Structure and Thermal *E–Z* Isomerization of Substituted 4-Phenylimino-5-pyrazolones and Hexafluoroacetone Anils

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The structure of the title compounds was examined by means of *ab initio* MO theory employing the STO-3G basis set. The optimized geometries represent a good basis for the discussion of conformation and configuration of these molecules. A quantum-chemical solvation model was applied for the estimation of the solvent influence. Dependent on the extent of push-pull conjugation in the investigated systems, the conformation of the linear inversion state, which has to be passed during the isomerization process, changes between a planar and perpendicular orientation of the *N*-phenyl ring. These conformation differences could be responsible for deviations of Hammett plots of the isomerization rate from linearity for special groups of aromatic azomethines.

Substituted 4-phenylimino-5-pyrazolones (**1**) and hexafluoroacetone anils (**2**) are of special interest in the discussion of the mechanism of *E–Z* isomerization of aromatic azomethines.[1,2] In most cases, the inversion mechanism, where the azomethine nitrogen atom is rehybridized to *sp* in the linear inversion state, seems to be the best explanation for this process, whereas the rotation mechanism, where rotation about the C=N double bond occurs, is improbable because of energetic reasons (Scheme 1).[3,4]

However, the finding of nonlinear, e.g. V-shaped, Hammett plots for the isomerization rate of a series of derivatives of **1** and **2**[5,6] stimulated the suggestion of a change between the inversion and rotation mechanisms dependent on the nature of the substituents. Considering similar results for benzoylacetanilide azomethines[7] and iminomalonates,[8] the tendency to nonlinear Hammett plots increases when push-pull conjugation dominates at the azomethine bond.

Recently, one of us unequivocally demonstrated by the study of solvent, temperature and pressure effects on the rate of isomerization of substituted *N*-benzylideneanilines and the title compounds that the rotation mechanism can be excluded for these compounds.[1,2] In order to explain the deviations from linearity in the Hammett plots based on the inversion mechanism, conformation differences in the linear inversion state could be assumed for the various derivatives. An examination of the conformation of the *N*-phenyl ring in the linear inversion state of some selected derivatives of **1** and **2** by means of quantum chemical methods shows the perpendicular orientation of the ring ($\theta=90°$, cf. Scheme 1) usually as the most stable conformation. However in case of strongly electron-donating substituents, the situation may change and the planar arrangement ($\theta=0°$) could be favored.[9]

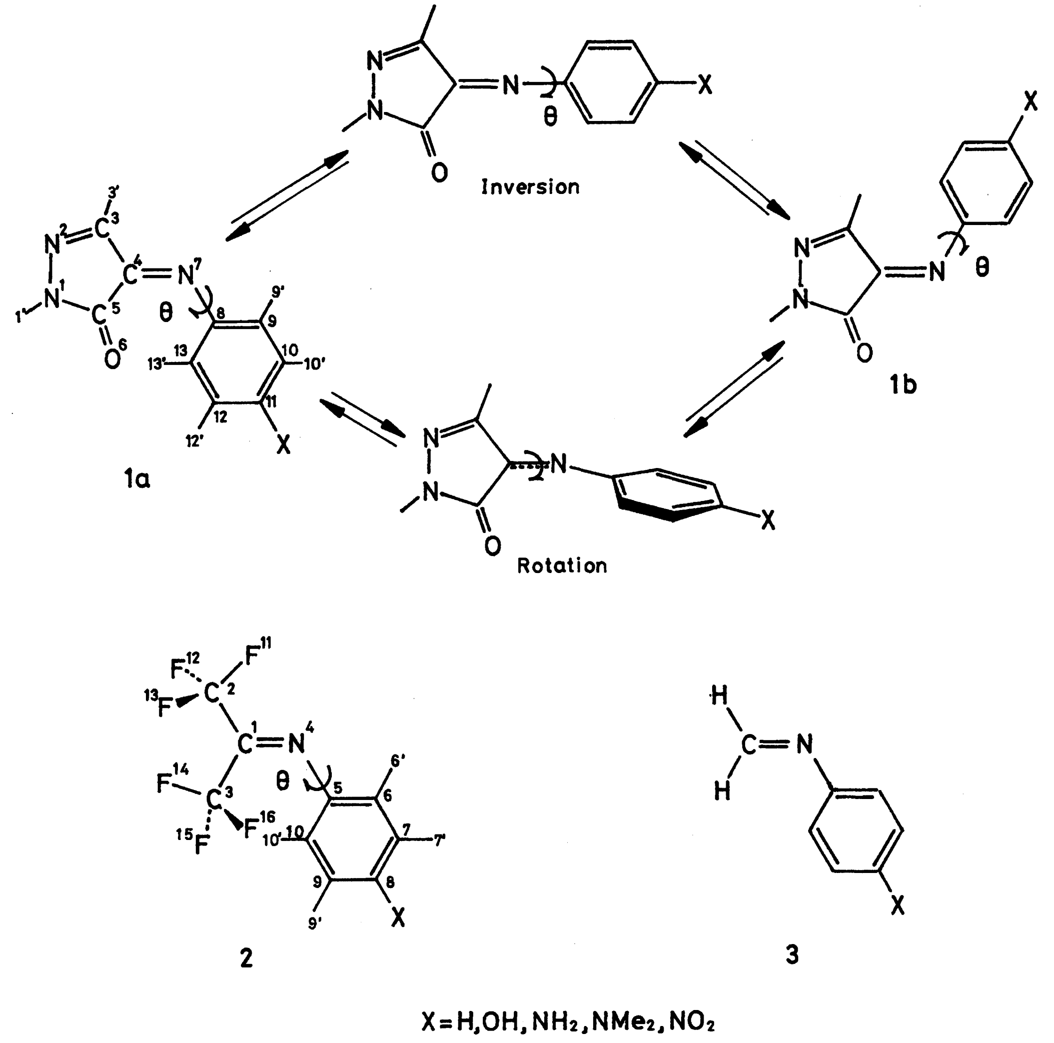
In this paper, we want to present results of a systematic structural investigation of the title compounds by means of quantum chemical methods as a basis for the discussion of the peculiarities of the *E–Z* isomerization in both groups of compounds. Additionally, the influence of solvents on the structure, which also represents an important indicator for the differentiation of inversion and rotation mechanism, was examined. Apart from our main interest in the relation between molecular structure and isomerization mechanism, the structural information given here could be of special importance for the interpretation of the spectral properties of the derivatives **1** which are used as image formers in color photography.

Methods

All calculations are based on *ab initio* SCF MO theory employing the STO-3G basis set.[10] The HONDO7 program package was used.[11] The STO-3G basis set has been proved to be reliable enough for the description of conformational problems of this type.[12] The geometries of all molecular forms were completely optimized. The solvent influence was estimated by a quantum-chemical reaction field model introduced some years ago,[13,14] which describes the electrostatic part of the solvation energy. The calculations are referred to the solvent water with standard computational parameters.

Results and Discussion

Structure of *p*-Substituted 4-Phenylimino-5-pyrazolones. The Tables 1 and 2 present the STO-3G optimized bond lengths and angles of the unsubstituted compound **1a**. The geometry parameters of the parent compound reflect also the situation in all substituted derivatives. Thus, those geometries are not explicitly given here. Bond lengths and angles may partially be compared with those from the X-ray study of two 1-phenyl-5-pyrazolone azomethine dyes which are used as image formers in color photography.[15] There is generally good agreement for most parameters. The only remarkable deviation concerns the CNC angle of the azomethine bond which is 131° in one of the two molecules examined by X-ray but 118.8° in the calculation of **1a** (120.3° for $X=NMe_2$). The agreement between the



Scheme 1.

theoretical and measured values (124.4°) for the other derivative bearing two *ortho* methyl groups in the N-phenyl ring is much better. This can be explained by the crystal forces which enforce the N-phenyl ring in the unsubstituted compound into a nearly planar arrangement ($\theta=13.9°$). Thus, the increased steric hindrance is compensated by an enlargement of the CNC angle. The two methyl groups in the other derivative *a priori* prevent an approximately planar orientation of the N-phenyl ring ($\theta=56.6°$). In the gas phase and in solution, the N-phenyl ring is generally more twisted than in the crystal also in the unsubstituted aromatic azomethines, e.g. the rotation angle in N-benzylideneaniline amounts to $\theta=52°$ and 65° based on experimental[16] and theoretical examinations,[17] respectively. The calculated values for the Z and E forms **1a,b** of 65.1° and 55.9°, respectively, confirm this experience. Whereas the substituent influence on bond lengths and bond angles is negligible, the torsion of the N-phenyl ring is more concerned. In agreement with experimental and theoretical results for substituted N-benzylideneanilines and N-methyleneanilines,[12,18] electron-donating substituents decrease and electron-attracting substituents increase the rotation angle. This can be explained by the improved conjugation possibility of the azomethine nitrogen lone-pair into the phenyl π system by ring rotation in case of electron deficiency. The actual torsion angle values (Table 3) show a stronger substituent influence in the Z than in the E forms. The considerable twist of the N-phenyl ring is an important aspect for the interpretation of the electronic spectra of anils of type **1** used in color photography.[19]

The calculated energy differences between Z (**1a**) and E (**1b**) configuration, which represent a reference point for the gas phase (Table 3), show no significant preference for the one or the other form. A very small substituent influence becomes visible. Electron-donating groups favor the E and electron-withdrawing substituents the Z form, respectively. NMR examinations[20] indicate the occurrence of both configurations in solution with a distinct predominance of the E form. This is well reproduced by our theoretical es-

Table 1. STO-3G Optimized Bond Lengths of Compound **1a** in Comparison with X-Ray Data for Two Photographic Image Dyes

Bond	STO-3G [a]	Experiment [a,b]	
N(1)N(2)	1.415	1.407	1.413
N(2)C(3)	1.294	1.290	1.292
C(3)C(4)	1.494	1.447	1.451
C(4)C(5)	1.538	1.499	1.494
N(1)C(5)	1.421	1.369	1.377
C(5)O(6)	1.218	1.219	1.217
C(4)N(7)	1.279	1.297	1.292
N(7)C(8)	1.468	1.374	1.399
C(8)C(9)	1.392	1.403	1.414
C(9)C(10)	1.385	1.362	1.377
C(10)C(11)	1.387	1.413	1.407
C(11)C(12)	1.387	1.415	1.409
C(12)C(13)	1.385	1.366	1.379
C(8)C(13)	1.392	1.403	1.410
N(1)H(1′)	1.019	—	—
C(3)H(3′)	1.082	—	—
C(9)H(9′)	1.082	—	—
C(10)H(10′)	1.083	—	—
C(11)H(11′)	1.082	—	—
C(12)H(12′)	1.083	—	—
C(13)H(13′)	1.082	—	—

a) In Å. b) X-Ray data from Ref. 15, the first value for 4-(4-diethylaminophenylimino)-3-methyl-1-phenyl-5-pyrazolone and the second value for 4-(4-diethylamino-2, 6-dimethylphenylimino)-3-methyl-1-phenyl-5-pyrazolone.

Table 2. STO-3G Optimized Bond Angles of Compound **1a** in Comparison with X-Ray Data for Two Photographic Image Dyes

Bond angle	STO-3G [a]	Experiment [a,b]	
N(1)N(2)C(3)	106.8	106.9	107.5
N(2)C(3)C(4)	113.7	112.8	112.0
C(3)C(4)C(5)	103.1	103.6	104.4
C(4)C(5)N(1)	102.1	103.8	103.7
C(5)N(1)N(2)	114.3	112.9	112.4
O(6)C(5)N(1)	126.4	125.5	126.6
N(7)C(4)C(5)	132.4	135.0	131.4
C(8)N(7)C(4)	118.8	131.0	124.4
C(9)C(8)N(7)	118.2	115.4	115.7
C(9)C(8)C(13)	120.2	116.6	119.0
C(10)C(9)C(8)	119.7	123.1	119.7
C(11)C(10)C(9)	120.3	120.4	122.0
C(12)C(11)C(10)	119.9	116.5	116.6
C(13)C(12)C(11)	120.3	122.2	122.6
N(2)N(1)H(1′)	119.0	118.7 [c]	118.4 [c]
H(3′)C(3)N(2)	121.5	122.2 [d]	122.1 [d]
H(9′)C(9)C(10)	120.8	124.0	119.6 [d]
H(10′)C(10)C(9)	119.7	122.0	117.0
H(11′)C(11)C(10)	120.1	122.0 [e]	122.1 [e]
H(12′)C(12)C(13)	119.6	120.0	117.0
H(13′)C(13)C(12)	120.5	123.0	117.9 [d]

a) In degrees. b) Dyes as in Table 1. c) N(2)N(1)-phenyl angle. d) Methyl group for hydrogen. e) NEt_2 for hydrogen.

Table 3. Substituent Influence on the *N*-Phenyl Ring Rotation of Anils **1a,b** and **2** and *E,Z* Energy Differences for the Anils **1a,b** in the Gas Phase and in Solution

Substituent X	Torsion angle θ [a]			$\Delta E_{E,Z}$ [b,c]	$\Delta E_{E,Z}$ [b,d]
	1a	**1b**	**2**		
NO_2	74.5	58.5	64.5	2.1	−19.4
H	65.1	55.9	59.0	−0.1	−5.3
NH_2	55.0	51.5	21.1	−1.2	−4.6

a) In degrees. b) In kJ mol^{-1}. c) Gas phase. d) Solvent water.

timations of the solvent influence, which confirm the preference of this form for all substituted derivatives (Table 3). It is obvious, that the *Z* configuration dominates in the case of derivatives of **1** bearing substituents in the 5-position because of steric reasons as found for some typical photographic image dyes.[15,20]

Structure of Hexafluoroacetone Anils. Table 4 lists the STO-3G optimized bond lengths and bond angles for the hexafluoroacetone anil molecule **2**. The substituent influence on the rotation angle of the *N*-phenyl ring is described by the theoretical values in Table 3. These results confirm the general conclusions about the structure of aromatic azomethines discussed for the derivatives of **1**. Due to missing experimental data, an explicit comparison with the quantum-chemical results is impossible.

***E–Z* Isomerization** In order to confirm the hypothesis that different conformations are preferred in the linear inversion states dependent on the nature of the substituents in the *N*-phenyl ring, we calculated the energy differences between the perpendicular and planar conformations ($\theta=90°$ and 0°, respectively, cf. Scheme 1) after complete geometry optimization. As expected from symmetry arguments, both conformations are zero-gradient points in the energy hypersurface. This was confirmed by the calculation of the complete potential curves for the *N*-phenyl ring rotation, which are monotonously decreasing or increasing between both conformations dependent on the corresponding substituents, and by the determination of the force constants matrix in selected cases for a further characterization of the zero-gradient points. The energy differences between the two conformations are given in Table 5. For the *N*-methyleneanilines (**3**) without any push-pull conjugation, which are included for comparison,[12] the perpendicular *N*-phenyl ring orientation is the most stable one on examining the rotation in the linear inversion state. This conformation corresponds to a transition state as indicated by the existence of one negative eigenvalue in the force constants matrix. The preference of the perpendicular arrangement is obviously caused by a favoring of the conjugation of the nitrogen p_z electrons into the *N*-phenyl ring. This effect is increased by electron-attracting substituents, but

Table 4. STO-3G Optimized Bond Lengths and Bond Angles for Hexafluoroacetone Anil **2**

Bond lengths a)		Bond angles b)	
C(1)C(2)	1.573	C(2)C(1)N(4)	117.3
C(1)C(3)	1.576	C(3)C(1)N(4)	128.6
C(1)N(4)	1.272	C(1)N(4)C(5)	120.7
N(4)C(5)	1.468	C(1)C(2)F(11)	110.9
C(5)C(6)	1.393	C(1)C(2)F(12)	110.4
C(6)C(7)	1.384	C(1)C(2)F(13)	110.9
C(7)C(8)	1.388	C(1)C(3)F(14)	109.6
C(8)C(9)	1.386	C(1)C(3)F(15)	111.6
C(9)C(10)	1.386	C(1)C(3)F(16)	111.3
C(5)C(10)	1.391	C(6)C(5)N(4)	117.6
C(2)F(11)	1.369	C(7)C(6)C(5)	119.6
C(2)F(12)	1.374	C(8)C(7)C(6)	120.2
C(2)F(13)	1.374	C(9)C(8)C(7)	120.0
C(3)F(14)	1.372	C(10)C(9)C(8)	120.4
C(3)F(15)	1.372	C(6)C(5)C(10)	120.4
C(9)H(9′)	1.083	H(10′)C(10)C(9)	120.5
C(10)H(10′)	1.082		

a) In Å. b) In degrees.

Table 5. Calculated Energy Differences between the Perpendicular and Planar Phenyl Ring Conformations of the Linear Inversion States and *E–Z* Inversion Barriers of Various Aromatic Azomethines in the Gas Phase and in Solution

Substituent X	ΔE a)	ΔE_s a)	ΔE_{inv} b)	$\Delta E_{s,inv}$ b)
		Anils **1**		
NO_2	−19.8	−22.2	104.0	104.4
H	−7.7	−6.2	109.5	110.7
NH_2	3.9	—	110.1	—
NMe_2	5.8	6.7	109.2	110.0
		Anils **2**		
NO_2	−17.6	−18.2	96.1	97.2
H	−6.5	−4.6	101.8	104.9
NH_2	5.0	5.7	102.1	103.6
		Anils **3** c)		
NO_2	−34.2	—	113.5	—
H	−21.8	—	121.8	—
OH	−12.8	—	127.1	—

a) $E(90°)-E(0°)$ in kJ mol^{-1}. b) Inversion barriers in kJ mol^{-1}. c) See Ref. 12.

diminished by donator groups considering the actual energy differences between the two alternative conformations. For azomethines without push-pull substituents, linear Hammett plots with positive slopes should, therefore, be expected when correlating the inversion rates of these derivatives. This is supported by theoretical and experimental data.3,4,12)

In the case of the title compounds **1** and **2**, the situation changes (Table 5). Based on our calculations, the perpendicular conformation remains the most stable one for the unsubstituted compounds and the derivatives with acceptor substituents. However, introduction of electron-donating substituents into the *N*-phenyl ring supports the conjugation through the azomethine bond in these molecules, which are push-pull systems now. Thus, the planar conformations become competitive and even correspond to the most stable phenyl ring orientations. The calculated solvent influence on the energy differences between the two alternative conformations is small (Table 5). Thus, the original conclusions can be maintained. The consequences of the conformational differences in the linear inversion states for the inversion barriers are also illustrated in Table 5. The favoring of the planar *N*-phenyl ring orientation in the push-pull systems decreases the inversion barrier. Thus, the inversion barriers of the amino-substituted and unsubstituted derivatives have nearly the same value. The dimethylamino-substituted derivative of **1** has a lower inversion barrier than the unsubstituted compound now. These results explain the deviations from linearity in the Hammett plots and make the tendency to V-shaped plots with increasing electron-donating power of the substituents understandable in these groups of compounds.

The solvent influence on the inversion barriers estimated by means of the quantum-chemical reaction field model is small (Table 5). This is in good accordance with experimental data showing a near constancy of the activation enthalpies and isomerization rate constants over a wide range of solvents differing in chemical nature and permittivity.1,2) The small barrier increase calculated for the solvent water in comparison to the gas phase value, demonstrates that the linear inversion state is somewhat less stabilized by solvents than the ground-state minimum structure because of a decreased polarity. This result provides a good basis for the interpretation of some experimental findings about the thermal *E-Z* isomerization suggesting the inversion mechanism,1,2) whereas for the isomerization via the rotation mechanism a highly polar transition state can be expected. In such a case, a considerable solvent effect should appear.

Conclusions

The results of our quantum-chemical calculations confirm the justification of the assumption of conformation differences in the linear inversion state of aromatic azomethines dependent on the nature of the substituents at the azomethine bond. Obviously, a planar structure of the inversion state is favored in push-pull azomethines, whereas otherwise the perpendicular orientation of the *N*-phenyl ring is preferred. The conformational differences seem to be the reason for the non-linear Hammett plots observed in these groups of compounds. The solvent influence on the inversion barrier is small leading to a slight increase of the barrier height. There is a polarity decrease in the inversion process when passing the linear inversion state. The results for the aromatic azomethines could at least partially be transferred to aromatic azo compounds.21)

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