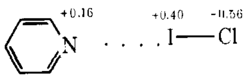
$$\psi_{\mathrm{ES-CT}} = c\Phi_{\mathrm{III}} + d\Phi_{\mathrm{IV}} \qquad (6)$$

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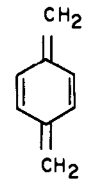
Abstract: The benzene-, naphthalene-, and anthracene-*p*-quinodimethanes, formed by pyrolysis of the corresponding paracyclophanes, were isolated in the solid state at 77°K. Their ir and uv spectra were recorded and confirm the quinonoid nature of the species in the condensed phase at 77°K. Direct spectroscopic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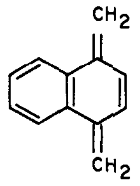

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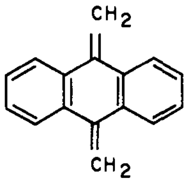

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Experimental Section

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).

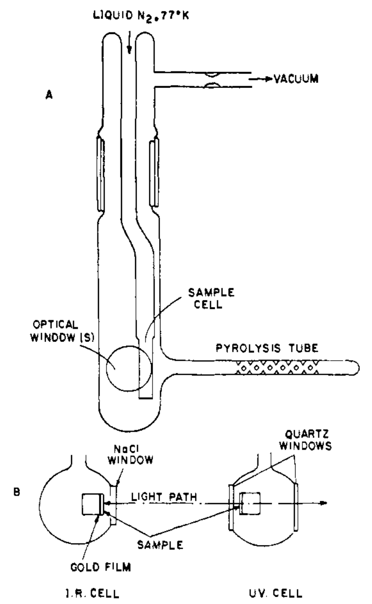

Figure 1. Pyrolysis and spectroscopic unit: (A) pyrolysis configuration, (B) spectroscopic configuration.

Tetrabenzo[2.2]paracyclophane was prepared from 9,10-bis-(chloromethyl)anthracene using the procedure of Golden[4] and recrystallized from chloroform. Spectral analysis confirmed the structure.

Pyrolysis Procedure. The basic design of the apparatus used in both the ir and uv experiments is shown in Figure 1. The quinodimethanes were generated by vacuum pyrolysis of the corresponding paracyclophane and condensed as thin transparent films on the window of a sample cell at 77°K. A series of small indentations in the pyrolysis tube prevented any direct transfer of the paracyclophane to the cold finger from sputtering and also ensured good thermal contact with the walls of the vessel. For the ir studies a unit with a single sodium chloride optical window was used. Prior to deposition of the quinodimethane film, a thin reflecting gold film was deposited on the sample cell. Ir spectra were recorded on a Beckman IR 12 spectrophotometer using a specular reflectance technique. For the uv studies a unit with two optically flat quartz windows was used and the spectra of the quinodimethane films were recorded on a Cary 14 spectrophotometer. In both devices the optical cell assembly could be conveniently rotated 90° to bring the deposited film into the light beam.

Results and Discussion

The uv spectra of the quinodimethanes at 77°K are shown in Figure 2. The following absorption maxima of the longest wavelength band were obtained: **1**, 301; **2**, 310; and **3**, 295 mμ. Because of problems in determining film thickness, reflection, scattering, etc., the extinction coefficients of the bands could not be estimated. Attempts to measure these from low-temperature solution spectra were also unsuccessful. The overlap of the quinodimethane spectrum with that of the polymer, which was always produced in low concentrations in solutions of the monomer, did not permit any reliable estimation of the ε values.

A detailed MO treatment of a series of *p*-quinodimethane molecules was reported by Pullman, *et al.*[5] On the basis of the theoretical treatment and absorption spectra of a series of stable tetraphenyl-substituted derivatives, the position and intensity of the longest wavelength absorption band ($N \rightarrow V_1$) were predicted. In going from **1** to **2** to **3**, a hypsochromic shift and a decrease in intensity were postulated, with absorption maxima at 320 mμ for **1**, 300 for **2**, and 275 for **3**. The longest wavelength absorption bands in the present work for the condensed phase are in reasonable agreement with the predicted values, although the hypsochromic shift is not observed.

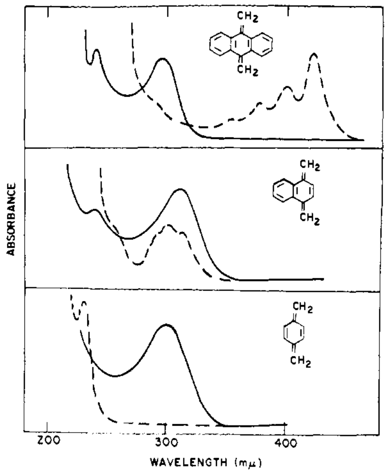

Figure 2. Uv spectra of the quinodimethanes at 77°K (———) and polymers formed on warming to 20°C (— — —). The quinodimethane and the polymer spectra are not reproduced on the same absorption scale.

Tardieu[6] reported the preparation of **3** by the alkali treatment of the dimethanesulfonic acid ester of bis(9,-10-hydroxymethyl)anthracene in THF at −25°. The structure of the unstable intermediate **3** was inferred from chemical evidence (isolation and identification of derivatives), and the uv spectrum was reported, $\lambda_{\max}$ (THF, −25°) 283 mμ. This value is in good agreement with the value obtained in this study. The solution spectra of a series of stable phenyl-[7] and cycloalkyl-[8] substituted derivatives of **3** exhibit absorption maxima in the region of 273–283 mμ. There are no reported values for the uv spectrum of **2** or any of its derivatives. Unlike the case of the anthracene analog, substituted derivatives of **2** may not be stable. Substitution of bulky groups in the 5 and 8 positions may not introduce enough steric hindrance to prevent the methylene–methylene interaction which presumably causes dimerization or polymerization. The longest wavelength bands in the uv spectrum of the gaseous quinodimethane **1** were reported[9] at 274–280 mμ, and absorption maxima in the region of 300–312 mμ were observed in the solution spectra of a number of stable *exo*-methylenecyclohexadienes.[10–12] From the data obtained in this investigation it appears that the longest wavelength absorption bands of **1**, **2**, and **3** in their condensed phases at 77°K occur at lower energies than either Pullman's predictions or in solution or in the gas phase.

Warming the quinodimethane films from 77°K to room temperature resulted in disappearance of their ab-

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(4) J. H. Golden, *J. Chem. Soc.*, 3741 (1961).

(5) A. Pullman, B. Pullman, E. D. Bergmann, G. Berthier, E. Fisher, D. Ginsburg, and Y. Hirschberg, *Bull. Soc. Chem. Fr.*, 707 (1951).

(6) P. Tardieu, *C. R. Acad. Sci.*, **248**, 2885 (1959).

(7) S. C. Dickerman, J. H. Berg, J. R. Haase, and R. Varma, *J. Amer. Chem. Soc.*, **89**, 5457 (1967).

(8) R. R. Hill and G. H. Mitchell, *Chem. Commun.*, 1243 (1968).

(9) I. Tanaka, *Nippon Kagaku Zasshi*, **75**, 218, 320 (1954).

(10) L. A. Errede, *J. Amer. Chem. Soc.*, **83**, 949 (1961).

(11) J. F. Eastham and V. F. Raaen, *Proc. Chem. Soc. London*, 149 (1958).

(12) P. N. Van Eenam and C. R. Hauser, *J. Amer. Chem. Soc.*, **79**, 5512 (1957).

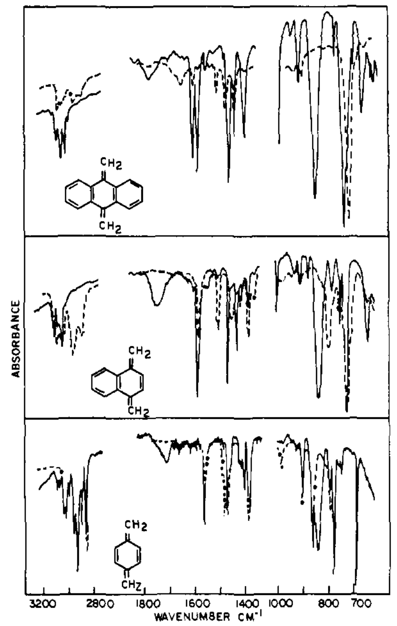

Figure 3. Ir spectra of the quinodimethanes at 77 °K (———) and polymers formed on warming to 20 °C (— — —).

sorption bands and formation of new bands characteristic of the respective aromatic compounds. It is well known that the quinodimethanes are extremely reactive and polymerize readily, and the spectra in Figure 2 (dashed lines) are identical with those of the polymers formed by phenyllithium coupling of the corresponding di(bromomethyl) compounds.[13,14]

The ir spectra of the quinodimethanes at 77 °K and of the polymers produced on warming to ambient temperature are shown in Figure 3. Absorption arising from the vinylidene wag in the quinodimethanes appears at 877 cm^{-1} in **1**, 872 in **2**, and 890 in **3**.[15-17] Bands consistent with overtones of the wagging modes are observed at 1750, 1760, and 1790 cm^{-1}, respectively. Further evidence for the olefinic group can be obtained from the CH stretching mode at approximately 3100 cm^{-1}. Conjugation of the exocyclic double bond with the aromatic rings results in a diminution of the 1500-cm^{-1} band in the quinodimethanes, whereas in the polymers where the extended conjugation is absent this band is easily detected. The band at 680 cm^{-1} from the endocyclic double bond in **2** is analogous to the out-of-plane bending of a cis-disubstituted ethylene. This vibration is symmetry forbidden in **1** and is not observed. The bands attributed to the quinodimethanes disappear rapidly as the films are warmed to room temperature, and a new spectrum characteristic of the aromatic polymer[13,14] is produced.

The ir and uv spectra of the quinodimethanes **1**, **2**, and **3** clearly establish their quinonoid structure in the condensed phase at 77 °K and provide direct spectroscopic evidence of the polymerization process that results on warming. The techniques used in this investigation also open the way for kinetic studies of the polymerization of quinodimethane monomers.

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(13) J. H. Golden, *J. Chem. Soc.*, 1604 (1961).

(14) J. H. Golden, *ibid.*, 3741 (1961).

(15) L. J. Bellamy, "Infrared Spectra of Complex Molecules," 2nd ed, Methuen, London, 1968.

(16) L. J. Bellamy, "Advances in Infrared Group Frequencies," Methuen, London, 1968.

(17) N. B. Coltup, L. H. Daly, and S. E. Wiberly, "Introduction to Infrared and Raman Spectroscopy," Academic Press, New York, N. Y., 1964.

An Electron Paramagnetic Resonance Study of Nitrosylmyoglobin

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Received December 5, 1970

Abstract: Paramagnetic resonance spectra of nitrosylmyoglobin have been obtained at 77°K for both the ^{15}NO and ^{14}NO derivatives. Principal values of the g tensor are $g_{zz} = 2.0068$, $g_{yy} = 1.9850$, and $g_{xx} = 2.0728$. The g tensor is oriented such that the principal axis x is aligned along the crystallographic c^* axis and y and z are directed at 13° from the b and a axes, respectively. This result is interpreted in terms of the orientation of the NO ligand. Two hyperfine splittings are observed near the a axis: 24.5 ± 1 G from the nitrogen in ^{15}NO (18.6 ± 1 G for ^{14}NO) and 6.4 ± 1 G attributed to the ϵ nitrogen of the 92-histidine residue (F8) are reported. The Fe–N–O bond angle appears to be 108–110°, resembling the 110° bond angle found previously in nitrosylhemoglobin.

The binding of ligands to hemoproteins has been a problem of keen and continuous interest to chemists and biochemists alike. The reasons reside with both the biological functions of these molecules and their prominent role as models for allosteric enzymes. Although X-ray crystallographic electron density maps, nuclear magnetic resonance contact shifts, Mössbauer spectra splittings, and electron paramagnetic resonance (epr) data have contributed toward some understanding of the bonding situation, the lack of a detailed description is obvious. In particular, very little is known regarding the bonding interactions between the metal and oxygen and the relevant histidines. It is to this problem that the work of this laboratory has been directed.

The classical epr work on hemoproteins was done by