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RadiationInduced Isomerization of [2,2,1] Bicycloheptadiene (Norbornadiene) to [2,2,1,02,6,03,5] Quadricycloheptane (Quadricyclene) in Cyclohexane Solutions

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Radiation-Induced Isomerization of [2,2,1] Bicycloheptadiene (Norbornadiene) to [2,2,1,$0^{2,6}$,$0^{3,5}$] Quadricycloheptane (Quadricyclene) in Cyclohexane Solutions

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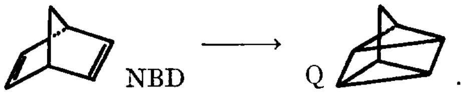
Radiation-induced isomerization of norbornadiene (NBD) into quadricyclene (Q) was studied in cyclohexane solutions. From the effects of charge and radical scavengers it could be concluded that at low NBD concentrations isomerization is initiated by a reaction of NBD with electrons and probably proceeds via singlet excited NBD. Low yields of Q show that this is not an efficient process. At higher NBD concentrations the isomerization becomes more efficient, indicating that other reactions may begin to contribute. Selfquenching of NBD* also becomes important at higher concentrations. In the presence of SF_6, electron transfer from NBD^- to this second solute occurs. Enhanced isomerization yields are observed in the presence of benzene, toluene, and acetophenone. Scavenger studies indicate that triplet-excited states of these solutes contribute to this increase in G(isom). They are formed by charge transfer from cyclohexane positive ions to the aromatic additives followed by neutralization. Complex formation between triplet-excited aromatic molecules and NBD is suggested to be an essential step in the isomerization reaction. Relative reactivities towards cyclohexane positive ions, estimated for methanol, toluene, and benzene, are, respectively, 1.0, 0.32, and 0.27. Calculated lifetimes of triplet-excited acetophenone, toluene, and benzene are between 10^{-6} and 10^{-7} sec. The excited states all react with NBD with rate constants between 5×10^8 and 5×10^9 $M^{-1}\cdot$sec^{-1}.

INTRODUCTION

In the course of our investigations of the gamma radiolysis of solutions of olefins in cyclohexane[1–4] we have studied solutions containing [2,2,1]bicycloheptadiene (norbornadiene, NBD). Like the mono-olefins studied, NBD reduces the yields of products originating from cyclohexane. In addition, sensitized isomerization of NBD to [2,2,1,$0^{2,6}$,$0^{3,5}$]quadricycloheptane (quadricyclene, Q) occurs:



This isomerization reaction has been studied photochemically.[5–7] From experimental results obtained with triplet sensitizers such as acetophenone and benzophenone it was concluded that isomerization proceeds via triplet-excited NBD.[6] However, recent quantum-mechanical calculations have indicated that similar isomerizations often occur from singlet-excited states.[8,9] We have studied the radiation-sensitized isomerization reaction in the presence of various additives, notably radical scavengers, scavengers of charged intermediates, quenchers of excited molecules, and some aromatic compounds. Results are reported in this paper.

EXPERIMENTAL SECTION

The purification of cyclohexane has been described.[4] Norbornadiene (Shell Chemie N.V.) was purified by distillation in a spinning band column. The following chemicals were used as obtained (with purities as stated by the suppliers). Quadricyclene[10] (purity >98%), toluene (Fluka purum, >98.5%), benzene (Baker analyzed, >99.5%), acetophenone (Fluka puriss., >99%), CH_3OH (Baker analyzed, >99.5%), SF_6 (Baker, >98%), NH_3 (Fluka puriss., ≥99.8%), NO (Baker, >99%) and O_2 (Air Products, >99.5%).

Samples were prepared and irradiated according to previously described methods.[1] The dose rate and total dose were 0.7×10^{19} eV/(g·min) and 7×10^{19} eV/g, unless otherwise specified.

Measurement of H_2, C_6H_{10}, and $C_{12}H_{22}$ has been described.[1] Norbornadiene and quadricyclene were separated gas chromatographically, using a 4-m column with 20% polyglycol 400 on Embacel 60-80 mesh.

RESULTS

Major products from cyclohexane radiolysis (H_2, C_6H_{10}, and $C_{12}H_{22}$) are reduced in yield in the presence of norbornadiene as can be seen in Fig. 1. Isomerization of this additive to quadricyclene is observed and yields of this product are given in Figs. 2 and 3 as a function of NBD concentration. The isomerization yield was found to be independent of dose rate from 0.1–2.4×10^{17} eV/(g·min) and of total dose in the range from 0.1–10×10^{19} eV/g.

Effects of additives are shown in Fig. 2 and Table I. It is evident that positive ion scavengers (NH_3, CH_3OH) have no effect on G(isom). The same is true for O_2 and NO which are known as free radical scavengers and as quenchers of excited molecules. On the other hand, a strong decrease in G(isom) was observed in the presence of SF_6, which is an efficient electron scavenger[11,12] (Table I).

Irradiation of solutions containing benzene, toluene, or acetophenone as additive resulted in increased isomerization yields (Fig. 4). Figure 5 shows G(isom) as a function of toluene concentration at NBD concentrations of 0.10M and 0.59M. The increase in G(isom) was also determined as a function of NBD concentration at constant concentrations of aromatic additives (Fig. 6).

Further information about this increase was obtained

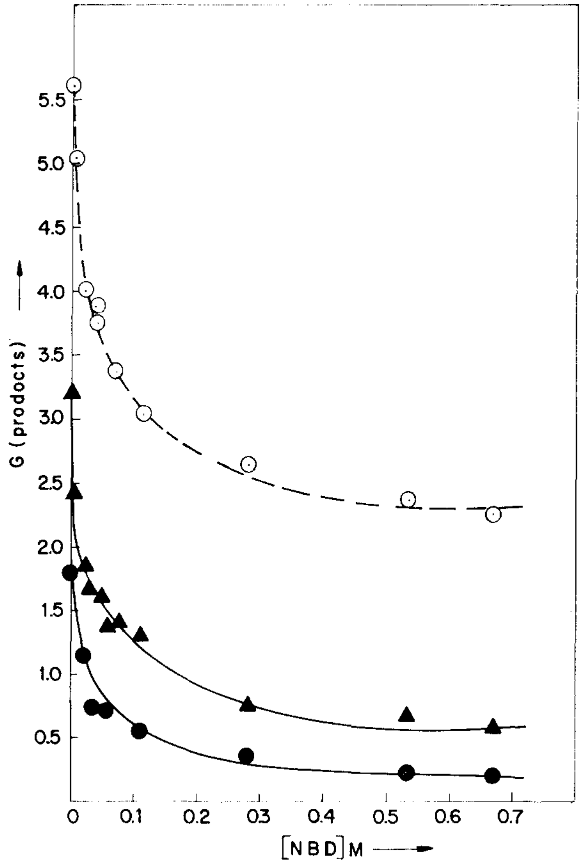


FIG. 1. Product yields from irradiated cyclohexane as functions of NBD concentration. ⊙, hydrogen; ▲, cyclohexene; ●, dicyclohexyl.

by investigating effects of CH_3OH, SF_6, and O_2. It was found that SF_6 reduces G(isom) to approximately zero (Table II). The effect of CH_3OH is shown in Fig. 7. It can be seen that the increase in G(isom) caused by $0.19M$ toluene, is nearly completely suppressed at $[CH_3OH] \geq 1M$. At $0.85M$ toluene, methanol at concentrations up to $1.4M$ causes a considerable reduction but no complete suppression of the increase in G(isom). A reduction is also observed when O_2 is added (Figs. 5 and 8).

TABLE I. Effect of SF_6 on G(isom) at $[NBD]=0.20M$.

$[SF_6]$ $10^{-2}M$	G(isom)
···	0.47
0.1	0.33
0.2	0.24
0.3	0.16
0.4	0.10
0.8	0.07
5.0	0.08
10	0.07
30	0.08

DISCUSSION

Mechanism of Energy Transfer and Isomerization

It can be seen in Fig. 2 that neither scavengers of positive ions (NH_3, CH_3OH) nor radical scavengers or quenchers of excited molecules (O_2, NO) affect G(isom). On the other hand, this yield can be reduced to practically zero in the presence of SF_6 (Table I). These results suggest that sensitized isomerization is initiated by a reaction of NBD with electrons [Reaction (1)]:

$$\mathrm{NBD}+e^- \rightarrow \mathrm{NBD}^-. \qquad (1)$$

This behavior of NBD is markedly different from that observed for mono-olefins in cyclohexane, as sensitized reactions of these solutes are due to positive charge transfer.[2,4] Attempts to demonstrate a contribution of free electrons by experiments at very low NBD concentrations were unsuccessful because of low Q yields and limitations in the gas chromatographic separation.

TABLE II. Effect of SF_6 on G(isom) at $[NBD]=0.10M$.

$[SF_6]$ (M)	Additive	G(isom)
···	···	0.29
0.10	···	0.03
···	Benzene $0.2M$	0.72
0.10	Benzene $0.2M$	<0.05
···	Toluene $0.2M$	0.80
0.10	Toluene $0.2M$	<0.05
···	Acetophenone $0.2M$	1.10
0.10	Acetophenone $0.2M$	<0.05

Isomerization might proceed according to $\mathrm{NBD}^- \rightarrow \mathrm{Q}^-$ followed by neutralization of Q^- or to NBD^-+positive ion$\rightarrow \mathrm{NBD}^* \rightarrow \mathrm{Q}$. It has been shown photochemically that electronically excited molecules can initiate isomerization of NBD.[6] Our results in the presence of aromatic additives are consistent with such a mechanism as will be discussed later. Moreover, from ESR measurements it has been concluded that NBD^- in 1,2-dimethoxyethane at −96°C does not isomerize to Q^-.[13] It will therefore be assumed that NBD* is an intermediate in the isomerization reaction. The following reactions are proposed:

$$\mathrm{NBD}+e^- \rightarrow \mathrm{NBD}^- \qquad (1)$$

$$\mathrm{NBD}^- + C_6H_{12}^+ \rightarrow \mathrm{NBD}^* + C_6H_{12} \qquad (2)$$

$$\mathrm{NBD}^* \rightarrow \mathrm{Q} \qquad (3)$$

$$\mathrm{NBD}^* \rightarrow \mathrm{NBD}. \qquad (4)$$

Positive ion scavengers do not affect G(isom). This indicates that formation of NBD* by neutralization of NBD^- is not sensitive to the positive ions involved. Hence, it cannot be excluded that in addition to Reac-

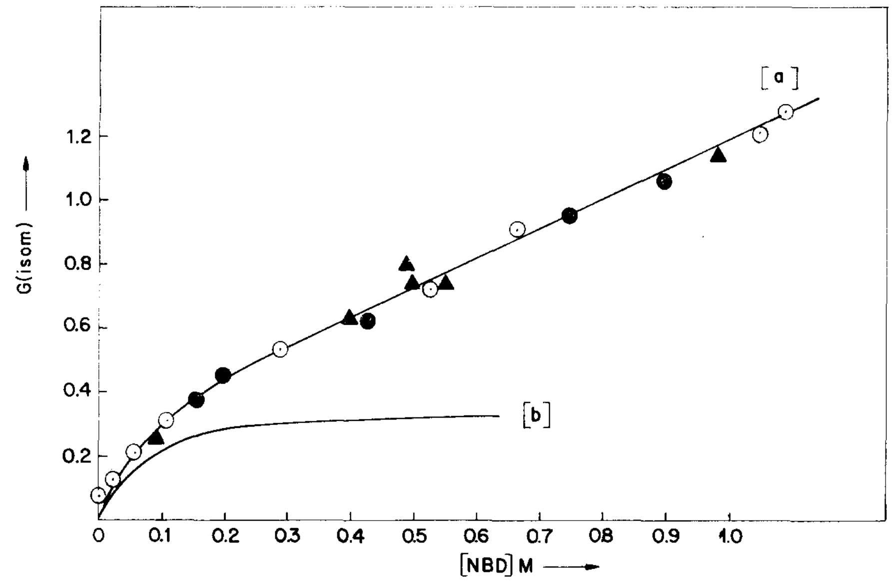


FIG. 2. Isomerization yields as functions of NBD concentration. Curve a: observed G values; curve b: calculated G values for sensitized isomerization (see text). ▲ with positive ion scavengers present ($[CH_3OH]$ or $[NH_3] \leq 1.0M$). ● with radical scavengers present ($[O_2]$ or $[NO]$ $0.1M$).

TABLE III. $G(\mathrm{isom})_{\mathrm{sens}}/\Delta G(H_2)$ and $G(\mathrm{isom})_{\mathrm{sens}}/[\Delta G(H_2)-0.8]$ at various NBD concentrations.

[NBD] (M)	$G(\mathrm{isom})_{\mathrm{sens}}$	$\Delta G(H_2)$	$G(\mathrm{isom})_{\mathrm{sens}}/\Delta G(H_2)$	$\Delta G(H_2)-0.8$	$G(\mathrm{isom})_{\mathrm{sens}}/[\Delta G(H_2)-0.8]$
0.025	0.08	1.50	0.05	0.7	0.11
0.05	0.14	1.90	0.08	1.1	0.13
0.075	0.19	2.20	0.09	1.4	0.14
0.10	0.22	2.40	0.09	1.6	0.14
0.20	0.26	2.80	0.09	2.0	0.13
0.30	0.29	3.00	0.10	2.2	0.13
0.40	0.31	3.10	0.10	2.3	0.13
0.50	0.32	3.20	0.10	2.4	0.13

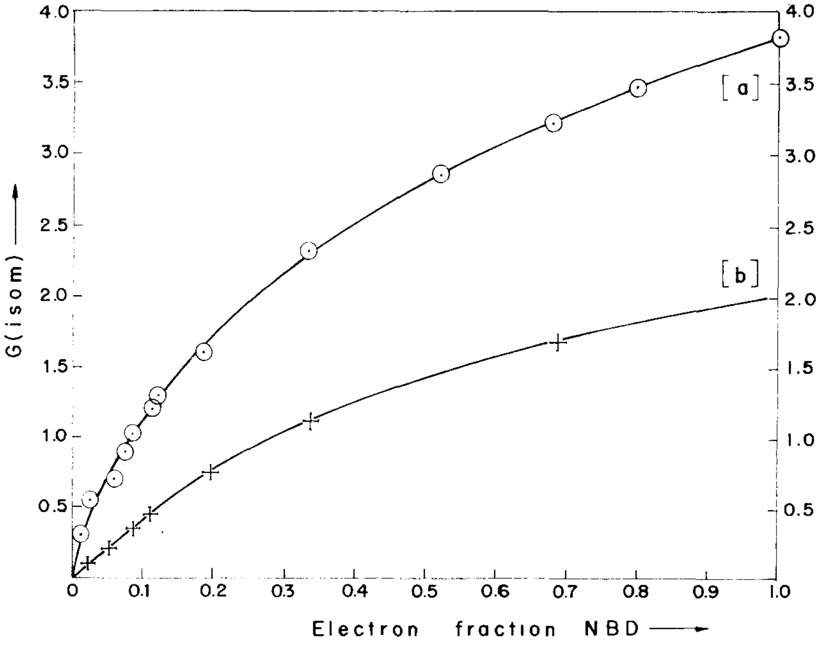


FIG. 3. Isomerization yields as functions of NBD electron fraction. Curve a: without additives; curve b: with $0.3M$ SF_6 present.

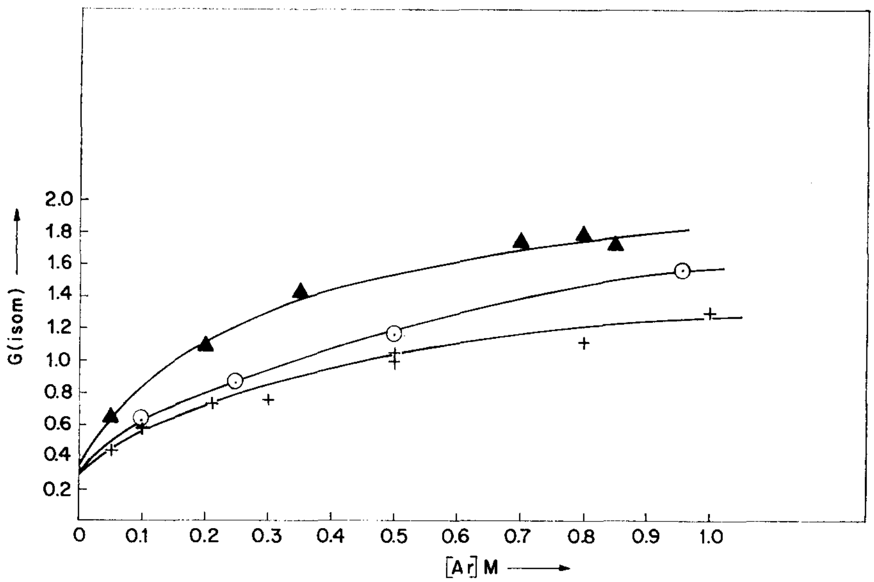


FIG. 4. Isomerization yields at 0.1M NBD as functions of additive concentration. +, benzene; ⊙, toluene; ▲, acetophenone.

tion (1) charge transfer from $C_6H_{12}^+$ to NBD also occurs as is the case with mono-olefins, followed by a reaction between NBD^+ and NBD^- leading to NBD*.

Oxygen and nitrous oxide are well-known quenchers of excited molecules. However, at concentrations up to 0.1M they have no effect on NBD isomerization initiated by gamma radiation (Fig. 2), nor on this isomerization when it results from direct excitation of NBD in cyclohexane with light of 2537 Å. Assuming a rate constant for quenching by $O_2 > 10^9\ M^{-1}\cdot sec^{-1}$,[14] it follows that the lifetime of NBD*, $\tau(NBD^*) < 10^{-10}$ sec.

Sensitized and Unsensitized Isomerization

Isomerization as a result of direct absorption of energy in NBD will become increasingly important at higher solute concentrations. In order to determine the true G values for sensitized isomerization, the contribution due to direct absorption of energy must be subtracted from the total G(isom). This contribution cannot be calculated from the G(isom) in pure NBD, as, for example, self-quenching may occur at high NBD concentrations. The following observations are relevant. At 0.2M NBD the sensitized isomerization can be completely suppressed by $8\times10^{-3}M$ SF_6 (Table I). Hence, at 0.3M SF_6 sensitized isomerization will be suppressed over the whole NBD concentration range studied, provided that no change in mechanism of energy transfer occurs with changing solute concentration. Residual yields of G(isom) with 0.3M SF_6 present are therefore assumed to result from direct radiation effects (Fig. 3, curve b and Fig. 9 curve a). The nonlinearity of curve b in Fig. 3 is suggestive for the occurrence of self-quenching at an NBD electron fraction >0.2.[15]

Residual G(isom) values in the presence of 0.3M SF_6 are not identical to G(isom) caused by direct absorption of energy in NBD in the absence of SF_6. This latter value can be calculated from the residual yields assuming that SF_6 reduces G(isom) resulting from direct absorption of energy in NBD with a factor equal

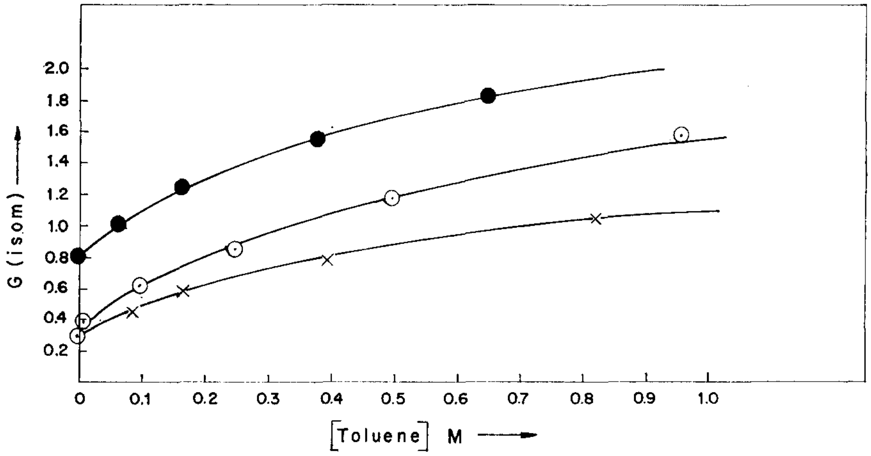


FIG. 5. Isomerization yields as functions of toluene concentration. ●, 0.59M NBD; ⊙, 0.10M NBD; ×, 0.10 NBD+0.02M O_2.

to 2.0/3.8 as in pure NBD (Fig. 3). Calculated G values are given in Fig. 9 curve b. Subtracting these calculated values from the total G(isom) results in values for the radiation-sensitized isomerization, $G(\text{isom})_{\text{sens}}$. This is shown in Fig. 2 curve b.

REDUCED HYDROGEN YIELDS

Yields of products from irradiated cyclohexane are reduced when electron scavengers are present. From the decrease in $G(H_2)$ Warman *et al.* estimated relative efficiencies of electron capture for a number of these scavengers.[16] Observed H_2 yields as a function of NBD concentration (Fig. 1) coincide with results in the presence of SF_6 as reported by Warman *et al.*[16] (dotted line in Fig. 1). As part of the reduction in $G(H_2)$ caused by NBD will be the result of reactions of thermal H atoms with olefinic double bonds, the identical behavior of $G(H_2)$ with either SF_6 or NBD present indicates that NBD is somewhat less reactive towards e^- than is SF_6.

As is shown in Table III, $G(\text{isom})_{\text{sens}}/\Delta G(H_2)$ is not constant but increases with increasing NBD concentration. This is consistent with the notion that scavenging of thermal H atoms by NBD, which is complete at relatively low solute concentrations,[1] contributes to $\Delta G(H_2)$. Subtracting from $\Delta G(H_2)$ the contribution due to H-atom scavenging equal to ~0.8,[1] a constant ratio $G(\text{isom})_{\text{sens}}/[\Delta G(H_2)-0.8]$ is obtained. It is also evident from Table III that $\Delta G(H_2)$ is much larger than $G(\text{isom})_{\text{sens}}$ and that only about 13% of NBD^- isomerizes into quadricyclene.

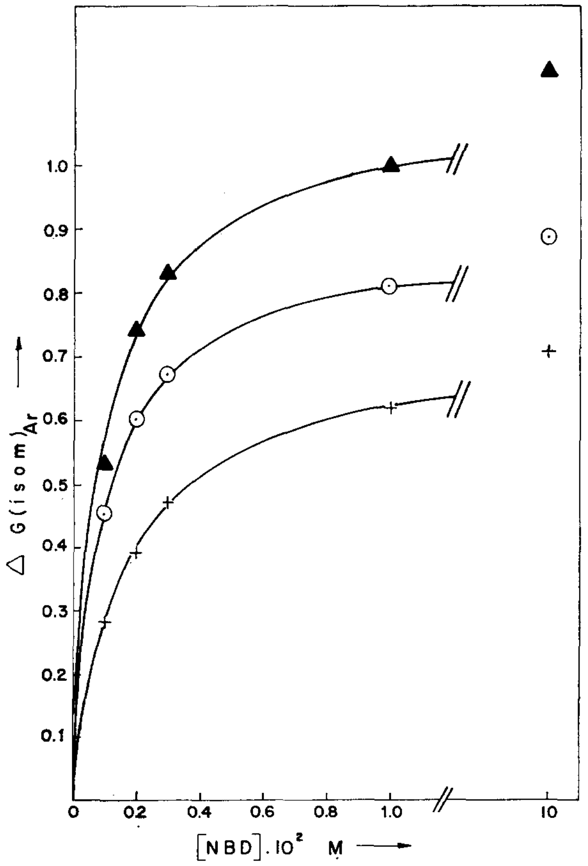


FIG. 6. Increase in isomerization yields as functions of NBD concentration. +, 0.50M benzene; ⊙, 0.50M toluene; ▲, 0.30M acetophenone.

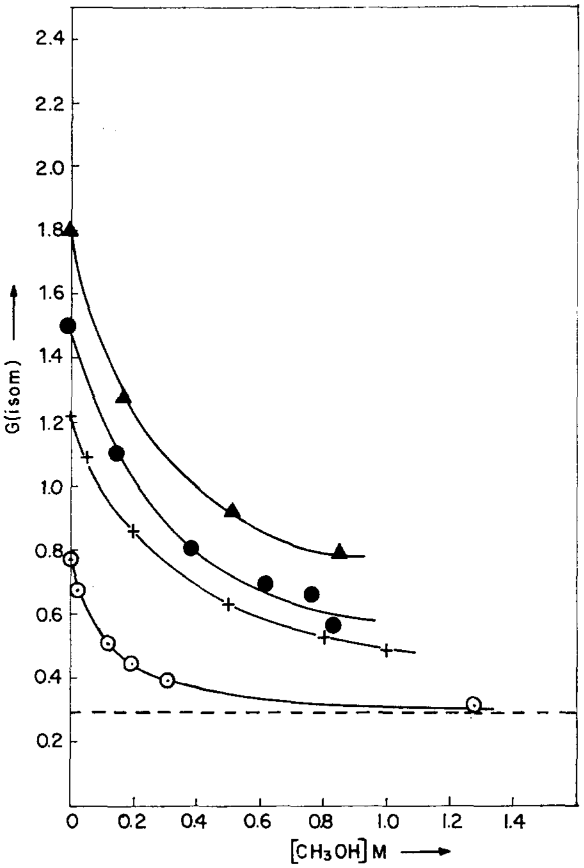


FIG. 7. Isomerization yields, at 0.10M NBD and with additives present, as functions of CH_3OH concentration. +, 0.85M benzene; ⊙, 0.19M toluene; ●, 0.85M toluene; ▲, 0.85M acetophenone. The dotted line represents G(isom) with only 0.10M NBD present.

It can be seen in Table I that sensitized isomerization of 0.20M NBD is completely suppressed by $8\times10^{-3}M$ SF_6. Since the reactivities for electrons of these two solutes are of the same order of magnitude, these results suggest that electron transfer from NBD^- to SF_6 occurs. Similar transfer reactions between a number of electron scavengers have been reported.[16]

ENHANCED ISOMERIZATION IN THE PRESENCE OF AROMATIC ADDITIVES

Increased NBD isomerization is observed in solutions containing benzene, toluene, or acetophenone (Fig. 4). The increase as a function of toluene concentration is the same for solutions containing either 0.10M or 0.59M NBD (Fig. 5). The enhanced yields are reduced by methanol. These observations suggest

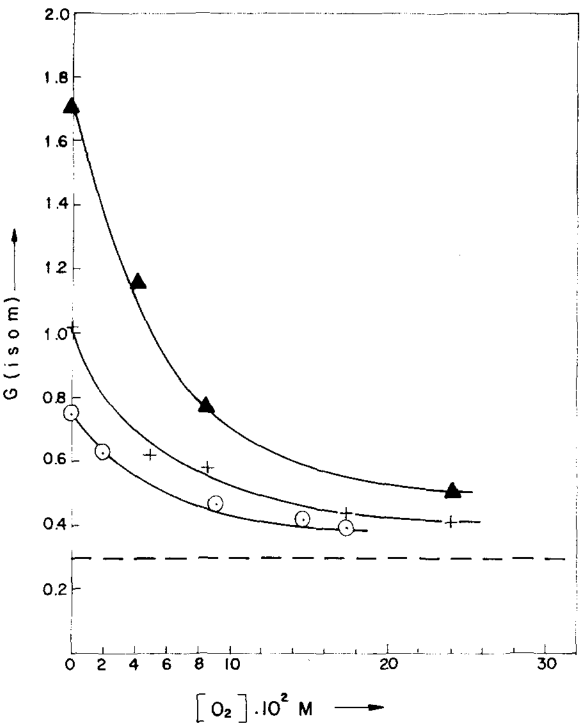


FIG. 8. Isomerization yields, at 0.10*M* NBD and with additives present, as functions of O_2 concentration. +, 0.50*M* benzene; ⊙, 0.19*M*, toluene; ▲, 0.50*M* acetophenone. The dotted line represents *G*(isom) with only 0.10*M* NBD present.

that cyclohexane positive ions react with the solutes. Charge transfer from cyclohexane to benzene has already been proposed in irradiated mixtures of these two compounds.[17,18] Ionization potentials of cyclohexane, benzene, toluene, and acetophenone are, respectively, 9.88, 9.25, 8.82, and 9.27 eV.[19]

The effect of O_2 on the enhanced isomerization yield suggests that reactions of excited molecules contribute to the observed increase. Probably oxygen competes with excitation transfer from Ar*, formed by neutralization of Ar^+, to NBD. The following reactions are proposed:

$$\mathrm{NBD}+e^-\rightarrow\mathrm{NBD}^-, \qquad (1)$$

$$\mathrm{NBD}^-+\mathrm{C_6H_{12}}^+\rightarrow\mathrm{NBD}^*+\mathrm{C_6H_{12}}, \qquad (2)$$

$$\mathrm{C_6H_{12}}^++\mathrm{Ar}\rightarrow\mathrm{Ar}^++\mathrm{C_6H_{12}}, \qquad (5)$$

$$\mathrm{Ar}^++\mathrm{NBD}^-\rightarrow\mathrm{Ar}^*+\mathrm{NBD}^*, \qquad (6)$$

$$\mathrm{Ar}^++e^-\rightarrow\mathrm{Ar}^*, \qquad (7)$$

$$\mathrm{Ar}^*\rightarrow\mathrm{Ar}, \qquad (8)$$

$$\mathrm{Ar}^*+\mathrm{NBD}\rightarrow\mathrm{NBD}^*+\mathrm{Ar}, \qquad (9)$$

$$\mathrm{NBD}^*\rightarrow\mathrm{Q}, \qquad (3)$$

$$\mathrm{NBD}^*\rightarrow\mathrm{NBD}. \qquad (4)$$

Reactions (3), (5), and (9) will be dealt with in more detail in a subsequent section of this paper. The complete reduction of *G*(isom) by SF_6 in the presence of aromatic additives (Table II) indicates that no Ar* is formed by neutralization of the positive ion with SF_6^-.[20]

RELATIVE REACTIVITIES OF BENZENE, TOLUENE, ACETOPHENONE, AND METHANOL TOWARDS CYCLOHEXANE POSITIVE IONS

Warman *et al.*[21] used the following equation to describe product formation from a charge scavenger S_1, in the absence $[G(P)_0]$ and in the presence $[G(P)_{S_2}]$ of a second scavenger S_2:

$$G(P)_0/G(P)_{S_2}=1+\alpha_2[S_2]/\alpha_1[S_1]. \qquad (I)$$

In this equation α_1 and α_2 are proportional to the reactivities of S_1 and S_2 towards the charged species. In our proposed mechanism the aromatic additives act as charge scavengers (S_1) resulting in increased isomerization $[\Delta G(\mathrm{isom})]$. This increase is reduced by methanol (S_2). The experimental results are plotted according to Eq. (I) in Fig. 10. The predicted linear dependence is indeed observed. In the derivation of Eq. (I) it was assumed that (a) no charge transfer occurs from one scavenger to the other and (b) the total yield of scavenged ions is not affected by the second scavenger. Therefore high concentrations of aromatic additives (0.85*M*) have been used in these experiments. However, even at these concentrations not all ions will be scavenged. As a consequence, the values for α_2/α_1 determined from the slope of the lines in Fig. 10 will be too low. From results reported by Warman *et al.* in the presence of two electron scavengers,[16] and by using the ratio of efficiencies for scavenging of positive ions and electrons,[22] it can be calculated that the actual ratio of α_2/α_1 is about 1.1× the observed ratio. Taking this into account, one obtains for the relative reactivities:

$$\alpha_{\mathrm{CH_3OH}}:\alpha_{\mathrm{acetophenone}}:\alpha_{\mathrm{toluene}}:\alpha_{\mathrm{benzene}}=1.0:0.43:0.32:0.27.$$

It has been implicitly assumed that the actual increase in isomerization caused by the aromatic additives is equal to the observed ΔG(isom) or that formation of NBD* in Reactions (2) and (6) is equally efficient. This is consistent with the previous conclusion that formation of NBD* by neutralization of NBD^- is not sensitive with regard to the positive ions involved. Also in support with this assumption is the fact that the results, when plotted according to Eq. (I), give straight lines. Nevertheless, the relative reactivities as calculated from the slope of these lines should be considered with some reserve.

Determination of Relative Rate Constants for Excitation Transfer from Aromatic Additives to Norbornadiene and the Lifetimes of Excited Aromatic Molecules

The observed decrease in ΔG(isom) in the presence of oxygen can be explained by a competition between O_2 and NBD for Ar* [Reactions (9) and (10)]:

$$\mathrm{Ar}^*+\mathrm{O_2}\rightarrow\mathrm{Ar}+\mathrm{O_2}. \qquad (10)$$

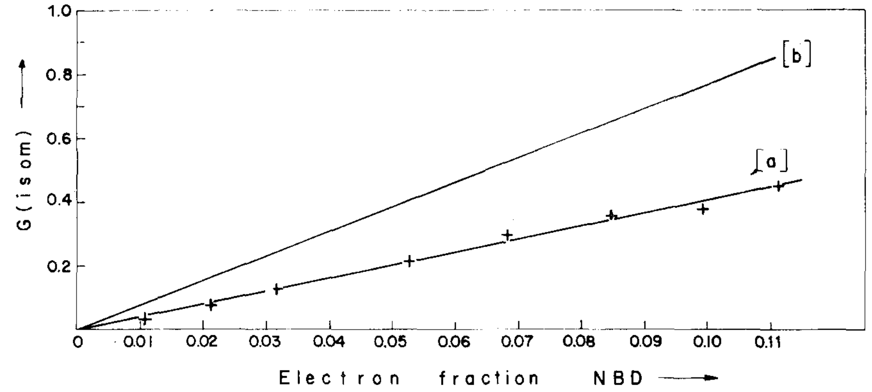


FIG. 9. Isomerization yields as functions of NBD electron fraction. Curve a: with $0.3M$ SF_6 present; curve b: calculated isomerization yields due to direct absorption of energy by NBD (see text).

Using a steady-state treatment the following equation can be derived:

$$\Delta G(\text{isom})_{\text{Ar}}/\Delta G(\text{isom})_{\text{Ar}+\text{O}_2} = 1+\{k_{10}[\text{O}_2]/(k_8+k_9[\text{NBD}])\}. \quad \text{(II)}$$

It will be shown later than at a NBD concentration of $0.1M$, as used in these experiments, $k_8 \ll k_9[\text{NBD}]$. Hence, a plot of $\Delta G(\text{isom})_{\text{Ar}}/\Delta G(\text{isom})_{\text{Ar}+\text{O}_2}$ as a function of $[\text{O}_2]/[\text{NBD}]$ is expected to give a straight line from which k_{10}/k_9 can be determined. Figure 11 shows not only the expected linear dependence, but also that within experimental error k_{10}/k_9 has the same value of 2.2 for the three solutes studied. It follows from Eq. (II) that at constant concentrations of NBD and O_2, $\Delta G(\text{isom})_{\text{Ar}}/\Delta G(\text{isom})_{\text{Ar}+\text{O}_2}$ should be independent of concentration of the aromatic additives. A constant ratio is indeed observed as is shown in Table IV. The experimental results were taken from Fig. 5.

Lifetimes of the aromatic additives can be estimated from experiments in which $\Delta G(\text{isom})_{\text{Ar}}$ is measured at constant [Ar] as a function of NBD concentration. The following equation can be derived from the proposed reaction mechanism:

$$\frac{1}{\Delta G(\text{isom})_{\text{Ar}}} = \frac{k_3+k_4}{k_3 G(\text{Ar}^*)} \times \left(1+\frac{k_8}{k_9[\text{NBD}]}\right). \quad \text{(III)}$$

A plot of $1/\Delta G(\text{isom})_{\text{Ar}}$ vs $1/[\text{NBD}]$ gives straight lines for the three additives, from which k_8/k_9 can be determined (Fig. 12). Using the observed value of 2.2 for k_{10}/k_9, one can calculate k_8/k_{10} values for the aromatic additives. Assuming for k_{10} a value between 10^9 and 10^{10} M^{-1} sec^{-1},[14] the following approximate values are found for k_8 and the corresponding lifetimes:

$k_8(\text{benzene}) = 7\times10^5\text{–}7\times10^6$ sec^{-1}

or $\tau(\text{benzene}) = 10^{-6}\text{–}10^{-7}$ sec,

$k_8(\text{toluene}) = 4\times10^5\text{–}4\times10^6$ sec^{-1}

or $\tau(\text{toluene}) = 2\times10^{-6}\text{–}2\times10^{-7}$ sec,

$k_8(\text{acetophenone}) = 5\times10^5\text{–}5\times10^6$ sec^{-1}

or $\tau(\text{acetophenone}) = 2\times10^{-6}\text{–}2\times10^{-7}$ sec.

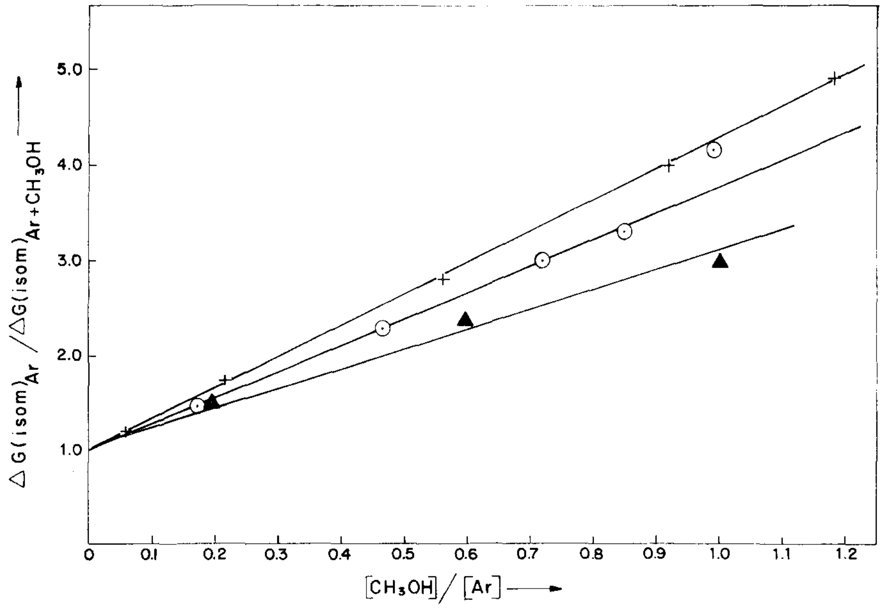


FIG. 10. Experimental results plotted according to Eq. (I) (see text). +, benzene; ⊙, toluene; ▲, acetophenone.

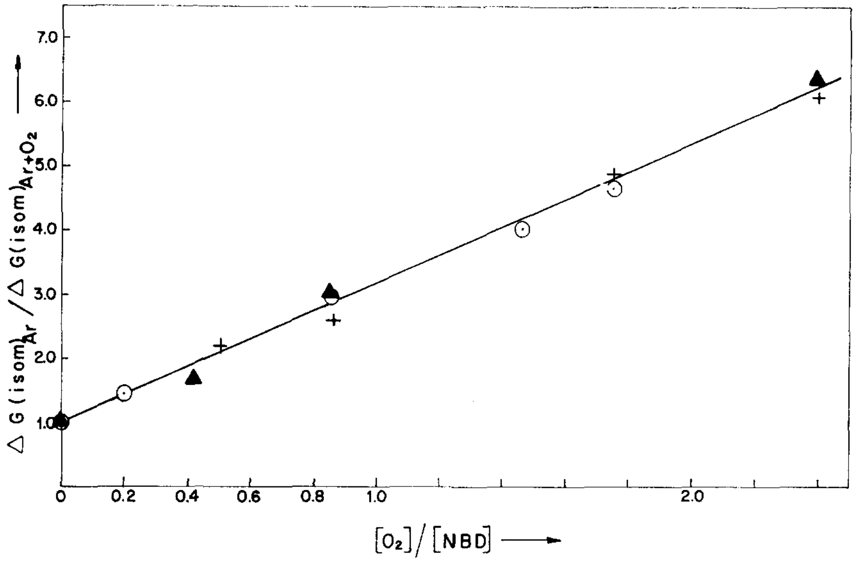


FIG. 11. Experimental results plotted according to Eq. (II) (see text). +, benzene; ⊙, toluene; ▲, acetophenone.

These calculated lifetimes correspond with known lifetimes (10^{-6}–10^{-7} sec) for the lowest triplet states of these molecules,[23–25] suggesting that energy transfer to NBD occurs from the lowest triplet state. This is energetically possible as the triplet energies of toluene (82 kcal/mol),[26] benzene (84 kcal/mol),[27] and acetophenone (73.6 kcal/mol)[26] are higher than of norbornadiene (59–68 kcal/mol).[28]

SOME DETAILS CONCERNING THE PROPOSED MECHANISM

Recent quantum-mechanical calculations indicate that valence isomerizations like the one discussed in this paper proceed via singlet excited states with the same symmetry as the ground state.[8,9] Such a mechanism is consistent with the estimated lifetime of NBD*, $<10^{-10}$ sec. The observed inefficiency of quadricyclene formation via NBD$^-$ may be due to small yields of singlet-excited states formed in the neutralization of NBD$^-$ or to inefficient isomerization of NBD^S to Q.

On the other hand, the increase in G(isom) in the presence of aromatic compounds was found to proceed via triplet-excited states of these additives. Similar results have been obtained photochemically by using triplet sensitizers.[6] Possibly, a complex between triplet aromatic molecules and NBD is formed with a symmetry that allows isomerization into quadricyclene to occur. It has recently been concluded that energy transfer from triplet-excited benzene and acetone to olefins requires formation of a "chemical complex" which is longer lasting than a mere "collision complex"[29]:

$$\text{Ar}^T + \text{NBD} \rightarrow (\text{Ar}\cdots\text{NBD})^* \rightarrow \text{Ar} + \text{Q} \qquad (11)$$

$$\text{Ar}^T + \text{NBD} \rightarrow (\text{Ar}\cdots\text{NBD})^* \rightarrow \text{Ar} + \text{NBD}. \qquad (12)$$

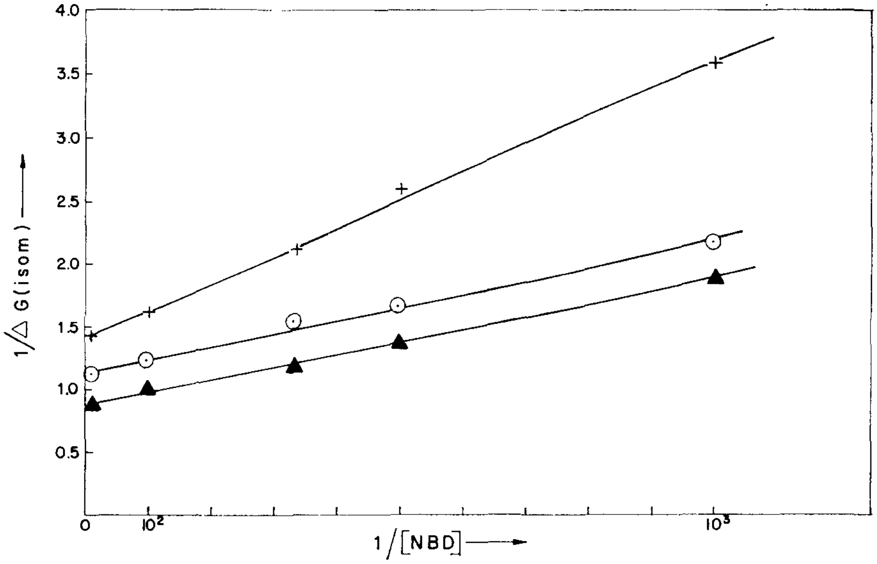
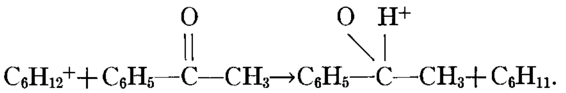


FIG. 12. Experimental results plotted according to Eq. (III) (see text). +, benzene; ⊙, toluene; ▲, acetophenone.

It can be seen in Fig. 4 that at $0.1M$ NBD, G(isom) is increased by a factor of 2 or 3, respectively, in the presence of $0.1M$ toluene or $0.1M$ acetophenone. Taking into account that scavenging of positive ions (by the aromatic additives), even in the presence of electron scavenger (NBD), is less efficient than electron scavenging itself,[30] it is evident that Ar^+ is more efficient in causing isomerization of NBD to Q than NBD^-. This is consistent with our previous conclusion that different excited states of NBD are involved in the isomerization reaction.

Figure 4 shows that at the same concentration, acetophenone causes a larger ΔG(isom) than toluene and that toluene is again slightly more effective than benzene. The difference between benzene and toluene is consistent with other observations indicating that the contribution of charge transfer increases with increasing difference in ionization potential.[3] However, the large ΔG(isom) caused by acetophenone (I.P.= 9.27 eV) requires another explanation. Probably this increase is not solely the result of triplet formation according to Reactions (5)-(7). Another process that may contribute is proton transfer from $C_6H_{12}^+$ to acetophenone:



$$C_6H_{12}^+ + C_6H_5-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 \rightarrow C_6H_5-\overset{O\ H^+}{\overset{\diagdown\ |}{C}}-CH_3 + C_6H_{11}. \qquad (13)$$

Proton transfer will be favored by resonance stabilization of the product positive ion. Neutralization of this ion may result in triplet acetophenone formation. Also, electron capture by acetophenone followed by neutralization might contribute to triplet formation.[31]

From isomerization yields at relatively high NBD concentrations it is evident that a more efficient mechanism is operative than the singlet isomerization in dilute solutions. Whereas triplet-excited states of NBD probably do not isomerize in dilute solutions, they might contribute to Q formation at higher solute concentrations. Reaction (14) may, for example, become increasingly important with increasing NBD concentration:

$$NBD^T + NBD \rightarrow (NBD\cdots NBD)^* \rightarrow Q + NBD. \qquad (14)$$

The similarity between Reactions (11) and (14) is evident.

TABLE IV. $\Delta G(\text{isom})_{\text{Tol}}/\Delta G(\text{isom})_{\text{Tol}+O_2}$ at various toluene concentrations; $[\text{NBD}]=0.10M$, $[O_2]=0.02M$.

[Toluene] (M)	$\Delta G(\text{isom})_{\text{Tol}}$	$\Delta G(\text{isom})_{\text{Tol}+O_2}$	$\Delta G(\text{isom})_{\text{Tol}}/\Delta G(\text{isom})_{\text{Tol}+O_2}$
0.09	0.26	0.17	1.53
0.16	0.42	0.28	1.50
0.39	0.72	0.47	1.54
0.82	1.15	0.75	1.53

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[11] SF_6 does not affect the isomerization when NBD is directly excited with light of 2537 Å.

[12] O_2 is also known to react with hydrated electrons. However, there is no evidence of an efficient reaction between O_2 and e^- in hydrocarbons, like cyclohexane. The different effects of O_2 and SF_6 on G(isom) suggest either that reactions between O_2 and e^- are inefficient or, more probable, that O_2^- reacts with NBD by e^- transfer. A similar transfer reaction from NBD^- to SF_6 is proposed in a following section of this paper. Apparently, in these solutions NBD has a higher electron affinity than O_2.

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$$C_6H_{12}^+ + SF_6^- \rightarrow HF + SF_5\cdot + C_6H_{11}.$$

Reduced yields with SF_6 present might also be taken as evidence for a mechanism in which increased isomerization in the presence of aromatic solutes is due to electron scavenging by these additives followed by excited molecule formation in the neutralization reaction. The effect of CH_3OH then suggests that neutralization with $CH_3OH_2^+$ does not produce excited solute molecules. With this mechanism a linear dependence of $1/-\Delta G(Q)$ on $1/([CH_3OH])^{1/2}$ is expected,[16] where $-\Delta G(Q)$ is the observed reduction in isomerization due to methanol addition. The experimental results do not show this dependence although the deviations are not very large. On the other hand, it can be shown by kinetic analysis of the data that the results are consistent with a competition between CH_3OH and aromatic additive for $C_6H_{12}^+$ ions. This will be discussed in the next paragraph. The latter mechanism will therefore be assumed to be predominant.

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Vibrational Exciton Density of States in Solid Benzene*

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Computer-aided calculations, based on experimentally-fitted pairwise interaction terms, give the complete exciton density-of-states profile for the entire Brillouin zone. The restricted Frenkel model, with short-range interactions, is the key assumption. Results are given and discussed for the out-of-plane a_{2u} normal mode ν_{11}(C_6H_6 and C_6D_6), for $\nu_{12}(b_{1u})$, and for $\nu_{15}(b_{2u})$. The wide range of parameters used makes this investigation pertinent to other vibrational and electronic exciton bands of benzene and any other molecular crystal with the same interchange symmetry. Also, Van Hove singularities are found to be more important for symmetry-based critical points than for "accidental" critical points. Present-day experimental and theoretical intermolecular excitation exchange interaction terms are compared.

INTRODUCTION

The usual experimental investigations of the vibrational and electronic states of molecular crystals involve the observations of the infrared or ultraviolet transitions between the ground and excited states of the crystal. Since the ground state is characterized by the reduced wave vector $\mathbf{k}=0$, the general crystal selection rule for this region, $\Delta\mathbf{k}\cong 0$, restricts the optically allowed transitions to those involving only the $\mathbf{k}\cong 0$ states of the vibrational or electronic exciton band. Recently, however, the study of the band contours of carefully selected "hot-band" transitions in crystals of benzene and naphthalene have led to the observation of the density-of-states distribution of the entire exciton band of the first excited singlet states of these systems.[1] These band profiles were then compared to theoretically calculated density-of-states distributions based on independent empirical data. No vibrational exciton bands in molecular crystals have yet been observed experimentally, but we have attempted to predict the band shape of some of the benzene vibrational excitons by applying the same theoretical formalism used to calculate the electronic exciton bands. The restricted Frenkel model used here[2] is applicable not only to many vibrational excitons, but also to all electronic Frenkel exciton states that are not associated with strong transition dipole moments.[3] It is particularly applicable to triplet exciton bands.[4]

Another aim of this investigation was to follow the changes in a density-of-states function with changes in pairwise interaction parameters, within the restricted Frenkel exciton theory. A large number of computations have been collected (only a few shown here), providing some insight into the nature of these relationships. Another point of interest has been the role of critical points in restricted Frenkel density-of-states functions. The computed curves are also of interest because they encourage experiments designed to investigate the density-of-states function in the liquid as well as the solid state.

THEORY

The energy distribution of the density of exciton states of a molecular crystal can be easily determined once the eigenvalue problem for the exciton band has been solved. For molecular crystals such as benzene and naphthalene, Frenkel exciton theory and the assumption of pairwise molecular interactions are the standard approaches for obtaining exciton energies.[5,6] References 1 and 6 contain the formalism for deriving the matrix elements for the excited state of crystalline benzene. These matrix elements, $L_{qq'}{}^{f}(\mathbf{k})$, defined by Eq. (7) of Ref. 6, correspond to the excited state of the molecule, whether electronic or vibrational:

$$
\begin{aligned}
L_{qq'}{}^{f}(\mathbf{k}) &= \langle \phi_{q}{}^{f}(\mathbf{k}) \mid H \mid \phi_{q'}{}^{f}(\mathbf{k}) \rangle \\
&= \sum_{n'=1}^{N/h} [\exp(i\mathbf{k})\cdot(\boldsymbol{\tau}_{q'}-\boldsymbol{\tau}_{q})] \\
&\qquad \times[\exp(i\mathbf{k})\cdot(\mathbf{r}_{n'}-\mathbf{r}_{n})]\int \phi_{nq}{}^{f*} H \phi_{n'q'}{}^{f} dR. \qquad (1)
\end{aligned}
$$

In general, the diagonal element $L_{qq}{}^{f}(\mathbf{k})$ is not equal to the diagonal element $L_{q'q'}{}^{f}(\mathbf{k})$ because the dot products of a given $\mathbf{k}$ with the vectors $(\mathbf{r}_n+\boldsymbol{\tau}_q)$ of sublattice q are different[2,3,5] from the dot products with the vectors $(\mathbf{r}_n+\boldsymbol{\tau}_{q'})$, associated with sublattice q'.