

The bond lengths listed in Table 2 are normal with an average non-phenyl C—C distance of 1.518 Å. The S—C(8) distance of 1.796 (5) Å lies within the range of S—C(*sp*³) distances observed in the case of various 1,3-thiazine systems (Amirthalingam & Jakkal, 1972; Talberg, 1974; Sacerdoti, Bertolasi, Gilli, Dondoni & Battaglia, 1977; Menczel, Kiss, Simon, Hornyák & Lempart, 1974; Argay, Kálmán, Kapor & Ribár, 1980).

The value found in the present case for the S—C(6) bond length, 1.747 (4) Å, matches well with the value found for the S—C(*sp*²) distance (Andreotti, Bocelli & Sgarabotto, 1980, and references therein).

Comparing the results of the present work with those of the study on 2,3,8,8a-tetrahydro-2-methyl-5,8a-diphenyl-1H-imidazo[2,1-c][1,4]thiazine (TDIT), it is found that N(4)—C(5), C(2)—C(3), N(4)—C(9), C(9)—C(21) and C(8)—C(9) distances are shorter by 0.025, 0.057, 0.015, 0.018 and 0.026 Å respectively. The C—S—C bond angle of 97.6 (4)° agrees well with 97.8 (2)° observed in the present case.

Intensity data were measured for us at Queen Mary College, London, by Dr M. B. Hursthouse. One of us (MSH) is grateful to CSIR (India) for financial assistance.

Acta Cryst. (1982). B38, 844–848

X-ray Structure Analysis of 3-[3-Benzoyl-4-(diethylamino)-5-methyl-1-pyrazolyl]-3-(diethylamino)-2-methyl-1-phenyl-2-propen-1-one, the 1:2 Reaction Product of Dibenzoyldiazomethane and 1-(Diethylamino)propyne

BY ALFRED GIEREN AND VIKTOR LAMM

Max-Planck-Institut für Biochemie, Abteilung Strukturforschung I, Am Klopferspitz,
8033 Martinsried/München, Federal Republic of Germany

(Received 24 April 1981; accepted 21 September 1981)

Abstract

X-ray structure analysis of the title compound (C₂₉H₃₆N₄O₂) has established its chemical constitution and the pathway of its formation. The crystals are monoclinic, space group *P*2₁, *a* = 8.978 (2), *b* = 16.522 (4), *c* = 19.307 (6) Å, γ = 106.07 (2)°, *V* = 2752.0 Å³, *D*_x = 1.141, *D*_m = 1.135 Mg m⁻³, *Z* = 4. The structure was solved by direct methods and refined to *R* = 0.043 for 5114 reflexions with *I* > 2σ(*I*). The π-resonance system of the vinylogous acid amide system of the 2-methyl-1-phenyl-2-propen-1-one residue on N(1) of the pyrazole ring is not planar and shows only a small π interaction with the aromatic

0567-7408/82/030844-05\$01.00

References

- AMIRTHALINGAM, V. & JAKKAL, V. S. (1972). *Acta Cryst.* B28, 2612–2614.
 ANDREOTTI, G. D., BOCELLI, G. & SGARABOTTO, P. (1980). *Acta Cryst.* B36, 1839–1846.
 ARGAY, C., KÁLMÁN, A., KAPOR, Á. & RIBÁR, B. (1980). *Acta Cryst.* B36, 363–368.
 CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* 53, 1891–1898.
 CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A24, 321–324.
 MAIN, P., LESSINGER, L., WOOLFSON, M. M., GERMAIN, G. & DECLERCQ, J. P. (1978). *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univ. of York, England, and Louvain, Belgium.
 MENCZEL, G. V., KISS, J., SIMON, K., HORNYÁK, GY. & LEMPART, L. (1974). *Acta Cryst.* B30, 1613–1615.
 SACERDOTI, M., BERTOLASI, V., GILLI, G., DONDONI, A. & BATTAGLIA, A. (1977). *Acta Cryst.* B33, 2816–2819.
 SANDHU, S. S. & HUNDAL, M. S. (1982). *Acta Cryst.* B38, 697–699.
 SANDHU, S. S., TANDON, S. S. & SINGH, H. (1980). *Indian J. Chem.* B19, 1023–1027.
 SHELDRIK, G. M. (1976). *SHELX*. Program for crystal structure determination. Univ. of Cambridge, England.
 TALBERG, H. J. (1974). *Acta Chem. Scand. Ser. A*, 28, 903–909.

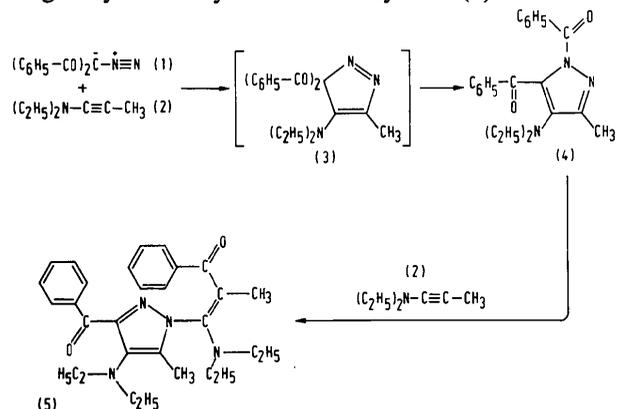
pyrazolyl residue. The diethylamino groups have different conformations. The nitrogen of the diethylamino group bound to the pyrazole ring is on the apex of a pyramid. The nitrogen within the vinylogous acid amide system is *sp*²-hybridized and almost coplanar with its bonding neighbours. The two molecules of the asymmetric unit, which show some significant differences in conformation, are related in the crystal by an approximate *n* glide plane.

Introduction

From the reaction of dibenzoyldiazomethane (1) with 1-(diethylamino)propyne (2) two products (4) and (5)

© 1982 International Union of Crystallography

could be isolated which were characterized analytically as 1:1 and 1:2 adducts of (1) and (2) (Huisgen, Bosch Verderol, Gieren & Lamm, 1981). Because (5) can also be obtained by the reaction of (4) with (2), (4) can be regarded as an intermediate in the synthesis of (5). The chemical constitution of (4) and (5) could not be determined by spectroscopic (^1H -, ^{13}C -NMR, MS) or chemical methods. We have therefore performed a single-crystal X-ray structure analysis of (5).



According to the results of the structure analysis the reaction pathway can be described as follows: the first step of the reaction is a [3 + 2]-cycloaddition of the 1,3-dipole (1) and the dipolarophile (2) to the 3*H*-pyrazole (3) based on the known regioselectivity (Huisgen, Reissig & Huber, 1979). (3) cannot be isolated because of fast aromatization to the 1,5-dibenzoyl-4-diethylamino-3-methylpyrazole (4). The isolable (4) reacts with another ynamine (2) resulting in 3-[3-benzoyl-4-(diethylamino)-5-methyl-1-pyrazolyl]-3-(diethylamino)-2-methyl-1-phenyl-2-propen-1-one (5).

Experimental

Yellow crystals of (5) were grown from benzene solution. (5) crystallizes in the monoclinic space group $P2_1$ with two molecules per asymmetric unit. Cell dimensions were obtained by least squares from the setting angles of 25 reflexions measured on an Enraf-Nonius CAD-4 diffractometer. With Cu $K\alpha$ radiation (Ni filter) intensities were collected on a punch-tape-controlled diffractometer (Siemens AED) using

Table 1. Atom coordinates and equivalent isotropic thermal parameters

B_{eq} = one third of the trace of the orthogonalized B_{ij} tensor.

	x	y	z	B_{eq} (\AA^2)		x	y	z	B_{eq} (\AA^2)
O(1)	0.9490 (3)	0.6712 (1)	-0.0716 (1)	7.4 (1)	O(1')	0.4099 (3)	1.1905 (1)	0.6885 (1)	7.7 (1)
O(2)	0.9087 (2)	0.3782 (1)	0.1444 (1)	6.5 (1)	O(2')	0.4499 (2)	0.9380 (1)	0.4417 (1)	6.5 (1)
N(1)	0.9345 (2)	0.4415 (1)	-0.0802 (1)	4.1 (1)	N(1')	0.4298 (2)	0.9653 (1)	0.6710 (1)	4.2 (1)
N(2)	0.8781 (2)	0.4624 (1)	-0.0200 (1)	4.0 (1)	N(2')	0.3781 (2)	0.9922 (1)	0.6120 (1)	4.1 (1)
N(3)	0.8215 (2)	0.4126 (1)	-0.1915 (1)	4.7 (1)	N(3')	0.3008 (2)	0.9104 (1)	0.7728 (1)	4.7 (1)
N(4)	1.1173 (2)	0.3236 (1)	0.0287 (1)	4.9 (1)	N(4')	0.6445 (2)	0.8727 (1)	0.5549 (1)	5.1 (1)
C(1)	1.0000 (3)	0.6167 (1)	-0.0974 (1)	5.3 (1)	C(1')	0.4599 (3)	1.1326 (1)	0.7079 (1)	5.2 (1)
C(2)	0.9065 (3)	0.5567 (1)	-0.1488 (1)	4.8 (1)	C(2')	0.3627 (3)	1.0617 (1)	0.7492 (1)	4.9 (1)
C(3)	0.9357 (2)	0.4226 (1)	0.0289 (1)	4.0 (1)	C(3')	0.4493 (2)	0.9634 (1)	0.5609 (1)	4.1 (1)
C(4)	1.0323 (2)	0.3756 (1)	-0.0012 (1)	4.1 (1)	C(4')	0.5477 (2)	0.9157 (1)	0.5878 (1)	4.3 (1)
C(5)	1.0284 (2)	0.3897 (1)	-0.0705 (1)	4.2 (1)	C(5')	0.5318 (2)	0.9189 (1)	0.6583 (1)	4.4 (1)
C(6)	0.8897 (2)	0.4733 (1)	-0.1436 (1)	4.3 (1)	C(6')	0.3631 (2)	0.9819 (1)	0.7351 (1)	4.4 (1)
C(7)	1.1621 (3)	0.6155 (1)	-0.0815 (1)	5.1 (1)	C(7')	0.6263 (3)	1.1390 (1)	0.6972 (2)	5.3 (1)
C(8)	1.2316 (3)	0.6489 (2)	-0.0190 (2)	5.6 (1)	C(8')	0.7030 (3)	1.1780 (2)	0.6378 (2)	6.2 (1)
C(9)	1.3854 (4)	0.6550 (2)	-0.0063 (2)	6.6 (1)	C(9')	0.8598 (4)	1.1900 (2)	0.6305 (3)	7.6 (2)
C(10)	1.4719 (4)	0.6286 (3)	-0.0551 (3)	8.5 (2)	C(10')	0.9437 (4)	1.1662 (2)	0.6823 (3)	8.6 (2)
C(11)	1.4060 (4)	0.5955 (3)	-0.1158 (3)	9.1 (2)	C(11')	0.8698 (4)	1.1296 (2)	0.7413 (3)	8.3 (2)
C(12)	1.2511 (4)	0.5879 (2)	-0.1295 (2)	7.1 (2)	C(12')	0.7124 (3)	1.1150 (2)	0.7486 (2)	6.7 (1)
C(13)	0.8227 (4)	0.5931 (2)	-0.2033 (2)	7.0 (2)	C(13')	0.2542 (5)	1.0847 (2)	0.7998 (2)	7.4 (2)
C(14)	0.8797 (3)	0.4191 (2)	-0.2631 (1)	5.8 (1)	C(14')	0.2919 (4)	0.9159 (2)	0.8476 (1)	6.2 (1)
C(15)	0.7589 (4)	0.4097 (3)	-0.3185 (2)	6.9 (2)	C(15')	0.3290 (7)	0.8436 (3)	0.8839 (3)	9.1 (2)
C(16)	0.7151 (4)	0.3337 (2)	-0.1690 (2)	5.6 (1)	C(16')	0.2035 (3)	0.8350 (2)	0.7384 (2)	5.7 (1)
C(17)	0.5614 (4)	0.3432 (3)	-0.1461 (3)	8.4 (2)	C(17')	0.0365 (4)	0.8297 (4)	0.7384 (3)	8.6 (2)
C(18)	1.1108 (3)	0.3597 (2)	-0.1279 (1)	6.0 (1)	C(18')	0.6111 (3)	0.8834 (2)	0.7137 (2)	6.3 (1)
C(19)	1.2344 (3)	0.3671 (2)	0.0791 (2)	6.3 (1)	C(19')	0.7716 (3)	0.9283 (2)	0.5150 (2)	6.8 (1)
C(20)	1.3577 (4)	0.4356 (2)	0.0468 (3)	7.7 (2)	C(20')	0.8892 (5)	0.9839 (3)	0.5602 (3)	8.9 (2)
C(21)	1.0204 (3)	0.2421 (2)	0.0524 (2)	6.3 (1)	C(21')	0.5617 (3)	0.7970 (2)	0.5173 (2)	6.6 (1)
C(22)	0.9288 (4)	0.1906 (2)	-0.0050 (3)	7.6 (2)	C(22')	0.4424 (4)	0.7371 (2)	0.5607 (3)	8.1 (2)
C(23)	0.8863 (2)	0.4272 (1)	0.1014 (1)	4.4 (1)	C(23')	0.4107 (2)	0.9775 (1)	0.4885 (1)	4.5 (1)
C(24)	0.8078 (2)	0.4928 (1)	0.1227 (1)	4.2 (1)	C(24')	0.3214 (2)	1.0395 (1)	0.4710 (1)	4.3 (1)
C(25)	0.8332 (3)	0.5703 (1)	0.0918 (1)	4.9 (1)	C(25')	0.3229 (3)	1.1099 (1)	0.5092 (1)	4.8 (1)
C(26)	0.7658 (3)	0.6299 (2)	0.1194 (2)	5.8 (1)	C(26')	0.2444 (3)	1.1661 (2)	0.4864 (2)	5.9 (1)
C(27)	0.6719 (3)	0.6124 (2)	0.1754 (2)	6.4 (1)	C(27')	0.1631 (4)	1.1513 (2)	0.4251 (2)	6.7 (1)
C(28)	0.6436 (3)	0.5339 (2)	0.2063 (2)	6.0 (1)	C(28')	0.1578 (4)	1.0806 (2)	0.3874 (2)	7.1 (1)
C(29)	0.7111 (3)	0.4741 (2)	0.1807 (1)	5.0 (1)	C(29')	0.2377 (3)	1.0248 (2)	0.4098 (1)	5.9 (1)

the five-point-measurement procedure (Hoppe, 1969) in the $\theta/2\theta$ scan mode. In the range $1^\circ < \theta \leq 70^\circ$ 5114 independent reflexions with $I > 2\sigma_I$ were measured. Lorentz-polarization corrections were applied in the usual way but no correction was made for absorption [$\mu(\text{Cu } K\alpha) = 0.5 \text{ mm}^{-1}$].

Structure determination and refinement

The computations were performed mainly on a VAX-11/780 with *SHELX76* (Sheldrick, 1976). The *E* statistics indicated a non-centrosymmetric space group. The structure was solved by direct methods. For phase determination 471 reflexions with $E \geq 1.4$ were used. Ten reflexions were provided with starting phases. In an *E* map selected by the R_α criterion a partial structure, containing 45 of the 70 non-hydrogen atoms, could be recognized. The missing non-hydrogen atoms were located from Fourier syntheses. Least-squares refinement was carried out first with isotropic then anisotropic temperature parameters. H atoms were found from difference maps, or were placed at theoretical positions. All H atoms were included in the refinement with isotropic temperature factors. The arrangement of N and C in positions 1 and 3 of the pyrazole ring was established by comparison of the isotropic temperature parameters obtained from parallel refinements of both models. The structure was refined in overlapping blocks because of the large number of parameters. The refinement converged to a weighted $R = \sum w^{1/2} ||F_o| - |F_c|| / \sum w^{1/2} |F_o| = 0.049$ ($R = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.043$) with $w = 2.13 / (\sigma^2_{F_o} + 0.002|F_o|^2)$. Atomic scattering factors for C, N and O were taken from Cromer & Mann (1968) and for H from Stewart, Davidson & Simpson

(1965). Positional and isotropic temperature parameters of the non-hydrogen atoms are listed in Table 1.*

Results and discussion

The structures of both molecules of the asymmetric unit are shown in Fig. 1. Bond distances and angles are listed in Table 2. Due to differences in conformation corresponding bond angles differ by up to 2.7° .

All the bond lengths in the aromatic pyrazole ring indicate intermediate bond orders between single and double bonds. They show a predominant influence of the valence-bond structure given in formula (5). N(2)–C(3) and C(4)–C(5), shown there as double bonds, are significantly shorter than the formal single bonds N(1)–C(5) and C(3)–C(4). π interactions between the substituents and the aromatic system of the pyrazole ring are small. Although the N(4)–C(4) distance between the diethylamino group and the five-membered ring is shorter than the distance N(1)–C(6), a π interaction can be excluded for the following reasons: N(4) is sp^3 -hybridized [the sum of the angles at N(4) is 341.7° and N(4) lies 0.36 \AA out of the plane of its bonding neighbours] and furthermore the N(4)–C(4) bond is twisted in such a way (Fig. 2a) that the lone pair at N(4) is positioned in the plane of the pyrazole ring, so that a π interaction with the *p* orbitals of this ring is impossible.

* Lists of structure factors, anisotropic temperature parameters of the non-hydrogen atoms, coordinates and isotropic temperature factors of the H atoms, bond distances and angles involving H atoms and torsion angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36417 (31 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

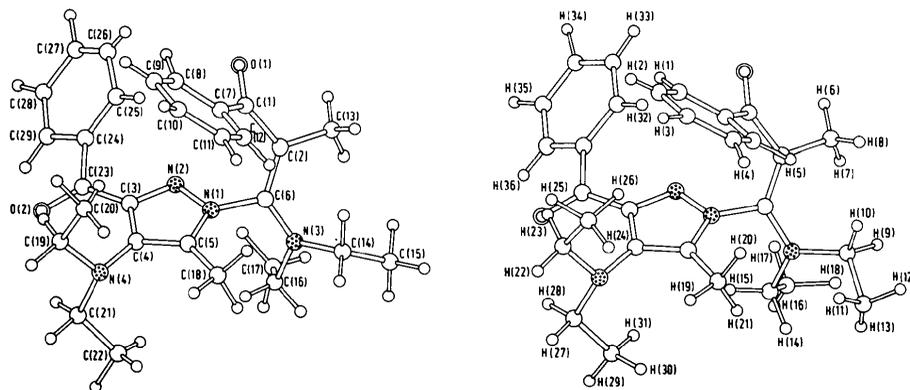


Fig. 1. Structures of both molecules of the asymmetric unit in a similar projection of the central five-membered ring. The numbering scheme for the non-hydrogen atoms is shown in the left molecule which is referred to in this paper as 'molecule 1'. On the right side 'molecule 2' contains the numbering scheme for the H atoms and is shown as its mirror image for better conformational comparison.

Steric interactions of adjacent substituents lead to a displacement of the bonding vectors to the pyrazole ring from the plane of the ring. The substituents at N(1) and C(3) avoid steric hindrance with their neighbours by a diminution of the angles formed with the unsubstituted N(2).

π resonance can be clearly observed in the vinyl-ogous acid amide system (merocyanine system) O(1) \rightarrow N(3). The amino N(3), for example, has a nearly planar arrangement of bonds in contrast to the N atom of the diethylamino group at C(4). But for steric reasons the system O(1) \rightarrow N(3) is not planar. Remarkably large out-of-plane rotations occur at the formal single bonds N(3)–C(6) and C(2)–C(1) (Fig. 2*c,d*). Also the p_z orbitals of the phenyl ring C(7) \rightarrow C(12) and those of the pyrazolyl residue are twisted with respect to the neighbouring p_z orbitals of the merocyanine system around C(1)–C(7), and C(6)–N(1), respectively (Fig. 2*e,f*). These twists lead to a diminution of up to 60% of the π resonance [resonance energy decreases as $\cos^2(\text{twist angle})$]. The shortest

Table 2. Bond distances (Å) and angles (°) not involving hydrogen atoms

	Molecule 1	Molecule 2	Mean value
O(1)–C(1)	1.223 (3)	1.223 (3)	1.223 (2)
O(2)–C(23)	1.215 (3)	1.222 (3)	1.219 (2)
N(1)–N(2)	1.350 (3)	1.351 (3)	1.351 (2)
N(1)–C(5)	1.370 (3)	1.369 (3)	1.370 (2)
N(1)–C(6)	1.433 (3)	1.434 (3)	1.434 (2)
N(2)–C(3)	1.334 (3)	1.333 (3)	1.334 (2)
N(3)–C(6)	1.377 (2)	1.368 (2)	1.373 (1)
N(3)–C(14)	1.471 (3)	1.451 (3)	1.461 (2)
N(3)–C(16)	1.453 (3)	1.468 (3)	1.461 (2)
N(4)–C(4)	1.420 (3)	1.416 (3)	1.418 (2)
N(4)–C(19)	1.467 (4)	1.469 (3)	1.468 (2)
N(4)–C(21)	1.460 (3)	1.459 (4)	1.460 (2)
C(1)–C(2)	1.487 (3)	1.485 (3)	1.486 (2)
C(1)–C(7)	1.493 (4)	1.483 (4)	1.488 (3)
C(2)–C(6)	1.348 (2)	1.347 (3)	1.348 (2)
C(2)–C(13)	1.512 (5)	1.501 (5)	1.507 (4)
C(3)–C(4)	1.437 (3)	1.434 (3)	1.436 (2)
C(3)–C(23)	1.477 (3)	1.474 (3)	1.476 (2)
C(4)–C(5)	1.360 (3)	1.371 (3)	1.366 (2)
C(5)–C(18)	1.491 (3)	1.492 (4)	1.492 (3)
C(7)–C(8)	1.400 (4)	1.400 (5)	1.400 (3)
C(7)–C(12)	1.381 (5)	1.382 (5)	1.382 (4)
C(8)–C(9)	1.378 (5)	1.374 (5)	1.376 (4)
C(9)–C(10)	1.367 (7)	1.373 (7)	1.370 (5)
C(10)–C(11)	1.358 (8)	1.372 (7)	1.365 (5)
C(11)–C(12)	1.387 (5)	1.373 (5)	1.380 (4)
C(14)–C(15)	1.500 (4)	1.500 (7)	1.500 (4)
C(16)–C(17)	1.498 (6)	1.478 (5)	1.488 (4)
C(19)–C(20)	1.484 (5)	1.478 (6)	1.481 (4)
C(21)–C(22)	1.497 (6)	1.497 (5)	1.497 (4)
C(23)–C(24)	1.504 (3)	1.504 (3)	1.504 (2)
C(24)–C(25)	1.373 (2)	1.374 (3)	1.374 (2)
C(24)–C(29)	1.398 (3)	1.385 (3)	1.392 (2)
C(25)–C(26)	1.396 (4)	1.384 (4)	1.390 (3)
C(26)–C(27)	1.352 (5)	1.376 (5)	1.364 (4)
C(27)–C(28)	1.386 (5)	1.366 (5)	1.376 (4)
C(28)–C(29)	1.385 (5)	1.385 (5)	1.385 (4)

Table 2 (cont.)

	Molecule 1	Molecule 2	Δ	Mean value
N(2)–N(1)–C(5)	112.4 (2)	112.2 (2)	0.2	112.3
N(2)–N(1)–C(6)	118.6 (2)	117.7 (2)	0.9	118.2
C(5)–N(1)–C(6)	129.0 (2)	129.9 (2)	0.9	129.5
N(1)–N(2)–C(3)	105.0 (2)	105.3 (2)	0.3	105.2
C(6)–N(3)–C(14)	120.0 (2)	119.5 (2)	0.5	119.8
C(6)–N(3)–C(16)	120.1 (2)	119.8 (2)	0.3	120.0
C(14)–N(3)–C(16)	118.6 (2)	118.3 (2)	0.3	118.5
C(4)–N(4)–C(19)	113.9 (2)	113.6 (2)	0.3	113.8
C(4)–N(4)–C(21)	113.7 (2)	114.5 (2)	0.8	114.1
C(19)–N(4)–C(21)	114.0 (2)	113.5 (2)	0.5	113.8
O(1)–C(1)–C(2)	120.3 (2)	121.3 (3)	1.0	120.8
O(1)–C(1)–C(7)	119.4 (2)	118.8 (2)	0.6	119.1
C(2)–C(1)–C(7)	120.1 (2)	119.5 (2)	0.6	119.8
C(1)–C(2)–C(6)	121.0 (2)	120.2 (2)	0.8	120.6
C(1)–C(2)–C(13)	116.8 (2)	115.5 (2)	1.3	116.2
C(6)–C(2)–C(13)	122.1 (2)	123.8 (2)	1.7	123.0
N(2)–C(3)–C(4)	110.8 (2)	110.9 (2)	0.1	110.9
N(2)–C(3)–C(23)	118.9 (2)	119.2 (2)	0.3	119.1
C(4)–C(3)–C(23)	130.2 (2)	129.6 (2)	0.6	129.9
N(4)–C(4)–C(3)	131.9 (2)	132.1 (2)	0.2	132.0
N(4)–C(4)–C(5)	123.2 (2)	123.3 (2)	0.1	123.3
C(3)–C(4)–C(5)	104.9 (2)	104.6 (2)	0.3	104.8
N(1)–C(5)–C(4)	106.9 (2)	107.0 (2)	0.1	107.0
N(1)–C(5)–C(18)	123.6 (2)	123.9 (2)	0.3	123.8
C(4)–C(5)–C(18)	129.4 (2)	129.1 (2)	0.3	129.3
N(1)–C(6)–N(3)	114.8 (2)	112.7 (2)	2.1	113.8
N(1)–C(6)–C(2)	118.4 (2)	118.4 (2)	0.0	118.4
N(3)–C(6)–C(2)	126.6 (2)	128.8 (2)	2.2	127.7
C(1)–C(7)–C(8)	120.1 (2)	120.3 (3)	0.2	120.2
C(1)–C(7)–C(12)	121.4 (2)	120.8 (3)	0.6	121.1
C(8)–C(7)–C(12)	118.2 (3)	118.5 (3)	0.3	118.4
C(7)–C(8)–C(9)	120.7 (3)	120.3 (4)	0.4	120.5
C(8)–C(9)–C(10)	120.0 (4)	120.4 (4)	0.4	120.2
C(9)–C(10)–C(11)	120.0 (4)	119.6 (4)	0.4	119.8
C(10)–C(11)–C(12)	121.0 (4)	120.8 (4)	0.2	120.9
C(7)–C(12)–C(11)	120.0 (4)	120.4 (4)	0.4	120.2
N(3)–C(14)–C(15)	115.5 (2)	112.8 (3)	2.7	114.2
N(3)–C(16)–C(17)	113.0 (3)	114.0 (3)	1.0	113.5
N(4)–C(19)–C(20)	112.2 (3)	112.1 (3)	0.1	112.2
N(4)–C(21)–C(22)	112.7 (3)	112.9 (3)	0.2	112.8
O(2)–C(23)–C(3)	120.4 (2)	120.1 (2)	0.3	120.3
O(2)–C(23)–C(24)	119.4 (2)	119.0 (2)	0.4	119.2
C(3)–C(23)–C(24)	120.2 (2)	120.9 (2)	0.7	120.6
C(23)–C(24)–C(25)	124.3 (2)	125.0 (2)	0.7	124.7
C(23)–C(24)–C(29)	116.5 (2)	116.0 (2)	0.5	116.3
C(25)–C(24)–C(29)	119.1 (2)	118.9 (2)	0.2	119.0
C(24)–C(25)–C(26)	120.0 (2)	120.6 (2)	0.6	120.3
C(25)–C(26)–C(27)	121.4 (3)	119.9 (3)	1.5	120.7
C(26)–C(27)–C(28)	119.1 (3)	120.1 (4)	1.0	119.6
C(27)–C(28)–C(29)	120.7 (3)	120.1 (3)	0.6	120.4
C(24)–C(29)–C(28)	119.7 (3)	120.4 (3)	0.7	120.1

bond in the merocyanine system, the double bond C(6)–C(2), is only slightly elongated and shows, consistent with its high double-bond character, the smallest twist (Fig. 2*b*). This twist nevertheless diminishes the rotation barrier in such a way that in solution there is an equilibrium in the proportion 5:1 of the conformation found in the crystalline state which has a *cis* arrangement of diethylamino and methyl

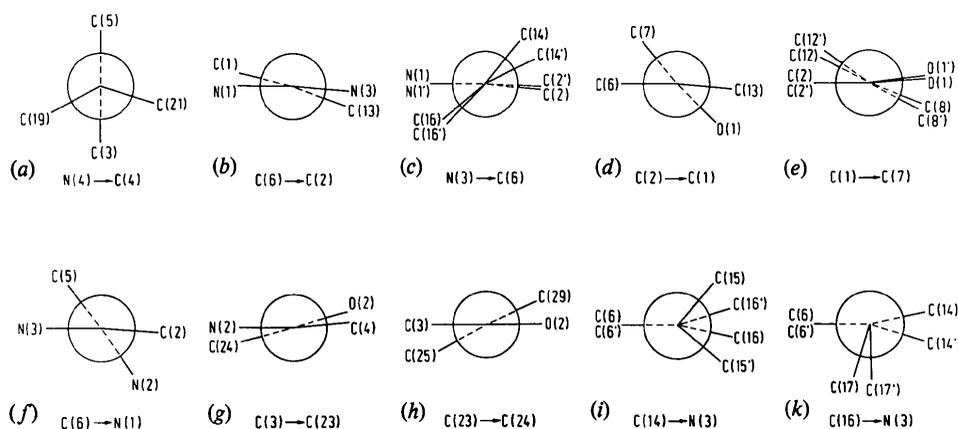


Fig. 2. Newman diagrams of the torsion angles around selected bonds for molecule 1 and the mirror image of molecule 2. For small differences between the molecules mean values are shown.

groups and of an isomer with a *trans* arrangement (Huisgen *et al.*, 1981). Compared with C(6)–N(1) there is a significant shortening of N(3)–C(6) although the twists at both bonds are nearly equal. This fact indicates that the π resonance in the system O(1)→N(3) is stronger than in the system O(1)→N(1) which can also be regarded as a vinylogous acid amide system. The reason is the availability of the lone pair of N(3) for the π resonance in a merocyanine system, whereas at N(1) the lone pair is involved in the aromatic π cloud of the pyrazole ring.

Within the benzoyl group attached to C(3) the torsion angles around the C(3)–C(23) and C(23)–C(24) bond (Fig. 2*g,h*) are smaller than those around comparable bonds in the merocyanine system. The greater planarity of this group is correlated with a significant difference between the bond angles at the 1 position [C(24)] of the phenyl ring: the angle C(23)–C(24)–C(29), inclined to the CO group, is about 8° smaller than the angle C(23)–C(24)–C(25).

The conformations of the two molecules in the asymmetric unit are nearly enantiomeric apart from some noteworthy differences. The absolute values of the torsion angles differ by more than 10° at the bonds N(3)–C(6) and C(1)–C(7) (Fig. 2*c,e*), and in the chain C(17)–C(16)–N(3)–C(14)–C(15) (Fig. 2*i,k*), where the greatest differences occur.

A feature of the molecular packing (Fig. 3) is that it approximates the higher centrosymmetric space group $P2_1/n$; there is a relationship of the form $x + 0.5, y + 0.5, -z + 0.58$ between the two molecules of the asymmetric unit. Nevertheless the deviations from the additional symmetry are such that no systematic or pseudo extinctions characteristic of a glide plane can be observed.

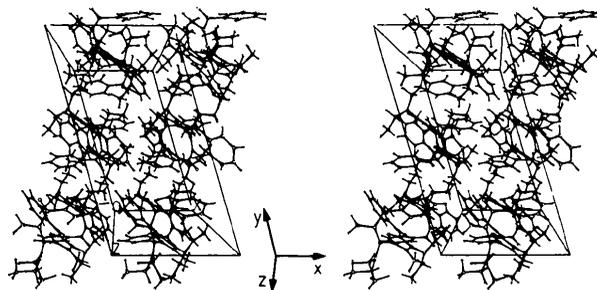


Fig. 3. Stereoscopic view of the molecular packing. The packing follows, instead of *b*, a new axis $b' = a + b$ ($b' = 16.476 \text{ \AA}$ and $\gamma' = 74.49^\circ$), where *a* and *b* refer to the unit cell given in the *Abstract*.

We thank Professor R. Huisgen for supplying crystals of the title compound and Dr C. Krüger for the opportunity to measure the cell dimensions on his Nonius CAD-4 diffractometer.

References

- CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.
 HOPPE, W. (1969). *Acta Cryst.* **A25**, 67–76.
 HUISGEN, R., BOSCH VERDEROL, M. P., GIEREN, A. & LAMM, V. (1981). *Angew. Chem.* **93**, 710–712; *Angew. Chem. Int. Ed. Engl.* **20**, 694–695.
 HUISGEN, R., REISSIG, H.-U. & HUBER, H. (1979). *J. Am. Chem. Soc.* **101**, 3647–3648.
 SHELDRICK, G. M. (1976). *SHELX*. Program for crystal structure determination. Univ. of Cambridge, England.
 STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.