Molecular conformation of isolated and hydrogen bonded *N,N'*-diformohydrazide: an *ab initio* study

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The molecular conformation of *N,N'*-diformohydrazide has been studied by *ab initio* molecular orbital calculations including electron correlation corrections up to the MP4/6-31G*//MP2/6-31G* level. The calculations indicate that the stable structures of the molecule are non-planar at nitrogen and show twisted conformation about the N–N bond. Structures and rotational barrier heights have been compared with those of *N,N'*-dimethylhydrazine, calculated at uniform levels of theory. A simulation of the crystal field has been proposed to investigate the effects of intermolecular hydrogen bonding on the structural properties of *N,N'*-diformohydrazide. Our crystal model, studied by HF/4-31G* calculations, shows that hydrogen bonding causes not only a concerted change in the length of the C–N, C=O and N–H bonds, but also a significant conformational change. In agreement with the neutron diffraction structure, the crystal molecule of our model is predicted to be planar. The overall geometrical perturbations due to self-association reveal an increase of π-conjugation between the nitrogen and carbonyl groups which can rationalize the conformational change. The effect of intermolecular hydrogen bonding on the vibrational spectrum is also discussed.

Hydrogen bonding is known to cause considerable effects on molecular geometry. Accurate investigations of gas phase and solid state molecular geometries reveal that crystal field is responsible for appreciable changes in the bond lengths, valence and torsion angles.[1] The low rotational barrier heights about single bonds makes the torsion angles most likely to be affected by hydrogen bonding and quite often the conformation of the isolated molecule is different from that observed in the crystal.[2–4]

Theoretical investigations show that such geometrical changes are a consequence of perturbations of the electronic structure induced by intermolecular association. In particular for species containing conjugated π-systems, hydrogen bonding appreciably affects the electron distribution on the molecular skeleton and in most cases cooperative effects contribute to reinforce hydrogen bonding interactions.[5,6]

The *N,N'*-diformohydrazide molecule, H–C(=O)–N–N–C(=O)–H, is an example where the crystal forces induce conformational changes. The effect of hydrogen bonding on its structure has been studied by comparing the geometry of the gas phase with that of the solid state molecule determined using single-crystal neutron diffraction data measured at 15 K.[7] The crystal consists of layers where the molecules, close to being exactly planar, are connected *via* strong N–H ··· O=C hydrogen bonding, as witnessed by the exceptionally short (N)H ··· O(=C) bond lengths [1.7543(7) Å]. The geometry of the isolated molecule has not been reported until now, however *ab initio* molecular orbital calculations reported in the previous paper[7] suggest that the planar conformation observed in the crystal is not the lowest energy structure. The HF/3-21G level[7] showed that the minimum energy structure has C_2 symmetry with a C–N–N–C torsion angle of 84.5°. On the basis of these results it emerges that the symmetry of the isolated molecule could be different from that of the crystal molecule, which is indeed C_{2h}. From symmetry considerations, the crystal field should therefore exert considerable effects not exclusively on the molecular geometry but even on the overall molecular properties, *e.g.*, the vibrational spectrum. For example, the centrosymmetric molecular conformation found in the crystal is expected to show IR spectra deeply different from the C_2 symmetry conformation of the free molecule, where all the vibrational modes are IR active.

Bearing in mind the lack of any accurate experimental geometry of the gas phase molecule, it is worthwhile reconsidering firstly the structural features of isolated *N,N'*-diformohydrazide by higher levels of the *ab initio* theory. As it is well known,[8] reliable estimates of valence angles and inversion barrier at nitrogen may be often obtained if polarization functions are added to an extended basis set and electron correlation corrections are possibly included. On the basis of these premises, distinct conformations of the isolated molecule, previously studied at the HF/3-21G level,[7] were therefore examined in this study using the Moller–Plesset perturbation theory[9] through MP2/6-31G* geometry optimizations and MP4/6-31G* single-point energy calculations with the aim to localize the lowest energy conformation. In order to gain further insight on the role of hydrogen bonding in determining the conformation of the solid state molecule, a simple but suitable molecular model simulating the neighbouring intermolecular association in the crystal was proposed and studied by *ab initio* methods. This theoretical approach was successfully followed in our recent studies on hydrogen bonding of imidazole,[5] diacetamide,[6] phenol[10] and thioacetamide[11] crystals. The molecular model proposed in this paper offers the possibility to investigate the effects of hydrogen bonding on the geometry as well as on the vibrational spectra of *N,N'*-diformohydrazide.

Computational details

The geometry of *N,N'*-diformohydrazide was optimized at the Hartree–Fock (HF) and at the second order of the Moller–Plesset perturbation theory (MP2) employing all the orbitals active by analytic gradient based technique. The stationary points determined on the potential energy surface were then identified by frequency calculations obtained by analytic second derivatives. Dipole derivatives were finally calculated for the evaluation of the IR band intensities. The split-valence basis sets 4-31G* and 6-31G*[12] were used for geometry optimizations and frequency calculations and 6-31G**[12] for population analysis. Since the normal mode calculations were accomplished using the Wilson GF matrix method,[13] the force constants in cartesian coordinates were transformed to force constants in a complete set of local coordinates.

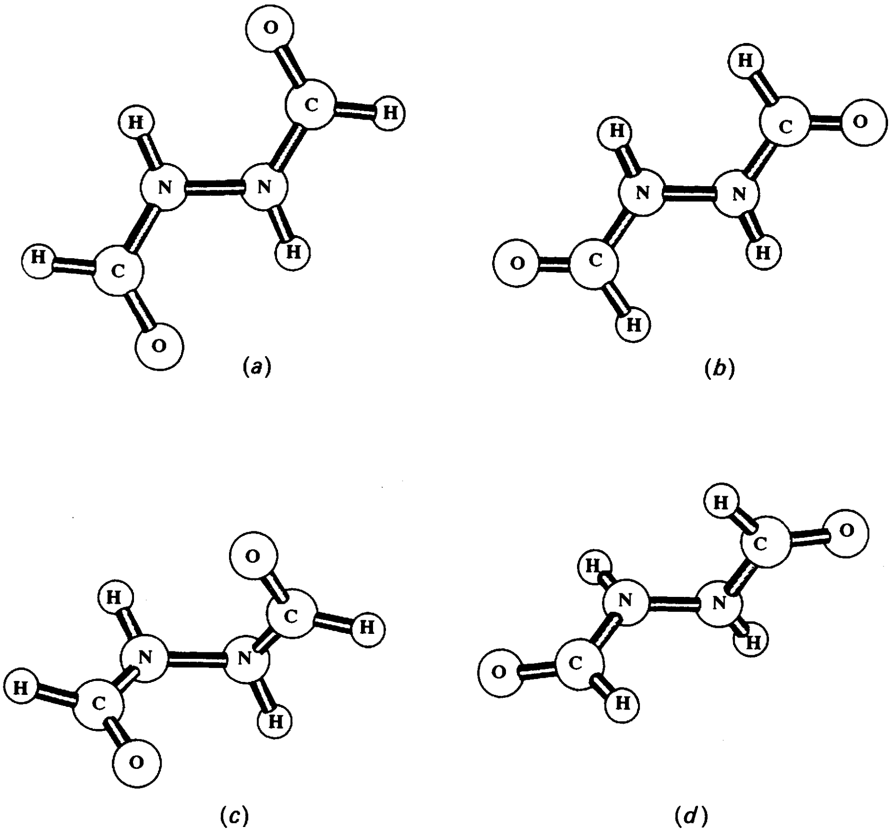

Fig. 1 C_{2h} (*a* and *b*) and C_2 (*c* and *d*) symmetry structures of *N*,*N*′-diformohydrazide

Geometry optimizations and frequency calculations of the crystal model proposed in this study were carried out at the HF/4-31G* level for a homogeneous comparison with the results obtained for the isolated molecule.

The relative stability between some rotamers of the free molecule was evaluated by single-point calculations at the MP2/6-31G* geometries using the frozen core approximation (fc) up to the fourth order of the Moller–Plesset theory by including single, double, triple and quadruple excitations and using the 6-31G* basis set. The designation of these calculations is MP4(fc)/6-31G*//MP2/6-31G*.

All *ab initio* molecular orbital calculations were carried out by using the Unix version of GAUSSIAN 92/DFT package[14] on an Alpha AXP-3000/500 cluster at the University of Rome.

Results and discussion

Isolated molecule

Molecular conformation. Rotations about the N–N and C–N bonds may originate different molecular conformations. Two orientations of the formyl groups of *N*,*N*′-diformohydrazide were considered (see Fig. 1). These correspond to the conformations where the formyl groups are oriented with the C=O bond located on the same (isomer I) or opposite (isomer II) side of the N–N bond. Geometry optimizations at the HF/4-31G* level were firstly carried out imposing the constraint of the C_{2h} symmetry [see Figs. 1(*a*) and (*b*)]. Frequency calculations revealed that both the planar structures are high-order saddle points. Relaxation of the planarity constraint was then introduced to localize stable structures of the molecule. Under the C_2 symmetry constraint, two stationary points corresponding to the structures reproduced in Figs. 1(*c*) and (*d*) were localized and characterized as local minima by frequency calculations.

To examine the effects of electron correlation corrections on the molecular structure, the geometries of the planar C_{2h} and twisted C_2 symmetry structures of both the isomers were optimized at the MP2/6-31G* level. Once again, the non-planar form of each configuration is preferred on the respective planar conformation and the analysis of the vibrational frequencies shows that both the structures are the true minima on the potential energy surface. The relative stability between the planar and non-planar conformations was finally calculated by higher levels of perturbation theory at the MP2/6-31G* geometries. As it can be seen from Table 1, the MP4/6-31G* energy calculations are in agreement with the MP2/6-31G*, HF/4-31G* and HF/3-21G[7] results and confirm that the stable structures of the molecule are non-planar at nitrogen and prefer twisted conformations about the N–N bond. The tendency of the molecule to destabilize the planar structures is a typical feature of the hydrazine derivatives and, as discussed previously,[7] was ascribed to the antibonding effect of the four π electrons in the planar conformation. However, the structural features of the hydrazine derivatives are expected to be considerably affected by the electronic nature of the substituent. In our case, the π-electron-withdrawing properties of the formyl group contribute to delocalize partly the nitrogen atom lone-pair onto the carbonyl group and consequently to reduce the destabilization of the planar form with respect to the hydrazine molecule itself.

It is interesting to note that the isomers I and II of *N*,*N*′-diformohydrazide show different barriers to planarity. For the isomer II the planar structure is destabilized by 55 kJ mol^{-1} with respect to the twisted conformation, whereas the isomer I is predicted to have a much lower barrier height, namely 7 kJ mol^{-1}. The nearly free rotation about the N–N bond predicted for the latter one can be explained by observing that the planar structure of such an isomer is more favourable for a stabilizing NH • • • O=C intramolecular interaction than the non-planar conformer. This clearly emerges by analysing the respective

Table 1 Total energies (atomic units) of *N*,*N*′-diformohydrazine and *N*,*N*′-dimethylhydrazide, relative stabilities, Δ*E* (kJ mol^{-1}), of the C_2 and C_{2h} symmetry conformers and zero-point energy corrections, ZPE (kJ mol^{-1})

	N,*N*′-Diformohydrazide					
	Isomer I		Isomer II		*N*,*N*-Dimethylhydrazine	
	C_2	C_{2h}	C_2	C_{2h}	C_2	C_{2h}
HF/3-21G[a]	−334.769 99	−334.767 96				
Δ*E*	0.0	5.3				
HF/4-31G*	−336.340 27	−336.335 34	−336.340 42	−336.315 80	−189.047 248	−188.990 27
Δ*E*	0.0	12.9	0.0	64.6	0.0	149.6
MP2/6-31G*	−337.608 36	−337.606 94	−337.607 05	−337.586 21	−189.835 75	−189.774 85
Δ*E*	0.0	3.7	0.0	54.7	0.0	159.9
ZPE/MP2/6-31G*	194.87		193.27			
MP4/6-31G*[b]	−337.649 25	−337.646 70	−337.647 86	−337.627 25	−189.881 22	−189.819 50
Δ*E*	0.0	6.7	0.0	54.1	0.0	162.0

[a] Ref. 7. [b] Short for MP4(SDTQ)(fc)/6-31G*//MP2/6-31G*.

(N)H · · · O(=C) distances, namely 2.897 Å for C_2 and 2.276 Å for C_{2h} symmetry structures.

In order to gain further insight into how *N*-substitution may affect the conformation of hydrazine, we extended this study to a different *N*-derivative, that is, *N*,*N*′-dimethylhydrazine. The comparison between *N*,*N*′-diformohydrazide and *N*,*N*′-dimethylhydrazine constitutes a suitable way both to examine the effect of a weak π-electron donor, such as the methyl group, on the barrier to planarity of hydrazine derivatives and to check the accuracy of the calculations adopted here for describing the hydrazine framework. In contrast to *N*,*N*′-diformohydrazide, the dimethyl derivative was in fact the subject of accurate experimental gas phase investigations.[15–17] The most recent study does report the molecular geometry as determined by *ab initio* HF/4-31G(N*) calculations, microwave spectroscopy and gas phase electron diffraction.[16] Our study on *N*,*N*′-dimethylhydrazine was limited to one of the most abundant conformers, indicated in the previous paper as the O,O conformer,[16] and which is reproduced in Fig. 2(*a*). For a homogeneous comparison with *N*,*N*′-diformohydrazide, the geometry of the dimethyl derivative was optimized at the HF/4-31G* and MP2/6-31G* levels imposing C_2 symmetry. The stability of the twisted conformer was then compared with that of the C_{2h} symmetry structure, shown in Fig. 2(*b*), obtained from the non-planar conformation by constraining planarity at nitrogen. As for the diformyl derivative, the twisted structure of *N*,*N*′-dimethylhydrazine is the preferred conformation. However, the energy difference of 162 kJ mol^{-1} was found to be much larger than the value determined for the diformyl compound, namely 54 kJ mol^{-1}, as a proof of the fact that the formyl group helps to stabilize the planar structure by delocalizing the nitrogen atom lone-pair onto the carbonyl system.

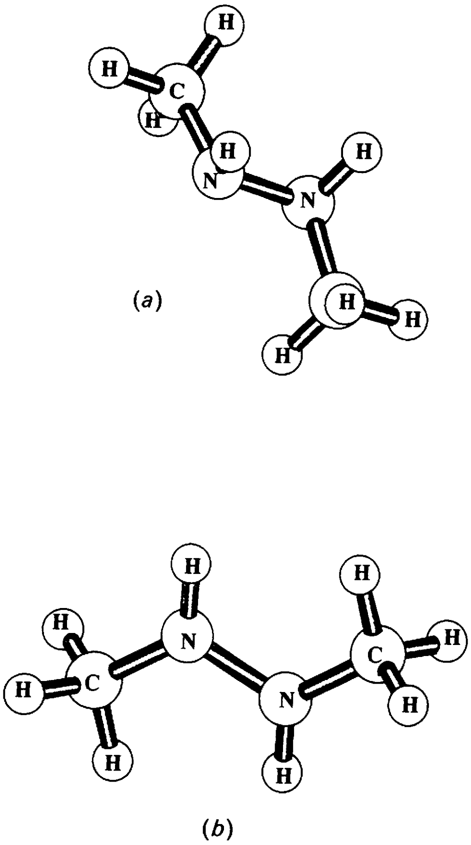

Fig. 2 C_2 (*a*) and C_{2h} (*b*) symmetry structures of *N*,*N*′-dimethylhydrazine

Molecular geometry. In Table 2 we present our theoretical results for *N*,*N*′-diformohydrazide along with the previous HF/3-21G results[7] which are useful for comparison purposes. A quick scan of the data reveals that there are appreciable changes in some of the geometrical parameters with respect to the level of calculation. For example, inclusion of electron correlation causes a general and expected[8] lengthening of the bond distances. Major changes occur in the torsional angles. In particular, the non-planarity at nitrogen progressively increases in going from the HF/3-21G, to the HF/4-31G* and MP2/6-31G* levels.

The lack of experimental structural data for the gas phase molecule does not allow us to evaluate easily the accuracy of our theoretical results. The main point of contact with experiment is the accurate crystal structure determined from low temperature neutron diffraction.[7] However, it should be realized that the strong intermolecular interactions occurring in the crystal may deform the molecular geometry appreciably with respect to the isolated molecule.[1] In addition, the crystal consists of planar molecules and the results of Table 2 clearly indicate that the geometries of the planar and twisted conformations are substantially different. In the planar structure, a favourable alignment of the nitrogen lone-pair allows the maximum π-conjugation with the formyl group. As a consequence of this fact, the π-character of the C–N bond increases, as suggested by the shortening of the relative distance, and that of the C=O bond decreases, as revealed by the lengthening of the respective distance.

Notwithstanding this, we can reasonably suppose that the MP2/6-31G* structural determination should be more accurate than the SCF geometry. This suggestion is in fact fully

Table 2 Geometrical parameters of C_2 and C_{2h} symmetry structures of *N*,*N*′-diformohydrazide

	Isomer I						Isomer II	
	HF/3-21G[a]		HF/4-31G*		MP2/6-31G*		MP2/6-31G*	
	C_2	C_{2h}	C_2	C_{2h}	C_2	C_{2h}	C_2	C_{2h}
Bond length (Å)								
r(C-N)	1.365	1.342	1.365	1.335	1.384	1.352	1.378	1.361
r(N-N)	1.391	1.412	1.369	1.378	1.387	1.383	1.375	1.395
r(C=O)	1.207	1.218	1.185	1.196	1.219	1.231	1.219	1.224
r(C-H)	1.082	1.079	1.089	1.087	1.103	1.100	1.103	1.105
r(N-H)	0.996	0.998	0.995	0.994	1.014	1.015	1.017	1.014
Bond angle (deg.)								
∠O=C-N	124.8	123.3	124.5	123.7	124.0	122.8	123.4	123.6
∠C-N-N	119.3	117.4	119.3	119.1	117.8	118.2	120.8	123.7
∠O=C-H	123.7	123.8	123.6	123.8	124.3	124.5	125.0	123.9
∠N-C-H	111.4	112.9	111.8	112.5	111.7	112.7	111.6	112.6
∠C-N-H	122.2	129.3	118.9	126.0	117.8	127.7	117.9	119.6
∠N-N-H	116.8	114.3	114.8	114.9	113.9	114.1	119.1	116.8
Torsional angle (deg.)								
∠C-N-N′-C′	84.5	180.0	71.2	180.0	65.5	180.0	107.2	180.0
∠N′-N-C=O	8.2	0.0	14.4	0.0	16.4	0.0	171.5	180.0
∠O=C-N-H	172.9	180.0	163.5	180.0	159.0	180.0	8.4	0.0
∠C′-N′-N-H	−81.1	0.0	−79.1	0.0	−78.6	0.0	−89.9	0.0
∠N′-N-C-H	−173.3	180.0	−168.7	180.0	−167.7	180.0	−9.9	0.0
∠H-N-C-H	−8.6	0.0	−19.5	0.0	−25.0	0.0	−173.0	180.0
∠H-N-N′-H′	113.4	180.0	130.5	180.0	137.3	180.0	73.1	180.0

[a] Ref. 7.

Table 3 Selected geometrical parameters of *N*,*N*′-dimethylhydrazine

	Ab initio[a]		Experimental	
	HF/ 4-31G*	MP2/ 6-31G*	r_g[b]	r_z[b]
Bond length (Å)				
r(C-N)	1.444	1.456	1.459(10)	1.455(10)
r(N-N)	1.405	1.428	1.441(2)[c]	1.439(2)[c]
r(N-H)	1.005	1.026	1.030[c]	1.012[c]
r(C-H)	1.084	1.093		
r(C-H′)	1.081	1.090	1.115(4)[c]	1.092(4)[c]
r(C-H″)	1.090	1.102		
Bond angle (deg.)				
∠C-N-N	111.1	109.2		109.8(5)
∠H-N-N	110.9	110.1		
∠H-N-C	110.3	109.1		
Torsional angle (deg.)				
∠C-N-N-C	158.0	165.2		165.3(18)
∠H-N-N-H	44.0	44.6		

[a] C_2 symmetry. [b] Ref. 16. The number in parentheses represent estimated limits of error. [c] Average value of inequivalent bond lengths.

supported by our computational results on *N*,*N*′-dimethylhydrazine. The quality of the MP2/6-31G* structure is proved by the good agreement with the experimental geometry determined by gas phase electron diffraction, r_g,[16] and microwave spectroscopy, r_z,[16] as shown in Table 3. The most evident discrepancy regards the N-N bond length for which the MP2 value (1.428 Å) is underestimated with respect to the r_g (1.441 Å) and r_z (1.439 Å) values. An accurate evaluation of the N-N bond distance could be obtained only at higher level of correlation corrections. For comparison purposes, we determined the geometry of unsubstituted hydrazine at various levels of the Moller-Plesset theory. When compared with the experimental geometry,[18] it emerges that an accurate determination of the N-N bond could be found only at the MP4/6-31G* level (see Table 4).

Hydrogen bonded molecule

We now turn our attention to the structural modifications induced by intermolecular hydrogen bonding. The simple model described in Fig. 3 was constructed with the aim of describing the neighbouring intermolecular interactions occurring in the crystal by *ab initio* methods. Within the proper orientation of the formyl groups found in the crystal, the isomer I of *N*,*N*′-diformohydrazide was therefore arranged to form four $C{=}O\cdots H{-}N$ hydrogen bonds. In this model, each carbonyl group is hydrogen bonded to one NH_3 molecule whereas each N-H group of *N*,*N*′-diformohydrazide interacts with one $H_2C{=}O$ molecule. All the $H\cdots O$ separations were assumed from the crystal (1.743 Å) and the interacting molecules were constrained to make $(N)H\cdots O{=}C$ and $N{-}H\cdots O({=}C)$ angles the values of which were fixed at those determined from low-temperature neutron diffraction crystallography,[7] namely 118.4° and 162.2°, respectively. To facilitate the geometry optimization procedure, the $N{-}H\cdots O{=}C$ sequence was assumed to be coplanar. The geometries of the NH_3 and $H_2C{=}O$ species used to model the crystal field was kept fixed at the values obtained by the isolated molecule at the HF/4-31G* level [$H_2C{=}O$: *r*(CH) = 1.091 Å, *r*(CO) = 1.182 A, ∠H-C=O = 122.2°; NH_3: *r*(NH) = 1.003 Å, ∠H-N-H = 107.0°]. Otherwise, the geometry of the central molecule was fully optimized within the C_2 symmetry constraint, as for the free molecule.

The twisted conformer, found as the stable structure in the gas phase, is no longer a stationary point when intermolecular association occurs and the molecule relaxes to a planar conformation. On the basis of our *ab initio* calculations we can conclude that hydrogen bonding stabilizes the planar structure in accordance with the crystal molecule. In addition, *ab initio* methods allow us to distinguish the geometrical modifications induced by intermolecular association from the intrinsic

Table 4 Geometrical parameters of hydrazine (C_2 symmetry) (bond lengths in Å and bond angles in deg.)

	Ab initio				
	HF/6-31G*[b]	MP2/6-31G*[b]	MP3/6-31G*[b]	MP4/6-31G*[c]	Experimental[a]
r(N–N)	1.413	1.439	1.440	1.446	1.449(2)
r(N–H)	0.999	1.016	1.016	1.020	1.021(3)[d]
r(N–H′)	1.003	1.021	1.020	1.025	1.021(3)[d]
∠N–N–H	107.9	106.3	106.3	105.9	106(2)
∠N–N–H′	112.3	111.5	111.3	111.0	112(2)
∠H–N–H′	108.2	107.0	106.9	106.5	—
τ[e]	90.2	90.5	90.9	90.2	91(2)

[a] Molecular geometry obtained from electron diffraction and microwave data. Bond distances are listed as r_g. Estimated errors are given in parentheses. [b] Ref. 8. [c] Present study. [d] Average value of inequivalent bond lengths. [e] H–N–N–H′ dihedral angle, τ, defined as the angle between the two bisectors of the H–N–H bond angles.

Table 5 Geometrical parameters of planar structures of *N*,*N*′-diformohydrazide

	Isolated molecule (HF/4-31G*)		Complex (HF/4-31G*)	Crystal[a]
	Isomer II	Isomer I		
Bond length (Å)				
r(C–N)	1.345	1.335	1.321	1.3321(4)
r(N–N)	1.389	1.378	1.377	1.3808(4)
r(C═O)	1.189	1.196	1.208	1.2384(4)
r(C–H)	1.090	1.087	1.085	1.0997(7)
r(N–H)	0.995	0.994	1.021	1.0385(7)
Bond angle (deg.)				
∠O═C–N	123.9	123.7	125.3	123.65(3)
∠C–N–N	123.2	119.1	119.9	119.34(2)
∠O═C–H	123.1	123.8	122.6	123.23(5)
∠N–C–H	113.0	112.5	112.1	113.12(4)
∠C–N–H	119.7	126.0	121.6	122.14(4)
∠N–N–H	117.2	114.9	118.5	118.51(4)

[a] Neutron diffraction of single crystal at 15 K, ref. 7. The standard deviations in parentheses refer to the last significant digit.

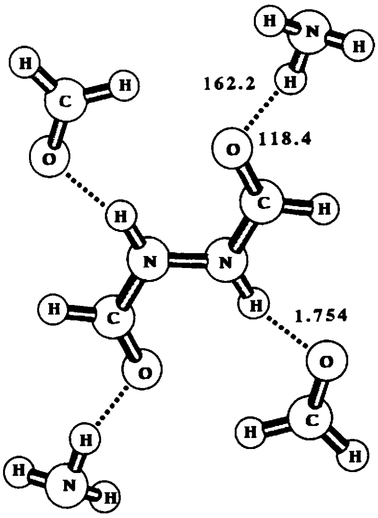

Fig. 3 Model of the crystal field of *N*,*N*′-diformohydrazide. The values of the (N)H ··· O(═C) bond distance, and of the (N)H ··· O═C and N–H ··· O(═C) bond angles are obtained from low temperature single crystal neutron diffraction (ref. 7).

geometrical perturbations due to the conformational change. Within this aim, we compared the geometry of the molecule in the model crystal field with that of the free molecule in the planar structure, that is the same conformation adopted in the crystal. The salient result emerging from Table 5 is that intermolecular hydrogen bonding causes appreciable geometrical changes, the most conspicuous of which occurs for the N–H bond which increases by 0.027 Å. The significant lengthening of the C═O bond (0.012 Å) and the simultaneous shortening of the C–N bond (0.014 Å) reveal changes in the π-character of the respective bonds. It is worth observing that similar geometrical changes are also predicted when we compare the planar conformations of the isomers I and II of the molecule. The intramolecular C═O ··· H–N hydrogen bond occurring in the isomer I causes indeed the lengthening of the C═O bond as well as the shortening of the C–N bond with respect to the values calculated for the isomer II.

The structural modifications emerging from Table 5 suggest that the contribution of the polar canonical form $^{+}$N═C–O^{-} as a resonance structure of *N*,*N*′-diformohydrazide increases progressively upon intramolecular (isomer I) and intermolecular (crystal model) hydrogen bonding formation. The natural bond orbital analysis, carried out in this study by HF/6-31G**//HF/4-31G* single point calculations, supports such a polarization of the wavefunction. The variations in the π-charge due to intermolecular association indicate in fact that the oxygen atom gains 0.06 e.s.u. whereas the nitrogen atom losses 0.05 e.s.u. The conformational change observed in going from the isolated to crystal molecules is a further evidence of polarization of the wavefunction since the canonical form $^{+}$N═C–O^{-} allows an appreciable overlap of the N lone-pair with the C p-orbital and a consequent decrease of the antibonding effect of the nitrogen π-electrons, responsible for the preference of twisted conformations for the isolated molecule. On the ground of these considerations, the barrier to planarity of *N*,*N*′-diformohydrazide decreases when intramolecular hydrogen bonding occurs (isomer I), as already discussed in the previous section, and vanishes when the molecule is involved both in intramolecular and intermolecular hydrogen bonding (crystal molecule).

There are noticeable discrepancies between the neutron diffraction and theoretical geometries of isolated *N*,*N*′-diformohydrazide. Bearing in mind that such a comparison should be made with caution because the *ab initio* geometries are basis and computational method dependent approximations of an equilibrium structure, outstanding differences are matched in bond lengths and bond angles. In our case the comparison between experimental and theoretical structures becomes particularly significant for bond angles since their values are not drastically affected by the choice of the computational method. From all our theoretical levels, the C–N–H and N–N–H bond angles of the equilibrium structure of the isolated molecule are predicted systematically narrower than those obtained from neutron diffraction crystallography. Such discrepancies are not only the obvious consequence of the flattening at nitrogen in the

Table 6 *Ab initio* (MP2/6-31G*) and experimental vibrational spectrum of *N*,*N*′-diformohydrazide

	C_2 (isomer I)			C_{2h} (isomer I)					
	Ab initio			*Ab initio*				Experimental[a]/ cm^{-1}	
N°	sym	cm^{-1} [b]	PED[c]	sym	cm^{-1} [b]	PED[c]	$\Delta\omega$[d]/ cm^{-1}	IR	Raman
ω_1	B	3487	S_3 (0.99)	B_u	3502	S_3 (0.99)	−294	2930s	
ω_2	A	3479	S_2 (0.99)	A_g	3493	S_2 (0.99)	−277		2910m
ω_3	A	2949	S_8 (0.98)	A_g	2982	S_8 (0.99)	+17		2912m
ω_4	B	2948	S_9 (0.98)	B_u	2982	S_9 (0.99)	+17	2920s	
ω_5	A	1768	S_6 (0.78)	A_g	1749	S_6 (0.65), S_4 (0.19), S_{16} (0.11)	−27		1675w
ω_6	B	1740	S_7 (0.79)	B_u	1692	S_7 (0.73), S_5 (0.14), S_{17} (0.12)	−58	1610vs	
ω_7	A	1501	S_{12} (0.75), S_4 (0.13)	A_g	1567	S_{12} (0.53), S_4 (0.23), S_1 (0.16)	+62		1552vs
ω_8	B	1434	S_{13} (0.79), S_5 (0.16)	B_u	1407	S_5 (0.40), S_{13} (0.38)	+106	1480s	
ω_9	A	1381	S_{16} (0.88)	A_g	1384	S_{16} (0.81)	—		1385s
ω_{10}	B	1377	S_{17} (0.89)	B_u	1357	S_{17} (0.83), S_{13} (0.10)	+14	1368vs	
ω_{11}	A	1279	S_1 (0.51), S_4 (0.26), S_{14} (0.19)	A_g	1248	S_1 (0.35), S_{12} (0.26), S_{14} (0.13), S_4 (0.26)	+32		1250vs
ω_{12}	B	1091	S_5 (0.63), S_{13} (0.13), S_{15} (0.10)	$\mathrm{B_u}$	1140	S_{13} (0.52), S_5 (0.40)	+83	1229s	
ω_{13}	A	1003	S_{20} (0.92)	A_g	1020	S_{10} (0.26), S_4 (0.24), S_1 (0.19), S_{12} (0.15)	+33		1062s
ω_{14}	A	985	S_4 (0.40), S_1 (0.20), S_{10} (0.19)	B_g	971	S_{21} (0.93)	+13		846sh
ω_{15}	B	980	S_{21} (0.85)	A_u	954	S_{20} (0.95)	+16	800sh	
ω_{16}	B	877	S_{11} (0.48), S_{15} (0.40)	A_g	833	S_{14} (0.48), S_1 (0.29), S_{10} (0.12)	+13		865m
ω_{17}	A	778	S_{14} (0.46), S_{10} (0.24), S_1 (0.20)	B_u	733	S_{15} (0.73), S_{11} (0.15)	+19	753s	
ω_{18}	A	549	S_{18} (0.35), S_{23} (0.26), S_{22} (0.12)	B_g	567	S_{24} (0.99)	—		460m
ω_{19}	B	441	S_{19} (0.40), S_{24} (0.34), S_5 (0.11)	A_u	419	S_{23} (0.73), S_{22} (0.23)	—	350sh	
ω_{20}	A	394	S_{23} (0.57), S_{10} (0.11)	A_g	268	S_{10} (0.48), S_{14} (0.37)	—		295s
ω_{21}	B	379	S_{19}(0.45), S_{15} (0.30), S_{11} (0.16)	B_u	189	S_{11} (0.75), S_{15} (0.21)	—		
ω_{22}	B	210	S_{11} (0.34), S_{19} (0.29), S_{24} (0.19)	A_u	153	S_{22} (0.93)	—		
ω_{23}	A	176	S_{18} (0.38), S_{10} (0.21), S_{14} (0.17), S_{22} (0.16)	B_g	104	S_{19} (0.47), S_{24} (0.35), S_{21} (0.18)	—		780vw
ω_{24}	A	72	S_{22} (0.77), S_{18} (0.13)	A_u	69i		—	765m	

[a] Ref. 19; vs: very strong, s: strong, m: medium; w: weak, vw: very weak, sh: shoulder. [b] Scaled frequencies. Scale factor = 0.96. [c] The potential energy distribution (contributions > 10) is expressed in terms of the internal coordinates reported in Table 7. [d] Frequency shift (> 10 cm^{-1}) obtained as difference between $\omega_{complex} - \omega_{free\ molecule}$ (C_{2h} conformation) both calculated at the HF/4-31G* level.

crystal molecule. For example, the C–N–H bond angle of the planar conformer is indeed larger than that of the twisted structure but is also much larger than the experimental value. A reasonable agreement with the crystal geometry is gained only if intermolecular interactions are included in the theoretical model, as shown in Table 5. Thus, although the crystal model is, admittedly, only a crude simulation of the crystal field, we may conclude that the structural differences observed when the molecule goes from gas phase to solid state, between which the conformational changes, are indeed due to intermolecular hydrogen bonding occurring in the crystal.

Vibrational spectra

Finally, we focus our attention on the vibrational properties of *N*,*N*′-diformohydrazide. As for the molecular structure, *ab initio* calculations allow us to investigate separately the modifications of the vibrational spectrum induced by the conformational change and the frequency shifts due to hydrogen bonding. All the vibrational frequencies calculated at the MP2/6-31G* level for both conformers of the isomer I are listed in Table 6 and numbered according to the order of frequencies. The respective simulated spectra are shown in Fig. 4. The description of each normal mode in terms of the internal coordinate listed in Table 7 is also reported in Table 6.

Table 7 Internal coordinate definitions[a] for *N*,*N*′-diformohydrazide

Coordinate	Definition	Description
S_1	Δr_{NN}	N–N stretching
$S_{2,3}$	$\Delta r_{NH} \pm \Delta r_{N'H'}$	N–H stretching
$S_{4,5}$	$\Delta r_{CN} \pm \Delta r_{C'N'}$	C–N stretching
$S_{6,7}$	$\Delta r_{CO} \pm \Delta r_{C'O'}$	C=O stretching
$S_{8,9}$	$\Delta r_{CH} \pm \Delta r_{C'H'}$	C–H stretching
$S_{10,11}$	$(2\Delta\alpha_{CNN'} - \Delta\alpha_{CNH} - \Delta\alpha_{HNN'}) \pm (2\Delta\alpha_{C'N'N} - \Delta\alpha_{C'N'H'} - \Delta\alpha_{H'N'N})$	C–N–N bending
$S_{12,13}$	$(\Delta\alpha_{CNH} - \Delta\alpha_{HNN'}) \pm (\Delta\alpha_{C'N'H'} - \Delta\alpha_{H'N'N})$	H–N–C bending
$S_{14,15}$	$(2\Delta\alpha_{OCN} - \Delta\alpha_{NCH} - \Delta\alpha_{OCH}) \pm (2\Delta\alpha_{O'C'N'} - \Delta\alpha_{N'C'H'} - \Delta\alpha_{O'C'H'})$	N–C=O bending
$S_{16,17}$	$(\Delta\alpha_{NCH} - \Delta\alpha_{OCH}) \pm (\Delta\alpha_{N'C'H'} - \Delta\alpha_{O'C'H'})$	H–C–N bending
$S_{18,19}$	$\gamma_{NH} \pm \gamma_{N'H'}$	N–H out-of plane bending
$S_{20,21}$	$\gamma_{CH} \pm \gamma_{C'H'}$	C–H out-of-plane bending
S_{22}	τ_{NN}	N–N torsion
$S_{23,24}$	$\tau_{CN} \pm \tau_{C'N'}$	C–N torsion

[a] $\Delta r_{a,b}$ represents change in bond length between atoms a and b; $\Delta\alpha_{abc}$ represents change in angle a–b–c.

N,*N*′-diformohydrazide has 24 fundamental vibrational modes having irreducible representations 13 A + 11 B of the C_2 point group and 9 A_g + 8 B_u + 4 A_u + 3 B_g of the C_{2h} point group. On the basis of symmetry considerations, one can readily predict that the vibrational spectra are quite different for the two structures. All the bands of the twisted conformer are IR active, whereas only 12 vibrations are expected to have IR activity in the case of a planar structure. The simulated vibrational absorption spectra, obtained from the calculated IR intensities and reported in Fig. 4, confirm that the overall spectral pattern changes greatly with the molecular conformation. Thus, it would be possible to investigate the structural deformations caused by intermolecular association even by looking at the overall pattern of absorption bands of the gas phase and condensed phase vibrational spectra. Unfortunately, no gas phase vibrational spectrum of the molecule has been

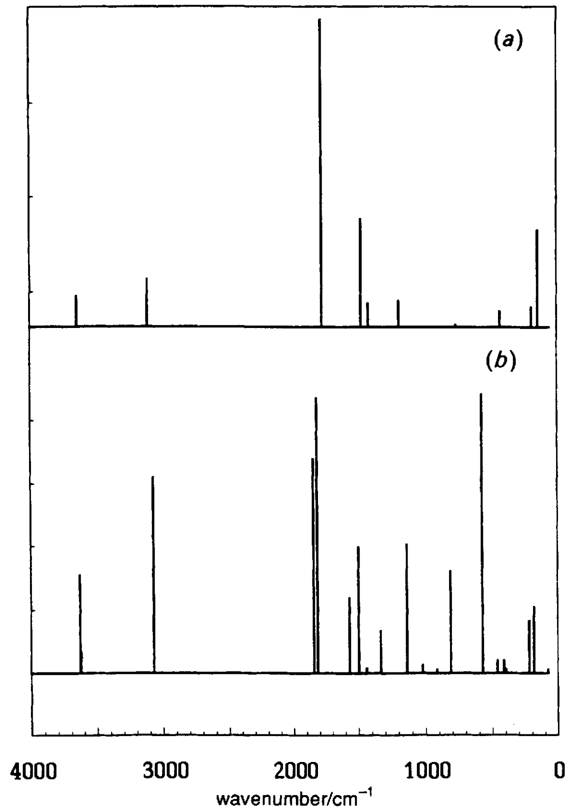

Fig. 4 MP2/6-31G* *ab initio* IR absorption spectra for the C_{2h} (*a*) and C_2 (*b*) symmetry structures of the isomer I of *N,N'*-diformohydrazide

reported so far and the only experimental spectroscopic evidence comes from the accurate study of the Raman and IR spectra of *N,N'*-diformohydrazide in the crystalline state.[18] Notwithstanding this, we can find interesting indications on the effects of hydrogen bonding from the comparison between the theoretical and experimental spectra.

Taking into account that the crystal molecule is planar, the frequencies of the crystal spectra were first compared with those predicted for the planar conformer of the isolated molecule (see Table 6). The assignment of the theoretical frequencies was based on the dominant internal coordinates expressed by the Potential Energy Distribution reported in Table 6 and on the basis of the frequency shifts calculated upon *N*-deuteriation from *ab initio* force field. The typical high frequency amide bands were therefore identified in the ω_5 and ω_6 modes (I amide band), ω_7 and ω_8 (II band) and ω_{11} and ω_{12} (III band). The isotopic shifts determined for each mode, ω_5 (-3), ω_6 (-1), ω_7 (-89), ω_8 (-89), ω_{12} (-173) and ω_{13} (-251), match well the experimental results, ω_5 (0), ω_6 (-5), ω_7 (-82), ω_8 (-91), ω_{11} (-213) and ω_{12} (-244).[19] As concerning the out-of-plane modes, the N–H bending coordinates (S_{18} and S_{19}) enter exclusively in the two lowest frequency modes. However, one of them shows an imaginary value and the remaining one is predicted at too low wavenumbers (104 cm^{-1}) to make significant any comparison with experiment. With the exception of these two normal modes and after providing for the typical scale factor of 0.96 for the MP2 calculated frequencies, there is satisfactory agreement with the experimental values for most of the vibrational modes. The agreement is however significantly improved when intermolecular interactions are included in the theoretical model. The effects of intermolecular association on the vibrational frequencies were evaluated by comparing each normal mode of the planar conformation of the isolated molecule with that of the crystal molecule proposed in this paper. The values of the frequency shifts are reported in Table 6 and were obtained from an homogeneous comparison at the HF/4-31G* level. Our results show that the typical frequencies of the amide bands, particularly sensitive to hydrogen bonding, come into better agreement with experiment. For example, the C=O (ω_5 and ω_6) and N–H (ω_1 and ω_2) stretching frequencies are lowered whereas the NH bending modes, usually indicated as II amide band (ω_7 and ω_8), exhibit a remarkable blue-shift by intermolecular association. The overall pattern of these frequency shifts reflects the structural modifications previously discussed. In particular, the slight increase of the modes containing prominent contribution from the C–N stretching, usually indicated as amide III bands, is actually consistent with the increase in the π-character of the C–N bond due to hydrogen bonding.

In addition, there is one other quantity that we can compare with the experiment, *i.e.*, the difference between the frequencies of the symmetric and antisymmetric modes of each amide band. It is worth observing that not only the single modes but also their frequency difference is sensitive to hydrogen bonding. In the isolated molecule, the A_g (ω_7) and B_u (ω_8) modes of the II amide band differ from each other by 160 cm^{-1} whereas those of the III amide mode (ω_{11} and ω_{12}, respectively) are separated by 120 cm^{-1}. The corresponding values for the crystal model lower at 116 and 57 cm^{-1}, respectively, and they match with a better agreement the experimental ones, 72 and 21 cm^{-1}.

In summary, we can conclude that crystal field is responsible for remarkable modifications in the vibrational spectrum of *N,N'*-diformohydrazide which find their origin, as structural considerations suggest, both from the conformational change and from the geometrical distortions induced by intermolecular hydrogen bonding.

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