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Diethyl 2,4-Bis(*o*-chlorophenylhydrazono)-3-oxopentanedioate

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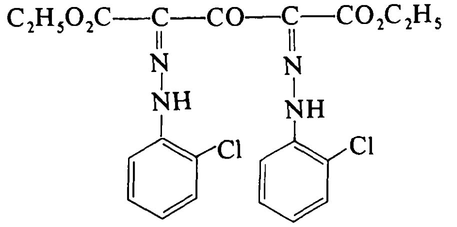
Abstract. $C_{21}H_{20}Cl_2N_4O_5$, $M_r = 479{\cdot}1$, triclinic, $a = 6{\cdot}944\ (8)$, $b = 16{\cdot}062\ (11)$, $c = 13{\cdot}543\ (11)$ Å, $\alpha = 124{\cdot}4\ (1)$, $\beta = 112{\cdot}3\ (1)$, $\gamma = 75{\cdot}6\ (1)^\circ$, $U = 1152{\cdot}3$ Å^3, $Z = 2$, $D_m = 1{\cdot}37$, $D_c = 1{\cdot}38$ Mg m^{-3}, $F(000) = 958$, Mo $K\alpha$ radiation, $\lambda = 0{\cdot}7107$ Å, $\mu = 0{\cdot}325$ mm^{-1}, space group $P\bar{1}$ from the successful structure determination. 1475 independent reflections were refined to R 0·082. The two halves of the dimer (numbered A and B) are not coplanar and intersect at 68·8°. This allows hydrogen bonding from the N—H group to an ester oxygen in A and to a carbonyl oxygen in B.

Introduction. Previously we have reported the spectral and structural characterization of a series of phenylhydrazones involving various substituent types (Kaberia, Vickery, Willey & Drew, 1980; Vickery, Willey & Drew 1981*a*). Our main interest concerns an evaluation of H bonding effects and the correlation of bond-length variations within the ring—NH—N=C< skeleton with changes in ring and imino carbon substitution. As a further study of bond relationships in phenylhydrazones, we have determined the structure of the title compound (I).



(I)

Slow addition of a threefold excess of a solution of the diazonium salt formed from *o*-chloroaniline and sodium nitrite in 50:50 aqueous hydrochloric acid to a methanol solution of diethyl 3-oxopentanedioate and sodium acetate was carried out at 263 K. The resulting solution was maintained at 263 K with mechanical stirring for several hours. Work-up gave the product as an orange solid which was recrystallized as fine needles from methanol/chloroform/*n*-hexane. Calc. for $C_{21}H_{20}Cl_2N_4O_5$: C, 52·6; H, 4·2; N, 11·7%. Found C, 52·5; H, 4·1; N, 11·7%.

A needle crystal of size 0·5 × 0·2 × 0·2 mm was set up to rotate around **a** on a Stoe STADI-2 diffractometer equipped with a graphite monochromator. Data

Table 1. *Atomic parameters* (×10^4) *with e.s.d.'s in parentheses*

	x	y	z	$\bar{U}$ (×10^3) (Å^2)
Cl(1*A*)	2902 (7)	1313 (3)	4393 (3)	265 (8)
C(1*A*)	−1692 (25)	3365 (12)	5419 (12)	183 (29)
C(2*A*)	−310 (25)	2565 (11)	5247 (12)	194 (28)
C(3*A*)	1180 (21)	2353 (8)	4637 (10)	163 (23)
C(4*A*)	1106 (19)	2913 (9)	4131 (10)	138 (21)
C(5*A*)	−317 (18)	3717 (8)	4288 (10)	164 (21)
C(6*A*)	−1755 (20)	3917 (9)	4913 (11)	174 (24)
N(7*A*)	2609 (14)	2650 (7)	3497 (9)	173 (17)
N(8*A*)	2578 (13)	3188 (6)	3019 (8)	154 (15)
C(9*A*)	3792 (15)	2933 (7)	2355 (9)	143 (18)
C(10*A*)	5244 (14)	2042 (7)	2050 (9)	148 (17)
O(10*A*)	5478 (11)	1434 (5)	2355 (7)	191 (13)
O(11*A*)	6397 (10)	2005 (5)	1429 (6)	193 (12)
C(12*A*)	7842 (23)	1117 (10)	963 (13)	252 (28)
C(13*A*)	7385 (21)	668 (9)	−322 (13)	207 (27)
Cl(1*B*)	3945 (5)	6840 (2)	2531 (3)	166 (6)
C(1*B*)	2091 (17)	6377 (10)	−907 (13)	197 (24)
C(2*B*)	2790 (15)	6802 (8)	351 (13)	195 (23)
C(3*B*)	3051 (14)	6272 (8)	919 (10)	143 (19)
C(4*B*)	2566 (14)	5242 (8)	155 (11)	137 (18)
C(5*B*)	1870 (14)	4798 (8)	−1137 (11)	136 (19)
C(6*B*)	1626 (16)	5371 (11)	−1640 (12)	181 (23)
N(7*B*)	2912 (12)	4704 (6)	741 (8)	114 (15)
N(8*B*)	2498 (10)	3752 (6)	39 (7)	130 (14)
C(9*B*)	2795 (13)	3225 (6)	553 (9)	110 (16)
C(10*B*)	2161 (16)	2152 (8)	−335 (10)	148 (20)
O(10*B*)	1845 (10)	1617 (5)	−66 (7)	157 (13)
O(11*B*)	1965 (15)	1863 (6)	−1505 (8)	173 (17)
C(12*B*)	1306 (34)	802 (10)	−2559 (14)	205 (37)
C(13*B*)	2287 (38)	415 (13)	−3469 (16)	297 (44)
C(14)	3577 (14)	3601 (7)	1878 (9)	134 (17)
O(14)	3983 (10)	4487 (4)	2630 (5)	135 (11)

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† Deceased.

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Table 2. *Bond distances* (Å) *and angles* (°)

	Part *A*	Part *B*
Cl(1)–C(3)	1·736 (12)	1·728 (11)
C(1)–C(2)	1·358 (21)	1·351 (21)
C(1)–C(6)	1·38 (3)	1·380 (20)
C(2)–C(3)	1·422 (26)	1·381 (25)
C(3)–C(4)	1·389 (24)	1·414 (15)
C(4)–C(5)	1·380 (17)	1·387 (18)
C(4)–N(7)	1·434 (20)	1·401 (22)
C(5)–C(6)	1·412 (23)	1·372 (26)
N(7)–N(8)	1·332 (19)	1·302 (12)
N(8)–C(9)	1·298 (17)	1·310 (19)
C(9)–C(14)	1·486 (20)	1·441 (15)
C(9)–C(10)	1·473 (13)	1·498 (13)
C(10)–O(10)	1·214 (18)	1·195 (20)
C(10)–O(11)	1·336 (17)	1·334 (18)
O(11)–C(12)	1·481 (14)	1·515 (14)
C(12)–C(13)	1·388 (22)	1·39 (3)
C(14)–O(14)	1·219 (10)	
C(2)–C(1)–C(6)	119·8 (17)	117·9 (18)
C(1)–C(2)–C(3)	119·8 (18)	122·7 (12)
Cl(1)–C(3)–C(2)	119·3 (12)	121·5 (8)
Cl(1)–C(3)–C(4)	120·5 (11)	119·8 (12)
C(2)–C(3)–C(4)	119·8 (12)	118·7 (10)
C(3)–C(4)–C(5)	120·3 (14)	118·9 (14)
C(3)–C(4)–N(7)	117·5 (11)	118·1 (10)
C(5)–C(4)–N(7)	122·1 (15)	122·9 (9)
C(4)–C(5)–C(6)	118·4 (15)	119·4 (10)
C(1)–C(6)–C(5)	121·6 (12)	122·4 (13)
C(4)–N(7)–N(8)	118·3 (9)	118·3 (9)
N(7)–N(8)–C(9)	120·9 (8)	120·0 (8)
N(8)–C(9)–C(14)	114·8 (8)	125·8 (8)
N(8)–C(9)–C(10)	123·4 (12)	115·6 (9)
C(14)–C(9)–C(10)	121·7 (11)	118·6 (12)
C(9)–C(10)–O(10)	126·6 (12)	126·2 (11)
C(9)–C(10)–O(11)	110·4 (11)	110·2 (13)
O(10)–C(10)–O(11)	122·8 (8)	123·5 (8)
C(10)–O(11)–C(12)	118·1 (11)	118·9 (13)
O(11)–C(12)–C(13)	109·0 (12)	111·1 (19)
C(9)–C(14)–C(9)	120·8 (7)	
C(9)–C(14)–O(14)	119·0 (9)	120·1 (12)

were taken *via* an ω scan of width $(1\cdot5 + \sin\theta/\tan\mu)^\circ$. The scan speed was 60 s deg^{-1} and the background was measured at the ends of the ω scan for 30 s. 3146 reflections were measured with $2\theta < 50^\circ$ of which 1475 with $I > 2\sigma(I)$ were used in subsequent calculations.

The positions of the two Cl atoms were obtained by direct methods using *SHELX* 76 (Sheldrick, 1976). The remaining C, O and N atoms were located from Fourier maps. The H atoms bonded to C were fixed in trigonal or tetrahedral positions. Atoms bonded to the same C atom or to C atoms in the same benzene ring were given common refinable thermal parameters. The methyl H atoms on C(13*A*) were located by rigid-body refinement, those on C(13*B*) were not. The H atoms on N(7) were refined independently but the two N–H bond lengths were constrained to be equivalent. The structure was refined (Cl, O, C, N anisotropic, H isotropic) to *R* 0·082 using two large blocks. The weighting scheme was $w = 1/[\sigma^2(F) + 0\cdot002F^2]$ where $\sigma(F)$ was obtained from counting statistics. In the final cycle of refinement, no shift was $>0\cdot1\sigma$ and the difference Fourier map showed no significant peaks. Calculations were carried out using *SHELX* 76 (Sheldrick, 1976) at the University of Manchester Computer Centre. Scattering factors and dispersion corrections were taken from *International Tables for X-ray Crystallography* (1974). Atomic coordinates are given in Table 1, bond lengths and angles in Table 2.*

Discussion. Crystals of the title compound were obtained from the reaction of diethyl 3-oxopentanedioate with an excess of *o*-chlorobenzenediazonium chloride. Direct equimolar addition however results in single coupling to give diethyl 2-(*o*-chlorophenylhydrazono)-3-oxopentanedioate (Vickery, Willey & Drew, 1981*b*). The presence of two NH proton signals $\delta_{\rm NH}$ 14·09, 12·94 and the absence of a methylenic singlet (–CH$_2$–) provided initial ^{1}H NMR (CDCl$_3$, 220 MHz) confirmation of a bis(phenylhydrazone) formulation. Other chemical shifts include: $\delta_{\rm CH_3}$ 1·37, 1·30 (superposed triplets), $\delta_{\rm CH_2}$ 4·46, 4·32 (superposed quartets) and $\delta_{\rm CH(ring)}$ 6·92–7·95 (complex multiplets). The extremely low-field $\delta_{\rm NH}$ values and the low-energy IR shift in ν(NH) 3228 cm^{-1} (broad) implicate both NH sites in hydrogen bonding.

The structure is shown in Fig. 1, together with the atomic numbering scheme. The two parts of the dimer have been numbered *A* and *B*. In both parts, H(7) is rotated around the C(4)–N(7) bond so that it is adjacent to Cl(1) leaving N(8) adjacent to H(5). This is presumably so that N(8) and Cl(1) can avoid close contacts. The most striking feature of the dimer (Fig. 1) is that the two halves are not coplanar and indeed the two phenyl rings intersect at 68·8°. This is because

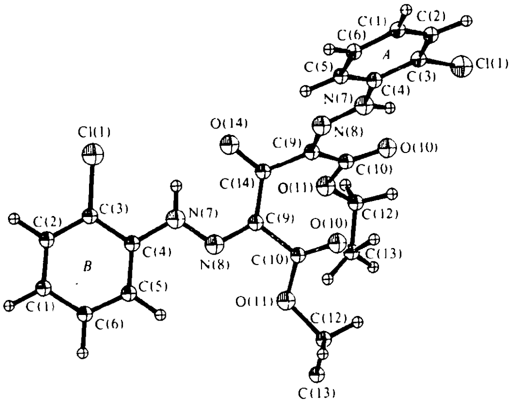

Fig. 1. Projection of the molecule with atomic numbering.

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* Lists of structure factors, anisotropic thermal parameters and H atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35821 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Least-squares planes through atoms* C(*n*), *n* = 1 *to* 6

Deviations of atoms from the planes are given in Å. Standard deviations are 0·01 Å in displacements and 0·1° in angles.

	A	*B*		*A*	*B*
Cl(1)	0·07	0·00	N(8)	0·02	0·06
C(1)	0·02	0·00	C(9)	0·12	0·10
C(2)	−0·02	0·00	C(10)	0·25	0·04
C(3)	0·02	−0·01	O(10)	0·31	−0·24
C(4)	−0·01	−0·01	O(11)	0·24	0·24
C(5)	0·01	−0·00	C(12)	0·47	0·32
C(6)	0·01	−0·00	C(14)	0·12	0·14
N(7)	0·01	0·04			

Angles between planes

A and *B*	68·8°
A and C(9*A*), C(10*A*), O(10*A*), O(11*A*)	4·5
A and C(10*A*), C(10*B*), C(14), O(14)	75·5
B and C(9*B*), C(10*B*), O(10*B*), O(11*B*)	15·0
B and C(10*A*), C(10*B*), C(14), O(14)	25·7

H(7*A*) is hydrogen bonded to O(10*A*) [N(7*A*)···O(10*A*) 2·68Å] while H(7*B*) is hydrogen bonded to O(14) [N(7*B*)···O(14) 2·58 Å]. The difference in N···O distances indicates that the hydrogen bond involving the carbonyl group C(14)—O(14) is stronger than that involving the ester at O(10*A*).

The difference in hydrogen-bonding pattern is not strictly necessary on steric grounds as the *B* moiety could rotate around the N(8*B*)—C(9*B*) bond and the —CO_2Et group around the C(9*B*)—C(10*B*) bond to leave O(10*B*) hydrogen bonded to N(7*B*). However, it seems unlikely that both H(7*A*) and H(7*B*) could be hydrogen bonded to O(14) as this would lead to a planar dimer and considerable crowding between the two —CO_2Et groups and between the lone pairs on N(8*A*) and N(8*B*).

In a previous paper (Vickery, Willey & Drew, 1981*a*), we have described the relationships between hydrogen bonding and bond order in phenyl hydrazones. In molecules where there is hydrogen bonding between N(7) and a carbonyl group conjugating to N(8)—C(9), the N(7)—N(8) bond is particularly short and the N(8)—C(9) bond is comparatively long and this is found in the present molecule with mean lengths of 1·317 and 1·304 Å respectively. [The range of bond lengths in our sample of 17 structures is 1·308 to 1·424 (mean 1·36 Å) and 1·25 to 1·33 (mean 1·29 Å)].

The angles in the phenylhydrazones do not follow such regular trends as the bond lengths, although it was noted that in compounds with *o*-nitro groups, the C(3)—C(4)—N(7) angle was increased to 123·1° (mean) from 117·4° (mean) in compounds without such a group. It is interesting that in the present case, these angles are only 117·5 (11), 118·1 (10)° suggesting that the steric repulsion of the *o*-chloro group is considerably less than that of the *o*-nitro group. Indeed, unlike the *o*-nitro group, an *o*-chloro cannot form hydrogen bonds with H(7) because the Cl···N distance is perforce too large.

The most remarkable angles in Table 2 are those for N(8)—C(9)—C(10) and N(8)—C(9)—C(14). In part *A*, the former is the larger by 8·6° to allow for the N(7)···O(10*A*) hydrogen bond. In part *B*, the latter is the larger by 10·2° to make room for the N(7*B*)···O(14) hydrogen bond.

There are no intramolecular distances less than the sum of the van der Waals radii. Table 3 lists deviations from the least-squares planes.

We thank the SRC for support.

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