A Theoretical Study of the Different Isomers of 2-Propen-1-imine

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A complete geometry optimization has been performed for the four isomers s-trans anti (TA), s-trans syn (TS), s-cis anti (CA) and s-cis syn (CS) of the molecule 2-propen-1-imine. Energy differences between the isomers have been estimated. The method used is the gradient technique of Pulay based on an ab initio SCF wave function constructed from a 4-31G basis. The lowest energy form is found to be the TA-form in accordance with a recent microwave study. The rotamer TS, having the ground state heavy-atom arrangement, is estimated to be 1.1 kcal/mol (1 kcal = 4.184 kJ) higher in energy than the ground state. The cis-forms, for which no experimental information is available, are found to be 1.8 kcal/mol (CA) and 3.8 kcal/mol (CS) above the ground state. The structures of all forms are discussed in comparison with available experimental information.

Imines, having the general formula $RR'C=NH$, are known to be extremely reactive species. Consequently very little is known about their structural properties.

Very recently Penn has been able to identify the aldimine 2-propen-1-imine by its microwave spectrum.[1] He claims to have detected the existence of two planar molecular forms both having a *trans* heavy atom arrangement. The forms are distinguished by the position of the imino hydrogen atom. The ground state is the rotamer having an *anti*-form, whereas the higher energy rotamer has a *syn*-form. The energy difference between the two forms is estimated to be 0.9 ± 0.1 kcal/mol.[1]

The structure determination of the *trans-anti* (TA) ground state conformation is based on five different isotopic species, and the structural parameters are supposed to be rather accurate. For the *trans-syn* (TS) rotamer only one isotopic species (imine-d_1), in addition to the normal species has

been observed. Consequently the estimates of the structural parameters for this rotamer are very uncertain.

In order to obtain quantitative information about the structural properties of the two molecular forms observed, as well as of the two possible *cis*-forms, (CA) and (CS), which have not been detected experimentally, we have carried through a complete geometry optimization of all planar forms using SCF calculations combined with the gradient method of Pulay.[2]

A detailed knowledge of the electronic and molecular structure of 2-propen-1-imine may be of great interest in the search for organic species in interstellar dust as the isomeric form ethyl cyanide has been detected in interstellar space.[3,4]

METHOD OF CALCULATION

All geometry optimizations were performed using the program TEXAS written by Pulay.[5] The essential feature of this program system is that, beyond the usual SCF procedure, it calculates the gradient of the energy in exact analytic form. Complete geometry optimization is carried out by the force relaxation method.[2]

The basis set applied was the 4-31G basis of Pople et al.[6] It has been demonstrated previously that a split valence basis like this one or the closely related 4—21 basis of Pulay et al.[7] is adequate for studies of this kind.[7,8] It has been found particularly suitable for the prediction of differences between related bond distances such as changes induced in a particular bond length by substitution.[9-11]

Predicted absolute values obtained by using such basis sets, have to be corrected in order to bring

them in accordance with experimental values. Systematic studies have demonstrated that for a particular type of bond, such as a carbon–carbon single bond, the correction needed is fairly independent of the surroundings of the bond.[7]

In the optimization of the structural parameters the end points were defined by changes in bond distances less than 0.002 Å and by changes in angles less than 0.4°.

In the end points Mulliken population analyses were performed using the program GAUSSIAN 76 by which also molecular energies were calculated using a scaled 4-31G basis.

Table 1. Energies in kcal/mol of the planar rotamers of 2-propen-1-imine relative to the rotamer of lowest energy (TA).[a]

ΔE	0	1.1	1.8	3.8
Rotamer	TA	TS	CA	CS

[a] Total energy of TA: −170.665159 a.u.

Table 2. Optimized geometries of the four rotamers of 2-propen-1-imine. The structural parameters are defined with reference to the labelling of atoms given in Fig. 1.

	Rotamer			
Parameter	TA	TS	CA	CS
$R(N1-C2)$	1.262 (1.274)[a]	1.261	1.262	1.262
$R(C2-C3)$	1.460 (1.454)	1.467	1.469	1.477
$R(C3-C4)$	1.322 (1.336)	1.321	1.321	1.322
$R(N1-H8)$	1.014 (1.014)	1.018	1.014	1.017
$R(C2-H7)$	1.087	1.082	1.085	1.080
$R(C3-H9)$	1.077 (1.086)*	1.081	1.078	1.078
$R(C4-H5)$	1.078	1.078	1.078	1.078
$R(C4-H6)$	1.081	1.080	1.078	1.080
$A(C2N1H8)$	115.0 (111.7)	114.9	115.0	115.8
$A(N1C2C3)$	121.4 (121.5)	126.5	122.9	128.8
$A(C2C3C4)$	123.2 (122.9)	123.4	124.0	125.8
$A(C3C4H5)$	122.0	121.8	121.0	122.8
$A(C3C4H6)$	121.9 (120)*	121.8	121.5	121.5
$A(C2C3H9)$	115.4	116.5	115.8	114.8
$A(C3C2H7)$	115.9	115.8	115.0	114.7

[a] Experimental values, Ref. 1. Values marked with asterix are assumed values in Ref. 1.

RESULTS AND DISCUSSION

Calculated molecular energies are given in Table 1. As revealed by the table the lowest energy is found for the TA-form, in accordance with experiment.[1] The other *trans* rotamer (TS) is predicted to be 1.1 kcal/mol higher in energy, a value that correlates satisfactorily with the experimental estimate of 0.9 kcal/mol.[1] It is worth noticing that the *anti* rotamer of the *cis*-form (CA) is only 1.8 kcal/mol above the ground state, whereas the *syn* rotamer of this form (CS) is found to be 3.7 kcal/mol above this state. The unfavourable energetics of the CS-form can at least partly be interpreted in terms of hydrogen overcrowding. On the other hand the CA-form will undoubtedly be partially stabilized by an attractive interaction between H6 and the lone-pair on the nitrogen atom. This assumption is supported by the small but significantly positive overlap population found in this region. See Table 3. The four different molecular forms studied are depicted in Fig. 1.

The completely optimized geometries of the four rotamers are given in Table 2. For comparison

Table 3. Mulliken population analysis of the different rotamers of 2-propen-1-imine. Optimized geometries. Labelling of atoms given in Fig. 1.

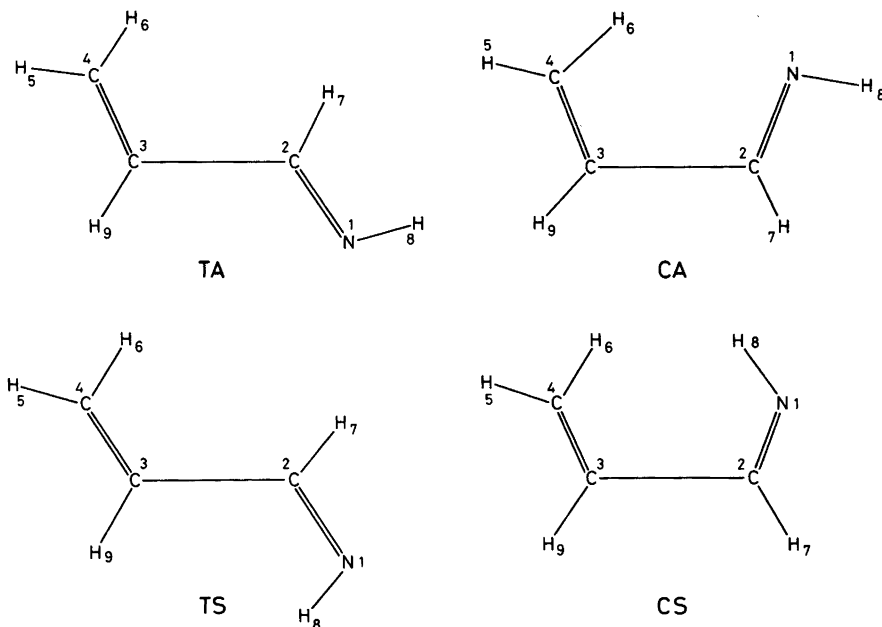|	Rotamer			
	TA	TS	CA	CS
Atomic charges				
N1	−0.597	−0.599	−0.599	−0.589
C2	+0.071	+0.096	+0.083	+0.085
C3	−0.163	−0.210	−0.215	−0.211
C4	−0.339	−0.326	−0.293	−0.317
H5	+0.180	+0.182	+0.169	+0.185
H6	+0.168	+0.180	+0.211	+0.169
H7	+0.170	+0.196	+0.166	+0.192
H8	+0.299	+0.294	+0.300	+0.295
H9	+0.210	+0.188	+0.179	+0.190
Overlap populations				
N1−C2	1.020	1.046	1.072	1.110
C2−C3	0.626	0.644	0.592	0.602
C3−C4	1.120	1.082	1.162	1.170
C2−H7	0.800	0.784	0.794	0.790
C3−H9	0.778	0.780	0.790	0.770
C4−H5	0.784	0.780	0.778	0.786
C4−H6	0.796	0.800	0.794	0.792
N1−H8	0.650	0.674	0.656	0.662
N1···H6			0.010	

Fig. 1. Atomic arrangements and labelling in the four rotamers of 2-propen-1-imine. The rotamers are *s-trans anti* (TA), *s-trans syn* (TS), *s-cis anti* (CA), and *s-cis syn* (CS).

the spectroscopically determined parameters for the TA-form are included in the table. On the whole the experimentally determined bond distances are in fair agreement with the predicted ones. The same is definitely true for the valence angles describing the heavy-atom skeleton. For the CCH-angles and the CNH-angle, however, there are substantial discrepancies.

The discrepancies appearing in Table 2 are interesting in view of the assumptions underlying the estimate of the experimental values. According to Penn[1] substitution coordinates have been evaluated only for the carbon atoms and the imino hydrogen. The coordinates for the nitrogen atom were determined on the basis of assumed $C-H$ bond lengths of 1.086 Å and CCH-angles of 120°. Our results clearly demonstrate that there is a large spread in $C-H$ bond lengths and particularly in CCH valence angles.

In spite of the fact that the relative mass of the H-atoms is low, the assumptions mentioned above have led to inaccurate experimental coordinates for the nitrogen atom. This has also been mentioned by Penn.[1] In this context it is worth observing that a displacement of the nitrogen atom

toward the neighbouring carbon atom will lead to a shortening of $R(N_1-C_2)$ and to a simultaneous increase in the $C_2N_1H_8$ valence angle. According to our predicted geometry parameters both these changes are wanted.

In the experimental work only the normal and imino-d_1 species have been observed for the TS rotamer. Accordingly the structural information available for this rotamer is very limited.

The recorded differences between the rotational constants for the TA and TS rotamers suggested that the TS form was elongated along the *a*-axis as compared to the TA form.[1] It was indicated that this elongation could take place by an increase in the CCC and CCN valence angles. Our calculations lead to the conclusion that the CCC angle is the same in the two forms whereas the CCN angle shows an increase of 5°. Furthermore we predict that the CNH angle has the same value in the two rotamers. The distinct pattern of two CCH angles around 120° and two that are definitely smaller (115−116°) is also the same in the two rotamers. This result is in sharp contrast to the assumption made in the experimental work that all CCH valence angles are 120°.[1]

Table 4. π-Electron contributions to the overlap populations in the heavy-atom part of the different rotamers of 2-propen-1-imine. Optimized geometries. Labelling of atoms given in Fig. 1.

Bond	Rotamer			
	TA	TS	CA	CS
N1−C2	0.474	0.473	0.479	0.478
C2−C3	0.029	0.032	0.014	0.018
C3−C4	0.504	0.504	0.506	0.507

As mentioned above, the other possible rotamers, CA and CS, have so far not been detected. In a possible search for these rotamers it might be helpful to know that for the CA rotamer our results suggest a slightly longer C_2-C_3 bond, and a small increase in the valence angles for the heavy atom skeleton as compared to the TA ground state. As shown by Table 2 the structural differences between the rotamers CA and CS are expected to be nearly the same as those between the forms TA and TS.

The results obtained by the population analysis, presented in Table 3 and Table 4, show that the total overlap population for the C_2-C_3 bond is slightly smaller for the *cis*-forms than for the *trans*-forms, and that a part of this difference is due to a larger accumulation of π-electrons in this region for the *trans*-forms. This is in accordance with the assumption of a more extensive conjugation in the *trans*-forms. The differences are minute, however, and are not reflected in the optimized bond lengths.

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