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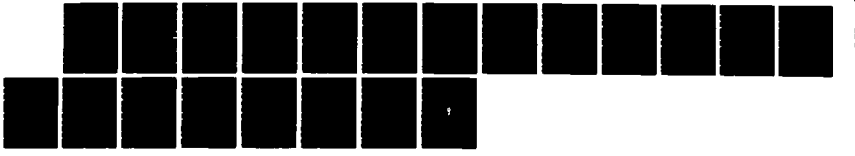

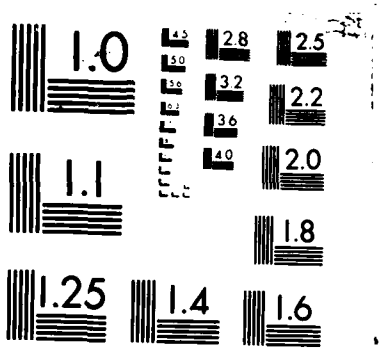

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A Planar Binuclear Phthalocyanine and its Di-Cobalt Derivatives

By

C.C. Leznoff, H. Ham, S.M. Marcuccio, W.A. Nevin, P. Janda, N. Kobayashi, and A.B.P. Lever

in

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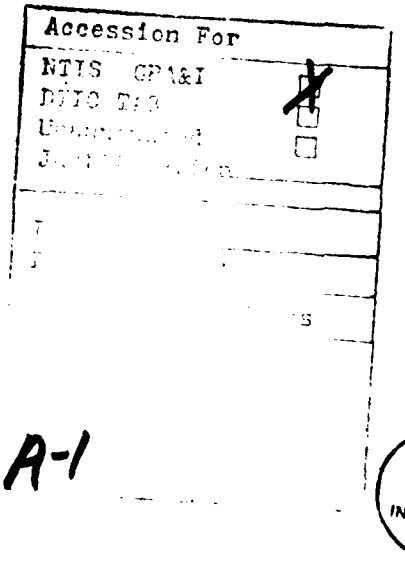

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"A Planar Binuclear Phthalocyanine and its Di-Cobalt Derivatives"

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The synthesis, characterisation and intramolecular interactions of a metal-free planar binuclear phthalocyanine and its cobalt derivatives are described.

Binuclear phthalocyanines covalently linked by $5^{1a,b}$, 4^{1c}, 2^{1c}, 1^{1d} and 0^{2} atom bridges have been recently described. We now report a new planar binuclear phthalocyanine (**1**) in which two phthalocyanine rings share a common benzene ring. Lacking a benzene ring relative to the other binuclear phthalocyanines, this is referred to as the (-1) linked binuclear phthalocyanine (**1a**).

We have previously studied intramolecular interactions in binuclear phthalocyanines[2] as a function of bridge link and it was obviously of interest to observe such interactions in (**1**). Indeed (**1a**) and its derivatives show spectroscopic and electrochemical evidence for greater intramolecular interactions than have been seen previously in binuclear phthalocyanines. Compound (**1**) also has value as a building block in making doubly-linked stacked conducting metallomacrocyclic polymers.[3]

Treatment of 4-neopentoxyphthalonitrile[1a,b] and 1,2,4,5-tetracyanobenzene[4] with ammonia[1b] gave the isoindolines (**2**) and (**3**) respectively (Scheme). A mixed condensation of excess (**2**) with (**3**) in 2-N,N-dimethylaminoethanol under standard conditions[1a-d] gave bis-2,3-b[7^{2},12^{2},17^{2}-trineopentoxytribenzo-[g,l,q]-5,10,15,20-tetraazaporphyrino[a,d]benzene (**1a**) after flash and gel-permeation chromatography.[5] The dicobalt(II) derivative (**1b**) was prepared by previously described insertion methods[1] in 63% yield from (**1a**). Compounds (**1a**) and (**1b**) gave parent ions in their mass spectra at 1468 and 1581 respectively using the FAB technique[1] and were fully characterised by

i.r., n.m.r. and elemental analysis. The inner NH protons of (**1a**) gave broad absorption peaks between -2 and -3ppm typical of other binuclear phthalocyanines.[1]

Both species (**1a**) and (**1b**) have electronic spectra (Figs.1,2) which are quite atypical, with broad absorption in the Q band region[6] indicative[2] of intramolecular electronic coupling. The characteristic double Q band of metal-free phthalocyanines[2] is barely evident even at 10^{-7}M concentrations. Q band S_1 emission is still observed but with an unusually broad[2] excitation spectrum (Fig.1).

Given the flat nature of the species (**1**), aggregation, prevalent in the phthalocyanine series[7] is important. Both the metal free and cobalt(II) species aggregate in micromolar concentration solutions. In o-di-chlorobenzene (DCB), the aggregation constants, for dimer formation, for (**1a**) and (**1b**) are (9.9 $\pm$ 0.9) x 10^4M^{-1} and (8.6 $\pm$ 0.6) x 10^4M^{-1} respectively, more than an order of magnitude higher than our previously investigated binuclear species[8], but an order lower than for a tetra-nuclear species.[5]

Cyclic voltammetry of (**1b**) in DCB solution (with 0.3M tetrabutyl-ammonium perchlorate, TBAP, Pt disc working electrode) consists of a series of broad peaks. Half-wave potentials were obtained by differential pulse voltammetry. Species (**1b**) shows oxidation at +0.17 and +0.59V and reduction at -0.81, -1.69 and -1.96V versus Fc^+/Fc[9]. The three most positive waves show evidence for splitting being broad or having well pronounced shoulders. Species (**1b**) is easier to reduce and more difficult to oxidise than previously described cobalt(II) mononuclear and binuclear analogues,[1,10] being reduced at some 0.3V less negative a potential.

Oxidised and reduced species were obtained using an optically transparent thin layer electrode (OTTLE) cell utilising a gold minigrid

working electrode. Stepwise oxidation across the first oxidation couple gives a spectrum typical of a phthalocyanine cation radical species[5,6b,10,11] (Fig.2a), corresponding to the oxidation of each of the phthalocyanine rings and with no clear spectroscopic evidence of any one-electron oxidised intermediate. In contrast, reduction over the double peak of the first reduction couple (-0.81V) occurs via two consecutive one-electron steps, corresponding to the consecutive reduction of each of the two cobalt atoms to Co(I) (Fig.2b). This is the first report of a mixed valence Co(I)-Co(II) phthalocyanine species, (**1c**). It displays a specific electronic spectrum (Fig.2b) different from either (**1b**) or the doubly reduced bis-Co(I) species, (**1d**). This is in contrast to cofacial mixed valence Co(II)-Co(I) porphyrin species[12] whose spectra show little evidence for interaction between the two halves of the molecule. The spectrum of (**1d**) shows some unusual features not seen previously with Co(I)Pc[10,6b,13,14] species, having a split Q band and an additional strong absorption peak at 825 nm. Both (**1c**) and (**1d**) show Q band and MLCT absorption (near 500nm) red shifted relative to less electronically coupled species.[1,10] Polarisation of the OTTLE negative of the couple at -1.69 V results in formation of a ring-reduced species, whose quite typical, but red shifted spectrum is also shown in Fig. 2b.

Electrocatalytic reduction of oxygen was examined at electrodes (glassy carbon and ordinary and stress annealed pyrolytic graphite) with adsorbed (**1b**). Oxygen reduction occurred at -0.34 V versus SCE in cyclic voltammetric curves through pH 1 to 13, and the limiting current corresponding to two electron reduction of oxygen to hydrogen peroxide was observed in rotating disc experiments. The absence of any dependence of the oxygen reduction potential upon pH down to pH = 1, is noteworthy.

This system represents an important new class of phthalocyanine

species which should prove of importance in photovoltaic and photo- and electrocatalytic applications, as well as in the field of molecular metals.[15]

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1. a) C.C.Leznoff, S.Greenberg, S.M.Marcuccio, P.C.Minor, P.Seymour, A.B.P.Lever, and K.B.Tomer, Inorg.Chim.Acta, 1984, 89, L35. b) C.C.Leznoff, S.M.Marcuccio, S.Greenberg, A.B.P.Lever and K.B.Tomer, Can.J.Chem., 1985, 63, 623. c) S.M.Marcuccio, P.I.Svirskaya, S.Greenberg, A.B.P.Lever and K.B.Tomer, Can.J.Chem., 1985, 63, 3057. d) S.Greenberg, S.M.Marcuccio, C.C.Leznoff and K.B.Tomer, Synthesis, 1986, 406.

2. E.S.Dodsworth, A.B.P.Lever, P.Seymour and C.C.Leznoff, J.Phys.Chem., 1985, 89, 5698.

3. C.W.Dirk, T.Inabe, K.F.Schoch,Jr. and T.J.Marks, J.Am.Chem.Soc., 1983, 105, 1539; B.N.Diel, T.Inabe, N.K.Jaggi, J.W.Lyding, O.Schneider, M.Hanack, C.R.Kannewurf, T.J.Marks, and L.H.Schwartz, J.Am.Chem.Soc., 1984, 106, 3207.

4. a) C.Piechocki and J.Simon, J.Chem.Soc. Chem.Commun., 1985, 259. b) D.Wöhrle and W.Wahl, Tetrahedron Lett., 1979, 227.

5. W.A. Nevin, W. Liu, S.Greenberg, M.R. Hempstead, S.M.Marcuccio, M. Melnik, C.C. Leznoff and A.B.P.Lever, Inorg.Chem., 1987, 26, 0000.

6. a) A.B.P.Lever, Adv.Inorg.Chem.Radiochem., 1965, 7, 27. b) P.C.Minor, M.Gouterman and A.B.P.Lever, Inorg.Chem., 1985, 24, 1894.

7. a) K.Bernauer, and S.Fallab, Helv.Chim.Acta, 1961, 44, 1287; b) Y-C.Yang, J.R.Ward and R.P.Seiders, Inorg.Chem., 1985, 24, 1765; c) A.R.Monahan, J.A.Brado, and A.F.DeLuca, J.Phys.Chem., 1972, 76, 1994.

8. W.A.Nevin. W.Liu and A.B.P.Lever, Can.J.Chem., 1987, 65, 0000.

9. Potentials were referenced internally to the ferrocenium/ferrocene couple, which lies at +0.16 V versus SCE. see R.R. Gagne, C.A. Koval, and D.C. Lisensky, Inorg. Chem. 1980, 19, 2854; G. Gritzner and J.Kuta, Electrochim. Acta, 1984, 29, 869.

10. W.A. Nevin, M.R. Hempstead, W. Liu, C.C. Leznoff, and A.B.P. Lever, Inorg.Chem., 1987, 26, 0000.

11. T.Nyokong, Z. Gasyna, and M.J. Stillman, Inorg. Chim. Acta, 1986, 112, 11; G. Ferraudi, S. Oishi, and S. Muraldiharan, J. Phys. Chem., 1984, 88, 5261; D. Dolphin, B.R. James, A.J. Murray, and J. Thornback, Can.J. Chem., 1980, 58, 1125.

12. a) J.P.Collman, M.Marrocco, C.M.Elliot and M.L'Her, J.Electroanal. Chem., 1981, 124, 113. b) Y.Le Mest, M.L'Her, J.Courtot-Coupez, J.P.Collman, E.R.Evitt and C.S.Bencosme, J.Electroanal.Chem., 1985, 184, 331.

13. W.A.Nevin, W. Liu, M. Melnik, and A.B.P. Lever, J.Electroanalytical Chem., 1986, 213, 217.

14. M.J.Stillman and A.J.Thompson, J.Chem.Soc., Far. Trans. II, 1974, 70, 790.

15. A.B.P.Lever, M.R.Hempstead, C.C.Leznoff, W.Liu, M.Melnik, W.A.Nevin and P.Seymour, Pure and Appl.Chem., 1986, 58, 1467.

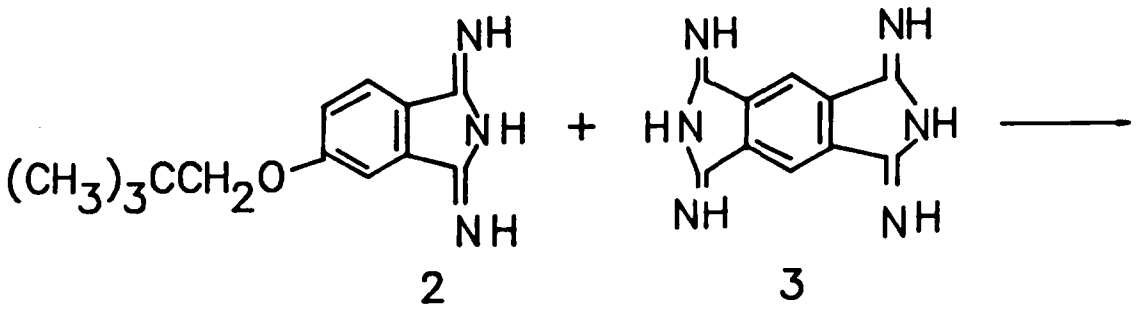
Figure Legends

Figure 1. Electronic absorption spectrum of (**1a**) in DCB (———————) at 1 x 10^{-6}M. Emission (λ_{ex} = 340nm)(-----) and excitation (λ_{em} = 715nm)(.....) spectra of (**1a**) in 1:1 ethanol/dichloromethane. a.u. = arbitrary units.

Figure 2. a) Development of the electronic spectrum with time, during the oxidation of (**1b**) at +0.55V vs Fc^+/Fc in DCB (0.3M TBAP) to a Co(II)-Co(II) ring oxidised di-cation radical.

b) Electronic absorption spectra of (**1b**) in DCB, after electrolysis at -0.90V (———), -1.25V (-----) and -1.85V(.....) vs Fc^+/Fc. The species are, neglecting axial ligands, the mixed valence Co(II)/Co(I), the Co(I)-Co(I) and a Co(I)-Co(I) ring reduced species respectively.

The insets show the near infrared region.



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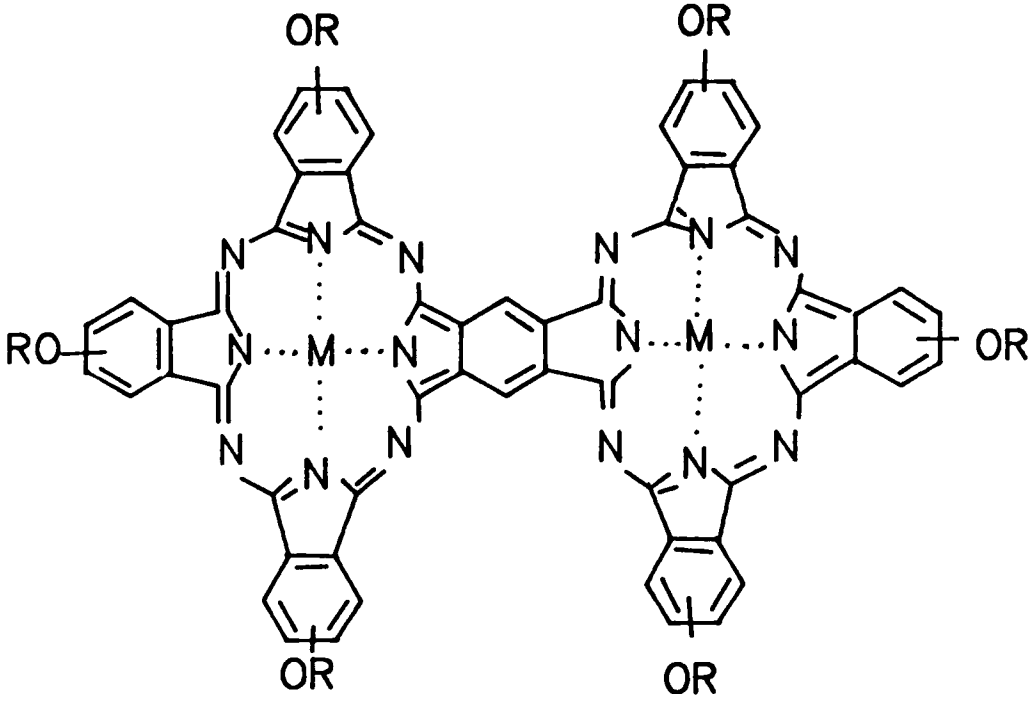
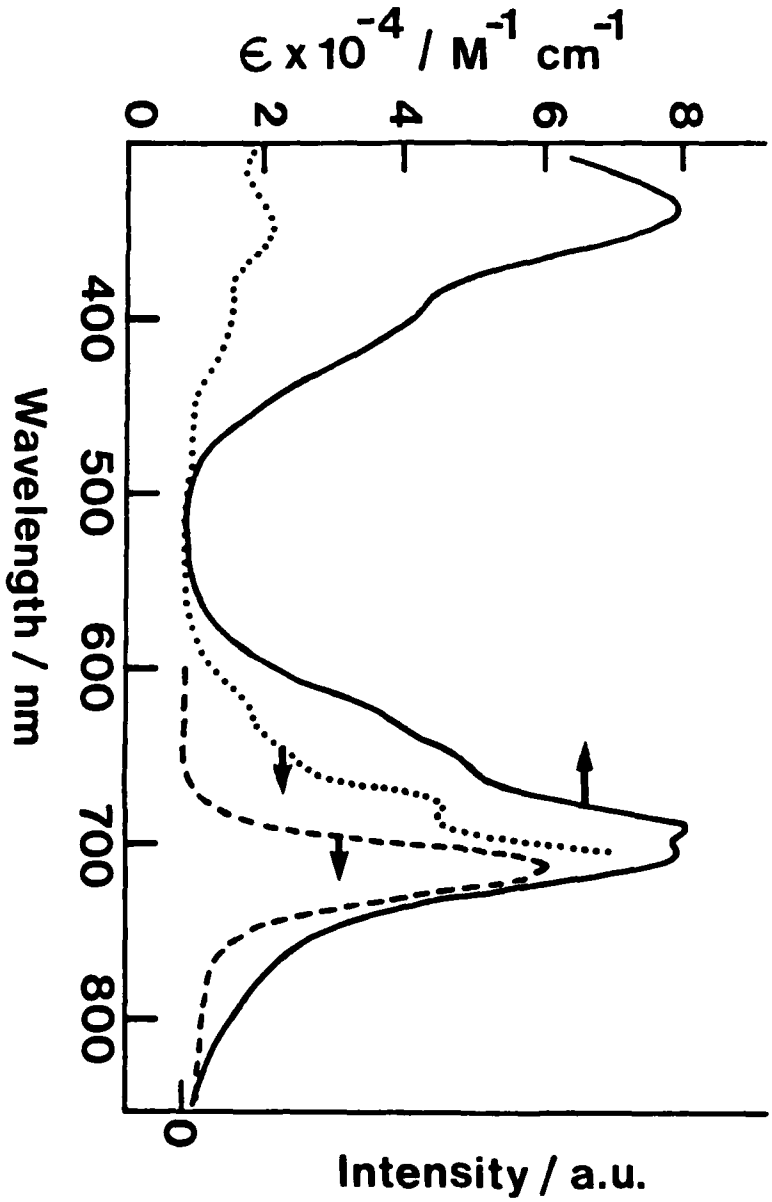
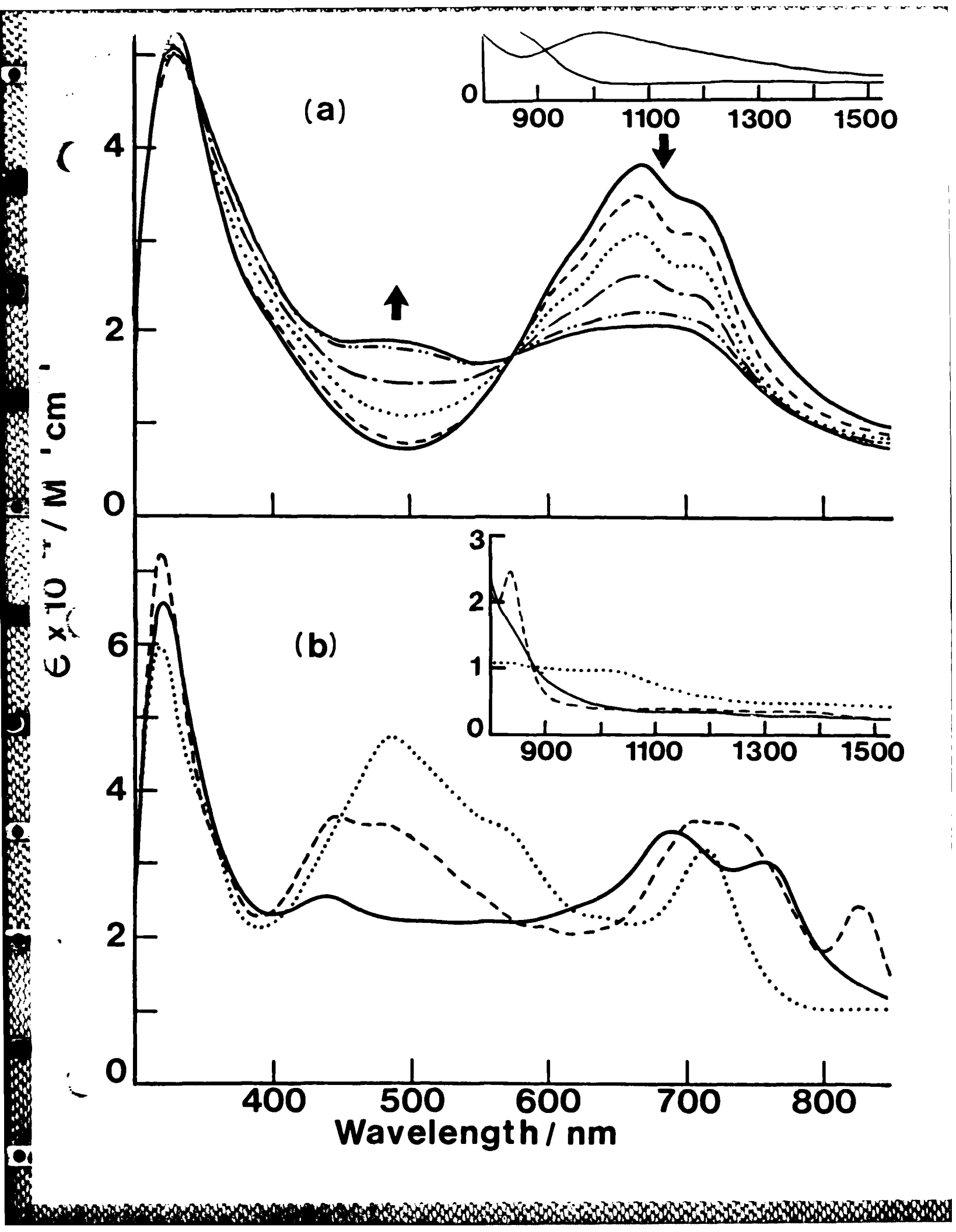


<u>1a</u> R = $CH_2C(CH_3)_3$,M = H_2

<u>1b</u> R = $CH_2C(CH_3)_3$,M = Co


ε x 10^-4 / M^-1 cm^-1
0
2
4
6
8
400
500
600
700
800
Wavelength / nm
0
Intensity / a.u.


(a)
(b)
0
900
1100
1300
1500
4
2
0
3
2
1
6
4
2
400
500
600
700
800
Wavelength / nm
ε x 10⁻³ / M⁻¹cm⁻¹

END

4-[redacted]-87

DTIC