

A packing diagram of the crystal structure, drawn with the aid of the program *STER* (van de Waal, 1973), is given in Fig. 2. The molecules are linked by hydrogen bridges. Each oxygen atom is involved in three hydrogen bonds of the type O...H-N. The geometries of these bonds are given in Table 4. The separations between the oxygen atom and the hydrogen atoms are much less than the sum of the van der Waals radii of these atoms, which is 2.53 Å (Kitaigorodsky, 1961). As stated by Hamilton & Ibers (1968), this is an unmistakable criterion for hydrogen bonding.

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4b,9a,13b-Triazadibenzo[*a,e*]acephenanthrylene-9,14-dione

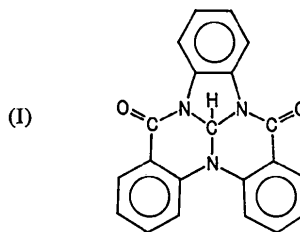
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Abstract. C₂₁H₁₃N₃O₂, *M* = 339.35, orthorhombic, *Pca*2₁ (No. 29), *Z* = 4. At -40°C, *a* = 18.458 (4), *b* = 10.924 (2), *c* = 7.673 (2) Å, *V* = 1547 Å³, *D_c* = 1.457 g cm⁻³. At 25°C, *D_m* = 1.44 g cm⁻³. Mo *K*α radiation, λ = 0.71069 Å, μ = 1.04 cm⁻¹. *R* = 0.065, 1118 reflections measured on a Syntex diffractometer. The structure of a novel, fused-ring heterocyclic compound is confirmed. As a result of an H...H intramolecular interaction, the conformations of the two chemically-equivalent halves of the molecule are found to be quite different.

Introduction. The synthesis and preliminary structural information for the title compound (1) have been previously communicated (Cass, Katritzky, Harlow & Simonsen, 1976). Thin, plate-like crystals were grown by sublimation; the yellow crystal selected for this investigation had dimensions of 0.09 × 0.27 × 0.44 mm perpendicular to (100), (010) and (001). The possible space groups, *Pcam* and *Pca*2₁ (systematic absences: *Ok*l, *k* odd and *h*0l, *h* odd), and a set of approximate unit-cell dimensions were determined from oscillation and Weissenberg photographs. Space group *Pcam*, with *Z* = 4, requires that the molecule be situated on a twofold axis, across a mirror plane, or about a center of symmetry; because the molecule can possess none of these symmetries (assuming an ordered structure), *Pca*2₁ was selected as the correct space group. This choice was later confirmed by the 'E' statistics and, of course, by the successful refinement of the structure.



The crystal was mounted on a Syntex *P2*₁ diffractometer equipped with a low-temperature apparatus which kept the crystal cooled to -40°C. Mo *K*α radiation, monochromated with a graphite crystal, was used throughout this study. The unit-cell parameters were refined using the Bragg angles (as determined by the Syntex centering routine) of 52 reflections.

Intensity data for 1322 unique reflections (4° < 2θ < 48°) were collected using the ω-scan technique. Scans of 1.0° were employed with scan rates which ranged from 0.5 to 5.0° min⁻¹, depending on the number of counts accumulated in a rapid preliminary scan. Background measurements were taken at both ends of the scan with ω displaced by ± 1.0° from the *K*α peak; the time of each measurement was one-half of the scan time. The intensities of four standard reflections were monitored after every 96 reflections; only statistical variations were noted. The intensities were corrected for Lorentz and polarization effects but not for absorption.

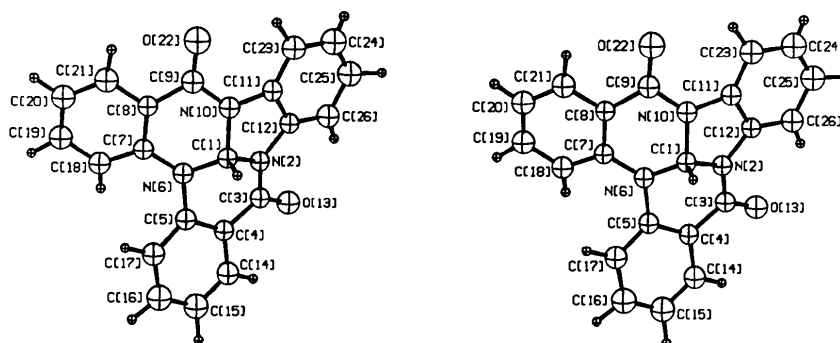


Fig. 1. Geometry and atom numbering scheme of the molecule. The hydrogen atoms are numbered in accord with the carbon to which each is bonded.

The structure was solved by direct methods (*MULTAN*) but required the separate normalization of each parity group (the *l*-odd reflections were systematically weak) and some hand phasing to find a suitable set of

starting reflections. The third best solution (absolute FOM) yielded the positions of all the non-hydrogen atoms. Refinement of the structure by the full-matrix least-squares method was carried out using only those

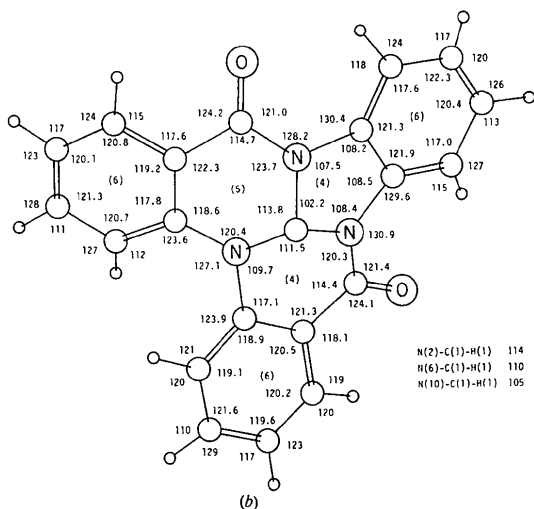
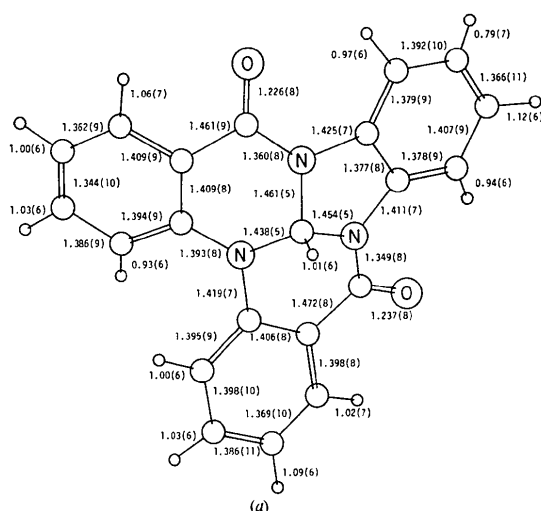


Fig. 2. (a) Bond distances and (b) angles for 4b,9a,13b-triazadibenzo[*a,e*]acephenanthrylene-9,14-dione. The average estimated standard deviation for the angles associated with each ring is given in parentheses inside the ring.

Table 1. Atomic coordinates and thermal parameters

(a) Non-hydrogen atoms

	<i>x</i> ($\times 10^4$)	<i>y</i> ($\times 10^4$)	<i>z</i> ($\times 10^4$)	<i>B</i>
C(1)	3798 (3)	1244 (5)	2700	2.58 (12)
N(2)	4351 (2)	1004 (4)	1394 (11)	2.60 (9)
C(3)	4390 (3)	-101 (5)	615 (12)	2.86 (12)
C(4)	3796 (3)	-942 (5)	1070 (12)	2.74 (12)
C(5)	3165 (3)	-520 (5)	1900 (13)	2.84 (12)
N(6)	3107 (2)	760 (4)	2184 (11)	2.69 (10)
C(7)	2475 (4)	1426 (5)	2476 (13)	2.64 (11)
C(8)	2535 (4)	2625 (5)	3139 (12)	2.49 (11)
C(9)	3227 (3)	3271 (6)	3228 (12)	3.14 (13)
N(10)	3815 (3)	2578 (5)	2825 (11)	2.83 (10)
C(11)	4504 (3)	2976 (5)	2209 (12)	2.75 (13)
C(12)	4821 (3)	2020 (5)	1324 (12)	2.52 (11)
O(13)	4898 (2)	-369 (4)	-363 (11)	3.87 (10)
C(14)	3884 (3)	-2186 (6)	697 (12)	3.48 (13)
C(15)	3362 (4)	-3009 (7)	1171 (14)	4.10 (15)
C(16)	2754 (4)	-2607 (7)	2062 (14)	4.26 (16)
C(17)	2651 (4)	-1370 (6)	2453 (13)	3.32 (14)
C(18)	1785 (3)	996 (6)	2070 (12)	3.16 (13)
C(19)	1178 (3)	1707 (6)	2396 (12)	3.45 (13)
C(20)	1235 (4)	2823 (6)	3119 (12)	3.45 (14)
O(21)	1900 (3)	3306 (6)	3456 (13)	3.48 (14)
O(22)	3287 (2)	4367 (4)	3533 (11)	4.34 (11)
C(23)	4828 (4)	4111 (6)	2287 (13)	3.70 (13)
C(24)	5497 (4)	4236 (7)	1471 (15)	4.38 (16)
C(25)	5814 (4)	3298 (6)	577 (13)	4.07 (15)
C(26)	5484 (3)	2138 (6)	515 (13)	3.55 (14)

(b) Hydrogen atoms

The hydrogen atoms are numbered in accord with the carbon atom to which each is attached.

	<i>x</i> ($\times 10^3$)	<i>y</i> ($\times 10^3$)	<i>z</i> ($\times 10^3$)	<i>B</i>
H(1)	392 (3)	94 (5)	390 (8)	3.3
H(14)	432 (3)	-246 (6)	-2 (10)	4.7
H(15)	342 (3)	-399 (6)	98 (10)	5.0
H(16)	232 (3)	-311 (5)	253 (10)	4.5
H(17)	220 (3)	-111 (6)	308 (9)	4.2
H(18)	180 (3)	25 (6)	149 (9)	4.0
H(19)	71 (3)	125 (5)	206 (8)	4.1
H(20)	80 (3)	333 (5)	343 (9)	4.4
H(21)	198 (3)	416 (6)	407 (10)	4.6
H(23)	454 (3)	479 (5)	271 (8)	4.3
H(24)	566 (3)	491 (6)	141 (11)	5.6
H(25)	638 (3)	329 (5)	4 (10)	4.9
H(26)	563 (3)	146 (6)	-15 (10)	4.3

Table 2. *Selected torsion angles*

The angles in the right- and left-hand columns are arranged to contrast the two chemically-equivalent halves of the molecule. (The unsymmetrical conformation is evident; if the molecule possessed a mirror plane, each pair of angles would have equal magnitudes but opposite signs.)

C(1)—N(2)—C(3)—C(4)	6.0°	C(1)—N(10)—C(9)—C(8)	-13.5°
C(1)—N(2)—C(3)—O(13)	-172.4	C(1)—N(10)—C(9)—O(22)	170.6
C(1)—N(2)—C(12)—C(11)	-13.4	C(1)—N(10)—C(11)—C(12)	15.2
N(2)—C(3)—C(4)—C(5)	14.4	N(10)—C(9)—C(8)—C(7)	-7.7
O(13)—C(3)—C(4)—C(5)	-167.3	O(22)—C(9)—C(8)—C(7)	168.1
C(3)—C(4)—C(5)—N(6)	3.7	C(9)—C(8)—C(7)—N(6)	11.5
C(4)—C(5)—N(6)—C(1)	-39.7	C(8)—C(7)—N(6)—C(1)	5.7
C(4)—C(5)—N(6)—C(7)	159.2	C(8)—C(7)—N(6)—C(5)	165.0
C(5)—N(6)—C(1)—N(2)	58.3	C(7)—N(6)—C(1)—N(10)	-24.2
C(5)—N(6)—C(1)—N(10)	173.2	C(7)—N(6)—C(1)—N(2)	-139.1
N(6)—C(1)—N(2)—C(3)	-42.9	N(6)—C(1)—N(10)—C(9)	29.2
N(6)—C(1)—N(2)—C(12)	143.5	N(6)—C(1)—N(10)—C(11)	-142.5
N(2)—C(12)—C(11)—N(10)	-1.2		

1118 reflections for which $I > 2\sigma(I)$. The non-hydrogen atoms were refined with isotropic thermal parameters. The hydrogen atoms were located from a difference Fourier and each was assigned an isotropic thermal parameter equal to 1.0 plus the value for the carbon atom to which it was bonded. The refinement of all positional parameters and the isotropic thermal parameters of the non-hydrogen atoms (143 variables, observation-to-variable ratio of 7.8) converged at a conventional R of 0.065. No attempt to refine the non-hydrogen atoms with anisotropic thermal parameters was made as this would have reduced the observation-to-variable ratio to the uncomfortable value of 3.9. The largest non-hydrogen parameter shift in the final cycle of the refinement was 0.16σ . The final positional and thermal parameters are given in Table 1.* The largest peak in the final difference map was $0.30 \text{ e } \text{Å}^{-3}$. The mathematical and computational details are noted elsewhere (Harlow, Loghry, Williams & Simonsen, 1975).

Discussion. Although the molecule is divisible into two chemically-equivalent halves, mirror symmetry is not possible because of a steric interaction between the hydrogen atoms attached to C(17) and C(18). The resulting conformation is easily seen in Fig. 1, supported by the torsion angles listed in Table 2 and the additional note that all three benzo groups are planar to within $0.03 (1) \text{ Å}$. The bond distances and angles are given in Fig. 2, and, as a rule, show reasonable agreement between the two halves of the molecule.

In an effort to minimize the H(17)···H(18) interaction, the molecule has distorted in a somewhat 'unsymmetrical' fashion, particularly with respect to the bond parameters associated with atom N(6). For example, angles C(1)—N(6)—C(5) and C(1)—N(6)—C(7) differ markedly: 109.7 vs 120.4° , respectively. The chemically-equivalent torsion angles involving N(6) are also

quite different and reflect the dissimilar conformations of the two six-membered rings containing N(6). The ring made up of atoms 1–6 assumes the standard half-chair conformation generally found for cyclohexenes; atoms N(2), C(3), C(4) and C(5) are nearly planar while C(1) and N(6) deviate significantly (in opposite directions) from the plane. The chemically-equivalent ring which contains atoms 1, 6–10 is almost planar throughout, but does take on a slight boat conformation with atoms C(1) and C(8) above the plane of the other four. Fig. 1 and Table 2 show the effects quite well. This unsymmetrical distortion is in contrast to the 'symmetrical' distortion reported for benzo[*c*]phenanthrene (Hirshfeld, Sandler & Schmidt, 1963) where a similar H···H steric interaction was found. The resulting H···H and C···C intramolecular distances agree very well however: for benzo[*c*]phenanthrene, H···H = 2.04 and C···C = 3.030 Å ; for the present structure, H(17)···H(18) = $2.06 (9)$ and C(17)···C(18) = $3.054 (9) \text{ Å}$. Also in good agreement are the angles C(17)—C(5)—N(6), C(5)—N(6)—C(7) and N(6)—C(7)—C(18), all significantly greater than 120° .

The intermolecular interactions are of the van der Waals type with the possible exception of a short contact between the central hydrogen atom, H(1), and a neighboring oxygen atom, O(13)' [related to O(13) by $1-x, -y, \frac{1}{2}+z$]. The distance, $2.33 (5) \text{ Å}$, is much less than 2.60 Å , the sum of the standard van der Waals radii for the two atoms. The C(1)—H(1)···O(13)' angle of $122 (4)^\circ$ weakens the argument for labeling this interaction as a hydrogen bond.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31447 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.