Anal. Calcd. for $C_9H_{17}O_5P$: C, 45.77; H, 7.26; P, 13.11. Found: C, 45.88; H, 7.76; P, 12.77.

Polydiethylphosphonomethyl methacrylate. Polymerization as described above gave a white, powdery, benzene-soluble polymer.

Anal. Calcd. for $C_9H_{17}O_5P$: C, 45.77; H, 7.26; P, 13.11. Found: C, 45.50; H, 7.62; P, 12.64.

Infrared spectra.[5a,b] The infrared spectra of the prepared compounds exhibit the customary ester (1735 cm.$^{-1}$), carbon-carbon double bond (1640 cm.$^{-1}$), P → O (1250 cm.$^{-1}$), P-O-C (1020 cm.$^{-1}$), 1050 cm.$^{-1}$ and 815 cm.$^{-1}$), and P–O (965 cm.$^{-1}$) absorption. In addition, an OH peak (3500 cm.$^{-1}$) probably due to traces of water is also observed.

Acknowledgment. We gratefully acknowledge the assistance of the Department of the Army who supported this project on Contract DA-49-007-MD-557.

DEPARTMENT OF CHEMISTRY
POLYTECHNIC INSTITUTE OF BROOKLYN
BROOKLYN 1, N. Y.

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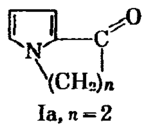
(5)(a) L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, Wiley, New York, 1958. (b) R. Sasin, R. M. Nauman, and D. Swern, *J. Am. Chem. Soc.*, 81, 4335 (1959).

Effect of Ring Size on the Spectra of Some Ketocycloalkano[*a*]pyrroles

JOHN M. PATTERSON, JAY BRASCH, AND PETER DRENCHKO

Received April 17, 1961

During an investigation of the chemistry of substituted pyrroles, some ketocycloalkano[*a*]pyrroles of the type were synthesized as intermediates



Ia, $n = 2$
Ib, $n = 3$
Ic, $n = 4$

Because of the recent interest in the spectra of pyrrole compounds[1] the ultraviolet spectra and carbonyl absorption frequencies of these compounds are reported herein. These spectral data are recorded in Table I.

TABLE I
ULTRAVIOLET MAXIMA AND CARBONYL FREQUENCIES OF THE PYRROLES

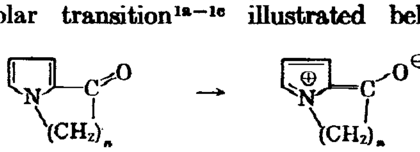
	95% Ethanol		Cyclohexane		Carbonyl Frequencies, Cm.$^{-1}$
	λ (mμ)	ε × 10^{-3}	λ (mμ)	ε × 10^{-3}	
1-Methyl-2-acetylpyrrole	287[a,b]	10.4	—	—	—
Ia	288	19.1	276[c] 282.5	29.6 39.6	1700
Ib	294	17.3	278[c] 288	19.5 21.8	1650
Ic	294[c]	4.74	279.5[c] 288.5	1.71 1.68	1645

[a] Also λ = 245 mμ; ε × 10^{-3} = 4.89. [b] Reference 1a. [c] Shoulder appears in the range 250–270 mμ.

For convenience the bands will be designated by an adaptation of the method used by Doub and Vandenbelt[2,3] in the substituted benzene series. The most displaced intense bands, relative to those of pyrrole, are designated as primary bands and the less intense bands as secondary bands. In the terminology of Eisner and Gore[1c] the primary band is called the K-band and the secondary band is called the B-band. A primary band (λ, 287 mμ) and a secondary band (λ, 245 mμ) have been reported[1a] for 1-methyl-2-acetylpyrrole. In the spectra reported here, only the primary band is observed; the secondary band is either masked completely or appears as a poorly defined shoulder of the primary band. The interpretation of these spectra will be limited to the primary band.

The ultraviolet maxima shifts and ε variations parallel those reported by Schubert and Sweeney[4] and those of Hedden and Brown[5] for the benzocyclanone series. The results can be rationalized by the application of the ideas used by Braude[6] in the substituted acetophenone series.

The primary band is usually ascribed to the nonpolar-polar transition[1a–1c] illustrated below. A



comparison of the spectra of 1-methyl-2-acetylpyrrole and 4-ketocyclopentano[*a*]pyrrole (Ia) shows only an increase in the intensity of the primary band and a masking of the secondary band. The increase in the transition probability can be attributed to the fixing of the carbonyl group in the plane of the pyrrole ring system.

With 5-ketocyclohexano[*a*]pyrrole (Ib) a shift, relative to the five-membered ketone system, of the primary band to longer wave lengths along with a slight decrease in the transition probability

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(1) (a) R. Andrisano, G. Pappalardo and L. Bolognari, *Gazz. chim. ital.*, 85, 1430 (1955). (b) G. H. Cookson, *J. Chem. Soc.*, 2789 (1953). (c) U. Eisner and P. H. Gore, *J. Chem. Soc.*, 922 (1958). (d) U. Eisner and R. L. Erskine, *J. Chem. Soc.*, 971 (1958).

(2) L. Doub and J. M. Vandenbelt, *J. Am. Chem. Soc.*, 69, 2714 (1947).

(3) The referee points out that the "secondary" bands identified by Doub and Vandenbelt in benzenoid spectra have no analogs in the pyrrole spectra and that it is possible that both intense bands of the pyrroles are "primary" bands. It has not been established that the transitions involved are equivalent to those of the benzene series.

(4) W. M. Schubert and W. A. Sweeney, *J. Am. Chem. Soc.*, 77, 2297 (1958).

(5) G. D. Hedden and W. G. Brown, *J. Am. Chem. Soc.*, 75, 3744 (1953).

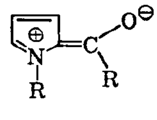
(6) E. A. Braude and E. S. Wright, *Progress in Stereochemistry*, Vol. 1, W. Klyne, ed., Butterworth, London, 1954, pp. 144–153.

is observed. This decrease in the transition energy may be associated with the difference in the steric strain of the two ring systems. The highly strained five-membered ring system should make the allowable electronic transition more difficult relative to the strainless six-membered ring system. The slight decrease in the ϵ_{max} is probably due to a decrease in the number of molecules in which the carbonyl group is coplanar with the pyrrole ring. Models show that in the strainless six-membered ring molecule the carbonyl group is slightly skewed with respect to the pyrrole ring.

In the spectrum of 6-ketocycloheptano[*a*]pyrrole the primary band is not displaced from that observed in the six-membered ring system, but there is a large decrease in the intensity of the band. Braude[7] suggests that changes of this type are due to relatively weak steric inhibitions. Models show that if the carbonyl group is to assume a coplanar conformation with the pyrrole ring, strain is introduced into the system because of C-H oppositions in the seven-membered ring. Fewer molecules, then, would be capable of undergoing the allowable electronic transition.

The use of the less polar cyclohexane solvent resulted in a constant shift of λ_{max} to shorter wave lengths, in an increase in the ϵ_{max} and in the appearance of fine structure in the curves. Such solvent effects have been attributed[8] to a hindrance in molecular rotation and a perturbation of the electrical forces in the solute molecule by the polar solvent. The increase in the ϵ_{max} suggests that the ethanol solvent may have reacted with the carbonyl group to a certain extent.

Eisner and Erskine[1d] have suggested that the low carbonyl stretching frequencies observed in the acylpyrrole series are due to significant contributions of the polar structure to the resonance hybrid.



The carbonyl frequencies of the ketocycloalkano[*a*]pyrroles fall within this range and are found to decrease with increasing size of the cycloalkano ring system. Similar decreases in carbonyl frequencies have been reported in the benzocyclanone series[9] and in the cyclanone series.[9,10]

The higher carbonyl stretching frequencies in the five-membered ring compounds compared to the six-membered ring compounds is due, according to Ingraham,[11] to the increased *s* character of the carbonyl carbon resulting from a rehybridization in the carbonyl orbitals caused by the angular strain associated with the five-membered ring.

EXPERIMENTAL

The infrared spectra were measured with a Perkin-Elmer Model 21 recording spectrophotometer using a sodium chloride prism. Chloroform solutions of 1 to 2% concentration were used. The ultraviolet spectra were measured with a Beckman Model DK-2 ratio recording spectrophotometer. Concentrations of the solutions were 10^{-4} to 10^{-5} *M*. The wave length maxima and the carbonyl absorption frequencies are given in Table I.

The ketocycloalkano[*a*]pyrroles (Ia–Ic) were synthesized by a modification and extension of the procedure described by Clemo *et al.*[12] Details of the synthesis will be described in a future report.

Acknowledgment. This investigation was sponsored by the Office of Ordnance Research, U. S. Army.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF KENTUCKY
LEXINGTON, KY.

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[10] T. Bürer and H. Günthard, *Helv. Chem. Acta*, **39**, 356 (1956).

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Some 3,5-Disubstituted Benzotrichlorides as Possible Insecticides

WALTER T. SMITH, JR., H. H. CHEN, AND JOHN M. PATTERSON

Received April 19, 1961

The structure and insecticidal activity of DDT is well known. Various explanations have been advanced to explain its activity.[1-6] It has been suggested[6] that the effect of the trichloromethyl group is to give the required steric orientation to the rest of the molecule, and that this orientation produces a maximum toxicity when the chlorine atoms on the aromatic nucleus are in the *para* positions. An alternate way to generalize the structural features required is to employ a unique spatial arrangement of the active substituents

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