

case some reflexions, which had large $F_o - F_c$ differences or were suspect for other reasons, were left out of the refinements. The tables of F_o and F_c include all observed reflexions.*

Results and discussion

The coordinates from both refinements are listed in Table 1: the agreement is excellent, in most cases well within a single standard deviation (as computed by the block-diagonal least-squares program). Bond lengths and angles are given in Table 2. Several mean planes with the interplanar angles are listed in Table 3. The mean bond length in the benzene ring is 1.389 Å and the C—H lengths given by the full-matrix refinement lie between 0.75 and 1.01 Å. One might have expected mirror symmetry in the molecule through N(1), C(1), C(4) and N(3), but the two nitro groups [N(2), N(4)] are rotated about their respective C—N bonds to dif-

ferent extents (Fig. 2). However, the shortest contacts between the *ortho* nitro groups and the ethyleneimine are the same: O(2)—N(1) = 2.807, O(5)—N(1) = 2.803 Å. Each O atom has one intermolecular contact to a H atom of less than 2.71 Å (Table 4).

There are no significant differences in bond lengths or angles between this compound and the corresponding values in 2,4-dinitro-5-ethyleneiminobenzamide (Iball, Scrimgeour & Williams, 1975), so the difference in biological activity is probably dependent on the presence of the CONH₂ group in the latter compound.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32118 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

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The Crystal Structure of *syn*-5,7-Diformyltricyclo[9.4.1.1^{3,9}]heptadeca-2,4,7,9,11,13,15-heptaene

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The title compound, C₁₉H₁₆O₂ (DIAL), an open 18 π -electron system, is an intermediate in the synthesis of *syn,syn*-trismethano[18]annulene and of its homologues. DIAL crystallizes in the monoclinic space group $P2_1/n$, with $a = 13.305$ (3), $b = 9.254$ (2), $c = 11.371$ (2) Å, $\beta = 95.89^\circ$, $Z = 4$, $D_o = 1.318$, $D_x = 1.318$ g cm⁻³. Intensities were collected on a four-circle diffractometer. The structure was solved by direct methods and refined by full-matrix least squares. The final R was 0.055 and the weighted R 0.041. The distance between H(16') and H(17'') is 1.83 Å. Steric hindrance between the methano bridges is reflected in a large deviation from planarity of the perimetral ring.

Introduction

The synthesis of polymethano-bridged annulenes is difficult because of the steric hindrance between the H atoms at the bridges. Knowledge of the geometry of these molecules is useful in understanding H...H non-

bonded interaction at short distances. This work is part of a project aimed at studying the relation between geometry and steric hindrance in annulenes. Geometrical analogies between DIAL and other similar compounds are evident and will be discussed. In particular we will compare the geometry of DIAL with SYNDIM

{*syn*-1,6:8,13-bismethano[14]annulene (Destro, Pilati & Simonetta, 1977)}, BUT {1,6:8,13-butane-1,4-diylidene[14]annulene (Gramaccioli, Mugnoli, Pilati, Raimondi & Simonetta, 1972)} and SYNO {tricyclo-[9.4.1.1^{3,9}]heptadeca-2,4,7,9,11,13,15-heptaen-6-one, (Von Wagemann, Mullen, Vogel, Pilati & Simonetta, 1977)}.

Experimental

The well formed red crystals of DIAL have a melting point of 264–266 °C.* A crystal, 0.45 × 0.25 × 0.20 mm, mounted on a Syntex P1 diffractometer was used for the analysis. Systematic extinctions (*Ok0* for *k* odd, *h0l* for *h* + *l* odd) confirmed the space group *P2₁/n*. Cell parameters were obtained from a least-squares fit of 50 reflexions centred on the diffractometer with Mo *Kα* radiation ($\lambda = 0.71069$ Å). The density was measured by flotation in a dilute Thoullet (K₂HgI₄) solution. The intensities were collected with graphite-monochromated Mo *Kα* radiation by the θ – 2θ technique, variable scan speed between 2 and 12° min⁻¹, and dead time coincidence correction 2.1 × 10⁻⁶ s. The background was counted for half the total scanning time 1° on each side of the *Kα*₁ and *Kα*₂ positions. After every group of 50 reflexions, two standard reflexions were monitored. They showed no significant change in their intensity. In the range explored ($2\theta_{\max} = 55^\circ$) 3209 independent reflexions were measured, of

* We thank Professor E. Vogel for kindly providing us with a crystalline sample of the product.

which 2815 had intensities above background. 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. Lorentz and polarization factors were applied; absorption effects were neglected ($\mu = 0.9$ cm⁻¹ for Mo *Kα* radiation).

Structure determination and refinement

The structure was solved by direct methods (Long, 1965). 199 reflexions in the range $0^\circ < 2\theta < 40^\circ$ and $E > 1.4$ were used with three reflexions chosen as origin and another four as variable phases. The first set (consistency index 0.78) was ignored because too many positive phases were present (171 *versus* 28 negative). The second (consistency index 0.76) gave an *E* map that showed all the non-hydrogen atoms. Initial coordinates of the H atoms were derived from geometrical considerations. Refinement on all 2815 observed reflexions was by full-matrix least squares with a modified version of *ORFLS* (Busing, Martin & Levy, 1962).

In the last cycle 255 parameters were included in a single matrix: coordinates of all the atoms, anisotropic temperature coefficients for 21 heavy atoms, isotropic *B*'s for 16 H atoms, a scale factor and a secondary extinction parameter, *g* (Larson, 1967; Zachariasen, 1963). The quantity minimized was $\sum w(\Delta F)^2$ with weights $w = 1/\sigma^2(F)$. Scattering factors for C and O were from Cromer & Waber (1965); for H from Stewart, Davidson & Simpson (1965). Since in the last cycle all shifts were less than 0.3 σ , convergence was assumed.

Table 1. Final atomic parameters ($\times 10^5$) and standard deviations (in parentheses) for heavy atoms

The anisotropic temperature coefficients are of the form: $T_i = \exp[-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + 2b_{12}hk + 2b_{13}hl + 2b_{23}kl)]$.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>b</i> ₁₁	<i>b</i> ₂₂	<i>b</i> ₃₃	<i>b</i> ₁₂	<i>b</i> ₁₃	<i>b</i> ₂₃
C(1)	15855 (11)	56564 (18)	-30406 (14)	449 (9)	966 (21)	790 (15)	174 (11)	-29 (9)	167 (14)
C(2)	11556 (11)	51089 (19)	-20187 (14)	354 (8)	1019 (21)	844 (15)	53 (11)	-17 (9)	17 (15)
C(3)	15357 (10)	51791 (16)	-8601 (13)	347 (8)	805 (19)	748 (13)	137 (10)	66 (8)	-28 (13)
C(4)	11232 (11)	41761 (17)	-571 (14)	324 (8)	888 (20)	812 (14)	40 (10)	75 (8)	-125 (14)
C(5)	14845 (11)	37321 (17)	10374 (14)	406 (9)	881 (20)	765 (14)	81 (10)	144 (9)	-53 (13)
C(6)	24434 (13)	41612 (21)	17867 (15)	584 (10)	1056 (23)	625 (14)	22 (13)	57 (9)	-44 (15)
C(7)	34154 (11)	37548 (16)	12851 (13)	399 (8)	826 (19)	696 (13)	-62 (10)	-66 (8)	-69 (13)
C(8)	37780 (10)	41896 (17)	2789 (14)	315 (8)	877 (19)	799 (14)	-51 (10)	-41 (8)	-112 (14)
C(9)	33663 (10)	51806 (16)	-6301 (13)	324 (7)	751 (18)	752 (14)	-125 (10)	-16 (8)	-61 (13)
C(10)	37537 (11)	51156 (17)	-16996 (14)	348 (8)	828 (19)	846 (15)	-62 (11)	23 (8)	8 (14)
C(11)	33339 (11)	56797 (17)	-28190 (14)	460 (9)	787 (19)	806 (15)	-116 (11)	97 (9)	65 (13)
C(12)	36105 (14)	50925 (20)	-38534 (16)	611 (11)	1076 (23)	916 (17)	69 (14)	213 (11)	181 (16)
C(13)	29908 (16)	50308 (20)	-49323 (16)	906 (15)	1102 (24)	694 (16)	39 (16)	171 (12)	109 (16)
C(14)	19534 (16)	50073 (21)	-50569 (17)	914 (15)	1209 (25)	646 (15)	-53 (17)	-24 (12)	89 (17)
C(15)	13290 (14)	50448 (22)	-41333 (15)	592 (11)	1368 (26)	771 (16)	-89 (15)	-113 (10)	176 (17)
C(16)	24514 (13)	66911 (18)	-29674 (17)	672 (11)	693 (18)	769 (15)	46 (12)	69 (10)	111 (15)
C(17)	24483 (12)	60530 (17)	-4005 (15)	529 (9)	631 (18)	707 (14)	-15 (10)	36 (9)	-74 (13)
C(18)	8435 (14)	26719 (20)	15589 (19)	522 (11)	1159 (25)	1149 (20)	92 (14)	205 (12)	227 (18)
C(19)	40756 (13)	27480 (20)	19972 (17)	489 (10)	1143 (24)	959 (17)	-87 (13)	-88 (11)	148 (17)
O(1)	9902 (10)	21389 (17)	25295 (13)	825 (11)	1984 (26)	1367 (16)	27 (13)	242 (10)	766 (17)
O(2)	39344 (10)	22544 (16)	29524 (12)	734 (9)	1894 (24)	1109 (13)	36 (12)	-55 (9)	619 (15)

No correction for thermal libration was made because the molecule cannot be considered rigid in the part near C(6) and at the formyl groups.

DIAL includes an open 18 π -electron system and the sequence of single and double bonds is evident. As expected, the difference between single and double bond lengths decreases on going from the outer to the central part of the system (Heilbronner & Straub, 1966), but not very regularly because of the large torsion angles imposed by the two methano bridges (Fig. 3).

The C—O bond in both formyl groups is *trans* to the nearest double bond. The *trans* form, normally more stable than the *cis*, is further stabilized in this case by a small attractive interaction with H(6') [O(1)—H(6') = 2.42, O(2)—H(6') = 2.36 Å]. This is in line with the absence of short intermolecular distances among the O and H atoms. [The shortest distance is O_{v,r,z}...H(6'')^{1/2-x,-1/2+y,1/2-z} = 2.63 Å, greater than the sum of the van der Waals radii.]

The *syn* position of C(6) with respect to C(17) is not surprising, in spite of the short distance (2.00 Å) be-

tween H(17') and H(6''). It is easily seen on a model that the *cis* position would cause complete interruption of conjugation in the 18 π -electron system at the level of C(3)—C(4) and C(9)—C(8) where torsion angles would be near to 90°. The same condition is found for SYNO in which the formyl groups are absent and the H atoms at C(6) are substituted by an O atom.

The most interesting feature of the molecule is the conformation of the two methano bridges. The methylene groups both lie in the symmetry plane, as was found in SYNO and SYNDIM. Twisting of the CH₂ groups is in fact quite unfavourable energetically (Gavezzotti & Simonetta, 1976). Room for the two internal H atoms is obtained by distortion of the dihedral angles at the base of the methano bridges with consequent deviation from planarity of the perimetral ring

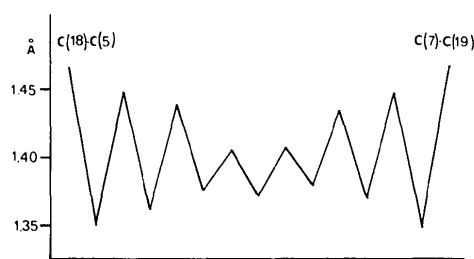


Fig. 3. C—C bond lengths (Å) in the π -electron system from C(18)—C(5) to C(7)—C(19).

Table 4. Bond angles (°)

C(15)—C(14)—C(13)	126.0	C(12)—C(13)—C(14)	125.7
C(1)—C(15)—C(14)	125.1	C(11)—C(12)—C(13)	125.1
C(16)—C(1)—C(15)	115.6	C(16)—C(11)—C(12)	115.1*
C(2)—C(1)—C(16)	123.3	C(10)—C(11)—C(16)	123.8*
C(2)—C(1)—C(15)	120.1	C(10)—C(11)—C(12)	120.0
C(3)—C(2)—C(1)	128.7	C(9)—C(10)—C(11)	128.6
C(17)—C(3)—C(2)	124.5	C(17)—C(9)—C(10)	124.2*
C(4)—C(3)—C(2)	116.8	C(8)—C(9)—C(10)	117.2*
C(4)—C(3)—C(17)	118.0	C(8)—C(9)—C(17)	118.0
C(5)—C(4)—C(3)	130.8	C(7)—C(8)—C(9)	130.8
C(6)—C(5)—C(4)	129.7	C(6)—C(7)—C(8)	129.8
C(18)—C(5)—C(4)	114.2	C(19)—C(7)—C(8)	114.3
C(18)—C(5)—C(6)	116.1	C(19)—C(7)—C(6)	115.9
C(5)—C(6)—C(7)	115.2		
C(1)—C(16)—C(11)	101.4		
C(3)—C(17)—C(9)	106.9		
C(5)—C(18)—O(1)	126.7	C(7)—C(19)—O(2)	126.6
C(13)—C(14)—H(14)	115.1	C(14)—C(13)—H(13)	114.7
C(15)—C(14)—H(14)	117.7	C(12)—C(13)—H(13)	118.4
C(14)—C(15)—H(15)	118.2	C(13)—C(12)—H(12)	116.9
C(1)—C(15)—H(15)	116.6	C(11)—C(12)—H(12)	117.8
C(1)—C(16)—H(16'')	109.2	C(11)—C(16)—H(16'')	108.1
C(1)—C(16)—H(16')	115.1	C(11)—C(16)—H(16')	113.1*
C(1)—C(2)—H(2)	114.0	C(11)—C(10)—H(10)	114.3
C(3)—C(2)—H(2)	116.5	C(9)—C(10)—H(10)	116.3
C(3)—C(17)—H(17'')	111.7	C(9)—C(17)—H(17'')	111.2
C(3)—C(17)—H(17')	110.6	C(9)—C(17)—H(17')	111.2
C(3)—C(4)—H(4)	114.5	C(9)—C(8)—H(8)	112.8*
C(5)—C(4)—H(4)	114.7	C(7)—C(8)—H(8)	116.3*
C(5)—C(18)—H(18)	113.0	C(7)—C(19)—H(19)	113.8
C(5)—C(6)—H(6'')	110.0	C(7)—C(6)—H(6'')	111.5
C(5)—C(6)—H(6')	108.5	C(7)—C(6)—H(6')	105.5*
O(1)—C(18)—H(18)	120.2	O(2)—C(19)—H(19)	119.6
H(16'')	109.7		
H(17'')	105.3		
H(6'')	105.5		

* The difference between the values for this pair is more than 2 σ .

Table 5. Some distances (Å) and dihedral angles (°) in DIAL, SYNO, SYNDIM and BUT

The capital letters refer to the dihedral angles in Fig. 2. The values are the average values assuming *m* symmetry for DIAL and SYNO, *mm*2 for SYNDIM. BUT has crystallographic symmetry *mm*2.

	DIAL	SYNO	BUT	SYNDIM
C(13)—C(14)	1.373	1.381	1.418	1.403
C(14)—C(15)	1.406	1.402	1.362	1.370
C(15)—C(1)	1.378	1.386	1.422	1.412
C(1)—C(16)	1.496	1.495	1.505	1.498
C(1)—C(2)	1.437	1.430		
C(2)—C(3)	1.367	1.367	1.397	1.393
C(3)—C(17)	1.508	1.508	—	—
C(3)—C(4)	1.448	1.441	—	—
C(4)—C(5)	1.350	1.342	—	—
C(5)—C(6)	1.513	1.475	—	—
C(16)...C(17)	2.978	2.924	2.957	2.921
H(16'')...H(17'')	1.83	1.84	—	1.78
A	157.7	157.3	164.3	163.4
B	112.1	111.4	110.2	109.2
C	132.5	134.6	133.4	134.9
D	115.4	113.9	116.4	115.9
E	154.3	154.3	153.4	154.7
F	118.7	119.3	—	—
G	133.7	137.2	—	—
H	107.6	103.5	—	—
I	155.3	155.1	—	—
L	132.7	148.1	—	—

(Fig. 2). For all three molecules these angles are very similar and the same situation is found in BUT. These similarities are remarkable in view of the different nature of the molecules: SYNDIM and BUT are aromatic annulenes, while DIAL and SYNO are polyenes showing alternation of short and long bonds. Some significant parameters of these four molecules are collected in Table 5 to make the similarity of these systems more evident.

Despite the distortion from planarity of the ring, the distance $H(16') \cdots H(17'')$ in DIAL, SYNO and SYNDIM is very short.

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The Crystal and Molecular Structure of Phenylurea

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The crystal structure of phenylurea has been determined from visually estimated $Cu K\alpha$ X-ray data. The crystals are monoclinic, space group $P2_1$, with $a = 14.01$ (2), $b = 5.36$ (2), $c = 4.66$ (1) Å, $\beta = 94.7$ (3)° and $Z = 2$. The structure was solved by the Patterson method and refined by block-diagonal least-squares calculations to $R = 0.081$ for 573 non-zero reflexions. The molecules related by a c -translation are linked together by two kinds of $N-H \cdots O$ hydrogen bonds [$N \cdots O$ 2.924 (9) Å, $N-H \cdots O$ 147 (11)°, $H \cdots O$ 2.14 (13); $N \cdots O$ 2.935 (9) Å, $N-H \cdots O$ 154 (7)°, $H \cdots O$ 2.10 (8) Å] to form a ribbon extending along c . The ribbons are held together by another $N-H \cdots O$ hydrogen bond [$N \cdots O$ 3.013 (9) Å, $N-H \cdots O$ 161 (5)°, $H \cdots O$ 2.14 (6) Å] between the molecules related by a twofold screw axis to form a sheet parallel to (100). The sheets are stacked along a by van der Waals interactions. The dihedral angle between the benzene ring and the urea moiety is 46.4°. The imino $N-C$ (carbonyl) distance, 1.375 (10) Å, is longer than the amino $N-C$ (carbonyl) 1.326 (10) Å. The $C=O$ distance, 1.245 (9) Å, is longer than those in acetanilides.

Introduction

As part of a programme of investigation of the molecular structure and packing mode of the aromatic compounds containing the amide grouping, $-NH-CO-X$ ($X = CH_3, NH_2, etc.$) (Haisa, Kashino, Kawai & Maeda, 1976), the structure of phenylurea has been determined by X-ray analysis. The molecule is

of interest since it is an activator as well as a competitive inhibitor of trypsin-catalysed hydrolysis (Sanborn & Heim, 1967). Its activity has been related by Pullman & Pullman (1963) and Amatuni & Krylov (1974) to the electronic structure of the amide group.

The present paper also extends the scope of study on the relation between the s -character of hybrid orbitals and the bond lengths, explored in a previous paper (Kawai, Kashino & Haisa, 1976).