Fig. 1. Molecular structure of 2-methyl-2$H$-naphtho[1,8-$de$]triazine. The bond lengths and angles are mean values averaged over the molecular symmetry and those in parentheses are the corresponding values of Hazell & Mariezcurrena (1980). The e.s.d.'s are between 0·006 (0·007) and 0·010 (0·011) Å for bond distances and between 0·4 (0·6) and 0·6 (0·9)° for bond angles with the exception of those defined by H atoms, where they are 0·06 (0·05–0·10) Å and 3–5 (4–7)° respectively.

for both $CH_3$ group orientations show almost identical intermolecular environments in the crystal packing.

We thank Drs A. Hazell and R. Mariezcurrena for placing their manuscript on the same subject at our disposal, Professor M. J. Perkins, Dr P. Flowerday, Dr R. C. Haddon and Dr M. L. Kaplan for supplying the crystals, and the Deutsche Forschungsgemeinschaft for financial support.



Fig. 2. Stereoscopic view of the crystal packing. At the $CH_3$ group only one statistical position for the H atoms is shown.

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# Structure of 3,5-Diformylbicyclo[5.4.1]dodeca-2,5,7,9,11-pentaene

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**Abstract.** $C_{14}H_{12}O_2$, orthorhombic, *Pccn*, $a = 13·738$ (2), $b = 13·472$ (2), $c = 11·658$ (2) Å, $Z = 8$, $D_c = 1·307$, $D_m = 1·306$ Mg m$^{-3}$ (flotation), $\mu$(Mo $K\alpha$) $= 0·094$ mm$^{-1}$, $F(000) = 896$. The structure has been solved by an iterative least-squares rigid-body process, and refined to $R = 0·062$ for 1243 independent reflexions. Bond lengths of the structure indicate an open
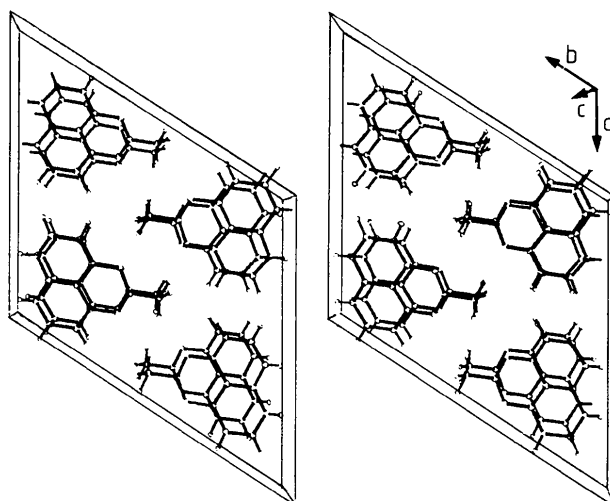
14$\pi$-electron system. Of the six strongest intermolecular interactions, four are of the type O···H, one is C···C and the last is C···H.

**Introduction.** The present analysis forms part of a structural study of bridged annulenes. We report here the structure of the title compound (hereafter ALD).

Table 1. *Atomic coordinates and equivalent isotropic thermal parameters*

Fractional coordinates are multiplied by $10^4$ for heavy atoms, by $10^3$ for hydrogen atoms. The equivalent isotropic thermal parameter is taken as $B$ (Å$^2$) = $\frac{4}{3}(\sum_i \sum_j B_{ij}\, \mathbf{a}_i \cdot \mathbf{a}_j)$.

| | $x$ | $y$ | $z$ | $B_{eq}/B$ |
|---|---|---|---|---|
| C(1) | 180 (2) | 3226 (2) | −191 (3) | 2·9 (1) |
| C(2) | 1148 (2) | 3531 (2) | 129 (3) | 3·0 (1) |
| C(3) | 1556 (2) | 3580 (2) | 1186 (3) | 3·0 (1) |
| C(4) | 1101 (3) | 3324 (3) | 2333 (3) | 3·2 (1) |
| C(5) | 222 (2) | 3922 (2) | 2677 (2) | 3·0 (1) |
| C(6) | −678 (2) | 3914 (2) | 2215 (3) | 3·0 (1) |
| C(7) | −1021 (2) | 3417 (2) | 1193 (3) | 3·1 (1) |
| C(8) | −1813 (2) | 3779 (2) | 615 (3) | 3·5 (1) |
| C(9) | −1978 (3) | 3628 (3) | −584 (4) | 4·0 (1) |
| C(10) | −1270 (3) | 3534 (2) | −1393 (3) | 4·1 (1) |
| C(11) | −248 (3) | 3547 (3) | −1173 (3) | 3·5 (1) |
| C(12) | −427 (2) | 2636 (2) | 619 (3) | 3·2 (1) |
| C(13) | 2555 (3) | 3930 (2) | 1201 (4) | 3·6 (1) |
| C(14) | 351 (3) | 4642 (3) | 3606 (3) | 3·9 (1) |
| O(1) | 3060 (2) | 4019 (2) | 2055 (2) | 4·8 (1) |
| O(2) | 1106 (2) | 4840 (2) | 4081 (2) | 5·3 (1) |
| H(2) | 152 (2) | 378 (2) | −46 (2) | 4·4 (6) |
| H(4A) | 159 (2) | 341 (2) | 286 (3) | 5·4 (7) |
| H(4B) | 101 (2) | 262 (2) | 239 (2) | 4·9 (7) |
| H(6) | −114 (2) | 437 (2) | 253 (2) | 3·8 (6) |
| H(8) | −227 (2) | 420 (2) | 107 (2) | 5·0 (7) |
| H(9) | −268 (3) | 376 (2) | −84 (3) | 6·8 (8) |
| H(10) | −148 (2) | 360 (2) | −227 (3) | 8·2 (9) |
| H(11) | 15 (2) | 386 (2) | −169 (2) | 5·3 (8) |
| H(12A) | −3 (2) | 223 (2) | 115 (2) | 4·7 (7) |
| H(12B) | −88 (2) | 217 (2) | 20 (2) | 5·4 (7) |
| H(13) | 290 (3) | 407 (3) | 48 (4) | 10·5 (13) |
| H(14) | −29 (3) | 496 (2) | 378 (3) | 7·0 (9) |

Crystals of ALD were kindly supplied by Professor E. Vogel. The cell parameters were obtained by least squares from the $\sin^2\theta$ values of 44 reflexions measured on a diffractometer. Systematic absences were consistent with the space group *Pccn*. Data were collected below $2\theta = 45°$ at room temperature on a computer-controlled four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0·71069$ Å) and a variable $\theta–2\theta$ scan technique. Each reflexion was assigned a variance $\sigma^2(I)$ based on counting statistics plus a term $(0·03S)^2$, where $S$ is the scan count (Peterson & Levy, 1957).

Of the 1412 measured reflexions, 1243 were accepted as observed on the criterion $I > 2\sigma(I)$ and used in the calculations. Data were corrected for Lorentz–polarization effects, but not for absorption.

The structure was found by the use of a method proposed by Bianchi, Gramaccioli, Pilati & Simonetta (1980). This method determines the positions and the orientations of molecular fragments of known internal geometry. In our case the internal geometry of the rigid group of atoms (excluding H atoms) was derived from the structure of *syn*-5,7-diformyltricyclo[9.4.1.1$^{3,9}$]-heptadeca-2,4,7,9,11,13,15-heptaene (DIAL: Pilati & Simonetta, 1977).

A few refinement cycles were carried out by the full-matrix least-squares method starting from the atomic coordinates of the solution. Starting values for the scale and overall temperature factors were estimated from a Wilson plot. The program used for refinement was a modified version of *ORFLS* (Busing, Martin & Levy, 1962). Form factors were from Cromer & Waber (1965), except those for H which were from Stewart, Davidson & Simpson (1965). H-atom positions were located from a difference map and recalculated according to stereochemical criteria.

Refinement was then continued on all position parameters, with anisotropic thermal parameters for non-hydrogen atoms and isotropic for the H atoms. A final $R = \sum \|kF_o\| - |F_c\|/\sum |kF_o| = 0·062$ was obtained for all 1243 observed reflexions with the final parameters (Table 1).* A final difference map showed no peak $>0·18$ e Å$^{-3}$.

**Discussion.** Bond distances and angles are listed in Tables 2 and 3; in both tables the two columns are referred to the two halves of the molecule that may be symmetry-related. Torsion angles along the perimeter ring are shown in Fig. 1 together with the numbering scheme.

As can be argued from Tables 2 and 3 and Fig. 1, the molecule of ALD shows a distortion from $m$ symmetry in the crystal. The deviation from $m$ symmetry is more pronounced here than in the related DIAL: this is emphasized in Table 3 from all the pairs marked by an asterisk; and also in Fig. 1 by the differences (up to ~8°) between selected torsion angles related by $m$ symmetry.

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* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35420 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond distances* (Å) ($\sigma = 0·004–0·006$ Å *for* C—C, C—O, $0·02–0·04$ Å *for* C—H)

| | | | |
|---|---|---|---|
| C(10)—C(9) | 1·361 | | |
| C(11)—C(10) | 1·428 | C(8)—C(9) | 1·430 |
| C(11)—C(1) | 1·358 | C(8)—C(7) | 1·369 |
| C(1)—C(12) | 1·490 | C(7)—C(12) | 1·491 |
| C(2)—C(1) | 1·441 | C(6)—C(7) | 1·446 |
| C(3)—C(2) | 1·356 | C(5)—C(6) | 1·348 |
| C(3)—C(4) | 1·516 | C(5)—C(4) | 1·506 |
| C(3)—C(13) | 1·452 | C(5)—C(14) | 1·464 |
| C(13)—O(1) | 1·220 | C(14)—O(2) | 1·206 |
| C(10)—H(10) | 1·07 | C(9)—H(9) | 1·02 |
| C(11)—H(11) | 0·92 | C(8)—H(8) | 0·99 |
| C(2)—H(2) | 0·92 | C(6)—H(6) | 0·96 |
| C(13)—H(13) | 0·98 | C(14)—H(14) | 0·99 |
| C(4)—H(4A) | 0·92 | | |
| C(4)—H(4B) | 0·97 | | |
| C(12)—H(12A) | 0·99 | | |
| C(12)—H(12B) | 1·01 | | |

Table 3. *Bond angles* (°) ($\sigma = 0\cdot2$–$0\cdot4°$ *for* C—C—C,
C—C—O, $1\cdot4$–$2\cdot3°$ *for* C—C—H, O—C—H, H—C—H)

| | | | |
|---|---|---|---|
| C(11)—C(10)—C(9) | 125·3 | C(10)—C(9)—C(8) | 125·2 |
| C(1)—C(11)—C(10) | 125·0 | C(7)—C(8)—C(9) | 123·8* |
| C(11)—C(1)—C(12) | 117·5 | C(8)—C(7)—C(12) | 117·7 |
| C(2)—C(1)—C(11) | 121·9 | C(6)—C(7)—C(8) | 120·1* |
| C(2)—C(1)—C(12) | 120·3 | C(6)—C(7)—C(12) | 121·2* |
| C(1)—C(2)—C(3) | 129·1 | C(5)—C(6)—C(7) | 129·3 |
| C(2)—C(3)—C(4) | 128·4 | C(6)—C(5)—C(4) | 128·6 |
| C(2)—C(3)—C(13) | 114·7 | C(6)—C(5)—C(14) | 114·4 |
| C(4)—C(3)—C(13) | 116·9 | C(4)—C(5)—C(14) | 117·0 |
| C(3)—C(4)—C(5) | 116·3 | | |
| C(1)—C(12)—C(7) | 102·4 | | |
| C(3)—C(13)—O(1) | 125·5 | C(5)—C(14)—O(2) | 126·2 |
| C(9)—C(10)—H(10) | 117·5 | C(10)—C(9)—H(9) | 119·1 |
| C(11)—C(10)—H(10) | 116·0 | C(8)—C(9)—H(9) | 114·2 |
| C(10)—C(11)—H(11) | 118·8 | C(9)—C(8)—H(8) | 120·0 |
| C(1)—C(11)—H(11) | 115·8 | C(7)—C(8)—H(8) | 116·1 |
| C(1)—C(12)—H(12A) | 112·2 | C(7)—C(12)—H(12A) | 114·3 |
| C(1)—C(12)—H(12B) | 111·6 | C(7)—C(12)—H(12B) | 108·5 |
| C(1)—C(2)—H(2) | 115·2 | C(7)—C(6)—H(6) | 113·0 |
| C(3)—C(2)—H(2) | 115·4 | C(5)—C(6)—H(6) | 117·0 |
| C(3)—C(4)—H(4A) | 104·7 | C(5)—C(4)—H(4A) | 110·4* |
| C(3)—C(4)—H(4B) | 109·7 | C(5)—C(4)—H(4B) | 113·9* |
| C(3)—C(13)—H(13) | 120·2 | C(5)—C(14)—H(14) | 109·2* |
| O(1)—C(13)—H(13) | 114·2 | O(2)—C(14)—H(14) | 124·7* |
| H(12B)—C(12)—H(12A) | 107·8 | | |
| H(4B)—C(4)—H(4A) | 100·3 | | |

\* The difference between the values for these pairs is equal to or greater than $3\sigma$.

Table 4. *Selected intermolecular contacts* (Å)

| | Symmetry operation applied to second atom | |
|---|---|---|
| C(9)···C(9) | $-\frac{1}{2}-x, \frac{1}{2}-y, z$ | 3·360 (6) |
| C(11)···H(4B) | $x, \frac{1}{2}-y, -\frac{1}{2}+z$ | 2·87 (3) |
| O(1)···H(4B) | $\frac{1}{2}-x, \frac{1}{2}-y, z$ | 2·58 (3) |
| O(1)···H(6) | $\frac{1}{2}+x, 1-y, \frac{1}{2}-z$ | 2·48 (3) |
| O(2)···H(8) | $\frac{1}{2}+x, 1-y, \frac{1}{2}-z$ | 2·59 (3) |
| O(2)···H(13) | $\frac{1}{2}-x, y, \frac{1}{2}+z$ | 2·37 (3) |

The packing within the unit cell (see Table 4) is responsible for the asymmetry of ALD. In particular, the O atoms of the two formyl groups are involved in four short intermolecular contacts of the type O···H
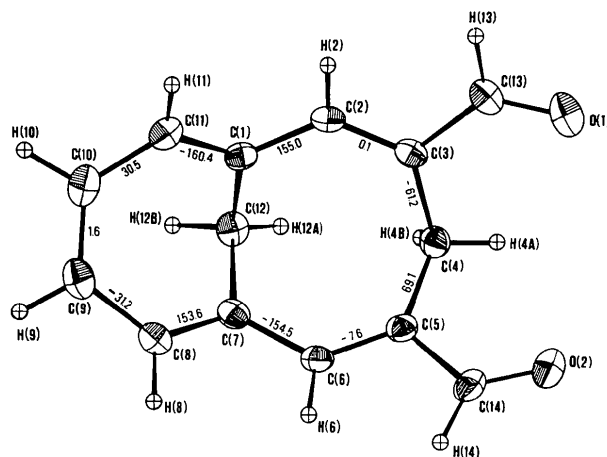


Fig. 1. A drawing of the molecule showing the numbering scheme and torsion angles (°) along the perimeter ring. Thermal ellipsoids are at the 20% probability level. H atoms are on an arbitrary scale. The signs of the torsion angles follow the convention proposed by Klyne & Prelog (1960).

that have not been found in DIAL. The two C—O bonds are in positions *trans* to their nearest double bonds for steric reasons.

The alternation of short and long bonds along the perimeter ring indicates an open $14\pi$-electron system. As expected, the variation of bond lengths decreases on going from the outer to the central part of the $\pi$ system.

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# Structure of 1,6-Methano[10]annulene

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**Abstract.** $C_{11}H_{10}$, orthorhombic, *Fdd2*, $a = 33\cdot9690\,(39)$, $b = 15\cdot1117\,(13)$, $c = 6\cdot1811\,(6)$ Å, $Z = 16$, $D_c = 1\cdot191\,(145\,\text{K})$, $D_m = 1\cdot129$ Mg m$^{-3}$ (flotation at 291 K), $\mu(\text{Mo }K\alpha) = 0\cdot073$ mm$^{-1}$, $F(000) = 1216$. The structure was solved by a constrained least-squares method and refined to $R = 0\cdot051$ for 1210