SHORT STRUCTURAL PAPERS

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2,6-Bis(diethylamino)-3,5-diphenyl-γ-pyrone*

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Abstract. $C_{25}H_{30}N_2O_2$, monoclinic, space group $P2_1/c$, $a=11{\cdot}554$ (2), $b=13{\cdot}372$ (3), $c=14{\cdot}581$ (3) Å, $\beta=106{\cdot}24$ (1)° at $-150\,^{\circ}$C, $Z=4$, $M=390{\cdot}5$, $D_c=1{\cdot}20$ and $D_m=1{\cdot}22$ g cm^{-3}. The structure was solved by direct methods and refined to $R=0{\cdot}110$ for 3361 non-zero intensities.

Introduction. Crystals suitable for single-crystal X-ray analysis were obtained by recrystallization from benzene of samples provided by Professor Jacqueline Ficini. An approximately equidimensional crystal measuring less than 0·5 mm in each dimension was selected. Intensity data were collected at $-150\,^{\circ}$C with Mo $K\alpha$ radiation on a Picker FACS-1 diffractometer equipped with a graphite monochromator and a nitrogen cold stream of local design (Huffman, 1974). Systematic absences of $0k0$ for $k=2n+1$ and $h0l$ for $l=2n+1$ identified the space group as $P2_1/c$. Unit-cell parameters were refined by least-squares calculations with the orientation angles of 15 carefully centered ($\pm 2\theta$) reflections having $30° < 2\theta < 40°$ (λMo $K\alpha=0{\cdot}71069$ Å). 6742 reflections were scanned in the range $1° \leq 2\theta \leq 50°$ by the θ–2θ scan mode with a scan rate of 2° min^{-1} and 20 s background counts at both ends of the scan range of 2·5° + dispersion. Three standard reflections were measured every 30 reflections. The crystal was realigned several times during the data collection when a drift in the standard reflections was observed. We believe that the alignment problem was

Table 1. *The final atomic coordinates and thermal parameters* ($\times 10^4$) *with standard deviations in parentheses*

The anisotropic thermal parameters are in the form $\exp[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2hl\beta_{13}+2kl\beta_{23})]$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
O(1)	7897 (2)	3125 (2)	1294 (1)	26 (2)	22 (2)	14 (1)	−11 (2)	−1 (1)	2 (1)
C(2)	8888 (3)	3386 (2)	2044 (2)	21 (3)	20 (2)	20 (2)	1 (2)	10 (2)	−4 (2)
C(3)	9229 (3)	2816 (2)	2854 (2)	22 (3)	15 (2)	17 (2)	2 (2)	5 (2)	−0 (1)
C(4)	8391 (3)	2060 (2)	3025 (2)	22 (3)	23 (2)	20 (2)	7 (2)	11 (2)	−2 (2)
C(5)	7308 (3)	1860 (2)	2234 (2)	24 (3)	19 (2)	15 (2)	4 (2)	5 (2)	3 (2)
C(6)	7178 (3)	2326 (2)	1381 (2)	21 (3)	15 (2)	19 (2)	2 (2)	−1 (2)	−6 (2)
N(7)	9399 (2)	4240 (2)	1830 (2)	43 (3)	29 (2)	20 (1)	−2 (2)	5 (2)	1 (1)
C(8)	9241 (3)	4556 (2)	833 (2)	50 (4)	25 (2)	15 (2)	−5 (2)	10 (2)	7 (2)
C(9)	8226 (3)	5318 (3)	480 (2)	56 (4)	31 (3)	27 (2)	−6 (3)	−1 (2)	8 (2)
C(10)	9984 (3)	4974 (2)	2581 (2)	24 (3)	17 (2)	25 (2)	−4 (2)	3 (2)	−4 (2)
C(11)	9164 (3)	5319 (3)	3177 (3)	47 (4)	38 (3)	36 (2)	−3 (3)	16 (2)	−11 (2)
C(12)	10459 (3)	2900 (2)	3535 (2)	31 (3)	10 (2)	21 (2)	−3 (2)	3 (2)	1 (2)
C(13)	11467 (3)	2906 (3)	3174 (2)	32 (3)	26 (2)	22 (2)	4 (2)	5 (2)	3 (2)
C(14)	12632 (3)	2971 (3)	3784 (3)	25 (3)	30 (2)	36 (2)	4 (2)	8 (2)	2 (2)
C(15)	12806 (3)	3024 (3)	4769 (3)	32 (3)	29 (2)	33 (2)	0 (2)	−6 (2)	−2 (2)
C(16)	11817 (3)	3008 (3)	5131 (2)	46 (3)	22 (2)	23 (2)	2 (2)	−1 (2)	−4 (2)
C(17)	10649 (3)	2945 (2)	4522 (2)	34 (3)	18 (2)	20 (2)	−1 (2)	3 (2)	−1 (2)
C(18)	6401 (3)	1120 (3)	2364 (2)	33 (3)	27 (2)	12 (2)	−3 (2)	8 (2)	−1 (2)
C(19)	6739 (3)	156 (3)	2725 (2)	40 (3)	25 (2)	21 (2)	−6 (2)	11 (2)	1 (2)
C(20)	5859 (3)	−522 (3)	2823 (2)	73 (4)	29 (3)	27 (2)	−13 (3)	20 (3)	2 (2)
C(21)	4650 (3)	−257 (3)	2573 (2)	56 (4)	55 (3)	22 (2)	−24 (3)	10 (2)	2 (2)
C(22)	4314 (3)	707 (3)	2232 (3)	28 (3)	61 (3)	28 (2)	−14 (3)	5 (2)	6 (2)
C(23)	5179 (3)	1389 (3)	2135 (2)	32 (3)	39 (3)	16 (2)	0 (2)	1 (2)	2 (2)
N(24)	6349 (2)	2095 (2)	516 (2)	45 (2)	26 (2)	22 (1)	−2 (2)	8 (2)	2 (1)
C(25)	6378 (3)	1046 (2)	188 (2)	46 (3)	19 (2)	22 (2)	−5 (2)	8 (2)	−4 (2)
C(26)	7485 (3)	828 (3)	−159 (2)	59 (4)	31 (3)	33 (2)	8 (3)	16 (3)	−5 (2)
C(27)	6112 (3)	2851 (2)	−266 (2)	39 (3)	23 (2)	15 (2)	1 (2)	−2 (2)	6 (2)
C(28)	5393 (3)	3741 (2)	−58 (2)	39 (3)	26 (2)	29 (2)	5 (2)	3 (2)	4 (2)
O(29)	8590 (2)	1583 (2)	3791 (1)	33 (2)	27 (2)	17 (1)	−2 (2)	4 (1)	8 (1)

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caused by pulling of the Duco cement used for mounting the crystal. We have since discontinued its use for low-temperature studies. The data collection was terminated before complete twofold redundant data were collected when realignment failed to restore the standard reflections, presumably because of radiation damage. Intensities, I, were assigned variances, $\sigma^2(I)$, according to counting statistics plus a term $(0{\cdot}03I)^2$ to allow for unaccountable errors. Lorentz and polarization corrections were made in the usual manner. Of 3787 independent reflections only 1776 had $(F_o)^2 \geq \sigma(F_o)^2$, and 426 were less than or equal to zero and were not used in further calculations.

The structure was solved by direct methods. The refinement was carried out with the full-matrix least-squares program of Busing, Martin & Levy (1962), $\sum w(|F_o|^2-|F_c|^2)^2$ with $w=1/\sigma^2(F_o^2)$ being minimized. Atomic scattering factors for C, N and O were obtained from *International Tables for X-ray Crystallography* (1962), while those of Stewart, Davidson & Simpson (1965) were used for hydrogen. To save computer time the initial refinements were carried out with only 1776 observed reflections; in the final cycles 3361 non-zero reflections were used in order to improve the ratio of observations to variables. All H atoms were located in a difference Fourier map and were found to be in excellent agreement with the expected H positions. For this reason calculated values were used throughout the refinements. An isotropic thermal parameter $B=4$ was used. The non-hydrogen atoms were refined anisotropically. The refinement converged at $R=0{\cdot}110$ ($R=\sum||F_o|-|F_c||/\sum|F_o|$), and $R_{wF2}=0{\cdot}087$, $R_{wF2}=[\sum w(|F_o|^2-|F_c|^2)^2/\sum w|F_o|^4]$. This relatively high value was quite acceptable in view of the large number of low intensities. The corresponding residuals calculated from the final coordinates with only 1776 observed reflections were 0·054 and 0·077 respectively. The final positional and thermal parameters are given in Table 1.*

Discussion. It has been shown (Ficini & Pouliquen, 1971) that carbon dioxide reacts with certain ynamines to form allenic diamides. If the ynamine carries an aromatic substituent the reaction unexpectedly takes a different route leading to a γ-pyrone structure (Ficini & Pouliquen, 1972). The present investigation was undertaken to establish unequivocally the structure of the reaction product.

The interatomic distances and bond angles for non-hydrogen atoms are shown in Fig. 1. A few close non-bonded intramolecular contacts are indicated in the figure. A perspective view of the molecule with the numbering scheme used is given in Fig. 2. Further intramolecular contacts are given in Table 2, and equations for various least-squares planes in the molecule are given in Table 3.

Table 2. *Selected non-bonded intramolecular contacts* (<3·3 Å)

O(1)—C(8)	2·667	C(4)—C(19)	3·139
O(1)—C(9)	3·226	O(29)-C(12)	2·891
O(1)—C(27)	2·634	O(29)-C(17)	2·948
O(1)—C(28)	3·122	O(29)-C(18)	2·857
C(2)—C(11)	3·036	O(29)-C(19)	2·962
C(2)—C(13)	3·043	C(5)—C(25)	3·073
C(10)-C(3)	3·074	C(6)—C(23)	3·087
C(10)-C(12)	3·082	C(6)—C(26)	3·103
C(10)-C(13)	3·242	C(6)—C(28)	3·134
C(4)—C(17)	3·127	C(25)-C(18)	3·167

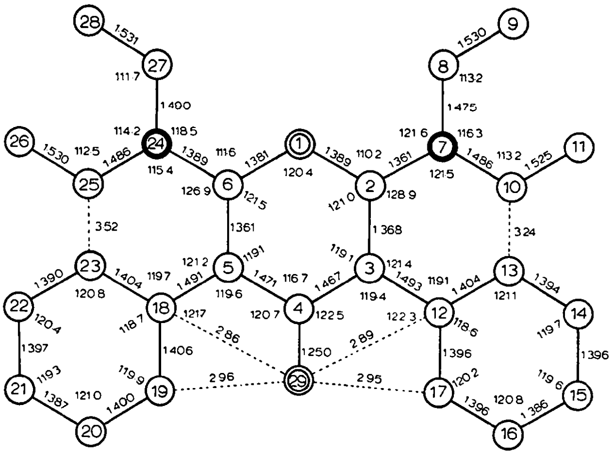

Fig. 1. Molecular dimensions for 2,6-bis(diethylamino)-3,5-diphenyl-γ-pyrone. Average e.s.d. for bond lengths 0·004 Å, for bond angles 0·3°. The open circles represent the C atoms, the double circles represent the O atoms, and the dark circles represent the N atoms.

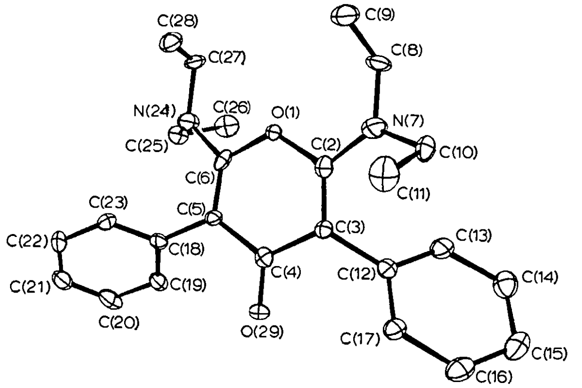

Fig. 2. Perspective view of 2,6-bis(diethylamino)-3,5-diphenyl-γ-pyrone drawn by *ORTEP* (Johnson, 1965). The numbering scheme is indicated. Thermal ellipsoids are scaled to 50% probability. Hydrogen atoms are omitted for clarity.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31506 (38 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England. Supplemental data are also available, in microfiche form only, for $2·00 from Chemistry Department Library, Indiana University, Bloomington, Indiana 47401, U.S.A. Request Molecular Structure Center Report No. 7507.

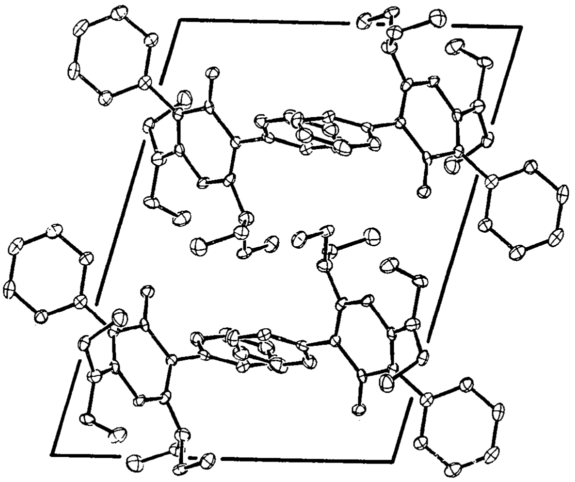

Fig. 3. Packing of the molecules viewed along the *b* axis. The origin is in the top left corner with **a** → and **c** ↓.

Table 3. *Equations of the best molecular least-squares planes and the distances* (Å) *of the atoms from their respective planes*

Equations of the planes are expressed in crystal space as:

$$Ax+By+Cz=D$$

$P1$ $-7\cdot6146x+8\cdot8712y+7\cdot6476z=-2\cdot2663$

$P2$ $-0\cdot3904x+13\cdot345y-0\cdot6167z=3\cdot2385$

$P3$ $-1\cdot7878x+4\cdot3190y+13\cdot702z=2\cdot5908$

Dihedral angles $\angle P1$–$P2$ 48·3° $\angle P1$–$P3$ 49·7° $\angle P2$–$P3$ 73·9°

Plane 1		Plane 2		Plane 3	
γ-Pyrone ring		Ring I benzene		Ring II benzene	
O(1)	0·016 Å	C(12)	0·006 Å	C(18)	−0·012 Å
C(2)	0·066	C(13)	−0·004	C(19)	0·006
C(3)	−0·080	C(14)	0·000	C(20)	0·004
C(4)	0·018	C(15)	0·003	C(21)	−0·008
C(5)	0·060	C(16)	−0·001	C(22)	0·002
C(6)	−0·080	C(17)	−0·003	C(23)	0·008
O(29)*	0·029	C(3)*	−0·017	C(5)*	−0·033
N(7)*	0·271				
N(24)*	−0·315				
C(12)*	−0·422				
C(18)*	0·194				

* Atoms excluded from the calculation of the plane.

The γ-pyrone ring is slightly, but significantly nonplanar, with C(3) and C(6) 0·08 Å below the mean plane of the ring and C(2) and C(5) 0·06 Å above the plane. Thus there appears to be a slight fold along the line from C(3) to C(6). The bond lengths are essentially in agreement with the values reported for 2,6-dimethyl-γ-pyrone (Brown, Norment & Levy, 1957), a normal covalent ketonic structure. The atoms attached to the γ-pyrone ring show large deviations from coplanarity with the ring; N(7) and N(24) are displaced 0·27 and −0·31 Å and C(12) and C(18) are displaced −0·42 and 0·19 Å respectively from the plane of the ring. These deviations can be ascribed to steric hindrance between the diethylamino groups and the benzene rings. The two benzene rings are twisted around the bonds C(3)–C(12) and C(5)–C(18) in such a way that the best planes through these rings make angles of 48·3 and 49·7° respectively with the plane of the central ring.

The molecular packing is illustrated in Fig. 3. None of the intermolecular contacts is shorter than the corresponding van der Waals distance.

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