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Quantum Chemical Investigation of Structures, Rotational Barriers, and Vibrational Spectra of the Rotamers of Ethyl Nitrite (CH_3CH_2ONO)

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Ab initio and density functional (DFT) methods were used to investigate the rotamers of ethyl nitrite. The potential energy surface for rotations around the C−O and the N−O bonds was calculated at different levels of theory. From the four geometrically possible conformers, only three were found to be stable when correlation effects are taken into account in the calculations. This result is consistent with a microwave study of Turner (*J. Chem. Soc.*, Faraday Trans. *2* **1979**, 317.) as well as with the presented IR spectrum of matrix-isolated ethyl nitrite which clearly distinguishes three different N═O stretching modes. A simulated IR spectrum generated from the results of the DFT calculations is in good agreement with this matrix spectrum and allows us to tentatively assign groups of frequencies.

Introduction

Alkyl nitrites (R−ONO) exist as a mixture of cis and trans (syn and anti) conformers. In the case of the smallest nitrite, nitrous acid (HONO), the trans form has been found to be the more stable conformer.[1,2] Already in 1952 Tarte[3] has suggested that the gas-phase infrared (IR) and ultraviolet (UV) spectra of alkyl nitrites can be explained as caused by a mixture of cis and trans conformers. From these spectra information about the more stable conformers could be extracted. According to this study, the cis conformation should be more stable in the case of methyl nitrite (CH_3ONO) while for higher *n*-alkyl nitrites the trans conformer has been proposed to be the more stable form. The stabilization of the cis conformation of methyl nitrite had been attributed later to the formation of internal hydrogen bonds.[4] The cis conformer of methyl nitrite was also found to be the more stable form in microwave and matrix IR experiments[5,6] as well as in photofragment yield spectra in a supersonic jet.[7]

On the basis of NMR experiments, Piette et al.[8] had proposed opposite relative stabilities for *n*-alkyl nitrites. According to their data, the trans form should be stabilized in the case of methyl nitrite, whereas the cis form should be the more stable conformation in higher *n*-alkyl nitrites. Piette's suggestion was supported by an investigation of Phillips et al.[9] The interpretation of Piette et al. was however doubted by an NMR investigation of a series of alkyl nitrites by Brown and Hollis.[10] An NMR investigation of Lazaar and Bauer[11] revealed relative stabilities which were in agreement with the original suggestions by Tarte. Also by means of NMR spectroscopy, gas-phase, and solution-phase thermodynamic parameters had been determined for several alkyl nitrites.[12] According to these data, methyl nitrite is clearly in the cis conformation for a wide range of temperatures while ethyl nitrite (EtONO) should be found in the cis form at low temperature but in the trans conformation at room temperature due to entropic effects.

Using microwave spectroscopy, Turner[13] was able to detect three conformers of ethyl nitrite. From relative intensities in spectra recorded at room temperature, he concluded that the cis−trans conformer (cis with respect to the N−O bond and trans with respect to the C−O bond) corresponds to the most stable form followed by the trans−gauche and the cis−gauche conformers. Microwave spectroscopy revealed the only evidence for three conformers of ethyl nitrite, whereas IR[14] and NMR[11,12] spectra allowed only the assignment of the cis and trans form with respect to the N−O bond.

At a first glance one would expect that the energies of all four possible conformers are very close to each other. An explanation for the experimental findings discussed above is therefore needed. State-of-the-art quantum chemical methods offer an attractive possibility to gain additional insight into the ground state properties of this molecule. To our knowledge no quantum chemical study of the ground state of EtONO has yet been published. We have therefore decided to carry out quantum chemical calculations of EtONO with the aim to identify the stable isomers of EtONO, to estimate their relative energies, and to provide information about their IR spectra.

We have calculated potential energy surfaces with respect to the dihedral angles $\tau_{O=N-O-C}$ and $\tau_{N-O-C-C}$ at different levels of theory to locate all possible stable conformers. By applying MP2, as well as density functional methods, possible effects of electron correlation have been studied. Relative energies of stable conformers have been calculated using extensive quantum chemical methods. Vibrational spectra of all stable conformations in the electronic ground state have been determined at the BLYP, B3LYP, and MP2 levels of theory. On the basis of the frequencies determined by means of the BLYP density functional method, an IR spectrum of a mixture of the stable conformations has been simulated and compared to a recently recorded IR spectrum of matrix isolated EtONO[15] in argon at low temperature.

Methods of Calculation

All calculations were performed with the Gaussian 94[16] program. The used AO basis set is the 6-31G** basis of Pople and co-workers.[17−19] The Gaussian 2 theory (with MP2: G2MP2),[20,21] as well as the complete basis set theories (CBS-4, CBS-q and CBS-Q),[22,23] was used to estimate the relative energies of the conformers. These methods try to extrapolate the errors inherent in the calculation, for example by scaling the frequencies empirically. Thereby, it is in most cases possible

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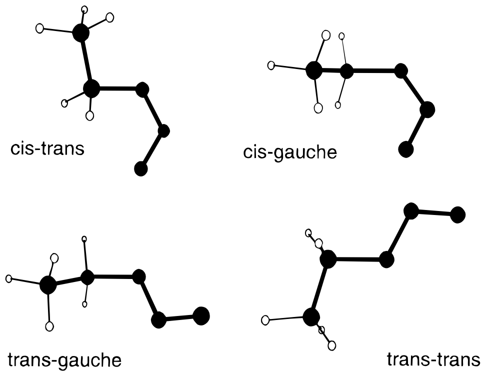

Figure 1. AM1 optimized structures of the rotamers of ethyl nitrite.

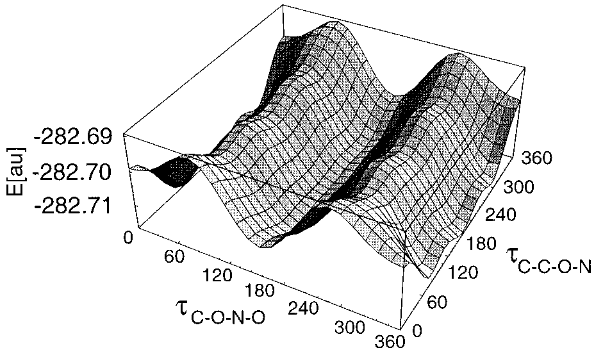

Figure 2. Two-dimensional PES of ethyl nitrite calculated at the HF/6-31G** level of theory.

to extrapolate thermodynamic functions to an accuracy of 10 kJ/mol for CBS-4, 9 kJ/mol for CBS-q, 5 kJ/mol for CBS-Q, and 8 kJ/mol for G2MP2. Occasionally, these procedures are described as “model chemistries”. For the DFT calculations, the BLYP[24,25] and B3LYP[26,27] functionals were used. The quantum chemically derived cartesian force constant matrix was then read into the program GAMESS[28] which was employed to compute normal modes, force constants of internal coordinates, total energy distributions in order to assign the normal vibrations,[29,30] and frequencies of isotopically labeled compounds. IR spectra from the results of the Gaussian 94 calculations have been generated with the program G92ToSpec.[31]

Results and Discussion

Geometries and Energetics. Four isomer of ethyl nitrite can be expected with cis and trans configurations with respect to the O−N and C−O bonds. Energy optimization by means of the semiempirical AM1 method reveals the four isomers depicted in Figure 1.

A potential energy surface with respect to the two dihedral angles $\tau_{O=N-O-C}$ and $\tau_{N-O-C-C}$ calculated at the HF/6-31G** level of theory is presented in Figure 2. In agreement with the semiempirical calculations, energy minima are found for combinations of $\tau_{O=N-O-C}$ and $\tau_{N-O-C-C}$ of (0,180) (cis−trans), (0,90) (cis−gauche), (180,90) (trans−gauche), and (180,180) (trans−trans). A more detailed presentation of the trans−trans minimum is given in Figure 3a. At this level of theory, a very small barrier for a trans−trans → trans−gauche isomerization of only about 1.1 kJ/mol is calculated. The existence of four rotamers, however, disagrees with experimental findings of only three conformers in microwave investigations[13] and only two species by IR spectroscopy[3,14] or in NMR investigations.[11,12] Upon inclusion of correlation effects at the MP2 level, the minima for the conformations cis−gauche, cis−trans, and trans−gauche are retained while the trans−trans conformation corresponds to a saddle point as presented in Figure 3b.

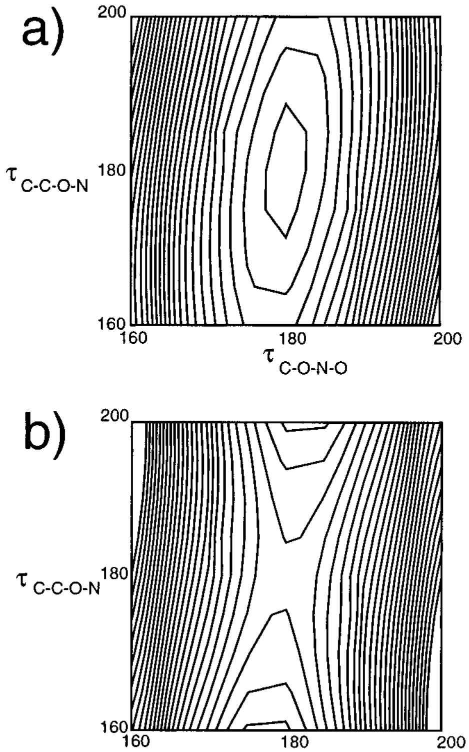

Figure 3. Contour plots of the PES of the 180°/180° region. (a) A local energy minimum is predicted at the HF/6-31G** level. (b) A transition state is predicted at the MP2/6-31G** level.

Consideration of correlation effects, thus, reveals only three stable conformers which agrees with the experimental findings.

Geometrical parameters for the stable conformers determined at different levels of theory are depicted in Table 1. We will confine our discussion to the bond lengths of the NO single and double bonds. In agreement with experimental values found in methyl nitrite[32] MP2 and B3LYP calculations predict a longer N=O double bond (∼+0.01 Å) and a shorter N−O single bond (∼−0.02 Å) for the $N-O^{cis}$ isomer compared to the $N-O^{trans}$ isomer. The same result was already predicted in an ab initio SCF study on methyl nitrite.[4] The stabilization of the cis conformer had been attributed to the formation of internal hydrogen bonds between methylene protons and the terminal −N=O group.[4]

Besides small differences in the bond lengths of the C−O, N−O, and N=O bonds of the cis and trans isomers, our calculations predict significantly different force constants for the N=O bonds of the cis and trans isomers. The trans isomer is predicted to have an N=O force constant which is by 0.7−0.8 mdyn/Å larger than those found in the two cis isomers. All these findings are consistent with a resonance model. The validity of the resonance model was, however, questioned by Wiberg and co-workers on the basis of results obtained for formamid and small carbonic acids and their methyl esters.[33,34] On the other hand, recent results of Fogarasi and Szalay on formamide using coupled cluster calculations support the resonance model.[35] The validity of the resonance model, thus, is the topic of ongoing discussions. Such resonance structures would favor the formation of an internal hydrogen bond in the $N-O^{cis}$ conformers and thus give an explanation for the stabilization of this conformer and its experimentally found higher rotational barrier. Evidence for differences in the electron density between the groups $-CH_2$ and O=N− in the different isomers can be drawn from the Mulliken overlap population matrices. At the B3LYP level, this overlap population is

TABLE 1: Optimized Structural Parameters of the Isomers of Ethyl Nitrite[a]

	HF[b]	MP2	B3LYP	exptl[13]
cis−gauche				
r_{O-N}	1.325	1.399	1.401	
$r_{N=O}$	1.163	1.210	1.191	
r_{C-O}	1.432	1.445	1.451	
r_{C-C}	1.518	1.516	1.523	
ONO	115.8	114.8	115.2	
CON	119.3	116.0	117.1	
CONO	0.5	0.1	0.2	
CCON	-82.2	-83.2	-85.7	
μ [D]	2.437	2.250	2.317	2.221
E +282.0	−0.714 491 2	1.535 712 2	−2.332 584 5	
cis−trans				
r_{O-N}	1.323	1.395	1.395	
$r_{N=O}$	1.163	1.211	1.193	
r_{C-O}	1.430	1.447	1.448	
r_{C-C}	1.513	1.511	1.517	
ONO	115.4	114.2	114.5	
CON	118.3	115.2	116.2	
CONO	0.0	0.0	0.0	
CCON	180.0	180.0	180.0	
μ [D]	2.508	2.332	2.425	2.306
E +282.0	−0.716 323 4	−1.536 278 9	−2.333 454 4	
trans−gauche				
r_{O-N}	1.337	1.419	1.422	
$r_{N=O}$	1.157	1.200	1.181	
r_{C-O}	1.424	1.445	1.442	
r_{C-C}	1.516	1.513	1.521	
ONO	111.7	110.6	110.9	
CON	111.9	109.0	110.4	
CONO	178.1	177.7	178.7	
CCON	-87.6	-102.9	-108.4	
μ [D]	3.164	2.487	2.627	2.50
E +282.0	−0.714 461 2	−1.533 695 6	−2.331 834 8	
trans−trans				
r_{O-N}	1.337			
$r_{N=O}$	1.157			
r_{C-O}	1.424			
r_{C-C}	1.513			
ONO	111.6			
CON	111.7			
CONO	180.1			
CCON	179.0			
μ [D]	3.170			
E +282.0	−0.714 375 3			

[a] Bond lengths are in angstroms, bond angles and dihedral angles in degrees, energies in atomic units, and dipole moments in debyes. [b] HF = Hartree−Fock.

approximately zero in the case of the trans−gauche isomer but sums up to 0.02 and 0.026 in the case of cis−trans and cis−gauche isomer, respectively.

From microwave spectroscopy results it was concluded that the trans−gauche and cis−gauche conformations are 970 ± 240 and 2860 ± 600 J/mol above the cis−trans conformation, respectively.[13] True and co-workers[12,36] determined ΔH^0 and ΔS^0 for the cis ⇌ trans isomerization of various nitrites. They showed that in the case of ethyl nitrite, the enthalpy favors the cis isomer, but that the entropic term $-T\Delta S^0$ favors the trans isomer and causes it to predominate at room temperature. This is completely consistent with the calculations at the CBS-Q and G2MP2 levels (see Table 2), where total energy and enthalpy favor the cis−trans conformer while the free enthalpy at 298 K favors the trans−gauche conformer. The theoretical values for the entropy S^0 at 298 K are 309 J/mol T for the cis−trans and 316 J/mol T for the trans−gauche isomer at the CBS-Q level. At the G2MP2 level the corresponding values are 311 and 317 J/mol T.

On the MP2 potential energy surface three different cis−trans isomerization reactions are possible. The cis−gauche → cis−trans and cis−gauche → trans−gauche isomerizations correspond to simple rotation around either the C−O or the N−O bonds, respectively. The corresponding torsional barriers determined at the MP2 level are 7.6 and 53.3 kJ/mol. The third possible isomerization corresponds to the reaction cis−trans → trans−gauche and is associated with a simultaneous rotation around the C−O and N−O bonds. The barrier for this reaction at the same level of theory has been calculated to 52.3 kJ/mol. Structural parameters and energies of these three transition states are listed in Table 3. Only very small effects on the C−O, N−O, and N═O bond lengths are found during a rotation around the C−O bond. Rotation around the N−O bond, however, causes an elongation of the N−O single bond of about 0.01−0.02 Å and a shortening of the N═O double bond of ca. 0.02 Å. Originally present mesomeric structures which strengthen the N−O bond and thus cause a high barrier for a rotation around the N−O bond are weakened during such a rotation.

Two clearly different rotational barriers of approximately 8 and 0.8 kJ/mol for a rotation of the methyl group had however been found in cis and trans methyl nitrite, respectively.[37] These findings suggest that the rotational barriers around the C−O bond need some further investigations.

Microwave spectra of ethyl nitrite also allowed the investigation of several isomerization reactions which all involve rotations around the C−O bond.[13] Barriers between 16.8 and 50.4 and of 9.6 ± 2.9 kJ/mol had been assigned to the isomerizations cis−gauche → cis−gauche and cis−trans → cis−gauche, respectively, and 1.7 ± 0.1 and 3.1 ± 16.8 kJ/mol for transitions trans−gauche → trans−gauche with either a trans−trans or a trans−cis transition state.[13] In agreement with the findings in methyl nitrite, a higher torsional barrier has generally been found in conformers having a cis conformation with respect to the N−O bond.

Our calculated barrier of 7.6 kJ/mol (MP2−level) for the cis−trans → cis−gauche isomerization agrees well with the corresponding experimental values of methyl nitrite and ethyl nitrite. For the cis−gauche → cis−gauche isomerization a barrier of 43.0 kJ/mol is calculated assuming a "cis−cis" transition state. Again, the calculated barrier is very close with the experimental estimate. In the case of the trans isomer (trans−gauche → trans−gauche), the agreement with experimental data is less satisfactory. Barriers of 4.1 and 15.8 kJ/mol are calculated at the MP2 level for transition states of "trans−trans" and "trans−cis" structure, respectively, which are clearly higher than the experimental estimates.

In methyl nitrite MP2 calculations predict torsional barriers of 8.6 and 2.3 kJ/mol for a rotation of the methyl group in the cis and trans conformer, respectively. These results parallel our findings in the case of ethyl nitrite where we also find a very good agrement with experimental data in the case of the barrier of the cis isomer while that of the trans conformer is considerably overestimated. The calculation, however, correctly predicts a smaller barrier for the trans than for the cis conformer.

Relative energies of stable conformations and of transition states at the MP2 level are listed in Table 4. Diagonal elements denote the relative energies of the stable conformations and nondiagonal elements represent the energy of the transition state for the indicated isomerization. The cis−trans conformer is predicted to be more stable than the cis−gauche and trans−gauche isomers.

We have also determined theoretical estimates for the dissociation energies for the process $CH_3CH_2ONO \rightarrow CH_3$-$CH_2O^\bullet$ ($X^2\Sigma$) + $NO^\bullet$ ($X^2\Pi$). Both radicals are in their doublet ground state. Experimental dissociation energies are within the range of 12 250 to 16 375 cm^{-1} [38,39] with a most recent value

TABLE 2: Thermodynamical Analysis[a]

	E	H^0	G^0	S^0	ΔH^0_{diss}	ΔG^0_{diss}	ΔS^0_{diss}
			CBS-4				
NO	−129.746 018	−129.745 074	−129.768 604	207			
EtO	−154.126 258	−154.125 314	−154.156 981	279			
cis−gauche	−283.946 860	−283.945 916	−283.981 113	310	−198	−146	−174
cis−trans	−283.947 575	−283.946 631	−283.982 185	313	−200	−149	−171
trans−gauche	−283.948 983	−283.948 039	−283.984 386	320	−204	−154	−168
			CBS-q				
NO	−129.775 088	−129.774 144	−129.797 674	207			
EtO	−154.150 958	−154.150 014	−154.181 681	279			
cis−gauche	−283.993 430	−283.992 485	−284.027 682	310	−179	−127	−174
cis−trans	−283.993 834	−283.992 889	−284.028 446	313	−180	−129	−171
trans−gauche	−283.995 346	−283.994 402	−284.030 749	320	−184	−135	−164
			CBS−Q				
NO	−129.744 655	−129.743 711	−129.766 956	205			
EtO	−154.096 927	−154.095 983	−154.126 776	271			
cis−gauche	−283.910 588	−283.909 644	−283.944 639	308	−184	−134	−168
cis−trans	−283.911 413	−283.910 469	−283.945 585	309	−186	−136	−168
trans−gauche	−283.910 940	−283.909 996	−283.945 894	316	−185	−137	−161
			G2MP2				
NO	−129.733 860	−129.732 916	−129.756 174	205			
EtO	−154.087 241	−154.086 297	−154.117 321	273			
cis−gauche	−283.891 828	−283.890 883	−283.926 031	310	−188	−138	−168
cis−trans	−283.892 708	−283.891 763	−283.927 025	311	−190	−140	−168
trans−gauche	−283.892 143	−283.891 199	−283.927 225	317	−189	−141	−161

[a] Absolute values of energy, enthalpy and free enthalpy are given in hartrees. Absolute entropies are given in J/mol T. Relative values were calculated for the dissociation EtONO → $NO^\bullet$ + $EtO^\bullet$ with respect to the double ground states of NO($X^2\Pi$) and EtO ($X^2\Sigma$) at 298 K. The units of the relative values are kJ/mol for ΔH^0_{diss} and ΔG^0_{diss} and J/mol T for ΔS^0_{diss}. ΔH^0_{diss} corresponds to the dissociation enthalpy.

TABLE 3: Optimized Transition State Structures for Rational Isomerizations[a]

	MP2	B3LYP
	cis−trans → cis−gauche	
E	−283.533 577	−284.331 481 6
$r_{(N=O)}$	1.205	1.188
$r_{(O-N)}$	1.414	1.411
$r_{(C-O)}$	1.447	1.449
C−O−N=O	−1.62	−1.53
C−C−O−N	−124.18	−123.49
	trans−gauche → cis−gauche	
E	−283.513 404	−284.309 584 0
$r_{(N=O)}$	1.191	1.175
$r_{(O-N)}$	1.494	1.472
$r_{(C-O)}$	1.446	1.445
C−O−N=O	−81.72	−83.61
C−C−O−N	87.34	85.13
	trans−gauche → cis−trans	
E	−283.513 772 7	−284.309 938 6
$r_{(N=O)}$	1.188	1.173
$r_{(O-N)}$	1.507	1.486
$r_{(C-O)}$	1.439	1.439
C−O−N=C	−91.31	−90.53
C−C−O−N	−72.22	−72.77

[a] Bond lengths are in angstroms, bond angles and dihedral angles in degrees, and energies in atomic units.

TABLE 4: Energy Diagram of Stable Conformers and of Transition States Calculated at the MP2 Level[a]

	cis− gauche^{I}	cis− gauche^{II}	cis− trans	trans− gauche^{I}	trans− gauche^{II}
cis−gauche^{I} →	169				
cis−gauche^{II} →	3577	169			
cis−trans →	637	637	0		
trans−gauche^{I} →	5064	5064	4983	611	
trans−gauche^{II} →	5064	5064	4983	339	611

[a] Energies are given in cm^{-1}.

of 14 800 cm^{-1}.[40,41] Calculated dissociation enthalpies are depicted in Table 2. The calculated dissociation enthalpies of the most stable isomer (cis−trans) are 16 700, 15 085, 15 500, and 15 900 cm^{-1} for CBS-4, CBS-q, CBS-Q, and G2MP2, respectively. Thus, a satisfactory agreement between the more recent experimental data and all calculations is found, favoring a dissociation energy of (185 ± 10) kJ/mol for the N−O bond. The error estimate is thus consistent with the reported accuracy of the used methods.

Vibrations. An IR spectrum of EtONO in an argon matrix is depicted in Figure 4.[15] Due to the existence of three rotamers, the spectrum is very complex and a complete assignment of the vibrational frequencies is most likely not possible without additional experimental data. Selected calculated frequencies together with an approximate assignment based on the total energy distribution are listed in Tables 5, 6, and 7.

In contrast to previous studies,[3,14] the matrix spectrum clearly shows the three N=O stretching modes of the three stable conformers of ethyl nitrite. In agreement with previous assignments, calculations at the BLYP, B3LYP, and MP2 level predict the N=O stretching mode of the trans−gauche isomer to be found at higher energy than the other two N=O stretching modes. All three calculations predict the same sequence for the three N=O modes, namely, $\nu^{N=O}_{trans-gauche} > \nu^{N=O}_{cis-gauche} > \nu^{N=O}_{cis-trans}$. We assign therefore the modes at 1659, 1609, and 1594 cm^{-1} to the conformers trans−gauche, cis−gauche, and cis−trans, respectively. The small energy difference between the N=O modes of the cis−gauche and cis−trans conformers (5 cm^{-1} in an argon matrix) makes clear that a good resolution is needed in order to resolve the two absorptions. In solution or solid IR spectra, the two bands can most likely not be resolved.

Absorptions at ∼800 cm^{-1} and at 617 and 565 cm^{-1} had been assigned to ν^{trans}_{N-O} and to the ONO bending mode of the cis and trans conformer, respectively, by Tarte.[3] A similar assignment is also found in the work of Klaboe et al.[14] who assigned absorptions at 813 and 771 cm^{-1} to the N−O stretching modes ν^{trans}_{N-O} and ν^{cis}_{N-O}, respectively, and bands at 625 and 582 cm^{-1} to the ONO bending modes of cis and trans EtONO, respectively.

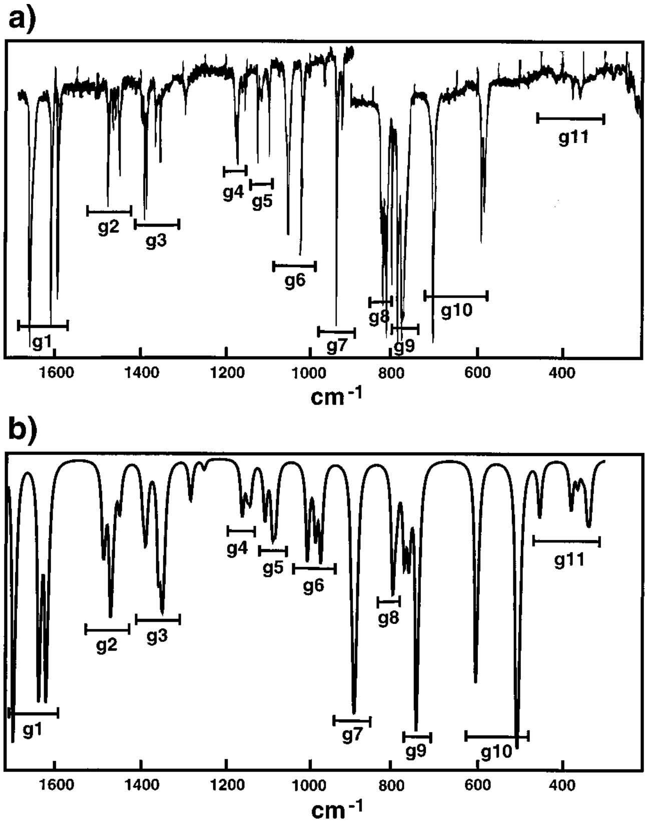

Figure 4. (a) IR spectrum of ethyl nitrite in an argon matrix. (b) Simulated IR spectrum on the basis of the BLYP calculation and assuming a 1:1:1 mixture of the three conformers.

TABLE 5: Calculated IR Frequencies and Total Energy Distribution of Selected Frequencies of the cis−gauche Conformer[a]

ν	intensity	TED[b]
		B3LYP
1701	(147)	95% N=O
1116	(11)	22% C−C + CH bending
1022	(69)	43% C−C + 40% C−O
956	(107)	42% ONO
818	(6)	42% C−O
810	(34)	21% N−O + CH bending + CH torsion
664	(109)	62% N−O
476	(5)	47% OCC
377	(3)	54% NOC
		BLYP
1633	(168)	95% N=O
1078	(10)	21% C−C + 14% OCC + CH bending
970	(29)	57% C−C + 31% C−O
886	(64)	38% ONO + 20% C−O
790	(3)	24% C−O + CH bending + CH torsion
761	(27)	28% ONO + 18% C−O
501	(137)	72% N−O
453	(10)	50% OCC
352	(0)	48% CON
		MP2
1586	(74)	81% N=O
1152	(8)	29% C−C + CH bending
1070	(94)	46% C−O + 32% C−C
979	(134)	33% ONO + 21% C−C + 13% N−O
837	(5)	30% C−O + 13% ONO + CH bending + CH torsion
825	(59)	25% N−O + 14% C−O
681	(124)	55% N−O + 14% ONO + 12% NOC
483	(5)	47% OCC
390	(3)	52% CON

[a] Frequencies are in cm^{-1} and intensities (in brackets) in km/mol. [b] TED = total energy distribution.

According to our calculations at the BLYP, B3LYP, and MP2 levels, modes below 1000 cm^{-1} are strongly mixed and occasionally no clear assignments are possible. The strong mode mixing can also cause isotopic shifts to be distributed among several modes. In contrast to earlier assignments, the BLYP calculations predict ONO bending modes at higher frequencies than N−O stretching modes in all three conformers. N−O stretching modes are predicted between 500 and 600 cm^{-1}, while modes with strong ONO bending character are usually found above 700 cm^{-1}. The same energetic sequence is also predicted by the B3LYP and MP2 methods. The two cis conformations cis−gauche and cis−trans exhibit a dominant ONO bending character in modes at 886 and 890 cm^{-1}, while in the case of the trans−gauche conformer, the dominant ONO bending character is found at lower energy in the mode at 741 cm^{-1}. In the cis conformers, significant ONO bending character is also found in modes at 761 cm^{-1} (cis−gauche) and 772 cm^{-1} (cis−trans).

Klaboe et al.[14] have furthermore assigned absorptions at 1044 and 1006 cm^{-1} to the C−O stretching mode of the cis and trans conformers, respectively. According to the BLYP calculations, C−O, C−C, and ONO modes are strongly mixed which makes a clear assignment of such modes difficult. Strong C−O stretching character is found in vibrations at 970, 886, 790, and 761 cm^{-1} for the cis−gauche conformer; at 983, 890, and 772 cm^{-1} for the cis−trans conformer; and at 1002, 897, and 741 cm^{-1} for the trans−gauche conformer.

A somewhat smaller degree of mode mixing is predicted by the B3LYP calculations. Here, dominant C−O stretching character is found in modes at 1022 and 818 cm^{-1} (cis−gauche), 1029 and 826 cm^{-1} (cis−trans), and 1065 and 853 cm^{-1} (trans−gauche). The mode at higher energy is nearly a 1:1 C−O/C−C mixture, while the mode at lower energy has clearly dominant C−O character, except in the case of the trans−gauche conformer.

Despite the discussed problems with an unambiguous mode assignment, comparison of a simulated spectrum, based on frequencies and intensities calculated with the BLYP method and under the assumption of a 1:1:1 mixture of the three conformers, with the experimental spectrum (Figure 4) suggests that at least *groups* of experimental frequencies can be assigned. We have defined 11 groups which are qualitatively assigned as follows: The frequencies contained in group g1 can clearly be attributed to the N=O stretching modes of the three stable conformers. The frequencies of g2 are predominant torsional modes of the methyl and methylen protons. HCC bending modes of the methyl and methylen groups are the predominant contributions of the modes belonging to group g3. HCC bending modes are also contributing predominantly to the modes of group g4. The modes contained in g5 are combinations of C−C stretch and OCC bending modes with significant contributions of HCC bending modes. The absorptions belonging to group g6 are combinations of C−C and C−O stretching vibrations. The strong band of group g7 is made up by all three conformers and contains mainly C−O stretching and ONO bending character. Only the trans−gauche conformer is predicted to contain also a considerable contribution of the C−C stretching mode in this spectral region. Bending modes of the CH_3 group and torsional modes of the CH_2 group are found in group g8 while g9 consists of combinations of C−O and N−O stretching and ONO bending modes. The two modes of group g10 clearly correspond to the N−O stretching mode of the cis−

trans (601 cm^{-1}) and cis−gauche and trans−gauche (∼500 cm^{-1}) conformers. Finally, OCC and CON bending modes are found in group g11.

TABLE 6: Calculated IR Frequencies and Total Energy Distribution of Selected Frequencies of the cis−trans Conformer[a]

ν	intensity	TED[b]
		B3LYP
1694	(158)	96% N=O
1146	(12)	18% C−C + 17% OCC + CH bending
1029	(34)	58% C−C + 30% C−O
960	(134)	37% ONO + 12% N−O
826	(53)	40% C−O + 21% N−O
753	(121)	50% N−O + 15% C−O
374	(1)	48% OCC + 18% N−O + 13% ONO + 12% CON
254	(1)	59% CON + 31% OCC
		BLYP
1616	(170)	96% N=O
1103	(11)	19% C−C + 15% OCC + CH bending
983	(14)	62% C−C + 22% C−O
890	(63)	34% ONO + 24% C−O
772	(23)	39% ONO + 38% C−O
601	(165)	58% N−O
335	(7)	41% OCC + 11% ONO
232	(1)	61% CON
		MP2
1580	(47)	61% N=O
1564	(50)	33% N=O
1177	(10)	22% C−C + 16% OCC + CH bending
1075	(57)	49% C−C + 37% C−O
984	(164)	25% ONO + 15% N−O + 11% C−C
842	(92)	35% C−O + 26% NO + 19% ONO
769	(126)	43% N−O + 22% ONO + 11% C−O
385	(1)	46% OCC + 17% N−O
266	(1)	58% CON + 32% OCC

[a] Frequencies are in cm^{-1} and intensities (in brackets) in km/mol. [b] TED = total energy distribution.

TABLE 7: Calculated IR Frequencies and Total Energy Distribution of Selected Frequencies of the trans-gauche Conformer[a]

ν	intensity	TED[b]
		B3LYP
1768	(231)	95% N=O
1124	(17)	13% C−C + 11% CO + CH bending
1065	(41)	45% C−O + 42% C−C
940	(28)	30% C−C + 22% ONO
853	(304)	33% N−O + 22% C−O + 11% ONO
601	(40)	48% N−O + 26% ONO
404	(2)	63% OCC + 11% CON
372	(5)	57% CON + 13% ONO
		BLYP
1693	(266)	95% N=O
1085	(11)	16% C−C + 12% OCC + CH bending
1002	(31)	44% C−C + 42% C−O
897	(15)	25% C−C + 21% ONO + 12% C−O
741	(231)	30% ONO + 27% C−O + 17% N−O
506	(78)	57% N−O + 16% ONO
379	(8)	50% OCC + 20% N−O + 14% CON
341	(6)	50% CON + 13% ONO
		MP2
1631	(121)	93% N=O
1154	(10)	24% C−C + CH bending
1101	(61)	52% C−O + 33% C−C
958	(10)	28% C−O + 19% ONO + 12% C−C
866	(355)	32% N−O + 16% C−O + 14% ONO
807	(123)	11% N−O + 10% ONO
605	(57)	49% N−O + 26% ONO
410	(5)	70% OCC
382	(6)	63% CON

[a] Frequencies are in cm^{-1} and intensities (in brackets) in km/mol. [b] TED = total energy distribution.

Conclusion

We presented a state-of-the-art quantum chemical investigation of the rotamers of ethyl nitrite together with the first IR spectrum that gives clear evidence for the existence of three stable conformers of this molecule.[15] Noncorrelated quantum chemical methods are shown to predict the trans−trans conformation as a stable structure, whereas after taking correlation effects into account by means of MP2 or density functional methods, this structure is predicted to correspond to a transition state. The prediction of three stable conformations agrees both with the findings of the microwave study of Turner[13] as well as with the recorded Ar matrix IR spectrum at 20 K. The energy difference between the N=O modes of the cis−gauche and cis−trans conformers was found to be merely ∼5 cm^{-1}. This explains why in earlier IR spectra, which had been recorded at lower resolution, only two species could be identified. The assignment of the relative stabilities was a topic of interest in the past. Our calculations make clear that this question can also not easily be answered by computational methods. G2MP2 and CBS-Q calculations, however, agree with the thermodynamic data of Conboy et al.[12] in that the cis−trans conformation would be preferred by the enthalpy but that the entropic term $-T\Delta S$ favors the trans−gauche isomer at room temperature.

The IR spectra of all stable rotamers were calculated. A surprisingly strong mixing of the modes was found which makes an interpretation in terms of localized modes not feasible for a great number of observed vibrational frequencies. A simulated IR spectrum using all three rotamers shows a reasonable agreement with recent experimental findings.

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References and Notes

(1) Bongartz, A.; Kames, J.; Welter, F.; Schurath, U. *J. Phys. Chem.* **1991**, *95*, 1076.
(2) Cotting, R.; Huber, J. R. *J. Chem. Phys.* **1996**, *104*, 6208.
(3) Tarte, P. *J. Chem. Phys.* **1952**, *20*, 1570.
(4) Cordell, F. R.; Boggs, J. E.; Skancke, A. *J. Mol. Struct.* **1980**, *64*, 57.
(5) Ghosh, P. N.; Bauder, A.; Günthard, H. H. *Chem. Phys.* **1980**, *53*, 39.
(6) Felder, P.; Ha, T. K.; Dwivedi, A. M.; Günthard, H. H. *Spectrochim. Acta* **1981**, *37A*, 337.
(7) Kades, E.; Rösslein, M.; Huber, J. R. *Chem. Phys. Lett.* **1993**, *209*, 275.
(8) Piette, L. H.; Ray, J. D.; Ogg, R. A. *J. Chem. Phys.* **1957**, *26*, 1341.
(9) Phillips, D. W.; Looney, C. E.; Spaeth, C. P. *J. Mol. Spectrosc.* **1957**, *1*, 35.
(10) Brown, H. W.; Hollis, D. P. *J. Mol. Spectrosc.* **1964**, *13*, 305.
(11) Lazaar, K. I.; Bauer, S. H. *J. Phys. Chem.* **1984**, *88*, 3052.
(12) Conboy, C. B.; Chauvel, J. P.; Moreno, P. O.; True, N. S.; Ott, C. M. *J. Phys. Chem.* **1986**, *90*, 4353.
(13) Turner, P. H. *J. Chem. Soc., Faraday Trans. 2* **1979**, 317.
(14) Klaboe, P.; Jones, D.; Lippincott, E. R. *Spectrochim. Acta* **1967**, *23A*, 2957.
(15) Nonella, M.; Huber, J. R. Unpublished results.
(16) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*, Revision d.2; Gaussian, Inc.: Pittsburgh, PA, 1995.
(17) Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724.
(18) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257.

(19) Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, D. J.; Pople, J. A. *J. Chem. Phys.* **1982**, *77*, 3654.

(20) Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J. Chem. Phys.* **1991**, *94*, 7221.

(21) Curtiss, L. A.; Raghavachari, K.; Pople, J. A. *J. Chem. Phys.* **1993**, *98*, 1293.

(22) Petersson, G. A.; Tensfeldt, T. G.; Montgomery, J. A. *J. Chem. Phys.* **1991**, *94*, 6091.

(23) Petersson, G. A.; Bennett, A.; Tensfeldt, T. G.; Al-Laham, M. A.; Shirley, W. A.; Mantzaris, J. *J. Chem. Phys.* **1988**, *89*, 2193.

(24) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.

(25) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(26) Becke, A. D. *J. Chem. Phys.* **1988**, *98*, 1372.

(27) Becke, A. D. *J. Chem. Phys.* **1988**, *98*, 5648.

(28) Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Jensen, J. H.; Koseki, S.; Gordon, M. S.; Nguyen, K. A.; Windus, T. L.; Elbert, S. T. *QCPE* **1990**, *10*, 52.

(29) Pulay, P.; Török, F. *Acta Chim. Hung.* **1965**, *47*, 273.

(30) Keresztury, G.; Jalsovszky, G. *J. Mol. Struct.* **1971**, *10*, 304.

(31) Brousseau, J.-L. University of Miami, Program G92ToSpec.

(32) Corkill, M. J.; Cox, A. P.; Turner, P. H. *Proceedings of the 7th Austin Symposium on Molecular Structure*, Austin, TX, 1978.

(33) Wiberg, K. B.; Laidik, K. E. *J. Am. Chem. Soc.* **1987**, *109*, 5953.

(34) Wiberg, K. B.; Breneman, C. M. *J. Am. Chem. Soc.* **1992**, *114*, 831.

(35) Fogarasi, G.; Szalay, P. G. *J. Phys. Chem.* **1997**, *A101*, 1400.

(36) Chauvel, J. P.; True, N. S. *J. Phys. Chem.* **1983**, *87*, 1622.

(37) Gwinn, W. D.; Anderson, R. J.; Stelma, D. *Proceedings of the 2nd Austin Symposium on Molecular Structure*, Austin, TX, 1968.

(38) Gray, P.; Williams, A. *Chem. Rev.* **1959**, *59*, 239.

(39) Williams, J. M.; Hamill, W. H. *J. Chem. Phys.* **1968**, *49*, 4467.

(40) Batt, L.; Christie, K.; Milne, R. T.; Summers, A. J. *Int. J. Chem. Kinet.* **1974**, *6*, 877.

(41) Heicklen, J. P. *Adv. Photochem.* **1988**, *14*, 177.