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Theoretical study on *O*-, *N*- and *S*-ylidic photoisomers derived from phenylvinylethers, phenylvinylthioethers and phenylvinylamines

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Abstract

In order to reveal the nature of the primary short-lived photoproducts (Y) of phenylvinylethers, phenylvinylthioethers and phenylvinylamines and to rationalize their photophysical properties, quantum chemical calculations were performed at the restricted and unrestricted Hartree–Fock (HF) level of theory and beyond employing split valence basis sets plus polarization functions. According to the population of the p_π (and d_π) orbitals within the Mulliken population analysis, the non-classical compounds Y are ylidic with carbon–heteroatom bonds shortened with respect to those of compounds with a classical structure. The ylidic character, however, is lower than that calculated for the formaldehyde methide, thioformaldehyde methide and azomethine methide parent compounds. The long-wavelength absorptions are due to an allowed $\pi \rightarrow \pi^*$ transition. They are satisfactorily reproduced by HF-based single configuration interaction (CIS) calculations in spite of the well-known limitations of this approach. The S_0/T_1 splitting energies alter in the sequence $O \sim S \ll N$. The inability to detect spectroscopically the triplet state $^3Y^*$ of the *O*- and *S*-ylidic photoproducts is probably due to the low S_0/T_1 gap of these compounds.

Keywords: *O*-, *N*- and *S*-ylidic photoisomers; Phenylvinylether; Phenylvinylthioether; Phenylvinylamine; Quantum chemical calculations

1. Introduction

Previous experimental studies on the conrotatory photocyclization of phenylvinylamines (*N*-aryl enamines [1]) and diphenylamines [2] have revealed a reaction mechanism involving triplet states and ylidic intermediates according to Scheme 1 ($X \equiv NR$), where **E** denotes the photoreactant, $^3\mathbf{E}^*$ the excited triplet state of the reactant, $^3\mathbf{Y}^*$ the triplet state of the primary (intermediate) ylidic product, **Y** the ground state of that intermediate and **P** the final product formed after suprafacial 1,4-hydrogen migration. The adiabatic pathway of formation of the primary product in its excited triplet state was proven via flash photolysis experiments. In the analogous photocyclization of phenylvinylethers [3] ($X \equiv O$ in Scheme 1) and phenylvinylthioethers [4] ($X \equiv S$ in Scheme 1), the adiabatic step $^3\mathbf{E}^* \rightarrow {}^3\mathbf{Y}^*$ could not be resolved, i.e. an absorption attributable to the triplet state of the ylide was not found in the flash experiments. Two rationalizations can be given for the missing $^3\mathbf{Y}^*$ signal: the reaction does not proceed adiabatically in these cases, or the triplet state of the *O*-ylide or *S*-ylide is so short lived that its decay is faster than its formation. In the latter case, an acceleration of the triplet decay via heavy atom effects may be discussed, but is not likely since the differences in atomic numbers of the heteroatoms are small, particularly between N and O. Another cause of rapid triplet–singlet crossover may be a small difference between the singlet (S_0, Y) and triplet (T_1, $^3Y^*$) states of the respective ylides.

The structure of **Y** in Scheme 1 was drawn ylidic rather than as a diradical since side products originating from radical reactions were not found. In the case of $X \equiv O$ and $X \equiv S$, the ylidic structure is further supported by possible scavenging reactions using dipolarophiles [5]. Direct proof of the structure, however, is still missing. Nevertheless, the molecules show non-classical structures. They cannot be represented by classical uncharged valence bond structures in their normal valence states. The basic structural subunits are usually presented either by resonance hybrids of several dipolar canonic forms, such as $C{=}X^+{-}C^- \rightleftharpoons C^-{-}X{=}C^+$, or by hypervalent structures, such as C=X=C. Another classification in organic chemistry assigns them as 1,3-dipolar species [6]:

$$C^+{-}X{-}C^- \rightleftharpoons C^-{-}X{-}C^+$$

The uncertainty in the structural description is reflected in the nomenclature [7].

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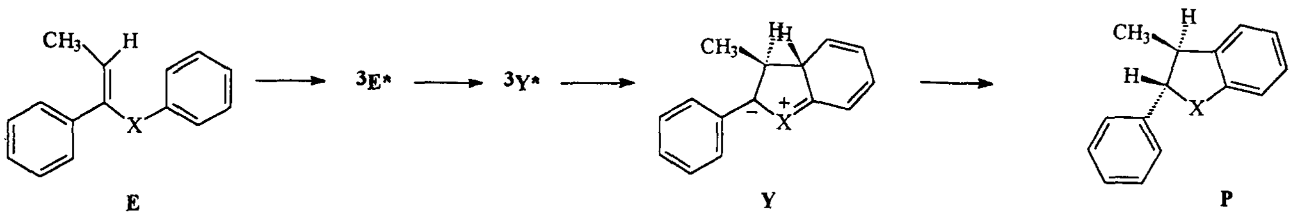
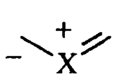


Scheme 1. Photocyclization of phenylvinylethers ($X \equiv O$), phenylvinylthioethers ($X \equiv S$) and phenylvinylamines ($X \equiv NR$).



X = NH, O, S

1

Scheme 2. Parent chromophores 1.

The purpose of this investigation is to extend former theoretical studies on ylidic structures [8,9] to the more complex photoproducts **Y**. Two main questions have been posed. Firstly, what is the molecular and electronic structure of the compounds of series **Y** that cannot be described by a single resonance formula? This requires the calculation of the geometry-optimized ground states and electron distributions. Secondly, does the relative S_0/T_1 splitting energy of the heteroanalogous compounds **Y** favour the distinct photophysical deactivation behaviour found experimentally? This requires the lowest excited states to be calculated.

In principle, reliable numerical predictions can only be made by state-of-the-art ab initio quantum chemistry. Such calculations would be prohibitively expensive for compounds the size of **Y** or are not available. The goal of this study is, however, to reveal trends rather than numbers. This can be done at a lower and more practicable level of theory.

For comparison, this study includes the ylidic parent structures **1** (Scheme 2) which are reactive transients in organic reactions [6]. In a previous ab initio quantum chemical study of **1** ($X \equiv S$), a singlet ground state and a low S_0/T_1 gap of 24 kcal mol^{-1} were found [8]. According to recent calculations by density functional theory (DFT), the S_0/T_1 gaps of compounds of series **1** and of the heterocyclic ylides 3,4-dimethylenefuran, 3,4-dimethylenethiophene and 3,4-dimethylenepyrrole alter in the sequence $O < S < N$ [9].

2. Computational details

Ab initio molecular orbital (MO) calculations were performed using the *GAUSSIAN-92* suite of ab initio programs [10]. Singlet molecules were calculated by the restricted Hartree–Fock (RHF) and triplet molecules by the unrestricted HF (UHF) procedures [11]. The valence double zeta basis sets 3-21G and 6-31G augmented by d-polarization functions were used throughout (basis sets 3-21G* and 6-31G* respectively). Electron correlation was accounted for using single reference Møller–Plesset perturbation theory to second order for closed shell (RMP2) and open shell (UMP2) compounds. In the case of **Y**, the core electrons were kept frozen. The molecular geometries were optimized by analytical gradients. The energy minima with respect to the nuclear coordinates were obtained by simultaneous relaxation of all geometry parameters without symmetry constraint.

The vertical transition energies from the ground state to the lowest excited singlet and triplet state were obtained by full configuration interaction of the singly excited configurations (RHF ground state geometries). In the case of diradicaloid species, this approach provides triplet states considerably too low in energy relative to the singlet ground state. The same failure occurs when singlet–triplet excitation energies are calculated by the energy difference method from RHF and UHF energies of the singlet ground and triplet excited states respectively. The calculations of **Y** even suggest triplet ground states. This particular feature is also reflected in the HF stability test. All compounds of series **Y** show RHF/UHF instability. This is an indicator of diradicaloid behaviour.

More useful results are obtained if electron correlation is taken into account at the R(U)MP2 level. In this paper, the S_0/T_1 splitting energies of **Y** were estimated by single point R(U)MP2 calculations with RHF optimum geometries. At this level of theory, molecules of series **Y** are singlet molecules. However, the wavefunctions of the triplet states are contaminated by contributions of higher spin. In the case of **Y**, the spin contamination is relatively large. The eigenvalue of the spin square operator is about 2.9 in both UHF and UMP2 calculations, rather than 2.0 (pure triplet state). Spin projection at the MP2 level reduces the eigenvalue to about 2.7. The S_0/T_1 splitting energies calculated in this paper were derived from UMP2 spin projected energies (PUMP2).

In order to estimate the electron distribution of **Y**, atomic charges were derived by conventional Mulliken population analysis (MPA) [11] and, in addition, by natural population analysis (NPA). The NPA procedure differs completely from the conventional method [12] in the use of natural orbitals. It is clearly superior to MPA in some cases.

3. Results and discussion

The calculated RHF/3-21G* geometries of the compounds of series **1** and **Y** are closely related. A perspective view of **Y** ($X \equiv NH$) is given in Fig. 1. Apart from the bond lengths CX specific for the heteroatoms X, the bond parameters differ slightly in the torsional angle δ(XCCC) between the five-membered ring and the attached phenyl group. The torsion is about 30° on average. Some geometric data of the calculated geometries of **Y**, together with those of the ylidic parent structures **1**, are given in Table 1. In view of the changes in the calculated CX bond lengths in the series furan, thiophene and pyrrole on passing from the RHF/3-21G* (1.380, 1.727 and 1.377 Å respectively) to the more accurate RMP2(full)/6-31G* (1.365, 1.715 and 1.372 Å respectively) level, the calculated bond lengths CX of **Y** (Table 1) are about 0.01 Å too large. The CX bond lengths of **Y** are remarkably short compared with those of the above-mentioned five-membered heterocyclic rings. The contraction of the bonds is compatible with the ylidic substructure of CXC in **Y** represented by the resonance structures

$$C{=}X^+{-}C^- \rightleftharpoons C^-{-}X{=}C^+$$

Shortening of the CX bonds is also found with the MP2(full)/6-31G* geometries of the parent structures **1** (cf. footnote to Table 1). The extremely short CS bonds in thioformaldehyde methide **1b**, which are only about 0.3 Å longer than in thioformaldehyde, may even suggest a hypervalent sulphur atom. Although d orbitals strongly contribute to the short CS bonds, they are not involved in the valence. Rather, the d orbitals act as polarization functions. Neglect of the d orbitals leads to a pronounced overestimation of the CS bond length. This amounts to 0.06 Å in the case of **1b** (RHF/3-21G* level). The charge distribution is also markedly affected.

At first glance, the ylidic structure of the *O*- and *N*-ylides of **Y** seems to be completely in contradiction with the calculated charge distribution of the compounds. Irrespective of the origin of the calculated charges, the result is opposite to the charge distribution expected from $C{=}X^+{-}C^- \rightleftharpoons C^-{-}X^+{=}C$. The atomic total charges of the *O*- and *N*-ylides, derived from MPA or NPA, are negative at the heteroatoms and positive at the adjacent carbon atoms. The same holds for the *O*- and *N*-ylides of series **1**. The characteristics of the *S*-ylides are different in both series **Y** and **1**. A partial positive charge is calculated at the heteroatom and a partial negative charge at the carbon atoms. However, the charge separation in the CSC fragments does not differ greatly from that in classical structures such as the non-ylidic thiophene (cf. Table 2).

Table 1
Selected geometric parameters of **Y** optimized at the RHF/3-21G* level of theory [a,b]

Parameter [c]	X≡O	X≡S	X≡NH
Bond length (see Fig. 1)			
a	1.355	1.644	1.344
b	1.317	1.643	1.331
c	1.393	1.419	1.407
d	1.357	1.345	1.351
e	1.453	1.459	1.458
f	1.336	1.329	1.333
Bond angles			
β(CXC)	114.5	99.3	116.4
δ(XCCC)	16.3	40.2	30.5

[a] CX bond lengths of **1** (Å). RHF/3-21G*: X≡O, 1.302; X≡S, 1.601; X≡NH, 1.324; RMP2/6-31G*: X≡O, 1.332; X≡S, 1.644; X≡NH, 1.342.
[b] Total energies (Hartree). **Y**(X≡O), −647.26963; **Y**(X≡S), −968.51531; **Y**(X≡NH), −627.58624; 1 Hartree = 627.5 kcal mol^{-1}.
[c] Bond lengths in Å, bond angles in degrees. For labelling of the bonds, see Fig. 1.
δ(XCCC) denotes the angle of torsion around the inter-ring bond.

In contrast with other types of ylide [7], the ylidic structures considered in this paper are conjugated. Resonance formulae define the charge distribution of the π systems rather than the total charge distribution. Consequently, any theoretical estimation of the ylidic charge distribution should be carried out in terms of the population of the π-type orbitals. This has been done by inspection of the Mulliken gross orbital population and extraction of the atomic populations of the π-type atomic orbitals (p_π, d_π). According to the πMO theory, π charges are defined by the population of the π-type orbitals and the core charges presumed for each type of atom. The core charge of carbon is one, and that of the heteroatoms X

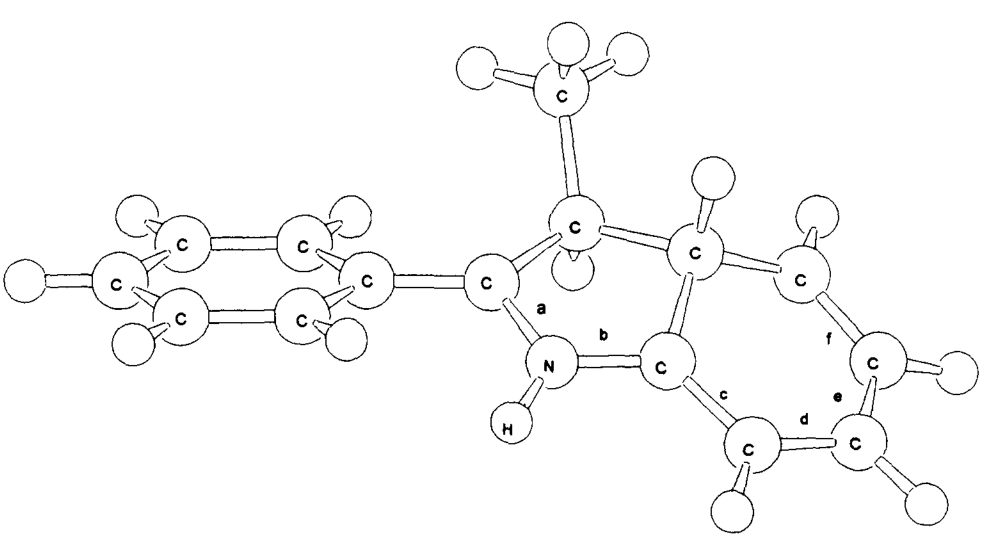


Fig. 1. RHF/3-21G* structure of **Y** (X≡NH). Labelling of the bonds in Table 1.

Table 2
Atomic total and π charges at the ylidic $C_\alpha XC_{\alpha'}$ fragments [a] calculated by Mulliken population analysis (MPA) and by natural orbital population analysis (NPA) at the RHF/3-21G* level of theory. Dipole moments μ are given in Debye

Compound	Atom [a]	MPA	NPA	π charges	μ
Y(X≡O)	O	−0.66	−0.41	+0.44	1.66
	C_α	+0.43	+0.28	−0.15	
	$C_{\alpha'}$	+0.47	+0.36	−0.05	
Y(X≡S)	S	+0.70	+0.85	+0.57	0.18
	C_α	−0.32	−0.40	−0.23	
	$C_{\alpha'}$	−0.35	−0.40	−0.19	
Y(X≡NH)	N	−0.92	−0.47	+0.58	1.31
	C_α	+0.40	+0.13	−0.16	
	$C_{\alpha'}$	+0.40	+0.13	−0.14	
1(X≡O)	O	−0.53	−0.35	+0.56	0.74
	C_α, $C_{\alpha'}$	−0.16	−0.19	−0.28	
1(X≡S)	S	+0.65	+0.89	+0.66	0.07
	C_α, $C_{\alpha'}$	−0.81	−0.94	−0.33	
1(X≡NH)	N	−0.67	−0.43	+0.68	1.53
	C_α, C_α'	−0.27	−0.40	−0.34	
Furan	O	−0.64	−0.52	+0.27	1.10
	C_α, $C_{\alpha'}$	+0.14	+0.13	−0.05	
Thiophene	S	+0.41	+0.47	+0.24	0.77
	C_α, $C_{\alpha'}$	−0.41	−0.46	−0.09	
Pyrrole	N	−0.87	−0.64	+0.37	1.92
	C_α, $C_{\alpha'}$	+0.10	−0.03	−0.08	

[a] C_α of **Y** is the carbon adjacent to X bearing the phenyl group; $C_{\alpha'}$ is the second carbon atom involved in the five-membered ring.

in **Y** and **1** is two. The compounds **Y** are not good candidates for such an analysis since the molecules are not planar and the π orbitals are consequently mixed with σ orbitals. However, the ylidic substructure CXC of **Y** is planar. MPA has been performed after positioning these atoms of CXC in a definite plane.

The calculated π charges are listed in Table 2. They display the expected ylidic electron distribution for all compounds of the series **Y** and **1**. The *O*-ylides appear to be less ylidic than the *S*- and *N*-ylides. Furthermore, the ylidic character of **Y** is weaker than that of **1**. The classical five-membered ring systems of furan, thiophene and pyrrole display a distinctly lower charge separation than the ylidic compounds (cf. Table 2). Again, attention has been paid to trends rather than to numbers. However, the charge distribution of **1** is not strongly changed on progressing from the HF level of theory to beyond (see data in Ref. [8]).

In spite of some ylidic charge separation, the calculated dipole moments of **Y** and **1** are low (cf. Table 2). The dipole moments are lower than 2 D. The high "1,3-dipolar" reactivity in both series of compounds, however, is not defined by the molecular dipole moment.

According to the quantum chemical calculations of **1** at the highest level of theory employed in this paper, namely R(U)MP2/3-21G*//R(U)HF/3-21G*, all compounds of this series are singlet molecules. The S_0/T_1 splitting increases in the sequence O ~ S ≪ N. The S_0/T_1 gap is less than 25 kcal mol^{-1} for the *O*- and *S*-ylides (Table 3). According to the definition of diradicaloid compounds given by Wirz [13], these are more or less diradicaloid, while the *N*-ylides are appreciably more stable in the singlet state (more than 30 kcal mol^{-1}). Remarkably, the above-mentioned sequence of the S_0/T_1 energies is also predicted at lower levels of theory such as at the R(U)HF (energy differences) and CIS level if the consistent overestimation of the triplet energies relative to the singlet energies is considered. The low S_0/T_1 gap of the oxygen- and sulphur-containing **Y** is in agreement with the assumption that a large rate may exist for the singlet–triplet crossover in these cases. On the other hand, the definitely higher gap of the *N*-ylides may entail a higher lifetime of these compounds which enables the triplet state to be detected experimentally.

The CIS approach proved to be more useful in calculating the vertical S_0/S_1 transition energies than the S_0/T_1 transition energies. According to Table 3, the theoretical (gas phase) energies agree satisfactorily well with the experimental data corresponding to the absorption maxima of **Y** and **1** in solution. The ab initio calculations predict correctly light absorption of **Y** in the visible and of **1** in the near-UV region. The colour-determining absorptions are due to $\pi \rightarrow \pi^*$ transitions. According to the calculated oscillator strengths, the colour bands are due to allowed and intense electron

Table 3
S_0/T_1 energy gaps ΔE_{ST} ((U)MP2(fz)/3-21G*) [a] and the lowest S_0/S_1 transition energies ΔE (CIS/3-21+G*) [b] based on (U)RHF/3-21G* optimum geometries

Compound	Theoretical ΔE_{ST} (kcal mol^{-1})	Theoretical		Experimental [c]	
		ΔE (eV)	λ (nm)	ΔE (eV)	λ (nm)
Y (X≡O)	18.8	2.25	551 (0.96) [h]	2.16	575 [d]
Y (X≡S)	16.1	2.49	497 (0.65)	2.10	590 [e]
Y (X≡NH)	32.5	2.67	464 (0.99)	2.10	590 [f]
1 (X≡O)	17.7	3.57	348 (0.51)		
1 (X≡S)	24.5	4.16	298 (0.52)	≈3.54	≈350 [g]
1 (X≡NH)	36.5	4.03	307 (0.49)		

[a] Energies of the triplets refer to values obtained after spin projection. The values of $\langle S^2 \rangle$ are deduced to about 2.7 after spin projection in series **Y** and to 2.01 in series **1**. The ΔE_{ST} values of **1** are those of the R(U)MP2(full)/6-31G* geometry optimization.

[b] The ΔE values of **1** obtained by CIS/6-31+G* are based on MP2(full)/6-31G* optimum geometries.

[c] In methylcyclohexane.

[d] Ref. [3].

[e] Ref. [4a].

[f] Ref. [1b]; in diethylether; *N*-methylated compound.

[g] Substituted thioformaldehyde methides [14].

[h] Oscillator strength given in parentheses.

transitions. The absorption wavelengths are also correctly predicted in another series of related deeply coloured ylidic compounds, such as the heterocyclic compounds 3,4-dimethylenefuran, 3,4-dimethylenethiophene and 3,4-dimethylenepyrrole [9] which are more diradicaloid than **Y** and **1**.

4. Conclusions

The results of this theoretical study support the assumption that ^{3}**Y*** is experimentally detectable only in the case of X≡NR because of its larger S_0/T_1 splitting, whereas the low gap in the case of X≡O and X≡S favours rather rapid intersystem crossing from the lowest triplet to the ground state. The ylidic substructure of **Y** is in keeping with the occupation analysis of the p_π-type orbitals in the Mulliken gross population. Some closed shell diradicaloid character is another intrinsic molecular property of this series of compounds. Any hypervalency in terms of d orbital occupation in the valence shell is not supported by the calculations, but the d orbitals play an important role as polarization functions in describing the molecular and electronic structure of sulphur organic ylidic compounds.

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