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THE CIRCULAR DICHROISM OF AN AZOALKANE

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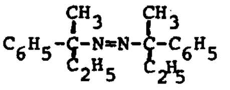
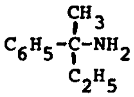
No spectroscopic data have been reported for optically active azoalkanes, and only a brief summary of optical rotatory dispersion data for phenylazosugars by Guthrie and his coworkers(1) has been published. With the hope that the circular dichroism curve for an optically active azoalkane might provide fundamental information on the $n \rightarrow \pi^*$ transitions of the azo group, about which there is still doubt and controversy(2,3,4,5), we have prepared the compound **1**, 3,6-diphenyl-3,6-dimethyl-4,5-diazaoctene-4, in optically active form.



$C_6H_5\text{-}\underset{C_2H_5}{\overset{CH_3}{C}}\text{-}N{=}N\text{-}\underset{C_2H_5}{\overset{CH_3}{C}}\text{-}C_6H_5$

1



$C_6H_5\text{-}\underset{C_2H_5}{\overset{CH_3}{C}}\text{-}NH_2$

2

The amine **2** was prepared from the corresponding alcohol via the Ritter reaction (acetonitrile and sulfuric acid) and hydrolysis with potassium hydroxide in ethylene glycol. The amine was resolved through the L-malate salt. Recovered amine had $\alpha]_D -16.8^\circ$, similar to the value of $\alpha]_{5460}$ -18.2° for amine synthesized from the corresponding optically active acid.(6) The amine was converted into the azoalkane 1 by oxidation with iodine pentafluoride in dichloromethane.(7) Chromatographic purification of 1 on neutral Woelm alumina at 7° provided a yellow oil in 25% yield. (Anal. Calcd. for $C_{20}H_{26}N_2$ C 81.59 H 8.91 N 9.29 Fd. C 81.95 H 8.91 N 9.47) The azoalkane 1 was stored in the freezer to preclude decomposition ($k_{49.5}$ 2.6 x 10^{-5}sec.$^{-1}$; Nelson and Bartlett(8) report $k_{49.5}$ 4.33 x 10^{-5}sec.$^{-1}$, $\Delta H^{\ddagger}$ 29.0 kcal./mole for the closely related azocumene) The n.m.r. spectrum for the (+)-isomer (derived from (-)-amine) in carbon tetrachloride with an internal tetramethylsilane reference was in excellent accord with that expected. (phenyl multiplet, 2.75τ, methylene quartet 7.98τ, methyl singlet 8.56τ, methyl triplet 9.25τ)

Ultraviolet (UV) absorption spectra were measured with a Cary model 14 spectrophotometer, circular dichroism (CD) with a Jouan Dichrograph and optical rotatory dispersion (ORD) with a Cary model 60 spectropolarimeter. The results are shown in Fig. 1 and the relevant dataare given in Table 1.

TABLE 1

(+)-Azoalkane 1 in Isooctane: CD, ORD and UV data[a]

UV	λ_{max} 3750 (ϵ_{max} 37)		
CD	λ_{max} 3832 ($\Delta\epsilon_{max}$ 0.90)	g_{max} 0.025^{b,c}	$[\theta]_{3830}$ 2970
ORD	$[\phi]_{500}$ +237°	$[\phi]_{450}$ +592°	$[\phi]_{412}$ +1420°
	$[\phi]_{400}$ +1160°	$[\phi]_{390}$ +406°	$[\phi]_{380}$ -666°
	$[\phi]_{360}$ -2190°	$[\phi]_{355}$ -2250°	$[\phi]_{310}$ -1280°

[a] c = 0.0143 M. Maximum slit width in CD measurements was 0.88 mm.

[b] ratio of $\Delta\epsilon_{max}$ to ε

[c] at 3830 A

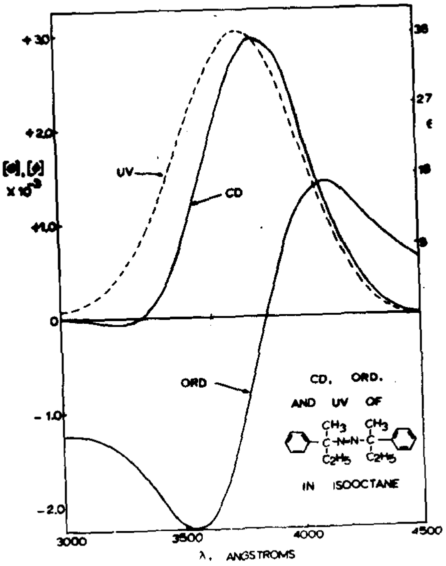


FIG. 1

The UV, CD and ORD curves for
azo bis-2-phenyl-2-butane (compound **1**) in isooctane solution.

Careful examination of the CD curve revealed that the short wavelength side included a contribution from a transition with a small rotational strength and a sign opposite to that of the main CD band. This finding was confirmed with the CD curve of the enantiomer, (-)-**1**, which gave the same result with reversed sign. (This enantiomer was only about 60% optically pure) The weak band varied in the expected way with concentration. Assuming that the CD curve for one transition is Gaussian when plotted against wavelength, a CD curve for a second transition may be derived as shown in Fig. 2.

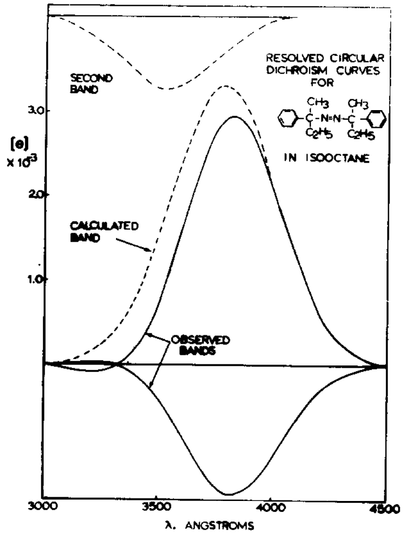


FIG. 2

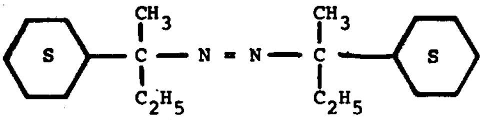
CD Curves for the Two Transitions of the Azoalkane **1**, Based on a Gaussian Shape for the Longwavelength Component.

Kortüm and Rau(3) have proposed that ultraviolet absorption in the same region as that in which our second CD band occurs be assigned to a second transition on the basis of its failure to fit under a Gaussian curve for the main ultraviolet band. They postulated that this second transition was a singlet-triplet transition but its intensity (ε3) seems far too high for such an assignment.

Our results suggest that there may be a second transition, but another interpretation is also possible. With the selection rules (g ↔ u, electric dipole transition, g ↔ g and u ↔ u, magnetic dipole transition)(9), the two transitions might be $(n_a - n_b) \rightarrow \pi^*(g \rightarrow g$, CD strong, UV weak) and $(n_a + n_b) \rightarrow \pi^*(u \rightarrow g$, CD weak, UV strong), with the first at longer wavelengths than the second. This assignment implies that there is a weak UV absorption band on the long wavelength side of the observed band. Most calculations suggest that the $n_a - n_b$ level would actually be lower than the $n_a + n_b$ level.(2,10)

Hochstrasser and Lower(10) report only one $n \rightarrow \pi^*$ transition for azobenzene in a stilbene crystal based on polarization measurements and the similarity of the spectrum of o-hydroxyazobenzene to that of azobenzene. More recent work on other molecules, however, implies that this result might not be universal.(11)

Another interpretation of our results could involve the coupling of two vibrations with different polarizations for one electronic transition. Our present results do not permit us to distinguish between these two possibilities. We propose to probe this matter further by an examination of the optically active saturated azoalkane, **3**. We should also note that it is necessary to use azoalkanes carrying no hydrogen on the α-position because of the possibility of isomerization to the hydrazone.



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