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PROBES OF NONREACTIVE ENVIRONMENT
IV. 1-METHYL-4-CYANOFORMYLPYRIDINIUM OXIMATE

by

Raymond A. Mackay
Edward J. Poziomek

February 1972

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The compound 1-methyl-4-cyanoformylpyridinium oximate (CPO) possesses two electronic absorption bands, which are measures of solvent polarity. These transitions are attributed to an intramolecular charge-transfer from oximate oxygen to the pyridinium ring ($n \rightarrow \pi^*$) and vanish on protonation, metal complexation, or chemical reaction of the oxygen. The solubility, spectral solvent dependence, and zinc and cobalt metal complexes of CPO are described. An outline is given of the factors affecting the choice of CPO as a reagent for probing environment in solution.

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February 1972

Task 1B662710AD2901

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FOREWORD

The work described in this report was authorized under Task 1B662710AD2901, Chemical Detection and Identification Technology, Detection and Identification Concepts. The work was performed at a low level effort over the past several years.

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DIGEST

The compound 1-methyl-4-cyanoformylpyridinium oximate (CPO) possesses two electronic absorption bands, which are measures of solvent polarity. These transitions are attributed to an intramolecular charge-transfer from oximate oxygen to the pyridinium ring ($n \rightarrow \pi^*$) and vanish on protonation, metal complexation, or chemical reaction of the oxygen. The solubility, spectral solvent dependence, and zinc and cobalt metal complexes of CPO are described. An outline is given of the factors affecting the choice of CPO as a reagent for probing environment in solution.

CONTENTS

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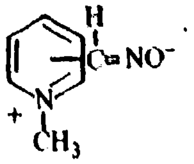
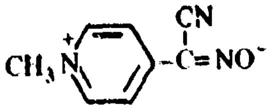
I. INTRODUCTION.

The charge-transfer (c-t) spectra of numerous substances have been used to correlate solute-solvent interactions with physical and chemical properties of interest. These include reaction rates, micelle formation, ion-pairing, and donor-acceptor excited states.[1] A study of the properties of aldoximates (PA) derived from 2,3- and 4-pyridinium aldoxime methiodides[2] showed that the long wavelength electronic absorption band, which had extinction coefficients of 10,000 to 20,000, correlated with Kosower's[3] Z values[*] and was designed as a c-t band. Unfortunately, these aldoximates are not very stable when isolated from solution. In the course of studies on c-t interactions involving pyridinium compounds, we have found that 1-methyl-4-cyanoformylpyridinium oximate (CPO), a very stable compound, has unusual characteristics that render it a useful reagent and probe of solute-solvent interactions. We report here a survey of some of the chemical and physical properties of CPO.



PA



CPO

II. EXPERIMENTATION.

A. 1-Methyl-4-Cyanoformylpyridinium Oximate.

This compound was prepared according to the method of Poziomek and coworkers.[4]

B. Zinc (II) and Cobalt (II) Chlorides of CPO.

A stoichiometric excess of the hydrated metal chloride was dissolved in ethanol and filtered to remove any cloudiness. The ligand (CPO) was added, and the suspension was stirred for about 1 day. The metal complex was filtered off, washed with ethanol and ether, and dried in vacuo.

Anal for $Zn(C_8H_7N_3O)_2Cl_2$. Calcd: C, 41.9; H, 3.1; N, 18.3; O, 7.0; Cl, 15.5; Zn, 14.2. Found: C, 41.9; H, 2.9; N, 18.5; O, 6.7; Cl, 15.3; Zn, 14.2.

Anal for $Co(C_8H_7N_3O)_2Cl_2 \cdot 0.14\ CoCl_2$. Calcd: C, 40.9; H, 3.0; N, 17.9; Co, 14.3. Found: C, 41.1; H, 3.1; N, 17.6; Co, 14.2. No attempt was made to extract the excess $CoCl_2$.

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[1] Mackay, R. A., Landolph, J. R., and Poziomek, E. J. Experimental Evidence Concerning the Nature of the Two Charge-Transfer Bands. J. Amer. Chem. Soc. *93*, 5026 (1971), and references therein.

[2] Engelhard, N., and Werth, B. Tetrahedron Letters *10*, 661 (1963).

[3] Kosower, E. M. The Effect of Solvent on Spectra. I. A New Empirical Measure of Solvent Polarity : Z Values. J. Amer. Chem. Soc. *80*, 3253 (1958).

[4] Poziomek, E. J., Poirier, R. H., Fromm, B. W., Kramer, D. N., Stockiner, J. A., and Pankau, M. D. 4-Cyanoformyl-1-Methylpyridinium Iodide Oxime and Derivatives. J. Org. Chem. *29*, 217 (1964).

[*] Energy in kilocalories $mole^{-1}$ of the peak maximum of the intermolecular c-t band of 1-ethyl-4-carbomethoxy-pyridinium iodide.

C. Physical Measurements.

The electronic spectra were obtained on a Cary 14 spectrophotometer. Liquid samples were run in 1-cm quartz cells with the solvent as reference. Solid samples were run as Nujol mulls on Whatman #1 filter paper with Nujol as reference. Solubilities were determined by dissolving the solid hot and letting it equilibrate to 20°C in a constant temperature bath. Aliquots were then withdrawn, appropriate dilutions made, and the concentrations determined spectrophotometrically on a Cary 14 spectrophotometer. Infrared spectra were obtained on a Perkin-Elmer 621 spectrophotometer, the samples being run as Nujol mulls between KRS-5 plates.

III. RESULTS AND DISCUSSION.

A. Solubility.

The solubility of CPO in a number of solvents at 20°C is given in table I. The compound has some solubility in a wide range of solvents from methylene chloride to water. It is insoluble in very nonpolar solvents such as hexane and benzene. There is no single correlation between solubility and either spectroscopic solvent polarity parameters, dielectric constant (*D*) of the solvent, or any of the usual functions of *D*.

Table I. Solubility and First and Second Charge-Transfer Bands of 1-Methyl-4-Cyanoformylpyridinium Oximate in Various Solvents

Solvent	Solubility[a]	E_{T1}[b]	ϵ_1[c]	E_{T2}[b]	ϵ_2[c]
Water	140	65.7	0.10	83.8	24
0.05 *M* H_2SO_4 (aq)	–	d	d	d	d
Methanol	9.0	59.6	0.08	78.7	29
0.05 *M* H_2SO_4 (MeOH)	–	d	d	d	d
Ethanol	1.5	57.2	0.09	77.1	30
Ethyl formate	e	e	e	76.3	e
2-Propanol	0.26	55.1	0.07	75.9	29
n-Pentanol	0.28	e	e	75.9	29
Dimethyl sulfoxide	87	51.3	0.10	75.3	41
Acetonitrile	7.5	51.0	0.08	74.9	36
Acetone	2.5	49.5	0.08	73.6	37
Ethylacetate	0.12	e	e	72.5	21
Methylene chloride	0.74	48.8	0.06	71.9	30

[a] Solubility at 20°C in moles $l^{-1} \times 10^3$.

[b] Band energy in kcal $mole^{-1}$ (±0.2 kcal $mole^{-1}$).

[c] Extinction coefficient in l $mole^{-1}$ $cm^{-1} \times 10^3$.

[d] Absent.

[e] Solubility too low for measurement

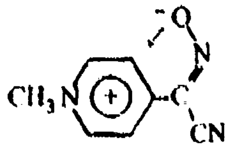
B. Electronic Spectra.

The first two (longest wavelength) absorption maxima and extinction coefficients of CPO in various solvents are given in table I. The lowest energy (E_{T1}) band is in the visible range with a molar extinction coefficient of about 100. The second band energy (E_{T2}) is in the near UV with a molar extinction coefficient of about 30,000. Both band energies are quite solvent sensitive and correlate linearly with empirical solvent polarity parameters such as Z values[3] and $E_{T(30)}$* values.[5] The color of the solution is thus an indication of the polarity of the solvent, ranging from blue in methylene chloride, to red in acetone, to yellow in water. The solid itself is dark red.

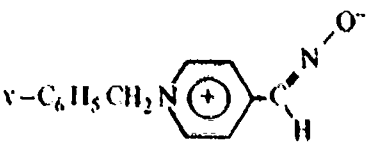
C. Nature of the Transition.

The magnitude and direction of the solvent dependence of E_{T1} and E_{T2} and their correlation with other inter- and intramolecular c-t band energies suggest that the transitions are of a similar nature. The absence of these bands in acid indicate that the oximate oxygen atom is involved.** In addition, the bands are seen to vanish with reactions (such as alkylation) of the oxygen, providing the anion (e.g., iodide, perchlorate, etc.) has a sufficiently high ionization potential so that the anion-to-ring intermolecular c-t bands do not interfere.

We believe that the first two transitions in CPO arise from an intramolecular charge transfer from oximate oxygen to the pyridinium ring ($n \rightarrow \pi^*$). It is also interesting to note that there exists the possibility of direct "through-space" interaction (A) because 4-pyridineglyoxylonitrile oxime (mp 276° to 278°C) and its alkylated derivatives have been assigned an E configuration (oxime group *cis* to pyridinium ring).[6,7] This is consistent with the large spectral solvent shifts of CPO, which indicate a significant change in direction of the electric dipole moment between ground and excited states. On the other hand, 1-(*p*-substituted benzyl) oximate derivatives (B) of *syn*-isonicotinaldehyde oxime show little shift of the lowest band energy between methylene chloride and methyl formate (table II).†



A



B

The question arises as to why two c-t bands are observed for pyridinium oximates. One possibility is that the electron is being promoted to either the first or second vacant molecular orbital (M.O.) on the ring. Evidence has been presented that indicates that this is the explanation for the c-t spectra of pyridinium iodides.[1] In the case of 4-substituted-1-alkylpyridinium iodides in CH_2Cl_2, the separation between the two c-t bands (ΔE_T) is about 28 kcal mole^{-1}. For CPO, ΔE_1 in CH_2Cl_2 is 23.1 kcal mole^{-1}. However, both bands were of comparable intensity in the iodide

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*Energy in kilocalories mole^{-1} of the peak maximum of the intramolecular c-t band of a pyridinium-N-phenol-betaine.

**The *p*Ka is reported to be 4.6 (Poziomek, et al.[4]).

†Reger, D. W., and Poziomek, E. J. Unpublished results.

[5] Reichardt, C. Indicators of Solvent Polarity. Agnew. Chem. (Int. Edn.) *4*, 29 (1965).

[6] Tyson, B. C., Jr., Poziomek, E. J., and Danielson, E. R. Chemistry of 4-Pyridineglyoxylonitrile Oxime and Methyl-4-Pyridineglyoxylate Oxime Ethers. J. Org. Chem. *34*, 3635 (1965).

[7] Tyson, B. C., Jr. Polarographic and Related Studies of *O*-Substituted Pyridinium Oximes. Ph.D. thesis. University of Delaware. June 1969.

Table II. Low Energy Charge-Transfer Band of Some 1-(*p*-Substituted Benzyl)-4-Formylpyridinium Oximates

p-Substituent	E_T*(CH_2Cl_2)	E_T*(methyl formate)
$-OCH_3$	45.2	45.8
$-Cl$	44.8	45.6
$-H$	45.1	45.8
$-NO_2$	44.8	45.8

*Band energy in kcal mole^{-1} (±0.3 kcal mole^{-1}).

salts (about 1000 liter mole^{-1} cm^{-1}), whereas in CPO the second band is about 300 times more intense. The ΔE_T of 1 ev (23 kcal mole^{-1}) is on the order of the energy difference between a singlet and triplet state. A second possibility then is that the two c-t bands are a result of triplet and singlet excited states arising from promotion of the electron to the first vacant M.O. Because the ground state is a singlet, the first band should be several hundred times less intense than the second.

The observation of phosphorescence from excitation of the long wavelength band would help to support the explanation based on triplet and singlet excited states. However, no emission was observed between room and liquid nitrogen temperatures in a variety of solvents. Unfortunately, our instrument was limited to a long wavelength maximum of 700 nm, and anomalously large Stokes shifts (10,000 to 20,000 cm^{-1}) have been reported for fluorescence from excitation of the c-t bands of pyridinium salts.[8]

D. Metal Complexation.

As mentioned, alkylation or protonation of CPO leads to a disappearance of the c-t bands. It seemed interesting to examine the spectral properties of CPO metal complexes. Accordingly, the metal complexes $M(CPO)_2Cl_2$, where M = Zn, Co, were prepared. Attempts to prepare iron (II) or copper (II) complexes lead to materials of uncertain composition. The cobalt and zinc complexes form cleanly and appear to be air stable and not hygroscopic. Solution spectra could not be obtained because the complexes are not soluble in most solvents. Some dissolution can be effected in dimethylformamide, pyridine, or acetonitrile. In all cases, however, ligand dissociation or replacement by solvent occurs. The zinc complex is yellow due to the tailing of UV absorption into the visible as shown by a solid state (Nujol mull) spectrum. As is the case with protonation or alkylation of the oxygen, the c-t bands are absent. Infrared mull spectra (table III) show that on coordination, the C=N stretching frequency of the oximate group is raised by 10 to 15 cm^{-1} and the C≡N frequency by 20 to 30 cm^{-1}, whereas the N-O stretching frequency is lowered by about 100 cm^{-1}. These results are consistent with metal ion coordination via the oximate oxygen because complexation should increase the contribution of the primary resonance form C relative to the resonance forms D and E. The zinc complex is presumably tetrahedral. The electronic spectrum of the solid cobalt complex is consistent with tetrahedral coordination, the visible absorption occurring about 16,000 cm^{-1}.

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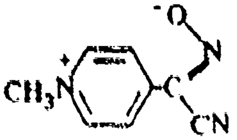
[8] Briegleb, G., Trencseni, J., and Herre, W. Chem. Phys. Lett. *3*, 146 (1969).

Table III. Infrared Stretching Frequencies of Zn(II) and Co(II) Chloride Complexes of CPO[a]

Compound	C–N[b]	C–N[c]	N–O[d]
CPO	2185	1620	1265, 1250
$Zn(CPO)_2Cl_2$	2215	1635	1173, 1157
$Co(CPO)_2Cl_2$	2205	1630	1155, 1145

[a] Frequency in cm^{-1}.
[b] $\pm 10\ cm^{-1}$.
[c] $\pm 2\ cm^{-1}$ (C=N of oximate group).
[d] $\pm 3\ cm^{-1}$.



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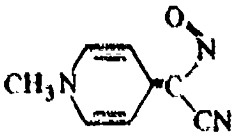

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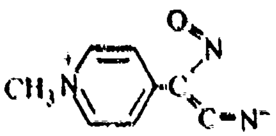

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E. Reasons for Selecting CPO as a Reagent for Probing Environment in Solutions.

Following is a list of the factors affecting the selection of CPO to use in probing solution environment.

1. CPO is easily prepared[4] from 4-pyridineglyoxylonitrile oxime, which, in turn, can be purchased or synthesized from isonicotinaldehyde oxime.[9]

2. CPO is very stable and has been stored for years under ambient laboratory conditions without decomposition.

3. A choice of CPO concentrations for probing solvent polarity is available because CPO possesses both weak and strong c-t bands with energies that correlate linearly with empirical solvent polarity parameters.

4. Modification of solubility properties can be accomplished easily by preparing CPO derivatives with appropriate pyridinium N-substituents.

5. The c-t bands of CPO are a result of intramolecular effects and follow Beer's law.

6. CPO reacts easily with a variety of alkylating, acylating, and sulfonylating chemicals[5] with a loss of the c-t bands. Analytical methods for these materials based on the resulting c-t band intensity could be developed.[10]

7. CPO reacts with certain metal ions to give insoluble complexes.

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[9] Poziomek, F. J., and Melvin, A. R. A New Synthetic Route to α-Isonitrosoacetonitriles. The Chlorination of Isonicotinaldehyde Oxime. J. Org. Chem. *26*, 3769 (1961).

[10] Poziomek, E. J., and Reger, D. W. Analytical Uses of Charge-Transfer Complexation: Spectrophotometric Method for Iodide in Water. Paper presented at the American Chemical Society Middle Atlantic Regional Meeting, Baltimore, Maryland, February 1971.

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