Spectra of Tetracyanoquinodimethane Monovalent Anion: Vibrational Structure and Polarization of Electronic Transitions

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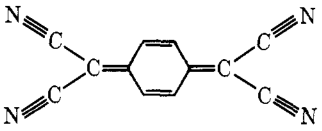
Abstract: The absorption spectra of tetracyanoquinodimethane (TCNQ) anion in the 960- to 350-nm range have been determined (a) in 2-methyltetrahydrofuran glass at 77 K, which allows resolution of vibronic structure, and (b) oriented in a liquid crystal solvent to obtain directions of the transition moments. The first electronic transition at 1.447 eV exhibits a vibronic structure indicative of two active upper-state vibrations, $\omega_1' = 1260 \pm 3$ and $\omega_2' = 331 \pm 3$ cm^{-1}. Both this and the second electronic transition occurring at 2.84 eV are polarized along the molecular long axis, requiring the symmetry of the two lowest lying electronic excited states to be B_{1u}. No transverse polarized transition was observed in the entire wavelength range; detection would have been possible if $\epsilon_{\text{transverse}}/\epsilon_{\text{long-axis}}$ exceeded 0.13 at any wavelength. The results are in satisfactory agreement with predictions of previously published SCF-LCAO-MO calculations.

Introduction

Chemists have long been interested in stable organic ion radicals as a result of their fascinating chemical and physical properties. A case in point is the anion radical of *p*-tetracyanoquinodimethane, TCNQ (I). This species became the subject of much research after its discovery in the early sixties because of its stability in nonaqueous polar solvents and because of its ability to form a variety of unique ion-radical solids with appropriate closed-shell cations.[2,3] Subsequently, magnetic resonance[4] and optical[1,5,6] experiments, as well as theoretical calculations[6-9] on the monomer ion radical, were performed to obtain an understanding of the ground- and excited-state properties of this species as they relate to the electronic states in the solid.



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Recently, a new class of TCNQ ion-radical solid was discovered which is structurally characterized by separate stacks of TCNQ anion radicals and separate stacks of cation radicals that are derivatives of the TTF (tetrathiofulvalene) molecule.[10,11] Undoubtedly, the elucidation of specific mechanisms of solid-state interaction in these double stack systems will require the ability to separate the contributions due to each stack. Recent electron paramagnetic resonance studies[12] on oriented single crystals of (TTF)(TCNQ) and optical polarization measurements on epitaxial films[13] of the same material suggest the feasibility of this approach if the relevant donor or acceptor stack contributions to the total behavior can be identified.

Unfortunately, the progress in assigning electronic transitions in these solids has been hampered by the unavailability of reliable information on electronic and vibrational band assignments, relative oscillator strengths, and optical polarization for the relevant monomer ion radicals and their self-associated species. Furthermore, neither TCNQ nor TTF has yet been shown to form solids in which the ion radicals are as electronically isolated from each other, as in the case of *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine perchlorate.[14] As a result, the spectroscopic properties of the parent monomer ion radical must be obtained by dilution of the solid in a suitable medium.

Under these restraints a common means of orienting the radical species has been to prepare them photolytically from the neutral species in a suitable matrix using a polarized excitation source. This photoselection technique[15] can be extremely powerful, but it is obviously limited to those systems which have appropriate photochemistry in low-temperature glasses. An orientation method of more general potential utility seemed to be the use of liquid-crystal solvents.

Nematic liquid crystals which can be oriented by physical means have been shown to be useful matrices in a variety of spectroscopic studies[16,17] on neutral closed-shell molecular species. Unfortunately, the relatively low dielectric constants of the available liquid crystals have limited their use to nonpolar molecules. For the few reported instances of their utility in studying polar ion radicals,[19] the low solubility was overcome by electrochemical generation of the free radical in situ and by subsequent detection of the free radical via the EPR technique.

Previous work in this laboratory[20] in a different context has demonstrated that the solubility of organic anions in liquid crystal solvents can be increased dramatically by complexation of the countercation K^+ with macrocyclic crown ethers.[21] We now find that the dicyclohexyl-18-crown-6 complex of potassium TCNQ (abbreviated as CKTCNQ) dissolves in a liquid crystal in concentrations high enough for optical spectroscopy at the small path lengths required for orientation.

We wish to describe in this paper our measurement of the polarization directions of the electronic transitions of TCNQ$\cdot^-$ occurring in the 960- to 350-nm wavelength range. We also present in detail the spectrum of TCNQ$\cdot^-$ in the same wavelength range obtained in 2-methyltetrahydrofuran (MTHF) glass at 77 K. A vibronic analysis allows us to remove ambiguities from previous interpretations of the TCNQ$\cdot^-$ spectrum. We further discuss our results in terms of the predictions of LCAO-MO calculations,[6,7] excited state geometry, and their relation to solid-state results.

Experimental Section

The LiTCNQ solid was prepared by means of the standard method.[2] CKTCNQ was prepared by refluxing an equivalent amount of dicyclohexyl-18-crown-6 (Aldrich Chemical Co.) and potassium TCNQ for 2 h in methanol. After removal of the solvent in a rotary evaporator, the solid was taken up in a small amount of methanol, recrystallized, filtered, and dried under vacuum. Potassium and carbon-hydrogen analyses[22] indicated the presence of

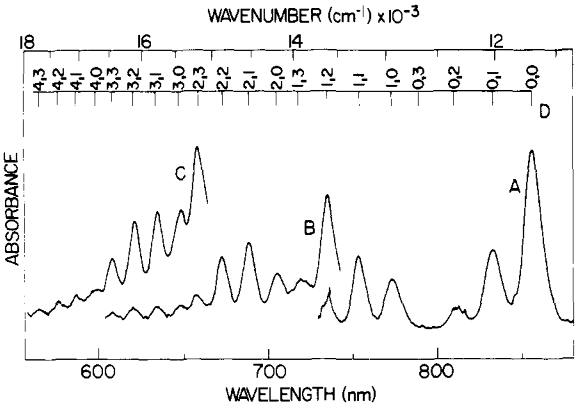

Figure 1. Near-infrared electronic spectrum of TCNQ$\cdot^-$ [as LiTCNQ(A,B) or CKTCNQ(C)] in 2-methyltetrahydrofuran solvent at 77 K. Relative concentrations are A:B:C = 1:4.4:33.3. Vibrational assignments are shown in D by indicating the number of quanta in vibrations 1 and 2 in the upper state.

about 10% impurity, probably unreacted crown ether. Both TCNQ salts were stored under nitrogen in the dark.

Low-temperature spectra were taken in 2-methyltetrahydrofuran solvent obtained from Aldrich and used without further purification. Solutions were prepared in a glove box under nitrogen atmosphere and red safelight and were cooled to liquid nitrogen temperature in an optical Dewar. Spectra were taken on a Cary 14 spectrophotometer equipped with a pen period attachment. Spectral slit widths used were <1 nm above 750 nm and <0.3 nm below, corresponding to a resolution better than 20 cm^{-1} over the entire range.

Oscillator strengths were measured in room-temperature acetone solution. We found this advisable because we wished to avoid the necessity of using uncertain corrections for volume contraction on freezing and because room-temperature solutions of LiTCNQ in MTHF proved extremely photosensitive.

The nematic solvent used in obtaining the polarization spectra was a eutectic mixture[23] of 4-pentyl- and 4-heptyl-4′-cyanobiphenyl.[24] Its relatively high dielectric constant, transparency in the near-ultraviolet, and a nematic-temperature range that includes room temperature, made it particularly well suited for our purpose. The absorption cell was made by clamping together two quartz slides 25 × 38 × 1.6 mm separated by U-shaped Teflon spacers 0.512 mm thick. To establish the optic axis direction, the inner faces of the slides were treated with *p*-octylphenoxyethanol (Triton X-15, TM Rohm & Haas Corp.) prior to assembly and rubbed along the long edge.[25] The cell was filled under nitrogen atmosphere and red safelight with a filtered saturated solution of CKTCNQ in the nematic solvent. An identically prepared cell filled with the pure solvent served as reference. The sample and reference compartments of the Cary 14 were equipped for the polarization measurements with a matched pair of Glan-Thompson prisms (Karl Lambrecht Co.).

In polarization measurements, compensation in the solvent absorption region of the spectrum can be expected only if the orientational order parameter of the solvent (to which its dichroism is proportional) is the same in the solution and in the pure solvent. To confirm this, the sample cell and the reference cell were scanned separately in the sample compartment of the Cary 14 between polarizers oriented 45° with respect to the optic axis. Identical series of transmission maxima and minima resulted, demonstrating that the retardation, hence the birefringence, of the two samples were identical to within an experimental error of 0.6%. This indicates that the small amount of solute caused no significant decrease in the order parameter of the nematic solvent.[26]

Results

(A) Low-Temperature Spectra. The spectra of LiTCNQ and CKTCNQ in MTHF glass at 77 K were recorded between 960 and 350 nm. Absorption was observed in two distinct regions: between 860 and 560 nm, and below 470 nm.

Table I. Assignment of Vibronic Frequencies of TCNQ$\cdot^-$ in the 860- to 560-nm Region[a]

Transition	ν_{obsd}, cm^{-1}	ν_{obsd} − ν_{ls}, cm^{-1}	ϵ_{rel}
$1^0 2^0$	11 669	−1	(100.0)
$1^0 2^1$	12 000	−1	44
$1^0 2^2$	12 315	−18	14.2
$1^0 2^3$	(12 664)		2.0
$1^1 2^0$	12 937	6	28
$1^1 2^1$	13 273	12	41
$1^1 2^2$	13 605	13	18.0
$1^1 2^3$	13 900	−24	6.2
$1^2 2^0$	14 184	−6	7.2
$1^2 2^1$	14 529	7	11.3
$1^2 2^2$	14 870	17	9.5
$1^2 2^3$	15 205	20	4.2
$1^3 2^0$	15 432	−18	2.7
$1^3 2^1$	15 785	4	2.7
$1^3 2^2$	16 116	3	2.4
$1^3 2^3$	16 641	17	1.5
$1^4 2^0$	16 722	12	0.75
$1^4 2^1$	17 036	−6	0.64
$1^4 2^2$	17 346	−27	0.47
$1^4 2^3$	17 699	−5	0.30

[a] Deviations from least-squares fit relative to the first band. The absolute value of molar extinction coefficient of the first band is approximately 5.2 × 10^4 assuming a 25% volume contraction.

The band structure in the 860–560 nm region, as illustrated in Figure 1, is strikingly simple. With the higher concentrations afforded by the greater solubility of the crown ether salt, 19 bands are resolved. In the regions where spectra have been obtained for both the lithium and the crown ether potassium salts, the wavelengths and intensity patterns of the vibronic bands coincide, as is expected for the TCNQ$\cdot^-$ radical anion unperturbed by the cations.

The observed bands, which are listed in Table I, can be interpreted as progressions of two molecular vibrations in a single electronic excited state. That is, the observed frequencies can be adequately represented by

$$\nu = \nu_{00} + \omega_1' v_1' + \omega_2' v_2' \qquad (1)$$

Here, v_1' and v_2', which extend from 0 to 4 and 0 to 3, respectively, are the quantum numbers of, and ω_1' and ω_2' are the frequencies of, the two active vibrations in the electronic excited state. Least-squares fitting resulted in ν_{00} = 11 670 ± 14 cm^{-1}, ω_1' = 1260 ± 3 cm^{-1}, and ω_2' = 331 ± 3 cm^{-1}. The root-mean-square deviation between the frequencies of the observed bands and those reproduced by the fit does not exceed the experimental precision of the wavelength readings (1 nm ≈ 15 cm^{-1}), which is limited by the observed line widths and signal to noise ratio. We conclude that the simple assignment adequately describes the observed spectrum, and neither the inclusion of other vibrational modes nor the postulation of a second electronic transition in this region is required.

The spectrum in the 470- to 350-nm region is shown in Figure 2. In the low-temperature glass the onset of absorption is sharp enough to assign the first observed maximum (22 920 cm^{-1} = 2.84 eV) as the 0–0 band of the second electronic transition. While the vibrational structure is more pronounced than in room-temperature solution spectra, the number of bands resolved is inadequate for a meaningful vibrational analysis. It is clear, however, that the two frequencies that dominated the lower energy transition are not important in the vibronic structure here.

(B) Polarized Absorption Spectra. The spectra of CKTCNQ at room temperature, with light polarized parallel and transverse to the alignment direction of the liquid-crystalline solvent, are shown in Figure 3. The spectra, as in other solvents, consist of two electronic transitions in the ac-

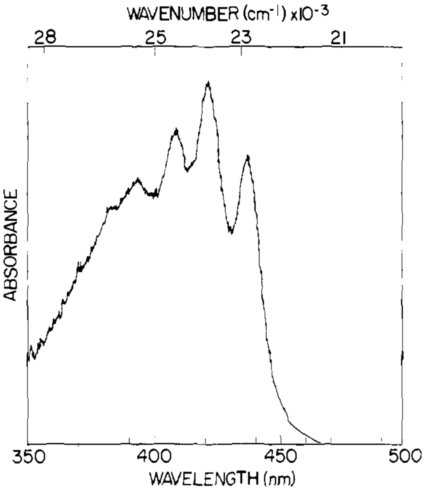

Figure 2. Electronic spectrum of TCNQ·$^-$ in 2-methyltetrahydrofuran solvent at 77 K (visible region).

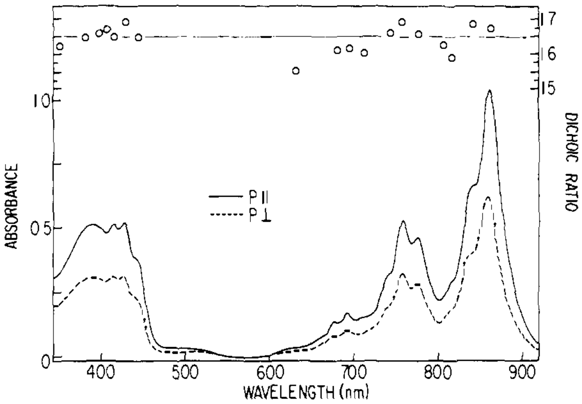

Figure 3. Polarized absorption spectrum of CKTCNQ in liquid-crystalline matrix with polarizer parallel (∥) and perpendicular (⊥) to orientation (rubbing) axis. See text for details.

cessible region. The envelopes of both transitions show a close correspondence to the vibronic structure observed in MTHF glass. The minor absorption near 500 nm was shown in a separate experiment to belong to a photodecomposition product. It is immediately apparent that all absorption features are similarly polarized along the nematic optic axis.

The nematic liquid-crystalline phase is characterized by the long-range orientational ordering of the long axes of its constituent molecules, an orientation that arises from repulsive (steric) interactions and dispersion forces. Molecules or molecular ions dissolved in a nematic liquid observe an anisotropic environment and themselves become ordered. If the dominant anisotropic interactions between solute and solvent are those responsible for the nematic order in the pure solvent, then the solute molecules orient with their long axes parallel to the long axes of the solvent molecules, i.e., along the optic axis of the nematic liquid. This was found to be the case in numerous NMR[17] and polarized absorption-spectroscopic experiments[16,27] where the direction of the transition moment was known a priori. The absence of significant shifts between the CKTCNQ spectra in MTHF and in the cyanobiphenyl solvents indicate that no unusual interactions between this solute and the nematic solvent need to be considered. Furthermore, EPR measurements[19] in another liquid crystalline solvent indicate that the normal to the molecular plane of TCNQ·$^-$ lies perpendicular to the alignment direction. It is thus reasonable to assume that TCNQ·$^-$ orients with its long axis along the optic axis of the cyanobiphenyl solvent. We conclude, therefore, that both electronic transitions observed here are polarized along the molecular long axis.

The dichroic ratio, $R = A_{\parallel}/A_{\perp}$, is also shown in Figure 3 for all maxima and several minima of the spectrum. Photometric error in the absorbances, $A_{\parallel}$ and $A_{\perp}$, limits the accuracy of R to ±0.03 for stronger bands and to ±0.10 in regions of weaker absorption. Within this error, the dichroic ratio of the 0–0 bands is the same as for the transitions to higher vibrational levels of the excited states. This indicates[28] that vibronic mixing of excited states of different symmetry is not important. It is consistent with the conclusion reached from the reasonably high observed intensities ($f_1 \simeq 0.28 \pm 0.05$ and $f_2 \simeq 0.45 \pm 0.07$ for the low- and high-energy transitions, respectively, in acetone solution) that both observed electronic transitions are symmetry allowed. It further implies[29] that the relative intensities of individual vibronic bands are determined by the Franck-Condon factors alone.

The dichroic ratio is related to the extinction coefficients, ϵ_x, ϵ_y, and ϵ_z, along the molecular axis and to the components of the ordering tensor, S_{ii}, by the expression[28]

$$R = \frac{3\bar{\epsilon} + 2(\epsilon_x S_{xx} + \epsilon_y S_{yy} + \epsilon_z S_{zz})}{3\bar{\epsilon} - (\epsilon_x S_{xx} + \epsilon_y S_{yy} + \epsilon_z S_{zz})} \tag{2}$$

Here $\bar{\epsilon} = \frac{1}{3}(\epsilon_x + \epsilon_y + \epsilon_z)$. If the molecule absorbs at a given wavelength, λ_0, only along its long axis,[30] x, then $\epsilon_y = \epsilon_z = 0$, and eq 2 is easily rearranged to give

$$S_{xx} = (R_0 - 1)/(R_0 + 2) \tag{3}$$

From the experimentally observed dichroic ratio, $R_0 = 1.65$, we obtain the order parameter that measures the average orientation of the long axis of the TCNQ·$^-$ solute in the cyanobiphenyl liquid crystal at 23°C as $S_{xx} = 0.18$.

We can place an upper limit on the extinction coefficient of a transition polarized perpendicular to the molecular long axis that might be buried under one of the two long-axis polarized transitions. Assume that at a wavelength different from λ_0, ϵ_z equals zero but $\epsilon_y = \gamma\epsilon_x$. Substitution into (2) and rearrangement results in the expression

$$\gamma = (R_0 - R)(1 - S_{xx})/[R - 1 - S_{yy}(R + 2)] \tag{4}$$

We do not have an independent measurement of S_{yy}. However, S_{yy} for similar but less elongated molecules, such as 1,2,4,5-tetracyanobenzene, *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine, and 1,3,6,8-tetrachloropyrene, are all negative,[27] and we take for TCNQ·$^-$ also $S_{yy} < 0$. Then, if the scatter in our dichroic ratio measurements, $R_0 - R \approx 0.10$, were caused by an underlying transverse polarized absorption, we find $\gamma < 0.13$. Thus we conclude that if there is a transverse polarized transition of TCNQ·$^-$ in the 900–360-nm region at all, its intensity at any wavelength in this region must be less than 13% of the intensity of the long-axis polarized transition.

Discussion

It is fruitful to compare our experimental results with the self-consistent-field molecular orbital calculations on TCNQ·$^-$. The most extensive calculations of Lowitz[6] used several theoretical basis sets and molecular geometries. All combinations yielded a single low-energy electronic transition (of about 1.6 eV), yet he suggested that the two broad spectral bands at 840 and 740 nm in the room-temperature solution spectrum of TCNQ were, in fact, two separate electronic transitions. It should be clear, however, from the vibrational analysis presented earlier[1] and completed here, that the experimental data do not require the presence of a second electronic transition in this energy range. All of

Lowitz's basis sets, as well as other calculations,[6,7,31] predict the lowest electronic excited state to belong to the B_{1u} representation. Since the ground state is B_{2g}, this requires the first electronic transitions to be long axis (x) polarized, which is observed.

Most theoretical calculations predict an A_u state, as well as a second B_{1u} state, to lie in the 2.5- to 3.5-eV region. The exact locations and even the order of these two states, as well as the oscillator strengths for transitions from the ground state, vary a great deal with the parameters assumed. Our polarization spectra show only the existence of the second long-axis polarized transition in this region, although we cannot rule out the presence of the y axis polarized $B_{2g} \rightarrow A_u$ transition as long as its intensity at any wavelength does not exceed 13% of the intensity of the x-polarized transition. Those basis sets that lead to a lower calculated energy for the A_u state than for the second B_{1u} state are clearly incorrect, since even a very weak transverse polarized transition should be experimentally observable in the relatively absorption-free region between the two observed transitions. Those calculations, however, that predict a higher energy for the A_u state are compatible with experiment, since the predicted oscillator strengths for the transition to this state are generally an order of magnitude lower than for the transition to the second B_{1u} state. We note, however, that all calculations, with the exception of ref 31, greatly overestimate the ratio of the oscillator strengths for the two observed long-axis polarized transitions.

Consideration of all the available calculations on the spectral transitions of TCNQ$\cdot^{-}$ [6,7,31] suggests that the open-shell Pople-like SCF–LCAO–MO treatment of Lowitz[6] gives the best agreement between theory and experiment. In this treatment, evaluation of the electronic interaction matrix elements using the equation of Mataga and Nishimato[32] with bond lengths and bond angles from the crystallographic data on (NMP) (TCNQ) yields calculated values of the spectral parameters[33] which are in good agreement with experiment. The poorer agreement when different geometrical parameters are employed may indicate the structural similarity of TCNQ$\cdot^{-}$ in solution and in the (NMP)(TCNQ) crystal environment.

The polarization directions reported here for the TCNQ radical anion cannot be verified by examination of the optical spectra of ion-radical solids which contain this ion in self-stacked arrays. The large (intrastack) interactions obscure the major spectral details of the isolated ion. However, the weaker intrastack coupling in alternate stacked ion-radical solids such as (TMPD)(TCNQ)[34] should preserve the major features of the spectra of the individual ions so that polarization directions could be determined on single crystals. Unfortunately, the inability to grow large single crystals of (TMPD)(TCNQ) has hampered attempts to obtain complete polarization data.[35]

Another interesting aspect of the TCNQ$\cdot^{-}$ spectrum is the domination of the vibronic structure of the lowest energy transition by just two upper-state vibrations. Since the transition is electronically allowed, the upper vibrational levels must be totally symmetric. There are ten normal modes of A_g symmetry which, together with the even harmonics of modes of other symmetry, could, in principle, appear in the vibronic structure. The Franck–Condon factors for nonzero change in the vibrational quantum numbers are apparently very small in all but two of these molecular vibrations. In Figure 4 we show a three-dimensional view of the Franck–Condon factor (square roots of the relative intensities) as a function of the quantum numbers of the two active vibrations. It is clear that the Franck–Condon factors are larger when a given number of quanta are distributed in both these two modes than when they are just found in one or the other.

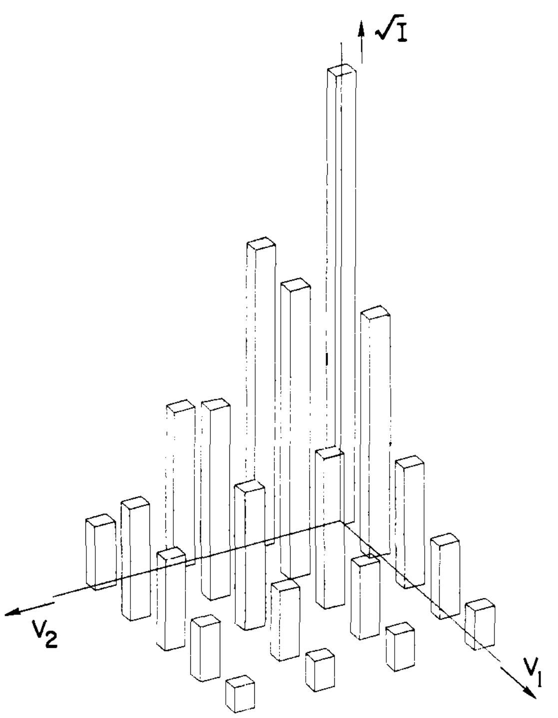

Figure 4. Three-dimensional plot of relative Franck–Condon coefficients ($\sqrt{I}$) vs. the vibrational quantum numbers V_1 and V_2.

The semiclassical interpretation of these observations is that the equilibrium internuclear distances in the ground and the first electronic excited states do not differ significantly, except along two normal coordinates. Furthermore, the deformation upon electronic excitation corresponds to a particular combination of these two modes. It would therefore be interesting to know which bond coordinates contribute significantly to these normal modes.

Although a theoretical framework exists for the evaluation of ground- and excited-state equilibrium potential energy surfaces and vibronic intensities,[36] such calculations have not been carried out for TCNQ$\cdot^{-}$. In a more empirical fashion, we can compare the observed vibrational frequencies in the first electronic excited state of TCNQ$\cdot^{-}$ with the ground-state frequencies of TCNQ and TCNQ$\cdot^{-}$ observed in Raman spectra, which have been assigned in normal coordinate analyses at least in the neutral species. Thus we find that ω_2' (331 cm^{-1}) is coincident within experimental error with one of the A_g vibrations of both TCNQ (334 or 340 cm^{-1})[37-39] and TCNQ$\cdot^{-}$ (335 or 334 cm^{-1}).[40,41] Since this frequency is apparently insensitive to the π-electron distribution and is well separated from other frequencies in the ground-state molecules, it most likely represents the same $C(CN)_2$ scissoring coupled with ring bending motions as assigned[38,39] in neutral TCNQ. There are several unassigned vibrations in the ground state of TCNQ$\cdot^{-}$ observed in the Raman spectrum[41] close to ω_1'; the nearest A_g vibration in TCNQ is between 1206 and 1210 cm^{-1}. The latter is a nearly pure C–H bending motion, according to the more recent normal coordinate analyses,[38,39] but it is unlikely that this assignment should carry over unchanged to the TCNQ$\cdot^{-}$ excited state. If it did, the implication would be that the equilibrium geometries of the ground and the first electronic excited states of TCNQ$\cdot^{-}$ differ mostly in bond angles and not in bond lengths.

In highly conducting TCNQ (self-stacked) solids there is evidence for specific interaction of intramolecular vibrations with the conduction electrons. Kaplunov et al.[39] has shown that the infrared spectrum of conductive TCNQ salts is characterized by broadening of the absorption bands in the 1000-1400-cm^{-1} region. Other optical experiments on (TTF)(TCNQ) in the infrared[42] suggest that a vibrational band at ~1200 cm^{-1} is involved in the electron-optical phonon interference effects observed. It may be possible that these phenomena are associated with one of the two molecular vibrations (i.e., $\omega_1' = 1264$ cm^{-1}) that we have identified as active in the lowest electronic transition of TCNQ$\cdot^-$. This would imply that the deformation of TCNQ$\cdot^-$ due to polarization by charge carriers is similar to that occurring on photon excitation.

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Heats of Alkylation of Substituted Pyridines. A Comparison of Carbon Basicity, Proton Affinity, and Nucleophilicity

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Abstract: Heats of reaction for a series of pyridines with methyl and ethyl fluorosulfonate in nonbasic solvents are reported. These correlate well with the equivalent protonation heats in fluorosulfuric acid and the gas phase. Furthermore, a remarkably good correlation ($r = 0.968$) is found between heats of ethylation for a series of pyridines and the free energies of activation for their reaction with ethyl iodide.[2] Apparently, charge delocalization in the pyridine ring is an important factor in all of these reactions, but some difficulties in specifying the reaction coordinate for this "simple" reaction are considered.

By virtue of their planar ring structure in which a basic n-electron pair is coupled to a polarizable π system, the pyridines are an ideal series for the quantitative investigation of electronic factors in nucleophilic substitution. This role was previously overshadowed by the brilliant studies of Brown,[1,2] who used alkylated pyridines to demonstrate the importance of steric effects and, hence, deliberately employed systems in which electronic variations would be minimized.

Recently Taft,[3-5] Beauchamp,[3] Liotta,[6] Aue,[7] Katritsky,[8] and their colleagues, as well as a number of other workers,[9] have developed a considerable body of good thermodynamic data for the protonation of pyridines, covering a broad range of electron-attracting and -releasing groups both in the gas phase[3,5,7] and in solution.[6,8,9] It is now clear that there is a close correlation between the response of ring substituents to the development of positive charge on the pyridine nitrogen atom by gas-phase protonation,[3,4,5,7] by