Mearsinium Picrate,* $C_9H_{14}NO^+.C_6H_2N_3O_7^-$

By Glen B. Robertson and Uncharee Tooptakong

Research School of Chemistry, The Australian National University, GPO Box 4, Canberra, ACT 2601, Australia

Abstract. $M_r = 380.3$, orthorhombic, $P2_12_12_1$, $a = 23.4614$ (11), $b = 10.8541$ (6), $c = 6.6458$ (4) Å, $U = 1692.4$ Å^3, $Z = 4$, $D_m = 1.48$ (1), $D_x = 1.49$ g cm^{-3}, Cu $K\bar{\alpha}$, $\lambda = 1.54184$ Å, $\mu = 10.7$ cm^{-1}, $F(000) = 792$, $T = 293$ (2) K, $R = 0.037$, $wR = 0.047$ for 2412 unique reflections $[I \geq 3\sigma(I)]$. The mearsine cation $[C_9H_{14}NO]^+$ is bicyclic with an isoquinuclidine skeleton and is strongly H-bonded [N$\cdots$O $= 2.686$ (2) Å; α(N–H$\cdots$O) $= 171$ (3)°] to the ketonic oxygen of the picrate group. Picrate anions stack face to face in columns parallel to **c** with an interplane separation of approximately $c/2$. The arrangement is unusual for similarly charged aromatic ions. The probability that the structure proposed depicts absolute configuration exceeds 99%.

Introduction. Mearsine is one of a series of minor alkaloids isolated from the north Queensland rainforest tree *Peripentadenia mearsii* (C. T. White) L. S. Smith by I. R. C. Bick and co-workers (Lamberton, Gunawardana & Bick, 1983). The empirical formula $C_9H_{13}NO$ was established by mass spectrometry, and by microanalysis, and the functional groups present were characterized by NMR, IR and UV spectroscopy. However, for reasons detailed elsewhere (Robertson, Tooptakong, Lamberton, Gunawardana & Bick, 1984) those structural features indicated by the spectroscopic data could not be interpreted satisfactorily in terms of the bicyclic system required by the formula. The present work, results of which are summarized briefly by Robertson *et al.* (1984), was undertaken accordingly.

Experimental. Light yellow-brown acicular crystals (parallel **c**) from methanol–water. D_m by flotation in carbon tetrachloride–*m*-xylene. Crystal $0.11 \times 0.11 \times 0.24$ mm perpendicular to bounding forms $\{110\}$, $\{1\bar{1}0\}$ and $\{001\}$; Picker FACS-1 diffractometer, θ–2θ continuous-scan mode [scan velocity 2° min^{-1} 2θ, 2×10 s backgrounds at extremes, $3 < 2\theta < 127°$, Cu $K\bar{\alpha}$, graphite-crystal monochromator, forms recorded $\pm h$, $+k$, $+l$, h 0–27, k 0–12, l 0–7, 3413 reflections including standards (3 every 97 data, 16,0,0, 0$\bar{8}$0 and 004, total degradation 2.7, 4.2 and 0.9% respectively)], data corrected for absorption (de Meulenaer & Tompa,

1965) [transmission factors: 0.926 (max.), 0.824 (min.)] and for crystal degradation (Churchill & Kalra, 1974); sorting and averaging (point group 222) yielded 2412 data (2 Bijvoet sets) with $I \geq 3\sigma(I)$; R_s $[= \sum \sigma_s(F_o)/\sum |F_o|$ where $\sigma_s(F_o) = \sigma_I/2\text{Lp}(|F_o|)]$ for this data set (Robertson & Whimp, 1975) was 0.019; cell dimensions from 12 well dispersed reflections with $88 < 2\theta < 117°$ [Cu $K\alpha_1$ radiation, $T = 293$ (2) K]; structure solved using *MULTAN*80 (Main *et al.*, 1980), H-atom location from difference syntheses; full-matrix least-squares refinement on F with weights $w = [\sigma^2{}_s(F_o) + 0.0005|F_o|^2]^{-1}$ (Busing & Levy, 1957; Corfield, Doedens & Ibers, 1967), anisotropic thermal parameters for C, N and O, isotropic thermal parameters for H and correction for extinction (Zachariasen, 1963), $R = 0.037$, $wR = 0.047$, $\sum [w\Delta^2/(n-s)]^{1/2} = 1.66$, extinction coefficient $= 2.3$ (2) $\times 10^{-4}$, $-0.3 < (\rho_o - \rho_c) < 0.5$ e Å^{-3}, max. $\Delta/\sigma = 0.19$; scattering factors, with dispersion corrections for C, N and O, from *International Tables for X-ray Crystallography* (1974); calculations performed with *ANUCRYS* programs (McLaughlin, Taylor & Whimp, 1977) and the Australian National University Univac 1100/82 computer.

Discussion. Atom nomenclature is defined in Fig. 1 (*ORTEP* II; Johnson, 1976) and the corresponding coordinates are listed in Table 1.† Bond distances and angles are in Table 2.

Crystals are composed of discrete H-bonded ion pairs $[C_9H_{14}NO]^+[C_6H_2N_3O_7]^-$, one pair per asymmetric unit. The crystal packing features a columnar arrangement (parallel to **c**) of interleaved near-parallel anions (Fig. 2) with a conventional van der Waals interplane separation (*ca* 3.32 Å, $c/2$). Relative displacements of successive anions from the column centres (2_1 axis) serve to generate a near-cylindrical negative-charge surface, which is effectively encapsulated by two helical cation arrays – one of which is closely contacting (H bonded) with pitch 1/2 and the other is more distant (in van der Waals contact) with pitch 1/4.

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† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42225 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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* Mearsine is 3,8-dimethyl-2-azabicyclo[2.2.2]oct-2-en-5-one.

Face-to-face stacking of molecules or molecular ions is a common feature of aromatic donor–acceptor complexes (Herbstein, 1971). However, so far as we are aware, the only such arrangements of *similarly* charged ions reported to data are those for the radical ions dimethyl-*p*-phenylenediamine in Würsters red bromide

(Tanaka & Sakabe, 1968) and (tetracyanoquino-dimethane)$_2^-$ in its tetramethyl-*p*-phenylenediamine salt (Hanson, 1968).
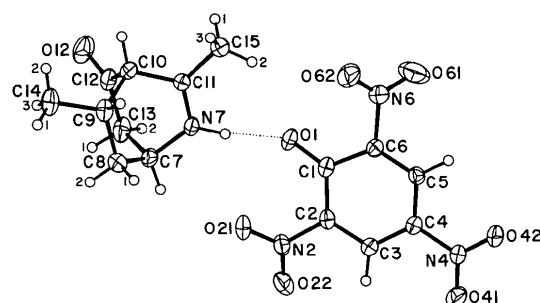

Fig. 1. Conformation and atom nomenclature in mearsinium picrate. Vibration ellipsoids correspond to 30% probability surfaces. H atoms are depicted as 0·11 Å radius spheres.

Table 1. *Atomic coordinates and equivalent isotropic thermal parameters*

$B_{eq} = \frac{1}{3}\sum_i\sum_j B_{ij}a^*_i a^*_j \mathbf{a}_i\cdot\mathbf{a}_j$; actual B values for H atoms.

	x	y	z	$B_{eq}(Å^2)$
C(1)	−0·2621 (1)	0·1152 (2)	−0·1625 (3)	3·1
C(2)	−0·2895 (1)	−0·0034 (2)	−0·1565 (4)	3·1
C(3)	−0·2608 (1)	−0·1136 (2)	−0·1559 (4)	3·2
C(4)	−0·2019 (1)	−0·1137 (2)	−0·1512 (4)	3·1
C(5)	−0·1715 (1)	−0·0043 (2)	−0·1505 (4)	3·1
C(6)	−0·2005 (1)	0·1040 (2)	−0·1536 (4)	3·1
N(2)	−0·3514 (1)	−0·0104 (2)	−0·1593 (3)	4·0
N(4)	−0·1717 (1)	−0·2293 (2)	−0·1428 (4)	3·8
N(6)	−0·1671 (1)	0·2179 (2)	−0·1553 (4)	4·5
O(1)	−0·2861 (1)	0·2164 (1)	−0·1825 (3)	4·7
O(21)	−0·3786 (1)	0·0779 (2)	−0·0994 (4)	6·9
O(22)	−0·3741 (1)	−0·1048 (2)	−0·2172 (4)	6·3
O(41)	−0·1979 (1)	−0·3247 (2)	−0·1636 (4)	6·2
O(42)	−0·1205 (1)	−0·2267 (2)	−0·1140 (4)	5·6
O(61)	−0·1240 (1)	0·2185 (2)	−0·2567 (5)	9·0
O(62)	−0·1820 (1)	0·3039 (2)	−0·0523 (5)	7·5
C(7)	−0·4410 (1)	0·3352 (2)	−0·1607 (4)	3·9
C(8)	−0·4661 (1)	0·3790 (3)	0·0393 (5)	4·3
C(9)	−0·4492 (1)	0·5141 (2)	0·0770 (4)	3·9
C(10)	−0·4120 (1)	0·5586 (2)	−0·1041 (4)	3·5
C(11)	−0·3637 (1)	0·4711 (2)	−0·1204 (4)	3·3
C(12)	−0·4487 (1)	0·5447 (2)	−0·2919 (4)	3·9
C(13)	−0·4644 (1)	0·4137 (3)	−0·3314 (5)	4·6
C(14)	−0·4999 (1)	0·5988 (3)	0·1081 (6)	5·2
C(15)	−0·3038 (1)	0·5083 (3)	−0·1026 (7)	5·3
N(7)	−0·3793 (1)	0·3587 (2)	−0·1490 (3)	3·5
O(12)	−0·4639 (1)	0·6317 (2)	−0·3917 (3)	6·2
H(N)	−0·349 (1)	0·303 (3)	−0·163 (5)	5·9 (7)
H(3)	−0·284 (1)	−0·187 (2)	−0·160 (4)	4·0 (5)
H(5)	−0·130 (1)	−0·006 (2)	−0·148 (3)	2·7 (4)
H(7)	−0·449 (1)	0·248 (2)	−0·187 (4)	4·9 (6)
H(81)	−0·452 (2)	0·332 (3)	0·156 (5)	8·0 (9)
H(82)	−0·507 (1)	0·366 (2)	0·026 (4)	4·3 (6)
H(9)	−0·422 (1)	0·522 (2)	0·195 (4)	5·2 (6)
H(10)	−0·399 (1)	0·644 (2)	−0·089 (4)	4·0 (5)
H(131)	−0·506 (1)	0·409 (3)	−0·330 (4)	5·2 (6)
H(132)	−0·450 (1)	0·381 (3)	−0·644 (5)	5·2 (6)
H(141)	−0·519 (1)	0·573 (3)	0·226 (6)	7·0 (9)
H(142)	−0·485 (2)	0·680 (4)	0·128 (6)	8·4 (10)
H(143)	−0·522 (1)	0·595 (3)	−0·008 (5)	4·8 (7)
H(151)	−0·298 (1)	0·570 (3)	−0·181 (5)	5·8 (8)
H(152)	−0·279 (1)	0·439 (3)	−0·106 (4)	4·9 (6)
H(153)	−0·301 (2)	0·552 (3)	0·025 (6)	7·5 (10)

Table 2. *Bond lengths* (Å) *and angles* (°)

C(1)–C(2)	1·439 (3)	C(8)–C(9)	1·539 (4)
C(1)–C(6)	1·452 (3)	C(8)–H(81)	0·99 (4)
C(1)–O(1)	1·241 (3)	C(8)–H(82)	0·97 (3)
C(2)–C(3)	1·373 (3)	C(9)–C(10)	1·563 (4)
C(2)–N(2)	1·453 (3)	C(9)–C(14)	1·517 (4)
C(3)–C(4)	1·381 (3)	C(9)–H(9)	1·01 (3)
C(3)–H(3)	0·96 (3)	C(10)–C(11)	1·483 (3)
C(4)–C(5)	1·385 (3)	C(10)–C(12)	1·523 (4)
C(4)–N(4)	1·442 (3)	C(10)–H(10)	0·98 (3)
C(5)–C(6)	1·358 (3)	C(11)–C(15)	1·467 (3)
C(5)–H(5)	0·98 (2)	C(11)–N(7)	1·288 (3)
C(6)–N(6)	1·465 (3)	C(12)–C(13)	1·491 (4)
N(2)–O(21)	1·219 (3)	C(12)–O(12)	1·208 (3)
N(2)–O(22)	1·217 (3)	C(13)–H(131)	0·97 (3)
N(4)–O(41)	1·213 (3)	C(13)–H(132)	1·00 (3)
N(4)–O(42)	1·216 (2)	C(14)–H(141)	0·95 (4)
N(6)–O(61)	1·214 (3)	C(14)–H(142)	0·96 (4)
N(6)–O(62)	1·209 (3)	C(14)–H(143)	0·93 (3)
O(1)–H(N)	1·76 (3)	C(15)–H(151)	0·86 (3)
C(7)–C(8)	1·531 (4)	C(15)–H(152)	0·96 (3)
C(7)–C(13)	1·521 (4)	C(15)–H(153)	0·97 (4)
C(7)–N(7)	1·472 (3)	N(7)–H(N)	0·93 (3)
C(7)–H(7)	0·98 (3)		

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C(2)–C(1)–C(6)	111·6 (2)	C(8)–C(7)–N(7)	106·2 (2)
C(2)–C(1)–O(1)	126·3 (2)	C(13)–C(7)–N(7)	107·3 (2)
C(6)–C(1)–O(1)	121·9 (2)	C(8)–C(7)–C(13)	109·5 (2)
C(1)–C(2)–C(3)	124·0 (2)	N(7)–C(7)–H(7)	111 (2)
C(1)–C(2)–N(2)	119·5 (2)	C–C(7)–H(7)	110–113 (2)
C(3)–C(2)–N(2)	116·4 (2)	C(7)–C(8)–C(9)	109·8 (2)
C(2)–C(3)–C(4)	119·5 (2)	C–C(8)–H	105–114 (2)
C(2)–C(3)–H(3)	116 (1)	H(81)–C(8)–H(82)	109 (3)
C(4)–C(3)–H(3)	124 (1)	C(8)–C(9)–C(10)	108·2 (2)
C(3)–C(4)–C(5)	120·9 (2)	C(8)–C(9)–C(14)	113·4 (2)
C(3)–C(4)–N(4)	119·6 (2)	C(10)–C(9)–C(14)	110·8 (2)
C(5)–C(4)–N(4)	119·5 (2)	C–C(9)–H(9)	103–112 (2)
C(4)–C(5)–C(6)	119·0 (2)	C(9)–C(10)–C(11)	106·6 (2)
C(4)–C(5)–H(5)	120 (1)	C(9)–C(10)–C(12)	106·6 (2)
C(6)–C(5)–H(5)	121 (1)	C(11)–C(10)–C(12)	108·0 (2)
C(5)–C(6)–C(1)	124·8 (2)	C–C(10)–H(10)	110–113 (1)
C(5)–C(6)–N(6)	117·6 (2)	C(10)–C(11)–C(15)	123·4 (2)
C(1)–C(6)–N(6)	117·5 (2)	C(10)–C(11)–N(7)	113·6 (2)
C(2)–N(2)–O(21)	118·6 (2)	C(15)–C(11)–N(7)	123·0 (2)
C(2)–N(2)–O(22)	119·0 (2)	C(10)–C(12)–C(13)	112·2 (2)
O(21)–N(2)–O(22)	122·4 (2)	C(10)–C(12)–O(12)	122·6 (2)
C(4)–N(4)–O(41)	119·2 (2)	C(13)–C(12)–O(12)	125·1 (2)
C(4)–N(4)–O(42)	118·2 (2)	C(7)–C(13)–C(12)	108·3 (2)
O(41)–N(4)–O(42)	122·6 (2)	C–C(13)–H	107–114 (2)
C(6)–N(6)–O(61)	117·0 (2)	H(131)–C(13)–H(132)	108 (2)
C(6)–N(6)–O(62)	119·5 (2)	C–C(14)–H	107–108 (2)
O(61)–N(6)–O(62)	123·4 (2)	H–C(14)–H	109–114 (3)
C(7)–N(7)–C(11)	116·8 (2)	C–C(15)–H	105–112 (2)
C(7)–N(7)–H(N)	129 (2)	H–C(15)–H	98–120 (3)
C(11)–N(7)–H(N)	115 (2)		
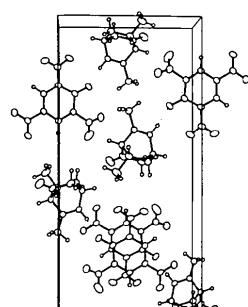
Fig. 2. Crystal packing arrangement viewed down **c**.
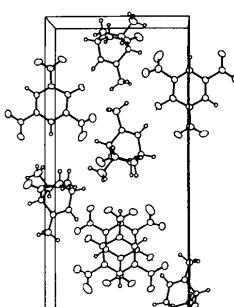
Cation dimensions bear a close similarity to those reported for a series of molecules containing bicyclo[2.2.2]octenone fragments (Becker, Ruge, Skelton & White, 1979; Karlsson, Lindgren, Pilotti & Söderholm, 1977, and references therein). The half-rings C(7)—N(7)—C(11)—C(10) (plane 1) and C(10)—C(9)—C(8)—C(7) are accurately planar [maximum deviation 0·0001 (22) Å] and the exocyclic methyl carbon atom [C(15)] is only marginally displaced from plane 1 [0·020 (5) Å]. The remaining half-ring C(10)—C(12)—C(13)—C(7) is just significantly nonplanar [maximum deviation 0·021 (3) Å]. In this case, however, the exocyclic substituent O(12) is substantially out of the plane [0·092 (2) Å] apparently as a result of unfavourable non-bonding contacts [e.g. O(12)···C(7) = 3·159 (3) Å, O(12)···H(7) = 2·47 (3) Å] to a neighbouring cation. Mean C—C bond lengths are in good agreement with standard values, with endocyclic Csp^2—Csp^3 distances ranging from 1·483 (3) to 1·523 (3) Å and Csp^3—Csp^3 distances from 1·521 (4) to 1·563 (4) Å. In both instances the spread of values is statistically significant and probably results from steric strain. Karlsson et al. (1977) have observed similar (but larger) effects in a range of more heavily substituted and sterically crowded bicyclo[2.2.2]octenone analogues. In common with values reported for the octenone analogues, the exocyclic C—C(Me) distances in the mearsine cation [1·517 (4), 1·467 (3) Å] are substantially shorter than their expected values [1·54, 1·51 Å]. After correction for libration shortening (riding model assumed) the discrepancy is largely eliminated, the corrected values being 1·534 (4) and 1·491 (4) Å. Application of Hamilton's R-factor ratio test (Hamilton, 1965) indicates a probability of ca 99·5% for the absolute configuration depicted in the figures as against ca 0·5% only for the enantiomer [wR = 0·0472, wR (enantiomer) = 0·0473, ratio = 1·002, significance level = 0·5%]. With anomalous-scattering contributions from C, N and O only (f'' = 0·009, 0·018, 0·32 e respectively) the sharp discrimination afforded by the R-factor ratio test is somewhat surprising and, presumably, reflects the fact that both members of each Bijvoet pair were included in the refinement schemes.

The occurrence of strong H-bonding interactions to the ketone oxygen of the picrate ion is a common feature of both organic and inorganic picrate salts. Relevant data for five such salts are summarized in Table 3. The procedure adopted by Taylor, Kennard & Versichel (1984) is followed: the Table 3 data relate to normalized N—H distances (N—H' = 1·030 Å; Jeffrey & Lewis, 1978). In all instances the N···O and H'···O values lie well to the extreme left (high-energy end) of the distributions reported by Taylor et al. (1984) for both inter- and intramolecular N—H···O=C bonds. Possibly because it provides the only instance where both the donor and acceptor groups are each involved

Table 3. N—H···O=C bond distances (Å) and angles (°) for picrate salts

H···O and α(N—H···O) values are those calculated with N—H distances normalized to 1·030 Å.

Cation	N···O	H···O	α(N—H···O)	C=O	Reference
NH_4^+	2·836 (4)	1·89 (7)	151 (6)	1·239 (6)	Maartmann-Moe (1969)
Serotonin⁺	2·705 (2)	1·74 (2)	154 (2)	1·241 (3)	Thewalt & Bugg (1972)
Tryptamine⁺	2·813 (4)	1·82 (4)	159 (1)		
	2·787 (2)	1·89 (2)	143 (2)	1·248 (3)	Gartland, Freeman & Bugg (1974)
Tryptophan⁺	2·734 (3)	1·81 (3)	148 (3)		
	2·736 (3)	1·99 (3)	127 (2)	1·251 (3)	
Mearsine⁺	2·686 (2)	1·66 (3)	171 (3)	1·241 (3)	This work

in just one H bond, the mearsine–picrate bond is arguably the most energetic and is the most nearly linear of those surveyed in Table 3. The α(N—H'···O) [171 (3)°] vs H'···O [1·66 (3) Å] correlation reported by Taylor et al. (1984) is maintained as, too, is the C=O vs H···O correlation. Nevertheless, long C=O distances (e.g. 1·244 Å av., Table 3) are not necessarily diagnostic of H bonding, as is evidenced by the value [1·243 (7) Å] in potassium picrate (Maartmann-Moe, 1969).

The aromatic nucleus of the picrate ion is slightly nonplanar [maximum deviation 0·019 (2) Å]. The nitrogen substituents lie close to the mean ring plane [maximum deviation 0·027 (2) Å] but the ketone oxygen is out of the plane by 0·126 (2) Å. The p-nitro group is twisted 8·2 (1)°, and the o-nitro groups are twisted 22·5 (1) [N(2), O(21), O(22)] and 41·3 (1)° [N(6), O(61), O(62)] from the ring plane. Twist angles are clearly very dependent on the environment (particularly the H-bonding environment) of the ion, with previously reported values ranging from 3 to 53° for o- and from 2 to 7° for p-NO_2 groups. Other dimensional data are in good agreement with those reported for potassium picrate (Maartmann-Moe, 1969) and for those salts surveyed in Table 3.

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# 5-Acetyl-7-(N-methylanilino)cyclohepta-2,4-dien-1-one, $C_{16}H_{17}NO_2$

BY CAROLYN B. KNOBLER,* DOUGLAS E. BUGNER, ORVILLE L. CHAPMAN AND KENNETH N. TRUEBLOOD

J. D. McCullough Laboratory for X-ray Crystallography, Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90024, USA

Abstract. $M_r = 255.32$, orthorhombic, $P2_12_12_1$, $a = 6.219$ (2), $b = 14.176$ (5), $c = 15.432$ (4) Å, $V = 1360.5$ Å^3, $Z = 4$, $D_x = 1.25$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu = 0.76$ cm^{-1}, $F(000) = 544$, $T = 298$ K, $R = 0.099$ for 1133 unique observed reflections. An interesting feature of this molecule is the very close intramolecular nonbonded N⋯O distance of 2.69 (1) Å; this appears to result in displacements of some atoms from what would otherwise be coplanar configurations. The methylanilino group is in the pseudo-equatorial position, with its plane nearly perpendicular (87°) to the best plane of the diene–dione system.

Introduction. 5-Acetyl-7-(N-methylanilino)cyclohepta-2,4-dien-1-one (1) is an intermediate in the course of synthesis of 4-vinyltropone from 2-(1-acetoxyethyl)-tropone. The red color and UV spectrum of (1) have been interpreted as resulting from some form of electron donor–acceptor complexation (Bugner, 1982).

(1)

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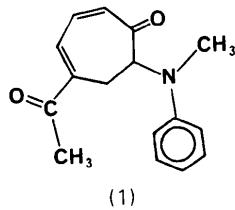
* To whom correspondence should be addressed.

Experimental. Preparation according to a modification (Bugner, 1982) of a synthesis developed by Dennis, Katritzky, Parton, Nomura, Takahashi & Takeuchi (1976) and adapted by Jackson (1980); red, blade-shaped, single crystal, $0.14 \times 0.14 \times 0.40$ mm; Weissenberg photographs have systematic absences $h00$ for h odd, $0k0$ for k odd, $00l$ for l odd; Syntex $P\bar{1}$ diffractometer, graphite monochromator, unit-cell parameters by least-squares refinement of 15 reflections $(16.45 \le 2\theta \le 22.23°)$, θ–2θ scan, $4.0°$ min^{-1} in 2θ, $2\theta_{max} = 50°$ for range $0 \le h \le 7$, $0 \le k \le 16$, $0 \le l \le 18$, three reflections monitored every 97 reflections with 2% maximum intensity variation from average, average variation ±1%, e.s.d. of standards about 1%, 1317 unique data, 1133 with $I > 0$ used in subsequent calculations, Lorentz and polarization but no absorption correction; direct methods, all atoms (including H atoms) located on Fourier and difference Fourier maps. The phenyl ring was treated as a rigid C_6H_5 group, C—C = 1.395 Å, C—H 1.0 Å, C—C—C and C—C—H = 120°, with individual isotropic displacement parameters for C and fixed isotropic displacement parameters for each H atom based on that of the attached C. All other H atoms were kept in geometrically reasonable positions with C—H = 1.0 Å and with fixed displacement parameters, as described for those attached to phenyl C atoms. All other nonhydrogen atoms have anisotropic displacement parameters; refined by full-matrix least-squares procedure based on F with