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P. A. Levene and Alexandre Rothen

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Rotatory Dispersion of Configurationally Related Alkyl Azides

P. A. LEVENE AND ALEXANDRE ROTHEN

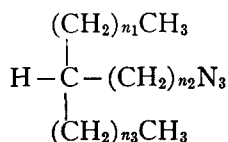
The Rockefeller Institute for Medical Research, New York, N. Y.

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From the viewpoint of chemical behavior, the $-N_3$ group may be regarded as a pseudohalogen. Like iodides, azides possess an absorption band in the near ultraviolet region. For both practical and theoretical reasons it was important to obtain information on the rotatory properties of the azides as compared with those of the corresponding halides. The correlation of the configurations of primary and secondary azides is discussed in this communication. From the analysis of the rotatory dispersion of the primary azides and halides it became evident that the partial

rotations of the azido group and of the halogen atom may be of opposite sign in configurationally related substances. An unexpected observation was made with regard to the members of a homologous series of secondary azides, namely, the rotation in the visible region as well as the partial rotation of the azido group, changes sign on passing from the second member of the series to the third. A tentative explanation of the phenomenon is given. It was found that in all alkyl azides the absorption band at $\lambda 2880$ is not anisotropic or at best, insignificantly so.

THE rotatory dispersions of azides of the general type



are presented in this communication.

The azido group possesses chemical properties analogous to those of the halogen atoms. Similarly to iodides, azides possess an absorption band in the near ultraviolet region. The azides can be converted into the corresponding amines without change of configuration.¹ The configurations of the primary and secondary amines were correlated with a sufficient degree of certainty. Thus it may be accepted that the configuration of primary and secondary azides are likewise correlated. With this knowledge it is now possible to investigate the effect of the value of n_2 on the partial rotation of the N_3 group and furthermore to test the applicability of this information to the correlation of the configurations of primary and secondary halides.

At the outset it may be stated that in homologous series of primary and of secondary azides, a phenomenon was encountered which does not occur in the corresponding halides. In azides having $n_2=0$ the rotation of the higher members of the series homologous with respect to n_1 are of opposite sign from those of the lower members. In the azides having $n_2=1$ the same phenomenon

is observed in the series homologous with respect to n_3 . In the halides, however, the rotations remain of the same sign all through the series. To find an explanation of this phenomenon, a knowledge of the rotatory dispersion of the azides was required.

All data concerning the dispersions can be seen in Tables I to III. The values found in the

TABLE I. Rotatory dispersion of configurationally related secondary azides in heptane.

<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>DEXTRO 2-AZIDOBUTANE $d_r^{25} = 0.8619$ (in vacuum) $n_D^{25} = 1.4122$ Conc. 1.673 M Visible region: $l = 40$ cm U.V. region: $l = 10$ cm 0.1 cm for $\lambda 2450$ $[M]^{25}_{\text{calc}} = \frac{12.712}{\lambda^2 - 0.0296}$</p> </div> <div style="width: 45%;"> <p>DEXTRO 2-AZIDOOCTANE $d_r^{25} = 0.8555$ (in vacuum) $n_D^{25} = 1.4332$ Conc. 0.645 M Visible region: $l = 40$ cm U.V. region: $l = 5$ cm 0.5 cm from $\lambda 3370$ to $\lambda 2450$ $[M]^{25}_{\text{calc}} = \frac{15.970}{\lambda^2 - 0.0309}$</p> </div> </div>				
λ	α^{25}	$[M]^{25}$	α^{25}	$[M]^{25}$
5892.6	—	—	10.718	50.49
5875.6	11.938	40.22	—	—
5780.1	12.379	41.71	11.171	52.68
5460.7	14.048	47.33	12.681	59.74
4358.3	23.53	79.27	21.31	100.39
4046.6	28.04	94.47	25.47	120.00
3830	7.90	106.5	—	—
3760	8.40	113.2	—	—
3750	—	—	3.82	144
3720	8.50	114.5	—	—
3585	—	—	4.32	163
3370	—	—	0.52	196
3220	—	—	0.62	234
3020	—	—	0.35	264
			(conc. 0.322 M)	
2800	—	—	0.38	360
			(conc. 0.258 M)	
2450	0.35	470	0.60	570
			(conc. 0.258 M)	

¹ P. A. Levene and A. Rothen, J. Biol. Chem. **115**, 415 (1936).

TABLE II. Rotatory dispersion of configurationally related secondary azides.

DEXTRO 3-AZIDOHEPTANE $d_4^{25} = 0.8583$ (in vacuum) $n_D^{25} = 1.4298$			DEXTRO 3-AZIDONONANE $d_4^{25} = 0.8575$ (in vacuum) $n_D^{25} = 1.4373$		LEVO 4-AZIDOOCTANE $d_4^{25} = 0.8591$ (in vacuum) $n_D^{25} = 1.4337$			
Conc. 0.854 M (in heptane) $l = 100$ cm			Conc. 0.7824 M (in heptane) $l = 40$ cm		in heptane Conc. 0.8885 M $l = 100$ cm		homogeneous state $l = 40$ cm	
$[M]^{25}_{\text{calc}} = \frac{1.2413}{\lambda^2 - 0.024}$			$[M]^{25} = \frac{1.3482}{\lambda^2 - 0.025}$		$[M]^{25} = -\frac{0.4167}{\lambda^2 - 0.023}$		$[M]^{25} = -\frac{0.3594}{\lambda^2 - 0.0288}$	
λ	α^{25}	$[M]^{25}$	α^{25}	$[M]^{25}$	α^{25}	$[M]^{25}$	α^{25}	$[M]^{25}$
5875.6	1.357	3.861	1.260	4.207	-1.150	-1.294	-2.508	-1.132
5780.1	1.412	4.018	1.307	4.364	-1.191	-1.340	-2.608	-1.177
5460.7	1.591	4.527	1.478	4.935	-1.351	-1.520	-2.952	-1.332
4358.3	2.64	7.51	2.45	8.18	-2.22	-2.498	-4.94	-2.23
4046.6	3.14	8.93	2.95	9.85	-2.68	-3.016	-5.86	-2.64 ₆

columns headed $[M]^{25}_{\text{max}}$ have been obtained from the experimental α values multiplied by the ratio

$$\frac{[M]^{25}_{\text{max}} \text{ of corresponding halide}}{[M]^{25} \text{ of sample used of corresponding halide}}$$

These values are minimum values of the maximum molecular rotations. In the case of the secondary azides, where a high degree of racemization is possible, these values should not be considered as representing even the order of magnitude of the maxima rotations.

ABSORPTION SPECTRA

All azides show a characteristic weak absorption band at $\lambda 2880$. The intensity as well as the position of this band is independent of the nature of the alkyl groups (see Fig. 1). In that respect they differ from the iodides where a slight displacement of the first absorption band was observed between primary and secondary iodides. In fact, intensity and position of the first band in the azides are uninfluenced by the presence in the molecule of phenyl or carboxyl groups. On the contrary, it has been shown that the first absorption band of the iodine atom is different with

TABLE III. Rotatory dispersion of configurationally primary alkyl azides in heptane.

DEXTRO 1-AZIDO-2-METHYLBUTANE $d_4^{25} = 0.8770$ (in vacuum) $n_D^{25} = 1.4235$ Conc. 0.895 M Visible region: $l = 40$ cm U.V. region: $l = 5$ cm, 0.5 for $\lambda 2500$ $[M]^{25}_{\text{max}} = \frac{3.211}{\lambda^2 - 0.0362}$			LEVO 1-AZIDO-2-METHYLNONANE $d_4^{25} = 0.8658$ (in vacuum), $n_D^{25} = 1.4430$ Conc. 0.410 M $l = 100$ cm $[M]^{25}_{\text{max}} = -\frac{0.717}{\lambda^2 - 0.0043}$		DEXTRO 1-AZIDO-3-METHYLPENTANE $n_D^{25} = 1.4300$ Conc. 0.898 M Visible region: $l = 40$ cm U.V. region: $l = 10$ cm $[M]^{25}_{\text{max}} = \frac{8.300}{\lambda^2 - 0.0352}$		DEXTRO 1-AZIDO-4-METHYLHEXANE $d_4^{25} = 0.8636$ (in vacuum), $n_D^{25} = 1.4324$ Conc. 1.062 M $l = 40$ cm $[M]^{25}_{\text{max}} = \frac{5.340}{\lambda^2 - 0.0312}$	
λ	α^{25}	$[M]^{25}_{\text{max}}$	α^{25}	$[M]^{25}_{\text{max}}$	α^{25}	$[M]^{25}_{\text{max}}$	α^{25}	$[M]^{25}_{\text{max}}$
5875.6	1.863	10.40	—	—	3.460	26.78	2.227	17.05
5780.1	1.932	10.79	-0.324	-2.17	3.587	27.76	2.302	17.63
5460.7	2.195	12.26	-0.363	-2.43 ₅	4.083	31.60	2.613	20.01
4358.3	3.74 ₇	20.93	-0.57 ₆	-3.86	6.935	53.68	4.39 ₆	33.65
4046.6	4.51	25.19	-0.67	-4.49	8.34	64.56	5.28	40.4
3790	—	—	—	—	2.50	77.4	—	—
3710	—	—	—	—	—	—	1.60 (10 cm)	49.0
3675	—	—	—	—	2.75	85.2	—	—
3580	0.77	34	—	—	—	—	—	—
2500	0.12	130	—	—	—	—	—	—
conc. 0.358 M								

respect to intensity as well as position in α -iodoacids as compared with alkyl iodides.²

In all the alkyl azides which we have tested—and most probably in all alkyl azides—the rotatory contribution of the band λ_{2880} is entirely negligible.

Precise dispersion measurements could not be carried out very far into the U.V. region on account of the proximity of the first absorption band. The dispersion of all compounds could be expressed satisfactorily for the wave-length interval covered, by a one term Drude formula.

AZIDES HAVING $n_2=0$

In the case of two of the secondary azides, the rotations were sufficiently large to permit measurements on the lower wave-length side of the first band, and it was found that, for that region, departures from the one term formula were small which brings additional evidence to the effect that the contribution of this band is negligible.

The value of the dispersion constant of the secondary azides of the methyl series ($n_2=0$) is very low ($\lambda_0 \approx 1700\text{\AA}$), if one considers that from λ_{2200} down, there is a strong absorption region ($\epsilon=380$ at λ_{2200}).

Now that a sufficiently large number of simple organic molecules with one asymmetric carbon atom have been investigated, it becomes more and more evident that when the molecule possesses only one functional group, the first weak absorption bands of the latter are generally weakly or not at all anisotropic (aliphatic aldehydes being an exception). This is contrary to the statement of Kuhn who maintains that the first weak ultraviolet absorption bands practically rule the course of the rotatory power. His statement was based on the fact that most of the substances which he examined had two functional groups attached to the asymmetric carbon atom (halogeno acids or azido acids, for example). It is the presence of the second functional group which renders these weak bands anisotropic.

It was previously found that in a series of substances with one functional group and homologous with respect to one of the alkyl groups (R_3 for instance), the sign of the rotatory contribution of the functional group remains the same in the whole

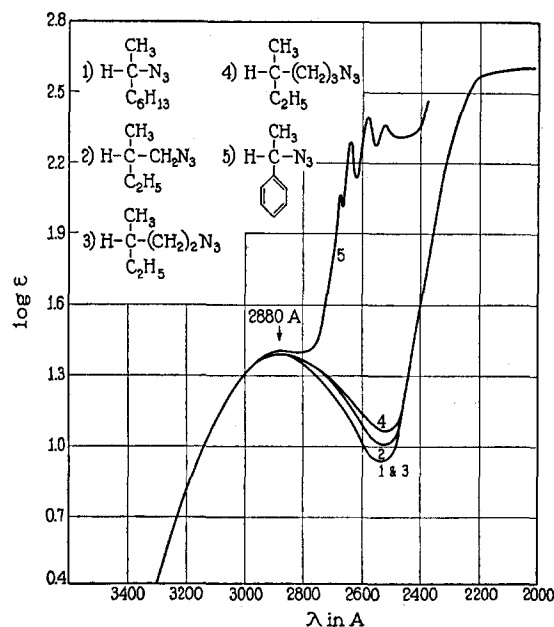


FIG. 1. Absorption curves of alkyl and phenyl azides.

series. It is apparent from Table II that the sign of rotation of 4-azidooctane is opposite to that of the 2-azido- or 3-azido-substituted hydrocarbons (homologous series with respect to R_1), but the constant of dispersion is practically the same for all the derivatives.

These facts seem to be contradictory to the rule just enunciated. But when one considers the low value of the dispersion constant and the narrow wave-length interval where rotatory measurements could be carried out, one must conclude for the present that it is quite possible that there are in the azides two active absorption regions corresponding to two different electronic states furnishing partial rotations of opposite sign. These active absorption regions may be so closely located as to produce only a very small difference in the course of the rotatory dispersion.

AZIDES HAVING $n_2=1$

In the primary azides with $n_2=1$ (see Table III), one observes that the members with $n_3=1$ and $n_3=6$ have rotations opposite in sign. This change of sign is connected with a corresponding change in the rotatory dispersion curve. The dispersion curves of the lower members of the series homologous with respect to n_3 are normal and those of the higher members are anomalous.

² P. A. Levene and A. Rothen, J. Biol. Chem. **107**, 533 (1934).

TABLE IV. Rotatory dispersion of a phenylazide and an azido acid.

1-AZIDO-1-PHENYLMETHANE IN HEPTANE			DEXTRO 2-AZIDOPROPIONIC ACID-1 IN HEPTANE		LEVO SODIUM* SALT of 2-AZIDOPROPIONIC ACID-1 IN WATER
$d_n^{25} = 1.0321$ (in vacuum), $n_D^{25} = 1.5233$ Conc. 0.700 M Visible region: $l = 100$ cm U.V. region: $l = 10$ cm $[M]^{25} = \frac{0.4584}{\lambda^2 - 0.052}$			Conc. 0.400 M Visible region: $l = 40$ cm U.V. region: $l = 5$ cm, 0.5 cm for $\lambda 3100$ $[M]^{25} = -\frac{2.525}{\lambda^2 - 0.0801} + \frac{4.710}{\lambda^2 - 0.020}$		$\alpha = -\frac{1.202}{\lambda^2 - 0.100}$
λ	α^{25}	$[M]^{25}$	α^{25}	$[M]^{25}$	
5892.6					-4.867
5875.6	21.130	35.627			
5780.1	21.969	37.042	+0.808	+5.05	-5.141
5460.7	25.194	42.480	+0.858	+5.32 ₆	-6.144
4358.3	44.96	75.81	+0.755	+4.72	-13.4
4046.6	55.40	93.41	+0.41	+2.56	
3858	6.37	107.4	—	—	
3765	6.85	115.5	—	—	
3710	—	—	—	—	
3685	7.35	123.9	—	—	
3610	7.85	132.3	—	—	
3520			-0.30	-15.0	
3430			-0.40	-20.0	
3320	1.05 (1 cm)	177			
3160			-0.15	-75.0	
3050	0.15 (0.1 cm)	250			
2800	0.25	420			

* The levo sodium salt on which the dispersion measurements were made was obtained from a sample of dextro azidopropionic acid of different rotation from that used for dispersion measurements.

Thus, the direction of the corresponding partial rotations remains the same in all members, but the numerical value of the first contribution is larger in the lower homolog and smaller in the compound with $n_3 = 6$.

The dispersion constants of the *primary azides* with $n_2 = 2$ or 3 are approximately the same and correspond to $\lambda_0 \approx 1800\text{\AA}$.

Rotatory dispersion data concerning methylphenylazido methane and α -azidopropionic acid and its sodium salt are given in Table IV. Inspection of the equation representing the dispersion curve shows that the presence of a phenyl group on the asymmetric carbon atom does not render anisotropic the band $\lambda 2880$ of the azido group. On the other hand, this band is strongly coupled in the azidopropionic acid. The course of the dispersion of the free acid is anomalous and analogous to that of the methyl-ester investigated by Kuhn *et al.*³ The sodium salt, on the other hand, is opposite in sign to the free acid or its ester. The dispersion runs a normal

course, the partial contribution of the band $\lambda 2880$ being predominant. The higher value ($\lambda_0^2 = 0.100$) of the dispersion constant of a one term Drude formula representing the dispersion is due to the fact that the second term is opposite in sign to the first and not much smaller in absolute value.

EXPERIMENTAL

The instruments described in a previous article were used to determine the rotatory dispersion⁴ and the same precision is claimed. Care was taken to insure purity of the samples. For each of them, indices of refraction were taken at the beginning and at the end of the last distillation to be certain of the homogeneity of the product.

Since such azides have not been prepared before, it may be interesting to mention here the value obtained for the refraction of the N_3 group. The mean value computed from the Lorentz formula is as follows: $R_D^{25} = 9.0$.

³ W. Kuhn and E. Braun, *Zeits. f. physik. Chemie* **B8**, 281 (1931).

⁴ P. A. Levene, A. Rothen and R. E. Marker, *J. Chem. Phys.* **1**, 662 (1933).