We conclude that the CT mechanisms given by eq 4 and 6 best explain the available experimental data, and that the CT contribution to the ground state of the ion pair is quite small. The ground-state stabilization of the CT complex is thus primarily electrostatic. In this regard the complex behaves as would any ion pair.

Two CT bands have also been observed in spectra of tropylium[18] and pyrylium[19] iodides. The ΔE_t for tropylium iodide in CH_2Cl_2 was found to 19.9 kcal mol^{-1}; the energy difference for 2,4,6-trimethylpyrylium iodide CT bands ($CHCl_3$ solvent) was found to be 14.5 kcal mol^{-1}. More work is needed before assigning the two-band pattern in these ring systems to properties of either the donor or acceptor.

Experimental Section

Compounds. Most of the compounds used for this study were reported previously (Table IV). They were prepared by reaction of the appropriate pyridine compound with either methyl or ethyl iodide. The absence of trace amounts of triiodide in each compound was confirmed spectrophotometrically in methylene chloride. 1-Ethyl-4-cyanopyridinium perchlorate was prepared according to the procedure of Schwarz.[9]

Polarography. The polarographic studies were performed using a Leeds and Northrup Electro-Chemograph, Type E, and a dropping mercury electrode (dme). The reference electrode was aqueous saturated calomel (sce); a three-compartment cell was employed to prevent water from entering the sample (dme) compartment. The middle compartment contained the nonaqueous solvent (CH_3CN) and 0.1 *M* $[CH_3(CH_2)_3]_4N^+ClO_4^-$ electrolyte only. The acetonitrile was dried over Na_2CO_3 and then distilled from molecular sieve. The polarographic grade $[CH_3(CH_2)_3]_4N^+ClO_4^-$ was obtained from Southwestern Chemical Co. and was dried overnight at 110° before use. The pyridinium salt concentrations were approximately 10^{-3} *M*.

Kinetics. All visible absorption data were obtained on a Cary 14 spectrophotometer using 1-cm cells with the solvent as reference. Temperature control was maintained using a constant-temperature bath with the water circulating through a metal block cell holder. Kinetic studies were performed by mixing the reagents, placing a sample in the spectrophotometer, and scanning optical density as a function of time at a fixed wavelength corresponding to the first CT band maximum. A methyl tosylate concentration of 0.1 *M* was used throughout; the initial pyridinium iodide concentrations were about 10^{-3} *M*.

Analyses. Elemental analyses were performed by the Analytical Research Department, Chemical Research Laboratory, Edgewood, Arsenal.

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A Nuclear Quadrupole Resonance Investigation of Iodine Monochloride Complexed with Pyridines[1a]

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Contribution from the Department of Chemistry, University of Colorado, Boulder, Colorado 80302. *Received October 10, 1970*

Abstract: The ^{35}Cl and ^{127}I nqr absorption frequencies of pyridine–ICl and 4-methylpyridine–ICl have been measured as a function of temperature. Their respective values at 273.2°K are 21.136 ± 0.01, 21.175 ± 0.01, 464.28 ± 0.04, and 462.76 ± 0.04 MHz. Their temperature coefficients were +2.2, +2.5, −28, and −24 kHz/°K. Application of the Townes and Dailey theory with neglect of s hydridization at the halogen atoms results in the following charge densities in each complex: pyridine (or 4-methylpyridine), +0.26; iodine, +0.35; and chlorine, −0.61 electron. A valence-bond interpretation indicates a 57% contribution of the "no-bond" wave function to the ground state. A representation in which the charge-transfer and electrostatic wave functions are explicitly included contains a maximum of 26% charge-transfer character in the ground-state wave function. Classical electrostatic forces thus appear to play a dominant role in the stabilization of these complexes. The charge-transfer contributions are nonnegligible, but a picture of the complex structure based completely on the charge-transfer model is likely to give misleading results.

In many instances stable molecules have been found to interact to form associated species, called molecular, charge-transfer, or donor–acceptor complexes. The literature concerning these complexes is voluminous, and the reader is referred to a number of books[2,3] and reviews[4-7] treating the subject in greater detail.

The properties of these complexes have usually been interpreted within the context of the charge-transfer (CT) model developed by Mulliken.[8] This model not only accounted for the "CT band" observed in many of these complexes, but also provided a theoretical basis for interpreting their ground-state properties. As is well known, this model proposes that the ground-state wave function for a donor–acceptor complex may be represented by

$$\psi_G = a\Phi_0(D,A) + b\Phi_1(D^+\text{–}A^-) \qquad (1)$$

where Φ_0 represents a "no-bond" structure and Φ_1 represents a "dative" structure in which an electron has been transferred from the donor to the acceptor molecule. The inclusion of Φ_1 in ψ_G results in a reso-

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[1] (a) Supported in part by the National Science Foundation under Grant No. GP 11387; (b) NASA Trainee, 1966–1969.

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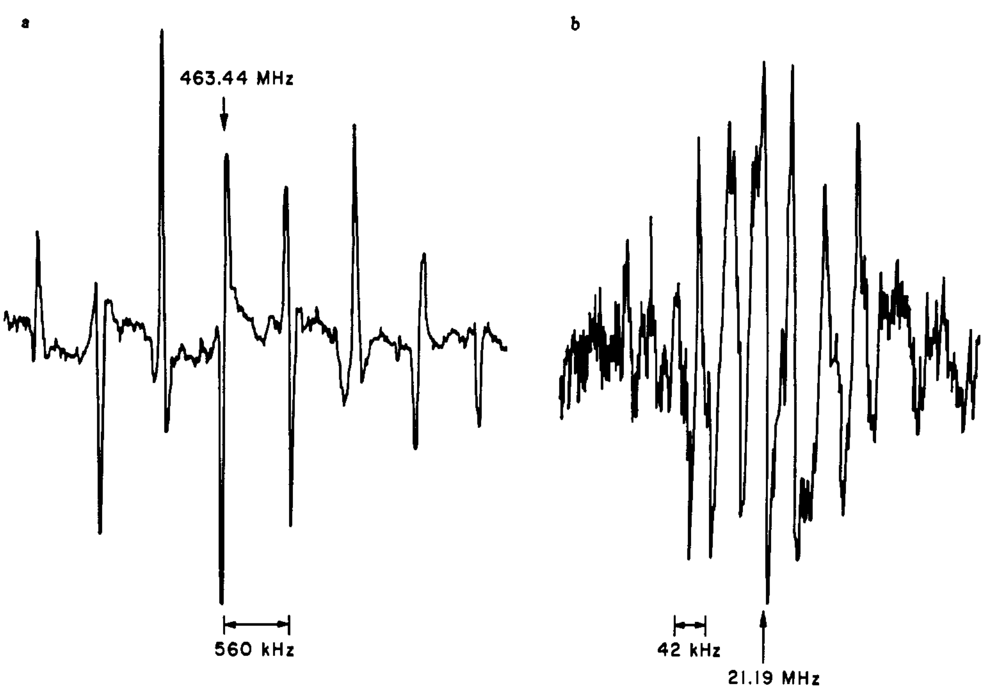

Figure 1. (a) Nqr absorption of ^{127}I in 4-methylpyridine–ICl. Experimental conditions were temperature = −26.4°C, sweep rate = 8 MHz/hr, time constant = 3 sec, and sample weight = 5.1 g. (b) Nqr absorption of ^{35}Cl in pyridine–ICl. Experimental conditions were temperature = 0°C, sweep rate = 1 MHz/hr, time constant = 10 sec, sample weight = 11 g.

nance stabilization which lowers the energy of ψ_G below the energy of Φ_0.

It has recently been suggested, however, that electrostatic interactions in the no-bond wave function may make substantial contributions to the ground-state properties of these complexes.[9–13] In fact, in aromatic halogen and aromatic–TCNE complexes, the electrostatic interactions accounted for a major portion of the stabilization energy. Also, electrostatic interactions make a significant contribution to such ground-state properties as dipole moments, infrared intensity enhancements, and frequency shifts. Ground-state properties had previously been solely attributed to the properties of the dative structure in the ground-state wave function. The results of the above studies suggested that the relative contributions of electrostatic and charge-transfer interactions to the ground-state properties of donor–acceptor complexes needed further study.

A possible experimental approach to investigating the relative importance of CT and electrostatic contributions to the ground-state wave function is nuclear quadrupole resonance (nqr). Several previous nqr studies[14–17] of weak CT complexes have indicated little, if any, CT character in the ground state. We therefore decided to investigate some strong CT complexes to compare the importance of CT and electrostatic interactions. Pyridine–iodine monochloride (py–ICl) and 4-methylpyridine–iodine monochloride (pic–ICl) are considered to be strong CT complexes and are ideal for studying the halogen nqr absorptions as they are relatively stable and isolable as solids. In addition, both chlorine and iodine nqr experiments can be performed, providing one with a double probe of the electron distribution. For both complexes, a CT contribution in the ground state would give rise to an increase in charge density about both halogen atoms, which is manifested by lower nqr absorption frequencies relative to pure ICl. However, the electrostatic contribution would give rise to an induced dipole in ICl which lowers the electron density about iodine and increases the electron density about chlorine. Thus the iodine nqr frequency should increase and the chlorine nqr frequency should decrease relative to the corresponding resonances in pure ICl. Hence the two types of contributions give rise to the same chlorine nqr frequency shifts, but opposite iodine shifts.

The crystal structure of py–ICl[18] has been determined with the following results. (1) The ICl lies in the pyridine plane on an axis passing through the nitrogen and the opposite carbon atom. The iodine is adajacent to nitrogen. (2) py–ICl appears to be a molecular crystal without significant intermolecular interactions. (3) The N–I separation is 2.26 Å and the I–Cl separation is 2.51 Å (compared with 2.37 and 2.44 Å in α-ICl).

A number of workers have studied the N–I and I–Cl infrared vibrations[19–22] of py–ICl and similar complexes and interpreted the results in light of the CT model. The association constant[23] for pyridine and

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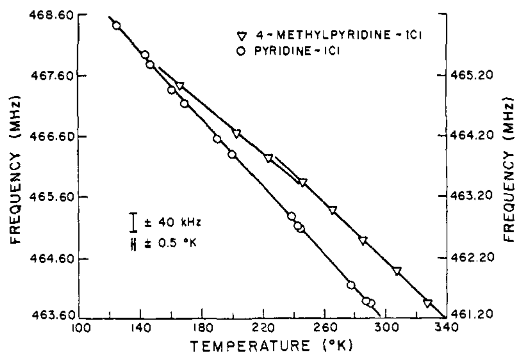

Figure 2. The temperature dependence of the ^{127}I nqr absorption frequency in ICl complexes.

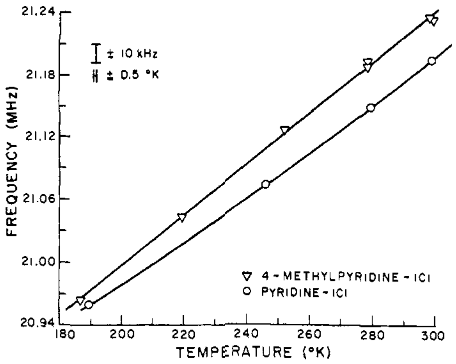

Figure 3. The temperature dependence of the ^{35}Cl nqr absorption frequency in ICl complexes.

iodine monochloride is $k_c = 4.8 \pm 10^5$ l./mol, indicating sizable interactions between the donor and acceptor molecules.

Experimental Section

The nqr studies were conducted using self-quenched super-regenerative oscillator detectors similar to those discussed by Peterson and Bridenbaugh.[24,25] The chlorine oscillator employed a 6CW4 (Nuvistor) tube and had an 11-44-MHz range with two sample coils. For a 1.2-g sample of *p*-dichlorobenzene at 20°C, the spectrometer had a ^{35}Cl signal-to-noise ratio (S/N) of 7, when a 6-MHz/hr sweep rate and a plate voltage of +105 V were used. The iodine oscillator had a frequency range of 200-540 MHz, with the weak member of the $^{127}\mathrm{I}_{1/2 \rightarrow 3/2}$ doublet in ICl having an S/N of 7 in a 3-g sample with the following experimental conditions: 8-MHz/hr sweep rate, 300-msec time constant on the phase-sensitive detector (PAR HR-8), −80°C, and +160 V on the plate of the oscillator tube. The nqr results reported for the complexes were for an 11-g sample for the ^{35}Cl absorptions and a 4-5 g sample for the ^{127}I absorptions. Typical ^{35}Cl and ^{127}I nqr spectra are shown in Figure 1. More detailed information concerning the construction, circuitry, and operation of the spectrometers may be obtained elsewhere.[26]

The temperature of the samples in the chlorine and iodine spectrometers was controlled by passing nitrogen gas at the desired temperature over the sample. The temperature control system was similar to one described in the literature.[27] The heart of the system was a Hallikainen Instruments Thermotrol Model 1053A temperature controller and a Hallikainen Instruments Model 1358A53 platinum resistance sensing element. This system regulated the temperature to better than ±0.1°C; however, the sample size for this investigation was large, so there were sizable temperature gradients across the sample. The chlorine samples were 2.5 in. long, and with large gas flow rates the temperature varied ±0.5°C over the sample. The iodine samples were much smaller (±1 in. in length) and between copper plates, so their estimated temperature variation (±0.3°C) was lower than that for the chlorine samples.

A copper-constantan thermocouple imbedded directly in the sample provided the temperature measurement during an actual frequency measurement.

Iodine monochloride was synthesized by the method of Cornog and Karges[28] and purified by fractional crystallization. All the ICl used in the complex syntheses had a freezing point greater than 26.7°C (pure α-ICl has a melting point (mp) of 27.2°C). py-ICl, pic-ICl, and 2,4,6-trimethylpyridine-ICl (col-ICl) were prepared in the usual manner.[29]

The complexes were stored in desiccators under nitrogen and away from light to prevent decomposition. Their uncorrected melting points and literature values are given in Table I.

To obtain good chlorine nqr spectra, the complexes usually had to be annealed. Both pic-ICl and py-ICl yielded iodine resonances without annealing. Chlorine nqr resonances were very weak, and annealing improved the signal-to-noise ratios in these samples. Also, observable resonance absorptions were detected after annealing in samples which previously gave none. The complexes were sealed into 4-dram vials and warmed in a vacuum oven to 80-90°C for 15-20 min; the oven was then evacuated and the samples were allowed to slowly cool to room temperature over a period of 2-3 hr. The annealed complexes were slightly darker yellow, but retained their melting points; hence it is unlikely that the nqr absorptions observed were due to impurities present before, or produced during, the annealing process.

Table I. Melting Points of Pyridine-ICl Complexes

Complex	Mp, °C	Lit.
Pyridine-ICl	132.5-135	132[a] (134-135)[b]
4-Methylpyridine-ICl	108.0-108.5	107-108[c]
2,4,6-Trimethylpyridine-ICl	125-126	

[a] A. I. Popov and R. H. Rygg, *J. Amer. Chem. Soc.*, **79**, 4622 (1957); recrystallized from CCl$_4$. [b] G. B. Kaufman and K. L. Steven, *Inorg. Syn.*, **7**, (1963); recrystallized from EtOH. [c] R. D. Witaker, J. R. Ambrose, and C. W. Hickam, *J. Inorg. Nucl. Chem.*, **17**, 254 (1961).

Results and Discussion

The ^{127}I and ^{35}Cl nqr absorption frequencies obtained as a function of temperature for py-ICl and pic-ICl are given in Figures 2 and 3. Values for the absorption frequencies at 273.2°K taken from these curves are given in Table II, along with the corresponding frequencies in ICl. No iodine nqr absorptions were found in 2,6-lutidine-ICl (408-488 MHz) or col-ICl

Table II. Nuclear Quadrupole Resonance Frequencies of ^{127}I and ^{35}Cl in ICl and Its Complexes with Pyridine and 4-Methylpyridine

Complex	Nucleus	Frequency, MHz	dν/dT, kHz/°K	Coupling constant, MHz
α-ICl[a]	^{127}I	452.42 ± 0.01	−48	3016.1
Pyridine-ICl	^{127}I	464.28 ± 0.04	−28	3095.2
4-Methylpyridine-ICl	^{127}I	462.76 ± 0.04	−24	3085.1
α-ICl[b]	^{35}Cl	37.184		74.368
Pyridine-ICl	^{35}Cl	21.136 ± 0.01	+2.2	42.272
4-Methylpyridine-ICl	^{35}Cl	21.175 ± 0.01	+2.5	42.350

[a] S. Kojima, A. Shimauchi, S. Hagiwara, and Y. Abe, *J. Phys. Soc. Jap.*, **10**, 930 (1955). [b] S. Kojima, K. Tsukada, S. Ogawa, and A. Shimauchi, *J. Chem. Phys.*, **23**, 1963 (1955); measured at 293°K.

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(362–508 MHz). No other iodine resonance absorption was found for py–ICl in the range 225–513 MHz. An annealed sample of col–ICl was searched unsuccessfully for a ^{35}Cl nqr absorption in the range 15.2–35.4 MHz.

The absorption frequencies are related to the quadrupole coupling constant, e^2Qq, and the asymmetry parameter, η, in a manner shown in eq 2 and 3 for ^{35}Cl and ^{127}I, respectively, for $\eta \leq 0.1$. The Townes

$$\nu_{\pm 1/2 \rightarrow \pm 3/2}(^{35}\mathrm{Cl}) = \frac{e^2Qq}{2h}\left(1 + \frac{\eta^2}{3}\right)^{1/2} \qquad (2)$$

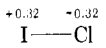
$$\nu_{\pm 1/2 \rightarrow \pm 3/2}(^{127}\mathrm{I}) = \frac{3e^2Qq}{20h}\left(1 + \frac{59}{54}\eta^2\right) \qquad (3)$$

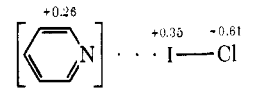
and Daily (TD) theory[30] was employed to determine the charge densities localized on the halogen atoms in the complexes. This theory has been applied by Das and Hahn[31] to ICl, for which they have related the electric field gradients eq at the halogen atoms to the amount of s hybridization in the bonding σ orbital (s^2), the fractional double bond character (π), and the ionic character (I) of the I–Cl bond. For ^{35}Cl and ^{127}I one can, therefore, write that

$$e^2Qq(\mathrm{i}) = -(1 - s_{\mathrm{i}}^2 - I - \pi)e^2Qq_{\mathrm{at}}(\mathrm{i}) \qquad (4)$$

where the index i designates either ^{35}Cl and ^{127}I and where e^2qQ_{at} is the free atom value of the quadrupole coupling constant. For the calculation of the p-electron defect (f), e^2Qq_{at} for chlorine and iodine were taken[31] as 109.7 and 2293 MHz. The average values of the halogen atom coupling constants in the complexes were $e^2Qq_{\mathrm{I}} = 3090$ and $e^2Qq_{\mathrm{Cl}} = 42.31$ MHz. The f's obtained were $f_{\mathrm{I}} = 1.348$ and $f_{\mathrm{Cl}} = -0.386$.

The double bond character of the halogen atoms in the complexes was assumed to be zero, as was the s hybridization. The charge densities localized about the halogen atoms in ICl and the complexes as determined from the nqr data are


$\overset{+0.32}{\mathrm{I}}\text{——}\overset{-0.32}{\mathrm{Cl}}$



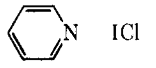
The +0.26 charge may be distributed throughout the pyridine ring but it is likely to be largely localized at the nitrogen atom.

The interpretation of these results is clouded by the use in the literature of model structures which are either not well defined or not orthogonal to one another. The most straightforward way to interpret the data is by means of a whole complex molecular orbital calculation. Here the electron densities on the ring and the halogen atoms can be assigned in an unambiguous way. Although an interpretation based on such a molecular orbital calculation is the method of choice, the actual computation is beyond our present means because of its complexity.

Because of this complexity, valence-bond (VB) and charge-transfer (CT) constructs have been used to describe these complexes. The valence-bond wave function that has been proposed[19] has the form

$$\psi_{\mathrm{VB}} = a\Phi_{\mathrm{I}} + b\Phi_{\mathrm{II}} \qquad (5)$$

where Φ_{I} and Φ_{II} correspond to the structures I and II, respectively. Assuming that in structure I ICl has its unperturbed nqr frequencies and that in structure II the ^{35}Cl nqr frequency is zero, one can calculate from the observed nqr frequencies in the complex that $a^2 \approx 0.57$ and $b^2 \approx 0.43$. The nqr data would then predict a value of $e^2Qq(^{127}\mathrm{I}) = 480$ MHz for Φ_{II}, which is quite reasonable. It should be pointed out that these numbers agree well with the estimate of 0.40–0.50 for b^2 from the earlier infrared work.[19]



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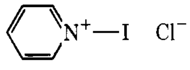
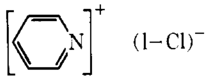
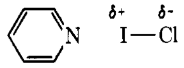


II

Two comments need to be made about this valence-bond interpretation, however. One is that structure II has sometimes been called a charge-transfer structure and b^2 has been used as a measure of the charge-transfer contribution. We feel that this is a mistake that confuses the picture. Strictly defined, the charge-transfer structure is III. It was previously proposed[19] that if the transferred electron was strongly localized on the chlorine atom in structure III, then III and II would be identical. The antibonding orbital into which the transferred electron goes in III is *not* strongly localized on the chlorine atom, however. In a simple MO approach, the σ orbital of ICl is more localized about the Cl atom. The σ* antibonding orbital consists of reversed atomic orbital coefficients with a sign change to maintain orthogonality. Hence, in theory, the σ* orbital is more localized about the iodine atom, and any charge placed in this orbital would result in a larger percentage being localized about the iodine atom. Experimental proof of this has been obtained by producing X_2^- and XY^- halogen radical anions (V_k centers) in alkali halide crystals.[32–34] Not only can the charge densities be determined, but the hybridization of the σ* orbital (and σ orbtial) may also be deduced. Extrapolation of the other XY^- radicals indicates that 54–55% of the transferred charge in III is localized about the iodine atom. Thus it is not correct to equate the charge-transfer structure III with the valence-bond structure II.



III



IV

The second comment about the valence-bond interpretation is that the assumption that the ICl in structure I has its unperturbed nqr coupling constants is certainly false. In other work, we have shown that electric fields from lone pairs[35] and from aromatic rings[9,11] can induce substantial dipole moments in halogens. Thus, structure I should really be the polarized structure IV, in which the electric field of the pyridine lone pair has induced an additional dipole in ICl. If one wishes to discuss these complexes in terms of a model in which the only two constructs used are electrostatic polarization and charge-transfer resonance, one can write a wave function of the form

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[30] C. H. Townes and B. P. Dailey, *J. Chem. Phys.*, 17, 782 (1949).

[31] T. P. Das and E. L. Hahn, *Solid State Phys., Suppl.*, No. 1, (1958).

[32] D. Schoemaker, *Phys. Rev.*, **149**, 693 (1966).

[33] D. Schoemaker, *Bull. Amer. Phys. Soc.*, **9**, 629 (1964).

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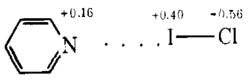
[35] P. J. Berkeley, Jr., and M. W. Hanna, *J. Chem. Phys.*, **41**, 2530 (1964).

$$\psi_{\mathrm{ES-CT}} = c\Phi_{\mathrm{III}} + d\Phi_{\mathrm{IV}} \qquad (6)$$

where Φ_{III} and Φ_{IV} are wave functions corresponding to structures III and IV. Using this formulation and neglecting overlap between Φ_{III} and Φ_{IV}, one obtains $c^2 = 0.26$ assuming that the s hybridization in the I–Cl bond is zero.

V_k center data[32-34] indicate that there is 4–5% s hybridization at the halogen atoms. If 5% s hybridization is assumed to be present at the halogen atoms, then the charge densities from the nqr data are



If the s hybridization correction to the electron densities is taken into account, there would only be 16% CT character in the $\psi_{\mathrm{ES-CT}}$ wave function. It would appear therefore, that there is between 16 and 26% CT character in py–ICl and pic–ICl. Thus, if one chooses to discuss these complexes in terms of a combined charge-transfer, electrostatic model, one is again forced to the conclusion that electrostatic interactions play a dominant role in determining the ground-state properties even of strong complexes. Of course, the charge-transfer interaction is necessary, and it is also true that the charge-transfer contribution is more significant in these strong complexes than in the weak complexes discussed in earlier work. Our main point is to emphasize that, in thinking about these complexes, conclusions drawn by only considering the charge-transfer contribution may be incorrect. The electrostatic contributions in the no-bond wave function cannot be neglected.

The positive temperature dependance of the ^{35}Cl nqr absorption frequencies and the reduced magnitude of the ^{127}I nqr absorption frequency temperature coefficients relative to ^{127}I in ICl were unexpected. The general theory[31,36] predicts negative temperature coefficients. Positive temperature coefficients have been observed before, and these have usually been correlated with a decrease in π bonding with increasing temperature. As discussed elsewhere,[26] the anomalous positive temperature coefficient of chlorine and the reduced size of the iodine temperature coefficient may be accounted for by employing vibrationally dependent coefficients of the valence-bond structures comprising the ground-state wave function of the complex. The contribution of the wave function representing the "no-bond" covalent structure increases as the temperature is raised.

Acknowledgment. The authors gratefully acknowledge the assistance of Dr. Donald W. Halford of the National Bureau of Standards in the construction of the instrumentation.

[36] H. Bayer, *Z. Phys.*, 130, 227 (1951).

Spectroscopic Studies of Quinodimethanes

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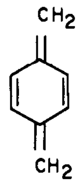
Abstract: The benzene-, naphthalene-, and anthracene-*p*-quinodimethanes, formed by pyrolysis of the corresponding paracyclophanes, were isolated in the solid state at 77°K. Their ir and uv spectra were recorded and confirm the quinonoid nature of the species in the condensed phase at 77°K. Direct spectroscopic evidence of the polymerization process which results on warming the samples was obtained.

The high reactivity of quinodimethanes which do not possess substituents on the methylene groups has generally precluded any attempts to isolate and characterize them. The structure of the reactive intermediate has been inferred from the nature of the products formed in their reactions. In an earlier communication[2] we reported the nmr spectra of the benzene-, **1**, naphthalene-, **2**, and anthracene-, **3**, -*p*-quinodimethanes in solution in THF-d_8 at −80°. The observed chemical shifts and the absence of any esr signal were fully consistent with the quinonoid rather than the biradical nature of the species. We have now established that these quinodimethanes can also be isolated in the solid state at 77°K. Their vibrational and electronic spectra, which further substantiate the quinonoid structures, are presented here. This technique has also permitted us to observe directly the transformation of the monomer species into polymer by spectroscopic methods.



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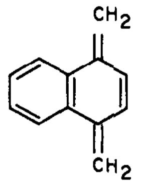

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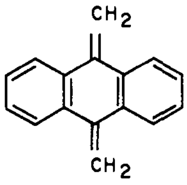

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Experimental Section

Materials. [2.2]Paracyclophane was obtained from Aldrich and was purified by repeated vacuum sublimation to mp 288–289°. Dibenzo[2.2]paracyclophane was synthesized from (4-methyl-1-naphthylmethyl)trimethylammonium bromide using toluene as reaction medium.[3] Recrystallization of the reaction product from benzene gave the anti isomer, mp 299–300° (with decomposition).

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[1] Visiting Scientist on sabbatical leave from the Weizmann Institute, Rehovot, Israel.

[2] D. J. Williams, J. M. Pearson, and M. Levy, *J. Amer. Chem. Soc.*, 92, 1436 (1970).

[3] H. H. Wasserman and P. M. Keehn, *ibid.*, 91, 2374 (1969).