

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (\AA^2)
$$B_{\text{eq}} = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i.a_j.$$

	x	y	z	B_{eq}
S1B	0.23005 (5)	0.1739 (1)	0.11781 (5)	3.92 (4)
O1B	0.2918 (1)	0.2306 (3)	0.1160 (2)	5.1 (1)
O2B	0.2390 (2)	0.0546 (3)	0.1520 (2)	5.6 (1)
N1B	-0.0771 (2)	0.1314 (3)	-0.1716 (2)	4.1 (1)
C1B	-0.0395 (2)	0.0459 (4)	-0.1899 (2)	4.0 (2)
C2B	-0.0579 (2)	-0.0110 (5)	-0.2581 (2)	5.1 (2)
C3B	-0.0101 (3)	-0.1024 (5)	-0.2582 (3)	5.7 (2)
C4B	0.0548 (2)	-0.1322 (4)	-0.1931 (3)	5.3 (2)
C5B	0.0735 (2)	-0.0721 (4)	-0.1265 (3)	4.8 (2)
C6B	0.0264 (2)	0.0195 (4)	-0.1242 (2)	3.8 (2)
C7B	0.0278 (2)	0.0947 (4)	-0.0657 (2)	3.5 (1)
C8B	-0.0371 (2)	0.1628 (4)	-0.0965 (2)	3.8 (2)
C9B	0.0879 (2)	0.0932 (4)	0.0141 (2)	4.1 (2)
C10B	0.1557 (2)	0.1654 (4)	0.0255 (2)	3.5 (1)
C11B	0.1648 (2)	0.2208 (4)	-0.0265 (2)	4.2 (2)
C12B	0.1767 (2)	0.2730 (6)	-0.0776 (3)	6.8 (2)
C13B	0.1971 (2)	0.2780 (4)	0.1622 (2)	4.0 (2)
C14B	0.1565 (2)	0.2332 (5)	0.1943 (2)	5.7 (2)
C15B	0.1286 (3)	0.3196 (8)	0.2262 (3)	7.6 (3)
C16B	0.1426 (3)	0.4431 (8)	0.2258 (3)	8.2 (3)
C17B	0.1834 (3)	0.4860 (6)	0.1942 (3)	7.4 (3)
C18B	0.2099 (2)	0.4047 (5)	0.1612 (3)	5.3 (2)
C19B	-0.0674 (2)	0.2434 (4)	-0.0596 (2)	3.8 (2)
C20B	-0.0243 (2)	0.3257 (4)	-0.0022 (3)	5.2 (2)
C21B	-0.0531 (3)	0.3908 (5)	0.0355 (3)	6.2 (2)
C22B	-0.1270 (3)	0.3800 (5)	0.0144 (3)	6.3 (2)
C23B	-0.1706 (3)	0.3014 (5)	-0.0423 (3)	5.5 (2)
C24B	-0.1414 (2)	0.2330 (4)	-0.0791 (2)	4.4 (2)

Table 2. Selected bond lengths (\AA) and angles ($^\circ$)

S1B—O1B	1.430 (3)	C7B—C8B	1.383 (5)
S1B—O2B	1.424 (3)	C7B—C9B	1.495 (5)
S1B—C10B	1.764 (4)	C8B—C19B	1.466 (5)
S1B—C13B	1.764 (4)	C9B—C10B	1.519 (5)
N1B—C1B	1.365 (5)	C10B—C11B	1.300 (5)
N1B—C8B	1.382 (5)	C11B—C12B	1.301 (6)
C1B—C2B	1.387 (6)	C19B—C20B	1.389 (6)
C1B—C6B	1.403 (5)	C19B—C24B	1.388 (5)
C2B—C3B	1.393 (6)	C20B—C21B	1.365 (6)
C3B—C4B	1.394 (6)	C21B—C22B	1.378 (7)
C4B—C5B	1.375 (6)	C22B—C23B	1.361 (7)
C5B—C6B	1.397 (6)	C23B—C24B	1.375 (6)
C6B—C7B	1.425 (5)		
N1B—C1B—C6B	107.2 (3)	C10B—C11B—C12B	177.3 (5)
C2B—C1B—C6B	122.4 (4)	S1B—C13B—C14B	119.7 (4)
C1B—C2B—C3B	117.1 (4)	S1B—C13B—C18B	119.2 (3)
C2B—C3B—C4B	121.3 (4)	C8B—C19B—C20B	122.9 (4)
C3B—C4B—C5B	120.9 (4)	C8B—C19B—C24B	119.3 (4)
C4B—C5B—C6B	119.3 (4)	C20B—C19B—C24B	117.7 (4)
C1B—C6B—C5B	118.9 (4)	C19B—C20B—C21B	121.2 (4)
C1B—C6B—C7B	107.4 (3)	C20B—C21B—C22B	119.9 (5)
C5B—C6B—C7B	133.6 (4)	C21B—C22B—C23B	120.0 (5)
C6B—C7B—C8B	107.2 (3)	C22B—C23B—C24B	120.3 (4)
C6B—C7B—C9B	124.8 (3)	C19B—C24B—C23B	120.9 (4)
C8B—C7B—C9B	128.0 (4)	O1B—S1B—O2B	119.0 (2)
N1B—C8B—C7B	107.9 (4)	O1B—S1B—C10B	109.1 (2)
N1B—C8B—C19B	122.0 (3)	O1B—S1B—C13B	108.3 (2)
C7B—C8B—C19B	129.7 (4)	O2B—S1B—C10B	108.3 (2)
C7B—C8B—C10B	112.6 (3)	O2B—S1B—C13B	108.0 (2)
S1B—C10B—C9B	117.2 (3)	C10B—S1B—C13B	102.9 (2)
S1B—C10B—C11B	116.5 (3)	C1B—N1B—C8B	110.3 (3)
C9B—C10B—C11B	126.3 (3)	N1B—C1B—C2B	130.4 (4)

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Lists, for both molecules A and B, of structure factors, anisotropic thermal parameters, H-atom coordinates, complete intermolecular distances including H atoms, and torsion angles, and positional parameters for Molecule A have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71360 (69 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: LI1050]

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Structure of [2]Benzoxepino[4,3-*b*]indole

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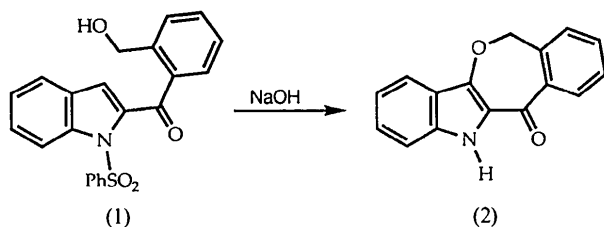
(Received 5 January 1993; accepted 29 April 1993)

Abstract

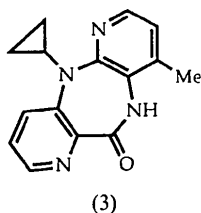
The crystal structure of [2]benzoxepino[4,3-*b*]indole, (2), shows that this tetracyclic molecule comprises two essentially flat 'wings', the indole and benzene aromatic moieties, linked *via* a 'hinge' comprising the CH_2O and carbonyl groups, and producing a butterfly shape; the angle between the wings is $29.2 (7)^\circ$.

Comment

We have described the process of intramolecular nucleophilic substitution in 2-acyl-1-phenylsulfonylindoles by which products having a six- or seven-membered heterocyclic ring fused to the indole 2,3-positions can be efficiently formed (Cooper, Hignett & Joule, 1981; Beal, Ashcroft, Cooper & Joule, 1982; Ashcroft, Dalton, Beal, Humphrey & Joule, 1983); for example, only a brief treatment of the keto-alcohol, (1), with hot alcoholic base is required to produce [2]benzoxepino[4,3-*b*]indole, (2), in 90% yield. We have shown that it is possible to produce such structures where the benzene ring is replaced by a pyridine (Beal, Ashcroft, Cooper & Joule, 1982) or the indole by an aza-indole (Dalton & Joule, unpublished results), and that it is possible to utilize nitrogen as a nucleophile in the cyclizing process (Cooper & Joule, unpublished results).



We were interested in determining the three-dimensional shape of molecules that can be produced using this technology, for example (2) (Fig. 1), because of the evident structural parallelism and a possible three-dimensional similarity to nevirapine (Mui, Jacober, Hargreave & Adams, 1992) showed nevirapine to adopt a butterfly-like conformation with an angle of approximately 59° between the 'wings'.



The structure determined for (2) shows the molecule to adopt a butterfly conformation with the angle between the two essentially flat portions, the indole and benzene moieties, being 29.2 (7)°.

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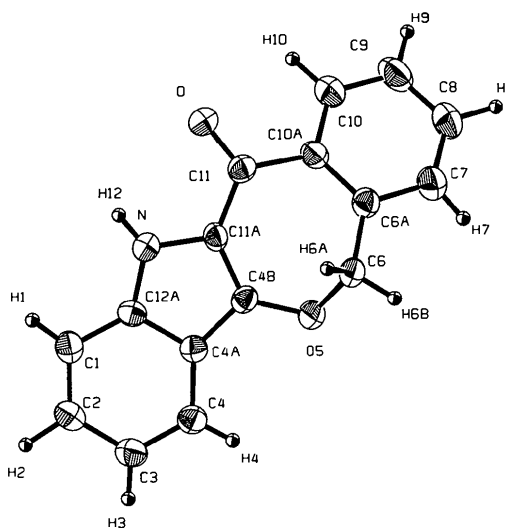


Fig. 1. ORTEP (Johnson, 1965) drawing of [2]benzoxepino[4,3-*b*]indole showing the numbering scheme used. Ellipsoids are depicted at the 30% probability level for non-H atoms and H atoms are shown at an arbitrary level.

Experimental

Crystal data

$C_{16}H_{11}NO_2$

$M_r = 249.27$

Monoclinic

$P2_1/n$

$a = 14.442$ (1) Å

$b = 4.561$ (6) Å

$c = 18.037$ (2) Å

$\beta = 93.959$ (6)°

$V = 1185.3$ (16) Å³

$Z = 4$

$D_x = 1.397$ Mg m⁻³

Cu $K\alpha$ radiation

$\lambda = 1.5418$ Å

Cell parameters from 23 reflections

$\theta = 62.57$ – 79.87 °

$\mu = 0.711$ mm⁻¹

$T = 294$ (1) K

Prism

$0.60 \times 0.25 \times 0.10$ mm

Yellow

Data collection

Rigaku AFC-5R diffractometer

$\omega/2\theta$ scans

1780 measured reflections

1724 independent reflections

1076 observed reflections

$[I \geq 3\sigma(I)]$

$R_{int} = 0.024$

$\theta_{max} = 120$ °

$h = -9 \rightarrow 15$

$k = -4 \rightarrow 4$

$l = -18 \rightarrow 20$

3 standard reflections

monitored every 150 reflections

intensity variation: 0.2%

Refinement

Refinement on F

$R = 0.048$

$wR = 0.048$

1706 reflections

216 parameters

All H-atom parameters refined

Weights from default scheme in TEXSAN (Molecular Structure Corporation, 1985)

$(\Delta/\sigma)_{max} = 0.01$

$\Delta\rho_{max} = 0.17$ e Å⁻³

$\Delta\rho_{min} = -0.15$ e Å⁻³

Atomic scattering factors from Cromer & Waber

(1974) with anomalous-dispersion effects from

Ibers & Hamilton (1964)

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (\AA^2)
$$B_{\text{eq}} = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j$$

	x	y	z	B_{eq}
O	0.3891 (2)	0.5614 (8)	0.5490 (2)	5.5 (2)
O5	0.1921 (2)	-0.0116 (8)	0.4194 (2)	4.6 (2)
N	0.4289 (3)	0.198 (1)	0.4336 (2)	4.5 (2)
C1	0.5015 (3)	-0.094 (1)	0.3361 (3)	4.9 (3)
C2	0.4817 (3)	-0.292 (1)	0.2814 (3)	5.1 (3)
C3	0.3914 (3)	-0.403 (1)	0.2668 (3)	5.0 (3)
C4	0.3208 (3)	-0.315 (1)	0.3081 (2)	4.5 (3)
C4A	0.3383 (3)	-0.111 (1)	0.3650 (2)	3.8 (2)
C4B	0.2852 (3)	0.033 (1)	0.4163 (2)	3.9 (2)
C6	0.1433 (3)	0.243 (1)	0.4423 (3)	4.5 (3)
C6A	0.1532 (3)	0.298 (1)	0.5237 (2)	4.5 (2)
C7	0.0757 (4)	0.284 (1)	0.5654 (3)	5.7 (3)
C8	0.0805 (4)	0.345 (2)	0.6398 (3)	6.6 (3)
C9	0.1644 (4)	0.422 (2)	0.6749 (3)	7.0 (4)
C10	0.2419 (4)	0.442 (1)	0.6348 (3)	5.9 (3)
C10A	0.2373 (3)	0.380 (1)	0.5598 (2)	4.5 (2)
C11	0.3258 (3)	0.402 (1)	0.5217 (2)	4.3 (2)
C11A	0.3409 (3)	0.219 (1)	0.4589 (2)	3.8 (2)
C12A	0.4290 (3)	-0.000 (1)	0.3781 (2)	4.0 (2)

Table 2. Geometric parameters (\AA , $^\circ$)

O—C11	1.243 (5)	C4A—C12A	1.410 (5)
O5—C4B	1.364 (5)	C4B—C11A	1.370 (6)
O5—C6	1.435 (6)	C6—C6A	1.486 (6)
N—C11A	1.384 (5)	C6A—C7	1.392 (6)
N—C12A	1.348 (6)	C6A—C10A	1.390 (6)
C1—C2	1.353 (7)	C7—C8	1.368 (7)
C1—C12A	1.401 (6)	C8—C9	1.373 (8)
C2—C3	1.407 (7)	C9—C10	1.378 (7)
C3—C4	1.366 (6)	C10—C10A	1.379 (6)
C4—C4A	1.393 (6)	C10A—C11	1.496 (6)
C4A—C4B	1.405 (6)	C11—C11A	1.433 (6)
C4B—O5—C6	113.4 (4)	C6A—C7—C8	122.1 (5)
C11A—N—C12A	110.0 (4)	C7—C8—C9	119.2 (5)
C2—C1—C12A	118.0 (5)	C8—C9—C10	119.9 (5)
C1—C2—C3	121.6 (5)	C9—C10—C10A	121.0 (5)
C2—C3—C4	120.6 (5)	C6A—C10A—C10	119.8 (4)
C3—C4—C4A	119.6 (5)	C6A—C10A—C11	123.3 (4)
C4—C4A—C4B	135.8 (4)	C10—C10A—C11	116.9 (4)
C4—C4A—C12A	118.9 (4)	O—C11—C10A	119.0 (4)
C4B—C4A—C12A	105.3 (4)	O—C11—C11A	120.4 (4)
O5—C4B—C4A	122.7 (4)	C10A—C11—C11A	120.4 (4)
O5—C4B—C11A	127.7 (4)	N—C11A—C4B	106.7 (4)
C4A—C4B—C11A	109.6 (4)	N—C11A—C11	119.7 (4)
O5—C6—C6A	113.9 (4)	C4B—C11A—C11	133.5 (4)
C6—C6A—C7	120.0 (4)	N—C12A—C1	130.2 (4)
C6—C6A—C10A	122.0 (4)	N—C12A—C4A	108.5 (4)
C7—C6A—C10A	118.0 (4)	C1—C12A—C4A	121.4 (4)

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Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71288 (24 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HA1045]

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N,N',N''-Triphenyl-1,3,5-triaminobenzene and its σ Complex on Protonation: a Stable *N,N',N''*-Triphenyl-2,4,6-triaminocyclohexadienylum Cation

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Abstract

Protonation of *N,N',N''*-triphenyl-1,3,5-triaminobenzene (*N,N',N''*-triphenyl-1,3,5-benzenetriamine) (1) by *p*-toluenesulfonic acid occurs at one of the C atoms of the central benzene ring, rather than at an N atom, to form the stable σ complex *N,N',N''*-triphenyl-2,4,6-triaminocyclohexadienylum *p*-toluenesulfonate (*N,N',N''*-triphenyl-2,4,6-triamino-1*H*-benzenium *p*-toluenesulfonate) (2). Changes in bond lengths clearly show the disruption of the aromaticity of the central ring in (1) on protonation and the stabilizing role of the N atoms in the delocalization of the positive charge. One of the outer benzene rings is probably involved in electronic stabilization since it approaches planarity with the central system. The other outer benzene rings do not show any obvious changes that would indicate a strong electronic contribution to the stability of (2), but are probably involved sterically.

Comment

Cationic σ complexes of arenes are of considerable importance as reactive intermediates in electrophilic