# Electronic Spectra of Ion Radicals and Their Molecular Orbital Interpretation. III. Aromatic Hydrocarbons

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**Abstract:** Utilizing the radiation-induced one-electron oxidation and reduction, a number of new ion radicals of aromatic hydrocarbons have been produced and comprehensive data are analyzed in terms of SCF–MO calculations. Some spectral data in the literature are discussed critically. A relatively simple correlation of the transition among the ions of the same molecular symmetry is pointed out. A systematic difference between the cation and anion of alternant hydrocarbons was found and is suggested to be due to the involvement of a $\sigma$–$\pi$ interaction. With new spectra of cations and anions of some nonalternant hydrocarbons the failure of the pairing property is demonstrated. The cyclooctatetraene cation seems to undergo a peculiar photoinduced rearrangement reaction.

During the past few decades numerous ion radicals have been produced and studied by esr and optical spectroscopy. The number of esr studies, however, by far exceeds the optical studies due to the presence of deceiving by-products which mask absorptions of the ion radical under study. In previous papers we have shown that $\gamma$-irradiation of rigid solutions is a reliable method for the ion radical production and the optical study of anions of aromatic nitro compounds[1] and the anthracene system.[2] In this paper we present comprehensive data for aromatic hydrocarbons which have been studied repeatedly. Reinvestigation of familiar systems may be justified for the following reasons.

(1) With the method employed herein any hydrocarbon is capable of affording anion and cation radicals provided that it is dissolved to a sufficiently high concentration ($\gtrsim 10^{-2}$ mol/l.) in an ethereal and an alkyl halide solvent (see the next section). Thus, an extensive comparison can be made over a variety of homologs which do not yield ion radicals by the conventional alkali metal reduction and the oxidation by means of Lewis acids. Since the hydrocarbon system is fundamental both in theory and in experiment, a systematic compilation of data would be useful.

(2) By irradiating simply over a long time interval the ion radical accumulates sufficiently to manifest weak absorptions (see next section). Thus, a comparison with calculations can be extended to finer details.

(3) Hoijtink's simplified theoretical treatment[3] has been replaced with an SCF–MO plus CI treatment as in Carsky's work.[4] In Carsky's paper only theoretical predictions were made for a number of hydrocarbons whose experimental data had not been available.

(4) Although a part of the experimental data was previously presented in radiation-chemical papers,[5] the region of wavelength measured in the papers was not wide enough for detailed spectroscopic discussions.

## Principles and Features of Experiment

In view of the relative unfamiliarity of the method, the principle of radical production will be briefly reviewed.[5] The details of experimental procedure are described in previous papers.[1,2]

For the production of an anion radical of an aromatic hydrocarbon, the substance is dissolved in 2-methyltetrahydrofuran (MTHF, $C_5H_{10}O$), frozen to a glassy solid at 77°K, and irradiated with $\gamma$-rays to induce the following reactions.

$$C_5H_{10}O \xrightarrow{\gamma} C_5H_{10}O^+ + e^- \quad (1)$$

$$C_5H_{10}O^+ + C_5H_{10}O \longrightarrow C_5H_{11}O^+ + \cdot C_5H_9O \quad (2)$$

$$e^- + \text{solute} \longrightarrow \text{solute anion} \quad (3)$$

Positive ions of MTHF decompose by reaction 2 while the electron moves through the body to be scavenged by the solute. For the production of cation radicals alkyl halides (RX) are used as the solvent. The following reactions lead to the production of solute cation.

$$RX \xrightarrow{\gamma} RX^+ + e^- \quad (4)$$

$$e^- + RX \longrightarrow R\cdot + X^- \quad (5)$$

$$RX^+ + \text{solute} \longrightarrow RX + \text{solute cation} \quad (6)$$

*sec*-Butyl chloride (BuCl) was used principally as the solvent, but a Freon mixture ($CCl_3F$ + $CF_2BrCF_2Br$; equivolume solution)[6] abbreviated as FM was also used in some cases for the following reasons.

(1) The same spectrum obtained from the two different halide matrices, hydrogenous and nonhydrogenous, should ensure that the spectrum is due to the common solute cation produced by reactions 4–6.

(2) The spectrum of solute cation in two different matrices should give a measure of the general solvent shift of the spectrum.

(3) Although FM is a poorer solvent than BuCl, the former is superior to the latter in revealing the vibrational structure of solute cation (see, *e.g.*, Figure 11a and 11b). It is to be noted that the positive charge in reactions 4 and 6 conducts electronically through the halide molecules until it is scavenged by a solute molecule doped at a site remote from the initial ionization.

The method has several advantages over the conventional methods.

(a) No chemical reagent such as sodium or Lewis acids is required. The spectral data are, therefore, free from complications originating from the presence of such a reagent. The accompanying by-products, $C_5H_{11}O^+$, $\cdot C_5H_9O$, and $R\cdot$, absorb only in the near uv,

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[1] T. Shida and S. Iwata, *J. Phys. Chem.*, **75**, 2591 (1971).

[2] T. Shida and S. Iwata, *J. Chem. Phys.*, **56**, 2858 (1972).

[3] P. Balk, S. Bruijn, and G. J. Hoijtink, *Recl. Trav. Chim. Pays-Bas*, **76**, 907 (1957); (b) G. J. Hoijtink, N. H. Velthorst, and P. J. Zandstra, *Mol. Phys.*, **3**, 533 (1960).

[4] R. Zahradnik and P. Carsky, *J. Phys. Chem.*, **74**, 1240, 1235 (1970).

[5] T. Shida and W. H. Hamill, *J. Chem. Phys.*, **44**, 2375, 4372 (1966).

[6] A. Grimison and G. A. Simpson, *J. Phys. Chem.*, **72**, 1776 (1968).

and absorptions appearing at longer wavelengths are solely attributable to the ion radical of the solute.

(b) The ion radicals by reactions 3 and 6 are formed at a distance from the counterions, $C_5H_{11}O^+$ and $X^-$, respectively, and remain immobile. Therefore ambiguity due to the formation of ion pairs such as $Na^+$-$Ar^-$ (Ar, aromatic hydrocarbon) is obviated.

(c) Being frozen at low temperatures, a trace of moisture and oxygen, even if they are present in the system, do not induce decompositions such as

$$Ar^- + H_2O \longrightarrow \cdot ArH + OH^- \qquad (7)$$

$$Ar^- + O_2 \longrightarrow Ar + O_2^- \qquad (8)$$

Also, the immobility of the mononegative ion eliminates the possibility of the disproportionation

$$2Ar^- \longrightarrow Ar + Ar^{2-} \qquad (9)$$

The low temperature makes the vibrational structure of the spectrum distinct which renders the identification of absorption bands easier.

(d) The extinction coefficient of anion radical can be determined easily because the yield of electrons in reaction 1 is known for a unit energy absorbed by the solution.[1,7] (The extinction coefficient of cation radical cannot be determined quantitatively because not all the positive charges in reactions 4 and 6 may be transferred to the solute owing to the competition between the conduction of positive charge and the decomposition of $RX^+$ during the conducting stage or in the final step of charge transfer to the solute.)

(e) Weak absorptions of ion radical can be magnified by giving higher doses in reactions 1 and 4. Prolonged irradiation does not lead to significant secondary decompositions of the radical contrary to the usual case in photoirradiation. This is because the electron in reaction 1 or the positive charge in reaction 4 is continuously scavenged by the overwhelmingly large number of unreacted solute molecules present. A number of forbidden bands of extremely small intensity have been found by the high dose irradiation.

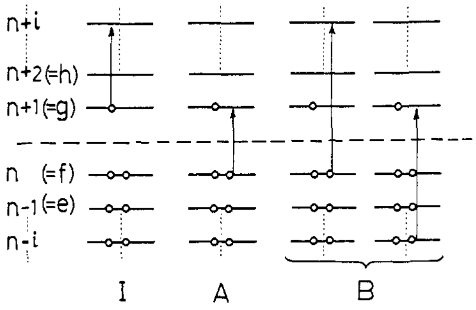
(f) Since for most ion radicals several well-separated electronic bands appear in the near uv through near ir regions, each band can be selectively photobleached using a tungsten lamp and a suitable glass filter. The selective photoexcitation provides useful information on the electronic state of the radicals.

## Results and Discussion

The absorption spectra in the following figures are obtained as the difference of absorption before and after $\gamma$-irradiation of MTHF and RX frozen solutions which is ascribed to the anion and the cation of the solute, respectively. In the near uv region the concomitantly produced solvent radicals and/or the strong absorption of the solute molecule interfere with the precise measurement or the absorption of the solute ion. A broken curve implies less accuracy of the measurement. In some figures the broken curve represents the spectrum cited from the literature as indicated in the caption.

The results of calculations in terms of SCF-MO plus CI for 40 configurations including some of the two-electron excitations[1] are shown in the stick spectrum. Sticks in the dotted line indicate symmetry-forbidden transitions, only the first of which is shown in the figure. In order to describe the character of the theoretical transition of anion, we chose configurations having a coefficient larger than 0.3 in the wave function and classified them as I ($n + 1 \rightarrow n + i$, $i \geqq 2$), A ($n \rightarrow n + 1$), B ($n - i$, $i \geqq 1 \rightarrow n + 1$ and $n \rightarrow n + i$, $i \geqq 2$), and D (two-electron excitation) where the sequential integers in parentheses correspond to the SCF-MO counting from the orbital of the lowest energy (see Scheme I for the notations I, A, and B). In the following spectral charts this notation for molecular orbitals is further replaced by an alphabetical expression in such a way as indicated in the diagram, that is, $n$, $n + 1$, $n + 2$, ..., corresponding to f, g, h, ..., and $n - 1$, $n - 2$, $n - 3$, ..., to e, d, c, .... For class B there are three manifolds depending on the spin $\alpha$ and $\beta$, that is, $\alpha$, $(1/\sqrt{2})(\alpha\beta\alpha - \beta\alpha\alpha)$, and $(1/\sqrt{6})(2\alpha\alpha\beta - \alpha\beta\alpha - \beta\alpha\alpha)$.[3,4] The second and the third are marked with 1 and 2, respectively, in the stick spectrum. The direction of transition moment with reference to the molecular arrangement in the figure is shown by the small arrows. In the following the observed spectra will be discussed in relation to the calculated results.

**Scheme I**



**(I) Benzene.** Figure 1a shows the spectrum of the benzene anion. In the previous work by Gardner using the alkali metal reduction[8] the absorption of the benzene anion was partially masked by the absorption of the alkali metal appearing at 600–700 nm. Gardner's rough estimation of the intensity ratio for the visible and the near uv bands as 1 : 1 ~ 2 seems reasonable with reference to the present results.

The theory predicts that the first forbidden transition occurs in the ir region which should remain forbidden even if the ion is distorted to some extent by the Jahn-Teller effect to lower the symmetry from $D_{6h}$ to $D_{2h}$. The broad visible and the near uv bands are, therefore, safely assigned to the first two allowed transitions of the opposite direction of polarization. The extraordinarily broad bandwidth is an interesting problem, and a possible explanation for the short lifetime of the excited states will be discussed elsewhere.[9]

**(II) Naphthalene and Its Derivatives.** Compared with the relative difficulty of anion formation of benzene[10] the second of the benzenoid homologs easily yields its anion by conventional methods.[11,12] Utilizing the features e and a of the preceding section,

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(7) T. Shida, *J. Phys. Chem.*, 73, 4311 (1969).

(8) C. L. Gardner, *J. Chem. Phys.*, 45, 572 (1966).

(9) T. Watanabe and T. Shida, to be published.

(10) T. R. Tuttle, Jr., and S. I. Weissman, *J. Amer. Chem. Soc.*, 80, 5342 (1958).

(11) P. Balk, G. J. Hoijtink, and J. W. H. Schreurs, *Recl. Trav. Chim. Pays-Bas*, 76, 813 (1957).

(12) K. K. Brandes and R. J. Gerdes, *J. Phys. Chem.*, 71, 508 (1967), and references cited therein.

special attention was paid to the feeble absorption in the near-ir and visible regions. Hoijtink's finding of the weak absorption at $<10$ kK[11] is confirmed. The vibrational structure at 20–25 kK is also magnified in proportion to the radiation dose. The band at $>40$ kK was not precisely measured owing to the strong absorption of the parent molecule.

There should be no doubt as to the assignment of the four long-axis polarized absorption bands in Figure 1b, the three B's and I ($g \rightarrow i$) corresponding to the bands at $>30$ kK and at $\sim 12.5$ kK, respectively. However, there is controversy and apparently some confusion as to the feeble absorption at $<10$ kK and the absorption at 20–30 kK. Hoijtink, *et al.*, assigned the former to the first forbidden transition and the latter to the second short-axis polarized allowed transition ($y_2$) in their first report.[3a] The first $y$-polarized allowed transition ($y_1$) was predicted as hidden on the high-energy side of the allowed $x$-polarized transition ($x_1$) appearing as the absorption at 11–17 kK.[3a] In a later publication, however, they concluded that most of the absorption at 20–30 kK was due to some impurity, possibly the adducts $H^+Ar^{2-}$ and/or $Na^+Ar^{2-}$.[13] This conclusion is based on their finding that no polarization was found in the region of 18–28 kK except for a slight indication of the $y$-polarized absorption at 29.2–30.5 kK[13] and that the absorption at 22 kK increased on standing.[3a] As a result, the two theoretical transitions $y_1$ and $y_2$ were considered not quite apparent in the experimental spectrum.[3b] However, we considered on the following basis that the absorption at 20–30 kK is not spurious, contrary to the Hoijtink's revision.

(1) With our experimental method the suggested adducts cannot be expected because of the impossibility of reaction 9 and of the absence of $H^+$ and/or $Na^+$ in the frozen solution.

(2) When the $\gamma$-irradiated sample was photobleached with a narrow band filter passing light of $\lambda < 300$ nm (corresponding to the anion band at 34 kK), the whole absorption diminished homogeneously which implies that the absorption at 20–30 kK is associated with the anionic absorption.

(3) The pairing property of the anion and cation should make the spectra resemble each other. The spectrum of naphthalene cation, first measured by us and shown in Figures 11a and 11b, shows an absorption at 20–30 kK which seems to be the counterpart of the absorption of the anion in the same region. In the halide matrices the formation of $H^+Ar^{2-}$ and/or $Na^+Ar^{2-}$ is inconceivable because the electrons produced by reaction 4 are almost exclusively scavenged as shown in reaction 5.

(4) As shown in Figures 8 and 9, the anions as well as the cations of naphthalene derivatives always exhibit similar absorptions in the visible region. It seems improbable that all the derivatives are commonly contaminated by some foreign species absorbing in the visible region.

Therefore, we suppose that the "very weak" $y$-polarized absorption of the previous work[3b] is the cause for the possible misinterpretation of the absorption at 20–30 kK and ascribe the absorption at 20–25 kK to $y_1$ (= IA) and that at 25–30 kK to $y_2$ (= AI) (Figure 1b). In other words, the $y_1$ is not overshadowed on the high-energy side of the strong $x_1$ nor is the $y_2$ masked by a "foreign species." Hoijtink's original assignment for the forbidden transition[3a] remains valid and is in agreement with our interpretation of the spectrum. Hinchliffe, *et al.*,[14] apparently thought that Hoijtink had considered the absorption at $<10$ kK as due to the $y_1$ transition in his revised paper[3b] and claimed that the absorption should be ascribed to the forbidden transition.

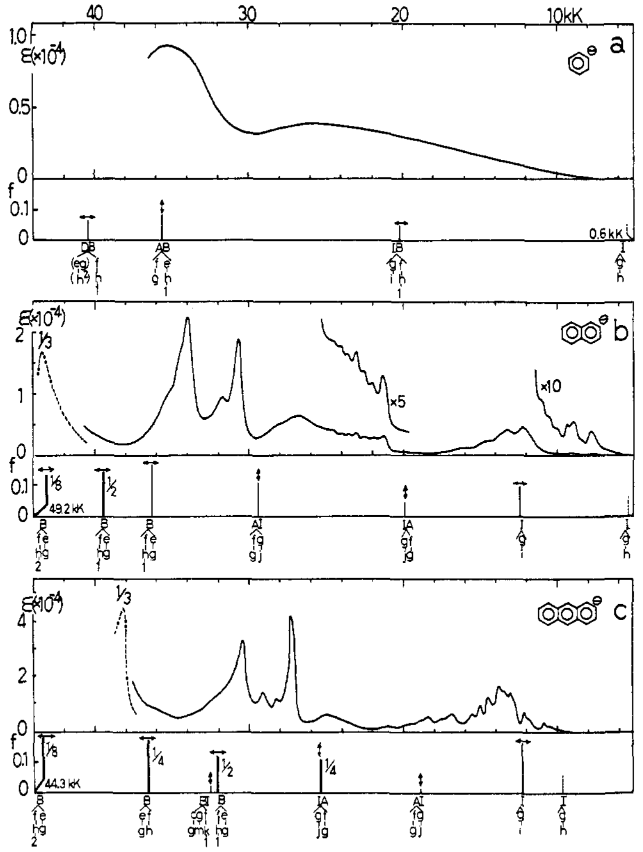

Figure 1. Observed and calculated spectra of anions of benzene (a), naphthalene (b), and anthracene (c). The broken curve in 1b is reproduced from ref 12 and 13.

Figures 1b and 11a,b and Figures 8 and 9 compare the spectra of the anion and cation of naphthalene and some of its derivatives. It is seen that the vibrational structure is more distinct for the cations than for the anions. The set of Figures 11a and 11b shows representatively the effect of the two halide matrices on the cation. The sharp vibrational structure in FM is remarkable. Although there is a slight solvent shift between the two solutions, the shift is small compared with the difference between the anion (Figure 1b) and the cation. As will be discussed later, the $x$-polarized transitions responsible for the absorption at 10–20 and $>30$ kK are blue-shifted for the cations relative to the anions while the absorption bands at 20–30 kK assigned to the $y$-polarized transitions are either red-shifted or almost unchanged. Since acenaphthene and 5,12-dihydronaphthacene give spectra similar to those of naphthalene, the hyperconjugative effect of the methylene groups seems insignificant in the optical excitation. The weak, near ir absorption is manifested for the acenaphthene anion and cation. This fact is

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(13) G. J. Joijtink and P. J. Zandstra, *Mol. Phys.*, 3, 371 (1960).

(14) A. Hinchliffe, J. N. Murrell, and N. Trinajstic, *Trans. Faraday Soc.*, 62, 1362 (1966).

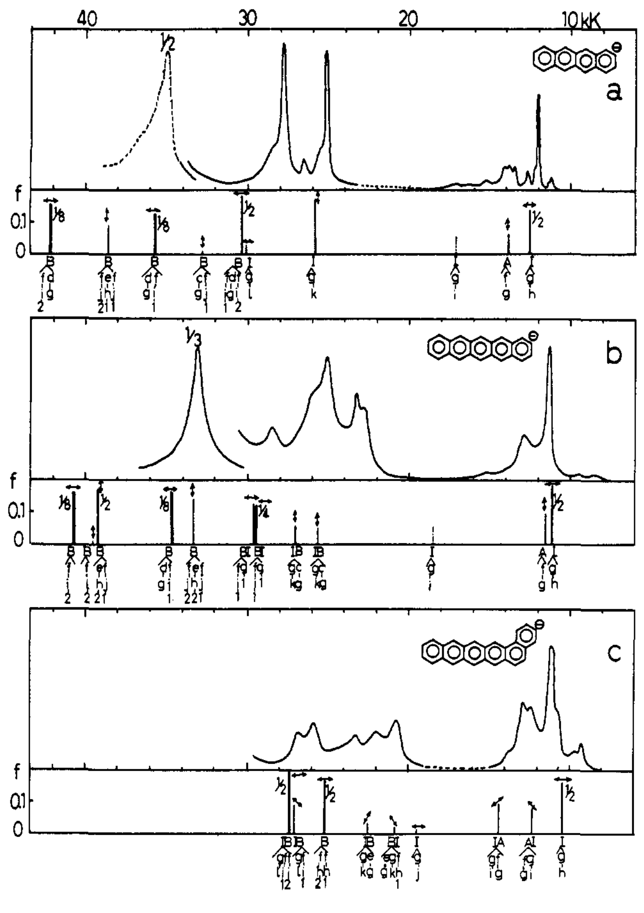

Figure 2. Observed and calculated spectra of anions of tetracene (a), pentacene (b), and 1,2-benzopentacene (c). In this and the following figures the absence of extinction coefficient $\epsilon$ implies that the hydrocarbon was not soluble enough for the precise determination of $\epsilon$ (see text and ref 1 and 2).

not inconsistent with our supposition that the transition for the absorption is symmetry forbidden but is partially allowed by the coupling with a $y$-polarized vibration; the methylene bridge of acenaphthene may affect the coupling specifically as compared with other less strained derivatives.

Figure 11c demonstrates the spectrum of naphthalene dimer cation[15] which was obtained by limitedly warming the sample for Figure 11b. Similar broad spectra of dimer cations were observed also for other hydrocarbons in FM but the discussion of such dimers will not be made here.[2]

**(III) Other Benzenoid Hydrocarbons.** Figures 1–7 compare the experimental and theoretical results of the anion of other benzenoid alternant hydrocarbons. The experimental data of Figures 2c, 3b, 3c, 4a, 4b, 5b, 5c, 6b, 6c, and 7b are new. The polyacenes (except 2c) and the pericondensed hydrocarbons of the symmetry of $D_{nh}$ (pyrene, perylene, triphenylene, and coronene) have been thoroughly studied by the Hoijtink's group[3,11,13,16] as well as by others.[4,14] The spectra of these authentic hydrocarbons are also included in the figures to demonstrate the reproducibility of the present experiments.

In general, the calculated intensity is a good guide for the identification of the observed bands. It is natural that the deviation of the calculated transition energy becomes larger for larger molecules and for higher energies because the number of configurations considered is limited to 40 in our program.

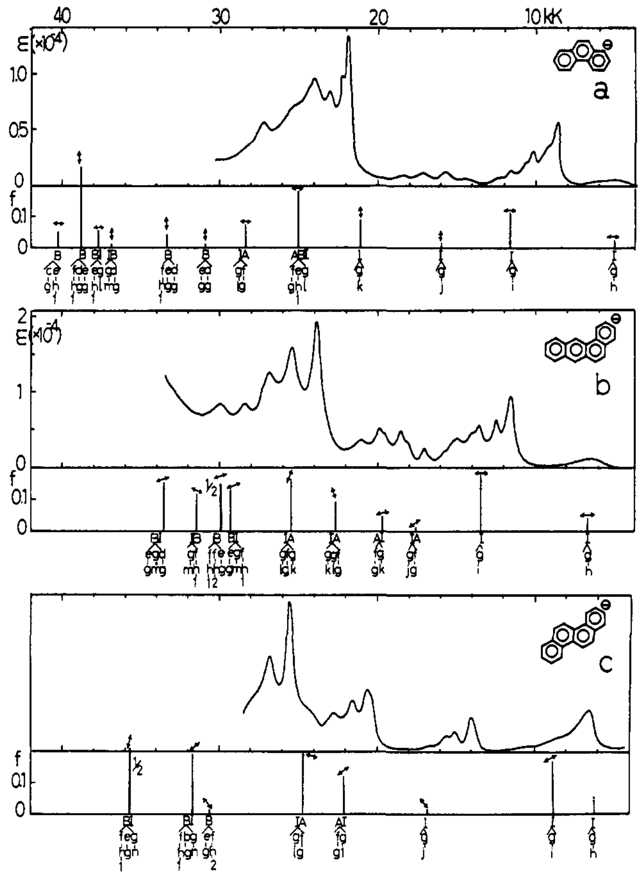

Figure 3. Observed and calculated spectra of anions of phenanthrene (a), 1,2-benzanthracene (b), and chyrsene (c).

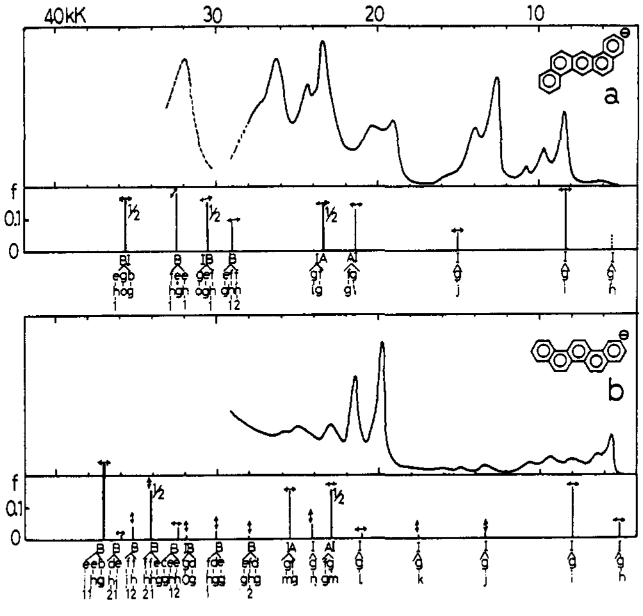

Figure 4. Observed and calculated spectra of anions of 1,2:5,6-dibenzanthracene (a) and picene (b).

As for the polyacenes which have been studied intensively, the assignment of the major bands seems to be established. However, there remains some ambi-

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(15) B. Badger and B. Brocklehurst, *Trans. Faraday Soc.*, **65**, 2576, 2582, 2588 (1969).

(16) G. J. Hoijtink, *Mol. Phys.*, **2**, 85 (1959).

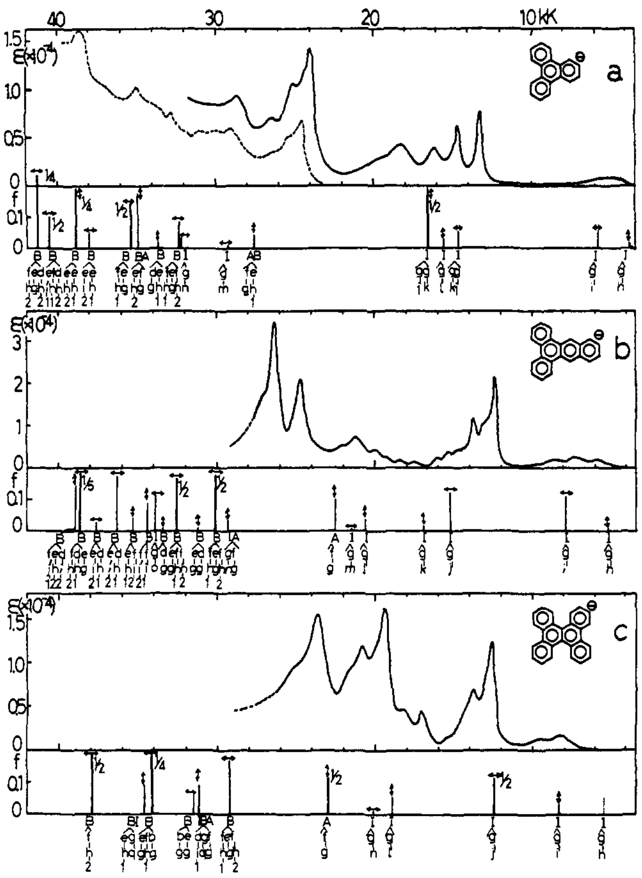

Figure 5. Observed and calculated spectra of anions of triphenylene (a), 2,3-benztriphenylene (b), and tetrabenzonaphthalene (c). The broken curve in 5a is reproduced from ref 16.

guity regarding minor bands. For example, although the small absorption at 10–12 kK of anthracene anion was regarded by Hoijtink, *et al.*, as due to the first allowed $y$-polarized transition,[3b] Hinchliffe, *et al.*, questioned this assignment because the CI splitting between $y_1$ (=AI) and $y_2$ (=IA) cannot be so large as to correspond to the absorptions at <12 and 25 kK, respectively.[14] They (Hinchliffe, *et al.*) proposed that the former absorption is due to the first forbidden transition and that the $y_1$-band is hidden on the *high*-energy side of the $x_1$-band at 13.5 kK.[14] We agree with this proposal because of the similar appearance of the weak, near ir absorption for both naphthalene and anthracene anions and because of the general agreement of the calculation with the experiment (Figure 1c). For tetracene and pentacene also the weak absorption at <12 kK may be due to the forbidden transition as claimed by previous workers,[14] but for these higher polyacenes a definite conclusion seems to be more difficult in view of the predicted proximity of the allowed $y_1$-band to the $x_1$ (Figures 2a and 2b).

Another minor correction of previous assignments may be made for the pyrene anion. Hoijtink, *et al.*, ascribed the absorption at 17–19 and 21–25 kK of the anion to the proton adduct as in the case of the naphthalene anion[13] (Figure 6a). However, since the absorption appears also in our experiment and since the present calculation predicts a weak short-axis polarized absorption on the low-energy side of the major visible band, we consider that the absorption is intrinsic to the pyrene anion. Also, the absorption at 21–25 kK can

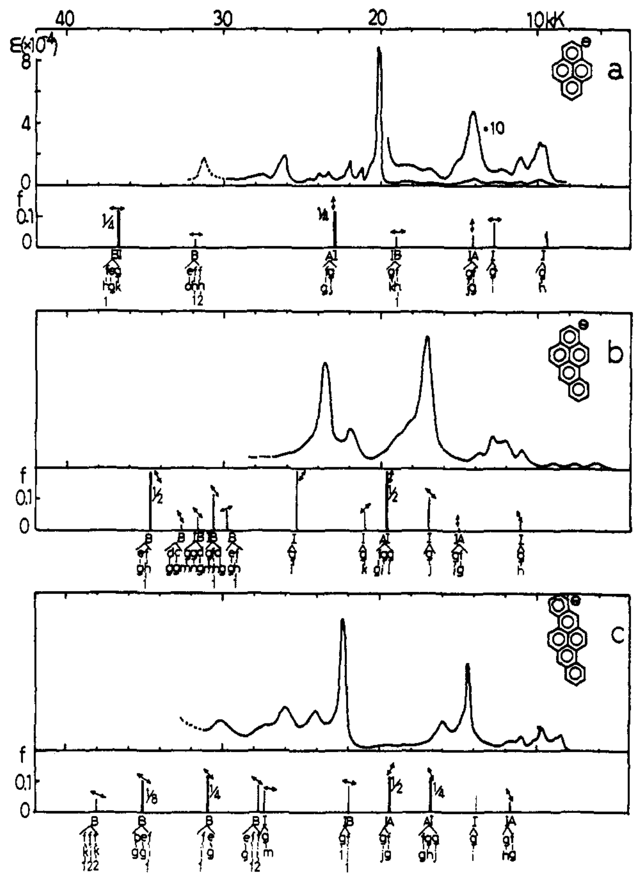

Figure 6. Observed and calculated spectra of anions of pyrene (a), 3,4-benzpyrene (b), and 3,4:8,9-dibenzpyrene (c).

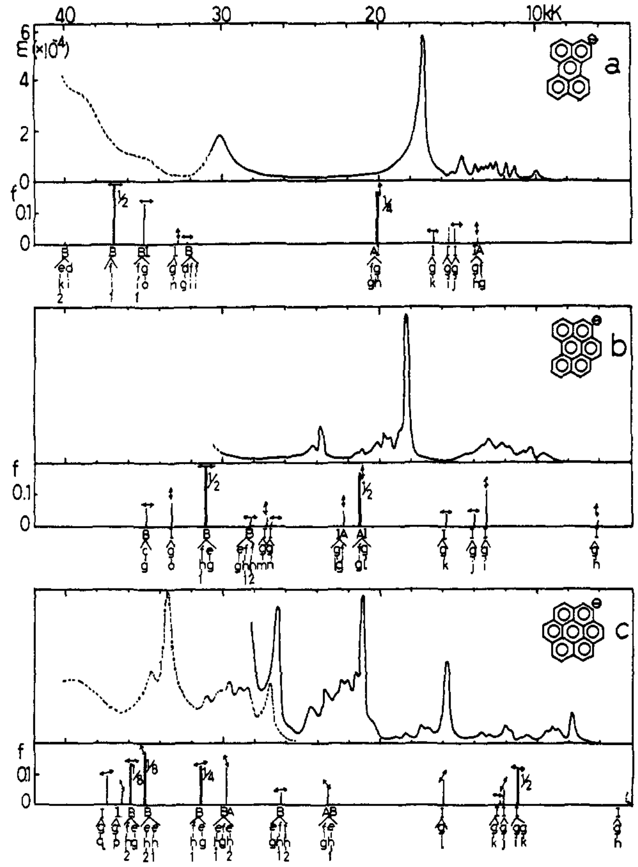

Figure 7. Observed and calculated spectra of anions of perylene (a), 1,12-benzperylene (b), and coronene (c). The broken curve in 7c is taken from ref 16.

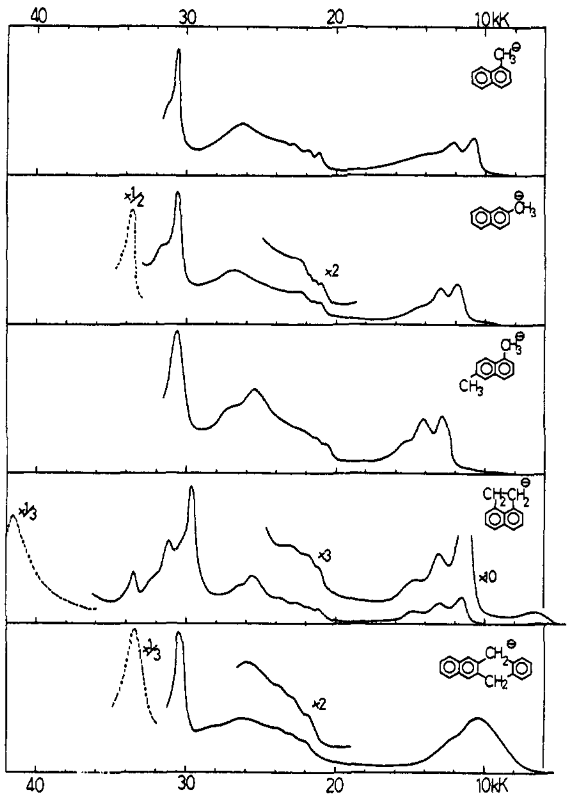

Figure 8. Observed spectra of anions of some naphthalene derivatives.

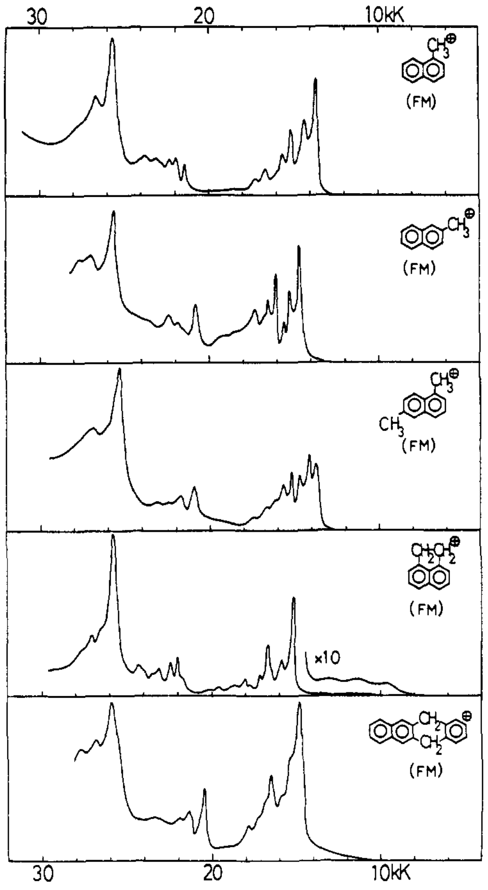

Figure 9. Observed spectra of cations of some naphthalene derivatives in the Freon mixture.

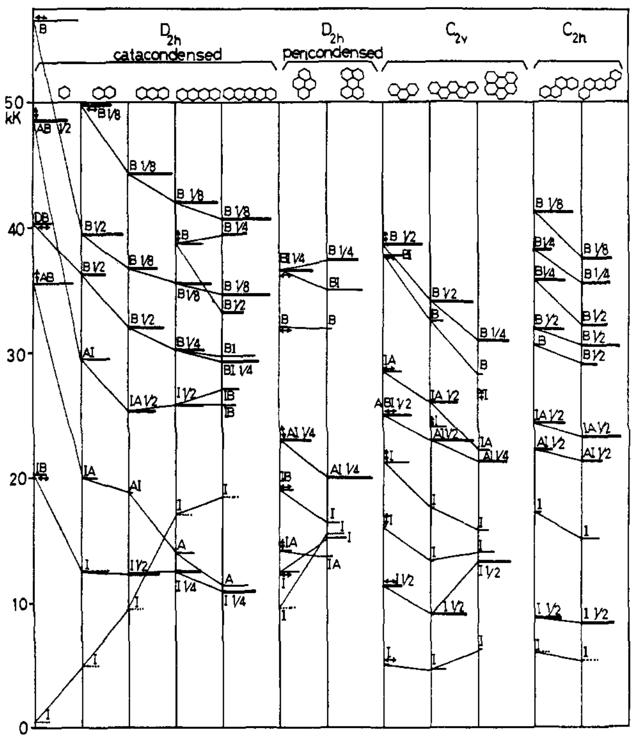

Figure 10. Correlation diagram of calculated spectra of anions. For the notation A, B, I, and D see the text. The small arrow represents the direction of transition moment referred to the molecular arrangement shown in the top of the diagram.

be regarded as the vibrational structure of the major peak at 20.32 kK because the small peaks at 21.59, 22.22, 22.99, and 24.09 kK can be analyzed in terms of two fundamental modes of $\nu \sim 1300$ and $1900 \text{ cm}^{-1}$.

Compared with the other ions, the calculated intensities for the anions of triphenylene and coronene markedly deviate from the observed spectrum. Such disagreement is attributable to the Jahn–Teller distortion as pointed out previously[16] (Figures 5a and 7c). For example, if we assign, following previous workers,[16] the two bands at 15.8 and 21 kK of the coronene anion to the transitions involving the pairs of orbitals e, f, and g, h which are degenerate and belong to $e_{2u}$ and $e_{1g}$ in the Hückel approximation,[16] the discrepancy of intensity between the experiment and the theory is obvious. Similarly, the intensity distribution of low-energy transitions of I-type for the two anions is quite different in theory and practice. (For these highly symmetric molecules the odd electron in the ground state was put into the orbital of the lower SCF energy between the nearly degenerate orbitals.)

Figure 10 shows the correlation of the calculated electronic state of some anions having the symmetries, $D_{2h}$, $C_{2v}$, and $C_{2h}$. The correlation was obtained by consulting the dominant configurations of each transition. It is seen that the lowest (doublet) transition is associated with the configuration I (g → h or i) which is dipole forbidden for the $D_{2h}$ and $C_{2h}$ symmetries. The lowest transition is followed by various I-type transitions responsible for most of the visible bands. Another ionic transition of type A is sandwiched between the transitions starting at about 30 kK and residing mostly in the region of 30–40 kK.

Although the chemical method using various Lewis

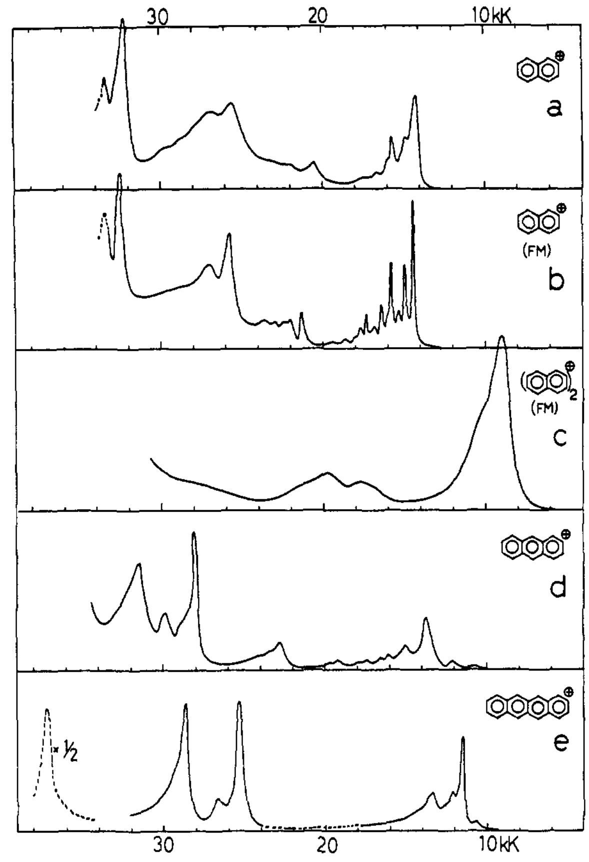

Figure 11. Observed spectra of cations of polyacenes. Figures 11b and 11c were obtained for FM solutions immediately after irradiation at 77°K and after limited warming and recooling to 77°K, respectively.[2] The scale of ordinate is common to b and c.

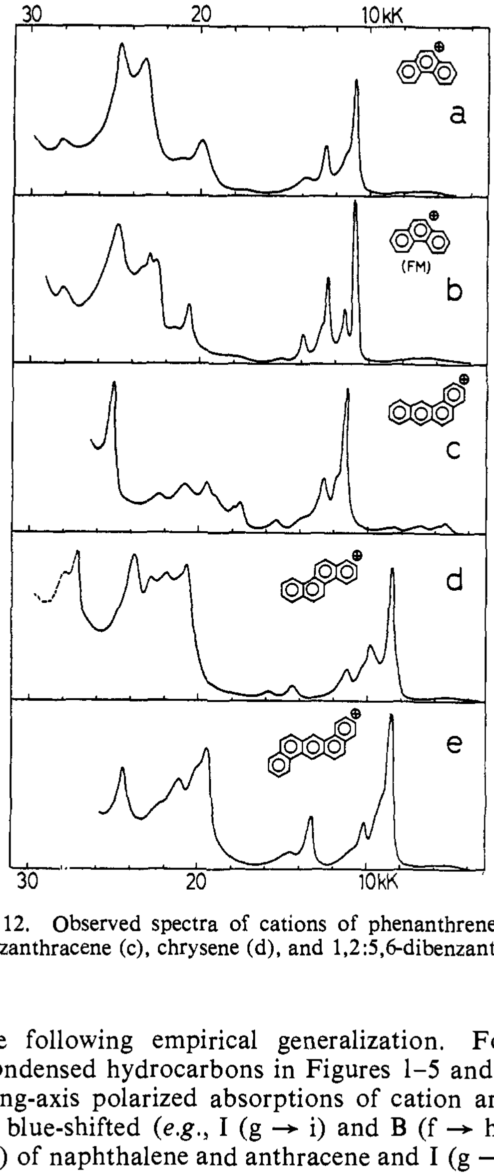

Figure 12. Observed spectra of cations of phenanthrene (a, b), 1,2-benzanthracene (c), chrysene (d), and 1,2:5,6-dibenzanthracene (e).

acids can produce cations of aromatic hydrocarbons,[17] intensely colored Lewis acids and/or the tendency to produce $ArH^+$ (protonated molecule[17b]) as well as other by-products prevent the precise measurement of the optical absorption spectrum of cation radicals under study. So far reliable spectra of alternant hydrocarbons have been recorded only for anthracene, tetracene, triphenylene, pyrene, perylene, 3,4-benzpyrene, and coronene.[17a,b]

Figures 11–14 demonstrate the spectra of cations produced by reactions 4–6. Although the MO calculation was made also for the cations, the results are not shown in the figures because of the insignificant differences from those for the anions. Since solvent power of the halide solvents at 77°K is relatively low, not all the hydrocarbons in anion studies were converted to the corresponding cation by reaction 6. Benzene was sufficiently soluble but because of its comparatively high ionization potential it was not effectively oxidized by reaction 6. (In order to scavenge the positive charge of reaction 4, it was necessary to add large amounts of benzene. This resulted in the formation of the benzene dimer cation[15] instead of the isolated cation radical.)

Comparison of Figures 11–14 with Figures 1–7 leads to the following empirical generalization. For the catacondensed hydrocarbons in Figures 1–5 and 11–13 the long-axis polarized absorptions of cation are generally blue-shifted (*e.g.*, I (g → i) and B (f → h – l, e → g) of naphthalene and anthracene and I (g → h) of phenanthrene and picene) while the short-axis polarized absorptions are somewhat varied but most of them are either red-shifted or almost unchanged (*e.g.*, IA (g → j, f → g) and AI (f → g, g → j) of naphthalene and anthracene, and I (g → k) of phenanthrene). For the pericondensed hydrocarbons in Figures 6, 7, 13, and 14 both the long- and short-axis polarized absorptions of the cation are blue-shifted (*e.g.*, pyrene and perylene). Survey of the spectra in literature also reveals the same general tendency. Examples of the systematic shifts are seen for perylene cation in boric acid[18] *vs.* its anion in liquid ether[11] and tetracene cation in $CF_3COOH-BF_3$, $H_2O$[17b] *vs.* the anion in tetrahydrofuran.[19] However, it would have been difficult to draw a general conclusion as to the spectral shift because the solvents used in the cited literature vary drastically. Since both MTHF and RX used in the present work are aprotic and the static dielectric constant of the frozen matrices at 77°K should be roughly the same and equal to ~2–3, we consider that the spectral shifts found in the present work are not due to the difference of solvent but are characteristic of the hydrocarbon ions. As is

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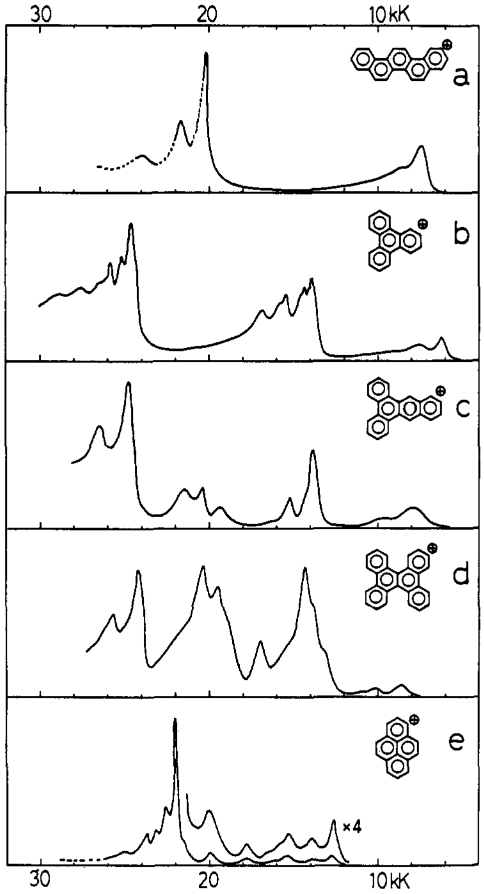

Figure 13. Observed spectra of cations of picene (a), triphenylene (b), 2,3-benztriphenylene (c), tetrabenzonaphthalene (d), and pyrene (e).

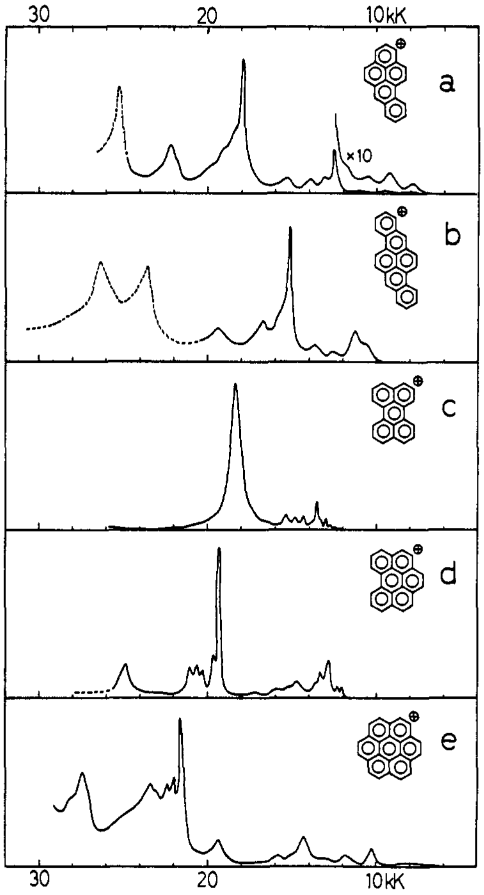

Figure 14. Observed spectra of cations of 3,4-benzpyrene (a), 3,4:8,9-dibenzpyrene (b), perylene (c), 1,12-benzperylene (d), and coronene (e).

shown representatively for naphthalene and phenanthrene cations in Figures 11 and 12, the spectral shift between the two halide matrices is relatively small. Although the reason for the shift is not immediately known, the difference might be a manifestation of the different effect of $\sigma$ electrons in both ions. The possibility that there is a difference in the structure of both ions does not seem plausible for such large molecules as perylene and coronene.

**(IV) Nonbenzenoid Alternant Hydrocarbons.** Figure 15 shows the spectra of an anion of the "$4n$-type" alternant hydrocarbons where $n = 2$, 3, and 4. The spectrum of the cyclooctatetraene (COT) anion has been measured by Kimmel and Strauss.[20] In agreement with their work the calculation assuming the regular octagon with the C–C distance of 1.39 Å is reproduced fairly well in the observed spectrum. Contrary to the benzenoid ($4n + 2$ type) hydrocarbons the inversion symmetry of the $4n$-type hydrocarbons is such that the f and g orbitals have the same parity, *i.e.*, ungerade for COT. As a consequence, the transition having the character of A (f → g) is forbidden. Because of the high symmetry of the COT anion the pairs of d, e and h, i are degenerate as is indicated by the crossed arrows in Figure 15a.

Although both experimental[21a] and theoretical[20,21d] evidence suggests the planarity of the COT anion, there is no reason for the cation to favor the planar form. If it were planar, one would expect a similar absorption spectrum to that of the anion by the pairing property. The top of Figure 16 shows the spectrum of irradiated COT solution in BuCl (bold curve) and in FM (fine curve) which should be associated with the cation radical of COT according to reactions 4–6. The structureless broad band is quite different from that of the COT anion but is similar to those observed for a number of cations of simple aliphatic olefins[22] which suggests that the COT cation retains the same olefinic structure as the neutral tub-shaped molecule. Although the nature of the absorption of the olefin cations observed in the previous work[22] is still not fully understood, the absorption could be due to the dimer cation as proposed by Badger and Brocklehurst.[15] The fact that the two ethylene units are adjacent in the COT molecule should, then, make the nonplanar COT cation similar to a dimer cation of ethylene. Whatever the character of the absorption of the COT cation may be, it shows rather remarkable changes upon photoexcitation; the spectral changes induced by successive bleaching with selected light (Figures 16b and 16c) took place in both halide matrices which indicates that the photoinduced reactions do not involve solvent molecules. Our conjecture is that the first bleaching changes the olefinic cation to another cation which is essentially olefinic but has a

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[20] P. I. Kimmel and H. L. Strauss, *J. Phys. Chem.*, **72**, 2813 (1968).

[21] (a) T. J. Katz and H. L. Strauss, *J. Chem. Phys.*, **32**, 1873 (1960); (b) F. J. Smentowski and G. R. Stevenson, *J. Amer. Chem. Soc.*, **90**, 4661 (1968); (c) H. L. Strauss, T. J. Katz, and G. K. Fraenkel, *ibid.*, **85**, 2360 (1963); (d) A. D. McLachlan and L. C. Snyder, *J. Chem. Phys.*, **36**, 1159 (1962).

[22] T. Shida and W. H. Hamill, *J. Amer. Chem. Soc.*, **88**, 5376 (1966).

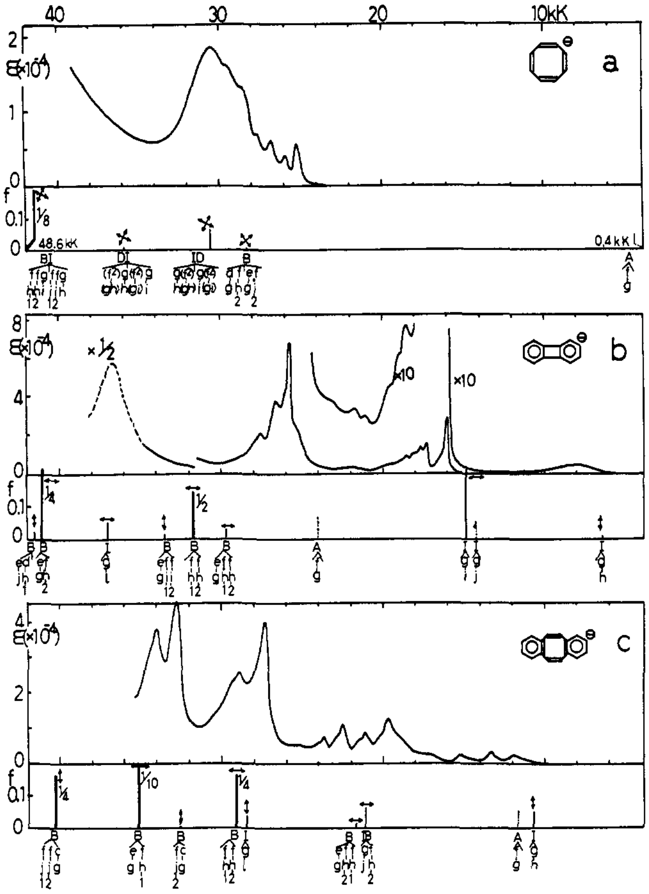

Figure 15. Observed and calculated spectra of anions of COT (a), biphenylene (b), and dibenzo-COT (c).

different conformation from the initial one (*e.g.*, from the tub to the crown shape). On the second bleaching the olefinic cation may undergo a rather drastic change involving a rearrangement of the carbon skeleton. This conjecture is based on the similarity of the first and the second broad absorptions to those of the olefin cations[22] and on the fact that the photoexcited COT neutral molecule is known to undergo various rearrangement reactions.[23]

Biphenylene anion and cation were produced and the optical spectra were compared with an approximate SCF-MO calculation by Hush and Rowlands.[24] Their spectrum of the anion agrees with ours except that the reported lowest transition at 6.58 kK is missing in our spectrum (Figure 15b). Instead of the band at 6.58 kK we found a near ir band at about 7.5 kK. This may correspond to the 6.58 kK, but the intensity is by far smaller than that of the previously reported band. As in the case of the COT anion, the transition comprising the A configuration should be forbidden.

As for the cation of biphenylene, the discrepancy between the previous and the present work is more serious. Although the shapes of the reported bands at 16.1 and 27.9 kK resemble those in Figures 17a and 17b, the band maximum is shifted toward blue by about 3 kK in our spectrum. The high polarity and a potential reactivity of concentrated sulfuric acid used as the solvent in the previous work might be responsible for the discrepancy. Since the cation in the present work should be less influenced by the solvent, the spectrum in Figure 17 should be more safely comparable with the

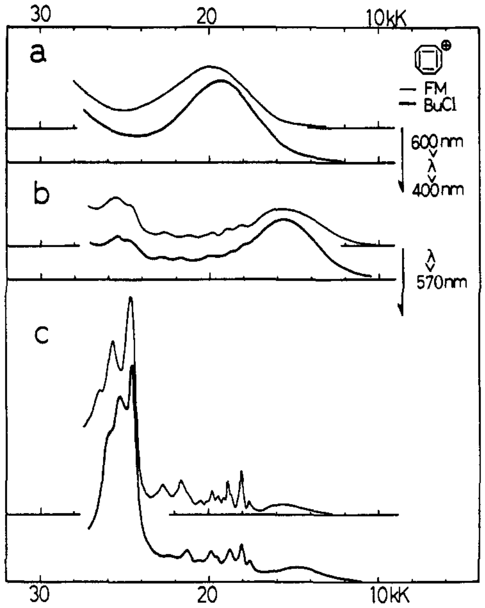

Figure 16. Observed spectra of COT cation (a) immediately after irradiation in BuCl (bold curve) and in FM (fine curve), (b) after the subsequent bleaching with blue light, and (c) after the succeeding bleaching with red light.

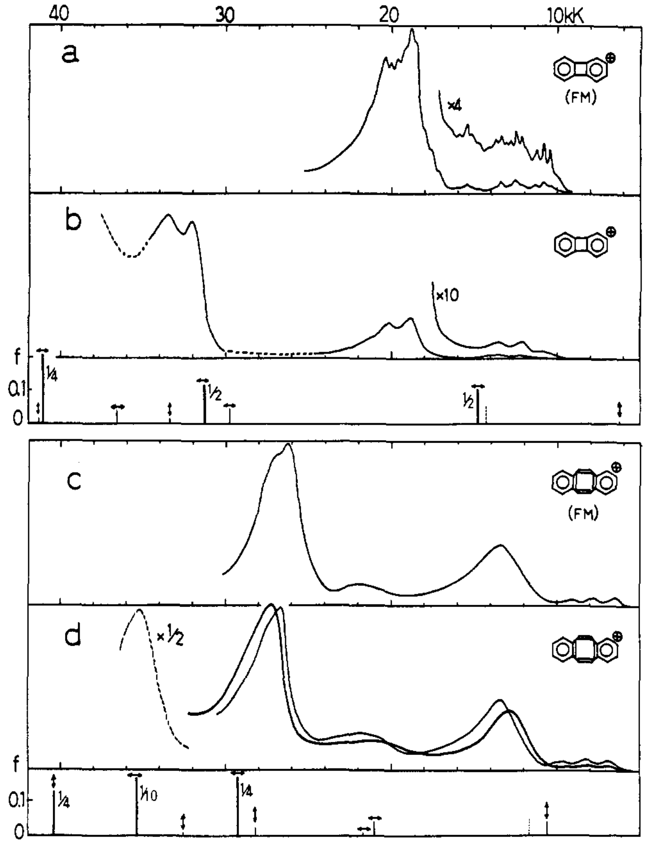

Figure 17. Observed and calculated spectra of cations of biphenylene (a, b) and dibenzo-COT (c, d). The bold curve in d was obtained immediately after irradiation in BuCl. Limited warming of the sample gave the fine curve after recooling at 77 °K.

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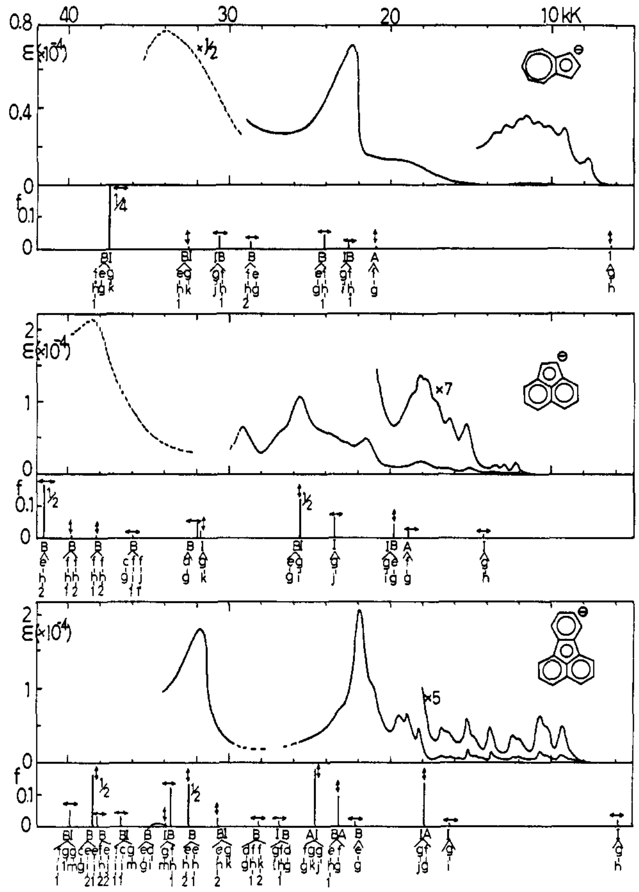

Figure 18. Observed and calculated spectra of anions of nonalternant hydrocarbons.

theoretical spectrum (in the calculation we used more recent structural information[25] than that used by Hush and Rowlands). By the technique of magnification, we have found a weak absorption which should be ascribed to the lowest energy $y$-polarized transition. The FM solution (Figure 17a) reveals the superposition of a low-frequency vibrational mode upon another of a higher frequency. The stepwise structure, partially seen on the low-energy shoulder of the strong visible band, may correspond to the forbidden transition predicted at 14.3 kK. Similar to the pericondensed hydrocarbons, both the $x$- and $y$-polarized transitions of the cation are blue-shifted compared with the anion. However, the degree of the shift seems to be larger than in benzenoid hydrocarbons which may be attributed to the partial break of the pairing property due to the presence of the cyclobutadiene ring.

Since no experimental data concerning the structure of dibenzo-COT ions are available, we assume by analogy with the COT anion that the dibenzo anion is also planar. The calculation based on such an assumption gives fair agreement with the observed spectrum (Figure 15c). Although the uncertainty of the structure of the cation should be greater, the experimental spectrum in Figures 17c and 17d suggests that the cation retains the pairing property. The blurring of the vibrational structure, however, may be related to the possible deviation from the planar structure. The close resemblance of the spectrum in FM (Figure 17c) to the

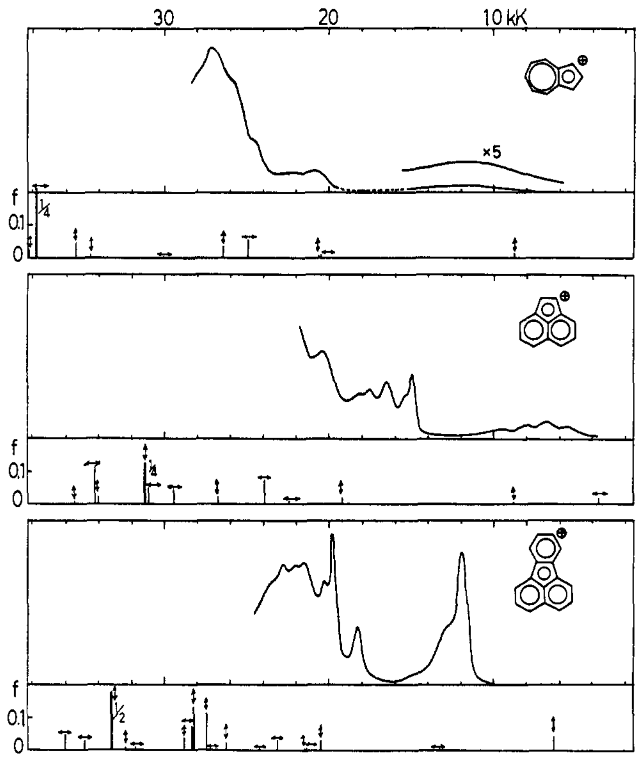

Figure 19. Observed and calculated spectra of cations of nonalternant hydrocarbons.

spectrum of softened BuCl solution (fine curve of Figure 17d) suggests that the FM glass at 77°K is softer than the BuCl at 77°K and that the cation in FM relaxes instantly upon irradiation while the cation in BuCl takes the relaxed conformation only after a limited warming of the matrix.

Figures 18 and 19 show the spectra of ions of nonalternant hydrocarbons. Although the esr study of azulene cation[26] and anion[27] has been repeatedly carried out, corresponding optical studies are rare. The electronic spectra of anions of azulene,[28,29] acenaphthylene,[30] and fluoranthene[30] are reported in the literature but the complete spectrum over the spectral region of 5–40 kK has not been determined. The cation of an alkylated azulene was studied recently[29] but the unsubstituted azulene ion is new as are the cations of the other two hydrocarbons in Figure 19. Except for the fact that the spectra of azulene cation and anion are accidentally similar, the spectra of both ions of the other two hydrocarbons are quite different as should be the case for a nonalternant hydrocarbon.[31]

**Notice.** The method of production of ion radicals described in this paper is widely applicable provided that the substance is sufficiently soluble in the solvents described above. However, the combination of a γ-ray irradiation facility and an apparatus for low-temperature optical measurements may not be readily accessible

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to those who need spectroscopic information of ion radicals. We are most willing to provide the data from our measurements on several hundred substances which will be published in due course.

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# Electron Spin Resonance Spectra of $\gamma$-Irradiated or Photolyzed Arsines

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**Abstract:** Exposure of trialkylphosphonium and trialkylarsonium ions in sulfuric acid glasses at 77 K to $^{60}$Co $\gamma$-rays gave radicals whose esr spectra are shown to be characteristic of the radical cations $R_3P^+$ and $R_3As^+$. The results confirm that these radicals are pyramidal with $C_{3v}$ symmetry, the unpaired electron being in an orbital having a p:s ratio of about 8 which is strongly confined to the central atom. No proton hyperfine coupling was detected. These results are discussed in relation to a recent suggestion that $R_3As^+$ radicals have a very low spin density on As when R is aromatic. Results recently reported for $R_2As$ radicals are largely confirmed, and attention is called to the remarkable similarity between the hyperfine tensor components for $Me_2As$ and $Ph_2As$ radicals. These results show conclusively that $\pi$ delocalization of the unpaired electron into the aromatic rings in $Ph_2As$ radicals is negligibly small.

In a most interesting paper, Preer, *et al.*, have recently presented esr spectra for various uv irradiated arsines in rigid alcoholic solutions.[1] In view of the importance of these compounds as ligands in transition-metal complexes, it seemed of interest to outline some of our own work in this area and to call attention to a remarkable facet of the results which was not previously mentioned.

Some time ago we reported esr results for the series of isoelectronic radicals $R_3Al^-$, $R_3Si$, and $R_3P^+$,[2] and deduced from the derived orbital populations on the central atoms that, while all three types of radical are pyramidal, there is a pronounced flattening on going from aluminum to phosphorus. This, we suggested, is best understood in terms of Pauling's electronegativity principle.[3]

More recently,[4] we showed that when pure alkyl phosphines or arsines are $\gamma$-irradiated, cation dimers, $R_3P{-}PR_3^+$ and $R_3As{-}AsR_3^+$, are formed rather than the simple cations. We have not, however, reported results for the $R_3As^+$ cations themselves. Also, in some of these radiation studies, we have obtained esr spectra very similar to those assigned by Preer, *et al.*,[1] to $R_2As$ radicals; we agree entirely with their assignment, but differ slightly in the derived magnetic parameters.

## Experimental Section

**Materials.** Trimethyl-, triethyl-, and triphenylphosphines and -arsines were of the highest grade available and were used, in general, as supplied since further purification had no effect on the esr results. Sulfuric acid was *ca.* 98% AnalaR grade. Solutions were prepared at *ca.* 273 K and immediately frozen, as small beads, to 77 K.

**Irradiation.** These samples were exposed at 77 K to $^{60}$Co $\gamma$-rays in a Vickrad source at a nominal dose rate of 4 Mrad hr$^{-1}$. Irradiation times ranged from 0.1 to 2 hr.

**Esr Spectroscopy.** Spectra were obtained at 77 K using a Varian E3 spectrometer and were calibrated with diphenylpicrylhydrazyl. Samples were annealed *in situ* either using a Varian variable-temperature accessory or by removing the liquid nitrogen from the dewar insert and allowing the sample to warm slowly, liquid nitrogen being added again as soon as appreciable changes in the esr spectra were noticed.

## Results

For the trimethyl and triethyl compounds in sulfuric acid, the central region ($\pm$ 100 G) of the esr spectra was dominated by features from $R_2\dot{C}{-}PH^+R_2$ or $R_2\dot{C}As^+{-}HR_2$ radicals, as described previously.[5,6] However, except for the triphenyl compounds, the outer spectral regions for the phosphonium salts comprised a doublet with distinct parallel and perpendicular features as indicated in Figure 1. These features are assigned to $Me_3P^+$ radical cations for reasons that have been outlined previously.[2] The arsonium ions gave rather similar outermost features (Figure 2) which are assigned to the $M_I = \pm {}^3/_2$ parallel and perpendicular components of spectra for $R_3As^+$ radical cations. The $M_I = \pm {}^1/_2$ lines are hidden by features previously assigned to $\beta$ radicals, $R_2\dot{C}CH_2AsH^+R_2$.[7] Some derived parameters are given in Table I. These have been obtained using the Breit–Rabi equation.

Also given in Table I are the corresponding orbital populations for the unpaired electron on phosphorus and arsenic. Although admittedly very approximate,

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