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Structures of *N*-Acetyldibenz[*b,f*]azepine, $C_{16}H_{13}NO$, and its Photodimer, $C_{32}H_{26}N_2O_2$, and of *N*-(Bromoacetyl)dibenz[*b,f*]azepine, $C_{16}H_{12}BrNO$

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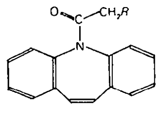
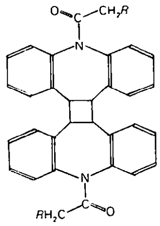
Abstract. $C_{16}H_{13}NO$ (I): $M_r = 235{\cdot}1$, $R\bar{3}$, $a = 36{\cdot}00\,(6)$, $c = 5{\cdot}43\,(1)$ Å, $V = 6094$ Å^3, $Z = 18$, $D_x = 1{\cdot}15$ g cm^{-3}, Cu $K\alpha$ radiation, $\lambda = 1{\cdot}5418$ Å, $\mu = 4{\cdot}96$ cm^{-1}, $F(000) = 2232$, final $R = 0{\cdot}081$ for 623 observed reflections. $C_{16}H_{12}BrNO$ (II): $M_r = 314$, *Pbca*, $a = 13{\cdot}867\,(4)$, $b = 7{\cdot}231\,(3)$, $c = 27{\cdot}867\,(10)$ Å, $V = 2794{\cdot}3$ Å^3, $Z = 8$, $D_x = 1{\cdot}49$ g cm^{-3}, Mo $K\alpha$ radiation, $\lambda = 0{\cdot}71069$ Å, $\mu = 28{\cdot}5$ cm^{-1}, $F(000) = 1264$, final $R = 0{\cdot}079$ for 823 observed reflections. $C_{32}H_{26}N_2O_2$ (III): $M_r = 470{\cdot}2$, $R\bar{3}$, $a = 28{\cdot}08\,(1)$, $c = 8{\cdot}926\,(4)$ Å, $V = 6095{\cdot}1$ Å^3, $Z = 9$, $D_x = 1{\cdot}15$ g cm^{-3}, Mo $K\alpha$ radiation, $\lambda = 0{\cdot}71069$ Å, $\mu = 0{\cdot}40$ cm^{-1}, $F(000) = 2232$, final $R = 0{\cdot}086$ for 733 observed reflections, $R_w = 0{\cdot}090$. In all three compounds the seven-membered azepine ring has a boat conformation, and bond lengths and torsion angles suggest very little π-electron delocalization. The dimer (III) has molecular geometry $\bar{1}$ (i) with stereochemistry *endo,trans,endo* at the central cyclobutane ring.

Introduction. Photodimerization, using benzophenone as sensitizer, of the *N*-substituted dibenzazepine (I) (in benzene) gives a dimer (III); this type of reaction may be used for controlled chain extension in polymers (Âlimoğlu, Bamford, Ledwith & Mullik, 1977). The stereochemistry of the resulting dimer, previously unknown, is established here, together with details of the monomer (I) which has pharmacological activity (Kricka & Ledwith, 1973), and its bromo derivative (II).



(I) R = H
(II) R = Br



(III) R = H

Experimental. (I), (II) and (III) were prepared by Mr D. B. Sykes and Dr A. K. Âlimoğlu using methods described by Kricka & Ledwith (1973,1974); (II) was crystallized from dichloromethane and *n*-hexane, (I) and (III) by vapour diffusion of petroleum ether into a solution of each compound in dichloromethane. Weissenberg photographs of (I) for the layers *hk*0 to *hk*3 were taken from a hexagonal needle crystal of length 0·65 mm and thickness 0·08 mm; they were measured by the SERC Microdensitometer Service to give 630 unique reflections; approximate interlayer scale factors were derived from exposure times and subsequently refined (in the early rounds of least

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squares, using isotropic vibration parameters for all atoms). After preliminary oscillation and Weissenberg photographs, crystals of (II) and (III) were mounted on the Stoe Stadi-2 diffractometer at Edinburgh University and intensity data recorded using an ω scan and $\theta_{\max} = 25°$; the crystal of (II), 0·32 × 0·90 × 0·32 mm, was mounted along **b**, and the hexagonal needle of (III), 0·8 mm long and 0·25 mm thick, was mounted along **c**; absorption corrections were not applied; 2445 independent reflections were recorded for (II), 2328 for (III); only those with $I > 2{\cdot}5\sigma(I)$ were used in the final refinement of (II), and $I > 3\sigma(I)$ in that of (III). The multisolution direct-methods procedure in *SHELX* (Sheldrick, 1976) gave an '*E* map' for (I) from which all but four of the C, N and O atom positions could be found; these four were found from a Fourier series. A Patterson series followed by a Br-phased Fourier series led to the structure of (II). *MULTAN* 80 (Main, Hull, Lessinger, Germain, Derclercq & Woolfson, 1978) was used to solve (III); eleven C, N and O positions were found from an '*E* map' and the remaining seven from a difference Fourier map. All three sets of parameters were refined by the full-matrix least-squares procedure using *SHELX*; the positions of H(10), H(11), and H(18) in (III) were taken from a difference map (where peaks in suitable positions for most of the other H atoms were also seen), but all other H atoms were placed at the stereochemically expected positions and allowed to 'ride' on the appropriate C atoms. Unit weights were used for (I) and (II), and weights $1{\cdot}48/[\sigma(F^2) + 0{\cdot}004F^2]$ for (III). Anisotropic thermal vibration parameters were refined for Br only in (II), but for all C, N and O atoms in (I) and (III). The crystal of (II) showed evidence of deterioration during data collection; some compensation for this was made by allowing the layer scale factors (up k) to refine. Difference maps for compounds (I) and (III) both showed several small peaks near the threefold axis where there is a substantial void in the packing (see Fig. 4), a possible location for solvent. Refinement of these led to positions with site occupancy ~0·3 C in (I) and ~0·1–0·2 C in (III), but the peaks could not be sensibly fitted to a solvent molecule. There were no suggestions from the difference maps that structures (I) or (III) have the noncentrosymmetric space group $R3$, rather than the centrosymmetric $R\bar{3}$. Scattering factors were from *International Tables for X-ray Crystallography* (1976).

Discussion. Positional parameters and average isotropic thermal parameters are in Table 1.[*]

The monomer molecule (II) and the atom numbering system are illustrated in Fig. 1 and the dimer in Fig. 2,

Table 1. *Atomic positions* (×10⁴) *and average vibration parameters* (×10³) *and their estimated standard deviations*

$$U = \tfrac{1}{3}(U_{11} + U_{22} + U_{33}).$$

	x	*y*	*z*	*U*(Å²)
(*a*) Compound (I)				
C(1)	849 (5)	1387 (5)	7028 (32)	56 (8)
C(2)	554 (5)	1352 (6)	8863 (36)	60 (9)
C(3)	618 (5)	1696 (7)	10341 (32)	64 (8)
C(4)	993 (4)	2089 (5)	10007 (27)	53 (8)
N(5)	1684 (3)	2545 (3)	7831 (18)	31 (5)
C(6)	2318 (4)	2844 (4)	10486 (27)	37 (7)
C(7)	2719 (4)	2882 (4)	11200 (27)	39 (7)
C(8)	2872 (4)	2660 (5)	9753 (30)	50 (8)
C(9)	2649 (4)	2399 (5)	7751 (28)	39 (7)
C(10)	1993 (4)	2051 (4)	5078 (27)	39 (7)
C(11)	1555 (4)	1807 (4)	4884 (25)	35 (7)
C(12)	1238 (4)	1783 (4)	6707 (26)	36 (7)
C(13)	1292 (4)	2131 (4)	8210 (25)	29 (6)
C(14)	2235 (4)	2344 (4)	7110 (25)	27 (6)
C(15)	2094 (4)	2579 (4)	8533 (26)	24 (6)
C(16)	1678 (4)	2875 (4)	6568 (26)	39 (7)
O(17)	2017 (3)	3210 (3)	6109 (17)	45 (5)
C(18)	1250 (5)	2813 (5)	5695 (31)	50 (7)
(*b*) Compound (II)				
C(1)	6344 (14)	4084 (31)	3988 (5)	44 (6)
C(2)	6075 (15)	5825 (36)	4170 (7)	54 (6)
C(3)	5108 (15)	6338 (36)	4199 (7)	48 (6)
C(4)	4438 (14)	4982 (29)	4033 (6)	39 (6)
N(5)	4013 (10)	1779 (24)	3763 (5)	30 (4)
C(6)	3024 (16)	1724 (34)	3050 (7)	54 (6)
C(7)	2890 (17)	1211 (34)	2557 (8)	66 (7)
C(8)	3652 (17)	282 (38)	2332 (8)	71 (7)
C(9)	4499 (17)	−155 (34)	2541 (8)	68 (7)
C(10)	5569 (17)	−15 (37)	3271 (8)	66 (7)
C(11)	6016 (15)	1005 (32)	3602 (6)	45 (6)
C(12)	5673 (13)	2725 (31)	3815 (6)	35 (5)
C(13)	4731 (12)	3200 (31)	3868 (6)	29 (5)
C(14)	4644 (15)	387 (34)	3035 (7)	47 (6)
C(15)	3889 (13)	1283 (31)	3265 (6)	39 (5)
C(16)	3496 (14)	775 (30)	4101 (5)	31 (4)
O(17)	2990 (9)	−545 (22)	4009 (4)	43 (3)
C(18)	3715 (13)	1508 (30)	4595 (5)	33 (5)
Br	3496 (2)	−551 (4)	5070 (1)	59 (3)
(*c*) Compound (III)				
C(1)	9407 (5)	1677 (5)	4499 (12)	49 (8)
C(2)	9813 (6)	1533 (5)	4401 (13)	60 (9)
C(3)	9942 (5)	1351 (5)	5740 (15)	63 (8)
C(4)	9693 (5)	1316 (5)	7115 (13)	51 (8)
N(5)	9027 (4)	1444 (4)	8572 (8)	37 (5)
C(6)	9533 (4)	2170 (5)	10393 (10)	41 (7)
C(7)	9685 (5)	2670 (5)	11005 (12)	49 (8)
C(8)	9475 (5)	2979 (5)	10409 (12)	43 (8)
C(9)	9111 (5)	2774 (5)	9193 (11)	46 (8)
C(10)	8581 (4)	2083 (5)	7208 (11)	34 (4)
C(11)	8669 (5)	1757 (5)	5857 (11)	39 (4)
C(12)	9127 (4)	1634 (4)	5877 (11)	29 (3)
C(13)	9288 (5)	1453 (5)	7127 (11)	37 (4)
C(14)	8965 (4)	2269 (5)	8541 (11)	35 (7)
C(15)	9172 (4)	1964 (4)	9218 (10)	34 (7)
C(16)	8731 (5)	951 (5)	9321 (13)	40 (8)
O(17)	8646 (4)	520 (4)	8744 (9)	63 (7)
C(18)	8476 (5)	958 (5)	10825 (12)	55 (8)
H(10)	8528 (41)	2435 (43)	6895 (94)	51 (*)
H(11)	8696 (40)	1931 (40)	4783 (111)	51 (*)

* One *U* value refined to 0·051 (10) for all ten H atoms. The other eight H atoms H(1) to H(4) and H(6)–H(9) were placed at the stereochemically expected positions on the corresponding C atoms by *SHELX*.

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[*] Lists of structure factors and anisotropic thermal parameters for (I), (II) and (III) have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38255 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

both drawn by *PLUTO* (Motherwell, 1976). The accuracy of the final bond lengths is not high [σ(C—C) ~ 0·01–0·02 Å] and they do not differ significantly from expected values. In Fig. 3 are presented some bond lengths and angles averaged for chemically equivalent parts of the molecule, and torsion angles for the seven-membered ring. In all three compounds this ring has a boat conformation; neither the bond lengths nor the torsion angles suggest any substantial π-electron delocalization around this ring; the three bonds to N are coplanar. (I) and (II) do not differ from each other and (III) differs only in the bond C(10)—C(11) which is double in the former, and single in the latter, and in small adjustments of bond angles and torsion angles to accommodate this.

The cyclodimer (III) has molecular symmetry $\bar{1}$ with stereochemistry *endo,trans,endo* around the cyclobutane ring (see Fig. 2). In an extended polymer chain, the two components attached in place of C(16) could therefore be parallel.

The packing of dimer molecules (III) in the rhombohedral lattice is illustrated in Fig. 4, which shows a large void near the origin. There are no unexpectedly short intermolecular contacts in any of the structures.

I am grateful to Dr R. O. Gould for recording the intensity data for (II) and (III) and to the SERC for financial support.

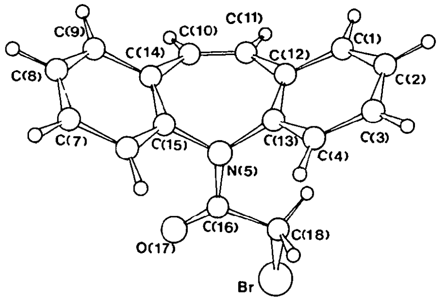

Fig. 1. One molecule of (II) indicating the atom numbering used for all three compounds.

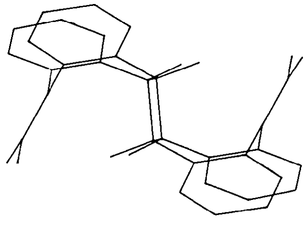

Fig. 2. The dimer (III); H atoms have been omitted for clarity except those on the cyclobutane ring.

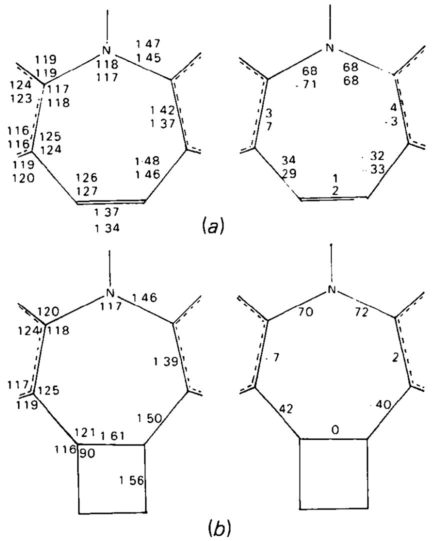

Fig. 3. Molecular geometry (in Å and degrees) of the azepine ring, averaged over chemically equivalent bonds and angles (left), and torsion angles of the ring (right), for (*a*) monomers (I) and (II) (lower figures) and (*b*) dimer (III). Estimated standard deviations are 0·01–0·02 Å and 1–1·5° in (I), 0·020–0·025 Å and 1·5–2° in (II), and 0·010–0·018 Å and 1° in (III).

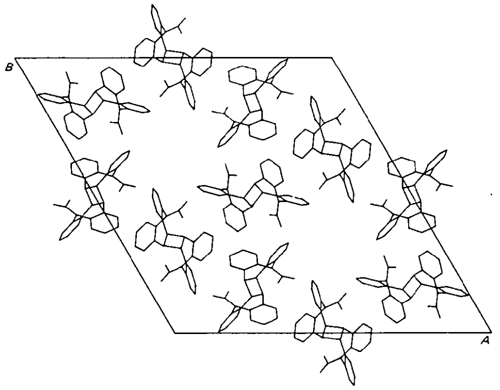

Fig. 4. *c*-axis projection to illustrate packing of dimer molecules in the crystal of (III).

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