Proc. R. Soc. Lond. A **381**, 443–455 (1982)
Printed in Great Britain

Quantum chemical computations on rotational isomers of hydrogen nitrite and nitritomethane

BY L. FARNELL AND J. F. OGILVIE
Research School of Chemistry, Australian National University,
P.O. Box 4, *Canberra, A.C.T.* 2600, *Australia*

(*Communicated by D. P. Craig, F.R.S. – Received* 18 *November* 1981)

Ab initio molecular-orbital computations with a split-valence 4-31G basis set have been carried out on syn- and antiperiplanar conformers of both HONO and H_3CONO, and on the transition structures in the unimolecular isomerization process. Calculated values of geometric structural and rotational parameters, dipole moments, wavenumbers of vibrational transitions, energies of vertical electronic transitions to both neutral and ionized excited states, and thermodynamic properties are compared with experimental data; generally good agreement is found. No explanation of the anomalous stability of antiperiplanar HONO has been discovered.

1. INTRODUCTION

Hydrogen nitrite and nitritomethane are two compounds of which the relatively simple molecules exhibit rotational isomerism. For both molecules, synperiplanar (s.p.) and antiperiplanar (a.p.) conformers have been well characterized by means of various spectroscopic methods. For this reason they provide sensitive tests of the ability of quantum chemical computations to reflect the relatively small differences of properties between rotamers. Moreover these molecules present a rather puzzling phenomenon (Ogilvie & Hasan 1981): although s.p. H_3CONO is more stable than a.p. H_3CONO, a.p. HONO is more stable than s.p. HONO. This observation cannot easily be attributed to any of the following: steric repulsions, hydrogen bonding, dipole–dipole interactions, electronic repulsion, or other attractive interactions. In the present work we attempt to explore this problem.

Several previous calculations on HONO have been reported (Schwartz *et al.* 1970; Radom *et al.* 1971; Skaarup & Boggs 1976; Benioff *et al.* 1976; Dargelos *et al.* 1977). These calculations differ according to the basis sets, number of configurations in the wavefunction, and degree of geometry optimization. The Hartree–Fock model, with use of a single determinantal wavefunction, is known (Payne & Allen 1977) to be adequate to reproduce potential energy functions for internal rotation; furthermore, although minimal basis sets are generally inadequate to give quantitative agreement with properties determined accurately from experiment, improvement of the basis set may not yield a monotonic improvement in these energy functions, for instance. The best agreement with the experimental value for the energy difference between a.p. HONO and s.p. HONO was obtained by Radom *et al.* (1971) using a 4–31G basis set and standard geometries. This basis set has been used in the present work, but molecular structures have been optimized. HONO has been reexamined to ensure that the same level of approximation is applied to all conformers of both HONO and H_3CONO. A computational study by Cordell *et al.* (1980) using a 4–21G basis set was directed at the rotational barriers in H_3CONO conformers.

Since completion of our computations, papers by Günthard & coworkers (Felder *et al.* 1981; Ghosh & Günthard 1981; Ha *et al.* 1981) have appeared that provide both theoretical and experimental results on nitritomethane, including a potential energy surface related to the internal rotational motion, thermodynamic properties and vibrational spectra. These results complement and extend previously available data, both published and unpublished (J. F. Ogilvie), and will be discussed in the appropriate sections.

After a summary of the computational method, we present results for comparison with various experimental data from spectroscopy of the free molecules, in order of increasing transition energies. Finally we address the problem of the apparently anomalous rotameric energies.

2. METHOD OF COMPUTATION

We have performed calculations using a modified (L. Farnell & R. Nobes, unpublished) version of the GAUSSIAN 80 system of computer programs (Pople *et al.* 1981). We used the split-valence 4-31G basis set (Ditchfield *et al.* 1971) throughout. Closed-shell computations were done in the usual fashion (Roothaan 1951), but open-shell calculations were made by the restricted Hartree–Fock method of Guest & Saunders (1974). We obtained by either of two methods the geometric parameters of structures, within the Born–Oppenheimer (1927) separation of nuclear and electronic motions, corresponding to stationary points on the potential energy hypersurface: the relative minima of energy were located by a quasi-Newton optimization (Poppinger 1975*a*), but saddle points (with one negative eigenvalue of the matrix of second derivatives) were found by minimization of the gradient norm (Poppinger 1975*b*). Both a.p. and s.p. conformers of each of HONO and H_3CONO were optimized under constraint of C_s symmetry: depending on the orientation of the methyl group in H_3CONO (eclipsed or staggered with respect to the terminal NO group), this constraint leads to either a true (relative) minimum of energy or the structure at the top of the energy barrier for rotation of the methyl group. The saddle points representing the barrier to interconversion of s.p. and a.p. conformers were located without symmetry constraint. We investigated the shape of the curve of potential energy for rotation of the nitrito group by fixing the torsional angle θ (defined so that $\theta = 0$ for the s.p. conformer) and then by interpolating other structural parameters between the optimized values at the stationary points. In addition, for HONO we made a full optimization of structure at each value of θ; because the energies thus differed insignificantly from those for the interpolated structures, the corresponding much more extensive computations for H_3CONO were omitted (see Ha *et al.* 1981). The energy values were fitted exactly by an expansion of the form

$$E(\theta) = \sum_{n=0}^{6} a_n \cos(n\theta).$$

(Terms of the form sin $(n\theta)$ vanish by symmetry.)

We computed wavenumbers of vibrational transitions by standard methods (Wilson *et al.* 1955), using second derivatives of the energy (with respect to Cartesian displacement coordinates) calculated by numerical differentiation of analytic first derivatives using a step length of 0.015 bohr radius (7.9×10^{-13} m).

3. RESULTS

3.1. *Geometrical structure*

We present in tables 1 and 2 the structural parameters (internuclear separations and angles between internuclear vectors) for s.p. and a.p. conformers of HONO and H_3CONO, compared with such experimental information as is available (Finnegan *et al.* 1972; Turner *et al.* 1979). Results are also given for structures at the saddle points. Following previous usage (Benioff *et al.* 1976) we apply the term 'gauche' structure to that corresponding to the energy maximum in the H–O–N–O or C–O–N–O torsional coordinate, although this torsional angle is nearer $\frac{1}{2}\pi$ than $\frac{1}{3}\pi$ rad. We call 'eclipsed' the structure at the point of maximum energy in the potential energy of H–C–O–N torsion.

TABLE 1. CALCULATED AND EXPERIMENTAL STRUCTURES OF HONO

(Bond lengths/10^{10} m, and bond and dihedral angles/rad; experimental data from Finnegan *et al.* (1972).)

	synperiplanar			antiperiplanar	
	calc.	exp.†	*gauche* calc.	calc.	exp.‡
H–O	0.965	0.982	0.960	0.954	0.954
O–N	1.378	1.392	1.450	1.400	1.433
N=O	1.177	1.185	1.163	1.167	1.163
H–O–N	1.948	1.815	1.930	1.883	1.782
O–N–O	1.988	1.983	1.951	1.944	1.932
θ	0	0	1.494	π	π

† Substitution structure. ‡ Equilibrium structure.

Because of the effect of zero-point vibration in the actual quantum state of minimum energy, the equilibrium structure of a molecule (defined within the Born–Oppenheimer approximation) is not directly determined by experiment. An extrapolation procedure in the analysis for a.p. HONO (Finnegan *et al.* 1972) has enabled an experimental estimate of the equilibrium structure. In the other cases, a substitution structure has been deduced from spectra of isotopic molecules. The primary quantities derived from rotational analyses, whether for pure rotational transitions in the microwave region or for rotational transitions accompanying vibrational or electronic transitions, are the rotational parameters; these are formally related through the Born–Oppenheimer separation to reciprocals of moments of inertia with respect to the principal inertial axes of a molecule. The calculated rotational parameters, applicable to equilibrium structures, are compared to available experimental quantities for all four rotamers, in table 3.

Table 2. Calculated and experimental (substitution) structures of H_3CONO

(Bond lengths/10^{-10} m, bond angles and dihedral angles (θ and τ)/rad; experimental data from Turner *et al.* (1979).)

(*a*) *Staggered methyl group*

	synperiplanar			antiperiplanar	
	calc.	exp.	*gauche* calc.	calc.	exp.
H–C	1.073	1.09	1.074	1.074	—
H′–C	1.077	1.10	1.079	1.078	—
C–O	1.455	1.437	1.453	1.442	1.436
O–N	1.367	1.398	1.432	1.388	1.415
N=O	1.181	1.182	1.168	1.171	1.164
H–C–O	1.812	1.777	1.827	1.831	—
C–O–N	2.075	2.002	1.981	1.965	1.918
H′–C–O	1.925	1.918	1.923	1.923	—
O–N–O	2.009	2.004	1.953	1.950	1.951
θ	0	0	1.503	π	π
τ(HCON)	π	π	3.098	π	—
τ(H′CON)	± 1.063	± 1.035	1.114, 1.026	± 1.066	—

(*b*) *Eclipsed methyl group*

	synperiplanar	antiperiplanar
H–C	1.075	1.079
H′–C	1.075	1.076
C–O	1.458	1.443
O–N	1.373	1.386
N=O	1.179	1.170
H–C–O	1.941	1.915
H′–C–O	1.859	1.881
C–O–N	2.119	1.979
O–N–O	2.026	1.953
θ	0	π
τ(HCON)	0	0
τ(H′CON)	± 1.031	± 1.042

3.2. *Dipole moments*

Another quantity that may be derived from rotational transitions is the electric dipole moment. Both in microwave spectroscopy and also recently by means of laser sources in vibration–rotational spectroscopy, use of the Stark effect allows the determination of the magnitudes of the components of electric dipole moment parallel to the principal inertial axes. The computed quantities, with signs related to the directions of axes in figures 1 and 2, are presented with experimental data in table 4. Again the computed values pertain to equilibrium structures (presented in tables 1 and 2), whereas the experimental values pertain to structures vibrationally and rotationally averaged in quantum states.

3.3. *Vibrational spectra*

Wavenumbers of transitions from the ground vibrational level to various singly excited vibrational states may in general be determined spectroscopically by means of infrared absorption and Raman scattering, although obtaining Raman spectra of the compounds here considered has proved problematical (Klaboe *et al.* 1967). Available data from experiment are presented in table 5 together with the computed wavenumbers. Because we used the harmonic approximation in the computation, we do not expect exact agreement with experiment: it might seem preferable to compare force field coefficients, but the unambiguous derivation of these from

TABLE 3. ROTATIONAL PARAMETERS/10^9 Hz

	synperiplanar		antiperiplanar	
	calc.	exp.	calc.	exp.
		$^1H^{16}O^{14}N^{16}O$		
A	85.993	84.1018†	97.941	93.6834‡
B	13.316	13.1690†	12.783	12.6345‡
C	11.530	11.3643†	11.307	11.1339‡
		$^1H_3{}^{12}C^{16}O^{14}N^{16}O$§		
A	21.077	20.27238	50.828	49.4277
B	7.223	7.43781	4.948	4.95337
C	5.566	5.63058	4.639	4.62732

† Substitution structure from Finnegan *et al.* (1972).
‡ Equilibrium structure from Finnegan *et al.* (1972).
§ Experimental data from Turner *et al.* (1979).

TABLE 4. DIPOLE MOMENTS, $\mu/(10^{-30}\,\mathrm{C\ m})$

	synperiplanar		antiperiplanar	
	calc.	exp.	calc.	exp.
		HONO†		
μ_A	−1.693	1.0244	−7.054	4.6129
μ_B	+5.749	4.6509	+6.095	4.4924
μ_C	0	0	0	0
μ	5.990	4.7623	9.318	6.4391
		H_3CONO‡		
μ_A	−7.834	5.5322	−10.839	7.2717
μ_B	+4.780	4.0028	+4.293	2.9687
μ_C	0	0	0	0
μ	9.173	6.8284	11.675	7.8543

† Experimental data from Allegrini *et al.* (1980).
‡ Experimental data from Gwinn *et al.* (1968).

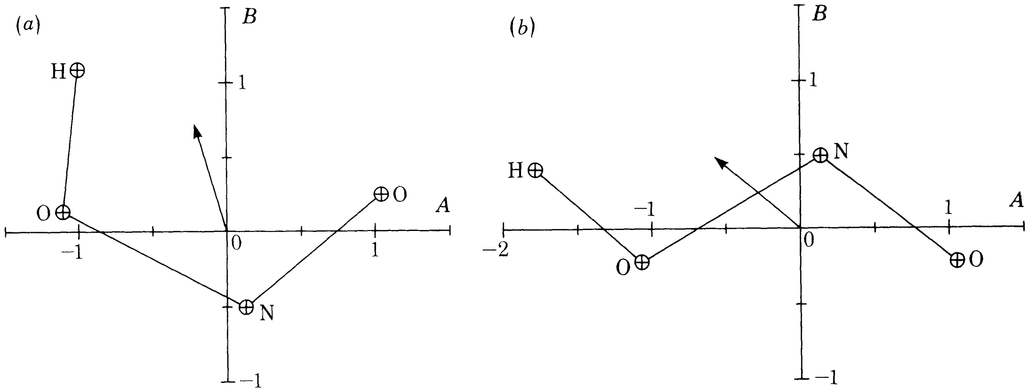

Figure 1. Computed structures of (*a*) synperiplanar HONO and (*b*) antiperiplanar HONO. Scale: 1 division represents 5×10^{-11} m. The arrow indicates the direction of the dipole moment.

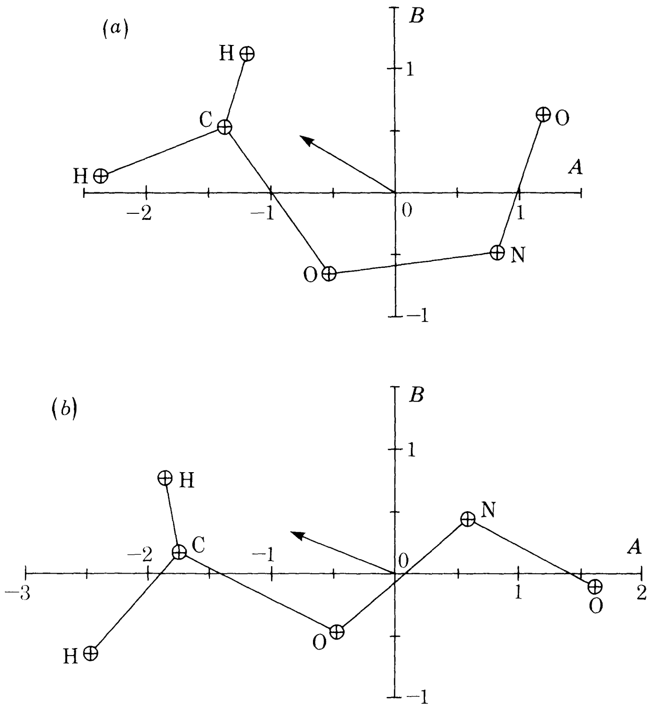

Figure 2. Computed structures of (*a*) synperiplanar H_3CONO and (*b*) antiperiplanar H_3CONO. Scales: 1 division represents 5×10^{-11} m. The arrow indicates the direction of the dipole moment.

TABLE 5. WAVENUMBERS OF VIBRATIONAL TRANSITIONS/10^2 m^{-1}

	synperiplanar		antiperiplanar		s.p. – a.p.	
HONO†	calc.	exp.	calc.	exp.	calc.	exp.
A′ ν_1	3818.5	3424	3987.9	3588	–169.4	–164
ν_2	1825.7	1640	1890.5	1699	–64.8	–59
ν_3	1458.0	1261	1415.3	1265	42.7	4
ν_4	953.8	853	900.7	791	53.1	62
ν_5	703.1	608	721.9	593	–18.8	15
A″ ν_6	669.9	638	552.8	540	117.1	98
H_3CONO‡						
A′ ν_1	3374.0	3038	3358.1	2921	15.9	117
ν_2	3242.4	2956	3230.5	2829	11.9	127
ν_3	1781.2	1620	1863.4	1677.5	–82.2	–57.5
ν_4	1657.9	1458.5	1663.9	1463	–6.0	–4.5
ν_5	1607.3	1410	1618.8	1429	–11.5	–19
ν_6	1304.7	1240	1309.1	1190	–4.4	50
ν_7	1104.0	990.5	1142.4	1046	–38.4	–55.5
ν_8	896.5	841	915.5	812.2	–19.0	28.8
ν_9	802.5	628	673.3	564.2	129.2	63.8
ν_{10}	357.4	346.2	359.9	379	–2.5	–32.8
A″ ν_{11}	3330.2	2993	3314.1	2887	16.1	106
ν_{12}	1648.5	1444.7	1653.7	1451.2	–5.2	–6.5
ν_{13}	1275.3	1003.5	1284.5	1031	–9.2	–27.5
ν_{14}	341.9	(260)§	192.4	(185)	149.5	(75)
ν_{15}	200.4	(153)	70.5	—	129.9	—

† Experimental data from McGraw *et al.* (1966).

† Experimental data from Ghosh & Günthard (1981).

§ Values in parentheses are indirectly determined from combination bands.

experiment is indeed problematical for even these molecules of only moderate complexity.

3.4. *Electronic spectra*

Some electronic transitions have been observed for HONO and H_3CONO, both in the ultraviolet region (transitions to electronically excited states of the neutral molecules) and by means of the photoelectric effect (ionization to the cation), the latter for only H_3CONO. We may estimate the ionization energies by using the theorem of Koopmans (1933). For excitation energies, an analogous approximation (Richards & Horsley 1970) produces the following relations:

$$E_{\text{triplet}} - E_{\text{ground}} = \epsilon_{\text{b}} - \epsilon_{\text{a}} - J_{\text{ba}};$$

$$E_{\text{singlet}} - E_{\text{ground}} = \epsilon_{\text{b}} - \epsilon_{\text{a}} - J_{\text{ba}} + 2K_{\text{ba}}.$$

Here we consider transitions from a closed-shell ground state to states with the electronic configurations designated by single occupancy of virtual orbitals b in the excited state as a result of promotion of one electron from the doubly occupied orbital a. J, K and ϵ are coulomb integrals, exchange integrals and s.c.f. eigenvalues respectively. Results are presented in tables 6 and 7. The electronic transitions of the neutral molecules are assigned to be to states with configurations involving

TABLE 6. PHOTON ENERGIES/10^{19} J FOR ELECTRONIC TRANSITIONS AND PHOTOIONIZATION OF HONO

transition	synperiplanar		antiperiplanar	
	calc.	exp.	calc.	exp.
$^3A'' \leftarrow {}^1A'$	3.92	—	4.11	—
$^1A'' \leftarrow {}^1A'$	5.90	5.2284†	6.03	5.1716†
electron ionized				
10a′	21.05	—	20.09	—
2a″	23.53	—	23.12	—
9a′	26.39	—	27.15	—
1a″	30.81	—	30.35	—
8a′	32.77	—	31.56	—
7a′	34.22	—	34.85	—

† Data from King & Moule (1962) for the adiabatic transition.

TABLE 7. PHOTON ENERGIES/10^{-19} J FOR ELECTRONIC TRANSITIONS AND PHOTOIONIZATION OF H_3CONO

	synperiplanar		antiperiplanar	
transition	calc.	exp.	calc.	exp.
$^3A'' \leftarrow {}^1A'$	4.43	—	4.54	—
$^1A'' \leftarrow {}^1A'$	6.41	5.457†‡	6.29	5.093†‡
$^3A' \leftarrow {}^1A'$	10.68	—	10.73	—
$^1A' \leftarrow {}^1A'$	16.30	9.69†§	15.76	7.79†§

electron ionized	s.p. calc.	exp.‖	a.p. calc.
13a′	20.14	17.51	19.35
3a″	21.55	18.83	21.04
12a′	23.74	21.47	24.72
2a″	26.76	23.39	26.97
11a′	26.83	24.51	26.50
1a″	31.23	26.92	30.88
10a′	31.63	—	31.57
9a′	33.36	—	32.61

† Data of J. F. Ogilvie, unpublished.

‡ Adiabatic transition.

§ Apparent vertical transition (overlapping broad lines).

‖ Data from Ogilvie (1975).

promotion of electrons from either of the two occupied orbitals of greatest energy to the unoccupied orbital of least energy.

3.5. *Thermodynamic properties*

In table 8 we present the computed energies that define the torsional potential energy function, and the relative energies in table 9. In these tables appear also the results of computations for the cations at the geometries optimized for the neutral molecules. The results of Fourier analysis of these energy data are given in table 10 with the corresponding coefficients derived from experimental data (Ogilvie & Hasan 1981).

TABLE 8. CALCULATED ENERGIES/hartree FOR HONO, H_3CONO AND THEIR CATIONS AS A FUNCTION OF TORSIONAL ANGLE/rad

(1 hartree = 4.3598×10^{-18} J.)

θ	HONO†	HONO‡	$HONO^+$§	H_3CONO†	H_3CONO‖	H_3CONO^+§
0	−204.31089	−204.31089	−203.89186	−243.28245	−243.27942	−242.89199
$\pi/6$	−204.30648	−204.30654	—	−243.27737	—	—
$\pi/3$	−204.29904	−204.29910	—	−243.26989	—	—
1.492	−204.29649	−204.29649	−203.88322	—	—	—
1.503	—	—	—	−243.26750	—	−242.87980
$2\pi/3$	−204.30084	−204.30089	—	−243.27103	—	—
$5\pi/6$	−204.30821	−204.30825	—	−243.27746	—	—
π	−204.31191	−204.31191	−203.90819	−243.28078	−243.28054	−242.90193

† S.p., a.p. and *gauche* geometries optimized; remainder interpolated.
‡ All geometries optimized.
§ Geometries used optimized for neutral species.
‖ Optimized with methyl group eclipsed.

TABLE 9. RELATIVE ENERGIES/10^{-21} J OF CONFORMERS OF HONO AND H_3CONO

	HONO		$HONO^+$	H_3CONO		H_3CONO^+
	calc.	exp.	calc.	calc.	exp.	calc.
synperiplanar	4.45	2.585†	71.20	0	0	43.34
antiperiplanar	0	0	0	7.28	9.73‡	0
gauche	67.23	60.37§	108.86	65.18	73.00‖	96.48
eclipsed s.p.	—	—	—	13.21	14.53‖	
eclipsed a.p.	—	—	—	8.33	9.75‖	

† Data from Varma & Curl (1976).
‡ Data from Felder *et al.* (1981).
§ Data from Hall & Pimentel (1963).
‖ Data from Turner *et al.* (1979).

TABLE 10. COEFFICIENTS/10^{-21} J IN EXPANSIONS OF TORSIONAL POTENTIAL ENERGY FUNCTIONS AS A COSINE SERIES

	calculated		
HONO	interpolated	optimized	experimental†
a_0	35.70	35.55	30.8
a_1	4.04	4.02	1.29
a_2	−32.43	−32.08	−29.5
a_3	−1.94	−1.93	—
a_4	−1.15	−0.98	—
a_5	0.03	0.05	—
a_6	−0.13	−0.15	—

CH_3ONO	calculated	experimental
a_0	36.32	38.1
a_1	−0.52	−3.12
a_2	−30.17	−34.9
a_3	−2.96	—
a_4	−2.14	—
a_5	−0.30	—
a_6	−0.23	—

† Data from Ogilvie & Hasan (1981).

4. Discussion

Our computed structural geometries for HONO rotamers are similar to those of Skaarup & Boggs (1976). By comparison with experiment, the notable defects are overestimation of HON interbond angle and underestimate of the central O–N bond length. In contrast, the computations with minimal basis set by Dargelos *et al.* (1977) produced an underestimation of the ONO angle and a marked overestimation of the N=O separation. There is close agreement between our results for s.p. H_3CONO and those computed by Ha *et al.* (1981) and Cordell *et al.* (1980); the small differences may be attributable to the slightly different basis set, 4–21G. The defects in the computed results on H_3CONO are similar to those for HONO: an underestimated O–N bond length and an overestimated CON interbond angle. However, in all cases the differences between a.p. and s.p. conformers are qualitatively correct. In agreement with Skaarup & Boggs (1976), we find that the most significant geometric changes in the *gauche* structure, the transition structure in the unimolecular isomerization process, are the increase of the O–N bond length and decrease of N=O bond length, for both HONO and H_3CONO; we attribute these effects to decrease of π-electron delocalization in the *gauche* structure, as indicated by the eigenvector coefficients.

Computed rotational parameters, reflecting the accuracy of the structures, are in good agreement with the experimental quantities. The components of electric dipole moment are qualitatively in agreement with experiment, but are 25–65 % too large: this feature is a common result of use of Hartree–Fock (uncorrelated) wavefunctions (Bader 1975).

The computed wavenumbers for fundamental vibrational transitions are almost all too large, and are rather more in error for HONO than previous results (Skaarup & Boggs 1976). Wavenumbers greater than about $8 \times 10^4\,m^{-1}$ are overestimated by about 12 %, as expected from other computations (Pulay 1977); the errors in the smaller wavenumbers are less consistent. Differences between a.p. and s.p. conformers are mostly qualitatively correct: exceptions are the ν_5 vibration of HONO and the ν_1, ν_2, ν_6, ν_8 and ν_{11} vibrations of H_3CONO. These vibrations are an ONO in-plane deformation in HONO, CH_3 stretching (ν_1 ν_2, ν_{11}), CH_3 deformation (ν_6) and a delocalized skeletal deformation (ν_8). Significant differences in the wavenumbers of torsional modes of H_3CONO were predicted, the smaller wavenumbers belonging to the a.p. conformer; these results, qualitatively reflecting the very recent experimental data (Ghosh & Günthard 1981), are consistent with the relatively small torsional barrier in the a.p. conformer.

Photon energies for electronic transitions and ionizations are all too large, as we expect from use of the approximation due to Koopmans (Richards 1969). The differences between the transition energies of the two conformers of H_3CONO are qualitatively correct, but the relatively smaller difference for s.p. and a.p. HONO is not reproduced. We predict differences in ionization energies between conformers of less than $10^{-19}\,J$; such small differences make observation difficult because linewidths are of comparable magnitude. The published photoelectron spectrum of H_3CONO was associated (Bergmann & Bock 1975) with the a.p. conformer although the s.p. conformer is proved to be the more abundant (Ghosh *et al.* 1980); both that spectrum and other (Ogilvie 1975) consist of broad lines. Incorporation of a methyl group into a molecule to replace a hydrogen atom is commonly associated with increased breadth of the less energetic lines in the photoelectron spectrum (Turner *et al.* 1970); thus the predicted slightly greater separation of the first photoelectron energies of the two conformers of HONO, relative to H_3CONO, together with potentially narrower lines, may permit the resolution of lines of the two conformers of HONO, for which no photoelectron spectrum has yet been published.

Magnitudes of the barrier height in the torsional potential energy function of HONO, in this and previous computations (Schwartz *et al.* 1970; Radom *et al.* 1971; Skaarup & Boggs 1976; Benioff *et al.* 1976; Dargelos *et al.* 1977), are all in reasonable agreement with experiment; likewise for H_3CONO (Cordell *et al.* 1980; Ha *et al.* 1981; Felder *et al.* 1981). Unlike some previous reports, we find good agreement also for the s.p.–a.p. energy difference. In particular, the difference in favoured conformer between HONO and H_3CONO is reproduced. We also obtain good agreement for the relative energies of the eclipsed and staggered (pertaining to the methyl group) structures of H_3CONO.

Because some effects in features appearing in microwave spectroscopy have been attributed to the nature of the torsional potential energy function (Gordy & Cook 1970), through the coupling of internal and external rotation, the nature of this function is of interest. We find that the empirical function, having three terms, is of the right form for HONO: the coefficients of higher terms are relatively small. The results for H_3CONO are less satisfactory in that the coefficient of $\cos\theta$ is smaller than the coefficients of $\cos 3\theta$ and $\cos 4\theta$. Felder *et al.* (1981) have concluded that there is strong coupling between the internal rotational motions of the CH_3 and NO groups in both conformers.

Computations for the cations indicate that loss of an electron associated with the occupied orbital of greatest energy substantially favours the a.p. conformer of both HONO and H_3CONO. We therefore examined the form of this orbital. In the neutral species its description as N=O orbital antibonding in the plane of molecular symmetry is appropriate, but in the cations this orbital tends to be localized on the terminal oxygen atoms. The most obvious change accompanying ionization occurs for s.p. H_3CONO; in the neutral molecule there is significant electronic density on the carbon atom, thus forming a bonding combination with the terminal oxygen atom, according to our computations. In the s.p. H_3CONO^+ cation and all other conformers, neutral or cationic, this orbital does not extend to the carbon atom (or hydrogen in HONO species). By localizing the molecular orbitals, Cordell *et al.* (1980) have studied in some detail the non-bonded interactions between the terminal atoms in H_3CONO; these authors regard the attractive interactions as an explanation of the difference in torsional barriers between methyl groups of the a.p. and s.p. H_3CONO conformers, and, in agreement with our results, also as a rationalization of the fact that the s.p. conformer is the more stable. Our computations fail to reveal any features that obviously lead to a.p. HONO being the more stable conformer; indeed computed charge densities of the two structures of the HONO conformers are very similar, so that electrostatic effects would favour the s.p. conformer.

5. Conclusions

We have compared our results of quantum chemical computations with experimentally derived data from spectra over a broad range of photon energies. We found good agreement for structural parameters but less good agreement for dipole moments and transition energies. The computations nevertheless reproduce well the small differences between the synperiplanar and antiperiplanar conformers of hydrogen nitrite and nitritomethane, with qualitative agreement in almost all cases. In particular, remarkable accuracy of energy differences between conformers, and also barriers to internal rotation, has been achieved, despite the relatively modest level of the basis sets. Perhaps this extent of agreement is fortuitous in the sense that use of increasingly more sophisticated basis sets may not yield monotonically increasing accuracy, but we believe that our results are characteristic of the extent of success that such computations can currently attain.

With regard to the anomalous stability of a.p. HONO, we can discover no obvious features of the wavefunction capable of explaining this observation.

References

Allegrini, M., Johns, J. W. C., McKellar, A. R. W. & Pinson, P. 1980 *J. molec. Spectrosc.* **79**, 446.
Bader, R. F. W. 1975 In *International review of science, physical chemistry*, vol. 1 (ed. A. D. Buckingham & C. A. Coulson). London: Butterworth.
Benioff, P., Das, G. & Wahl, A. C. 1976 *J. chem. Phys.* **64**, 710.
Bergmann, H. & Bock, H. 1975 *Z. Naturf.* **30**b, 629.
Born, M. & Oppenheimer, J. R. 1927 *Annls Phys.* **84**, 457.
Cordell, F. R., Boggs, J. E. & Skancke, A. 1980 *J. molec. Struct.* **64**, 57.
Dargelos, A., El Ouadi, S., Liotard, D., Chaillet, M. & Elguero, J. 1977 *Chem. Phys. Lett.* **51**, 545.
Ditchfield, R., Hehre, W. J. & Pople, J. A. 1971 *J. chem. Phys.* **54**, 724.
Felder, P., Ha, T. K., Dwivedi, A. M. & Günthard, H. H. 1981 *Spectrochim. Acta* A **37**, 337.
Finnegan, D. J., Cox, A. P., Brittain, A. H. & Smith, J. G. 1972 *J. chem. Soc. Faraday Trans.* II, **68**, 548.
Ghosh, P. N., Bauder, A. & Günthard, H. H. 1980 *Chem. Phys.* **53**, 39.
Ghosh, P. N. & Günthard, H. H. 1981 *Spectrochim. Acta* A **37**, 347.
Gordy, W. & Cook, R. L. 1970 *Microwave molecular spectra*. New York: Wiley.
Guest, M. F. & Saunders, V. R. 1974 *Molec. Phys.* **28**, 819.
Gwinn, W. D., Anderson, R. J. & Stelman, D. 1968 *Bull. Am. phys. Soc.* **13**, 831.
Ha, T. K., Meyer, R., Ghosh, P. N., Bauder, A. & Günthard, H. H. 1981 *Chem. Phys. Lett.* **81**, 610.
Hall, R. D. & Pimentel, G. C. 1963 *J. chem. Phys.* **38**, 1889.
King, G. W. & Moule, D. 1962 *Can. J. Chem.* **40**, 2057.
Klaboe, P., Jones, D. & Lippincott, E. R. 1967 *Spectrochim. Acta* A **23**, 2957.
Koopmans, T. 1933 *Physica, 's Grav.* **1**, 104.

McGraw, G. E., Bernitt, D. L. & Hisatsune, I. C. 1966 *J. chem. Phys.* **45**, 1392.

Ogilvie, J. F. 1973 *J. chem. Soc. chem. Commun.* 450.

Ogilvie, J. F. 1975 Paper presented to North American Chemical Congress, Mexico City.

Ogilvie, J. F. & Hasan, M. H. A. 1981 *J. molec. Struct.* **75**, 255.

Payne, P. W. & Allen, L. C. 1977 In *Applications of electronic structure theory* (ed. H. F. Schaefer). New York: Plenum Press.

Pople, J. A. *et al.* 1981 *Quantum Chem. Program Exchange* **13**, 406.

Poppinger, D. 1975*a* *Chem. Phys. Lett.* **34**, 332.

Poppinger, D. 1975*b* *Chem. Phys. Lett.* **35**, 550.

Pulay, P. 1977 In *Applications of electronic structure theory* (ed H. F. Schaefer). New York: Plenum Press.

Radom, L., Hehre, W. J. & Pople, J. A. 1971 *J. Am. chem. Soc.* **93**, 289.

Richards, W. G. 1969 *Int. J. Mass Spectrom. Ion Phys.* **2**, 419.

Richards, W. G. & Horsley, J. A. 1970 *Ab initio molecular orbital calculations for chemists*, ch. 6. Oxford: Clarendon Press.

Roothaan, C. C. J. 1951 *Rev. mod. Phys.* **23**, 69.

Schwartz, M. E., Hayes, E. F. & Rothenberg, S. 1970 *Theor. chim. Acta* **19**, 98.

Skaarup, S. & Boggs, J. E. 1976 *J. molec. Struct.* **30**, 389.

Turner, D. W., Baker, C., Baker, A. D. & Brundle, C. R. 1970 *Molecular photoelectron spectra*. London: Wiley.

Turner, P. H., Corkill, M. J. & Cox, A. P. 1979 *J. phys. Chem.* **83**, 1473.

Varma, R. & Curl, R. F. 1976 *J. phys. Chem.* **80**, 402.

Wilson, E. B., Decius, J. C. & Cross, P. C. 1955 *Molecular vibrations*. New York: McGraw-Hill.