Ab initio Study of Some $N_3^•$ Radical Properties

R. KLEIN and S. BISKUPIČ*

Department of Physical Chemistry, Faculty of Chemical Technology, Slovak Technical University, CS-812 37 Bratislava

Received 1 June 1992

Ab initio CI-SD study of some electric and magnetic properties of the $N_3^•$ radical in its ground state was carried out in 9*s*5*p*1*d*/4*s*2*p*1*d* basis set for four different molecular geometries. Dependence of isotropic and anisotropic hyperfine coupling constants on the geometry of the species under consideration and also on configuration space was investigated. Possible existence of the nonlinear form of the trinitrogen radical is discussed.

Molecular orbital calculations along with EPR data have been proved to be useful in elucidating of the electronic and geometrical structures of the open shell systems. However, the calculation of hyperfine coupling constants (hfc constants) and spin densities on the *ab initio* level remains a difficult problem [1—4], especially for nitrogen atom [5—9]. There are several known sources of the discrepancies: *i*) basis set size, its finite and contraction, *ii*) spin-polarization contributions from inner shell electrons, *iii*) choice of the right molecular geometry, and *iv*) use of correlated wave functions.

Recently, much attention was paid to the electronic structure of $N_3^•$ radical both on *ab initio* [10—21] and semiempirical levels [22—24]. *Ab initio* calculations were mostly carried out in order to find the optimal geometry. An early Hartree—Fock calculation [10] gives also dipole moment, ionization potential, and enthalpy of formation. In this study the authors investigated the angle region 120—180° only, discussing symmetry or asymmetry of the bonds. *Tian et al.* [11, 12] and *Kaldor* [13] calculated vibrational frequencies for optimized geometries. The electron affinity was investigated by *Baker et al.* [14]. *Petrolongo* [15] calculated ground state geometry and vertical spectrum of $N_3^•$ radical using the multi-reference configuration interaction (MRD-CI) method. Detailed analysis of the complete active space SCF (CAS-SCF) potential energy surface for $N_3^•$, N_3^+, and N_3^- species was given by *Wasilewski* [21] and by *Martin et al.* [25]. According to all previous calculations linear $^2\Pi_g$ state with internuclear distance 1.1815 Å was predicted as a ground state.

To our knowledge no electric and only a few magnetic properties were published for $N_3^•$ molecule on *ab initio* level. *Claxton et al.* [18] calculated hfc constants for $N_3^•$ and N_3^{2-} species by *ab initio* unrestricted Hartree—Fock SCF (UHF-SCF) wave function using STO orbitals taking geometries from *Archibald* [10]. *Adams* and *Owens* [22] calculated hfc constant for the same species with the help of the INDO method. *Higgins et al.* [24] evaluated heat of formation and ionization potential for MNDO optimal geometry. Only hfc constants of the nitrogen atom in state ^4S [5—8] and of N_4^+ radical [9] were studied in detail. The most recent high-level *ab initio* investigation of the potential energy surface of $N_3^•$ radical (up to the fourth order of the projected Moller—Plesset perturbation theory, UHF-PMP4/6-31G*) by *Martin et al.* [25] showed that nine stationary points can be localized. But only two of them had linear structure. This conclusion was also confirmed by *Wasilewski* [21], who has found at least two minima for $N_3^•$ radical in ground and various excited states. The aim of this study is the investigation of some NQR and EPR properties for both linear and nonlinear $N_3^•$ species found in the work of *Martin et al.* [25].

THEORETICAL

The interaction between the nuclear spin and the spin of an unpaired electron in molecule causes a splitting of energy levels and is usually analyzed in terms of hfc constants [26]. The isotropic part a_N^{iso} of the hfc constant (Fermi contact term)

$$a_N^{iso} = \frac{8\pi}{3} g_e \mu_B g_N \mu_N \langle \Psi_0 | S_a^{-1} \sum_{k=1}^{n} \mathcal{S}_{ka}\, \delta(r_{Nk}) | \Psi_0 \rangle \quad (1)$$

measures the net unpaired spin density at the nucleus N in the molecule (g_e = 2.002319 is g value for the electron in free radical, μ_B is Bohr magneton, g_N nuclear g-factor, μ_N nuclear magneton, Ψ_0 wave function of the ground state, $\delta(r_{Nk})$ Dirac delta-function at the position r_{Nk}, $\mathcal{S}_{ka}$ operator of the spin momentum with the eigenvalue S_a).

The anisotropic (dipole) part of the hfc constant is in the molecule-fixed coordinate system defined as

$$A_{N_{ab}}^{aniso} = \sum_{k=1}^{n} 2S_a^{-1} \langle \Psi_k | \mathcal{S}_{ka} (r_{Nk}^2 \delta_{ab} - 3 r_{Na} r_{Nb}) r_N^{-5} | \Psi_k \rangle \quad (2)$$

* The author to whom the correspondence should be addressed.

and it is the measure for the spatial distribution.

Cartesian components g_{ab} of electronic **g**-tensor were calculated according to Stone's equation [27]

$$g_{ab} = g_e\delta_{ab} + \sum_{n \neq m} \frac{\langle\Psi_n|\mathcal{L}_{ka}|\Psi_m\rangle\langle\Psi_m|\sum_k \xi_k \mathcal{L}_{kb}|\Psi_n\rangle}{E_n - E_m} + \sum_{n \neq m} \frac{\langle\Psi_n|\sum_k \xi_k \mathcal{L}_{ka}|\Psi_m\rangle\langle\Psi_m|\mathcal{L}_{kb}|\Psi_n\rangle}{E_n - E_m} \quad (3)$$

where $\mathcal{L}_{ka}$ is the a-component of the angular momentum about the kth nucleus, ξ_k is the spin-orbit coupling constant for the kth atom and E_m, E_n are orbital energies.

Cartesian components of the electric field gradient [28] (efg) tensor $V_{N_{ab}}$ are generally evaluated as the expectation value of the operator

$$V_{N_{ab}} = \sum_{I \neq M} Z_I(3\boldsymbol{R}_{a_{IM}}\boldsymbol{R}_{b_{IM}} - \delta_{ab}\boldsymbol{R}_{IM}^2)\boldsymbol{R}_{IM}^5 - \sum_{p,q} \rho_{pc}\langle p|(3\boldsymbol{r}_{aM}\boldsymbol{r}_{bM} - \delta_{ab}\boldsymbol{r}_M^2)/\boldsymbol{r}_M^5|q\rangle \quad (4)$$

where $\boldsymbol{R}_a$ and $\boldsymbol{r}_a$ represent the nuclear and electron Cartesian coordinates, respectively, and $\boldsymbol{R}_{IM}$ is the distance between nucleus I (with the charge Z_I) and nucleus M, ρ_{pq} is reduced one-particle density matrix in appropriate atomic orbital basis p, q. efg Tensor characterizes the spatial variation of the electric field created by other nuclei and electrons.

Asymmetry parameter [28], defined for $|V_{N_{zz}}| \geq |V_{N_{yy}}| \geq |V_{N_{xx}}|$ labeled principal axes as

$$\eta = (V_{N_{xx}} - V_{N_{yy}})/V_{N_{zz}} \quad (5)$$

is used for the characterization of the nuclear quadrupole interaction in given molecule. The coordinate system used for the calculation of molecular properties mentioned above is given in Fig. 1.

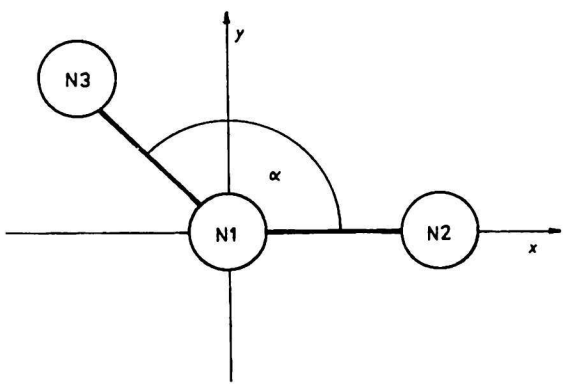

Fig. 1. Coordinate system for $N_3^\bullet$ radical.

All calculations were carried out within single and double configuration interaction method (CI-SD) [29, 30] by MELDF package [31]. Mono- and biexcitations were performed by using MO's acquired from a restricted Hartree—Fock open shell (RHF-SCF) [32—34] wave function. *Huzinaga*'s [35] 9*s*5*p* basis set with *Dunning*'s contraction [36] to 4*s*2*p* augmented with one diffuse function (ξ_d = 0.80) was used for each nitrogen atom. This size of basis set should be flexible enough to describe the spin-polarization effects in individual nitrogen atoms [5]. The property integrals were obtained according to the algorithm described by *Chandra* and *Buenker* [37, 38]. In this preliminary computational study we did not investigate either the influence of the multi-reference set involved in CI-SD calculation or vibration-rotation averaging of calculated hfc constants. No symmetry conditions ($\mathbf{C}_{2v}$ or $\mathbf{D}_{\infty h}$ point groups) were considered.

RESULTS AND DISCUSSION

First a small topological study has been done with the help of INDO method [39]. Full geometry optimization within this framework led always to the symmetric structures (opposite than in [10], where asymmetric geometries were preferred). *Petrolongo* [15] has found that asymmetric geometry is preferred by SCF calculation, but on MRD-CI level the symmetric structure is optimal. Using the INDO method two stationary points were found. Some characteristics are given in Table 1. The second (bent) structure, which is more stable than the linear form by 0.154634 hartree, was not found by *Adams* and *Owens* [22]. The distribution of the spin density obtained is opposite both in signs and size for central and terminal nitrogen atoms, respectively. To investigate the possibility of the existence of nonlinear $N_3^\bullet$ species suggested by INDO method and also by *Martin* [25] and *Wasilewski* [21] we have expanded our studies and undertook *ab initio* calculations in 9*s*5*p*1*d*/4*s*2*p*1*d* basis set. Initial geometries (Table 2) were taken from the most complete UHF-PMP4 geometry investigation [25]. The real existence of both linear and bent structures at the room temperatures and their lifetime remains still as open question, because $N_3^\bullet$ radical in the gas and/or liquid phase dissociates spontaneously to molecular nitrogen [40]

$$2\ N_3^\bullet(X^2\Pi_g) \rightarrow 2\ [N_2(X^1\Sigma_g^+) + N(^2D_u)] \rightarrow 3\ N_2(^1\Sigma_g^+) \quad (A)$$

Estimated half-life time is 10^{-5}—10^{-6} s [41]. It should be mentioned that the low-temperature experiment in solid matrix [11, 12] for N_3^- closed shell does show the possible existence of the nonlinear species. No

Table 1. INDO Optimized Geometries, Their **g**-Tensors, and hfc Constants for $N_3^•$ Radical

r(NN)	α(NNN)	Total energy	hfc Constants a_{N1}^{iso}	$a_{N2,N3}^{iso}$	Dipole moment μ	g_{xx}	g_{yy}	g_{zz}	$\langle g \rangle^b$
Å	°	hartree[a]	MHz	MHz	10^{-30} C m				
1.2073	180.0	− 33.157832	− 23.76	+ 12.41	0.000	2.00216	2.00270	2.00520	2.00335
1.2901	63.5	− 33.312466	+ 7.26	− 18.97	2.491	2.00216	2.00261	2.00362	2.00280

a) 1 hartree = 4.3598×10^{-18} J; *b*) $\langle g \rangle = (g_{xx} + g_{yy} + g_{zz})/3$.

Table 2. Molecular Geometries [25] and RHF-SCF Energies in 9*s*5*p*1*d*/4*s*2*p*1*d* Basis Set for $N_3^•$ Species under Consideration

Species	Symmetry	Term	Electronic structure	r(NN)	α(NNN)	SCF energy
				Å	°	hartree
N007	C_{2v}	$^2B_1$	$a_1^2\, b_2^2\, a_1^2\, a_1^2\, a_1^2\, b_2^2\, b_1^2\, a_1^2\, a_1^2\, b_2^2\, b_1$	1.4173	49.49	− 163.216869
N005	C_{2v}	$^2A_2$	$a_1^2\, a_1^2\, b_2^2\, a_1^2\, b_2^2\, a_1^2\, b_1^2\, a_1^2\, b_2^2\, a_1^2\, a_2$	1.2803	69.13	− 163.197797
N010	C_{2v}	$^4B_1$	$a_1^2\, a_1^2\, b_2^2\, a_1^2\, b_2^2\, a_1^2\, b_1^2\, b_2^2\, a_1^2\, b_2\, a_2\, a_1$	1.2693	116.34	− 163.169796
N009	$D_{\infty h}$	$^2\Pi_g$	$\sigma_g^2\, \sigma_u^2\, \sigma_g^2\, \sigma_g^2\, \sigma_u^2\, \sigma_g^2\, \pi_u^4\, \sigma_u^2\, \pi_g^3$	1.1593	180.00	− 163.236678

similar experiments were published for electroneutral $N_3^•$ species.

RHF-SCF energies for given structures in 9*s*5*p*1*d*/4*s*2*p*1*d* basis set are in Table 2. During the AO → MO integral transformation all of the 48 MO's were kept active. In Table 3 we report CI-SD energies with estimated full CI energies according to Davidson's formula [42]. Both on SCF and CI-SD level the most stable is the linear structure N009 (notation according to Fig. 4 in [25]), followed by N007 (+ 127.4 × 10^{-3} hartree), N005 (+ 133.9 × 10^{-3} hartree) and much higher lying N010 (+ 292.4 × 10^{-3} hartree) bent structures. *Wasilewski* [21] reported the order N009, N010, N005, N007. Dependence of CI-SD energies on the number of core MO's is almost linear. Inclusion of a part of the correlation energy lowers the total energy (first of all N005 and N010 structures) about 60 × 10^{-3} hartree.

The reference space in all CI-SD calculation contained only one spin-adapted configuration (ten doubly occupied MO's and one single occupied MO, c_0^2 = 0.8794—0.9324). But the obtained results showed that $N_3^•$ radical requires the multireference zeroth order wave function description as its starting point. For the first four to eight MO's considered as core orbitals, 69308, 49068, 32306, 19022, and 9216 spin-adapted configurations within CI-SD framework were generated. The lowest root was extracted by diagonalizing CI matrix according to the *Davidson* algorithm [43] and for these CI-SD vectors appropriate molecular properties were computed.

The analysis of the electron excitations showed that the most relevant excitations are: *i*) from upper doubly occupied to the upper lying virtual MO's, which underlines the importance of the appropriate basis size and of the diffuse functions (*s*→*d*), and *ii*) from upper doubly occupied orbitals to low lying virtual MO's (*s*→*p*). Unlike the atomic nitrogen for $N_3^•$ molecule are important double excitations into *p* orbitals. The influence of the higher (triple) excitations on the a_N^{iso} value has not been solved satisfactorily yet [8, 44].

Values of isotropic part and values of components of the anisotropic part of the hfc constant depending on CI space and molecular geometry are given in Table 4. The RHF calculation gives $a_N^{iso} = 0$ for all centres, so these values should be determined solely by spin-polarization effects. Larger CI space does not affect these values substantially, except for central nitrogen in N005 molecule. The opposite signs, as could be expected from the INDO calculation were not observed. It is well known that for correct sign prediction much larger basis set must be used [7]. Isotropic hfc constant of central nitro-

Table 3. Dependence of Energies on Geometry and Orbital CI Space

Number of core MO's	Species	CI-SD energy	Full CI energy
		hartree	hartree
4	N005	− 163.569072	− 163.6138
5		− 163.502968	− 163.5372
6		− 163.438862	− 163.4634
7		− 163.436568	− 163.3566
8		− 163.288917	− 163.2936
4	N007	− 163.575658	− 163.6165
5		− 163.508941	− 163.5391
6		− 163.443850	− 163.4642
7		− 163.357336	− 163.3657
8		− 163.304088	− 163.3077
4	N009	− 163.703049	− 163.7691
5		− 163.641985	− 163.6996
6		− 163.576031	− 163.6229
7		− 163.523682	− 163.5616
8		− 163.397353	− 163.4059
4	N010	− 163.410393	− 163.4335
5		− 163.461539	− 163.5011
6		− 163.388859	− 163.4156
7		− 163.316189	− 163.3292
8		− 163.264919	− 163.2715

Table 4. Dependence of the hfc Constants (in Principal Magnetic Axis System) on Geometry and Orbital CI Space

Number of core MO's	Species	a_{N1}^{iso} / MHz	$a_{N2,N3}^{iso}$ / MHz	$A_{N1_{xx}}^{aniso}$ / MHz	$A_{N1_{yy}}^{aniso}$ / MHz	$A_{N1_{zz}}^{aniso}$ / MHz	$A_{N2,N3_{xx}}^{aniso}$ / MHz	$A_{N2,N3_{yy}}^{aniso}$ / MHz	$A_{N2,N3_{zz}}^{aniso}$ / MHz
4	N007	49.99	5.69	−45.238	−41.401	86.639	−3.666	−3.685	7.350
5		11.86	3.30	−45.379	−41.101	86.479	−3.614	−3.614	7.228
6		13.06	4.21	−45.095	−41.391	86.486	−3.636	−3.627	7.263
7		14.67	4.70	−45.982	−41.374	87.356	−3.042	−3.031	6.074
8		12.92	4.47	−46.480	−40.750	87.231	−3.035	−3.035	6.070
4	N005	1.09	29.32	4.330	1.360	−5.689	−26.212	−27.325	53.538
5		1.10	13.26	2.972	4.220	−7.192	−26.487	−27.632	54.119
6		3.46	9.41	3.439	4.746	−8.185	−27.087	−27.675	54.762
7		4.07	9.68	−0.642	0.575	0.068	−24.429	−25.531	49.960
8		4.57	7.66	−0.511	0.396	0.115	−24.378	−25.655	50.033
4	N010	23.13	32.24	6.100	−0.774	−5.326	−17.395	39.965	−22.169
5		24.11	18.59	5.899	−0.026	−5.870	−17.154	39.543	−22.388
6		16.74	11.17	6.387	0.037	−6.425	−17.173	39.238	−22.065
7		17.61	11.31	6.236	−0.867	−5.369	−16.632	39.300	−22.668
8		14.99	16.99	6.130	−0.199	−5.931	−18.646	40.572	−21.926
4	N009	252.39	433.45	1.146	−0.573	−0.573	15.183	−7.591	−7.592
5		252.48	423.58	0.597	−0.299	−0.298	15.117	−7.559	−7.559
6		249.70	418.98	0.266	0.329	−0.595	14.948	−7.177	−7.772
7		246.87	413.80	0.205	−0.102	−0.102	14.535	−7.268	−7.268
8		249.22	427.77	2.285	−1.142	−1.142	15.601	−7.801	−7.800

gen N1 is much more sensitive to bond angle changes than hfc constants of the terminal nitrogens N2 and N3. However, the hfc constants ratio $|a_{N1}^{iso}/a_{N2,N3}^{iso}| \approx 1.92$ for linear and *ca.* 0.383 for bent structures expected according to the INDO method was not observed (Table 4). In literature only hfc constants for $N_3^{\bullet}$ adducts with different spin traps [41, 45] were published. Our hfc constants are in fair agreement with these experimental data, which points to the qualitative character of the obtained results. We can just predict 2—8 times higher $a_{N2,N3}^{iso}$ value for linear structure than for the nonlinear one. We have found that enlarging CI space also does not affect anisotropic part of hfc constants very much. Also according to the previous investigations [1—4] these values are influenced more by basis set deficiencies than by correlation effects. Experimental values for **A**-tensor of the $N_3^{\bullet}$ radical are missing (Table 5). There were reported experimental values for N_3^{2-} anion radical only [46]. *Claxton et al.* [18] evaluated A_N^{aniso} components by UHF wave function in minimal STO basis set, taking geometries from INDO [22] and *ab initio* [10] calculations. *Adams* and *Owens* [22] just determined signs of the experimentally measured **A**-tensor components to satisfy the relation

$$a_N^{iso} = (A_{N_{xx}} + A_{N_{yy}} + A_{N_{zz}})/3 \qquad (6)$$

All these values are collected in Table 5. It is well known that the signs of the hfc constants cannot be

Table 5. Experimental hfc Constants (MHz) for $N_3^{\bullet}$ Radical

Method	a_{N1}^{iso}	$a_{N2,N3}^{iso}$	$A_{N1_{xx}}^{aniso}$ / $A_{N2,N3_{xx}}^{aniso}$	$A_{N1_{yy}}^{aniso}$ / $A_{N2,N3_{yy}}^{aniso}$	$A_{N1_{zz}}^{aniso}$ / $A_{N2,N3_{zz}}^{aniso}$	Species
exp. [46]	–	–	21.0 ± 1.4 54.9 ± 1.4	39.2 ± 1.4 78.5 ± 1.4	17.4 ± 1.4 44.0 ± 1.4	N_3^{2-}
exp. [44]	41.2 ± 0.1	8.3 ± 0.1	–	–	–	$N_3^{\bullet}$ + DMPO
exp. [45]	42.18	5.77	–	–	–	$N_3^{\bullet}$ + PBN
	41.14	5.46	–	–	–	$N_3^{\bullet}$ + PyBN
INDO [22]	−23.77	12.39	−21.0 +54.9	+39.2 −78.5	+17.4 −44.0	$N_3^{\bullet}$
UHF [18] *ab initio*	−50.4	20.7	−46.24 0.0	−28.9 −5.0	−76.2 +66.9	$N_3^{\bullet}$
UHF-AA *ab initio* [18]	−16.5	7.0	−17.1 −11.8	−7.0 −11.5	−25.2 +45.9	$N_3^{\bullet}$

DMPO – 5,5-dimethylpyrrolin-1-one, PBN – *N*-benzylidene-*tert*-butylamine *N*-oxide, PyBN – *N*-(4-pyridyl)-*N*-*tert*-butylamine *N*-oxide, UHF-AA – unrestricted Hartree—Fock after annihilation.

Table 6. Mulliken Charge Distribution and Spin Densities

Species	N1 (central)		N2, N3 (terminal)		Dipole moment μ
	charge density	spin density	charge density	spin density	10^{-30} C m
N007	6.59691	0.86063	7.20154	0.06969	3.95371
N005	6.88559	0.00910	7.05721	0.49546	2.05926
N010	6.99654	0.48110	7.00173	0.25945	0.99546
N009	6.43987	0.68004	7.28006	0.15998	0.00000

Table 7. Dependence of the Components of Electric Quadrupole Moment*, Electric Field Gradient, Quadrupole Splitting Constant, and Asymmetry Parameter on the $N_3^•$ Geometry

Species	θ_{xx}	θ_{yy}	θ_{zz}	θ_{yx}	Atom	efg gradient	e^2Qq/h	η
	10^{-40} C m^2	10^{-40} C m^2	10^{-40} C m^2	10^{-40} C m^2		10^{12} C m^{-3}	MHz	
N007	−4.621	−3.312	7.933	−0.897	N1	0.752787	1.513100	0.0572
					N2, N3	0.813255	1.634650	0.8821
N005	−2.437	−5.225	7.659	0.785	N1	1.216944	2.446000	0.5421
					N2, N3	0.378608	0.760995	0.6634
N010	−4.205	2.924	1.280	7.089	N1	0.578089	1.521600	0.7522
					N2, N3	0.384904	0.795972	0.5933
N009	−5.161	2.581	2.581	0.000	N1	0.032169	0.064660	0.2216×10^{-3}
					N2, N3	1.111312	2.233700	0.2750×10^{-5}

*With the centre-of-mass as the origin ($\theta_{xz} = \theta_{yz} = 0.000$).

determined from EPR measurements. When we assume close A_N^{aniso} values both for N_3^{2-} and $N_3^•$ radicals, the best agreement can be found for N009 species, but absolute values are still underestimated about 50 %. The similar poor agreement for anisotropic hfc components was obtained by *Claxton* [18], where either spin-annihilation procedure did not improve calculated A_N^{aniso} values. It is noteworthy that components of the anisotropic hfc constant on terminal nitrogens are relatively stable against the geometry changes.

The results of the Mulliken population analysis [47, 48] are given in Table 6. Canonical structures for the linear form $|N \equiv \overset{+}{N}-\underline{N}| \rightleftarrows |\overset{\bullet}{N}=\overset{+}{N}=\underline{N}|$ have a positive formal charge on the central nitrogen atom, which could explain the high degree of charge polarization found in the Mulliken population analysis. The unpaired electron resides primarily on the central nitrogen atom with significant $2p_\pi$ character. All bent structures have nonzero dipole moment.

Electric field gradient, nuclear quadrupole splitting constant, and asymmetry parameter calculated from the "best" (*e.g.* four core MO's only) CI-SD wave function are collected for individual nitrogen atoms in Table 7 together with the components of the electric quadrupole moment. Again (to our knowledge) no experimental results are available, so it is rather problematic to discuss these results. One common feature can be observed from Table 7: quadrupole splitting constants are for linear structure higher on central atoms than on terminal nitrogens. Opposite is true for all bent forms. Linear structure exhibits low values of the asymmetry parameter. Also components of the electric quadrupole moment are approximately twice and more higher for linear than for bent structures. Generally all these values are not very sensitive (in single-reference CI-SD approximation) to the CI space used.

CONCLUSION

The primary aim of these calculations was to evaluate some electric and magnetic properties for four different geometries of the $N_3^•$ radical. We tested the contribution of the electron correlation on CI-SD level of theory for hfc constants (both isotropic and anisotropic parts), electric field gradient, asymmetry parameter, and electric quadrupole moment. To our knowledge only few experimental data are available for the radical under consideration as a consequence of its big instability. It is well known [49] that for example N_2O^+ isoelectronic species can be strongly stabilized upon bending. We propose existence of a cyclic isomer, which should be a Jahn—Teller species (analogous to $C_3H_3^•$ radical). The real existence of the bent species is in our opinion possible at low temperatures in solid matrices and remains as an open question for the spectroscopists. However, the obtained numerical values have qualitative meaning only due to relatively small basis set for property calculation and single-reference CI space.

Acknowledgements. All calculations have been carried out on CDC-4680 computer at the Central Computer Centre of the Slovak Technical University, the services of which have been very valuable for this study.

REFERENCES

1. Chipmann, D., *J. Chem. Phys. 71*, 761 (1979).
2. Chipmann, D., *J. Chem. Phys. 78*, 3112 (1983).
3. Chipmann, D., *J. Chem. Phys. 94*, 6632 (1983).
4. Feller, D. and Davidson, E. R., *J. Chem. Phys. 80*, 1006 (1984).
5. Bauschlicher, C. W., Jr., *J. Chem. Phys. 92*, 518 (1990).
6. Feller, D. and Davidson, E. R., *J. Chem. Phys. 88*, 7580 (1988).
7. Engels, B., Peyerimhoff, S. D., and Davidson, E. R., *Mol. Phys. 62*, 109 (1987).
8. Engels, B. and Peyerimhoff, S. D., *J. Phys. B 21*, 3459 (1988).
9. Knight, L. B., Johannensen, K. D., Cobranchi, D. C., Earl, E. A., Feller, D., and Davidson, E. R., *J. Chem. Phys. 87*, 885 (1987).
10. Archibald, T. W. and Sabin, J. R., *J. Chem. Phys. 55*, 1821 (1971).
11. Tian, R., Facelli, J. C., and Michl, J., *J. Phys. Chem. 92*, 4073 (1988).
12. Tian, R., Facelli, J. C., and Michl, J., *J. Am. Chem. Soc. 110*, 7225 (1988).
13. Kaldor, U., *Int. J. Quantum Chem. S 24*, 291 (1990).
14. Baker, J., Nobes, R. H., and Radom, L., *J. Comput. Chem. 7*, 349 (1986).
15. Petrolongo, C., *J. Mol. Struct. 175*, 215 (1988).
16. Dyke, J. M., Jonathan, N. B. H., Lewis, A. E., and Morris, A., *Mol. Phys. 47*, 1231 (1982).
17. Novaro, O. and Castilo, S., *Int. J. Quantum Chem. S 26*, 41 (1984).
18. Claxton, T. A., Overill, R. E., and Symons, M. C. R., *Mol. Phys. 26*, 75 (1973).
19. Alcamí, M., de Paz, J. L. G., and Yanes, M., *J. Comput. Chem. 10*, 468 (1989).
20. Knight, L. B., Martin, R. L., and Davidson, E. R., *J. Chem. Phys. 71*, 3991 (1979).
21. Wasilewski, J., *Int. J. Modern Phys.*, to be published.
22. Adams, G. F. and Owens, F. J., *J. Chem. Phys. 57*, 2212 (1972).
23. Chuvilkin, N. D., Zhidomirov, G. M., and Umanskii, I. M., *Chem. Phys. Lett. 33*, 576 (1975).
24. Higgins, D., Thompson, C., and Thiel, W., *J. Comput. Chem. 9*, 702 (1988).
25. Martin, J. M. L., Francois, J. P., and Gijbels, R., *J. Chem. Phys. 90*, 6469 (1989).
26. Harriman, J. E., *Theoretical Foundation of the Electron Spin Resonance*. Academic Press, New York, 1978.
27. Stone, J. A., *Proc. R. Soc. London A 271*, 424 (1963).
28. Urban, M., Černušák, I., Kellö, V., and Noga, J., in *Methods in Computational Chemistry*, Vol. *1*, p. 117. (Wilson, S., Editor.) Plenum Press, New York, 1987.
29. Shavitt, I., in *Methods of Electronic Structure Theory*. (Schaefer, H. F., Editor.) P. 323. Plenum Press, New York, 1977.
30. Saunders, V. R. and van Lethe, J. H., *Mol. Phys. 48*, 923 (1983).
31. Davidson, E. R., in *Modern Techniques in Computational Chemistry MOTECC-90*. (Clementi, E., Editor.) P. 553 and references cited therein. Plenum Press, New York, 1991.
32. Davidson, E. R., *Chem. Phys. Lett. 21*, 565 (1973).
33. Davidson, E. R., *Int. J. Quantum Chem. 8*, 707 (1974).
34. Hsu, H., Davidson, E. R., and Pitzer, R. M., *J. Chem. Phys. 65*, 609 (1976).
35. Huzinaga, S., *J. Chem. Phys. 42*, 1293 (1965).
36. Dunning, T. H., *J. Chem. Phys. 78*, 2823 (1970).
37. Chandra, P. and Buenker, R. J., *J. Chem. Phys. 79*, 358 (1983).
38. Chandra, P. and Buenker, R. J., *J. Chem. Phys. 79*, 366 (1983).
39. Pople, J. A., Beveridge, D. L., and Dobosh, P. A., *J. Chem. Phys. 46*, 2026 (1967).
40. Continetti, R. E., Cyr, D. R., Metz, R. B., and Neumark, D. M., *Chem. Phys. Lett. 182*, 406 (1991).
41. Kremers, W. and Singh, A., *Can. J. Chem. 58*, 1592 (1980).
42. Langhoff, S. R. and Davidson, E. R., *Int. J. Quantum Chem. 8*, 61 (1974).
43. Davidson, E. R., *J. Comput. Phys. 17*, 87 (1975).
44. Glas, R. and Hibbert, A., *J. Phys. B 11*, 2257 (1978).
45. Rehorek, D., *Z. Chem. 24*, 228 (1984).
46. Marinkas, P. L., *J. Chem. Phys. 52*, 5144 (1970).
47. Mulliken, R. J., *J. Chem. Phys. 23*, 1833 (1955).
48. Davidson, E. R., *J. Chem. Phys. 46*, 3320 (1967).
49. Hopper, D. G., *J. Chem. Phys. 76*, 1068 (1982).

Translated by R. Klein