A Theoretical Approach to the Vibrational Analysis of the Nitroenamine System[1]

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A comparative *ab initio* and semi-empirical study of the vibrational spectra of a series of nitroenamines with intramolecular hydrogen-bonds has been performed. Although the semi-empirical MNDO/H calculations reproduce qualitatively some of the observed spectral properties, the $\nu(NO_2)$ frequencies are considerably overestimated. The minimal basis set STO-3G gives the correct order for the frequencies of the characteristic vibrations of the nitroenamine system, and reproduces many of the observed structural effects. Better results still are obtained with the split-valence 3-21G basis set. The calculation of force constants, infrared and Raman intensities, and isotope frequency shifts has confirmed the previous assignment of the experimental spectra. The analysis of the normal modes reveals the complex vibrational couplings occurring in these molecules and explains the unusual vibrational spectra of the nitroenamine system. The comparison between theoretical and experimental spectra also allowed an independent assignment of the nature of the isomers present in the molecules studied.

The spectral properties of 'push-pull' ethylenes have been extensively investigated because of the information they provide on the electron distribution in such mesomeric systems, and on their static and dynamic conformational properties.[2] NMR spectroscopy has been the most popular technique for these studies; the only investigations of the IR and Raman spectra of 'push-pull' ethylenes have been performed mostly on enamines having one or two electron-withdrawing groups, usually acyl, at C(2).[3,4]

In principle, vibrational spectra can provide information on the nature and relative populations of the isomers present in the sample, at temperatures where the isomeric equilibrium is fast on the NMR chemical exchange time-scale. However, the application of vibrational spectroscopy to the study of isomeric equilibria relies on a previous assignment of the vibrational spectrum of every possible isomer. For this assignment to be made some independent information is often required which, in turn, is usually provided by NMR spectroscopy. A different approach to the problem consists of the calculation of the theoretical vibrational spectrum of every isomer by means of quantum-mechanical methods. Theoretical spectra have been shown to be useful not only in identifying unstable organic species, but also in interpreting the IR bands of otherwise well-characterized molecules.[5,6] The calculation can also be very helpful for the interpretation of the observed vibrational properties and the structural effects on these properties in terms of the conformational-dependent force constant and normal modes.

We have previously shown[7] how the combined use of NMR and IR spectroscopy provides a complete picture of the isomeric equilibria of a group of typical 'push–pull' ethylenes, the nitroenamines. The study of nitroenamines[8] has recently been stimulated by the potential use of these compounds in organic synthesis,[9–11] and by their possible biological activity.[12] We have also shown that semi-empirical calculations can give a reasonable description of the static and dynamic properties of these systems.[13,14] As a part of these studies we report herein a theoretical investigation of the vibrational spectra of a series of structurally related nitroenamines (1)–(4) (Scheme),† and of several of their deuteriated isotopomers. All these compounds were recently characterized and thoroughly studied by ^{1}H and ^{13}C NMR, IR, and Raman spectroscopy.[7] The spectra show that compounds (1) and (2) exist in solution as an equilibrium mixture of geometrical isomers with a strong intramolecular hydrogen-bond in the *Z*-isomer.[7b] In compounds (3) and (4), with a second electron-withdrawing group, up to four planar isomers are theoretically possible. However, the *EE* isomer, which in principle is expected to be the less stable,[13] has never been detected.[7] The presence of the other three isomers, with strong intramolecular hydrogen-bonds, has been demonstrated only for compound (3), which has easily distinguishable IR spectra for the three isomers, although the corresponding ^{1}H and ^{13}C NMR spectra present a single set of signals for the rapidly interconverting *ZE* and *ZZ* isomers.[7a,b] In compound (4), the steric hindrance introduced by the methyl group at C(1) precludes the existence of planar structures in the *Z* configuration,[13] and it has been proposed[7b,c,13] that this compound exists in solution as a mixture of the planar *EZ* isomer and a non-planar *Z*,*quasi*-s-*cis* isomer (Scheme). Compounds (1)–(4) and related nitroenamines show a band at 1 650–1 600 cm^{-1}, intense in IR and weak in Raman, assigned from the frequency to the C=C stretching mode. However, this intensity pattern as well as the fact that *N*-deuteriation causes a drop in the frequency of up to 50 cm^{-1}, reveal the complex composition of the corresponding normal mode of vibration. The isotopic effect is negligible in the *E* isomers of (1) and (2), with no intramolecular hydrogen-bond. In each compound the band is typically of higher frequency in the *Z* isomer (Δν 5–20

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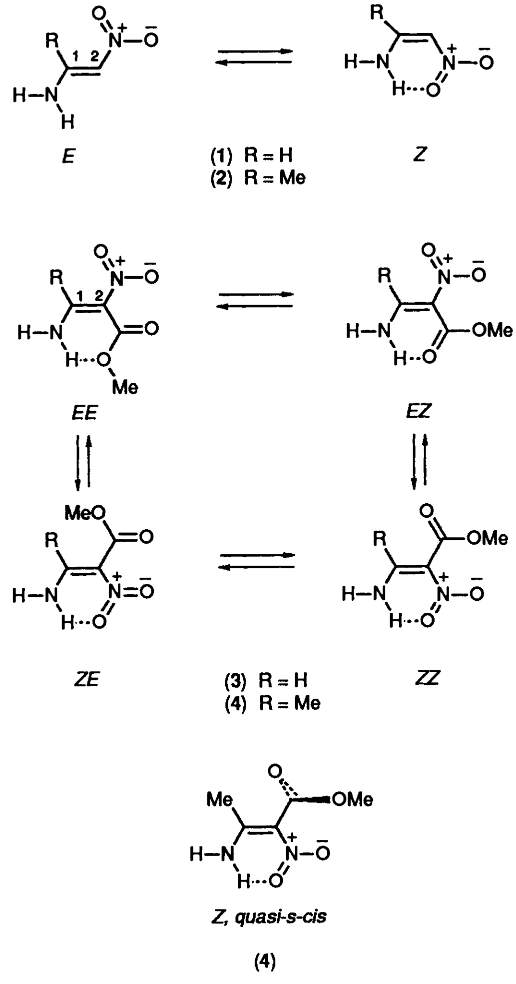
† For comparative purposes, the numbering system for compound (1) has been preserved in the structural formulae of the remaining compounds. The symbols below the formulae of compounds (3) and (4) indicate, in the order shown, the configuration around the carbon–carbon double bond, and the alignment of the C=O group with respect to the C=C group.



Scheme.

cm^{-1}), the difference being smaller for the compounds (3) and (4), with two electron-withdrawing groups. Methyl substitution at C(1) causes a frequency drop of this band ($\Delta\nu$ 25–40 cm^{-1}) as deduced by comparing compounds (1) and (3) with (2) and (4), respectively. Another unusual feature of the nitroenamine system is the low frequency of the NO_2 stretchings (ν_{as} 1 520–1 435 cm^{-1}, ν_s 1 315–1 230 cm^{-1}) and their anomalous IR intensities in the simple nitroenamines (1) and (2), where ν_{as} is typically weak or medium in IR and Raman while ν_s is very strong in IR as well as in Raman. The presence of a second electron-withdrawing group in compounds (3) and (4) causes the NO_2 stretches to recover their normal intensity pattern. For these two compounds, the frequency of the C=O stretch is a function of the spatial orientation of the CO_2Me group with respect to the nitroenamine moiety. The frequency is lower (1 675–1 655 cm^{-1}) in the *E* isomer, where the C=O group takes part in a strong intramolecular hydrogen-bond with the NH_2 group. For compound (3), with two planar *Z* isomers, the highest frequency corresponds to the *ZE* isomer, where the C=O bond is parallel to one of the N–O bonds of the nitro group. For the amino group, the ν_{as} stretch remains practically at the same frequency along the series, while the corresponding ν_s values follow the changes observed on the strength of the intramolecular hydrogen-bond, *i.e.* they are lower in the *Z* isomers for all the compounds and diminish with increasing substitution in the double bond. Ostercamp and Taylor[15] had previously studied the vibrational spectra of a series of simple nitroenamines. They proposed an assignment for the characteristic bands of the nitroenamine system, and explained some of the peculiar features observed in terms of the high degree of electronic polarization and mechanical coupling between the NO_2, C=C, and C–N bonded units. This interpretation was based on a proposed similarity between nitroenamines and amino enones.

The purpose of our investigation is first to confirm in a completely independent way our previous assignment of the vibrational spectra of compounds (1)–(4),[7] and second to obtain a theoretical interpretation of the unusual vibrational properties of these compounds in terms of structure-dependent force constants and normal modes. To reach this goal we have calculated the vibrational spectra of all the possible different isomers of compounds (1)–(4) using the semi-empirical method MNDO/H. For the simplest compound in the series, (1), and for (3) a more reliable force field has been tried using the *ab initio* STO-3G basis set. A more extended basis set, the split-valence 3-21G, has also been used for (1).

Computational Methods.—The semi-empirical calculations have been carried out by means of the GEOMO program.[16] The *ab initio* calculations have been performed by means of the GAUSSIAN 86 program.[17] The vibrational properties were obtained by solving the Coupled Perturbed Hartree–Fock equations (CPHF).[18]

Results and Discussion

Semiempirical Calculations.—Due to the number and complexity of the structures included in this study, and to the extensive geometry optimizations that are required to perform the vibrational calculations, a semi-empirical method was considered to be an appropriate method of calculation. We have shown[13] that the MNDO/H method[19] gives a reasonable description of the geometries, isomeric equilibria, and energy barriers to isomerization of the nitroenamines included in this study. The original MNDO method[20] fails to predict an acceptable energy difference between the two geometrical isomers of the parent nitroenamine (1),[13] due to an underestimation of the hydrogen-bonding interaction.

We will restrict our analysis of the spectra to those vibrations considered as most characteristic of the nitroenamine system, *i.e.* those corresponding roughly to stretchings of the NH_2, C=C, and NO_2 (and C=O) bonded units. Table 1 shows the diagonal stretching force constants for the nitroenamine framework of the planar isomers of compounds (1)–(4) calculated by the MNDO/H method. Completely optimized geometries have been used in all cases except for compounds (3) and (4) where a planarity constraint was imposed for the conjugated system in order to obtain a simplified view of the isomeric equilibria.[13] The corresponding MNDO/H harmonic frequencies for the characteristic vibrations of the nitroenamine moiety are included in Table 2. For comparison purposes, the corresponding experimental frequencies appear in Table 3.

The salient feature of the semi-empirical results is the large overestimation of the $F_{N\text{-}O}$ constants and, correspondingly, of the NO_2 stretching frequencies. The error is specially evident in compounds (3) and (4), with an ester group, where the calculated $F_{N\text{-}O}$ and $\nu_{as}(NO_2)$ values are higher than the corresponding $F_{C=O}$ and ν(C=O) values in some of the isomers. For comparison, the spectroscopically determined[21] values for the $F_{N\text{-}O}$ and $F_{C=C}$ constants in nitroethene are 8.21 mdyn Å^{-1} and 9.86 mdyn Å^{-1}, respectively.* This strong deviation can be attributed to the poor parametrization of

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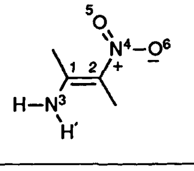
* 1 dyn = 10^{-5} N.

Table 1. Harmonic stretching force constants (mdyn Å^{-1}) calculated by the MNDO/H method for the planar isomers of compounds (**1**)–(**4**).



Compd.	Isomer	$F_{C(1)=C(2)}$	$F_{C(1)-N(3)}$	$F_{C(2)-N(4)}$	$F_{N(4)-O(5)}$	$F_{N(4)-O(6)}$	$F_{C=O}$	$F_{N(3)-H'}$	$F_{N(3)-H}$
(**1**)	*E*	10.62	10.54	6.88	17.60	17.91	—	7.40	7.43
	Z	10.69	10.98	7.06	16.09	18.29	—	5.75	7.46
(**2**)	*E*	10.40	10.16	6.86	17.68	17.79	—	7.39	7.42
	Z	10.64	10.85	7.16	15.95	18.27	—	5.33	7.43
(**3**)	*EE*	10.23	11.27	6.87	17.23	18.20	18.24	6.00	7.39
	EZ	10.39	11.48	7.13	17.22	18.09	15.67	4.51	7.38
	ZE	10.51	11.47	7.20	15.32	18.76	18.01	4.88	7.38
	ZZ	10.40	11.52	7.28	15.30	18.75	17.38	4.90	7.37
(**4**)	*EE*	10.32	10.96	6.73	17.38	18.08	18.18	5.74	7.36
	EZ	10.48	11.20	6.98	17.36	17.99	15.54	4.25	7.34
	ZE	10.65	11.21	7.09	15.16	18.77	17.89	4.54	7.34
	ZZ	10.50	11.28	7.21	15.14	18.76	17.41	4.56	7.37

Table 2. Harmonic frequencies (cm^{-1}) calculated by the MNDO/H method for the characteristic vibrations of the planar isomers of compounds (**1**)–(**4**).

Compd.	Isomer	$\nu_{as}(NH_2)$	$\nu_s(NH_2)$	$\nu(C=O)$	ν(enamine)	$\nu_{as}(NO_2)$	$\nu_s(NO_2)$
(**1**)	*E*	3 656	3 641	—	1 752	2 086	1 840
	Z	3 661	3 244	—	1 825	2 079	1 825
(**2**)	*E*	3 652	3 640	—	1 748	2 084	1 832
	Z	3 654	3 134	—	1 773	2 076	1 810
(**3**)	*EE*	3 644	3 298	2 133	1 773	2 074	1 827
	EZ	3 641	2 914	1 987	1 781	2 082	1 829
	ZE	3 641	3 016	2 122	1 810	2 070	1 784
	ZZ	3 639	3 020	2 060	1 807	2 086	1 784
(**4**)	*EE*	3 636	3 223	2 126	1 671	2 067	1 830
	EZ	3 632	2 828	1 988	1 796	2 075	1 834
	ZE	3 631	2 911	2 111	1 788	2 061	1 823
	ZZ	3 630	2 917	2 062	1 787	2 083	1 820

Table 3. Experimental frequencies[a] (cm^{-1}) for the characteristic vibrations of the different isomers of compounds (**1**)–(**4**).[b]

Compd.	Isomer	$\nu_{as}(NH_2)$	$\nu_s(NH_2)$	$\nu(C=O)$	ν(enamine)	$\nu_{as}(NO_2)$	$\nu_s(NO_2)$	ν[C(2)–H]	ν[C(1)–H]
(**1**)	*E*[c]	d	d	—	1 632vs[e]	d	d	d	d
	Z	3 505m	3 350m	—	1 642vs	1 450s	1 263vs	3 140w	3 055vw
(**2**)	*E*	d	d	—	d	d	d	d	—
	Z	3 490m	3 320m	—	1 620vs	1 445s	1 294vs	d	—
(**3**)	*EZ*	3 490m	3 340w	1 673s	1 635sh	1 495m	1 310s	—	d
	ZE	3 490m	3 340w	1 733m	1 642vs	1 470m	1 310s	—	d
	ZZ	3 490m	3 340w	1 692w	1 642vs	1 470m	1 310s	—	d
(**4**)	*EZ*	3 485m	3 310w	1 675m	1 618vs	1 515s	1 270s	—	—
	Z-quasi-s-*cis*	3 485m	3 310w	1 722m	1 618vs	1 515s	1 270s	—	—

[a] In $CDCl_3$ unless otherwise stated. [b] Values taken from ref. 6. [c] In $(CD_3)_2SO$. [d] Not measured. [e] Intensity abbreviation: s, strong; m, medium; w, weak; sh, shoulder; v, very.

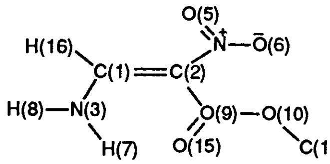
MNDO for molecules containing N and O atoms, and has been previously observed by other authors.[22]

Despite these errors, the semiempirical calculations reproduce qualitatively some of the vibrational properties of nitroenamines (**1**)–(**4**), and the structural effects observed on these properties. The $F_{C(1)=C(2)}$ and $F_{C(1)-N}$ stretching constants are calculated to have very similar values thus reflecting a strong conjugation of the amino group with the double bond. As a consequence, both internal co-ordinates strongly interact and the normal mode with the highest contribution from the C(1)=C(2) stretching co-ordinate has also a strong participation of the C(1)–N stretch. This normal mode can be described, in the MNDO/H approximation, as an asymmetric combination of both co-ordinates with participation of the in-plane C(1)–N–H and C=C–H bendings. A small contribution to this mode of the N–O and C(2)–N stretchings is also predicted by MNDO/H, most likely due to the considerable overestimation of the corresponding force constants. For its complex composition, also deduced experimentally (see above), and for its localization on the enamine moiety of the molecule, we have proposed[7] the names of *enamine mode* and *enamine band* for this mode and its corresponding assigned band. The contribution of the C–N–H in-plane bending can explain the observed isotopic effects, produced by *N*-deuteriation, on the frequency of the enamine band. The effect of methyl substitution at C(1) is also qualitatively reproduced. As can be seen from comparing compounds (**1**) and (**3**) with (**2**) and (**4**), respectively, the introduction of a methyl group on C-(1) causes a decrease of the $F_{C(1)-N}$ force constant and, in the simple nitroenamines (**1**) and (**2**), also of the $F_{C(1)=C(2)}$ constant. The change in the composition of the enamine mode caused by the disappearance of the in-plane C(2)=C(1)–H bending co-ordinate in compounds (**2**) and (**4**) could also contribute to the observed effect (*vide infra*). The influence of isomerism on the frequency of the enamine band is also correctly predicted, except for compound (**4**). For each compound, the calculated frequency is higher in the *Z* than in the *E* isomer, as a result of the higher $F_{C(1)-N}$ and $F_{C(1)=C(2)}$ constants in the former isomer. (See, however, the *ab initio* results below.)

In compounds (**3**) and (**4**), the calculated $F_{C=O}$ constants are different for every isomer and diminish in the series *EE* > *ZE* > *ZZ* > *EZ*. The intramolecular hydrogen-bond in the *EZ* isomer, and the through-space dipolar interaction between the NO_2 and the C=O group, which is maximum in the *EE* and *ZE* orientations, may explain the observed effects. The theoretical and the experimental frequencies for the C=O stretching also follow this order, showing that the variation is not due to a change in the composition of the corresponding normal mode, as suggested for other amino enones,[3,4] but rather reflects directly the change in the C=O bond order. Besides, the fact that no other ν(C=O) bands can be observed in the IR spectra of (**3**) and (**4**) at frequencies higher than that assigned to the *ZE* isomer rules out the existence of the *EE* isomer, in agreement with our previous energy calculations.[13] The ν(C=O) frequencies calculated for the planar isomers of compound (**4**) are very similar to those calculated for (**3**). As indicated above, compound (**4**) shows only two ν(C=O) bands in the IR spectra in solution, which have been assigned to its two geometrical isomers. For the *Z* isomer of (**4**), the experimental frequency is in between those found for the *ZE* and *ZZ* isomer of (**3**). This observation and the fact that, as deduced from our theoretical results, the introduction of the methyl group at C(1) is predicted to have an almost nil effect on the ν(C=O) values of the *ZE* and *ZZ* isomers, strongly support the proposed[7b,c] nonplanar structure for the *Z* isomer of (**4**).

The stretching force constants for the two N–H bonds have very similar values in the structures *E*-(**1**) and *E*-(**2**), with no intramolecular hydrogen-bonds. As expected, the presence of an intramolecular hydrogen-bond diminishes significantly the stretching force constant of the N–H involved, $F_{N-H'}$. Considering that $F_{N-H'}$ is a measure of the strength of the hydrogen-bond, the values in Table 1 indicate that, in the MNDO/H approximation, this strength increases with substitution on the double bond, in agreement with our experimental observations.[7] However, contrary to the experimental evidence[7] and the *ab initio* results (*vide infra*), MNDO/H predicts for compounds (**3**) and (**4**) a stronger intramolecular hydrogen-bond for the ester group (*EZ* isomer) than for the nitro group (*ZE* and *ZZ* isomers). The calculated frequencies for the ν_{as} and ν_s stretching modes of the NH_2 group have very similar values in the structures *E*-(**1**) and *E*-(**2**). In the presence of the intramolecular hydrogen-bond, $\nu_s(NH_2)$ diminishes significantly while $\nu_{as}(NH_2)$ remains approximately at the same position. The $\nu_s(NH_2)$ values follow the changes in $F_{N-H'}$, reflecting the high contribution of this stretching co-ordinate to the ν_s mode. However, in contrast to the rest of the calculated spectrum, the $\nu_s(NH_2)$ values are in general underestimated, indicating that the MNDO/H approximation overestimates the strength of the intramolecular hydrogen-bond in these systems.

Table 4. Optimized geometrical parameters calculated by the STO-3G basis set for the stable isomers of compound (**3**).

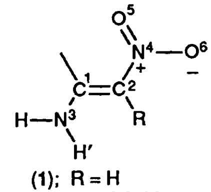


Geometrical parameter	*EZ*	*ZZ*	*ZE*
C(1)–C(2)	1.350[a]	1.359	1.358
N(3)–C(1)	1.362	1.351	1.352
N(4)–C(2)	1.491	1.482	1.482
O(5)–N(4)	1.287	1.315	1.314
O(6)–N(4)	1.276	1.266	1.266
C(9)–C(2)	1.496	1.501	1.498
O(10)–C(9)	1.385	1.391	1.402
C(11)–O(10)	1.439	1.438	1.436
O(15)–C(9)	1.230	1.222	1.217
N(3)–H(7)	1.024	1.029	1.029
N(3)–H(8)	1.015	1.015	1.015
C(1)–H(16)	1.092	1.092	1.092
N(3)–C(1)–C(2)	122.93[b]	123.32	122.66
N(4)–C(2)–C(1)	116.73	118.31	118.49
O(5)–N(4)–C(2)	117.09	119.40	119.95
O(6)–N(4)–C(2)	119.89	120.29	119.27
C(9)–C(2)–C(1)	120.43	119.36	123.41
O(10)–C(9)–C(2)	115.00	114.21	109.30
C(11)–O(10)–C(9)	112.06	111.74	111.85
O(15)–C(9)–C(2)	122.42	122.74	128.11
H(7)–N(3)–C(1)	115.75	111.53	111.74
H(8)–N(3)–C(1)	121.65	121.83	121.75
H(16)–C(1)–C(2)	118.89	117.56	118.23

[a] Bond lengths in Å. [b] Bond angles in degrees.

ab initio Calculations.—The considerable deviations in the semiempirical force field associated with the nitro group may seriously affect the reliability of the MNDO/H spectra. It has been shown that *ab initio* vibrational spectra are accurate enough to give correct overall vibrational patterns for a wide range of small to medium-sized molecules.[5] Consequently, we have obtained *ab initio* force fields for the observed isomers of two compounds in the series: the parent nitroenamine (**1**) and the ester (**3**). The STO-3G minimal basis set was employed for both compounds. In the case of compound (**1**), the more flexible 3-21G split-valence basis set was also used in order to test the level of reliability attainable at this higher level of theory. Completely optimized geometries have been considered, except for (**3**) where the optimization was performed within the C_s symmetry group of this molecule. No attempt has been made to fit the theoretical force fields to the observed spectra (solution phase) by scaling the force field. Instead, to compensate for the effect of anharmonicity and the neglect of electron correlation in the SCF wave function, we have scaled the calculated frequencies. It has been found that a direct proportionality exists between harmonic calculated frequencies obtained at the

Table 5. *ab initio* harmonic stretching force constants (F/mdyn Å^{-1}) for planar isomers of compounds (**1**) and (**3**).



(**1**); R = H
(**3**); R = CO_2Me

Compd.	Basis set	Isomer	$F_{C(1)=C(2)}$	$F_{C(1)-N(3)}$	$F_{C(2)-N(4)}$	$F_{N(4)-O(5)}$	$F_{N(4)-O(6)}$	$F_{C=O}$	$F_{N(3)-H'}$	$F_{N(3)-H}$
(**1**)	STO-3G	*E*	12.61	9.17	6.14	10.82	11.29	—	9.68	9.72
		Z	12.64	9.47	6.32	9.05	12.02	—	8.38	9.68
	3-21G	*E*	10.01	8.24	5.56	6.93	8.13	—	8.13	8.22
		Z	9.90	8.65	5.69	6.42	8.14	—	7.82	8.22
(**3**)	STO-3G	*EZ*	11.62	9.67	6.08	10.46	11.50	15.37	8.84	9.64
		ZE	11.72	10.07	6.35	8.11	12.59	16.76	7.84	9.59
		ZZ	11.66	10.08	6.35	8.00	12.62	16.35	7.84	9.59

theoretical geometry and anharmonic observed frequencies, which are based on the experimental geometry.[23,24]

The optimized geometries of the two isomers of compound (**1**) at the STO-3G and 3-21G levels have been published elsewhere.[13] Those for the three lower energy isomers of compound (**3**) obtained at the STO-3G level are reported in Table 4. Unfortunately, there are no experimental parameters for comparison available for these compounds.

The *ab initio* diagonal force constants for the nitroenamine framework of the different isomers of compound (**1**) and (**3**) are included in Table 5. By comparing these values with those in Table 1 it can be seen that they are significantly different and in better accordance with the values which could be anticipated (see above). The main improvement corresponds to the F_{N-O} values that are now lower than the corresponding $F_{C(1)=C(2)}$ constants. Only the F_{N-H} and $F_{C(1)=C(2)}$ constants are higher in STO-3G than in MNDO/H. The structural effects on the calculated force field predicted at the STO-3G level for both molecules correspond in general to those derived from MNDO/H. The only exception refers to the effect of isomerism on the values of the stretching force constant of the N–H bond involved in the intramolecular hydrogen-bond, $F_{N-H'}$, in compound (**3**). The *ab initio* results show that the $F_{N-H'}$ values for the *ZZ* and *ZE* isomers are lower than that of the *EZ* isomer, indicating a stronger intramolecular hydrogen-bond with the nitro group than with the ester group. This result is in agreement with our experimental observations[7] and opposed to the MNDO/H predictions. As in the MNDO/H force field, the $F_{C(1)=C(2)}$ and $F_{C(1)-N}$ constants are very similar, and $F_{C(2)-N}$ is significantly smaller as expected for a preferential conjugation of the amino group with the double bond.

The use of the 3-21G split-valence basis results in lower values for the diagonal force constants of the two isomers of compound (**1**) (Table 5). The main change corresponds to the $F_{C(1)=C(2)}$ and F_{N-O} constants, which are now very close to those determined spectroscopically for nitroethene (see above). The $F_{C(1)=C(2)}$ constant is predicted to have a lower value for the *Z* than for the *E* isomer, contrary to the MNDO/H and STO-3G predictions. However, this result is in agreement with the experimental evidence for a *hydrogen-bond assisted conjugation* in this[7] and related systems.[25] The presence of the intramolecular hydrogen-bond in the *Z*-isomer promotes the resonance interaction ('push-pull' effect) between the hydrogen-bond donor and the hydrogen-bond acceptor. The dependence of the calculated 3-21G force field on the configuration of the C(1)=C(2) bond in compound (**1**) can be easily rationalized on this basis. For compound (**3**), the additional interaction between the two acceptor groups precludes such a straightforward analysis.

The *ab initio* harmonic frequencies for the most characteristic vibrations of compound (**1**) calculated by the STO-3G and 3-21G basis are included in Table 6. The comparison with the experimental frequencies for the *Z* isomer (Table 3) show that the calculated values are overestimated. However, the order of the frequencies corresponding to the main vibrations of (**1**) is correctly reproduced with both basis sets, in contrast to the semi-empirical results. There is a marked trend towards lower frequencies on going from the minimal basis set STO-3G to the split-valence 3-21G. For comparison with the observed frequencies (solution phase), the STO-3G and 3-21G values have been scaled by the factors 0.83 and 0.9, respectively. The agreement is exceptional in both cases, but especially for the STO-3G results with a standard deviation for the scaled frequencies included in Table 6 of only 17 cm^{-1}. The standard deviation increases to 48 cm^{-1} (10 cm^{-1} if the two N–O stretches are omitted) on going to the 3-21G values. The scaled 3-21G frequencies for the ν_{as} and ν_s stretchings of the NO_2 group are too low by 132 and 65 cm^{-1}, respectively. However, only the 3-21G calculation predicts correctly the effect of the configuration of the double bond on the frequencies. The frequency of the enamine mode of the *Z* isomer is calculated to be 18 cm^{-1} higher than that of the *E*-isomer. This value is very close to the experimental difference ($\Delta\nu$ 20 cm^{-1}) determined[7b] in Me_2SO solution, although the calculated values are harmonic frequencies and correspond to the gas phase. With respect to the ν_{as} and ν_s stretchings of the NO_2 group, the experimental evidence[7b] is not as clear, although it has been observed[7b] for other nitroenamines that ν_{as} is slightly lower in the *Z* isomer, where the NO_2 group participates in an intramolecular hydrogen-bond. The effects predicted by the STO-3G basis for the enamine, $\nu_{as}(NO_2)$ and $\nu_s(NO_2)$ modes are the opposite of those predicted by 3-21G.

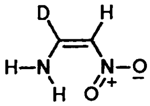
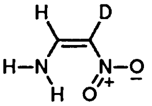
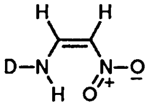
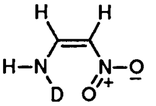
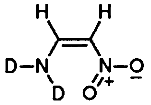
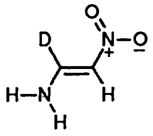
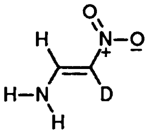
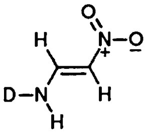
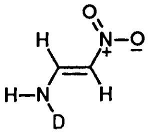
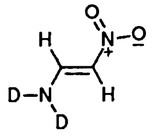
Since theoretical frequencies can be in error by as much as a few hundred wavenumbers, some complementary information is required to reach a definite assignment for the observed bands. It has been shown[5] that when theoretical intensities are computed together with the frequencies very useful results can be obtained without employing any scale factors. The IR absorption intensities and the corresponding Raman activities calculated by the 3-21G basis set for the two isomers of compound (**1**) are also included in Table 6. The overall pattern of observed relative intensities (solution phase) is correctly

Table 6. *ab initio* vibrational frequencies (cm^{-1}), IR intensities (km mol^{-1}), and Raman activites (Å^4 amu) for the characteristic vibrations of compound (**1**).

	STO-3G				3-21G							
	ν		$\nu_{sc.}$[a]		*Z*			*E*			$\nu_{sc.}$[b]	
	Z	*E*	*Z*	*E*	ν	I_{IR}	A_R	ν	I_{IR}	A_R	*Z*	*E*
$\nu_{as}(NH_2)$	4 231	4 292	3 512	3 562	3 884	131.4	82.6	3 895	76.8	73.3	3 495	3 506
$\nu_s(NH_2)$	3 861	4 075	3 347	3 400	3 719	96.3	77.6	3 778	125.2	140.1	3 347	3 400
ν[C(2)–H]	3 781	3 766	3 138	3 126	3 483	7.5	52.6	3 466	10.9	43.8	3 135	3 119
ν[C(1)–H]	3 703	3 701	3 073	3 072	3 362	3.8	69.9	3 396	3.7	31.8	3 026	3 056
ν(enamine)	1 983	2 015	1 646	1 672	1 817	482.8	7.3	1 799	395.1	76.1	1 635	1 619
$\nu_{as}(NO_2)$	1 807	1 742	1 500	1 446	1 464	204.3	3.5	1 489	83.2	16.2	1 318	1 340
$\nu_s(NO_2)$	1 502	1 527	1 247	1 267	1 331	511.0	132.2	1 310	552.6	218.7	1 198	1 179

[a] Scaled frequencies (scale factor 0.83). [b] Scaled frequencies (scale factor 0.9).

Table 7. Isotope frequency shifts (cm^{-1}) obtained by 3-21G *ab initio* calculations for the characteristic vibrations of the two isomers of compound (**4**).

			Z isomer		
					
Assignment	$\Delta\nu$	$\Delta\nu$	$\Delta\nu$	$\Delta\nu$	$\Delta\nu$
$\nu_{as}(NH_2)$	0	0	−1 072	−30	−1 009
$\nu_s(NH_2)$	0	1	42	−976	−1 030
ν[C(2)–H]	0	−906	0	0	0
ν[C(1)–H]	−873	1	0	0	1
ν(enamine)	−14	−3	−17	−37	−43
$\nu_{as}(NO_2)$	−28	−3	−65	−73	−62
$\nu_s(NO_2)$	8	−77	−2	−7	−2
			E isomer		
					
Assignment	$\Delta\nu$	$\Delta\nu$	$\Delta\nu$	$\Delta\nu$	$\Delta\nu$
$\nu_{as}(NH_2)$	0	0	−1 083	−43	−1 010
$\nu_s(NH_2)$	0	0	51	−984	−1 049
ν[C(2)–H]	0	−899	0	0	0
ν[C(1)–H]	−883	0	0	0	0
ν(enamine)	−28	−21	3	−1	−9
$\nu_{as}(NO_2)$	−8	−41	−17	−1	10
$\nu_s(NO_2)$	0	−6	−5	−8	−12

reproduced by the calculation. The observed bands designated as strong, medium, and weak are generally reproduced as such. This applies even to the Raman spectrum, in spite of the considerable error which may affect the theoretical Raman activities at the 3-21G level. The normal mode with the highest theoretical IR intensity and Raman activity corresponds to $\nu_s(NO_2)$, in agreement with the experimental assignment.[7b] The enamine mode is correctly predicted to be very intense in IR, and of weak activity in Raman. For $\nu_{as}(NO_2)$, the theoretical IR intensity and Raman activity are significantly lower than those calculated for the symmetric stretching, also in agreement with the experimental observation.[7b]

The isotope frequency shifts calculated with the 3-21G force field for several deuteriated isotopomers of the two isomers of compound (**1**) are included in Table 7. Besides further confirming the assignment of the experimental spectra, the theoretical isotope effects clearly reveal the complex vibrational couplings that occur in this molecule (*vide infra*). The qualitative agreement between theoretical and experimental effects provides a reasonable basis for their interpretation in terms of structure-dependent normal modes. The effect of *C*-deuteriation predicted for the enamine mode is higher for the *E* isomer and when the substitution is performed at C(1). This result indicates that the observed difference between the

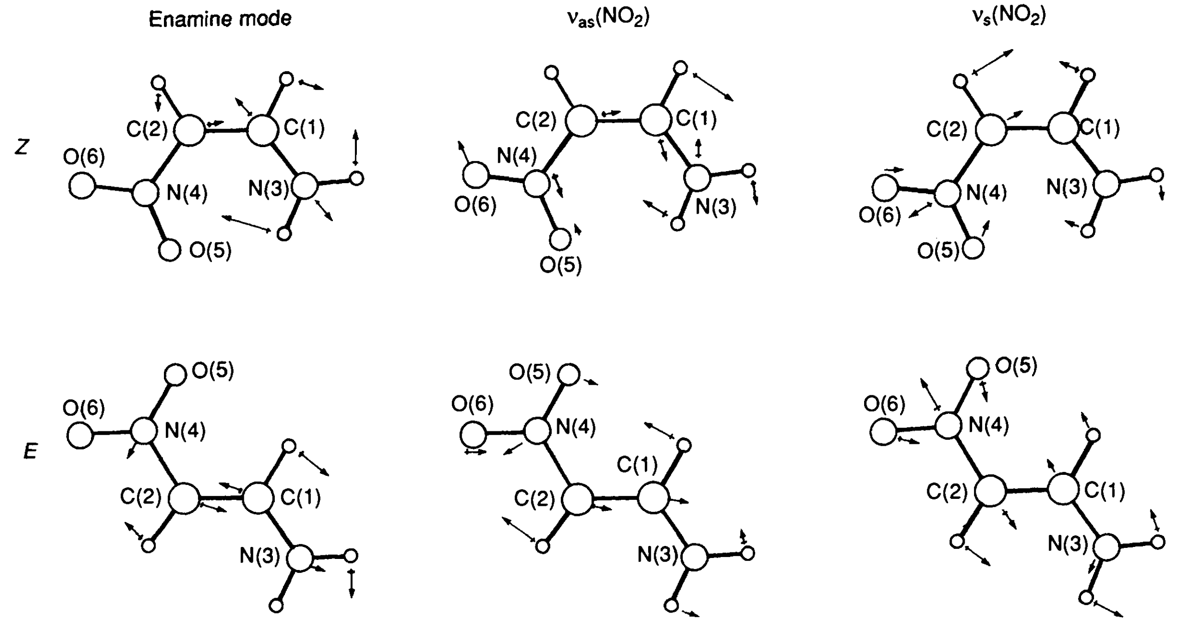


Figure 1. Displacement vectors for the enamine, $v_{as}(NO_2)$ and $v_s(NO_2)$ vibrations of the two isomers of compound (**1**).

Table 8. Harmonic frequencies (cm^{-1}) and IR intensities (km mol^{-1}) for the characteristic vibrations of the more stable planar isomers of compound (**3**), calculated by the STO-3G basis set.

	ZZ isomer			*ZE* isomer			*EZ* isomer		
Assignment	v	v_{sc}[a]	I_{IR}	v	v_{sc}[a]	I_{IR}	v	v_{sc}[a]	I_{IR}
$v_{as}(NH_2)$	4 207	3 492	205.1	4 208	3 493	202.9	4 236	3 516	135.7
$v_s(NH_2)$	3 764	3 124	253.0	3 765	3 125	246.8	3 940	3 270	148.0
v[C(1)–H]	3 698	3 069	12.6	3 709	3 078	15.7	3 703	3 073	34.9
v(C=O)	2 061	1 711	118.0	2 099	1 742	138.8	2 027	1 682	161.8
v(enamine)	1 941	1 611	810.0	1 946	1 615	785.2	1 925	1 598	615.9
$v_{as}(NO_2)$	1 798	1 492	140.1	1 796	1 491	63.3	1 777	1 475	137.8
$v_s(NO_2)$	1 570	1 303	63.3	1 572	1 305	167.2	1 509	1 252	72.7

[a] Scale factor 0.83.

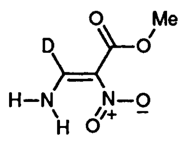
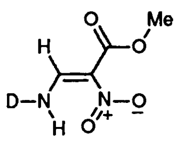
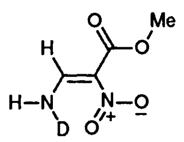
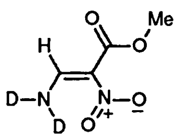
frequencies of the enamine mode of compounds (**1**) and (**2**) is due, at least partially, to the disappearance of the in-plane C(2)=C(1)–H bending co-ordinate in compound (**2**). However, the electronic effects introduced by the methyl group in (**2**) may also contribute as deduced from the MNDO/H results (see above). The effect of the *N*-deuteriation on the frequency of the enamine mode is predicted to be almost negligible for the *E* isomer, but considerable (Δv up to −43 cm^{-1}; observed[7b] −17 cm^{-1} in $CHCl_3$) for the *Z* isomer, especially when the substituted hydrogen is that involved in the intramolecular hydrogen-bond. It seems, therefore, that the contribution of the in-plane C(1)–N–H bending to the enamine mode is directly related to the presence of the intramolecular hydrogen-bond, in agreement with our observations.[7b] The isotope shifts predicted for the v_{as} and v_s stretchings of the NO_2 group clearly show their complex composition and that our assignment as N–O stretches is probably oversimplified.

It is clear now that in order to reproduce the vibrational properties of the parent nitroenamine (**1**), an *ab initio* calculation using a split-valence basis set is necessary. The minimal split-valence 3-21G basis predicts correctly the overall pattern of IR and Raman intensities and the structural effects (including isotope shifts) on the main vibrations of (**1**). Consequently, the predicted force field should also be correct, except for a proportionality constant (scale factor) which cannot affect the description of the normal modes deduced for the molecule using this force field. The displacement vectors for the enamine, $v_{as}(NO_2)$, and $v_s(NO_2)$ vibrations of the two isomers of (**1**) as calculated for the 3-21G force field are represented in Figure 1. The calculated isotope frequency shifts can now be easily rationalized in terms of the complex vibrational couplings expected for this molecule. The enamine mode is described, like in the MNDO/H approximation (see above), as an asymmetric combination of the C(1)=C(2) and C(1)–N stretching motions with contribution of the C=C–H and C(1)–N–H in-plane bendings. However, in contrast to the MNDO/H predictions, there is no participation of the stretching co-ordinates of the NO_2 group. The contributions of the different co-ordinates depend on the configuration of the double bond: those of the C(1)–N stretch and the C(1)–N–H in-plane bendings are larger in the *Z* isomer, while the C(1)=C(2) stretch and the C=C–H in-plane bendings participate more in the *E* isomer. From Figure 1 it is clear that the vibrations assigned to the v_{as} and v_s stretchings of the NO_2 group correspond in fact to complex modes including other co-ordinates such as the C=C–H and C(1)–N–H in-plane bendings, but no contribution of the C(1)=C(2) stretching is predicted. These results seriously question the alleged[15] vibrational coupling between the C=C and NO_2 units to explain the observed vibrational properties of simple nitroenamines.

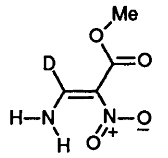
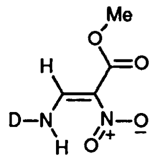
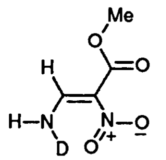
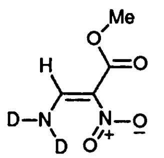
The harmonic frequencies for the characteristic vibrations of

Table 9. Isotope frequency shifts (cm^{-1}) calculated by the STO-3G basis set for the characteristic vibrations of the planar isomers of compound (**3**).

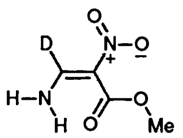
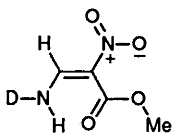
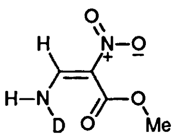
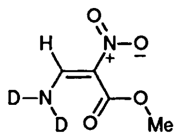
ZZ isomer

				
Assignment	$\Delta\nu$	$\Delta\nu$	$\Delta\nu$	$\Delta\nu$
$\nu_{as}(NH_2)$	0	−1 180	−32	−1 090
$\nu_s(NH_2)$	0	+69	−973	−1 032
ν[C(1)–H]	−953	0	0	0
ν[C=O]	−1	0	0	0
ν(enamine)	−30	−6	−40	−42
$\nu_{as}(NO_2)$	0	−11	−39	−42
$\nu_s(NO_2)$	−22	−1	−24	−37

ZE isomer

				
Assignment	$\Delta\nu$	$\Delta\nu$	$\Delta\nu$	$\Delta\nu$
$\nu_{as}(NH_2)$	0	−1 181	−32	−1 090
$\nu_s(NH_2)$	−1	−69	−973	−1 031
ν[C(1)–H]	−956	0	+1	+1
ν[C=O]	−1	0	0	−1
ν(enamine)	−29	−6	−40	−42
$\nu_{as}(NO_2)$	−1	−13	−45	−48
$\nu_s(NO_2)$	−17	+3	−38	−40

EZ isomer

				
Assignment	$\Delta\nu$	$\Delta\nu$	$\Delta\nu$	$\Delta\nu$
$\nu_{as}(NH_2)$	0	−1 194	−101	−1 094
$\nu_s(NH_2)$	−1	+79	−1 017	−1 090
ν[C(1)–H]	−955	0	0	0
ν[C=O]	−2	−2	−3	−5
ν(enamine)	−22	−8	−40	−42
$\nu_{as}(NO_2)$	−7	−24	−23	−28
$\nu_s(NO_2)$	−1	−11	−2	+13

the three stable isomers of compound (**3**) using the STO-3G force field are included in Table 8. As previously observed for (**1**), the *ab initio* force field provides the correct order of frequencies for the characteristic vibrations of this compound (*cf.* Table 3), in contrast again to the MNDO/H results. For comparison with the experimental values, the theoretical frequencies have been scaled by 0.83, the same factor used for (**1**) at the STO-3G level, resulting in a standard deviation of only 64 cm^{-1} for the vibrations included in the Table. The effect of isomerism on the frequencies is also qualitatively reproduced. Thus, the enamine mode is calculated to have very similar frequencies in the *ZZ* and *ZE* isomers, and a lower value in the *EZ* isomer, in agreement with the experimental results[7] and the MNDO/H predictions. The same effects are predicted for the $\nu_{as}(NO_2)$ and $\nu_s(NO_2)$ modes, although the experimental evidence[7] is not clear for these modes. The ν(C=O) frequencies are predicted to diminish in the series *ZE* > *ZZ* > *EZ*, in agreement with the experimental assignment and the MNDO/H calculations. But contrary to the semiempirical predictions, the two NH stretchings have lower frequencies in the *ZZ* and *ZE* isomers, as expected for a stronger hydrogen-bond with the NO_2 group.

In spite of the errors which may affect the IR intensities calculated at the STO-3G level (Table 8), some features of the spectra are correctly reproduced. The enamine mode is predicted to be more intense than the corresponding ν(C=O). With the exception of the *ZE* isomer, the $\nu_{as}(NO_2)$ mode has also a high theoretical intensity, in contrast with the 3-21G results

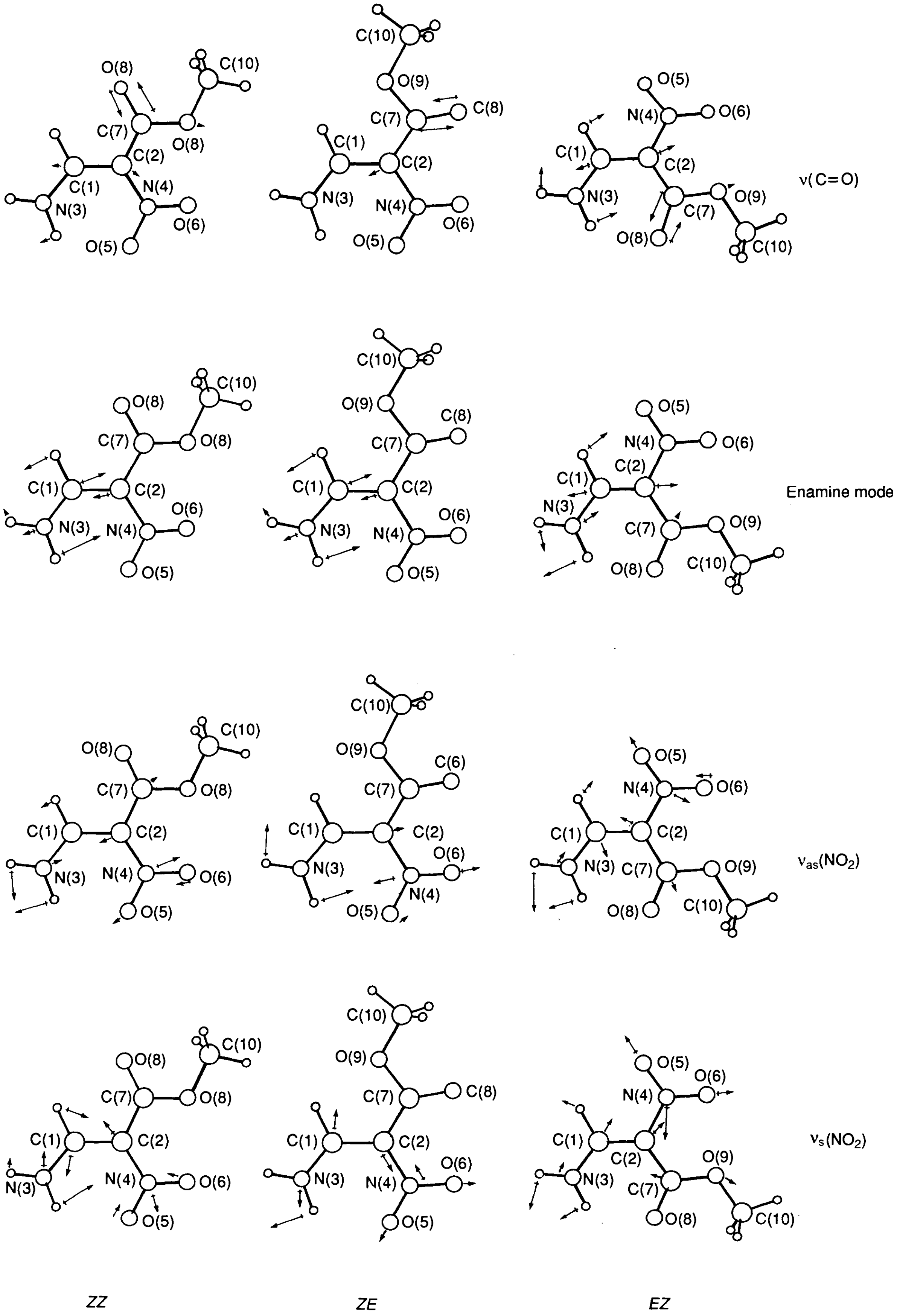


Figure 2. Displacement vectors for some characteristic vibrations of the stable isomers of compound (**3**).

for (**1**), but in agreement with the experimental observation.[7] However, contrary to that observed, the $\nu_s(NO_2)$ mode is predicted to have a lower IR intensity than the corresponding asymmetric mode, with the exception again of the *ZE* isomer.

The isotope frequency shifts calculated with the STO-3G force field for several deuteriated isotopomers of the three isomers of compound (**3**) are included in Table 9. The predicted effects are very similar to those calculated for (**1**) using the 3-21G force field. For the enamine mode, *N*-deuteriation is predicted to have a significant effect ($\Delta\nu$ up to -42 cm^{-1}) when the hydrogen substituted is that involved in the intramolecular hydrogen-bond. However, the same values are calculated for the three isomers, contrary to the experimental observation ($\Delta\nu$ $-$ 20 cm^{-1} for the *ZZ* and *ZE* isomers; -50 cm^{-1} for the *EZ* isomer, in $CHCl_3$).[7] Similarly, as calculated for (**1**), deuteriation at C(1) also affects ($\Delta\nu$ -22 to -30 cm^{1}) the enamine vibration. This shift is very similar to the observed frequency difference between the enamine vibrations of (**3**) and (**4**) ($\Delta\nu$ -24 cm^{-1}, in $CHCl_3$).[7] Again, as for (**1**) and (**2**), the similarity between theoretical shifts predicted for deuteriation at C(1) and the experimental shift observed for methylation at this carbon reveals that the change in the composition of the normal mode is probably the main factor responsible for the difference between the enamine vibrations of (**3**) and (**4**). The ν(C=O) mode shows negligible theoretical isotope shifts, by contrast to the NO_2 stretchings.

The theoretical isotope effects can be easily understood in terms of the different composition of the eigenvectors shown in Figure 2. The ν(C=O) vibration is highly localized, except for the *EZ* isomer. Therefore, the effects of isomerism on the ν(C=O) values are due to changes in the C=O bond order, and not to a conformational-dependent coupling between the C=C and C=O stretching co-ordinates suggested[3,4] for related amino enones. The composition of the enamine mode is practically the same for the three isomers, and very similar also to that calculated for (**1**) with the 3-21G force field. These results clearly show that, in spite of their complex composition, the normal modes are roughly transferable[26] between these molecules and their different isomers. It becomes also clear from the Figures that the vibrations assigned as $\nu_{as}(NO_2)$ and $\nu_s(NO_2)$ correspond in fact to complex modes.

Conclusions

We have shown that theoretical calculations can be very useful for the interpretation of vibrational spectra complicated by conjugation, vibrational couplings, and isomerism, as occurs in nitroenamines. Although the semi-empirical MNDO/H calculations reproduce qualitatively some of the observed properties, the frequencies of the NO_2 stretchings are considerably overestimated. A more accurate force field is provided by the *ab initio* calculations. The minimal basis STO-3G gives the correct order for the frequencies of the characteristic vibrations of the nitroenamine system, and reproduces many of the observed structural effects. Better results are obtained with the split-valence 3-21G basis. The generally good reproduction of experimental relative intensities and isotope frequency shifts for the parent nitroenamine (**1**) is a strong indication of the accuracy of the 3-21G force field. The analysis of the normal modes provided by the calculations reveal the complex vibrational couplings that occur in these molecules. The so-called *enamine* mode can be described as an asymmetric combination of the C(1)=C(2) and C(1)–N stretchings with contribution of the in-plane C=C–H and C(1)–N–H bendings. The ν_{as} and ν_s stretchings of the NO_2 group also participate in complex vibrational couplings. Finally, but no less important, the general agreement between theoretical and experimental spectra has independently confirmed our previous assignment of the nature of the isomers present in the compounds studied.

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