

Table 4. *Hydrogen bonds*E.s.d.'s for $D \cdots A$ are 0.004 Å.

	Donor	Acceptor	$D \cdots A$	$D-H$	$H \cdots A$	$DH \cdots A$	Symmetry of A
Dimer (I)	N(2)	O(1)	2.872 Å	1.00 Å	1.91 Å	159°	$1-x, 1-y, 1-z$
	N(2')	W	2.903	0.99	1.91	175	$2-x, 2-y, 1-z$
	W	O(1')	2.836	0.92	1.95	162	$x, 2-y, -\frac{1}{2}+z$
	W	N(3')	2.909	0.92	1.99	172	$x, -1+y, z$
Addition compound (II)	N(2)	O(1)	2.869	0.99	1.88	177	$x, 1-y, 1-z$
	O(2)	O(1)	2.791	1.12	1.73	157	$1+x, y, z$

the OH group can make a hydrogen bond with N(2) of the dimer.

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The Tricyclic Photorearrangement Product from the Addition of 3-Methyl-5,6-diaza-2,4-cyclohexadien-1-one to 2-Propenol, 7-Hydroxymethyl-8-methyl-2,3-diazatricyclo[3.3.0.0^{2,8}]octan-4-one, C₈H₁₂N₂O₂

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Abstract. C₈H₁₂N₂O₂, triclinic, $P\bar{1}$, $a = 6.953$ (4), $b = 7.811$ (8), $c = 8.328$ (7) Å, $\alpha = 94.34$ (7), $\beta = 91.43$ (6), $\gamma = 115.29$ (6)°, $V = 407.0$ Å³, $Z = 2$, $M_r = 168.2$, m.p. = 413 K (decomp.), $D_x = 1.372$ g cm⁻³, $R = 6.4\%$ for 1039 independent reflections measured to $2\theta = 112^\circ$. Irradiation of a solution containing 3-methyl-5,6-diaza-2,4-cyclohexadien-1-one and 2-propenol produces a cyclobutane addition compound which, upon further irradiation, opens and switches bonds to form a tricyclic molecule. Crystal-structure analysis has established that the molecule contains one three-membered ring and two five-membered rings.

Introduction. The irradiation by ultraviolet light of a solution containing 4-methyl-5,6-diaza-2,4-cyclohexadien-1-one and 2-propenol leads to a cyclobutane-type addition product with the hydroxyl group *anti* with respect to the carbonyl O (Karle, 1982; Kanaoka, Hasebe & Sato, 1980; Hasebe, 1980). The same procedure with the isomeric 3-methyl-5,6-diaza-2,4-cyclohexadien-1-one (I) leads to a cyclobutane addition

product (II) and then proceeds further to yield a rearrangement product. The objective of the crystal-structure analysis presented in this paper was to elucidate the structural formula, and stereochemistry, of the rearrangement product which has been shown to be (III).

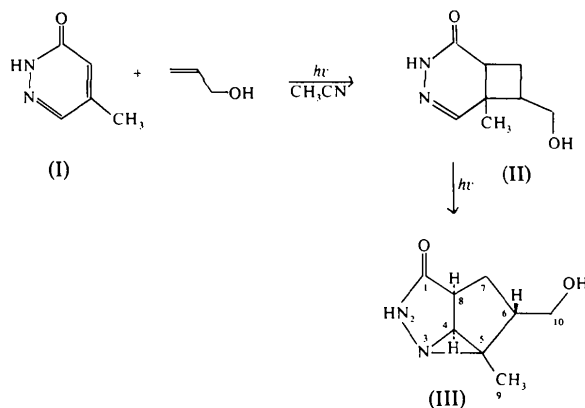


Table 1. Fractional coordinates and B_{eq} values

The e.s.d.'s for x , y and z are 0.0006, 0.0005 and 0.0004 respectively. For B_{eq} the e.s.d. is less than 0.1 Å². $B_{eq} = \frac{4}{3} \sum_i \sum_j \beta_{ij} a_i \cdot a_j$.

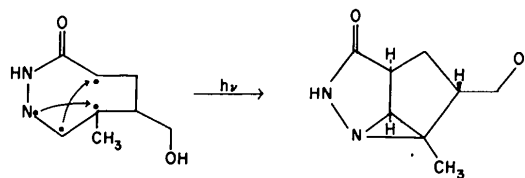
	x	y	z	B_{eq} (Å ²)
O(1)	0.5604	0.2319	1.0749	3.5
O(2)	0.0540	0.5178	0.7744	3.6
C(1)	0.5029	0.1996	0.9310	2.9
N(2)	0.6230	0.2773	0.8096	3.0
N(3)	0.5297	0.1947	0.6511	3.0
C(4)	0.3124	0.0458	0.6798	3.0
C(5)	0.3283	0.2195	0.6061	2.7
C(6)	0.2645	0.3392	0.7272	2.4
C(7)	0.1614	0.2048	0.8597	2.8
C(8)	0.2773	0.0751	0.8563	2.9
C(9)	0.2981	0.2209	0.4263	4.1
C(10)	0.1181	0.4160	0.6546	3.3

Crystals of (III) in the form of colorless plates, grown from a mixture of acetone and ethyl acetate, were provided by Professor Yuichi Kanaoka, Hokkaido University. Diffraction data were collected on a Nicolet P3F diffractometer equipped with a graphite monochromator. The θ - 2θ scanning mode was used with variable scanning speed dependent upon the magnitude of the intensity and data were collected to $2\theta_{max} = 112^\circ$ with Cu $K\alpha$ radiation (1.54178 Å). Three reflections used as standards were measured at intervals of 50 measurements. Their intensities remained constant during the data collection. The data were corrected for Lorentz and polarization effects but not for absorption.

The structure was solved by direct phase determination using the symbolic addition procedure. The positions of the H atoms were derived from a difference map. Anisotropic full-matrix least-squares refinement of the non-H atoms and refinement of only the coordinates for the H atoms resulted in an R factor of 6.4% for all 1039 data. The function minimized was $\sum w(|F_o| - |F_c|)^2$ with weighting based on counting statistics (Gilardi, 1973). Coordinates and B_{eq} values for the non-H atoms are listed in Table 1.*

Discussion. The tricyclic photorearrangement product (III) is shown in Fig. 1 (the numbering of the atoms does not correspond to the numbering required for the chemical name of the molecule). The derivation of the tricyclic product from its precursor, the cyclobutyl photoaddition product (II), is easily conceived by the opening of the C-N double bond and the bond separating the four- and six-membered rings, and subsequently switching bonds as indicated:

* Lists of structure factors, anisotropic thermal parameters and coordinates for H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36471 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.



The tricyclic compound (III) is presumably more stable than the cyclobutyl compound (II). Although the structure of (II) has not been determined, the structure of an isomer of (II), the cyclobutyl addition product of 4-methyl-5,6-diaza-2,4-cyclohexadien-1-one and 2-propenol, has been described in the preceding paper (Karle, 1982). In that molecule, the C-C bond lengths in the cyclobutyl ring range from 1.551 to 1.563 Å, whereas the C-C bond lengths in the five- and three-membered rings in the tricyclic molecule range from 1.513 to 1.551 Å, Fig. 2. The contraction of the C-C bond lengths is correlated with a rearrangement to a more stable molecule. A similar contraction of C-C bond lengths upon rearrangement to a more

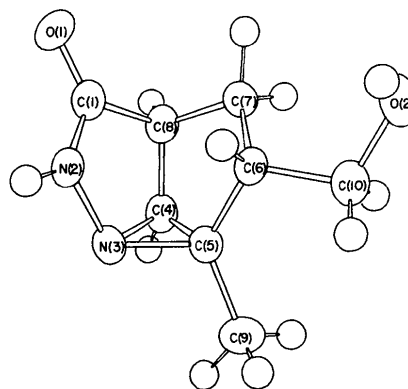


Fig. 1. Computer drawing of the photorearrangement product 7-hydroxymethyl-8-methyl-2,3-diazatricyclo[3.3.0.0^{2,8}]octan-4-one. (The crystallographic numbering does not correspond to the chemical name.) The thermal ellipsoids are drawn at the 50% probability level.

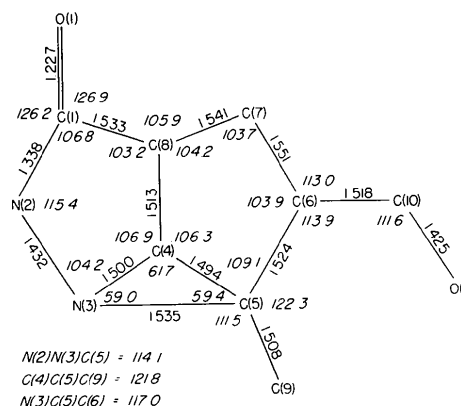


Fig. 2. Bond lengths (Å) and angles (°). The e.s.d.'s for bond lengths are near 0.006 Å and for bond angles they are near 0.3°.

stable isomer that involved changing four-membered rings to five- and three-membered rings has been observed in two photodimers obtained from tyramine (Iwakuma, Nakai, Yonemitsu, Jones, Karle & Witkop, 1972).

Torsional angles are shown in Table 2. The five-membered ring containing a planar C(1) atom and a planar N(2) atom is approximately planar with maximum deviations of ± 0.10 Å from the least-squares plane. The five-membered ring containing all saturated C atoms has the usual envelope conformation with

atoms C(8), C(4), C(5) and C(6) nearly in a plane, with maximum deviations of ± 0.05 Å from a least-squares plane and atom C(7) placed at 0.53 Å from that plane.

Pairs of hydrogen bonds between the OH and carbonyl O atoms link pairs of molecules around a center of symmetry. In the O(2)H...O(1) hydrogen bond, the O(2)—O(1) length is 2.751 Å. Another hydrogen bond, N(2)H...O(2), where N(2)—O(2) is 2.813 Å, links molecules head-to-tail along the *a* direction to complete a hydrogen-bonded layer, two molecules thick, in the *a* and *c* directions.

Table 2. Torsional angles (°)

E.s.d.'s are of the order of 0.6°.

C(8)C(1)N(2)N(3)	-13	C(5)C(6)C(7)C(8)	+30
C(1)N(2)N(3)C(4)	+2	C(6)C(7)C(8)C(4)	-36
N(2)N(3)C(4)C(8)	+10	C(7)C(8)C(4)C(5)	+29
N(3)C(4)C(8)C(1)	-17	N(3)C(4)C(5)C(9)	98
C(4)C(8)C(1)N(2)	+18	C(5)C(6)C(10)O(2)	177
C(8)C(4)C(5)C(6)	-10	C(6)C(10)O(2)H	61
C(4)C(5)C(6)C(7)	-13		

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Structure of 1-(*p*-Methoxyphenyl)-*trans*-1,2-diphenylbut-1-ene

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Abstract. C₂₃H₂₂O, triclinic, *P*1, *a* = 9.644 (3), *b* = 10.0001 (3), *c* = 10.4999 (3) Å, α = 78.77 (3), β = 67.53 (3), γ = 74.91 (2)°, *V* = 898.3 Å³, *d*_c = 1.16 Mg m⁻³, *Z* = 2. There are two independent molecules in the asymmetric unit, which have very similar conformations. The structure was refined to a final *R* of 0.0586 for 2294 significant reflections.

Introduction. The title compound, 1-(*p*-methoxyphenyl)-*trans*-1,2-diphenylbut-1-ene, synthesized according to the method of Sohár, Ábráham, Schneider, Horváth & Fuggerth (1979), is a synthetic precursor of the

antiœstrogenic drug tamoxifen {1-[*p*-(2-dimethylaminoethoxy)phenyl]-*trans*-1,2-diphenylbut-1-ene} which is in current use for the treatment of disseminated breast cancer.

A majority of breast tumours have identifiable œstrogen receptors, and their presence indicates a potential starting point for hormonal therapy (Camerman, Chan & Camerman, 1980). Œstradiol (the natural œstrogen) normally forms a complex with a protein receptor in the cytoplasm and this complex can then enter the nucleus and activate protein synthesis. Antiœstrogens compete with œstradiol for this receptor