

The Structures of 6-(*N,N*-Dimethylamino)pentafulvene and 2-Formyl-6-(*N,N*-dimethylamino)pentafulvene. Bond Length Evidence for Dipolar Resonance Forms

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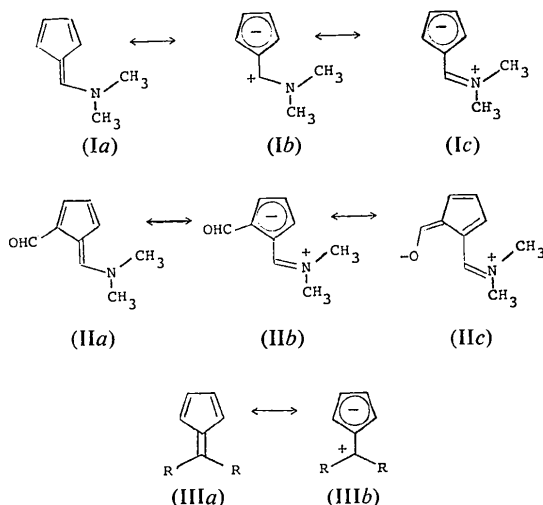
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The structural consequences of dipolar resonance forms of the pentafulvenes have been studied for 6-(*N,N*-dimethylamino)pentafulvene (NMEFUL) and 2-formyl-6-(*N,N*-dimethylamino)pentafulvene (AMFORF). NMEFUL: $P2_12_12_1$; $a = 5.872$, $b = 17.293$, $c = 7.273$ Å; $Z = 4$. AMFORF: $P\bar{1}$; $a = 9.793$, $b = 11.971$, $c = 7.608$ Å, $\alpha = 91.90$, $\beta = 110.03$, $\gamma = 90.72^\circ$, $Z = 4$. Three-dimensional intensity data, Mo for NMEFUL and Cu for AMFORF, were collected on automatic diffractometers. The structures were solved by direct methods and refined with full-matrix least-squares techniques. The final R indices were 0.040 for NMEFUL and 0.044 for AMFORF. Bond lengths in the five-membered rings and the $-C=C-N(CH_3)_2$ portions of the molecules differ from normal values and show the effects of significant contributions of dipolar resonance forms to the structures.

Introduction

The crystal structures of two 6-aminopentafulvenes, 6-(*N,N*-dimethylamino)pentafulvene (I, NMEFUL) and 2-formyl-6-(*N,N*-dimethylamino)pentafulvene (II, AMFORF) have been investigated as part of a program to delineate the structural consequences of charge separation in the nitrogen-containing pentafulvenes.



Although dipolar canonical forms such as (IIIb) contribute little to the ground state resonance hybrids of alkyl-substituted pentafulvenes [(III); see Yates (1968) for a review], the introduction of a 6-amino substituent (Ia) can help to stabilize the charge-separated form by delocalization of the exocyclic positive charge in (Ib) to nitrogen (Ic). Several characteristic features of the 6-aminopentafulvenes which reflect this dipolarity are dipole moments, C=C and C-N rotational barriers

and vicinal proton coupling constants in the 5-ring. For example, the 4.5 D dipole moment of (I) (Hafner, Vöpel, Ploss & König, 1963) is considerably larger than the 1.48 D of 6,6-dimethylpentafulvene (III, R = CH₃; Wheland & Mann, 1949). Crabtree & Bertelli (1967) have estimated a charge magnitude of 1.33 esu (0.28 e) for (I) assuming the negative end of the dipole was located in the middle of the 5-ring and the positive end was positioned on N. We have obtained an identical value (Wheeler, 1973; Ammon & Wheeler, 1973) for the total 5-ring charge (5 C's + 4 H's) from CNDO/2 calculations. The energy barriers restricting rotation about the C(1)=C(6) and C(6)-N bonds in (I) are, respectively, 22.1 and 13.5 kcal mole⁻¹ (ΔG^\ddagger ; Downing, Ollis & Sutherland, 1969). These values can be put in perspective by a comparison with the 36.7 kcal mole⁻¹ C=C barrier in stilbene (Taylor & Murray, 1938) and 4.4 kcal mole⁻¹ C-N barrier in trimethylamine (Lide & Mann, 1958). Additionally, the dipolar natures of these aminofulvenes can be detected in their 5-ring vicinal proton coupling constants which are inversely proportional to the lengths of the carbon-carbon bonds to which the H's are attached. The $J_{34} = 3.1$ Hz and $J_{45} = 4.5$ Hz values in (II) (Mannschreck & Kölle, 1969) are between the $J_{C-C} = 1.94$ Hz and $J_{C-C} = 5.06$ Hz values for cyclopentadiene (Lambert, Durham, Lepoutere & Roberts, 1965), indicating that the 5-ring lengths in (II) are more equal than the C=C-C=C distances in cyclopentadiene.

Experimental

X-ray measurements

The X-ray measurement techniques and data analyses employed here have been previously described (Ammon, & Wheeler, 1974; Ammon & Mueller-Westerhoff, 1974). Intensity data for NMEFUL were obtained on

a Picker FACS-I diffractometer with monochromatic Mo radiation; the data for AMFORF were obtained on a Siemens AED diffractometer with Ni-filtered Cu radiation. Crystal and intensity measurement data are reported in Table 1.

Intensity corrections were made for (a) crystal decomposition and intensity fluctuations with the standard reflection data, and (b) for Lp. Absorption corrections were not made.

Structure solution

NMEFUL: space group $P2_12_12_1$; $Z=4$. The structure was solved, and initially refined, in the monoclinic space group $P2_1$. I am grateful to an unknown referee for indicating the space group error. The structure was solved by direct methods. Following calculation of the

pseudo-normalized structure factors (E), an initial set of 18 symbolic phases, based on three origin-defining reflections (103, 201, $21\bar{7}$) and a fourth unrestricted reflection (1,14,2) was derived by hand. The 1,14,2 phase was set to $\pi/2$ for enantiomorph specification, and the initial 18 phases were expanded to 250 phases ($E > 1.3$) by tangent refinement. An E map computed with these 250 data revealed all of the C and N atoms. The initial R index ($\sum|F_o - F_c|/\sum F_o$) was 0.28.

AMFORF: space group $P\bar{1}$, $Z=4$. The structure was solved by direct methods, with the 253 largest E 's (> 1.1). Preliminary studies showed that an extensive phase pyramid could be constructed with a starting set of seven phases (3 origin, 4 arbitrary). The problem was then to compute the 15 solutions ($2^4 - 1$) and their associated E maps, and to pick the correct map. The

Table 1. Crystal and intensity measurement data

	NMEFUL	AMFORF
Molecular formula	$C_8H_{11}N$	$C_9H_{11}NO$
Method of crystal formation	Sublimation	Recrystallization from hexane-isopropyl alcohol
Crystal color, shape, size	Light yellow, cube <i>ca.</i> 0.4 mm	Light yellow, cube <i>ca.</i> 0.3 mm
Space group	$P2_12_12_1$	$P\bar{1}$
Number of 2θ 's measured (average $ 2\theta_o - 2\theta_c $)	21 by manual centering at $\pm 2\theta$ (0.013°)	34 by automatic centering (0.025°)
Cell parameters (e.s.d.'s)	$a = 5.872$ (3) Å $b = 17.293$ (10) $c = 7.273$ (4)	$a = 9.793$ (2) Å $b = 11.971$ (3) $c = 7.608$ (2) $\alpha = 91.90$ (2)° $\beta = 110.03$ (2) $\gamma = 90.72$ (2)
Z	4	4
ρ_{exp} (by neutral buoyancy in aqueous KI)	1.070 g cm ⁻³	1.173 g cm ⁻³
ρ_{x-ray}	1.089 g cm ⁻³	1.182 g cm ⁻³
Reciprocal lattice vector parallel to diffractometer φ axis	[100]	[001]
2θ - θ scan range, scan rate, background time	1.4° + 0.69 tan θ , 0.5° min ⁻¹ , 40 s	1.92–2.64°, 1–20° min ⁻¹ depending on peak intensity, variable
Maximum 2θ , radiation, λ	50°, Mo $K\alpha$, 0.71069 Å	120°, Cu $K\alpha$, 1.5418 Å
Number of data measured, unique data, data 3σ above background	2979 ($h \pm k \pm l$), 795, 685	2662, 2362, 1620

Table 2. Fractional coordinates, temperature factors (Å^2) and e.s.d.'s for 6-(*N,N*-dimethylamino)pentafulvene

	x	y	z	U or U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	0.5173 (4)	0.0451 (1)	0.5798 (3)	0.063 (1)	0.088 (2)	0.051 (1)	-0.002 (1)	-0.003 (1)	-0.001 (1)
C(2)	0.6102 (5)	0.1180 (2)	0.5216 (4)	0.075 (2)	0.112 (2)	0.065 (2)	-0.022 (2)	0.004 (2)	0.005 (2)
C(3)	0.4633 (6)	0.1751 (2)	0.5679 (4)	0.115 (2)	0.085 (2)	0.074 (2)	-0.010 (2)	-0.013 (2)	0.004 (2)
C(4)	0.2744 (6)	0.1410 (2)	0.6571 (4)	0.086 (2)	0.105 (2)	0.069 (2)	0.010 (2)	0.002 (2)	-0.007 (2)
C(5)	0.3049 (5)	0.0630 (2)	0.6650 (4)	0.073 (2)	0.102 (2)	0.058 (1)	-0.015 (2)	0.004 (1)	0.005 (1)
C(6)	0.6337 (5)	-0.0228 (2)	0.5418 (3)	0.063 (2)	0.113 (2)	0.054 (1)	-0.008 (2)	0.000 (1)	0.002 (1)
C(7)	0.7312 (6)	-0.1586 (2)	0.5208 (4)	0.104 (2)	0.115 (2)	0.086 (2)	0.021 (2)	-0.005 (2)	-0.006 (2)
C(8)	0.3697 (6)	-0.1175 (2)	0.6664 (5)	0.091 (2)	0.101 (2)	0.082 (2)	-0.010 (2)	0.008 (2)	0.008 (2)
N	0.5787 (4)	-0.0960 (1)	0.5770 (3)	0.076 (1)	0.085 (1)	0.060 (1)	0.000 (1)	-0.002 (1)	0.002 (1)
H(2)	0.748 (5)	0.120 (1)	0.459 (4)	0.094 (8)					
H(3)	0.481 (5)	0.232 (2)	0.545 (4)	0.11 (1)					
H(4)	0.146 (5)	0.168 (2)	0.698 (4)	0.09 (1)					
H(5)	0.208 (5)	0.028 (1)	0.720 (4)	0.087 (9)					
H(6)	0.779 (6)	-0.021 (1)	0.473 (4)	0.108 (9)					
H(8A)	0.388 (4)	-0.177 (1)	0.662 (3)	0.082 (8)					
H(8B)	0.358 (7)	-0.092 (2)	0.805 (6)	0.17 (1)					
H(8C)	0.241 (6)	-0.093 (2)	0.582 (5)	0.12 (1)					

selection criteria were based on the relative numbers of 0 and π phases (the correct solution should have approximately equal numbers of each) and on the absence of large peaks close to centers of symmetry. The 'best' E map (127 0, 126 π phases) did not reveal the structure. The next five best solutions on the basis of the numbers of 0 and π phases were unacceptable because of the center of symmetry criterion. The correct solution was No. 7 (120 0, 133 π). Several 'artifact' peaks in the E map were higher than real atom peaks, and two of the 22 C, N and O atoms were incorrectly selected. The initial R index for the correct 22 atom trial structure was 0.31 for 0.4 $\sin \theta/\lambda$ data.

Refinement

The structure refinement was by the full-matrix least-squares method and used anisotropic temperature factors for C, N and O and isotropic terms for H. The minimization function was $\sum w(F_o - F_c)^2$; the weights (w) were calculated from a Hughes (1941) type function

[$w = 1$ for $F_o \leq K$, $w = (K/F_o)^2$ for $F_o > K$] with K selected to make the $w(F_o - F_c)^2$ differences approximately equal for all ranges of F_o . Isotropic secondary extinction corrections were applied [r^* , equation (22) in Larson (1970)]: $r^* = 0.021(4)$ for NMEFUL and 0.00312 (9) for AMFORF. The form of the anisotropic t.f.'s reported in the atomic parameters tables is $T = \exp[-2\pi^2(U_{11}h^2a^{*2} + \dots + 2U_{23}klb^*c^*)]$.

NMEFUL: H atoms were located from a difference map, with the exception of the three atoms attached to C(7). The methyl hydrogens were represented by a circle of 12 H's (0.25 weight; C-H = 1.04 Å, N-C-H = 109.5°) with $B = 9.0 \text{ Å}^2$ ($U = 0.114 \text{ Å}^2$); the H parameters were not refined. The value of K for the weight (w) calculations was 10.0. The final R and weighted R ($[\sum w(F_o - F_c)^2 / \sum w F_o^2]^{1/2}$) were 0.040 and 0.045. The atomic parameters are listed in Table 2.

AMFORF: all H atoms were located from a difference map and refined normally. The value of K was 28.0. The final R and weighted R values were 0.044

Table 3. Fractional coordinates, temperature factors (Å^2) and e.s.d.'s for 2-formyl-6-(*N,N*-dimethylamino)-pentafulvene

	x	y	z	U or U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	1.0794 (3)	0.4758 (2)	0.7826 (4)	0.052 (2)	0.056 (2)	0.046 (2)	0.000 (1)	0.011 (1)	-0.002 (1)
C(2)	1.1778 (3)	0.3852 (3)	0.8511 (4)	0.055 (2)	0.059 (2)	0.047 (2)	0.001 (1)	0.009 (1)	0.000 (1)
C(3)	1.3149 (4)	0.4213 (3)	0.8590 (5)	0.051 (2)	0.076 (2)	0.075 (2)	0.004 (2)	0.013 (2)	-0.004 (2)
C(4)	1.3071 (4)	0.5309 (3)	0.7991 (5)	0.059 (2)	0.079 (2)	0.081 (2)	-0.015 (2)	0.023 (2)	-0.006 (2)
C(5)	1.1655 (4)	0.5645 (3)	0.7525 (4)	0.068 (2)	0.059 (2)	0.062 (2)	-0.004 (2)	0.018 (2)	0.002 (1)
C(6)	0.9330 (4)	0.4644 (3)	0.7608 (4)	0.055 (2)	0.062 (2)	0.051 (2)	0.002 (2)	0.014 (1)	-0.006 (1)
C(7)	0.6798 (4)	0.4997 (4)	0.6846 (6)	0.047 (2)	0.119 (3)	0.106 (3)	0.007 (2)	0.021 (2)	-0.030 (3)
C(8)	0.8472 (4)	0.6461 (3)	0.6445 (5)	0.085 (3)	0.081 (3)	0.086 (3)	0.024 (2)	0.024 (2)	0.009 (2)
C(9)	1.1498 (4)	0.2757 (3)	0.9037 (5)	0.080 (3)	0.063 (2)	0.073 (2)	0.005 (2)	0.018 (2)	0.004 (2)
N	0.8277 (3)	0.5351 (2)	0.7025 (4)	0.058 (2)	0.074 (2)	0.056 (2)	0.012 (1)	0.012 (1)	-0.008 (1)
O	1.0338 (3)	0.2354 (2)	0.9003 (4)	0.090 (2)	0.067 (2)	0.115 (2)	-0.010 (1)	0.036 (2)	0.012 (1)
H(3)	1.404 (3)	0.376 (2)	0.899 (4)	0.08 (1)					
H(4)	1.388 (3)	0.574 (2)	0.788 (4)	0.08 (1)					
H(5)	1.129 (3)	0.637 (2)	0.703 (4)	0.08 (1)					
H(6)	0.900 (3)	0.389 (2)	0.795 (4)	0.06 (1)					
H(7A)	0.661 (7)	0.440 (6)	0.77 (1)	0.24 (4)					
H(7B)	0.629 (4)	0.564 (4)	0.706 (6)	0.13 (2)					
H(7C)	0.625 (5)	0.477 (4)	0.562 (7)	0.15 (2)					
H(8A)	0.747 (5)	0.687 (3)	0.618 (6)	0.13 (2)					
H(8B)	0.922 (4)	0.691 (3)	0.735 (5)	0.10 (1)					
H(8C)	0.892 (4)	0.647 (3)	0.551 (5)	0.11 (2)					
C(1')	0.5763 (4)	0.0003 (2)	0.3167 (4)	0.062 (2)	0.052 (2)	0.064 (2)	0.000 (1)	0.003 (2)	0.005 (1)
C(2')	0.6630 (4)	0.0969 (3)	0.4145 (5)	0.075 (3)	0.063 (2)	0.065 (2)	-0.009 (2)	0.035 (2)	0.000 (2)
C(3')	0.8004 (4)	0.0598 (4)	0.5146 (5)	0.075 (3)	0.099 (3)	0.079 (3)	-0.015 (2)	0.023 (2)	0.000 (2)
C(4')	0.8039 (5)	-0.0550 (4)	0.4844 (6)	0.069 (2)	0.100 (3)	0.109 (3)	0.011 (2)	0.022 (2)	0.017 (3)
C(5')	0.6697 (4)	-0.0920 (3)	0.3648 (5)	0.081 (3)	0.063 (2)	0.086 (3)	0.008 (2)	0.033 (2)	0.009 (2)
C(6')	0.4312 (4)	0.0102 (2)	0.2085 (4)	0.069 (2)	0.049 (2)	0.069 (2)	-0.001 (2)	0.036 (2)	0.008 (2)
C(7')	0.1876 (4)	-0.0356 (3)	0.0007 (6)	0.064 (3)	0.094 (3)	0.101 (3)	-0.007 (2)	0.018 (2)	0.020 (2)
C(8')	0.3716 (5)	-0.1803 (3)	0.0848 (6)	0.106 (3)	0.059 (2)	0.102 (3)	-0.005 (2)	0.023 (2)	-0.010 (2)
C(9')	0.6234 (5)	0.2118 (3)	0.4163 (6)	0.098 (3)	0.066 (2)	0.106 (3)	-0.022 (2)	0.052 (3)	-0.015 (2)
N'	0.3360 (3)	-0.0648 (2)	0.1057 (4)	0.067 (2)	0.056 (2)	0.072 (2)	-0.006 (1)	0.025 (1)	0.008 (1)
O'	0.5075 (4)	0.2530 (2)	0.3337 (5)	0.104 (3)	0.055 (2)	0.184 (3)	0.002 (2)	0.062 (2)	-0.002 (2)
H(3')	0.888 (4)	0.109 (3)	0.591 (5)	0.11 (2)					
H(4')	0.895 (4)	-0.102 (3)	0.534 (5)	0.12 (2)					
H(5')	0.640 (4)	-0.169 (3)	0.314 (4)	0.09 (1)					
H(6')	0.390 (3)	0.087 (2)	0.209 (4)	0.08 (1)					
H(7A')	0.164 (4)	0.040 (3)	0.042 (5)	0.11 (2)					
H(7B')	0.158 (5)	-0.040 (4)	-0.137 (6)	0.14 (2)					
H(7C')	0.114 (4)	-0.081 (3)	0.025 (5)	0.11 (2)					
H(8A')	0.281 (6)	-0.221 (4)	0.008 (8)	0.18 (3)					
H(8B')	0.464 (5)	-0.183 (4)	0.045 (6)	0.14 (2)					
H(8C')	0.407 (5)	-0.218 (3)	0.199 (6)	0.12 (2)					

and 0.060. The atomic parameters are listed in Table 3.

The AMFORF structure shows a pseudo-symmetry close to that expected for the monoclinic space group $P2_1/n$. The approximate relationship between the two molecules is $x, y, z \approx \frac{1}{2} + x', \frac{1}{2} - y', \frac{1}{2} + z'$. Intensity variations corresponding to the $P2_1/n$ systematic absences for $0k0$ and $h0l$ are most pronounced for the $0k0$'s. The overall Laue symmetry deviates considerably from the $2/m$ necessary for the monoclinic system.

X-ray scattering curves for C, N and O were taken from the work of Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955); the H curve was taken from Stewart, Davidson & Simpson (1965).†

Computer programs

The Picker diffractometer was controlled by Lenhart & Henry's (1970) disc control package; the Siemens diffractometer used software supplied by the manufacturer. The major calculations were performed on the University of Maryland's UNIVAC 1108 with The X-RAY System of Crystallographic Programs (Stewart, Kruger, Ammon, Dickinson & Hall, 1972).

Discussion

The NMEFUL molecule and two AMFORF molecules are essentially (individually) coplanar. There are only small deviations of the non-5-ring atoms from the 5-ring planes (Tables 4 and 5). The dimethylamino groups $=CH-N(CH_3)_2$ are coplanar and the angles between the dimethylamino and 5-ring planes are 2.6° in NMEFUL, and 4.2° and 1.1° in AMFORF.

Table 4. *Least-squares planes and deviations* (Å) for NMEFUL

	Plane 1	Plane 2
C(1)	-0.002*	-0.009
C(2)	0.002*	-0.064
C(3)	-0.002*	-0.109
C(4)	0.001*	-0.077
C(5)	0.001*	-0.016
C(6)	-0.046	-0.002*
C(7)	-0.149	-0.002*
C(8)	-0.124	-0.002*
N	-0.095	0.007*

Plane 1: $2.7085x + 1.7109y + 6.4132z = 5.1979$

Plane 2: $2.7029x + 0.9392y + 6.4450z = 5.1859$

* Used for plane definition.

Bond lengths and angles for the two compounds are given in Figs. 1 and 2. The most significant aspect of these structures is the departure of the 5-ring and

† The tables of structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30398 (35 pp., 1 microfiche). Copies of these tables may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 5. *Least-squares planes and deviations* (Å) for AMFORF

	Plane 1	Plane 2
C(1)	0.000*	-0.044
C(2)	0.001*	-0.060
C(3)	-0.001*	-0.088
C(4)	0.001*	-0.086
C(5)	0.000*	-0.061
C(6)	0.011	-0.006*
C(7)	-0.035	-0.005*
C(8)	-0.003	-0.005*
C(9)	-0.001	-0.056
N	0.015	0.017*
O	-0.012	-0.046

Plane 1: $-1.4064x + 3.7427y + 6.9961z = 5.7382$

Plane 2: $-1.5972x + 3.7478y + 7.0236z = 5.6002$

C(1')	0.001*	-0.007
C(2')	0.000*	-0.071
C(3')	-0.001*	-0.011
C(4')	0.002*	0.088
C(5')	-0.002*	0.086
C(6')	0.045	-0.003*
C(7')	0.060	-0.003*
C(8')	-0.102	-0.003*
C(9')	0.002	-0.173
N'	0.014	0.008*
O'	-0.004	-0.239

Plane 1': $-5.8103x - 2.0895y + 7.1983z = -1.0706$

Plane 2': $-5.5583x - 2.9125y + 7.1521z = -0.9315$

* Used for plane specification.

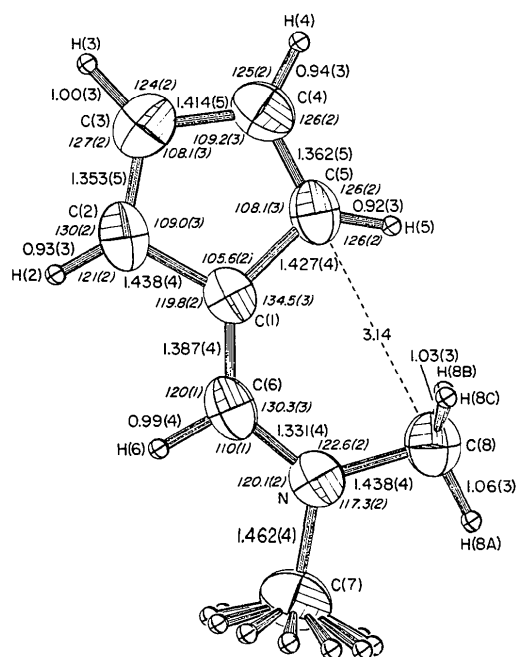


Fig. 1. Bond lengths (Å), angles ($^\circ$) and e.s.d.'s for the NMEFUL molecule superimposed on an ORTEP-II (Johnson, 1971) drawing. 30% probability ellipsoids were used for C and N with 0.1 Å radius spheres for H. The circle H atoms on C(7) have been included. The C angles which have not been included are $N-C(8)-H(8A) = 99(1)$, $N-C(8)-H(8B) = 111(2)$, $N-C(8)-H(8C) = 104(2)$, $H(8A)-C(8)-H(8B) = 115(2)$, $H(8A)-C(8)-H(8C) = 117(2)$, $H(8B)-C(8)-H(8C) = 109(3)^\circ$.

C=C–N bond lengths from standard values. The 5-ring lengths do not have the single and double bond values characteristic of cyclopentadiene, pentafulvene or 6,6-dimethylpentafulvene (Fig. 3). These compounds have

Table 6. $C(sp^2)$ – $N(sp^2)$ bond lengths and double-bond character

Structure	Length (Å)	Percent double bond character*	Reference
	1.470	0	Camerman, Jensen & Balaban (1969); Camerman (1970)
	1.404	—	Yakushi, Ikemoto & Kuroda (1971)
	1.371	25	Smith & Luss (1972)
	1.318	50	Sax, Fletcher, Yoo & Stewart (1971)
	1.311	33	McClure & Craven (1973)
	1.279	100	Iball & Motherwell (1969)

*Estimated from the canonical resonance forms for each compound.

butadiene-like bond distances (Fig. 3), which are close to the 'pure' $C(sp^2)=C(sp^2)$ and $C(sp^2)-C(sp^2)$ distances of ca. 1.34 Å (ethylene C=C=1.337 Å; Bartell, Roth, Hollowell, Kuchitsu & Young, 1965) and 1.48 Å (1.485 Å; Dewar & Schmeising, 1960). The 5-ring and C(1)–C(6) distances in NMEFUL and AMFORF reflect a decrease of π -bond character in the double bonds and concomitant increase of π -bond character in the single bonds, indicating that dipolar resonance forms such as (Ic) and (IIb) contribute substantially to the molecular ground states.

Several selected carbon–nitrogen bond distances and estimates of their percentages of double-bond character are listed in Table 6. From these data, it can be seen that the NMEFUL 1.331 Å and AMFORF 1.309 Å average C(6)–N distances correspond to double-bond characters of about 50%. The shorter C–N in AMFORF, compared to NMEFUL, accords with the C–N rotational energies (ΔG^\ddagger) of 17.9 kcal for AMFORF and 13.5 kcal mole⁻¹ for NMEFUL (Downing, Ollis & Sutherland, 1969), since the shorter bond should be the stronger bond.

Because C(1)–C(6) rotation in AMFORF is sufficiently hindered by the 2-formyl substituent, the rotational barrier (which is unknown) for this bond can not be associated with the bond length in a meaningful way. However, a comparison of this kind can be made for NMEFUL: the long C(1)–C(6) bond, 1.387 Å, coincides with the low C=C rotational energy of 22.1 kcal mole⁻¹ (Downing, Ollis & Sutherland, 1969).

Additional structural effects of the formyl group

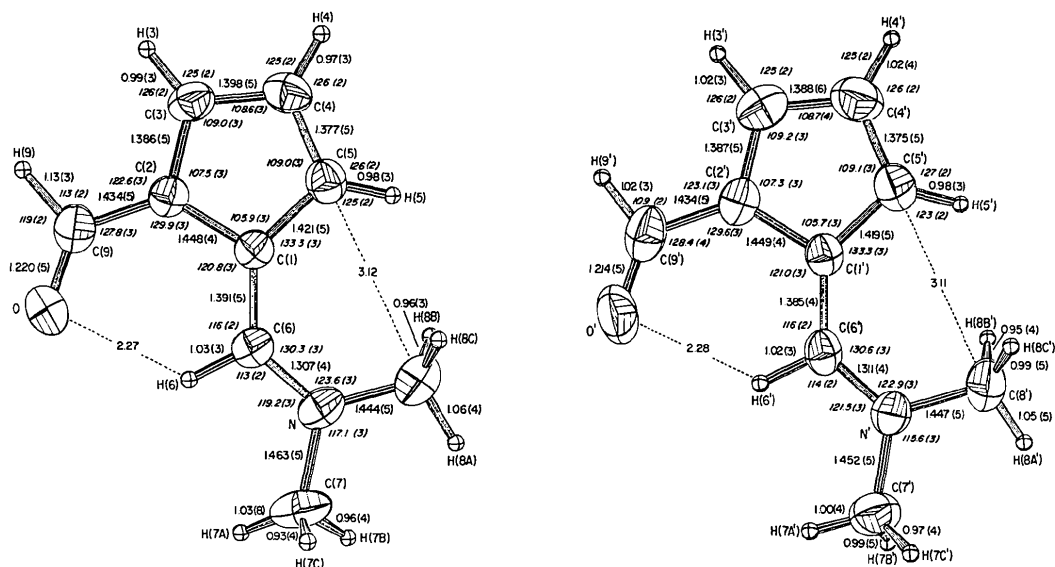
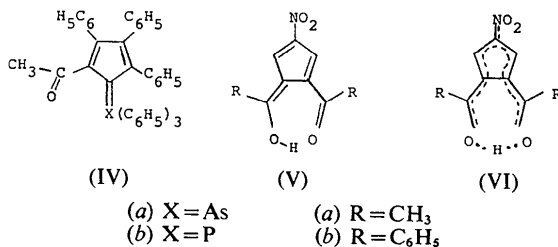


Fig. 2. Bond lengths (Å), angles (°) and e.s.d.'s for the two AMFORF molecules superimposed on ORTEP-II (Johnson, 1971) drawings. 30% probability ellipsoids were used for C, N and O with 0.1 Å radius spheres for H. The angles which have not been included are N–C(7)–H(7A)=121 (3), N–C(7)–H(7B)=108 (3), N–C(7)–H(7C)=112 (3), H(7A)–C(7)–H(7B)=105 (5), H(7A)–C(7)–H(7C)=106 (5), H(7B)–C(7)–H(7C)=102 (4), N–C(8)–H(8A)=107 (3), N–C(8)–H(8B)=114 (2), N–C(8)–H(8C)=114 (2), H(8A)–C(8)–H(8B)=109 (3), H(8A)–C(8)–H(8C)=118 (3), H(8B)–C(8)–H(8C)=95 (3), N'–C(7')–H(7A')=111 (2), N'–C(7')–H(7B')=117 (3), N'–C(7')–H(7C')=114 (2), H(7A')–C(7')–H(7B')=109 (3), H(7A')–C(7')–H(7C')=100 (3), H(7B')–C(7')–H(7C')=103 (3), N'–C(8')–H(8A')=108 (3), N'–C(8')–H(8B')=109 (2), N'–C(8')–H(8C')=114 (3), H(8A')–C(8')–H(8B')=120 (4), H(8A')–C(8')–H(8C')=106 (4), H(8B')–C(8')–H(8C')=99 (4)°.

can be seen in the unequal carbon-carbon bond lengths, $C(1)-C(2)=1.448 \text{ \AA}$ and $C(1)-C(5)=1.420 \text{ \AA}$, and in the greater uniformity in the $C(2)=C(3)-C(4)=C(5)$ region of AMFORF compared to NMEFUL. These features, including the shorter C-N in AMFORF can be rationalized by a contribution of resonance form (IIc) to the ground-state resonance hybrid. A similar bond-length pattern was reported for triphenylarsonium and triphenylphosphonium 2-acetyl-3,4,5-triphenylcyclopentadienyliide (IVa) and (IVb) (Ferguson Rendle, Lloyd & Singer, 1971; Rendle, 1972). However, the 1.240 \AA C=O distances in these ylides are more in line with the decrease in carbonyl double bond character required by a structure like (IIc), than is the 1.217 \AA distance in AMFORF. (The negative charge on O in (IVa) and (IVb) presumably is stabilized by short $As \cdots O$ and $P \cdots O$ contacts.) Diffraction studies of two 6-hydroxy-2-carbonyl substituted pentafulvenes, (Va) and (Vb), by G. Ferguson and coworkers (1973, unpublished) have provided a $1.27-1.28 \text{ \AA}$ value for the C=O length with 50% double-bond character. The carbon-oxygen double-bond character in these compounds can be placed at *ca.* 50% because the X-ray data show that the structures are most properly depicted by (VI).



An interesting part of the AMFORF structure is the close approach bond between O and H(6) [$O \cdots H(6)=2.27 \text{ \AA}$]. The most energetically reasonable conformation of the C(2)-C(9) bond, the formyl to 5-ring bond, is with O and H(6) in proximity since this arrangement enables the negative oxygen to interact with and stabilize the positive charge developed in the C(6) portion of the molecule. The opposite C(2)-C(9) conformation, with O and H(9) interchanged, would put H(9) and H(6) together and offer none of the charge stabilizing features of the $O \cdots H(6)$ interaction.

The effects of steric interactions can be seen in most of the exocyclic angles in both AMFORF and NMEFUL. Interactions of the C(8) methyl group with the near side [C(5)] of the 5-ring have produced the following angle variations: (1) the $C(5)-C(1)-C(6)$ angle is $12-15^\circ$ larger than the $C(2)-C(1)-C(6)$ angle; (2) the $C(1)-C(6)-N$ angle, *ca.* 130° , is $5-10^\circ$ larger than an unperturbed sp^2 value; (3) the inside $C(8)-N-C(6)$ angle is about $2-4^\circ$ greater than the outside $C(7)-N-C(6)$ angle. In AMFORF, the *ca.* 7° difference in the exocyclic angles at C(2) probably reflects the steric environment of the C(6) portion of the molecule.

The C(8) H's in NMEFUL were located in a difference map and refined normally, whereas the C(7) H's could not be found in the map. The C(7) H's were approximated by an appropriately positioned circle of 0.25 weight H atoms for subsequent calculations. All C(7) and C(8) H's in AMFORF were located from a difference map. In both NMEFUL and AMFORF, the conformations of the C(8) methyls are probably determined by the proximity of the H(5)'s. Similar intramolecular restrictions on the C(7) conformation do not exist, and one must look to intermolecular interactions in an attempt to explain the difference between the C(7)'s in the two compounds.

A packing diagram for NMEFUL, Fig. 4, illustrates

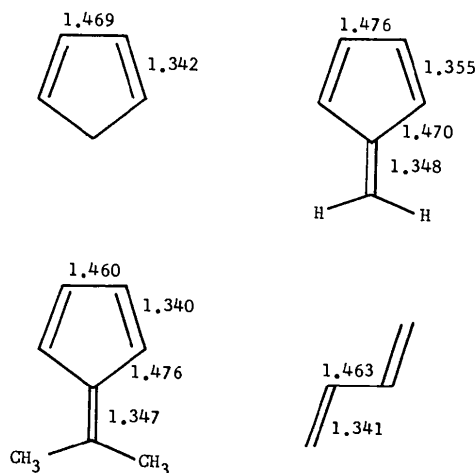


Fig. 3. Bond distances (\AA) in cyclopentadiene (Scharpen & Laurie, 1965), pentafulvene (Baron, Brown, Burden, Domaille & Kent, 1972), 6,6-dimethylpentafulvene (Chiang & Bauer, 1970) and butadiene (Kuchitsu, Fukuyama & Morino, 1968).

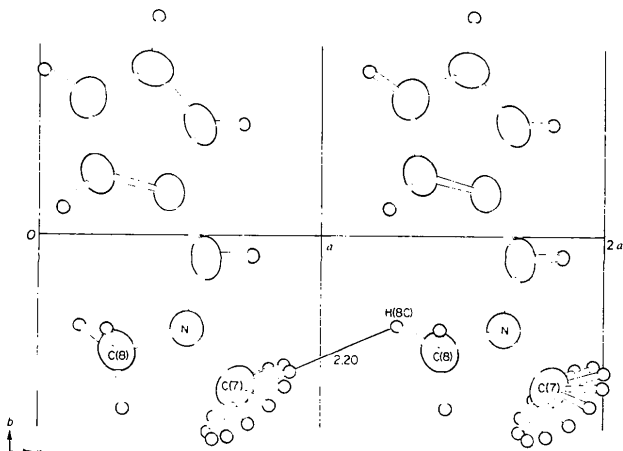


Fig. 4. Packing diagram for NMEFUL normal to the ab plane drawn with ORTEP-II (Johnson, 1971). The C and N atoms are drawn as 25% ellipses, with 0.1 \AA circles for H. Two molecules related by the unit translation parallel to a are shown.

two molecules related by a unit translation parallel to **a**. The only intermolecular contact less than the corresponding van der Waals distances is the 2.20 Å contact between H(8c) at x, y, z and one of the C(7) circle H's at $-1+x, y, z$. Although these contacts are smaller than the normally quoted 2.4 Å H...H van der Waals distance (Pauling, 1960), they are longer than the recently revised distance of 2.0 Å (Baur, 1972). Thus it would appear that the H...H interaction is either weak or nonexistent.

A packing diagram for AMFORF is shown in Fig. 5, along with the most significant intermolecular contacts. Only two of these contacts, $O' \cdots H(7B) = 2.55$ Å and $O \cdots H(7B') = 2.53$ Å, are shorter than the 2.6 Å $O \cdots H$ van der Waals distance obtained from the Pauling (1960) radii of 1.2 Å for H and 1.4 Å for O. In both cases, however, the H's are associated with methyl groups whose conformations are not fixed by intramolecular interactions. Although the $O \cdots H$ interactions are weak, they might be responsible for fixing the C(7) conformations in AMFORF.

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References

- AMMON, H. L. & MUELLER-WESTERHOFF, U. (1974). *Tetrahedron*. In the press.
- AMMON, H. L. & WHEELER, G. L. (1973). Unpublished.
- AMMON, H. L. & WHEELER, G. L. (1974). *Acta Cryst.* **B30**, 1146–1154.
- BARON, P. A., BROWN, R. D., BURDEN, F. R., DOMAILLE, P. J. & KENT, J. E. (1972). *J. Mol. Spect.* **43**, 401–410.
- BARTELL, L. S., ROTH, E. A., HOLLOWELL, C. D., KUCHITSU, K. S. & YOUNG, J. E. (1965). *J. Chem. Phys.* **42**, 2683–2686.
- BAUR, W. H. (1972). *Acta Cryst.* **B28**, 1456–1465.
- BERGHUIS, J., HAANAPPEL, IJ. M., POTTERS, M., LOOPSTRA, B. O., MACGILLAVRY, C. H. & VEENENDAAL, A. L. (1955). *Acta Cryst.* **8**, 478–483.
- CAMERMAN, A. (1970). *Canad. J. Chem.* **48**, 179–181.
- CAMERMAN, A., JENSEN, L. H. & BALABAN, A. T. (1969). *Acta Cryst.* **B25**, 2623–2630.
- CHIANG, J. F. & BAUER, S. H. (1970). *J. Amer. Chem. Soc.* **92**, 261–265.
- CRABTREE, J. H. & BERTELLI, D. J. (1967). *J. Amer. Chem. Soc.* **89**, 5384–5389.
- DEWAR, M. J. S. & SCHMEISING, H. N. (1960). *Tetrahedron*, **11**, 96–120.
- DOWNING, A. P., OLLIS, W. D. & SUTHERLAND, I. O. (1969). *J. Chem. Soc. (B)*, pp. 111–119.
- FERGUSON, G., RENDLE, D. F., LLOYD, D. & SINGER, M. I. C. (1971). *Chem. Commun.* pp. 1647–1648.
- HAFNER, K., VÖPEL, K. H., PLOSS, G. & KÖNIG, C. (1963). *Liebigs Ann.* **661**, 52–75.
- IBALL, J. & MOTHERWELL, W. D. S. (1969). *Acta Cryst.* **B25**, 882–888.
- HUGHES, E. W. (1941). *J. Amer. Chem. Soc.* **63**, 1737–1752.
- JOHNSON, C. K. (1971). *ORTEP*. Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee.
- KUCHITSU, K., FUKUYAMA, T. & MORINO, Y. (1968). *J. Mol. Struct.* **1**, 463–479.
- LAMBERT, J. B., DURHAM, L. J., LEPOUTERE, P. & ROBERTS, J. D. (1965). *J. Amer. Chem. Soc.* **87**, 3896–3899.

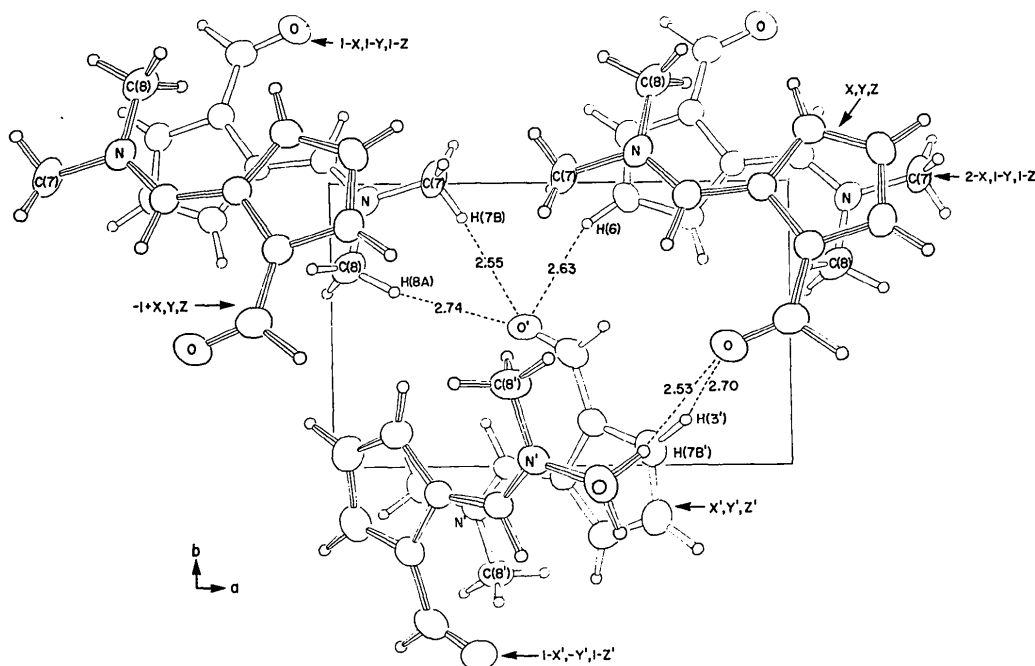


Fig. 5. Packing diagram for AMFORF normal to the ab plane drawn with *ORTEP-II* (Johnson, 1971). The C, N and O atoms are represented as 25% ellipsoids, with 0.1 Å circles for H. The rectangular figure has a horizontal dimension of 0 to a and a vertical dimension of 0 to $b/2$.

- LARSON, A. C. (1970). *Crystallographic Computing*, edited by F. R. AHMED, S. R. HALL & C. P. HUBER, pp. 291–294. Copenhagen: Munksgaard.
- LENHART, P. G. & HENRY, D. (1970). Abstracts ACA Meeting, Spring 1970, New Orleans, La., M8, p. 71.
- LIDE, D. R. & MANN, D. E. (1958). *J. Chem. Phys.* **28**, 572–576.
- MCCLURE, R. J. & CRAVEN, B. M. (1973). *Acta Cryst.* **B29**, 1860–1863.
- MANNSCHRECK, A. & KÖLLE, U. (1969). *Chem. Ber.* **102**, 243–254.
- PAULING, L. (1960). *The Nature of the Chemical Bond*, p. 260. Ithaca: Cornell Univ. Press.
- RENDLE, D. F. (1972). *The Crystal Structures of Two Steroid Hormones and Three Cyclopentadienylides*, Ph. D. Dissertation, Univ. of Guelph.
- SAX, M., PLETCHER, J., YOO, C. S. & STEWART, J. M. (1971). *Acta Cryst.* **B27**, 1635–1644.
- SCHARPEN, L. H. & LAURIE, V. W. (1965). *J. Chem. Phys.* **43**, 2765–2766.
- SMITH, D. L. & LUSS, H. R. (1972). *Acta Cryst.* **B28**, 2793–2806.
- STEWART, J. M., KRUGER, G. J., AMMON, H. L., DICKINSON, C. & HALL, S. R. (1972). The X-RAY System of Crystallographic Programs, TR-192, Computer Science Center, Univ. of Maryland, College Park, Md.
- STEWART, R. F., DAVIDSON, E. & SIMPSON, W. (1965). *J. Chem. Phys.*, **42**, 3175–3187.
- TAYLOR, T. W. J. & MURRAY, A. R. (1938). *J. Chem. Soc.* pp. 2078–2086.
- WHEELER, G. L. (1973). *Synthesis, Molecular Structure and Charge Separation of Cyclopentadienylidene Dihydropyridines and Dihydroisoquinolines, and Related Compounds*, Ph. D. Dissertation, Univ. of Maryland.
- WHELAND, G. W. & MANN, D. E. (1949). *J. Chem. Phys.* **17**, 264–268.
- YAKUSHI, K., IKEMOTO, I. & KURODA, H. (1971). *Acta Cryst.* **B27**, 1710–1718.
- YATES, P. (1968). *Advances in Alicyclic Chemistry*, edited by H. HART & G. J. KARAKATSOS, Vol 2., pp. 59–184.

Acta Cryst. (1974). **B30**, 1738

The Crystal Structures of the Molecular Complexes between Benzidine and 7,7,8,8-Tetracyano-*p*-quinodimethane. III.* Benzidine–TCNQ Complex Containing Benzene

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Crystals of the (1:1) complex of benzidine and 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ), containing benzene in the crystal lattice, are monoclinic, space group $P2_1/m$, with $a = 17.184$, $b = 9.852$, $c = 7.680$ Å, $\beta = 100.03^\circ$, $Z = 2$. The structure was refined by the method of constrained least-squares. The benzidine and the TCNQ molecules form alternately stacked molecular columns along the c axis. Benzidine and TCNQ in the nearest-neighbour columns are connected by hydrogen bonds to form infinite net planes parallel to the (201) plane. Between the columns there are channels running along the c axis in which benzene molecules are accommodated.

Introduction

Benzidine (BD) and 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ) have been found to form, in addition to the solvent-free complex, solid molecular complexes which contain solvent molecules (Ohmasa, Kinoshita & Akamatu, 1969). The crystal structures of these complexes can be classified into three types. Type I is that found for the solvent-free complex, and type II, that for the dichloromethane-containing complex. The complexes which contain acetone, acetonitrile and 1,2-dichloroethane give X-ray powder diffraction patterns very similar to that of the dichloromethane-containing complex, and seem to have a type II structure. Type III comprises the complexes containing benzene, toluene, chlorobenzene, bromobenzene, nitrobenzene and benzonitrile.

We have already reported the crystal structure of the BD–TCNQ solvent-free complex (Yakushi, Ikemoto & Kuroda, 1974) and that of the dichloromethane-containing complex (Ikemoto, Chikaishi, Yakushi & Kuroda, 1972). In the present paper, we report the crystal structure of the benzene-containing complex, as a typical example of a type III complex.

Experimental

Dark purple crystals of the complex were obtained from a benzene solution. They grow, with slow cooling of the solution, into thick needle-like crystals elongated along the c axis. Chemical analysis of these crystals indicated that the molecular ratio of the components, BD:TCNQ:benzene, was $1:1:1.1 \pm 0.15$. Considering the crystal structure and the standard deviation of the chemical analysis, we decided that the molecular ratio was 1:1:1.

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