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THE STRUCTURE OF N,N'-DIPHENYL-6-AMINOPENTAFULVENE-2-ALDIMINE

UNSYMMETRICAL HYDROGEN LOCATION IN A DEGENERATE INTRAMOLECULAR N···H—N BOND

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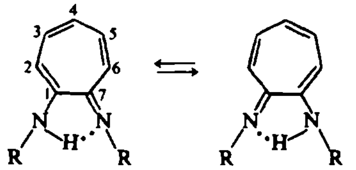
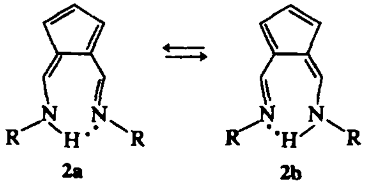
Abstract—The structure of the title compound (hereinafter called PALDIM) has been determined by a 3-dimensional X-ray crystallographic analysis. The space group is orthorhombic, $P2_12_12_1$, and cell parameters are $a = 5{\cdot}468$, $b = 20{\cdot}442$, $c = 13{\cdot}088$ Å. X-ray intensity data were measured on a computer-controlled diffractometer with Cu radiation. Least-squares structure refinement used anisotropic temperature factors for C and N and isotropic terms for H. The final R factor was 0·021. An electron density difference map showed evidence for solid state disorder in terms of two half-hydrogen atoms positioned in the N···N region. A single, symmetrical H location also could be ruled out from X-ray photoelectron spectroscopic data. Bond lengths and angles in the N···H—N regions of PALDIM and 1-methylamino-7-methylimino-1,3,5-cycloheptatriene indicate that the intramolecular H bond should be stronger in PALDIM, despite the fact that the PALDIM N···N distance is 0·28 Å longer than that in the cycloheptatriene. This conclusion is confirmed by IR data.

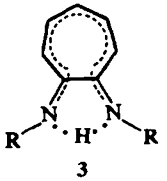
In compounds like 1-amino-7-imino-1,3,5-cycloheptatrienes **1** and the 6-aminopentafulvene-2-aldimines **2**, the N—H···N moiety provides the structural environement for either facile tautomerism or a symmetrical hydrogen bond. IR, NMR and dipole moment data[1-3] for the aminotroponeimine **1** usually have been interpreted in favor of a symmetrical structure, e.g. **3**, although a rapid intramolecular proton shift, **1a** ⇄ **1b**, could not be eliminated unequivocally. An X-ray crystallographic investigation[4] of **1** (R = CH_3) revealed two "half-hydrogen" atoms (from a difference electron density calculation) in the N···N region of the molecule, similar to what might be obtained by the superposition of one-half molecule of **1a** on one-half molecule of **1b**. However, the in-plane components of the anisotropic temperature factors of the seven-ring carbon atoms were interpreted[4] as evidence against the superposition possibility (i.e. solid state disorder). In the case of the pentafulvenes, Mueller-Westerhoff[5] concluded that neither the symmetrical structure **4** or the 10π electron nonclassical aromatic structure **5** are correct descriptions of the system; that the pentafulvenes have classical structures; and that the tautomers **2a** and **2b** interconvert very rapidly.



1a **1b**



2a **2b**



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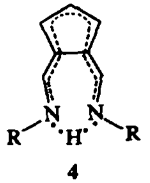

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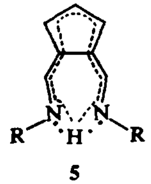

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We have carried out an X-ray crystallographic investigation of N,N'-diphenyl-6-aminopentafulvene-2-aldimine (2, R = C_6H_5; PAL-DIM) to further examine the symmetrical–unsymmetrical hydrogen problem, and our results are reported in this paper.

DISCUSSION

Bond lengths and angles and an ORTEP representation of PALDIM are given in Fig 1. The 6-aminopentafulvene-2-aldimine portion of the molecule (excluding the phenyls) has close to C_{2v} symmetry. The five-membered ring and the two phenyls are individually planar; (Table 1) the 5-ring/phenyl A and 5-ring/phenyl B angles are respectively, 19·6 and 6·7°. Coplanarity of the phenyls with the 6-aminopentafulvene-2-aldimine moiety presumably is restricted by steric interactions between the "inside" H's; H(9)···H(19) = 2·40 Å.

With the exception of the C(1)–C(2) length, the 6-aminopentafulvene-2-aldimine carbon–carbon and carbon–nitrogen distances are approximately half way between the usual single and double bond values for these elements. A similar pattern was observed in aminotroponeimine 1,[4] although the 7-ring to N distances, *av* 1·335 Å, were *ca* 0·03 Å longer than the corresponding PALDIM C–N's. A further difference between the two structures is the 1·447 Å C(1)–C(2) length in PALDIM compared to the 1·490 Å central bond (C(1)–C(7)) in **1**. In general, the PALDIM bond lengths are essentially what one would expect for either a superposition of the unsymmetrical H structures (**2a** + **2b**) or to a symmetrical H structure (e.g., **4**–**5**). A similar conclusion holds for the aminotroponeimine.

The PALDIM structure refinement initially varied the carbon, nitrogen and all hydrogen parameters except the hydrogen(s) on nitrogen. A difference electron density map evaluated in the least-squares plane[6] of the N(1)–C(6)–C(1)–C(2)–C(7)–N(2) moiety revealed two 0·20 e $Å^{-3}$ maxima separated by a shallow 0·14 e $Å^{-3}$ minimum in the N(1)···N(2) vicinity (Fig 2). The two peaks were about one-half to one-third the normal height (0·4–0·6 e $Å^{-3}$) for a full difference map H atom. Although the difference between the maxima and the minimum electron densities, *ca* 0·06 e $Å^{-3}$, is less than the 0·08 e $Å^{-3}$ ESD of the difference map, the peak magnitudes and their locations were highly suggestive of a disordered structure represented by one-half of **2a** plus one-half of **2b**. Interpolation of the difference map gave initial H(N1)–N(1) and H(N2)–N(2) distances of 1·03 and 1·00 Å, respectively.

Attempts at least-squares refinement of the posi-

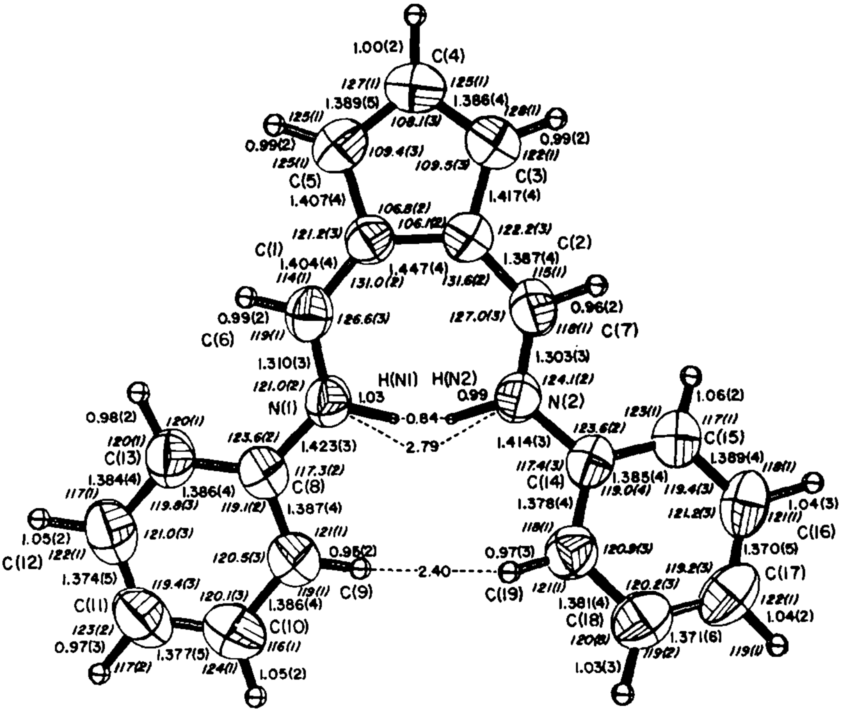


Fig. 1. An ORTEP-II[11] drawing viewed normal to the five-membered ring. 50% probability ellipsoids were used for C and N; 0·1 Å spheres were used for all H's except H(N1) and H(N2) which were plotted as 0·05 Å spheres. Bond distances (Å) and angles (°) are given. Estimated standard deviations are in parentheses. The phenyl A and B rings are, respectively, the left-most and right-most six-membered rings.

Table 1. PALDIM least squares planes and distances (Å) of the atoms from the planes

Atom	5-ring	Phenyl A	Phenyl B
N(1)	−0·037	−0·049	−0·206
N(2)	−0·014	0·394	0·058
C(1)	−0·001*	−0·622	0·073
C(2)	0·001*	−0·400	0·200
C(3)	−0·001*	−0·757	0·339
C(4)	0·000*	−1·174	0·307
C(5)	0·001*	−1·093	0·147
C(6)	−0·030	−0·474	−0·120
C(7)	0·001	0·057	0·196
C(8)		−0·013*	
C(9)		0·003*	
C(10)		0·009*	
C(11)		−0·010*	
C(12)		−0·001*	
C(13)		0·012*	
C(14)			0·019*
C(15)			−0·018*
C(16)			0·003*
C(17)			0·011*
C(18)			−0·011*
C(19)			−0·004*

5-ring plane: $3{\cdot}28645x - 2{\cdot}13761y + 10{\cdot}37026z = 3{\cdot}86470$

Phenyl A plane: $2{\cdot}73098x + 4{\cdot}56773y + 10{\cdot}95509z = 4{\cdot}21778$

Phenyl B plane: $2{\cdot}82217x - 3{\cdot}47562y + 10{\cdot}98697z = 4{\cdot}24443$

*Used for definition of the plane.

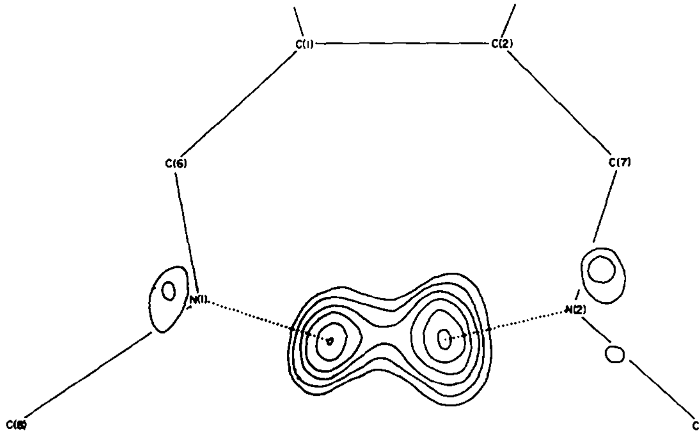
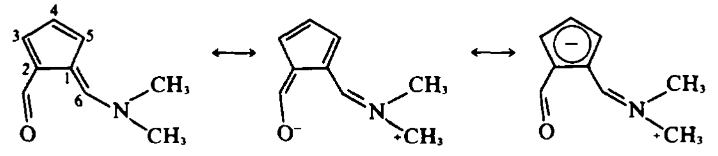


Fig. 2. A difference electron density map in the N ··· N region of 6-aminopentafulvene-2-aldimine. Contours are at 0·02 e Å^{-3}; the lowest contour is at 0·10 e Å^{-3}.

tions and isotropic temperature factors of the two half-H's generally led to unsatisfactory values for these parameters. Subsequently, the H's were fixed at their initial locations with temperature factors (U's) of 0·08 Å^2, and their refinement was limited to a single population parameter, $P_{H(N1)}(P_{H(N2)} = 1 - P_{H(N1)})$. The final value for $P_{H(N1)}$ was 0·25 ($P_{H(N2)}$ = 0·75) with an ESD of 0·03. However, the behavior of these atoms in the position and temperature factor refinement, as well as the equal peak magnitudes in the difference map, indicate that these population parameters are not significantly different from 0·5. Two cycles of refinement on C, N and the other H's, with $P_{H(N1)}$ and $P_{H(N2)}$ equal to 0·5, led to an R factor of 0·021.

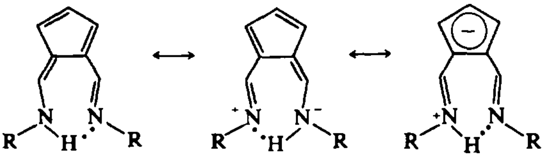
The 6-aminopentafulvene-2-aldimine bond lengths are very similar to the distances found in a X-ray crystallographic investigation of 2-formyl-6-(dimethylamino)pentafulvene **6**.[7] The similarity extends to both the exocyclic distances, C=C and C–N, and to the 5-ring lengths, all of which have close to 50% double bond character values. Dipolar



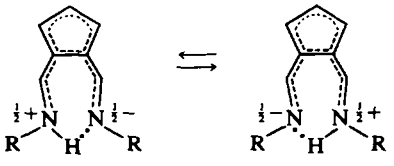
6a **6b** **6c**

canonical forms such as **6b** and **6c** probably constitute an important contribution to the ground state resonance hybrid; structure **6c** may be responsible for the decrease in the C(1)–C(2) bond length, 1·451 Å, from the 1·47–1·49 Å value for a Csp^2–Csp^2 single bond.

The similarities between the aldimine **2** and formyl **6** structures suggest that canonical forms such as **7a** and **7b** could make appreciable contributions to the ground state structure of PALDIM. **7a** should be energetically favored over the analogous formyl structure, **6a**, because of the stabilizing effect of the intramolecular hydrogen bond on the negatively charged nitrogen atom. A possible resonance hybrid for PALDIM, made from equal contributions of **2a** and **7a**, plus some **7b**, is shown in structure **8a**. The fast proton exchange would then occur between structures **8a** and **8b** which have identical C and N locations, limiting the solid state disorder to the central H atom.

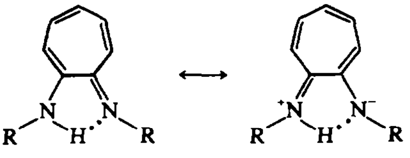


2a **7a** **7b**

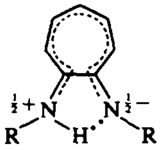


8a **8b**

This kind of analysis can be readily extended to the aminotroponeimine (**1**), by using equal contributions of canonical forms **1a** and **9** to give resonance hybrid **10**. Any contribution from a cycloheptatrienium structure (**11**) is improbable because the 1·490 Å C(1)–C(7) distance is right for a Csp^2–Csp^2 single bond.* In their analysis of the crystallographic data for **1** (R = CH$_3$), Goldstein and Trueblood[4] cited the absence of high tangential motion of the ring atoms as evidence against the coexistence of the distinct tautomers (**1a** and **1b**) in the crystal. However, from the data and arguments presented in this paper, we feel that the possibility of a solid state disorder cannot be dismissed because the existence of resonance hybrids like **8** for PALDIM and **10** for **1**, would result in structures with apparent C_{2v} symmetry and make any solid state disorder of the C and N atoms impossible to detect. Therefore, the analysis of solid state disorder is restricted to the central H of the aminotroponeimine.



1a **9**



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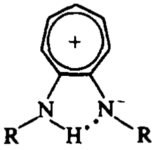

11

Since difference electron density maps for both the 5- and 7-ring compounds have revealed two H minimia, we conclude that there is no evidence for a symmetrical H location in either case. However, the structural data indicate that the intramolecular hydrogen transfer from nitrogen to nitrogen should be quite facile.

A further investigation of the symmetrical–unsymmetrical hydrogen position was made using the X-ray photoelectron spectra (XPS) of the N,N′-dimethyl, di-t-butyl and diphenyl derivatives of **2**. The rationale behind these experiments was that an unsymmetrical H location would correspond to two different nitrogen atoms (one amino and one imino),

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*Although the cycloheptatrienium form **11** is unimportant for the aminotroponeimine resonance hybrid, the corresponding cyclopentadienide structure **7b** makes a significant contribution to the PALDIM resonance hybrid **8**. The structural data which suggest that this difference exists are: (1) the N(1)–C(6) and N(2)–C(7) distances in PALDIM are *ca* 0·03 Å shorter than the aminotroponeimine N(1)–C(1) and N(2)–C(7) distances, indicating more C=N character in PALDIM; (2) the 1·447 Å C(1)–C(2) distance in PALDIM is shorter than a normal Csp^2–Csp^2 single bond (1·47–1·49 Å), indicating that there is some C=C character in this connection, whereas the 1·490 Å C(1)–C(7) aminotroponeimine length is a single bond length.

whereas a symmetrical location would have but one nitrogen. The N(1s) XPS spectra of all three compounds consisted of a single broadened peak which remained unchanged throughout the temperature range from ambient to *ca* −150°. The peaks (FWHH = 3·1–3·3 eV) could be deconvoluted, however, into two components (FWHH = 2·3 eV) of equal area, separated by energies of 1·36, 1·45 and 1·45 eV for the methyl, *t*-butyl and phenyl compounds, respectively. These data demonstrate the existence of two different N atoms in **2**, and confirm the unsymmetrical H location.

It is conceivable that an increase in nitrogen basicity from the N-phenyl to the N-alkyl compounds could lead to a stronger N–H···N linkage with a concomitant decrease in the N···N separation. This possibility was explored using the IR spectra of the methyl, *t*-butyl and phenyl compounds. The N–H bands were broad and very characteristic of a strong intramolecular hydrogen bond.[5] The band shapes and positions in the three compounds were virtually identical; 2304, 2305 and 2310 cm^{-1}, respectively. The IR and XPS experiments indicate that the N–H···N structures are essentially identical and that nitrogen atom basicity must have a negligible structural influence.

The 2·51 Å N···N distance in **1** (R = CH_3)[4] compared to the 2·79 Å distance in PALDIM suggests that the first compound should represent the better possibility for a symmetrical H location and for a strong intramolecular H bond, whereas the opposite is indicated by the IR spectra of the compounds. The N–H stretch in **1** appeared as a relatively sharp band at 3226 cm^{-1},[3] while the PALDIM absorption appeared as a broad band centered at 2310 cm^{-1}, features which can be attributed to a stronger and more symmetrical H bonding situation in the latter. Semiempirical MO studies[7] of the linear N···H–N association in the pyridinium–pyridine and pyridine–pyrrole systems suggested that a single potential minimum for the H atom (symmetrical location) occurred below N···N distances of 2·5 Å, while a double potential minimum (unsymmetrical) prevailed above this value. Although the 2·51 Å N···N distance in **1** is just on the symmetrical–unsymmetrical border line, the N···H distances and N···H–N angles in PALDIM are more appropriate to a strong interaction than are the corresponding parameters in **1**. For example, the H···N distance and N–H···N angle in **1** are 2·03 Å and 107°* (Fig 3) compared to values of 1·84 Å and 156° in PALDIM (Fig 4). Since PALDIM has both a shorter N···H and more linear N···H–N contact than in **1**, the PALDIM hydrogen bond should be stronger, and the PALDIM hydrogen location should be more symmetrical than that in the aminotroponeimine.

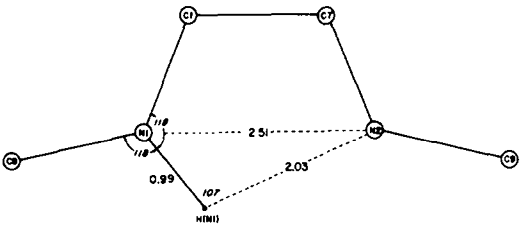

Fig. 3. Distances (Å) and angles (°) in the N···N region of 1-methylamino-7-methylimino-1,3,5-cycloheptatriene.

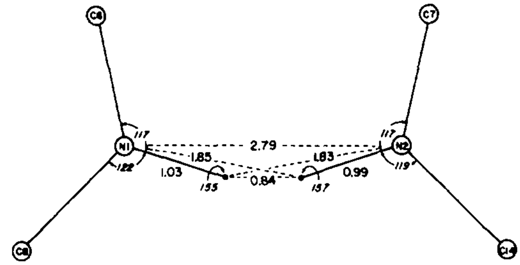

Fig. 4. Distances (Å) and angles (°) in the N···N region of PALDIM.

EXPERIMENTAL

X-ray diffraction. N,N′-Diphenyl-6-aminopentafulvene-2-aldimine[5] crystallized from cyclohexane as bright yellow-orange needles. A 0·23 × 0·1 × 0·2 mm specimen, obtained by cutting one of the needles, was mounted parallel to the needle axis (*c*). Oscillation and Weissenberg photographs (Cu radiation) revealed the acentric, orthorhombic space group $P2_12_12_1$. Intensity and accurate cell constant data were obtained on a Siemens AED diffractometer using Ni-filtered Cu radiation (CuK$\alpha\lambda$ = 1·5418 Å). The unit cell parameters were calculated by least-squares from 33 2θ's measured with an automatic reflection centering program. The crystal data are: formula $C_{19}H_{16}N_2$; mol wt 272·3; a = 5·468 (1), b = 20·442 (6), c = 13·088 (3) Å; V = 1462·9 Å^3; ρ_{calcd} = 1·236 g cm^{-3} for Z = 4.

Intensity data were collected by the 2θ–θ scan method using the Siemens 5-point scan technique.[9] The instrument performs a 0·01° (θ) step scan and the counting time at each step is varied according to an initial evaluation of the peak intensity. The counting times ranged from 1·2 sec per step for the weakest to 0·06 sec per step for the strongest reflections; the 2θ maximum = 120°. A single standard reflection was measured at 20 reflection intervals to monitor intensity fluctuations. a total of 2913 data were measured (2 octants, hkl and $h\bar{k}l$), which gave 1293 unique data (1314 including space group absent data). 533 of the 1293 data were less than 3σ above background.

The data were reduced, scaled and normalized structure factors (E's) were calculated.† The structure was solved by direct methods using a combination of symbolic addition and tangent refinement. The three origin (0,2,3 = 0°, 1,0,3 = 90°, 0,17,5 = 90°) and one enantiomorph (5,11,0 =

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*These data are given only for H(N1). The H(N2) position is improbable.

†All calculations were performed on a UNIVAC 1108 computer with the *X-ray System*[10] of crystallographic programs.

Table 2. Atomic fractional coordinates, temperature factors (Å^2)^a and estimated standard deviations (in parentheses)

ATOM	X	Y	Z	U or U11	U22	U33	U12	U13	U23
C(1)	−0·1741(5)	−0·0901(1)	0·4092(2)	0·059(2)	0·055(2)	0·063(2)	0·001(2)	0·006(2)	−0·002(1)
C(2)	−0·3803(5)	−0·0802(1)	0·4768(2)	0·059(2)	0·053(1)	0·053(2)	0·001(1)	0·003(1)	0·003(1)
C(3)	−0·4800(6)	−0·1431(1)	0·4952(2)	0·074(2)	0·067(2)	0·073(2)	−0·008(2)	0·010(2)	0·007(2)
C(4)	−0·3448(7)	−0·1897(1)	0·4428(2)	0·093(2)	0·055(2)	0·094(2)	−0·004(2)	0·011(2)	−0·005(2)
C(5)	−0·1587(6)	−0·1577(1)	0·3905(2)	0·082(2)	0·063(2)	0·091(2)	−0·001(2)	0·016(2)	−0·013(2)
C(6)	−0·0102(6)	−0·0460(1)	0·3635(2)	0·057(2)	0·072(2)	0·060(2)	0·002(2)	0·007(2)	−0·012(1)
C(7)	−0·4787(6)	−0·0240(1)	0·5195(2)	0·056(2)	0·069(2)	0·050(1)	0·001(2)	0·004(2)	0·005(1)
C(8)	0·1612(5)	0·0572(1)	0·3198(2)	0·049(2)	0·066(2)	0·045(1)	−0·010(1)	−0·003(1)	−0·004(1)
C(9)	0·1037(5)	0·1229(1)	0·3082(2)	0·056(2)	0·066(2)	0·065(2)	−0·005(2)	0·001(2)	−0·002(1)
C(10)	0·2568(6)	0·1640(1)	0·2534(2)	0·074(2)	0·074(2)	0·075(2)	−0·013(2)	−0·004(2)	0·005(2)
C(11)	0·4669(6)	0·1398(2)	0·2094(2)	0·069(2)	0·096(2)	0·065(2)	−0·026(2)	−0·008(2)	0·015(2)
C(12)	0·5264(5)	0·0750(2)	0·2224(2)	0·049(2)	0·106(2)	0·053(2)	−0·010(2)	−0·001(2)	−0·001(2)
C(13)	0·3770(5)	0·0336(1)	0·2781(2)	0·052(2)	0·077(2)	0·052(2)	−0·001(2)	−0·003(2)	−0·003(1)
C(14)	−0·5175(6)	0·0913(1)	0·5498(2)	0·056(2)	0·062(2)	0·043(1)	0·010(2)	−0·005(1)	0·001(1)
C(15)	−0·7374(6)	0·0889(1)	0·6022(2)	0·065(2)	0·078(2)	0·064(2)	0·009(2)	0·011(2)	0·007(2)
C(16)	−0·8303(6)	0·1456(2)	0·6459(2)	0·080(2)	0·094(2)	0·072(2)	0·025(2)	0·014(2)	0·003(2)
C(17)	−0·7128(7)	0·2043(2)	0·6351(3)	0·100(3)	0·078(2)	0·081(2)	0·026(2)	0·008(2)	−0·009(2)
C(18)	−0·5007(8)	0·2071(1)	0·5795(3)	0·108(3)	0·064(2)	0·103(3)	0·004(2)	0·013(3)	−0·015(2)
C(19)	−0·4033(6)	0·1509(1)	0·5373(2)	0·076(2)	0·064(2)	0·085(2)	0·001(2)	0·016(2)	−0·009(2)
N(1)	−0·0072(4)	0·0176(1)	0·3750(1)	0·051(1)	0·057(1)	0·053(1)	−0·004(1)	0·004(1)	−0·002(1)
N(2)	−0·4031(4)	0·0359(1)	0·5065(2)	0·054(1)	0·057(1)	0·048(1)	0·003(1)	0·004(1)	−0·001(1)
H(N1)	−0·138	0·038	0·422	0·08					
H(N2)	−0·258	0·042	0·461	0·08					
H(3)	−0·631(4)	−0·150(1)	0·535(2)	0·080(8)					
H(4)	−0·379(5)	−0·238(1)	0·443(2)	0·090(8)					
H(5)	−0·038(5)	−0·179(1)	0·345(2)	0·094(8)					
H(6)	0·109(4)	−0·0665(9)	0·317(2)	0·073(7)					
H(7)	−0·615(4)	−0·0313(9)	0·564(1)	0·052(6)					
H(9)	−0·045(4)	0·1401(9)	0·335(2)	0·072(7)					
H(10)	0·202(5)	0·213(1)	0·248(2)	0·092(8)					
H(11)	0·569(5)	0·171(1)	0·173(2)	0·13(1)					
H(12)	0·683(4)	0·054(1)	0·190(2)	0·086(8)					
H(13)	0·423(4)	−0·012(1)	0·287(2)	0·081(7)					
H(15)	−0·838(5)	0·045(1)	0·613(2)	0·103(9)					
H(16)	−0·995(6)	0·142(1)	0·686(2)	0·12(1)					
H(17)	−0·777(5)	0·247(1)	0·670(2)	0·092(8)					
H(18)	−0·413(6)	0·251(1)	0·572(2)	0·12(1)					
H(19)	−0·251(5)	0·152(1)	0·499(2)	0·096(8)					

^{a}The form of the anisotropic temperature factors is exp $[-2\pi^2(U_{11}h^*a^{*2}+\cdots 2U_{23}klb^*c^*)]$.

90°) fixing phases, plus one other (1,1,3) provided a satisfactory start for the entire phase determination. An E-map computed with 219 terms revealed the 21 C and N atoms. The structure refinement was by full-matrix least-squares with anisotropic temperature factors for the C and N atoms, isotropic terms for H (initially located from a difference map). The calculation included a secondary isotropic extinction correction ($r^* = 0{\cdot}00065(1)$[11]). The function minimized was $\Sigma(F_0 - F_c)^2$. Unit weights were justified by the data collection procedure, which tended to equalize the standard deviations of the intensities. The final R index ($\Sigma|F_o - F_c|/\Sigma F_o$) was 0·021. Atomic scattering factors were taken from the work of Cromer and Mann.[12] The atomic parameters are given in Table 2; a structure factor list may be obtained from the authors on request.

Photoelectron spectra. The spectra were obtained using a Varian IEE-15 spectrometer equipped with a Mg X-ray source ($K\alpha$, 1253·6 eV). All samples were run as powders which were mixed with alumina and dusted onto double-backed cellophane tape. The spectra were referenced to a 73·55 eV Al line, which had been previously calibrated using gold decoration as the reference (Au $4f_{7/2}$ = 83·0 eV). The N(1s) spectra from the three aminopentafulvene-aldimines consisted of a single, broad peak with full-width half heights (FWHH's) in the range of 3·1–3·3 eV. The individual spectra were resolved into two peaks of almost equal intensity with a DuPont 310 Curve Resolver. The component functions used with the Resolver were Gaussian with a FWHH of 2·3 eV (from measurements on ammonium chloride). In a typical run on the diphenyl isomer at ambient temperature, the experimental peak (FWHH = 3·3 eV) was resolved into two components with relative areas of 49 and 51. The data reported in the text are average values from at least three runs for each compound.

IR spectra. The IR spectra were recorded as fluorolube mulls on a Perkin-Elmer 225 spectrometer.

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