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## Ab initio study of formazan and 3-nitroformazan

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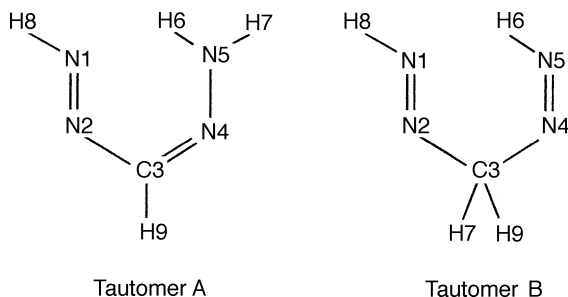
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Formazan and 3-nitroformazan have been investigated at *ab initio* level (MP2/6-31G\*\* and B3LYP/6-31G\*\*) in all their possible conformations, for studying the various possibilities of intramolecular hydrogen bonding formation. The *trans-syn-s-cis* (TSSC), known also as *yellow form*, has been found to be the most stable conformer (at least in the gas phase) in both compounds. This particular structure is strongly stabilized by a N—H···N hydrogen bridge, which gives rise to a hexatomic chelate ring, with the possibility of a proton transfer process. This closely resembles that of malondialdehyde, previously studied, in the evolution of the potential energy shape but with a greater barrier height. Various approaches for obtaining a quantitative estimate of the energy of the hydrogen bridges are discussed. The electronic structures of the most favoured TSSC, TSST (*trans-syn-s-trans*) and TAST (*trans-anti-s-trans*) conformations of formazan have been compared with those of the corresponding forms of 1,5-diphenylformazan, in order to account for the UV spectra available in the literature and the different colours exhibited by the molecule on passing from one conformation to another.

### Introduction

Malondialdehyde is perhaps the most studied molecule among  $\beta$ -dicarbonyls because of its tautomerism and strong O—H···O intramolecular hydrogen bond (see, *e.g.*, ref. 1). Formazan resembles malondialdehyde in that it has —N=N—H and =N—NH<sub>2</sub> sub-units instead of C=O and C—O—H frameworks and also shows tautomerism involving an amino proton, which can produce N—H···N hydrogen bridges having different strengths, depending on the molecular conformation. Analogous to malondialdehyde, formazan is also able to give chelate complexes with metals (Cu, Ni, Zn, *etc.*); moreover its tetrazolium salts, as 2-(4-iodophenyl)-3-(4-nitrophenyl)-5-phenyl tetrazolium chloride and 5-cyano-2,3-ditolyl tetrazolium chloride, are very important in view of their use as indicators of respiratory activity and cytotoxicity assays.<sup>2,3</sup>

Theoretically the following two tautomers (A and B) can be expected for formazan:



Scheme 1

Even if A is more stable than B, owing to its conjugate system, the study of tautomer B is also interesting for investigating the strength of the possible N—H···N bridge involving the imino group in the absence and presence of conjugation.

As shown in Fig. 1 and 2, eight conformations are possible for tautomer A and ten conformations for tautomer B. They

are labelled according to the following nomenclature: the *trans-cis* isomers are described with respect to the N1=N2 and N2—C3 bonds, whereas the *syn-anti* conformers are described with respect to the C3—N4 bond (although in B the single and double bonds have different positions, the same labels as used for A are preserved for continuity). Whilst no experimental information is available for simple formazan, to the best of our knowledge, it is known from the literature that formazan derivatives (*e.g.* 1,5-diphenylformazan, and its related 3-methyl, 3-nitro, 3-ethyl, 3-phenyl, 3-*tert*-butyl derivatives and so on) can exist in linear, half folded and fully folded forms.<sup>4,5</sup> The available experimental findings suggest that the relative stability and conformational equilibrium of these isomers are mainly governed by intramolecular and/or (in solid and liquid phase) intermolecular hydrogen bond formation and by the bulkiness of the substituent groups, the linear form (TAST, *trans-anti-s-trans*, often indicated as the *yellow form*) being the most stable when substituents are small.<sup>4,5</sup> The fully folded, TSSC (*trans-syn-s-cis*) and half folded TSST (*trans-syn-s-trans*) conformers, both with the possibility of N—H···N bridge formation, are referred to as red II and red I forms, respectively.<sup>4</sup> In solution these isomers are in equilibrium and the relative abundance also depends upon the nature of the solvent.<sup>4–7</sup> It has been also reported that the above cited conformers have low interconversion barriers<sup>8,9</sup> and have interesting ground and excited state absorption characteristics,<sup>10</sup> responsible for the solvatochromism and photochromism<sup>11–13</sup> exhibited by formazans.

Strangely, if a CNDO/2 study on the quasiaromaticity of fully folded formazan<sup>14</sup> and a report in the PhD thesis of one of us<sup>15</sup> are excluded, no theoretical investigation on these systems has been found in the literature. The order of stability of the most probable conformations in the gas phase seems to be highly dependent on the calculation approach adopted for the geometrical optimization procedure. In fact, the semi-empirical AM1 method predicts TSSC to be the most stable conformer, in contrast with PM3 and *ab initio* (3-21G and

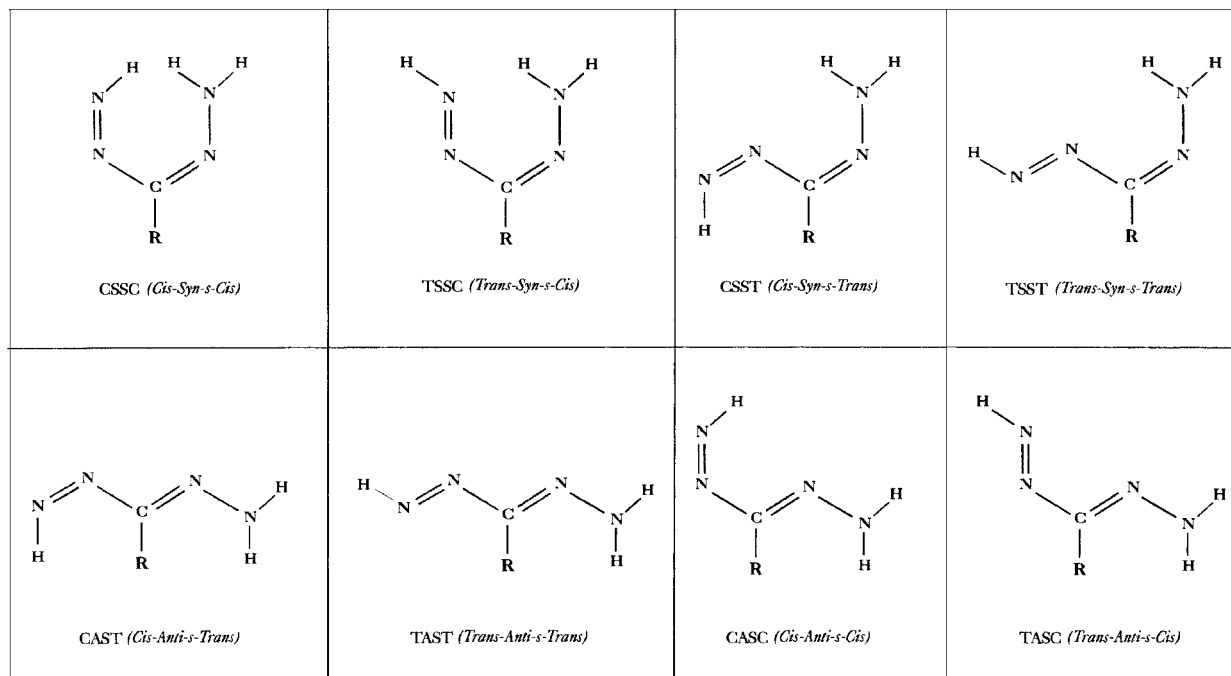


Fig. 1 Possible conformations of tautomer A of formazan.

6-31G\*) results, according to which TSST is the preferred form.<sup>15</sup> Obviously, such results also point out the important role played by intramolecular hydrogen bridges.

Substitution of the hydrogen at the carbon atom with a nitro group, should give rise to additional hydrogen bonding possibilities (N—H...O bridges), so it appears advisable to carry out a more complete *ab initio* study for these systems, taking into account all the possible molecular conformations, and including the correlation energy and the zero point vibration energy correction. In particular it would be a very important goal to estimate the hydrogen bond strengths of the

various N—H...N and N—H...O bridges for comparison with the values previously obtained for the O—H...O bridge of malondialdehyde, acetylacetone and related 3-substituted derivatives. At the same time it is interesting to investigate the potential energy curve of the proton transfer process for comparison with that of malondialdehyde, previously studied.

In the present paper, formazan (I) and 3-nitroformazan (II) together with the most favoured conformations of 1,5-diphenylformazan have been studied. The investigation has also been extended to the electronic structure of each conformation in order to obtain detailed information on the elec-

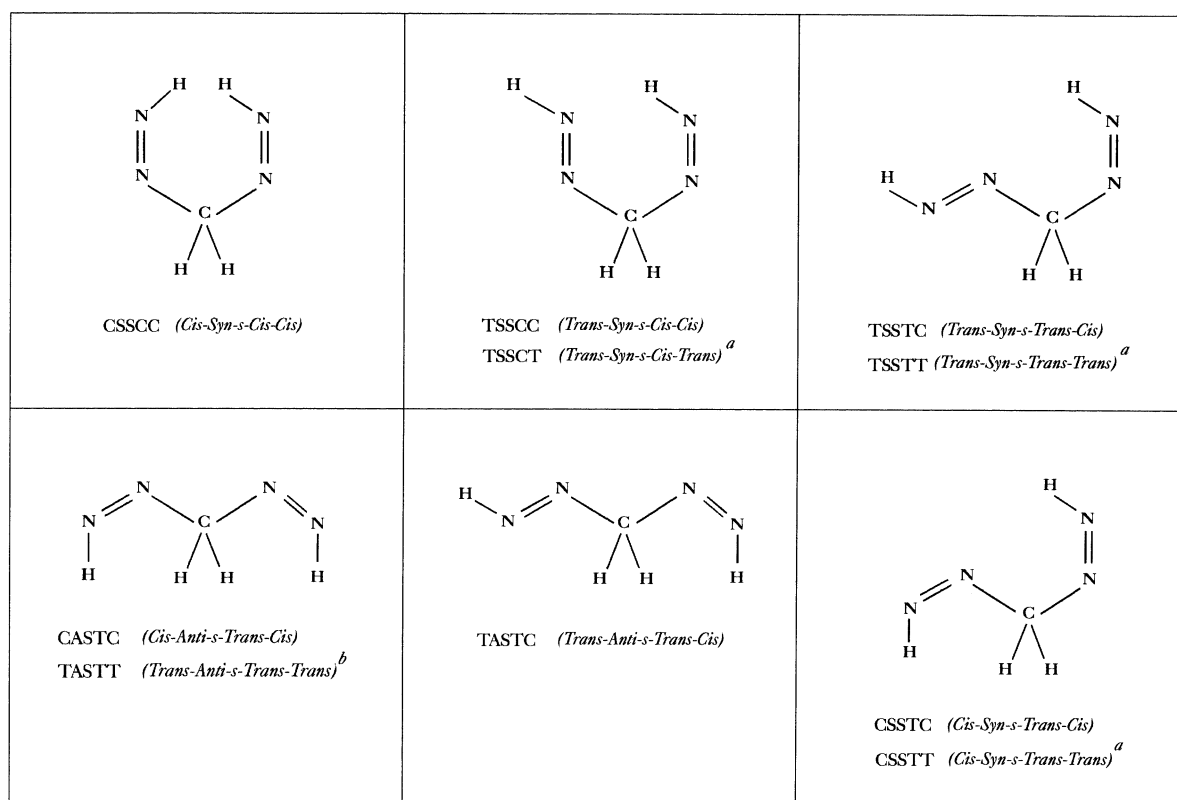


Fig. 2 Possible conformations of tautomer B of formazan.<sup>a</sup> H6 rotated by 180°. <sup>b</sup> H6 and H8 rotated by 180°.

tronic transitions, responsible for the colour of the compound. Finally the vibrational frequencies were calculated in order to evaluate the zero point energy.

## Calculations

The present study was performed at *ab initio* level by means of GAUSSIAN92 and GAUSSIAN94 programs.<sup>16,17</sup> All the possible conformations shown in Fig. 1 and 2 were fully optimized using the standard 6-31G\*\* basis and correlation energy inclusion, evaluated both at the Møller–Plesset second order and at the density functional theory (DFT) levels. In the B tautomer conformations, H7 and H9 were assumed to lie perpendicularly to the N<sub>2</sub>C<sub>3</sub>N<sub>4</sub> plane.

Owing to the limited hard disk capacity of the available computers, the vibrational frequencies of the nitro derivative conformations, were calculated only at DFT level (for the cumbersome 1,5-diphenylformazan the 3-21G basis was used). The B3LYP keyword<sup>18–21</sup> was adopted for this approach, which implies the adoption of the Becke's three parameters hybrid method, where the non-local correlation is provided by the Lee, Yang and Parr functional.<sup>20</sup> Ultraviolet spectroscopic transition energies and oscillator strengths have been computed using the default CI procedure for singlet states (doubly excited configurations were not taken into account). All calculations were carried out on an ALPHA-3400 and a SUN-Ultra1 workstation.

## Results and discussion

### (a) Molecular geometries and stability order

The possible conformations of tautomer A are shown in Fig. 1. Their optimized geometries are omitted for space saving, but are available upon request. All conformations of **I** adopt a full planar geometry, except the CSSC, CASC and TASC ones, in which the H–N1–N2 framework undergoes non-negligible rotation around the C–N single bond, and the

amino group tends to assume a pyramidal arrangement.<sup>22</sup> As it can be seen from the  $\Delta E$ s collected in Table 1, the relative stabilities among the possible conformations of tautomer A of formazan do not change when the zero point vibration energy correction is considered, but MP2 and B3LYP approaches predict different stability order for the CAST, CASC and TASC forms. In any case, independently of the adopted method, the preferred conformers are, in the order, the TSSC, TSST and TAST ones. On the grounds of the related  $\Delta E$  values and Boltzman equation, TAST should be present in low quantity in the conformational equilibrium, at least in the gas phase.

Comparison (Table 2) with results available in the literature<sup>15</sup> shows that the stability order is basis set independent only when the correlation energy is enclosed. It is also noteworthy that semiempirical AM1 results agree with the *ab initio* ones better than those of the PM3 method since this latter method predicts relevant torsion angles.

The stability of the chelate TSSC form derives mainly from the N5–H6···N1 hydrogen bridge, as evidenced by the related N···N and N···H distances ( $r_{5-1} = 2.586 \text{ \AA}$ ,  $r_{6-1} = 1.851 \text{ \AA}$ ), which are shorter than the sum of the van der Waals radii (1.55  $\text{\AA}$  for N, 1.2  $\text{\AA}$  for H<sup>23</sup>). The presence of hydrogen bonding is also evident from the greater conjugation present in the N1=N2–C3=N4 framework. Quantitative evaluation of its hydrogen bond energy ( $E_{\text{HB}}$ ) is however a hard task because a reference "open form" analogous to that adopted for malondialdehyde (O–H group rotated by 180°) is not possible here. Alternative reference conformations for this purpose could be CAST, TAST or TASC, whilst CSST, TSST and CASC are to be excluded because they also have weak hydrogen bridges (N5–H6···N2 and N1–H8···N4). With respect to CAST, TAST and TASC,  $E_{\text{HB}}$  values of 30.56, 9.84 and 29.08  $\text{kJ mol}^{-1}$  (24.02, 7.29 and 32.49  $\text{kJ mol}^{-1}$  at B3LYP level) are obtained after zero point vibration energy correction. The 9.84  $\text{kJ mol}^{-1}$  value is too low (it is lower than the energy of the intermolecular hydrogen bridge of water)

**Table 1** Stability order and energy differences ( $\text{kJ mol}^{-1}$ ) among the possible conformations of **I** and **II**

Formazan	3-Nitroformazan							
	MP2/6-31G**		B3LYP/6-31G**		MP2/6-31G**	B4LYP/6-31G**		
	$\Delta E$	$\Delta E'^a$	$\Delta E$	$\Delta E'^a$		$\Delta E$	$\Delta E'^a$	
TSSC	0.0	0.0	0.0	0.0	TSSC	0.0(0.0)	0.0	0.0
TSST	4.5	3.1	2.9	0.7	TAST	7.0(3.8)	13.1	12.4
TAST	12.4	9.8	10.8	7.3	TASC	10.4(25.6)	8.8	7.5
CSST	19.7	16.9	15.2	11.4	CASC	13.7(27.0)	13.8	11.4
CASC	27.4	26.8	34.5	32.2	TSST	15.9(7.0)	21.2	19.9
TASC	29.7	29.1	32.7	30.6	CSST	21.0(27.4)	13.5	12.8
CAST	35.1	30.6	29.7	24.0	CAST	25.1(32.9)	17.8	16.8
CSSC	43.5	43.2	53.7	52.4	CSSC	50.3(51.8)	60.7	58.4

<sup>a</sup> Values corrected for the zero point vibration energy. <sup>b</sup> Values in parentheses refer to the conformations having the nitro group perpendicular to the heavy atom skeleton.

**Table 2** Comparison between AM1, PM3 and *ab initio* results concerning the most stable conformations of formazan ( $\Delta E$  in  $\text{kJ mol}^{-1}$ )

	AM1 <sup>a</sup>	PM3 <sup>a</sup>	HF/3-21G <sup>a</sup>	MP2/3-21G <sup>b</sup>	HF/6-31G* <sup>a</sup>	MP2/6-31* <sup>b</sup>	MP2/6-31G** <sup>b</sup>
$\Delta E$							
TSSC	0.0	6.9	1.3	0.0	0.0	0.0 <sup>c</sup>	
TSST	15.9	0.0	0.0	17.0	0.0	4.0	4.5 <sup>d</sup>
TAST	29.5	4.9	16.5	32.8	5.8	12.0	12.4 <sup>e</sup>

<sup>a</sup> Ref. 15. <sup>b</sup> Present work. <sup>c</sup>  $E = -258.687072 E_{\text{h}}$ ; thermal correction to enthalpy = 196.9  $\text{kJ mol}^{-1}$ ; thermal correction to Gibbs free energy = 106.1  $\text{kJ mol}^{-1}$ . <sup>d</sup>  $E = -258.685348 E_{\text{h}}$ ; thermal correction to enthalpy = 194.2  $\text{kJ mol}^{-1}$ ; thermal correction to Gibbs free energy = 106.4  $\text{kJ mol}^{-1}$ . <sup>e</sup>  $E = -258.682359 E_{\text{h}}$ ; thermal correction to enthalpy = 193.4  $\text{kJ mol}^{-1}$ ; thermal correction to Gibbs free energy = 105.3  $\text{kJ mol}^{-1}$ .

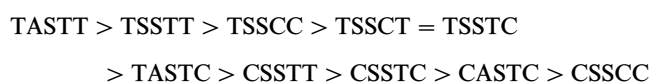
perhaps because the TAST conformation, stabilised by attractive interaction between the lone pair of N1 and H9, is not a valid reference for our purpose. On the contrary, the other two values, very close to each other, appear to be reasonably acceptable, being sufficiently strong for an intramolecular bridge stabilised by conjugation. It should be noted that  $E_{\text{HB}}$  values are significantly lower than that found in malondialdehyde, where the more electronegative oxygen atom is involved. TASC seems to be the most suitable reference conformer since it differs from TSSC only in the orientation of the amino group and the  $\text{H9}\cdots\text{H6}$  repulsion is damped by the small planarity loss.

The bridges possible in CSST and TSST are expected to be weaker than in TSSC because their  $\text{N}\cdots\text{N}$  distances are longer than in TSSC and, mainly, because such bridges give rise to a pentatomic instead of a hexatomic ring. A rough estimate of their strengths can be done assuming CAST and TAST, respectively, as reference conformations: under these assumptions,  $E_{\text{HB}}$  is  $13.69\text{ kJ mol}^{-1}$  for CSST ( $r_{\text{N5}\cdots\text{N2}} = 2.669\text{ \AA}$ ,  $r_{\text{N2}\cdots\text{H6}} = 2.321\text{ \AA}$ ), and  $6.72\text{ kJ mol}^{-1}$  for TSST ( $r_{\text{N5}\cdots\text{N2}} = 2.697\text{ \AA}$ ,  $r_{\text{N2}\cdots\text{H6}} = 2.345\text{ \AA}$ ). These lower values, qualitatively in line with the longer  $\text{N}\cdots\text{N}$  and  $\text{N}\cdots\text{H}$  distances, confirm the weakness of the hydrogen bridges; in any case they point out that the relative stability order of these structures is governed mainly by the balance between repulsive and attractive interactions instead of the presence of a true hydrogen bond.

The hydrogen bridge possibly present in the CASC conformation ( $r_{\text{N1}\cdots\text{N4}} = 2.700\text{ \AA}$ ,  $r_{\text{N4}\cdots\text{H8}} = 2.187\text{ \AA}$ ) is different from the other conformations because it involves the imino proton instead of amino proton. Its  $E_{\text{HB}}$ , evaluated once again as the stability difference with respect to the TASC form, is only  $2.24\text{ kJ mol}^{-1}$ . It is therefore a very weak bridge, but its strength should be the most correct and reliable, according to the adopted  $E_{\text{HB}}$  definition, because CASC and TASC differ only in the orientation of the  $\text{N1-H8}$  bond and the geometrical parameters are not appreciably different in the two conformations.

The best CSSC geometry is not planar and, notwithstanding hydrogen bond interactions, seems to be possible on the grounds of non-bonded distances, an  $E_{\text{HB}}$  estimate should be trivial because of the conjugation broken by non-planarity, and by the unfavourable directions of the nitrogen lone pairs.

As far as the possible conformations of tautomer B is concerned (Fig. 2), the following stability order is predicted at MP2/6-31G\*\* level ( $\Delta E$  in  $\text{kJ mol}^{-1}$ ):



$\Delta E$  values are 0.00, 1.35, 12.81, 14.42, 14.43, 20.86, 24.51, 34.80, 44.18 and 54.60, respectively.

TSSTC is the only conformation showing planar geometry, but the most stable is the symmetric TASTT form (characterized by  $r_{\text{C-N}} = 1.469\text{ \AA}$ ,  $r_{\text{N=N}} = 1.265\text{ \AA}$ ,  $\theta_{\text{N-C-N}} = 108.1^\circ$ ,  $\theta_{\text{C-N=N}} = 110.1^\circ$  and a torsion angle of  $132.2^\circ$  around the  $\text{C-N}$  single bond) followed by the nearly isoenergetic TSSTT form ( $\Delta E = 1.35\text{ kJ mol}^{-1}$ ). However, TASTT is predicted to be  $44\text{ kJ mol}^{-1}$  higher in energy than the (most stable in absolute) TSSC form of tautomer A. Owing to this remarkably lower stability of the B tautomer, no correction for the zero point vibrational energy was considered and no B3LYP calculation was carried out. Tautomer B, though by far less stable, has been considered here in order to analyse the terms governing the hydrogen bond energy in tautomer A.

Shorter  $\text{N}\cdots\text{N}$  and  $\text{N}\cdots\text{H}$  distances confirm the presence of a hydrogen bridge in the TSSCC, TSSTC and CSSTC forms. In the TSSTC and CSSTC conformations, however, the  $\text{N2}\cdots\text{N5}$  distances (2.694 and 2.698  $\text{\AA}$ , respectively, according to MP2 results) are longer than those of TSSTT (2.569  $\text{\AA}$ ) and CSSTT (2.581  $\text{\AA}$ ), indicating negligible or the absence of a

hydrogen bridge. Support for this conclusion comes also from the lower stability of the former with respect to the latter forms. Therefore, only in the TSSCC conformation can hydrogen bonding stabilization (but not enough to ensure molecular planarity) be expected. Assuming that the hydrogen bond energy for TSSCC ( $E_{\text{HB}}$ ) is roughly coincident with the stabilization of the considered conformation with respect to TSSCT or TSSTC, an  $E_{\text{HB}}$  value of only  $1.6\text{ kJ mol}^{-1}$  is produced.

Apart from the non-quantifiable error implicit in the adopted definition of hydrogen bond strength, the value of  $1.6\text{ kJ mol}^{-1}$  concerning TSSCC could be acceptable because in this tautomer the two double bonds are separated by two single  $\text{C-N}$  bonds, with consequent conjugation breaking with respect to A. This shows the importance of conjugation in stabilizing the hydrogen bridge in the corresponding isomer of tautomer A. When comparison of the energies between the corresponding conformations of tautomers A and B (isomerization energy) is made, it is noted that the  $\Delta E$  values are constantly in the range of  $50\text{--}60\text{ kJ mol}^{-1}$ , except for the TAST form, where  $\Delta E$  is about  $32\text{ kJ mol}^{-1}$ .

Formazan and 3-nitroformazan have TSSC as the most stable conformation (Table 1), but the stability order of their other forms is different; this is in view of the interaction of the  $\text{NO}_2$  group with the neighbouring hydrogen atoms. No conformation of 3-nitroformazan is fully planar: all of them are mainly characterized by a more or less significant rotation angle of the nitro group and by the tendency of the  $\text{NH}_2$  group to evolve towards a pyramidal accommodation. At the B3LYP level the torsion angles are substantially lower than at the MP2 level (TSSC and CSST conformations are predicted to have an essentially planar formazan skeleton and the nitro group is rotated by only  $7$  and  $3^\circ$  in the two forms, respectively). Energy values, summarized in Table 1, show that the stability order is highly dependent on the approach used for the correlation energy evaluation. In any case, TAST and TASC are the most favoured conformations after TSSC. According to B3LYP results, the order of stability of TAST and TASC is reversed with respect to MP2 prediction; moreover CASC, TASC and CSST differ very little in energy and their relative order is modified when the zero point vibration energy is taken into account.

In addition to those seen in formazan,  $\text{N-H}\cdots\text{O}$  type hydrogen bridges are present in 3-nitroformazan and this gives rise to non-planar hexatomic chelate rings, stabilizing the various conformations in different ways. Two  $\text{N-H}\cdots\text{O}$  bridges are simultaneously present in CAST, but their contribution to the energy lowering of this form seems to be modest, given that it is about  $18\text{ kJ mol}^{-1}$  less stable than the TAST form, where only one such bridge is possible. Indeed, the stability order and the related  $\Delta E$  values are not easily understandable if one takes into account the number and type of hydrogen bonding because the total energy of each conformation is the final result of a balance of many different energy terms which cannot be considered constant. What one notes is that the CAST, TAST, CASC and TASC conformations of 3-nitroformazan, where hydrogen bonding with the nitro group is possible, undergo stabilization with respect to the corresponding conformation of formazan (the exception is CSST), whilst TSST, CSST and CSSC, where such hydrogen bonding interactions are absent, undergo some degree of destabilization. This trend is confirmed also by the B3LYP results, except for the CSST and TAST forms. When the nitro group is frozen perpendicularly to the  $\text{N-C=N}$  plane, so that the possibility of  $\text{N-H}\cdots\text{O}$  bridge formation is avoided, the formazan heavy atom skeleton regains its near planarity, except in the TASC ( $\omega_{1-2-3-4} = -20.3^\circ$ ), CASC ( $\omega_{1-2-3-4} = -11.1^\circ$ ) and CSSC ( $\omega_{1-2-3-4} = 43.6^\circ$ ) conformations. From the stability order obtained in this situation (Table 1) it can be seen that the energy differences, with respect to the most stable TSSC form, concerning CAST and TASC are 32.9 and

25.6 kJ mol<sup>-1</sup>, respectively. They are not far from the value found for the corresponding structures of formazan and allow us to conclude that the hydrogen bond energy of TSSC is not changed appreciably on going from **I** to **II**.

The CASC conformation of 3-nitroformazan is 3.4 kJ mol<sup>-1</sup> less stable than TASC (in formazan the stability order is reversed), which confirms that the N1—H8···N4 bridge in the former structure is not as apparent.

Attempts to estimate the strength of other hydrogen bridges in 3-nitroformazan were made, but a discussion on them is omitted here in view of the fact that quantitative evaluation of the hydrogen bond energy is not possible as a well defined hydrogen bond free reference structure is not available. It can only be said that the strongest hydrogen bridge is the one present in the TSSC conformation and that the hydrogen bridges involving NO<sub>2</sub> should be weaker owing to the ring non-planarity, which does not allow good conjugation.

Analysis of the normal vibration modes concerning the atoms involved in the hydrogen bridge shows that the N5—H7 and N5—H6 stretching modes are partially coupled and give rise to two bands, whose positions in the IR spectrum depend on the considered conformation and on the approach adopted in evaluating the correlation energy. For unsubstituted formazan they are calculated in the ranges of 3710–3850 and 3350–3650 cm<sup>-1</sup>, respectively, according to MP2 and shifted towards lower values by about 100 cm<sup>-1</sup> according to the B3LYP approach. From inspection of the obtained frequencies it can be noted that on passing from the hydrogen bond free TAST to the hydrogen bonded TSSC conformation,  $\nu_{\text{H6}}$  shifts towards lower frequencies by about 170 cm<sup>-1</sup>. The value of 3350 cm<sup>-1</sup>, predicted at the B3LYP level for  $\nu_{\text{H6}}$  of the TSSC form agrees very well with the experimental band observed at 3337 cm<sup>-1</sup> in the IR spectrum of the red form of 3-ethyl-1,5-diphenylformazan.<sup>6</sup>

On passing to 3-nitroformazan, one notes that the trend of the stretching frequencies involving H6 parallels those found for formazan. In particular, the stretching mode frequency of N—H6 is 3336 cm<sup>-1</sup> in TSSC and in the range of 3450–3500 cm<sup>-1</sup> in the remaining forms. The shift towards lower frequencies with respect to the possible reference conformations are of the same order found in formazan, suggesting that the potential energy well of the strongest hydrogen bridge is not remarkably affected by 3-substitution.

### (b) Hydrogen bonding energy from rotation barriers

As previously discussed, the difficulty in calculating the energetic values,  $E_{\text{HB}}$ , of the hydrogen bridges present in several formazan conformations arises from the impossibility in finding a fully reliable reference conformation that is free of hydrogen bonding. Rotation of the hydrogen atom of the bridge by 180°, as done in malondialdehyde and its derivatives is impracticable here (except for the CASC conformation). Moreover, as we pointed out in previous papers for  $\beta$ -diketones,<sup>24,25</sup> the difference in stability between the chelate and open conformations is not the best solution because the values obtained may not be the actual strength of the bridge since they can be affected by other terms extraneous to the hydrogen bond strength. This is especially true in formazan in view of the different strain and non-bonded interactions operating in the two conformers compared. Therefore, to check the reliability of  $E_{\text{HB}}$  values discussed in the previous section for TSSC and other forms of formazan, we tried to obtain the hydrogen bond strength in a different way.

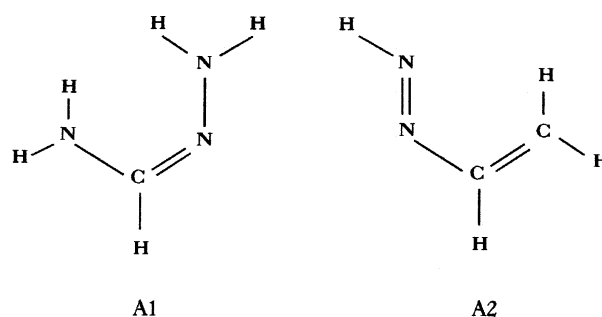
An alternative reference free hydrogen bonded structure of TSSC could be obtained after rotation by 90° (or more, if the maximum of the curve does not lie at 90°) of the NH<sub>2</sub> or the HN1=N2 groups. In this case the energy difference between the planar and rotated forms (here indicated as  $\Delta E_{0-90}$ ) should be the sum of the hydrogen bond strength ( $E_{\text{HB}}$ ) and of

the internal rotation barrier (RB):

$$\Delta E_{0-90} = E_{\text{HB}} + \text{RB}$$

If one calculates the RB of the NH<sub>2</sub> or of the HN1=N2 groups in simple, hydrogen bridge free molecules,  $E_{\text{HB}}$  could be easily deduced from the above equation. If  $E_{\text{HB}}$  estimated in this way agrees with  $E_{\text{HB}}$  evaluated as the energy difference between the open and chelate conformers for simple compounds where geometries and strain are not excessively different in the two forms, then we can use this approach with confidence in more complicated compounds when it is not possible, or it is not convenient, to select an open conformation as the free hydrogen bonding reference structure.

When applied to malondialdehyde (selecting vinyl alcohol as the reference compound) a value of 58.87 kJ mol<sup>-1</sup> is obtained for the hydrogen bond strength. The excellent agreement with  $E_{\text{HB}}$  previously obtained (58.60 kJ mol<sup>-1</sup><sup>25</sup>) is an encouraging support to the validity of such an idea. According to this method,  $E_{\text{HB}}$  for the TSSC conformer of formazan could be obtained by considering the barrier of the NH<sub>2</sub> or that of the H—N=N groups, whilst RB can be obtained from the following A1 and A2 reference compounds:



Scheme 2

In calculating the barrier of A1, the left side amino group was oriented in such a way that the lone pair of its N atom is always directed towards the nitrogen atom of the right side amino group so that most of the N···N interactions present in formazan, except those concerning the hydrogen bonding, are preserved. In such conditions a RB of 50.52 kJ mol<sup>-1</sup> was attained for NH<sub>2</sub> which, compared with the analogous barrier of formazan gives  $E_{\text{HB}} = 39.26$  kJ mol<sup>-1</sup>. This could be an acceptable value because it is lower than that found in malondialdehyde (as expected) and only a few kJ mol<sup>-1</sup> higher than those deduced in the previous section when CAST and/or TASC were assumed as hydrogen bond free reference conformations.

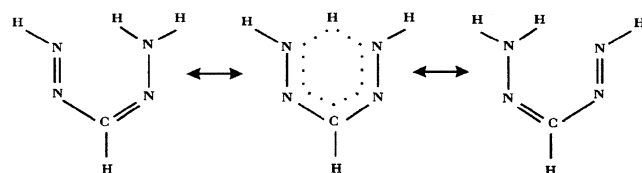
Rotation of the H—N=N framework of formazan produces a barrier of 47.70 kJ mol<sup>-1</sup> when full planarity (sp<sup>2</sup> hybridization) was imposed on the NH<sub>2</sub> group, and 33.88 kJ mol<sup>-1</sup> when NH<sub>2</sub> is free to adjust the spatial position of the hydrogen atoms during rotation. Comparison with the corresponding barrier in the A2 reference molecule (13.59 kJ mol<sup>-1</sup>) gives  $E_{\text{HB}}$  values of 34.11 or 20.29 kJ mol<sup>-1</sup>, in the two cases, respectively. Both of these are reasonable values, but the former is closer to that obtained in the previous section as the stability difference between the chelate (TSSC) and non-chelate (TASC and CASC) structures. Such results, however, are rather different from each other and do not allow us to judge whether  $E_{\text{HB}}$ , estimated through the proposed procedure, is as good as it appears or not when applied to malondialdehyde. Bearing in mind that there can be an error due to the non-transferability of the barrier from one molecule to another, one can conclude that the energy of the hydrogen N5—H6···N1 bridge is in the range 20–40 kJ mol<sup>-1</sup>, but, taking into account  $E_{\text{HB}}$  obtained in the previous section, its most probable strength is closer to an average value of 30 kJ mol<sup>-1</sup>.

When applied to the CSST and TSST conformations for evaluating the strength of the N5—H6···N2 bridge, an  $E_{\text{HB}}$  value of 2.2 kJ mol<sup>-1</sup> was found for the former and zero for the latter conformation. Such results confirm the weakness of the N5—H6···N2 bridge and suggest that the lowest  $E_{\text{HB}}$  value deduced in the previous section (6.72 kJ mol<sup>-1</sup>) should be taken as correct.

An attempt to evaluate the strength of a possible hydrogen bond involving the N1—H8 imino group was done by considering the TSSC conformation of formazan having the NH<sub>2</sub> group rotated by 90°. Unfortunately, no useful datum was obtained because when H8 points towards the lone pair of N5 the total energy is higher and  $r_{\text{N1} \cdots \text{N5}}$  longer (2.826 Å) than those obtained for the conformation having H8 oriented in opposite direction ( $r_{\text{N1} \cdots \text{N5}} = 2.715$  Å).

### (c) Proton transfer

Further information on  $E_{\text{HB}}$  can be obtained from comparison of the potential energy well of formazan with that, previously studied, of malondialdehyde<sup>26</sup> since, as for malondialdehyde, formazan in its TSSC conformation can also exist in two energetically equivalent forms interconverting with each other as follows:



Scheme 3

The evolution of the potential energy curve on going from double ( $C_s$  symmetry) to single ( $C_{2v}$  symmetry) minimum shape, shows that the barrier between the two potential energy wells becomes practically negligible at  $r_{\text{N1} \cdots \text{N5}} = 2.3$  Å and vanishes completely at  $r_{\text{N1} \cdots \text{N5}} = 2.2$  Å, giving rise to a single, rather flat, well. Analysis of the molecular geometrical parameters evidences that at these short N1···N5 distances the two N—N as well as the two C—N bonds become equivalent, even if no symmetry restriction was imposed. When the exact  $C_{2v}$  symmetry is imposed, the minimum energy geometry is characterized by  $r_{\text{N} \cdots \text{N}} = 1.314$  Å,  $r_{\text{C} \cdots \text{N}} = 1.347$  Å and  $\theta_{\text{N-N-C}} = 114.5^\circ$ . H6 is at 1.246 Å from N5 and from N1 whilst  $r_{\text{N5} \cdots \text{N1}}$  is 2.3537 Å (in the TSSC minimum energy structure  $r_{\text{N5} \cdots \text{N1}} = 2.5856$  Å). In the corresponding  $C_{2v}$  conformation of malondialdehyde  $r_{\text{O} \cdots \text{O}}$  was 2.363 Å and  $r_{\text{O} \cdots \text{H}} = 1.204$  Å (2.592 and 1.697 Å, respectively, in the  $C_s$  form).

The  $\Delta E$  between the energy of the TSSC conformation of formazan in its H-centred,  $C_{2v}$ , and most stable,  $C_s$  forms, *i.e.* the barrier to the proton transfer process, is 26.75 kJ mol<sup>-1</sup> (15.20 kJ mol<sup>-1</sup> in malondialdehyde<sup>26</sup>). From these data it is found that malondialdehyde and formazan behave very similarly, but the higher value of the proton transfer barrier in the present case indicates that the hydrogen bridge energy in formazan is weaker than in malondialdehyde.

### (d) Electronic spectra

The theoretical information gained in the present work can be useful to account for the solvatochromism shown by formazan derivatives. Experimental reports on the UV spectra of simple formazan are not available but those of 1,5-diphenylformazan and several of its 3-substituted derivatives are known,<sup>4-7</sup> although not deeply studied from the theoretical point of view. On the grounds of the absorption bands and resonance Raman spectra of such molecules, it was concluded that the yellow colour is peculiar to the TAST form, whilst the red-I and red-II forms are to be identified with the TSST and TSSC

conformations, respectively.<sup>4</sup> It was also observed that the spectrum of 1,5-diphenylformazan and 3-methyl-1,5-diphenylformazan (TAST, yellow form) in freshly prepared CCl<sub>4</sub> solution shows the most intense absorption band at 406 and 398 nm, respectively. At equilibrium, the band at 406 nm of the former compound is slightly reduced in intensity and a weak shoulder appears near 500 nm,<sup>4</sup> whilst in the 3-methyl derivative spectrum two bands having comparable intensities were observed at 398 and 477 nm. Analogously a fresh solution of the yellow form of 3-ethyl-1,5-diphenylformazan also shows an absorption peak at 398 nm, which at equilibrium becomes a shoulder of the band at 477 nm. No time dependence was noted in the spectra of 3-isopropyl- and 3-*tert*-butyl-1,5-diphenylformazan, whose main absorption band lies at 469–473 nm.<sup>4</sup> Other bands, which preserve their shape in all the above compounds are present near 300 and 250 nm. Moreover, from X-ray crystal structure analysis of the 3-ethyl-1,5-diphenylformazan TAST form an intermolecular hydrogen bridge between H6 and N2 of adjacent molecules was noted ( $r_{\text{N} \cdots \text{H}} = 2.48$  Å), together with a somewhat shorter intramolecular hydrogen bridge between the same atoms inside the TSST form.<sup>6</sup> These hydrogen bridges in the solid state and those possible with solvent molecules in solution, suggest that the stability order from calculations may be completely different from that of the solid state. In other words, if strong steric effects originating from the size of the group attached at the 3-position are absent, the stability of the TAST and TSST conformations in the solid state is governed by crystalline forces and intermolecular hydrogen bridges with adjacent molecules, whilst in solution a relevant role can be played by possible intermolecular hydrogen bonds with solvent molecules too. On the contrary, when a very cumbersome 3-substituent group is present, only the TSSC conformation, stabilized by its intramolecular hydrogen bridge, is allowed by steric effects.

Our theoretical results, both at the 6-31G\*\* and 3-21G levels, predict the lowest electronic transition of formazan ( $n \rightarrow \pi^*$ ), in the TSSC conformation, on the boundary of the UV and visible region (370 nm) with a shift towards shorter wavelengths in the less stable TSST and TAST conformations. The first  $\pi \rightarrow \pi^*$  transition, having rather strong intensity, is predicted to lie at 242 nm in TSSC and it also shifts towards shorter wavelengths in the TSST and TAST forms. Even if this calculated value refers to the gas phase, it is to be excluded that the red shift expected on passing to the liquid phase can be the only effect responsible for its shift up to the value of 400 nm observed in the 1,5-diphenylformazans and related 3-substituted derivatives. On the other hand, that the experimental band at 400 or 477 nm reported in the literature could originate from an  $n \rightarrow \pi^*$  transition is excluded by its strong intensity.

Comparison of formazan and 1,5-diphenylformazan optimized geometrical parameters (MP2/3-21G) points out that the N1—N2 and C3—N4 bonds become longer and the N2—C3 bond becomes shorter on passing from the parent to its derivative, whilst the phenyl rings (for which the standard benzene geometry was adopted) are coplanar with the heavy atoms skeleton of formazan. This increased conjugation shifts the lowest energy  $\pi \rightarrow \pi^*$  transition to 351 (TSSC), 299 (TSST) and 280 nm (TAST) and increases its intensity. Bearing in mind that a further red shift is expected when the compounds experience solvent interactions, the agreement with the experimental data is considered very good. In light of the present results it can be deduced that in the freshly prepared CCl<sub>4</sub> solution of the yellow (TAST) form of 1,5-diphenylformazan, the absorption peak is at 406 nm whilst at equilibrium it shifts to 477 nm (which is the absorption characteristic of the red forms) because both TSST and TSSC forms are present. In 3-isopropyl- and 3-*tert*-butyl-1,5-diphenylformazan no time dependence of such peaks is observed because only the red,

TSSC, conformation is possible for such compounds and the band is always in the range of 470 nm.

Finally, it is noteworthy that the weak band near 300 nm is very likely the  $n \rightarrow \pi^*$  transition calculated at 210–220 nm, whilst the bands at 250 and lower wavelengths are due to transitions between molecular orbitals, that are essentially benzenic.

## Conclusions

The present study confirms that intramolecular N—H $\cdots$ N hydrogen bonding (in the absence of strong steric effects) is the determining factor governing the stability order of the most probable formazan conformations in the gas phase. The experimental findings derived from measurements in the solid state and in solution can be accounted for by considering solvent effects and/or intermolecular hydrogen bridge formation. The highest hydrogen bond strength (the most probable value is in the range of 30 kJ mol<sup>-1</sup>) is reached in the intramolecular hydrogen bridge of the TSSC conformation of formazan, where it is enhanced by conjugation. This value should not change appreciably in 3-nitroformazan. The strength of the N5—H6 $\cdots$ N2 hydrogen bridge in the formazan CSST and TSST conformations is roughly estimated at ca. 10 kJ mol<sup>-1</sup> or lower. In the CASC conformation, where the imino group is involved, a negligible strength was estimated for the N1—H8 $\cdots$ N4 bridge, which, on energetic grounds, is completely absent in the corresponding conformation of the nitro derivative.

The conformations of tautomer B are by far less stable than those of A, mostly because conjugation and molecular planarity are broken so that the hydrogen bonding, no longer assisted by resonance, becomes very weak or disappears completely. It has also been proved that  $E_{\text{HB}}$  can be evaluated from  $\Delta E_{0-90}$  of the considered conformation after correction for the internal rotation barrier deduced from appropriate, hydrogen bond free, simpler compounds. Selection of the reference molecule is a very delicate task. The energetic terms so evaluated, as well as the shifts of the frequencies concerning the N—H vibration stretching mode, on the whole, agree fairly well for accounting the relative stability order of the conformations having different hydrogen bridges.

Inspection of the calculated electronic transitions indicated that the lowest energy  $\pi \rightarrow \pi^*$  transition is centred near 210 nm, whilst the lowest energy  $n \rightarrow \pi^*$  transition lies at about 370 nm in the TSSC form and at lower wavelengths in the less stable TSST and TAST conformations. It shifts 70–110 nm towards longer wavelengths in 1,5-diphenylformazan and its 3-substituted derivatives as a consequence of the extended conjugated system, so reaching good agreement with the available experimental findings. The results obtained for 3-nitroformazan parallel those of the unsubstituted molecule, but energy estimates for the various hydrogen bridges, simultaneously present, are not possible because they are unable to be isolated to be treated separately. However we feel that further investigations should be done on analogous hydrogen bridges and various suitable reference conformations to test and generalize the method proposed here for estimation of  $E_{\text{HB}}$ . Further work along these lines is in progress in our laboratory.

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