H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0348P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$

Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

N15—C11	1.361 (3)	N25—C21	1.361 (3)
N15—C14	1.358 (3)	N25—C24	1.363 (3)
C11—C12	1.363 (3)	C21—C22	1.351 (3)
C12—C13	1.417 (4)	C22—C23	1.417 (3)
C13—C14	1.344 (3)	C23—C24	1.345 (4)
N15—C11—C1	122.1 (2)	N25—C21—C1	121.3 (2)
N15—C11—C12	106.6 (2)	N25—C21—C22	106.9 (2)
C1—C11—C12	131.3 (3)	C1—C21—C22	131.5 (2)
C11—C12—C13	107.7 (3)	C21—C22—C23	108.5 (2)
C11—N15—C14	110.4 (2)	C21—N25—C24	109.7 (2)

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N25—H25···*Cg*1^{i}†	0.86	2.42	3.219 (3)	154
N15—H15···*Cg*2^{ii}	0.86	2.52	3.324 (3)	156

Symmetry codes: (i) $1-x, 1-y, -z$; (ii) $1-x, y-\frac{1}{2}, \frac{1}{2}-z$.

† *Cg*1 and *Cg*2 are the centroids of the N15 and N25 rings, respectively.

Molecule (I) crystallized in the monoclinic system: space group $P2_1/c$ from the systematic absences. H atoms were allowed for as riding atoms with N—H 0.86, and C—H 0.93 and 0.98 Å. At an intermediate stage in the analysis, the site occupancies of the atom pairs N15/C12 and N25/C22 were allowed to vary in order to check for possible N/C disorder; the occupancy factors obtained did not differ significantly from unity and accordingly in the final refinement cycles, no N/C disorder was allowed for. Difference Fourier maps in the plane of the pyrrole rings clearly supported the present atom designation.

Data collection: *CAD-4-PC Software* (Enraf–Nonius, 1992). Cell refinement: *SET*4 and *CELDIM* in *CAD-4-PC Software*. Data reduction: *DATRD*2 in *NRCVAX*96 (Gabe *et al.*, 1989). Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997*a*). Program(s) used to refine structure: *NRCVAX*96 and *SHELXL*97 (Sheldrick, 1997*b*). Molecular graphics: *NRCVAX*96, *ORTEP*II (Johnson, 1976), *PLATON* (Spek, 1997*a*) and *PLUTON* (Spek, 1997*b*). Software used to prepare material for publication: *NRCVAX*96, *SHELXL*97 and *WordPerfect* macro *PRPCIF*97 (Ferguson, 1997).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1144). Services for accessing these data are described at the back of the journal.

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3-Methoxy-2,4,6-triphenylpyridine at 173 K

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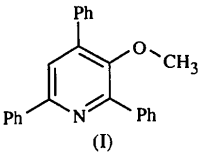
Abstract

In the title compound, $C_{24}H_{19}NO$, the methoxy group attached at C3 avoids steric hindrance with the neighbouring phenyl rings by emerging almost orthogonally from the pyridine ring [C2—C3—O31—C31 −95.3 (2)°]. The phenyl rings show a disrotatory arrangement and the angles between them and the pyridyl ring range from 22.66 (6) to 47.91 (5)°, whereas these angles differ by only approximately 6° in 2,4,6-triphenylpyridine.

Comment

3-Methoxy-2,4,6-triphenylpyridine serves as a precursor for oxyl radicals of heterocycles. The synthesis proceeds from the title compound, (I), *via* the corresponding phenol to the triphenylpyridyloxyl (Teuber, Schütz & Bader, 1977). The crystal structure determination was performed to establish unambiguously the pattern of substitution of the heterocycle.



(I)

The methoxy group attached at C3 avoids steric hindrance with the neighbouring phenyl rings by emerging almost orthogonally from the pyridine ring, with C2—C3—O31—C31 −95.3 (2)°. The three phenyl rings display a disrotatory conformation and form different angles with the pyridine ring. The observed increase of these angles can be explained by steric hindrance caused by the neighbouring substituents. The phenyl ring attached at C6 forms the smallest angle with the heterocycle, 22.66 (6)°, because there is only the free electron pair of the N atom and one H atom in the *ortho* positions. The angle formed by the phenyl ring attached at C2 is increased, to 32.97 (6)°, because of the steric influence of the methoxy group. The remaining phenyl ring forms the widest angle with the heterocycle, 47.91 (5)°, as there are two substituents in the *ortho* positions, compared to only one in the neighbourhood of the other two phenyl rings. In 2,4,6-triphenylpyridine (Ondráček *et al.*, 1994), the angles between the phenyl rings and the heterocycle are in a much smaller range. Whereas steric arguments serve to explain the differing angles in the title compound, this approach is not appropriate for 2,4,6-triphenylpyridine: the two phenyl rings in the *ortho* positions with respect to the N atom form angles of 31.12 and 36.29° with the pyridine ring, while the phenyl ring in the *para* position displays an angle of 30.50°, similar to that formed by one of the *ortho* phenyl rings.

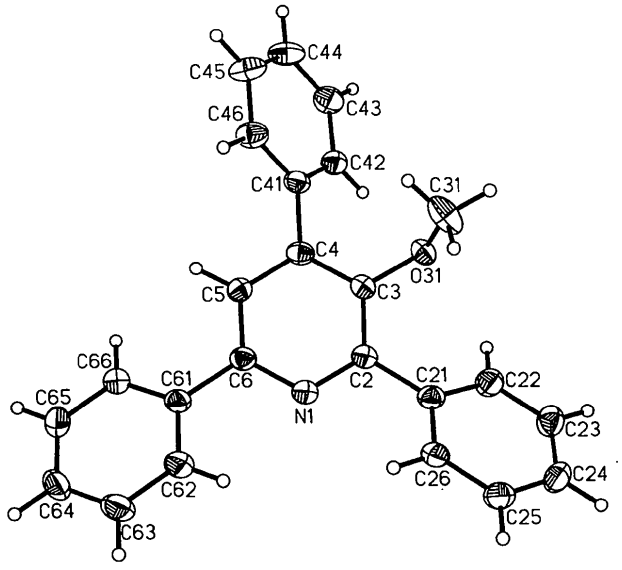


Fig. 1. Perspective view of the title compound with the atom numbering; displacement ellipsoids are at the 50% probability level.

Experimental

The title compound was prepaired according to the method of Kröhnke & Zecher (1962) by mixing ω-methoxyacetophenone, benzaldehyde and *N*-phenacylpyridinium bromide in a boiling solution of ammonium acetate and glacial acetic acid (Teuber, Schütz & Bader, 1977). Suitable crystals were obtained from ethyl acetate.

Crystal data

$C_{24}H_{19}NO$
M_r = 337.40
Monoclinic
Cc
a = 9.8982 (1) Å
b = 20.4966 (2) Å
c = 9.7322 (1) Å
β = 112.472 (1)°
V = 1824.53 (3) Å^3
Z = 4
D_x = 1.228 Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 7550 reflections
θ = 1–26°
μ = 0.075 mm^{-1}
T = 173 K
Block
0.40 × 0.40 × 0.40 mm
Colourless

Data collection

Siemens CCD three-circle diffractometer
ω scans
Absorption correction: none
8415 measured reflections
3398 independent reflections
3314 reflections with $I > 2\sigma(I)$
R_{int} = 0.033
θ_{max} = 26.31°
h = −12 → 12
k = −25 → 24
l = −12 → 11

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.086
S = 1.048
3398 reflections
236 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0475P)^2 + 0.6444P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.180 e Å^{-3}
$\Delta\rho_{min}$ = −0.165 e Å^{-3}
Extinction correction: *SHELXL96* (Sheldrick, 1996)
Extinction coefficient: 0.0077 (10)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

N1—C6	1.3486 (18)	C3—O31	1.3823 (17)
N1—C2	1.3497 (18)	O31—C31	1.435 (2)
C6—N1—C2	119.24 (12)	O31—C3—C4	119.77 (12)
N1—C2—C3	121.27 (12)	O31—C3—C2	120.26 (12)
N1—C2—C21	115.90 (12)		

The data collection nominally covered over a sphere of reciprocal space, by a combination of three sets of exposures; each set had a different φ angle for the crystal and each exposure covered 0.3° in ω. The crystal-to-detector distance was 6.0 cm. Coverage of the unique set was over 99% complete to at least 25° in θ. Crystal decay was monitored by repeating the initial frames at the end of data collection and analysing the duplicate reflections. All H atoms were located by difference Fourier synthesis and refined with fixed individual displacement parameters [U(H) = 1.5U_{eq}(C_{methyl}) or U(H) = 1.2U_{eq}(C)] using a riding model, with sp^2 C—H =

0.95 and methyl C—H = 0.98 Å. As the structure contains only C, H, N and O atoms, and due to the kind of radiation used, the absolute structure could not be determined.

Data collection: *SMART* (Siemens, 1995). Cell refinement: *SMART*. Data reduction: *SAINT* (Siemens, 1995). Program(s) used to solve structure: *SHELXS*96 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*96 (Sheldrick, 1996). Molecular graphics: *XP* in *SHELXTL-Plus* (Sheldrick, 1991).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1146). Services for accessing these data are described at the back of the journal.

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7-Methoxy-2,2-dimethyl-3-phenyl-4-(4-hydroxyphenyl)-2*H*-1-benzopyran†

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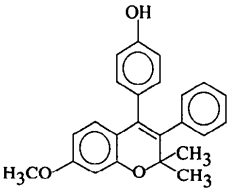
Abstract

The crystal structure of the title compound, $C_{24}H_{22}O_3$, shows that both the pendant phenyl substituents at C3 and C4 have a twist conformation, while the pyran ring adopts a distorted sofa conformation due to puckering at C2 by the dimethyl substitutions.

† CDRI Communication No. 5662.

Comment

In the course of our ongoing work on the synthesis and structure–activity relationship studies of a series of non-steroidal antiestrogens, the title compound, (I), which elicited an estrogenic response, was synthesized (Ray *et al.*, 1976). A closely related compound, centchroman, was found to be associated with potent estrogen antagonistic activity along with weak estrogenic activity (Kamboj *et al.*, 1977). Since both estrogen agonist and antagonist activities are mediated through the estrogen receptor, it was of interest to study the spatial differences in the molecular structures of the two compounds which would account for this differential behaviour. Recently, the X-ray structures of both the racemate and *d*-enantiomer of centchroman (as the *N*-methyl iodide salt) have been reported in order to explore their configuration–activity relationships (Ray *et al.*, 1994; Srivastava *et al.*, 1996). In this communication, we report the X-ray single-crystal structure determination of the title compound and use molecular graphics to compare it's structure with both the *dl*-centchroman methyl iodide salt and estradiol.



(I)

The conformation of the title molecule along with the atom-numbering scheme is shown in Fig. 1. The molecule contains one fused-ring system (*A*/*B*) and two phenyl rings (*C* and *D*). All three aromatic rings, *A*, *C* and *D*, are planar [deviations of the atoms from their least-squares planes are within the range −0.018 (1)–0.025 (1) Å], while ring *B* is puckered. In ring *B*, atoms C2 and O25 deviate by 0.423 (3) and −0.216 (3) Å, respectively, from the least-squares plane through C3, C4, C5 and C1, which indicates that the ring has a tendency to adopt a sofa conformation. Both the 3- and 4-substituted pendant phenyl rings showed a tendency to be perpendicular with respect to the plane through the *A*/*B* chromene ring (the dihedral angles between the planes *A*/*B* and *C* is 99.4°, and between *A*/*B* and *D* is 109.4°) as has been found in the centchroman structure (Ray *et al.*, 1994). Fig. 2 shows that the molecules are connected by intermolecular hydrogen bonding [O27—H···O25 2.848 (2) Å], thus, the crystal structure is stabilized mainly by hydrogen-bonding and van der Waals interactions.

It has been speculated (Durani *et al.*, 1979) that estrogen antagonists, which act through competitive inhibition of estradiol action, carry a substructural entity in their molecular framework which simulates estradiol and is responsible for its binding to the receptor.