Stereochemistry of Eight-Membered Cyclic Azo Compounds[1]

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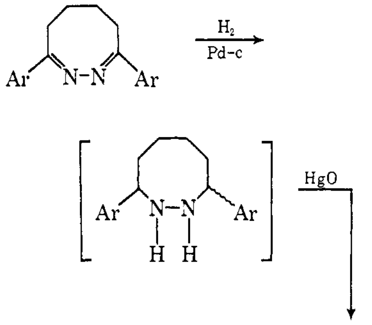
Abstract: The isolation of two isomers of 3,8-diphenyl- and of 3,8-bis(*p*-methoxyphenyl)-1,2-diaza-1-cyclooctene is reported. The evidence obtained indicates that these compounds are *cis–trans* diaryl isomeric pairs possessing *cis*-azo linkages.

Since its original synthesis, the lower melting isomer (I) of 3,8-diphenyl-1,2-diaza-1-cyclooctene has been of particular interest because of its thermal stability and its anomalous azo ultraviolet absorption maximum and dipole moment.[4] A second, higher melting isomer (II) of this compound now has been isolated. The ultraviolet maximum, dipole moment, and thermal stability of II, unlike the corresponding data for I, were comparable to those of the six- and seven-membered cyclic *cis*-azo compounds. The isomeric di-*p*-anisylazocyclooctenes (III and IV) were also prepared and exhibited behavior similar to that of the two diphenyl analogs. The availability of both pairs of diastereomers (I and II, III and IV) prompted the study of their properties in an attempt to determine the configuration of the azo linkage and of the aryl substituents.

Results and Discussion

The eight-membered cyclic azo compounds (I–IV) were prepared *via* the route illustrated in Scheme I.

Scheme I



I, Ar = C_6H_5 (56%) II, Ar = C_6H_5 (4.3%)
III, Ar = *p*-$MeOC_6H_4$ (45%) IV, Ar = *p*-$MeOC_6H_4$ (20%)

Both the diphenyl- and the bis(*p*-methoxyphenyl)-1,2-diaza-1-cyclooctenes have previously been reported;[4,5] however, only gross structures were given, and no stereochemical assignments were made. Evidence presented in this paper suggests the stereochemistry of these two compounds to be that depicted in structures I and III. Isomers II and IV, which were isolated recently by fractional recrystallization, have also been shown to possess the stereochemistry indicated by the appropriate structures in Scheme I.

Assignment of Stereochemistry

Dipole moment measurements and ultraviolet absorption data have been used to assign the configuration of the azo linkage. For example, the dipole moments of 3,5-diaryl-*cis*-1-pyrazolines,[6] 3,7-diphenyl-*cis*-1,2-diaza-1-cycloheptene,[7,8] and *cis*-azobenzene[9] are 2.2–2.3, 2.42, and 3.0 D, respectively. On the other hand, *trans*-1-azobis(1-phenylpropane)[6] has a dipole moment of 0.5 D, whereas *trans*-azobenzene[9] and *trans*-azomethane[10] have zero dipole moments. In addition, the ultraviolet absorption maxima for compounds possessing *cis*-azo configurations appear at greater wavelengths than those of compounds with *trans*-azo linkages. As illustrated in Table I, compounds such as 3,7-diphenyl-*cis*-1,2-diaza-1-cycloheptene[7] and 3,6-diphenyl-*cis*-1,2-diaza-1-cyclohexene[11] exhibit absorption maxima at 389 and 390 mμ, whereas *trans*-1-azobis(1-phenylpropane) shows an azo absorption band at 359 mμ. Rates of thermal decomposition of azo compounds have also been useful in the assignment of *cis*-azo linkages in the six- and seven-membered rings. The rates of these compounds are more than 200 times greater than that of *trans*-1-azobis(1-phenylpropane) at 80°.

Isomers II and IV exhibited dipole moments comparable to those for five- and seven-membered cyclic *cis*-azo compounds. Moreover, the ultraviolet absorption maxima associated with the azo linkages of II and IV, and their corresponding rates of thermal decomposition more closely paralleled those of the six- and seven-membered *cis*-azo ring systems. In addition,

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[1] This is the 46th in a series of papers concerned with the preparation and decomposition of azo compounds. For the previous paper, see C. G. Overberger, M. Valentine, and J.-P. Anselme, *J. Amer. Chem. Soc.*, in press.

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[3] This paper comprises in part (a) portions of a thesis submitted by John W. Stoddard in partial fulfillment of the requirements for the Ph.D. degree, 1969, The University of Michigan; (b) portions of theses submitted by Carmela Yaroslavsky in partial fulfillment of the requirements for the Ph.D. degree, 1966, and by Hyman Katz in partial fulfillment of the requirements for the B.S. degree, 1966, Polytechnic Institute of Brooklyn.

[4] C. G. Overberger and I. Tashlick, *J. Amer. Chem. Soc.*, **81**, 217 (1959).

[5] J. M. Van der Zanden and G. De Vries, *Rec. Trav. Chim. Pays-Bas*, **75**, 1159 (1956).

[6] C. G. Overberger, J.-P. Anselme, and J. R. Hall, *J. Amer. Chem. Soc.*, **85**, 2752 (1963).

[7] C. G. Overberger and J. Lombardino, *ibid.*, **80**, 2317 (1958).

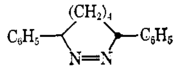
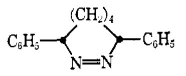
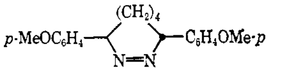
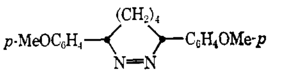
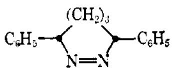
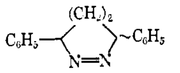
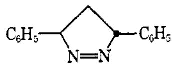
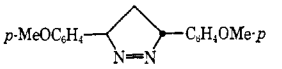
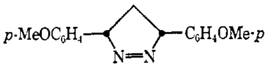
[8] C. G. Overberger and C. Yaroslavsky, *Tetrahedron Lett.*, 4395 (1965).

[9] G. S. Hartley and R. J. W. LeFevre, *J. Chem. Soc.*, 531 (1939).

[10] W. West and R. B. Killingsworth, *J. Chem. Phys.*, 6, 1 (1938).

[11] S. G. Cohen, S. Hsaio, E. Saklad, and C. H. Wang, *J. Amer. Chem. Soc.*, **79**, 2661, 4400 (1957).

Table I. Dipole Moment, Spectral, and Kinetic Data of Azo Compounds

Compound	μ, D[a]	Uv maxima[b] mμ	ϵ	-N=N-, cm^{-1}	sec^{-1} at 80°	E_a, kcal/mol	Ref
trans-$CH_3N{=}NCH_3$	0	340	4.5		6.9×10^{-16}	50.2	8, *f*
cis-$CH_3N{=}NCH_3$		353	240				*g*
$(CH_3)_2CHN{=}NCH(CH_3)_2$		355	18		2.9×10^{-12}	40.9	*h*
$C_6H_5(Et)CHN{=}NCH(Et)C_6H_5$	0.50	359	47		1.9×10^{-6}	32.3	4
	1.20	368	45	1538	3.5×10^{-8}	36.7	4, this work
	2.86	381	111	1545	2.3×10^{-4}	26	This work[d]
	1.76	361	46		2.7×10^{-8}	28	This work[e]
	2.77	379	106		1.8×10^{-4}	25	This work[d]
	2.42	390	127	1542	4.3×10^{-4}	29.7	7, 8
		387	775	1548	6.0×10^{-4}		11
	2.23	329[c]	291	1548	1.2×10^{-8}	17.9	6, *i*
		332[c]	533	1555	2.5×10^{-3}	16.3	*j*
		329[c]	329	1545	4.25×10^{-3}	11.8	*j*

[a] Probable error ±0.05 D. [b] In chloroform unless otherwise noted. [c] In ethanol. [d] Rates were determined at 80, 100, and 116°. [e] Rates were determined at 154, 167, and 180°. [f] C. Rice and D. V. Sickman, *J. Chem. Phys.*, **4,** 239, 242, 608 (1936). [g] R. F. Hutton and C. Steel, *J. Amer. Chem. Soc.*, **86,** 745 (1964). [h] H. C. Ramsperger, *ibid.*, **50,** 714 (1928); B. W. Langley, B. Lythgoe, and L. S. Rayner, *J. Chem. Soc.*, 4191 (1952). [i] C. G. Overberger and J.-P. Anselme, *J. Amer. Chem. Soc.*, **86,** 658 (1964). [j] C. G. Overberger, N. Weinshenker, and J.-P. Anselme, *ibid.*, **87,** 658 (1964).

compounds II and IV were found to isomerize to hydrazones at a much slower rate than does the seven-membered *cis*-azo derivative.[7] On this basis structures II and IV were assigned *cis*-azo linkages.

The assignment of the configuration of the azo linkages of isomers I and III, however, could not be based solely on the above criteria. For these two compounds, the lower dipole moments, the lower azo ultraviolet absorption maxima, and the extremely slow rates of thermal decompositions could be rationalized in terms of either a *trans*-azo linkage, or a *cis*-azo linkage with the anomalous physical properties of the linkage being attributed to the configuration of the aryl substituents. The evidence obtained favors the latter possibility, and thus would establish the configuration of the diaryl groups as being *trans* in structures I and III and *cis* in II and IV.

Hydrogenation–Oxidation Studies. The two significant stereochemical aspects of 3,8-diaryl-1,2-diaza-1-cyclooctenes are concerned with the configurations of (a) the azo linkage and (b) the aryl substituents. Thus, consideration of azo derivatives I and II, for example, would necessarily involve the possibility of the existence of four diastereomers: the *cis*- and *trans*-3,8-diphenyl-*cis*-1,2-diaza-1-cyclooctenes and *cis*- and *trans*-3,8-diphenyl-*trans*-1,2-diaza-1-cyclooctenes.

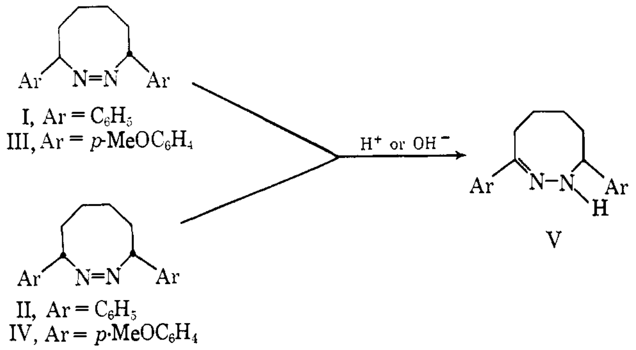
The existence of *trans*-azo linkages for the isomers of 3,8-diphenyl-1,2-diazacyclooctene was rendered unlikely by the results of the following reduction–oxidation experiments, thus reducing to two the number of possible diastereomers. Isomer II, already assigned a *cis*-azo linkage on the basis of ultraviolet absorption maximum, dipole moment, and rate of decomposition data, was reduced to the corresponding hydrazine and reoxidized with mercuric oxide. If the mixture of products obtained in Scheme I was due to a nonstereoselective oxidation, isomer II, upon reduction and subsequent oxidation would be expected to give some *trans*-azo linked product in addition to regenerated isomer II. However, only isomer II was isolated from the reaction mixture in nearly quantitative yield.

A similar argument would apply to isomer I. Repetition of the experiment on this isomer resulted in the formation of isomer I in quantitative yield. It was concluded, therefore, that isomers I and II possess *cis*-azo linkages and that both isomers differ only in the configuration of their phenyl substituents.

Rates of Isomerization. A study of the rates of isomerization of each of the 3,8-diaryl-1,2-diazacyclooctenes (I–IV) to the corresponding hydrazones (V) provided additional evidence for the existence of *cis*-azo linkages in isomers I and III. Furthermore, the results of this investigation allowed the assignment of the *trans* configuration to the aryl groups of compounds I and III and the *cis* configuration to the aryl groups of compounds II and IV.

In the presence of dilute acid or base, isomers II and IV isomerized 1000 times faster to hydrazone (V) than isomers I and III (Scheme II). This observation is opposite to that expected if cyclic isomers I or III had possessed *trans*-azo linkages.

Scheme II



This difference in rate can be rationalized in terms of the configuration of the phenyl groups. Models indicate that in structures II and IV, which possess *cis*-diaryl substituents, the aryl groups are coplanar to the $>CN{=}NC<$ system. Removal of the axial hydrogen is therefore facilitated not only by maximum overlap with the π orbital of the azo bond, but also by resonance stabilization by the equatorial aryl group. On the other hand, a *trans*-aryl configuration introduces some strain into the molecule, and prevents the phenyl groups from being coplanar with the carbon–nitrogen bonds. This deviation from coplanarity is far greater for the aryl substituent in the axial position than for the one in the equatorial position. Moreover, molecular models also indicate that the removal of the C_3 axial hydrogen is severaly hindered by the C_8 axial aryl group lying directly above it, and consequently a slower isomerization is observed. This position of the C_8 phenyl ring (axial) lying above that of the C_3 axial hydrogen is further substantiated by the nmr spectra of compounds I and III. In both of these structures, the signal for the axial benzylic hydrogen is shifted upfield by τ 0.5 from that of the corresponding structures (II and IV) having two *cis*-diaryl substituents because of the shielding effect of the overlying aromatic ring.[12]

This model can also be used to explain the large difference in rates of thermal decomposition between the two diastereomeric pairs (I and II, III and IV—Table I). In the case of II and IV, coplanarity of both aryl substituents with the carbon–nitrogen bonds can easily be achieved in the transition state, thereby stabilizing the incipient diradical formed.[4] In structures I and III, although some resonance stability is probably gained by the equatorial aryl group, none is furnished by the axial aromatic substituent. The effect of phenyl substituents on decomposition rates of azo compounds is dramatic: for example, the replacement of α-hydrogens in azomethane by two phenyl groups results in a ten-billion-fold increase in the rate of decomposition (Table I).

Rates of Hydrogenation. The eight-membered azo isomer II was found to hydrogenate at a rate 1.35 times greater than that of the corresponding structural isomer I. In a similar fashion the *p*-anisyl derivative IV hydrogenated 1.30 times that of isomer III. These results further supported a *cis*-azo linkage for each of these compounds because a *trans*-azo linkage in an eight-membered ring would be expected to undergo hydrogenation at a considerably faster rate than a *cis*-azo bond.[13,14] These results also suggest the *cis* configuration for the diaryl substituents in isomers II and IV, and a *trans* configuration for the aryl substituents in isomers I and III. The slightly greater rates of hydrogenation of II and IV can be rationalized by the assigned stereochemistry of the aryl groups. The rate of hydrogenation would be expected to be somewhat greater for a 1,2-diazacyclooctene possessing *cis*-3,8-diaryl groups (II and IV) because for the corresponding compounds possessing *trans*-diaryl substituents (I and III), the axial aromatic rings would hinder the approach of hydrogen to the azo linkage.

Photochemical and Thermal Decompositions. Analysis of the products resulting from photochemical decomposition of *trans*- and *cis*-3,8-diphenyl-*cis*-1,2-diaza-1-cyclooctenes (I and II) provided additional evidence for the assigned configuration of the diphenyl substituents.

The photochemical decomposition of isomer I was carried out at two different temperatures in the solid state. The results, listed in Table II, indicate that the ratio of *trans*- to *cis*-1,2-diphenylcyclohexanes is significantly higher in solid state photolysis at −78°. The increase in the ratio of *trans*- to *cis*-1,2-diphenylcyclohexanes (4:1) at −78° as compared to that (1.3:1) at the higher decomposition temperature suggests that the phenyl groups of isomer I possess the *trans* configuration. A similar stereospecificity has been reported in the photolytic decomposition of 1-pyrazolines.[15,16]

Table II. Products of Photolysis I and II

Compd	Conditions	Temp, °C	1,2-Diphenylcyclohexane, % *cis*	*trans*	1,6-Diphenyl-1-hexene, %
I	Solid state	0	15.4	20	64.6
I	Solid state	−78	9	35	56
II	Solid state	−78	18	10	72
II	Solid state	19	20	17	63

The major product of the solid state photochemical decomposition of compound II was again olefin (Table II). When the temperature was lowered from 19 to −78°, the amount of olefin increased. In this case *cis*-1,2-diphenylcyclohexane was formed in larger amount than the corresponding *trans* isomer. The *cis* to *trans* ratio of 1.16 at 19° increased to 1.76 at −78°. It should be noted that no isomerization occurred when a mixture of *cis*- and *trans*-1,2-diphenylcyclohexanes was irradiated for 20 hr at room tem-

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(12) J. R. Dyer, "Absorption Spectroscopy of Organic Compounds," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1965, pp 80–82.

(13) I. Jardine and F. J. McQuillin, *J. Chem. Soc., C*, 458 (1966).

(14) K. Ziegler and H. Wilms, *Ann.*, 567, 1 (1950).

(15) See Table I, footnote *j*.

(16) T. V. Van Auken and K. L. Rinehart, *J. Amer. Chem. Soc.*, 84, 3736 (1962).

perature. These results suggest the *cis* configuration for the phenyl groups of isomer II.

The predominance of olefinic products in the solid state photolysis of isomers I and II may be due to a conformation effect.[8] Models indicate that in both the chair and boat forms of the eight-membered ring, C_3 and C_8 are in close proximity, a situation favoring cyclization. On the other hand, in a twisted form, C_3 (or C_8) is closer to the C–H bond of C_7 (or C_4) than to C_8 (or C_3). In this case, the radical can more easily abstract a hydrogen atom to give olefin.

The products of thermal decomposition are summarized in Table III. The percentages reported were determined from peak areas of vapor-phase chromatograms. The order of elution of the decomposition products of III and IV was assumed to be the same as that of authentic samples of *cis*- and *trans*-1,2-diphenylhexanes and *cis*- and *trans*-1,2-diphenyl-1-hexenes, and their assignment must, therefore, be regarded as tentative. In all cases, the ratio of *trans*- to *cis*-1,2-diarylcyclohexane was greater than 1. The relatively large quantities of olefin formed may be attributed to the high decomposition temperatures.

Table III. Thermal Decomposition Products of the Diaryldiazacyclooctenes

	1,2-Diarylcyclohexane, %		1,6-Diaryl-1-hexene, %	Hydrazone, %	Unknown, %
Compd	*cis*	*trans*			
I	16.6	27.9	50.4	5.1	0.0
II	14.7	48.3	30.4	3.9	2.7
III	19.6	38.2	37.0	3.0	2.2
IV	14.2	31.0	40.8	9.5	4.5

Experimental Section[17]

Synthesis and Separation of *cis*- and *trans*-3,8-Diphenyl-1,2-diaza-1-cyclooctenes (I and II). A mixture of isomers I and II was prepared according to the procedure of Overberger and Tashlick.[4] The separation of the diastereomers was accomplished by two methods.

a. **Recrystallization.** The crude oxidation product (from 18.4 g, 0.070 mol of azine), obtained by the above procedure, was recrystallized from boiling hexane. The first portion of material to crystallize was dissolved in a slight excess of hexane. On cooling, 0.8 g (4.3%) of a colorless solid precipitated, mp 113–116° dec. Recrystallization from cyclohexane yielded an analytical sample of II, mp 115–116° dec; $\lambda_{max}^{CHCl_3}$ 381 mμ (ϵ 111); nmr ($CDCl_3$): τ 2.6–2.8 multiplet (10 H, aromatic), 4.66 two doublets (2 H, C_6H_5CH), and 7.8–9.2 multiplet (8 H, CH_2); infrared (KBr) 1545 cm^{-1} (–N=N–).

Anal. Calcd for $C_{18}H_{20}N_2$: C, 81.77; H, 7.63; N, 10.60; mol wt, 264. Found: C, 81.53; H, 7.69; N, 10.46; mol wt, 256.

The combined mother liquors gave isomer I in 56% yield after recrystallization from methanol. An analytical sample melted at 90–91° (lit.[3] mp 90–91°); nmr ($CDCl_3$): τ 2.7–2.92 multiplet (10 H, aromatic), 5.25 two doublets (2 H, C_6H_5CH), and 7.6–9.2 multiplet (8 H, CH_2); infrared (KBr) 1538 cm^{-1} (–N=N–).

b. **Sublimation.** A mixture of isomers I and II (see above), mp 84–86°, was sublimed at 55° (0.2 mm). The sublimate, isomer I, melted at 86–88°. Recrystallization from methanol raised the melting point to 90–91°. The sublimed residue, isomer II, melted at 108–110°. Recrystallization from methanol raised the melting point to 115–116°.

Synthesis and Separation of *cis*- and *trans*-3,8-Bis(*p*-methoxyphenyl)-1,2-diaza-1-cyclooctene (III and IV). A mixture of isomers III and IV was prepared by the same procedure as that employed for the diphenyl derivatives. The separation of isomers however, was accomplished by an alternate procedure which had previously been used for the separation of *cis*- and *trans*-1-pyrazolines.[15] A slurry of 2.0 g of 3,8-bis(*p*-anisyl)-1,2-diaza-1-cyclooctene,[5] in benzene was filtered, to yield filtrate A and residue B. Residue B was slurried in 5 ml of benzene and filtered, yielding filtrate C and residue D. Filtrate C was an inseparable mixture of the isomers. Residue D was recrystallized from ethanol and gave 0.39 g (20%) of IV, mp 135–137° dec; $\lambda_{max}^{CHCl_3}$ 379 mμ (ϵ 106); nmr ($CDCl_3$): τ 2.2–3.1 multiplet (8 H aromatic); 4.72–4.80 two doublets (2 H C_6H_5CH) 6.22 singlet (6 H, CH_3O); 7.6–9.2 multiplet (8 H, CH_2). Evaporation of filtrate A left a residue which was recrystallized from absolute ethanol to yield 0.90 g (45%) of III, mp 125–126°, lit.[5] mp 126–126.5°, $\lambda_{max}^{CHCl_3}$ 361 mμ (ϵ 46), nmr ($CDCl_3$): τ 2.5–3.1 multiplet (8 H aromatic); 4.19–5.26 two doublets (2 H, C_6H_5CH); 6.23 singlet (6 H, CH_3O); 7.6–9.2 multiplet (8 H, CH_2).

Anal. Calcd for $C_{20}H_{24}O_2N_2$: C, 74.05; H, 7.46; N, 8.64; mol wt, 324. Found for III: C, 74.15; H, 7.46; N, 8.72; mol wt, 329. Found for isomer IV: C, 74.08; H, 7.49; N, 8.81; mol wt, 323.

Hydrogenative–Oxidative Conversions of Isomers I and II. A solution of 110 mg (0.416 mmol) of isomer I in 25 ml of tetrahydrofuran (freshly distilled from $LiAlH_4$) was hydrogenated for 6 hr at 45 lb pressure at room temperature with 10 ml of 5% palladium-on-charcoal in a Parr apparatus. After the reduction was completed; the catalyst was removed by filtration, and 500 mg (2.31 mmol) of mercuric oxide was immediately added. The mixture was stirred for 26 hr under a nitrogen atmosphere; the solid removed by filtration and the tetrahydrofuran removed *in vacuo* at room temperature. The resulting yellow solid was dissolved in warm methanol, decolorized with Norit, and filtered. Upon cooling 70 mg of isomer I crystallized, mp 89–90°. Evaporation of the filtrate and recrystallization of the residue from cyclohexane afforded 20 mg more of isomer I. A mixture melting point with the starting material was undepressed. The nmr and ir spectra of the material remaining in the mother liquor (cyclohexane) indicated only the presence of isomer I. In a larger run, the presence of the intermediate hydrazine was established by nmr and ir analysis. Isomer II (100 mg) was reduced and reoxidized under the same conditions as those given for isomer I. The final methanol solution, when allowed to stand at room temperature yielded crystals (40 mg) of II, mp 115–116° dec, whose ir spectrum was identical with that of the starting material (II). Concentration of the mother liquor and subsequent cooling to 0° afforded 15 mg more of isomer II. The remaining methanol solution was evaporated to dryness, and the residual white solid recrystallized from cyclohexane yielding an additional 15 mg of isomer II. The nmr and ir spectra of the remaining material in the mother liquor indicated mostly isomer II; in this fraction a small amount (1–2%) of hydrazone was also present.

Rates of Isomerization. The rates of isomerization (acidic or basic) of isomers I and II were determined by following the increase in absorption at 260 mμ (hydrazone). The isomerization could also be followed in compound II by the decrease of the azo absorption at 389 mμ; however, this was not practical because of the small ϵ max at this wavelength. In the *p*-methoxy derivatives (III and IV) the increase in rate of hydrazone formation was followed at 320 mμ. The experimental procedure was the same used for each of the four compounds. The azo derivative to be isomerized was dissolved in 3 ml of isopropyl alcohol containing either 0.02 *M* hydrochloric acid or 0.13 *M* sodium hydroxide. While isomers II and IV rearranged to hydrazone (V) within minutes, I and III took several days.

The presence of hydrazone was demonstrated by nmr analysis, and the ultraviolet absorption spectra of solutions of I and II after acidic isomerization were identical. A comparison of the rate of isomerization of isomers II and IV with that of the seven-membered cyclic azo compound[7] was made in ethanolic solution. Their rates were observed to be several orders of magnitude slower than that of the seven-membered ring analog.

Rates of Hydrogenation. In order to measure small amounts of hydrogen uptake accurately, a microsloping-manifold atmospheric

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(17) The melting points are uncorrected. The analyses were performed by the Galbraith Laboratories, Inc., Knoxville, Tenn. The infrared spectra were run as KBr pellets on a Perkin-Elmer "21" spectrophotometer. The ultraviolet curves and isomerization data were obtained either on a Cary "14" or Perkin-Elmer "202" recording spectrophotometer. Nuclear magnetic resonance spectra were recorded on a Varian Model A-60 spectrometer using tetramethylsilane as an internal standard.

hydrogenation apparatus was constructed.[18] A 10-ml buret was used in combination with a water manometer for measurement of the absorption of hydrogen. The conditions used were identical for all four isomers (I–IV), namely, 13 ml of THF (freshly distilled from $LiAlH_4$), 33 mg Pd–C catalyst (5%), and 0.30 mmol of compound were used. In each case the solvent and the catalyst were allowed to equilibrate for 50 min in a hydrogen atmosphere before addition of the substrate. The rates of hydrogen uptake were first order with respect to hydrogen. Rate constants (k_H) were obtained from the slopes of plots of log $[V_\infty/(V_\infty - V_t)]$ *vs.* time (where V_∞ = total volume of hydrogen uptake, V_t = volume of hydrogen uptake recorded at time t) and are as follows: for I, k_H 0.0320 min^{-1}; II, k_H 0.0432 min^{-1}; III, k_H 0.0326 min^{-1}; IV, k_H 0.0480 min^{-1} (av deviation $\pm 2 \times 10^{-4}$).

Solid State Photolyses. All solid state photolyses were carried out in nmr tubes (equipped with a drying tube) as reaction vessels. A Hanovia medium pressure mercury lamp was used as the light source. An evacuated silvered quartz dewar flask which had a narrow clear strip was used as the cooling chamber for the nmr tubes. The photolysis of I and II at −78° were run for 3 weeks on 0.04–0.15-mmol samples. The photolysis of I (at 0°) and II (at 19°) were carried out for 36 hr. Liquefaction occurred soon after irradiation had begun. The completion of the photolyses was determined by the absence of absorption of the azo band in the uv spectrum and by the disappearance of the benzylic protons of I and II in the nmr spectra. The photolytic mixtures were analyzed by vapor phase chromatography on both a 6-ft D.C. 200 silicone oil column at 200° and a 6-ft FFAP column at 220°. Comparisons of retention times were made with authentic samples.[19]

Kinetics of Thermal Decomposition. The rates of decomposition were determined in duplicate using a microapparatus modified from that used by Overberger and Gainer.[20] It consisted of an inner chamber into which the sample was introduced, and an outer chamber in which a suitable liquid was refluxed. A 10-mm tube allowed the nitrogen evolved to pass from the inner chamber, through a cooling coil (temperature 27°), into a 100-ml buret. The course of the decomposition of the azo compound was followed by the evolution of nitrogen. The quantity of nitrogen collected ranged from 90 to 110% of theory with the lower yields of nitrogen occurring at lower temperatures. The decompositions were found to obey first-order kinetics; the rate constants were determined from plots of log $[V_\infty/(V_\infty - V_t)]$ *vs.* time. The values were calculated by a computer using the least-squares method. Values differing from the calculated rate by more than the average deviation were discarded. Energies of activation were also calculated by the method of least squares and the values are summarized in Table I.

An induction period was observed, but was eliminated by bubbling nitrogen through the solvent when it had reached the temperature of the decomposition. Elimination of the induction period resulted in a high initial rate.

In all cases, the boiling point of the liquid refluxing in the outer chamber of the apparatus was used as the decomposition temperature. Previously, the decomposition temperature was determined by direct measurement. For a typical run, 5 ml of tetralin (dried over Drierite and redistilled) was placed in the inner chamber. A suitable liquid, chosen according to the temperature desired, was refluxed in the outer chamber. When the tetralin temperature had reached equilibrium, nitrogen was bubbled through the tetralin for 15 min. The sample (100 mg) was then quickly introduced. Stirring of the tetralin was effected continuously with a Teflon-covered magnet. Measurements were taken through several half-lives. When the evolution of nitrogen had ceased, the volume reading was taken as V_∞; these values agree well with the stoichiometric values.

Thermal Decomposition Products. The samples obtained in the thermal decompositions were combined and the tetralin distilled under reduced pressure. Samples (1 μl) were injected into a vpc equipped with a 10% Carbowax column (column temperature, 170°). In the case of the 3,8-diphenylazo derivatives retention times were compared with authentic materials.[19] The order of elution for the decomposition products of isomers III and IV were assumed to be the same as for the diphenyl analogs, and therefore, their assignment is tentative. The percentages reported were determined from peak areas of the chromatograms (Table III).

Dipole Moments. The dielectric constants (Table IV) were measured in benzene solution at 20.0° with DMOL Dipolemeter (Kahl Scientific Instrument Corp.). Spectro grade benzene was dried over molecular sieves. The dielectric constant of benzene was taken to be $2.2825 \pm 2 \times 10^{-4}$.[21] The refractive indices were measured using a dipping refractometer (Carl Zeiss, Jena). The dipole moments were calculated as described by Guggenheim[22] and are given in Table IV.

Table IV. Dielectric Constant Data[a]

Isomer	w_2	e_{12}	$n^{20}D$
I	0.00000	2.2825	1.501100
	0.00103	2.2840	1.501205
$a_e = 0.9253$	0.00263	2.2853	1.501358
	0.00498	0.2880	1.501678
$a_n = 0.3037$	0.00750	2.2900	1.501992
	0.00991	2.2929	1.502116
	0.02436	2.3041	1.503501
II	0.00000	2.2825	1.501100
	0.00160	2.2894	1.501223
$a_e = 3.8089$	0.00412	2.2998	1.501490
$a_n = 0.3279$	0.00607	2.3074	1.501815
	0.00998	2.3187	1.502191
III	0.00000	2.2825	1.501065
	0.00258	2.2830	1.501239
$a_e = 1.2631$	0.00477	2.2885	1.501457
$a_n = 0.1862$	0.01004	2.2935	1.501760
	0.02336	2.3131	1.502757
IV	0.00000	2.2825	1.501065
	0.00100	2.2862	1.501114
$a_e = 2.8852$	0.00171	2.2888	1.501200
$a_n = 0.2122$	0.00238	2.2891	1.501220
	0.00343	2.2917	1.501316

[a] $a_e = [(e_{12} - e_1)/w_2]\ w_2 \rightarrow 0$, $a_n = [(n_{12}^2 - n_1^2)/w_2]w_2 \rightarrow 0$; e_1, dielectric constant of solvent; e_{12}, dielectric constant of solution; w_2, weight fraction of solute; n_1, refractive index of solvent; n_{12}, refractive index of solution.

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