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The Crystal Structures of Two Photodimers of 6,6-Dimethyl-2,3-benzo-2,4-cycloheptadienone

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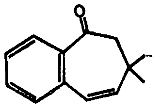
The structures of two photodimers of 6,6-dimethyl-2,3-benzo-2,4-cycloheptadienone, $C_{26}H_{28}O_2$, have been determined from room temperature X-ray diffractometer data. Dimer *A* crystallizes in the monoclinic space group $C2/c$ with $a=30{\cdot}141$ (16), $b=8{\cdot}536$ (4), $c=15{\cdot}979$ (6) Å and $\beta=103{\cdot}1$ (2)° and $Z=8$. Dimer *B* crystallizes in the monoclinic space group $P2_1/c$ with $a=7{\cdot}774$ (2), $b=15{\cdot}503$ (6), $c=16{\cdot}752$ (5) Å and $\beta=100{\cdot}95$ (2)° and $Z=4$. Both structures were solved by direct methods and refined by block-diagonal least-squares techniques to *R* values of 0·050 (1761 independent reflections) and 0·043 (1172 independent reflections) for dimer *A* and dimer *B* respectively. In both molecules the five- to six-membered ring juncture has been found to be *cis* and the six- to seven-membered ring juncture *trans*; however, in dimer *A* the hydrogen atoms H_b and H_c are *trans*, whereas, in dimer *B* they are *cis*. The location of strain in different regions of the two dimers is shown through a comparison of bond lengths and angles and dihedral angles. The conformations of the non-aromatic rings differ in the two molecules, those in dimer *A* being more flattened than those in dimer *B*.

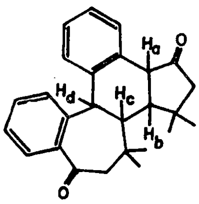
Introduction

Recent studies (Hart, 1973; Hart, Miyashi, Buchanan & Sasson, 1974) have indicated that photolysis of 6,6-dimethyl-2,3-benzo-2,4-cycloheptadienone (I) yields two crystalline dimers and no monomeric products.



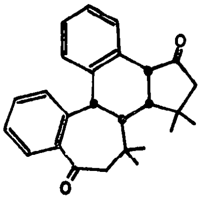
(I)

An infrared spectroscopic analysis of the reaction products shows that only one of the carbonyl groups remains conjugated, an indication that the products are not simple cyclobutane dimers. Chemical and p.m.r. techniques have established the dimers to be stereoisomers with the general structure (II) which contains four chiral centers.

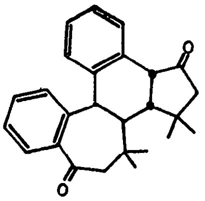


(II)

Mechanistic considerations (only two of eight possible dimers were detected, so the mechanism must be geometrically constrained) coupled with the knowledge gained from the chemical and spectroscopic investigations lead to two possible sets of structures. If a non-concerted mechanism with diradical intermediates is postulated (Hart, 1973) dimers (III) and (IV) would

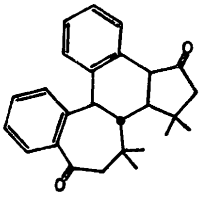


(III)

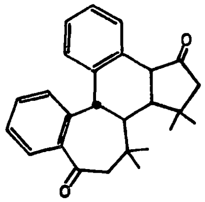


(IV)

result; if a concerted cycloaddition mechanism (*e.g.*, the Woodward–Hoffmann allowed $\pi 4s+\pi 2a$) is considered (Hart, Miyashi, Buchanan & Sasson, 1974) dimers (V) and (VI) would be produced. Spectroscopic and chemical data cannot distinguish conclusively between the two sets of possibilities. Thus, structural investigations of photodimers *A* and *B* were initiated.



(V)



(VI)

Experimental section

Crystals of 6,6-dimethyl-2,3-benzo-2,4-cycloheptadienone photodimers *A* and *B* (henceforth dimer *A* and dimer *B* respectively), $C_{26}H_{28}O_2$, were supplied by Professor H. Hart.

Dimer A

Crystals were in the form of clear, colorless, flat plates. Preliminary measurements of the lattice parameters and space-group determination were made by precession camera techniques with Mo $K\alpha$, Zr-filtered radiation. All subsequent measurements were made *via* a computer-controlled, four-circle, Picker goniostat with Mo $K\alpha$ radiation, graphite monochromator, and at a temperature of 23 (2) °C. The crystal used was roughly a rectangular prism ($0{\cdot}29 \times 0{\cdot}073 \times 0{\cdot}44$ mm) mounted with the long dimension [001] parallel to the φ axis of the goniostat. Cell constants were obtained from least-squares refinement of 12 reflections which had been carefully centered (Vandlen & Tulinsky, 1971). The density was determined by flotation in aqueous potassium bromide. Crystal data for both dimers are given in Table 1.

Three-dimensional, single-crystal intensity data in one quadrant (hkl, $hk\bar{l}$) to the limit $2\theta = 45°$ were collected by the ω-scan technique with a scan range of 0·7°, scan rate of 0·5° min^{-1}, and a $K\alpha_1$–$K\alpha_2$ dispersion factor of 0·692 (Furnas, 1966). The counting system employed a scintillation counter with pulse-height discrimination. Individual background measurements were made at the endpoints of the scan range for 10 s each. Filters were not used; three attenuators were used. The maximum standard deviation from the average intensities of three periodically monitored reflections ($00\bar{4}$, 204, $1\bar{3}1$) was 1·2%, an indication that the crystal had not suffered appreciable radiation damage during the seven days of data collection. 2916 reflections were collected, exclusive of standards.

The raw data were reduced as described previously (Biefeld & Eick, 1974) and considered for use in the refinement by the criterion $I > 2\sigma(I)$. An absorption correction was considered unnecessary in view of the small μ. The data were corrected for Lorentz and polarization effects by the program *INCOR* (Zalkin), which was altered to include a perpendicular monochromator correction. After Friedel pairs and equivalent reflections had been averaged, 2635 independent reflections remained with 1761 of these with intensities $> 2\sigma(I)$.

Dimer B

Crystals were in the form of clear, colorless, rectangular prisms. Preliminary space-group determination was made from an intensity-weighted plot of reciprocal space measured with a manual G.E. goniostat Measurement of cell dimensions and all subsequent measurements were made as described for dimer *A*. The crystal used was roughly a rectangular prism (*ca.* $0{\cdot}21 \times 0{\cdot}34 \times 0{\cdot}42$ mm) mounted with the long dimension [001] parallel to the φ axis of the goniostat. Three-dimensional single-crystal intensity data in one quadrant (hkl, $\bar{h}kl$) to the limit $2\theta = 40°$ were collected by the ω-scan technique with a scan range of 1·0° and scan rate of 1° min^{-1}. The counting system and individual background measurements were as described above. The random fluctuation of the three periodically monitored reflections (200, 040, 006) had excursions of less than 4·7% from the average for all three standards; an indication that the crystal had not suffered appreciable radiation damage during the data collection. 2041 reflections were measured exclusive of standards.

The data were reduced with the program *NUFACS* (Ibers, 1971). Errors in the intensities are calculated from equation (1):

$$\sigma(I) = [CT + 0{\cdot}25(t_c/t_b)^2(B_1 + B_2) + (pI)^2]^{1/2} \qquad (1)$$

in which CT is the total integrated peak count obtained in time t_c, B_1 and B_2 are the background counts each obtained in time t_b, $I = CT - (t_c/2t_b)\,(B_1 + B_2)$, and p is an instrumental drift factor chosen as 0·03. An absorption correction was considered unnecessary in view of the small μ. The data were corrected for Lorentz and polarization effects by *NUFACS*. Of 1836 independent reflections measured, 1172 had intensities $> 2\sigma(I)$.

Determination and refinement of the structures

Dimer A

Normalized structure factor magnitudes were calculated from the corrected intensity data *via* the program *FAME* (Dewar & Stone, 1969). The statistical distribution of the E's calculated from a Wilson plot of 20 intervals with the 2635 measured reflections is

Table 1. *Crystal data for dimers A and B*

	Dimer *A*	Dimer *B*
Molecular formula	$C_{26}H_{28}O_2$	$C_{26}H_{28}O_2$
M.W.	372·512	372·512
a	30·141 (16) Å	7·774 (2) Å
b	8·536 (4)	15·503 (6)
c	15·979 (6)	16·752 (5)
β	103·1 (2)°	100·95 (2)°
Systematic absences	hkl, $h+k=2n+1$	$h0l$, $l=2n+1$
	$h0l$, $l=2n+1$; $0k0$, $k=2n+1$	$0k0$, $k=2n+1$
Space group	$C2/c$, No. 15	$P2_1/c$, No. 14
V	4003·7 Å^3	1982·2 Å^3
Z	8	4
$F(000)$	1600 e	800 e
μ	0·823 cm^{-1} (Mo $K\alpha$)	0·830 cm^{-1} (Mo $K\alpha$)
D_{exp}	1·228 (2) g cm^{-3}	
D_{calc}	1·236 g cm^{-3}	1·248 g cm^{-3}
λ(Mo $K\alpha$, graphite monochromator)	0·70926 Å	0·70926 Å

consistent with a centrosymmetric distribution; thus, the space group was assumed to be $C2/c$ (No. 15).

The phase determination was accomplished by the symbolic addition procedure (Karle & Karle, 1966), facilitated through use of the program *MULTAN* (Germain, Main & Woolfson, 1971). Initial attempts at automatic phase determination with *MULTAN* with several different sets of origin-specifying reflections produced solutions, and subsequently E maps, in which the molecule was located too near a symmetry element. To give the program a better set of starting signs, a hand determination of the phases was initiated with the 200 reflections of largest E magnitudes. The phases of 39 reflections were determined in terms of signs or three symbols. The two origin-specifying reflections and the three reflections which had been assigned symbolic phases along with the 200 reflections of largest E magnitudes were processed through *MULTAN*. Of the eight possible solutions, the phases from the solution with the highest absolute figure of merit, ABS FOM (Germain, Main & Woolfson, 1971), produced an E map which contained peaks corresponding to the positions of all 28 nonhydrogen atoms.

Four cycles of full-matrix least-squares refinement (Zalkin) of positional and isotropic thermal parameters followed by two cycles of refinement on positional and anisotropic thermal parameters yielded an R value

Table 3. *Hydrogen atom positional* ($\times 10^4$) *and thermal parameters and their estimated standard deviations in parentheses for dimer A*

	x	y	z	B(Å^2)
H(2*A*)	4549 (8)	−3339 (30)	4041 (15)	4·0 (6)
H(2*B*)	4483 (9)	−1859 (32)	4620 (17)	5·4 (7)
H(4)	4065 (7)	22 (26)	2804 (14)	2·6 (6)
H(5)	3232 (7)	−977 (27)	2611 (14)	3·0 (6)
H(7*A*)	2575 (10)	460 (37)	1612 (19)	7·0 (8)
H(7*B*)	2605 (10)	2460 (34)	1558 (18)	6·3 (8)
H(9)	2945 (9)	−370 (34)	3757 (17)	5·4 (7)
H(11)	2642 (8)	2759 (30)	4182 (15)	3·9 (6)
H(12)	2983 (9)	4538 (33)	5359 (17)	5·8 (8)
H(13)	3789 (8)	4512 (33)	5916 (16)	5·0 (7)
H(14)	4281 (9)	2947 (33)	5348 (17)	5·6 (8)
H(16)	4169 (7)	90 (28)	4615 (15)	3·6 (6)
H(18)	4332 (8)	3798 (30)	3888 (15)	4·2 (7)
H(19)	5027 (10)	4893 (37)	3660 (18)	7·8 (10)
H(20)	5615 (8)	3028 (32)	3479 (16)	4·7 (7)
H(21)	5496 (8)	456 (30)	3525 (15)	3·7 (6)
H(23*A*)	3631 (10)	−2833 (35)	2221 (18)	6·5 (8)
H(23*B*)	4178 (9)	−2464 (32)	2345 (17)	5·5 (8)
H(23*C*)	4010 (10)	−4094 (38)	2766 (20)	7·9 (9)
H(24*A*)	3301 (9)	−2694 (35)	3631 (17)	6·3 (8)
H(24*B*)	3772 (9)	−3741 (32)	4233 (17)	5·6 (8)
H(24*C*)	3628 (8)	−2119 (30)	4468 (15)	4·4 (7)
H(25*A*)	3827 (11)	2634 (37)	2443 (20)	8·0 (9)
H(25*B*)	3408 (12)	3484 (42)	2728 (22)	10·3 (11)
H(25*C*)	3401 (10)	3353 (37)	1714 (19)	7·4 (9)
H(26*A*)	3709 (9)	344 (33)	1356 (17)	5·5 (8)
H(26*B*)	3288 (9)	1196 (35)	819 (18)	6·3 (8)
H(26*C*)	3176 (13)	−680 (49)	1037 (25)	12·2 (13)

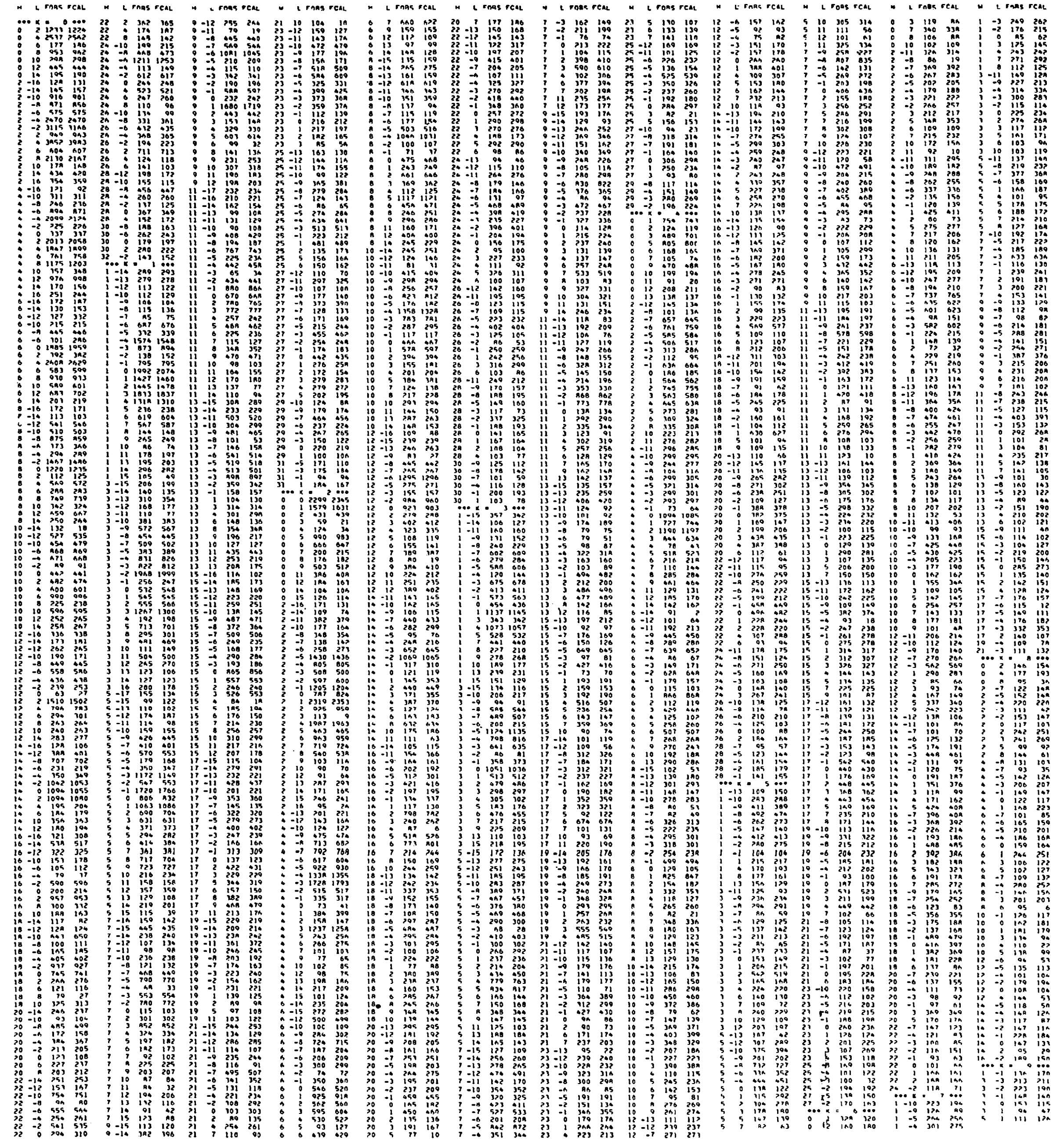
Table 2. *Final positional and thermal parameters* ($\times 10^4$) *of the nonhydrogen atoms and their estimated standard deviations in parentheses for dimer A*

The temperature factor is of the form $\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	4839 (1)	−1272 (4)	3755 (2)	9 (0)	184 (7)	38 (2)	10 (2)	−1 (1)	−14 (3)
C(2)	4465 (1)	−2161 (4)	4032 (2)	13 (1)	121 (6)	43 (2)	9 (2)	2 (1)	−8 (3)
C(3)	3979 (1)	−1975 (4)	3481 (2)	11 (0)	112 (6)	33 (2)	2 (1)	2 (1)	−9 (3)
C(4)	3866 (1)	−233 (4)	3258 (2)	9 (0)	115 (6)	33 (2)	2 (1)	4 (1)	0 (2)
C(5)	3362 (1)	60 (3)	2839 (2)	9 (0)	107 (6)	35 (2)	−1 (1)	2 (1)	−1 (2)
C(6)	3258 (1)	1185 (4)	2050 (2)	10 (0)	164 (7)	34 (2)	2 (1)	2 (1)	7 (3)
C(7)	2744 (1)	1424 (4)	1919 (2)	11 (0)	237 (8)	44 (2)	8 (2)	1 (1)	15 (3)
C(8)	2643 (1)	1269 (4)	2791 (2)	8 (0)	240 (8)	56 (2)	3 (2)	2 (1)	−6 (3)
C(9)	3058 (1)	648 (4)	3429 (2)	9 (0)	163 (7)	40 (2)	1 (1)	6 (1)	4 (3)
C(10)	3279 (1)	1860 (4)	4086 (2)	10 (0)	133 (6)	34 (2)	2 (1)	7 (1)	6 (3)
C(11)	3002 (1)	2810 (4)	4465 (2)	11 (0)	177 (7)	45 (2)	7 (2)	8 (1)	5 (3)
C(12)	3187 (1)	3833 (4)	5124 (2)	16 (1)	184 (7)	52 (2)	10 (2)	16 (1)	−2 (3)
C(13)	3652 (1)	3892 (4)	5421 (2)	17 (1)	159 (7)	35 (2)	6 (2)	10 (1)	−7 (3)
C(14)	3931 (1)	2959 (4)	5059 (2)	12 (0)	141 (6)	32 (2)	3 (1)	5 (1)	−0 (3)
C(15)	3751 (1)	1948 (4)	4370 (2)	10 (0)	116 (6)	33 (2)	1 (1)	5 (1)	5 (3)
C(16)	4071 (1)	824 (4)	4064 (2)	9 (0)	113 (6)	33 (2)	2 (1)	2 (1)	−6 (3)
C(17)	4517 (1)	1497 (4)	3918 (2)	9 (0)	142 (6)	30 (1)	−3 (1)	2 (1)	−13 (3)
C(18)	4588 (1)	3095 (4)	3858 (2)	11 (0)	157 (6)	46 (2)	−2 (1)	6 (1)	−7 (3)
C(19)	4985 (1)	3712 (4)	3694 (2)	14 (1)	180 (7)	56 (2)	−9 (2)	10 (1)	−19 (3)
C(20)	5324 (1)	2711 (4)	3584 (2)	12 (1)	225 (8)	58 (2)	−14 (2)	11 (1)	−25 (3)
C(21)	5259 (1)	1132 (4)	3612 (2)	9 (0)	221 (8)	48 (2)	1 (2)	5 (1)	−28 (3)
C(22)	4864 (1)	497 (4)	3776 (2)	8 (0)	154 (6)	36 (2)	0 (1)	2 (1)	−15 (3)
C(23)	3950 (1)	−2911 (4)	2651 (2)	13 (1)	155 (7)	50 (2)	1 (2)	3 (1)	−14 (3)
C(24)	3655 (1)	−2715 (4)	3976 (2)	15 (1)	156 (7)	55 (2)	2 (2)	9 (1)	21 (3)
C(25)	3500 (1)	2759 (4)	2230 (2)	16 (1)	178 (7)	49 (2)	−9 (2)	1 (1)	28 (3)
C(26)	3375 (1)	399 (5)	1262 (2)	15 (1)	283 (9)	39 (2)	4 (2)	3 (1)	10 (4)
O(1)	5135 (1)	−2022 (3)	3528 (2)	13 (0)	221 (5)	82 (2)	18 (1)	9 (1)	−27 (3)
O(2)	2280 (1)	1561 (4)	2958 (2)	10 (0)	514 (9)	74 (2)	24 (2)	6 (1)	−7 (3)

of 0·124 where $R=[\sum w(\Delta F)/w(F_o)]$, $w=1/\sigma_F^2$ and $\sigma_F=\sigma(I)F/2I$. The large number of parameters prevented simultaneous refinement of nonhydrogen and hydrogen atom parameters. Thus, block-diagonal least-squares refinement procedures (Sparks & Trueblood, undated) were used in the calculations. Four cycles of block-diagonal least-squares treatment on the non-hydrogen atom positional and anisotropic thermal parameters yielded an R of 0·119. A difference Fourier map (Rao, 1966) calculated at this point revealed the positions of all 28 hydrogen atoms. Three cycles of block-diagonal refinement were carried out with the carbon and oxygen atomic parameters variable and the hydrogen atom positional and isotropic thermal (6·00 Å^2) parameters fixed; the R value decreased to 0·080. Nine cycles of least-squares refinement with all atomic parameters varying served to complete the structure refinement. The largest parameter shift in the final cycle was less than 0·4 of one estimated standard deviation (e.s.d.). A final difference Fourier map contained

Table 4. *Calculated and observed structure factor magnitudes for dimer A*



no features other than a randomly fluctuating background below 0·2 e.Å^{-3}.

Cromer & Waber's (1965) scattering factors for neutral atoms were used for carbon and oxygen, while those of Stewart, Davidson & Simpson (1965) were used for hydrogen. The final atomic positional and thermal parameters appear in Tables 2 and 3; the hydrogen-atom numbers match those of the carbon atoms to which they are bonded. The e.s.d.'s were calculated from the inverse matrices of the final block-diagonal least-squares cycle. Final R values, weighted and unweighted, respectively, are 0·043 and 0·050 for the 1761 reflections with $I > 2\sigma(I)$. Calculated and observed structure factor magnitudes ($\times 10$) appear in Table 4.

Dimer B

Normalized structure factor magnitudes were calculated from the corrected intensity data *via* the program *FAME* (Dewar & Stone, 1969). The statistical distribution calculated from a Wilson plot of 20 intervals with the 1836 measured reflections is consistent with a centrosymmetric distribution as required by the space group $P2_1/c$.

The phase determination was accomplished by the symbolic addition procedure (Karle & Karle, 1966), facilitated by the program *MULTAN* (Germain, Main

Table 6. *Hydrogen atom positional* ($\times 10^3$) *and thermal parameters and their estimated standard deviations in parentheses for dimer B*

	x	y	z	B(Å^2)
H(2*A*)	−458 (6)	89 (3)	−14 (3)	4·9 (13)
H(2*B*)	−479 (5)	178 (3)	24 (3)	3·7 (11)
H(4)	−255 (4)	229 (2)	136 (2)	1·3 (8)
H(5)	−161 (5)	169 (2)	251 (2)	1·8 (9)
H(7*A*)	53 (6)	132 (3)	379 (3)	4·1 (11)
H(7*B*)	268 (6)	131 (3)	374 (3)	4·2 (12)
H(9)	−80 (5)	312 (2)	251 (2)	1·5 (8)
H(11)	319 (6)	360 (3)	294 (3)	4·4 (12)
H(12)	532 (5)	393 (3)	221 (2)	2·8 (10)
H(13)	497 (5)	362 (3)	88 (2)	2·4 (9)
H(14)	248 (6)	281 (3)	28 (3)	4·4 (12)
H(16)	10 (4)	185 (2)	43 (2)	0·9 (8)
H(18)	−34 (5)	407 (3)	75 (3)	3·4 (10)
H(19)	−204 (6)	506 (3)	−14 (3)	4·4 (12)
H(20)	−398 (7)	457 (4)	−127 (3)	7·7 (16)
H(21)	−440 (6)	303 (3)	−148 (3)	5·5 (13)
H(23*A*)	−456 (6)	29 (3)	119 (3)	5·9 (13)
H(23*B*)	−315 (6)	42 (3)	189 (3)	5·6 (13)
H(23*C*)	−455 (6)	118 (3)	154 (3)	5·9 (14)
H(24*A*)	−211 (6)	−15 (3)	47 (3)	5·8 (13)
H(24*B*)	−43 (7)	21 (4)	105 (3)	7·7 (16)
H(24*C*)	−86 (6)	52 (3)	20 (3)	4·9 (12)
H(25*A*)	−97 (6)	24 (3)	299 (3)	4·3 (12)
H(25B)	−27 (7)	−15 (3)	224 (3)	5·9 (14)
H(25*C*)	100 (6)	−19 (3)	303 (3)	5·4 (13)
H(26*A*)	308 (7)	152 (3)	221 (3)	6·4 (15)
H(26*B*)	197 (6)	85 (3)	163 (3)	4·3 (12)
H(26*C*)	311 (6)	52 (3)	247 (3)	4·7 (12)

Table 5. *Final positional and thermal parameters* ($\times 10^4$) *of the nonhydrogen atoms and their estimated standard deviations in parentheses for dimer B*

The temperature factor is of the form $\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	−3123 (7)	1758 (4)	−586 (3)	142 (12)	58 (4)	31 (2)	8 (5)	−17 (5)	−12 (3)
C(2)	−3863 (7)	1364 (4)	98 (3)	152 (12)	49 (3)	45 (3)	−11 (5)	5 (5)	−12 (3)
C(3)	−2581 (7)	1091 (3)	884 (3)	180 (12)	34 (3)	31 (2)	−4 (5)	14 (4)	−10 (2)
C(4)	−1543 (6)	1886 (3)	1299 (3)	119 (10)	34 (3)	22 (2)	−4 (4)	11 (4)	−3 (2)
C(5)	−645 (6)	1790 (3)	2215 (3)	131 (11)	34 (3)	28 (2)	−7 (4)	25 (4)	3 (2)
C(6)	767 (7)	1104 (3)	2611 (3)	169 (12)	34 (3)	29 (2)	3 (5)	12 (4)	6 (2)
C(7)	1351 (7)	1519 (4)	3465 (3)	219 (14)	55 (3)	29 (3)	1 (6)	18 (5)	12 (2)
C(8)	1066 (7)	2475 (4)	3388 (3)	229 (13)	51 (3)	29 (2)	−25 (6)	25 (5)	−1 (2)
C(9)	164 (7)	2670 (3)	2524 (3)	165 (11)	39 (3)	24 (2)	3 (5)	10 (4)	0 (2)
C(10)	1499 (6)	2979 (3)	2029 (3)	140 (11)	29 (3)	22 (2)	0 (4)	2 (4)	1 (2)
C(11)	2995 (7)	3417 (4)	2394 (3)	176 (13)	49 (3)	20 (2)	−3 (5)	−1 (4)	4 (2)
C(12)	4293 (7)	3630 (4)	1961 (3)	184 (13)	43 (3)	34 (3)	−31 (5)	−21 (5)	1 (2)
C(13)	4093 (7)	3396 (3)	1145 (3)	132 (12)	40 (3)	43 (3)	−3 (5)	9 (5)	11 (2)
C(14)	2597 (6)	2966 (3)	791 (3)	128 (11)	41 (3)	27 (2)	2 (4)	4 (4)	5 (2)
C(15)	1287 (6)	2762 (3)	1217 (3)	133 (10)	28 (3)	19 (2)	5 (4)	2 (4)	−0 (2)
C(16)	−368 (6)	2330 (3)	760 (3)	143 (11)	31 (3)	27 (2)	7 (4)	18 (4)	−3 (2)
C(17)	−1444 (6)	2981 (3)	181 (3)	128 (10)	29 (3)	20 (2)	9 (4)	7 (4)	−1 (2)
C(18)	−1275 (6)	3863 (3)	287 (3)	141 (11)	41 (3)	25 (2)	−1 (5)	6 (4)	−2 (2)
C(19)	−2252 (7)	4444 (3)	−246 (3)	184 (13)	39 (3)	43 (3)	5 (5)	3 (5)	10 (2)
C(20)	−3386 (8)	4147 (4)	−920 (4)	213 (14)	51 (4)	49 (3)	16 (6)	−13 (5)	20 (3)
C(21)	−3581 (7)	3279 (4)	−1049 (3)	180 (13)	64 (4)	32 (3)	3 (6)	−17 (5)	8 (3)
C(22)	−2654 (6)	2690 (3)	−491 (3)	155 (11)	44 (3)	28 (2)	−1 (5)	9 (4)	1 (2)
C(23)	−3770 (7)	729 (4)	1438 (4)	194 (14)	48 (3)	58 (3)	−26 (5)	35 (6)	−3 (3)
C(24)	−1434 (8)	376 (4)	636 (3)	225 (14)	39 (3)	42 (3)	4 (5)	19 (5)	−8 (2)
C(25)	49 (8)	207 (4)	2732 (3)	288 (16)	36 (3)	49 (3)	8 (6)	39 (6)	14 (3)
C(26)	2363 (7)	1016 (4)	2213 (3)	186 (13)	39 (3)	41 (3)	25 (5)	17 (5)	11 (2)
O(1)	−3036 (6)	1354 (3)	−1205 (2)	347 (12)	72 (3)	35 (2)	−5 (4)	3 (4)	−17 (2)
O(2)	1493 (6)	3000 (3)	3922 (2)	437 (13)	66 (3)	24 (2)	−34 (5)	2 (4)	−9 (2)

& Woolfson, 1971). The phases from the solution with the highest absolute figure of merit, ABS FOM (Germain, Main & Woolfson, 1971), produced an E map which contained peaks corresponding to all 28 non-hydrogen atoms.

Eleven cycles of block-diagonal least-squares (Sparks & Trueblood, undated) refinement of positional and isotropic thermal parameters followed by twelve cycles of refinement on positional and anisotropic thermal parameters yielded an R value of 0·102 where R is as defined above. A difference Fourier map (Rao, 1966) calculated at this point contained peaks (of more than 0·3 e.Å^{-3}) which corresponded to probable positions of all hydrogen atoms. Nine cycles of block-diagonal least-squares refinement were carried out with the carbon and oxygen parameters variable and the hydrogen atom positional and isotropic thermal parameters fixed; the R value decreased to 0·050. Seven

Table 7. *Calculated and observed structure factor magnitudes for dimer B*

K	L	FOBS	FCAL
*** H = -7 ***			
0	2	65	16-
0	4	109	103
0	6	67	6-
0	8	76	124-
1	1	66	3-
1	2	133	116
1	3	145	149
1	4	106	124
1	5	130	136
1	6	71	83-
1	7	68	7-
1	8	69	47-
2	1	207	208
2	2	67	59-
2	3	67	52-
2	4	130	132
2	5	66	41-
2	6	83	72
2	7	68	9-
2	8	134	135
3	1	106	105
3	2	114	121
3	3	130	126
3	4	161	157
3	5	135	142
3	6	68	50-
3	7	69	36-
4	1	72	67
4	2	118	127
4	3	67	16-
4	4	78	87
4	5	120	106
4	6	124	121
5	1	69	43-
5	2	69	23-
5	3	68	40-
5	4	69	36-
*** H = -6 ***			
0	2	63	22-
0	4	63	24-
0	6	67	37-
0	8	234	234
0	10	69	17-
1	0	133	132
1	1	65	10-
1	2	203	204
1	3	98	91
1	4	138	156
1	5	65	5-
1	6	66	40-
1	7	65	26-
1	8	177	180
1	9	196	192
1	10	103	100
1	11	98	87
2	0	61	31-
2	1	79	86
2	2	99	95
2	3	264	260
2	4	78	78
2	5	69	60-
2	6	111	100
2	7	69	59-
2	8	217	222
2	9	69	20-
2	10	72	52-
2	11	69	3-
3	0	82	81
3	1	66	44
3	2	92	96
3	3	143	146
3	4	119	118
3	5	171	173
3	6	69	74-
3	7	68	43-
3	8	71	71-
3	9	68	36-
3	10	92	76
3	11	73	46
4	0	133	141
4	1	67	14
4	2	196	207
4	3	237	253
4	4	71	36
4	5	68	27-
4	6	110	106
4	7	131	133
4	8	121	122
4	9	72	50-
4	10	72	68-
5	0	63	6-
5	1	161	158
5	2	235	242
5	3	104	92
5	4	109	117
5	5	293	288
5	6	83	78
5	7	72	4-
5	8	70	35-
5	9	72	3-
5	10	72	7-
6	0	99	97
6	1	67	36-
6	2	71	85-
6	3	66	1-
6	4	78	75
6	5	68	3-
6	6	134	130
6	7	142	137
6	8	68	23-
6	9	71	33-
7	1	67	38-
7	2	69	90-
7	3	120	139
7	4	94	100
7	5	127	110
7	6	71	63
7	7	68	18-
7	8	72	80-
8	2	67	27-
8	3	95	83
8	4	64	45-
8	5	68	41-
8	6	68	6-
*** H = -5 ***			
0	2	58	87-
0	4	125	126
0	6	164	163
0	8	454	462
0	10	193	203
0	12	69	23-
1	1	67	60
1	2	133	114
1	3	55	21-
1	4	101	92
1	5	61	27-
1	6	75	86
1	7	77	75
1	8	66	62-
1	9	71	49-
1	10	78	61
1	11	73	43-
1	12	88	89
1	13	71	16-
2	1	148	157
2	2	56	5-
2	3	175	173
2	4	94	92
2	5	60	38-
2	6	176	168
2	7	93	99
2	8	82	97
2	9	244	252
2	10	92	73
2	11	179	191
2	12	104	109
2	13	74	2-
3	1	55	6-
3	2	119	130
3	3	44	62
3	4	95	75
3	5	61	1-
3	6	64	56-
3	7	149	134
3	8	65	46-
3	9	69	59-
3	10	103	116
3	11	105	111
3	12	117	103
3	13	100	95
4	1	81	98
4	2	81	87
4	4	327	322
4	5	105	110
4	6	230	237
4	7	139	147
4	8	68	52-
4	9	67	11-
4	10	168	148
4	11	73	17-
4	12	71	46-
4	13	121	93
5	1	62	70-
5	2	59	39-
5	3	92	75
5	4	62	55
5	5	272	289
5	6	65	45-
5	7	65	4-
5	8	67	50-
5	9	83	82
5	10	73	50-
5	11	201	196
5	12	127	139
6	1	61	16-
6	2	157	168
6	3	101	111
6	4	64	24-
6	5	67	53-
6	6	85	99
6	7	64	19-
6	8	70	15-
6	9	70	3-
6	10	71	8-
6	11	75	74
6	12	75	5-
7	1	195	202
7	2	257	256
7	3	181	181
7	4	343	338
7	5	325	324
7	6	69	38-
7	7	75	72
7	8	117	132
7	9	71	15-
7	10	70	16-
7	11	75	32-
8	1	117	95
8	2	116	116
8	3	243	256
8	4	66	13-
8	5	233	245
8	6	72	77
8	7	65	54-
8	8	70	70-
8	9	138	129
8	10	72	40-
9	1	170	178
9	2	149	153
9	3	147	147
9	4	120	115
9	5	91	69
9	6	71	5-
9	7	82	64
9	8	87	83
9	9	76	67-
10	1	66	26-
10	2	93	107
10	3	69	59-
10	4	49	26-
10	5	70	52-
10	6	67	7-
10	7	68	2-
11	1	68	44-
11	2	174	177
11	3	68	7-
*** H = -4 ***			
0	2	49	19-
0	4	826	826
0	6	775	774
0	8	115	113
0	10	80	85
0	12	146	155
0	14	75	48
1	1	128	122
1	2	168	168
1	4	247	250
1	5	64	61
1	7	60	59-
1	8	456	464
1	9	162	154
1	10	127	143
1	11	118	120
1	12	255	259
1	13	87	103
1	14	264	266
1	15	151	156
2	1	50	11-
2	2	149	143
2	3	53	49-
2	4	226	225
2	5	222	220
2	6	283	276
2	7	58	1-
2	8	139	146
2	9	65	36-
2	10	74	95
2	11	95	96
2	12	175	180
2	13	124	134
2	14	74	23-
3	1	329	328
3	2	68	81
3	3	55	88-
3	4	258	253
3	5	119	128
3	6	116	120
3	7	60	62-
3	8	194	189
3	9	66	44-
3	10	128	127
3	11	71	55-
3	12	69	3-
3	13	86	76
3	14	90	89
4	1	67	59
4	2	56	53-
4	3	226	227
4	4	203	186
4	5	140	127
4	6	102	94
4	7	127	101
4	8	63	15-
4	9	67	44-
4	10	72	93-
4	11	74	71-
4	12	75	61-
4	13	93	67
4	14	75	64-
5	1	136	125
5	2	105	106
5	3	142	157
5	4	57	58-
5	5	58	13-
5	6	154	145
5	7	247	252
5	8	67	11-
5	9	72	83
5	10	100	95
5	11	82	86
5	12	194	183
5	13	128	130
6	1	98	90
6	2	55	15-
6	3	59	36
6	4	83	76
6	5	60	49-
6	6	118	102
6	7	63	46-
6	8	67	65-
6	9	70	50-
6	10	83	85
6	11	261	256
6	12	73	67-
6	13	75	58-
7	1	149	148
7	2	238	249
7	3	60	51
7	4	143	148
7	5	128	119
7	6	71	81
7	7	65	40-
7	8	127	141
7	9	162	178
7	10	70	7-
7	11	76	37-
7	12	77	78
8	1	142	147
8	2	196	198
8	3	149	144
8	4	184	193
8	5	64	13
8	6	171	166
8	7	78	70
8	8	78	83
8	9	71	7-
8	10	76	94
8	11	146	151
8	12	75	10-
9	1	185	185
9	2	69	61
9	3	198	208
9	4	264	258
9	5	66	31-
9	6	69	32-
9	7	72	87-
9	8	185	185
9	9	100	85
9	10	73	8-
9	11	73	14-
10	1	158	166
10	2	68	44-
10	3	116	101
10	4	67	50-
10	5	211	220
10	6	77	95
10	7	86	38-
10	8	70	20-
10	9	72	65-
11	1	64	24-
11	2	68	64-
11	3	212	212
11	4	106	105
11	5	115	111
11	6	82	65
11	7	71	71-
11	8	88	99
12	1	68	65-
12	2	67	5-
12	3	150	148
12	4	144	132
12	5	119	122
*** H = -3 ***			
0	2	745	747
0	6	1224	1222
0	8	155	169
0	10	311	319
0	12	479	484
0	14	241	261
1	1	113	116
1	2	152	169
1	3	47	33-
1	4	335	326
1	5	557	553
1	6	132	149
1	7	346	350
1	9	60	18-
1	10	151	161
1	11	109	108
1	12	74	9-
1	13	127	118
1	14	354	352
1	15	77	69-
2	1	96	96
2	2	103	113
2	3	179	159
2	4	135	135
2	5	596	581
2	6	484	469
2	7	59	71-
2	8	213	228
2	9	60	27-
2	10	64	13-
2	11	83	76
2	12	248	255
2	13	170	172
2	14	99	108
2	15	135	133
3	1	72	63
3	2	198	200
3	3	70	66
3	4	202	200
3	5	519	504
3	6	255	250
3	7	60	69-
3	8	252	252
3	9	64	56-
3	10	66	27-
3	11	345	360
3	12	119	114
3	13	172	174
3	14	79	77-
3	15	140	126
4	1	217	233
4	2	369	359
4	3	57	53
4	4	53	67-
4	5	130	119
4	6	67	66
4	7	62	63-
4	8	97	91
4	9	135	140
4	10	141	148
4	11	256	249
4	12	76	33-
4	13	73	20-
4	14	76	46-
4	15	81	45-
5	1	181	174
5	2	93	101
5	3	51	21-
5	4	264	266
5	5	142	147
5	6	243	238
5	7	75	68
5	8	66	39
5	9	69	73-
5	10	68	44-
5	11	70	32-
5	12	80	86
5	13	75	9-
5	14	79	7-
6	1	345	335
6	2	81	87
6	3	93	85
6	4	155	162
6	5	305	304
6	6	68	63
6	7	110	104
6	8	140	134
6	9	87	92
6	10	69	7-
6	11	84	82
6	12	77	67-
6	13	94	97
6	14	80	59-
7	1	99	102
7	2	271	268
7	3	176	169
7	4	78	85
7	5	242	249
7	6	216	216
7	7	67	60
7	8	63	27-
7	9	69	9-
7	10	71	38-
7	11	76	68-
7	12	175	162
7	13	78	66-
8	1	56	36-
8	2	58	40-
8	3	219	234
8	4	102	92
8	5	63	51
8	6	64	28-
8	7	65	20-
8	8	93	81
8	9	71	28-
8	10	72	65-
8	11	119	101
8	12	76	30-
8	13	78	30-
9	1	188	184
9	2	170	161
9	3	155	159
9	4	70	65
9	5	63	38-
9	6	66	9-
9	7	69	22-
9	8	70	57-
9	9	72	68-
9	10	73	16-
9	11	73	26-
9	12	76	67-
10	1	78	67
10	2	62	21-
10	3	83	81
10	4	65	27-
10	5	69	76-
10	6	66	28-
10	7	68	2-
10	8	69	14-
10	9	69	3-
10	10	136	155
10	11	76	63-
11	1	145	148
11	2	61	12-
11	3	164	153
11	4	99	74
11	5	69	69-
11	6	69	2-
11	7	155	146
11	8	93	81
11	9	158	158
12	1	158	159
12	2	69	52
12	3	215	215
12	4	201	182
12	5	159	161
12	6	94	107
12	7	71	63-
12	8	69	4-
13	1	70	4-
13	2	99	111
13	3	185	189
13	4	67	0-
13	5	91	118
*** H = -2 ***			
0	2	2130	2157
0	4	164	159
0	6	139	134
0	8	217	218
0	10	203	200
0	12	128	134
0	14	144	135
0	16	154	147
1	1	322	330
1	2	409	388
1	3	431	423
1	4	1060	1059
1	5	51	52
1	6	51	16-
1	7	282	285
1	8	58	33-
1	9	59	18-
1	10	63	24-
1	11	75	73
1	12	71	33-
1	13	152	164
1	14	112	108
1	15	80	70-
1	16	78	45-
2	1	439	438
2	2	576	587
2	3	510	512
2	4	189	184
2	5	118	122
2	6	249	259
2	7	357	365
2	8	106	107
2	9	65	62
2	10	80	92
2	11	119	119
2	12	148	142
2	13	109	96
2	14	183	168
2	15	78	46-
3	1	87	82
3	2	45	10-
3	3	197	189
3	4	82	96
3	5	516	511
3	6	181	181
3	7	57	0-
3	8	59	12-
3	9	94	84
3	10	67	74-
3	11	115	132
3	12	74	13-
3	13	389	408
3	14	128	140
3	15	78	25-
4	1	177	164
4	2	101	96
4	3	286	277
4	4	161	162
4	5	530	531
4	6	477	459
4	7	212	206
4	8	58	49-
4	9	131	128
4	10	228	234
4	11	136	148
4	12	195	197
4	13	79	15-
4	14	83	89
4	15	208	199
5	1	339	335
5	2	314	302
5	3	185	182
5	4	420	408
5	5	53	43-
5	6	74	75
5	7	194	192
5	8	61	26-
5	9	122	108
5	10	77	71
5	11	72	51-
5	12	78	71
5	13	213	206
5	14	137	140
5	15	80	2-
6	1	443	441
6	2	425	431
6	3	51	35-
6	4	118	115
6	5	125	117
6	6	333	327
6	7	87	84
6	8	63	7-
6	9	284	284
6	10	84	86
6	11	74	72-
6	12	101	91
6	13	132	136
6	14	106	113
7	1	55	80-
7	2	177	172
7	3	59	62
7	4	57	53-
7	5	58	9-
7	6	60	39-
7	7	80	83
7	8	182	178
7	9	67	23-
7	10	71	22-
7	11	102	115
7	12	81	89
7	13	75	3-
7	14	114	91
8	1	188	187
8	2	54	11-
8	3	63	71
8	4	356	345
8	5	191	186
8	6	179	181
8	7	65	78-
8	8	144	138
8	9	71	1-
8	10	75	63-
8	11	75	16-
8	12	141	131
8	13	85	46
9	1	59	52-
9	2	74	77
9	3	63	46
9	4	59	30-
9	5	158	167
9	6	278	279
9	7	256	255
9	8	176	173
9	9	123	124
9	10	84	70
9	11	77	2-
9	12	74	8-
10	1	60	10-
10	2	63	53-
10	3	62	54-
10	4	62	73-
10	5	208	203
10	6	131	108
10	7	97	91
10	8	74	73-
10	9	99	118
10	10	276	278
10	11	74	13-
11	1	92	90
11	2	62	1-
11	3	63	41-
11	4	133	133
11	5	64	43-
11	6	75	70
11	7	79	88
11	8	88	63
11	9	73	61-
11	10	139	127
12	1	69	51-
12	2	65	3-
12	3	182	177
12	4	68	23-
12	5	149	164
12	6	71	1-
12	7	70	60-
12	8	74	75-
12	9	185	179
13	1	189	196
13	2	75	59
13	3	70	63
13	4	69	34-
13	5	150	151
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0	4	54	6-
0	6	160	150
0	10	162	146
1	0	277	281
1	1	80	96
1	3	210	211
1	4	278	275
1	5	57	32-
1	6	61	13-
1	7	91	84
1	8	67	27-
1	9	69	5-
1	10	388	408
2	0	168	179
2	1	54	67-
2	2	109	104
2	3	100	104
2	4	55	5-
2	5	120	125
2	6	182	181
2	7	177	181
2	8	284	295
2	9	72	58-
2	10	261	260
2	11	308	307
3	0	54	45
3	1	102	95
3	2	55	4-
3	3	244	254
3	4	97	84
3	5	237	229
3	6	69	86-
3	7	67	9-
3	8	192	177
3	9	84	85
3	10	69	7-
3	11	121	114
4	0	205	204
4	1	58	67-
4	2	192	190
4	3	54	17
4	4	257	253
4	5	62	41-
4	6	87	101
4	7	164	186
4	8	75	72
4	9	68	14-
4	10	84	81
5	0	140	160
5	1	84	63
5	2	114	110
5	3	165	159
5	4	137	130
5	5	194	197
5	6	66	10-
5	7	163	168
5	8	69	12-
5	9	74	69
6	0	218	208
6	1	59	49-
6	2	143	149
6	3	102	112
6	4	69	92
6	5	92	103
6	6	88	75
6	7	96	58
6	8	93	91
6	9	105	95
6	10	75	46-
7	0	61	47
7	1	57	10-
7	2	62	42-
7	3	164	161
7	4	65	16-
7	5	152	145
7	6	69	45-
7	7	69	2-
7	8	73	76-
7	9	72	67-
8	0	181	188
8	1	74	51
8	2	62	5-
8	3	154	144
8	4	65	42-
8	5	68	47-
8	6	155	163
8	7	86	59
8	8	71	37-
9	0	63	31-
9	1	92	83
9	2	83	86
9	3	168	158
9	4	82	58
9	5	109	99
9	6	96	116
9	7	89	77
10	0	65	9-
10	1	86	81
10	2	92	100
10	3	179	131
10	4	137	152
10	5	112	114
10	6	74	24-
11	0	70	67
11	1	104	111
11	2	69	44-
11	3	104	102
11	4	73	35-
12	0	70	38-
12	1	69	66-
12	2	69	20-
*** H = 5 ***			
0	2	61	56-
0	4	58	8-
1	0	63	66
1	1	100	96
1	2	242	254
2	0	181	181
2	1	73	69
2	2	60	11-
2	3	60	59-
2	4	72	66
2	5	171	178
2	6	70	3-
2	7	148	152
2	8	69	45-
2	9	70	3-
3	0	260	270
3	1	61	36-
3	2	59	18-
3	3	165	170
3	4	126	109
3	5	269	262
3	6	158	160
3	8	149	136
3	9	71	13-
4	0	77	84
4	1	136	113
4	2	106	95
4	3	64	13-
4	4	64	50-
4	5	65	63-
4	6	138	145
4	7	65	10-
4	8	74	111-
5	0	151	152
5	1	58	6-
5	2	202	203
5	3	66	84-
5	4	65	13-
5	5	110	113
5	7	70	47-
5	8	68	22
6	0	59	33-
6	1	112	110
6	2	65	16-
6	3	67	62-
6	4	109	118
6	5	67	9-
6	6	200	193
6	7	67	21-
7	0	64	60-
7	1	62	39-
7	2	154	162
7	3	102	107
7	4	96	109
7	5	69	52-
7	6	161	130
7	7	68	11-
8	0	68	15-
8	1	179	142
8	2	80	64
8	3	68	41-
8	4	209	215
8	5	70	37-
8	6	186	191
9	0	68	52-
9	1	109	109
9	2	69	75-
9	3	180	199
9	4	84	72
10	0	69	44-
10	1	68	47-
10	2	68	51-
10	3	72	42-
*** H = 6 ***			
0	0	63	10-
0	2	67	59
0	4	94	89
0	6	70	24-
1	0	141	132
1	1	61	30-
1	2	64	5-
1	3	114	101
1	4	67	42-
1	5	66	25-
1	6	68	57-
2	0	61	31-
2	1	61	18-
2	2	63	46-
2	3	66	28-
2	4	112	120
2	5	239	237
2	6	146	140
3	0	80	81
3	1	65	44-
3	2	142	135
3	3	66	54-
3	4	71	56-
3	5	71	76-
3	6	84	88
4	0	150	141
4	1	68	1-
4	2	74	61
4	3	69	75-
4	4	166	166
4	5	163	149
4	6	70	61-
5	0	68	6-
5	1	120	103
5	2	67	39-
5	3	66	47-
5	4	155	157
5	5	135	128
6	0	93	97
6	1	81	84
6	2	67	49-
6	3	110	102
6	4	69	46-
7	0	66	50-
7	1	66	1-
7	2	82	82
7	3	68	2-
8	0	145	132
8	1	205	199
*** H = 7 ***			
0	0	242	237
0	2	68	47-
1	0	110	94
1	1	70	13-
1	2	102	100
2	0	191	196
2	1	130	141
2	2	129	106
3	0	103	92
3	1	68	51-
4	0	69	68-

cycles of block-diagonal least-squares refinement with all atomic parameters varying served to complete the structure refinement. The largest parameter shift in the final cycle was less than 0·35 of one e.s.d. A final difference Fourier map contained no features other than a randomly fluctuating background below 0·3 e.Å^{-3}.

The scattering factors were those employed for dimer *A*. The final atomic positional and thermal parameters appear in Tables 5 and 6; the atom numbering scheme is the same as that used for dimer *A*. The e.s.d.'s were calculated from the inverse matrices of the final least-squares cycle. Final *R* values, weighted and unweighted, respectively, are 0·043 and 0·044 for the 1172 reflections with $I > 2\sigma(I)$. Calculated and observed structure factor magnitudes (×10) appear in Table 7.

Results

The X-ray structural analyses have established the configurations of dimers *A* and *B* as those of (V) and (VI) respectively. The structures of dimers *A* and *B* are illustrated in the stereoscopic drawings (Johnson, 1965) of Figs. 1 and 2, respectively, which show 20% equiprobability ellipsoids derived from the anisotropic thermal parameters. In both dimers the five- to six-membered ring junctures have been found to be *cis*, while the six- to seven-membered ring junctures have been found to be *trans*. Bond distances and angles, shown in Figs. 3, 4, 5 and 6 were calculated with the program *DAESD* (Harris, 1964).

The average bond lengths* involving hydrogen atoms are 1·02 (5) and 0·98 (4) Å and range from 0·95 to 1·11 Å and 0·89 to 1·10 Å, for dimers *A* and *B* respectively. The average bond angles* involving hydrogen atoms are 111 (6) and 111 (7)° for dimers *A* and *B* with corresponding ranges of 99 to 125° and 97 to 127°.

The aryl groups were found to be planar. In dimer *A* the maximum deviations from the least-squares plane through atoms C(10) to C(15) (ring 1) are 0·015 and 0·13 Å for carbon and hydrogen atoms, respectively, while those from the plane through C(17) to C(22) (ring 2) are 0·016 and 0·04 Å. In dimer *B* the analogous deviations are 0·009 and 0·10 Å (ring 1) and 0·021 and 0·10 Å (ring 2) for carbon and hydrogen atoms, respectively.

Discussion

Overall the two structures have bond lengths and angles which not only are similar, as a comparison of the average lengths* of chemically equivalent bonds helps demonstrate, but also compare well, on the

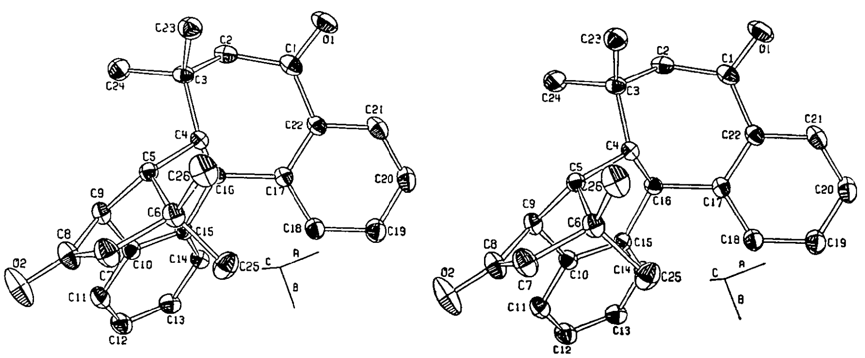

Fig. 1. Stereoscopic view of dimer *A*.

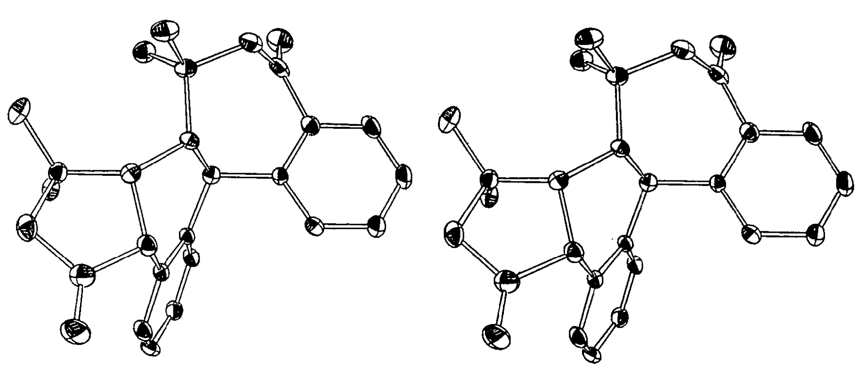

Fig. 2. Stereoscopic view of dimer *B*.

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* Estimated standard deviations for the average bond distances and angles were calculated from the equation $\sigma = \{[\sum_{i=1}^{N} (X_i - \bar{X})^2]/(N-1)\}^{1/2}$, where X_i is the *i*th bond length or angle and $\bar{X}$ is the mean of the *N* equivalent bond lengths or angles

whole, with expected values (Sutton, 1965) as summarized in Table 8. None of these average values is significantly (*i.e.*, the values lie approximately within 3σ of one another) different either between the two dimers or between the dimers and the expected values.

Even though the average values of bond lengths are in agreement for the two dimers, there are several individual differences which are significant. The longest C_{sp3}–C_{sp3} bond length in dimer *A* is C(4)–C(16) of 1·580 (4) Å and is at the *trans* six- to seven-membered ring juncture. The dimer *B* C(4)–C(16) bond length of 1·562 (7) Å, although still longer than the normal value [1·537 (5) Å] for C_{sp3}–C_{sp3} bonds, is not the longest bond of this type in the molecule. Instead, the longest bond in dimer *B* occurs at C(5)–C(6) [1·582 (7) Å] adjacent to the bridgehead bond between the five- and six-membered rings and opposite the carbonyl in the five-membered ring. Several other substantially different bond lengths in the two molecules occur in the regions of the *gem*-dimethyl groups. The bonds C(4)–C(5) and C(6)–C(7) of 1·568 (7) and 1·556 (7) Å, respectively, are much longer in dimer *B* than in dimer *A* [1·534 (4) and 1·529 (4) Å, respectively]. The lengthening of specific but different bonds in each molecule probably implies that strain in the systems is centered in different regions. In dimer *A* it appears that the greatest stress is present at the six- to seven-membered ring juncture, while in dimer *B* the area of greatest strain is in the region of the *gem*-dimethyl groups.

Additional indications that stress is located in different areas of the two molecules is provided by a critical comparison of the bond angles in the two dimers. In the area of the molecule where the *gem*-dimethyl groups are located, the angles in dimer *B* differ from corresponding ones in dimer *A*. For example, angles C(4)–C(5)–C(6) and C(3)–C(4)–C(5) of 128·2 (4) and 117·2 (4)°, respectively, in dimer *B* are much larger than the same angles of 116·8 (2) and 113·7 (2)° in dimer *A*, while the angle C(2)–C(3)–C(23) of 104·4 (4)° in dimer *B* is smaller than the same angle of 107·6 (3)° in dimer *A*. However, the angles in the area of the six- to seven-membered ring juncture and aryl- to seven-membered ring juncture are nearer the anticipated values in dimer *B* than in dimer *A*. For instance, the angle C(15)–C(16)–C(17) of 109·6 (4)° in dimer *B* is closer to the expected value than that of 117·3 (3)° in dimer *A*. The endocyclic angles of the C_{sp3}-hybridized carbon atoms in the seven-membered ring in dimer *B* more closely resemble those observed previously in cycloheptanes than do the same angles in dimer *A*. In two reported structures which contained cycloheptane rings, the observed endocyclic angles were greater than those found in paraffin chain molecules and range from an average of 115·3° in one case (Groth, 1967) to 118·1° in the other (Chacko, Srinivasan & Zand, 1971). Thus, the angles at sp^3-hybridized atoms in a seven-membered ring are larger than those usually expected. Therefore, the angles C(4)–C(16)–C(17) and C(3)–C(4)–C(16) of 110·3 (4) and 113·6 (4)° in dimer *B* are probably nearer the anticipated value, while the same angles of 106·6 (2) and 109·6 (2)° in dimer *A* are substantially smaller than those observed in seven-membered rings. The angle C(1)–C(22)–C(21) of 118·4 (5)° in dimer *B* approximates the expected 120° more closely than that of 115·3 (3)° in dimer *A*. Finally, the closing of the angle C(2)–C(1)–C(22) to 115·6 (5)° in dimer *B* contrasted to a slight opening of the same angle in dimer *A* is probably due to a difference in ring conformation at these atoms.

In summary, the major differences in bond angles and bond lengths between the two structures are prob-

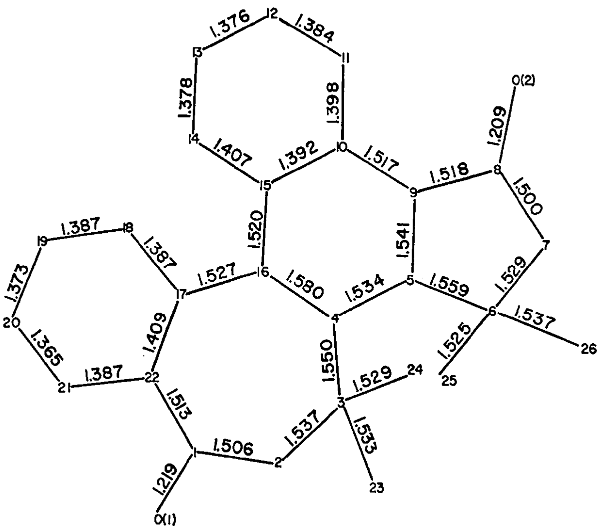


Fig. 3. Bond distances (Å) in dimer *A* with estimated standard deviations in the range 0·004 to 0·005 Å.

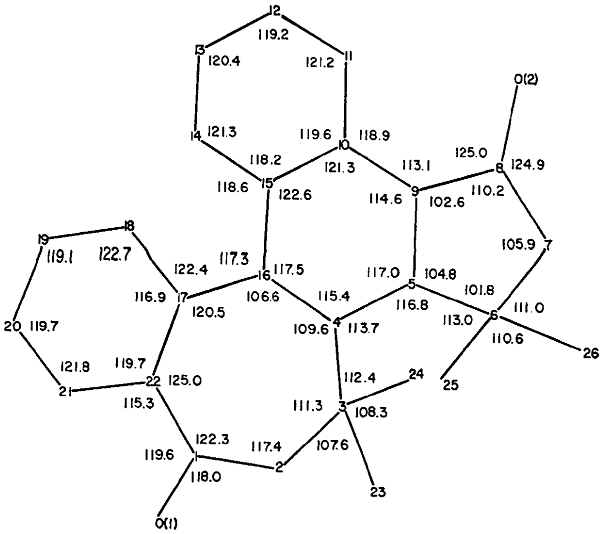


Fig. 4. Bond angles (°) in dimer *A* with estimated standard deviations in the range 0·2 to 0·3°.

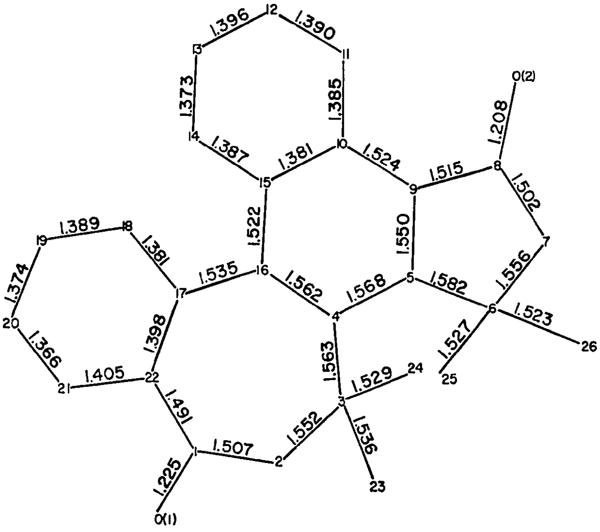


Fig. 5. Bond distances (Å) in dimer *B* with estimated standard deviations in the range 0·006 to 0·009 Å.

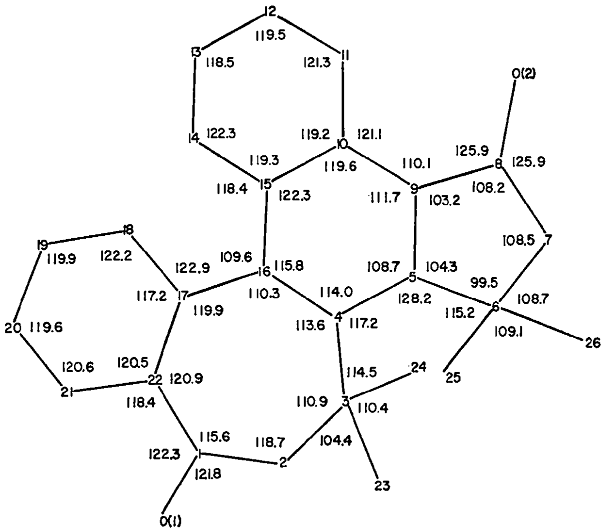


Fig. 6. Bond angles (°) in dimer *B* with estimated standard deviations in the range 0·4 to 0·5°.

ably due to a different distribution of strain in the two molecules. In dimer *A* the greatest point of stress is at the six- to seven-membered ring juncture, whereas, in dimer *B*, it is in the region of the *gem*-dimethyl groups.

As stated previously, the five- to six-membered ring juncture is *cis* and the six- to seven-membered ring juncture is *trans* in both molecules. Thus, the difference in these molecules is not one of gross ring junctures which are identical in both molecules, but in the relationship of the hydrogen atoms at these junctures, (II). In both dimers H_a and H_b are *cis* and H_c and H_d are *trans*; however, the relationship of H_b and H_c is *trans* in dimer *A* but *cis* in dimer *B*. The effect that this structural difference has on the manner in which the strain in the molecules is distributed has been demonstrated by the bond lengths and angles. Another way to assess the effect of the junctional difference on the strain involved in dimers *A* and *B* is to examine the conformations of the nonaromatic cyclic moieties. A tabular comparison of the dihedral angles (Hendrick-

Table 9. *A comparison of the dihedral angles in dimers A and B*

	Dimer *A*	Dimer *B*
Five-membered ring		
C(5) → C(6)	38·8°	−39·1°
C(6) → C(7)	−29·8	27·1
C(7) → C(8)	10·4	−5·0
C(8) → C(9)	13·8	−20·1
C(9) → C(5)	−32·3	37·3
Six-membered ring		
C(4) → C(5)	29·4	−48·7
C(5) → C(9)	−40·5	58·6
C(9) → C(10)	25·1	−31·2
C(10) → C(15)	1·5	−8·8
C(15) → C(16)	−13·0	18·6
C(16) → C(4)	−3·3	11·9
Seven-membered ring		
C(1) → C(2)	−66·5	79·9
C(2) → C(3)	45·8	−61·4
C(3) → C(4)	39·5	62·0
C(4) → C(16)	−80·8	−85·0
C(16) → C(17)	56·7	73·7
C(17) → C(22)	−0·1	−9·7
C(22) → C(1)	10·5	−58·2

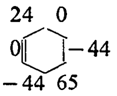
Table 8. *Comparison of the average lengths of chemically equivalent bonds in dimers A and B with the expected values*

Bond type	Dimer *A*	Dimer *B*	Expected
C_{sp3}–C_{sp3}	1·541 (16) Å	1·550 (19) Å	1·537 (5) Å
C_{sp3}–C_{sp2}			
C_{sp3} = aryl carbon atom	1·521 (5)	1·527 (7)	1·505 (5)
C_{sp2} = carbonyl carbon atom	1·508 (9)	1·508 (7)	1·506 (5)
C_{sp2}–C_{sp2}			
C_{sp2} = nonaryl carbon atom	1·513 (5)	1·491 (8)	1·47 (2)
C_{sp2} = aryl carbon atom	1·387 (13)	1·385 (11)	1·394 (5)
C=O			1·215 (5)
Conjugated	1·219 (4)	1·225 (7)	
Nonconjugated	1·209 (4)	1·208 (7)	

son, 1961) in dimers *A* and *B* is given in Table 9. From this table it can be seen that the rings of dimer *B* are much more puckered than those of dimer *A*, since with only two exceptions the dihedral angles for the cyclic moieties in dimer *B* are larger than those in dimer *A*. The exceptions, both of which occur in the five-membered ring, arise because this ring is in the envelope configuration rather than the half-chair conformation as in dimer *A*; thus, the angle down the bond C(7)–C(8) should approach 0° as the conformation of the ring approaches that of an ideal envelope.

Observation of different conformations for the five-membered rings in the dimers can be used as an additional indication for the strain in dimer *B* being centered in the region of the *gem*-dimethyl groups. Calculations (Pitzer & Donath, 1959) have suggested that the half-chair conformation for cyclopentanone rings is a low-energy form for this moiety. Although the five-membered ring in dimer *A* deviates slightly from ideal half-chair conformation, the dihedral angles are consistent with this form. In contrast the five-membered ring in dimer *B* resembles an envelope configuration which probably results from the crowding of the *gem*-dimethyl groups.

If, however, the conformations of the cyclohexene rings are examined, one finds that the more normal configuration is found in dimer *B* instead of dimer *A*. A comparison of the dihedral angles found for the cyclohexene rings in the dimers with those calculated for cyclohexene (Bucourt & Hainaut, 1965), (VII), reveals that the six-membered ring in dimer *A* is much more flattened than that in dimer *B*. This observation is consistent with the indications for strain being located in the region of the ring junctures, particularly the six- to seven-membered ring junction, in dimer *A*.



(VII)

The conformation of the seven-membered rings should be affected [*i.e.*, flattened in the region of C(1)] by the possible conjugation of the carbonyl groups, C(1)–O(1), with the aryl group, C(17) through C(22). In dimer *A* the largest deviation from the best least-squares plane through C(1), C(2), C(17), C(22) and O(1) is 0·08 Å. The tolerably good plane formed by these atoms is one indication for conjugation of the carbonyl group C(1)–O(1) with the aryl group. As an additional check on the planarity of this section of the dimer *A* molecule, the angle between the plane formed by C(1), C(2), C(22), and O(1) and that formed by the aryl group was found to be 8·9°. This angle is the same as that found between the carboxylate and the phenyl planes in *trans*-bicyclo[4,2,0]octyl 1-3,5-dinitrobenzoate (Barnett & Davis, 1970). Thus, the carbonyl group at C(1) in dimer *A* can be considered conjugated as was indicated in the infrared data (Hart, 1973; Hart, Miyashi, Buchanan & Sasson, 1974). Examination of the same region of the dimer *B* molecule for conjugation reveals the following: C(17) is 0·97 Å out of the best least-squares plane formed by C(1), C(2), C(22) and O(1). Furthermore, the angle between this latter plane and that formed by the aryl carbon atoms C(17) through C(22) is 60·0°. Both of these observations are substantially different from those noted for dimer *A* and lead to the conclusion that the carbonyl group C(1)–O(1) in dimer *B* appears less conjugated with the aryl group than that in dimer *A*. This conclusion is supported by a comparison of the bond distance C(1)–C(22) of 1·513 (5) and 1·491 (8) Å in dimers *A* and *B* respectively. If C(1)–O(1) is indeed conjugated with the aryl group, one would expect the C(1)–C(22) bond to be slightly lengthened from the normal C_{sp2}–C_{sp2} bond length of 1·47 (2) Å; this bond is seen to be substantially longer in dimer *A* than in dimer *B*. Since there is an indication in the infrared data that each dimer contains both a conjugated and non-conjugated carbonyl group, either the dimer *B* molecule must be more flexible than the dimer *A* molecule, consistent with a lack of indications for stress at the ring junctures, or the configuration which dimer *B* assumes must be more susceptible to crystal packing forces than that which dimer *A* assumes.

The dihedral angles involving the hydrogen atoms attached to the four asymmetric carbon atoms remain to be discussed. These angles, designated by the hydrogen atoms involved where the hydrogen atoms are labelled as in (II), are 35, 85 and 124°, for *ab*, *bc*, and *cd*, respectively, in dimer *A* and 49, 45 and 146° in dimer *B*. The dihedral angle involving hydrogens *b* and *c* in dimer *A* is particularly important since in the p.m.r. studies on dimer *A* (Hart, 1973; Hart, Miyashi, Buchanan & Sasson, 1974) no coupling was observed between hydrogens *b* and *c*. This observation has led to the prediction that the dihedral angle involving these atoms must be approximately 90° in dimer *A* but substantially different from 90° in dimer *B*. These structural investigations have confirmed this prediction.

We are indebted to Professor H. Hart for his discusssions of the chemistry of these molecules. An NSF traineeship to CGB is acknowledged gratefully.

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Structural Researches on Metal Complexes of Polydentate Ligands Containing Carbonyl and α-Diimine Moieties. IV.* Pentacoordination in Dichloro-2-(2′-pyridyl)-3-(*N*-2-picolylimino)-4-oxo-1,2,3,4-tetrahydroquinazolinemanganese(II)

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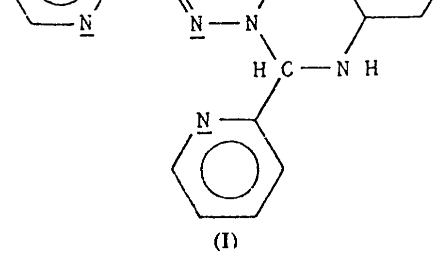
The crystals of the title compound ($C_{19}H_{15}Cl_2MnN_5O$) are triclinic ($P\bar{1}$); the unit-cell dimensions are $a=9{\cdot}306$ (4), $b=15{\cdot}493$ (6), $c=10{\cdot}200$ (4) Å, $\alpha=127{\cdot}1$ (2), $\beta=123{\cdot}6$ (2) $\gamma=74{\cdot}0$ (2)°; $Z=2$. The structure has been determined from diffractometer data by Patterson and Fourier methods and refined by block-diagonal least-squares calculations to $R=3{\cdot}6$% for 2011 independent reflexions. The manganese atom is five-coordinated through two chlorine atoms (Mn–Cl = 2·338, 2·341 Å), two nitrogen atoms (Mn–N = 2·261, 2·259 Å) and an oxygen atom (Mn–O = 2·203 Å). The organic molecule behaves as a tridentate ligand as has already been observed for the Cu(II) and Co(II) complexes, but now the oxygen atom takes the place of a pyridine nitrogen. Packing is mainly determined by a N–H···Cl hydrogen bond, which gives rise to chains running parallel to **c**.

Introduction

The structure analysis of the title compound was undertaken as a part of a programme of research currently in progress in our laboratory on metal complexes of polydentate ligands containing carbonyl and α-diimine groups. Our work on this subject includes three X-ray structural determinations carried out on the following complexes: $Cu(PPQ)Cl_2$ (Mangia, Nardelli, Pelizzi & Pelizzi, 1974), $[Co(PPQ)(NCS)(SCN)]_2$ (Mangia, Nardelli & Pelizzi, 1974), $Cu_2(DIP)Cl_2.H_2O$ (Mangia, Pelizzi & Pelizzi, 1974) [PPQ and DIP denote 2-(2′-pyridyl)-3-(*N*-2-picolylimino)-4-oxo-1,2,3,4-tetrahydroquinazoline and 2,6-diacetylpyridinebis(picolinoylhydrazone) respectively] and a comprehensive spectroscopic study of the behaviour of PPQ as a ligand (Pelizzi & Pelizzi, 1974).

The crystal analyses of the PPQ complexes revealed that in both cases the ligand acts as tridentate through the underlined nitrogen atoms:



(I)

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