Diazenes. IV. Circular Dichroism of Dialkyldiazenes (Azoalkanes)[1,2]

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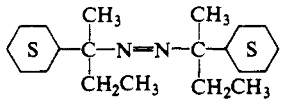
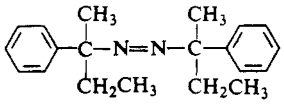
Abstract: The long-wavelength absorption band of a 1,2-dialkyldiazene (RN=NR, "azoalkane," R = 2-cyclohexyl-2-butyl) with λ_{max} 3805 Å (ε 22) in isooctane is accompanied by a single Gaussian-shape circular dichroism band (λ_{max} 3790 Å, $[\theta]_{max}$ 4450). This observation supports the recent conclusion that the low energy "$n \rightarrow \pi^*$ absorption band" of diazenes is a single $n_+ \rightarrow {}^*\pi$ transition. The optically active dialkyldiazene with R = 2-phenyl-2-butyl exhibits two overlapping CD bands *of opposite signs*. Of the two possible explanations for two CD bands, two species or two (or more) vibronic couplings, the latter is preferred. The reversal of sign in the CD absorptions of certain cyclic ketones is reexamined and interpreted in the same way. The opposite signs of the CD curves are explained as a natural consequence of the difference in the polarizability of the highest and lowest vibrational states of the n,π^* electronic state. The syntheses of the optically active dialkyldiazenes and 1,2-bis(1-adamantyl)diazene are described. The shift of the $n_+ \rightarrow \pi^*$ transition to longer wavelengths with (a) increasing substitution on the α carbon and (b) increasing steric hindrance between the alkyl and diazene groups is noted.

The diazene group (–N=N–, "azo")[1] is an important component of many dyes and free-radical sources. It is surprising that it is only recently that serious efforts have been made to understand the electronic transitions of molecules containing the diazene group. As late as 1962, a textbook on ultraviolet spectroscopy suggested that only one long-wavelength absorption band was observed because the splitting between the nonbonding levels is too small.[5] Another text of the same vintage implied that the splitting should be large on the basis of the large difference between the $n \rightarrow \pi^*$ transitions of the imine ($R_2C{=}NR$) and diazene (RN=NR) groups.[6] Robin and Simpson[7] were the first to indicate that the splitting should be of substantial magnitude, largely on theoretical grounds. Their conclusion was confirmed by the extensive theoretical study of diazene (diimide, HN=NH) carried out by Robin, Hart, and Kuebler[8] and supported by the assignments made possible by complete spectra for the simple *trans*-1,2-dialkyldiazenes, **1**-CH_3, **1**-CH_3CH_2, **1**-$(CH_3)_2CH$, and **1**-$(CH_3)_3C$ (RN=NR, **1**-R). Suzuki[9] has also predicted a large splitting for the nonbonding orbitals of the diazene group by a molecular orbital treatment.

A qualitative energy level scheme for the diazene group is illustrated in Figure 1 and includes the combinations arising from two of the orbitals on each nitrogen. The difference between the levels labeled n_+ and n_- is the splitting between the nonbonding orbitals of the diazene group. In order to gain further insight into the relationship between this level scheme and the electronic transitions of diazenes, we examined the ultraviolet absorption (uv), optical rotatory dispersion (ORD), and circular dichroism (CD) curves for two optically active dialkyldiazenes, **1-C** and **1-P**.



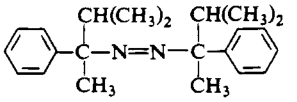
1-C



1-P

The compound **1-P** has been prepared by Bartlett and McBride[10] in racemic form along with **1**-*i*-**P** in optically active form. Very limited ORD data were given for **1**-*i*-**P**, and the primary purpose of their efforts was to examine the triplet pair arising from photodissociation of **1**-*i*-**P** at 77°K along with other aspects of radical recombination within cages.

There have been few studies on optically active diazene derivatives. Guthrie and his students have reported ORD data for some phenylazo sugars and phenylazo steroids,[11] and Snatzke has described the CD curves for several pyrazoline derivatives.[12]



1-*i*-**P**

As the discussion and results will indicate, the diazene

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(1) Previous articles in this series are P.-k. C. Huang and E. M. Kosower, *J. Am. Chem. Soc.*, **90**, 2354, 2362, 2367 (1968). Diazene nomenclature has been discussed in article II, but see also H. Bock, *Angew. Chem. Intern. Ed. Engl.*, **4**, 457 (1965).

(2) A preliminary report of a portion of this work has appeared: E. M. Kosower and D. J. Severn, *Tetrahedron Letters*, 3125 (1966).

(3) (a) Based in part on the Ph.D. Thesis, of D. J. Severn, Feb 1969; (b) National Science Foundation Trainee, 1966–1969.

(4) Support from the National Institutes of Health, the Army Research Office (Durham), and the National Science Foundation is gratefully acknowledged.

(5) H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley & Sons, Inc., New York, N. Y., 1962, pp 185–186.

(6) J. N. Murrell, "The Theory of the Electronic Spectra of Organic Molecules," John Wiley & Sons, Inc., New York, N. Y., 1963, p 183.

(7) M. B. Robin and W. T. Simpson, *J. Chem. Phys.*, **36**, 580 (1962).

(8) M. B. Robin, R. R. Hart, and N. A. Kuebler, *J. Am. Chem. Soc.*, **89**, 1564 (1967).

(9) H. Suzuki, "Electronic Absorption Spectra and Geometry of Organic Molecules," Academic Press, Inc., New York, N. Y., 1967, pp 499–503.

(10) P. D. Bartlett and J. M. McBride, *Pure Appl. Chem.*, in press. We are grateful to Professor Bartlett for a preprint of the paper.

(11) E. O. Bishop, G. J. F. Chittenden, R. D. Guthrie, A. F. Johnson, and J. F. McCarthy, *Chem. Commun.*, 93 (1965); J. Buckingham and R. D. Guthrie, *ibid.*, 570, 1241 (1967).

(12) G. Snatzke and J. Himmelreich, *Tetrahedron*, **23**, 4337 (1967).

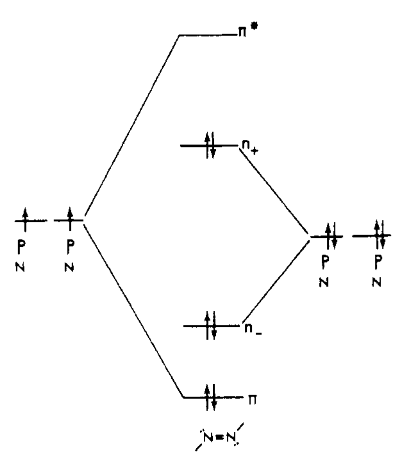


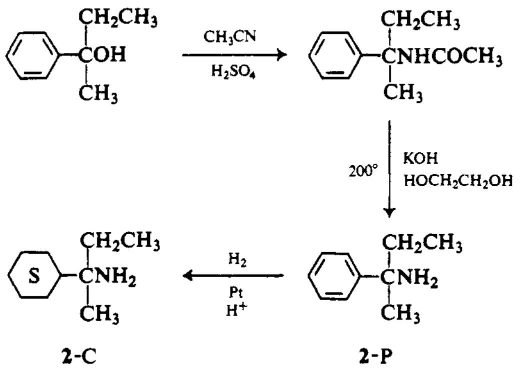
Figure 1. A qualitative energy level scheme for the combination arising from two nitrogen orbitals involved in formation of the diazene (-N=N-) group. The difference between the n+ and n− orbitals represents the splitting between the nonbonding nitrogen orbitals of the diazene group.

group (a small symmetric group) is of utility in investigations involving optically active compounds.[13,14]

Results

Synthesis of Dialkyldiazenes. The tertiary amines, 2-phenyl-2-butylamine (**2**-P) and 2-cyclohexyl-2-butylamine (**2**-C), were prepared by the route outlined in Chart I. The tertiary alcohol, 2-phenyl-2-butanol, was

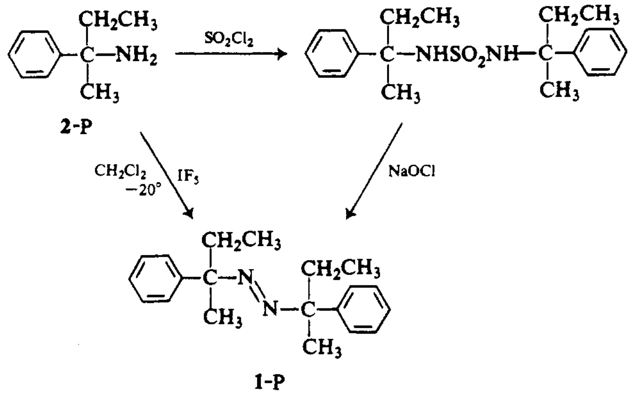
Chart I



converted to the N-acetyl derivative of **2**-P by acetonitrile and sulfuric acid (the Ritter reaction[15]). Hydrolysis of the sterically hindered amide to the free amine proceeded in relatively poor yield (33%) with potassium hydroxide in refluxing ethylene glycol. (The N-formyl derivative of **2**-P required similar conditions.[10]) Hydrogenation of amine **2**-P over platinum under acidic conditions[16] produced 2-cyclohexyl-2-butylamine with no light absorption ($\varepsilon < 1$) in the region in which the benzene ring exhibits light absorption coefficients of over 200.

The tertiary amine **2**-P yielded a sulfondiamide with sulfuryl chloride. In the case of optically active amine as starting material, recrystallization of the sulfondiamide appeared to result in further optical purification. However, the temperature required for the sodium hypochlorite reaction[17] with the sulfondiamide was high enough (40°) to cause some decomposition of the desired diazene (**1**-P). The iodine pentafluoride procedure developed by Stevens[18] and utilized for 2-phenyl-2-propylamine (*t*-cumylamine)[19] and related amines by Bartlett and his students[10] proved to be a superior method for the preparation of the diazenes from the tertiary amines (Chart II). The same procedure was used to prepare 1,2-bis(1-adamantyl)diazene (**1**-A).

Chart II



The amine **2**-P was resolved through the L-malate salt to yield a liquid with the specific activity $[\alpha]_D$ −16.8°. Amine derived through Curtius degradation of the corresponding acid had a specific activity $[\alpha]_{5460}$ −19.6°.[20] Typical simple dispersion curves for compounds which absorb in the far ultraviolet give values for the ratio of rotations at the D line of sodium and at 5460 Å, α_D/α_{5460}, of about 0.85.[21] On the basis of this criterion, the optical purity of amine **2**-P prepared by us is probably the same as that obtained from the acid.[20]

Optically active 2-cyclohexyl-2-butylamine (**2**-C), $[\alpha]_D$ +2.0°, was prepared by hydrogenation of optically active 2-phenyl-2-butylamine (**2**-P) with $[\alpha]_D$ −17.0°.

The *trans* isomer of the dialkyldiazene **1**-P was produced from the amine **2**-P by iodine pentafluoride oxidation, purified by chromatography on neutral alumina at 7° and isolated as a yellow oil in 25% yield. Its structure was established by chemical analysis, nmr spectrum in carbon tetrachloride (phenyl multiplet τ 2.75, methylene hydrogens as pairs of peaks centered at 7.94 and 8.10, each with $J = 7$ cps, methyl singlet 8.56 and methyl triplets at 9.25 ($J = 7$ cps) with intensity ratios of 4.7:2:2.9:2.9), long-wavelength ultraviolet absorption band (low-intensity absorption characteristic of diazene $n \rightarrow \pi^*$ transition, λ_{max} 3750 Å (ε 37) in isooctane), and rate of decomposition ($k_{49.5°} = 2.6 \times 10^{-5}$ sec^{-1} *vs.* $k_{49.5°}$ =

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[13] *Cf.* G. Snatzke, Ed., "Optical Rotatory Dispersion and Circular Dichroism in Organic Chemistry," Sadtler Research Laboratories, Philadelphia, Pa., 1967.

[14] O. E. Weigang, Jr., and E. G. Höhn, *J. Am. Chem. Soc.*, **88**, 3673 (1966); *J. Chem. Phys.*, **48**, 1127 (1968).

[15] J. J. Ritter and P. Minieri, *J. Am. Chem. Soc.*, **70**, 4045 (1948).

[16] H. Ruhlen, L. Knopfle, and W. Sapper, *Ann.*, **534**, 272 (1938).

[17] R. Ohme and E. Schmitz, *Angew. Chem.*, **77**, 429 (1965).

[18] T. E. Stevens, *J. Org. Chem.*, **26**, 2531 (1961).

[19] S. F. Nelson and P. D. Bartlett, *J. Am. Chem. Soc.*, **88**, 137 (1966).

[20] D. J. Cram and J. S. Bradshaw, *ibid.*, **85**, 1108 (1963). The reported rotation was converted to specific rotation with our value for the density, $d^{25}{}_4$ 0.93.

[21] T. M. Lowry, "Optical Rotatory Power," Dover Publications, New York, N. Y., 1964, p 123.

Table I. Longest Wavelength Absorption Bands for *trans*-1,2-Dialkyldiazenes

Compd, RN═NR R	Solvent	λ_{max}, Å	ε_{max}	Ref
CH_3	Gas	3400	5	*a*
	H_2O	3430	25	*b*
CH_3, CH_3CH_2[c]	Gas	3520	6.4	*d*
	H_2O	3465	~15	*e*
$(CH_3)_2CH$	Gas	3560	8	*a*
$(CH_3)_3C$	Isooctane	3675	13.5	*e*
$C_6H_5C(CH_3)(CH_2CH_3)$	Isooctane	3760	36	*e*
	CH_3CN	3750	35	*e*
	CH_3OH	3750	37	*e*
$C_6H_{11}C(CH_3)(CH_2CH_3)$	Isooctane	3805	22	*e*
	CH_3CN	3795	23	*e*
	n-Hexane	3805	22	*e*
1-$C_{10}H_{15}$[f]	Isooctane	3680	15.8	*e*

[a] Reference 9. [b] R. F. Hutton and C. Steel, *J. Am. Chem. Soc.*, **86**, 745 (1964). [c] 1-Ethyl-2-methyldiazene. [d] S. Fujita, S. Kodama, and O. Toyama, *Bull. Chem. Soc. Japan*, **39**, 1323 (1966). [e] Present work. [f] 1-Adamantyl.

Table II. Uv, CD, and ORD Data for *trans*-1,2-Bis(2-phenyl-2-butyl)diazene (**1**-P)

	Uv		CD	
Solvent	λ_{max},[a] Å	ε_{max}	$\lambda([\theta]_{max})$, Å	$\Delta\varepsilon$
Isooctane	3760	36	3830 3825	+0.84, +0.83[b] −0.82[c]
Acetonitrile	3750	35	3850 3840	+0.59 −0.57[c]
Methanol	3750	37	3850 3840	+0.66, +0.64[b] −0.64[c]
g^{d-f} = 0.023 (isooctane)				

ORD		ORD	
λ, Å	[ϕ], deg	λ,Å	[ϕ], deg
4500	+590	3700	−1630
4300	985	3600	−2250 trough
4200	1310	3500	−2210
4120	1420 peak	3400	−1910
4000	1160	3200	−1360
3900	406	3000	−1270
3800	−666		

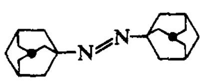
[a] In each solvent, the ultraviolet absorption curve had a minimum at 2980 Å, ε 1, a mark of high purity. [b] Duplicate value obtained after an interval of 2 years. [c] Values corrected by a factor of 17.0/10.0 to allow for the fact that the amine used to prepare this enantiomer was not optically pure. [d] Ratio of $\Delta\varepsilon_{max}$ to ε_{max}. [e] At 3830 Å. [f] Concentrations used ranged from 0.014 to 0.027 *M*.

4.33×10^{-5} sec^{-1} for 1,2-bis(2-phenyl-2-propyl)diazene).[19]

The *trans* isomer of the dialkyldiazene **1**-C was prepared in a manner similar to that used for **1**-P except that chromatographic purification could be carried out at room temperature. Its structure was established by chemical analysis, nmr spectrum (CCl_4) (complex absorption between τ 8 and 9.4 with a methyl singlet apparent at 9.11) and ultraviolet absorption (λ_{max} 3805 Å (ε 22) in isooctane).

The dialkyldiazene **1**-P derived from optically active amine has an nmr spectrum which may be explained on the basis of a single compound, whereas **1**-P produced from optically inactive amine has a number of peaks that may be assigned to the *meso* diastereomer. Differences between the nmr spectra of *meso*- and *dl*-**1**-*i*-P have been described.[10]

The *trans* configuration for the dialkyldiazenes is assigned on the grounds of the low intensity for the n → π* transitions (*cf.* Table V, article I[1]). The positions of the n → π* transitions for the diazenes **1**-P (3755 Å) and **1**-C (3805 Å) occur at considerably longer wavelengths than that for the analogous **1**-$(CH_3)_3C$ (3675 Å). To investigate the origin of the displacement of the n → π* transition to lower energies, we prepared 1,2-bis(1-adamantyl)diazene (**1**-A) (3680 Å), and find that the longest wavelength maximum is at a wavelength very close to that of **1**-$(CH_3)_3C$. Models show that the 1-adamantyl group is about the same size with respect to the diazene group as the *t*-butyl group, but that the CH_2 groups can interact sterically with the nonbonding orbital on the second nitrogen on the diazene group. The most reasonable explanation for the shifts found for **1**-P and **1**-C is one involving nonbonded repulsion between the n electrons of the diazene group and the substituents on the carbon bound to the diazene group. The "steric effect shift" from **1**-$(CH_3)_3C$ in the n → π* transition energy is



1-A

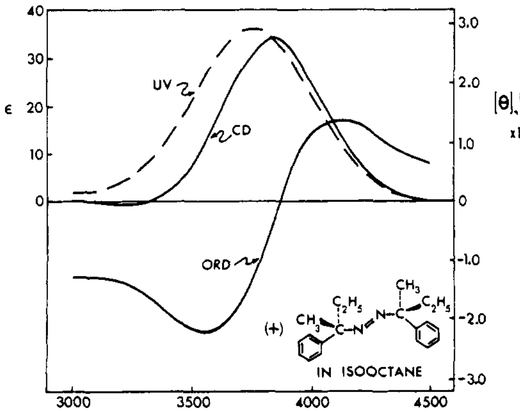


Figure 2. CD, ORD, and uv curves for *trans*-1,2-bis(2-phenyl-2-butyl)diazene (**1-P**) in isooctane. The short-wavelength portion of the CD curve with reversed sign has been confirmed as described in the text.

Table III. Uv, CD, and ORD Data for *trans*-1,2-Bis(2-cyclohexyl-2-butyl)diazene (**1-C**)

Solvent	Uv		CD	
	λ_{max}, Å	ε_{max}	$\lambda([\theta]_{max})$, Å	$\Delta\varepsilon$
Isooctane	3805	22	3790 3790	+1.35 -1.20^a
Acetonitrile	3795	23	3780 3790	+1.18 -1.06^a
n-Hexane	3805	22	3780	+1.34

$g^{b,c} = 0.061$ (isooctane)

ORD		ORD	
λ, Å	[ϕ], deg	λ, Å	[ϕ], deg
4600	+1030	3800	−41
4400	1530	3700	−1770
4200	2440	3500	−3470 trough
4100	2820 peak	3400	−3220
3900	1650	3200	−2180

[a] Values corrected by the factor 17.0/9.5 to allow for the fact that the amine used to prepare the diazene was not optically pure. [b] At 3790 Å. [c] Concentrations used ranged from 0.0034 to 0.0171 *M*.

1.7 kcal/mol for **1-P** and 2.7 kcal/mol for **1-C**. It may also be noted that increasing the substitution on the α-carbon of a 1,2-dialkyldiazene causes the n → π* transition to shift to lower energies, an effect which is probably an inductive effect. Data illustrating these points are listed in Table I.

Circular Dichroism (CD) and Optical Rotatory Dispersion (ORD) of Dialkyldiazenes. The dialkyldiazenes **1-P** and **1-C** derived from the optically active amines **2-P** and **2-C** exhibit strong Cotton effects in the region of the longest wavelength absorption band. A comparison of the CD, ORD, and uv data for diazene **1-P** is shown in Figure 2 with the numerical values summarized in Table II. Data for diazene **1-C** are illustrated in Figure 3 and listed in Table III.

The diazene **1-P** has a CD curve which changes sign on the short-wavelength side. The validity of this observation was confirmed by demonstrating that the oppositely signed contribution (a) increased in strength with concentration, (b) appeared in all solvents tested, and (c) occurred with reversed sign for the enantiomeric diazene.

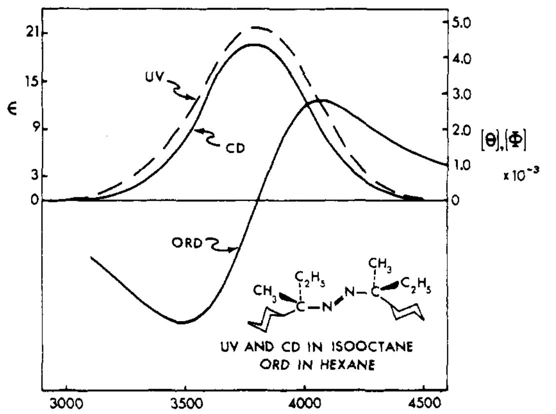


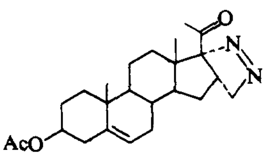
Figure 3. CD, ORD, and uv curves for *trans*-1,2-bis(2-cyclohexyl-2-butyl)diazene (**1-C**): CD, uv—isooctane; ORD—hexane.

Diazene **1-C** (the cyclohexyl derivative) has a CD curve which is Gaussian in shape. The positively signed CD curve was obtained for the diazene related to the diazene **1-P** which gave a positively signed curve (except for that short-wavelength portion with reversed sign).

Discussion

The rotational strength observed for the CD absorptions of 1,2-dialkyldiazenes is sufficient to demonstrate the value of the diazene group as a probe of asymmetric environment within molecules. The *g* value (ratio of $\Delta\varepsilon_{max}$, CD to ε_{max}, uv) for the cyclohexyldiazene **1-C** is 0.061 which is not much lower than that for a carbonyl compound like 3β-hydroxy-5α-androstan-16-one, which has the rather high value of 0.175. A high *g* value permits the CD curve to be measured under optimum experimental conditions. A list of *g* values for a number of other groups may be found in the review by Mason.[22]

A *cis*-diazene does not differ appreciably in rotational strength from a *trans*-diazene, to judge from the limited ORD data reported by Crawford and coworkers for optically active 3,5-dimethylpyrazoline.[23] Snatzke and Himmelreich[12] have suggested that the unusually high rotational strength found for the pyrazolino steroid **3**[24] is like that of an inherently disymmetric chromophore; many related examples (for homoconjugated chromophores) may be found in the review by Crabbé.[25]



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Nature of n → π* Transition of Diazenes. The long-wavelength absorption band of simple dialkyldiazenes can

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(22) S. F. Mason, *Quart Rev.* (London), **17**, 35 (1963).

(23) R. J. Crawford, A. Mishra, and R. J. Dummel, *J. Am. Chem. Soc.*, **88**, 3959 (1966).

(24) L. Velluz, M. Legrand, and M. Grosjean, "Optical Circular Dichroism," Academic Press, Inc., New York, N. Y., 1965, p 216.

(25) P. Crabbé, *Topics Stereochem.*, **1**, 93 (1967).

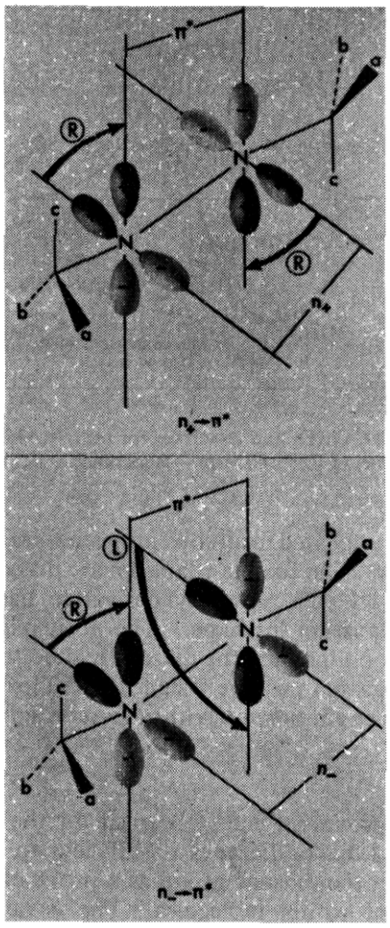

Figure 4. A representation of the $n_+ \rightarrow \pi^*$ (above) and $n_- \rightarrow \pi^*$ (below) transitions of the diazene group. The heavy arrows represent the rotational sense of the charge movement from the n_+ or n_- orbitals into the π^* orbital, with the interaction of the perturbing field of the asymmetric group localized to the charge originating on the nearest neighbor nitrogen. "Right-handed" polarized absorption would be favored for the $n_+ \rightarrow \pi^*$ transition, as shown in the upper portion of the figure for the particular absolute configuration shown. Circular dichroic absorption would not be observed for the $n_- \rightarrow \pi^*$ transition.

be identified as a singlet → singlet ($S \rightarrow S^*$) $n \rightarrow \pi^*$ transition of a *trans*-diazene group on the basis of (1) modest absorption intensity and (2) position as lowest electronic transition which can be readily observed. The absorption intensity (ε_{max} 36 for **1**-P and 22 for **1**-C) is much too high for a singlet → triplet ($S \rightarrow T$) transition, an order of magnitude too low for a typical *cis*-diazene $n \rightarrow \pi^*$ transition (Table V, article I[1]), and two orders of magnitude too low for a $\pi \rightarrow \pi^*$ transition. Figure 1 illustrates why the $n \rightarrow \pi^*$ transition is expected to be the lowest energy $S \rightarrow S^*$ transition.

One of the major remaining problems in defining the characteristics of the $n \rightarrow \pi^*$ transitions of diazenes is, as we have already pointed out in the introductory section, an evaluation of the splitting between the n_+ and n_- orbitals (Figure 1). The reasons for believing that the splitting is large are: (1) a large difference between the $n \rightarrow \pi^*$ transition energies for imines, $R_2C{=}NR$, and diazenes, $RN{=}NR$,[6] (2) simple smooth long-wavelength absorption bands for highly unsymmetrical diazenes like $C_6H_5N{=}NH$ and $C_6H_5N{=}NCH_3$, (3) molecular orbital calculations which uniformly suggest a large value.[7-9] We might also point out that tetraazadienes $RN{=}NN{=}NR$ have never been observed and molecules like 1-arylpentazoles[26] are very unstable. We can now support the contention that the splitting is large with our results for the cyclohexyldiazene **1**-C. In the long-wavelength absorption region, the CD curve is simple, of reasonable strength, and Gaussian in shape, indicating that only a single electronic transition occurs in this region. A consideration of how the magnetic transition moment may be induced by rotation of the charge from the "nonbonding" orbitals into the antibonding π^* orbitals suggests that the n_+ orbital is the originating orbital for the electronic transition. Observable intensity is produced by perturbations which lead to a small electric moment (Figure 4).

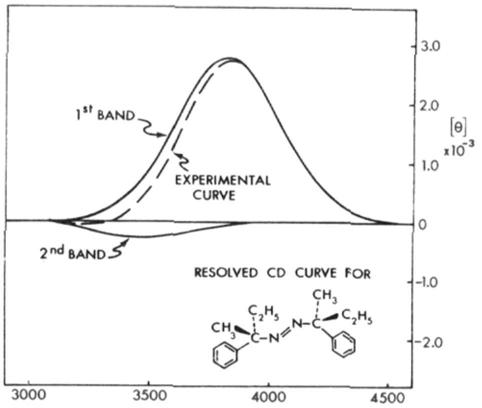

Figure 5. Circular dichroism curve for *trans*-1,2-bis(2-phenyl-2-butyl)diazene (**1**-P) in isooctane and the two Gaussian components resolved from the experimental curve.

The calculations of Robin and his coworkers[8] on diazene ($HN{=}NH$) suggest that the splitting might be as large as 7 eV for *trans*-diazene. It is predicted that the low energy $n_+ \rightarrow \pi^*$ transition would have low intensity and the high energy $n_- \rightarrow \pi^*$ transition would have considerable intensity. The high-energy band would be located around 1200 Å if the prediction is correct and would therefore be unobservable. Diazene **1**-C has a shoulder on a sharply rising absorption curve near 1875 Å (ε 8000 in hexane). Some rotational strength was detected in this region before the wavelength cutoff, but this circular dichroism and rotatory dispersion can not now be assigned.[27] According to the representation for the $n_- \rightarrow \pi^*$ transition shown in Figure 4, the rotational strength associated with the transition should be low in comparison to the absorption intensity.

Low-temperature spectra of crystalline azobenzene are in agreement with the idea that the longest wavelength absorption band is a single $n_+ \rightarrow \pi^*$ transition.[28]

Reversal of Sign in CD Curve. The phenyldiazene **1**-P has a CD curve which changes in sign on the short-wave-

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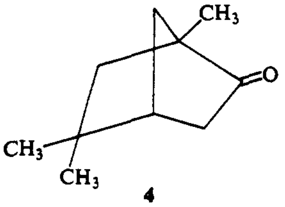
[26] I. Ugi, *Advan. Heterocyclic Chem.*, **3**, 373 (1964). Interaction of four n orbitals could lower the n,π^* energy to a thermally accessible level. No low-energy transition is cited for the 1-arylpentazoles and they are reported to be colorless or pale yellow.

[27] We thank Professor L. Verbit, Department of Chemistry, State University of New York at Binghamton, for the measurement, made with a JASCO instrument.

[28] R. M. Hochstrasser and S. K. Lower, *J. Chem. Phys.*, **36**, 3505 (1962).

length side. The magnitude of the contribution with a sign opposite to the most intense part of the CD curve may be seen more easily by a resolution into two curves as shown in Figure 5.[29] There is almost no solvent effect on the nature of the CD spectrum, although there is a small solvent effect on the rotational intensity. The contrast of the CD spectrum of the closely related cyclohexyldiazene **1-C** with that of **1-P** stimulated us to try to seek explanations for such behavior.

Reversal of sign in a CD curve may be taken as evidence for at least two overlapping CD curves, presumably of Gaussian shape, of opposite sign. The simplest explanation for two curves is that there are two species present, and examples which behave in this manner have been well elucidated by Moscowitz, Wellman, and Djerassi.[30,31] A solution containing two conformers of (+)-*trans*-2-chloro-5-methylcyclohexanone exhibits a CD curve with reversal of sign in EPA (ether–pentane–ethanol).[30] However, rigid bicyclic ketones like isofenchone (**4**)



4

exhibit a CD curve in cyclohexane which reverses in sign and which cannot be ascribed to the presence of two conformers. Coulombeau and Rassat[32] have rationalized the reversal which they discovered[33] with a theory put forward by Moscowitz and coworkers[30] to the effect that there were two species present in cyclohexane solutions of isofenchone: a solvated species and an unsolvated species.

We find this explanation unsatisfactory on two grounds. First, it is difficult to imagine an "unsolvated" molecule existing even in cyclohexane solution. Whatever the appropriate description might be for a collection of cyclohexane molecules around an isofenchone molecule, it does not seem likely that there would be two distinctly different groupings. No solvent effect whatsoever is found for the position of the n → π* transition of acetone on passage from the gas phase to cyclohexane solution.[9] Second, there is evidence that asymmetric induction by the solvent (required if we accept the notion that the solvated solute has a CD rather different from that of the unsolvated solute) is quite weak and can only be observed for especially favorable cases. Bosnich[34] has found a very weak CD curve for benzophenone in L-2,3-butanediol ($\Delta\varepsilon_{max}$ 0.05). This is not to say that solvent effects cannot be substantial, but only that a direct interaction mechanism (required for rigid ketones) is not strong enough to explain a reversal in sign ranging from a negative $\Delta\varepsilon_{max}$ of −0.3 to a positive $\Delta\varepsilon_{max}$ of +0.5 for **4**.[32]

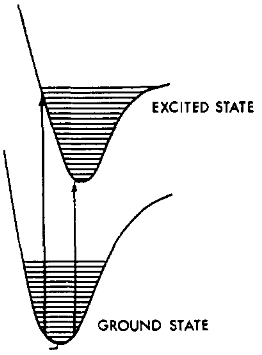


Figure 6. Ground-state and n,π* excited-state potential energy curves for an n → π* electronic transition. Transitions to low and high vibrational states are indicated.

An alternative explanation for the reversal of sign is that the vibrations of the excited state which couple to the electronic transition lead to CD absorptions of different magnitude and even different sign. It is our contention that this possibility when examined carefully will account for the reversal in sign in the CD spectra of molecules like **1-P** and **4**, and will also lead quite naturally to an explanation of the effect of solvent on the CD spectrum of **4**.

Let us first consider potential energy curves for the ground and n,π* excited states for a carbonyl compound. These are illustrated in Figure 6. The n,π* excited-state curve has a minimum at a distance greater than that of the ground-state curve because the addition of an antibonding electron to the region between carbon and oxygen will increase the equilibrium distance more than subtraction of an electron from the antibonding n_+ orbital will decrease the distance.[35] Electronic transitions from the ground vibrational state of the ground electronic state will produce, on the long-wavelength side, low vibrational states of the n,π* excited state molecule. On the short-wavelength side, high vibrational states of the n,π* excited state molecule will be the result of light absorption. The higher vibrational states of molecules will, in general, be more polarizable than the lower vibrational states.[36]

The difficulties in estimating rotational strengths arising from vibronic coupling to electronic transitions have been investigated by Weigang and Dodson.[38] We shall adopt here the assumption that higher vibrational states will respond to asymmetric polarization in a manner opposite to that for the ground state. The asymmetric polarization is provided by the portion of the molecule (the "perturber" in the language of Weigang and Höhn[14]) which does not belong to the absorbing group. Vibronic coupling between lower vibrational states (we emphasize the vibrational states of the excited electronic state since the ground electronic state will be normally coupled to

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[29] The short-wavelength oppositely signed curve is much stronger than one might suspect from the experimental CD spectrum. We have assumed that the strong CD curve must be Gaussian, using points from wavelengths longer than 3900 Å to establish the curve.

[30] A. Moscowitz, K. M. Wellman, and C. Djerassi, *Proc. Natl. Acad. Sci. U. S.*, **50**, 799 (1963).

[31] K. M. Wellman, P. H. A. Laur, W. S. Briggs, A. Moscowitz, and C. Djerassi, *J. Am. Chem. Soc.*, **87**, 66 (1965).

[32] C. Coulombeau and A. Rassat, *Bull. Soc. Chim. France*, 3752 (1966).

[33] C. Coulombeau and A. Rassat, *ibid.*, 2673 (1963).

[34] B. Bosnich, *J. Am. Chem. Soc.*, **89**, 6143 (1967).

[35] These remarks apply to the "instantaneous" (Franck–Condon) excited state molecule.

[36] The higher vibrational states may be located at an energy level at which anharmonicity becomes important.[37] It is clear that the electrons in bonds which are in high vibrational states are less strongly bound than those in low vibrational levels of the same electronic state. There is, however, little evidence on this point.

[37] G. Herzberg, "Molecular Spectra and Molecular Structure," Vol. II, D. Van Nostrand and Co., New York, N. Y., 1945, p 246.

[38] O. Weigang and P. T. Dodson, unpublished results.

only the lowest vibrational states) and the electronic transition will emphasize the interaction between the "nonbonding" electrons and the perturber. The "nonbonding" electrons (n_p in carbonyl compounds and n_+ in diazene derivatives) are the highest in energy and therefore the most polarizable electrons of the ground electronic state. The addition of the asymmetric interaction between the perturber and the n,π^* state coupled to the lower vibrational states does not, we presume, change the sign of the circular dichroic absorption. On the other hand, the coupling of the higher vibrational states to the n,π^* state leads to an interaction between these and the perturber which can sometimes change the sign of the circular dichroic absorption. This effect will normally be observed on the short-wavelength side. A detailed theoretical analysis of this problem is required for the proper inclusion of the vibrational states. We may regard the present discussion as an effort to provide a plausible physical picture for the effects which lead to a reversal in sign. Further, we note that the more polar the solvent, the stronger the interaction between the nonbonding electrons and the solvent. Thus, the less polarizable will the ground state be, and the more important will be the contribution of the excited state to the over-all asymmetric polarization responsible for the rotational strength. In general, the solvent effects reported by Coulombeau and Rassat fit this picture with the additional restriction that the "high vibrational state interaction" is limited in magnitude. The effect of the solvent on the sign of the CD spectrum is, of course, superimposed on the well-known solvent effect on the position of the carbonyl $n \to \pi^*$ transition. As expected, some characteristics of the solvent effect are correlated by the solvent polarity parameter **Z**.[39]

In the case of the diazene **1-P** and **1-C**, we may surmise from an examination of models that these molecules are almost rigid due to steric hindrance. The n,π^* excited state will have an equilibrium distance[35] between the nitrogens of the diazene group greater than that of the ground electronic state. The phenyldiazene **1-P** shows a reversal of sign on the short-wavelength side which we believe is explained by the theory. We would expect that the oppositely signed contribution would be diminished in the cyclohexyldiazene **1-C** because the excited states involved in the perturbation by the rest of the molecule, *i.e.*, the excited states of the perturber, on the diazene group are higher in energy. Indeed, no reversal of sign is seen in the CD spectrum of **1-C**.

Conclusions

Reversal in the sign of a CD spectrum through an absorption region thought to belong to a single ($n \to \pi^*$) electronic transition has been explained as an intrinsic property of the absorbing molecule, traceable to the difference in polarizability of upper and lower vibrational states of the excited n,π^* electronic states.[40] The simple Gaussian CD curve found for the diazene **1-C** has been used to support the identification of the long-wavelength absorption band of diazenes as an $n_+ \to \pi^*$ transition.

Experimental Section

Melting points are uncorrected. Nmr spectra were recorded with a Varian A-60, using tetramethylsilane as internal reference. Ir spectra were recorded with a Perkin-Elmer Model 137, uv and visible spectra with a Cary Model 14, and CD spectra with Jouan Dichrograph. Analyses were made by Huffman Laboratories, Wheatridge, Colo., and Schwarzkopf Analytical Laboratories, Woodside, N. Y.

2-Phenyl-2-butylamine (2-P). The N-acetyl derivative was obtained from the reaction of acetonitrile (1.9 mol), 2-phenyl-2-butanol (1.36 mol), and sulfuric acid (1.36 mol) in glacial acetic acid (700 ml) at 20° for 24 hr, followed by treatment with water, extraction with chloroform, and distillation as a colorless, viscous oil, bp 107° (0.08 mm) (50% yield). Hydrolysis was effected by excess potassium hydroxide in boiling ethylene glycol with removal of the product by distillation. Fractionation gave pure amine, a colorless liquid of faintly sweetish odor, bp 90° (10 mm) (lit.[20] 50–52° (2 mm) in 33% yield; ir broad band 3320–3080 cm^{-1}; nmr (CCl_4) multiplet at τ 2.78 (aromatic H), multiplet at 8.14 (J = 7 cps) (CH_2), singlet at 8.68 (CH_3), singlet at 8.75 (NH_2), and a triplet at 9.31 (J = 7 cps) in ratios 5:2:3:2:3; $d^{25}{}_4$ 0.93.

Anal. Calcd for $C_{10}H_{15}N$: C, 80.48; H, 10.13; N, 9.39. Found: C, 79.52; H, 9.95; N, 9.78.

Optical resolution was effected through the **acid L-malate salt,** mp 170–171°.

Anal. Calcd for $C_{14}H_{21}NO_5$: C, 59.35; H, 7.47; N, 4.94. Found: C, 59.77; H, 7.64; N, 5.01.

Six recrystallizations from water led to amine $[\alpha]_D$ −16.8° (neat). A seventh crystallization of the acid L-malate gave rise to amine $[\alpha]_D$ −17.0° (lit.[20] α_{5460} −18.2°).

2-Cyclohexyl-2-butylamine (2-C). Amine **2-P** (0.021 mol) was hydrogenated at atmospheric pressure over prereduced PtO_2 (1 g) in aqueous hydrochloric acid (8 ml of HCl, 50 ml of H_2O) at 60°. The solution was filtered and a further portion of catalyst added after 2 days. The filtration and addition of catalyst were repeated after an additional 5 days. At the end of another 5 days, uv absorption at 2600 Å corresponds to 99.5% reduction (total time, 12 days). Work-up with sodium hydroxide gave amine **2-C** which was fractionated to yield a clear liquid, bp 97–98° (26 mm) (33–46% yield).

Anal. Calcd for $C_{10}H_{21}N$: C, 77.34; H, 13.63; N, 9.02. Found: C, 77.47; H, 13.92; N, 9.22.

Optically active amines showed $[\alpha]_D$ −1.08° from **2-P**, $[\alpha]_D$ +9.5°; $[\alpha]_D$ +2.0° from $[\alpha]_D$ −17.0°. (The density of the amine was estimated as 0.80.)

Dialkyldiazenes. *trans*-1,2-Bis(2-phenyl-2-butyl)diazene (1-P). As in the general procedure of Stevens,[18] iodine pentafluoride (IF_5, Matheson Co., 4.2 g, weighed in a Teflon vial with cap) was added with stirring to a mixture of methylene chloride (40 ml) and pyridine (6 ml) held at −20°. Amine **2-P** (2-phenyl-2-butylamine, 4.5 g, $[\alpha]_D$ +10°) in methylene chloride (10 ml) was added dropwise over 1 hr. The mixture was allowed to come to room temperature, stirred 1 hr, carefully treated with water, hydrochloric acid (1 *N*), sodium thiosulfate solution (5%), and water, and dried over $MgSO_4$. The solvent was removed under reduced pressure and the yellow oily residue was chromatographed with pentane on neutral Al_2O_3 *with the column maintained at a temperature of 7°*. Fractions with strong light absorption between 3000 and 4000 Å and almost no absorption at 2950 Å were combined and evaporated to yield *trans*-1,2-bis(2-phenyl-2-butyl)diazene (**1-P**) as a yellow oil (0.9 g, 20%). The nmr spectrum is described in the text.

Anal. Calcd for $C_{20}H_{26}N_2$: C, 81.59; H, 8.91; N, 9.29. Found: C, 81.81; H, 8.85; N, 8.75.

***trans*-1,2-Bis(2-cyclohexyl-2-butyl)diazene (1-C).** Amine **2-C** (2-cyclohexyl-2-butylamine) was oxidized, worked up, and isolated by the above procedure in 16–22% yield as a thick yellow oil (chromatography could be carried out at 25°).

Anal. Calcd for $C_{20}H_{38}N_2$: C, 78.37; H, 12.49; N, 9.14. Found: C, 78.16; H, 12.67; N, 9.18.

***trans*-1,2-Bis(1-adamantyl)diazene (1-A).** 1-Aminoadamantane (2.9 g) was refluxed briefly with CH_2Cl_2 (250 ml) with stirring. The solution was filtered and oxidized as described above to yield a yellow solid, from which the diazene was extracted with hexane. Recrystallization from a large volume of acetone gave 0.35 g of **1-A**: mp 280–284° (slight apparent decomposition); λ_{max} 3680 Å (ϵ 15.8 in isooctane); ir, sharp bands at 1460 and 870 cm^{-1} in addition to the 3000-cm^{-1} region; nmr τ 7.8–8.5 with strongest peak at 8.29.

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[39] *Cf.* E. M. Kosower, "An Introduction to Physical Organic Chemistry," Part 2, John Wiley & Sons, Inc., New York, N. Y., 1968.

[40] A more concrete physical picture could be presented but should await confirmation of the theory.

Anal. Calcd for $C_{20}H_{30}N_2$: C, 80.48; H, 10.13; N, 9.38. Found: C, 80.30; H, 10.26; N, 9.41.

1-Ethyl-2-methyldiazene. Acetaldehyde methylhydrazone was generated from acetaldehyde and methylhydrazine in tetrahydrofuran (THF) with the aid of Molecular Sieve 4A pellets, filtered through Molecular Sieve powder, and reduced to the hydrazine with lithium aluminum hydride. The hydrazine was isolated in 12% yield, bp 92° (predicted 93 ± 3°,[41] with structure confirmed by nmr); ethyl group: methyl triplet centered at τ 8.98 and methylene quartet centered at 7.25 with $J = 7$ cps; methyl group: singlet at τ 7.53; hydrazino group: broad peak at τ 6.70 (the peaks had the appropriate ratios); ir with NH absorption at 3250–3400 cm^{-1}. Oxidation to the diazene was accomplished with mercuric oxide in water. The volatile diazene was distilled from the reaction mixture; $\lambda_{\max}$ 3465 Å (in H_2O); nmr τ 8.69 (triplet), 6.17 (quartet), 6.25 (singlet), in the ratio 3:5.

Attempts to discern a circular dichroism for the diazene group of this molecule in the presence of β-lactoglobulin failed (*cf.* the pentane binding observed by Wishnia and Pinder.)[42]

Circular Dichroism Spectra. The Jouan Dichrograph was calibrated before each run with a solution of epiandrosterone. Reproducibility of CD spectra was ±2% and the slit was maintained at less than 1.3-mm width. ORD spectra were obtained on a Cary Model 60 spectropolarimeter for which we are grateful to Professor S. Englard, Department of Biochemistry, Albert Einstein College of Medicine.

Analysis of Spectroscopic Curves. The simple CD curve for diazene **1-C** was fitted easily to a Gaussian expression

$$\theta = \theta_0 e^{-\left(\frac{\lambda - \lambda_0}{\Delta_0}\right)^2}$$

where θ = observed ellipticity, θ_0 = maximum ellipticity, λ = wavelength, λ_0 = wavelength of maximum ellipticity, Δ_0 = half-width at $\theta = \theta/e$ by means of a program operated on a LOCI-2A computer (Wang Laboratories) using points at 3900, 4100, and 4400 Å.

The complex CD curve for diazene **1-P** was resolved into two Gaussian curves by first calculating the major component as described above (3900, 4100, and 4300 Å), subtracting the observed values from the calculated and checking the Gaussian character of the second component.

Addition of the two components gave the observed CD curve.

Acknowledgment. Helpful criticisms and comments from Professor O. Weigang, Tulane University, and Dr. M. B. Robin, Bell Laboratories, are gratefully acknowledged.

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[41] L. Spialter, D. H. O'Brien, G. L. Untereiner, and W. A. Rush, *J. Org. Chem.*, **30**, 3278 (1965).

[42] A. Wishnia and T. W. Pinder, Jr., *Biochemistry*, **5**, 1534 (1966).