

# The Crystal and Molecular Structure of 1-Methylamino-7-methylimino-1,3,5-cycloheptatriene\*

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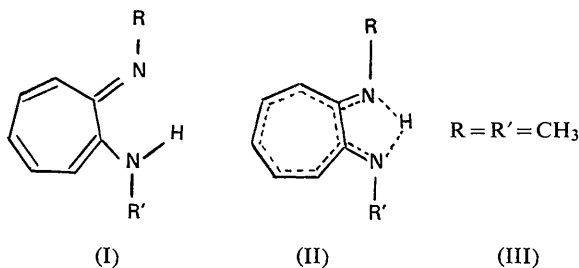
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1-Methylamino-7-methylimino-1,3,5-cycloheptatriene,  $C_9H_{12}N_2$ , a typical  $N,N'$ -disubstituted aminotroponimine, forms orthorhombic orange plates of space group  $Iba2$ , with eight molecules in the unit cell and  $a_0 = 14.518$ ,  $b_0 = 19.49$ ,  $c_0 = 5.982$  Å. The structure was solved with the help of a sharpened three-dimensional Patterson function, and was refined by full-matrix least-squares methods. The molecule has essentially  $mm2$  symmetry, including the methyl groups, which are staggered with respect to the nearest ring hydrogen atoms; the molecular structure seems best described in terms of a ten-electron  $\pi$ -system encompassing the seven-membered ring and the two attached nitrogen atoms. The single amino hydrogen atom appeared in a final difference Fourier synthesis as two peaks of half the normal height symmetrically situated with respect to the two nitrogen atoms, a finding consistent with the nuclear magnetic resonance, infrared, and chemical evidence that the nitrogen atoms are equivalent. Intermolecular contacts are normal.

## Introduction

$N,N'$ -Disubstituted aminotroponimines (I) are stable colored compounds which, like the structurally related tropolone, exhibit aromatic character in their physical and chemical properties (Brasen, Holmquist & Benson, 1960, 1961). However, differences between tropolone and the aminotroponimines in nuclear magnetic resonance (n.m.r.) spectra, in molecular dipole moments, and in rates of nucleophilic substitution on the ring indicate (Benson, 1960) that the latter compounds contain a ten-electron  $\pi$ -system delocalized over the seven ring carbons and the two nitrogen atoms (II) in contrast to tropolone, which is best understood in terms of a  $\pi$ -system involving only six electrons.



The proton n.m.r. absorption spectrum of a chloroform solution of  $N,N'$ -dimethylaminotroponimine (III), shows only one peak for the methyl protons, even at  $-80^\circ\text{C}$  and when the amino hydrogen is replaced by deuterium. This evidence implies that the two methyl groups are, on a time average, equivalent, which in turn

implies that the nitrogen atoms are equivalent, and either that the amino hydrogen is symmetrically situated with respect to the two nitrogen atoms [as in (II)], or that there is an extremely fast intramolecular hydrogen (or deuterium) exchange (Benson, 1960; Brasen *et al.*, 1961). As discussed below, we have independently concluded from the X-ray evidence that the two nitrogen atoms are chemically equivalent.

The aminotroponimines are of interest also because they form chelates with divalent ions such as  $Zn^{2+}$ ,  $Ni^{2+}$ ,  $Cu^{2+}$ , and  $Co^{2+}$ . The nickel chelates exist in both a diamagnetic and a paramagnetic form, which are in equilibrium with one another in solution. The diamagnetic form is presumed to correspond to a square planar configuration around the nickel atom and the paramagnetic form to contain tetrahedrally arranged ligands. The equilibrium appears to be governed by steric factors and depends on temperature, solvent, and the size of the substituents on the nitrogen atoms (Eaton, Phillips & Caldwell, 1963).

We undertook a precise single-crystal structure analysis of (III) in an effort to provide information about the aromatic character of the aminotroponimines and with the hope that we might possibly locate the  $N$ -proton. The determination should also provide a useful reference standard for any structural studies of the chelates of this and related molecules.

## Experimental

Crystals of  $N,N'$ -dimethylaminotroponimine (III),  $C_9H_{12}N_2$ , in the form of orange plates were kindly supplied to us by Dr B. C. Fratt. Preliminary Weissenberg photographs showed that the crystals are orthorhombic; the cell dimensions were determined by an iterative relaxation method from measurements on zero-layer Weissenberg photographs calibrated with  $CeO_2$  powder lines ( $a_0 = 5.411$  Å), using  $\lambda(\text{Cu } K\alpha) = 1.5418$  Å. They

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Table 1. Observed and calculated structure factors and phase angles

The columns are, respectively, h, 10F<sub>o</sub>, 10|F<sub>c</sub>|, and α. Values marked with U were below the observable limit; the F<sub>o</sub> listed is 7-1F<sub>min</sub>. Those marked with E are suspected of showing secondary extinction.

Table with multiple columns containing numerical data for structure factors and phase angles. The table is organized into several vertical sections, each with its own header (e.g., K=0, L=0, K=1, L=0, etc.). Each section lists values for h, 10F<sub>o</sub>, 10|F<sub>c</sub>|, and α, with some entries marked with U or E. The data is presented in a grid-like format across the page.

are  $a_0 = 14.518 \pm 0.010$ ,  $b_0 = 19.49 \pm 0.02$ , and  $c_0 = 5.982 \pm 0.004$  Å. The density calculated for an eight-molecule unit cell is  $1.163 \text{ g.cm}^{-3}$ ; the observed density is  $1.174 \pm 0.005 \text{ g.cm}^{-3}$ . The systematic extinctions are  $hkl$  with  $h+k+l=2n+1$ ,  $0kl$  with  $k=2n+1$  (or  $l=2n+1$ ), and  $h0l$  with  $h=2n+1$  (or  $l=2n+1$ ). These are consistent with two space groups,  $Iba2$  and  $Ibam$ , but the latter can be ruled out on the basis of packing considerations, since the molecules would be constrained to lie either on the mirror planes or on two-fold axes, and their size is such that they would then overlap. There is thus one molecule in the asymmetric unit of space group  $Iba2$ .

Intensity data were collected from crystals mounted about **b** and **c**, enclosed in 0.3 mm diameter thin-walled Lindemann-glass capillaries to minimize loss by evaporation of the moderately volatile substance. The crystal mounted about **b** was 0.5 mm high, with cross-section cut to approximately 0.17 by 0.20 mm; integrated intensities for levels 0–6 and non-integrated intensities for levels 7–18 were recorded with a Nonius camera by the multiple-film technique with Cu  $K\alpha$  radiation. Integrated intensities were similarly collected about **c** for levels 0–5 from a crystal 0.5 mm high, with cross-section cut to about  $0.16 \times 0.24$  mm. The integrated intensities, collected with Ni-filtered radiation, were measured both with a densitometer (Baird Atomic Model CB) and visually, by comparison with an integrated intensity scale. Estimation of the non-integrated intensities was done visually, using a standard scale having reflections of comparable size and shape. Lorentz and polarization corrections were applied; absorption corrections were ignored, since the maximum error due to absorption was calculated to be less than 5% for the *b*-axis data and less than 8% for that collected around **c** ( $\mu = 5.8 \text{ cm}^{-1}$  for Cu  $K\alpha$ ).

The data were correlated to a common scale in two steps by means of an iterative relaxation technique, similar to that described by Rollett & Sparks (1960) and programmed for the IBM 7090 computer by Dr Sparks. Of the 1131 reflections in the Cu  $K\alpha$  sphere, 1031 (91%) were accessible experimentally, and of these only 92 (9%) were too weak to be observed. These 92 are identified in Table 1 by the letter *U*; the  $F_o$  listed for them is approximately  $0.71 F_{\min}$ , where  $F_{\min}$  is the estimated minimum observable structure factor amplitude in the corresponding region of reciprocal space. This value was used when they were included in the least-squares refinements (Hamilton, 1955).

#### Determination and refinement of the structure

A trial structure was found by the application of elementary search techniques to a three-dimensional Patterson function which had been sharpened by modification of the coefficients by the factor  $(0.17 + s^2)e^{-Bs^2}$ , with  $s = \sin \theta/\lambda$  and  $B = 3.0$  (Jacobson, Wunderlich & Lipscomb, 1961). We did not have a three-dimensional automatic computer search program available; hence

the first step in the procedure was to find the plane of the (presumably planar) molecule by visual inspection of the Patterson distribution, searching for sections of high density which passed through the origin, corresponding to the coplanar intramolecular vectors of the molecule. A three-dimensional model of the peaks within 3.5 Å of the origin in the sharpened Patterson function revealed this plane rather quickly. Then the orientation of the molecule within the section was found by fitting to it a vector map constructed from a model of the molecule; only one good fit was evident. The correctness of this fit was indicated when the twofold axis of the molecule, not a crystallographic symmetry element, was found to correspond with a previously unnoticed approximate twofold axis in the Patterson section on which the search was made.

Once the orientation of the molecule had been established, only two translational parameters remained to be determined, corresponding to the position of some arbitrary point in the molecule relative to the origin of the unit cell; the third translational parameter is arbitrary because **c** is a polar axis in space group  $Iba2$ . These translational parameters were found by consideration of the Harker lines  $P(u, 0, \frac{1}{2})$  and  $P(0, v, \frac{1}{2})$  and their implications for the full Patterson function. Each Harker-line peak was analyzed by assuming it to arise first from a *given* unique atom of the molecule; this assumption then implied the existence of many other interactions, both on the Harker line and throughout the three-dimensional Patterson function. The fit for each unique atom in turn was considered. This method led to one and only one good fit for each of the two translational parameters to be specified. The trial structure so determined gave a discrepancy index, *R*, of 0.35 with all eleven carbon and nitrogen atoms included in the calculation, each with an isotropic temperature factor of  $3.0 \text{ Å}^2$ . However, a three-dimensional Fourier synthesis, and a calculation of the geometry of the molecule, showed that an inadvertent error had been made in the position of one of the atoms. When this was corrected, *R* was 0.25 and it appeared very likely that the trial structure was correct.

Refinement was begun at once by full-matrix three-dimensional least squares. The program used was a slightly modified version of that of Gantzel, Sparks & Trueblood (ACA no. 317), which minimizes  $\sum w(|F_o| - G|F_c|)^2$ , where *G* is a scale factor (the reciprocal of which is actually applied to  $F_o$ ). The scattering factors used in all calculations were those of Hoerni & Ibers (1954) for the carbon and nitrogen atoms, and the hydrogen scattering function given in *International Tables for X-ray Crystallography* (1962). Two separate weighting schemes were employed, first that of Hughes (1941) with  $4F_{\min} = 22.4$ , and second, one with weights inversely proportional to the e.s.d.'s of the data as estimated during the data-correlation. The results at parallel stages were not significantly different; the final parameters quoted here are those derived from the latter weighting scheme.

The initial refinement proceeded in stages during which the range of reflections included was successively increased by lowering the minimum value of  $F_o$  (from 21 to 0) and raising the maximum value of  $\sin \theta/\lambda$  (from 0.40 to 0.65). During this initial refinement, an arbitrarily chosen constant isotropic temperature factor of  $3.0 \text{ \AA}^2$  was used.  $R$  fell to 0.18. Three further cycles with individual isotropic temperature factors included as variable parameters reduced  $R$  to 0.13, and four more with anisotropic temperature factors gave  $R=0.107$ . A difference map then revealed the approximate positions of all twelve of the hydrogen atoms; the one attached to the nitrogen atom appeared as a broad peak about midway between the nitrogens. All of the hydrogen atoms except the one attached to the nitrogen atom were then included in further least-squares refinements, including all of the observed and unobserved reflections except for the seven strongest (which appeared to suffer from extinction); the positions and individual isotropic temperature factors of the hydrogen atoms were allowed to vary. Because of limitations of the program, it was necessary to give two of the heavier atoms isotropic temperature factors while refining the hydrogen parameters. Consequently, after the hydrogen parameters had converged, a few additional cycles of anisotropic refinement of all of the heavier atoms were done to insure convergence. All of the final shifts were less than 5% of the corresponding e.s.d. The final  $R$  was 0.070 for the observed and unobserved data, excluding the eleven strongest reflections. When these are included,  $R=0.082$ .

The parameters resulting from these refinements were used in a final difference Fourier synthesis. The ultimate hydrogen atom appeared in a broad region of electron density, with two maxima of heights 0.27 and 0.23  $\text{e.}\text{\AA}^{-3}$  and a saddle point of height 0.20  $\text{e.}\text{\AA}^{-3}$  between them (Fig. 1). The e.s.d. of the electron density is nearly 0.05  $\text{e.}\text{\AA}^{-3}$ ; only two other features of the map approached densities of even three times the e.s.d. and they were not near this region. The positions of the two maxima representing the amino hydrogen were about 1.0  $\text{\AA}$  apart and each was 1.1  $\text{\AA}$  from the nearer nitrogen atom. Hydrogen atoms with weight 0.5 were

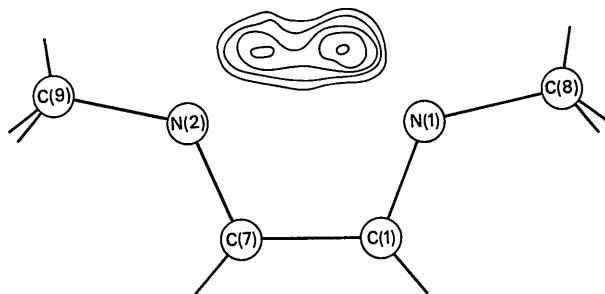


Fig. 1. Final difference electron density synthesis in the plane of the molecule, near the nitrogen atoms. All atoms except the amino hydrogen atom were used in the calculation of structure factors. Contour interval  $0.03 \text{ e.}\text{\AA}^{-3}$ , with the first contour at  $0.14 \text{ e.}\text{\AA}^{-3}$ , which is about  $3\sigma(\rho)$ .

put at these positions, assigned temperature factors of  $7 \text{ \AA}^2$ , and refined by three cycles of full-matrix least squares, together with all of the heavy atoms in the molecule. The shifts in the parameters of the latter were negligible, while those of the half hydrogens themselves converged; the positions shifted by only about one

Table 2. Final position parameters and their standard deviations\*

	x	y	z
C(1)	3006,2	1106,1	5120,9
C(2)	2236,2	0702,1	4514,10
C(3)	1365,2	0663,2	5433,11
C(4)	0984,2	1004,2	7236†
C(5)	1423,3	1462,2	8627,10
C(6)	2310,2	1726,2	8513,10
C(7)	3038,2	1587,1	7040,9
C(8)	3944,2	0632,2	2091,10
C(9)	4062,3	2393,2	8965,11
N(1)	3794,2	1077,1	3985,8
N(2)	3852,2	1894,1	7221,9
H(2)	233,3	045,2	297,8
H(3)	093,3	034,2	487,8
H(4)	028,3	093,2	754,8
H(5)	101,3	171,2	996,8
H(6)	253,3	213,2	980,8
H(8a)	386,3	013,2	235,9
H(8b)	349,3	072,2	081,9
H(8c)	458,3	074,2	128,9
H(9a)	479,3	255,2	876,9
H(9b)	355,3	279,2	899,9
H(9c)	402,3	220,2	1038,9
H(N1)	431,5	137,3	450,10
H(N2)	427,7	173,5	554,22

\*  $\times 10^4$  for all but hydrogen atoms, for which values are  $\times 10^3$ . E.s.d.'s are separated by a comma, and are given in the units of the least significant digit. The values of  $\sigma(z)$  appear abnormally large, but because of the polarity of  $c$  there are strong correlations between the  $z$  values of different atoms, the average correlation coefficient being about 0.65.

† This parameter was arbitrarily fixed.

Table 3. Thermal vibration parameters†

	$B_{11}$	$B_{22}$	$B_{33}$	$B_{12}$	$B_{13}$	$B_{23}$
C(1)	46	23	256	11	-17	23
C(2)	49	28	349	4	-31	-18
C(3)	46	34	473	-7	-50	26
C(4)	47	41	465	10	31	51
C(5)	59	43	341	24	55	20
C(6)	58	36	306	20	14	-17
C(7)	49	24	266	9	-26	2
C(8)	70	40	313	22	35	-30
C(9)	83	37	436	-11	-55	-78
N(1)	51	31	309	6	33	-5
N(2)	57	30	365	-3	-22	-25

	$B$		$B$
H(2)	3.8 $\text{\AA}^2$	H(8a)	3.5 $\text{\AA}^2$
H(3)	5.3	H(8b)	2.6
H(4)	5.8	H(8c)	4.3
H(5)	5.9	H(9a)	7.5
H(6)	6.0	H(9b)	5.3
H(N1)	2	H(9c)	5.0
H(N2)	7		

\*  $B_{ii}$  and  $B_{ij} \times 10^4$ . The e.s.d. of  $B_{ii}$  are ca. 4%, while for the hydrogen atoms  $\sigma(B) \approx 1.1 \text{ \AA}^2$  for all but H(N2), for which  $\sigma \approx 2 \text{ \AA}^2$ . The expression used for anisotropic temperature factors is:

$$\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{23}kl + B_{13}hl)].$$

e.s.d., although the temperature factor of one half-atom fell to  $2 \text{ \AA}^2$ . The significance of this observation of two 'half-hydrogens' is discussed below. The final position parameters, together with their e.s.d.'s, are given in Table 2, and the final temperature factors in Table 3.

The rigid-body tensors derived from the temperature factors are given in Table 4; the r.m.s. difference be-

tween observed and calculated  $U_{ij}$  was  $0.0023 \text{ \AA}^2$ . The analysis of the rigid-body motion of the molecule was made by the method of Schomaker & Trueblood (1966, 1967) because the molecule is non-centrosymmetric and consequently Cruickshank's (1956*a*) method is inapplicable. Neither the librational nor the translational motion is markedly anisotropic, and the maximum libration amplitude is only about  $4.3^\circ$ , so the librational corrections for rigid-body motion are not great. Comparison of results obtained by application of Cruickshank's method with those in Table 4, together with comments on the interpretation of the screw tensor  $S$  and quantities related to it, are given elsewhere (Schomaker & Trueblood, 1967).

### The molecular and crystal structure

The bond distances and angles in the molecule are shown in Figs. 2 and 3, and are given, with their e.s.d.'s, in Table 5. The e.s.d.'s include allowance for the high correlation in  $z$  (Templeton, 1960). Approximate corrections to the bond distances and angles to allow for the effects of molecular libration were made (Cruickshank, 1956*b*); the corrections to the distances were quite uniformly  $0.005\text{--}0.006 \text{ \AA}$ , while those to the angles were generally less than  $0.1^\circ$ . Because the principal vibrations of the methyl groups are appreciably greater than those of the attached nitrogen atoms, and are chiefly normal to the respective  $\text{N-CH}_3$  bond vectors, the rigid-body model is a poor approximation for

Table 4. Results of rigid-body analysis of thermal parameters\*

	Eigenvalues	Eigenvectors† (Direction cosines $\times 10^4$ )		
Librational tensor, $L$	$18.3 (\text{e})^2$	8317	-5031	2351
	11.9	4160	2842	-8638
	9.7	3678	8162	4456
Translational tensor, $T$	$0.0521 \text{ \AA}^2$	-7573	-6499	0645
	0.0480	-1458	2646	9533
	0.0415	-6365	7125	-2952
Symmetrized‡ screw tensor, $S$	$\begin{pmatrix} 37 & 109 & -108 \\ & 14 & 14 \\ & & -51 \end{pmatrix} \times 10^5 \text{ rad. \AA}$			

\* Calculated by the method of Schomaker & Trueblood (1966, 1967).

† Direction cosines of the eigenvectors are relative to  $a$ ,  $b$ , and  $c$  respectively.  $L$  is independent of the origin,  $T$  and  $S$  depend upon it and are here given relative to the unique origin which symmetrizes  $S$ . This unique origin is about  $0.52 \text{ \AA}$  from the centroid of the molecule, displaced along the three crystal axes by  $0.41$ ,  $-0.20$ , and  $-0.25 \text{ \AA}$ .

‡  $S$  is expressed relative to the principal axes of  $L$  and to the unique origin given above.

Table 5. Bond distances and bond angles

Bond distances						
	Uncorrected	Corrected*	E.s.d.	Uncorrected	E.s.d.	
C(4)–C(5)	1.378 $\text{ \AA}$	1.383 $\text{ \AA}$	$6 \times 10^{-3} \text{ \AA}$	C(2)–H(2)	1.06 $\text{ \AA}$	$4 \times 10^{-2} \text{ \AA}$
C(4)–C(3)	1.382	1.387	6	C(3)–H(3)	0.96	4
				C(4)–H(4)	1.05	4
C(5)–C(6)	1.388	1.393	6	C(5)–H(5)	1.10	4
C(3)–C(2)	1.381	1.386	6	C(6)–H(6)	1.15	4
C(6)–C(7)	1.402	1.407	6	C(8)–H(8 <i>a</i> )	1.00	5
C(2)–C(1)	1.414	1.420	6	C(8)–H(8 <i>b</i> )	1.03	5
				C(8)–H(8 <i>c</i> )	1.06	5
C(1)–C(7)	1.484	1.490	4	C(9)–H(9 <i>a</i> )	1.10	5
C(1)–N(1)	1.332	1.337	5	C(9)–H(9 <i>b</i> )	1.07	5
C(7)–N(2)	1.329	1.334	5	C(9)–H(9 <i>c</i> )	0.93	5
N(1)–C(8)	1.443	1.46 (0)	7	N(1)–H(N1)	1.0	0.1
N(2)–C(9)	1.458	1.47 (9)	7	N(2)–H(N2)	1.2	0.1
Bond angles†						
	C(3)–C(4)–C(5)	126.7°		C(2)–C(1)–N(1)	121.7°	
	C(4)–C(3)–C(2)	130.6		C(6)–C(7)–N(2)	122.2	
	C(4)–C(5)–C(6)	129.8		C(7)–C(1)–N(1)	113.2	
	C(3)–C(2)–C(1)	130.7		C(1)–C(7)–N(2)	112.1	
	C(5)–C(6)–C(7)	131.2		C(1)–N(1)–C(8)	123.7	
	C(2)–C(1)–C(7)	125.1		C(7)–N(2)–C(9)	123.0	
	C(6)–C(7)–C(1)	125.7				

\* Corrected for libration of the molecule (see text). The e.s.d.'s include an (arbitrary) uncertainty of  $0.001\text{--}0.002 \text{ \AA}$  in this correction.

† The e.s.d. of the bond angles are  $0.3\text{--}0.4^\circ$ , with the larger values for the angles within the ring, especially those away from C(1) and C(7). Most angles involving hydrogen atoms are shown in Fig. 3.

these atoms, and consequently these distances were corrected by the method of Leung & Marsh (1958).

The molecule has essentially  $mm2$  ( $C_{2v}$ ) symmetry, even including the hydrogen atoms of the methyl groups. The rotational conformation of these groups is apparently governed by steric interaction with the nearest hydrogen atoms on the ring, H(2) and H(6) respectively, the methyl hydrogen atoms nearest to these atoms straddling them at distances of about 2.0–2.3 Å (Table 6). The sum of the usually accepted van der Waals radii for two hydrogen atoms is 2.2–2.4 Å, so these contacts are just slightly short; however, if the

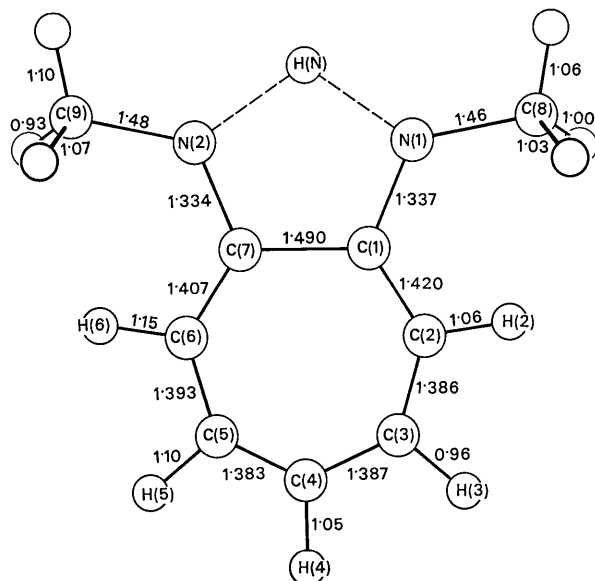


Fig. 2. Bond distances, including approximate corrections for molecular libration. The amino hydrogen atom is shown at the average of the two positions found (Fig. 1, Tables 2 and 5).

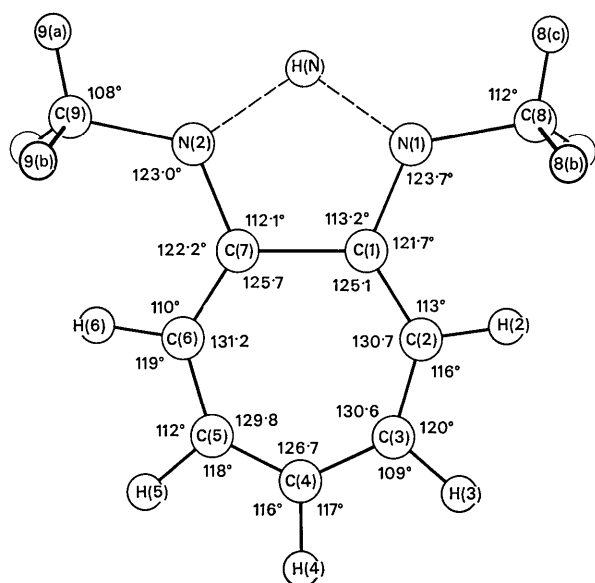


Fig. 3. Bond angles.

methyl groups were in the conformations  $60^\circ$  from those found here, the distances would be further reduced by about 0.3 Å. One further intramolecular distance of interest is that between hydrogen atoms on adjacent carbon atoms of the ring; the average value is 2.31 Å. In benzene, where the C–C and C–H bond distances are equal to those here, this distance is about 2.48 Å. The difference is of course due to the increase in the internal angle at each carbon atom of the planar seven-membered ring.

Table 6. Some non-bonded intramolecular distances\*

H(2)···H(8a)	2.34 Å	H(6)···H(9b)	2.03 Å
···H(8b)	2.19	···H(9c)	2.19
···C(8)	2.43	···C(9)	2.34
H(8c)···H(N1)	2.3	H(9a)···H(N2)	2.6

\* No intermolecular distances are listed here, although many are shown in Fig. 4. They were in no instance smaller than the sums of the accepted van der Waals radii.

The approximate twofold axis of the molecule, relating chemically equivalent distances and angles, is shown in Table 5 by the grouping of chemically equivalent geometrical features. The distances and angles that we find suggest strongly that the description in terms of an aromatic system containing 10  $\pi$ -electrons is a valid one. The simplest picture to consider is the superposition of two equivalent resonance forms, corresponding to (I) and the equivalent form with the double bonds all shifted to the neighboring position and the bond from H to N transferred to the other nitrogen atom. This view would lead one to expect the two exocyclic C–N bonds and all of the ring bonds with the exception of C(1)–C(7) to correspond to the aromatic distance, and indeed they do, for the aromatic C–N distance of about 1.34–1.35 Å in pyridine, pyrazine, and related substances is very close to that found here (1.34), and the average of the six appropriate C–C distances here is 1.396 Å (with an average deviation of about 0.01 Å), very close to that reported for crystalline benzene,  $1.392 \pm 0.004$  Å (Cox, Cruickshank & Smith, 1958) and gaseous benzene, *e.g.*  $1.397 \pm 0.001$  Å (Stoicheff, 1954). Furthermore, the N–CH<sub>3</sub> distances are in fair accord with expectation for a bond between trigonally hybridized nitrogen and tetrahedral carbon, about 1.45 Å. Finally, the C(1)–C(7) distance of 1.490 Å agrees well with that expected for a single bond between two trigonally hybridized carbon atoms and with, for example, the central ‘single’ bond in 1,3-butadiene, 1.483 Å (Almenningen, Bastiansen & Traetteberg, 1958) and the inter-ring bond in biphenyl, 1.497 Å (Robertson, 1961) or 1.492 Å (Almenningen & Bastiansen, 1958). The analogous bond in other 10  $\pi$ -electron systems has a similar length, *e.g.* in sodium tropolonate, 1.471 Å (Sasada & Nitta, 1956) and azulene, 1.483 Å (Robertson, Shearer, Sim & Watson, 1962). On the other hand, in tropolone hydrochloride, where a 6  $\pi$ -electron system prevails, the C(1)–C(7) bond length is only 1.39 Å (Sasada & Nitta, 1957).

Coplanarity of all of the atoms in the molecule (except for the hydrogen atoms in each methyl group) is also to be expected if the molecule does indeed have aromatic character. As Table 7 shows, the methyl carbon atoms, C(8) and C(9), are indeed in the plane of the ring. The deviations of C(4), C(5), and N(1) from this plane may be real, but in any event are small, amounting to no more than 0.02 Å at most. Furthermore the twin half-peaks corresponding to H(N1) and H(N2) also lie in the molecular plane, as expected.

Table 7. Planarity of the molecule\*

Atom	Deviation	Atom	Deviation
C(1)	0.007 Å	H(2)	0.14 Å
C(7)	-0.003	H(3)	-0.06
C(2)	-0.008	H(4)	0.12
C(6)	-0.002	H(5)	0.05
C(3)	0.002	H(6)	0.02
C(5)	-0.020		
C(4)	0.019	H(8a)	-0.79
		H(8b)	0.78
N(1)	0.015	H(8c)	0.14
N(2)	0.004		
		H(9a)	-0.04
C(8)	-0.014	H(9b)	0.79
C(9)	0.001	H(9c)	-0.77
		H(N1)	0.03
		H(N2)	0.09

\* The least squares plane, defined by the eleven heavy atoms, has the equation  $-0.3125X + 0.7374Y - 0.5988Z + 1.615 = 0$  in which  $X$ ,  $Y$ , and  $Z$  are coordinates in Å measured parallel to  $a$ ,  $b$ , and  $c$  (Schomaker, Waser, Marsh & Bergman, 1959).

One reasonable molecular axis is that given in Table 7 as the normal to the molecular plane. The other logical mutually perpendicular axes lie in the plane, with direction cosines 0.0516, 0.6426, 0.7645 [approximately parallel to C(1)-C(7)] and 0.9485, 0.2080, -0.2388.

The shape of the seven-membered ring in the present molecule is remarkably similar to that in sodium tropolonate (Table 8), with significant parallel trends in the averages of chemically equivalent bond angles and bond distances. The close similarity in the geometry of these two molecules evident in Table 8 is confirmed by  $\chi^2$  tests, which show that neither the distances nor angles are significantly different. The very slight deviations from planarity in sodium tropolonate also parallel those of the present molecule. It is noteworthy that the dipole moments of these molecules have opposite polarity, 4.4D in the tropolonate anion, with the ring positive, and 1.24D in the present molecule, with the ring negative.

One possible interpretation of our findings, both with regard to the two half-peaks for the amino proton and the aromatic character, might be that the crystal is statically disordered, containing a random mixture of two individual 'tautomers' corresponding to (I) and the equivalent form with the amino hydrogen and all the double bonds moved. These would properly be

Table 8. Comparisons of ring geometry

Distance or angle*	Present molecule	Sodium tropolonate†
1-7	1.490 Å	1.471 Å
1-2; 6-7	1.414	1.431
2-3; 5-6	1.390	1.389
3-4; 4-5	1.385	1.396
1; 7	125.4°	125.4°
2; 6	131.0	131.5
3; 5	130.2	129.5
4	126.7	127.0

\* Carbon atoms are identified by number; internal ring angles are identified by the number of the central carbon atom of the three which define the angle. The e.s.d.'s of the distances given are about 0.004 Å for the present molecule and 0.013 Å for sodium tropolonate.

† Sasada & Nitta (1956).

called 'tautomers' if there were a significant barrier to their interconversion; the evidence cited in the opening paragraphs is of course against this suggestion. However, even if in fact these two distinct species *might* exist, the evidence is against their co-existing in this crystal. The atomic parameters that we find give no evidence of the high apparent tangential motion of the atoms in the ring which such a disorder would simulate; in fact, for C(1), C(2) and C(7) the r.m.s. vibration amplitude in the radial direction is equal to or greater than that in the tangential direction. As Table 4 shows, neither the librational nor the translational motion is especially great or markedly anisotropic; the r.m.s. librational amplitude around the normal to the least-squares plane of the ring (Table 7) is only 3.9°.

Our results concerning the amino hydrogen atom cannot alone be considered definitive; although the heights of the half-peaks which represent it are between five and six times the e.s.d. of the electron density, the e.s.d. of the positions of these hydrogen atoms as estimated from the least-squares results are about 0.1 Å, and systematic errors of even a minor sort could make the actual uncertainties significantly larger. As Fig. 1 illustrates, the saddle-point between the maxima is only about one e.s.d. lower than the maxima themselves. However, while it is not unequivocally established that there are two equivalent proton positions rather than a single average one, our results do clearly suggest that the barrier in the potential function for movement of this proton must be relatively low, and the function itself nearly symmetrical. The infrared spectroscopic evidence for intramolecular hydrogen bonding (Brasen *et al.*, 1961) and the n.m.r. evidence of equivalence of the nitrogen atoms are, of course, in accord with this view. Dipole moment and reactivity studies have also been interpreted by Brasen *et al.* to support the presence of a 10- $\pi$ -electron aromatic system, as indicated by (II), with possibly a small degree of transfer of the hydrogen atom's electron to the ring, *i.e.* with small contributions from a zwitterion resonance form similar to (II), consisting of a proton and the remainder of the molecule with a negative charge. Short hydrogen bonds with apparently disordered hy-

drogen atoms have been reported in a number of structures recently, e.g. cytosine-5-acetic acid (Marsh, Bierstedt & Eichhorn, 1962) and  $\beta$ -5-n-propoxy-*o*-quinone-2-oxime (Romers, 1964). Proton tunneling in  $\text{N-H}\cdots\text{N}$  bonds has been discussed by Rein & Harris (1965) in connection with genetic mutations involving the guanine-cytosine base pair of deoxyribonucleic acid.

Webb & Fleischer (1965) have recently reported a precise X-ray study of porphine with results very similar to those found here: a half-hydrogen atom associated with each nitrogen atom, and apparent equivalence of chemical bonds which would be distinct in individual tautomers.

The eight molecules in the unit cell are packed in an efficient manner, without any unusually close intermolecular contacts. The shortest intermolecular distances are shown in Fig. 4. The molecules lie in four general orientations in the unit cell (the body-centering

operation repeating these), inclined to all three axes, as indicated by the equation for the molecular plane (Table 7). They are packed in the familiar herringbone fashion within layers normal to **b**. The molecules within any layer are inclined, with the methyl groups and nearby ring hydrogen atoms forming the bulk of the upper and lower surfaces of the layer – thus the contacts between layers are chiefly between methyl groups, or methyl groups and ring hydrogen atoms of different molecules. The molecular planes of the molecules within any layer are inclined to one another at  $36^\circ$  (when related by the *c*-glide normal to **a**, e.g. *A* and *C* of Fig. 4),  $74^\circ$  (when related by the  $2_1$  parallel to **c**, e.g. *A* and *F*) and  $95^\circ$  (when related by the *c*-glide normal to **b**, e.g. *A* and *D*).

It is a pleasure to acknowledge our indebtedness to Mary Burke Laing, who made preliminary studies of

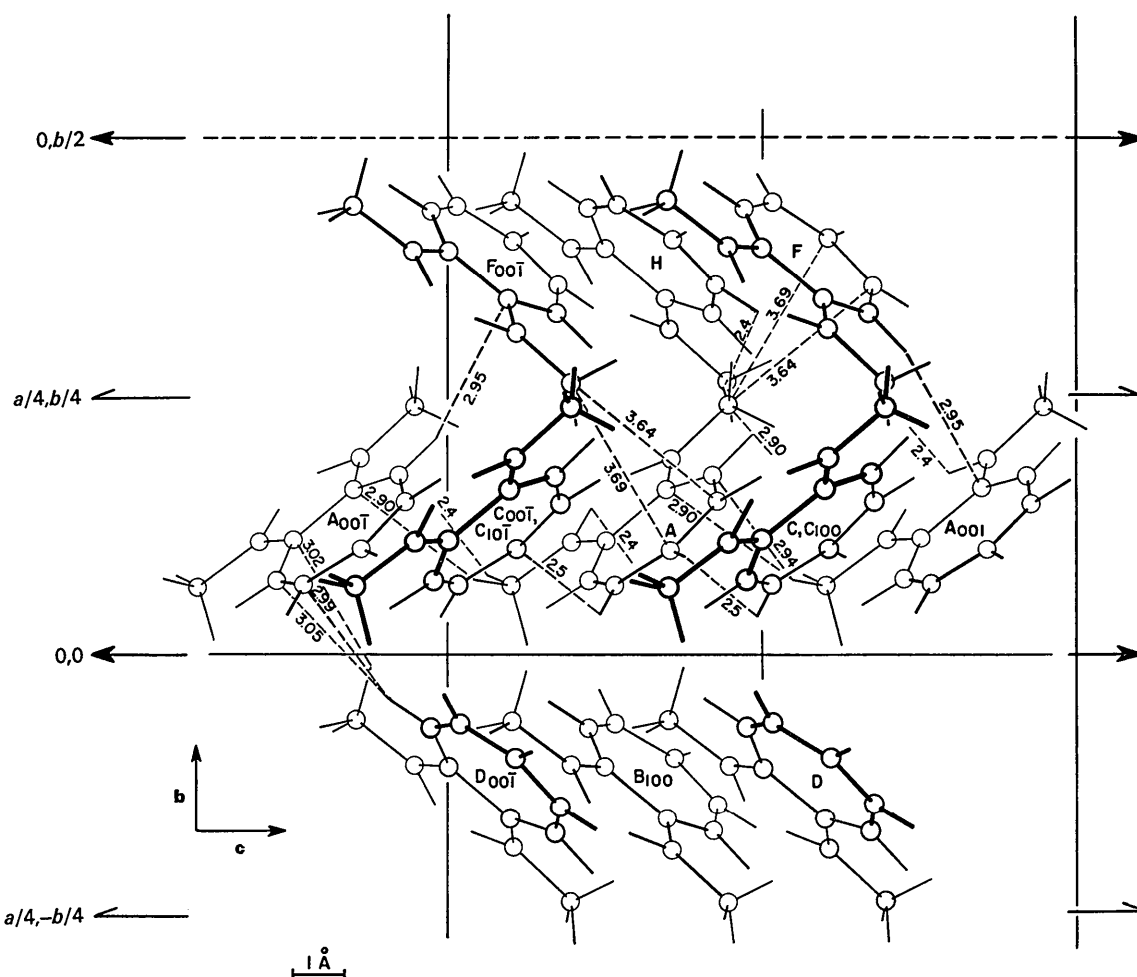


Fig. 4. View along **a** of the molecules bordering a reference molecule, *A*. The letters and subscripts associated with each molecule represent the symmetry transformations and axial translations which relate that molecule to the reference molecule, *A*, at position *x, y, z*. The positions of the symmetry-related molecules are *B*,  $-x, -y, z$ ; *C*,  $-x, y, \frac{1}{2} + z$ ; *D*,  $x, -y, \frac{1}{2} + z$ ; *F*,  $\frac{1}{2} - x, \frac{1}{2} - y, \frac{1}{2} + z$ ; *H*,  $\frac{1}{2} + x, \frac{1}{2} - y, z$ . Symbols appearing together refer to molecules superimposed upon one another; only the nearer molecule is shown. Distances to the further molecule, i.e. translations in the positive **a** direction, are depicted by incomplete dashed lines. All intermolecular H-H contacts less than  $2.6 \text{ \AA}$ , all C-H contacts less than  $3.0 \text{ \AA}$ , and some others of interest, are shown.



these crystals and determined their unit cell and space group, to Dr B.C. Pratt of the Central Research Department, E.I. du Pont de Nemours & Company, for the sample, to the U.S. Air Force for their partial support of this work, to Maryellin Reinecke for the illustrations, and to the staff of the UCLA Computing Facility for their cooperation in the machine calculations.

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## The Crystal Structure of Phenylethynyl(isopropylamine)gold(I).

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Phenylethynyl(isopropylamine)gold(I),  $i\text{-C}_3\text{H}_7\text{NH}_2\text{AuC}\equiv\text{CC}_6\text{H}_5$ , crystallizes in an orthorhombic cell with  $a = 17.92$ ,  $b = 17.15$ ,  $c = 7.22$  Å,  $Z = 8$ , space group *Pccn*. The structure was solved by the heavy atom method and refined by the method of least squares to an  $R$  value of 0.064, calculated on the 1032 observed reflexions. The gold atoms lie in infinite zigzag chains, extending along the direction of the  $c$  axis, with gold-gold distances of 3.72 Å along the chains and angles of  $153^\circ$ . The chains are related in pairs by the twofold axes through  $\frac{1}{2}\frac{1}{2}0$  and  $\frac{3}{2}\frac{1}{2}0$ , the gold-gold distances between the chains being 3.27 Å. Each gold atom is bonded, in an almost linear manner, to a nitrogen and to an ethynyl carbon atom with these atoms lying nearly in the plane of the zigzag. The gold-nitrogen and gold-carbon distances are 2.03 and 1.94 Å respectively. The amino hydrogen atoms are directed approximately towards neighbouring ethynyl groups and may be engaged in hydrogen bond formation.

### Introduction

The complexes formed by phenylethynylgold(I) with primary and secondary amines tend to be sparingly soluble in inert solvents. Molecular-weight measurements (cryoscopically in benzene) show the presence of associated species, the extent of association increasing with concentration. The *n*-octylamine complex has

degrees of association in the range 3.1–4.1 for the concentration range 1.3–5.7 wt.%; the *n*-nonylamine complex in the range 2.6–4.1 (0.7–5.2 wt.%). The isopropylamine complex was not sufficiently soluble to permit such measurements.

The ethynyl stretching frequencies for these complexes lie in the range 2122–2125  $\text{cm}^{-1}$  (in a potassium bromide disc) and those of bisphenylethynylmercury at 2149  $\text{cm}^{-1}$  with a weaker band at 2117  $\text{cm}^{-1}$ . The very slight lowering in the stretching frequencies of the gold complexes suggests that  $\pi$ -bonding between the

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