

Fig. 4. Packing diagram for 8-quinolyl cyanomethyl sulfone.

these two groups would explain the larger C–S–C angle, 107.4° , than is generally found for acyclic sulfones, $102\text{--}105^\circ$.

In summation, it appears that the general conformation of the molecule can be better explained as a balance of repulsive forces rather than in terms of an attractive C–H \cdots N force.

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Refinement of the Structure of 1-Methyl-2-(9'-fluorenylidene)-1,2-dihydropyridine. A Crowded Fulvalene

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Abstract. $C_{19}H_{15}N$; orthorhombic, *Pbca*; $a=16.674$ (2), $b=17.328$ (2), $c=9.525$ (1) Å; $Z=8$; $R=0.042$. Intramolecular nonbonded contacts are responsible for a 35.7° twist of the exocyclic C=C. Bond lengths in the five-ring and heterocyclic six-ring show the effect of π -electron delocalization, indicating that a dipolar resonance form makes a substantial contribution to the ground-state hybrid.

Introduction. A $0.1 \times 0.1 \times 0.2$ mm crystal was used to measure the lattice constants and intensities on a Picker FACS-I diffractometer equipped with a graphite monochromator and Mo X-ray source ($K\alpha, \lambda=0.71069$ Å). The cell parameters were determined by the least-squares method from 13 Bragg angles measured manually at $\pm 2\theta$ (average $|2\theta_o - 2\theta_c| = 0.004^\circ$). The intensities were measured with the θ - 2θ scan

method, a 2θ scan speed of $0.5^\circ \text{ min}^{-1}$, a 2θ scan range equal to $1.6^\circ + 0.692^\circ \tan \theta$, and 20 s backgrounds, to a 2θ maximum of 50° . Three standard reflection intensities, measured at 50 reflection intervals, were used to monitor and correct for intensity fluctuations and crystal decomposition (*ca* 3%). A total of 3038 reflections were measured: 2423 of these were unique and 1033 had $I > 3\sigma(I)$.

The initial atomic coordinates were taken from a previous film data investigation (Ammon, 1969). The structure refinement used the full-matrix least-squares method with anisotropic temperature factors assigned to C and N and isotropic terms to H. The function minimized was $\Delta = \sum w(|F_o| - |F_c|)^2$: weights of $w = [1/\sigma(F)]^2$ for $F < 20$, $w = 1$ for $F \approx 20-70$ and $w = (70/F)^2$ for $F > 70$ were selected to provide an approximately constant value of Δ as a function of $|F_o|$. The F_c 's were corrected for secondary isotropic extinction [$r^* = 0.0017(3)$; Larson, 1970], and only those reflections for which $I_c \geq 3\sigma(I_o)$ were included in the least-squares calculations. The source of the C and N scattering factors was Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955), and the H factors were taken from the work of Stewart, Davidson & Simpson (1965). The final R ($\sum ||F_o| - |F_c|| / \sum |F_o|$) and weighted R ($\{[\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2}\}$) indices were 0.042 and 0.035 respectively. All calculations were performed with the X-RAY system of programs (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) on a Univac 1108 computer at the University of Maryland's Computer Science Center. The atomic parameters are listed in Table 1.†

† A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31801 (10 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Discussion. The structure of the title compound (I) is of interest because of the strain inherent in planar form (Ia), and the potential importance of the mesomeric form (Ib) as a means of reducing the structural restraints imposed by the inter-ring C=C [C(2)-C(9)]. A previous study (Ammon & Wheeler, 1975) of the structure of (IIa) revealed an 18.6° twist of the exocyclic C=C, presumably arising from non-bonded interactions between the five-membered ring and the

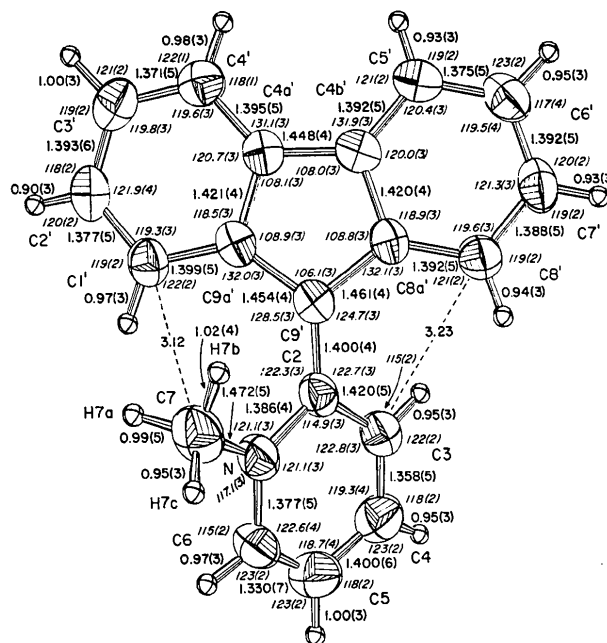


Fig. 1. An ORTEP drawing normal to the five-ring plane with bond lengths (Å), angles ($^\circ$) and e.s.d.'s (in parentheses). The angles at C(7) not given in the drawing are: N-C(7)-H(7a) = $114(2)$, N-C(7)-H(7b) = $115(3)$, N-C(7)-H(7c) = $108(2)$, H(7a)-C(7)-H(7b) = $101(3)$, H(7a)-C(7)-H(7c) = $111(3)$ and H(7b)-C(7)-H(7c) = $108(3)^\circ$.

Table 1. Fractional atomic coordinates, temperature factors ($\text{\AA}^2 \times 10^3$, for H $\times 10^2$) and estimated standard deviations (in parentheses)

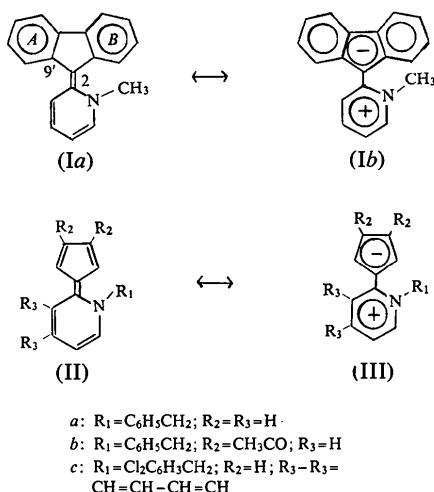
The form of the anisotropic temperature factors is $\exp[-2\pi^2(h^2a^{*2}U_{11} + \dots + 2klb^*c^*U_{23})]$.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
N	0.3348 (2)	0.5625 (1)	1.2932 (3)	55 (2)	39 (2)	48 (2)	2 (2)	8 (2)	-1 (2)
C(2)	0.3662 (2)	0.4922 (2)	1.2506 (3)	51 (2)	38 (2)	38 (2)	2 (2)	7 (2)	1 (2)
C(3)	0.4505 (2)	0.4848 (2)	1.2669 (4)	48 (2)	51 (2)	55 (3)	1 (2)	3 (2)	-7 (2)
C(4)	0.4962 (3)	0.5392 (2)	1.3315 (4)	56 (3)	71 (3)	71 (3)	-9 (2)	2 (3)	-2 (2)
C(5)	0.4594 (3)	0.6056 (2)	1.3848 (5)	75 (3)	67 (3)	72 (3)	-18 (3)	3 (3)	-11 (3)
C(6)	0.3812 (3)	0.6155 (2)	1.3638 (4)	79 (3)	47 (2)	59 (3)	-7 (2)	15 (3)	-13 (2)
C(7)	0.2550 (3)	0.5880 (2)	1.2464 (6)	67 (3)	45 (2)	65 (3)	13 (2)	4 (3)	5 (3)
C(1')	0.1927 (2)	0.4307 (2)	1.3627 (4)	47 (2)	47 (2)	50 (2)	7 (2)	5 (2)	1 (2)
C(2')	0.1245 (2)	0.3897 (2)	1.3956 (4)	49 (2)	64 (3)	55 (3)	12 (2)	12 (2)	1 (2)
C(3')	0.1007 (2)	0.3252 (2)	1.3187 (4)	42 (2)	63 (2)	69 (3)	1 (2)	4 (2)	7 (2)
C(4')	0.1482 (2)	0.2986 (2)	1.2117 (3)	48 (2)	48 (2)	56 (3)	0 (2)	-5 (2)	2 (2)
C(4a')	0.2190 (2)	0.3374 (2)	1.1787 (3)	42 (2)	46 (2)	36 (2)	5 (2)	-3 (2)	3 (2)
C(4b')	0.2832 (2)	0.3181 (2)	1.0826 (3)	49 (2)	37 (2)	39 (2)	3 (2)	-8 (2)	4 (2)
C(5')	0.2939 (2)	0.2564 (2)	0.9909 (4)	55 (2)	45 (2)	49 (2)	-2 (2)	-8 (2)	-3 (2)
C(6')	0.3620 (2)	0.2512 (2)	0.9101 (4)	59 (2)	56 (2)	54 (3)	10 (2)	-4 (2)	-14 (2)
C(7')	0.4193 (2)	0.3095 (2)	0.9171 (4)	47 (2)	74 (3)	46 (2)	12 (2)	5 (2)	-9 (2)
C(8')	0.4101 (2)	0.3720 (2)	1.0070 (4)	43 (2)	53 (2)	48 (2)	-2 (2)	-2 (2)	-6 (2)
C(8a')	0.3434 (2)	0.3757 (2)	1.0945 (3)	43 (2)	43 (2)	32 (2)	6 (2)	0 (2)	3 (2)
C(9')	0.3179 (2)	0.4325 (2)	1.1989 (3)	45 (2)	41 (2)	39 (2)	3 (2)	-1 (2)	0 (2)
C(9a')	0.2405 (2)	0.4063 (2)	1.2503 (3)	44 (2)	43 (2)	36 (2)	8 (2)	-2 (2)	1 (2)

Table 1 (cont.)

	x	y	z	U
H(3)	0.473 (2)	0.437 (2)	1.235 (3)	6 (1)
H(4)	0.552 (2)	0.529 (2)	1.342 (4)	6 (1)
H(5)	0.494 (2)	0.645 (2)	1.433 (4)	8 (1)
H(6)	0.353 (2)	0.661 (2)	1.397 (3)	5 (1)
H(7a)	0.232 (2)	0.557 (2)	1.165 (4)	8 (1)
H(7b)	0.212 (3)	0.581 (2)	1.317 (5)	13 (2)
H(7c)	0.259 (2)	0.641 (2)	1.223 (4)	8 (1)
H(1')	0.208 (2)	0.474 (2)	1.422 (3)	4.7 (9)
H(2')	0.095 (2)	0.404 (2)	1.471 (3)	4 (1)
H(3')	0.049 (2)	0.299 (2)	1.343 (3)	5 (1)
H(4')	0.136 (1)	0.251 (2)	1.160 (3)	3.5 (8)
H(5')	0.255 (2)	0.219 (2)	0.981 (3)	5 (1)
H(6')	0.373 (2)	0.208 (2)	0.850 (3)	6 (1)
H(7')	0.463 (2)	0.308 (1)	0.857 (3)	3.7 (9)
H(8')	0.450 (2)	0.410 (1)	1.010 (3)	3.8 (9)

N-benzyl group. CNDO/2 calculations on model systems suggested that a dipolar canonical form such as (IIIa) might make as much as a 40% contribution to the ground-state resonance hybrid. In the case of (I), the *A* ring effectively prevents relief of the $\text{CH}_3 \cdots$ ring *B* strain by bond-angle deformation at $\text{C}(9')$ and $\text{C}(2)$, setting the stage for an even larger $\text{C}=\text{C}$ twist than that found in (IIa).



ORTEP (Johnson, 1971) drawings of (I), one containing bond lengths and angles, are shown in Figs. 1 and 2. Both the heterocyclic six-membered ring and

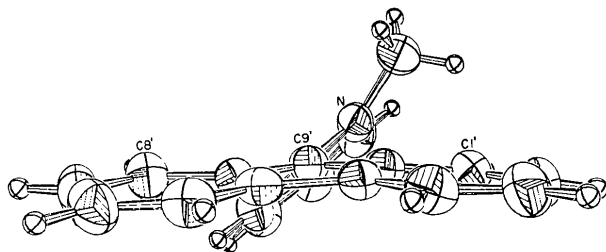


Fig. 2. An ORTEP drawing parallel to $\text{C}(9')-\text{C}(2)$ to illustrate the fluorenylidene bend and $\text{C}=\text{C}$ twist.

the fluorenylidene nucleus are slightly distorted from their ideal planar geometries (Table 2). The major fluorenylidene distortion occurs in ring *B*; atoms $\text{C}(1')$, $\text{C}(2')$ and $\text{C}(3')$ are found significantly below the plane of the central five-membered ring (see Fig. 2). The $\text{CH}_3 \cdots \text{C}(1')$ interaction appears to have caused these three atoms to bend as a unit since the out-of-plane distances are approximately the same for $\text{C}(1')$ and $\text{C}(3')$, whereas the $\text{C}(2')$ distortion is about 0.1 Å larger.

Table 2. Least-squares plane deviations (Å)

	Planes 1	2	3	4
N	0.440			-0.042*
C(2)	-0.157			0.044*
C(3)	-0.971		-1.074	-0.013*
C(4)	-1.250			-0.022*
C(5)	-0.722			0.027*
C(6)	0.102			0.006*
C(7)	1.595			-0.392
C(1')	-0.186	-0.005*		1.969
C(2')	-0.277	-0.020*		
C(3')	-0.172	0.021*		
C(4')	-0.047	0.002*		
C(4a')	0.005*	-0.027*	0.029	
C(4b')	-0.002*	-0.184	0.013*	
C(5')	-0.029		0.009*	
C(6')	-0.040		-0.018*	
C(7')	0.021		0.005*	
C(8')	0.057		0.017*	-1.209
C(8a')	0.002*		-0.026*	
C(9')	0.005*	-0.070	-0.037	0.210
C(9a')	-0.006*	0.028*		

$$\text{Plane 1: } -7.5192x + 9.2635y - 6.8079z = -6.5506$$

$$\text{Plane 2: } -8.6389x + 9.8274y - 6.0985z = -5.7378$$

$$\text{Plane 3: } -7.8185x + 8.8969y - 6.8456z = -6.8078$$

$$\text{Plane 4: } -2.9699x - 7.6365y + 8.3802z = 5.5895$$

* Used for calculation of the least-squares plane.

The principal mechanism for relief of the $\text{CH}_3 \cdots \text{C}(1')$ and $\text{C}(3) \cdots \text{C}(8')$ nonbonded interactions is a twist and bend of the inter-ring $\text{C}=\text{C}$ (Fig. 2), and displacement of the CH_3 from the plane of the dihydropyridine ring. The ring is surprisingly planar (Table 2) in view of the severe steric effects that must exist across the $\text{C}=\text{C}$. The 0.39 Å displacement of the CH_3 group from the heterocyclic plane is similar to the 0.34 Å distance found for the benzylic C atom in (IIc) (Ammon & Wheeler, 1975); in the case of (I), the displacement adds *ca* 0.03 Å to the $\text{CH}_3 \cdots \text{C}(1')$ separation. In a planar model of (I), the nonbonded distances would be approximately 3.05 Å for $\text{C}(3) \cdots \text{C}(8')$ and 2.56 Å for $\text{C}(7) \cdots \text{C}(1')$, both of which are smaller than the normal $\text{C} \cdots \text{C}$ van der Waals separation of 3.4 Å (Pauling, 1960). The 2.56 Å distance is impossibly short and the interaction is undoubtedly responsible for the magnitude of the $\text{C}=\text{C}$ twist. The staggered conformation of the CH_3 group (see Figs. 1 and 2) with respect to the dihydropyridine ring minimizes nonbonded interactions with both this ring and the $\text{C}(1')-\text{C}(9a')-\text{C}(9')$ region of the fluorenylidene nucleus.

From the normals to the least-squares planes of the five-membered ring and heterocyclic ring, the twist and tilt components [see Ammon & Wheeler (1975) for the algorithm] of the C=C are 35.7 and 15.1° respectively. This twist is similar to values observed in other overcrowded fulvalenes: e.g. 40° in bis(fluorenylidene) (Bailey & Hull, 1971) and 38.5° in octabromopentafulvalene (Ammon, Fallon, West & Rao, 1974). The 1.400 Å inter-ring C=C distance is similar to the lengths of 1.39 and 1.385 Å in these two crowded pentafulvalenes, and to the 1.410 Å in (IIa), and 1.412 Å in (IIc) (Ammon & Wheeler, 1975), but it is significantly shorter than the 1.442 Å observed in (IIb) (Ammon & Erhardt, 1975).

The degree of charge separation in unsymmetrical fulvalenes such as (I) and (II) depends upon two major structural characteristics: (1) the inherent abilities of the cyclic substituents at the termini of the inter-ring C=C to stabilize + and - charges; (2) steric effects which force a C=C twist and reduction in π -bond character, thereby increasing the dipolar contribution above that in a planar conformation. The pK_a 's of cyclopentadiene at 15, and fluorene at 22.9 (Buncel, 1975), suggest that the degree of charge separation arising from factor (1) above is (IIb) > (IIa) > (I).^{*} Since the charge separation in these compounds should be related to the extent of π -delocalization in the heterocyclic rings, we have attempted to evaluate this delocalization with a modified form of Julg's aromaticity index (Julg, 1971; Wheeler & Ammon, 1974). The indices, which are based on ring C-C and C-N bond lengths, are 1.00 for pyridine (100% delocalization) and 0.59 for cyclohexatriene (0% delocalization). The values of 0.90, 0.79 and 0.81 for (IIb), (IIa) and (I), respectively, correspond to 76, 49 and 53% of the delocalization in pyridine. Relative to (IIa), the increase in dipolar character in (I) presumably is due to a major contribution from factor (2).

The effects of negative charge delocalization on bond lengths in the five-membered ring portion of the fluorenylidene nucleus of (I) can be readily illustrated by a comparison with the appropriate distances in 9-

fluorenone (Luss & Smith, 1972). The single-bond distances in (I) [C(8a')-C(9'), C(9')-C(9a')=1.457; C(4a')-C(4b')=1.448 Å] are shorter than the corresponding 9-fluorenone bonds (1.486, 1.475 Å), whereas the benzenoid double-bond lengths in (I) [C(4a')-C(9a'), C(4b')-C(8a')=1.420 Å] are longer than the corresponding 1.390 Å ketone values.

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^{*} The position of (IIb) in this sequence is based on the assumption that the pK_a of diacetylcyclopentadiene would be smaller than 15. The stable form of diacetylcyclopentadiene is the fulvenoid tautomer 2-acetyl-6-hydroxy-6-methylpentafulvene.