NOTES

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Ultraviolet Spectral Studies in the Esters of Aroylphosphonic Acids

Ken-ichi TERAUCHI and Hiroshi SAKURAI

The Institute of Scientific and Industrial Research, Osaka University, Yamada-Kami, Suita, Osaka

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The yellow color and spectral properties of aroylphosphonates are of some interest since the carbon analog benzaldehyde derivatives are colorless and since the phosphorus atom obviously acts as part of the chromophoric system.

The infrared and NMR data[1] provide evidence for a moderately strong conjugation between phosphorus of the phosphoryl group and carbon of the adjacent carbonyl group; more especially, the infrared absorptions of the carbonyl group in Compounds I—VIII (Table 2) show significantly low frequencies (50—65 cm^{-1} less than those[2] of the corresponding aldehydes). Griffin[3] and Berlin[4] have investigated the ultraviolet spectral evidence for d_π–p_π bonding in tri-2-pyrryl-, 2-(1-methylpyrryl),- 2-thienyl-, and 2-furylphosphine oxides, all of which possess a number of *para*-substituents on the aromatic ring, and in some acylphosphonates, respectively. The *n*–π^* transitions, however, in esters of aroylphosphonic acids have not yet been elucidated. In the present work, the *n*–π^* bands of Compounds I—VIII have been investigated, and an interesting correlation of the *n*–π^* band with Hammett substituent constants has been found.

The ultraviolet spectra of benzoylphosphonates were shown in the 320—450 mμ region (Fig. 1). In the ultraviolet and visible regions, the I—VIII benzoylphosphonates have two absorptions (Table 1); that in the 258—295 mμ region is identified as a π–π^* transition (^{1}A–^{1}La) on the basis of the large extinction coefficients, and the other, occurring in the 373—385 mμ region, identified as an *n*–π^* transition of the carbonyl group, are involving interaction with the phosphorus d-orbitals. The high intensity π–π^* bands in Compounds I—VIII underwent a bathochromic shift of from 17 to 29 mμ from those of its carbon-analog benzaldehydes.[5] Such a red shift suggests the extended conjugation that electronic excitation would produce an excited electron, one which is probably partially delocalized over the P→O group perhaps through vacant d orbitals on the phosphorus. On the other hand, the *n*–π^* bands in I—VIII are, of course, at much longer wavelengths. When we compare the absorption data[6] with those of the benzaldehydes, we find that the *n*–π^* absorption maxima of benzoylphosphonates show an average bathochromic shift of 50 mμ, suggesting that the orbital on carbon atom overlaps with a vacant d orbital on the phosphorus. Also, the extinction coefficients of benzoylphosphonates are considerably greater than those of the corresponding benzaldehydes. The *n*–π^* transition of I occurred at a wavelength shorter by 17 mμ in methanol than in cyclohexane (hypsochromic shift). This change follows the pattern

TABLE 1. ULTRAVIOLET SPECTRAL DATA FOR AROYLPHOSPHONATES

Compound	$\overset{O}{\overset{\|}{RC}}-\overset{O}{\overset{\uparrow}{P}}(OR')_2$		Transition	
	R	R′	π–π^* λ_{max}, mμ ($\log \varepsilon_{max}$)	*n*–π^* λ_{max}, mμ ($\log \varepsilon_{max}$)
I	C_6H_5	C_2H_5	258 (4.05)	379 (1.92)
II	C_6H_5	*i*-C_3H_7	258 (4.11)	379 (1.91)
III	C_6H_5	*n*-C_4H_9	259 (4.11)	380 (2.01)
IV	C_6H_5	$CH_2CH{=}CH_2$	265 (4.31)	378 (2.18)
V	*p*-ClC_6H_4	C_2H_5	268 (4.10)	385 (1.97)
VI	*p*-BrC_6H_4	C_2H_5	271 (4.27)	385 (1.98)
VII	*p*-$CH_3OC_6H_4$	C_2H_5	294 (4.01)	373 (2.18)
VIII	*p*-$(CH_3)_3CC_6H_4$	C_2H_5	271 (4.06)	375 (2.16)

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[1] K. D. Berlin and H. A. Taylor, *J. Am. Chem. Soc.*, **86**, 3862 (1964).

[2] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, New York, N.Y. (1954).

[3] C. E. Griffin, R. P. Peller, K. R. Martin and J. A. Peters, *J. Org. Chem.*, **30**, 97 (1965).

[4] K. D. Berlin and D. H. Burpo, *ibid.*, **31**, 1304 (1965).

[5] J. C. Dearden and W. F. Forbes, *Can. J. Chem.*, **36**, 1362 (1958).

[6] H. E. Ungnade, M. E. Hill and M. J. Kamlet, Ed., "Organic Electronic Spectral Data," Vol. II, Interscience Publishers, Inc., New York (1957), p. 135.

usually observed in carbonyl compounds in changing from non-polar to polar solvents; hence, it substantiate the identification of the spectroscopic transition as n–π^*.

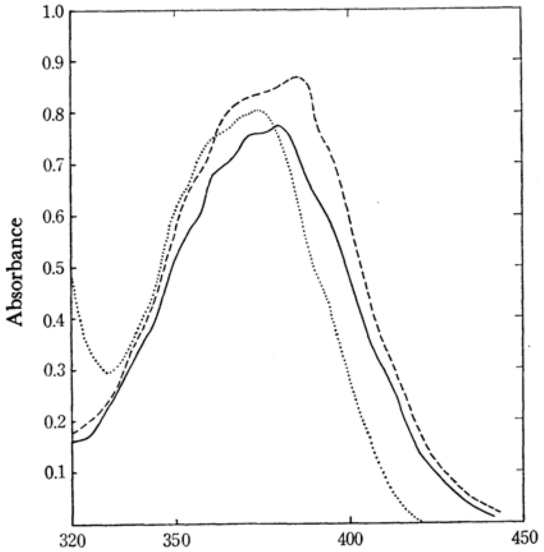

Fig. 1. The electronic spectra of I (——), 928×10^{-5} M; V (- - -), 958×10^{-5} M; and VI (········), 533×10^{-5} M; all spectra were recorded in cyclohexane.

An interesting correlation between the wavelengths of the most intense n–π^* bands and σ's, the Hammett substituent constants, was also noted (Fig. 2). Although it is recognized that ultraviolet data, which involve both ground and excited states, cannot normally be related to Hammett substituent effects, which involve ground states only, this apparent correlation appears worthy of comment. A linear correlation of wavelengths with σ's was found for benzoylphosphonate and its *p*-*t*-butyl-, *p*-methoxy-, *p*-chloro-, and *p*-bromo derivatives. Unfortunately, no kinetic data involving Hammett correlations in *para*-substituted benzoylphosphonates have yet been reported; however, we believe that this correlation is real and significant.

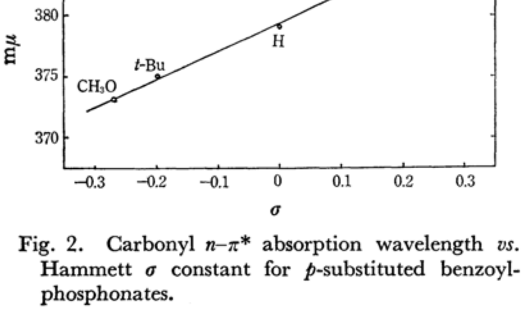

Fig. 2. Carbonyl n–π^* absorption wavelength *vs.* Hammett σ constant for *p*-substituted benzoylphosphonates.

Such a substituent effect prompts the question concerning the preferred conformation in the aroylphosphonates. The NMR data[1)] suggest free rotation around the C–P bond. On the other hand, dipole-moment measurements have been reported the values of 2.93 D for I, 3.20 D for VI, and 2.64 D for V.[7)]

These values of VI and V, lower and higher, respectively compared to those of the corresponding aldehydes (reported[8)] as 3.70 D and 2.03 D respectively) prompt the speculation that the powerful electron inductive abilities of the methoxy and chloro functions cause a change in the electron density on the carbonyl carbon atom. The more the electron density on the carbonyl carbon increases, the more the lifetime of the conformation in which the carbonyl and phosphoryl groups are opposite might increase.

Consequently, it is conceivable that, in Compound V, the interaction of a filled nonbonding orbital on the oxygen of the phosphoryl group with the π-orbital of the carbon atom of the carbonyl group could occur to a greater extent than in Compound VI and could result in the n–π^* band at a longer wavelength. Assuming sp^2-hybridization on the oxygen of the phosphoryl group, the overlap of these orbitals is possible and is probably at a maximum when the P→O bond is perpendicular to the plane composed of the aryl ring, carbon, and phosphorus. It is also known[9)] that, when there is a direct (σ-type) interaction of the π-orbital of the carbon atom of the carbonyl group with the lone-pair electron in another group, an intensification of the carbonyl n–π^* band is observed. Therefore, as is shown in Table 1, from the large intensity of the n–π^* band in Compounds I—VIII we will be able to deduce that such a direct

TABLE 2. INFRARED SPECTRA OF AROYLPHOSPHONATES (cm^{-1})

Compd.	C=O	P→O	P–O–C
I	1655	1255	1020
II	1648	1250	998
III	1640	1252	1020
IV	1642	1254	a
V	1645	1251	1015
VI	1640	1250	1014
VII	1630	1245	1021
VIII	1644	1255	1018

a) A broad absorption in the region of 988—1030 cm^{-1}.

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7) See Ref. 1. These values are measured in R=CH$_3$.

8) L. G. Wesson, "Tables of Electric Dipole Moment," The Technology Press, Cambridge, Mass. (1948).

9) J. N. Murrell, "The Theory of the Electronic Spectra of Organic Molecules," John Wiley and Sons, Inc., New York, N.Y. (1963), p. 165.

interaction (overlap effect) exists in benzoylphosphonates. This interactioni is supported by the findings concerning the carbonyl stretching frequency shown in Table 2. However, in view of the ultraviolet data, the p_π–d_π bonding in aroylphosphonates is apparently far less sensitive to rotation around the bond axis than is the p_π–p_π bonding such as that in α-diketones.[10] In arly sulfones, it is known that the formation of p_π–d_π bonds is independent of steric restraints because of the geometry and the large number of 3d orbitals.[11] In compounds of the R_3PO type it has been pointed out that some interaction of 3d orbitals with a π orbital of the chromophoric R group is possible, whatever the orientation of the chromophore plane with respect to the rest of the molecule.[12]

In addition, the β-keto compound diethylphosphonacetophenone has only one high intense band (λ_{max} 245 mμ, log ε 4.32), with no discrenible shoulders in the 220—450 mμ region; this shows the absence of any formation of d_π–p_π bonding.

Experimental

The ultraviolet spectra were determined in spectral-grade cyclohexane on a Hitachi EPU-2 spectrophotometer. The infrared spectra were obtained on a Hitachi EPI-S2 instrument run at a very slow speed in films of the esters of sodium chloride plates. The aroylphosphonates were synthesized by the reaction of trialkyl phosphites with acid chloride.[1] The diethylphosphonacetophenone was prepared by the methods of Borowitz *et al.*[13] Repeated distillation under reduced pressure was used to purify all the compounds needed. Tlc on a 0.25-mm thickness of silica gel, with acetone-chloroform in the volume ratio of 1 : 9, showed only one spot after development for each of the compounds examined.

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[10] N. J. Leonard and E. R. Blout *J. Am. Chem. Soc.*, **72**, 484 (1950), and references therein.

[11] H. H. Jaffe and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N.Y. (1962), p. 489.

[12] See Ref. 11, p. 474.

[13] I. J. Borowitz, M. Anschel and S. Firstenberg, *J. Org. Chem.*, **32**, 1723 (1967).