

Figure 1.

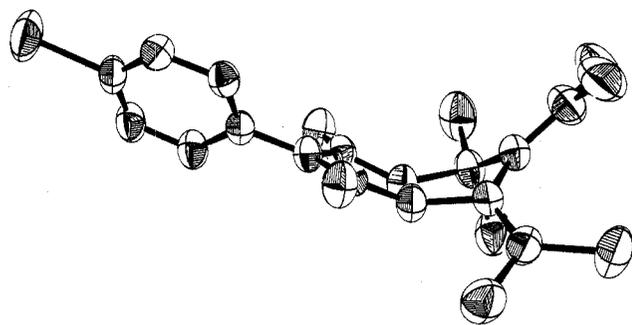
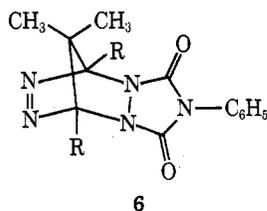


Figure 2.

12°) and bond angles deviate substantially from the normal [for example, C₁₈-C₁₄-C₁₅ (118.8°), C₁₅-C₁₉-C₂₀ (125.9°), C₂₀-C₁₉-C₂₁ (112.1°), and C₂₃-C₂₂-C₂₄ (114.4°)]. The C₁₉-C₂₀, C₁₉-C₂₁, and C₂₂-C₂₃ bond lengths are considerably longer (0.03–0.04 Å) than normal vinyl C–C bonds (such as C₂₂-C₂₄). These distortions arise from severe steric interactions between the C₁₈-C₂₀ and C₂₁-C₂₃ methyl groups, the C–C nonbonded distances being 3.124 (8) and 3.134 (8) Å, respectively. These distances are considerably less than the sum of the van der Waals radii for two methyls of 3.4 Å.¹⁰ The very close packing of the methyls is accomplished by intermeshing, or staggering, of the hydrogen atoms of the neighboring methyls. Inspection of a scale molecular model of 5a indicates that for racemization of the skewed diene chromophore to occur C₂₁ and C₂₃ must pass within ~2.1 Å of each other if no other bond angle deformations or distortions occur. This would seem to be a prohibitively short distance which would result in a very high energy barrier for enantiomerization (unless other distortions were to occur in the molecule to lengthen this distance in the transition state).

A structural feature of great interest with respect to possible dynamic processes in 5 is the nonplanarity about the N–N bridge (interplanar angle of 19.1° between planes C₈-N₁₀-N₁₁-C₁₂ and C₁₄-N₁₀-N₁₁-C₁₆). It had been implied previously from DNMR studies (over a temperature range of –60 to 60°) with 6 that the urazole ring in triazol-



6

inedione adducts was either rigid with the nitrogen atoms pyramidal or planar, or that inversion between pyramidal nitrogen forms was occurring rapidly at –60°.¹¹ Inspection of the scale molecular model of 5a indicates that the nonplanar N–N bridge is a structural characteristic of the molecule and is not the result of intra- or intermolecular inter-

Table I
Bond Lengths and Angles in Structure 5a

Bond type	Length, Å	Angle type	Value
Br–C ₁	1.895 (4)	C ₅ –C ₁ –C ₂	121.6 (4)
C ₁ –C ₂	1.387 (6)	C ₁ –C ₂ –C ₃	119.3 (4)
C ₂ –C ₃	1.386 (6)	C ₂ –C ₃ –C ₄	119.5 (4)
C ₃ –C ₄	1.374 (6)	C ₃ –C ₄ –C ₅	121.2 (4)
C ₄ –C ₅	1.398 (6)	C ₃ –C ₄ –N ₇	120.0 (4)
C ₅ –C ₆	1.387 (6)	C ₅ –C ₄ –N ₇	118.8 (4)
C ₆ –C ₁	1.383 (6)	C ₄ –C ₅ –C ₆	119.3 (4)
C ₄ –N ₇	1.433 (5)	C ₅ –C ₆ –C ₁	119.0 (4)
N ₇ –C ₈	1.404 (6)	C ₅ –N ₇ –C ₁₂	111.1 (3)
C ₈ –O ₉	1.207 (5)	O ₉ –C ₈ –N ₁₀	129.1 (4)
C ₈ –N ₁₀	1.362 (6)	C ₈ –N ₁₀ –N ₁₁	109.1 (3)
N ₁₀ –N ₁₁	1.419 (5)	C ₈ –N ₁₀ –C ₁₄	131.0 (4)
N ₁₁ –C ₁₂	1.377 (5)	N ₁₁ –N ₁₀ –C ₁₄	109.6 (3)
C ₁₂ –O ₁₃	1.205 (5)	N ₁₀ –N ₁₁ –C ₁₂	108.8 (3)
C ₁₂ –N ₇	1.395 (6)	N ₁₀ –N ₁₁ –C ₁₆	108.5 (3)
N ₁₀ –C ₁₄	1.515 (5)	C ₁₂ –N ₁₁ –C ₁₆	128.7 (4)
C ₁₄ –C ₁₅	1.539 (6)	N ₁₁ –C ₁₂ –O ₁₃	127.9 (4)
C ₁₄ –C ₁₇	1.538 (7)	N ₁₀ –C ₁₄ –C ₁₅	99.3 (3)
C ₁₄ –C ₁₈	1.525 (7)	C ₁₇ –C ₁₄ –C ₁₅	111.6 (4)
C ₁₅ –C ₁₆	1.464 (6)	C ₁₈ –C ₁₄ –C ₁₅	118.8 (4)
C ₁₅ –C ₁₉	1.336 (6)	C ₁₉ –C ₁₄ –C ₁₈	110.5 (4)
C ₁₆ –N ₁₁	1.453 (5)	C ₁₄ –C ₁₅ –C ₁₆	105.3 (3)
C ₁₆ –C ₂₂	1.325 (6)	C ₁₄ –C ₁₅ –C ₁₉	128.3 (4)
C ₁₉ –C ₂₀	1.521 (7)	C ₁₆ –C ₁₅ –C ₁₉	126.3 (4)
C ₁₉ –C ₂₁	1.516 (7)	C ₁₅ –C ₁₆ –N ₁₁	105.0 (4)
C ₂₂ –C ₂₃	1.524 (7)	C ₁₅ –C ₁₆ –C ₂₂	131.7 (4)
C ₂₂ –C ₂₄	1.485 (7)	N ₁₁ –C ₁₆ –C ₂₂	121.3 (4)
		C ₁₅ –C ₁₉ –C ₂₀	125.9 (5)
		C ₁₅ –C ₁₉ –C ₂₁	122.0 (5)
		C ₂₀ –C ₁₉ –C ₂₁	112.1 (4)
		C ₁₆ –C ₂₂ –C ₂₃	122.6 (4)
		C ₁₆ –C ₂₂ –C ₂₄	123.0 (4)
		C ₂₃ –C ₂₂ –C ₂₄	114.3 (4)

Table II
Interplanar Angles in 5a

Plane 1	Plane 2	Value, deg
Aromatic ring	C ₈ –N ₇ –C ₁₂	47.1
C ₈ –N ₁₀ –N ₁₁ –C ₁₂	C ₁₄ –N ₁₀ –N ₁₁ –C ₁₆	19.1
C ₁₄ –N ₁₀ –N ₁₁ –C ₁₆	C ₁₄ –C ₁₅ –C ₁₆	33.2
C ₁₄ –C ₁₅ –C ₁₆	C ₂₀ –C ₁₉ –C ₂₁	12.0
C ₁₅ –C ₁₆ –N ₁₁	C ₂₃ –C ₂₂ –C ₂₄	7.0
C ₁₅ =C ₁₉ —C ₂₁	C ₁₆ =C ₂₂ —C ₂₄	52.3
	—C ₂₀	
	—C ₂₃	

actions, or the distortion about the other five-membered ring. Further evidence in support of this is derived from the results of DNMR studies with 5b (vide infra).

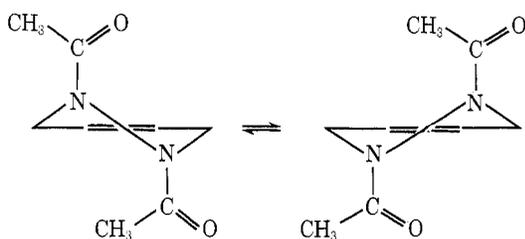
DNMR Studies with 5b. The room-temperature NMR spectrum of 5b in 1:1 dideuteriodichloromethane–trichlorofluoromethane displays methyl singlets at δ 1.67 (6 H), 1.72 (6 H), 1.87 (3 H), and 2.13 (3 H). On lowering the temperature the high-field singlet broadens and finally at temperatures below –48° becomes two symmetrical singlets¹² with $\Delta\delta$ 52.3 Hz (at 100 MHz). The coalescence temperature for the dynamic process is –28°, which gives $\Delta G^\ddagger_{-28} = 11.9$ kcal/mol. Further cooling to –110° resulted in no further changes.

Assignment of the resonances to the various methyl groups in 5b can be unambiguously made by comparison of chemical shifts with those observed for other adducts of similar structure,³ and by consideration of the environ-

ments of the methyl groups in **5b**. The lowest field methyl resonance represents the "outside" methyl of the C₆ isopropylidene group which resides in the plane of the neighboring carbonyl group and is thus deshielded.¹³ The δ 1.87 resonance represents the "outside" methyl of the C₇ isopropylidene group. The high-field resonance which broadens and forms two widely separated singlets at lower temperatures must represent the geminal methyls attached to C₈. The scale model of **5a** shows that one of the methyls is axially oriented while the other is equatorially oriented and resides in the plane of the neighboring carbonyl group and thus must be deshielded. It is this equatorial methyl which gives rise to the new low-field singlet at low temperatures.

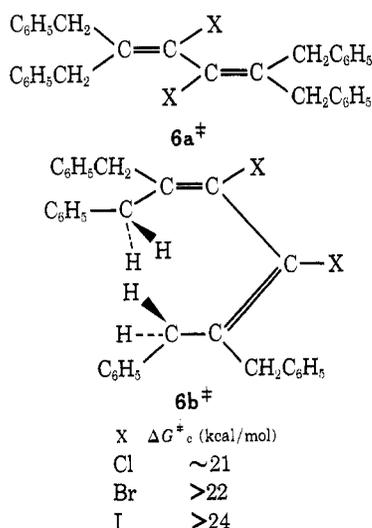
Two dynamic processes are possible in **5a** which would result in the exchange in the chemical environments of the two methyl groups attached to C₈: enantiomerization of the skewed diene chromophore or N-N bridge inversion. A number of considerations indicate that N-N bridge inversion is the phenomenon giving rise to the observed results.

The barrier for ring inversion in diacyltetrahydropyridazines and -piperidazines, i.e.



has been observed to be ~ 20 kcal/mol.¹⁴ In the planar transition state for this inversion process considerable steric strain must be generated between the acyl functions. In the inversion about the bridge nitrogens of **5**, however, the functions attached to the nitrogens are contained in a cyclic structure and the steric strain between these groups is not increased on going to the transition state. Therefore, the barrier for inversion should be considerably lower than 20 kcal/mol.

The studies of Mannschreck, Köbrich, and coworkers¹ have revealed enantiomerization barriers of ≥ 21 kcal/mol for the substituted butadienes **6**. They attribute this bar-



rier to rotation via the s-trans transition state (**6a[‡]**), which, on the basis of overall steric considerations, they believe to be lower in energy than rotation via the s-cis transition state (**6b[‡]**). As the inside benzyl groups in **6b[‡]** can adopt conformations in which the phenyl groups are oriented outward, the steric strain between the benzyl groups should

approximate that between the methyls in the transition state for enantiomerization of **5**. As the barrier in **6b[‡]** must be > 21 kcal/mol, one would similarly predict a barrier for enantiomerization in **5** of > 21 kcal/mol, a value far too high compared to the experimentally observed value of 11.9 kcal/mol for the dynamic process in **5**. Finally, our isolation of optically active **1** and **2**, which retain their optical activity unchanged for 10 days at 25°, indicates that the enantiomerization barrier must be considerable, certainly much greater than the observed 11.9 kcal/mol. Thus, all of the evidence thus far available indicates that the dynamic process observed with **5b** involves nitrogen bridge inversion and not enantiomerization of the skewed diene.

The barrier of 21.1 kcal/mol for the dynamic process observed with **4[‡]** is considerably higher than that observed with **5**. If the arguments and conclusions given in this paper are correct, the barrier in **4** is too high for ring nitrogen inversion. The lower barrier in **4** relative to that anticipated for enantiomerization of **5** could conceivably be due to the more flexible nature of the six-membered ring in **4** compared to the rather inflexible five-membered ring in **5**, thus allowing more facile distortion to lower the barrier to enantiomerization.

Experimental Section

Preparation of 5a. 4-(4-Bromophenyl)-1,2,4-triazoline-3,5-dione was prepared from 4-bromoaniline following the procedure of Cookson and coworkers¹⁵ giving a very reactive, purple-colored material. A solution of 0.26 g of the crude material in 10 ml of dichloromethane was added to 0.15 g of 2,2,3,3-tetramethylisobutylidene-cyclopropane dissolved in 5 ml of dichloromethane. The purple color of the triazolinedione was discharged immediately. The solvent was removed under reduced pressure and the residue was chromatographed on a 1.5 \times 10 cm column of silica gel. Elution with 5% ethyl acetate-chloroform gave 150 mg of product as colorless crystals, mp 122.5–124.0°. A crystal suitable for X-ray structural analysis was derived by evaporative recrystallization from methanol.

Crystal data: C₁₉H₂₂BrN₃O₂, mp 122.5–124.0°, monoclinic, space group *P*2₁/*c*, *a* = 12.418 (5), *b* = 15.799 (6), *c* = 10.095 (4) Å, and β = 102.70 (2)°. The calculated density was 1.416 g/cm³; an experimental density could not be determined owing to the limited amount of compound. Lattice constants were obtained from a least-squares refinement of the setting angles of 26 reflections, each collected at $\pm 20^\circ$, given by the automatic centering routine supplied with the diffractometer (λ 0.71069 Å) at the ambient laboratory temperature of 20 \pm 1°. Intensity data were collected on a Syntex P1 diffractometer using the θ - 2θ scanning technique with graphite-monochromated MO K α radiation. Details of the data collection and data reduction are essentially those given previously;¹⁶ 1983 reflections had $F_o > 3\sigma(F_o)$ and were considered to be observed. Only the observed data were used in the solution and refinement of structure. The structure was solved by the standard heavy-atom method¹⁷ and refined by full-matrix least-squares techniques¹⁸ to a final $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ of 0.043 and a weighted $R_2 = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$ of 0.055. The shift errors in the last cycle of refinement were all less than 0.05. All hydrogen atom positions were determined from a difference Fourier synthesis; electron density maxima appropriately located for hydrogen atom positions were about three times higher than the general background level in the map. These hydrogen atoms were included in the final cycles of least-squares refinement as fixed contributors. A final difference Fourier map was essentially featureless with the largest peak being 0.15 e/Å.³ (See paragraph at end of paper regarding supplementary material.)

Variable-Temperature NMR Studies with 5b. A dilute solution ($\sim 1\%$) of **5b[‡]** in 1:1 deuteriodichloromethane-trichlorofluoromethane (the low concentration was necessitated by the limited solubility of **5b** in the chosen solvent system at low temperatures) was triply freeze degassed in an NMR tube and sealed under a nitrogen atmosphere. The NMR spectra were recorded on a Varian XL100-15 spectrometer equipped with a variable-temperature probe and a Transform Technology TT100 Fourier transform. Because of the low concentration of the substrate and the different T1's of the hydrogens in **5b** the spectra were recorded using the Nicolet T1 Program/II (ten scans) with D1 = 10 sec, conditions

under which the hydrogens of **5b** are >98% relaxed giving singlets of appropriate relative intensities.

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Registry No.—**5a**, 54595-52-7; **5b**, 40755-74-6.

Supplementary Material Available. A listing of atomic coordinate positions and anisotropic thermal parameters will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for \$4.00 for photocopy or \$2.50 for microfiche, referring to code number JOC-75-1444.

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Photochemical Reactions of α,β -Unsaturated Acids, Esters, and Nitriles

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Cyclohexene-1-carboxylic acid, the corresponding methyl ester, and cyclohexene-1-carbonitrile undergo slow addition to electron-rich alkenes upon irradiation. Reaction occurs, very slowly, at the carbon-carbon double bond of the ester and nitrile to give [2 + 2] cycloadducts, sometimes accompanied by products of ene-like reactions. Cyclohexene-1-carboxylic acid gives ester **15** and lactone **16** via retro-type II processes.

The photochemical behavior of five- and six-membered ring conjugated enones is diverse and interesting, with reactions such as α -cleavage, oxetane formation, [2 + 2] cycloaddition to the carbon-carbon double bond, the lumirrearrangement to bicyclo[3.1.0]hexanones (in certain cases), and others being observed, depending on the presence or absence of coreactants.¹ It is believed that these molecules have lowest lying n,π^* and π,π^* triplet states of approximately equal energies, and that the precise structural details of the compound defines which state is of lowest energy, but that reactions from either state are possible in most cases.

On the other hand, the photochemical behavior of α,β -unsaturated acids and their derivatives, such as esters and nitriles, has, with the exception of a few specific compounds, been much less thoroughly investigated. The structures of the several [2 + 2] photodimers produced on irradiation of cinnamic acid in the solid state have been well worked out.² Cinnamic esters have been reported to undergo [2 + 2] photochemical addition to olefins in solu-

tion.³ Maleic anhydride, fumaric acid, and maleic acid, and also fumaronitriles, undergo [2 + 2] photodimerization most efficiently in the solid state.⁴ Coumarin undergoes direct and sensitized dimerization and sensitized addition to olefins, the former process apparently occurring via both singlet and triplet excited states.^{5a,c} α -Phenylcinnamic acids on irradiation close to β -lactones.⁶ Acrylonitrile dimerizes in the [2 + 2] fashion on photosensitization, whereas 2-cyanobutadiene undergoes two types of electrocyclic ring closure,⁷ just as does butadiene itself. This would imply that the reactive excited states of butadiene and the 2-cyano derivative are similar (i.e., π,π^*).

In other simple α,β -unsaturated acids, esters, and nitriles which have been examined, the photochemistry which has been observed has been similar to that exhibited by acyclic ketones. Both classes of compounds undergo processes such as (a) migration of the double bond to the β,γ position, probably via hydrogen abstraction by the carbonyl oxygen, as in the type II elimination (this has been observed in crotonic acid and crotonic esters);^{8,9} (b) cis-trans isomeriza-