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10-(*N*-Methylamino)benz[*f*]azulene

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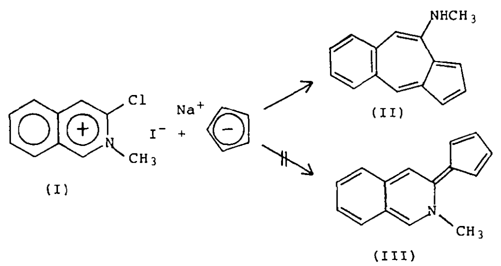
Abstract. $C_{15}H_{13}N$; M_r = 207·3; monoclinic, space group $P2_1/c$; a = 19·972 (5), b = 5·537 (1), c = 21·530 (4) Å, β = 110·22 (2)°; D_c = 1·232 g cm^{-3} for Z = 8. Mo $K\alpha$ radiation diffractometer data. Final R = 0·055. C–C bond lengths show the influence of considerable single–double bond alternation. Crystal-packing interactions in the *ac* plane are limited to H···H contacts, whereas C···C contacts are the primary interactions in the **b** direction.

Introduction. The title compound (II) was prepared as follows: 2-methyl-3-chloroisoquinolinium iodide (I) (13·5 g, 0·45 mol) was added to freshly prepared sodium cyclopentadienide (from 5·6 g, 0·24 mol, sodium sand and 33 ml, 0·43 mol, cyclopentadiene) in 250 ml dry dimethoxymethane under nitrogen with stirring. After 16 h at room temperature, the reaction was quenched with water, the aqueous solution was extracted with benzene, and alumina thin-layer chromatography (benzene eluent) of the concentrated benzene fraction revealed three mobile components (one major purple band, two minor yellow-green bands) in addition to a brown-black band at the origin. The purple component was isolated by column chromatography (neutral alumina, benzene eluent), and following sublimation and recrystallization from benzene, there was obtained a 2% yield of (II) as purple needles, m.p. 105–106·5 °C.



A specimen, *ca* 0·4 mm long and 0·2 mm in cross-section, mounted parallel to the needle axis (*b*), was used for all X-ray measurements. The space group was established with oscillation and Weissenberg photographs (Cu radiation), and all lattice parameter and intensity measurements were made with a Picker FACS-I diffractometer with Mo radiation [graphite monochromator, $\lambda(K\alpha)$ = 0·71069 Å]. The final unit-cell parameters were obtained by least squares from the Bragg angles of 16 reflections manually centered at $\pm 2\theta$ (average of $|2\theta_o - 2\theta_c|$ = 0·004°).

Intensities were measured with the θ–2θ scan method with a 2θ scan rate of 2·0° min^{-1}, and with 20 s background counts. Three standard reflections were counted at 80-reflection intervals. 4765 data were measured to a 2θ maximum of 50° giving 3986 unique reflections (excluding 460 systematically absent data); 1943 of these were 3σ above background. The structure was solved by the routine application of direct methods with the XRAY system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) subprogram *PHASE*. An E map computed with 398 phases (209+, 189−) clearly revealed 29 of the 32 C and N atoms, and the remaining three atoms were located in a difference map.

Structure refinement was by full-matrix least squares minimizing the function $\sum w(F_o - F_c)^2$, where $w = 1$ for $F_o \leq 30$ and $w = (30/F_o)^2$ for $F_o > 30$ (Hughes, 1941). The calculations used anisotropic temperature factors for C and N, and isotropic terms for H (initial coordinates for the six methyl H atoms were obtained from a difference map; positions for the ring and amino H atoms were calculated assuming a trigonal geometry for the appropriate heavy atoms (X) and an X—H distance of 1·0 Å). Computer storage limited the heavy-atom refinement to 25 atoms at one time, and the atoms refined in each of the final four cycles were selected more-or-less randomly with the restriction that each atom be varied in at least three cycles. H atoms were refined in separate cycles. For the final heavy and H atom refinement cycles, all parameter shift/σ ratios were less than 1. Atomic scattering factors for C and N were calculated from the analytical expressions of Cromer & Mann (1968); the scattering factors for H were interpolated from the tabulated values of Stewart, Davidson & Simpson (1965). The final R ($\sum |F_o - F_c| / \sum F_o$) and weighted R $\{[\sum w(F_o - F_c)^2 / \sum wF_o^2]^{1/2}\}$ factors were 0·055 and 0·066 respectively.[†] The

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[†] Lists of structure factors and thermal factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33395 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Fractional coordinates and estimated standard deviations (in parentheses) for* 10-(*N-methylamino*)-*benz*[*f*]*azulene*

	x	*y*	*z*		*x*	*y*	*z*
C(1)	0·6188 (2)	0·3196 (9)	0·9492 (2)	C(1′)	0·2274 (2)	0·034 (1)	0·9404 (2)
C(2)	0·5735 (3)	0·128 (1)	0·9556 (2)	C(2′)	0·2573 (2)	0·221 (1)	0·9118 (3)
C(3)	0·5537 (2)	−0·0093 (9)	0·8997 (2)	C(3′)	0·2046 (3)	0·3656 (9)	0·8738 (2)
C(3a)	0·5860 (2)	0·0928 (8)	0·8549 (2)	C(3a′)	0·1376 (2)	0·2733 (8)	0·8753 (2)
C(4)	0·5746 (2)	0·0042 (8)	0·7932 (2)	C(4′)	0·0731 (2)	0·3759 (8)	0·8407 (2)
C(4a)	0·5987 (2)	0·0836 (8)	0·7419 (2)	C(4a′)	0·0024 (2)	0·3057 (8)	0·8336 (2)
C(5)	0·5751 (2)	−0·0510 (9)	0·6820 (2)	C(5′)	−0·0534 (3)	0·4476 (9)	0·7903 (2)
C(6)	0·5943 (3)	0·006 (1)	0·6292 (2)	C(6′)	−0·1238 (3)	0·394 (1)	0·7765 (3)
C(7)	0·6394 (2)	0·204 (1)	0·6336 (2)	C(7′)	−0·1415 (2)	0·193 (1)	0·8065 (3)
C(8)	0·6633 (2)	0·3381 (9)	0·6900 (2)	C(8′)	−0·0896 (2)	0·0549 (9)	0·8492 (2)
C(8a)	0·6445 (2)	0·2850 (8)	0·7465 (2)	C(8a′)	−0·0154 (2)	0·1029 (8)	0·8654 (2)
C(9)	0·6757 (2)	0·4418 (7)	0·8016 (2)	C(9′)	0·0310 (2)	−0·0593 (8)	0·9118 (2)
C(10)	0·6709 (2)	0·4538 (7)	0·8639 (2)	C(10′)	0·1038 (2)	−0·0812 (7)	0·9366 (2)
C(10a)	0·6276 (2)	0·3028 (8)	0·8890 (2)	C(10a′)	0·1538 (2)	0·0624 (8)	0·9186 (2)
C(11)	0·7551 (2)	0·8049 (8)	0·8894 (2)	C(11′)	0·0930 (3)	−0·425 (1)	1·0080 (2)
N	0·7124 (2)	0·6229 (7)	0·9078 (2)	N′	0·1342 (2)	−0·2565 (7)	0·9836 (2)
H(1)	0·639 (2)	0·438 (8)	0·983 (2)	H(1′)	0·257 (2)	−0·088 (9)	0·973 (2)
H(2)	0·560 (2)	0·093 (8)	0·993 (2)	H(2′)	0·312 (2)	0·239 (8)	0·923 (2)
H(3)	0·522 (2)	−0·162 (9)	0·891 (2)	H(3′)	0·210 (2)	0·509 (6)	0·845 (2)
H(4)	0·545 (2)	−0·138 (7)	0·780 (2)	H(4′)	0·080 (2)	0·520 (8)	0·818 (2)
H(5)	0·546 (2)	−0·206 (8)	0·683 (2)	H(5′)	−0·041 (2)	0·571 (9)	0·768 (2)
H(6)	0·576 (2)	−0·105 (9)	0·586 (2)	H(6′)	−0·160 (3)	0·50 (1)	0·743 (3)
H(7)	0·655 (2)	0·249 (8)	0·595 (2)	H(7′)	−0·192 (2)	0·145 (9)	0·796 (2)
H(8)	0·696 (2)	0·490 (8)	0·695 (2)	H(8′)	−0·102 (2)	−0·102 (9)	0·875 (2)
H(9)	0·708 (2)	0·579 (6)	0·793 (2)	H(9′)	0·006 (2)	−0·184 (7)	0·931 (2)
H(N)	0·702 (2)	0·647 (9)	0·948 (2)	H(N′)	0·184 (2)	−0·293 (9)	0·996 (2)
H(11*a*)	0·790 (2)	0·729 (8)	0·869 (2)	H(11*a*′)	0·061 (3)	−0·33 (1)	1·029 (3)
H(11*b*)	0·724 (2)	0·905 (9)	0·847 (2)	H(11*b*′)	0·060 (3)	−0·53 (1)	0·970 (3)
H(11*c*)	0·780 (3)	0·90 (1)	0·930 (3)	H(11*c*′)	0·126 (3)	−0·52 (1)	1·043 (3)

atomic parameters are listed in Table 1. All calculations were carried out on Univac 1108 or 1100/40 computers at the University's Computer Science Center; the crystallographic calculations were performed with the XRAY system (Stewart *et al.*, 1972) of programs.

Discussion. The reaction of 2-methyl-3-isoquinolinium iodide (I) with sodium cyclopentadienide was investigated (Wheeler, 1973) as a potential route to 2-methyl-3-cyclopentadienylidene-2,3-dihydroisoquinoline (III), which presumably could arise from displacement of Cl from C(3) of (I) with cyclopentadienide, followed by loss of a proton from the intermediate. Although the isolated product had some of the expected properties for (III), it quickly became obvious that the material was probably (II), having been formed by the well-known preference of 2-alkylisoquinolinium salts to undergo nucleophilic aromatic substitution at C(1) over C(3). The reaction, which can be envisaged as an example of the Ziegler & Hafner (1957) method for azulene synthesis, undoubtedly proceeds by nucleophilic attack of cyclopentadienide at C(1) of (I), followed by ring opening, ring closure to give a seven-membered ring, and finally elimination of the elements of HCl. It is similar to that reported (Muth, DeMatte, Urbanik & Isner, 1966) for the preparation of benz[*f*]azulene in 4% yield from 2-methylisoquinolinium iodide and cyclopentadienide, which presumably involves the elimination of the elements of CH_3NH_2 in the final reaction step.

Although our crystallographic study of the material was initiated for the primary purpose of structure identification, the intermolecular packing became of particular interest following the discovery that there were two independent molecules in the unique structural unit.

ORTEP-II (Johnson, 1971) drawings of the two molecules with bond lengths and angles are given in Fig. 1. The benz[*f*]azulene rings in the two molecules are reasonably planar, the deviations of the atoms from their least-squares planes being 0·035 and 0·061 Å, respectively, for the unprimed and primed molecules (out-of-plane deviations are primarily due to the central seven-membered ring atoms). The two N atoms and methyl groups are significantly out of plane with distances of N = 0·167, C(11) = 0·126, N′ = 0·158 and C(11′) = 0·217 Å. These displacements may be due to non-bonded interactions between the CH_3—NH group and nearby atoms, such as C(9), H(9) and H(1). There are no significant bond distance and angle differences between the two molecules, and the N—CH_3 conformations are similar (see Fig. 1).

The C—C bond distances in the benz[*f*]azulene nucleus show considerable bond-length alternation,

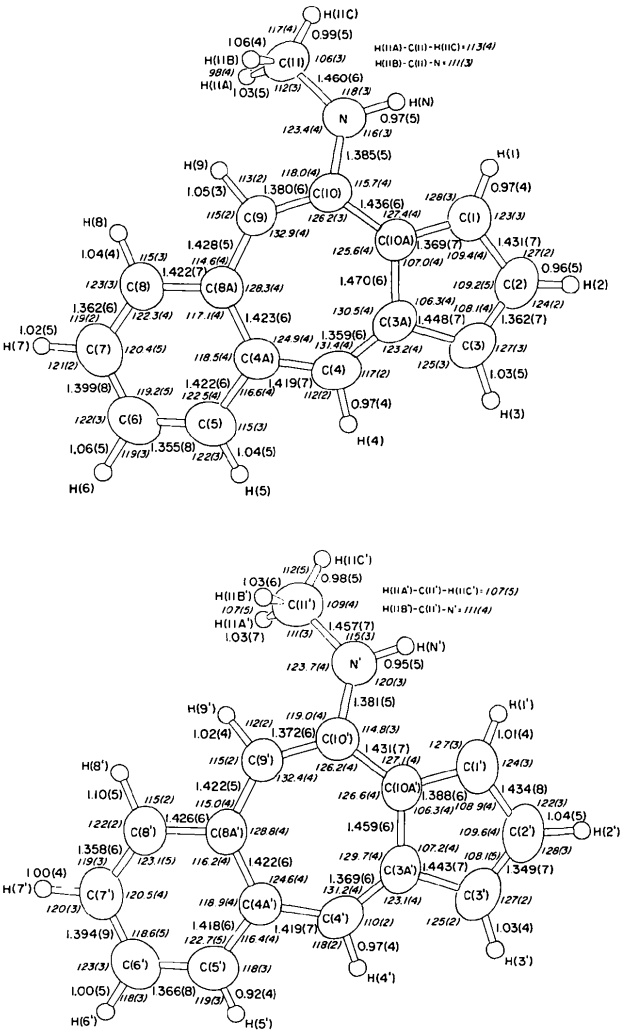

Fig. 1. Bond lengths (Å), angles (deg, italic numbers) and e.s.d.'s (in parentheses) for the two independent 10-(*N*-methylamino)benz[*f*]azulene molecules. 50% boundary ellipses are shown for the C and N atoms; the H atoms are drawn as 0·1 Å radius circles.

typical of many nonbenzenoid aromatics. In the present case, the peripheral single–double bond alternation is quite pronounced, with C(1)–C(10a), C(2)–C(3), C(3a)–C(4), C(5)–C(6), C(7)–C(8) and C(9)–C(10) being short, and C(1)–C(2), C(3)–C(3a), C(4)–C(4a), C(6)–C(7), C(8a)–C(9) and C(10)–C(10a) being long. This pattern strongly suggests that a single canonical structure (II) makes a major contribution to the resonance hybrid. Although the single–double bond pattern indicated by (II) would predict a shorter than normal distance for C(4a)–C(8a), the opposite is observed here with an average value of 1·422 Å. To investigate further the bond-length pattern, we have performed an ω-iteration, Hückel molecular-orbital calculation (Streitwieser, 1961) on a model of 10-aminobenz[*f*]azulene. The C–C and C–N resonance integrals were all set equal to $1\cdot0\beta$, and a value of $1\cdot5\beta$ was used for the Coulomb integral of N. The HMO π-

Table 2. *Hückel molecular orbital π-bond orders and average lengths* (Å) *for the* C–C *bonds*

	Bond order	Bond length
C(1)–C(2)	0·6089	1·432
C(1)–C(10a)	0·6471	1·378
C(2)–C(3)	0·6950	1·355
C(3)–C(3a)	0·5521	1·445
C(3a)–C(4)	0·6460	1·364
C(3a)–C(10a)	0·3849	1·464
C(4)–C(4a)	0·5638	1·419
C(4a)–C(5)	0·5562	1·420
C(4a)–C(8a)	0·4891	1·422
C(5)–C(6)	0·7185	1·360
C(6)–C(7)	0·6008	1·396
C(7)–C(8)	0·7175	1·360
C(8)–C(8a)	0·5588	1·424
C(8a)–C(9)	0·5588	1·425
C(9)–C(10)	0·6522	1·376
C(10)–C(10a)	0·5166	1·433

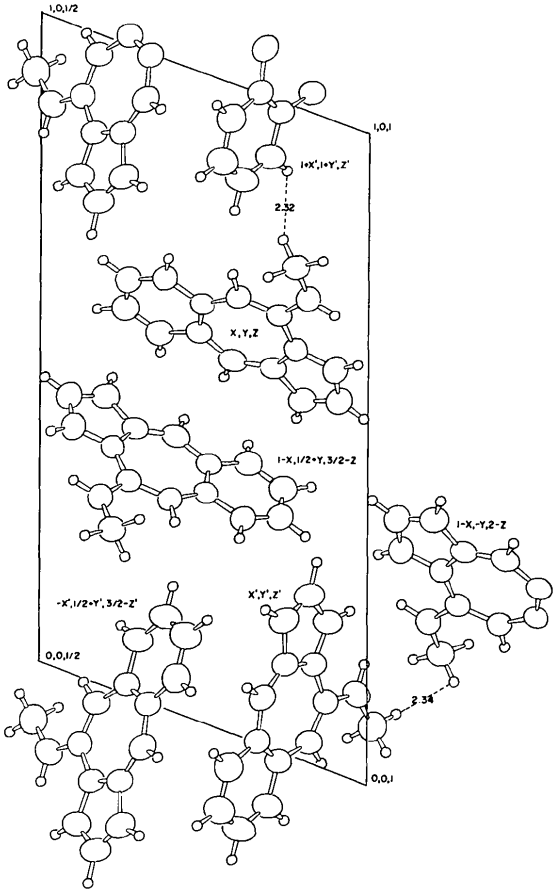

Fig. 2. Packing diagram drawn normal to the *ac* plane illustrating the intermolecular contacts less than 2·4 Å. One of the two independent molecules is designated by primes.

bond orders and mean bond distances from the two molecules (Table 2) show, with minor variations, a consistent pattern, including the C(4a)—C(8a) bond. However, the calculations do predict that the two ring-fusion bonds, C(3a)—C(10a) and C(4a)—C(8a), should be longer than observed by approximately 0·03 and 0·04 Å respectively. The bond orders reported for 10-aminobenz[*f*]azulene in Table 2 are quite similar to those of unsubstituted benz[*f*]azulene, suggesting that the amino substituent has a relatively minor influence on the ring geometry.

The length of the short *b* axis (5·537 Å) appears to be primarily determined by the stacking of parallel benz[*f*]azulene planes in van der Waals contact with each other. This can be illustrated by calculating the angle that a 3·4 Å thick aromatic ring (Pauling, 1960) must be inclined to [010], to make the [010] repeat distance equal to 5·537 Å. The 52·1° value [$\cos^{-1}(3{\cdot}4/5{\cdot}537)$] obtained is very close to the 52·5 and 53·3° angles between [010] and the least-squares-plane normals of the two benz[*f*]azulene nuclei. Because the molecules in these stacks are offset from their immediate neighbors, none of the intermolecular distances between a molecule at x,y,z and another at $x, \pm 1 + y, z$ are as small as 3·4 Å: the shortest of these contacts are C(3a)···N = 3·53 Å (N at $x, -1 + y, z$), and C(3a′)···N′ = 3·51, C(4′)···N′ = 3·54 and C(4′)···C(10′) = 3·58 Å (second atom of each pair is at $x, 1 + y, z$).

A packing diagram, viewed normal to the *ac* plane, is shown in Fig. 2. The intermolecular interactions are singularly uninteresting, consisting only of H···H contacts. The two contacts less than 2·4 Å are illustrated in the diagram. There are no contacts to suggest an N—H···N interaction.

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5-(4-Methylbenzoylimino)-5*H*-1,3λ^4,2,4-dithiadiazol

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Abstract. $C_9H_7N_3OS_2$, triclinic, $P\bar{1}$, $a = 7{\cdot}813$ (3), $b = 10{\cdot}967$ (4), $c = 6{\cdot}537$ (3) Å, $\alpha = 96{\cdot}68$ (4), $\beta = 106{\cdot}95$ (4), $\gamma = 105{\cdot}65$ (2)°, $V = 504{\cdot}2$ Å^3, $M_r = 237{\cdot}3$, $Z = 2$, $D_x = 1{\cdot}56$, $D_m = 1{\cdot}55$ g cm^{-3}. The molecule is almost planar with symmetry *m*. The S^{IV}=N bonds of the SN_2 group differ in length, but both are elongated compared with sulfur diimide compounds. The title compound contains a very short intramolecular C=O···S contact distance of 2·305 Å, suggesting a 'bond–non-bond' resonance.

Einleitung. Im Rahmen unserer Strukturuntersuchungen an S^{IV}—N-Mehrfachbindungssystemen, insbesondere von Verbindungen, die das SN_2-Fragment enthalten (Gieren & Pertlik, 1974, 1976; Gieren, Dederer, Roesky & Janssen, 1976) haben wir die Titelsubstanz (III) untersucht. (III) entsteht durch Umsetzung von *N*,*N*′-Bis(trimethylsilyl)schwefeldiimid (I) mit 1-Chlorthio-*N*-(*p*-toluoyl)formimidoylchlorid (II) (Neidlein, Leinberger, Gieren & Dederer, 1978). Für die Konstitution der Verbindung war neben der mono-