Subsequent elution with 1:1 hexane–benzene yielded 1.7 g of desired product whose distillation afforded 1.6 g of 1-diazo-2-octanone (**25**): bp 55° (0.3 Torr); infrared (neat) N_2 4.74 (s), C=O 6.08 (s) μ; pmr δ 0.7–1.0 (m, 3, Me), 1.1–1.9 (m, 8, methylenes), 2.1–2.5 (m, 2, ketomethylene), 5.28 (s, 1, CH).

A solution of 1.4 g of **25** in 3 ml of methylcyclohexane was added over a period of 1 hr to a refluxing mixture of 0.80 g of isopropenyl acetate and 0.2 g of copper–bronze[21c] in 5 ml of methylcyclohexane and the mixture refluxed for an additional 12 hr. It was filtered, the residue washed with methylcyclohexane, and the combined organic solutions were evaporated. Chromatography of the residual oil, 1.4 g, on alumina, activity I, and elution with hexane gave 1.0 g of colorless oil whose distillation produced a stereoisomeric mixture of 1-acetoxy-1-methyl-2-enanthylcyclopropane (**27**): bp 92–94° (1 Torr); infrared (neat) C=O 5.73 (s), 5.88 (s) μ; pmr δ 1.44 (s, 3, quaternary Me in one isomer), 1.53 (s, 3, quaternary Me in other isomer), 2.00 (s, 3, Ac in one isomer), 1.92 (s, 3, Ac in other isomer), 0.7–2.8 (m, 16, other Hs).

Anal. Calcd for $C_{13}H_{22}O_3$: C, 68.99; H, 9.80. Found: C, 69.13; H, 9.90.

A solution of 800 mg of **27** and 10 ml of 5% sodium hydroxide in 10 ml of methanol was kept at room temperature for 20 hr. The alcohol was removed under vacuum and the remaining aqueous solution extracted with ether. The extract was washed with water, dried, and evaporated. The residual oil, 590 mg, was chromatographed on activity I alumina. Elution with hexane yielded 490 mg of dihydrojasmone (**28**), infrared and pmr spectrally identical with an authentic specimen; semicarbazone, mp, mmp 173–175°.

Acknowledgment. The authors are indebted to Mr. Richard M. Charnah[56] for technical assistance and to Eli Lilly and Co. and the National Science Foundation for support of this investigation.

[56] National Science Foundation undergraduate research participant, summer 1969.

The Crystal and Molecular Structure of 3,7-Bis(*p*-iodophenyl)-4,5,6-triphenyl-4*H*-1,2-diazepine

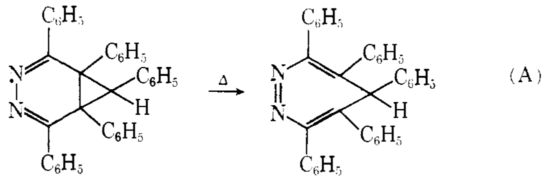
J. N. Brown, R. L. Towns, and L. M. Trefonas*

Contribution from the Department of Chemistry, Louisiana State University in New Orleans, New Orleans, Louisiana 70122. Received May 18, 1970

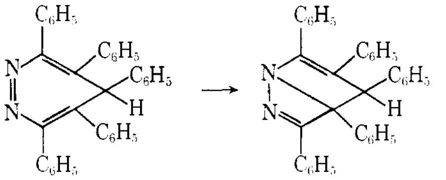
Abstract: The crystal and molecular structure of 3,7-bis(*p*-iodophenyl)-4,5,6-triphenyl-4*H*-1,2-diazepine has been determined by single-crystal X-ray diffraction methods. The compound crystallizes in space broup $P\bar{1}$ (No. 2) with unit cell constants: a = 10.463 (1), b = 13.418 (1), c = 12.082 (1) Å, α = 97.86 (1), β = 107.06 (1), and γ = 109.19 (1)°. The structure was solved by the heavy-atom method and refined by block-diagonal least-squares to a final R value of 0.072 for the 2654 independently measured, statistically significant reflections. The seven-membered ring differs in conformation and location of the double bonds from either of the previously postulated structures. A mechanism for the formulation of this thermal isomer is proposed herein.

The synthesis and characterization of heterocyclic unsaturated seven-membered ring systems is a relatively new field. The inherent synthetic difficulties with these compounds are further complicated by the ambiguities resulting in structure assignments based on routine physical techniques (ir, uv, nmr, mass spectrum fragmentation).

For example, the adduct of triphenylcyclopropene with diphenyl-*s*-tetrazine can be thermally isomerized at temperatures above 100° to a second stable compound. Sauer and Heinrich[1] postulated structures for the two isomeric forms on the bases of uv correlations as shown in (A). Battiste and Barton,[2] using ir, uv, and nmr techniques, reasonably established that the structure of the low-temperature isomer was that previously assigned to the high-temperature form, namely II. Battiste then suggested that the high-temperature thermal isomer was a bicyclic system (both are illustrated in (B)) from which one could then easily rationalize mass spectrum fragmentation products such as benzonitrile.

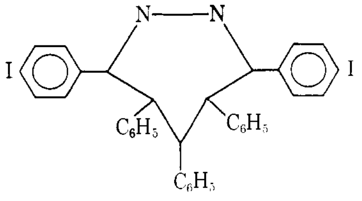


I II (A)



II III (B)

In order to resolve this difference and to establish definitely the structure of the high-temperature form, a single-crystal X-ray structure determination was undertaken. The compound studied, a heavy atom derivative, is shown in IV (bonding within the seven-membered ring not indicated here). The structure determination indicated that both previous authors



IV

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* To whom correspondence should be addressed.

(1) J. Sauer and E. Heinriche, *Tetrahedron Lett.*, 4979 (1966).

(2) M. A. Battiste and T. J. Barton, *ibid.*, 1227 (1967).

were incorrect in their structure assignments of the high-temperature form of this thermal isomer.

Experimental Section

3,7-Bis(*p*-iodophenyl)-4,5,6-triphenyl-4*H*-1,2-diazepine ($C_{33}H_{24}N_2I_2$) crystallized in the form of rhombohedral crystals from solvent exchange of carbon tetrachloride and diethyl ether. A crystal (approximately 0.15 × 0.11 × 0.04 mm) was mounted with the (00*l*)-axis coincident with φ. Polar plots of the reciprocal lattice showed no mirror symmetry, indicating space groups $P1$ (No. 1) or $P\bar{1}$ (No. 2). A primitive lattice was chosen and lattice constants were determined by a least-squares fit of 47 carefully measured 2θ values using copper radiation. The resultant lattice constants and their estimated standard deviations are $a = 10.463 \pm 0.001$ Å, $b = 13.418 \pm 0.001$ Å, $c = 12.082 \pm 0.001$ Å, $\alpha = 97.86 \pm 0.01$, $\beta = 107.06 \pm 0.01°$, $\gamma = 109.19 \pm 0.01°$. The calculated density (assuming two molecules per unit cell) is 1.64 g/cm^3 as compared to the experimental density of 1.63 g/cm^3 (determined by a flotation method).

Intensity data were collected on a General Electric XRD-490 fully automated diffractometer by the (stationary crystal)–(stationary counter) method using balanced zirconium and yttrium filters and molybdenum Kα radiation. A total of 5040 independent reflections were measured in the unique hemisphere to a 2θ maximum of 50° ($d = 0.840$ Å). The linear absorption coefficient with this radiation was only 21.76 cm^{-2}, therefore no absorption correction was deemed necessary. A reflection was considered observable if

$$(I_{\mathrm{Zr}} - 2\sigma(I_{\mathrm{Zr}})) - (I_{\mathrm{Y}} + 2\sigma(I_{\mathrm{Y}})) \geq I_{\mathrm{B}}$$

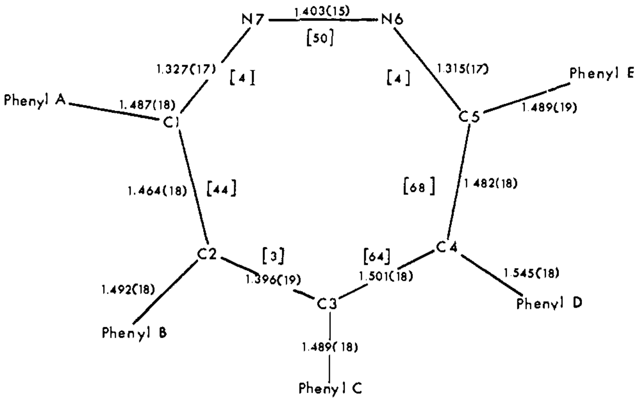
in which I_{B} is a background intensity determined as a function of 2θ and the σ's are based on counting statistics. Using this criterion, 2654 reflections (approximately 53% of the total measured) were in the observable range.[3] The Lorentz polarization corrections were applied, and the corrected intensities were then reduced to structure amplitudes in the usual manner.

Determination of Structure

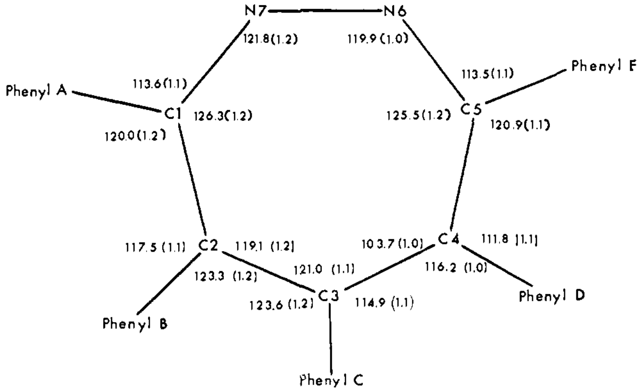
The Patterson function was calculated to locate the two iodines and to determine the space group. If the space group were $P1$, six unique iodine–iodine vectors, in addition to the origin, would be expected; if it were $P\bar{1}$, then four unique vectors, in addition to the origin, would be expected. Examination of the map showed only three unique peaks of sufficient density to be I–I vectors, one of which was more dispersed than the others. By assuming two I–I vectors partially overlapping in the region of the dispersed peak, coordinates were chosen for the two iodine atoms (in $P\bar{1}$) which were fully consistent with the remaining large peaks. Five cycles of block diagonal isotropic refinement of the iodine positions using unit weights gave an R value = 0.354. An electron density map phased by the iodines showed 37 peaks in addition to the two iodine peaks. A bond scan showed these peaks to be the nonhydrogen atoms needed. The nitrogen positions were easily determined since no phenyl rings were bonded to these atoms. Five more cycles of block diagonal least squares (weighted by $1/\sigma^2$) with isotropic temperature factors for all 39 atoms refined to an R value = 0.221. The isotropic temperature factors were converted to anisotropic temperature factors and several more cycles of similarly weighted anisotropic refinement yielded a final R value = 0.072.

Results and Discussion

The coordinates and anisotropic temperature factors of all of the atoms, together with their estimated standard deviations, are summarized in Table I. For the lighter (noniodine) atoms, estimated standard deviations are about 0.015 Å in the bond distances and 1.5° in the bond angles. Structures V and VI show the bond angles, dihedral angles, and bond distances (exclusive of those in the phenyl rings) for the molecule.



V



VI

One can further gauge the overall reliability of all of the molecular parameters by comparing those parts of the structure (namely, the phenyl rings) for which accurately determined literature values are available.[4] Our values averaged over all five phenyl rings in this structure are 1.415 Å for the bond distances and 120.0° for the bond angles. The average deviations for these 30 independently determined results (0.012 Å for the bond distances and 1.7° for the bond angles) are in agreement with the estimated standard deviations. Further corroboration is obtained by calculating the best least squares fit to a plane for each of the phenyl rings. Each of the phenyl rings fit a least squares equation of a plane of the form

$$Ax + By + Cz = D$$

with an average error of less than 0.016 Å for each atom. The two I–C distances (2.120 and 2.094 Å) lie within the literature range (2.03–2.13 Å) previously reported for such distances.[5] Table II summarizes the bond

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(3) A listing of the values of the observed and calculated structure factors has been deposited as Document No. 01143 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington, 25, D. C. A copy may be secured by citing the document number and by remitting $5.00 for photoprints, or $2.00 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

(4) "Tables of Interatomic Distances and Configuration in Molecules and Ions," Special Publication No. 11, The Chemical Society, London, 1958, Supplement 1964.

(5) (a) L. M. Trefonas and R. Majeste, *J. Heterocycl. Chem.*, **2**, 80 (1965); (b) H. Zacharis and L. M. Trefonas, *ibid.*, 7, 775 (1970).

Table I. Final Least Squares Parameters

Atom	Fractional coordinate (ESD × 10^4)			Anisotropic temperature factors[a] (ESD × 10^4)					
	X	Y	Z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
I1	−0.0783 (1)	−0.0314 (1)	−0.2258 (1)	104 (2)	94 (1)	186 (2)	−3 (1)	18 (1)	−44 (1)
I2	1.2769 (1)	0.9823 (1)	0.5888 (1)	129 (2)	48 (1)	171 (2)	5 (1)	−12 (1)	0 (1)
C1	0.5242 (13)	0.3543 (10)	0.0897 (11)	94 (19)	52 (11)	61 (15)	21 (11)	23 (13)	18 (10)
C2	0.6584 (12)	0.3421 (10)	0.0907 (11)	71 (17)	56 (11)	59 (14)	25 (11)	25 (13)	20 (10)
C3	0.7750 (12)	0.3762 (9)	0.1992 (11)	92 (19)	43 (10)	69 (15)	28 (11)	40 (13)	32 (10)
C4	0.7661 (13)	0.4283 (9)	0.3134 (10)	117 (19)	32 (9)	35 (13)	24 (11)	44 (13)	12 (8)
C5	0.7502 (12)	0.5305 (10)	0.2920 (11)	69 (18)	58 (11)	66 (15)	25 (11)	13 (13)	−3 (10)
N6	0.6366 (10)	0.5364 (8)	0.2143 (10)	88 (15)	44 (9)	105 (14)	27 (9)	26 (12)	9 (9)
N7	0.5139 (10)	0.4409 (8)	0.1481 (9)	76 (15)	59 (9)	87 (13)	25 (9)	25 (11)	14 (9)
C8	0.3813 (12)	0.2654 (9)	0.0154 (11)	81 (18)	50 (10)	53 (14)	13 (11)	21 (13)	2 (10)
C9	0.2613 (13)	0.2919 (10)	−0.0402 (11)	80 (19)	72 (12)	73 (16)	40 (12)	27 (14)	15 (11)
C10	0.1276 (13)	0.2071 (10)	−0.1102 (12)	105 (21)	58 (11)	73 (16)	13 (12)	19 (14)	−12 (11)
C11	0.1206 (13)	0.0997 (12)	−0.1186 (12)	51 (18)	105 (15)	79 (17)	−6 (13)	4 (14)	−28 (12)
C12	0.2374 (14)	0.0711 (11)	−0.0666 (12)	110 (22)	80 (13)	80 (17)	30 (14)	19 (15)	30 (12)
C13	0.3734 (14)	0.1578 (10)	0.0018 (12)	140 (23)	34 (10)	96 (18)	9 (12)	24 (16)	7 (11)
C14	0.8717 (13)	0.6386 (10)	0.3547 (11)	89 (19)	56 (11)	71 (16)	10 (12)	20 (14)	22 (11)
C15	1.0171 (13)	0.6444 (10)	0.3857 (11)	98 (20)	67 (12)	68 (15)	38 (13)	44 (14)	10 (11)
C16	0.1379 (14)	0.7450 (9)	0.4508 (12)	136 (22)	30 (9)	83 (16)	5 (12)	48 (15)	13 (10)
C17	1.1052 (13)	0.8354 (10)	0.4827 (12)	111 (21)	48 (11)	80 (17)	−8 (12)	10 (15)	2 (11)
C18	0.9629 (14)	0.8341 (11)	0.4522 (13)	119 (23)	59 (12)	124 (20)	20 (13)	27 (17)	14 (12)
C19	0.8439 (14)	0.7322 (9)	0.3827 (12)	133 (22)	23 (9)	103 (17)	13 (11)	36 (16)	2 (10)
C20	0.6439 (12)	0.3590 (9)	0.3512 (11)	72 (18)	51 (10)	61 (14)	29 (11)	2 (12)	17 (10)
C21	0.6107 (14)	0.4165 (11)	0.4398 (12)	127 (22)	75 (13)	73 (16)	39 (13)	55 (15)	23 (11)
C22	0.5073 (14)	0.3539 (12)	0.4844 (12)	131 (23)	107 (15)	64 (16)	57 (15)	32 (15)	33 (13)
C23	0.4395 (13)	0.2366 (11)	0.4410 (13)	75 (19)	89 (14)	113 (19)	39 (13)	24 (15)	40 (13)
C24	0.4756 (13)	0.1845 (10)	0.3546 (12)	96 (20)	67 (12)	85 (17)	27 (12)	31 (14)	30 (11)
C25	0.5779 (13)	0.2446 (10)	0.3104 (11)	83 (19)	64 (12)	67 (15)	15 (12)	12 (13)	22 (11)
C26	0.9210 (12)	0.3783 (9)	0.2092 (12)	57 (17)	45 (10)	97 (17)	21 (11)	29 (13)	1 (10)
C27	0.9875 (13)	0.3316 (11)	0.2953 (12)	82 (19)	74 (12)	73 (16)	43 (12)	9 (13)	12 (11)
C28	1.1259 (14)	0.3354 (11)	0.3062 (11)	124 (22)	98 (14)	44 (15)	60 (14)	12 (14)	−5 (11)
C29	1.1989 (14)	0.3867 (12)	0.2337 (13)	109 (22)	103 (15)	90 (18)	34 (15)	32 (16)	−31 (13)
C30	1.1320 (15)	0.4336 (12)	0.1474 (13)	120 (23)	110 (16)	102 (19)	26 (15)	55 (17)	6 (14)
C31	0.9914 (13)	0.4303 (11)	0.1355 (12)	88 (20)	84 (13)	82 (17)	28 (13)	46 (15)	6 (12)
C32	0.6599 (13)	0.2874 (10)	−0.0248 (11)	80 (18)	64 (11)	52 (14)	4 (11)	33 (13)	−10 (10)
C33	0.7106 (15)	0.2020 (11)	−0.0258 (13)	131 (23)	75 (13)	100 (18)	29 (14)	30 (17)	−13 (12)
C34	0.7148 (15)	0.1497 (13)	−0.1330 (13)	134 (25)	126 (18)	86 (19)	12 (17)	43 (17)	−18 (14)
C35	0.6593 (16)	0.1794 (13)	−0.2392 (15)	153 (27)	116 (17)	127 (22)	−21 (17)	75 (20)	−12 (15)
C36	0.6061 (16)	0.2653 (13)	−0.2361 (14)	151 (27)	113 (17)	115 (21)	−20 (17)	51 (19)	27 (15)
C37	0.6042 (14)	−0.3192 (11)	−0.1269 (11)	113 (21)	112 (15)	13 (13)	−5 (14)	26 (13)	13 (11)

[a] Anisotropic temperature factors in the form $\exp(-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}l^2 - 2\beta_{12}hk - 2\beta_{13}hl - 2\beta_{23}kl)$.

distances, bond angles, and deviations from planarity for the five phenyl rings.

The main focus of this study, of course, was not to reconfirm known molecular parameters but rather to determine the nature, conformation, bonding, and molecular parameters of the central ring (see V and VI). The bonding of the phenyl rings to this central ring is itself quite revealing. The four rings presumed to be trigonally bonded (phenyls A, B, C, E) are 1.489 ± 0.007 Å from the central ring and each forms angles of 118.4 ± 3.7° with the central ring. The ring presumed to be tetrahedrally bonded (phenyl D) is 1.545 Å from the central ring and forms angles of 111.8 and 116.2° with the central ring. The bond distances in all cases confirm the type of bonding assumed and the slight distortions in angles result from the steric difficulties in aligning five adjacent phenyl rings about a seven-membered ring.

The bonding pattern within the seven-membered ring is at variance with both previously predicted structures.[1,2] The N6–N7 bond length of 1.403 Å approximates the single bond distance of 1.383 which has been found previously in a system where the nitrogen atoms in turn form double bonds with the adjacent carbon atoms.[6] The NC double bond distances (1.315 and 1.327 Å) are in close agreement with the C=N distance of 1.302 Å given in the literature.[7] The remaining bond with multiple bond character (C2–C3 = 1.396 Å) would have a bond order of at least 1.75 based on a plot of π-bond order *vs.* inverse square of the bond length as suggested by Gordy[8] and calibrated on the basis of a large number of values taken from the Chemistry Society Tabulation.[4] It can thus be assumed to constitute the last of the multiple bonds within this ring. The angles involved at each of these double bond positions range in value from 119.1 to 122.5° with an average value of 120.0 ± 0.9°, again corroborating the assignment of the double bonds.

Although the somewhat shortened ring distances (N–N = 1.400 Å, C1–C2 = 1.464 Å) suggest a delocalization of charge through these bonds, the dihedral angles in the ring (shown in structure V) clearly indicate that these atoms deviate widely from planarity (which would be indicated by dihedral angles near 0°). At C4, where we have assumed that phenyl ring D is tetrahedrally attached, the dihedral angles lie very close to the theoretical value of 60° which would be predicted for tetrahedral bonding. Further support for this geometry is evident from the C4–C3 and C4–C5

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(6) B. Bak, D. Christensen, J. Rastrup-Andersen, and E. Tannenbaum, *J. Chem. Phys.*, **24**, 720 (1956).

(7) L. M. Trefonas, *et al.*, *J. Amer. Chem. Soc.*, **88**, 2145 (1966).

(8) W. Gordy, *J. Chem. Phys.*, **15**, 305 (1947).

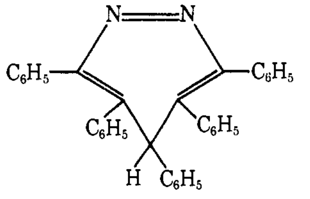
Table II. Data on Phenyl Rings. Bond Distances, Bond Angles, Least Squares Planes

		Distances (ESD × 10^{-3}), Å	Angles (ESD), deg
	Ring A	1.421 (19)	123.1 (1.2)
		1.402 (19)	118.9 (1.2)
		1.406 (21)	117.0 (1.3)
		1.401 (20)	125.3 (1.3)
		1.422 (20)	117.2 (1.3)
		1.403 (18)	118.4 (1.3)
C_{11}–I_1		2.120 (15)	116.1, 118.5 (1.1)
	Ring B	1.414 (20)	123.4 (1.3)
		1.406 (22)	119.6 (1.4)
		1.414 (24)	118.9 (1.5)
		1.436 (24)	120.4 (1.5)
		1.424 (21)	120.5 (1.5)
		1.389 (19)	117.5 (1.4)
	Ring C	1.415 (19)	122.3 (1.2)
		1.398 (20)	118.2 (1.2)
		1.427 (21)	120.8 (1.3)
		1.420 (22)	120.9 (1.4)
		1.421 (21)	118.7 (1.4)
		1.428 (19)	119.0 (1.3)
	Ring D	1.425 (19)	121.0 (1.2)
		1.426 (21)	117.7 (1.3)
		1.442 (22)	120.8 (1.3)
		1.388 (20)	119.3 (1.3)
		1.404 (19)	120.7 (1.3)
		1.404 (19)	120.6 (1.2)
	Ring E	1.429 (19)	120.9 (1.2)
		1.430 (19)	120.8 (1.2)
		1.400 (19)	116.4 (1.3)
		1.418 (21)	124.7 (1.3)
		1.442 (20)	117.3 (1.3)
		1.399 (19)	119.6 (1.3)
C_{17}–I_2		2.095 (14)	117.0, 118.2 (1.0)

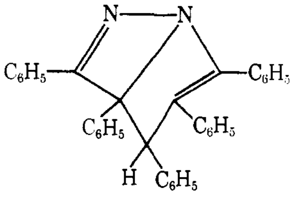
Ring	Av distance (av dev),[a] Å	Av angle (av dev),[b] deg	Equation of planes (std dev)
A	1.409 (0.010)	120.0 (2.8)	$-0.5247P - 0.2464Q + 0.8149R + 2.141 = 0$ (0.012)
B	1.414 (0.011)	120.0 (1.3)	$+0.7362P + 0.6496Q + 0.1899R - 6.561 = 0$ (0.012)
C	1.418 (0.009)	120.0 (1.3)	$-0.0739P + 0.7199Q + 0.6902T - 4.082 = 0$ (0.004)
D	1.415 (0.016)	120.0 (1.0)	$+0.6355P - 0.2744Q + 0.7217R - 4.355 = 0$ (0.003)
E	1.419 (0.015)	120.0 (2.0)	$-0.2367P - 0.4589Q + 0.85464R + 1.055 = 0$ (0.016)

[a] Overall distance $1.41_5 \pm 0.01_2$ A. [b] Overall angle 120.0 ± 0.7°.

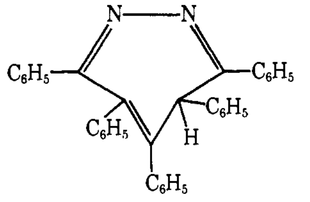
distances of 1.50_1 and 1.48_2 Å, respectively, and the internal angle at C4 of 103.7°. Thus a comparison of our result to those previously postulated (II, III, VII)



II, Sauer[1]



III, Battiste[2]



VII, this study

shows that neither previous author was correct in the structure assignment. It seems reasonable to assume that the conformation in solution would be similar to that determined for the crystal since there are no relatively close intermolecular contacts in the crystal. Only four iodine–carbon contacts of less than 4.0 Å (3.69, 3.74, 3.75, and 3.89 Å) are found between molecules and only one pair of light atom intermolecular contacts (N6–C9 = 3.45 Å) exists. To assist the reader in visualizing the conformation of the molecule, Figures 1 and 2 are included. Figure 1 is a three-dimensional ORTEP[9] drawing of the molecule and Figure 2 is a projectional drawing of the seven-membered ring.

Recent information regarding the structure to be assigned to the low-temperature isomer[10] leads to several plausible paths to the final product. The simplest to visualize is a 1,2 shift directly from the norcaradiene structure. Alternatively one can start with Sauer's low-temperature isomer and assuming Battiste's structure as an intermediate, a possible mechanism for the thermal conversion would involve either a 1–7 shift or two 1–5 shifts as illustrated in Scheme I. The latter choice (consecutive 1–5 shifts) seems more reasonable than a 1–7 shift by analogy to sigmatropic processes in the carboxyclic system, cyclohepta-1,3,5-triene.[11] Such a sequence of consecutive 1–5 shifts would not preclude an additional bicyclic

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[9] C. K. Johnson, ORTEP ORNL-3794, Oak Ridge National Laboratories, Nashville, Tenn., 1965.

[10] C. A. Fritchie, private communication (May 1970).

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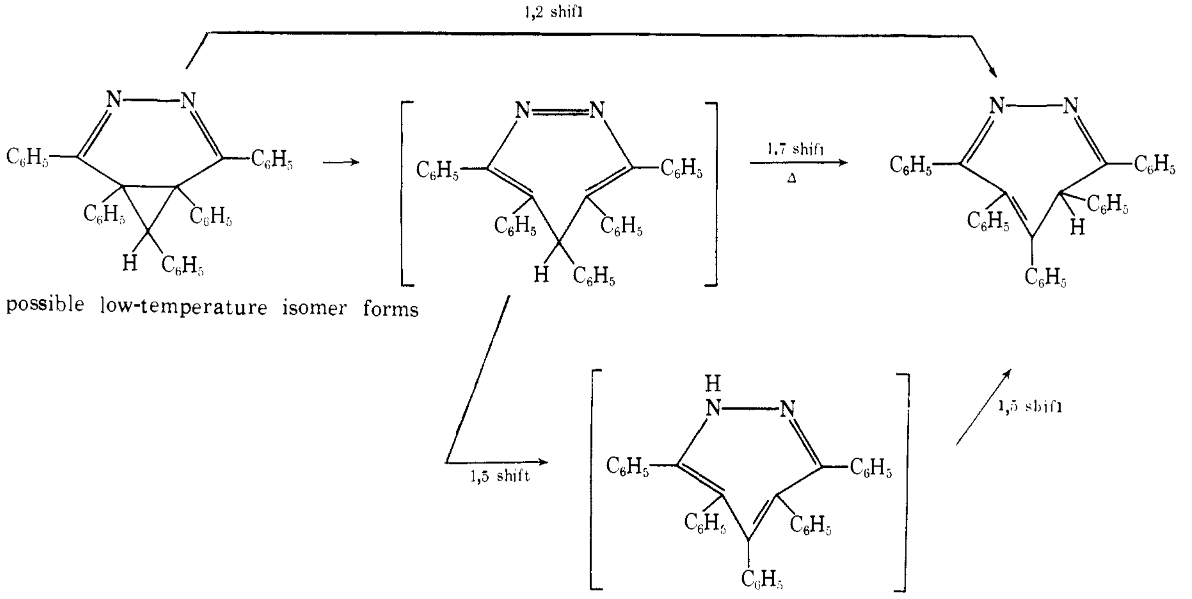
Scheme I



possible low-temperature isomer forms

intermediate also existing, perhaps in equilibrium with the indicated intermediate, and thus accounting for the unexpected thermal fragmentation products, such as benzonitrile, reported by Battiste.

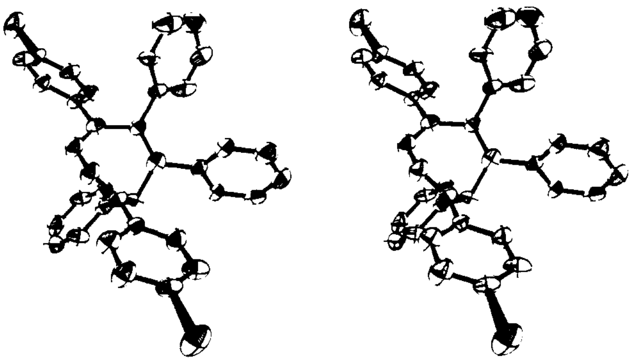


Figure 1. ORTEP drawing of the molecule.

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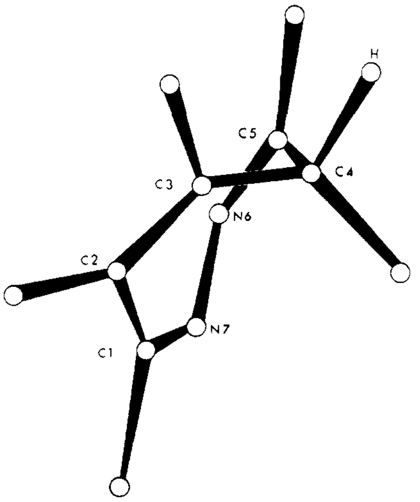

Figure 2. Projectional drawing of the seven-membered ring.