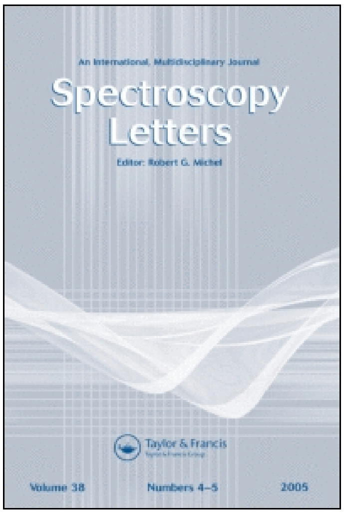
This article was downloaded by:
On: *30 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Spectroscopy Letters

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Spectroscopic Investigations on Polymeric Tetra Benzo 18-Crown-6 Ether Bridged Metal-Free Phthalocyanine

Mustafa Özdemir[a]; Erbil Ağar[a]
[a] Department of Chemistry, Faculty of Science and Arts, Ondokuz Mayis University, Samsun, Turkey

To cite this Article Özdemir, Mustafa and Ağar, Erbil(1991) 'Spectroscopic Investigations on Polymeric Tetra Benzo 18-Crown-6 Ether Bridged Metal-Free Phthalocyanine', Spectroscopy Letters, 24: 5, 741 — 748

To link to this Article: DOI: 10.1080/00387019108018154

URL: http://dx.doi.org/10.1080/00387019108018154

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

SPECTROSCOPY LETTERS, 24(5), 741-748 (1991)

SPECTROSCOPIC INVESTIGATIONS ON POLYMERIC TETRA BENZO 18-CROWN-6 ETHER BRIDGED METAL-FREE PHTHALOCYANINE

Key words: Crown ether, phthalocyanine, crown ether bridged phthalocyanine, spectroscopic investigation.

Mustafa Özdemir and Erbil Ağar

Department of Chemistry, Faculty of Science and Arts,
Ondokuz Mayıs University, 55139 Kurupelit, Samsun, Turkey

INTRODUCTION

Phthalocyanines, crown ethers, and crown ether bridged phthalocyanine compounds have recently attracted a great deal of attention because of their interesting properties[1-5]. The spectroscopic specifications of these molecules have been studied for a long time. However, their structures are not completely elucidated since they have relatively big monomers, and form giant polymers[4,6,7]. There are many studies on the spectroscopic specifications of phthalocyanines[8-10], but one of them which recently appeared in Journal of Chemical Physics may be important as a theoretical reference from now on[1]. Similarly, the spectroscopic properties of crown ethers have been investigated for about twenty years[11,12]. Meanwhile, some spectroscopic properties of crown ether bridged phthalocyanine compounds have also investigated previously[3-7,13,14].

In this study; UV/VIS, IR, and ^1H NMR spectroscopic characteristics of polymeric tetra -2,3-[1′, 2′-dicyano] benzo -1, 4,7,10,13,16 hexaoxacyclo octadecane bridged metal-free phthalocyanine (polymeric tetra benzo 18-crown-6 ether bridged metal-free phthalocyanine or polymeric H_2CRPc) were investigated in diverse solvents and compared with the values obtained in recent works[1,2,11]. Aside from the UV/VIS carried out of the samples, the first derivative spectra were taken to enhance the detectability of minor spectral features such as weak shoulders[15].

Phthalocyanine, dibenzo 18-crown-6, and their polymeric species were chosen as model compounds. The differences between the model compounds and the polymeric H_2CRPc were specified. The formula of polymeric H_2CRPc in this work was shown in Figure 1.

EXPERIMENTAL

Instruments

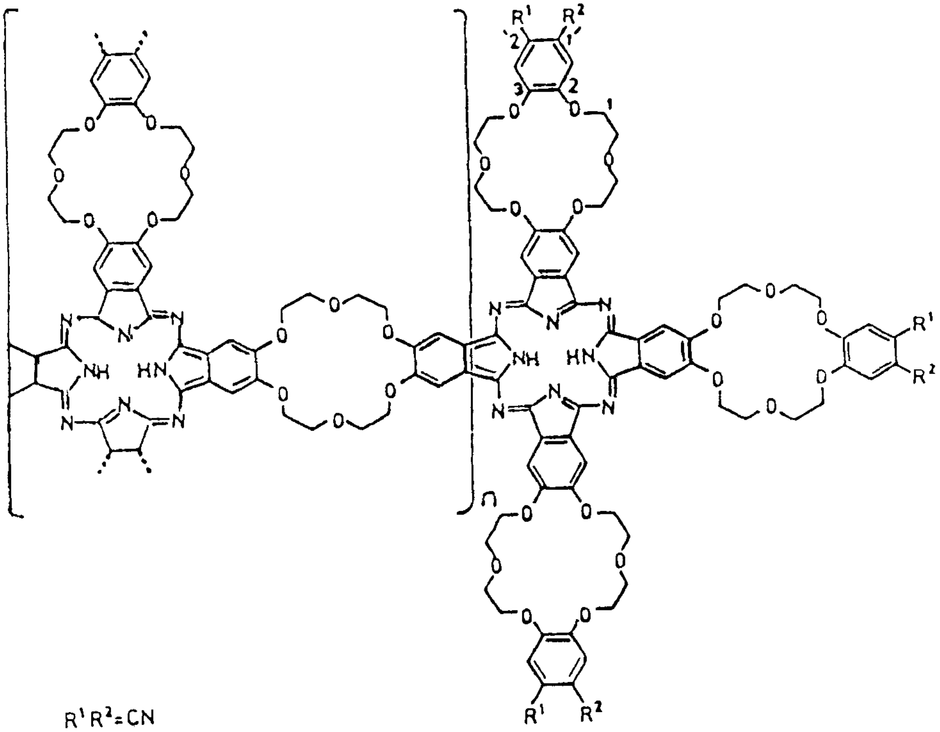
Instruments used in the experiments were UV Visible Varian DMS 100 double-beam spectrophotometer, Perkin Elmer 1430 Ratio Recording Spectrophotometer, and ^1H NMR, EM 360 Varian 60 MHz spectrometer.

Chemicals

Hydroquinone, ethylene glycol, N,N'-dimethyl formamide, ethanol were purchased from Merck (Germany). Solvents used in the experiments of DMSO, pyridine, DMF, dichloromethane, ethanol, chloroform, and aceton were also from Merck and were in spectroscopic quality.

Methods

Sym-dibenzo-18-crown-6, tetracyanodibenzo-18-crown-6, and polymeric H_2CRPc were synthesized according to published methods



$R^1R^2 = CN$

FIGURE 1

except the atmosphere of pure nitrogene used instead of argon[4,6,11].

RESULT AND DISCUSSION

UV/VIS, and first derivative spectra of the polymeric H_2CRPc were taken in DMSO, DMF, pyridine, chloroform, acetone, and dichloromethane. The results obtained from spectra were given in the Table 1.

TABLE 1

UV/VIS and First Derivative Spectral Transitions of the Polymeric H_2CRPc in the Diverse Solvents (λ_{max} and ε are in nm and $g^{-1}.cm^{-1}$. L, respectively)

DMSO : 677(33.2), 642(15.5), 610(12.6), 404(10.6) 337(23.3), 293(32.2), D_1: 556(0.12) $C = 5.15 \times 10^{-3}$ g/L

Pyridine : 675(32.4), 640(11.8), 620(9.8), D_1: 556(0.12), $C = 4.90 \times 10^{-3}$ g/L

DMF : 674(35.5), 642(19.3), 622(17.9), 290(277.1) D_1: 551(0.879), $C = 4.55 \times 10^{-3}$ g/L

Dichloromethane: 708(5.9), 671(8.5), 657(3.6), 347(33.4), 302(32.1), D_1: -, $C = 3.05 \times 10^{-3}$ g/L

Chloroform:752(1.4), 710(2.5), 672(5.6), 644(1.1), 620(0.8), 347(77.7), 302(360.5), D_1: - , $C = 3.55 \times 10^{-3}$ g/L

Acetone : 671(3.8), 654(4.0), 638(0.6), 550(5.8), D_1: - , $C = 2.96 \times 10^{-3}$ g/L

IR spectrum of polymeric H_2CRPc was taen in KBr and mulls (nujol mull and hexachlorobutadiene mull). The NMR spectrum of this polymer was obtained in DMSO-d_b. The bands of IR and ^{1}H NMR spectra are given in Table 2.

Polymeric H_2CRPc was relatively soluble in DMSO, DMF, and pyridine.

The experimental UV/VIS bands of polymeric H_2CRPc were slightly different from theoretical values[1], and the results of mononuclear and binuclear phthalocyanines[2]. The region of Q bands, and their ovartons were obtained in three transition levels in DMSO, DMF, and pyridine. In addition to these, there was a first derivative band between 548 and 556 nm in all of three solutions. The differences may probably arise from different solvent effects.

TABLE 2

IR and ^{1}H NMR Spectral Transitions of polymeric H_2CRPc
(IR: cm^{-1}, ^{1}H NMR: δ ppm ν)

IR Spectral Transitions in KBr-muls

3610 - 3620 ν(N-H) sh, 3380 - 3410 ν(N-H) s, 2918 - 2920
ν(Ar, C-H)s, 2845 - 2850 ν(Ar, C-H)s, 2230 - 2235 ν(C N)s
1715 - 1715 ν(Ar, C=C)s, 1592 - 1598 δ(Ar C=C) v
1510 - 1515 δ(C-N-C)v, 1465 - 1470 δ(-C-H)m, 1450 - 1455
δ(-C-H)v, 1410 - 1415 δ(-C-H)v, 1400 - 1402 δ(C-C)v
1380 - 1375 ν(C-C)s, 1350 - 1355 ν(C-C)s,
1280 - 1280 ν(O-C)s, 1210 - 1208 ν(O-C)v,
1170 - 1170 ν(C-N-C)s, 1108 - 1110 ν(-C-O-C)s.
1063 - 1065 ν(-C-O-C-)m, 1040 - 1040 β(C-H)m,
950 - 955 β(C-H)v, 910 - 915 γ(-C-H)m,
868 - 870 γ(C-H)v, 820 - 820 γ(C-H)s,
776 - 780 γ(C-H)v, 745 - 745 γ(-C-H)s

sh:shoulder s:strong m:medium v:very

^{1}H NMR Spectral Transitions in DMSO-d_b

Pyrrole N-H : -2.39 - (-2.65) ppm
Crown ether - H : 3.85 - 4.25 ppm
Aromatic - H : 7.95 - 8.15 ppm
Integration ratios : Pyrrole-H/CR-H/Aromatic-H were 1/20/5

The spectrum in DMSO has also 404, 337 and 293 nm bands. These bands may come from benzene units distant from phthalocyanine's benzene units. Because increasing polymerization of a monomer is responsible for red shift[16].

Polymeric H_2CRPc was slightly soluble in chloroform, acetone, and dichloromethane. Q bands of phthalocyanine units shifted to infrared side of spectrum. Spectra in dichloromethane, chloroform, and acetone did not have first derivative bands. Furthermore, there were likely benzene bands in 347 and 302 nm for polymeric compound.

Solvent effects on UV/VIS characteristics of polymeric H_2CRPc were not regular. Red shifts or blue shifts of spectra bands were not systematic changes. For more precise conclusion in the solvent effects, the complicated solvent influences also must be taken into consideration. The results obtained from UV/VIS experiments are given in the Table 1.

When IR spectra in KBr and mulls of polymeric H_2CRPc were compared with the H_2Pc and sym-dibenzo-18-crown-6 compounds, it was shown that some significant differences existed. We have obtained a broad band between 3620 and 3380 cm^{-1}. This was arise from pyrrole-N-H. The vibration modes of -C-H were in 2910-2845 cm^{-1}.

There were 2230-2350 ν(C $\equiv$ N), 1715-1715 ν(Ar-C=C), 1592-1595 δ(N-H), and 1510-1208 ν(C-C) ν(C-H) and ν(Ar-C-O-C) bands in spectra. Between 1170 and 1040 cm^{-1}; pyrrole β(C-H), aliphatic ether ν(C-O-C) and δ(N-H) were found. There were γ(C-H), ϕ(C-C), and (N-H) bands from 950 to 745 cm^{-1}. The detailed IR transitions are given in Table 2.

As shown from formula in Figure 1, there are many vibrational active groups in this compound. Main group bands were specified in spectrum, but many bending, scissoring, rocking, combination and overton bands were predicted in a definite band range. There were little shifts to greater wavelength numbers in the most of the IR bands with respect to H_2Pc and sym-dibenzo-18-crown-6[11,13,17,18].

Proton nuclear magnetic resonance spectrum of polymeric H_2CRPc was taken in DMSO-D_b. As expected, polymeric H_2CRPc gave three peaks arose from pyrrole H(N-H), aromatic H(Ar-H), and crown ether H(O-CH_2-CH_2-O). Polymeric materials showed the peak broadening in comparison with small molecules because of the lower mobility in polymer (19). In fact, ^{1}H NMR spectrum of polymeric H_2CRPc was obtained in broad bands in δ:(-2,39, -2,65) for pyrrole H, (3,85-4,25) for crown ether H, and (7,95-8,15) for aromatic H.

ACKNOWLEDGEMENTS

The authors would like to express their thanks to Prof.Dr. Özer Bekâroğlu, and Dr.Vefa Ahsen, researchers from TÜBİTAK, Gebze, İzmit for their assistances in the synthesis and structure determination of H_2CRPc.

REFERENCES

1. Orti E., Brédas J.L. Electronic Structure of Phthalocyanines: Theoretical Investigation of the optical properties of phthalocyanine monomers, dimers and crystals. J. Chem. Phys. 1990; 92(2): 1228-1235
2. Dodsworth E.S., Lever A.B.P. Intramolecular Coupling in Metal-Free Binuclear Phthalocyanines. J. Phys. Chem. 1985, 89, 5698-5705
3. Kobayashi N., Lever A.B.P. Cation- or Solvent -Induced Supermolecular Phthalocyanine Formation: Crown Ether Substituted Phthalocyanines. J. Am. Chem. Soc. 1987, 109, 7433-7441
4. Ahsen V., Yılmazer E., Bekâroğlu Ö. Synthesis and properties of (18-crown-6)-bridgen phthalocyanine network polymers. Makromol. Chem. 1988, 189, 2533-2543
5. Gasyna Z., Kobayashi N., Stillman M.J. Optical Absorbtion and Magnetic Dichroism Studies of Hydrogen Crown Ether-Substituted Monomeric and Dimeric Phthalocyanines J.Chem. Soc Dalton Trans. 1989, 2397-2405
6. Ahsen V., Yılmazer E., Bekâroğlu Ö. Preparation of a novel polymeric copper phthalocyanine containing crown ether moieties and its alkali metal binding property. Makromol. Chem., Rapid Commun. 1987, 8, 243-246
7. Sielcken Ot E., Tilborg M.M., Roks M.F.M., Hendriks R., Drenth W., Nolte R.J.M. Synthesis and Aggregation Behavior of Hosts Containing Phthalocyanine and Crown Ether Subunits. J.Am. Chem. Soc. 1987, 109, 4261-4265

8. Moser F.H., Thomas A.L. The Phthalocyanines Vol 1: Properties. Florida: CRC Press Inc. 1983

9. Fierro C., Anderson A.B., Scherson D.A. Electron Donor-Acceptor Properties of Porphyrins, Phthalocyanes, and Related Ring Chelates: A Molecular Orbital Approach J. Phys. Chem. 1988, 92, 6902-6907

10. Shurvell H.F., Pinzuti L. Sur Les Spectres Infrarouges des Phtalocyanines. Canadian Journal of Chemistry. 1966, 44, 125-136

11. Pedersen C.J. Cyclic Polyethers and Their Complexes with Metal Salts. J. Am. Chem. Soc. 1967, 89 (26), 7017-7036

12. Christensen J.J., Eatough D.J., Izatt R.M. The Synthesis and Ion Binding of Synthetic Multidentate Macrocyclic Compounds. Chem. Rew. 1974, 74, 351-383

13. Ahsen V., Yılmazer E., Ertaş M. Synthesis and Characterization of Metal-free and Metal Derivatives of a Novel Soluble Crown-Ether-Containing Phthalocyanine. J.Chem. Soc. Dalton Trans. 1988, 401-406

14. Koray A.R., Ahsen V., Bekâroğlu Ö. Preparation of Novel, Soluble Copper Phthalocyanine with Crown Ether Moieties J.Chem. Soc., Chem. Commun., 1986, 932-933

15. O'Haver T.C. Derivative and Wavelength Modulation Spectrometry. Analytical Chemistry, 1979, 51 (1), 91A-100A

16. Jaffé H.H., Orchin M. Theory and Applications of Ultraviolet Spectroscopy. London, Joh Wiley and Sons. Inc. London 1962

17. Wöhrle D., Marose U., Knoop R., Polymeric phthalocyanines and their precursors. Makromol. Chem., 1985, 186, 2209-2228

18. Wöhrle D., Preussner E. Polymeric phthalocyanines and their precursors. Makromol. Chem. 1985, 186, 2189-2207

19. Rodriguez F., Principles of Polymer Systems. Second Ed. London, McGraw-Hill Publ. Co. 1983

Date Received: 02/11/91
Date Accepted: 02/26/91