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p- and *o*-Bis(*N,N*-diacetylamino)benzene

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Abstract. *p*-C₁₄H₁₆N₂O₄ (I): $M_r = 276.29$, monoclinic, $C2/m$, $a = 13.883$ (8), $b = 6.967$ (3), $c = 7.720$ (1) Å, $\beta = 112.42$ (3)°, $V = 690.26$ Å³, $Z = 2$, $D_x = 1.329$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.106$ mm⁻¹, $F(000) = 292$, $T = 293$ K, $R = 0.044$ for 797 reflexions with $F > 3\sigma(F)$. *o*-C₁₄H₁₆N₂O₄ (II): $M_r = 276.29$, monoclinic, $C2/c$, $a = 29.546$ (9), $b = 9.626$ (2), $c = 16.126$ (5) Å, $\beta = 113.37$ (3)°, $V = 4210.13$ Å³, $Z = 12$, $D_x = 1.307$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.105$ mm⁻¹, $F(000) = 1752$, $T = 293$ K, $R = 0.057$ for 2488 reflexions with $F > 3\sigma(F)$. All of the diacetylamino groups in (I) and (II) adopt the usual *syn-anti* configuration. Structure (I) displays crystallographic C_{2h} symmetry with the diacetylamino functions lying in a mirror plane at right angles to the benzene ring. Structure (II) is composed of two conformers, one of which is bisected by a crystallographic twofold axis and the other, although similar, is asymmetric.

Introduction. Several structures are known in which a diacetylamino (DAA) group is bound to an sp^2 C, e.g. amino sugars (Ruzić-Toroš, Rogić & Kojić-Prodić, 1980), but it is only in 6-(*N,N*-diacetylamino)chrysene (Wieckowski & Krygowski, 1981) that the bonded C atom forms part of a delocalized hydrocarbon. The present work offers several opportunities to study this type of system, of which (I) is the first example where both ring substituents flanking the DAA groups are H atoms.

Experimental. The tetraacetyl compounds were prepared by treating the respective diamines with excess

acetic anhydride under reflux for 2h; residual acetic anhydride and acetic acid were removed *in vacuo*, and the acetylation procedure repeated twice. The resultant mixtures of tri- and tetraacetyl derivatives were extracted with 60–80° petroleum ether and evaporated to give the tetraacetyl derivatives, which were recrystallized from aqueous ethanol.

(I): Colourless 0.2 × 0.2 × 0.4 mm; CAD-4 diffractometer, graphite-monochromatized Mo $K\alpha$ radiation; lattice parameters from 25 reflexions ($10.0 < \theta < 10.9^\circ$); ω - 2θ scan; $-18 < h < 18$, $0 < k < 9$, $0 < l < 10$ with $0 < \theta < 25^\circ$; no systematic variations in intensities of standards (330, 603, 711); 1107 reflexions, 797 with $F > 3\sigma(F)$; $R_{\text{int}} = 0.013$; Lp correction applied but absorption ignored; direct methods, *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980); anisotropic full-matrix refinement on F , *SHELX76* (Sheldrick, 1976), H (from ΔF synthesis) isotropic; empirical extinction correction applied where $F_c^* = F_c(1 - 0.00000825F_c^2/\sin \theta)$; final $R = 0.044$, $wR = 0.050$, $w = 4.127/[\sigma^2(F_o) + 0.00004F_o^2]$; max. $\Delta/\sigma = 0.04$ for x of O(12); all features in final ΔF synthesis between -0.25 and $+0.25$ e Å⁻³.

(II): Colourless 0.2 × 0.3 × 0.4 mm; CAD-4 diffractometer, graphite-monochromatized Mo $K\alpha$ radiation; lattice parameters from 25 reflexions ($8.3 < \theta < 9.3^\circ$); ω - 2θ scan; $-31 < h < 31$, $0 < k < 11$, $0 < l < 18$ with $0 < \theta < 25^\circ$; no systematic variation in intensities of standards (822, 12,0,0,623); 4011 reflexions, 2488 with $F > 3\sigma(F)$; $R_{\text{int}} = 0.023$; Lp correction applied but absorption ignored; direct methods, *MULTAN80*; anisotropic full-matrix refinement on F , *SHELX76*, H

(riding on heavier atoms) isotropic; empirical extinction correction applied where $F_c^* = F_c(1 - 0.00001F^2/\sin\theta)$; final $R = 0.057$, $wR = 0.070$, $w = 2.6713/[\sigma^2(F_o) + 0.00015F_o^2]$; max. $\Delta/\sigma = 0.07$ for U of H(221A); all features in final ΔF synthesis between -0.30 and $+0.18 e \text{ \AA}^{-3}$. Scattering factors from *International Tables for X-ray Crystallography* (1974). Computations carried out on the joint CDC 7600/Amdahl 470V8 system of the University of Manchester Regional Computing Centre. The Cambridge Structural Database was surveyed using the *Crystal Structure Search Retrieval* (1984) interactive system.

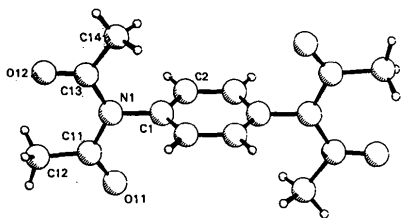


Fig. 1. *p*-Bis(diacetylamino)benzene (I) drawn using PLUTO (Motherwell & Clegg, 1978).

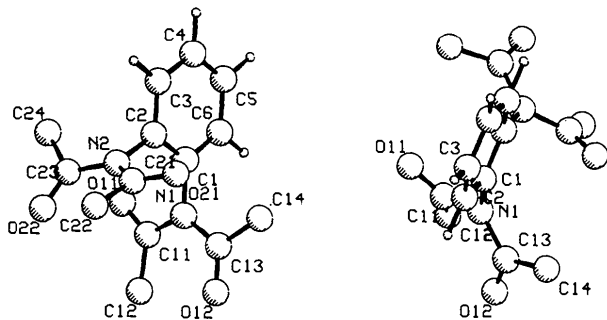


Fig. 2. *o*-Bis(diacetylamino)benzene (II). Methyl H atoms have been omitted for clarity.

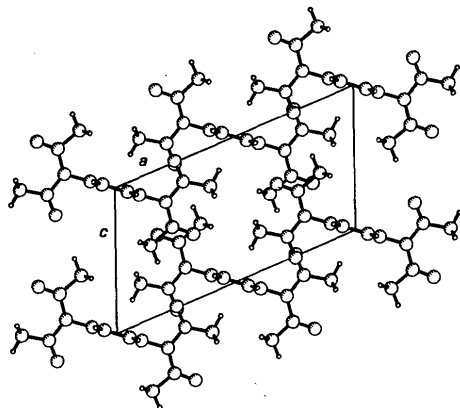


Fig. 3. Crystal packing in (I) projected on to the *ac* plane.

Table 1. Fractional atomic coordinates ($\times 10^4$) and vibrational parameters ($\text{\AA}^2 \times 10^4$) for non-H atoms

Molecule (I)	x	y	z	U_{eq}^*
C(1)	6027 (1)	5000	1197 (2)	459
C(2)	5520 (1)	3282 (2)	605 (2)	554
N(1)	7111 (1)	5000	2453 (2)	470
C(11)	7832 (2)	5000	1555 (3)	560
O(11)	7494 (1)	5000	-132 (2)	855
C(12)	8969 (2)	5000	2685 (4)	805
C(13)	7362 (2)	5000	4393 (2)	543
O(12)	8249 (1)	5000	5510 (2)	858
C(14)	6462 (2)	5000	5008 (4)	749
Molecule (IIA)				
C(1A)	1536 (1)	3675 (3)	6485 (2)	503
C(2A)	1821 (1)	4800 (3)	6912 (2)	526
C(3A)	1894 (1)	5101 (4)	7798 (2)	682
C(4A)	1691 (1)	4254 (4)	8253 (2)	767
C(5A)	1418 (1)	3103 (4)	7834 (2)	778
C(6A)	1341 (1)	2813 (4)	6947 (2)	666
N(1A)	1434 (1)	3388 (3)	5548 (2)	534
O(11A)	1787 (1)	2552 (4)	5400 (2)	630
O(11A)	2131 (1)	2145 (3)	6062 (2)	935
C(12A)	1741 (2)	2200 (5)	4473 (3)	923
C(13A)	993 (1)	3878 (4)	4871 (2)	700
O(12A)	910 (1)	3745 (4)	4087 (2)	1271
C(14A)	627 (1)	4544 (4)	5171 (3)	746
N(2A)	2044 (1)	5660 (3)	6444 (2)	560
C(21A)	1771 (1)	6807 (4)	5972 (2)	633
O(21A)	1363 (1)	6976 (3)	5955 (2)	1019
C(22A)	1991 (1)	7843 (4)	5552 (3)	833
C(23A)	2510 (1)	5310 (4)	6462 (2)	715
O(22A)	2629 (1)	5658 (3)	5867 (2)	1206
C(24A)	2849 (1)	4503 (5)	7277 (3)	843
Molecule (IIB)				
C(1B)	5034 (1)	6078 (3)	7100 (2)	515
C(2B)	5078 (1)	7324 (3)	6715 (2)	684
C(3B)	5043 (2)	8555 (4)	7112 (3)	845
N(1B)	5067 (1)	4791 (3)	6674 (2)	529
C(11B)	5512 (1)	4019 (4)	7107 (2)	637
O(11B)	5858 (1)	4618 (3)	7673 (2)	870
C(12B)	5518 (2)	2521 (4)	6904 (3)	942
C(13B)	4725 (1)	4495 (4)	5791 (2)	624
O(12B)	4810 (1)	3599 (3)	5344 (2)	897
C(14B)	4264 (1)	5329 (4)	5433 (2)	810

$$*U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i a_j a_i^* a_j^*$$

Discussion. Molecules (I) and (II) are illustrated in Figs. 1 and 2 respectively with an additional view of (I) showing the crystal packing presented in Fig. 3. The atomic coordinates are given in Table 1* and bond lengths and angles in Table 2. Compound (I) has crystallographic C_{2h} symmetry; the configuration of the DAA groups is *syn-anti*, with these groups lying in a mirror plane. The benzene ring is centred on inversion points at $\frac{1}{2}, \frac{1}{2}, 0$ or $0, 0, 0$ and lies at right angles to the *m* plane. The four acetyl π systems on each molecule overlap those from eight other molecules at interplanar spacings of $b/2$ to form infinite acetyl stacks parallel to *b*. Within each molecule the orthogonal DAA and benzene π systems support the view of Wieckowski & Krygowski (1981) that, in 6-(*N,N*-diacetylamino)-chrysenes, the chrysenes and DAA systems deviate from

* Lists of structure factors, anisotropic vibrational parameters, H-atom parameters and complete geometry tables have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44066 (28 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Selected bond lengths (Å), angles (°) and torsion angles (°)

Molecule (I)			
C(1)–C(2)	1.375 (2)	C(1)–N(1)	1.447 (2)
C(2)–C(2)	1.388 (2)	N(1)–C(11)	1.418 (2)
N(1)–C(13)	1.402 (2)	C(11)–O(11)	1.204 (2)
C(11)–C(12)	1.485 (3)	C(13)–O(12)	1.205 (2)
C(13)–C(14)	1.496 (3)		
N(1)–C(1)–C(2)	119.5 (1)	C(2)–C(1)–C(2 ⁱⁱ)	121.0 (2)
C(11)–N(1)–C(1)	114.8 (1)	C(13)–N(1)–C(1)	119.1 (2)
C(13)–N(1)–C(11)	126.0 (2)	O(11)–C(11)–N(1)	118.2 (2)
C(12)–C(11)–N(1)	120.2 (2)	C(12)–C(11)–O(11)	121.6 (2)
O(12)–C(13)–N(1)	122.3 (2)	C(14)–C(13)–N(1)	116.2 (2)
C(14)–C(13)–O(12)	121.5 (2)		
Molecule (IIA)			
C(1A)–C(2A)	1.377 (4)	C(1A)–C(6A)	1.383 (4)
C(1A)–N(1A)	1.446 (4)	C(2A)–C(3A)	1.389 (4)
C(2A)–N(2A)	1.444 (4)	C(3A)–C(4A)	1.383 (5)
C(4A)–C(5A)	1.379 (5)	C(5A)–C(6A)	1.386 (5)
N(1A)–C(11A)	1.411 (4)	N(1A)–C(13A)	1.409 (4)
C(11A)–O(11A)	1.211 (4)	C(11A)–C(12A)	1.485 (5)
C(13A)–O(12A)	1.196 (4)	C(13A)–C(14A)	1.492 (5)
N(2A)–C(21A)	1.401 (4)	N(2A)–C(23A)	1.404 (4)
C(21A)–O(21A)	1.206 (4)	C(21A)–C(22A)	1.492 (5)
C(23A)–O(22A)	1.196 (4)	C(23A)–C(24A)	1.512 (5)
C(6A)–C(1A)–C(2A)	120.4 (3)	N(1A)–C(1A)–C(2A)	120.3 (3)
N(1A)–C(1A)–C(6A)	119.3 (3)	C(3A)–C(2A)–C(1A)	119.5 (3)
N(2A)–C(2A)–C(1A)	120.4 (3)	N(2A)–C(2A)–C(3A)	120.1 (3)
C(4A)–C(3A)–C(2A)	120.0 (3)	C(5A)–C(4A)–C(3A)	120.5 (3)
C(6A)–C(5A)–C(4A)	119.4 (3)	C(5A)–C(6A)–C(1A)	120.1 (3)
C(11A)–N(1A)–C(1A)	115.1 (3)	C(13A)–N(1A)–C(1A)	119.4 (3)
C(13A)–N(1A)–C(11A)	125.4 (3)	O(11A)–C(11A)–N(1A)	117.0 (3)
C(12A)–C(11A)–N(1A)	121.4 (3)	C(12A)–C(11A)–O(11A)	121.6 (3)
O(12A)–C(13A)–N(1A)	121.4 (3)	C(14A)–C(13A)–N(1A)	117.4 (3)
C(14A)–C(13A)–O(12A)	121.2 (3)	C(21A)–N(2A)–C(2A)	116.8 (2)
C(23A)–N(2A)–C(2A)	119.9 (3)	C(23A)–N(2A)–C(21A)	123.4 (3)
O(21A)–C(21A)–N(2A)	118.4 (3)	C(22A)–C(21A)–N(2A)	120.7 (3)
C(22A)–C(21A)–O(21A)	120.8 (3)	O(22A)–C(23A)–N(2A)	121.0 (3)
C(24A)–C(23A)–N(2A)	116.6 (3)	C(24A)–C(23A)–O(22A)	122.4 (3)
C(2A)–C(1A)–N(1A)–C(11A)	88.0 (3)	C(1A)–N(1A)–C(11A)–O(11A)	1.1 (3)
C(2A)–C(1A)–N(1A)–C(13A)	95.3 (3)	C(1A)–N(1A)–C(13A)–O(12A)	174.9 (3)
C(1A)–C(2A)–N(2A)–C(21A)	91.0 (3)	C(2A)–N(2A)–C(21A)–O(21A)	–2.8 (3)
C(1A)–C(2A)–N(2A)–C(23A)	–87.7 (3)	C(2A)–N(2A)–C(23A)–O(22A)	153.7 (3)
Molecule (IIB)			
C(1B)–C(1B ⁱⁱⁱ)	1.381 (6)	C(1B)–C(2B)	1.381 (4)
C(1B)–N(1B)	1.439 (4)	C(2B)–C(3B)	1.369 (5)
C(3B)–C(3B ⁱⁱⁱ)	1.373 (8)	N(1B)–C(11B)	1.428 (4)
N(1B)–C(13B)	1.410 (4)	C(11B)–O(11B)	1.212 (4)
C(11B)–C(12B)	1.480 (5)	C(13B)–O(12B)	1.212 (4)
C(13B)–C(14B)	1.486 (5)		
N(1B)–C(1B)–C(2B)	119.7 (3)	C(3B)–C(2B)–C(1B)	120.2 (3)
C(11B)–N(1B)–C(1B)	116.0 (3)	C(13B)–N(1B)–C(1B)	120.0 (3)
C(13B)–N(1B)–C(11B)	122.8 (3)	O(11B)–C(11B)–N(1B)	117.3 (3)
C(12B)–C(11B)–N(1B)	119.2 (3)	C(12B)–C(11B)–O(11B)	123.3 (3)
O(12B)–C(13B)–N(1B)	120.7 (3)	C(14B)–C(13B)–N(1B)	117.5 (3)
C(14B)–C(13B)–O(12B)	121.8 (3)		
C(2B)–C(1B)–N(1B)–C(11B)	106.5 (3)	C(1B)–N(1B)–C(11B)–O(11B)	–14.6 (3)
C(2B)–C(1B)–N(1B)–C(13B)	–60.6 (3)	C(1B)–N(1B)–C(13B)–O(12B)	162.6 (3)

Symmetry code: (i) $1-x, y, -z$; (ii) $x, 1-y, z$; (iii) $1-x, y, \frac{1}{2}-z$.

being exactly perpendicular because of asymmetric chrysene bond lengths at the point of substitution. These workers also correlated the expanded valence angle in chrysene [$122.1(2)^\circ$] with the electron-withdrawing effect of DAA in accordance with Walsh's (1947) rule. This expansion is seen to a lesser though significant extent in (I) [C(2)–C(1)–C(2ⁱⁱ) = $121.0(2)^\circ$] and would place the electron-withdrawing influence of DAA alongside CN and SO_3^- according to

a survey of *para*-substituted benzenes (Domenicano & Murray-Rust, 1979).

The configuration of (II) is such that the free molecule would be bisected by a twofold axis as in (I). However, due to packing forces, only one of the two crystallographically independent molecules [(IIB)] retains this symmetry. In contrast to (I) the maintenance of planar *ortho*-DAA groups at right angles to the benzene ring would cause unfavourable steric interactions between C(14), C(24) and O(21), O(11). This has been avoided in (IIA) by tilting the DAA groups, moving C(14A) away from O(21A) [$3.10(1) \text{ \AA}$] with an associated twist around N(2)–C(23) to give an O(11A)···C(24A) distance of $3.19(1) \text{ \AA}$. In (IIB) the mutual orientations of the DAA groups and the benzene ring deviate considerably from being perpendicular. Planar DAA groups in this situation would have unfavourable interactions, with O(11) approaching N(1) and C(13) in the adjacent DAA. This has been limited in (IIB) by distorting the DAA groups, primarily *via* twists about N(1)–C(11) and N(1)–C(13) (see Table 2). However, several short non-bonded contacts still remain: C(2B)···C(13B) $3.08(1)$, C(2B)···C(14B) $3.13(1)$, C(1Bⁱⁱⁱ)···C(11B) $3.13(1)$, C(1Bⁱⁱⁱ)···O(11B) $3.13(1)$, N(1Bⁱⁱⁱ)···C(11B) $3.17(1)$, N(1Bⁱⁱⁱ)···O(11B) $3.30(1)$, O(11Bⁱⁱⁱ)···C(14B) $3.29(1) \text{ \AA}$, where (iii) denotes an atom at $1-x, y, \frac{1}{2}-z$, generated by the twofold axis. The highly symmetric crystal packing seen in (I) is absent from (II) and is reflected in its lower melting point [(II): $365, (I): 471 \text{ K}$].

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