

Evidence for a Cyclic Form of the Azide Anion

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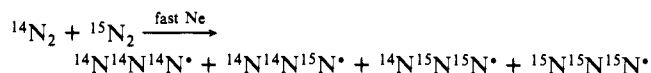
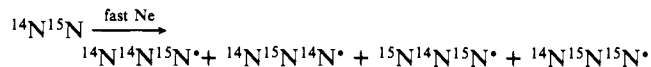
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We have obtained evidence for a transient cyclic N_3^- anion from isotopic labeling studies. Calculations suggest that the transient is the D_{3h} symmetry triplet ground state of the smallest possible antiaromatic anion, the cyclic azide anion.

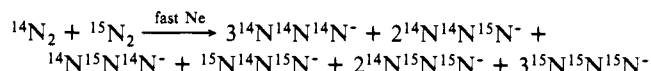
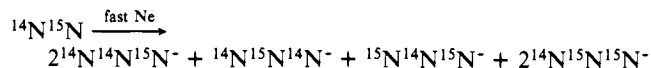
The IR and UV-vis absorption and emission spectra of a solid N_2 matrix which had been bombarded with 5-keV Ne atoms and/or ions revealed the presence of N_3^* radicals, and ESR demonstrated the presence of about 15 times as many $N(^4S)$ atoms.² The IR also contained weak peaks for the antisymmetric stretches of "free" and "ion-paired" N_3^- . With mixtures of $^{14}N_2$, $^{15}N_2$, and $^{14}N^{15}N$, the six expected isotopic peaks appeared for each IR band of N_3^* and N_3^- at the anticipated positions.²

We have now measured the isotopic intensity ratios for several such mixtures. Their composition was determined from the intensities of the weak IR peaks of the diatomics, assuming isotope-independent oscillator strengths.

The isotopic intensities of N_3^* fit an end-on attack mechanism of formation from N_2 and N, which is presumably generated in high-energy impact on N_2



The isotopic intensity distribution of the free N_3^- ion³ is different (Figure 1) and close to that expected if all three N atoms become equivalent in a three-membered ring at some time before the eventual observation of the linear N_3^- product.



The best fit was obtained assuming that the scrambling was incomplete, with about 20% of end-on attack (Table I). Attempts to fit the data to scrambling within groups of more than three N atoms failed (e.g., assuming transient formation of a five-membered cycle, N_5^-).

Two possibilities need to be considered: (i) N_3^- is formed initially in its usual linear geometry, by a process such as electron capture by N_3^* or an end-on attack⁴ by energetic N^- on N_2 , and the bulk of it subsequently undergoes label randomization via transient three-membered ring formation in a remarkably efficient process. This could be a hot singlet ground-state reaction immediately after initial $N_3^* + e$ recombination^{6,7} or a triplet reaction

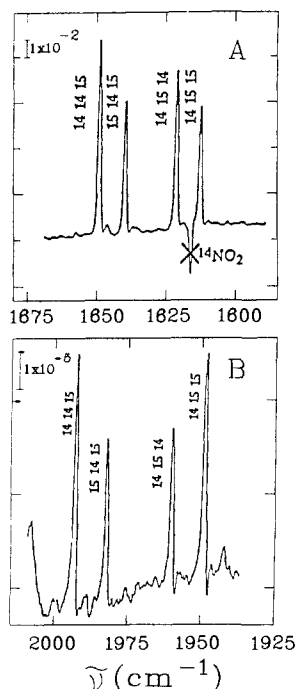


Figure 1. The ν_3 fundamental region for N_3^* (A) and N_3^- (B) in a $\approx 10:1$ $^{14}N^{15}N:^{14}N_2$ matrix bombarded with 4 keV Ne + Ne⁺ (20 K). Obtained as a difference of spectra recorded before and after bleaching.

sensitized by energy transfer from triplet $N_2(A^3\Sigma_u^+)$.⁸ (ii) Only $\sim 20\%$ of the N_3^- is formed via electron capture by linear N_3^* , without scrambling. The rest is formed in a process that avoids N_3^* altogether, such as a side-on attack on N_2 by N^- in its 3P ground state.^{4,9}

Either way, transient formation of a cyclic N_3^- structure needs to be postulated. Planar cyclic 4N-electron π -systems should be antiaromatic, with a destabilized lowest singlet and relatively stable lowest triplet, as was first pointed out for uncharged [4N]-annulenes.¹¹ This suggests that our cyclic N_3^- structure is only a transition state if reached in the singlet state but could be a metastable intermediate if reached in the triplet state. According to symmetry arguments,¹² unlike neutral [4N]annulenes, [n]-annulenes with a charged perimeter ($n \neq 4N$) have a triplet state well below the lowest singlet and will be triplet ground-state species ("axial" biradicals¹³) of D_{nh} symmetry.¹⁴ The smallest con-

(6) We have searched for such a thermal scrambling path in vain. No scrambling was observed upon heating neat $Na^{15}N^{14}N^{14}N$ to 180° for 72 h or its solution in HMPA to 150 °C for 2 h. The dissolved azide decomposed upon longer heating. The only indication that a thermal scrambling path might exist was provided by the observation of label scrambling upon extended irradiation of an aqueous solution at 248 nm. Since light of this wavelength is known to cause photodetachment [Treinin, A.; Hayon, E. *J. Chem. Phys.* 1969, 50, 538. Barat, F.; Hickel, B.; Sutton, J. *J. Chem. Soc., Chem. Commun.* 1969, 125], one possible way of accounting for this observation is a hot ground-state reaction after recombination. However, we believe it is far more likely that this scrambling is an excited state process.

(7) Ne bombardment of solid O_2 yields only the end-on isotopic intensity distribution for both the O_3 and the O_3^- products, demonstrating that at least in this case there is no scrambling by the hot ground-state mechanism in the matrix: Tian, R.; Magnera, T. F.; David, D. E.; Michl, J., unpublished results. However, the $N_3^* + e$ recombination is more exothermic than $O_3 + e$.

(8) Richards, D. S.; Setser, D. W. *Chem. Phys. Lett.* 1987, 126, 215. Cao, De Zhao; Setser, D. W. *J. Phys. Chem.* 1988, 92, 1169.

(9) We believe that both the end-on addition of $N(^2D)$ and the side-on addition of $N(^3P)$ to N_2 require activation energy, but this should be amply available in the impact region for a short period of time.¹⁰ An attempt to induce triplet-sensitized label scrambling in a solution of $Na^{15}N^{14}N^{14}N$ and acetophenone in *t*-BuOH by a 2-h irradiation at 308 nm was unsuccessful.

(10) Urbassek, H.; Michl, J. *Nucl. Instr. Meth.* 1987, B22, 480.

(11) Baird, N. C. *J. Am. Chem. Soc.* 1972, 94, 4941.

(12) Borden, W. T. *J. Chem. Soc., Chem. Commun.* 1969, 881. Borden, W. T. In *Diradicals*; Borden, W. T., Ed.; Wiley: New York, 1982; p 50.

(13) Bonačić-Koutecký, V.; Koutecký, J.; Michl, J. *Angew. Chem., Int. Ed. Engl.* 1987, 26, 170. Michl, J.; Bonačić-Koutecký, V. *Tetrahedron*, in press. Bonačić-Koutecký, V.; Schöffel, K.; Michl, J. *Proceedings of the Workshop on Quantum Chemistry*, Girona, Spain, July 1988, Carbó, R., Ed.; Elsevier: Amsterdam, in press.

(1) This project was initiated at the University of Utah.

(2) Tian, R.; Facelli, J. C.; Michl, J. *J. Phys. Chem.* 1988, 92, 4073.

(3) The isotopic peaks of the ion-paired N_3^- were too weak for reliable measurement.

(4) N^- is not bound in the gas phase but should keep its electrons in the N_2 matrix. E.g., the photodetachment thresholds of "free" and "ion-paired" N_3^- are ~ 4.5 and ~ 3.4 eV in an N_2 -Ar matrix,² compared with 2.76 eV in the gas phase.⁵ Gas-phase electron affinity of N is only slightly negative, -0.07 eV: Mazeau, J.; Giresteau, F.; Hall, R. I.; Huetz, A. *J. Phys. B: Atom. Molec. Phys.* 1978, 11, L557.

(5) Illenberger, E.; Comita, P. B.; Brauman, J. I.; Fenzlaff, H. D.; Henri, M.; Heinrich, N.; Koch, W.; Frenking, G. *Ber. Bunsenges. Phys. Chem.* 1985, 89, 1026.

Table I. Relative Integrated Intensities of ν_3 for N_3^- Isotomers

	$^{14}N^{14}N^{14}N^-$	$^{14}N^{14}N^{15}N^-$	$^{15}N^{14}N^{15}N^-$	$^{14}N^{15}N^{14}N^-$	$^{14}N^{15}N^{15}N^-$	$^{15}N^{15}N^{15}N^-$
	$^{14}N^{15}N;^{14}N_2$ (10:1)					
obsd	0.0	1.2	0.7	0.7	1.0	0.0
calcd scrambled	0.2	1.3	0.5	0.7	1.0	0.0
calcd end-on	0.2	1.4	1.0	1.2	1.0	0.0
calcd scrambled +20% end-on	0.2	1.3	0.6	0.8	1.0	0.0
	$^{15}N_2;^{14}N_2$ (1:1.4)					
obsd	1.6	1.1	0.3	0.4	0.9	1.0
calcd scrambled	2.0	0.9	0.5	0.5	0.9	1.0
calcd end-on	2.0	1.4	0.0	0.0	1.4	1.0
calcd scrambled +20% end-on	2.0	1.0	0.4	0.4	1.0	1.0

Table II. SCF^a Optimized Geometries for the N_3^- Anion

state	sym-metry	en ^b (au)	rel en ^b (kcal/mol)	R_{NN} (Å)	harmonic freq (cm ⁻¹)
$^1\Sigma_g^+$	$D_{\infty h}$	-163.319 68	0	1.151 ^c	2190 (σ_u), ^{d-f} 1553 (σ_g), ^{e,f} 706 (π_u) ^e
3B_2	C_{2v}	-163.281 32	24.0	1.240	1423 (a_1), 1181 (b_2), 708 (a_1)
$^3A_2'$	D_{3h}	-163.251 48	42.7	1.362	1567 (a_1'), 1025 (e')

^a6-311+G* (5 d components). Restricted HF for singlet, unrestricted HF for triplets. ^bNot corrected for zero-point energies. ^cObserved,¹⁹ 1.1884 Å. ^dObserved in gas phase,¹⁹ 1986.4672 cm⁻¹, for free N_3^- in N_2 matrix;² 2003.5 cm⁻¹. ^eFrequencies observed in KN_3 crystal;²⁰ 2036.4, 1344, 642.4 cm⁻¹. ^fBest available ab initio results;²³ 1950, 1295 cm⁻¹.

ceivable antiaromatic triplet ions should then be the D_{3h} symmetry triatomics N_3^- , P_3^- , O_3^{2+} , S_3^{2+} , etc. Our data constitute evidence for the transient existence of the singlet or triplet form of the first one of these.

In order to establish whether cyclic N_3^- of D_{3h} symmetry represents a bound chemical entity with a triplet ground state, we have performed ab initio calculations. Results of initial SCF optimizations are collected in Table II. We find that a cyclic (D_{3h}) N_3^- indeed is a bona fide isomer of the usual linear azide anion, with a triplet ground state. The ordinary bent triplet N_3^- is 18.7 kcal/mol lower on the same T_1 surface, separated by a barrier. The geometrical distortion from the optimal cyclic triplet N_3^- (D_{3h}) to the optimal bent acyclic triplet N_3^- (C_{2v}) stabilizes the lowest singlet state strongly and brings it below the lowest triplet. The optimized linear ground-state singlet lies 42.7 kcal/mol below the optimized D_{3h} triplet.

Our best value for the vertical triplet-singlet splitting in cyclic N_3^- at the SCF-optimized geometry is 39 kcal/mol, from 6-311+G* CI calculations starting with ROHF triplet orbitals and including up to quadruple excitations in the σ and π spaces until the T-S difference covered (up to ~25 000 configurations, degeneracy of the singlet satisfied to within 0.3 kcal/mol). This type of calculation is notoriously difficult,²¹ and the value should be viewed as an upper limit, but there is no doubt that the $^3A_2'$ triplet lies below the $^1E'$ singlet at this geometry, as it does in $C_3H_3^-$ and $N_3H_3^{2+}$,²¹ and that triplet cyclic N_3^- is a metastable isomer

of ordinary linear singlet N_3^- . Unlike $C_3H_3^-$ and $N_3H_3^{2+}$, the antiaromatic singlet cyclic N_3^- is not able to ease its misery by out-of-plane distortion.

The theoretical results suggest that an involvement of cyclic N_3^- triplet in the formation of isotopically scrambled N_3^- in our matrix experiments is plausible. One can expect the metastable cyclic triplet N_3^- to be relatively short-lived, and the cyclic triplet P_3^- , very recently calculated²² to have a D_{3h} equilibrium geometry as well, is a more promising candidate for direct observation.

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(22) Burdett, J. K.; Marsden, C. J. *Nouv. J. Chim.*, in press.

(23) Botschwina, P. *J. Chem. Phys.* **1986**, *85*, 4591.

Structure and Reactivity of Novel Lithium Di-*tert*-butylphosphido(alkyl)cuprates

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Organocopper reagents have been extensively exploited in organic synthesis as nucleophilic reagents for the formation of new carbon-carbon bonds.² Of the various organocuprates available, heterocuprates, $RCuXLi$ ($X =$ heteroatom ligand),³ play one particularly important role in that they prevent the waste of precious alkyl groups (R) that is inherent in the use of homocuprates, R_2CuLi . However, with the notable exception of those heterocuprates based upon certain phosphido and amido ligands,^{3b-d} the utility of heterocuprates may be restricted by their thermal instability. Although limited structural information is available for homocuprates R_2CuLi ,⁴ heterocuprate reagents have

(1) (a) Recipient of a National Institutes of Health (National Cancer Institute) Research Career Development Award, 1980-1985. (b) Fellow of the Alfred P. Sloan Foundation, 1985-1989.

(2) For some general reviews, see: (a) Posner, G. H. *An Introduction to Synthesis Using Organocopper Reagents*; John Wiley and Sons: New York, NY, 1980. (b) Normant, J. F. *J. Organomet. Chem. Lib.* **1976**, *1*, 219. (c) Lipshutz, B. H.; Wilhelm, R. S.; Kozlowski, J. A. *Tetrahedron* **1984**, *40*, 5005. (d) Taylor, R. J. K. *Synthesis* **1985**, 364. (e) Lipshutz, B. H. *Synthesis* **1987**, 325.

(3) (a) Posner, G. H.; Whitten, C. E.; Stirling, J. H. *J. Am. Chem. Soc.* **1973**, *95*, 7788. (b) Bertz, S.; Dabbagh, G. *J. Chem. Soc., Chem. Commun.* **1982**, 1030. (c) Bertz, S.; Dabbagh, G.; Villacorta, G. M. *J. Am. Chem. Soc.* **1982**, *104*, 5824. (d) Bertz, S.; Dabbagh, G. *J. Org. Chem.* **1984**, *49*, 1119.

(14) $C_3H_3^{+15}$ and $C_6Cl_6^{2+16}$ indeed are ground-state triplets, while C_4H_4 is a ground-state singlet,¹⁷ distorted by the pseudo-Jahn-Teller effect and rapidly tunneling between two D_{2h} minima.¹⁸

(15) Saunders, M.; Beyer, R.; Jaffe, A.; McBride, J. M.; O'Neill, J.; Breslow, R.; Hoffman, J. M.; Perchonok, C.; Wasserman, E.; Hutton, R. S.; Kuck, V. J. *J. Am. Chem. Soc.* **1973**, *95*, 3017. Borden, W. T.; Davidson, E. R. *J. Am. Chem. Soc.* **1979**, *101*, 3771.

(16) Wasserman, E.; Hutton, R. S.; Kuck, V. J.; Chandross, E. A. *J. Am. Chem. Soc.* **1974**, *96*, 1965.

(17) Bally, T.; Masamune, S. *Tetrahedron* **1980**, *36*, 343.

(18) Orendt, A. M.; Arnold, B. R.; Radziszewski, J. G.; Facelli, J. C.; Malsch, K. D.; Strub, H.; Grant, D. M.; Michl, J. *J. Am. Chem. Soc.* **1988**, *110*, 2648, and references therein.

(19) Polak, M.; Gruebele, M.; Saykally, R. J. *J. Am. Chem. Soc.* **1987**, *109*, 2884.

(20) Lamoureux, R. T.; Dows, D. A. *Spectrochim. Acta* **1975**, *31A*, 1945.

(21) Borden, W. T.; Davidson, E. R.; Feller, D. *J. Am. Chem. Soc.* **1980**, *102*, 5302.