

Can NO_2^+ exist in bent or cyclic forms?

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Abstract

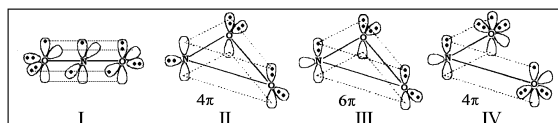
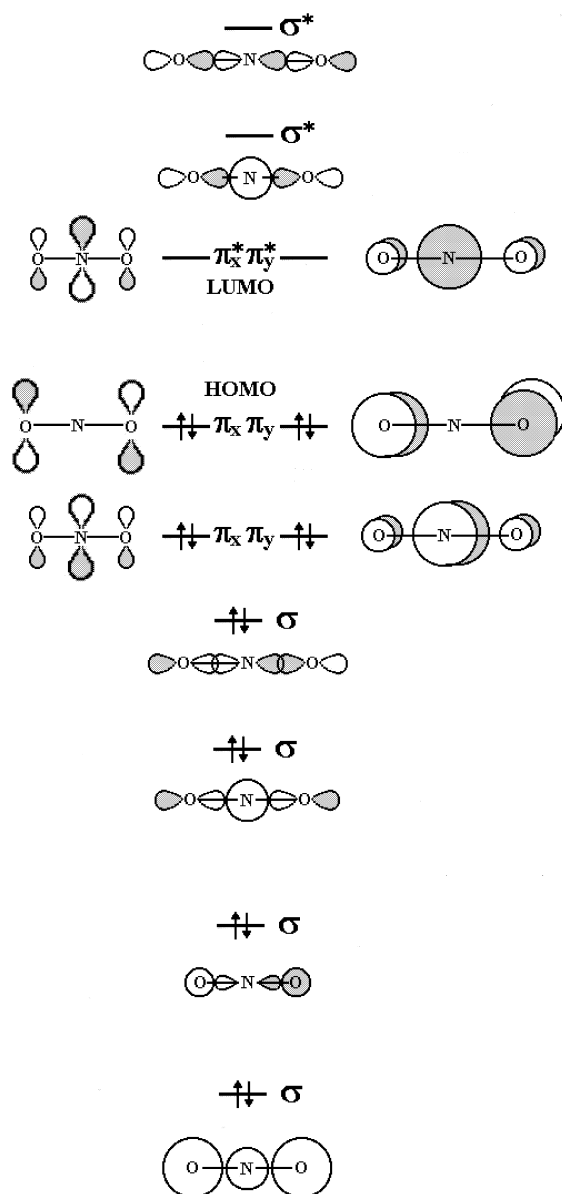
Calculations of NO_2^+ at HF, CBS-4, CASSCF, MBPT(2), MBPT(3), and MBPT(4) theory levels, using 3-21G and 6-31G(d) basis sets, found two C_{2v} structures along with the linear geometry. Computations using MBPT(2) and CCSD(T) approaches and the aug-cc-pvtz basis set confirmed these results. Harmonic vibrational frequency calculations, performed with MBPT(2) and CCSD(T) theories, indicated that the linear structure was the global minimum while one of the bent structures ($\angle\text{ONO} = 80^\circ$) was a higher energy local minimum. The second C_{2v} structure ($\angle\text{ONO} = 45^\circ$) exhibited a large imaginary vibrational frequency along the asymmetric stretching (B_2) mode, indicating its saddle point nature. © 2001 Elsevier Science B.V. All rights reserved.

Based on spectroscopic data, obtained in the middle of the 20th century, NO_2^+ is regarded as a linear molecule [1]. The description of the electronic structure of this linear molecule is straightforward, both in terms of qualitative valence bond theory (structure I in Fig. 1) and in terms of qualitative molecular orbital representations (see Fig. 2). Numerous ab initio computations support [2–16] the linear structure. This, however, does not

exclude the possibility of other isomeric forms. For instance, qualitative valence bond structures can be written for cyclic NO_2^+ involving either 4π (structure II in Fig. 1) or 6π (structure III in Fig. 1) electrons. One can also construct a bent valence bond structure (structure IV in Fig. 1) with four electrons. This suggests that bent or cyclic structures could perhaps exist on the potential energy surface (PES) as local minima. This implication would be particularly significant for understanding reactions where the nitronium ion interacts with nucleophiles, such as in nitration, and where it must go from its initial linear form into a bent one during the reaction process. Such a bending

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Fig. 1. Qualitative valence bond structures of NO_2^+ .Fig. 2. Qualitative molecular orbital description of linear NO_2^+ .

motion, without the presence of a reacting nucleophile, may be regarded as a reference process to which the effect of various nucleophiles may be compared. In addition to this, while bent forms of the isoelectronic CO_2 have been known for quite some time [17], a full study of the NO_2^+ PES has, to our knowledge, not yet been done and hence this paper is presented with the aim to do this.

Spectroscopy [18–25] and reaction kinetics [26–31] of NO_2^+ have been studied previously. However, no optimized bent or cyclic NO_2^+ structure has been reported in the literature, even though on the basis of four single point calculations ($\alpha = 110^\circ$, 100° , 90° and 80° at $r = 1.1205 \text{ \AA}$, where α is the ONO bond angle and r is the NO distance), Hopper has suspected [5] the existence of a high energy cyclic minimum in the vicinity of $\alpha = 90^\circ$.

In order to test this possibility, the potential energy curve, $E = E(\alpha)$, where α is the ONO bond angle, was scanned using ab initio computations, at various levels of approximation. A preliminary scan at the Hartree–Fock (HF) level of theory using a 3-21G basis set yielded three potential energy curves, each of which originated from a totally symmetric wave function (see Fig. 3).

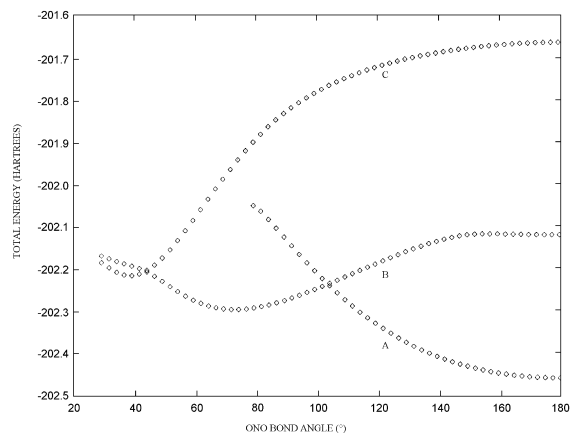


Fig. 3. The crossing of three potential energy curves associated with three different electronic configurations, as computed at the HF/3-21G level of theory. The horizontal axis corresponds to the ONO bond angle (α , in degree); the vertical axis describes the total energy (E , in hartree). The three curves correspond to the following 1A_1 electronic configurations: A: $\dots a_2^2 b_2^0 a_1^0 b_1^0$; B: $\dots a_2^2 b_2^0 a_1^2 b_1^0$; C: $\dots a_2^2 b_2^0 a_1^0 b_1^2$. The C_{2v} symmetry is employed throughout.

Based on the shapes of the curves obtained and based on the ‘non-crossing rule’, it is reasonable to expect that the correlated ground state potential energy curve may have up to three C_{2v} -symmetric minima. These minima should correspond to the linear ($\alpha = 180^\circ$), a higher energy bent ($\alpha > 60^\circ$), and an even higher energy cyclic ($\alpha < 60^\circ$) structures. The same can be seen by analyzing the crossings of the MO energy levels (see Fig. 4). Starting with the three minima, predicted by the HF/3-21G scans, geometry optimizations have been carried out at six levels of the theory: HF, complete active space self-consistent field (CASSCF), second through fourth-orders of the many-body perturbation theory (MBPT(2), MBPT(3), and MBPT(4)), using a standard 631+G(d) basis set, and complete basis set approximation (CBS-4). The results are summarized in Table 1.

Beyond these exploratory computations, an in depth study has been carried out on the linear and C_{2v} structures of NO_2^+ . The calculations were performed using two approaches, the MBPT(2) approach and the coupled cluster approach with single, double, and noniterative perturbative triple excitations (the CCSD(T) method) [32], both with the aug-cc-pvtz basis set [33]. All electrons were correlated in the MBPT(2) calculations, whereas in all CCSD(T) calculations performed

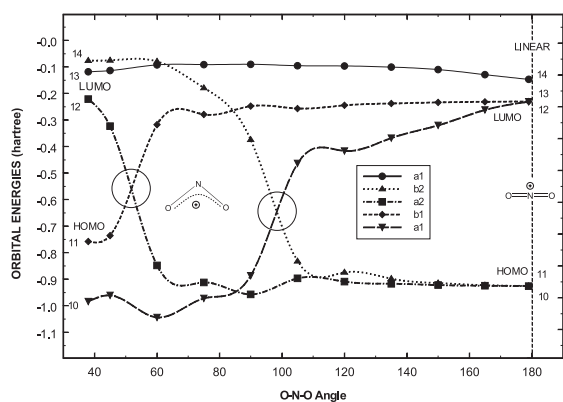


Fig. 4. A Walsh type diagram, illustrating the HOMO/LUMO level crossings as a function of the ONO bond angle (α , in degree) in NO_2^+ . Of the computed MO energy levels, ϵ_i (in hartree), only those with $i = 10, 11, 12, 13$, and 14 are shown.

Table 1
Results^a of exploratory geometry optimizations for NO_2^+ at various levels of theory using a standard 6-31G+(d) basis set

Method	Linear			Bent			Cyclic					
	α	r	E	ΔE	α	r	E	ΔE	α	r	E	ΔE
HF	180.0	1.091	-203.682385	0.0	74.97	1.228	-203.509745	108.33	38.16	1.746	-203.348737	209.37
CAS(4,6)	180.0	1.102	-203.776520	0.0	86.20	1.229	-203.638585	86.56	47.46	1.513	-203.497434	175.13
CAS(8,8)	180.0	1.115	-203.841256	0.0	86.26	1.260	-203.719213	76.85	41.72	1.720	-203.572209	168.83
CBS-4 (0 K)	180.0	1.111	-204.501607	0.0	73.10	1.349	-204.343483	99.22	38.50	1.872	-204.138882	227.61
CBS-4 E			-204.498860	0.0			-204.340525	99.36			-204.135865	227.78
CBS-4 H			-204.497916	0.0			-204.339580	99.35			-204.134921	227.78
CBS-4 G			-204.522341	0.0			-204.366576	97.74			-204.136236	242.28
MP2	180.0	1.157	-204.246347	0.0	82.17	1.282	-204.075301	107.33	47.80	1.629	-203.874875	233.1
MP3			-204.175726	0.0			-204.017788	99.10			-203.833086	215.01
MP4D			-204.211135	0.0			-204.058830	95.57			-203.874167	211.45
MP4DQ	180.0	1.181	-204.191964	0.0	84.39	1.313	-204.033298	99.56	45.06	1.690	-203.857770	209.71
MP4SDQ			-204.216121	0.0			-204.067311	93.38			-203.880686	210.49
MP4SDTQ			-204.275063	0.0			-204.121608	96.29			-203.919135	223.35

^aThe ONO angle (α) in degree, the NO bond length (r) in Å, the total energy (E) in hartree, and the relative energy (ΔE) in kcal/mol.

Table 2
The MBPT(2)/aug-cc-pvtz geometries and harmonic vibrational frequencies

Parameter ^{a,b}	Linear	Bent	Cyclic
r	1.1377	1.2690	1.6104
α	180.0	81.3	46.5
E	-204.46673380	-204.29123176	-204.09150732
ΔE	0.0	110.13	235.46
ν_1	602.2 (Π_u , bend)	759.7 (A_1 , bend)	845.4i (B_2 , asym)
ν_2	1306.7 (Σ_g , sym)	1371.7 (B_2 , asym)	720.3 (A_1 , bend)
ν_3	2536.6 (Σ_u , asym)	1542.5 (A_1 , sym)	1014.4 (A_1 , sym)

^a The NO bond length (r) in Å, the ONO bond angle (α) in degree, the total energy (E) in hartree, the relative energy (ΔE) in kcal/mol, and the harmonic vibrational frequencies (ν_1, ν_2, ν_3) in cm^{-1} .

^b sym = symmetric stretch, asym = asymmetric stretch.

Table 3
The CCSD(T)/aug-cc-pvtz geometries and harmonic vibrational frequencies

Parameter ^{a,b}	Linear ^c	Bent	Cyclic ^d
r	1.1253	1.2739	1.7046
α	180.0	80.0	41.2
E	-204.47063267	-204.31612455	-204.13292431
ΔE	0.0	96.96	211.91
ν_1	626.2 (Π_u , bend)	682.5 (A_1 , bend)	518.4i (B_2 , asym)
ν_2	1382.4 (Σ_g , sym)	748.4 (B_2 , asym)	596.5 (A_1 , bend)
ν_3	2389.9 (Σ_u , asym)	1461.6 (A_1 , sym)	1418.4 (A_1 , sym)

^a The NO bond length (r) in Å, the ONO bond angle (α) in degree, the total energy (E) in hartree, the relative energy (ΔE) in kcal/mol, and the harmonic vibrational frequencies (ν_1, ν_2, ν_3) in cm^{-1} .

^b sym = symmetric stretch, asym = asymmetric stretch.

^c Experimental values from [21,25]: $\nu_1 = 626.90$, $\nu_2 = 1386.84$, $\nu_3 = 2362.0 \text{ cm}^{-1}$.

^d The O–O distance in the cyclic structure of 1.1995 Å is virtually identical to the O–O distance in the isolated O_2 molecule (1.20752 Å).

Table 4
The CCSD(T)/aug-cc-pvtz geometries and harmonic vibrational frequencies of dissociation products N^+ , O_2 , N , O_2^+

Species ^a	E (hartree)	R_g (Å)	ν (cm^{-1})
$\text{N}(^4\text{S})$	-54.51692394	n/a	n/a
$\text{N}(^2\text{D})$ (*)	-54.41750320	n/a	n/a
$\text{N}^+(^3\text{P})$ (*)	-53.98500355	n/a	n/a
$\text{O}_2(^3\Sigma_g^-)$	-150.14102005	1.2132	1574.7
$\text{O}_2^+(^2\Pi_g)$ (*)	-149.69922259	1.1215	1907.0

^a The species denoted with (*) requires a multi-reference description. The expected quality of these data is lower than in the remaining cases.

Table 5
The CCSD(T)/aug-cc-pvtz dissociation energies for the linear NO_2^+ corresponding to the dissociation channels of the $(\text{N} + \text{O}_2)^+$ type

	D_c (kcal/mol)	D_0 (kcal/mol)
$\text{N}(^2\text{D}) + \text{O}_2^+(^2\Pi_g)$	222.08	218.52
$\text{N}^+(^3\text{P}) + \text{O}_2(^3\Sigma_g^-)$	216.25	212.21
$\text{N}(^4\text{S}) + \text{O}_2(^2\Pi_g)$	159.69	156.13

in this study, the core orbitals (three lowest orbitals in NO_2^+ , two lowest orbitals in O_2 and O_2^+ , and the lowest orbital in N and N^+) were kept frozen. The CCSD(T) calculations for the open-shell dissociation products (O_2 , O_2^+ , N , and N^+) were performed using the unrestricted HF (UHF) reference (we tried the restricted open-shell HF (ROHF) reference, too, but the results turned out to be virtually identical). It is necessary to point

out that some of these species are not properly described by a single determinant; the calculations of dissociation energies are therefore only semi-quantitative. The CCSD(T) and MBPT(2) calculations for NO_2^+ (a closed-shell species) used the restricted HF (RHF) reference. All MBPT(2) and CCSD(T) calculations employing the aug-cc-pvtz basis set (geometry optimizations and harmonic frequency calculations) were performed with GAUSSIAN 98 [34] (the MBPT(2) and CCSD(T) calculations) and Aces II [35] (the CCSD(T) calculations). The CCSD(T) analytic gradient capability of Aces II turned out to be very useful and greatly facilitated our optimization efforts.

We characterized three stationary points on a C_{2v} -symmetric PES, referred to as the linear, bent, and cyclic structures. In spite of numerous efforts, we were unable to locate any asymmetric minimum. All our attempts to locate the asymmetric structures failed, giving us the bent, C_{2v} -symmetric structure. We cannot rule out the existence of an asymmetric local minimum, but it is likely that if such a minimum exists, it is very shallow or high lying or has both these features.

The main findings of our calculations are collected in Tables 2 (MBPT(2)/aug-cc-pvtz results) and Table 3 (CCSD(T)/aug-cc-pvtz results). Table 4 lists the CCSD(T)/aug-cc-pvtz results for the dissociation products of the $(\text{N} + \text{O}_2)^+$ type and Table 5 provides information about the energetics of dissociation of the linear NO_2^+ into the spin-allowed $\text{N}(^2\text{D}) + \text{O}_2(^2\Pi_g)$ and $\text{N}^+(^3\text{P}) + \text{O}_2(^3\Sigma_g^-)$ channels and spin-forbidden $\text{N}(^4\text{S}) + \text{O}_2(^2\Pi_g)$ channel.

The harmonic vibrational analysis for the stationary points reveals that while all three structures represent minima within the C_{2v} symmetry, only the linear and bent structures are true local minima. The saddle-point nature of the cyclic structure, observed initially at the MBPT(2)/aug-cc-pvtz level, was confirmed in the subsequent CCSD(T)/aug-cc-pvtz calculations. The cyclic structure is a saddle point dividing two mirror-image C_s valleys representing asymmetric bent NO_2^+ geometries (notice that the imaginary frequency corresponds to asymmetric stretch). Fol-

lowing the coordinate corresponding to the negative eigenvalue of the Hessian leads to the lowering of the symmetry of the C_{2v} structure to C_s . Consequently, both HOMO and LUMO become the a'' orbitals and the path between the cyclic and bent structures, which is forbidden in Woodward–Hoffmann sense when the C_{2v} symmetry is preserved, becomes allowed when the C_{2v} symmetry is broken. Since the cyclic structure seems to represent the $\text{N}^+ \dots \text{O}_2$ configuration, the above described process of going from the cyclic saddle point to the bent minimum structure of NO_2^+ may play a role in the reaction $\text{N}^+ + \text{O}_2 \rightarrow \text{NO}_2^+$.

Both the linear and bent local minima are located below all dissociation channels of the $(\text{N} + \text{O}_2)^+$ type listed in Table 5. Finally, we should note that our CCSD(T) geometries and frequencies of the linear NO_2^+ molecule agree remarkably well with the experimental [24,25] and theoretical [14,16] results reported earlier. Also, our results are similar, although not identical, to the findings of Xantheas et al. [17] on the isoelectronic CO_2 . They found a bent $^1_1(C_{2v})$ local minimum for $\alpha \cong 70^\circ$ and a C_{2v} -symmetric transition state for $\alpha \cong 95^\circ$, the latter dividing the former from the linear minimum. This exploratory work on the bent and cyclic isomers of the otherwise linear triatomics is now being extended to the isoelectronic CO_2 and BO_2^- systems.

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