$$C_{17}H_{14}N_2O_8$$

References

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6-(3-Methoxybenzyl)-5-methyl-o-anisonitrile

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Abstract. $C_{17}H_{17}NO_2$, $M_r = 267.33$, monoclinic, $P2_1/c$, $a = 7.038$ (2), $b = 26.372$ (6), $c = 7.779$ (2) Å, $\beta = 100.93$ (2)°, $V = 1428.5$ (6) Å^3, $Z = 4$, $D_x = 1.25$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.76$ cm^{-1}, $F(000) = 568$, $T = 295$ K. Final $R = 0.051$ for 1275 observed reflections. The bond distances are H_2C—C(av.) = 1.509 (4), C=N = 1.135 (4), C—CH$_3$ = 1.444 (4), C—O(av.) = 1.360 (4) and C—C(benz., av.) = 1.383 (4) Å. The X-ray structure confirms regioselective addition to the 1 position of the 1,3-cyclohexadien-5-yne.

Experimental. Recently, we have observed a novel tandem-addition rearrangement via a benzocyclobutenimine intermediate (II) leading to contiguously substituted benzenes such as the title compound (I), which was obtained as an unexpected product in 49% yield by the reaction of 3-methoxylithioarylonitrile with 1-methoxy-4-methyl-1,3-cyclohexadien-5-yne (generated in situ with lithiodiisopropylamine in THF) followed by protonation.

(I)   (II)
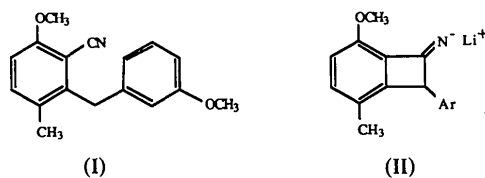
Crystals of (I) are colorless rectangular plates, unit-cell parameters by least-squares fit of 15 reflections in the range $10 < 2\theta < 25°$, crystal dimensions $0.34 \times 0.16 \times 0.35$ mm, space group $P2_1/c$ from systematic absences ($0k0$, k odd; $h0l$, $h+l$ odd); automatic

Syntex $P2_1$ diffractometer, graphite-monochromated Mo $K\alpha$ radiation, $\theta/2\theta$ scan mode, variable scan rate ($3.0–14.7°$ min^{-1}, depending on intensity), 2195 measured reflections, 1887 independent reflections in the range $3 < 2\theta < 45°$, $R_{int} = 0.017$, hkl range $h -7\rightarrow7$, $k\ 0\rightarrow28$, $l\ 0\rightarrow8$, 1275 observed reflections with $I > 3\sigma(I)$, $\sigma(I)$ from counting statistics; three standard reflections remeasured after every 100 reflections did not show any significant change ($\sim 3\%$) in intensity during data collection; Lorentz–polarization correction, no absorption or extinction corrections. Direct methods SHELXS86 (Sheldrick, 1986), refinement by full-matrix least squares using SHELX76 (Sheldrick, 1976), anisotropic; H atoms located in difference Fourier maps, H atoms included in the refinement with isotropic temperature factors and with the constraint as benzyl, methyl and —CH$_2$—; $w = 1/(\sigma^2 F + 0.003988F^2)$, $\sum w(|F_o| - |F_c|)^2$ minimized, $R = 0.051$ and $wR = 0.060$ for 1275 observed reflections; $S = 1.12$, $(\Delta/\sigma)_{max} = 0.03$, $\Delta\rho_{max, min} = 0.31$, -0.18 e Å^{-3} in final difference Fourier map. Atomic scattering factors were taken from International Tables for X-ray Crystallography (1974). The final atomic parameters are given in Table 1,† selected bond lengths, angles and torsion angles are given in Table 2. The identification of the atoms and the configuration are shown in the ORTEP (Johnson, 1965) drawing of Fig. 1, the packing of the molecules is shown in the unit cell in Fig. 2.

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Related literature. Polysubstituted benzenes such as (I) are easily hydrolyzed and oxidized to keto acids which serve as precursors to naturally occurring anthraquinones (de Silva, Watanabe & Snickus, 1979). Benzocyclobutenimine has been proposed as an intermediate in the reaction of 1,3-cyclohexadien-5-ynes derived from aryloxazolines and lithioalkanenitriles (Meyers & Pansegrau, 1984).
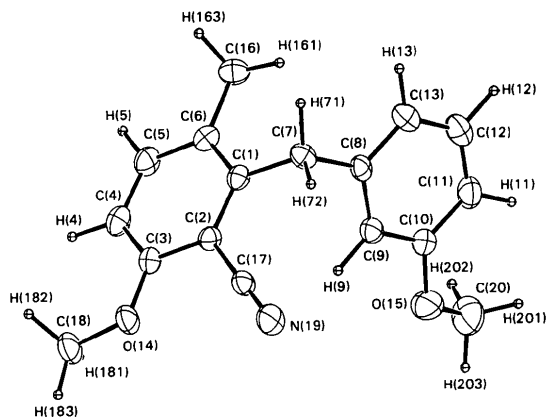
Fig. 1. ORTEP drawing of the molecule. Thermal ellipsoids are scaled to enclose 30% probability. H atoms are represented as spheres of arbitrary radii.
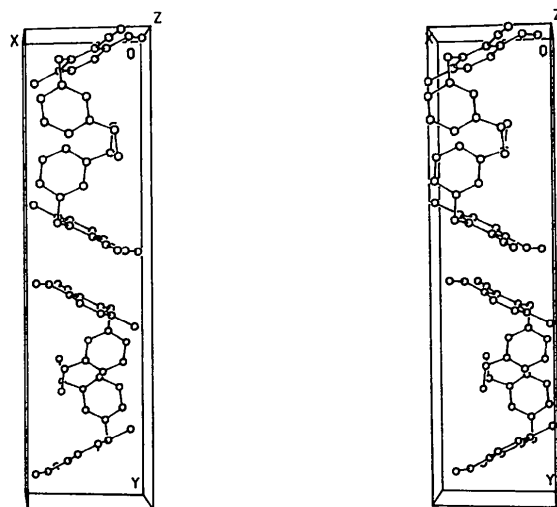
Table 1. *Fractional atomic coordinates with equivalent isotropic thermal parameters for the non-H atoms (e.s.d.'s in parentheses)*

	x	y	z	$U_{eq}*(\text{Å}^2)$
C(1)	0·6643 (4)	0·41298 (10)	1·2153 (3)	0·0396 (6)
C(2)	0·4818 (4)	0·43568 (10)	1·1723 (3)	0·0397 (6)
C(3)	0·3839 (4)	0·44081 (11)	0·9994 (3)	0·0427 (7)
C(4)	0·4694 (5)	0·42240 (12)	0·8671 (4)	0·0550 (8)
C(5)	0·6475 (5)	0·39953 (12)	0·9092 (4)	0·0552 (8)
C(6)	0·7478 (4)	0·39451 (11)	1·0796 (4)	0·0475 (7)
C(7)	0·7644 (4)	0·40818 (11)	1·4038 (4)	0·0459 (7)
C(8)	0·7455 (4)	0·35610 (11)	1·4771 (3)	0·0414 (6)
C(9)	0·5657 (4)	0·33390 (12)	1·4639 (4)	0·0480 (7)
C(10)	0·5455 (4)	0·28644 (13)	1·5288 (4)	0·0535 (8)
C(11)	0·7041 (5)	0·26019 (14)	1·6150 (4)	0·0652 (9)
C(12)	0·8839 (6)	0·28254 (14)	1·6292 (5)	0·0670 (9)
C(13)	0·9064 (5)	0·32924 (12)	1·5614 (4)	0·0542 (8)
O(14)	0·2119 (3)	0·46458 (8)	0·9782 (2)	0·0526 (5)
O(15)	0·3600 (3)	0·26800 (10)	1·4997 (4)	0·0830 (8)
C(16)	0·9435 (5)	0·36909 (14)	1·1142 (5)	0·0642 (9)
C(17)	0·3839 (4)	0·45278 (12)	1·3088 (4)	0·0441 (7)
C(18)	0·0956 (5)	0·46653 (14)	0·8052 (4)	0·0606 (9)
N(19)	0·3019 (4)	0·46469 (12)	1·4145 (3)	0·0644 (8)
C(20)	0·3336 (7)	0·21588 (17)	1·5197 (7)	0·0936 (14)

* The standard deviations of U_{eq}'s were calculated according to Schomaker & Marsh (1983).

Fig. 2. Stereoscopic drawing showing the packing of molecules in the unit cell. H atoms are removed for clarity.

Table 2. *Selected bond lengths (Å), bond angles (°) and torsion angles (°)*

C(1)–C(7)	1·507 (4)	C(10)–O(15)	1·372 (4)
C(2)–C(17)	1·444 (4)	O(14)–C(18)	1·437 (4)
C(3)–O(14)	1·347 (3)	O(15)–C(20)	1·407 (6)
C(6)–C(16)	1·511 (4)	C(17)–N(19)	1·135 (4)
C(7)–C(8)	1·511 (4)		

C(1)–C(2)–C(17)	120·2 (2)	C(1)–C(7)–C(8)	112·7 (2)
C(3)–C(2)–C(17)	117·4 (2)	C(9)–C(10)–O(15)	115·3 (3)
C(2)–C(3)–O(14)	115·5 (2)	C(11)–C(10)–O(15)	124·0 (3)
C(4)–C(3)–O(14)	125·8 (3)	C(3)–O(14)–C(18)	118·0 (2)
C(1)–C(6)–C(16)	121·6 (3)	C(10)–O(15)–C(20)	118·2 (3)
C(5)–C(6)–C(16)	119·7 (3)	C(2)–C(17)–N(19)	177·3 (3)

C(1)–C(2)–C(17)–N(19)	−108 (6)	C(3)–C(2)–C(17)–N(19)	69 (6)
C(1)–C(7)–C(8)–C(9)	−52·4 (3)	C(4)–C(3)–O(14)–C(18)	7·3 (4)
C(1)–C(7)–C(8)–C(13)	128·3 (3)	C(9)–C(10)–O(15)–C(20)	163·5 (3)
C(2)–C(1)–C(7)–C(8)	100·5 (3)	C(11)–C(10)–O(15)–C(20)	−16·0 (5)
C(3)–C(2)–C(1)–C(7)	−179·9 (2)		

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