

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY, NEW YORK 27, N. Y.]

The Electronic Structures and Spectra of the Azide Ion and Alkyl Azides

BY W. D. CLOSSON AND HARRY B. GRAY

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The electronic transitions of alkyl azides and hydrazoic acid have been assigned on the basis of molecular orbital theory and the electronic structure and energy levels in azide ion. The 2870 Å. band in alkyl azides has been assigned to a $\pi_y \rightarrow \pi_x^*$ (${}^1\Sigma_g^+ \rightarrow {}^1\Delta_u$) transition, and the 2160 Å. band to an $s-p_x \rightarrow \pi_y^*$ (${}^1\Sigma_g^+ \rightarrow {}^1\Delta_u$) transition. The effects of solvent polarity and electronegative substituents upon the spectra of alkyl azides have been rationalized in terms of this model.

Introduction

The azide ion, N_3^- , is a linear triatomic molecule ion with sixteen valence electrons. The principal bands in the electronic spectra of a number of linear triatomic molecules isoelectronic with N_3^- have been assigned previously in terms of a molecular orbital energy level scheme.¹

In the present paper the electronic spectrum of the N_3^- ion is analyzed in terms of molecular orbital theory. The observed energies of the excited states in N_3^- then are used to assign the electronic spectra of several azido compounds.

Molecular Orbital Theory for Linear Triatomic Molecules.—A linear triatomic molecule with $D_{\infty h}$ symmetry is illustrated in Fig. 1. The orbital transformation scheme for s and p valence orbitals is given in Table I.

σ -orbitals:

$$\Psi[\sigma_g^+] = C_M\Phi(s) + C_L\Phi[1/\sqrt{2}(\sigma_1 + \sigma_2)] \quad (1)$$

$$\Psi[\sigma_u^+] = C_M\Phi(p_x) + C_L\Phi[1/\sqrt{2}(\sigma_1 - \sigma_2)] \quad (2)$$

π -orbitals:

$$\Psi^{(1)}[(\pi_g)] = \Phi[1/\sqrt{2}(p_{x1} - p_{x2})] \quad (3)$$

$$\Psi^{(2)}[(\pi_g)] = \Phi[1/\sqrt{2}(p_{y1} - p_{y2})] \quad (4)$$

$$\Psi^{(1)}[(\pi_u)] = C_M\Phi(p_x) + C_L\Phi[1/\sqrt{2}(p_{x1} + p_{x2})] \quad (5)$$

$$\Psi^{(2)}[(\pi_u)] = C_M\Phi(p_y) + C_L\Phi[1/\sqrt{2}(p_{y1} + p_{y2})] \quad (6)$$

The C 's are subject to the usual conditions of normalization and orthogonality, and are different for σ_g^+ , σ_u^+ and π_u molecular orbitals.

TABLE I

Representation	M orbitals	L orbitals
σ_g^+	s	$(1/\sqrt{2})(\sigma_1 + \sigma_2)$
σ_u^+	p_x	$(1/\sqrt{2})(\sigma_1 - \sigma_2)$
σ_g^-
σ_u^-
π_g	..	$(1/\sqrt{2})(p_{x1} - p_{x2})$ $(1/\sqrt{2})(p_{y1} - p_{y2})$
π_u	p_x, p_y	$(1/\sqrt{2})(p_{x1} + p_{x2})$ $(1/\sqrt{2})(p_{y1} + p_{y2})$

The molecular orbital energy level scheme expected for such molecules is shown in Fig. 2. The single electron σ -bonding molecular orbitals are considered more stable than the single electron π -bonding molecular orbitals.

Azide Ion, N_3^- .—The azide ion is one of a number of important molecules and ions with sixteen valence electrons. The ground state of N_3^- is

$$[(\sigma_g^+)^2]2[2s_1]2[2s_2]2[(\sigma_u^+)^2]2[(\pi_u)^4]2[(\pi_g)^4] = {}^1\Sigma_g^+ \quad (7)$$

For N_3^- the π_u orbital coefficients are approximately²

$$C_M(\pi_u) = C_L(\pi_u) = 1/\sqrt{2} \quad (8)$$

Thus we calculate

$$\epsilon[(\pi_u)^* - (\pi_g)] = -\sqrt{2}\beta(N,N) \quad (9)$$

(1) (a) A. D. Walsh, *J. Chem. Soc.*, 2260 (1953); (b) R. S. Mulliken, *Can. J. Chem.*, **36**, 10 (1958).

(2) However, more exact orbital coefficients for N_3^- are given by E. Clementi, *J. Chem. Phys.*, **34**, 1468 (1961).

Here ϵ is a single electron molecular orbital energy difference and $\beta = \int \Phi_M H \Phi_L d\tau$. Singlet excited states due to a transition $\pi_g \rightarrow \pi_u^*$ are ${}^1\Sigma_u^+$, ${}^1\Sigma_u^-$ and ${}^1\Delta_u$. Of these, only the ${}^1\Sigma_g^+ \rightarrow {}^1\Sigma_u^+$ transition is allowed.

Electronic Spectrum of N_3^- .—The spectrum of N_3^- in water solution exhibits a weak band ($\epsilon = 430$) at 43,500 cm^{-1} .³ This band is partly masked by a strong absorption which does not reach a maximum at 53,000 cm^{-1} . These two bands are characteristic of linear triatomic molecules with sixteen valence electrons (CO_2 , CS_2)¹ and may be assigned as in (10) and (11)

$${}^1\Sigma_g^+ \longrightarrow {}^1\Delta_u \quad 43,500 \text{ cm}^{-1} \quad (10)$$

$${}^1\Sigma_g^+ \longrightarrow {}^1\Sigma_u^+ \quad >53,000 \text{ cm}^{-1} \quad (11)$$

Electronic Spectra of Azido Compounds.—The HN_3 and RN_3 molecules are not linear, the R-N-(NN) angles being about 120° .⁴ A consideration of bond distances⁴ suggests that most of the π -bonding takes place between the middle and the end nitrogen. For such an arrangement of atoms the molecular orbitals are

$$(\text{R-N})_{(1)} - \text{N}_{(M)} - \text{N}_{(2)}$$

σ -orbitals:

$$\Psi[\sigma_a] = C_M\Phi(s) + C_1\Phi(\sigma_1) + C_2\Phi(\sigma_2) \quad (12)$$

$$\Psi[\sigma_b] = C_M\Phi(p_x) + C_1\Phi(\sigma_1) - C_2\Phi(\sigma_2) \quad (13)$$

π -orbitals:

$$\Psi[\pi_x] = C_M\Phi(p_x) + C_2\Phi(p_x) \quad (14)$$

$$\Psi[\pi_y] = C_M\Phi(p_y) + C_2\Phi(p_y) + C_1\Phi(p_y) \quad (15)$$

Localized R-N orbital:

$$\Psi_{\text{RN}}[s-p_x] = \sqrt{1/3}\Phi(s) + \sqrt{2/3}\Phi(p_x) \quad (16)$$

The molecular orbital energy level scheme for RN_3 molecules is shown in Fig. 3. The relative energies of the single electron molecular orbitals are estimated using the level scheme for azide ion as a guide. For the fourteen valence electrons (sixteen minus the two in the σ^b R-N orbital) the ground state is

$$(\sigma_a^b)^2(2s_2)^2(\sigma_b^b)^2(\pi_y^b)^2(\pi_x^b)^2(s - p_x)^2(\pi_y)^2 \quad (17)$$

The most stable singlet excited state involves the one electron excitation $\pi_y \rightarrow \pi_x^*$. For any reasonable value of Δ_3 , the second most stable singlet excited state is due to the $s-p_x \rightarrow \pi_y^*$ transition. These excited states are related to the ${}^1\Delta_u$ state in the N_3^- ion.

In alkyl azides two electronic transitions are observed in the accessible portion of the ultraviolet region. These occur at about 46,000 cm^{-1} (2160 Å.) and 34,800 cm^{-1} (2870 Å.), and are assigned to the $s-p_x \rightarrow \pi_y^*$ and $\pi_y \rightarrow \pi_x^*$ transitions, respectively.

In the limit of isolated RN and NN molecules

$$\Delta_1 = (1/3)[\epsilon(2p) - \epsilon(2s)]$$

$$\Delta_2 = -\beta(N,N) \quad (19)$$

$$\Delta_3 = 0 \quad (20)$$

Assuming that the differences in the interelectronic-repulsion energies of the first excited states and the

(3) A similar absorption band is found in the NaN_3 crystal. See S. K. Deb, *ibid.*, **35**, 2122 (1961).

(4) L. Pauling and L. O. Brockway, *J. Am. Chem. Soc.*, **59**, 13 (1937).

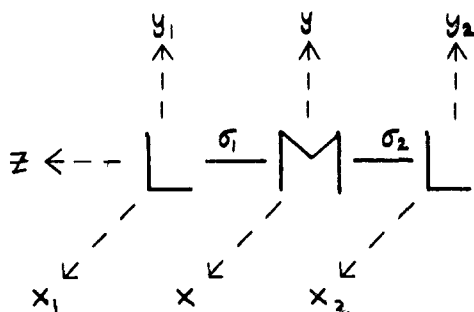


Fig. 1.—Coordinate system for a linear triatomic molecule with $D_{\infty h}$ symmetry.

ground states for N_3^- and RN_3 are equal, the $\pi_y \rightarrow \pi_x^*$ transition in RN_3 molecules is predicted at

$$(1/\sqrt{2})[\Delta E(^1\Sigma_g^+ \rightarrow ^1\Delta_u)] = 30,060 \text{ cm.}^{-1} \quad (21)$$

This is in reasonable agreement with the observed energy (Δ_2 is expected to be greater than $-\beta(N,N)$ due to the interaction of p_x in π_x^*).

The $s-p_x \rightarrow \pi_y^*$ transition is predicted at

$$(1/\sqrt{2})[\Delta E(^1\Sigma_g^+ \rightarrow ^1\Delta_u)] + \Delta_1 \quad (22)$$

For the nitrogen atom, Δ_1 may be estimated at about $14,000 \text{ cm.}^{-1}$, using atomic spectral data compiled by Moore.⁵ Thus the $s-p_x \rightarrow \pi_y^*$ should appear around $44,000 \text{ cm.}^{-1}$; the agreement between theory and experiment is quite satisfactory.

Spectral Measurements.—The ultraviolet absorption spectra (from *ca.* 1950 to 3100 \AA.) of several representative alkyl azides, as well as that of hydrazoic acid, have been measured in a series of solvents of varying polarity. The empirical polarity constant "Z," proposed by Kosower,⁶ was used as a guide in choosing the solvents. The positions of the absorption maxima in the neighborhood of 2870 \AA. ($34,800 \text{ cm.}^{-1}$) of the various azides are presented in Table II, and those of the maxima near 2160 \AA. ($46,300 \text{ cm.}^{-1}$) in Table III.

The short wave length band of hydrazoic acid in water is partially masked but a maximum is apparent at about 2000 \AA. The absorption spectrum of sodium azide in basic aqueous solution was measured over the range 1900 to 3100 \AA. No distinct maxima were observed, the intensity rising to large values in the short wave length region. A shoulder, however, indicative of a maximum near 2300 \AA. ($\epsilon_{\text{max}} = 440$) was observed.

The most noticeable feature seen in the data of Tables II and III is the insensitivity of the position of the maxima of most alkyl azides to gross changes in solvent polarity (as indicated by the polarity constant "Z"). For example, the first transition (at *ca.* 2870 \AA.) of cyclohexyl azide varies over a range of only 21 \AA. (250 cm.^{-1}). Indeed, the transition energy of the first absorption band in isoöctane and tetrafluoropropanol, solvents of vastly different polarity, are identical for *n*-butyl azide, and almost so for *t*-butyl and cyclohexyl azide. The position of the higher energy maximum is also quite insensitive to the polarity of the medium. The range for simple alkyl azides is about 32 \AA. (700 cm.^{-1}) but this is mainly due to the fact that the extremely polar solvent TFP (tetrafluoropropanol) appears to shift this transition to significantly shorter wave lengths. Water and $10 M$ lithium chloride in water also have a similarly large effect on 2-hydroxyethyl azide. Plots of transition energies *vs.* Z for the low energy (2870 \AA.) bands of cy-

(5) C. E. Moore, "Atomic Energy Levels," U. S. Natl. Bur. Standards Circular 467, 1949 and 1952.

(6) (a) E. M. Kosower, *J. Am. Chem. Soc.*, **80**, 3253, 3261, 3267 (1958).

(b) E. M. Kosower and G. Wu, *ibid.*, **83**, 3142 (1961).

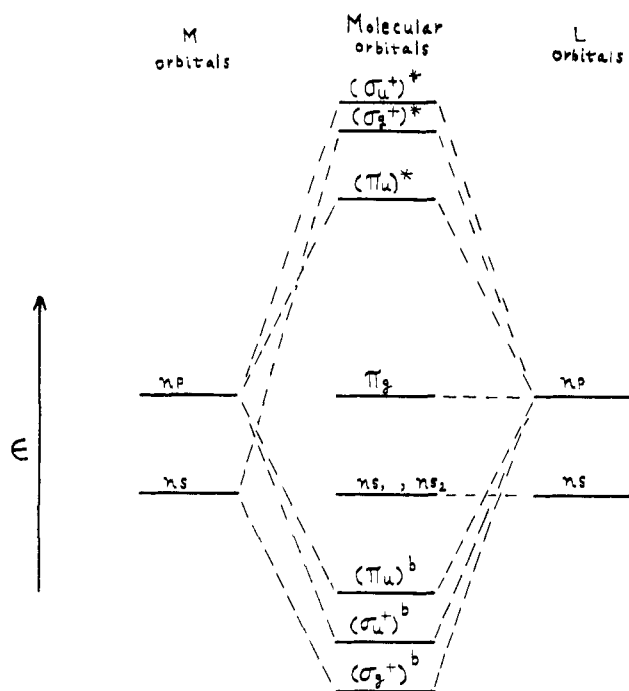


Fig. 2.—Molecular orbital energy level scheme for a linear triatomic molecule containing atoms with s and p valence orbitals.

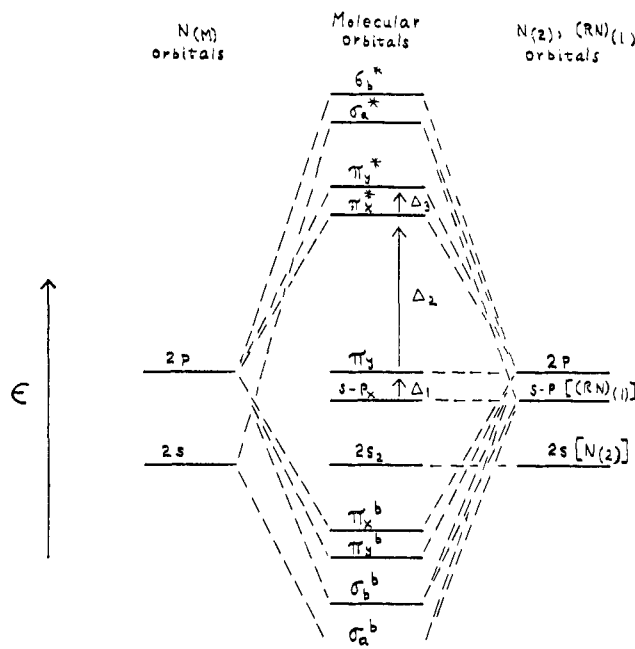


Fig. 3.—Molecular orbital energy level scheme for RN_3 type molecules.

clohexyl and 2-hydroxyethyl azide are presented in Fig. 4, and similar plots for the high energy transitions of some of the alkyl azides are shown in Fig. 5.

The introduction of electronegative groups or atoms into the aliphatic portion of alkyl azides is shown to shift both transitions to higher energies. Hydrazoic acid is apparently the extreme case, its lower intensity maximum being shifted about 230 \AA. , and the higher energy band apparently being moved about 160 \AA. (Hydrazoic acid in dilute hydrochloric acid solution exhibited a maximum at about 2000 \AA. , $\epsilon = 540$.)

Discussion

The low intensity ($\epsilon \approx 25$) of the 2870 \AA. maxima of alkyl azides might tempt one to consider it as a typical

TABLE II
 THE LONG WAVE LENGTH ABSORPTION MAXIMA OF ALKYL AZIDES^a

Compound	Solvent									
	10 M LiCl ^b (106.8) ^c		TFP ^d (96.3) ^c		Water (94.6) ^c		Methanol (83.6) ^c		Ethanol (79.6) ^c	
	λ_{\max}	ϵ_{\max}	λ_{\max}	ϵ_{\max}	λ_{\max}	ϵ_{\max}	λ_{\max}	ϵ_{\max}	λ_{\max}	ϵ_{\max}
<i>n</i> -Butyl azide	2860	22	2875	23	2874	24
Cyclohexyl azide	2862	26	2878	25	2877	25
<i>t</i> -Butyl azide	2869	^e	2886	^e	2884	^e
2-Chloroethyl azide	2822	27	2840	27	2840	27
2-Hydroxyethyl azide	2828	23	2836	22	2832	22	2853	19	2853	20
2-Acetoxyethyl azide	2819	24	2845	23	2843	24
Ethyl azidoacetate	2786	26	2816	23	2815	24
Hydrazoic acid	2603	43

Compound	Solvent					
	Acetonitrile (71.3) ^c		Chloroform (63.2) ^c		Isooctane (60.1) ^c	
	λ_{\max}	ϵ_{\max}	λ_{\max}	ϵ_{\max}	λ_{\max}	ϵ_{\max}
<i>n</i> -Butyl azide	2877	23	2872	29	2863	25
Cyclohexyl azide	2883	26	2881	31	2871	26
<i>t</i> -Butyl azide	2890	^e	2890	^e	2880	^e
2-Chloroethyl azide	2842	27	2837	33	2834	34
2-Hydroxyethyl azide	2859	19	2840	26
2-Acetoxyethyl azide	2850	21	2840	29	2835	25
Ethyl azidoacetate	2820	25	2813	29	2804	25
Hydrazoic acid	2644	^e	2643	^e

^a All values are considered valid to at least $\pm 5-6 \text{ \AA}$. ^b Solution of lithium chloride in water. ^c Z-value. ^d 2,2,3,3-Tetrafluoropropanol. ^e Not calculated.

$n \rightarrow \pi^*$ transition, similar to those of carbonyl compounds such as ketones and aldehydes and possibly to those of xanthate esters, alkyl nitrites, and nitro-

of ketones (and probably of the other systems mentioned above, as well) to the polarity of the medium is well known and documented.^{6,10} In a typical case,⁸

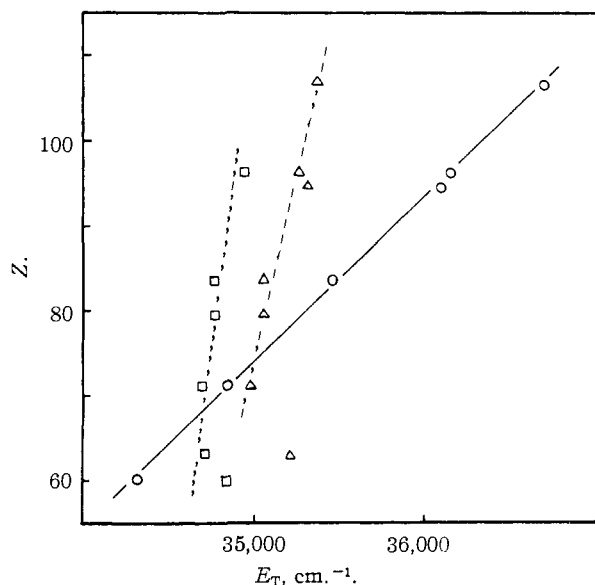


Fig. 4.— E_T (transition energies) versus Z (solvent polarity values): cyclohexanone --- O, cyclohexyl azide --- □, 2-hydroxyethyl azide --- Δ.

alkanes. Indeed, it is frequently labeled as such.⁷ However, while the low intensity transitions of these other systems are optically active in the proper asymmetric environment⁸ (*i.e.*, have Cotton effects associated with them in the corresponding rotatory dispersion curves), the 2870 Å. band of simple alkyl azides has been reported to be inactive,⁹ except in the case of α -azidopropionic acid derivatives as reported by Kuhn,^{7a} which may be a special instance. Also, the sensitivity of the energy of the low intensity transition

(7) (a) W. Kuhn, *Ann. Revs. Phys. Chem.*, **9**, 417 (1958), and references contained therein; (b) S. F. Mason, *Proc. Chem. Soc.*, 137 (1962).

(8) C. Djerassi, "Optical Rotatory Dispersion, Application to Organic Chemistry," Chapter 14 in particular, McGraw-Hill Book Co., New York, N. Y., 1960.

(9) P. A. Levene and A. Rothen, *J. Chem. Phys.*, **5**, 985 (1937).

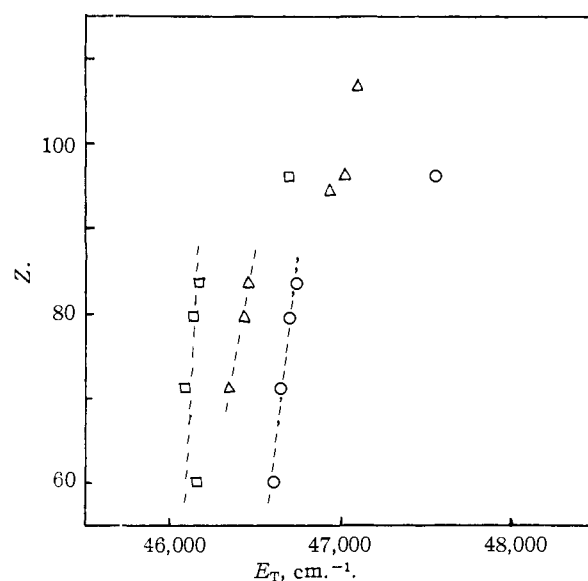


Fig. 5.— E_T (transition energies) versus Z (solvent polarity values): 2-acetoxyethyl azide --- O, cyclohexyl azide --- □, 2-hydroxyethyl azide --- Δ.

such as cyclohexanone, the maximum is shifted 248 Å. (1900 cm^{-1}) upon changing from isoöctane to TFP.^{6b} Moreover, the shift is very regular (linear in Z), moving to higher energies with increasing solvent polarity.^{6b}

A plot of the energy for the $n \rightarrow \pi^*$ transition of cyclohexanone *vs.* Z is included in Fig. 4 to illustrate the difference in solvent sensitivity of the ketone and azide transitions. The lack of such solvent sensitivity in the low energy transition of alkyl azides is another indication of a difference in nature of this band from that of typical $n \rightarrow \pi^*$ transitions.

(10) P. Maroni, *Ann. chim.*, [13] **2**, 757 (1957); R. P. Mariella, *et al.*, *J. Org. Chem.*, **19**, 678 (1954). See also A. E. Gillam and E. S. Stern, "Electronic Absorption Spectroscopy," Edward Arnold (Publishers) Ltd., London, 1954, p. 264.

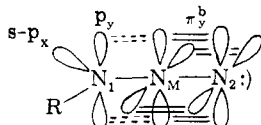
TABLE III
THE SHORT WAVE LENGTH ABSORPTION MAXIMA OF ALKYL
AZIDES^a

Compound	Solvent							
	10 M LiCl ^b (106.8) ^c		TFP ^d (96.3) ^c		Water (94.6) ^c		Methanol (83.6) ^c	
	λ_{\max}	ϵ_{\max}	λ_{\max}	ϵ_{\max}	λ_{\max}	ϵ_{\max}	λ_{\max}	ϵ_{\max}
<i>n</i> -Butyl azide	2134	547	2160	462
Cyclohexyl azide	2142	494	2166	410
<i>t</i> -Butyl azide	2135	^e	2157	^e
2-Chloroethyl azide	2118	611	2142	527
2-Hydroxyethyl azide	2124	535	2127	501	2131	479	2153	423
2-Acetoxyethyl azide	2114	582	2140	515
Ethyl azidoacetate	2116	646	2143	581

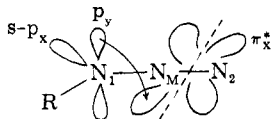
Compound	Ethanol ^e (79.6) ^c		Acetonitrile ^e (71.3) ^c		Isooctane ^e (60.1) ^c	
	λ_{\max}	ϵ_{\max}	λ_{\max}	ϵ_{\max}	λ_{\max}	ϵ_{\max}
<i>n</i> -Butyl azide	2161	446	2166	446	2161	540
Cyclohexyl azide	2168	400	2170	394	2167	440
<i>t</i> -Butyl azide	2159	^e	2160	^e	2158	^e
2-Chloroethyl azide	2144	516	2145	533	2141	609
2-Hydroxyethyl azide	2154	417	2158	398
2-Acetoxyethyl azide	2142	502	2144	500	2146	550
Ethyl azidoacetate	2147	592	2147	600	2153	610

^a All values are considered valid to at least $\pm 3-4$ Å. ^b Solution of lithium chloride in water. ^c Z-Value. ^d 2,2,3,3-Tetrafluoropropanol. ^e Not calculated.

A consideration of the electronic process which we propose is responsible for the long wave length transition of alkyl azides is in order. We assume the electronic structure of the azido group is as shown. While the two outer nitrogens (N_M-N_2) of the azido group



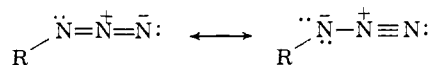
may be approximated by a nitrogen molecule, there is undoubtedly some interaction of the p_y orbital of N_1 with the π system of N_M-N_2 . Among other things, this will tend to raise the energy of the π_y^* orbital toward the value $-\sqrt{2}\beta_{(N-N)}$. The lowest energy orbital available for excitation then becomes the π_x^* orbital of the N_M-N_2 system. A $\pi_y \rightarrow \pi_x^*$ transition (the non-bonding π_y orbital is mainly localized as the p_y orbital of N_1), shown below, is probably the source of the 2870 Å. maximum of alkyl azides. Such a transition is "perpendicular" and is not allowed,



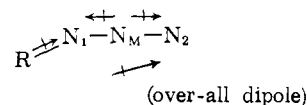
thus accounting for the low intensity ($\epsilon = 20-40$) of the 2870 Å. maximum.

In a discussion of the effect of solvent polarity upon the energy of a given absorption maximum one must consider both the nature of the cybotactic reaction^{6a} about the chromophore and the difference of the dipoles in the ground and excited states, keeping the role of the Franck-Condon principle in mind. Considering the inertness of simple alkyl azides toward bases and weak acids, specific interaction of the azido group with solvent (such as hydrogen bond formation) is probably not very important. In particular, the p_y orbital on N_1 is at least partially bonded to the π_y system, and probably not available for strong interaction with solvent. The azido group is known to be electron withdrawing with respect to carbon.¹¹ Recent measurements indicate that its Hammett substituent constant, σ_m , is very similar to that of the fluoro group.¹² In resonance terms the two structures shown

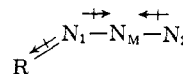
below are believed to be important contributors to the ground state.¹³ The dipoles in the ground state would



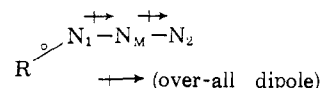
probably have roughly the directions and magnitudes as shown



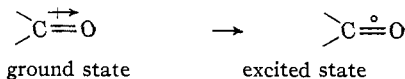
During the transition, charge would be transferred from N_1 to the vicinity of N_M and N_2 . The dipole changes during the 2870 Å. transition would be roughly as shown



leaving the excited state with the dipole system indicated



It can be seen from these crude approximations that the dipole moment will change very little, either in direction or magnitude, on shifting from the ground state to the excited state of the 2870 Å. transition. Thus, the degree of interaction between the functional group and the cybotactic region should be about the same in the ground and excited states no matter what the nature of the solvent. In comparison, for ketones and aldehydes the ground state dipole almost vanishes in the excited state¹⁴



The effect of solvent upon the low intensity maxima of ketones may be directly related to this large dipole change.¹⁴ The lack of appreciable dipole change in the $\pi_y \rightarrow \pi_x^*$ transition of alkyl azides may be a general phenomenon for similar multiply bonded linear triatomic functional groups, and further investigation is in progress.

The high energy transition of alkyl azides (near 2160 Å.) also appears to be quite insensitive to solvent polarity, except in the cases of extremely polar, strongly hydrogen bonding solvents (see Fig. 5). The effect of these latter solvents (TFP, water, 10 M aqueous lithium chloride) may be due to specific interaction with the $s-p_x$ orbital. Although this transition is an order of magnitude more intense than the $\pi_y \rightarrow \pi_x^*$ band it is still quite weak ($\epsilon \approx 500$). This is quite reasonable, since as mentioned above, the 2160 Å. band is probably $s-p_x \rightarrow \pi_y^*$ (${}^1\Sigma_g^+ \rightarrow {}^1\Delta_u$). Thus, like the $\pi_y \rightarrow \pi_x^*$, it is "perpendicular" and not allowed. The dipole changes during this transition should be quite similar to those outlined above for the $\pi_y \rightarrow \pi_x^*$ transition. As seen in Fig. 4 and Fig. 5, the $s-p_x \rightarrow \pi_y^*$ transition is about equally insensitive to solvent polarity over the range $Z = 60.1$ to 83.6 (isooctane to methanol). It would be interesting to extend rotatory dispersion measurements on suitable optically active azides through the region of the $s-p_x \rightarrow \pi_y^*$ transition and compare the results with those in the 2870 Å. region.

(12) P. A. S. Smith, J. H. Hall and R. O. Kan, *J. Am. Chem. Soc.*, **84**, 485 (1962).

(13) L. Pauling, "Nature of the Chemical Bond," 3rd ed., Cornell University Press, Ithaca, N. Y., 1960, p. 272.

(14) See pp. 3264 and 3265 of ref. 6a.

(11) J. H. Boyer and F. C. Cantor, *Chem. Revs.*, **54**, 1 (1954).

The effect of placing electronegative substituents in the aliphatic portion of alkyl azides appears quite reasonable. By simple inductive means, they would tend to lower the energy of the electrons on N₁, and thus increase the energies of both transitions. These are exactly the effects seen in the data of Tables II and III. According to this, the effect should fall off rapidly with the distance of separation of the electronegative group and N₁.

Acknowledgments.—Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. The authors thank Professor E. M. Kosower for the loan of some spectral equipment and for interesting and encouraging discussion.

Experimental

Solvents.—All solvents were of spectra-grade quality, or better. The 2,2,3,3-tetrafluoropropanol was received as gift from Dr. E. O. Langerak of the Organic Chemical Department, E. I. du Pont de Nemours and Company, and was purified according to the procedure of Kosower and Huang.^{5b}

Measurements.—The low energy transitions of the alkyl azides were measured with a Cary recording spectrophotometer, Model 14, using matched 1.0-cm. cells. In general, the maxima were measured by running over the maximal absorption at the slowest speed at least three times and averaging the maxima thus obtained. The maxima could be duplicated to at least ± 5 Å., and usually to ± 3 Å. The extinction coefficients probably are accurate to within $\pm 5\%$.

The high intensity maxima were measured in the same way, using a Cary Model 14 recording spectrophotometer and 0.01-cm. cells. The maxima could be duplicated to at least ± 4 Å., and usually to ± 2 Å.

A test of the obedience of the absorption maxima of *n*-butyl azide in isoöctane to Beer's law also was carried out. The results are shown in Table IV.

Materials.—*n*-Butyl azide was prepared by the method of Lieber, Chao and Rao¹⁵; b.p. 63–65° (200 mm.), *n*_D²⁰ 1.4196 (lit.¹⁵ b.p. 71° (225 mm.), *n*_D²⁰ 1.4192).

Cyclohexyl azide was prepared as above; b.p. 66–68° (20 mm.), *n*_D²⁰ 1.4681 (lit.¹⁵ b.p. 72° (30 mm.), *n*_D²⁰ 1.4693).

(15) E. Lieber, T. S. Chao and C. N. R. Rao, *J. Org. Chem.*, **22**, 238 (1957).

TABLE IV

BEER'S LAW DATA FOR <i>n</i> -BUTYL AZIDE IN ISOÖCTANE		
Concn., <i>M</i>	ϵ_{\max} , 2161 Å.	ϵ_{\max} , 2863 Å.
0.3150	468	..
.1575	465	..
.0788	474	24.7
.0394	[503]	24.7
.0197	466	24.5

t-Butyl azide also was prepared by the method of Lieber, *et al.*,¹⁵ but could not be separated completely from contaminating *t*-butyl alcohol. The material finally used for spectral measurements had b.p. 70–74°, *n*_D²⁰ 1.3955 (lit.¹⁵ b.p. 68–71°, *n*_D²⁰ 1.3865). The extinction coefficient of this material (for example in methanol at 2157 Å., ϵ_{\max} was 258) indicated that it was at least 60% *t*-butyl azide. The small amount of *t*-butyl alcohol present would be unlikely to affect the position of the maximum greatly.

2-Chloroethyl azide was prepared by the method of Wiley and Moffat,¹⁷ and had b.p. 39° (20 mm.), *n*_D²⁰ 1.4660 (lit.¹⁷ b.p. 45° (25 mm.), *n*_D²⁰ 1.4658).

2-Hydroxyethyl azide was prepared by the method of Forster and Fierz,¹⁸ and had b.p. 69–72° (20 mm.), *n*_D²⁰ 1.4587 (lit.¹⁹ b.p. 52–54° (5 mm.), *n*_D²⁰ 1.4588).

Ethyl azidoacetate was obtained by Lieber's method¹⁵ and had b.p. 72–73° (20 mm.), *n*_D²⁰ 1.4358 (lit.²⁰ b.p. 74–75° (23 mm.), *n*_D²⁰ 1.4341).

2-Acetoxyethyl azide was prepared by acetylating 2-hydroxyethyl azide with acetyl chloride in the presence of pyridine according to the method of Sarel and Newman.²¹ It had b.p. 71–73° (20 mm.), *n*_D²⁰ 1.4366.

Anal. Calcd. for C₄H₇N₃O: C, 37.21; H, 5.46; Found: C, 37.08; H, 5.62.

Hydrazoic acid in aqueous solution was obtained by acidifying with dilute hydrochloric acid a solution of sodium azide. Spectral measurements then were made directly on this solution. Solutions of hydrazoic acid in isoöctane and chloroform were obtained by shaking an aqueous solution of the acid with the appropriate solvent and drying the organic layer with sodium sulfate. Since the concentration of hydrazoic acid in these solvents was not known, no attempt was made to calculate the extinction coefficient in isoöctane or chloroform.

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(20) W. F. Huber, *ibid.*, **77**, 112 (1955).

(21) S. Sarel and M. S. Newman, *ibid.*, **78**, 5416 (1956).

[CONTRIBUTION FROM THE COLLEGE OF PHARMACY, UNIVERSITY OF ILLINOIS, CHICAGO 12, ILLINOIS, AND THE ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS]

Deuterium Isotope Effects in Transamination: L-Alanine and Pyridoxal^{1,2}

BY M. I. BLAKE, F. P. SIEGEL, J. J. KATZ AND M. KILPATRICK

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The reaction between pyridoxal and L-alanine at 100° depends on pH, the nature and concentration of added buffer constituents and metal ions. For the solvent H₂O, L-protio-alanine reacts with pyridoxal 2.4 times faster than the L-deuterio-alanine. For the solvent D₂O in similar buffer systems, L-protio-alanine reacts 2.9 times faster than L-deuterio-alanine.

In living systems a transfer of amino groups occurs between certain amino and keto acids. This important reversible process known as transamination has been reviewed recently by Snell,³ who discusses the mechanism of the enzymatic and non-enzymatic reactions. Although a number of rate studies have been carried out, velocity constants have not been reported until recently for the non-enzymatic reactions.^{4,5}

(1) Based on work performed under the auspices of the U. S. Atomic Energy Commission.

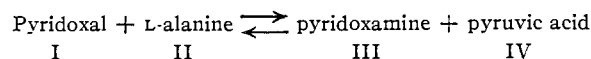
(2) Presented at the 141st Natl. Meeting of the American Chemical Society, Washington, D. C., March, 1962.

(3) E. E. Snell and W. T. Jenkins, *J. Cellular Comp. Physiol.*, **54**, Supplement p. 161 (1959).

(4) B. E. C. Banks, A. A. Diamantis and C. A. Vernon, *J. Chem. Soc.*, 4235 (1961).

(5) G. M. Fleck, Dissertation, University of Wisconsin, 1961.

As L-deuterio-alanine was available from *Scenedesmus obliquus* grown in deuterium oxide,⁶ it was of interest to design a set of relatively simple kinetic experiments to determine the kinetic isotope effect in the solvents H₂O and D₂O. The reaction chosen for study was



This reaction is not simple and both rapid and slow spectral changes occur on mixing the reactants. These changes are a function of temperature and pH and indicate a number of intermediates as well as species from the reactants. In addition, it is known that pyruvic acid hydrates and that pyridoxal may exist in solution

(6) M. I. Blake, H. L. Crespi, V. Mohan and J. J. Katz, *J. Pharm. Sci.*, **50**, 425 (1961).