61. Studies on Radical Cations, III.
The Type C Valence-Isomeric System Quadricyclane Radical Cation/Norbornadiene Radical Cation[1]

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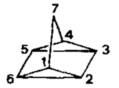
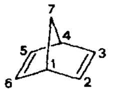
Summary

The previously discussed principles involved in electrocyclic reactions of open-shell ions are exemplified for a type C system, the radical cation couple quadricyclane^{+} (**Q**$^{+}$)/norbornadiene^{+} (**NBD**$^{+}$). Exhaustive calculations (MINDO/3) for the various states of the ions support the general predictions for such types of systems. The barrier of interconversion **Q**$^{+}$ → **NBD**$^{+}$ is estimated to be significantly lower than that for the corresponding neutrals. Experimental support to this prediction is obtained by γ-irradiation of **Q** or **NBD** in an electron scavenging matrix. In both cases only **NBD**$^{+}$ is observed, indicating that **Q**$^{+}$ is not stable at 77 K. Previous observations and propositions referring to the system **Q**$^{+}$/**NBD**$^{+}$ are discussed in view of the present findings.

Introduction. - In the previous paper of this series [1] we have discussed some principles pertaining to electrocyclic processes of open-shell cations. The present paper exemplifies a type C process using as substrates the radical cation couple quadricyclane^{+} (**Q**$^{+}$)/norbornadiene^{+} (**NBD**$^{+}$).



Q



NBD

Results and discussion. - *Thermochemical and PES. data relevant to* **Q**$^{+}$ → **NBD**$^{+}$. Recent work has established ΔH_{r}° (**Q** → **NBD**) = -113.5 kJ mol^{-1} [2]. Using benzene as calibration standard for the PE. spectra of **Q** and **NBD**, we have found I_{1}^{a} (**Q**) = 7.86 eV, I_{1}^{a}(**NBD**) = 8.43 eV[2]. These data yield ΔH_{r}°(**Q**$^{+}$ → **NBD**$^{+}$) = -54.4 kJ mol^{-1}, *i.e.*

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[1] Part II of this series: [1].

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[2] These values differ somewhat from those reported earlier [4-6], presumably due to the fact that the latter were based on calibration peaks situated at higher energies, concommitant with greater influence from scale non-linearities.

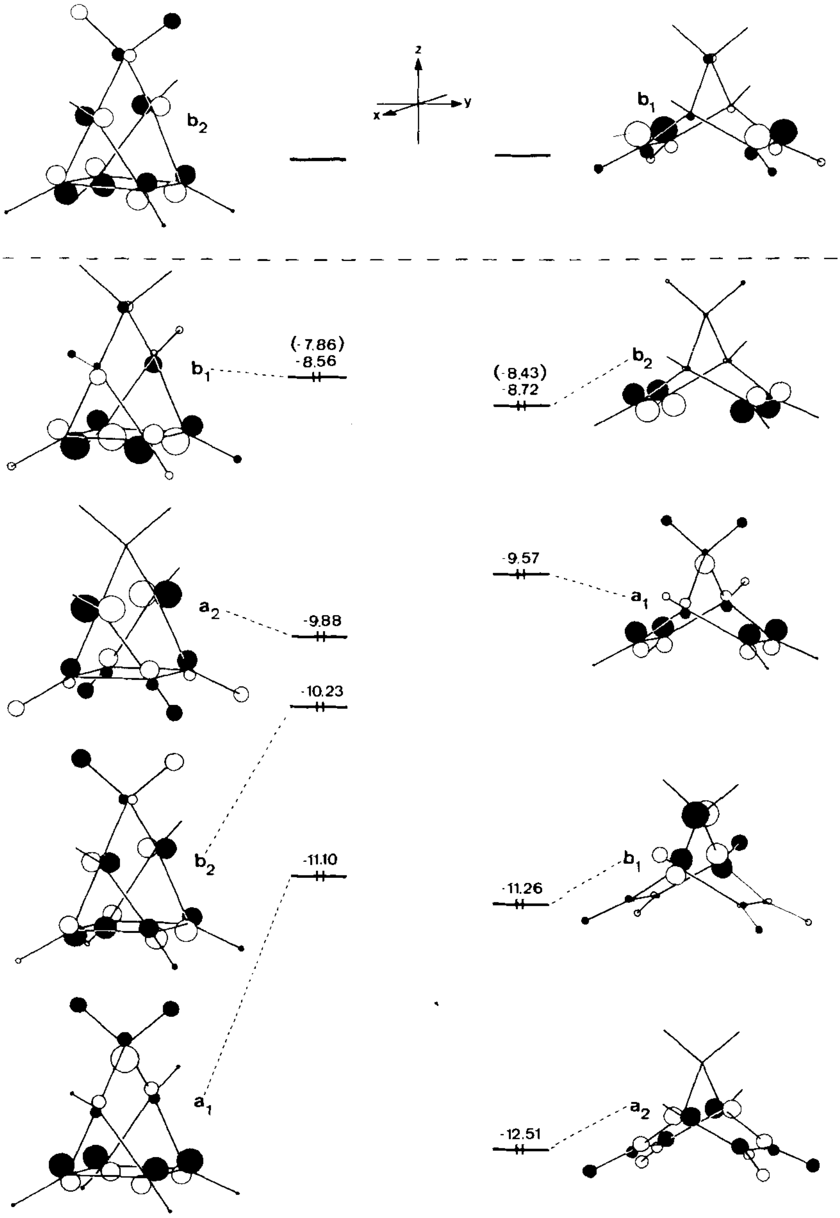

Fig. 1. *Energies, symmetry species and MOPLOT-representations* [3] *for some high lying MO's of* Q *and* NBD *from PES.* (I^a-values in parentheses)

the reaction is also exothermic for the ions. The difference in heat capacities of the two neutrals [2] indicates that the same will also hold at 77 K.

Figure 1 shows energies (from PES.), symmetry species and MOPLOT-representa-

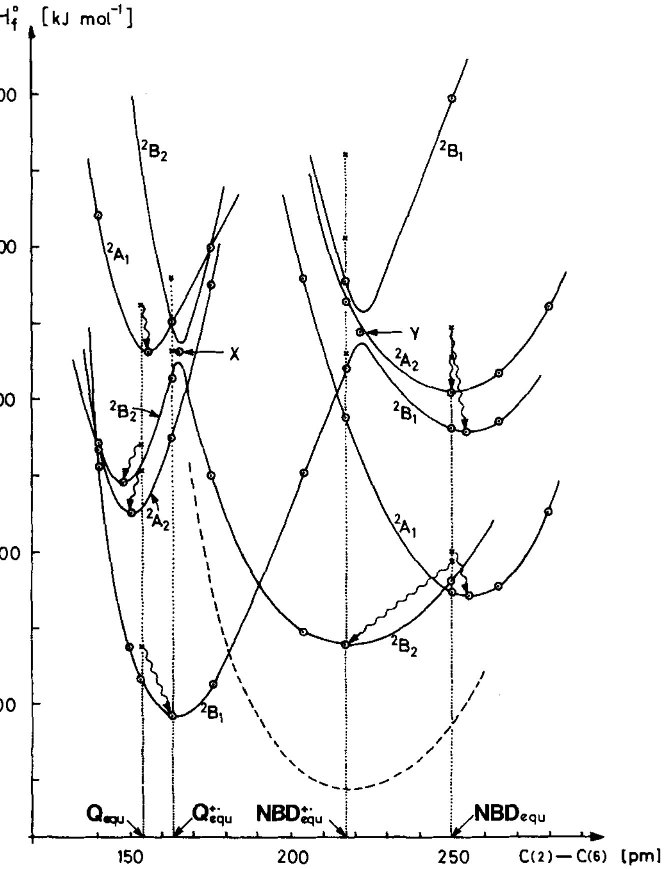

Fig. 2. *MINDO/3-potential surfaces for* $Q^+ \rightarrow ND^+$ (see text). ⊙: Optimized structures for given value of C(2)–C(6) ×: Vertically produced ions having same structure as optimized **NBD** or **Q**

tion [3] (based on MINDO/3-results) for some of the high lying occupied MO's of **Q** and **NBD** [5] [6][3]).

MINDO/3-potential surfaces for $\mathbf{Q}^+ \rightarrow \mathbf{NBD}^+$. *Figure 2* displays the results of an exhaustive investigation on the potential surfaces of various states of $\mathbf{Q}^+$ and $\mathbf{NBD}^+$ using the MINDO/3-method [8]. Every circled point corresponds to a geometry optimized in C_{2v} for the given value of the C(2)–C(6) reaction coordinate q^+. The *Table* lists some pertinent structural data of the species at the various potential minima.

Calculatory details. In order to calculate a state of a given symmetry the program is supplied with a set of signs of preferably large AO-coefficients characterizing the nodal structure of the MO from which ionization is intended to occur. After every iteration step the program checks the new eigenvectors against this pattern of signs starting from the closed-shell HOMO (or LUMO in the case of 'non-*Koopmans*'-configurations) and moving downwards along the scale of orbital energies until an MO shows the required disposition of AO-coefficients. This MO is then occupied by a single electron.

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[3]) Note [7] for other work relating the orbital structure of **Q** and **NBD** to various experimental observations.

Table. *Equilibrium geometries* (pm) *calculated by MINDO/3 for* **NBD** *and* **Q** *and for various states of their radical cations* **NBD**$^+$ *and* **Q**$^+$ (Exper. values in parentheses)

		C(2)–C(6)	C(2)–C(3)	C(1)–C(2)	C(1)–C(7)	C(1)–C(4)
Q	$^1A_1$	153	155	154	153	232
		(152)	(156)	(151)	(154)	(233) [9]
Q$^+$	$^2B_1$	163	149	153	155	235
	$^2A_2$	150	153	159	152	229
	$^2B_2$	148	160	156	151	231
	$^2A_1$	156	158	152	155	245
NBD	$^1A_1$	250	136	154	157	225
		(245)	(134)	(153.5)	(157)	(226) [10]
NBD$^+$	$^2B_2$	217	140	153	156	231
	$^2A_1$	255	139	151	159	235
	$^2B_1$	255	135	154	160	208
	$^2A_2$	250	135	154	156	224

Since convergence can sometimes not achieved for excited configurations of open-shell systems (especially 'non-*Koopmans*'-configurations), a remark is indicated on the techniques employed to perform these calculations. One of the main reasons for failure is that the symmetry of the wave functions is destroyed by rounding errors that are picked up and accumulated mainly during diagonalization. Whereas in closed-shell calculations these errors are smoothed out during the next SCF-cycle, open-shell systems often prove to be unstable with respect to such perturbations.Therefore, a routine was designed which in every SCF-step averages all elements of the F-Matrix that ought to be identical (apart from their sign) owing to the symmetry of the system. For configurations that still escape convergence under these circumstances a trick has to be applied which consists in a stepwise depopulation of the chosen MO by performing SCF-calculations with fractional occupation numbers. The SCF density matrix resulting for a given occupation number always serves as a first guess for the next SCF-calculation with a lower occupation number, until the ultimate value of 1.0 is reached.

A somewhat special situation is encountered in the case of states which are not the lowest ones of their symmetry. Variational procedures should not be used but for the lowest lying state of a given symmetry because the variational principle does not hold for higher states. However, our calculations involve geometry optimization which allows us to follow a potential valley along a reaction coordinate up to values for which an other state of the same symmetry has a lower energy at its relaxed geometry. But since for every new step along this reaction coordinate the SCF-density matrix of the previous point is used as a first guess, the procedure does sometimes only lately on the reaction coordinate 'recognize' that there exists an energetically more favourable electronic configuration of the same symmetry to which it will then drop down. By this 'sneaking' approach energies of higher lying configurations of a given symmetry are obtained in favourable cases.

The well known tendency of MINDO/3 to overestimate the stability of small ring compounds is apparently reflected also for radical cations, as **Q**$^+$ is erroneously predicted to be more stable than **NBD**$^+$ 4)). Equally disagreeing with experiment is the result that the relaxation energy of the ground state ions (*i.e.* I_1^v-I_1^a) is larger for **NBD**$^+$ than for **Q**$^+$ (compare *Fig. 1*). Finally, vertically produced **NBD**$^+$ ($^2A_1$) is calculated to be almost isoenergetic to **NBD**$^+$ ($^2B_2$) whereas I_2^v-$I_1^v = 0.85$ eV is found for **NBD** [6]. These failures for **NBD**$^+$ may be corrected if the $^2B_2$-curve is adjusted as shown by the dotted line. Note that it goes over into $\psi^*_{NK}(^2B_2)$ of **Q**$^+$ (*NK*: 'non-*Koopmans*', see [1]).

For **Q**$^+$ the diagram contains no evident contradictions to experimental facts, although one might note that the sequence of the first two excited states is predicted to

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4)) Recent MNDO-calculations for the ground state process **Q**$^+$ → **NBD**$^+$ [11] yield, however, a reaction enthalpy in good agreement with the experimental value deduced earlier in this paper.

be $^2A_2$ below $^2B_2$, which contrasts with the ordering proposed from MINDO/2-calculations in [5]. Notably, SPINDO- and MNDO-calculations give the same ordering as MINDO/3.

In spite of these shortcomings the results support what was qualitatively predicted in [1] for a type C reaction:

(i) The ground states of $\mathbf{Q}^+$ and $\mathbf{NBD}^+$ have different electronic symmetries, their least-motion interconversion being therefore *S*tatesymmetry *F*orbidden *(SF)*. Note that even the intervention of a non totally symmetric b_1-mode, rendering C(2)–C(6) and C(3)–C(5) bond rupture non-synchronous, would not lead to avoided crossing of the potential curves.

The ground configuration surfaces for $\mathbf{Q}^+$ and $\mathbf{NBD}^+$ do not correlate directly with the lowest lying $\psi^*_K(\mathbf{NBD}^+)$, $\psi^*_K(\mathbf{Q}^+)$, but with higher lying $\psi^*_{NK}(\mathbf{NBD}^+)$, $\psi^*_{NK}(\mathbf{Q}^+)$ of the same symmetry, respectively. As indicated in *Figure 2* (and *Fig. 4b* in [1]) CI. will eventually lead to correlation between the ground states and those states dominated by ψ^*_K. As a result of this feature, however, these ions rearranging along a C-type path exhibit low lying states which are non-dissociative with respect to the envisaged reaction coordinate.

(ii) Inspection of the *Table* and *Figure 1* reveals that ionic relaxation (with respect to the neutral ground states) occurs precisely in the directions indicated by the partial bond orders of the MO's from which ionization is effected. Note especially that $\Delta q^+ = 54$ pm for ground state $\mathbf{Q}^+/\mathbf{NBD}^+$, whereas $\Delta q^o = 97$ pm for **Q/NBD**. Hence, as predicted qualitatively in [1], ionization of the reactants leads for each of them to a structural relaxation directed toward the geometry of its counterpart, thus shortening q of the type C reaction and decreasing the thermal barrier. This feature is unique for the ground states of the ions, as all their excited states have their minima at C(2)–C(6) values closer to those for the neutrals.

The above points lead us to predict that the barrier for $\mathbf{Q}^+ \rightarrow \mathbf{NBD}^+$ is significantly reduced if compared to that for $\mathbf{Q} \rightarrow \mathbf{NBD}$, in agreement with the general arguments for type C ionic processes given in [1]. From *Figure 2* we deduce $\Delta H^{\ddagger}$ somewhere around 40 kJ mol^{-1} for $\mathbf{Q}^+ \rightarrow \mathbf{NBD}^+$, *i.e.* very much less than observed for $\mathbf{Q} \rightarrow \mathbf{NBD}$ ($\Delta H^{\ddagger} = 156.9$ kJ mol^{-1} [2]). Evidently, a major reason for this outcome is the almost 50% shortening of the reaction coordinate q^+ with respect to q^o as discussed in (ii). To investigate this aspect separately we assumed the C(2)–C(6) motion to be harmonic and the transition state to lie at the intersection of the parabolas. The ratio of the corresponding force constants for both **Q/NBD**, or $\mathbf{Q}^+/\mathbf{NBD}^+$, was taken as the square of the ratio of frequencies for $\nu_{11}(e')$ of cyclopropane [12] and $\nu_9(a_1)$ of propane [12]. With q^o, q^+ from the *Table* and the above given ΔH_1- and $\Delta H^{\ddagger}$-values, $\Delta H^{\ddagger}$ $(\mathbf{Q}^+ \rightarrow \mathbf{NBD}^+) = 48$ kJ mol^{-1} follows, indicating the importance of reaction coordinate shortening after ionization.

Concerning the significance of the calculations. All calculated points given in *Figure 2* correspond to optimized C_{2v}-geometries. Hence, points of intersection of different surfaces do not correspond to common geometries. Since all bonds and angles in a molecule undergoing isomerization will change continously, the system, at a certain point on the reaction coordinate, must leave its most favourable C_{2v}-structure in order to pass from one state to the other. Therefore, the height of a cros-

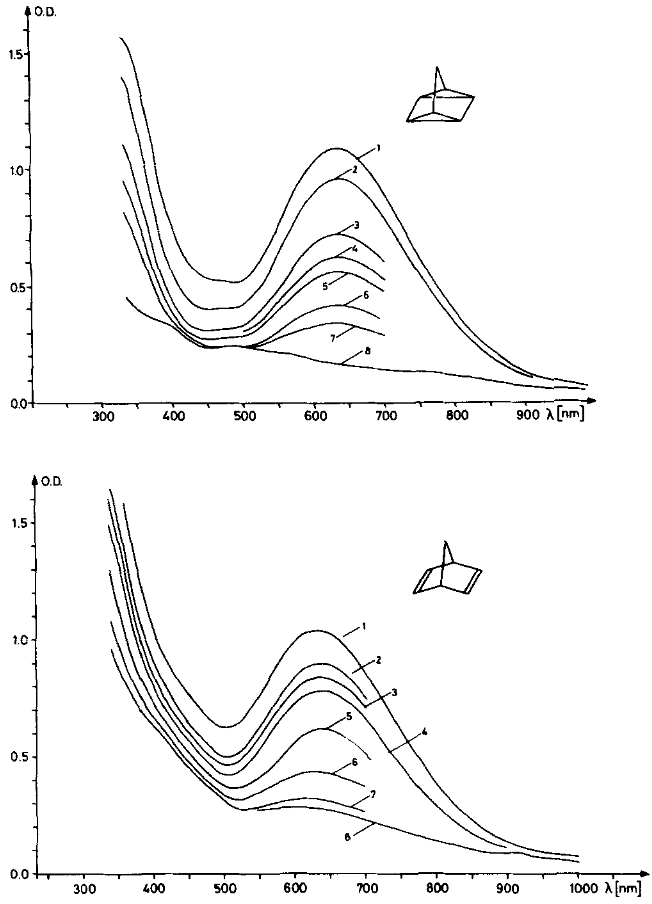

Fig. 3. *Optical spectra of γ-irradiated* **Q** *and* **NBD** *in BuCl/2MB* 1:1 *at 77 K* (see text):
1: immediately after γ-irradiation
2-8: progressively bleached with $\lambda = 580-710$ nm light

sing point relative to a potential minimum cannot (as done above) be readily interpreted as the activation barrier for the process leading across this point. The following remarks of general interest put our theoretical conclusions on a better perspective:

(i) As long as the whole reaction is discussed strictly within imposed C_{2v}-symmetry, crossing-over from one to the other potential curve must involve C_{2v}-nuclear arrangements of *non*-optimal energy. In the case of crossing states of different symmetry, when CI. does not yield any stabilization, the actual C_{2v}-barrier on a multi-dimensional C_{2v}-hypersurface may therefore be higher than that suggested by the crossing point in a two-dimensional diagram. This statement applies to the ground-state isomerization $\mathbf{Q}^{+} \rightarrow \mathbf{NBD}^{+}$. However, when no change in symmetry is involved (*e.g.* points denoted by X and Y in *Fig. 2*) CI. between the two crossing configurations may well turn out to cancel the effect described above, so that the crossing point will more adequately mimic the actual C_{2v}-barrier.

The charge distributions of the two crossing configurations can be taken as a rough measure to judge whether CI. will have a pronounced effect or not. In the case of the two states crossing at points X and Y in *Figure 2* the charge distributions, and therefore the total electronic wave functions, were found to differ markedly, so that no drastic CI. effect is expected.

(ii) Recent work [13] has suggested that some closed-shell isomerizations may proceed through nuclear configurations lacking any symmetry. A qualitative interpretation of this finding is difficult given that the investigated processes are of *SA*- and *OA*-type regardless of the symmetry of the reaction coordinate. Nevertheless, it forces one to conclude that the present open-shell process, classified as *SF* within C_{2v}-symmetry, may have all tendency to proceed through appropriately distorted nuclear configurations of lower symmetry (or no symmetry at all). It then achieves *SA*-behaviour and circumvents the high energy regions of 'crossing point' and intervening ridge. Recent MNDO-calculations for ground-state $\mathbf{Q}^+ \rightarrow \mathbf{NBD}^+$, though not being complete in many respects, nevertheless support this conclusion [11]. It follows that barrier-considerations based on crossing points in idealized high-symmetry correlation diagrams, as done here and in [1], provide *upper bounds* to the actual barriers. Nevertheless, the conclusion about open-shell processes being less activated than the corresponding closed-shell ones is still valid (see [1]).

Attempts to prepare $\mathbf{Q}^+$. γ-Irradiation [14] of $2 \cdot 10^{-2}$ M[5]) pure (99.9%) **Q** or **NBD** in a glassy matrix of butylchloride/2-methylbutane (BuCl/2MB 1:1) [15] at 77 K leads to the same blue cation $\mathbf{X}^+$, the longest wavelength transition in the visible being found for both samples with same absorbance at $\lambda_{\max} = 635$ nm ($E = 1.95$ eV, *Fig. 3*). The absorbing species $\mathbf{X}^+$ is assigned to $\mathbf{NBD}^+$ on the basis of the following combined arguments:

(i) The thermochemical estimates above indicate $\mathbf{NBD}^+$ to be more stable than $\mathbf{Q}^+$ at 77 K.

(ii) Thermal or optical bleaching of the matrix with unfiltered light and subsequent GC. analysis yields no trace of **Q** for irradiated **NBD**[6]), but ~7% of **NBD** for irradiated **Q**. γ-irradiation of **DABCO** (diazabicyclo[2.2.2]octane) [16] under the same conditions as used for **NBD** or **Q** (*e.g.* same concentration, solvent, dose) yields G = 1.60[7]), taking $\varepsilon_{\max} = 1600$ ($\lambda_{\max} = 470$ nm) for $\mathbf{DABCO}^+$ [17]. This corresponds to $9.2 \cdot 10^{-4}$ M active holes of the matrix migrating to the solute. It is reasonable to assume this concentration also to be effective in the case of **Q** (or **NBD**). Hence $[\mathbf{Q}^+] = 9.2 \cdot 10^{-4}$ M or 4.6% of the initial concentration of **Q** after the irradiation. The same percentage applies to $\mathbf{NBD}^+$ formed from $\mathbf{Q}^+$, and after subsequent bleaching to **NBD**. Given the assumptions and uncertainties in this estimate we find a reasonable agreement with the GC. analyzed value above.

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[5]) This concentration is sufficiently low to prevent association of the substrate on cooling, which would result in dimer cation formation upon γ-irradiation.

[6]) This observation agrees with the following consideration: Recombination of $\mathbf{NBD}^+$ ($EA(\mathbf{NBD}^+) = 8.43$ eV $= I_1^a(\mathbf{NBD})$) with the trapped e^- on Cl^- ($EA(Cl) = 3.8$ eV), taking for the combined polarization energy of the ions ~ −2 eV [14] liberates an energy of 2.6 eV. This amount is an upper bound; evidence exists [14] that during e^--return a degradation of *Coulombic* energy of 1-2 eV takes place. The final reaction thus yields **NBD** well below the barrier for **NBD** → **Q**; the energy liberated is also not sufficient to populate the triplet state of **NBD** lying ~4 eV vertically above ground state **NBD** [18] and presumably slightly less than that above **NBD** having the structure of equilibrium $\mathbf{NBD}^+$ ($^2B_2$). Hence, interconversion of hot **NBD** or ^{3}**NBD** [20] to **Q** is not feasible.

[7]) G = number of ions produced per 100 eV radiation deposited in the matrix.

(iii) Irradiation of the matrix at 77 K with 580-710 nm light (maximum intensity at 625 nm, *Balzers* K5+K6 and *Zeiss* KG1 filters) bleaches the broad band with λ_{max} = 635 nm (1.95 eV) readily. The electron affinity of the excited blue species $\mathbf{X}^+$, $EA(\mathbf{X}^{+*}) = I_1^a(\mathbf{X}) + 1.95$ eV is 9.81 eV if $\mathbf{X}^+ \equiv \mathbf{Q}^+$, and 10.38 eV if $\mathbf{X}^+ \equiv \mathbf{NBD}^+$. Only in the latter case is hole exchange with one of the matrix components (I_1^a(BuCl) = 10.45 eV, I_1^a(2MB) = 10.32 eV [21]) feasible. The validity of this argument is supported by the observation that excitation of $\mathbf{DABCO}^+$ with light of λ = 461–468 nm (E = 2.67 eV; *Balzers* B40 461-8 and *Zeiss* KG1 filters) does not bleach this ion [16]. Since I_1^a(**DABCO**) = 7.1 eV [22], $EA(\mathbf{DABCO}^{+*})$ = 9.77 eV follows which indeed does not suffice to extract an electron from the matrix.

Is $\mathbf{Q}^+ \rightarrow \mathbf{NBD}^+$ *a 'hot' or a 'photochemical' reaction?* At first sight the above finding that $\mathbf{Q}^+$ is not stable at 77 K agrees with the prediction of a low thermal barrier for the type C process $\mathbf{Q}^+ (^2B_1) \rightarrow \mathbf{NBD}^+ (^2B_2)$. We shall now discuss two alternative mechanisms of reaction which, though being for themselves very interesting phenomena, would unfortunately *not* yield a clue to our prediction:

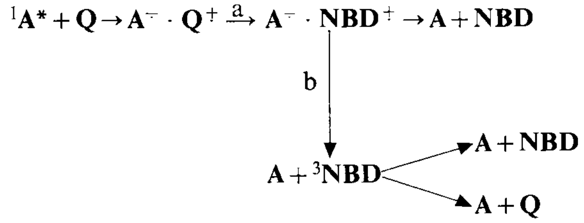
(i) 'Hot' reaction: Since I(matrix) = 10.3–10.5 eV, the resonant hole transfer from solvent to **Q** liberates just sufficient energy for a reasonably vertical population of the close lying excited $\mathbf{Q}^+$-states $^2B_2$ or $^2A_2$ (see crossing points in *Fig. 2*). Internal conversion into the $^2B_1$-ground vibronic manifold of $\mathbf{Q}^+$ will be very efficient in view of the equilibrium geometries (especially the C(2)–C(6) distances, see *Table*) which are rather different between the upper two with respect to the lower surface, assuring optimal *FC*-factors. It initially produces hot $\mathbf{Q}^+ (^2B_1)$ well above the ground state barrier, the energy being strongly concentrated in exactly that mode which interrelates $\mathbf{Q}^+$ with $\mathbf{NBD}^+$. Hence, the time available for quenching hot $\mathbf{Q}^+$ may not be sufficiently short to inhibit its straight pass-over to $\mathbf{NBD}^+$ within half of a vibrational period. There, more efficient energy degradation will take place in view of the higher density of states. Note that these arguments are still valid if the resonant hole transfer produces hot $\mathbf{Q}^+ (^2B_1)$ in the first place. This possibility seems, however, unlikely since a corresponding energy-matching state would have to be attained in a strongly non-vertical fashion. (See [23] for pertinent references on hot reactions in condensed media.)

(ii) 'Photochemical' reaction: There are precedents in the literature for non-resonant hole transfer in a number of cases [14]. Given this possibility, the excess energy on hole transfer from solvent to $\mathbf{Q}^+$ may suffice to populate its excited $^2B_2$-state in a non-vertical fashion. The system would either be prepared in the upper $^2B_2$-branch from which funneling through X to the lower branch would take place, or directly in the lower branch to the right of the funnel X *(Fig. 2)*. As this state directly correlates with the ground state of $\mathbf{NBD}^+$, adiabatic conversion $\mathbf{Q}^+ \rightarrow \mathbf{NBD}^+$ would take place in a manner well known in ordinary photochemistry.

In order to exclude these possibilities, 'hole-moderators' (**HM**) were introduced into the matrix at concentrations significantly higher than that of **Q**. These substances then first accept the hole from the matrix, degrade its energy and subsequently transfer it onto **Q** as long as $I_1^a(\mathbf{HM}) > I_1^a(\mathbf{Q})$ = 7.86 eV is satisfied. For these experiments the optical quality of the glass unfortunately became too poor to allow spectroscopic measurements and the colour changes were therefore followed by visual inspection. For **HM** = benzene (I_1^a = 9.25 eV), chlorobenzene (I_1^a = 9.06 eV) and naphthalene (**NA**) (I_1^a = 8.15 eV) the blue colour of $\mathbf{NBD}^{+}$ still appeared, for **HM** = 1-chloronaphthalene (I_1^a = 7.8 eV) and **DABCO** (I_1^a = 7.1 eV) only the colour of the respective radical cations $\mathbf{HM}^{+}$ could be observed. These results aduce evidence against the operation of mechanism *(ii):* the excess energy of 0.3 eV with which $\mathbf{Q}^{+}$ is burdened after $\mathbf{NA}^{+} + \mathbf{Q} \rightarrow \mathbf{NA} + \mathbf{Q}^{+}$ does not suffice to populate any of its excited states. This energy amount equivalent to ~30 kJ mol^{-1} may still lead to a hot reaction *(i)* of $\mathbf{Q}^{+}$. But this possibility does now not interfere with the scope of this work any more as a barrier of $\leqslant$30 kJ mol^{-1} must then be associated with $\mathbf{Q}^{+} \rightarrow \mathbf{NBD}^{+}$, not conflicting with the qualitative expectations outlined earlier.

Conclusions, Corollaries. - The observation, that the mass spectra of **Q** and **NBD** have identical patterns led to the conclusion, that 'their molecular ions are produced in states which are identical with regard to energy and structure' [24]. Identical product distributions were also obtained on anodic oxidation of **Q** and **NBD** in alcoholic solvents [25]. **Q** was found to quench naphthalene (NA) fluorescence efficiently, whereby extensive isomerization to **NBD** takes place [19]. This process was convincingly demonstrated to involve a complex $\mathbf{Q} \cdot \mathbf{NA}$ with strong CT-character $\mathbf{Q}^{+} \cdot \mathbf{NA}^{-}$ [4,26], the $\mathbf{Q}^{+}$-internal coordinates being proposed to be intermediate between those of **Q** and **NBD**. It was concluded, that 'therefore back charge transfer may produce either **Q** or **NBD**' [26].

PE. spectroscopy, however, reveals that the $\mathbf{Q}^{+}/\mathbf{NBD}^{+}$ system is a type C valence isomer couple [1], its interconversion being therefore state symmetry forbidden. According to present chemical thinking, the actual process involves a finite barrier which leaves $\mathbf{Q}^{+}$ and $\mathbf{NBD}^{+}$ as *two distinct species* with $\mathbf{NBD}^{+}$ being more stable on thermochemical grounds. As $\mathbf{Q}^{+}$ is unstable at 77 K, the thermal barrier for $\mathbf{Q}^{+} \rightarrow \mathbf{NBD}^{+}$ must be very low, *i.e.* much lower than for $\mathbf{Q} \rightarrow \mathbf{NBD}$. This finding supports the qualitative expectations for a type C system [1]. It furthermore suggests that for the room temperature experiments cited above reactions took place from $\mathbf{NBD}^{+}$, formed directly from **NBD** or *via* $\mathbf{Q}^{+} \rightarrow \mathbf{NBD}^{+}$ from **Q**. In case of the photochemical studies this latter process may in fact proceed within the quenching complex which exhibits strong CT-character (a):



Consideration of the energetics of the system in the case of **A** = naphthalene shows [27] that back transfer of the electron in $\mathbf{A}^{-} \cdot \mathbf{NBD}^{+}$ liberates sufficient energy to populate $^3\mathbf{NBD}$ (b) which is known to convert into **Q** and **NBD** [20]. This could explain why quenching of $^1\mathbf{A}^*$ by **Q** proceeds with Φ ($\mathbf{Q} \rightarrow \mathbf{NBD}$) < 1 [19].

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