Crystal and Molecular Structure of the Photoreductive Dimer of 5,6-Dihydro-3,5,5-trimethyl-1,4-oxazin-2-one

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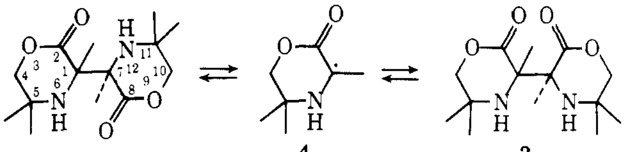
Abstract: The single-crystal x-ray analysis of the *dl* photoreductive dimer (**2**) of 5,6-dihydro-3,5,5-trimethyl-1,4-oxazin-2-one is described. The analysis was performed as a measure of structural features in **2** which contribute to the reported facile homolysis of the C(1)-C(7) bond. The dimer crystallizes in the monoclinic space group $P2_1/c$ with eight dimeric molecules per unit cell of dimensions a = 11.866 (8) Å, b = 28.133 (18) Å, c = 12.281 (7) Å, and β = 130.44 (4)°. From 1935 unique, observed reflections collected on an automated four-circle diffractometer, the structure was solved and refined to final values for the discrepancy indices of $R = 0.048$ and $wR = 0.051$. The two independent molecules of **2** are linked together by four N-H- - -O hydrogen bonds. The central C(1)-C(7) bond is long (1.591 (4) Å). The bond lengthening is explained primarily by steric strain resulting from short intramolecular contacts in the region around the bond.

Recently we reported that the meso and *dl* photoreductive dimers (**1** and **2**) of 5,6-dihydro-3,5,5-trimethyl-1,4-oxazin-2-one (**3**) in solution exist in equilibrium with a radical, 5,6-dihydro-3,5,5-trimethyl-1,4-oxazin-2-onyl (**4**).[1c] The enthalpy of dissociation for the homolysis is solvent dependent and ranges from 22 kcal/mol in benzene to 11 kcal/mol in ethanol. The enthalpy of dissociation in ethanol solvent is about the same as the ΔH for dissociation of the triphenylmethyl dimer.[2] The facile homolysis of **1** and **2** is intriguing because the resulting radical is an α-amino acid radical structurally related to the α-amino acid radicals produced by irradiation of amino acids and peptides with high-energy radiation[3] and by reaction of peroxy radicals with peptides.[4]



1 **4** **2**

We are interested in the structural features of the reductive dimers (**1** and **2**) and the radical **4** which contribute to the facile bond homolysis. We have proposed that steric interactions in the dimers may be important. Carbons 1 and 7 are fully substituted and further crowded by the *gem*-dimethyl groups at positions 5 and 11. To estimate the importance of steric crowding in the dimers we have now completed a single-crystal x-ray analysis of the *dl* dimer (**2**).

Results and Discussion

The results of the structure determination are displayed as follows. The atomic parameters defining the crystal structure are given in Table I, and Table II gives the root mean square vibrational amplitudes of the atoms refined anistropically. There are two molecules in the asymmetric unit linked by hydrogen bonds. A three-dimensional representation showing the relationship of the two dimers appears in Figure 1, and the numbering scheme adopted is shown in Figure 2. Table III gives the bond lengths and angles with standard deviations for both molecules.

Because of the low ratio of observations to parameters (approximately 5.4:1) in this structure determination, the statistical validity of standard deviations, especially those on bond angles, must be viewed as low estimates and with some skepticism. However, a comparison of the bond lengths between the four chemically equivalent units in the asymmetric unit shows no equivalent bonds that differ significantly from each other. A similar comparison of bond angles indicates only two sets of angles which differ significantly. The significance of variation in equivalent bond lengths and bond angles was determined by assuming that equivalent bond lengths and bond angles are in fact equal and comparing the magnitude of observed differences with the standard deviations for the bond lengths and bond angles in question.[5] In addition, weighted averages for bond lengths and angles with even lower statistical uncertainty may be calculated.[6] For example, for the carbonyl bonds, C(2)-O(2) and C(8)-O(8), $\bar{d} = \Sigma_i(X_i/\sigma_i^2)/\Sigma_i(1/\sigma_i^2) = 1.208$ and $\sigma(\bar{d}) = (\Sigma_i(1/(1/\sigma_i^2)))^{1/2} = 0.003$, and for the equivalent C-CH_3 bonds, C(1)-C(Me1) and C(7)-C(Me7), $\bar{d} = 1.535$ and $\sigma(\bar{d}) = 0.003$. Thus the presence of and close agreement between four crystallographically independent, chemically equivalent moieties in the asymmetric unit increases the statistical reliability and, more importantly, the chemical significance of the final results.

A comparison of the weighted average observed bond lengths and expected values for similar bonds as tabulated by Sutton[7] reveals only three bonds which differ significantly from the expected value. The C(4)-C(5) and C(10)-C(11) bonds, 1.508 (3) Å, are shorter than the expected value of 1.537 Å, and the C(1)-C(7) bond, 1.591 (4) Å, is longer than the expected value. The C(1)-C(7) bond length, however, is in the range of bond lengths found in the literature for fully substituted C-C bonds, 1.583-1.611 Å.[8]

Examination of the intramolecular contacts (Table V) in the region around the C(1)-C(7) bond reveals steric strain which is contributing to the C(1)-C(7) bond lengthening. The C(2)-N(12), N(6)-C(8) and C(Me1)-C(Me7) intramolecular contacts are all considerably less than the expected van der Waals contacts of approximately 3.3 Å for C-N distances and 4.0 Å for methyl-methyl distances.[9] In addition the short contacts between C(Me1) and C(Me5A) and between C(Me7) and C(Me11A) prevent C(Me1) and C(Me7) from bending away from each other to reduce their contribution to the steric strain. The remaining intramolecular contacts all involve one or two hydrogens. Because of these short hydrogen contacts, the hydrogens should be locked into positions. The ease with which hydrogens were located in a three-dimensional difference map and the lack of disorder in the methyl hydrogens' positions is further evidence of this locking phenomenon.

Least-squares planes were calculated for the conjugated

Table I. Final Structural Parameters[a]

	x/a[b]	y/b	z/c	β_{11}[c] or B[d]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Molecule A									
C(1)	−805 (4)	4008 (1)	2627 (4)	93 (7)	9 (1)	96 (6)	3 (2)	64 (6)	4 (2)
C(2)	−1590 (5)	4292 (2)	3032 (4)	100 (7)	15 (1)	65 (6)	−6 (2)	49 (6)	−2 (2)
O(3)	−1754 (3)	4759 (1)	2865 (3)	165 (6)	14 (1)	160 (5)	1 (1)	130 (5)	−7 (1)
C(4)	−1279 (5)	5002 (2)	2188 (5)	167 (9)	10 (1)	169 (8)	3 (2)	126 (8)	1 (2)
C(5)	179 (5)	4809 (1)	2697 (4)	120 (8)	10 (1)	95 (7)	1 (2)	74 (6)	−2 (2)
N(6)	−119 (3)	4310 (1)	2223 (3)	102 (5)	8 (1)	102 (5)	−3 (1)	72 (5)	−1 (1)
C(7)	−2097 (5)	3716 (1)	1231 (4)	107 (7)	11 (1)	118 (7)	1 (2)	84 (6)	−1 (2)
C(8)	−1445 (6)	3576 (2)	537 (7)	141 (9)	14 (1)	188 (10)	−18 (2)	116 (9)	−23 (3)
O(9)	−1947 (4)	3770 (2)	−695 (5)	191 (7)	32 (1)	172 (7)	−21 (2)	146 (6)	−24 (2)
C(10)	−2993 (7)	4162 (2)	−1297 (5)	192 (11)	34 (1)	116 (8)	−15 (3)	109 (8)	1 (3)
C(11)	−4160 (5)	4070 (2)	−1182 (5)	124 (8)	24 (1)	75 (7)	−13 (3)	54 (7)	−4 (2)
N(12)	−3362 (4)	4044 (1)	354 (3)	86 (5)	12 (1)	81 (5)	0 (1)	54 (4)	1 (1)
C(Me1)	343 (5)	3689 (2)	3902 (5)	131 (8)	17 (1)	170 (8)	8 (2)	90 (7)	24 (2)
O(2)	−2051 (3)	4094 (1)	3547 (3)	186 (6)	21 (1)	149 (5)	−16 (1)	137 (5)	−6 (1)
C(Me5A)	1404 (5)	4873 (2)	4305 (5)	165 (9)	16 (1)	108 (8)	−14 (2)	77 (7)	−13 (2)
C(Me5B)	604 (5)	5066 (2)	1919 (5)	172 (9)	13 (1)	154 (8)	−8 (2)	114 (8)	−1 (2)
C(Me7)	−2532 (5)	3258 (1)	1556 (5)	144 (8)	9 (1)	211 (9)	−2 (2)	121 (8)	2 (2)
O(8)	−473 (4)	3283 (1)	1087 (5)	192 (7)	17 (1)	343 (9)	0 (2)	208 (7)	−20 (2)
C(Me11A)	−5055 (6)	3618 (2)	−1995 (5)	215 (11)	37 (1)	136 (9)	−44 (3)	106 (8)	−31 (3)
C(Me11B)	−5195 (6)	4497 (2)	−1753 (6)	175 (10)	34 (1)	128 (9)	12 (3)	51 (8)	29 (3)
Molecule B									
C(1)	4455 (4)	3782 (1)	3003 (4)	96 (7)	9 (1)	115 (7)	−1 (1)	71 (6)	−1 (2)
C(2)	4055 (5)	3721 (2)	3958 (5)	100 (8)	14 (1)	120 (8)	−8 (2)	72 (7)	−16 (2)
O(3)	4724 (4)	3399 (1)	4997 (3)	147 (6)	21 (1)	116 (5)	1 (2)	100 (5)	5 (1)
C(4)	5736 (5)	3064 (2)	5155 (5)	129 (8)	14 (1)	135 (8)	5 (2)	89 (7)	11 (2)
C(5)	6734 (5)	3307 (1)	4962 (4)	95 (7)	11 (1)	99 (7)	−1 (2)	60 (6)	3 (2)
N(6)	5748 (4)	3490 (1)	3490 (3)	79 (5)	12 (1)	83 (5)	5 (1)	48 (4)	5 (1)
C(7)	3089 (4)	3584 (1)	1478 (4)	77 (6)	11 (1)	97 (6)	2 (2)	56 (6)	3 (2)
C(8)	3693 (5)	3467 (2)	726 (5)	90 (7)	20 (1)	88 (7)	3 (2)	50 (6)	6 (2)
O(9)	3844 (3)	3018 (1)	487 (3)	145 (6)	21 (1)	139 (5)	2 (2)	105 (5)	−11 (2)
C(10)	3562 (5)	2635 (2)	1057 (5)	143 (8)	14 (1)	154 (8)	0 (2)	98 (7)	−6 (2)
C(11)	2221 (5)	2728 (2)	910 (5)	102 (7)	13 (1)	100 (7)	0 (2)	57 (6)	−8 (2)
N(12)	2563 (3)	3161 (1)	1749 (3)	92 (5)	10 (1)	99 (5)	−2 (1)	61 (4)	−3 (1)
C(Me1)	4768 (5)	4312 (2)	3001 (5)	161 (9)	10 (1)	210 (9)	−1 (2)	116 (8)	4 (2)
O(2)	3126 (4)	3975 (1)	3785 (4)	145 (6)	22 (1)	187 (6)	5 (2)	122 (5)	−12 (2)
C(Me5A)	7676 (5)	3693 (2)	6099 (5)	131 (8)	20 (1)	100 (7)	−9 (2)	53 (7)	−7 (2)
C(Me5B)	7729 (5)	2938 (2)	5066 (5)	123 (8)	17 (1)	140 (8)	11 (2)	73 (7)	13 (2)
C(Me7)	1843 (5)	3952 (2)	561 (5)	123 (8)	15 (1)	161 (8)	9 (2)	86 (7)	13 (2)
O(8)	4028 (4)	3785 (1)	324 (3)	163 (6)	26 (1)	157 (6)	−1 (2)	122 (5)	17 (2)
C(Me11A)	836 (5)	2773 (2)	−673 (5)	126 (8)	19 (1)	134 (8)	−5 (2)	60 (7)	−13 (2)
C(Me11B)	2023 (5)	2326 (2)	1603 (5)	180 (9)	12 (1)	179 (9)	−11 (2)	109 (8)	−4 (2)

	x/a[b]	y/b	z/c	β_{11}[c] or B[d]	x/a[b]	y/b	z/c	β_{11}[c] or B[d]
	Molecule A				Molecule B			
H(1N6)	820	4168	2639	393	6351	3689	3418	425
H(1N12)	−4068	3940	447	412	1666	3253	1543	420
H(1C4)	−2002	4964	1184	532	5197	2819	4469	537
H(2C4)	−1162	5332	2419	532	6333	2929	6094	537
H(1C10)	−2478	4444	−796	770	4400	2595	2043	577
H(2C10)	−3459	4196	−2278	770	3407	2350	557	577
H(1CMe1)	−140	3475	4084	643	3895	4492	2613	635
H(2CMe1)	876	3513	3707	643	5033	4361	2429	635
H((3CMe1)	1018	3881	4732	643	5545	4415	3949	635
H(1CMe5A)	1110	4736	4789	617	7045	3917	6050	621
H(2CMe5A)	2280	4720	4599	617	8255	3850	5924	621
H(3CMe5A)	1595	5202	4519	617	8311	3552	7021	621
H(1CMe5B)	1473	4925	2166	587	8264	3079	4820	613
H(2CMe5B)	−181	5042	920	587	7151	2682	4439	613
H(3CMe5B)	797	5391	2197	587	8411	2822	6025	613
H(1CMe7)	−2930	3335	1999	585	1449	4028	1010	587
H(2CMe7)	−3253	3093	687	585	1083	3819	−357	587
H(3CMe7)	−1681	3064	2177	585	2227	4228	469	587
H(1CMe11A)	−5681	3549	−1785	894	−1	2841	−756	656
H(2CMe11A)	−5644	3673	−2992	894	674	2485	−1160	656
H(3CMe11A)	−4403	3362	−1711	894	971	3025	−1099	656
H(1CMe11B)	−4655	4762	−1149	933	2893	2296	2576	642
H(2CMe11B)	−5577	4565	−2692	933	1843	2037	1112	642
H(3CMe11B)	−5979	4424	−1760	933	1204	2395	1550	642

[a] Estimated standard deviations of the least significant figures are given here and in all succeeding tables. [b] Fractional cell coordinates ×10^4. [c] Aniosotropic thermal parameters (×10^4) are in the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$. [d] The isotropic thermal parameter for each hydrogen atom (×10^2) is calculated to be equal to 1.0 + the equivalent isotropic thermal parameter for the atom to which it is attached.

Table II. Root Mean Square Amplitudes (Å) of Vibration

	Molecule A			Molecule B		
	Min	Intermed	Max	Min	Intermed	Max
C(1)	0.184 (8)	0.191 (7)	0.215 (7)	0.185 (8)	0.194 (8)	0.228 (6)
C(2)	0.168 (8)	0.204 (8)	0.253 (8)	0.185 (8)	0.200 (8)	0.279 (8)
O(3)	0.182 (5)	0.243 (5)	0.278 (4)	0.188 (5)	0.248 (5)	0.293 (5)
C(4)	0.200 (7)	0.225 (7)	0.278 (7)	0.207 (7)	0.225 (7)	0.274 (7)
C(5)	0.187 (8)	0.203 (7)	0.223 (7)	0.197 (7)	0.201 (8)	0.230 (7)
N(6)	0.168 (6)	0.193 (6)	0.215 (5)	0.173 (6)	0.200 (5)	0.224 (5)
C(7)	0.178 (8)	0.210 (7)	0.230 (7)	0.173 (8)	0.204 (7)	0.218 (7)
C(8)	0.185 (9)	0.230 (9)	0.323 (8)	0.187 (8)	0.216 (9)	0.287 (8)
O(9)	0.204 (6)	0.262 (5)	0.382 (6)	0.191 (5)	0.251 (5)	0.306 (5)
C(10)	0.195 (9)	0.271 (8)	0.380 (8)	0.217 (7)	0.242 (7)	0.273 (7)
C(11)	0.182 (9)	0.231 (8)	0.321 (7)	0.189 (8)	0.207 (7)	0.257 (7)
N(12)	0.189 (6)	0.189 (6)	0.222 (5)	0.188 (6)	0.199 (6)	0.216 (5)
O(2)	0.178 (6)	0.257 (5)	0.318 (4)	0.193 (6)	0.272 (5)	0.329 (5)
O(8)	0.180 (6)	0.270 (5)	0.404 (5)	0.186 (6)	0.266 (5)	0.345 (5)
C(Me1)	0.200 (8)	0.234 (7)	0.332 (7)	0.200 (8)	0.255 (7)	0.318 (7)
C(Me7)	0.186 (8)	0.231 (7)	0.311 (6)	0.205 (8)	0.243 (7)	0.295 (6)
C(Me5A)	0.192 (8)	0.264 (7)	0.294 (7)	0.198 (8)	0.271 (7)	0.291 (7)
C(Me5B)	0.211 (7)	0.251 (7)	0.275 (7)	0.204 (8)	0.260 (7)	0.290 (7)
C(Me11A)	0.206 (9)	0.281 (8)	0.427 (8)	0.211 (8)	0.265 (7)	0.314 (7)
C(Me11B)	0.197 (9)	0.335 (8)	0.401 (8)	0.206 (8)	0.281 (7)	0.298 (7)

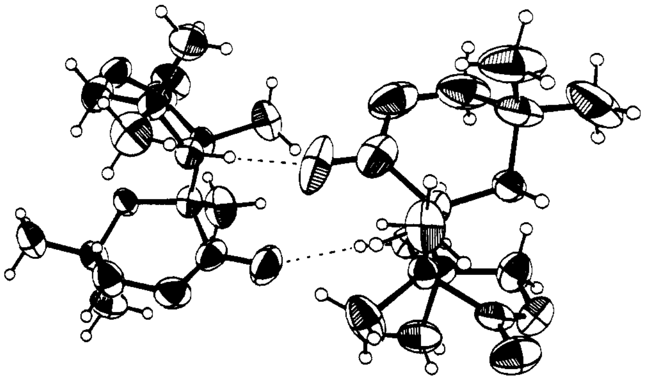


Figure 1. Perspective drawing of the two independent molecules of the *dl* dimer (**2**) in the asymmetric unit. The dotted lines represent hydrogen bonding interactions. Probability ellipsoids are shown at the 50% level. The size of the hydrogen atoms is reduced for clarity.

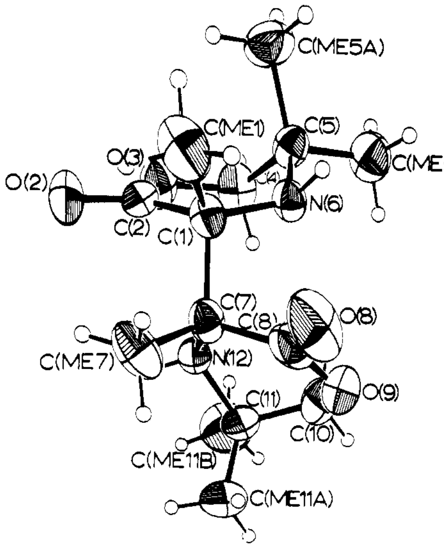


Figure 2. Perspective drawing of the *dl* dimer (**2**) showing the atomic numbering scheme. Probability ellipsoids are shown at the 50% level. The size of the hydrogen atoms is reduced for clarity.

regions of the dimer and dihedral angles were calculated for both molecules. The results of these calculations are given in Table IV. In each case the methylene carbons, C(4) and C(10), are significantly distorted from the plane. This distortion probably occurs to relieve some steric strain between C(Me1) and C(Me5A) and between C(Me7) and C(Me11A).

The hydrogen bonding between the molecules is illustrated in Figure 1. Each dimer is involved in four hydrogen bonds. The distances for these bonds, given in Table V, agree well with the expected N–H- - -O distance for amine nitrogens of 2.57–3.22 Å with a mean value of 3.04 Å.[10] The N–H- - -O angles for the hydrogen bonds range from 166 to 172°. The other intermolecular contacts are of normal van der Waals type.

Although there are several short intramolecular contacts in the dimer and there is evidence for some strain in the molecule, there appears from examination of the molecule and of models to be little freedom in this system. This rigidity and the lack of short intermolecular contacts suggests that the conformation observed in the molecule is the same as the predominant conformation found in solution.

The results of the x-ray analysis confirm our suspicions that the C(1)–C(7) bond is longer than the average carbon–carbon single bond and that steric strain contributes to this lengthening. Because of the work of Hoffmann and others[11] we were also concerned about possible electronic through-bond coupling of the amine and carboxyl functional groups as a contributing factor to the facile bond homolysis. The x-ray data do not support this type of electronic interaction insofar as bond lengths are sensitive to through-bond coupling. The C(1)–C(2), C(1)–N(6), C(7)–C(8), and C(7)–N(12) bonds are all of approximately normal length. Ultraviolet spectral data also provide no evidence for through-bond coupling. The dimers **1** and **2** show only weak end absorption in the UV, characteristic of the carboxyl functional group.[12]

Experimental Section

Crystal Data. Crystals of the *dl* photoreductive dimer (**2**) of 5,6-dihydro-3,5,5-trimethyl-1,4-oxazin-2-one (**3**) were prepared by irradiation of **3** in 2-propanol solvent.[1] They are colorless needles (mp 155–156 °C) which were grown at ambient temperature from a mixture of spectrograde isooctane and spectrograde methylene chloride. The unit cell is monoclinic. The cell dimensions, determined by least-squares fit of the cell parameters to 15 carefully measured reflections, are a = 11.866 (8), b = 28.133 (18), c = 12.281 (7) Å, and β = 130.44 (4)°. The volume is 3120 (3) Å^3. The measured density of the crystals, determined by pycnometry using zinc iodide solution, is 1.22 (2) g/cm^3. Assuming eight molecules of the dimer per

Table III. Bond Lengths (Å) and Angles (deg)

	Molecule			Molecule	
	A	B		A	B
C(1)-N(6)	1.469 (5)	1.482 (5)	C(7)-N(12)	1.471 (5)	1.478 (5)
C(1)-C(2)	1.533 (6)	1.534 (6)	C(7)-C(8)	1.527 (6)	1.528 (6)
C(1)-C(7)	1.598 (5)	1.583 (5)	C(7)-C(Me7)	1.536 (6)	1.537 (6)
C(1)-C(Me1)	1.531 (6)	1.538 (6)	C(8)-O(8)	1.208 (6)	1.206 (5)
C(2)-O(2)	1.207 (5)	1.212 (5)	C(8)-O(9)	1.332 (6)	1.336 (5)
C(2)-O(3)	1.325 (5)	1.328 (5)	O(9)-C(10)	1.452 (7)	1.439 (5)
O(3)-C(4)	1.444 (5)	1.436 (5)	C(10)-C(11)	1.503 (7)	1.503 (6)
C(4)-C(5)	1.509 (6)	1.513 (6)	C(11)-N(12)	1.464 (5)	1.473 (5)
C(5)-N(6)	1.472 (5)	1.469 (5)	C(11)-C(Me11A)	1.540 (7)	1.534 (6)
C(5)-C(Me5A)	1.524 (6)	1.534 (6)	C(11)-C(Me11B)	1.525 (7)	1.522 (6)
C(5)-C(Me5B)	1.522 (6)	1.515 (6)			
N(6)-C(1)-C(2)	113.3 (3)	112.4 (4)	N(12)-C(7)-C(8)	113.5 (4)	113.2 (4)
N(6)-C(1)-C(7)	106.9 (3)	106.3 (3)	N(12)-C(7)-C(1)	106.0 (3)	105.9 (3)
N(6)-C(1)-C(Me1)	111.4 (3)	110.6 (3)	N(12)-C(7)-C(Me7)	111.2 (3)	111.1 (3)
C(2)-C(1)-C(7)	104.7 (3)	106.1 (3)	C(8)-C(7)-C(1)	104.5 (3)	105.6 (3)
C(2)-C(1)-C(Me1)	107.3 (4)	107.8 (4)	C(8)-C(7)-C(Me7)	107.8 (4)	107.9 (4)
C(7)-C(1)-C(Me1)	113.2 (3)	113.7 (3)	C(1)-C(7)-C(Me7)	113.8 (3)	113.0 (3)
O(2)-C(2)-O(3)	117.8 (4)	118.7 (4)	O(8)-C(8)-O(9)	118.4 (5)	119.0 (5)
O(2)-C(2)-C(1)	120.5 (5)	119.9 (5)	O(8)-C(8)-C(7)	120.7 (6)	119.8 (5)
O(3)-C(2)-C(1)	121.7 (4)	121.5 (4)	O(9)-C(8)-C(7)	120.9 (5)	121.3 (5)
C(2)-O(3)-C(4)	119.1 (3)	120.2 (3)	C(8)-O(9)-C(10)	119.6 (4)	119.7 (4)
O(3)-C(4)-C(5)	111.2 (3)	110.7 (4)	O(9)-C(10)-C(11)	111.0 (5)	111.9 (4)
N(6)-C(5)-C(4)	105.3 (3)	105.7 (3)	N(12)-C(11)-C(10)	105.3 (4)	105.7 (4)
N(6)-C(5)-C(Me5A)	114.1 (3)	113.6 (3)	N(12)-C(11)-C(Me11A)	113.1 (4)	113.6 (4)
N(6)-C(5)-C(Me5B)	107.2 (3)	107.4 (3)	N(12)-C(11)-C(Me11B)	106.7 (4)	107.3 (3)
C(4)-C(5)-C(Me5A)	111.6 (4)	111.1 (4)	C(10)-C(11)-C(Me11A)	111.7 (5)	110.3 (4)
C(4)-C(5)-C(Me5B)	109.1 (4)	108.9 (4)	C(10)-C(11)-C(Me11B)	109.7 (5)	109.8 (4)
C(Me5A)-C(5)-C(Me5B)	109.4 (4)	109.9 (4)	C(Me11A)-C(11)-C(Me11B)	110.0 (5)	110.1 (4)
C(1)-N(6)-C(5)	117.5 (3)	118.8 (3)	C(7)-N(12)-C(11)	118.3 (3)	118.3 (3)

Table IV. Least-Squares Planes

A. Distances from Least-Squares Planes (Å)

	Molecule A (I)	Molecule B (III)		Molecule A (II)	Molecule B (IV)
C(1)	0.010 (4)	0.010 (4)	C(7)	−0.011 (4)	−0.012 (4)
C(2)	−0.005 (4)	−0.001 (4)	C(8)	−0.004 (5)	−0.001 (4)
O(3)	0.023 (3)	0.035 (3)	O(9)	−0.043 (4)	−0.031 (3)
C(4)	−0.035 (5)	−0.057 (5)	C(10)	0.077 (6)	0.050 (5)
O(2)	−0.011 (3)	−0.021 (3)	O(8)	0.023 (4)	0.020 (3)
C(Me1)	1.098	1.120	C(Me7)	−1.127	−1.113

B. Coefficients of the Equations of the Planes in the Form $ax + by + cz = d$[a]

	a	b	c	d
I	4.514	4.131	5.504	2.729
II	5.612	19.86	1.162	6.356
III	4.639	18.21	3.001	9.846
IV	5.680	0.2321	4.393	2.499

[a] The planes are calculated according to W. C. Hamilton, *Acta Crystallogr.*, **14,** 185 (1961). The parameters x, y, and z are fractional monoclinic coordinates.

unit cell, the calculated density is 1.210. Thus there are two crystallographically independent molecules of the dimer per asymmetric unit. From precision photographs and the absences observed in the measurement of the sphere of reflection, the space group is $P2_1/c$. The systematic absences are $h0l$ with l odd and $0k0$ with k odd. $F(000)$ is 1232. For Cu Kα radiation (λ = 1.5418 Å), the linear absorption coefficient is 7.4 cm^{-1}.

Intensity Measurements. Intensity measurements were made on a crystal of dimensions 0.6 × 0.2 × 0.15 mm using a Syntex P$\bar{1}$ autodiffractometer. The Syntex monochromator with a graphite crystal was used to obtain monochromatic radiation. The intensity measurements were made using the θ-2θ scanning techniques as programmed at Syntex. The scan speed was varied from 24°/min for reflections with more than 1500.0 counts in a 2-s scan to 4°/min for reflections with less than 150.0 counts in a 2-s scan. The scan ranges were calculated to start 1° below 2θ for Kα_1 and end 1° above 2θ for Kα_2. Background measurements were made at the beginning and end of each scan period for 1/4 of the scan time. Some 3500 independent reciprocal lattice points were surveyed within a single quadrant to $2\theta \leq 100.0°$. This corresponds to 49% of the copper sphere. The measurements were monitored every 40 measurement cycles by two reference reflections. The references showed no significant variation over the course of the experiment. Data were processed in the usual way with values of I_{obsd} and $\sigma(I_{\mathrm{obsd}})$ corrected for Lorentz and polarization effects. No correction was made for absorption. Of the 3500 independent points measured, 1935 were determined to have intensity significantly above background and were used in the solution and refinement of the structure. A reflection was taken as significant when $F_o^2 > 3.0*\sigma(F_o^2)$ and $\sigma(F_o^2) = \{\mathrm{TSC} + \mathrm{BACK} + [P*(\mathrm{TSC} - \mathrm{BACK})]^2\}^{1/2}*\mathrm{RLP}$. TSC is the total counts collected during the measurement scan and BACK, the total number of counts accumulated during the background measurements corrected for the difference between measurement scan time and background scan time. P, a damping factor to downweight stronger intensities, was given a value

Table V. Selected Intra- and Intermolecular Contacts

<table>
<tr><th></th><th>Molecule A</th><th>Molecule B</th></tr>
<tr><td colspan="3">Intramolecular Contacts (Å)</td></tr>
<tr><td>C(2)-N(12)</td><td>2.598 (5)</td><td>2.596 (5)</td></tr>
<tr><td>C(8)-N(6)</td><td>2.608 (5)</td><td>2.595 (6)</td></tr>
<tr><td>C(Me1)-C(Me5A)</td><td>3.481 (8)</td><td>3.519 (8)</td></tr>
<tr><td>C(Me1)-C(Me7)</td><td>2.943 (7)</td><td>2.926 (7)</td></tr>
<tr><td>C(Me7)-C(Me11A)</td><td>3.474 (8)</td><td>3.517 (8)</td></tr>
<tr><td>C(1)-H(1CMe7)</td><td>2.83</td><td>2.81</td></tr>
<tr><td>C(1)-H(3CMe7)</td><td>2.78</td><td>2.75</td></tr>
<tr><td>C(2)-H(1N12)</td><td>2.76</td><td>2.77</td></tr>
<tr><td>N(6)-H(1C10)</td><td>2.87</td><td>2.89</td></tr>
<tr><td>C(7)-H(1CMe1)</td><td>2.75</td><td>2.77</td></tr>
<tr><td>C(7)-H(2CMe1)</td><td>2.85</td><td>2.82</td></tr>
<tr><td>C(8)-H(1N6)</td><td>2.77</td><td>2.78</td></tr>
<tr><td>N(12)-H(1C4)</td><td>2.87</td><td>2.88</td></tr>
<tr><td>H(1CMe1)-H(3CMe7)</td><td>2.15</td><td>2.15</td></tr>
<tr><td>H(3CMe1)-H(1CMe5A)</td><td>2.41</td><td>2.41</td></tr>
<tr><td>H(3CMe5A)-H(3CMe5B)</td><td>2.41</td><td>2.43</td></tr>
<tr><td>H(2CMe5B)-H(1C4)</td><td>2.40</td><td>2.37</td></tr>
<tr><td>H(1CMe7)-H(1N12)</td><td>2.24</td><td>2.24</td></tr>
<tr><td>H(2CMe7)-H(3CMe11A)</td><td>2.43</td><td>2.38</td></tr>
<tr><td>H(1CMe11B)-H(1C10)</td><td>2.49</td><td>2.42</td></tr>
<tr><td>H(2CMe11B)-H(2C10)</td><td>2.45</td><td>2.52</td></tr>
<tr><td>H(3CMe11B)-H(1N12)</td><td>2.52</td><td>2.48</td></tr>
<tr><td colspan="3">Hydrogen Bonding Contacts (Å)^a</td></tr>
<tr><td>O(2)-N(6)^{I}</td><td colspan="2">3.08</td></tr>
<tr><td>O(2)-H(1N6)^{I}</td><td colspan="2">2.13</td></tr>
<tr><td>N(6)-O(2)^{II}</td><td colspan="2">3.13</td></tr>
<tr><td>H(1N6)-O(2)^{II}</td><td colspan="2">2.18</td></tr>
<tr><td>O(8)-N(12)^{II}</td><td colspan="2">3.16</td></tr>
<tr><td>O(8)-H(1N12)^{II}</td><td colspan="2">2.22</td></tr>
<tr><td>N(12)-O(8)^{I}</td><td colspan="2">3.16</td></tr>
<tr><td>H(1N12)-O(8)^{I}</td><td colspan="2">2.21</td></tr>
<tr><td colspan="3">Intermolecular Contacts (Å)^a</td></tr>
<tr><td>O(2)-C(Me1)^{I}</td><td colspan="2">3.43</td></tr>
<tr><td>O(3)-C(Me5A)^{III}</td><td colspan="2">3.38</td></tr>
<tr><td>C(Me1)-C(Me11A)^{IV}</td><td colspan="2">3.81</td></tr>
<tr><td>C(Me5B)-C(Me7)^{V}</td><td colspan="2">3.72</td></tr>
<tr><td>C(Me11A)-C(Me11A)^{VI}</td><td colspan="2">3.78</td></tr>
<tr><td>C(Me11B)-C(Me1)^{V}</td><td colspan="2">3.85</td></tr>
<tr><td>H(2C10)-H(3CMe5A)^{VII}</td><td colspan="2">2.59</td></tr>
<tr><td>H(1CMe1)-H(2CMe11B)^{IV}</td><td colspan="2">2.49</td></tr>
<tr><td>H(2CMe5A)-H(2CMe11B)^{VIII}</td><td colspan="2">2.60</td></tr>
<tr><td>H(2CMe5B)-H(2CMe5A)^{III}</td><td colspan="2">2.57</td></tr>
<tr><td>H(1CMe7)-H(1N6)^{I}</td><td colspan="2">2.59</td></tr>
</table>

[a] Contacts are between the first atom at x, y, z in molecule A and the second atom in molecule B at the symmetry related position denoted by the Roman superscript: I, $-1.0 + x, y, z$; II, x, y, z; III, $-x, 1.0 - y, 1.0 - z$; IV, $x, 0.5 - y, 0.5 + z$; V, $-x, 1.0 - y, -z$; VI, $-1.0 + x, 0.5 - y, -0.5 + z$; VII, $-1.0 + x, y, -1.0 + z$; VIII, $1.0 + x, y, 1.0 + z$.

of 0.04.[13] RLP, the reciprocal of the Lorentz and polarization correction, was defined as

$$\frac{2.0 * \sin\theta\cos\theta}{0.5\left(\dfrac{\cos^2 2\theta_{\rm mono} + \cos^2 2\theta}{1.0 + \cos^2 2\theta_{\rm mono}}\right) + 0.5\left(\dfrac{\cos 2\theta_{\rm mono} + \cos^2 2\theta}{1.0 + \cos 2\theta_{\rm mono}}\right)}$$

where $\theta_{\rm mono}$ is the monochromator angle.

Solution and Refinement of the Structure. The structure was solved by direct methods using the program MULTAN[14] which calculated phases for the 395 $|E|$s greater than or equal to 1.50. An E map was generated for the set of phases with the highest figures of merit; 35 of the 40 heavy atoms were found on this map. Two full-matrix least-squares[15] refinement cycles gave $R = 0.481$ and $wR = 0.485$. The remaining five nonhydrogen atoms were located on a subsequent Fourier map. Three more cycles of least-squares refinement of the 40 heavy atoms reduced R to 0.224 and wR to 0.222. Additional refinement with all atoms anisotropic converged with $R = 0.096$ and $wR = 0.118$. A three-dimensional difference map and maps in the planes of the methyl hydrogens revealed the positions of all 48 hydrogens. Idealized positions were determined for all hydrogens and their contribution to the structure factors were calculated. Final anisotropic refinement with the fixed contribution of the hydrogens removed converged with $R = 0.048$ and $wR = 0.051$. The standard deviation of an observation of unit weight was 1.405. The final difference map was flat and had no features with any structurally significant peaks. In the calculations atomic scattering curves were taken from the tabulations of Hanson and co-workers.[16]

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Supplementary Material Available. Observed and calculated structure factor amplitudes (7 pages). Ordering information is given on any current masthead page.

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