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The Crystal and Molecular Structures of Two Photodimers from *N*-Chloroacetyltyramine

By Daniel S. Jones* and Isabella L. Karle

Laboratory for the Structure of Matter, Naval Research Laboratory, Washington, D.C. 20375, *U.S.A.*

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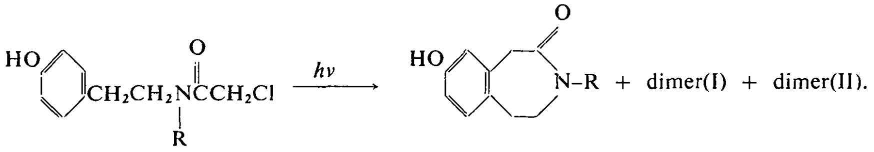
Ultraviolet irradiation of *N*-chloroacetyltyramine eliminates HCl and produces two unusual photodimers (I) and (II) whose molecular formulas have been identified by X-ray structure analyses. The *N*,*N'*-dimethyl derivative of (I), decahydro-7,14a,7a,14-ethanediylidenenaphtho[1,8-*de*:4,5-*d'e'*]bisazocine-4,6,11,13(1*H*,7*H*,8*H*,14*H*)-tetrone ($C_{22}H_{26}N_2O_4.2H_2O$), crystallizes in space group $P2_1/c$, with $a=12\cdot793$ (3), $b=12\cdot879$ (3), $c=13\cdot822$ (4) Å, and $\beta=120\cdot03$ (2)°, with four molecules per unit cell. The *N*,*N'*-diacetyl derivative of (II), 4,11-diacetyldodecahydro-7*H*-1,7,8a-ethanylylidene-8,14-methanocyclopropa[1,6]benzo[1,2-*d*:4,3-*d'*]bisazocine-3,12,15,17(4*H*,9*H*)-tetrone ($C_{24}H_{26}N_2O_6$), crystallizes in space group *Pbca*, with $a=24\cdot927$ (7), $b=12\cdot971$ (4), $c=12\cdot437$ (4) Å, and eight molecules in the unit cell. Data for both compounds were collected on an automatic four-circle diffractometer using the θ–2θ scan technique. The final agreement indices for the two compounds, at the conclusion of full-matrix anisotropic refinement, were 0·076 and 0·052, respectively.

Introduction

The photoreactions of derivatives of *N*-chloroacetyltyrosine and *N*-chloroacetyltyramine give cyclization products whose structures are strongly dependent upon the substituents present on the phenyl ring. The end products of any given reaction are difficult to predict, and crystallographic investigations play an important part in determining product structures. In previous studies, crystal structure analyses have shown that the photoreactions of similar compounds gave widely differing results (Karle, Karle & Estlin, 1967; Yonemitsu, Witkop & Karle, 1967; Karle, Gibson & Karle, 1969; Yonemitsu, Okuno, Kanaoka, Karle & Witkop, 1968; Karle & Karle, 1970; Yonemitsu, Nakai, Kanaoka, Karle & Witkop, 1970).

In the present study, the ultraviolet irradiation of a water–ethanol solution of *N*-chloroacetyltyramine gave a benzazepinone, plus two compounds whose composition, $C_{20}H_{22}N_2O_4$, indicated that they were dimers of the starting material (Iwakuma, Nakai, Yonemitsu, Jones, Karle & Witkop, 1972; Iwakuma, Nakai, Yonemitsu & Witkop, 1973). The reaction is shown below:



Additional ultraviolet irradiation of dimers of type (I) gave the corresponding dimers of type (II), but not conversely. A crystallographic investigation of dimers of type (I) and (II) was undertaken in order to establish their molecular formula, their structural configuration and to provide a basis for the elucidation of the mechanisms involved in the cyclization–dimerization reaction. The compounds studied were: (1) dimer (I), a dimer of type (I) with R=Me, and (2) dimer (II), the diacetate derivative of a dimer of type (II) with R=H, obtained upon refluxing the type (II) dimer with acetic anhydride.

Experimental

Dr Osamu Yonemitsu of Hokkaido University, Sapporo, Japan, and Dr Bernhard Witkop of the National Institutes of Health provided crystals of both dimers (I) and (II). Precession and Weissenberg photographs established their respective space groups. The crystals were then aligned on an automatic four-circle diffractometer and their unit-cell constants determined from a least-squares fit of the lattice and orientation parameters to the observed setting angles of 12 general reflections. These cell constants and other physical properties are given in Table 1. X-ray data were collected on the diffractometer using Cu $K\alpha$ radiation and the θ–2θ scan technique. For both compounds the scan width was $2\cdot1° + 2\theta(\alpha_2)° - 2\theta(\alpha_1)°$ with a scan rate of 2° per min and a background count of 10 s at each end of the scan. The three standard reflections chosen for dimer (II) remained constant in intensity throughout data collection within a standard deviation of 1%. The three standards for dimer (I) remained constant within this range during collection of the first 2500 intensities, then showed a discontinuous drop in intensity of about 2%, to a new level which held constant during the remainder of data collection.

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* National Academy of Sciences, National Research Council Resident Research Associate.

Table 1. *Physical data*

	Dimer (I)	Dimer (II)
Molecular formula	$C_{22}H_{26}N_2O_4.2H_2O$	$C_{24}H_{26}N_2O_6$
M.W.	382·46 + 36·03	438·48
Space group	$P2_1/c$	*Pbca*
a	12·793 ± 0·003 Å	24·927 ± 0·007 Å
b	12·879 ± 0·003	12·971 ± 0·004
c	13·822 ± 0·004	12·437 ± 0·004
β	120·03 ± 0·02°	90°
Volume	1971·6 ± 1·9 Å^3	4021·2 ± 3·6 Å^3
Density (calc.)	1·410 ± 0·001 g cm^{-3}	1·448 ± 0·001 g cm^{-3}
μ, linear absorption coefficient	8·6 cm^{-1}	8·8 cm^{-1}
Number of independent reflections observed	3132	3206
Radiation	Cu *Kα*	Cu *Kα*
Wavelength	1·54178 Å	1·54178 Å
Z, molecules per unit cell	4	8

Lorentz and polarization corrections were applied to the observed intensities, and the intensities were then approximately scaled to an absolute level by means of a *K* curve. Normalized structure factor magnitudes, $|E|$, were derived for use in the phase determination.

Phase determination and refinement

Dimer (I)

Phases for the reflections from both compounds were obtained from the normalized structure-factor magnitudes by means of the symbolic addition procedure for centrosymmetric crystals (Karle & Karle, 1966). An *E* map based on the phases of 561 reflections of $|E|$ value greater than 1·2 revealed the positions of the 28 non-hydrogen atoms of dimer (I), along with the positions of the oxygen atoms of the two water molecules in the asymmetric unit. Full-matrix least-squares refinement on the scale factor, atomic positions, and anisotropic thermal parameters yielded an agreement index of 0·116. A difference map revealed the positions of 19 of the 30 hydrogen atoms in the asymmetric unit. The hydrogen atoms not found were those of the water molecules and the two methyl groups. One additional hydrogen atom appeared in the difference map with an unacceptably long bond length. In all succeeding refinements, these 19 hydrogen positions were fixed and the thermal parameters of the hydrogen atoms were set equal to the parameters of the atoms to which they were bonded.

The function minimized was $\sum w_F(F_o-F_c)^2$ where $w_F=1/\sigma_F^2$. The quantity $\sigma_F^2=(A/4Lp)\,(\sigma_I^2/I)$ where *A* is the attenuator factor, Lp is the Lorentz–polarization

Table 2. *Fractional coordinates and thermal parameters for dimer* (I)

The thermal parameters are of the form $T=\exp\,[-\frac{1}{4}(B_{11}h^2a^{*2}+B_{22}k^2b^{*2}+B_{33}l^2c^{*2}+2B_{12}hka^*b^*+2B_{13}hla^*c^*+2B_{23}klb^*c^*)]$. The standard deviations are those calculated by the least-squares program.

	x	*y*	*z*	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C(1)	−0·2130 (3)	0·9069 (3)	0·0299 (2)	2·43 (12)	3·20 (14)	2·49 (12)	0·20 (10)	0·87 (10)	0·53 (10)
C(2)	−0·3349 (3)	0·8799 (3)	0·0186 (3)	2·33 (13)	2·88 (14)	3·99 (15)	0·18 (11)	1·06 (12)	−0·04 (12)
N(3)	−0·3576 (2)	0·7689 (2)	0·0147 (2)	2·12 (11)	3·14 (12)	2·37 (11)	−0·22 (9)	0·98 (9)	−0·63 (9)
C(4)	−0·3268 (3)	0·7094 (3)	0·1047 (2)	1·85 (12)	3·51 (15)	2·85 (13)	−0·27 (10)	1·25 (10)	−0·61 (11)
C(5)	−0·2706 (3)	0·7618 (3)	0·2180 (3)	1·85 (12)	4·90 (17)	2·73 (13)	−0·27 (11)	0·99 (11)	−1·11 (12)
C(5a)	−0·1319 (2)	0·7695 (2)	0·2741 (2)	1·88 (11)	2·79 (12)	2·05 (11)	−0·10 (9)	1·10 (9)	−0·05 (9)
C(6)	−0·0899 (3)	0·8539 (2)	0·3611 (2)	2·26 (12)	3·36 (14)	2·27 (12)	−0·07 (10)	1·16 (10)	−0·46 (10)
C(7)	−0·0088 (2)	0·9305 (2)	0·3528 (2)	2·33 (12)	2·57 (12)	2·43 (12)	−0·03 (9)	1·15 (10)	−0·69 (10)
C(7a)	0·1005 (2)	0·8889 (2)	0·3412 (2)	1·97 (11)	2·11 (11)	2·00 (10)	−0·03 (8)	1·00 (9)	−0·06 (8)
C(8)	0·2154 (3)	0·8986 (2)	0·4549 (2)	2·26 (12)	3·08 (14)	2·20 (11)	−0·39 (10)	0·91 (10)	−0·46 (10)
C(9)	0·3367 (3)	0·8667 (2)	0·4693 (3)	2·11 (12)	3·05 (14)	3·30 (14)	−0·40 (10)	1·09 (11)	−0·45 (11)
N(10)	0·3524 (2)	0·7544 (2)	0·4666 (2)	2·09 (10)	3·40 (12)	2·13 (10)	0·18 (8)	0·95 (8)	0·23 (9)
C(11)	0·3205 (2)	0·7009 (2)	0·3731 (2)	1·78 (12)	3·14 (14)	2·68 (13)	0·19 (10)	1·23 (10)	0·49 (10)
C(12)	0·2631 (3)	0·7600 (2)	0·2641 (2)	2·13 (12)	3·38 (14)	2·43 (12)	0·23 (10)	1·25 (10)	0·36 (10)
C(12a)	0·1238 (2)	0·7591 (2)	0·2085 (2)	1·97 (12)	2·55 (12)	1·98 (11)	−0·02 (9)	1·12 (9)	−0·18 (9)
C(13)	0·0775 (3)	0·8373 (2)	0·1148 (2)	2·06 (12)	3·18 (13)	2·04 (12)	−0·24 (10)	1·00 (10)	0·11 (10)
C(14)	0·0144 (3)	0·9251 (2)	0·1310 (2)	2·59 (12)	2·49 (12)	2·32 (12)	−0·02 (10)	1·28 (10)	0·54 (9)
C(14a)	−0·0981 (2)	0·8931 (2)	0·1426 (2)	2·05 (11)	2·13 (11)	2·14 (11)	0·06 (8)	0·99 (9)	0·04 (8)
C(14b)	−0·0721 (2)	0·7862 (2)	0·2013 (2)	1·83 (11)	2·04 (11)	1·78 (10)	−0·02 (9)	0·88 (9)	−0·02 (8)
C(14c)	0·0668 (2)	0·7826 (2)	0·2820 (2)	1·79 (11)	1·98 (11)	1·86 (11)	−0·08 (9)	0·95 (9)	−0·08 (8)
C(15)	−0·0587 (3)	0·9787 (2)	0·2359 (2)	2·70 (13)	1·97 (12)	2·83 (13)	0·13 (10)	1·19 (10)	−0·15 (10)
C(16)	0·0693 (3)	0·9734 (2)	0·2481 (2)	2·52 (13)	1·92 (11)	2·63 (12)	−0·16 (9)	1·13 (10)	−0·04 (10)
C(17)	−0·4046 (3)	0·7183 (3)	−0·0943 (3)	3·18 (15)	5·38 (19)	2·57 (13)	−0·56 (13)	1·38 (11)	−1·22 (13)
C(18)	0·3958 (3)	0·6971 (3)	0·5711 (3)	3·14 (15)	5·48 (19)	2·51 (13)	0·77 (13)	1·30 (11)	1·19 (13)
O(1)	−0·3424 (2)	0·6150 (2)	0·0969 (2)	3·72 (11)	2·98 (11)	4·22 (12)	−0·63 (9)	1·87 (10)	−0·39 (9)
O(2)	−0·1260 (3)	0·8603 (2)	0·4281 (2)	5·30 (14)	7·05 (16)	4·32 (13)	−2·30 (12)	3·91 (12)	−2·66 (11)
O(3)	0·3333 (2)	0·6059 (2)	0·3738 (2)	3·72 (11)	2·73 (11)	3·62 (11)	0·53 (8)	1·89 (9)	0·44 (8)
O(4)	0·0915 (2)	0·8268 (2)	0·0332 (2)	4·46 (12)	5·37 (13)	2·28 (9)	0·92 (10)	2·20 (9)	0·48 (8)
O(*W*1)	0·3832 (3)	0·5069 (3)	0·2272 (2)	7·41 (17)	6·44 (17)	5·45 (14)	0·54 (13)	4·11 (14)	−0·45 (12)
O(*W*2)	0·6253 (3)	0·5013 (3)	0·2554 (2)	7·54 (18)	6·02 (16)	4·94 (14)	0·45 (13)	2·95 (13)	0·85 (12)

correction and $\sigma_I^2=\sigma_P^2+\sigma_{B1}^2+\sigma_{B2}^2$, where P is the peak count, B_1 and B_2 are the scaled background counts and σ_N^2 for any count N is given by $\sigma_N^2=N+(0{\cdot}015)^2N^2$. Atomic scattering factors were those listed in *International Tables for X-ray Crystallography* (1959). To minimize the effects of secondary extinction, 15 reflections were removed for which $\sin\theta<0{\cdot}2$, $|F_c|$ was relatively large and $|F_c|\gg|F_o|$ (Stout & Jensen, 1968). The R value at the conclusion of this refinement was 0·078. Calculation of the R value on the full set of data, including the reflections with secondary extinction, gave a value of 0·097.

An analysis for multiple diffraction, using the computing program *MULREF*5 (Coppens, 1968),* was carried out for several moderately strong reflections for which $|F_o|$ was considerably greater than $|F_c|$, and five reflections identified as affected by multiple diffraction were removed from the least-squares procedure. Finally, additional refinement was carried out in which an isotropic secondary extinction correction was applied (program *ORXFLS*3, Busing, Martin & Levy, 1971). The resulting R value was 0·076, which was less than the value obtained by simply deleting reflections affected by secondary extinction. Inclusion of the five multiple-diffraction reflections in an R value calculation gave a value of 0·077.† Final parameters for the heavy atoms of dimer (I) are given in Table 2, while

Table 3. *Fractional coordinates for hydrogen atoms in dimer* (I)

	x	y	z
H(1-1)	−0·217	0·982	0·003
H(1-2)	−0·199	0·862	−0·021
H(2-1)	−0·339	0·920	0·076
H(2-2)	−0·400	0·916	−0·053
H(5)	−0·316	0·835	0·205
H(5a)	−0·095	0·699	0·315
H(7)	0·021	0·990	0·408
H(8-1)	0·202	0·857	0·499
H(8-2)	0·220	0·978	0·465
H(9-1)	0·354	0·902	0·418
H(9-2)	0·405	0·891	0·541
H(12-1)	0·305	0·833	0·271
H(12-2)	0·276	0·716	0·209
H(12a)	0·098	0·684	0·177
H(14)	−0·007	0·982	0·078
H(14b)	−0·101	0·729	0·142
H(14c)	0·088	0·723	0·334
H(15)	−0·114	1·042	0·214
H(16)	0·139	1·029	0·277

Table 4. *Fractional coordinates and thermal parameters for dimer* (II)

The thermal parameters and standard deviations are as defined in Table 2.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C(1)	0·28872 (8)	0·15424 (16)	0·34043 (15)	3·11 (8)	3·23 (9)	2·00 (7)	0·20 (7)	−0·12 (6)	−0·08 (6)
C(2)	0·22698 (9)	0·16426 (18)	0·33254 (17)	3·23 (9)	3·96 (10)	2·70 (8)	0·22 (8)	0·25 (7)	−0·14 (7)
C(3)	0·20493 (8)	0·20133 (17)	0·22591 (17)	2·85 (9)	3·15 (10)	3·21 (9)	0·07 (7)	−0·08 (7)	−0·09 (7)
N(4)	0·18939 (7)	0·12839 (13)	0·15000 (14)	2·76 (7)	2·85 (7)	2·85 (7)	0·05 (6)	−0·25 (6)	0·07 (6)
C(5)	0·21137 (9)	0·02273 (17)	0·15373 (18)	3·66 (9)	2·74 (9)	3·91 (10)	−0·14 (7)	−0·49 (8)	0·00 (8)
C(6)	0·26669 (8)	0·01555 (17)	0·10270 (17)	3·44 (9)	3·09 (9)	3·22 (10)	0·40 (7)	−0·74 (7)	−0·67 (7)
C(6a)	0·31073 (8)	0·07639 (15)	0·15897 (15)	2·92 (8)	2·79 (9)	2·21 (8)	0·31 (7)	−0·20 (7)	−0·10 (6)
C(7)	0·32413 (8)	0·18529 (16)	0·12274 (15)	3·37 (9)	3·05 (9)	2·05 (7)	0·36 (7)	−0·04 (6)	0·34 (6)
C(7a)	0·35947 (8)	0·09701 (16)	0·08801 (15)	3·35 (9)	3·46 (9)	2·05 (7)	0·59 (7)	0·02 (7)	0·13 (7)
C(8)	0·41437 (8)	0·10769 (16)	0·14098 (16)	3·16 (9)	3·13 (9)	2·53 (8)	0·18 (7)	0·33 (7)	0·34 (7)
C(8a)	0·39997 (8)	0·16587 (15)	0·24592 (16)	2·95 (8)	2·33 (8)	2·65 (8)	0·07 (7)	0·00 (7)	0·25 (7)
C(9)	0·44484 (8)	0·22731 (15)	0·29977 (19)	3·18 (8)	2·40 (9)	4·19 (10)	−0·11 (7)	−0·39 (7)	−0·06 (7)
C(10)	0·48591 (8)	0·16837 (17)	0·36550 (18)	3·21 (9)	2·95 (9)	3·42 (9)	0·11 (7)	−0·24 (8)	−0·44 (8)
N(11)	0·51555 (7)	0·08648 (13)	0·30727 (14)	2·89 (7)	2·67 (7)	3·23 (7)	0·08 (6)	−0·04 (6)	−0·07 (6)
C(12)	0·51012 (8)	−0·01603 (16)	0·34507 (16)	3·36 (9)	3·02 (9)	2·64 (8)	0·34 (7)	−0·29 (7)	−0·24 (7)
C(13)	0·45397 (8)	−0·05566 (16)	0·36522 (17)	3·30 (9)	2·93 (9)	3·19 (9)	0·22 (7)	−0·29 (7)	0·54 (7)
C(14)	0·40991 (8)	−0·02216 (15)	0·28491 (15)	2·85 (8)	2·36 (7)	2·82 (8)	−0·02 (6)	−0·17 (6)	0·08 (6)
C(14a)	0·37670 (8)	0·07450 (14)	0·31365 (15)	2·92 (8)	2·23 (8)	2·10 (7)	−0·02 (6)	−0·15 (3)	0·12 (6)
C(14b)	0·31706 (8)	0·06459 (15)	0·28166 (15)	3·00 (8)	2·55 (8)	2·13 (8)	−0·05 (6)	−0·10 (6)	0·23 (6)
C(15)	0·43306 (8)	0·00191 (16)	0·17463 (16)	2·81 (8)	3·02 (9)	2·80 (8)	0·04 (7)	−0·29 (7)	−0·31 (7)
C(16)	0·35344 (8)	0·24183 (15)	0·21265 (16)	3·06 (8)	2·52 (8)	2·89 (8)	0·17 (7)	−0·09 (7)	0·36 (7)
C(17)	0·31594 (8)	0·25514 (16)	0·30643 (16)	3·08 (8)	3·15 (9)	2·43 (8)	0·36 (7)	−0·69 (7)	−0·24 (7)
C(18)	0·16039 (8)	0·15341 (18)	0·05575 (18)	2·71 (9)	4·14 (11)	3·19 (9)	−0·05 (8)	−0·24 (7)	−0·04 (8)
C(19)	0·13157 (9)	0·25406 (18)	0·04718 (20)	3·67 (10)	4·26 (10)	3·73 (10)	0·61 (9)	−0·50 (8)	0·32 (8)
C(20)	0·55539 (9)	0·11590 (18)	0·23483 (18)	3·13 (9)	3·35 (10)	3·67 (10)	−0·30 (8)	−0·22 (8)	0·11 (8)
C(21)	0·58172 (10)	0·03417 (19)	0·16721 (20)	3·83 (10)	4·31 (11)	4·82 (11)	0·04 (9)	1·25 (9)	−0·20 (9)
O(1)	0·20108 (7)	0·29318 (12)	0·20946 (14)	5·70 (9)	2·93 (8)	5·23 (9)	0·21 (6)	−2·01 (7)	−0·24 (6)
O(2)	0·30839 (6)	0·33667 (12)	0·35267 (12)	4·81 (8)	3·13 (7)	3·55 (7)	0·40 (6)	−0·60 (6)	−1·21 (6)
O(3)	0·54926 (6)	−0·06951 (12)	0·36072 (13)	3·39 (7)	3·62 (7)	4·38 (8)	0·79 (6)	−0·35 (6)	0·42 (6)
O(4)	0·46078 (6)	−0·05623 (12)	0·12156 (12)	3·94 (7)	3·67 (7)	3·43 (7)	0·70 (6)	0·26 (6)	−0·74 (6)
O(5)	0·15788 (8)	0·08941 (14)	−0·01494 (14)	5·74 (10)	5·42 (9)	4·34 (8)	1·13 (7)	−1·94 (7)	−1·84 (7)
O(6)	0·56507 (7)	0·20683 (13)	0·22237 (14)	4·79 (8)	3·30 (8)	5·37 (9)	−0·73 (6)	0·72 (7)	0·24 (7)

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* The authors wish to thank Dr Coppens for providing them with a copy of this program.

† A table of observed and calculated structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30245 (16 pp., 1 microfiche). Copies of this table may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

the hydrogen atom positions, as obtained from the difference maps, are given in Table 3.

Dimer (II)

The positions of the 32 non-hydrogen atoms of dimer (II) were revealed in an *E* map based on the phases of 578 reflections of $|E|$ value greater than 1·0. Isotropic refinement yielded an *R* value of 0·131. A difference map then revealed the locations of 18 of the 26 hydrogen atoms. After one cycle of anisotropic refinement, which included these 18 hydrogen atoms in fixed positions, a difference map showed the positions of all of the remaining hydrogen atoms. In subsequent refinements, the hydrogen positions were fixed and the thermal parameters of the hydrogen atoms were set equal to the thermal parameters of the atoms to which they were bonded. Nine reflections affected by secondary extinction, as judged by the criteria discussed above, were removed from the refinement and one additional cycle of anisotropic refinement resulted in an *R* value of 0·054. Calculation of the *R* value with inclusion of the nine reflections with secondary extinction gave a value of 0·064.

Finally, one cycle of additional refinement was carried out in which the scale factor and an isotropic secondary extinction parameter were varied. All data were included, and atomic positions and thermal parameters were fixed at the values obtained from the refinement already completed. An *R* value of 0·052 was obtained.† There was no evidence of multiple diffraction effects among these data. Table 4 gives the final heavy atom parameters for dimer (II), and Table 5 gives the hydrogen-atom positions.

Table 5. *Fractional coordinates for hydrogen atoms in dimer* (II)

	x	*y*	*z*
H(1)	0·299	0·147	0·420
H(2-1)	0·217	0·224	0·379
H(2-2)	0·211	0·103	0·353
H(5-1)	0·211	0·003	0·223
H(5-2)	0·182	−0·025	0·116
H(6-1)	0·264	0·041	0·025
H(6-2)	0·281	−0·061	0·103
H(7)	0·298	0·221	0·067
H(7a)	0·357	0·060	0·012
H(8)	0·439	0·151	0·094
H(9-1)	0·464	0·269	0·239
H(9-2)	0·425	0·278	0·349
H(10-1)	0·512	0·220	0·397
H(10-2)	0·468	0·136	0·424
H(13-1)	0·457	−0·127	0·360
H(13-2)	0·444	−0·041	0·434
H(14)	0·384	−0·079	0·274
H(14a)	0·380	0·098	0·390
H(14b)	0·302	−0·001	0·307
H(16)	0·368	0·312	0·185
H(19-1)	0·158	0·311	0·037
H(19-2)	0·110	0·272	0·111
H(19-3)	0·108	0·251	−0·014
H(21-1)	0·603	0·065	0·113
H(21-2)	0·557	−0·020	0·145
H(21-3)	0·609	0·000	0·202

Discussion

The configuration of dimer (I) is shown in the stereodrawing of Fig. 1. The bond lengths and proper atom numbering are shown in Fig. 2, and the bond angles are given in Fig. 3. This compound has a central cage bounded by four six-membered rings and two four-membered rings. Each four-membered ring is puckered, with the torsion angles around the ring bonds having values of about 20°. The six-membered rings assume distorted boat conformations. Of special interest are the four bonds in the four-membered rings with lengths of 1·58 Å, [C(16)–C(7a), C(7a)–C(7), C(15)–C(14a), and C(14a)–C(14)]. These high values are understandable in terms of the irreversible photoreaction of dimers of type (I) to give dimers of type (II), implying that type (I) is the less stable form.

Cursory inspection of a model of this molecule reveals what appears to be a non-crystallographic twofold axis bisecting bonds C(15)–C(16) and C(14b)–C(14c). In fact, however, the deviation from twofold symmetry is well beyond experimental error, the largest deviation being associated with atoms O(2) and O(4). Torsion angles which would be related by a true twofold show the following discrepancies: the angle C(14b)–C(5a)–C(6)–C(7) is 2·0 (3)° while the 'corresponding' angle C(14c)–C(12a)–C(13)–C(14) is 12·3 (3)°; similarly, angle O(2)–C(6)–C(5a)–C(5) is 46·6 (4)° while angle O(4)–C(13)–C(12a)–C(12) is 64·0 (3)°. Also of interest is the fact that the least-squares line rep-

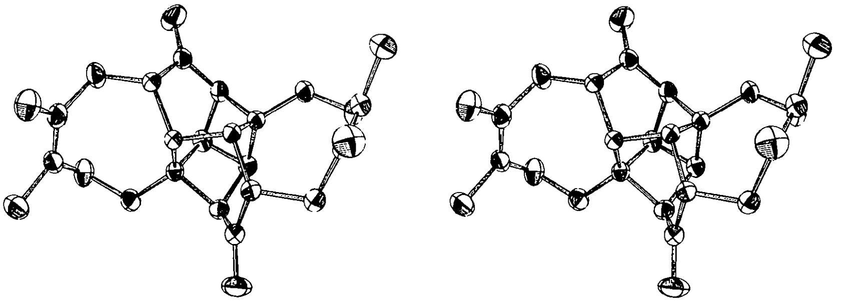

Fig. 1. A stereo illustration of the dimer (I) molecule. Hydrogen atoms are not shown. Figs. 1, 4, 5 and 6 were drawn with the aid of the *ORTEP* computing program (Johnson, 1965).

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† See footnote to p. 619.

resenting the pseudo-axis is in near-coincidence with the crystallographic twofold screw axis, although the discrepancy here is again beyond experimental error. 14 pairs of atoms are related by the pseudo-twofold axis. At the average *y* coordinate of the 14 midpoints (−0·189 fractional), the *x* and *z* fractional coordinates of the line are 0·002 and 0·240, respectively, where the *z* coordinate represents a displacement of about 0·15 Å from the location of the crystallographic axis. In addition, the least-squares line is tilted by about 1° with respect to the screw axis.

The packing arrangement for dimer (I) is shown in Fig. 4. The near-coincidence of the molecular pseudo-twofold and the crystallographic screw axes is clearly seen. Although the hydrogen atoms associated with the water molecules, indicated by shading in Fig. 4, were not found, the lengths and angles involved strongly suggest hydrogen bonding between O(3)···O(*W*1) at 2·726 Å, O(*W*1)···O(*W*2) at 2·923 Å and O(*W*2)···O(1^{α})* at 2·831 Å, thus forming an infinite chain in the **a** direction of the unit cell. The minimum intermolecular contact distance found was C(2)···O(3^{β}), 3·26 Å, while the shortest C···C contact was C(11)···C(17^{γ}), 3·47 Å. It should be noted that O(4) has a contact at 3·31 Å [O(4)···C(6^{δ})], while its pseudo-symmetry equivalent, O(2), has no C···O contact of less than 3·5 Å.

The configuration of dimer (II) is shown in the stereodrawing of Fig. 5. The bond lengths, with atom numbering, are given in Fig. 2 and the bond angles in

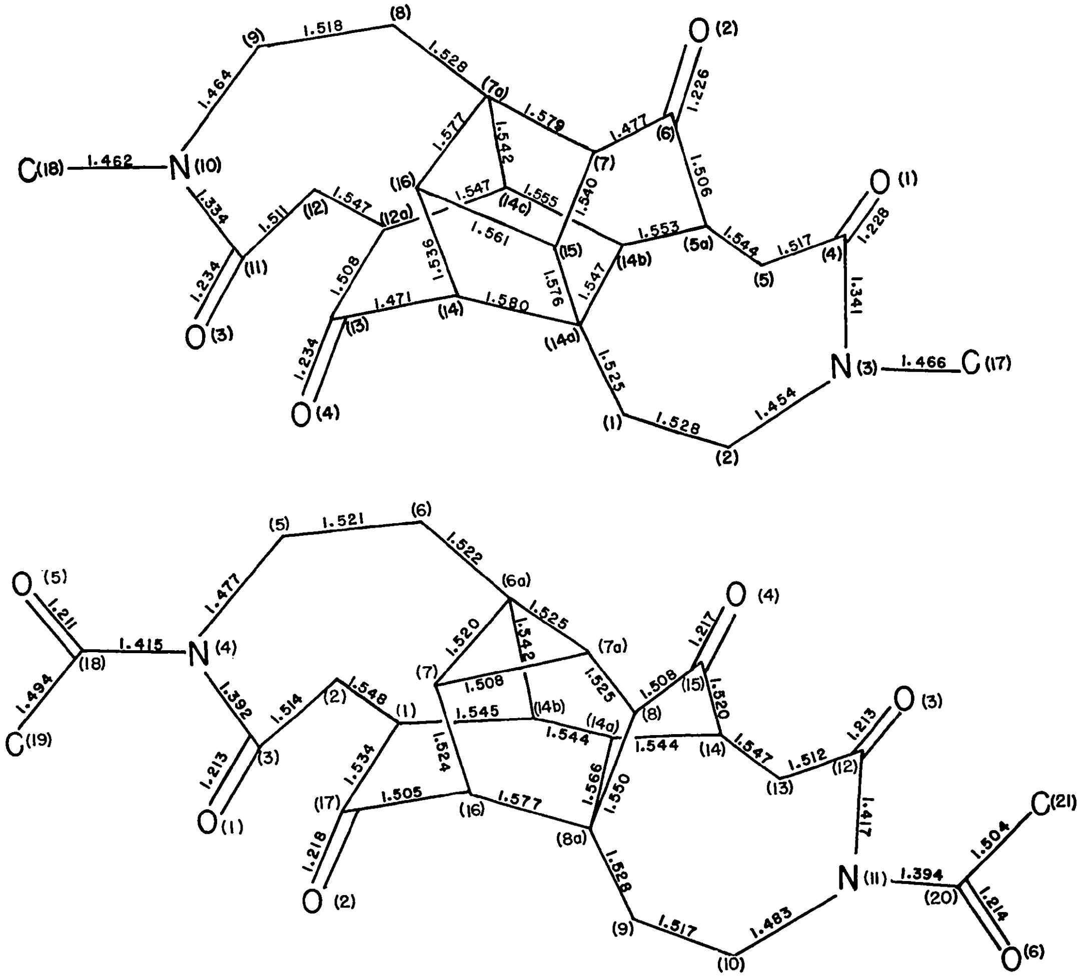

Fig. 2. Bond lengths and correct atom numbering for dimer (I) (above) and dimer (II) (below). Estimated standard deviations in the lengths range from 0·003 to 0·005 Å for dimer (I) and are all 0·003 Å for dimer (II). The systematic names for these compounds are: Dimer (I), decahydro-7,14a,7a,14-ethanediylidenenaphtho[1,8-*de*:4,5-*d′e′*] bisazocine-4,6,11,13(1*H*,7*H*,8*H*,14*H*)-tetrone. Dimer (II), 4,11-diacetyldodecahydro-7*H*-1,7,8a-ethanylylidene-8,14-methanocyclopropa[1,6]benzo[1,2-*d*:4,3-*d′*]bisazocine-3,12,15,17(4*H*,9*H*)-tetrone.

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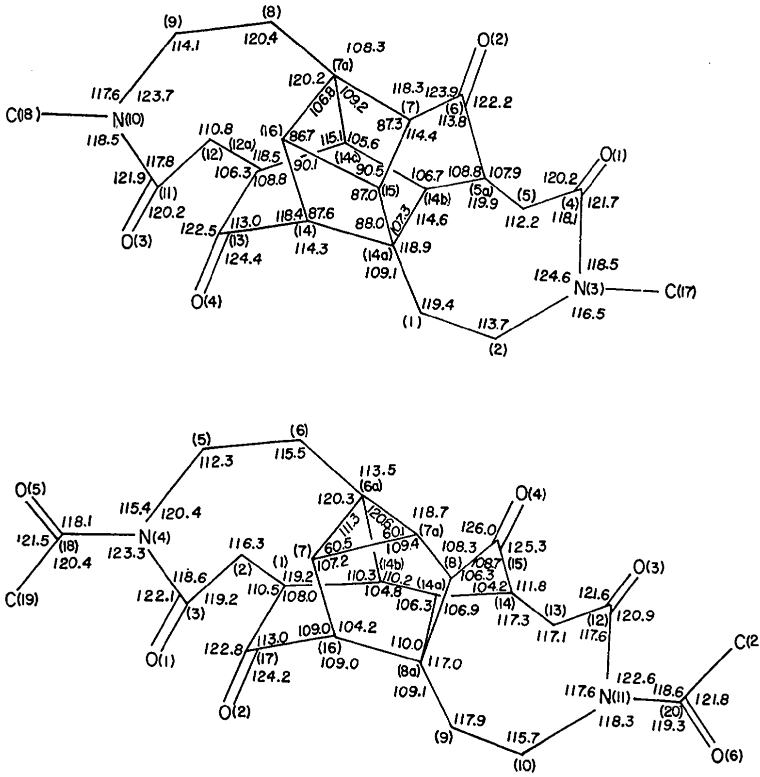
* The molecules whose atom numbers have superscripts are related to the molecule whose coordinates are given in Table 2 as follows:

(α)	$1+x$	y	z
(β)	$-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$
(γ)	$1+x$	$-\frac{1}{2}-y$	$\frac{1}{2}+z$
(δ)	x	$-\frac{1}{2}-y$	$-\frac{1}{2}+z$.

Fig. 3. Dimer (II) has a more complex, partially open, cage bounded by one three-, two five-, two six-, and one seven-membered ring. The six-membered rings are again in a distorted boat conformation. Fig. 2 shows the relationship between the cages of dimers (I) and (II). The postulated mechanism for the formation of the dimers is discussed elsewhere in detail (Iwakuma, Nakai, Yonemitsu, Jones, Karle & Witkop, 1972).

The stereodiagram in Fig. 6 shows the packing arrangement of dimer (II). The only contact distances



I

C(8)	C(7a)	C(14c)	119.2
C(16)	C(7a)	C(7)	88.5
C(1)	C(14a)	C(15)	120.3
C(14b)	C(14a)	C(14)	108.5
C(12a)	C(14c)	C(14b)	106.3
C(7)	C(15)	C(14a)	111.8
C(14)	C(16)	C(7a)	112.1
C(14a)	C(14b)	C(14c)	105.7

II

C(7)	C(6a)	C(7a)	59.4
C(6)	C(6a)	C(14b)	118.5
C(6a)	C(7)	C(16)	109.6
C(7a)	C(8)	C(8a)	106.3
C(9)	C(8a)	C(14a)	115.5
C(8)	C(8a)	C(14a)	99.8
C(8)	C(8a)	C(16)	104.7
C(14)	C(14a)	C(14b)	112.9

Fig. 3. Bond angles for dimer (I) (above) and dimer (II) (below). Estimated standard deviations range from 0·2 to 0·3° for dimer (I) and 0·1 to 0·2° for dimer (II).

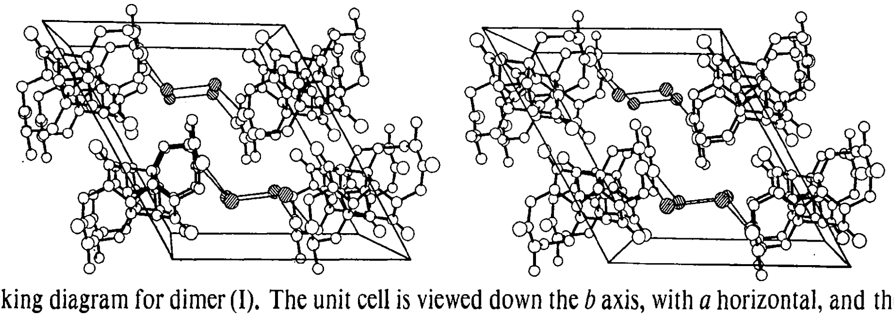


Fig. 4. A stereo packing diagram for dimer (I). The unit cell is viewed down the *b* axis, with *a* horizontal, and the *c* axis related to *a* through the angle *β*. The O atoms of the water molecules are shaded and hydrogen bonds between the water molecules and O(3) and O(1) are indicated by light lines.

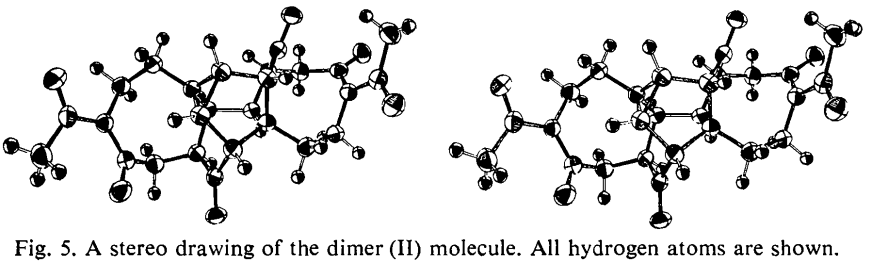


Fig. 5. A stereo drawing of the dimer (II) molecule. All hydrogen atoms are shown.

Table 6. *A comparison of bond lengths and torsion angles in the amide regions of Dimers* (I) *and* (II) *with expected values*

	Dimer (I)		Dimer (II)		Expected (Marsh & Donohue, 1967)
Bond lengths					
	C(5)—C(4)	1·517 (4) Å	C(13)–C(12)	1·512 (3) Å	1·51 Å
	C(12)–C(11)	1·511 (4)	C(2)—C(3)	1·514 (3)	
	C(4)—N(3)	1·341 (4)	C(12)–N(11)	1·417 (3)	$1{\cdot}32_5$
	C(11)–N(10)	1·334 (5)	C(3)—N(4)	1·392 (3)	
	N(3)—C(2)	1·454 (4)	N(11)–C(10)	1·483 (3)	$1{\cdot}45_5$
	N(10)–C(9)	1·464 (4)	N(4)—C(5)	1·477 (3)	
	C(4)—O(1)	1·228 (4)	C(12)–O(3)	1·213 (3)	1·24
	C(11)–O(3)	1·234 (4)	C(3)—O(1)	1·213 (3)	
Torsion angles					
	C(5)—C(4)—N(3)—C(2)	3·6 (5)°	C(13)–C(12)–N(11)–C(10)	49·3 (3)°	0·0°
	C(12)–C(11)–N(10)–C(9)	−1·0 (5)	C(2)—C(3)—N(4)—C(5)	−22·4 (3)	
	O(1)—C(4)—N(3)—C(2)	−176·0 (3)	O(3)—C(12)–N(11)–C(10)	−130·6 (2)	180·0°
	O(3)—C(11)–N(10)–C(9)	−178·8 (3)	O(1)—C(3)—N(4)—C(5)	158·0 (2)	

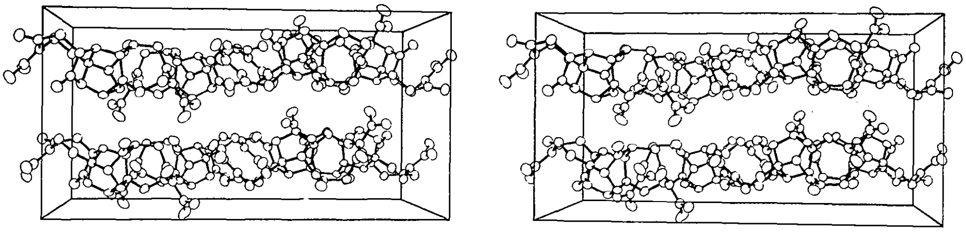


Fig. 6. A stereo packing diagram for dimer(II). The unit cell is viewed down the *b* axis, with the *a* axis horizontal and the *c* axis vertical.

of note are six C···O distances in the range 3·1–3·4 Å:† O(5)–C($14a^{\alpha}$), 3·13 Å; O(5)···C(14^{α}), 3·13 Å; O(5)···C(13^{α}), 3·19 Å; O(5)···C($14b^{\alpha}$), 3·28 Å; O(6)···C(13^{β}), 3·30 Å; and O(6)···C(19^{γ}), 3·37 Å. The shortest C···C contact observed was 3·73 Å.

Both dimer (I) and dimer (II) have cyclic amide linkages,

$$\begin{array}{c}\mathrm{R}\;\;\mathrm{O}\\ |\;\;\;\| \\ \mathrm{R'{-}N{-}C{-}R''}\end{array}$$

where, for dimer (I), R is a methyl group, and, for dimer (II), an acetyl group. Table 6 compares the bond lengths and torsion angles in these regions with generally accepted average values (Marsh & Donohue, 1967). For dimer (I), the observed values are close to those expected for an amide bond, while for dimer (II), there is a large deviation from the required planarity. In addition, the dimer-(II) N(11)–C(12) and N(4)–C(3) lengths of 1·417 and 1·392 Å, respectively, are closer to the 1·45 Å value expected for a single C–N bond adjacent to a double bond than to the $1{\cdot}32_5$ Å value for a C–N amide linkage. In light of the similarity of the ring structures in this region of the two dimers, it would appear that it is the introduction of the acetyl groups in dimer (II) that does away with the characteristic geometry of the amide linkage.

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† The molecules whose atom numbers have superscripts are related to the molecule whose coordinates are given in Table 5 as follows:

(α)	$\frac{1}{2}-x$	$-y$	$-\frac{1}{2}+z$
(β)	$1-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$
(γ)	$\frac{1}{2}+x$	y	$\frac{1}{2}-z$.

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