[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA]

A Qualitative Correlation of the Spectra of Some Heterocyclic Carbonyl Compounds

BY JEROME A. BERSON

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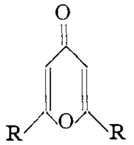
The spectra of pyrones, pyridones and their benzo homologs are treated theoretically by qualitative valence-bond reasoning. The integrated intensity in the monocyclic series is shown to be proportional to the square of the distance between the hetero atom and the carbonyl oxygen. Variations in the positions of the maxima are related to speculations on the important contributing structures in the ground and excited states.

The general structural similarities of pyrones and pyridones and of their benzo homologs have led us to an examination of the ultraviolet absorption data on these substances in the hope that a correlation of structure and spectroscopic behavior might be effected.[1] Table I gives the pertinent data for the substances concerned.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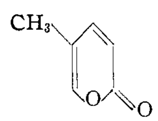
b, R = CH_3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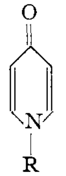
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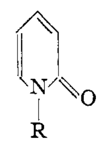
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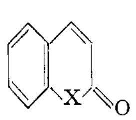
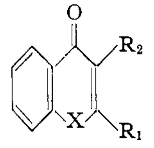

Va, X = O
b, X = NH
c, X = NCH_3


VIa, X = O; R_1 and R_2 = H
b, X = NH; R_1 and R_2 = H
c, X = NCH_3; R_1 and R_2 = H
d, X = NH; R_1 = CH_3; R_2 = H
e, X = NH; R_1 = H; R_2 = CH_3

Monocyclic Series.—The data for the monocyclic series (I–IV) reveal two general effects: (i) the nitrogen heterocycles absorb at slightly longer wave lengths than their oxygen analogs and (ii) the α-compounds absorb at pronouncedly longer wave lengths but with lower intensities than the γ-compounds.

These effects are interpretable in terms of a qualitative quantum mechanical picture of the absorption process. The electronic excitation associated with absorption of ultraviolet light involves transition from a ground state in which homopolar structures predominate to an excited state which partakes heavily of heteropolar resonance structures.[2] In the cases of I–IV, we consider the ground states to be hybrids of several canonical structures, the most important of which are of the type A_{1-3} and B_{1-3} ($X = O$, NH or NCH_3) with A_1 and B_1 predominant. It must be borne in mind that the wave functions describing the spectroscopic states must include terms representing contributions from structures such as A_{4-7} in the γ-series and B_{4-7} in the α-series. Inclusion of the "intermediate" dipolar structures is of particular significance in the γ-series since the prob-

TABLE I

ULTRAVIOLET ABSORPTION DATA[a]

	Monocyclic series	λmax (mμ)	Relative intensity	r^2 (Å.)	Ratio	Intensity	r^2
Ia	γ-Pyrone[b]	246	0.91	14.98	II:Ia	0.39	0.35
Ib	2,6-Dimethyl-γ-pyrone[b]	247	.98	14.98	II:Ib	.37	.35
II	5-Methyl-α-pyrone[c]	295	.36	5.20			
IIIa	γ-Pyridone[d]	256	1.00	15.37	IVa:IIIa	.42	.35
IIIb	N-Methyl-γ-pyridone[d]	262	.99	15.37	IVb:IIIb	.41	.35
IVa	α-Pyridone[d]	297	.42	5.38			
IVb	N-Methyl-α-pyridone[d]	300	.41	5.38			
	Benzo series						
Va	Coumarin[e]	312, 276	.28[k]	5.20	Va:VIa	.68	.35
Vb	2-Quinolone[f,g]	329, 270	.34[k]	5.38	Vb:VIb	.58	.35
Vc	N-Methyl-2-quinolone[g,h]	330,[i] 279[i]	.45[k]	5.38	Vc:VIc	.64	.35
VIa	Benzopyrone[b]	300,[i] 241[j]	.41[k]	14.98			
VIb	4-Quinolone[f,g]	332,[i] 288[i,j]	.59[k]	15.37			
VIc	N-Methyl-4-quinolone[g]	340,[i] 291[i]	.70[k]	15.37			
VId	2-Methyl-4-quinolone[f]	328,[i] 290[j]	.53[k]	15.37	Vb:VId	.64	.35
VIe	3-Methyl-4-quinolone[f]	340,[i] 290[j]	.39[k]	15.37			

[a] The positions of the maxima are estimated from the curves and may be in error by as much as ±2 mμ. Solvent for IIIa, IIIb, IVa and IVb was methanol; for all others, ethanol. [b] R. C. Gibbs, J. R. Johnson and E. C. Hughes, THIS JOURNAL, **52**, 4895 (1930). [c] J. Fried and R. C. Elderfield, *J. Org. Chem.*, **6**, 566 (1941). [d] H. Specker and H. Gawrosch, *Ber.*, **75**, 1338 (1942); *cf.* E. R. Riegel and M. C. Reinhard, THIS JOURNAL, **48**, 1334 (1926). [e] Determined in 95% ethanol with the Beckman spectrophotometer, model DU. *Cf.* T. Tasaki, *Acta Phytochim.*, **3**, 21 (1927); E. Rakower, *Acta Phys. Polinica*, **3**, 415 (1934) [*C. A.*, **31**, 2097 (1937)]. [f] G. W. Ewing and E. A. Steck, THIS JOURNAL, **68**, 2181 (1946). [g] Reference 1. [h] H. Ley and H. Specker, *Ber.*, **72**, 192 (1939). [i] The band shows fine structure. Only the longest wave length peak is given. [j] Plateau. [k] Intensity for the longest wave length band. The band was graphically resolved in the region of overlap with the neighboring band.

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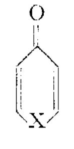
(1) R. D. Brown and F. N. Lahey, *Austr. J. Sci. Res.*, **A3**, 615 (1950), have discussed the qualitative relationship of the spectra of quinolones to that of naphthalene from the molecular orbital viewpoint.

(2) (a) A. Maccoll, *Quart. Rev.*, **1**, 11 (1947); (b) A. Sklar, *J. Chem. Phys.*, **5**, 669 (1937); (c) R. S. Mulliken, *Revs. Mod. Phys.*, **14**, 265 (1942).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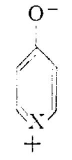
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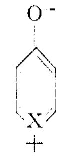
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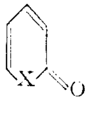
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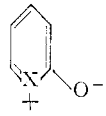
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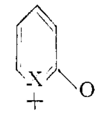
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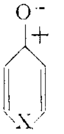
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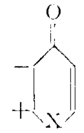
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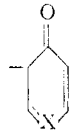
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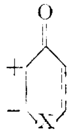
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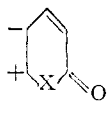
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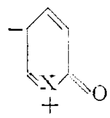
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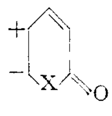
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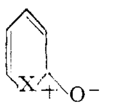
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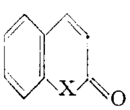
ability of direct electronic transitions between the homopolar structure (A_1) and the extreme heteropolar structures (A_2 and A_3) is very small.[3] In the first excited states, the importance of the heteropolar Kekulé structures (A_2, A_3, B_2, B_3) increases. The greater reluctance of oxygen to bear a positive charge (relative to that of nitrogen)[4] results in the observed longer wave length absorption for the nitrogen heterocycles.

The higher energy absorption for the γ-compounds may be ascribed to the fact that A_2 and A_3 must be of higher energy than B_2 and B_3 because of increased charge separation. While the stability relationship between the pairs of polar structures is the same in the ground state, the effects there must be diminished because of the smaller contributions of these structures.

The extinction coefficients in the γ-series are several times as large as those in the α-series. Qualitatively, this is to be expected, since the integrated intensity (measured by the area under the band envelope) is a function of the dipole strength of the chromophore and is therefore proportional to a quantity which may be taken, at least approximately, to be the square of the distance between the ends of the absorbing system.[5-7] It seemed probable, therefore, that the intensity variations in the monocyclic series were related to the greater N–O or O–O distances in the γ-compounds as compared to the α-compounds. In order to determine whether the intensity variations followed the second power relationship, we have calculated the relative integrated absorption intensities by replotting the literature curves as extinction coefficient *vs.* frequency in cm.$^{-1}$, extrapolating to zero extinction, measuring the areas planimetrically, and comparing the ratios of the integrated intensities to the ratios of the squares of the respective N–O and O–O distances (r^2). Since precise structural information on these substances is lacking, we have chosen reasonable values for the various bond lengths and angles by analogy to values reported in the literature for similar functional groups and have adjusted these to accommodate the changes in bond order accompanying resonance. Since the uncertainties in the structural parameters do not significantly affect the ratios of the squares of the distances, the particular values used in the calculations have not been recorded here. The satisfactory agreement between the integrated intensity ratios and r^2 ratios (Table I) lends strong support to our interpretation of the variations of the intensities with structure.

Benzo Series.—An extension of the correlations to the benzo series (Va-c and VIa-e) involves some new factors.

The ground states for the benzo series are hybrids in which structures of the type C_1, C_2 and D_1, D_2 (X = O, NH or NCH_3) predominate while smaller contributions are made by dipolar structures. In the excited state hybrids, the dipolar structures (only a few of which are shown) such as C_{3-9} make much more significant contributions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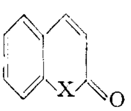
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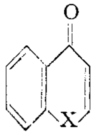
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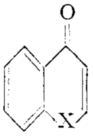
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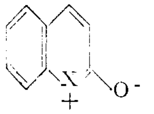
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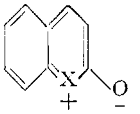
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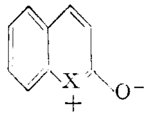
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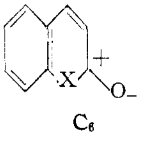
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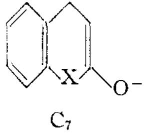
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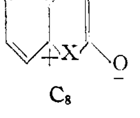
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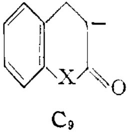
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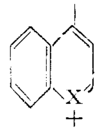
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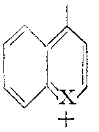
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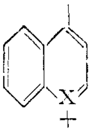
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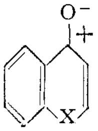
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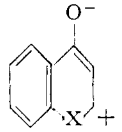
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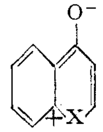
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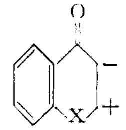
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The principal differences in spectroscopic behavior between the monocyclic and benzo series are now interpretable:

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(3) *Cf.* L. Pauling, *Proc. Nat. Acad. Sci.*, **25**, 577 (1939).

(4) *Cf.* V. Schomaker and L. Pauling, THIS JOURNAL, **61**, 1778 (1939).

(5) N. Q. Chako, *J. Chem. Phys.*, **2**, 644 (1934).

(6) R. S. Mulliken, *ibid.*, **7**, 14 (1939).

(7) This relationship has been conspicuously successful in correlations of spectral intensities of linear polyenes [L. Pauling, *Fortschr. Chem. organ. Naturstoffe*, **3**, 203 (1939); *Helv. Chim. Acta*, **32**, 2241 (1949); L. Zechmeister, A. L. LeRosen, W. A. Schroeder, A. Polgar and L. Pauling, THIS JOURNAL, **65**, 1941 (1943); L. Zechmeister and R. B. Escue, *ibid.*, **66**, 322 (1944)] and of α,β-unsaturated ketones (R. B. Turner and D. Voitle, *ibid.*, **73**, 1403 (1951)].

(i) The longest wave length maxima for the benzo compounds lie appreciably further toward the red than do those of the corresponding monocyclic derivatives (Table I). This is attributable to the far greater number of dipolar structures in the benzo series. While contributions from dipolar structures stabilize both ground and excited states in both series, their more significant contribution in the excited states is reflected in over-all decrease in excitation energy in the benzo series as compared to the monocyclic series.

(ii) The differences in excitation energies between the α- and γ-compounds are very much smaller in the benzo series (Table I). This results from the somewhat decreased relative importance of the dipolar naphthalenoid structures (C_{3-5} and D_{3-5}) in the benzo series. The greater spread of the integrated intensity values within both the α- and γ-groups of the benzo series as well as the substantial deviations of the intensity ratios from the r^2 ratios presumably is a consequence of the same circumstance. The anomalously low intensity of 3-methyl-4-quinolone (VIe) may be due to steric hindrance between the methyl and carbonyl groups.

(iii) All of the benzo compounds show either maxima or well-defined plateaus at wave lengths below the principal maxima, while the monocyclic compounds show only one band in the conventionally accessible region of the spectrum. The following explanation for this is in terms of the γ-compounds but applies equally well to the α-compounds. In the monocyclic series, we may represent the ground state energy essentially by that of A_1, slightly depressed by resonance contributions from the dipolar structures. The degenerate first-approximation excited state, made up largely of the energetically equivalent structures A_2 and A_3 is split by resonance into two-widely separated energy levels. Transition from the ground state to the lower of these two levels accounts for the observed single band, while transition to the higher level is presumably outside the range of the conventional instruments. In the benzo series, however, the first-approximation ground and excited states are both highly degenerate and markedly split by resonance, the ground state into two levels, principally by interaction between the benzenoid structures D_1 and D_2 and the excited state into three levels, principally by interaction among the naphthalenoid structures D_{3-5}. It seems probable that the upper level derived from the original ground state and the lower level derived from the original excited state will be sufficiently close together in energy so that significant further interaction will occur. The magnitude of the resultant resonance splitting will depend on the proximity of the levels. If these are only moderately close together, as seems reasonable, the split will be comparatively small and there will be two low-lying excited states with only a comparatively small difference in energy between them.[8] This energy difference should be roughly comparable throughout the benzo series, an expectation in good agreement with experiment. The average spacing for the eight members of the series is 16 ± 2 kcal./mole.

Acknowledgment.—The author is indebted to Dr. Verner Schomaker for stimulating comments and suggestions.

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[8] A further approximation would take into account an additional perturbation of the second excited state by interaction with the next higher state. If the energy relationships are similar in magnitude to those in our discussion above, the third excited state level might be experimentally observable. Indeed, this is found as a maximum in the region 230–240 mμ (not indicated in the table) in the spectra of all the nitrogen compounds of the benzo series (Vb, Vc, VIb, VIc, VId, VIe).

LOS ANGELES 7, CALIFORNIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

The Action of Elementary Fluorine upon Organic Compounds. XVIII. A New Type of Reactor and the Mild Fluorination of Carbon Disulfide[1]

BY EDWARD A. TYCZKOWSKI[2] AND LUCIUS A. BIGELOW

RECEIVED FEBRUARY 6, 1953

A new type of metal packed direct fluorination reactor incorporating a concentric tube burner designed from a study of fluorine diffusion flames has been built and operated. It has been shown by direct comparison to produce a very mild fluorination reaction in which both cleavage and polymerization appear to be reduced. The new reactor has been applied to the mild fluorination of carbon disulfide which has resulted in the isolation of the new and interesting perfluoro compound $SF_5CF_2SF_5$. This was accompanied by the new $SF_3CF_2SF_5$ and CF_3SF_3, as well as an unusually pure sample of S_2F_{10}, and a variety of additional cleavage products.

This paper describes the construction and operation of a novel design of fluorination reactor; and is also the second[3] of a group which will deal with the vapor phase fluorination, largely under mild conditions, of typical organic compounds containing nitrogen or sulfur.

In this Laboratory careful studies have been made of the performance of a considerable series of metal packed fluorination reactors, the efficiencies of which have increased with our experience; but nevertheless relatively little knowledge has been gained as to what actually takes place within such a unit. The last of these was the T-reactor, designed by Gilbert,[4] in which the sample on carrier

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[1] This paper was presented at the September, 1952, Meeting of the American Chemical Society in Atlantic City; and has been constructed from portions of the Doctorate Thesis to be offered by Edward A. Tyczkowski to Duke University in the Spring of 1953.

[2] Allied Chemical and Dye Corporation Fellow, 1950–1951; Atomic Energy Commission Fellow, 1951–1952.

[3] See J. A. Cuculo and L. A. Bigelow, THIS JOURNAL, **74**, 710 (1952).

[4] A. R. Gilbert and L. A. Bigelow, *ibid.*, **72**, 2411 (1950).