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Registry No. IA, 85082-23-1; Ib, 85082-29-7; Ic, 85082-30-0; Id, 85082-31-1; Ie, 85032-32-2; If, 85082-33-3; Ig, 85082-34-4; Ih, 85082-35-5; Ii, 85082-36-6; Ij, 85082-37-7; IIa, 85082-24-2; IIb, 85082-25-3; IIc, 85082-27-5; IIIa, 85082-28-6; IIIb, 82371-40-2; $C_6H_{13}CH{=}CH_2$, 111-66-0; Ph—CH=CH_2, 100-42-5; C_6H_5, 71-43-2; CH_4, 74-82-8; *cis*-2-butene, 590-18-1; *trans*-2-butene, 624-64-6; cyclohexene, 110-83-8; norbornene, 498-66-8; *trans*-1-phenyl-1-propene, 873-66-5; α-methyl styrene, 98-83-9; 2-methyl-2-pentene, 625-27-4; toluene, 108-88-3; 1,3,5-trimethylbenzene, 108-67-8; *cis*-decalin, 493-01-6; *n*-octane, 111-65-9.

Supplementary Material Available: Complex Ia: contact distances less than 3.5 Å (Table I), distances and angles (Table II), mean planes (Table III), positional and thermal parameters (Tables IV and V), observed and calculated structure factor amplitudes (Table VI). Complex IIIb: description of the structure, distances and angles (Table IX), least-squares mean planes (Table X), positional and thermal parameters (Table XI and XII), observed and calculated structure factor amplitudes (Table XIII). Complexes Ia and IIIb: X-ray experimental data (Table XVII). Experimental Section: preparation and analysis of complexes Ib–j (25 pages). Ordering information is given on any current masthead page.

Theoretical Studies in the Norbornadiene–Quadricyclane System

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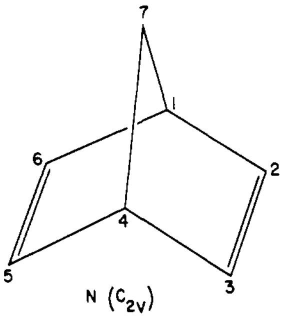
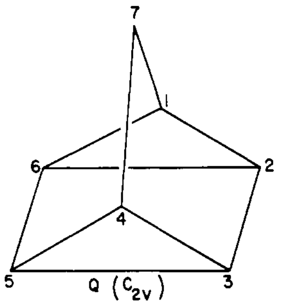
Abstract: Ab initio molecular orbital theory is used to investigate interesting aspects of the chemistry of norbornadiene (N) and quadricyclane (Q). Effects of polarization functions and electron correlation are included in these calculations. The optimized structures of N and Q are found to be in excellent agreement with those obtained from electron diffraction experiments. N is calculated to be 27 kcal/mol more stable than Q, slightly higher than the experimental thermochemical measurements. Detailed structural information which is not available experimentally is provided for the radical cations of N and Q (N$^+$ and Q$^+$). N$^+$ is calculated to be 11 kcal/mol more stable than Q$^+$, in good agreement with the experimental value. The nature of the triplet state is investigated in detail. The structure of the triplet state is found to be distorted to a symmetry (C_s) lower than that of the parent compounds (C_{2v}). An analysis of the orbital correlations for such a distorted triplet state reveals that conversion to Q on the singlet surface is more favorable than conversion to N. This explains the photochemical observations that reveal that the triplet state converts with a high yield (≃90%) to Q. Relative spin densities are calculated for both radical cations and are consistent with the measured nuclear spin polarization spectra.

Norbornadiene (N) and quadricyclane (Q) are strained hydrocarbons which have been the subject of intense experimental[1-13] and theoretical[14-21] investigations. They are structural isomers which can interconvert under appropriate conditions. Thermochemical as well as structural information about both molecules is known experimentally and hence provides a convenient testing ground for theoretical studies.



N (C_{2v})



Q (C_{2v})

The cations formed from both N and Q (N$^+$ and Q$^+$) have also been observed in photochemical[21-24] and nuclear spin polarization (CIDNP) experiments.[25,26] From the ionization potentials observed in the case of N and Q, thermochemical information about the cations can be inferred. However, no structural information is available, as is typical for most gas-phase ions. Hence, theory can provide valuable structural information to complement the energetic information known from experiments.

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Table I. Calculated and Experimental Geometries for N and Q[a,b]

geometrical parameter	norbornadiene			quadricyclane		
	STO-3G	6-31G	expt[c,d]	STO-3G	6-31G	expt[c,e]
$r(C_1–C_7)$	1.555	1.562	1.571	1.525	1.514	1.54
$r(C_1–C_2)$	1.547	1.544	1.533	1.511	1.519	1.51
$r(C_2–C_3)$	1.311	1.326	1.339	1.551	1.549	1.565
$\angle(C_1–C_7–C_4)$	91.9	91.7	92.2	98.0	99.0	98.5
$\angle(C_6–C_1–C_2)$	106.5	107.2	107	59.7	60.0	60.9
$r(C_2–C_6)$	2.479	2.486	2.465	1.505	1.519	1.515
θ[f]	114.2	114.9	114.7	61.9	62.1	63

[a] Not all the geometrical parameters are listed. The optimizations were, however, completely carried out within the given symmetry constraint. [b] Bond lengths in angstroms and bond angles in degrees. [c] The uncertainties are in the range 0.01–0.03 Å for bond lengths and 1–2° for bond angles. [d] References 7 and 8. [e] Reference 9. [f] θ is the angle between the planes $C_1C_2C_3C_4$ and $C_1C_6C_5C_4$.

Nuclear spin polarization (CIDNP) effects observed for N and Q have been interpreted[25,26] in terms of the relative spin densities of N^+ and Q^+. Theory can be applied to calculate such contact spin density contributions and hence used in confirmation of spectral assignments.

Another exciting aspect of the chemistry of N and Q is the interesting triplet-state photochemistry observed for this system.[6] Under triplet-sensitized (or direct triplet excited) conditions, N is converted with a very high yield (≃90%) to Q. The reverse reaction, i.e., conversion of Q to N, can be achieved thermally or in the presence of a transition-metal catalyst. Hence a thermochemical cycle can be established and this may be useful in energy storage and release under appropriate conditions.[6]

Turro et al.[6] have proposed that the triplet diradical formed from N is preferentially funneled from the triplet surface into the Q well. However, detailed understanding of the triplet state and the nature of the triplet minimum is lacking.

One of the important aims of this paper is to study the neutral systems N and Q, the ionic systems N^+ and Q^+, and the triplet state T at a uniform level of theory. We have used fairly large basis sets and sophisticated theoretical methods so that both structural and energetic information can be obtained accurately. The nature of the triplet state and the reason for the preferential conversion of such a state to Q are studied in detail. Spin density contributions are calculated and compared to the proton NMR spectra seen in CIDNP experiments.

Computational Methods

The Hartree–Fock (HF) method was used as the starting point throughout. For radical cations and triplet states, the spin-unrestricted version of the Hartree–Fock method was used. Preliminary investigations of the potential energy surface were carried out with the minimal STO-3G basis set[27] and initial geometries were determined at this level. The geometries of all the stationary points were then reoptimized with the split-valence 6-31G basis set.[28] These geometries were used for single-point calculations with the polarized 6-31G* basis set.[29] This basis set, which includes *d* functions on C (involving a total of 121 basis functions) is known to reliably describe the relative energetics of cyclic and noncyclic hydrocarbons.[29] In addition, effects of electron correlation were included by second order Møller–Plesset perturbation theory (MP2)[30,31] with the 6-31G basis. This correlation correction was then coupled with the 6-31G* calculations to give projected MP2 results with the 6-31G* basis.

Results and Discussion

Structures and Relative Energies of N and Q. The structures of both N and Q have been characterized experimentally by gas-phase electron diffraction.[7,9] The relative proton positions in N have also been determined by NMR studies of N partially oriented in a nematic phase.[8] Theoretically, the structure of N has been determined previously by different methods (STO-3G,[17] molecular mechanics,[18] and MINDO/3[21]). The structure of Q has been calculated with the semiempirical MINDO/3 method[21] and recently with a 4-21G basis.[19] Some of our calculated geometrical parameters are listed along with the experimentally determined values in Table I. The calculated relative energies at several levels of theory with these geometries are given in Table II.

Table II. Total and Relative Energies of N and Q Calculated at Various Theoretical Levels

theoretical method	total energy, hartrees		relative energy, kcal/mol	
	N	Q	N	Q
HF/STO-3G[a]	−266.42259	−266.41445	0	5.1
HF/6-31G[b]	−269.54545	−269.49220	0	33.4
MP2/6-31G[b]	−270.16501	−270.10421	0	38.2
HF/6-31G*[b]	−269.65217	−269.61725	0	21.9
MP2/6-31G*[b]			0	(26.7)[c]
expt			0	22 ± 1[d]

[a] Using STO-3G geometries. [b] Using 6-31G geometries. [c] Values in parentheses are projected estimates. [d] References 10–12.

It can be seen from Table I that all the geometrical parameters are described very well by theory. Even at the minimal STO-3G level, excellent agreement with experiment is obtained. In particular, all the bond angles (including the angles which are not listed) are calculated to be within the uncertainties of the experiment, even at this simple level of theory. The calculated 6-31G values do not change significantly from the STO-3G values though improvement is obtained for some bond lengths (e.g., $C_2–C_3$ in N which increases from 1.311 to 1.326 Å). Most of the calculated C–C bond lengths at this level are also within the experimental uncertainties (which mostly range from 0.01 to 0.03 Å). The calculated C–H distances with the 6-31G basis (not listed) are typically too short by ≃0.02 Å. This is partly due to the neglect of electron correlation in the determination of the theoretical geometries and partly due to vibrational effects which significantly affect the experimental C–H bond length determinations.[19]

The energy difference between N and Q is a sensitive test of the level of theory used in the calculations. Experimentally, thermochemical measurements of the energy difference[10–12] have obtained N to be 22 ± 1 kcal/mol more stable than Q, though a higher value of 27 kcal/mol has been reported[13] in a study of catalyzed N → Q isomerization. Previous MINDO/3 determinations[21] give only a small energy difference due to the well-known deficiency of semiempirical methods to overestimate the stability of three-membered rings.

Our calculated energy differences are listed in Table II. At the STO-3G level, N is calculated to be only 5.1 kcal/mol more stable than Q. This deficiency of the STO-3G basis is similar to that of semiempirical methods. At the HF/6-31G level the calculated difference (33.4 kcal/mol) is slightly overestimated. This tendency of the 6-31G basis to slightly underestimate the stability of three-membered rings has been noted before.[29] For example, cyclopropane is calculated to be 12.5 kcal/mol less stable than propene at this level, whereas the experimental value is only 7.4 kcal/mol. This is principally due to the neglect of *d*-type polarization functions on carbon. At the polarized HF/6-31G* level, the energy difference falls to 21.9 kcal/mol, bringing it into the experimental range. Electron correlation effects, calculated

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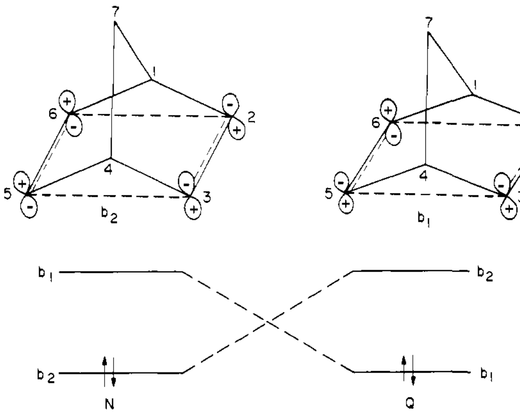


Figure 1. Schematic representation of the orbitals b_2 and b_1 (top) and their occupation in N and Q (bottom). Only the phases of the orbitals are shown to illustrate their bonding nature. The contributions of carbon p orbitals are shown. The symmetry allowed mixing of other atomic orbitals is not illustrated.

Table III. Calculated Geometries for N^+ and Q^+ [a,b]

geometrical parameter	norbornadiene cation		quadricyclane cation	
	STO-3G	6-31G	STO-3G	6-31G
$r(C_1-C_7)$	1.553	1.551	1.538	1.527
$r(C_1-C_2)$	1.535	1.528	1.513	1.505
$r(C_2-C_3)$	1.370	1.371	1.491	1.475
$\angle(C_1-C_7-C_4)$	94.4	94.1	98.0	98.0
$\angle(C_6-C_1-C_2)$	94.6	96.9	66.5	69.2
$r(C_2-C_6)$	2.256	2.287	1.660	1.710
θ [c]	100.6	103.1	69.6	72.5

[a] Not all geometrical parameters are listed. The optimizations were, however, carried out completely within the given symmetry constraint. [b] Bond lengths in angstroms and bond angles in degrees. [c] θ is the angle between the planes $C_1C_2C_3C_4$ and $C_1C_6C_5C_4$.

Table IV. Total and Relative Energies of N^+ and Q^+ Calculated at Various Theoretical Levels

theoretical level	total energy, hartrees		relative energy, kcal/mol	
	N^+	Q^+	N^+	Q^+
HF/STO-3G[a]	−266.20484	−266.20139	0	2.2
HF/6-31G[b]	−269.28262	−269.24777	0	21.9
MP2/6-31G[b]	−269.87653	−269.84331	0	20.8
HF/6-31G*[b]	−269.39527	−269.37647	0	11.8
MP2/6-31G*[b]			0	(10.7)[c]
expt			0	9[d]

[a] Using STO-3G geometries. [b] Using 6-31G geometries. [c] Values in parentheses are projected estimates. [d] References 10-12 and 21.

at the MP2/6-31G level, used in conjunction with the HF/6-31G* results worsen the agreement somewhat and give a projected energy difference of 26.7 kcal/mol. This is slightly higher than the experimental value of 22 kcal/mol but is within the expected uncertainty of the calculations performed at this level of theory (±5 kcal/mol).

The orbitals which are important for the chemistry of N and Q are the b_2 and b_1 orbitals shown in Figure 1. The b_2 orbital has bonding character between C_2 and C_3 but is antibonding between C_2 and C_6. N has two electrons in this orbital (highest occupied molecular orbital, HOMO) and this is responsible for the long C_2–C_6 distance in N (2.49 Å calculated with the 6-31G basis). The b_1 orbital is bonding between C_2 and C_6 and antibonding between C_2 and C_3. This orbital, which is doubly occupied in Q, is responsible for the short C_2–C_6 distance in Q (1.52 Å). It is clear that the interconversion between N and Q on the singlet C_{2v} potential surface involves a crossing between these two orbitals and hence has a significant barrier.

Structures and Relative Energies of N^+ and Q^+. As is typical in gas-phase ion chemistry, no information about the structures of the ions is known experimentally, though the energetics have been determined. The photoelectron spectra of N and Q[21-24] and the recent observation of different nuclear spin polarization patterns for N and Q[25,26] clearly reveal the existence of two different radical cations. This is compatible with simple molecular orbital ideas. N^+ has one electron in the b_2 orbital and hence has $^2B_2$ symmetry. Q^+ has one electron in the b_1 orbital resulting in $^2B_1$ symmetry. Hence, the interconversion between N^+ and Q^+ (within C_{2v} symmetry) also involves an orbital crossing,[20] but the barrier is likely to be smaller.[21]

Some of our geometrical parameters at the STO-3G and 6-31G levels are listed in Table III. These correspond to symmetrical (C_{2v}) structures for both cations. However, at the STO-3G level, the most stable structure for both cations has a strongly distorted C_s symmetry. However, this seems to be due to theoretical limitations at this level. At the 6-31G level, N^+ adopts a symmetrical C_{2v} structure but Q^+ still has a very small C_s distortion (the energy gained by such a distortion is only 0.2 kcal/mol). Calculations with electron correlation at the MP2/6-31G level reveal that even Q^+ has a symmetrical C_{2v} structure. Hence only the structures optimized with imposed C_{2v} symmetry are shown in Table III. It can be seen later that in the case of the triplet state, the symmetry is indeed reduced to C_s.

It should be remembered that the C_s distortions considered above still do not mix the $^2B_1$ and $^2B_2$ states. Hence an orbital crossing still persists and contributes significantly to the barrier separating Q^+ from N^+. We have also considered other modes such as C_2 or C_1 distortions which allow mixing between the $^2B_1$ and $^2B_2$ configurations. One might imagine that such distortions could allow a lower energy pathway for the crossing over of Q^+ to N^+. However, our calculations indicate that Q^+ is stable toward such distortions which cause the energy to increase. In fact, complete analytical evaluation of the force constants for Q^+ confirms that it is a local minimum on the potential surface. We did not, however, attempt to determine the magnitude of the barrier separating Q^+ from N^+.

The calculated geometrical parameters reveal that ionization of N and Q brings the cations structurally closer to each other. This has been pointed out before by Haselbach et al. from their MINDO/3 calculations.[21] This can be illustrated by taking the distance $r(C_2–C_6)$ as a reaction coordinate. N and Q have values of the reaction coordinate of 2.49 and 1.52 Å, respectively, at the 6-31G level. The corresponding values for N^+ and Q^+ are closer, viz. 2.29 and 1.71 Å. However, our calculated change in the reaction coordinate on ionization is significantly different from the previous MINDO/3 calculations.[21] For example, the difference in the reaction coordinate between N and N^+ is 0.20 Å at the 6-31G level whereas the MINDO/3 value is 0.33 Å. In the case of Q and Q^+, the 6-31G value of the difference is 0.19 Å whereas the MINDO/3 value is only 0.10 Å. Both deviations are principally due to the overestimation of the stability of three-membered rings by the MINDO/3 method. As expected, the STO-3G values lie between the MINDO/3 and 6-31G values.

Inspection of Table III reveals that the other geometrical parameters also behave in a similar manner. For example, the bond length $r(C_2–C_3)$ in both N^+ and Q^+ (1.37 and 1.48 Å, respectively) is intermediate between that of N and Q (1.33 and 1.55 Å corresponding to a double and single bond, respectively). θ, the angle between the planes $C_1C_2C_3C_4$ and $C_1C_6C_5C_4$, exhibits a similar behavior.

The energy difference between N^+ and Q^+ is known experimentally from the ionization potentials of N and Q (8.43 and 7.86 eV, respectively) measured by photoelectron spectroscopy.[21] Again, N^+ is known to be more stable and the experimental value of the energy difference is 9 kcal/mol.[21] This is very similar to the solution data (7 kcal/mol) based on the measured oxidation potentials[24] of N and Q. Previous MINDO/3 calculations[21] give the wrong ordering, predicting Q^+ to be more stable. However, the same authors report that MNDO calculations give the correct ordering.

Table V. Geometries Calculated for the Triplet State with the 6-31G Basis[a,b]

geometrical parameter	triplet structure T_1	T_2
$r(C_1-C_7)$	1.531	1.551
$r(C_4-C_7)$	1.557	1.551
$r(C_1-C_2)$	1.514	1.534
$r(C_1-C_6)$	1.514	1.532
$r(C_3-C_4)$	1.534	1.534
$r(C_2-C_3)$	1.491	1.549
$r(C_5-C_6)$	1.491	1.333
$r(C_2-C_6)$	1.561	2.420
$r(C_3-C_5)$	2.365	2.420
$\angle(C_1-C_7-C_4)$	96.8	94.0
$\angle(C_6-C_1-C_2)$	62.0	104.2
$\angle(C_5-C_4-C_3)$	100.9	104.2

[a] Not all geometrical parameters are listed. The geometries were, however, completely optimized within the given symmetry constraint. [b] Bond lengths in angstroms and bond angles in degrees.

Table VI. Total and Relative Energies (with Respect to N) Calculated for the Triplet State

theoretical level	total energy, hartrees T_1	T_2	relative energy, kcal/mol T_1	T_2
HF/6-31G	−269.48668	−269.47888	36.9	41.8
MP2/6-31G	−270.06110	−270.05325	65.2	70.1
HF/6-31G*	−269.60051	−269.58774	32.4	40.4
MP2/6-31G*			(60.7)[a]	(68.7)[a]

[a] Values in parentheses are projected estimates.

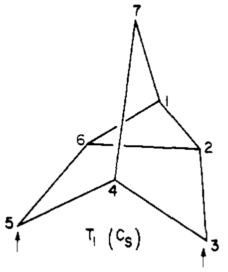
Our calculations at different levels of theory are listed in Table IV. The behavior is similar to that seen earlier in the case of the neutral N and Q. At the STO-3G level, N^+ is only 2.2 kcal/mol more stable than Q^+, but even at this simple level of theory, the correct ordering is obtained. At the 6-31G level, the energy difference (21.9 kcal/mol) is again overestimated. Inclusion of polarization functions at the 6-31G* level results in a enery difference of 11.8 kcal/mol, bringing it closer to the experimental value. When electron correlation effects are included at the MP2/6-31G level, the final projected energy difference of 10.7 kcal/mol is obtained, in good agreement with experiment.

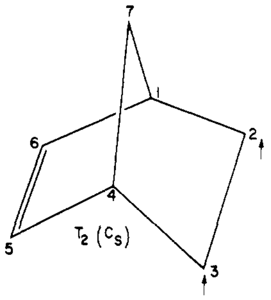
Nature of the Triplet State and Photochemistry of Interconversion of N and Q. The photochemical rearrangement of N to Q is well-known.[6] Under triplet-sensitized excitation (as well as upon direct $S_0 \rightarrow T_1$ excitation) of N, a high yield ($\simeq$90%) of Q is obtained. Turro et al.[6] proposed that the triplet diradical formed from N (or Q) is preferentially funneled from the triplet surface into the Q well.

We have extended our calculations to characterize the nature of the triplet state in order to understand this interconversion of N to Q. Simple inspection of the molecular orbitals important for the chemistry of N and Q (Figure 1) reveals that the triplet state resulting from N or Q has one electron in the b_2 orbital and one electron in the b_1 orbital (within C_{2v} symmetry) resulting in an overall $^3A_2$ symmetry. Hence, both N and Q may be expected to have a common triplet state whose geometry is intermediate between that of N and Q. This is indeed found to be the case with the triplet state (within C_{2v} symmetry) having a single minimum intermediate between N and Q. Since such a state is shared between N and Q, the triplet photochemistry of N and Q may be expected to be the same. While these aspects are indeed true, some important modifications seem necessary. In particular, such a C_{2v} triplet state does not explain the most important aspect of the triplet photochemistry, viz. preferential conversion to Q. On the contrary, such a structure is still dominated by the orbital correlating with the HOMO of N (namely b_2) and on conversion to the singlet surface would preferentially convert to N (the orbital energy for the b_2 orbital, -8.2 eV, is considerably lower than that of the b_1 orbital, -5.6 eV). In other words, such a triplet state lies much closer to N than Q. Thus the reaction coordinate previously has a value of 2.16 Å for such a triplet state with the corresponding values for N and Q being 2.49 and 1.52 Å, respectively. The location of the singlet barrier for the interconversion of N and Q is also important is this context, but we did not determine tha precise location of such a transition state. However, preliminary investigation at the HF level with complex molecular orbitals indicates that the singlet transition state has a reaction coordinate in the range 1.9–2.0 Å. Hence the symmetrical triplet states lies on the N side of the barrier and this again indicates that on crossing over to the singlet surface, it would preferentially give N. The same result is obtained with the 6-31G basis if the energy of the C_{2v} triplet structure is considered with the orbitals populated so as to correlate with N (46.2 kcal/mol above N) and Q (158.3 kcal/mol above N).

The above discussion illustrates that the symmetrical C_{2v} triplet state is not responsible for the conversion of N to Q. Consideration of structures with lower symmetries immediately shows that unlike the neutral N or Q, or the ionic N^+ or Q^+, the triplet state distorts very strongly to lower symmetries. This effect remains even with the larger 6-31G basis set and hence is not due to basis set limitations. In fact, the lower symmetry C_s triplet considered below is 28.7 kcal/mol lower in energy than the C_{2v} structure at the 6-31G level. Hence the symmetrical structure is not considered any further.

We considered two different C_s forms of the triplet state which may be approximately represented as follows:





The two triplets result from the two possible C_s distortions of the symmetric C_{2v} form. (We have also considered the diagonal C_2 distortion but this does not result in lower energies and leads back to the C_{2v} structure.) Both triplets have one unpaired electron in an orbital symmetric with respect to its plane of symmetry and the other unpaired electron in an antisymmetric orbital. One of these orbitals correlates with the orbital occupied in N and the other singly occupied orbital correlates with the orbital occupied in Q.

Both triplets, T_1 and T_2, are considerably more stable than the C_{2v} triplet (by 28.7 and 23.8 kcal/mol, respectively) at the HF/6-31G level. The two optimized structures are listed in Table V. It is possible that optimization of the structures with the inclusion of electron correlation might modify the geometries somewhat, but the essential features are not likely to change.

T_1 is the most stable structure for the triplet. It has an almost completely formed bond between C_2 and C_6 ($r(C_2-C_6)$ = 1.56 Å). The bond between C_2 and C_3 is just beginning to develop a double-bonded character ($r(C_2-C_3)$ = 1.49 Å compared to its value of 1.55 Å in Q). The other triplet, T_2, has a double bond between C_5 and C_6 ($r(C_5-C_6)$ = 1.33 Å) but has only a single bond between C_2 and C_3 ($r(C_2-C_3)$ = 1.55 Å).

The total and relative energies (relative to N) of the triplets are listed in Table VI. Even at the polarized HF/6-31G* level T_1 is only 32 kcal/mol higher than N. This is principally due to the deficiency of unrestricted Hartree-Fock theory which favors higher multiplicities. Inclusion of electron correlation favors N considerably and T_1 is calculated to be 61 kcal/mol higher at the projected MP2/6-31G* level. T_2 is 8 kcal/mol less stable and lies 69 kcal/mol above N. However, since a change in the multiplicity is involved, the uncertainty involved in the calculation of the singlet-triplet separation is expected to be much higher. Larger basis sets and higher levels of electron correlation may

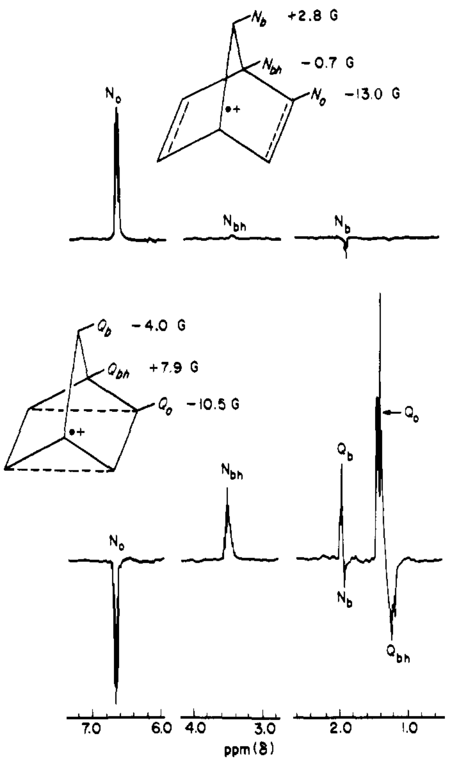


Figure 2. Calculated hyperfine coupling constants for the radical cations of N (top) and Q (bottom) and nuclear spin polarization effects ascribed to the intermediacy of these cations. For the comparison of the observed enhancements with the calculated hyperfine coupling constants it has to be noted that there are four protons of type N_o and Q_o but only two of types N_b, Q_b and N_{bh}, Q_{bh}, respectively.

be necessary to yield an accurate estimation of this difference.

Even though we have calculated two different C_s structures for the triplet state, it is only the lower T_1 state which is significant. It should be remembered that they are two different distortions of the same symmetric structure. We have not attempted to determine the interconversion pathways of the two different structures but interconversion through distortion to a lower C_1 symmetry is possible.

Inspection of the nondegenerate singly occupied orbitals in T_1 reveals that the orbital correlating with the HOMO of Q (b_1) is more favorable than the orbital correlating with the HOMO of N (b_2). In other words at this triplet geometry, the singlet formed by occupation of two electrons in the orbital correlating with b_1 is much more stable than the singlet formed by occupation of two electrons in the orbital correlating with b_2 (by 22.6 kcal/mol with the 6-31G basis). This suggests that when this triplet crosses over to the singlet surface, it would preferentially form Q. Hence the predominant interconversion of N to Q in the triplet state can be explained only by the distorted nature of the structure of the triplet state which funnels electrons preferentially to the orbital which correlates with the HOMO of Q.

Spin Densities of N^+ and Q^+ and CIDNP Spectra. Nuclear spin polarization effects have been observed in the case of both N and Q.[25,26] Roth et al.[25] have observed different proton NMR spectral patterns for the two hydrocarbons in their CIDNP experiments and have interpreted the relative enhancements in terms of the relative hyperfine coupling constants for the bridgehead (bh), bridge (b), and olefinic/cyclobutane (o) protons.

We have calculated the contact spin density contributions to the hyperfine coupling constants of the different protons in N^+ and Q^+ in order to understand and confirm the experimental assignments. In general, the use of Gaussian basis sets such as the ones used in this study may not be sufficient to accurately calculate nuclear properties. However, in the case of small hydrocarbon radicals Chipman[32] has calculated spin-projected Hartree–Fock calculations of spin densities with a variety of basis sets and obtained good agreement with experiment. We have used unrestricted Hartree–Fock theory without spin-projection to calculate the contact spin density contributions to the hyperfine coupling constants. Typically such calculations have significant contaminations from higher multiplicities and give proton hyperfine coupling constants too high compared to experiment.[32] However, both N^+ and Q^+ are almost pure doublets (as can be seen from the S^2 value of $\simeq 0.76$ which is very close to the pure doublet value of 0.75) and contaminations from higher multiplicities should be very small. Also we compare only the *relative* spin density contributions of the different kinds of protons in the two cations with experiment and, as can be seen below, these methods do seem adequate for such purposes.

The calculated hyperfine coupling constants for the different protons in N^+ and Q^+ are given in Figure 2 along with the nuclear spin polarization effects ascribed to the intermediacy of these cations. For the comparison of the observed enhancements with the calculated hyperfine coupling constants it has to be noted that there are four protons of type o but only two of types b and bh, respectively. In the case of N^+, most of the calculated spin density contribution (with the 6-31G* basis) is at the olefinic position. All the relative signs and magnitudes are in excellent agreement with the experimental assignments. In the case of Q^+, the spin density contribution is not dominated by any one proton position. Again the cyclobutane positions have the maximum contribution but the contributions of the other positions are also significant. The relative signs as well as the magnitudes are again in excellent agreement with the experimental assignments. The above results show that such computations may be of value in spectral assignments, at least in the case of proton NMR spectra.

Conclusions

The optimized structures of N and Q are calculated and found to be in excellent agreement with those determined from electron diffraction experiments. N is calculated to be 27 kcal/mol more stable than Q, slightly higher than the known thermochemical measurements. Detailed structural information which is not available experimentally is provided for both cations. N^+ is calculated to be 11 kcal/mol more stable than Q^+, in good agreement with the experimental value. The nature of the triplet state is investigated in detail. Both N and Q are found to share a common triplet state. The structure of the triplet state is found to be distorted to a symmetry (C_s) lower than that of the parent compounds (C_{2v}). An analysis of the orbital correlations for such a distorted triplet state reveals that conversion to Q on the singlet surface is more favorable than conversion to N. This explains the photochemical observations that reveal that the triplet state converts with a high yield ($\simeq 90\%$) to Q. Thus, at the same uniform level of theory, interesting aspects of the chemistry of N and Q, the radical cations N^+ and Q^+, and the triplet state can be understood in detail.

Registry No. N, 121-46-0; Q, 278-06-8; N^+, 41153-22-4; Q^+, 70254-62-5.

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[32] Chipman, D. M. *J. Chem. Phys.* **1979**, *71*, 761 and references therein.