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STRUCTURES AND DIPOLE MOMENTS OF NON-IONIC NITRITE ROTAMERS

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ABSTRACT

Results related to the geometric structures and dipole moments of hydrogen nitrite, HONO, and nitritomethane, H_3CONO, are presented. A novel procedure for constructing dipole moments for polynuclear molecules from vector sums of contributions from dinuclear fragments has been devised to include an explicit separation dependence; its validity is discussed.

INTRODUCTION

Simple molecules that exist in different conformations invite continuing investigation of details of molecular structure arising from intramolecular interactions. In this respect, rotational isomers are of particular interest, because the same molecular topology applies to conformations that have distinct spectroscopic properties, although the ease of interconversion (relatively small energy barriers between conformers) precludes isolation of separate rotamers under usual conditions [1, 2]. The non-ionic nitrites RONO are an especially convenient instance of such characteristics because they are readily prepared and observed by means of spectroscopic measurements throughout the range of transition energies from NMR in the radiofrequency region [3] to ionisation processes in photoelectron experiments [4].

Some features of molecular structure of these nitrites that have attracted attention in past experiments have been geometrical structure, dipole moments, and energy differences between rotamers, although the first and last of these three aspects are really details of the general potential-energy hypersurface within the Born—Oppenheimer approximation. Possibly the two simplest covalent nitrites for which abundant experimental data are now available are hydrogen nitrite, HONO, and nitritomethane, H_3CONO. In each case, both cisoid and transoid rotamers have been characterised to some extent by microwave spectroscopy, in addition to other studies, so that their geometrical structures, dipole moments and relative energies have been

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estimated within moderate experimental uncertainties. For HONO, the transoid rotamer is the more stable, by (2.585 ± 0.14) × 10^{-21} J [5], whereas for H_3CONO the cisoid rotamer is the more stable, by (6.24 ± 0.43) × 10^{-21} J [6]. The former case is exceptional, especially in regard to the latter, because in other known cases of relative stability of rotational isomers the rotamer having the smaller dipole moment is the more stable, unless what is often called a steric factor is operative. Thus, cisoid nitritomethane is the more stable; the energy difference is less for the rotamers of nitritoethane, whereas for 2-nitritopropane the transoid rotamer is definitely the more stable, and in the case of 2-methyl-2-nitritopropane the cisoid rotamer is scarcely observable [7]. The steric effect of the progressively more bulky alkyl moiety from methyl to 2-methylpropyl groups is thus seen to act in opposition to the electrostatic influence, so that the less polar rotamer can become in these cases also the less stable. For this reason, the greater stability of transoid HONO, having a dipole moment of 6.439 × 10^{-30} C m [8], relative to cisoid HONO, of dipole moment 4.762 × 10^{-30} C m [8], is indeed remarkable, for it can be easily attributed to none of steric repulsions, hydrogen bonding, dipole—dipole interactions, electronic repulsions nor other attractive interactions [9]. The difference in zero-point energy is only 5.2 × 10^{-22} J, estimated from spectroscopic data [10], so this effect does not account for the amount of 2.585 × 10^{-21} J [5].

In this paper we present some results related to the geometric structures and dipole moments of hydrogen nitrite and nitritomethane. These molecules are used as tests of methods of estimating these properties of other molecules for which data may be less abundant.

GEOMETRIC STRUCTURES

If we define θ as the torsional angle between the internuclear vectors connecting, on the one hand, nitrogen and terminal oxygen nuclei, and, on the other hand, central oxygen and hydrogen nuclei, along the axis of the central O—N internuclear vector, then the potential-energy function for rotation about this axis may be expected to have the form [11]

$$V(\theta)/\mathrm{J} = 1.29 \times 10^{-21}\ [2 - (1 - \cos\theta) + 22.9\,(1 - \cos 2\theta)]$$

with the energy difference between rotamers [5] and barrier [12] taken from experimental data. For nitritomethane, the corresponding function is

$$V(\theta)/\mathrm{J} = 3.12 \times 10^{-21}\ [(1 - \cos\theta) + 11.2\,(1 - \cos 2\theta)]$$

with the appropriate energy difference [13] and barrier [3]. In both cases the angle $\theta = 0$ corresponds to the cisoid rotamer. These functions are shown in Fig. 1.

The geometric structural parameters of hydrogen nitrite rotamers have been known for some years [8], whereas only recently have structural parameters been derived for the nitritomethane rotamers. Two sets of param-

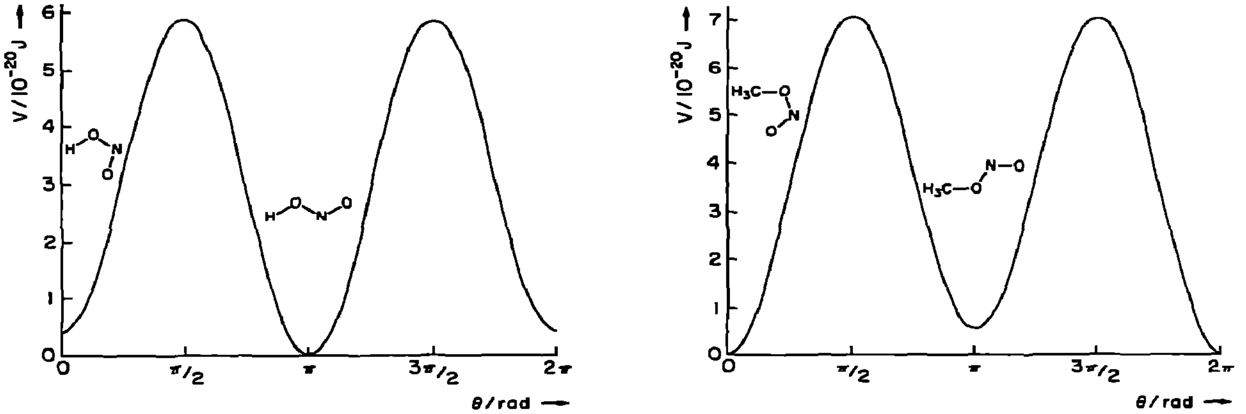

Fig. 1. Torsional potential-energy functions of (a) hydrogen nitrite, and (b) nitritomethane.

eters, one [14] from an incomplete set of isotopic molecules and the other [13] from a complete set, are available for the cisoid rotamer, whereas for the transoid rotamer only an incomplete structure is available [13]. For several years prior to the latter results, sets of rotational parameters for both rotamers, but only for ${}^{1}H_3{}^{12}C{}^{16}O{}^{14}N{}^{16}O$, had been available [15]. On the basis of these six rotational parameters, it was in fact possible [16] to make a quantitative estimate of the structure. If the methyl group is assumed to be trigonally symmetric about the internuclear axis containing the carbon and adjacent oxygen nuclei, then there still remain seven independent structural parameters to define the nuclear positions: these were taken to be four internuclear separations and three angles between internuclear vectors with a common vertex. Furthermore, the CH internuclear separations were fixed to an average value defined by means of the fundamental vibration wavenumbers near $3 \times 10^5\ \mathrm{m^{-1}}$ [1] and a spectra–structure correlation [17]. Then the remaining structural parameters were systematically varied in order to produce an objective minimum of the function r, an agreement index

$$r = 10^3\left[\left(\frac{A' - A}{A}\right)^2 + \left(\frac{B' - B}{B}\right)^2 + \left(\frac{C' - C}{C}\right)^2\right]^{1/2}$$

in which A', B' and C' are rotational parameters calculated from the trial geometry on a rigid-rotor basis and A, B and C are the experimental values [15]. Together with the structural parameters of hydrogen nitrite, the results are given in Table 1, in comparison with other structures [13, 14].

DIPOLE MOMENTS

The early microwave experiments [8, 15] established not only rotational parameters of HONO and H_3CONO but also the dipole moments μ (and components μ_a and μ_b parallel to the A and B inertial axes) for each rotamer. For nitritomethane, there was considerable discrepancy between these directly determined dipole moments μ and those derived indirectly by means

TABLE 1

Some structural parameters of nitritomethane and hydrogen nitrite rotamers[a]
(Units: R, 10^{-12} m; α, rad; ν, 10^2 m^{-1})

Nitritomethane	Cisoid			Transoid	
	b	c	d	b	d
R_{CH}	110	108.6*	109.8*	109.5	
R_{CO}	143	143	143.7	141.2	143.6
R_{ON}	142	141.5	139.8	142.5	141.5
R_{NO}	116.2	118.5	118.2	114.6	116.4
α_{HCO}	1.9714	1.8925*	1.8710*	1.9188	
α_{CON}	1.833	1.9897	2.0019	1.9234	1.9181
α_{ONO}	2.2026	2.0106	2.0036	2.0141	1.9513
ν_{CO}	985			1040	
ν_{ON}	837			806	
ν_{NO}	1611			1663	
Hydrogen nitrite	**Cisoid**			**Transoid**	
	e			e	
R_{HO}	98.2			95.8	
R_{ON}	139.2			143.2	
R_{NO}	118.5			117.0	
α_{HON}	1.8151			1.7823	
α_{ONO}	1.9818			1.9324	
ν_{HO}	3424			3588	
ν_{ON}	853			791	
ν_{NO}	1640			1699	

[a] Values marked with an asterisk are average values. [b] Internuclear separations and angles from the present work; vibrational wavenumbers from ref. 1. [c] Ref. 14. [d] Ref. 13. [e] Internuclear separations and angles from ref. 8; vibrational wavenumbers from ref. 10.

of dielectric measurements and the bond-moment hypothesis [18]. Careful consideration of these microwave data might have improved our understanding of the dipolar effects within these rotamers. If any internal contribution within the methyl group is ignored, then the observed values of μ_a, μ_b and μ could be attributed to contributions associated with the four sets of internuclear vectors, H—O or H_3C—O, O—N and N—O. There are, thus, at least three unknown contributions to be determined from the two independent data, μ_a and μ_b, for each rotamer. Furthermore only the magnitudes of these components are known, leading to ambiguity of relative signs. Possibly a reasonable procedure in these circumstances is to combine the data for the two cisoid rotamers, and separately for the two transoid rotamers, under the assumption that the two different corresponding NO contributions within the two cisoid (or transoid) rotamers are sufficiently similar. Even with the further supposition, on the basis of chemical experience, of the relative signs of two components, there is still a quadruple set of solutions for each set of rotamers. For instance, the results showed that the contribution associated with the terminal N—O internuclear vector assumed values from 2.27 to 11.6 ($\times 10^{-30}$ C m) in the sense N^+O^-, to be compared with a value of $+6.35 \times 10^{-30}$ C m used in earlier bond-moment schemes [18, 19]. For OH, the range is even wider, from —8.1 to +5.33 ($\times 10^{-30}$ C m), to be compared with $+5.34 \times 10^{-30}$ C m in H_2O. Whilst the latter values for the cisoid rotamer are sufficiently divergent, those for the transoid rotamer are even worse, —0.1 to 48.0 for OH and —55 to —7.9 (all $\times 10^{-30}$ C m) for the terminal NO. One can conclude that this method of decomposing molecular dipole moments into contributions associated with particular internuclear vectors is entirely unsuccessful.

Recently there has been success in development of dipole moment functions of dinuclear molecules, that express the dependence of instantaneous dipole moment on internuclear separation, over a large range of distance. Such results from hydrogen halides [20] required the combination of experimental data, mostly from vibration—rotation intensities, that applied to internuclear separations near equilibrium, with results of quantum computations for distances corresponding to potential energies near that of dissociation. The possibility arose to test the additivity of contributions to the dipole moment of polynuclear molecules, of known geometric parameters, through the vector sum of distance-dependent contributions of dinuclear fragments. In this case the hydrogen nitrite rotamers proved useful because only two types of adjacent internuclear couples occurred, either HO or NO, but a range of internuclear separations prevailed in the two rotamers (see Table 1).

We require data in order to construct the necessary dipole-moment functions. Because the available experimental data for each of hydroxyl and nitrogen(II) oxide molecules are insufficient, we have had recourse to the results of quantum computations, but their agreement with the (limited) experimental data is an assurance of satisfactory quality.

As previously [20], we have chosen to represent the dipole-moment function of the free dinuclear molecule by a Padé approximant, a ratio of polynomials of which the derivatives at equilibrium separation agree exactly with those of a function fitted numerically, according to standard statistical criteria, to tabulated data sets. For both OH and NO molecules in their $X^2\Pi$ ground states, a function of the form

$$\mu(R) = M_0(x+1)^2(x - x_0)/(-x_0 + \sum_{i=1}^{7} e_i x^i)$$

was devised to meet the following criteria [21]: (a) $\mu(R) = 0$ at $R = 0$ or $x = -1$, where $x = (R - R_e)/R_e$ (R_e is always the equilibrium internuclear separation of the appropriate free molecule); (b) $\mu(R) \to 0$ as R^3 in the limit as $R \to 0$; (c) $\mu(R) \to 0$ as R^{-4} as $R \to \infty$; (d) if the function changes sign within the defined region, then $x = x_0$ at the point where $\mu(R) = 0$; otherwise

$x_0 = -1$; (e) the function must fit adequately the tabulated data, but must have no additional roots or poles. It has been found that a function of the above form successfully meets these criteria in general.

The tabulated data for OH [22] and NO [23] were first fitted to a polynomial, truncated as required, of the form

$$\mu(R) = \sum_{i=0}^{k} M_i x^i$$

where $k = 4$ for OH and $k = 5$ for NO. Then this function was transformed [24] into the Padé form above. As previously [20], additional coefficients e_6 and e_7 were generated by trial to ensure reasonable behaviour at large R, but these values have practically no effect on the properties of $\mu(R)$ in the range of significance for the polynuclear molecules in question. The coefficients of the functions are listed in Table 2, and graphs of the two Padé functions appear in Fig. 2.

With the known geometric structures of the hydrogen nitrite rotamers, we have used the dipole-moment contributions generated from the Padé functions to sum vectorially in order to produce the results in Table 3.

DISCUSSION

With regard to Table 1, we conclude that in these cases it was possible to obtain approximate information about seven structural parameters from only three experimental rotational parameters of each rotamer. Although there are significant differences between our values of internuclear separation, and, more notably, the angles, and the corresponding ones from the

TABLE 2

Coefficients for dipole-moment functions of OH, NO, CO

	OH	NO	CO
$M_0(10^{-30}$ C m)	5.5965 ± 0.011	−0.4921 ± 0.008	−0.40795[a]
$M_1(10^{-30}$ C m)	2.0823 ± 0.043	7.984 ± 0.067	11.808[a]
$M_2(10^{-30}$ C m)	−3.4865 ± 0.14	1.911 ± 0.47	−1.0774[a]
$M_3(10^{-30}$ C m)	−5.9409 ± 0.32	7.279 ± 0.93	−11.875[a]
$M_4(10^{-30}$ C m)	4.191 ± 0.19	25.37 ± 5.3	8.172[a]
$M_5(10^{-30}$ C m)	0	25.18 ± 7.3	0
$R_e(10^{-12}$ m)	97.0161	115.0792	112.8327
x_0	−1	+0.062	+0.0347
e_1	2.6279	−0.12971	−0.07377
e_2	2.6452	−0.14235	−0.07829
e_3	2.7145	−0.34233	−0.06126
e_4	2.6787	−0.38404	−0.11418
e_5	0	−0.47665	0
e_6	3.4185	−2.0343	−0.19731
e_7	3.4	−0.55	−0.07096

[a] Ref. 24.

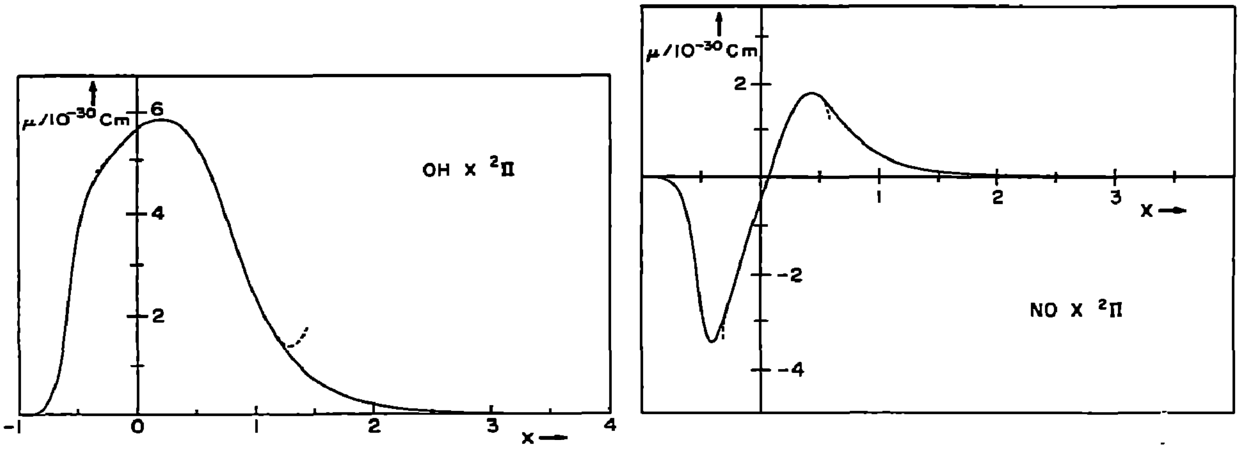

Fig. 2. Dipole-moment functions of (a) hydroxyl molecule, and (b) nitrogen(II) oxide molecule. The full curves represent the Padé functions and the broken curves show the polynomials. On the scale of the diagrams, all the original points lie on the curve where the full and broken lines coincide.

substitution method [13, 14], the latter are more meaningful physically, especially for cisoid nitritomethane from a complete substitution procedure [13]. In each case, the pattern of relative internuclear distances is consistent with the vibrational wavenumbers in the sense that the greater separation corresponds to a smaller transition energy; only the CO separations are remarkably similar, (143.7 and 143.6) × 10^{-12} m, in view of the marked difference of vibrational wavenumbers (98 500 and 104 000 m^{-1}). To attribute such a spectroscopic transition to a particular internuclear vibration is clearly a gross oversimplification, because the kinetic or potential energy associated with that transition is distributed among several vibrational modes, even in an harmonic approximation. Notwithstanding these reservations, the same

TABLE 3

Comparison of calculated and experimental dipole moments of some molecules (10^{-30} C m)

	μ_{calc}	$\lvert\mu_{exp}\rvert$		μ_{calc}	$\lvert\mu_{exp}\rvert$
HONO cisoid			*$HONO_2$*		
μ_a	2.0144	1.0244[a]	μ_a	5.137	6.638[b]
μ_b	4.670	4.6509[a]	μ_b	1.636	2.935[b]
μ_c	0	0	μ_c	0	0
μ	5.087	4.7632[a]	μ	5.834	7.238[b]
HONO transoid			*H_2O*		
μ_a	5.220	4.6129[a]	μ	5.567	6.170[c]
μ_b	3.839	4.4924[a]			
μ_c	0	0	*NO_2*		
μ	6.481	6.4391[a]	μ	1.856	1.054[d]

[a]Ref. 27. [b]Ref. 28. [c]Ref. 29. [d]Ref. 30.

trends in vibrational wavenumbers are observable for hydrogen nitrite rotamers, for which both geometrical [8] and vibrational [10] structures are better established.

To assign error limits (such as standard deviations) to our derived structural parameters of nitritomethane rotamers is difficult; probably the results would still not be meaningful without the accompanying specification of a correlation matrix because of the coefficients near unity therein. Furthermore the criterion of decrease of agreement index r may be illusory; the evidence is that although agreement indices of both rotamers of nitritomethane, 1.1 and 2.7, were much less than those quantities for hydrogen nitrite, 7.2 and 8.3, the latter pertain to a substitution structure compared to rotational parameters of one isotopic species. The discrepancy is readily attributed to the effect of motion associated with zero-point energy states, to which the rotational parameters refer in all cases. For other molecules, it remains possible that a structure of approximate validity might not result from our method, but as the size of molecule increases the practicality of a full substitution procedure rapidly diminishes. Perhaps a more reliable procedure would be to apply the molecular mechanics method [25] with rotational parameters imposed as constraints.

Our procedure of constructing a dipole moment, or its components, for a polynuclear molecule as a vector sum of contributions from nuclear fragments, including explicitly a quantitative dependence on internuclear separation, is believed to be novel. The results in Table 3 for hydrogen nitrite might seem impressive, only the small μ_a of cisoid HONO being estimated particularly poorly, and therefore to augur well for future applications. However, further cases prepared from the same functional dependences prove to be in worse agreement with experimental data; thus the hydrogen nitrate molecule shows only fair agreement, and the result for nitrogen(IV) dioxide is quite poor. Although this new method of estimating contributions to a total dipole moment cannot be expected to make fully reliable predictions, this procedure may nevertheless prove useful as a basis of estimates for some purposes. In this regard, the combination of the present function for the hydroxyl group, $\mu(R_{OH})$, with the function for the carbon oxygen group, $\mu(R_{CO})$ adapted from earlier results [24], also given in Table 2, would, when a similar function for the carbon hydrogen group $\mu(R_{CH})$ becomes available, facilitate estimates of dipole moment for a large group of organic molecules.

The measured dipole moment of a dinuclear molecule must actually be considered to constitute an average value of the dipole-moment function over the amplitude of nuclear oscillation in a particular quantum state, or some distribution thereof depending on the nature of the experiment. Such an averaging procedure is relatively easily applied to a dinuclear molecule; an analogous procedure may even be applied to dinuclear fragments within a polynuclear molecule, if we use the information derived from vibrational spectra. We have in fact investigated such a correction procedure for all the molecules listed in Table 3. In each case, the corrections were relatively small, and in many cases worsened the agreement with experimental results. Probably much more important corrections relate to deformation and torsional vibrations, but the requisite data are much less abundant than for stretching vibrations. Moreover the vibrational wavenumbers, although loosely attributed to a particular motion, are really related to a few modes among which vibrational energy is significantly distributed. Thus a thorough application of the correction procedure would require a knowledge of the molecular force field, preferably in not only the harmonic approximation.

Rather than to attribute the failure of agreement between calculated and experimental dipole moments in Table 3 to these vibrational effects, or to inductive [26] or "mesomeric" effects, we prefer to recognise the fallacy of the so-called additivity principle, according to which properties of molecules may be taken to be the sum of constituent parts. Only for mass is such a procedure quantitatively valid. For any other observable property, such as vibrational transition frequencies, structural parameters and dipole moments, that depend on electronic density about and between the various nuclei in a particular molecule, the fallacy is equivalent to the supposition that electrons do not move easily throughout the space surrounding the nuclei. There may be other assumptions implicit in our attempt to apply the dipole-moment functions of dinuclear molecules in their ground electronic states to similar fragments comprising a polynuclear molecule, but we would expect that none of them would have any particular validity.

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