over the whole spectrum.

The samples were kindly provided by the late Professor M. Scholtz (Sektion Chemie, Karl Marx Universität Leipzig, DDR). The purity of the samples was checked by mass spectrometry.

The MNDO calculations[19] were carried out with localization of the minimum on the energy hypersurface. The experimental values adopted[20–22] were for the C–H bond length in the methyl groups, the N–H bond length in the amino group, and the phenyl ring internal co-ordinates, while the other internal co-ordinates were allowed to relax. The pyrazole ring was allowed to become non-planar: the resulting dihedral angles in the ring did not exceed 6° and the C–C–C–O dihedral angle

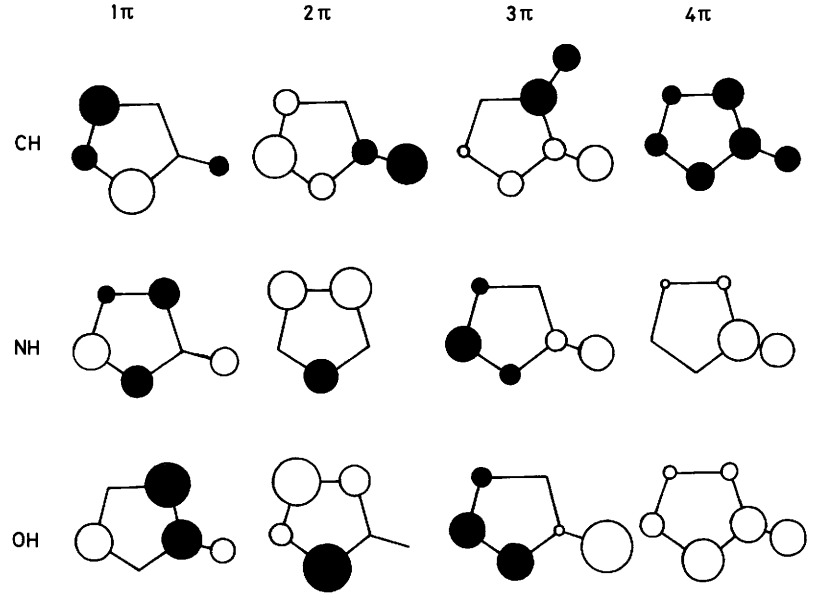


Figure 1. Schematic drawing of the π-orbitals of the tautomeric forms of dihydropyrazole-3-one (**1**)

Table 1. Calculated molecular orbital energies for tautomeric forms of dihydropyrazol-3-one

Form	MO Energy/ −eV			
CH	10.08 (1π)	11.27 (n_O)	12.85 (n_{N-1})	13.56 (2π)
	14.22 (3π)	15.05 (σ)	15.88 (σ)	16.60 (4π)
NH	9.71 (1π)	10.88 (2π)	11.61 (n_O)	13.14 (3π)
	14.76 (4π)			
OH	9.19 (1π)	10.04 (2π)	11.94 (n_{N-1})	13.74 (3π)
	14.48 (σ)	14.59 (σ)	15.78 (4π)	

deviated by less than 8° from planarity in all the molecules under study.

Results and Discussion

General Features of the Valence Orbitals.—Before discussing the interpretation of the PE spectra, we will first describe the character of the less tightly bound valence orbitals in the tautomeric forms of the parent 2,4-dihydropyrazol-3-one (**1**). In all the forms, the ring is nearly planar and the electronic structure can be described in terms of π- and σ-MOs. The six p_z orbitals give rise to four occupied π-MOs.

The HOMO (1π) of the CH form may be regarded as arising from the antisymmetric combination of the n_{N-2} orbital and $\pi_{C=N}$ orbital (Figure 1). The 2π-MO has the character of the out-of-phase combination of the $\pi_{C=O}$ orbital and the ring p_z orbitals. A significant contribution to the 3π-MO comes from the CH_2 group π-type orbital. The 4π-MO lacking any nodal plane perpendicular to the ring lies below the highest ring σ orbitals (Table 1). The non-bonding lone pair of the carbonyl oxygen (n_O) lies above that of the imine nitrogen atom.

The HOMO of the NH form (1π) has the character of a combination of the antibonding nitrogen lone pairs with the contribution of the $\pi_{C=C}$ orbital. The 2π-MO is mainly $\pi_{C=C}$ in character with the fairly high density in the N-2 p_z orbital. The shape of the 3π-MO is very close to that of the 2π-MO of the CH form. The lowest MO denoted as 4π has its main contribution from the $\pi_{C=O}$ orbital.

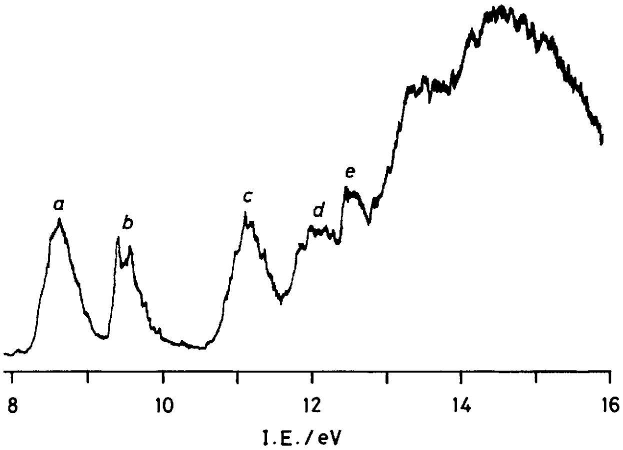


Figure 2. He^I Photoelectron spectrum of 2,5-dimethyl-2,4-dihydropyrazol-3-one (**2**)

In the OH form, the $\pi_{C=C}$ orbital can be considered as the main contribution to the HOMO (1π). The 2π-MO cannot be classified simply in terms of fragment analysis. The electron density in the 3π-MO is approximately equally divided between the hydroxy oxygen and the ring. The lowest 4π-MO is located below the highest ring σ-MOs.

2,5-Dimethyl-2,4-dihydropyrazol-3-one (**2**).—The He^I PE spectrum of (**2**) (Figure 2) has two low-energy bands and three less resolved features at the edge of the broad band envelope. Two sharp peaks and a shoulder on the high-energy side are resolved within band *b*. The spacing amounts to 1 210 and 1 170 cm^{-1} (Table 2). These values are very close to the vibrational intervals exhibited by the carbonyl lone pair band.[23] Thus, band *b* can be assigned to the carbonyl lone pair ionization. It follows that CH or NH is the predominant form. The MNDO calculations for (**2**) predict that the oxygen lone pair will lie just below the HOMO in the CH form, whereas in the NH form it is the third outermost MO (Figure 3). The nearly symmetric shape of band *a* indicates that it comes from one rather than two ionizations. Moreover, the calculation predicts a 1-eV gap

Table 2. Experimental ionization energies (eV) and band assignments[a]

Band	(2)	(3)	(4)	(5)	(6)
a	8.65 (1π)	8.00 (ph πb_1)	7.70 (ph πb_1)	7.88 (ph πb_1)	7.86 (ph πb_1)
b	9.42 (n_0)	9.09 (ph πa_2)	9.02 (ph πa_2)	8.94 (ph πa_2)	8.78 (1π)
	9.57[b]				
	9.72[b]				
c	11.15(n_{N-1})	9.33 (n_0)	9.42[c]	9.08 (n_0)	9.05 (ph πa_2)
d	12.06 (2π)	9.49[b]	11.01 (n_{N-1})	9.22[b]	9.37 (2π)
e	12.57 (3π)	9.90 (1π)	11.80 (ph + 2π)	9.76 (1π)	10.14 (n_0)
f		11.03 (n_{N-1})	12.41 (ph + 3π)	10.60 (n_{N-1})	11.16 (3π)
g		11.76 (ph + 2π)		11.67 (ph + 2π)	11.80 (ph)
h		12.44 (ph + 3π)		12.45 (ph + 3π)	

[a] Values quoted are for the band maxima; estimated acuracy ±0.05 eV. ph indicates phenyl orbitals [b] Vibrational progression of the n_0 ionization. [c] Overlapping ionization of n_0, $1\pi_{CH}$, and n_{NH_2} orbital.

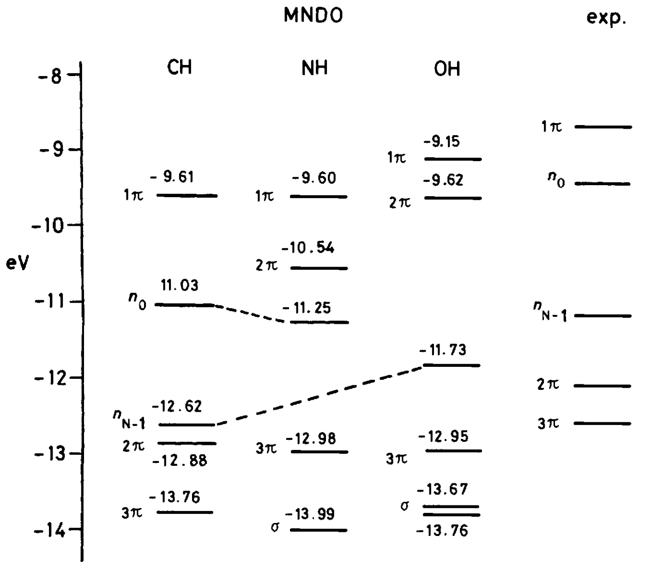


Figure 3. Comparison between orbital energies and experimental I.E.s of 2,5-dimethyl-2,4-dihydropyrazol-3-one (2)

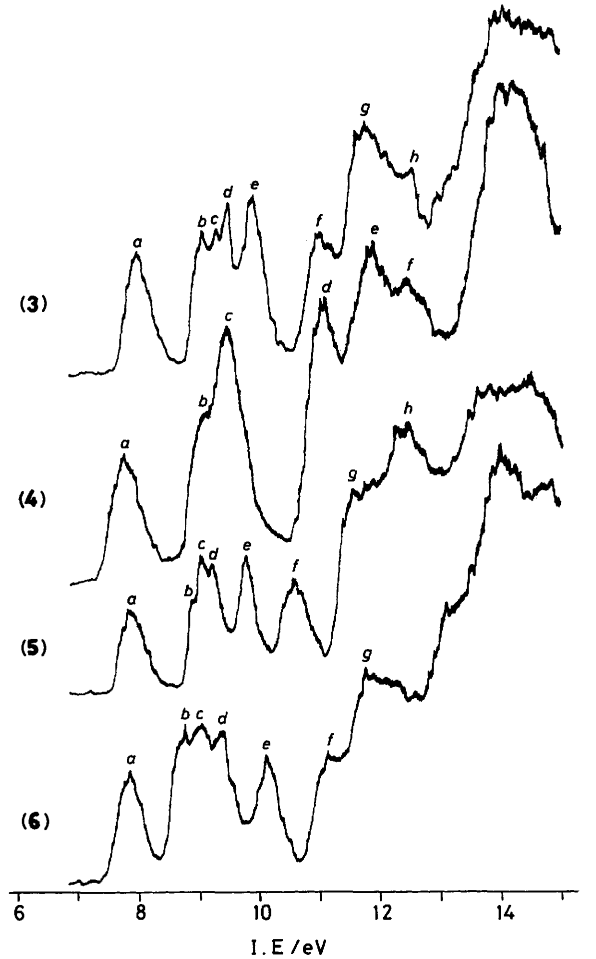


Figure 4. He^I Photoelectron spectra of 5-methyl-2-phenyl-2,4-dihydropyrazol-3-one (3), 5-amino-2-phenyl-2,4-dihydropyrazol-3-one (4), 4,4,5-trimethyl-2-phenyl-2,4-dihydropyrazol-3-one (5), and 1,5-dimethyl-2-phenyl-1,2-dihydropyrazol-3-one (6)

between the 1π- and the 2π-MO. For the OH form, four bands could be expected in the spectrum before the onset of the σ envelope. Thus the PE spectrum can be assigned to the CH form. In accordance with the MNDO calculations, band *a* is assigned to the 1π-MO and bands *c*, *d*, and *e* to the n_{N-1}, 2π-, and 3π-orbitals, respectively.

4,4,5-*Trimethyl*-2-*phenyl*-2,4-*dihydropyrazol*-3-*one* (**5**).—The methyl groups fix structure (**5**) in the CH form. The PE spectrum (Figure 4) features 6 bands below the sharp onset of the broad band envelope at *ca.* 11 eV. The first band peaks at 7.88 eV. This is close to the I.E. of the highest phenyl π-orbital in aniline.[24] The MNDO calculations predict the highest occupied phenyl π-MOs above those of the dihydropyrazole moiety (Figure 5). We assigned band *a* to the $e_{1g}\pi$ level of the phenyl ring, namely its b_1 component (C_{2h} local symmetry of the phenyl is adopted). The *b*, *c*, and *d* bands overlap considerably. the *b*–*c* and *c*–*d* spacing is equal to 1 130 and 1 210 cm^{-1}, respectively. The following bands *e* and *f* do not exhibit any fine structure. In the PE spectrum of (**2**), vibrational transitions are observed only within the n_0 band. It is unreasonable to suppose that band *e* peaking at 9.76 eV appears as a result of the n_0 ionization. The substitution of hydrogen atoms in the α position by methyl groups cannot lead to stabilization of the n_0 orbital nor can the phenyl group exert such an effect on the lone pair orthogonal to the ring π-orbitals. We assigned bands *c* and *d* to the vibrational progressions of the n_0 ionization event and band *b* to the phenyl $e_{1g}\pi$-orbital, namely the a_2 component. The assignment of bands *b* and *c* to the n_0 ionization and band *d* to the a_2-orbital seems less probable from the spectra of (**3**) and (**5**) (see below). The remaining bands, *e* and *f*, are assigned to the 1π- and n_{N-1}-orbitals, respectively. The steep onset of the unresolved

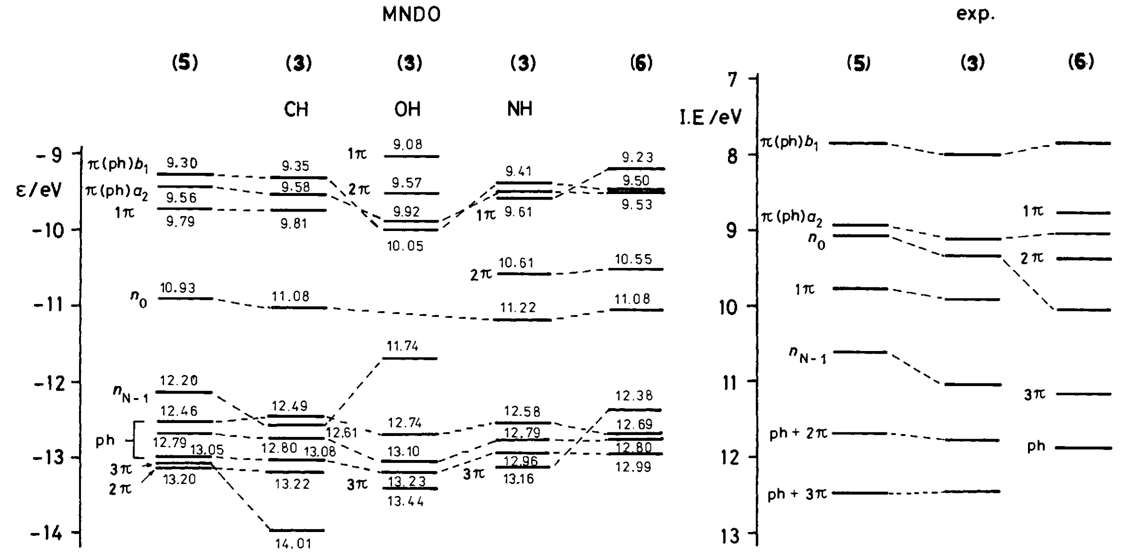


Figure 5. Comparison between the orbital energies of 4,4,5-trimethyl-2-phenyl-2,4-dihydropyrazol-3-one (**5**), tautomeric forms of 5-methyl-1-phenyl-2,4-dihydropyrazol-3-one, 1,5-dimethyl-2-phenyl-1,2-dihydropyrazol-3-one and experimental I.E.s

envelope with feature *g* at 10.67 eV can be tentatively assigned to the phenyl orbitals and the 2π-orbital; broad band *h* at 12.45 eV may be attributable to the 3π-orbital and the phenyl-ring orbitals (12.39 eV in aniline[24]). The substitution of the methyl group by phenyl leads to strong stabilization of the 1π-MO, which results in the reversed sequence of the two highest dihydropyrazol-3-one MOs. The MNDO calculation conserves the MO sequence of the dihydropyrazol-3-one on going from (**1**) to (**5**) and predicts a minute splitting of the phenyl e_{1g} π-level. This can be rationalized by the underestimation of the conjugative interaction between the two fragments by the MNDO method. The splitting of the e_{1g} level, 1.06 eV, found in the PE spectrum shows that there is a strong conjugative interaction between the phenyl and pyrazol-3(2*H*)-one π-orbitals.

1,5-*Dimethyl*-2-*phenyl*-1,2-*dihydropyrazol*-3-*one* (**6**).—The MNDO calculation yields the phenyl e_{1g} π-level and the highest orbital of the dihydropyrazole ring gathered close together, and, due to the substitution of the N-1 hydrogen the HOMO is the 1π-orbital (Figure 5). The first I.E. of (**6**) differs insignficantly from that of (**5**). Hence we assigned band *a* to the b_1 orbital of phenyl. The following bands *b*, *c*, and *d* are grouped close together. The tentative assignement of band *c* to the phenyl a_2 π-orbital implies a reasonable assumption that this orbital with a node at the point of substitution is only slightly influenced by the transition from the CH to the NH form. Then bands *b* and *d* can be assigned to the 1π- and 2π-orbitals, respectively. The oxygen lone pair is predicted to lie approximately 0.5 eV below the 2π-orbital and thus we assigned band *e* to the n_0 ionization. In agreement with the MNDO results, the n_0 orbital is stabilized compared with the CH form. The following band, *f*, may be assigned to the 3π-orbital and band *g* to the highest σ-orbitals of phenyl.

5-*Methyl*-2-*phenyl*-2,4-*dihydropyrazol*-3-*one* (**3**).—The PE spectrum of (**3**) resembles the spectrum of (**5**) rather than that of (**6**) (Figures 4 and 5). The slight shift in the maxima of bands *a*, *b*, and *e* by *ca.* 0.15 eV to higher I.E.s as compared with (**5**) is in agreement with the absence of methyl groups (Table 2). The assignment of bands *a* and *b* to the phenyl b_1- and a_2-orbitals and band *e* to the 1π-orbital was adopted. The spacing between bands *c* and *d* is equal to 1 290 cm^{-1}, which is nearly the same as in the spectrum of (**5**). The shift of bands *c* and *d* by 0.26 eV to higher I.E. is in agreement with the observed sensitivity of the carbonyl lone pair I.E. to α-methyl substituents.[23] Thus bands *c* and *d* were assigned to the n_0 ionization. In agreement with the MNDO results, band *e* originating from the n_{N-1} ionization exhibits a stabilization of 0.43 eV due to the absence of the methyl groups (Figure 5). Bands *f* and *g* can be assigned to the 2π- and 3π-orbitals, respectively, and the phenyl orbitals, as in the spectrum of (**5**).

5-*Amino*-2-*phenyl*-2,4-*dihydropyrazol*-3-*one* (**4**).—The PE spectrum exhibits only three bands in the range below 10.5 eV. Band *a*, peaking at 7.70 eV, has its counterpart in the spectra of the foregoing phenyl derivatives and hence was assigned to the phenyl b_1 π-orbital. The shape of the spectrum between 8.5 and 10.5 eV differs from that of (**3**) and (**5**), as only two bands, *b* and *c*, are observed at 9.02 and 9.42 eV, respectively. We believe that the absence of any band in the range 9.5—11 eV indicates that the NH form is absent from the gas phase. Taking into account that the MNDO calculations does not reproduce the stabilization of the 1π-orbital, we feel that the observed spectrum resembles more the calculated orbital energies of the CH form (Figure 6). The second band *b* peaks at 9.02 eV. This value is very close to that found for the phenyl a_2 π-orbital throughout the studied series. Because of the shape of this orbital, its interaction with π-orbitals of the dihydropyrazol-3-one moiety is very weak. Hence band *b* was assigned to the phenyl a_2-orbital. Then intense band *c* originates from overlapping ionizations of the 1π- and n_0-orbitals and the lone pair of the amino group. Band *d* may be tentatively assigned to the n_{N-1} ionization. The assignment of the features at 11.80 and 12.41 eV (*g*, *h*) parallels that adopted for (**3**).

Relative Stabilities of Tautomeric Forms.—The calculated relative stabilities of the tautomeric forms are summarized in Table 3. Irrespective of the character of the substituents, the stability increases in the order NH < OH < CH. The substituents in positions 2 and 5 have no significant effect on the relative energy of the OH form. The phenyl group in position 2 tends to stabilize the NH form.

Conclusions

The gas-phase ultraviolet PE spectra of the tautomerizable dihydropyrazol-3-one derivatives are interpreted in terms of the

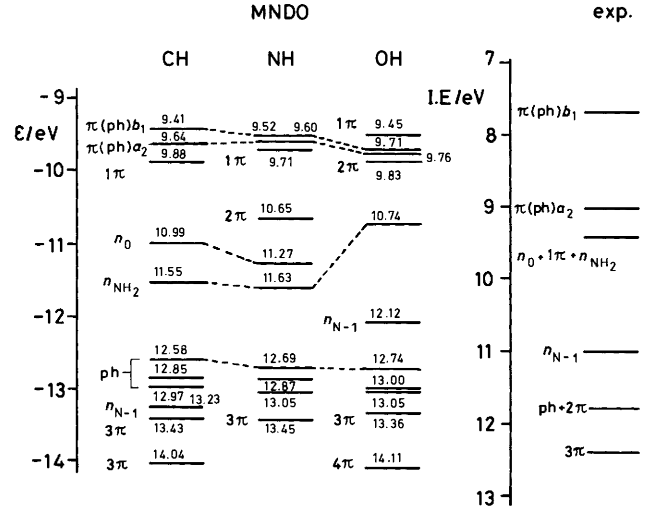


Figure 6. Comparison between orbital energies of tautomeric forms and experimental I.E.s of 5-amino-2-phenyl-2,4-dihydropyrazol-3-one (**4**)

Table 3. Calculated relative stabilities of tautomeric forms (kJ mol^{-1})^a

Compound	NH	OH
(**1**)	72.8	24.4
(**2**)	89.2	14.3
(**3**)	58.0	23.1
(**4**)	59.9	16.0

^{a} The CH form is most stable.

CH tautomeric form. Low I.E. spectral bands are assigned on the basis of observed vibrational fine structure, comparative arguments, and MNDO calculations. The ordering of the highest occupied MOs of the heterocycle depends on the substituent on the N-2 atom. In 2-alkyl derivatives the HOMO can be described in terms of the out-of-phase combination of the $\pi_{C=N}$-orbital and the nitrogen p_z orbital. The phenyl group brings about a stabilization of this MO, and the oxygen lone pair becomes the outermost MO of the 2,4-dihydropyrazol-3-one moiety. The calculated relative stability of the tautomeric forms increases in the order NH < OH < CH.

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Received 9*th March* 1987; *Paper* 7/433